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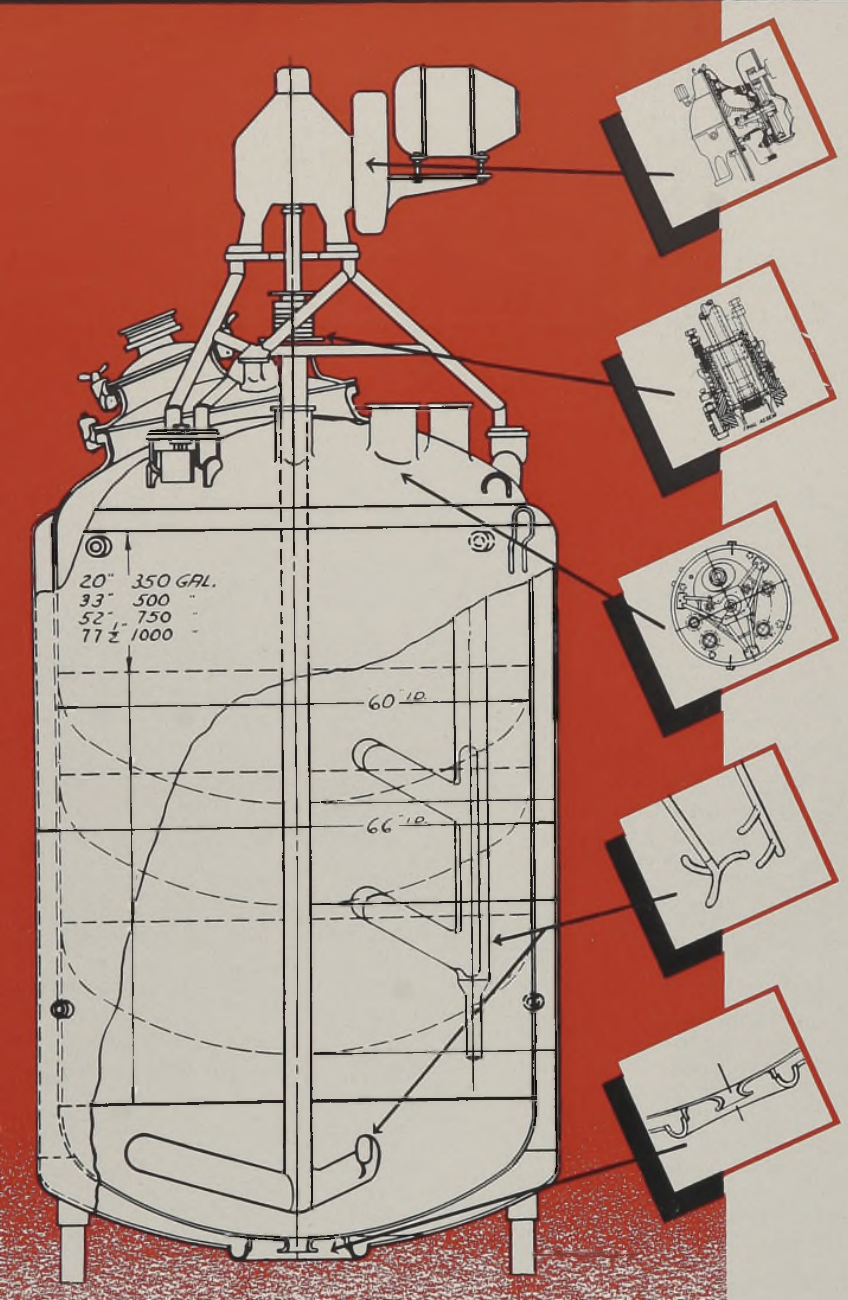
SOLVING "TOUGH" PROCESS PROBLEMS WITH STANDARD HIGH PRESSURE GLASS LINED STEEL REACTORS



Standard corrosion resistant equipment which stands up under the higher pressures, often increasing yields and speeding up reactions, is now available in the Pfaudler "R" Series of reaction kettles.

This series of ASME code built high pressure glass lined reaction kettles of all welded steel further extends the advantages of highly acid resisting Pfaudler Glass. Moreover, the range in which these standardized kettles are available—350 to 2000 gallons gives you a wide choice.

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CONSTRUCTION FEATURES

1. Standard Pfaudler spiral gear drives are motor driven and built for rugged service. Pedestal mounting makes it unnecessary to disturb drive while maintaining stuffing box.
2. High duty stuffing boxes for agitators feature replaceable wearing sleeves. Rotary seals are leak-proof and can be protected for full chemical service. Water jacket may be added or removed as required. Semi- and full- automatic oilers are available.
3. Ample top-head openings with machined flanges meet 95% of processing requirements. Include two 2", two 4", one 5" and one 6" openings besides opening for agitator. Additional openings may be added. Note 30" opening for assembly of agitator, fitted with 12" by 16" manhole with clamped cover—minimum gasket area.
4. The Pfaudler agitative system, consisting of glass covered impeller agitator, with or without adjustable upward or downward deflecting baffles, is capable of handling entire range of reaction problems. New thermometer well in baffles makes thermometer more responsive—gives almost instantaneous indication.
5. New welded outlet diaphragm eliminates cumbersome bottom outlet stuffing box. It is designed to take necessary expansion and contraction and meets ASME code requirements.

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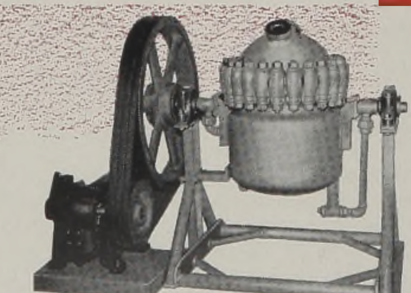

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INDUSTRIAL AND ENGINEERING CHEMISTRY • INDUSTRIAL EDITION

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CATALYSIS IN THE PETROLEUM INDUSTRY

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INDUSTRIAL AND ENGINEERING CHEMISTRY REPORTS ON THE CHEMICAL WORLD TODAY

Technology

Hoarding Helium. The Texas Panhandle, where the saying is it can rain more in five minutes and less in five years than in any other place in the world, will be the location of the greatest single helium storage reservoir in the world—a gigantic underground cache.

Deep in the heart of Texas (not quite) and thirty-two miles north of Amarillo is Exell, set down in the middle of the cow country. As you drive from Amarillo, you might easily miss the Bureau of Mines' biggest helium plant. For in the distance—and distances in that country are as far as the eye can reach—the plant looks like a dozen or more natural gasoline plants which still seem incongruous on the Texas range. Really Exell is not a town but merely several rows of small, neat, gray painted cottages acting as a front for the plant. The name "Exell" comes from the cow brand of the XL Ranch.

Just completed, between the new Exell plant and the older helium plant at Amarillo, is a 2-inch-high pressure-transport pipe line. Through it will flow part of Exell's helium output, and ultimately it will be piped back into the ground for conservation and future use, passing through pipe line connections to the near-by 60,000-acre government-owned Cliffside natural gas field.

Although the helium piped back into the ground must be repurified later when it is withdrawn, the gas from the cache will be much richer in helium content, the processing time will be reduced, and immediate supplies will be available on short notice.

In using the vast potential storage space, the helium will be injected under pressure into one of the eleven producing wells of the Cliffside field. Helium is extracted from natural gas, but only a relatively small quantity of the latter is subjected to processing. Limited storage facilities have made it necessary to allow large quantities of natural gas to go to market, still containing helium. The Exell plant is processing natural gas from fields other than Cliffside. Cliffside has the richest helium content.

In constructing the Exell-Amarillo line, several new features were embodied—among them, the relatively new method of pressure welding. In this machine process, which does not require welding rods, the connecting ends of the pipe are heated to welding temperature and forced together by hydraulic pressure to form a dense and uniform weld.

By this process, a virtually unbroken 2-inch cylinder was extended for thirty-two miles, under rivers (which sometime have water in them), through valleys, and over elevations. But before being coated and wrapped to minimize corrosion, the line was filled with natural gas and carefully examined for leaks. In checking for leaks, every inch of the line was submerged and passed through a movable water trough. By using gas for internal pressure, the slightest leak was detected when the line was placed in water.

To guard against damage and loss of helium when inadvertent breaks occur, the line is equipped with a series of special valves, designed by a Bureau of Mines' employee, which close the pipe line automatically on each side of the break in case of sudden upswing in flow from the predetermined rate of the line. The valves prevent a loss of the entire volume of helium in the lines, limiting the leakage to the section between check valves.

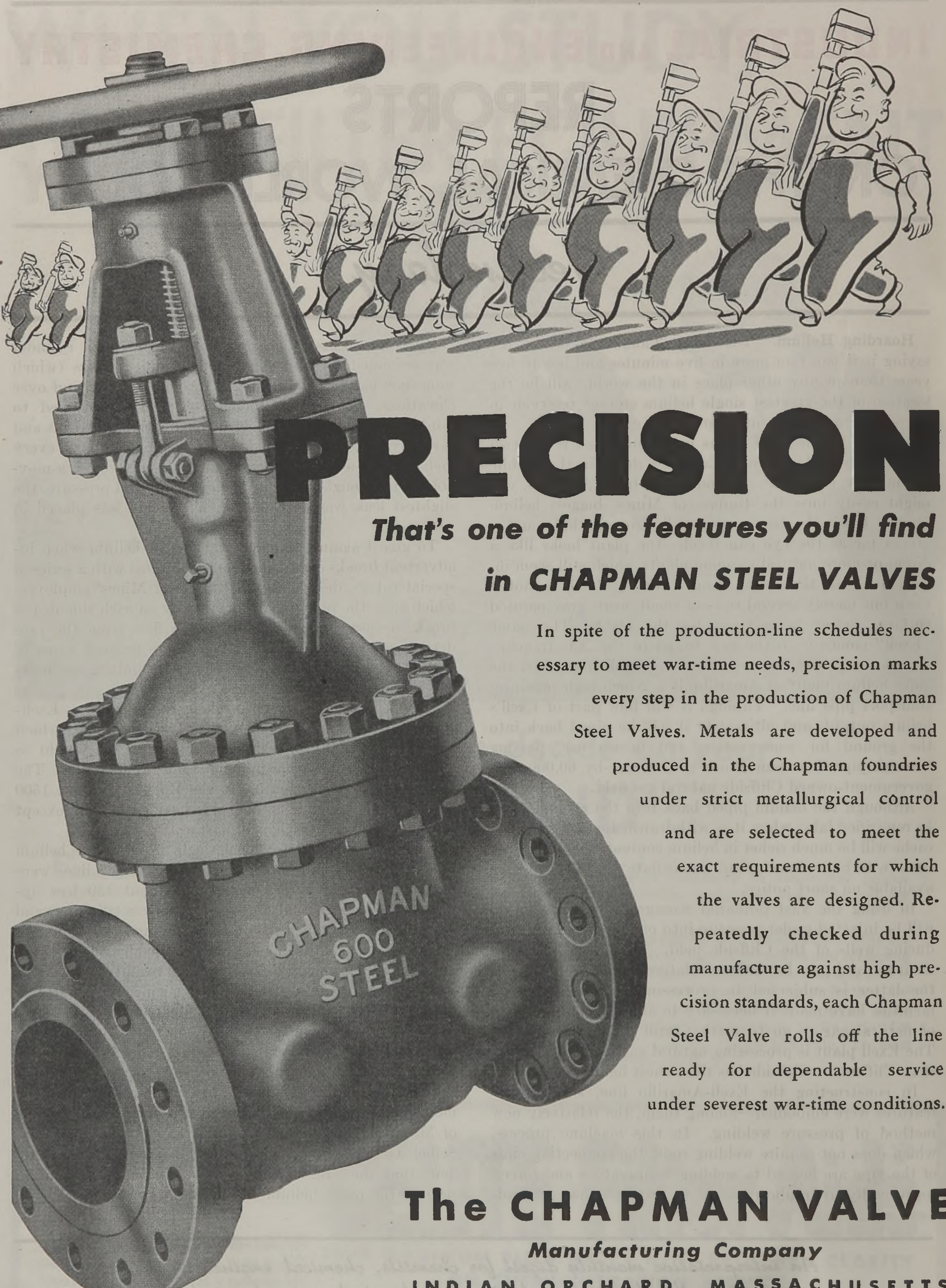
Special precautions were taken to guard the Exell-Amarillo line against floods of the Canadian River, which have broken many pipe lines lacking sufficient weight to keep them below the moving sand and water. The Canadian River, originating in the Rockies, is some 1500 miles long, as much as a mile wide near Exell, and, except for an occasional deluge, is almost as dry as a bone.

Instead of the conventional single crossing, the helium line was divided and two separate transmission lines were placed across the river, one looped about 150 feet upstream from the actual crossing to allow settling as sand and gravel are washed from under the line. As a further safeguard, each of the lines was surrounded by a 4-inch pipe and the annular space filled with cement to add more weight.

Hoarding helium in the ground in a concentrated status, as worked out by Bureau of Mines' experts, is a valuable war and postwar step. Despite continued demands for military use, Secretary Ickes expects more helium to be available in 1945 for nonmilitary purposes. He tells us that the Bureau's five plants are producing at a rate of more than twenty-five times that of prewar days. Bureau of Mines' experts at Amarillo and Exell, including C. W. Seibel, George Erlandson, and C. C. Anderson, are confident that the "Boss" will not be out on a limb in his promise of more helium for nonmilitary industries.

(Continued on page 8)

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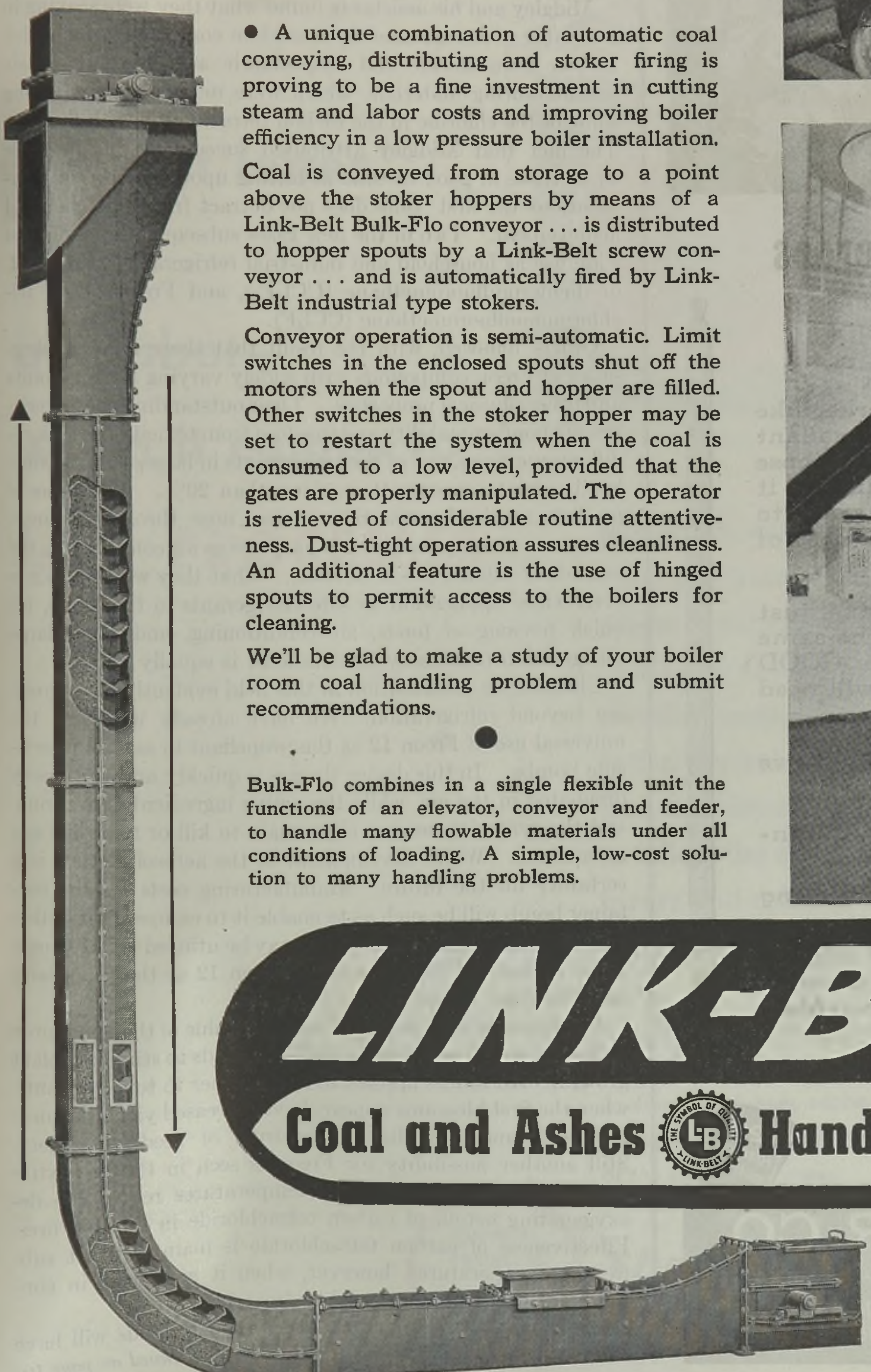

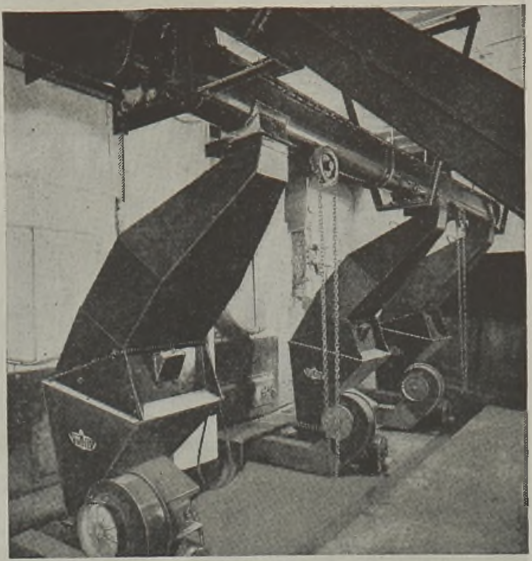

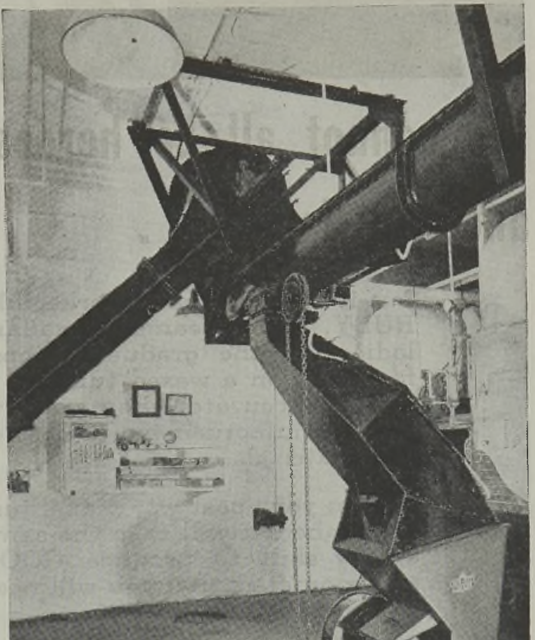

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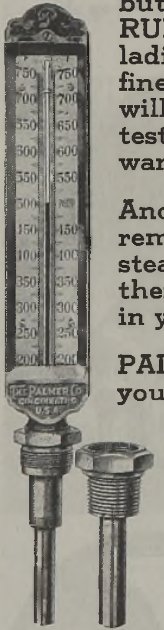

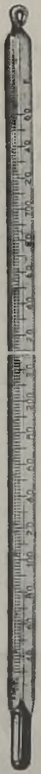

I. & E. C. Reports on the Chemical World Today

Technology

New Fluorine Refrigerants. The old Victorian idea that man is by nature metaphysical and arrogant and, hence, unsuited to the experimental method, is wholly refuted by the success which has attended experiments in new refrigerants. The late Thomas Midgley, Jr., and fellow workers were not metaphysicians, and they were arrogant only in a firm belief that chemistry could develop and supply refrigerants with desirable characteristics for particular purposes because of these peculiar properties.

Midgley and his assistants found what they were seeking in a number of halogenated hydrocarbon compounds, for which carbon tetrachloride and hydrofluoric acid were the basic manufacturing materials, which were modified by replacing some of the chlorine in the carbon tetrachloride with fluorine. The fact that Midgley attributed success in this instance to a stroke of good fortune in hitting upon the correct combinations the first time does not detract from this chemical achievement. Two of the new gases subsequently came into wide use as household and industrial refrigerants—Freon 12, or dichlorodifluoromethane (CCl_2F_2), and Freon 11, or trichloromonofluoromethane (CCl_3F).

Others followed, with the result that there is available a series of Freon compounds with widely varying boiling points and other physical properties. Their outstanding characteristics are nonflammability and freedom from toxicity. Dichlorodifluoromethane, one of the refrigerants in largest use, is odorless in air at concentrations of less than 20%. The vapor is nonirritating in all proportions to eyes, nose, throat, and lungs. The use of these gases for such purposes as air conditioning the interior of submarines is obvious. That they will experience even wider application as safe refrigerants in the home, for quick freezing of foods, air conditioning, and other large refrigeration machinery installations, is equally clear.

Chemistry's contribution in this field evidently is progressing beyond refrigeration. We have already witnessed the universal use of Freon 12 as the propellant in aerosol insecticide bombs. In this device the gas is quickly and harmlessly dissipated in the air, while the active ingredient, pyrethrum, and the synergist, sesame oil, remain to kill or repel flies and mosquitoes. Wider development of the aerosol method is a certainty for the future. Manufacturing costs for the container bomb will be such as to enable it to compete with other insecticidal sprays. Pyrethrum may be utilized for its knockdown values and killing powers, Freon 12 as the propellant, and Freon gas as the carrier.

Experiments have demonstrated the value of the same spray technique in the use of hormone compounds to stimulate plant growth. Hormones applied in this manner to tomato plants, when the first blossoms appear, have increased yields as much as 100% and provided larger fruit of seedless variety. Still another possibility for Freon is seen in the fire extinguisher field. Extremely low temperatures retard the deoxygenating action of carbon tetrachloride in fighting fires. Effectiveness of carbon tetrachloride is maintained at subfreezing temperatures, however, when it is utilized in conjunction with the halogenated hydrocarbons.

It must not be assumed that Freon compounds will have an uncontested market in these

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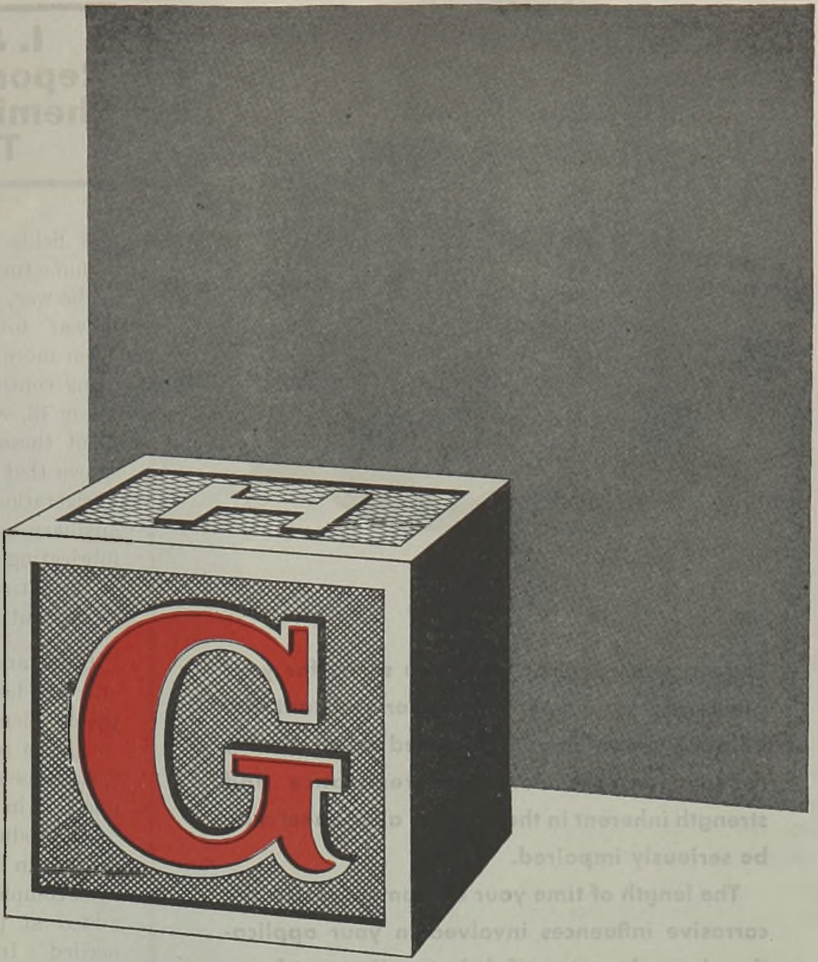
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I. & E. C. Reports on the Chemical World Today

Technology

new fields or even in refrigeration. On the other hand, manufacturers of Freon will be greatly fortified at the end of the war, with plant capacity for the Freons almost double prewar totals, through extensions and new facilities. Even more important is the fact that chemical research is being continued in this field, and that a new refrigerant, Freon 13, will be placed in postwar production to supplement those previously marketed. Pilot-plant trials have shown that it possesses great possibilities in low-temperature refrigeration. However, development of compressors and auxiliary equipment, study of the behavior of metals and lubricating oil at low temperatures, and further developments of insulating material must be completed before this new refrigerant will find general use.

Coke and Coal-Tar Chemicals. The by-product coke and coal-tar chemical industries are not, generally speaking, the recipients of much publicity these days; yet we must, if we pause to reflect, admit that coking operations come as close to being the heart of America's war effort as any other phase of industrial activity.

By-product coking operations, with a record of 73,618,000 net tons in 1944, are up 23% over 1940. Many old ovens have been completely rebuilt in the past four years and new ovens added at plants where more furnace coke was urgently needed. In addition, eight new plants have been completed; two are located in Texas and one in California, which raise to twenty-two the number of states producing by-product coke. An amazing total of 528 new ovens (not including old ovens completely rebuilt), with an annual coke capacity of 2,595,000 net tons, were built in 1944, raising the number of new ovens constructed since 1940 to 1988 with a yearly coke capacity of 10,844,000 tons.

Obviously most of the increased demand for coke comes from the tremendous wartime expansion of the iron and steel industry. Furnace requirements in 1944 took approximately 78% of the total. However, a substantial gain has been made in the quantity of coke used in the manufacture of water gas, used both as a fuel and as a starting point in chemical synthesis. The net increase in 1944 was 48% higher than that in 1940. The feverish expansion in ammonia synthesis to increase our explosives output still further should make this trend more pronounced in 1945.

Production of crude coal tar, ammonia, and coke-oven gas in 1944 followed the general pattern of coke production and reached levels never attained before; gains of 4, 5, and 5%, respectively, over 1943 were recorded. Although production of the primary by-products has substantially increased since 1940, the average yield of some by-products per ton of coal carbonized has declined because of increased oven temperatures and shorter coking period. Crude tar and ammonia production in 1943 fell short of the 1942 figures, although more coal was treated in that year. Production figure on crude light oil in 1944 has been withheld, but it is safe to assume that it is considerably above the 250,511,095 gallons of 1943. Ammonia liquor (in NH_3 content) recovery in 1944 was 63,329,677 pounds as compared with 56,938,798 in 1940.

(*Continued on page 12*)

Designed for longer life

TUBE-TURN welding fittings contribute to longer life for any piping system in which they are used—by their greater strength, their smooth walls of uniform thickness, and their resistance to wear and corrosion. Welded piping connections are permanently tight and leakproof, and the whole system becomes virtually a single pipe. Threading, caulking, gasket replacement and bolt tightening are eliminated, thus doing away with potential causes of trouble in systems where other type fittings are used.

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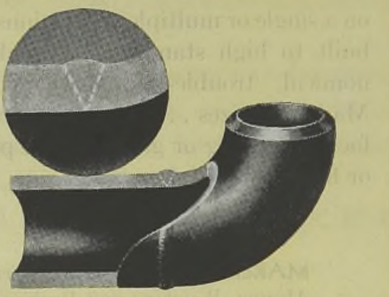

TUBE-TURN *Welding Fittings and Flanges*

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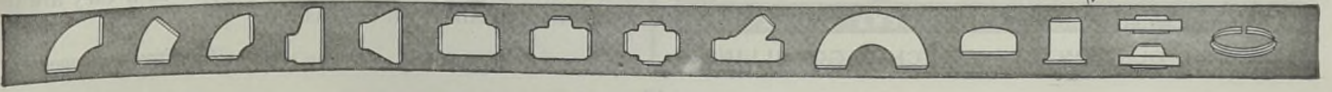

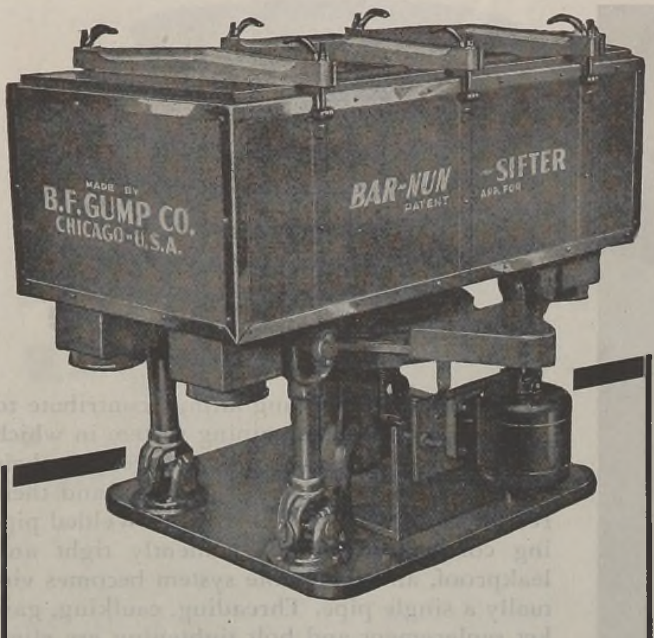

I. & E. C. Reports on the Chemical World Today

Technology

The 1945 outlook for by-product coke and coal-tar chemicals is uncertain but probably good. The impending end of the German war machine may bring some decline in military requirements for steel, but what is not needed will certainly find use in civilian goods. There should be no letup in the need for coal-tar chemicals which are mostly in short supply; some are really in the critical category.

The long-term pull is more uncertain. Will there be a sustained postwar demand for nearly 100 million tons of steel a year? Some can see consumption down to 70 million. One interesting angle of the steel and, hence, the coke industry will be the fate of the steel plants of the Southwest and the West Coast. War Production Board is still skeptical about the Texas plants. In the West you get arguments on both sides that either Geneva Steel (now operated for the Government by U. S. Steel), located in Utah, or Fontana (operated by Kaiser) located near Hollywood, Calif., will be operated in the postwar period. The more optimistic westerners think that Geneva's 1,300,000 tons of ingot steel capacity and Fontana's 700,000 can both be used, but are somewhat hazy as to how the West wants to utilize this steel productive capacity. In the fight to get the plants, it is probable that no holds will be barred.

No. 1 Corrosion Problem. The Southwest's fabulous natural gas industry has a number one corrosion problem which is giving considerable worry, for who the dark-eyed villain is, has not yet been determined. On high-pressure wells (2000 pounds or better) some rather mysterious corrosion effects were more or less accidently discovered close to the wellheads just about two and a half years ago. Nothing like them has been noted on low-pressure wells, but the industry is particularly concerned because there are definite indications that corrosion is spreading. There are reasons to suspect certain of the fatty acids.

A subcommittee of the Natural Gasoline Association of America is working on the problem in conjunction with a subcommittee of the American Petroleum Institute and a subcommittee of the National Association of Corrosion Engineers. The N.G.A.A. committee has retained one well-known research organization in an attempt to find the mysterious corrosive and, once it is identified, to provide the ways and means of nullifying the action.

Jet Propulsion. Our national pride in research was smitten when the Germans first zoomed over the skies in Europe with jet-propelled planes. Somehow it seemed that the United States should have been the leader in this field and the first to do the zooming. We recently heard the reason why. The American research teams recognized the necessity of first developing high-temperature alloys, and this they have done (I. & E. C. Reports, February, 1944, advertising section page 5). The Germans, however, have not done this. Their planes require special cooling apparatus, an encumbering disadvantage which will have to be junked if they are to compete with American designs.

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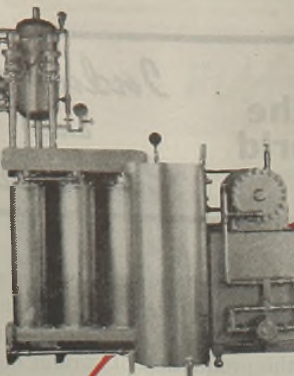
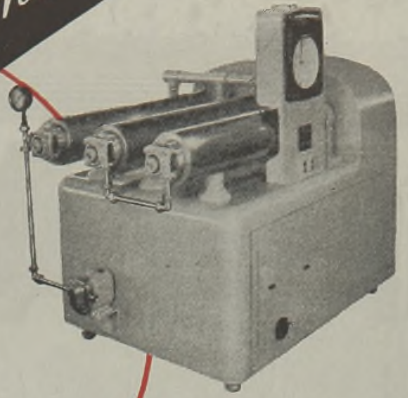
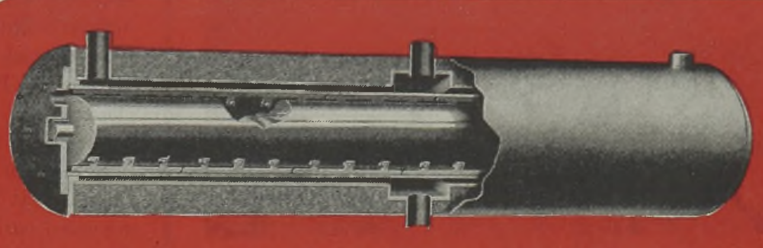
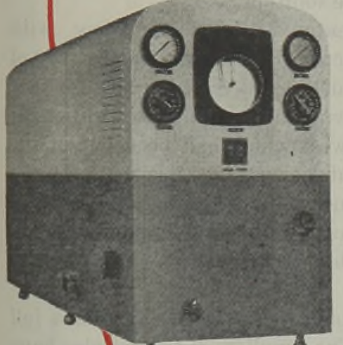


Variations upon a theme





SIMULTANEOUS HEAT TRANSFER AND PROCESSING IN A CONTINUOUS, CLOSED, CONTROLLED SYSTEM



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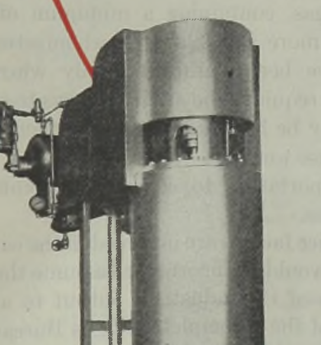

THE Votator*

A GIRDLER PRODUCT

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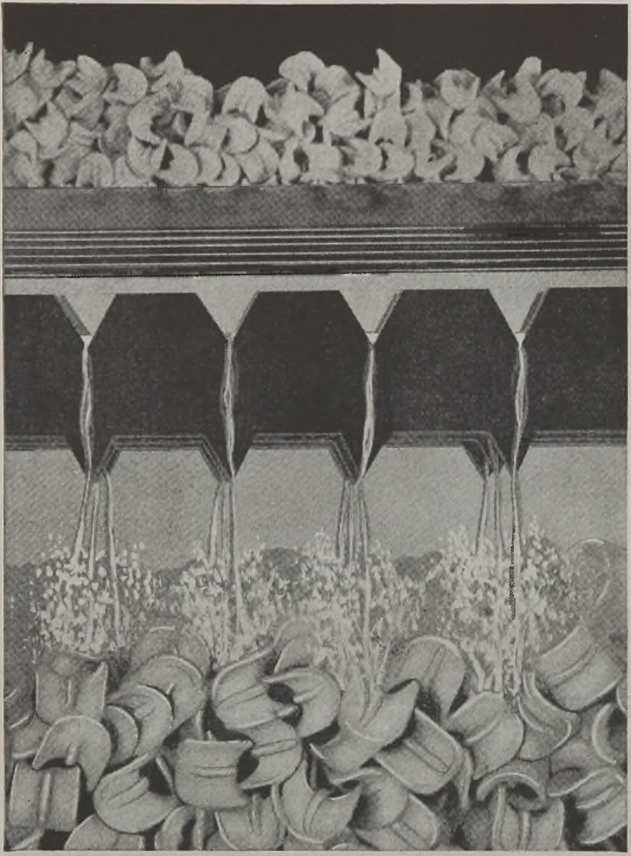


I. & E. C. Reports on the Chemical World Today

Industry and Commerce

Carbon Black Shortage. When several top war agencies get into a perspiring huddle over one supply shortage, while so many other things are deficient, it must be serious. Despite a large increase in the production of carbon black, the supply has fallen so far behind rubber and tire production that the Government recently was forced to curtail operations at tire factories from seven to six days a week. Its use was also war-restricted. Congress became alarmed, and the Mead Committee early in March set the wheels in motion for an inquiry into reasons for the shortage.

Supplies of carbon black for colloidal dispersion in synthetic rubber are being increased steadily through plant construction and extensions, but probably will not be wholly sufficient until the expansion program is complete late in 1945 or early in 1946. Congressional inquiry and all the efforts of WPB, OPA, DSC, WMC, PAW, OWM, and War Department to untangle the problem probably will contribute little to an immediate solution.

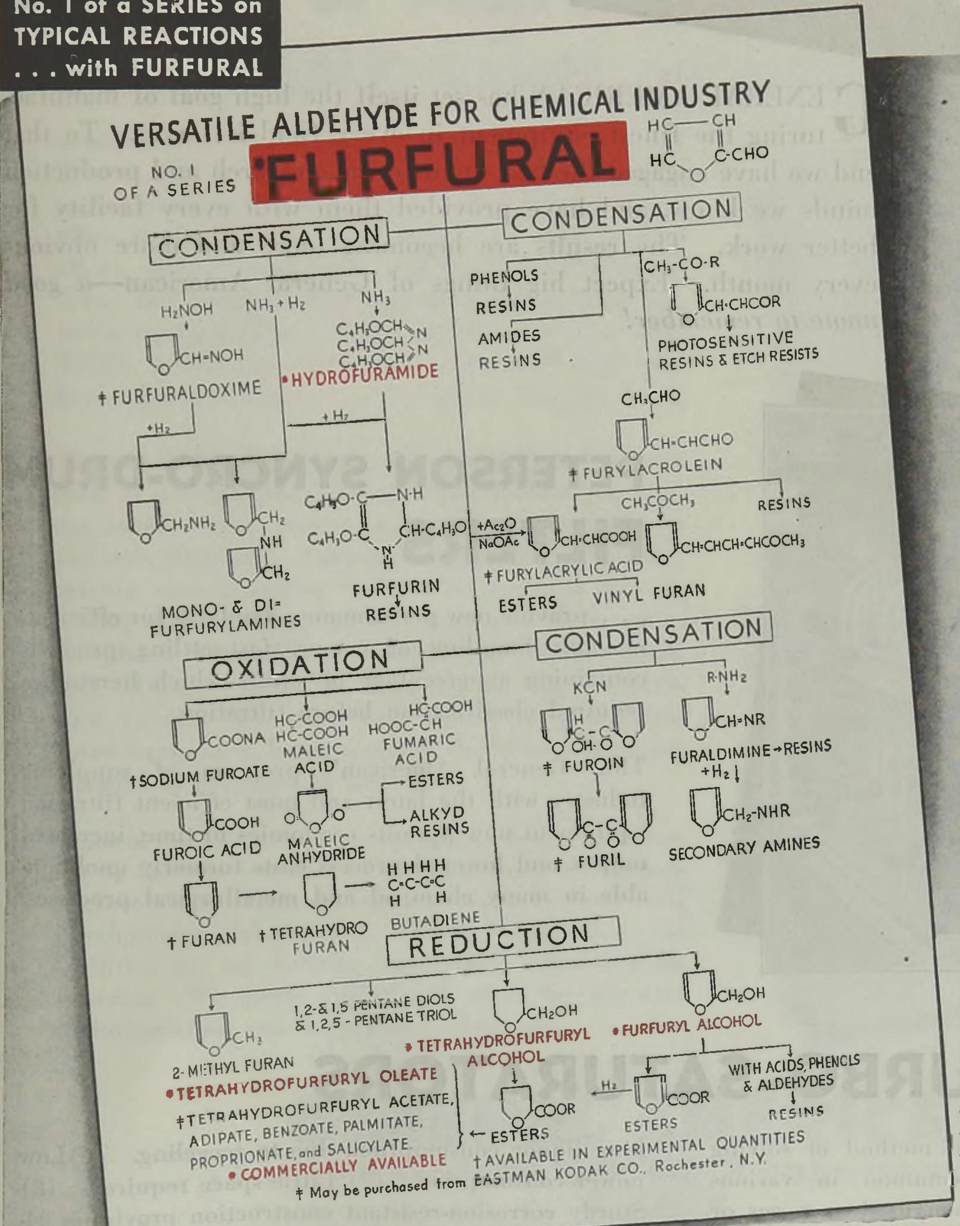
Newspaper columnists entered the controversy with charges that the War Production Board stood in the way of increased carbon black production by vetoing plans for new construction, and of approving instead the restoration of older facilities in the Southwest which had been out of the picture because of higher materials costs. The raw material in the manufacture of carbon black is natural gas, and some producers naturally sought an upward adjustment in carbon black ceilings to compensate for the higher costs at such plants.

The Office of Price Administration has come in for a full share of criticism as well. The suppliers of the gas also have demanded ceiling advances, and the OPA has granted such requests only in part. In one instance it approved an increase of 5 cents per 1000 cubic feet to the producer of sweet gas, while four or five companies selling sour gas were permitted to boost prices to carbon black manufacturers a maximum of 3.5 cents. Sweet gas, containing a minimum of sulfur, is usually considered more suitable for carbonization. These price increases have been authorized only where existing carbon black plants required the additional gas to supply new facilities, and it may be hard to explain to others that those obtaining the increase were not "teacher's pets". More pipe lines for gas transportation to consuming points are also needed in some areas.

Other cost and price factors are involved in the carbon black controversy, but it would be incorrect to assume that they are retarding expansion of the industry's output to any extent. Even on the basis of the incomplete Census Bureau data, we were producing carbon black in January at an annual rate of 457,500,000 pounds; WPB authorities contend that the figures for both channel and furnace types are currently close to 900,000,000 pounds annually. At the end of the summer we will be turning them out at a yearly rate of more than a billion pounds, compared with a few hundred million in prewar years.

Disputes over costs and government policies do not explain the carbon black shortage one tenth as much as the rubber

(*Continued on page 18*)


VERSATILE ALDEHYDE FOR CHEMICAL INDUSTRY
NO. I OF A SERIES
•FURFURAL
HC—CH HC C-CHO O
CONDENSATION
H₂NOH
NH₃ + H₂
NH₃
CH=NOH
‡ FURFURALDOXIME
C₄H₃OCH=N C₄H₃OCH<N C₄H₃OCH
• HYDROFURAMIDE
+H₂
+H₂
CH₂NH₂
CH₂ NH CH₂
MONO- & DI- FURFURYLAMINES
C₄H₃O-C—N-H C₄H₃O-C CH-C₄H₃O N H
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AMIDES
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PHOTOSENSITIVE RESINS & ETCH RESISTS
CH₃CHO
CH=CHCHO
‡ FURYLACROLEIN
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CH=CHCOOH
‡ FURYLACRYLIC ACID
CH=CHCH=CHCOCH₃
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VINYL FURAN
OXIDATION
COONA
† SODIUM FUROATE
HC-COOH HC-COOH
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MALEIC ANHYDRIDE
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ALKYD RESINS
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BUTADIENE
† FURAN
† TETRAHYDRO FURAN
CONDENSATION
KCN
R-NH₂
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‡ FUROIN
CH=NR
FURALDIMINE→RESINS
+H₂
C-C O O
‡ FURIL
CH₂-NHR
SECONDARY AMINES
REDUCTION
CH₃
2-METHYL FURAN
1,2-& 1,5 PENTANE DIOLS & 1,2,5 - PENTANE TRIOL
CH₂OH
• TETRAHYDROFURFURYL ALCOHOL
CH₂OH
• FURFURYL ALCOHOL
• TETRAHYDROFURFURYL OLEATE
‡ TETRAHYDROFURFURYL ACETATE, ADIPATE, BENZOATE, PALMITATE, PROPRIONATE, and SALICYLATE
← ESTERS
COOR
H₂
COOR
ESTERS
WITH ACIDS, PHENOLS & ALDEHYDES
RESINS
• COMMERCIALLY AVAILABLE
† AVAILABLE IN EXPERIMENTAL QUANTITIES
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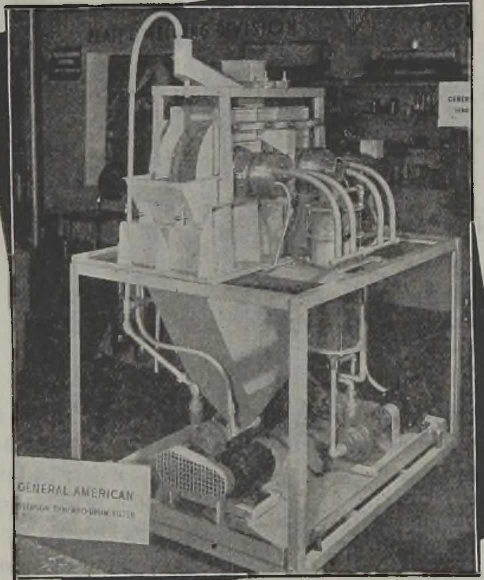

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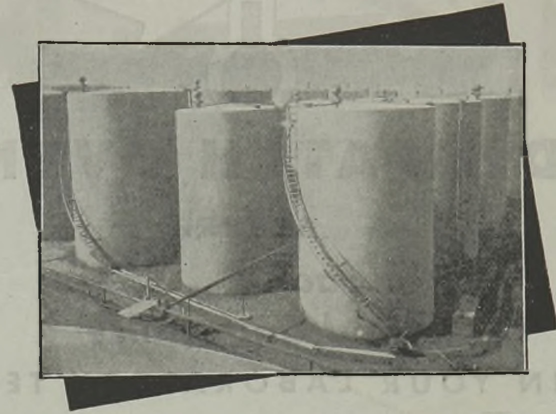

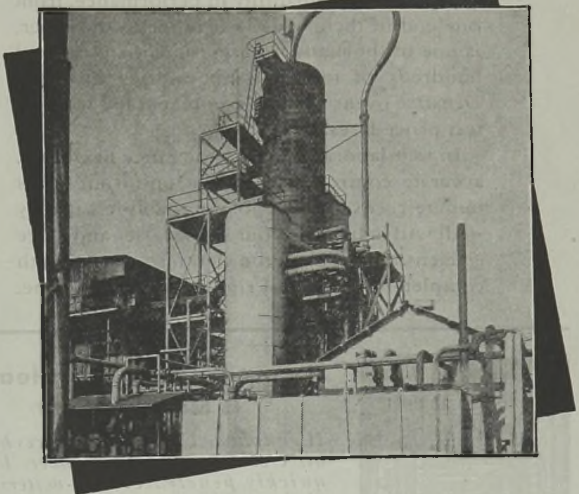

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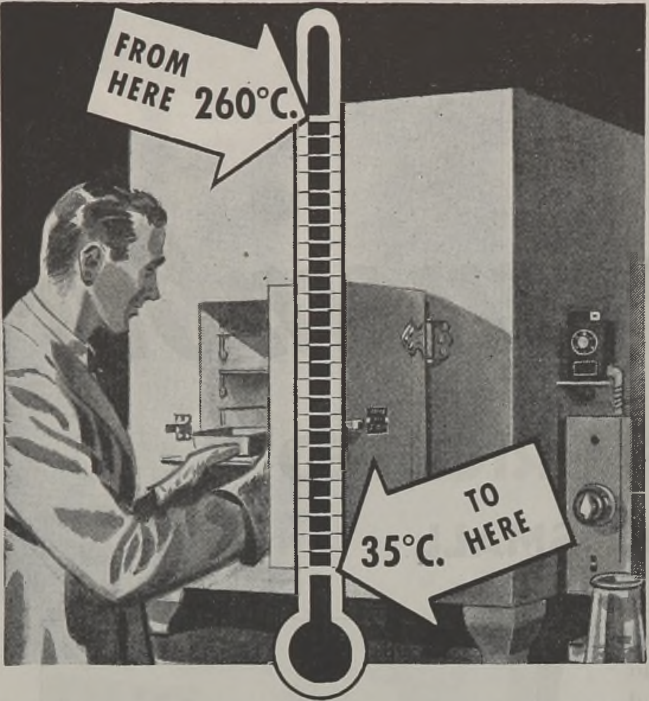


I. & E. C. Reports on the Chemical World Today

Industry and Commerce

program's requirements. As compared with the quantities which formerly entered natural rubber, synthetic has to be heavily loaded with carbon to obtain toughness, abrasion, tear resistance, and other properties. Rubber technicians point out that the addition of carbon black increases the tensile strength of natural rubber 10 to 15%, but that in synthetics such as GR-S the tensile is increased tremendously. The Government has placed its 1945 synthetic requirements at 1,000,000 tons, and those for 1946 at 1,200,000.

New carbon black capacity came into production during the first quarter, and still more will come in during the second and third. The assertion that no large increases can be attained until 1946, therefore, are not entirely correct. One large producer is trebling production over prewar totals, and another who accounted for 189,500,000 pounds in 1944 is increasing capacity sufficiently this year to raise this figure to 280,000,000 pounds annually. Total new capacity during 1945 alone is estimated at 170,000,000 pounds. Up to the end of November about 100,000,000 pounds of furnace-type black had been added to production; but from this point on more capacity devoted to the channel black can be expected, thereby providing a better balance as to grades.

Technology has not been standing still in carbon black processing, meanwhile. Under one ingeniously devised method the production of carbon black is increased through the use of supersonic vibration or very high frequencies. The essential features of this process, which is said to increase yields from 10 to 15%, are covered in several patents. In the standard channel process, natural gas is burned under conditions of insufficient oxygen for combustion, and the finely divided particles of carbon are deposited upon a revolving plate or drum. In the newer method gas is burned in a reducing atmosphere, and the carbon particles are mechanically shaken out of the flame by subjecting the latter, the atmosphere, and collector plate to supersonic vibration at frequencies higher than 300μ. The original work on this method was conducted at Antioch College.

New Source for Wax. Montan wax may now be added to the long list of those products imported before the war but now produced in this country. Fairly considerable quantities of montan were brought in from Germany and elsewhere in normal times for the manufacture of polishes, candles, phonograph records, paper-sizing preparations, paints, adhesives, and the like. Through extensive research at its laboratories in Belleville, N. J., the American Dyewood Company has perfected a process for producing montan wax from American lignite, and a plant for the purpose has been erected at Malvern, Ark. An interesting side light is that colors and pigments may also be provided from lignite through the same process. Montan is a dark brown wax with melting points between 80° and 90° C., and usually contains the ester montanic acid along with a large percentage of hydrocarbons. It is, in fact, more of a hydrocarbon than it is a wax, but its uses in industry are well established. In 1939 we imported 7,000,000 pounds.

vertisement. Prepared Monthly by U. S. Industrial Chemicals, Inc.

U.S.I. CHEMICAL NEWS

April ★ A Monthly Series for Chemists and Executives of the Solvents and Chemical Consuming Industries ★ 1945

Current Shortages Rouse New Interest In Natural Resins

Spectacular Pacific Successes Seen Hastening Large-Scale Availability

Synthetic resins, like other commodities required in the war effort, have been subjected to varied restrictions as a result of constantly changing Government specifications and raw-material shortages. The first serious shortage was in glycerine, which affected the availability of many synthetics. Then, when glycerine again became available, the demand for phthalic-alkyd type resins and paints by the armed forces increased to such an extent that WPB had to place these resins under allocation.

Next came allocation of phenolic resins and, later, of the raw materials required for maleic and other specialty resins. Each move reflected the changed requirements of the military and each, of course, affected the availability of the different resins for essential civilian uses. The only conventional synthetic resin that remained free of Government restrictions as to raw materials was Ester Gum; but here the quantities available were consumed in high-rated uses so that, in effect, even it could not be considered for civilian use.

New Resins Made

Protective coatings manufacturers were forced to shift from one type of resin to another, just as the resin manufacturers were forced to shift raw materials. U.S.I., for example, found itself turning "technological handsprings" in its research laboratories and plants to make available, first, the urgently needed war resins, and then to provide new and previously untried types for varied purposes. These purposes ranged all the way from resins for use as shellac substitutes and as replacements for phthalic and alkyd types, to resins that could be used in place of the natural resins usually imported from Far Eastern areas occupied by the enemy.

Rosin Allocated

During the past month, WPB has placed rosin under allocation, setting individual consumption and inventory quotas for specified industries. This has forced the use of resins that contain either very little rosin or none at all. Through the importation of currently available natural resins, U.S.I. has kept stocks available of Congo Gum, Kauri Gum, and Accroides (Yacca or Red Gum), none of which contain rosin. Of these types, the most widely used is Congo Gum, which, until two months ago, was available for use without restriction. However, in March, due to the shortage of rosin and the resulting heavy demand for all types of rosin-free resins, the WPB placed all natural resins under Allocation Order M300—Schedule 96.

Importation of the largest possible quantities of Congo Gum, Kauri Gum and Accroides are being continued. It must be remembered, however, that war-time conditions present difficulties in gathering the gum and shipping it. It is to be expected that the spectacular advances of our armed forces in the Pacific area will open the important gum pro-

(*Continued on next page*)

Sees Hope for Early Return of Many Prewar Denaturants

Freeing of Axis-Held Territories Already Reflected in Increased Supply of Essential Oils Used in Drugs and Cosmetics

Kwang-Si Province, Calabria, Java, Madagascar, Spain, Siberia—such were the widely scattered areas of the world upon which the alcohol industry depended for denaturants used in alcohols for making lotions, shampoos, bay rum, mouth washes and the rest. Starting with the fall of France, many of these areas fell into enemy hands. Spain presented political difficulties. In Siberia and Australia, as in America itself, available manpower had to be concentrated on the production of allied war materials.


Harvesting citronella grass in Ceylon. Oil of citronella is the starting point for the synthesis of menthol.

Measures taken by alcohol producers, the Treasury Department and Central and South American countries have, to a surprising extent, alleviated many of these shortages. U.S.I., for example, has followed a system of interplant transfers which, while costly, has helped to meet customers' needs equitably.

Italian Shipments Start

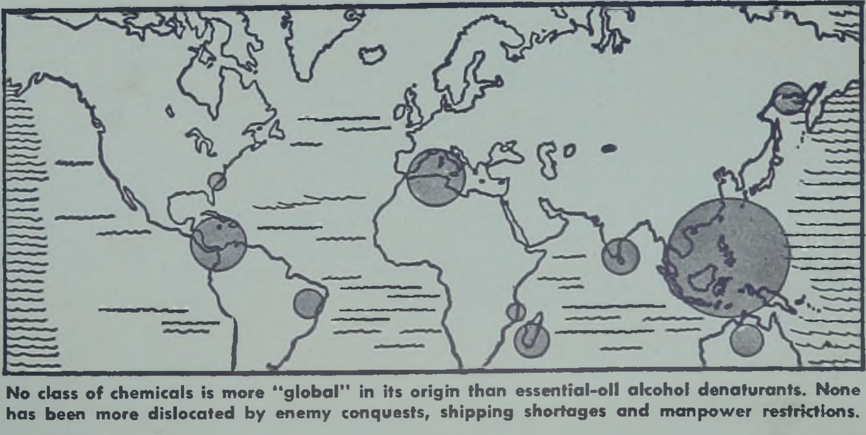
However, the shipment of 80,000 pounds of oil of bergamot from Italy, last year, was the signal for new hope for the early return of the many essential oils which cannot be produced economically in the Western Hemisphere. The freeing of France and the rapid rolling back of the Japs in the Pacific has given fresh impetus to these hopes. Here, briefly, is the current situation as it affects the more important odoriferous denaturants:

Oil of citronella — Important as the starting point for the synthesis of menthol, this oil came principally from Java. Currently, an inferior grade is available from Ceylon. Guatemala and other Central American Countries have started growing citronella grasses, but it will take a year or two to get real production.

Mint oil — This source of natural menthol is now coming in large quantities from Brazil. While higher in price than the product originally obtained from Japan, natural menthol is now cheaper than the product synthesized from oil of citronella.

Oil of cassia — This essential oil (USP), which is used as a substitute for oil of cinammon, was produced exclusively in Kwang-Si Province, China. Currently synthetic oil of

(*Continued on next page*)


No class of chemicals is more "global" in its origin than essential-oil alcohol denaturants. None has been more dislocated by enemy conquests, shipping shortages and manpower restrictions.

Claisen Reactions Yield Superior Drying Agents

Drying properties greatly superior to those found in naturally occuring oils, such as linseed, tung and certain fish oils, are claimed for a series of new esters described in a recent patent.

These esters are generally prepared by condensing, via a Claisen reaction, esters derived from the glycerides of natural oils such as tung, menhaden and sardine. These esters are heated in the presence of a condensing agent such as sodium hydride or U.S.I.'s Sodium Ethoxide until the conversion to the sodium derivative of the beta-keto-ester is substantially complete. The reaction mixture is then acidified and washed free of salt, acid and other soluble impurities. The water and diluent are removcd by distillation and the desired product recovered as a residue.

April ★ U.S.I. CHEMICAL NEWS ★ 1945

Natural Resins

(Continued from preceding page)

ducing centers in the Philippines, Netherlands, East Indies and Singapore — much sooner than we once thought. The availability of these important resins will alleviate continuing shortages of rosins and synthetic resins without placing an additional strain on our domestic manpower.

Removes Fatty Acids by New Technique

Vegetable and animal oils for many uses are said to be freed from color, lipoids and free fatty acids by a technique which uses a vacuum neutralizer, but no heat.

The oil to be treated is first washed with water. After agitation, the mixture of oil and water is allowed to stratify, the lipoids being drawn off as part of the water layer. The oil is made color-free by mixing with clay and filtering.

Rid of lipoids and color, the oil is treated with a mixture of ethanol and sufficient sodium hydroxide to saponify the free fatty acid, the final reaction in this step taking place as the mixture is sprayed, under vacuum, into a neutralizing chamber. The result of this reaction is alcohol soap and colorless oil, free from lipoids and fatty acids. Alcohol is recovered from the residue by distillation, leaving a by-product of relatively high-grade soap stock.

New Dry Mounting Tissue Uses Phthalates and Alcohol

A new type of dry mounting tissue, used to produce fast, flat mounts of photographs and the like, is described as overcoming the common tendency to "block" or stick together in the package. The new tissue, described in a recent patent, is coated with a thermoplastic adhesive which does not become tacky at temperatures below 125 F., and therefore is non-adhesive at normal room temperatures. The adhesive heat seals, however, when pressed with an iron maintained at 200 to 220 F.

The adhesive consists essentially of cellulose acetate butyrate, a compatible plasticizer, such as diethyl or dibutyl phthalate, and an alkyd resin. The adhesive may be applied to the tissue from a melted mixture or in a benzene-denatured alcohol solvent.

Prewar Denaturants

(Continued from preceding page)

cassia, denaturant grade, is substituting for this substitute.

Camphor — Synthetic camphor has been in large-scale production in this country ever since the Japanese monopoly was broken in the early 30's. However, its important uses in photographic film, plastics, etc., made it hard to get now.

Oil of lavender — When the price of this product of Southern France skyrocketed, the Treasury Department authorized the substitution of domestic oil of cedar leaf. It is hoped that lavender will soon again be available from France.

Oil of bay — This essential ingredient of the familiar bay rum is a product of Puerto Rico and the Virgin Islands. It is now being imported without serious difficulty.

Domestic products — Oils of sassafrass, turpentine, pine, wintergreen, peppermint and cedar leaf were, fortunately, in production in this country long before the war. However, the shortage of manpower and the needs of our armed forces have combined to seriously limit the use of these oils as denaturants.

Separating clove buds and stems on far-off Zanzibar. Oil of cloves also comes from the French Island of Madagascar.

Prolonged Penicillin Action

Following research in the Naval Medical Corps, it is indicated that the effective action of a mixture of penicillin and beeswax-peanut oil lasts much longer than penicillin alone. Action is still further prolonged by application of an ice-bag at the point of injection.

TECHNICAL DEVELOPMENTS

Further information on these items may be obtained by writing to U.S.I.

To seal waterproof bags, four adhesives are offered. Different characteristics claimed for each adapt them to four different types of jobs. They are said to meet Army-Navy packaging specifications. **(No. 921)**

USI

A range of filter aids is offered for tasks such as clarifying beer, refinery products and pectins. They range in size from one designed to remove colloidal matter of less than 0.1 micron diameter, up to those of several times that pore size and flow rate. The aids are milled from finest diatomaceous silica. **(No. 922)**

USI

Soap that lathers better, and requires less soap substance, is promised by the processor of a new colloidal clay, offered for use in soap manufacture. **(No. 923)**

USI

A new rolling-oil additive, for the metal working industry, is designed to blend with mineral oil at room temperature, and to be modified by adding kerosene. This refined fatty ester additive can be combined in proportions of 3 to 5 per cent of the mineral oil. **(No. 924)**

USI

Rigid synthetic rubber products of high electrical resistance can be produced by incorporating a new resin substitute for carbon black, according to an announcement. Proper mixtures of the three grades of the new resin are said to impart desired qualities of rigidity, hardness, elongation and tensile strength. **(No. 925)**

USI

A new wetting agent, claimed to contain no oil and only a trace of inorganic salts, is said to be particularly adapted to tasks such as scouring wool, wetting back dried skins, and in fulling soaps to assist rinsing, etc. **(No. 926)**

USI

A new adhesive, which should provide time and labor savings in merchandise handling, is designed to hold paperboard and wooden boxes together in unit loads. It is said to combine high shear strength with low tensile strength, thus preventing slippage during transit, yet making it easy to separate packages at their destination. **(No. 927)**

USI

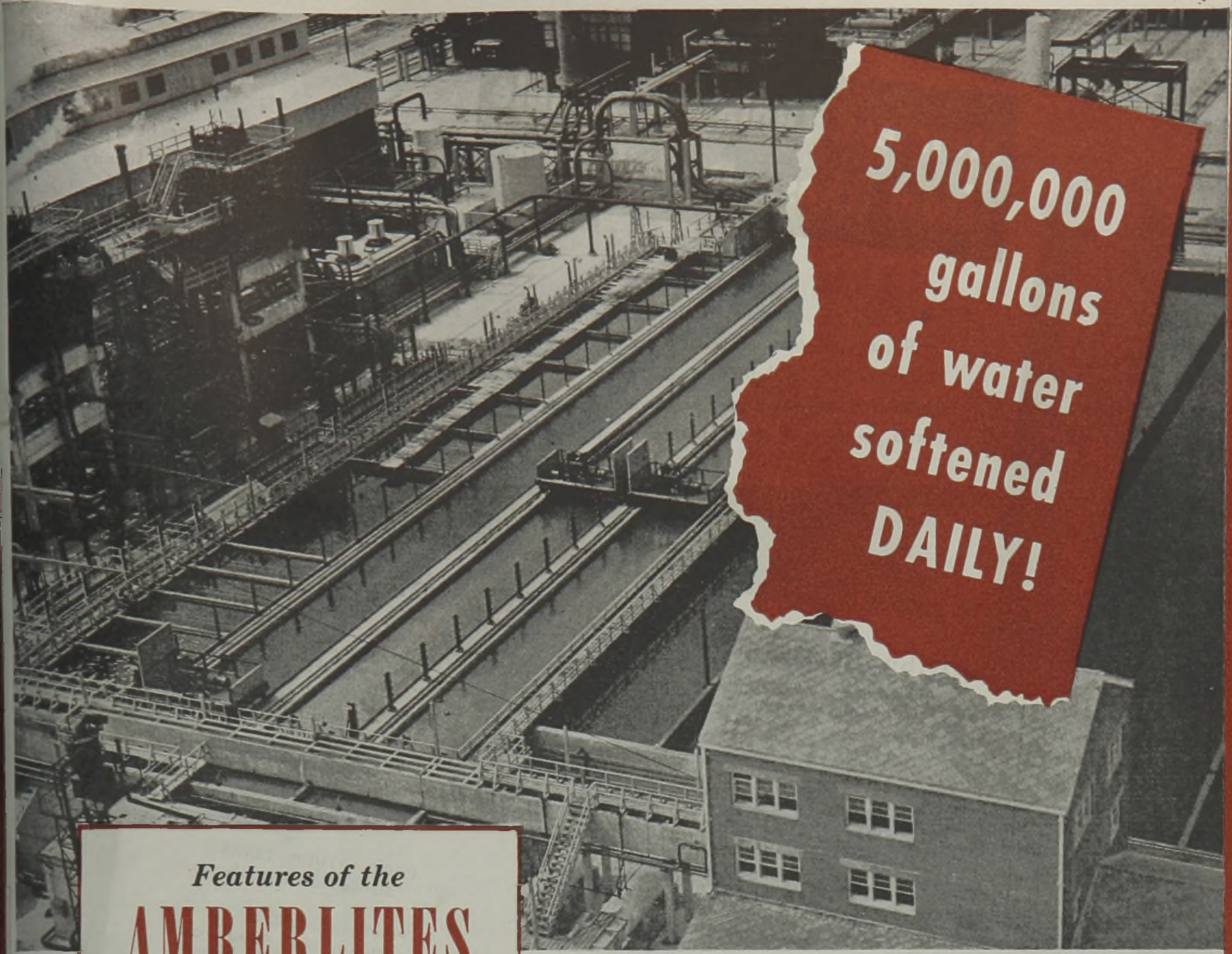
A fire- and shock-resistant plastic, that is said to generate no toxic gases when heated, and to be easily molded, has been developed. Key to the unusual properties of the new plastic is the use of asbestos instead of organic compounds as a filler. **(No. 928)**

USI

A new glass is being manufactured to withstand operating temperatures up to 650 F and thermal shock to 400 F. It is said to have four times the strength and six times the shock-resistance of plate glass, and is suggested for use in tanks for acids, alkalis and solvents. **(No. 929)**

USI

To recover valuable metals from waste solutions is the stated function of a new process using anion exchange resins. **(No. 930)**



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● Typical of the accomplishments of the AMBERLITE Ion Exchange Resins is the large-scale water softening installation at the Neches Butane Products Company plant, illustrated above. The large quantities of softened water required in the manufacture of butadiene are produced by the six 427 cu. ft. AMBERLITE softeners, shown at left center.

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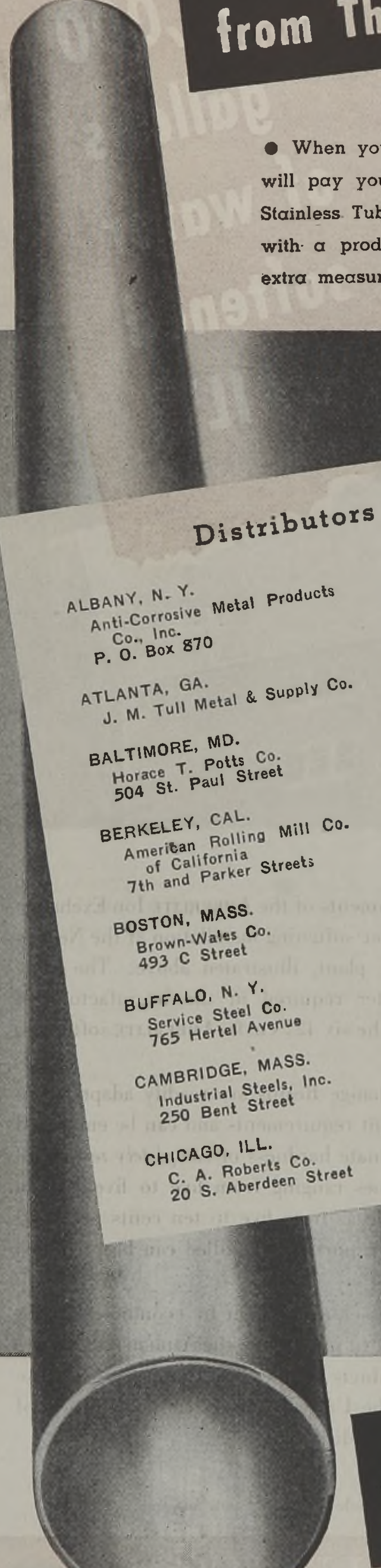

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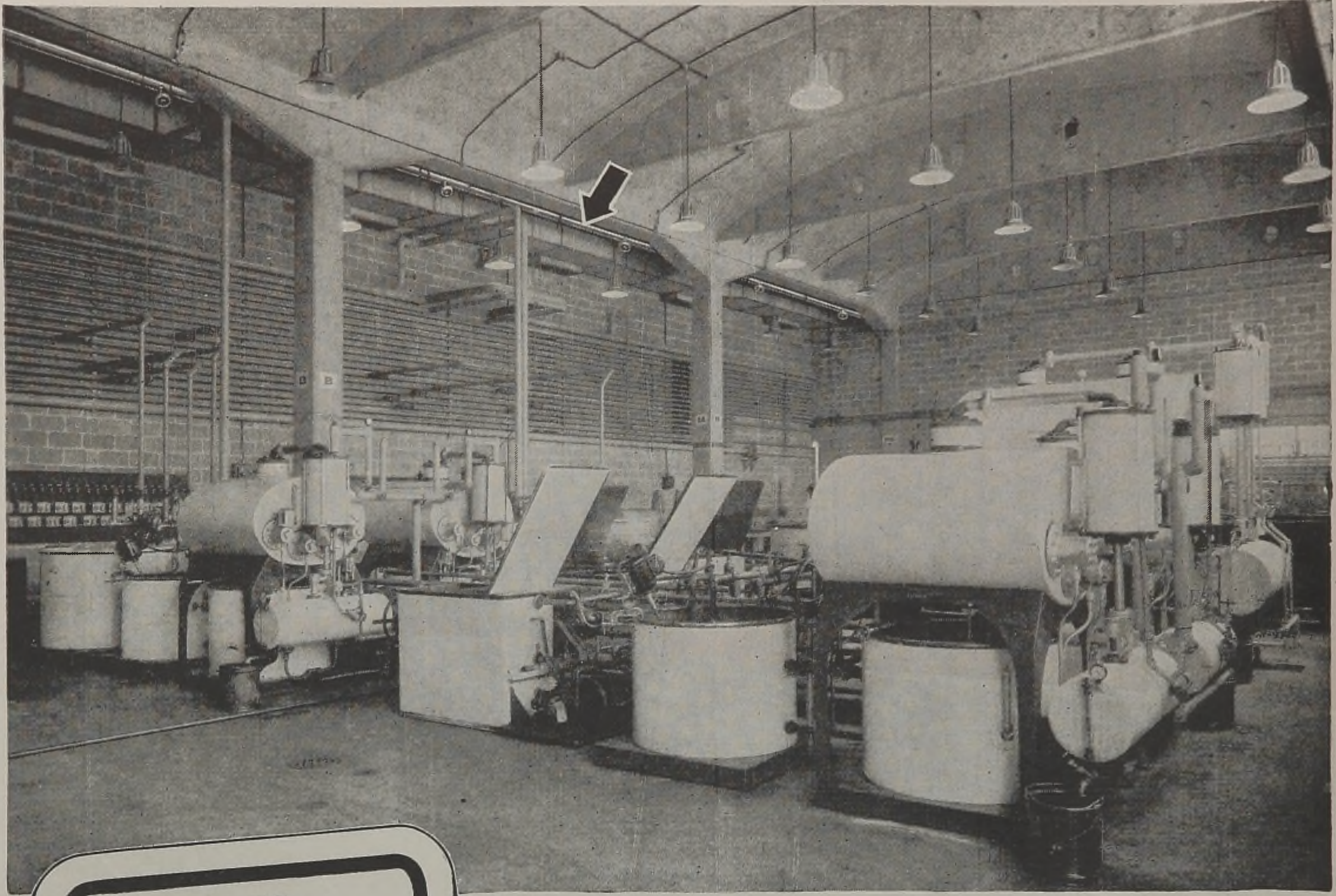
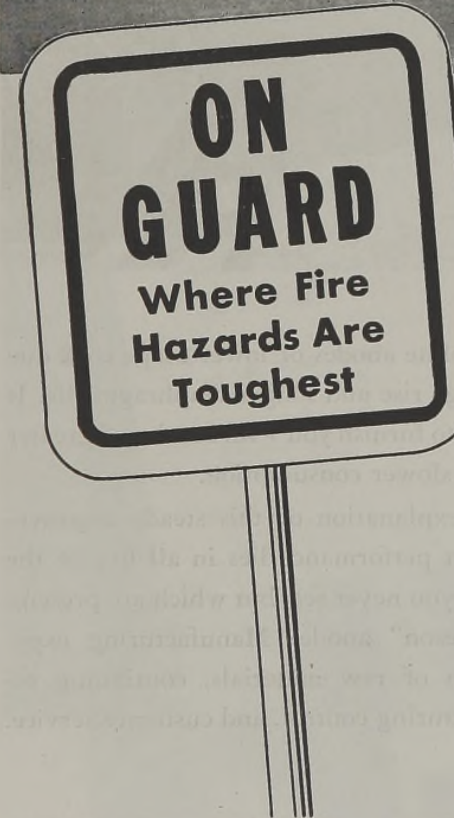
In Canada: Canadian National Carbon Company Limited, Welland, Ontario

KEEP YOUR EYE ON THE INFANTRY . . . THE DOUGHBOY DOES IT!



This oil reclamation plant is just one of 9 huge rooms protected by a single Cardox System



Cardox Fire Extinguishing Systems Give New Protection Scope with POUNDS or TONS of Carbon Dioxide

Inexpensive carbon dioxide is widely recognized as the fastest non-damaging fire extinguishing agent. Through Cardox methods of control and engineered application, carbon dioxide is supplied instantly . . . in *pounds* for small fires, in *tons* for large ones . . . to give new protection against a wide variety of indoor and outdoor hazards.

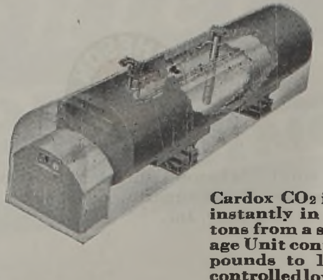
Effective Coverage for One Hazard or Many

The enhanced extinguishing performance of Cardox engineered applications of carbon dioxide for effective coverage of one hazard or many is due to a combination of basic factors: From ¼ to 125 tons of Cardox CO_2 . . . stored at 0°F and 300 p.s.i. in a single storage unit . . . is readily available for mass application at high rate, and for total flooding (when necessary) of large areas, *with ample reserve* for new emergencies. It has uniform extinguishing characteristics regardless of plant or atmospheric conditions. It provides high CO_2 "snow" yield for increased cooling effect upon fire zone and combustible. This heavy CO_2 snow yield also provides effective projection through relatively great distance . . . even outdoors through strong winds.

On the basis of this enhanced performance, Cardox Fire Extinguishing Systems have been given many of Industry's toughest peace-time and war-time fire protection assignments.

Bulletin 1735 should be in the files of everyone responsible for fire protection in industry. Ask for a free copy today on company letterhead.

CARDOX CORPORATION
BELL BUILDING • CHICAGO 1, ILLINOIS
New York • Boston • Washington
Detroit • Cleveland • Atlanta • Pittsburgh
San Francisco • Los Angeles • Seattle



Cardox CO_2 is supplied instantly in pounds or tons from a single Storage Unit containing 500 pounds to 125 tons at controlled low temperature of 0°F and 300 p.s.i.

CARDOX
CO_2 FIRE EXTINGUISHING SYSTEMS

"BOY— *bring me a pipe stretcher!*"

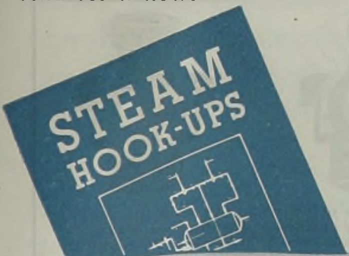
Unreasonable demands are made on the steam engineer every day, and many's the time he would like to call on his helper for tools that would enlarge the capacity of his lines, heating coils, and even the boiler.

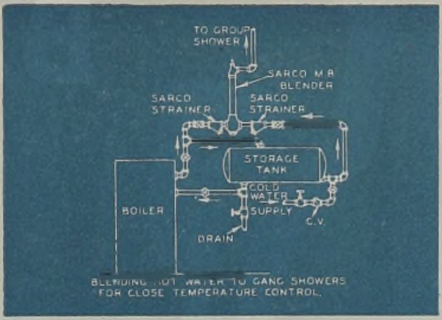
The actual fact is that, if the boy came back with a basketful of Sarco steam traps and controls, the job could be done with a pipe cutter and a wrench.

This in a nutshell is Sarco Service — To get more heat to the job by correctly dripping the lines. To use more of the heat before it leaves the coils, by individual trapping, and to regulate temperatures — both in heating and cooling, all over the plant.

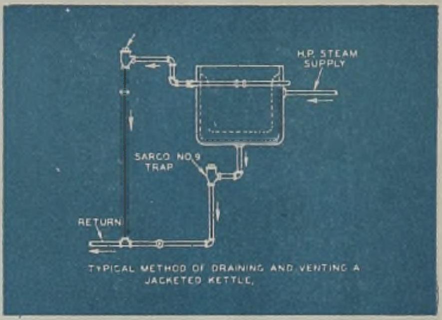
Time and again steam process production has been increased 25 to 50%, or the steam used greatly reduced, or the amount of metered water cut 50% or more.

The Sarco Hook-Up book contains a hundred or more ideas, with recommendations and sketches, and tells how each Sarco product will fit into your plant operation. Why not send for it now?

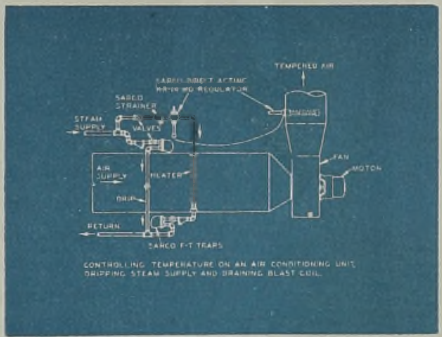




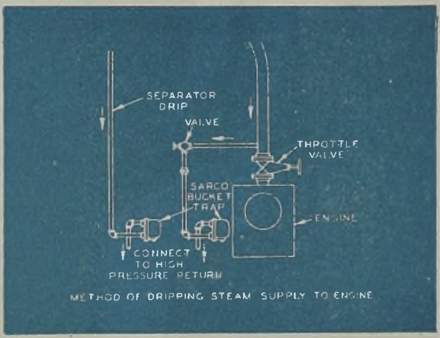
BLENDING HOT WATER TO GANG SHOWERS FOR CLOSE TEMPERATURE CONTROL.



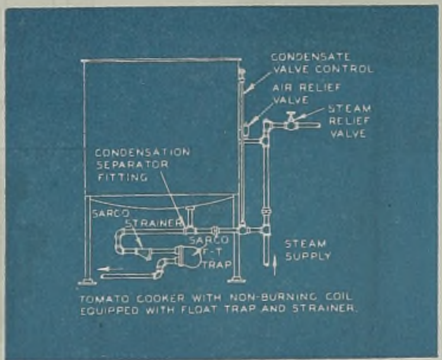
TYPICAL METHOD OF DRAINING AND VENTING A JACKETED KETTLE.



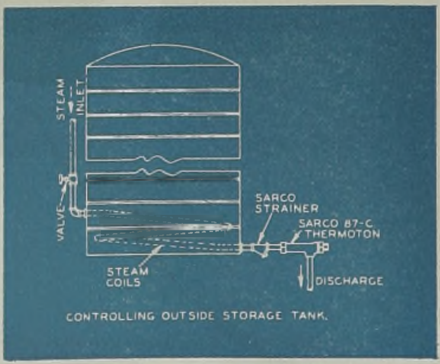
CONTROLLING TEMPERATURE ON AN AIR CONDITIONING UNIT, DRIPPING STEAM SUPPLY AND DRAINING BLAST COIL.



METHOD OF DRIPPING STEAM SUPPLY TO ENGINE



TOMATO COOKER WITH NON-BURNING COIL EQUIPPED WITH FLOAT TRAP AND STRAINER.



CONTROLLING OUTSIDE STORAGE TANK.

SARCO COMPANY, INC.
475 FIFTH AVENUE
NEW YORK 17, N. Y.

Represented in Principal Cities

SARCO Saves Steam

SARCO CANADA, LTD., 85 Richmond Street, West, TORONTO, ONTARIO

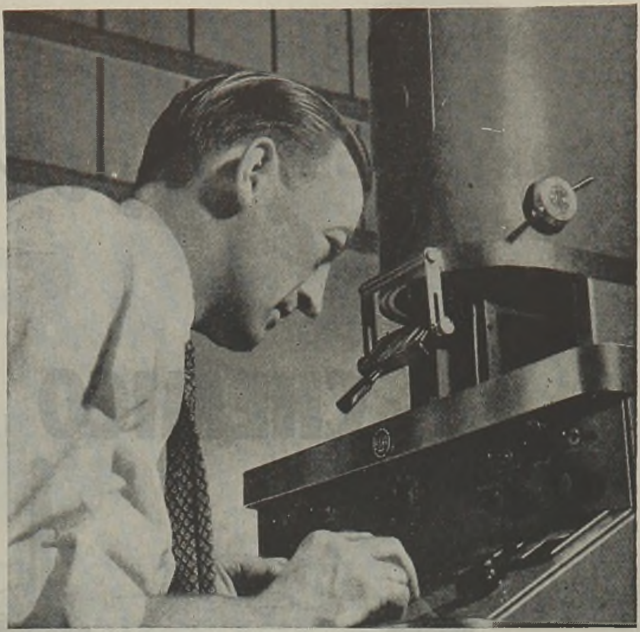
36


OIL
FOR THE ARTERIES OF PRODUCTION
THE ALMOST INDISPENSABLE
BARCO
FLEXIBLE JOINTS

These People

are seeing answers

to your problem



The RCA Electron Microscope may tell you why a process you banked on fails, and what procedure will bring success . . .

THE upper picture, at the right, shows an RCA Type EMU Universal Model Electron Microscope. Shown in the lower picture is a Type EMC Console Model RCA Electron Microscope. With the large "Universal" model, it is possible to observe objects directly at magnifications as high as 20,000 diameters. With the smaller "Console" model, objects studied are magnified to 5,000 diameters. With either instrument, sharp, clear micrographs can be obtained easily and quickly.

Images shown and photographed with both instruments are characterized by extremely high resolving power and remarkable depth of focus. For this reason, either instrument can be employed, if desired, to obtain stereoscopic pictures showing objects in strikingly effective and informative 3-dimensional perspective.

The "Console" instrument is, of course, less expensive than the "Universal" model. RCA Electron Microscopes are now used by an impressive number and variety of industrial companies and institutions of the highest standing. RCA engineers welcome inquiries from responsible industrial, scientific and educational sources. Please address Electron Microscope Section, Dept. 117V, RCA, Camden, New Jersey.

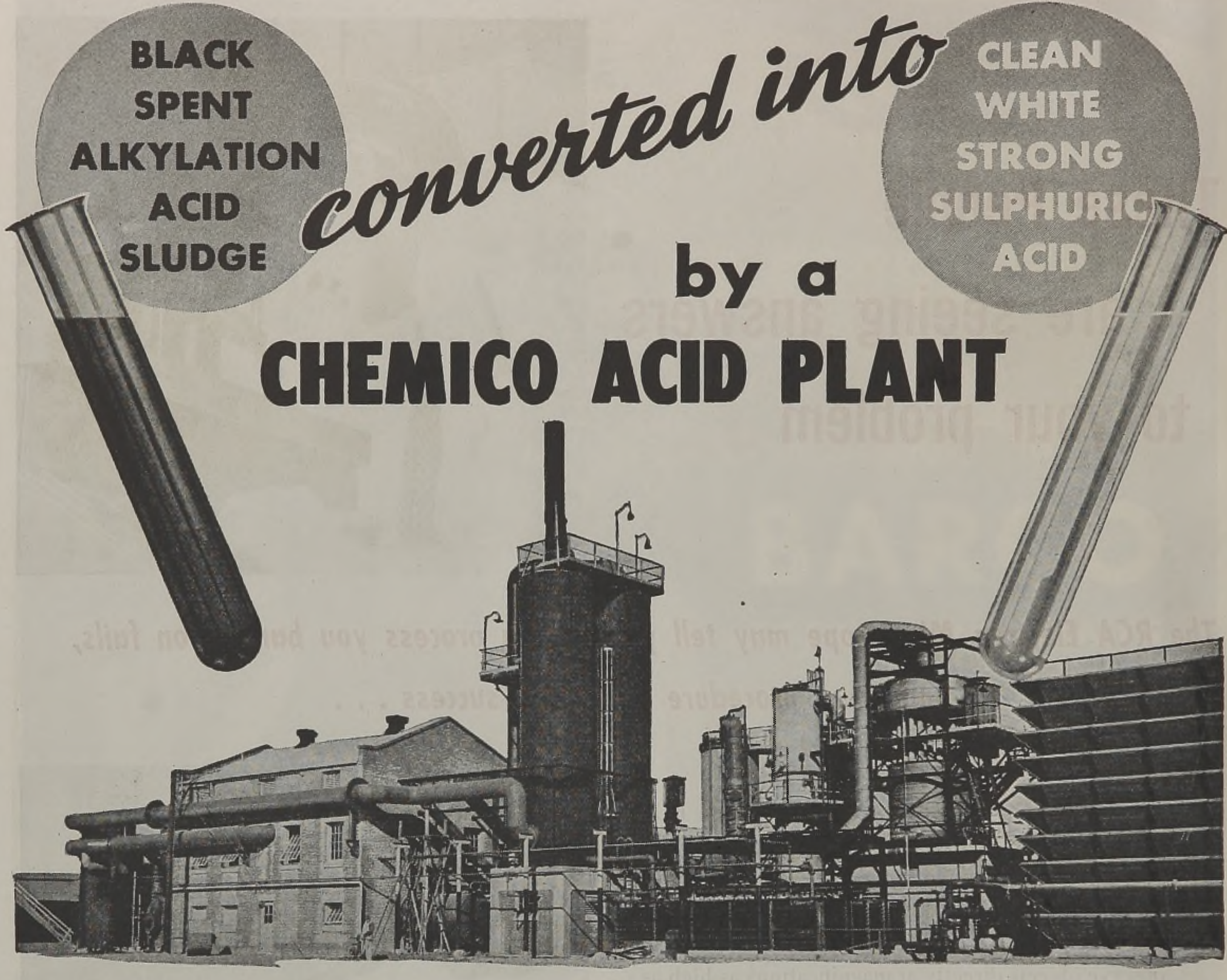
BUY MORE WAR BONDS

RCA

RADIO CORPORATION OF AMERICA

RCA VICTOR DIVISION • CAMDEN, N. J.

In Canada, RCA VICTOR COMPANY LIMITED, Montreal



Three large plants now in operation are daily proving the many advantages of a CHEMICO Acid Plant for producing a thoroughly dependable fresh supply of sulphuric acid from alkylation process spent acid sludge.

Some of these benefits . . . high recovery, an important factor in the present shortage of acid . . . *flexibility* to produce acid of any desired strength . . . *adaptability* to produce acid from either acid sludge or raw sulphur . . . *no economic loss* because hydrocarbon content of the acid sludge is utilized as fuel in the process . . . *no fumes or odors* escape to atmosphere and no pollution of streams . . . *acid recovered at moderate cost,* an important factor in the success of the alkylation process for making high octane gasoline.

Preliminary recommendations, with estimate of installation and operating costs, are submitted without charge or obligation. Your inquiry is invited.

CHEMICAL CONSTRUCTION CORPORATION

30 ROCKEFELLER PLAZA • NEW YORK 20, N. Y.

Cables, Chemiconst, New York • European Representatives, Cyanamid Products, Berkhamsted, Herts., England

CHEMICO PLANTS are PROFITABLE INVESTMENTS

ANHYDROUS HYDROFLUORIC ACID

FORMULA: HF

DESCRIPTION: A colorless, corrosive, fuming liquid. It volatilizes easily and on contact with the atmosphere, forms a visible cloud similar in appearance to steam.

PHYSICAL PROPERTIES:

AHF has a sp. gr. of 1.008 at 0°C (32°F); its boiling point is 19.4°C (66.9°F); its freezing point is about -85°C (-121°F). Its viscosity for all practical purposes is comparable to water. It flows freely and can be handled in comparatively small pipe lines. It can be used either in the liquid or gaseous form in reactions.

Its heat of solution with water is approximately 11,600 cal. per gram formula weight (1040 Btu/lb), and its heat of vaporization is approximately 6000 cal. per gram formula weight (540 Btu/lb).

CHEMICAL PROPERTIES:

The commercial AHF contains a minimum of 99.0% HF, and very low percentages of H_2SiF_6, SO_2, and H_2SO_4 as impurities. A very pure acid containing a higher percentage of HF, less than 0.35% of water, and virtually approaching a C.P. acid in respect to impurities is also available for reactions where needed. For methods of analysis of AHF, see analytical edition of Ind. Eng. Chem., Vol. 16, P. 483 (Aug. 15, 1944).

The acid reacts rapidly with silica, and attacks such materials as glass, porcelain, enamelware, asbestos, etc.

In addition, lead, cast iron, wood, rubber and most plastics are attacked and are unsatisfactory for handling the acid.

Monel, copper and mild carbon steel have excellent resistance to the anhydrous acid and are being used successfully in handling it in commercial installations. Platinum is probably the most resistant of all metals and silver has excellent resistance in the absence of sulphides.

The acid reacts violently with water, and where it is to be diluted or added to solutions, installations should be designed so as to guard against the possibility of water being forced or drawn into cylinders or containers of the strong acid. Special attention must be given to materials of construction when handling aqueous solutions of HF.

SOME USES FOR AHF:

AHF is being used in increasingly larger quantities as an alkylation catalyst in the production of high octane gasoline. It is also used in the production of organic fluorine compounds, and in the synthesis of other organic compounds.

It can be diluted to form very pure aqueous HF acid for the preparation of high purity inorganic fluorine compounds.

As suggested by its physical and chemical properties, new uses as a condensation reagent and fluorinating agent are being continually reported. Current work indicates that it is of increasing interest in polymerization, isomerization and acylation reactions.

PRECAUTIONS IN HANDLING:

Anhydrous Hydrofluoric Acid and its water solutions attack the skin and tissues strongly, producing painful burns. Strong concentration of the vapors may cause irritation of the throat, constricted breathing, and possibly inflammation of the lungs. Contact with the acid and vapor should be carefully avoided thru the observance of proper safety precautions, and in cases of accidental contact, approved first aid measures should be promptly followed. For additional information, refer to the Manufacturing Chemists' Assoc. Manual Sheets TC-5 and H-2. Copies of these will be furnished by us on request.

SHIPPING CONTAINERS:

AHF is regulated by ICC as a hazardous article, being classified as a "corrosive liquid." The shipping containers specified by ICC are pressure vessels, as commonly used for compressed gases.

The containers now available from Penn Salt are:

CYLINDERS: Sizes—6 lbs. net, 100 lbs. net, and 230 lbs. net. Type—ICC Specification 3A480.

TANK CARS: Sizes—11½ tons net, 22 tons net, and 42 tons net. Type—ICC Specification 105A series.

SHIPPING CLASSIFICATION:

Corrosive liquid—ICC white label required on cylinders. ICC corrosive liquid placard required on tank cars.

PENNSYLVANIA SALT MANUFACTURING COMPANY

Chemicals

1000 WIDENER BUILDING, PHILADELPHIA 7, PA.

New York • Chicago • St. Louis • Pittsburgh • Cincinnati • Minneapolis • Wyandotte • Tacoma

Molten sodium silicate for heat transmission?

Yes, it sounds like a paradox since PQ Silicates are fireproofing agents and are used as binders for insulating compounds.

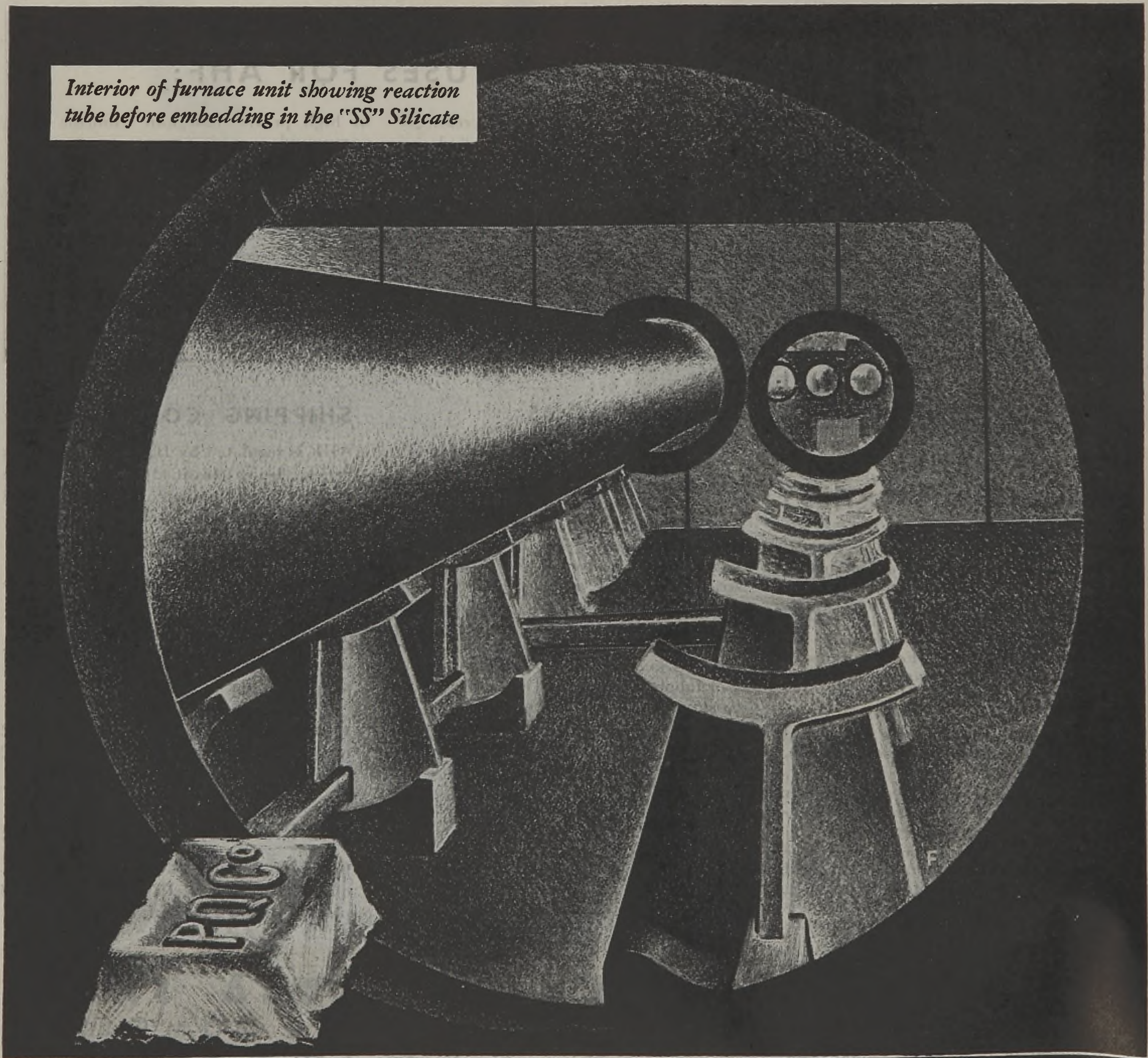
This new use was discovered when chrome-nickel steel for retorts in the production of magnesium became scarce and ordinary steel was substituted. The problem of corrosion by furnace gases was solved by surrounding each retort with molten silicate of soda glass, our "SS" Brand.

At 1600°F. the glass is fluid and transparent to infra-red rays. Reaction in the retorts proceeds as desired while the metal itself is "insulated" from corrosive atmospheres by the silicate in which it is immersed. And the silicate glass keeps in usable condition for long periods. The low iron and alumina content of "SS" Brand gives high transparency to infra-red rays.

Whether your problem is one of corrosion prevention, or special heat transmission, investigate sodium silicates. Let PQ help you get the right grade and the best method of application

PHILADELPHIA QUARTZ CO.

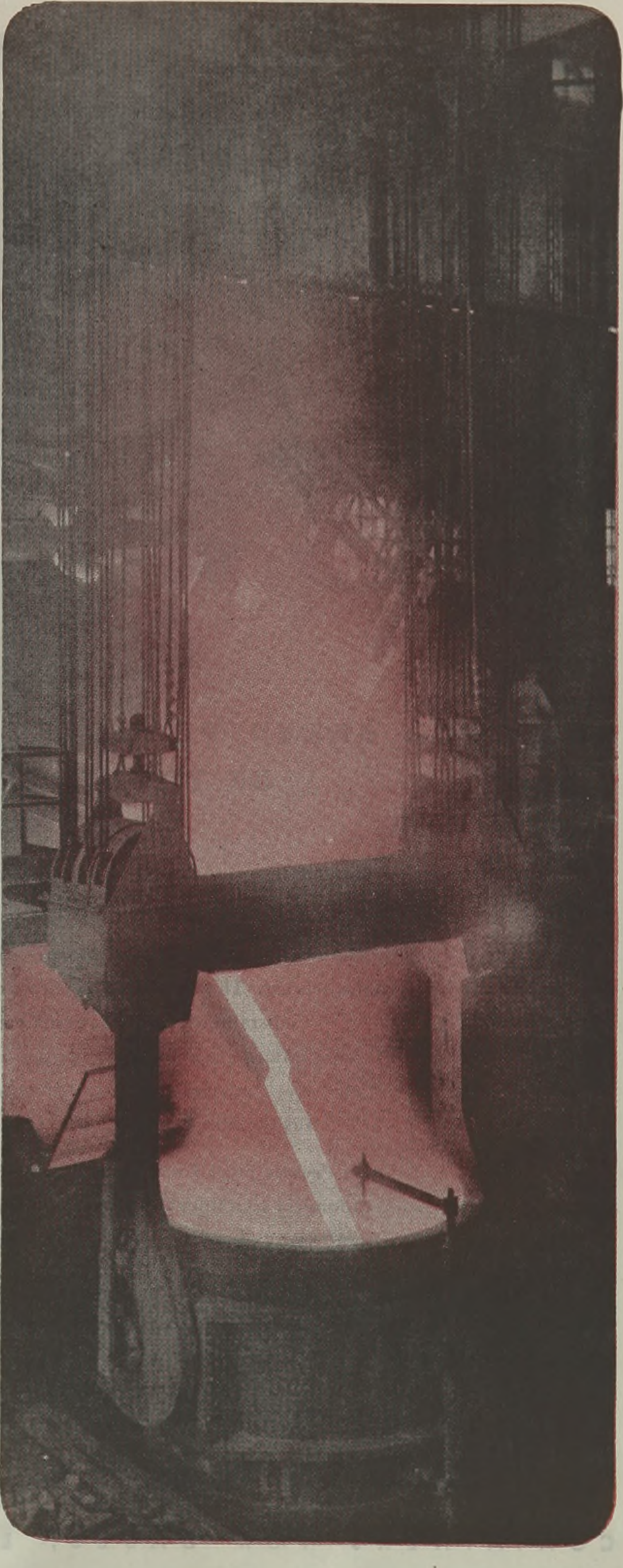
Dept. C, 119 South Third Street, Phila. 6, Pa.
Chicago Sales Office: 205 West Wacker Drive

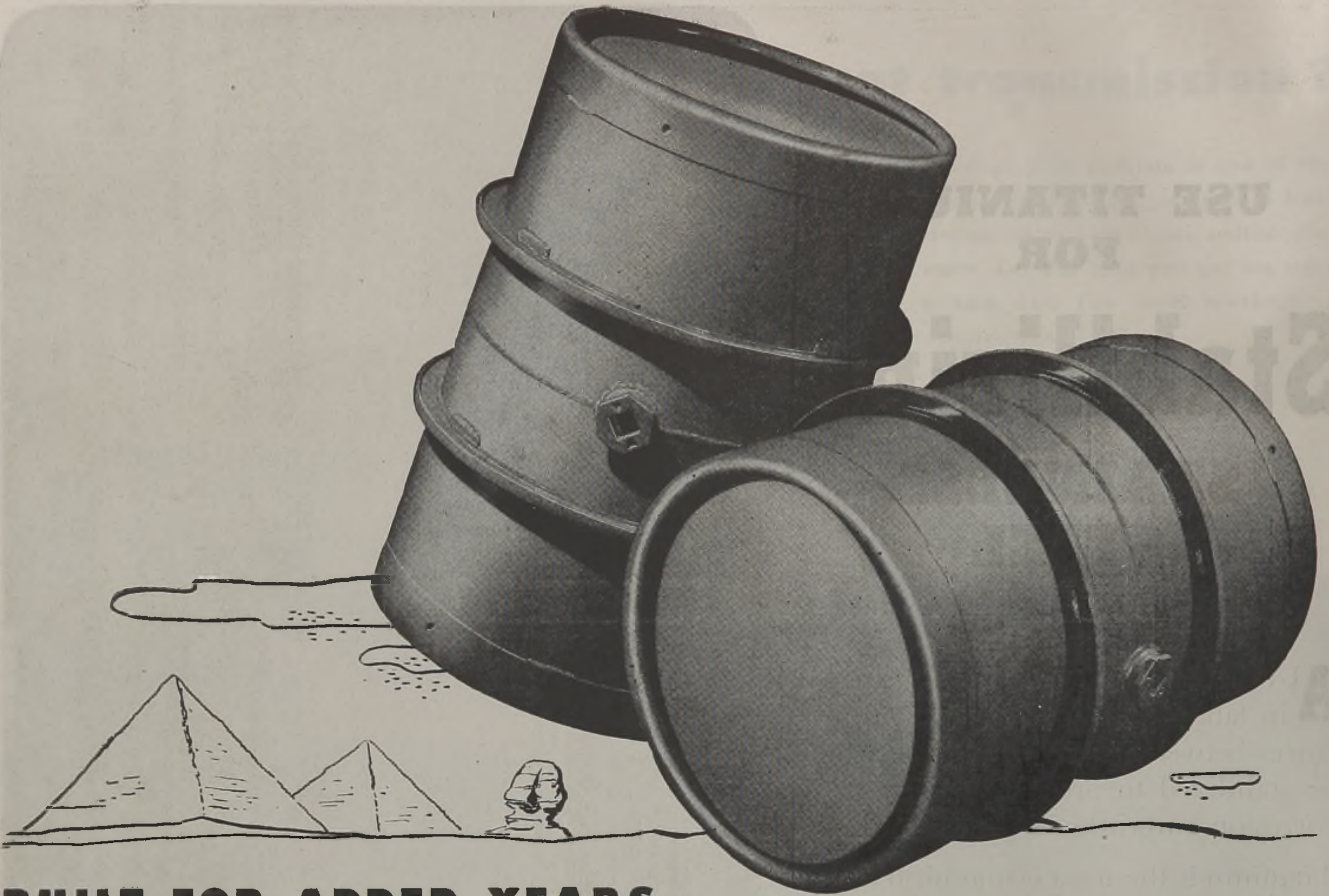


Interior of furnace unit showing reaction tube before embedding in the "SS" Silicate

WORKS: Anderson, Ind. • Baltimore, Md. • Chester, Pa. • Gardenville, N. Y.
Jeffersonville, Ind. • Kansas City, Kans. • Rahway, N.J. • St. Louis, Mo. • Utica, Ill.

PQ SILICATES OF SODA





BUILT FOR ADDED YEARS OF TROUBLE-FREE SERVICE

● To assure long life—design and construction must go hand in hand. Take Hackney two-piece acid drums, for instance. They're built to last—to afford maximum economy in the handling of such products as sulphuric acid, liquid caustic potash, aqua ammonia, etc.

The two-piece construction minimizes the possibilities of chime failure as it eliminates chime crevices. The reinforced, separate chime protectors, together with the I-bar hoops, substantially increase resistance to rough handling and abuse. Corrosion and bung failure are avoided by the two-pass single circumferential butt weld and careful attachment of heavy forged spuds. By heat-treating the finished container, it is possible even further to increase resistance to corrosion and prolong its life.

Let a Pressed Steel Tank Company representative help you determine the most practical and economical container for your individual requirements. You will be benefiting by more than 40 years of experience in precision manufacturing and designing. Write for details.

Hackney
MILWAUKEE

Pressed Steel Tank Company

Manufacturers of Hackney Products

1313 Vanderbilt Concourse Bldg., New York 17
208 S. La Salle Street, Room 2075, Chicago 4 558 Roosevelt Building, Los Angeles 14
1451 South 66th Street, Milwaukee 14

CONTAINERS FOR GASES, LIQUIDS AND SOLIDS

TOUGH CORROSION-PROOFING JOBS CALL FOR

PLIOWELD

RUBBER LINING

7 REASONS
why you should investigate
PLIOWELD

1. Effectively seals in corrosives that cannot be handled in metal.
2. Bonds permanently to metal surfaces by an exclusive Goodyear process.
3. Does not split or loosen with vibration or severe external impacts.
4. Does not crack or buckle under alternate wetting and drying, or temperature changes.
5. Surface will not disintegrate or slough off.
6. Protects chemicals from discoloration, iron "pick-up" and other contaminations.
7. Each installation specially formulated to provide maximum protection against chemical used.

A PRODUCT OF GOODYEAR RESEARCH

Interior of Plioweld-lined unit for continuous pickling of brass shell cases

THE continuous brass-pickling unit shown above illustrates the adaptability of Goodyear's Plioweld rubber lining to intricate equipment having numerous angles which complicate the task of installation. On this job the lining varies from ½″ to 1″ in thickness — a difficult application successfully handled by Goodyear's special bonding process that *permanently* welds the lining to any type of metal.

You will find Plioweld rubber lining superior for all tough corrosion-proofing jobs because it is impervious to most industrial acid solutions. It is comparable to natural rubber in its protection against alkalis, plating solution and organic materials.

Another important plus is Plioweld's extremely long life. It will not soften and slough off. It is highly resistant to cutting from tumbling objects. And it will not loosen from vibration when installed in operative units — fans, agitators, centrifuges, etc.

All Plioweld installations are made by Goodyear factory experts — a further guarantee of lasting satisfaction. With chemical equipment so busy and so hard to replace today, you'll be wise to get full information about Plioweld from the G.T.M. — Goodyear Technical Man. To consult him, write: Goodyear, Akron 16, Ohio or Los Angeles 54, California.

Plioweld—T.M. The Goodyear Tire & Rubber Company

GOODYEAR

THE GREATEST NAME IN RUBBER

BRIGHTON YEAST CULTURE APPARATUS . . .

. . . designed for the process industries

We illustrate the BRIGHTON yeast culture machine — built in accordance with customers' plans and specifications. Fabricated in stainless steel, with highly polished interior. This machine has a diameter of 60" and a capacity of 700 gallons.

Brighton produces

FRACTIONATING COLUMNS • COOLERS
HEAT EXCHANGERS • CONDENSERS
PILOT PLANTS • KETTLES • TANKS
WATER STILLS • PERCOLATORS

and every type of

PROCESSING VESSEL

fabricating in

COPPER • STAINLESS STEEL • NICKEL
BRASS • SILVER • ALUMINUM
NICKEL CLAD • STAINLESS STEEL CLAD

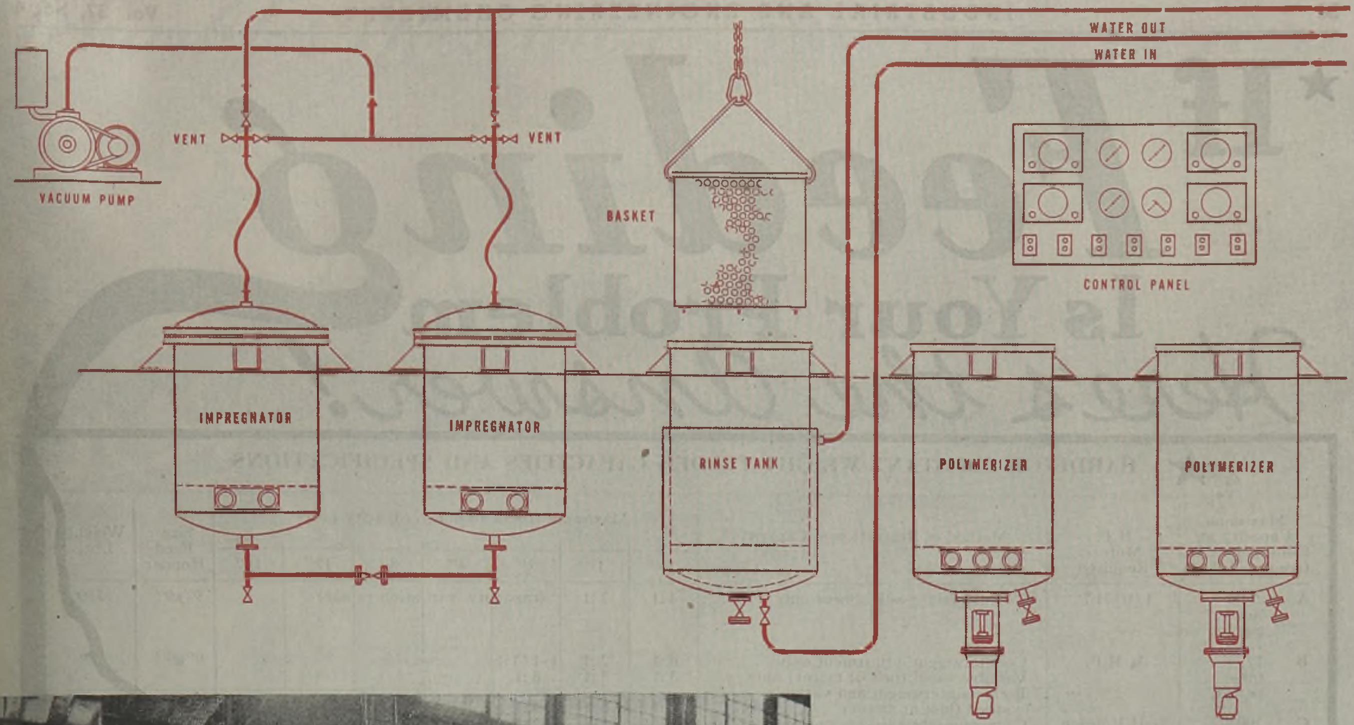
from 1/16" to 1/2" thickness

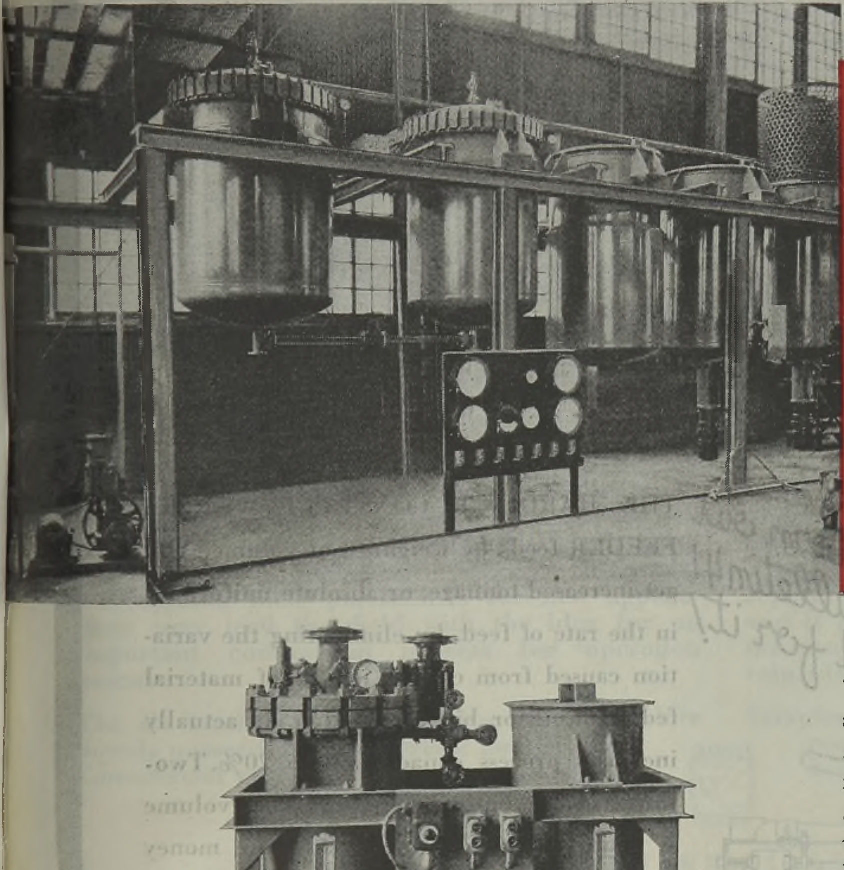
Write for Catalog 20C

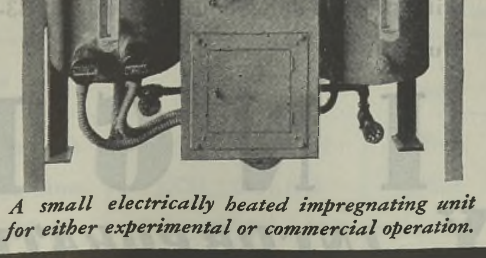
ESTABLISHED
1914

BRIGHTON
COPPER WORKS

BRIGHTON STATION • CINCINNATI 14, OHIO





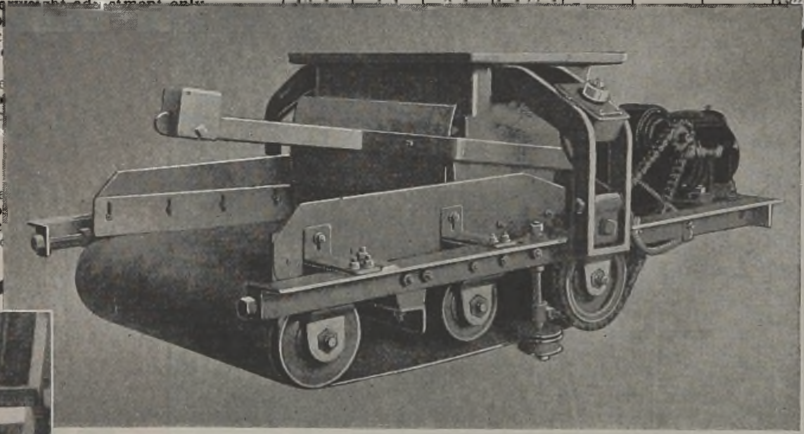


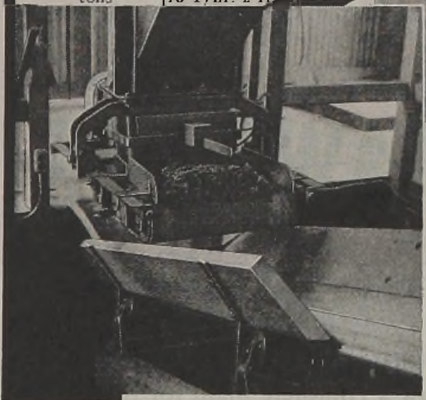
A small electrically heated impregnating unit for either experimental or commercial operation.

★ If *Feeding*
Is Your Problem
Here's the Answer!

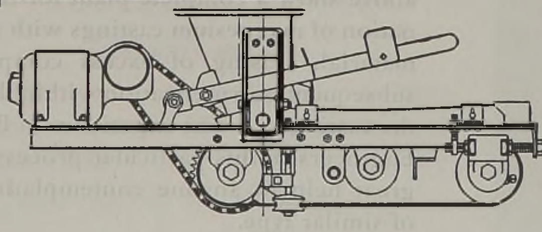
★ **HARDINGE CONSTANT WEIGHT FEEDER CAPACITIES AND SPECIFICATIONS**

	Maximum Capacity at 85lbs. per cu. ft. (see note below)	H.P. Motors Required	Method of Regulation of Capacity	Maximum size of feed also capacity range							Size Feed Hopper	Weight Lbs.
				¼″	1″	2″	4″	8″	12″	18″		
A	2500 lbs. per hr.	1/10 H.P.	Counterweight adjustment only........	4 :1	2 :1	(capacity variation range)					9″x9″	350
B	12 tons per hr.	¼ H.P.	Counterweight adjustment only........ Variable speed (belt or motor) only..... Both counterweight and variable speed (belt or motor)..............	6 :1 3 :1 18 :1	2 :1 3 :1 6 :1	1–1/3 :1 3 :1 4 :1					9″x9″	
C	200 tons per hr.	¼ H.P. below 20 T/hr. ½ HP above 20 T/hr.	Counte Variab Both c spee									
D	1000 tons per hr.	½ H.P. below 15 T/hr. 1 HP 15 to 100 T/hr. 2HP above 100 T/hr.	Counte Variab Both c spee									
E	2000 tons per hr.	½ H.P. below 5 T/hr. 1 H.P. 5 to 50 T/hr. 2 HP above 50 T/hr.	Counte Variab Both c spee									
F	200 tons	1 H.P. below 10 T/hr. 2 H.P.	Coun									





Page torn out of Bulletin 41 Send for it!



THE HARDINGE CONSTANT WEIGHT FEEDER feeds by weight—not volume. You get increased tonnage, or absolute uniformity in the rate of feed, by eliminating the variation caused from change in size of material fed, bulking or bin segregation. It actually increases process capacity 10 to 20%. Two-thirds of our rapidly mounting sales volume is made up of *repeat orders*. Make money with this Feeder. Send for Bulletin 33-C and Bulletin 41.

HARDINGE
COMPANY *INCORPORATED*
YORK, PENNSYLVANIA, *Main Office and Works*

Sharples Research... PIONEERING FOR THE FUTURE

The first steamboat, invented by John Fitch and built in Philadelphia, Pa., was launched and operated on the Delaware River on July 27, 1786.

THE advantages of being first in a new enterprise are well known to those who have traveled far along the road to success. Although now available in only experimental quantities, these secondary alkylamines are potentially important chemical raw materials of the future. Any research chemist investigating their possibilities for new applications may lead the field with the idea for an important commercial process for operation postwar.

The alkylamines described below are water-white liquids possessing characteristic amine odors. Commercial applications for these particular compounds have not been fully developed, but analogous members of this series have found extensive use as intermediates in the synthesis of pharmaceuticals, dyestuffs, textile assistants, emulsifying agents, inhibitors, antioxidants and rubber chemicals. Applications may be found which will represent improvements over existing practices and it is possible that the specific properties of the compounds listed in the table may render them valuable for entirely new uses.

Samples will be submitted for evaluation upon receipt of your request on company letterhead.

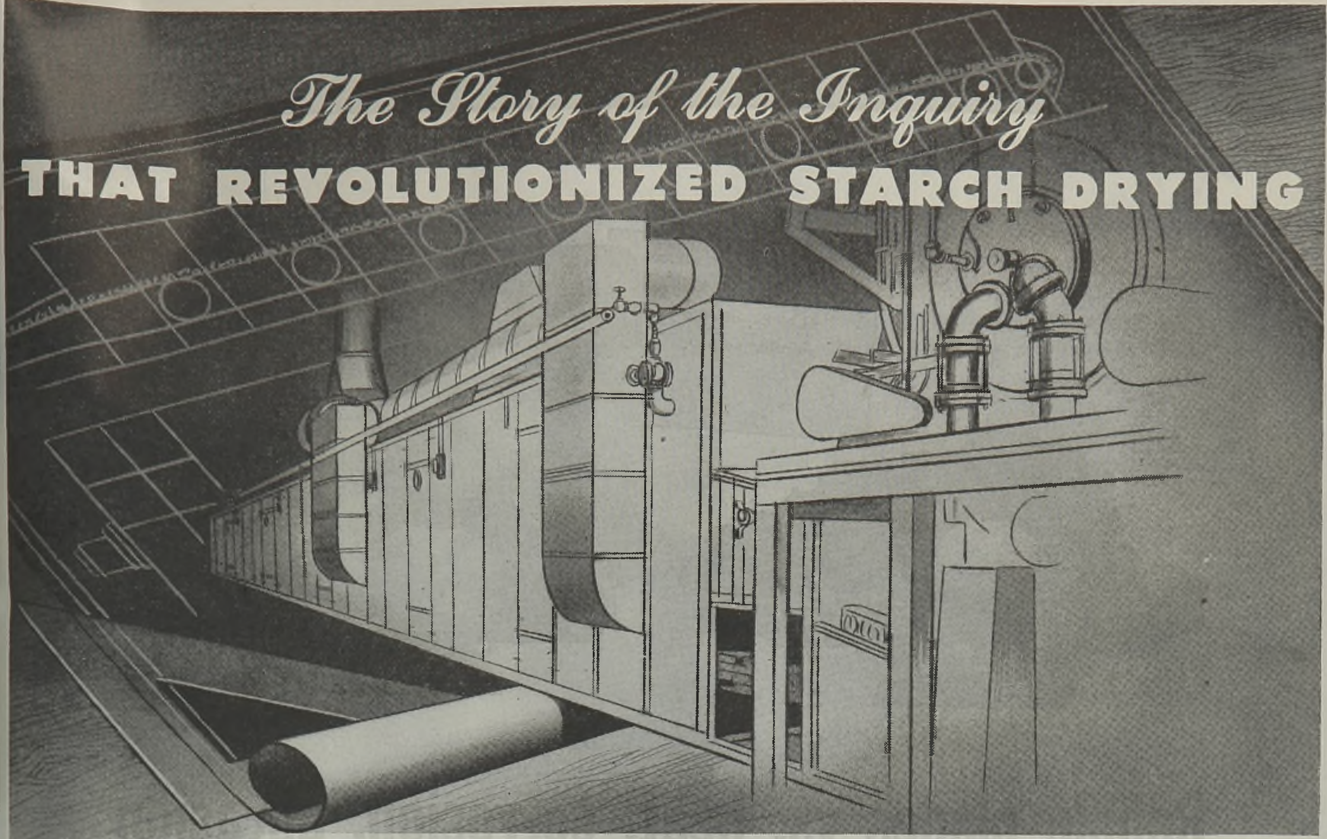
NEW SHARPLES AMINES

(Sec-Alkylamines)

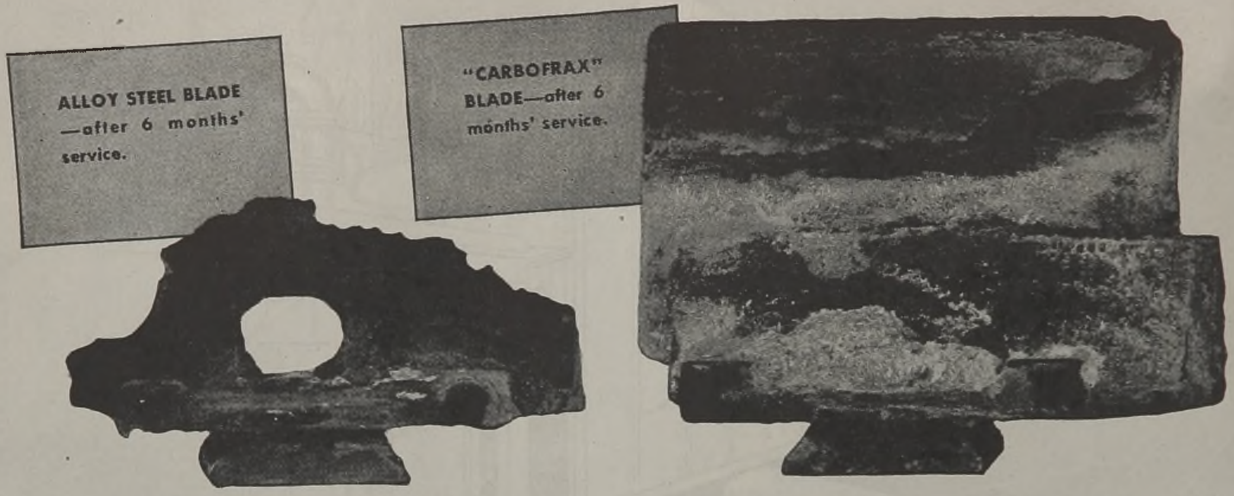
Name	Formula	Mol. Wt. (calcd.)	Sp. Gr. at 20/20° C.	Boiling Range °C.	Solubility in		
					Water	Ethanol	Benzene
Di-n-propylamine	$(CH_3CH_2CH_2)_2NH$	101.2	0.741	105-109	Partial	Complete	Complete
Diisopropylamine	$[(CH_3)_2CH]_2NH$	101.2	0.726	81-85	Partial	Complete	Complete
Diisobutylamine	$[(CH_3)_2CHCH_2]_2NH$	129.2	0.746	136-140	Slight	Complete	Complete
Di-sec-butylamine	$(CH_3CH_2CHCH_3)_2NH$	129.2	0.783	134-137	Slight	Complete	Complete

[illegible] *Inc.*

PHILADELPHIA • CHICAGO • NEW YORK


The Story of the Inquiry
THAT REVOLUTIONIZED STARCH DRYING

NO. 3 IN A SERIES DESCRIBING THE USE OF SUPER REFRACTORIES IN THE PROCESS INDUSTRIES



Rabble blades vs. heat, corrosion, abrasion

▶ High temperatures, corrosion and abrasion are triple threats to rabble blades transporting ores and other materials on the hearths of roasting furnaces.

Looking for a material that could withstand such extreme conditions, engineers have turned to "Carbofrax"—the silicon carbide super refractory by Carborundum. The above pictures of two rabble blades after six months in the same furnace show the result. The metal blade has been corroded to such an extent that little of the original shape remains. In fact, it was ineffective after only four months. Now look at the blade made of the refractory material "Carbofrax." Practically unaffected, it's still capable of considerable service.

This successful performance of "Carbofrax" is due to its unmatched resistance to abrasion and corrosion at elevated temperatures—plus an excellent hot strength that counters the cracking tendency imposed by heavy charges.

Rabble blades exemplify just one possible application for "Carbofrax." And "Carbofrax" is but one of many super refractories by Carborundum available for tough jobs in the process industries.

There are many processes in the chemical, metallurgical and petroleum fields to which one or more of Carborundum Brand Refractories can be advantageously applied to insure longer life—less maintenance—lower operating costs.

Call on a Carborundum engineer to determine how super refractories by Carborundum can be used to meet the threat of thermal, chemical and mechanical breakdown in either proposed or existing processes.

THE CARBORUNDUM COMPANY
Refractories Division, Perth Amboy, N. J.

District Sales Branches: Chicago, Philadelphia, Detroit, Cleveland, Boston, Pittsburgh. **Distributors:** McConnell Sales & Engineering Corp., Birmingham, Ala.; Christy Firebrick Company, St. Louis, Mo.; Harrison & Company, Salt Lake City, Utah; Pacific Abrasive Supply Company, Los Angeles & San Francisco, California; Denver Fire Clay Company, El Paso, Texas; Smith-Sharpe Company, Minneapolis, Minn.

"Carborundum" and "Carbofrax" are registered trade marks of, and indicate manufacture by, The Carborundum Company

Super Refractories by CARBORUNDUM
TRADE-MARK

***SEND FOR** this booklet and learn how super refractories are used in the process industries. Gives helpful charts of properties and many interesting applications.*

Clip coupon now!

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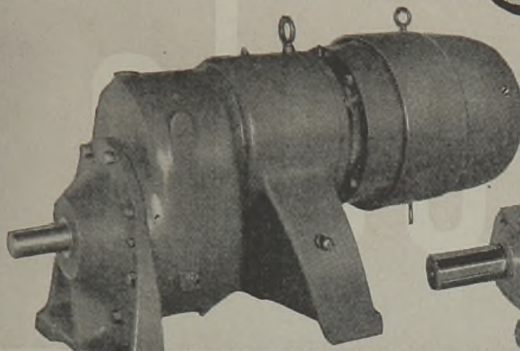
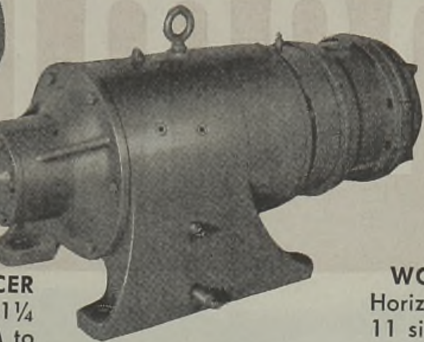
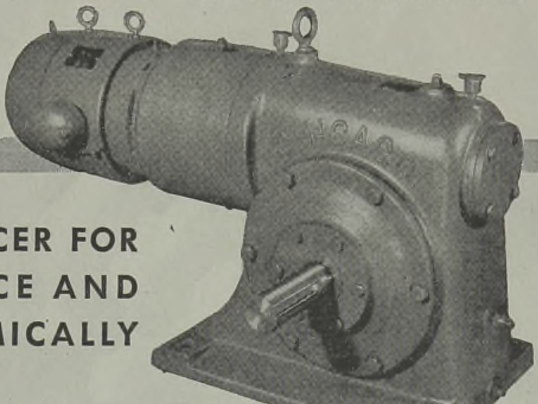
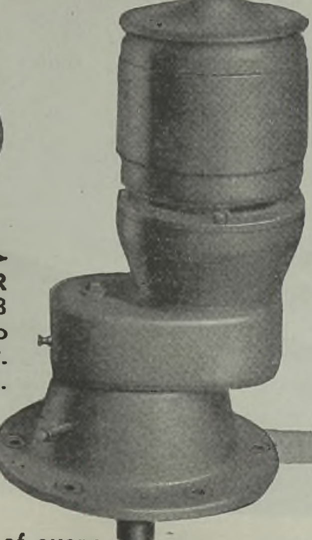
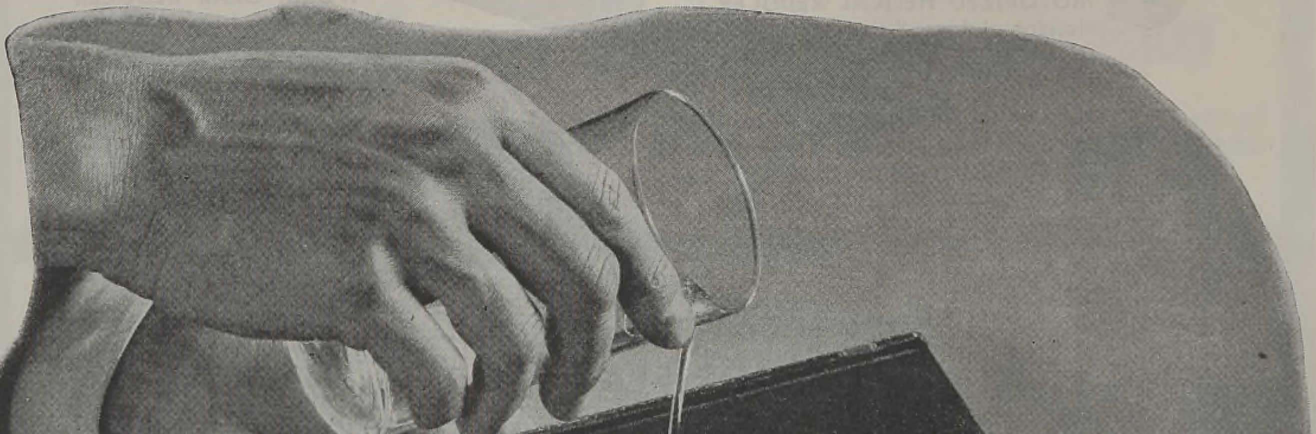










Precision and diversification typify research in synthetics

INDUSTRY, ever more concerned with advanced chemical processes, naturally turns to synthetics. For synthetics, by their very nature, can be more accurately tailored to individualized needs.

In exactly meeting these modern demands, Celanese research has produced precision results in widely diversified fields. For example, Celanese organic phosphate emulsions serve both in oil-in-water and water-in-oil processes to meet the demands of varied applications.

These stable compounds provide the key to many difficult situations. For instance, plasticizing water-soluble type plastics and water-soluble coating materials for paper and fabric, such as book and shade cloths. In addition to providing an improved plasticizer, these emulsions add the quality of water repellency—plus increased color value of pigments.

In common with the Lindol* group of organic phosphates, these emulsions also contribute high film strength and excellent lubricating characteristics. Consider their possibilities, too, as lubricants and coolants for wire drawing operations. They are non-corrosive, have high film strength lubricating characteristics, are fluxes for subsequent tinning operations and plasticizers for enamel coatings. This is the kind of *extra* performance which characterizes Celanese chemicals in the minds of engineers through such diversified products as Lindol, Lindol* E.P., Lindol* M.P., Celluflex* and Cellulube*.

Each is a specialized product, yet each has many specialized uses, often vital roles in industry and war. Lindol E.P., as a lubricant additive in oils for warplane engines, increases film strength to withstand long periods of terrific heat and acts to dissolve resinous deposits.

The point is that Celanese research isn't merely designed to serve everybody but to serve *you—your* needs. And not with *almost* what you want, but with precisely what you are looking for. What are *your* goals, present and near-future? Our Technical Staff would like to work with you. Celanese Chemical Corporation, a division of Celanese Corporation of America, 180 Madison Avenue, New York 16, N. Y.

PLASTICIZERS
ORGANIC PHOSPHATES
LUBRICANT ADDITIVES
INTERMEDIATES
DYE-STUFFS

*Reg. U. S. Pat. Off.

TEXTILES • PLASTICS • CHEMICALS

3 NEW CENTRIFUGAL IMPROVEMENTS *to help you* IMPROVE COST-PRICE RATIO

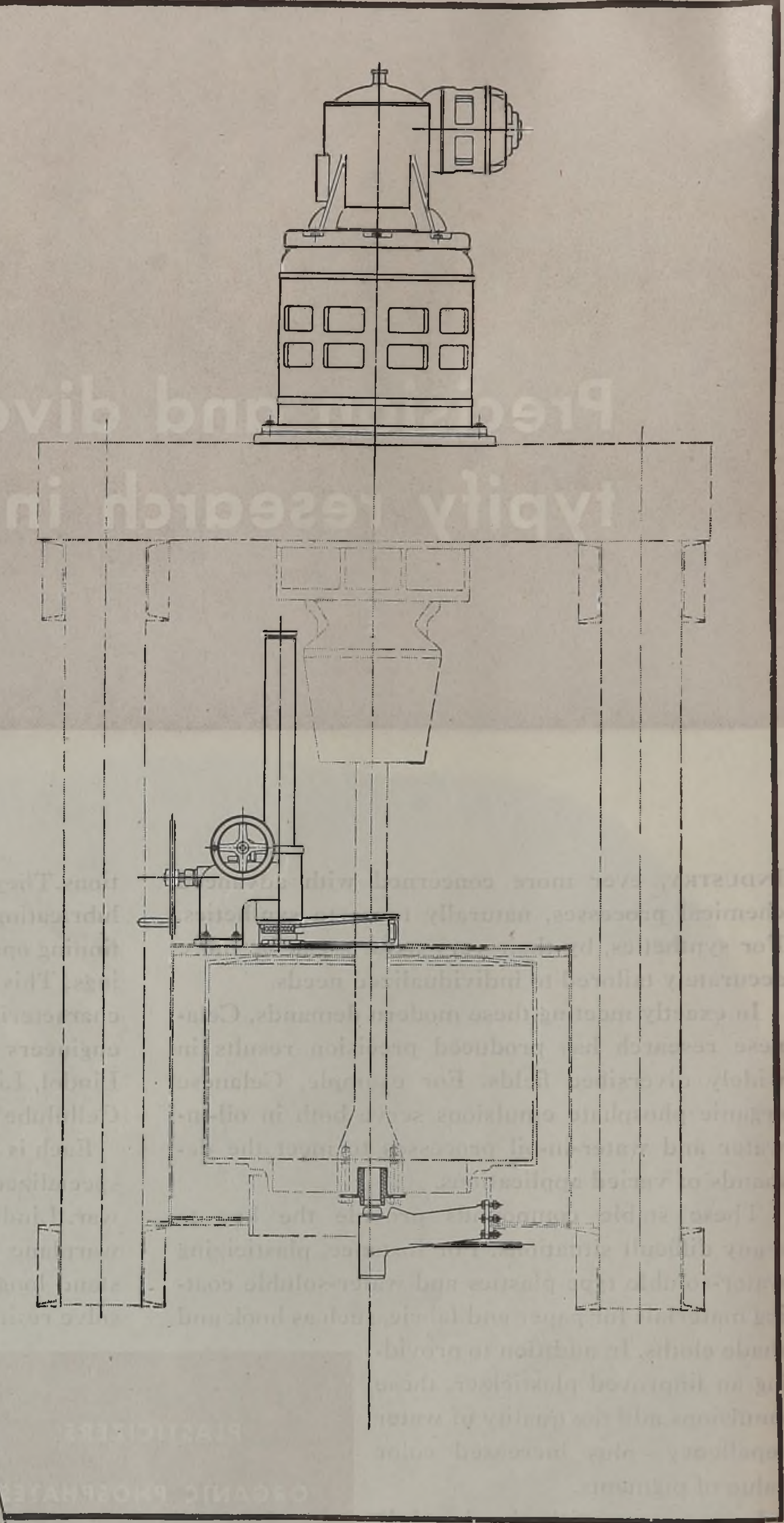
Again AT&M advances centrifugal design to provide even more efficient production in chemical processing . . . 3 new centrifugal improvements for absolute control in unloading hard-to-handle materials.

1. A radically redesigned, 2-motor free-wheeling drive with a much higher torque than before provides a constant low speed for discharging without load on the main motor.

2. A new *discharger gives positive, accurate control over the depth of cut — controlled by worm and worm wheel. The shoe rests on the top of the curb during spinning operation.

3. A *stabilizer located at the bottom of the basket prevents basket from gyrating. Operated by foot or power. It can be interlocked with cycle controls.

*Both discharger and stabilizer can be used with ordinary baskets.



Send for complete information on these new developments—also, a copy of AT&M's useful booklet entitled "Better, Cheaper, Faster Processing". Now is a good time to line up your new equipment for more profitable production. AMERICAN TOOL & MACHINE COMPANY, 1421 Hyde Park Avenue, Boston, Mass. 30C Church Street, New York 17, N.Y.

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CENTRIFUGING

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HOOKER CHEMICALS

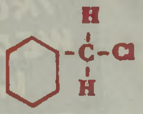
Where You Want the Benzyl, Benzal or Benzoyl Group, Choose from these Hooker Intermediates

Purity, chemical activity, ease of handling and comparative costs are some of the factors which should influence the choice of a chemical intermediate.

Where you need to incorporate a benzyl, benzal or benzoyl group into your product, Hooker gives you an opportunity of balancing these factors against chemical characteristics from a number of intermediates. Among Hooker chlortoluene compounds and derivatives, there are two chemicals that provide the benzyl group, one—the benzal group and four—the benzoyl group. From them we can help you select the one which best meets your requirements on all counts.

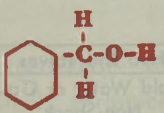
For the Benzyl Group ($C_6H_5CH_2$)—

BENZYL CHLORIDE, $C_6H_5CH_2Cl$



May be used in Friedel-Crafts reactions, may be reacted with alcohols in presence of caustic soda to produce mixed ethers; to introduce benzyl group in amino compounds; will react with sodium cyanide to form benzyl cyanide or phenyl acetonitrile; reacts with sodium sulfhydrate to form benzyl mercaptan; reacts with sodium sulfide to form benzyl sulfide. Produces esters with sodium salts of acids.

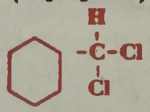
BENZYL ALCOHOL, $C_6H_5CH_2OH$



Reacts with some alcohols in presence of dehydrating agent such as sulfuric acid to produce ethers. Produces esters with acids, acid anhydrides or acid chlorides. Reacts with acetyl chloride to produce benzyl acetate.

For the Benzal Group (C_6H_5CH)=

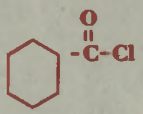
BENZAL CHLORIDE, $C_6H_5CH\ Cl_2$



Reacts with water to form benzaldehyde. May be used in Friedel-Crafts reactions as source of chloro group in production of triphenyl methane derivatives.

For the Benzoyl Group (C_6H_5CO)—

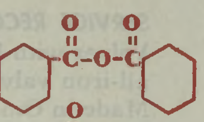
BENZOYL CHLORIDE, C_6H_5COCl



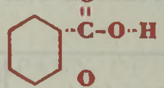
May be reacted with alcohols to produce esters. May be used in Friedel-Crafts reactions to produce ketones. Reacts with ammonia to form benzamide. Reacts with amines to give benzoyl substituted products.

Benzoyl Chloride is the most reactive chemical of the Hooker Benzoyl compounds. However, the following are also sources for the Benzoyl Group, and may be preferable in some cases:

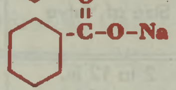
BENZOIC ANHYDRIDE, $(C_6H_5CO)_2O$



BENZOIC ACID, C_6H_5COOH



BENZOATE OF SODA, C_6H_5COONa



When requesting Bulletin 320, containing further information on these Hooker chemicals, please write on your letterhead.

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NEW YORK, N. Y. • TACOMA, WASH. • WILMINGTON, CALIF.

CAUSTIC SODA CHLORINE
PARADICHLORBENZENE MURIATIC ACID

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. . . Whatever You Need in Piping Materials

ONE SOURCE OF SUPPLY
ONE RESPONSIBILITY FOR ALL PARTS
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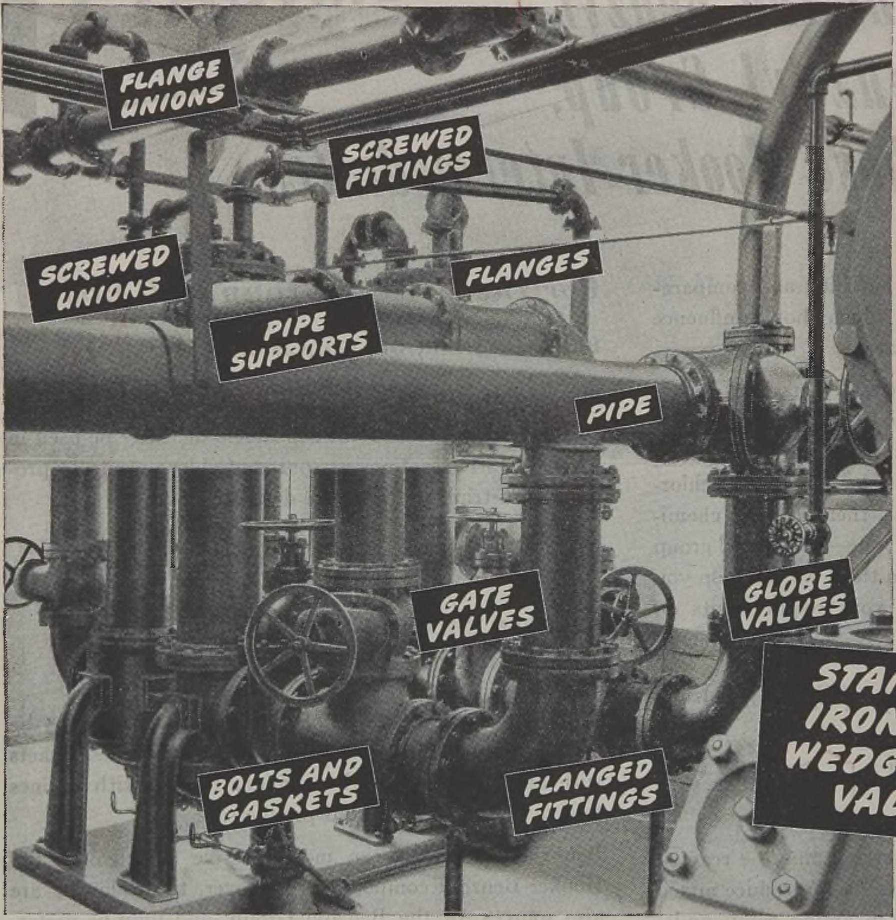
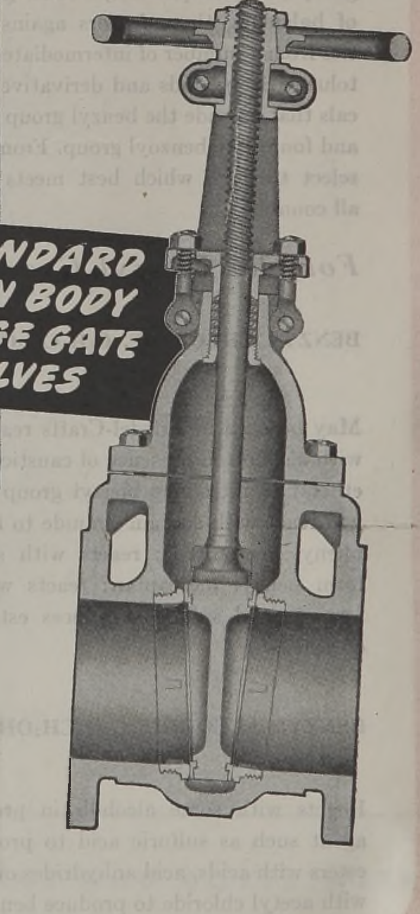


Aftercooler hook-up in Chemical Plant

It's easy to simplify and speed deferred replacement work . . . when you take advantage of Crane *complete* piping materials service. *All* your piping needs are supplied by a single source—your Crane Branch or Wholesaler. You get exactly what you need—you choose from the world's greatest line of piping materials, in brass, iron and steel. Uniform quality in all parts—and one responsibility for them—helps you get the best installations. Crane Co.'s 90 years' experience in meeting piping needs assures your complete satisfaction. In Standard Iron Body Wedge Gate Valves, for example, Crane offers the complete line listed below.



***SERVICE RECOMMENDATIONS:* Crane Standard Iron Body Wedge Gate Valves** with Brass trim are recommended for steam, water or oil lines; all-iron valves for oil, gas or fluids that corrode brass but not iron. Made in O.S. & Y. and Non-Rising Stem patterns.

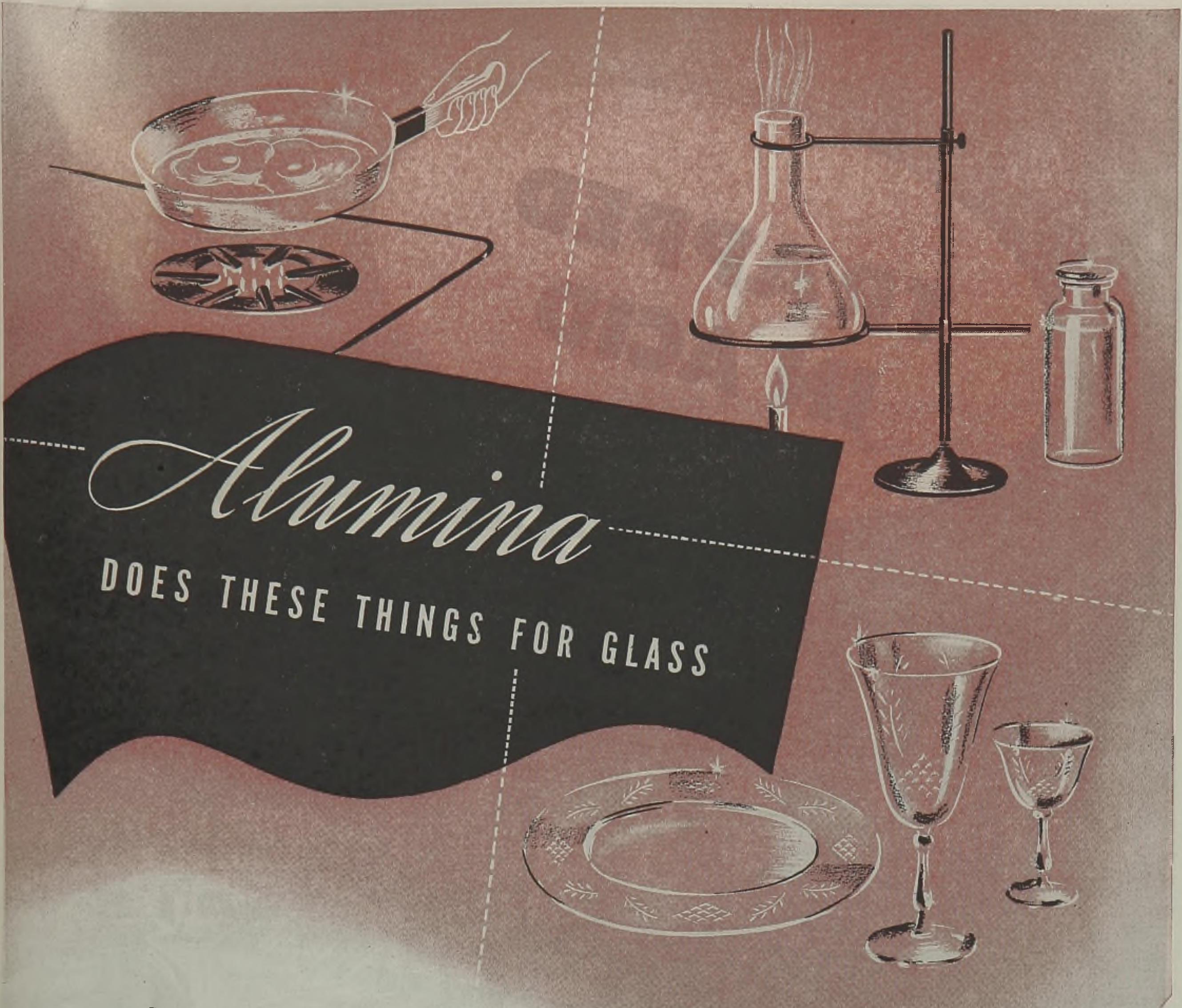
Working Pressures

Size of Valve	Screwed or Flanged End Valves		Hub End Valves
	Saturated Steam	Cold Water, Oil or Gas, Non-Shock	Cold Water or Gas Non-Shock
2 to 12 in.	125 pounds	200 pounds	200 pounds
14 and 16 in.	125 pounds	150 pounds	150 pounds
18 to 24 in.	*	150 pounds	150 pounds

*For steam lines larger than 16-in., Crane 150-Pound Cast Steel Gate Valves are recommended.
(For sizes under 2-in., use Crane Clamp Gate Valves.)

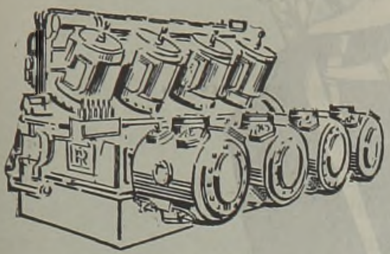
CRANE CO., General Offices: 836 S. Michigan Ave., Chicago 5, Ill. • *Branches and Wholesalers Serving All Industrial Areas*

CRANE 90 YEARS OF PROGRESS 1855 1945 VALVES • FITTINGS • PIPE
PLUMBING • HEATING • PUMPS

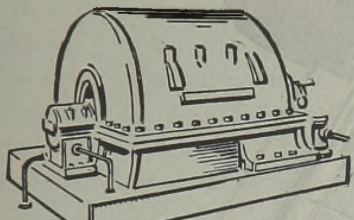

Alumina
DOES THESE THINGS FOR GLASS


TRAPPED
IN ACID

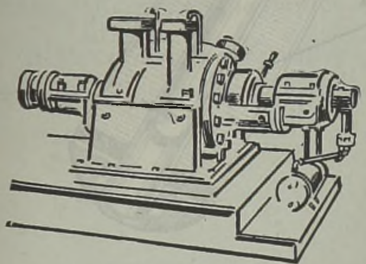
Gases and Liquids



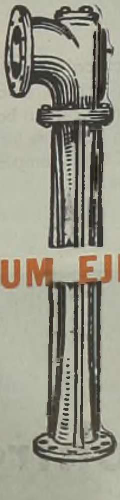
COMPRESSORS



TURBO-BLOWERS



CENTRIFUGAL PUMPS



VACUUM EJECTORS

● Inventive genius and ability to recognize a problem and lick it have always been associated with those in the Process Industries. It is because of their never-ceasing research, development and production that we have the countless products so essential to war and peace.

They face ever-changing problems involving new gases, new liquids, higher temperatures, higher pressures, greater volumes. For the compression of gases and transport of liquids in these processes — many of them continuous — the careful selection of machinery is of greater importance than ever before.

Sustained development of reciprocating compressors, of turbo-blowers and of centrifugal pumps and vacuum equipment to handle the many and varied gases and liquids has permitted Ingersoll-Rand to help the Process Industries to solve many of their problems. Through the years, many new machines have been built to meet ever-changing conditions—always built by men who appreciate the high standards of reliability and efficiency required for this service.

We will continue to meet and, where possible, to anticipate such requirements, no matter how severe these may be.

Ingersoll-Rand

11 BROADWAY, NEW YORK 4, N. Y.

COMPRESSORS • TURBO-BLOWERS • ROCK DRILLS • AIR TOOLS

CENTRIFUGAL PUMPS • CONDENSERS • OIL AND GAS ENGINES

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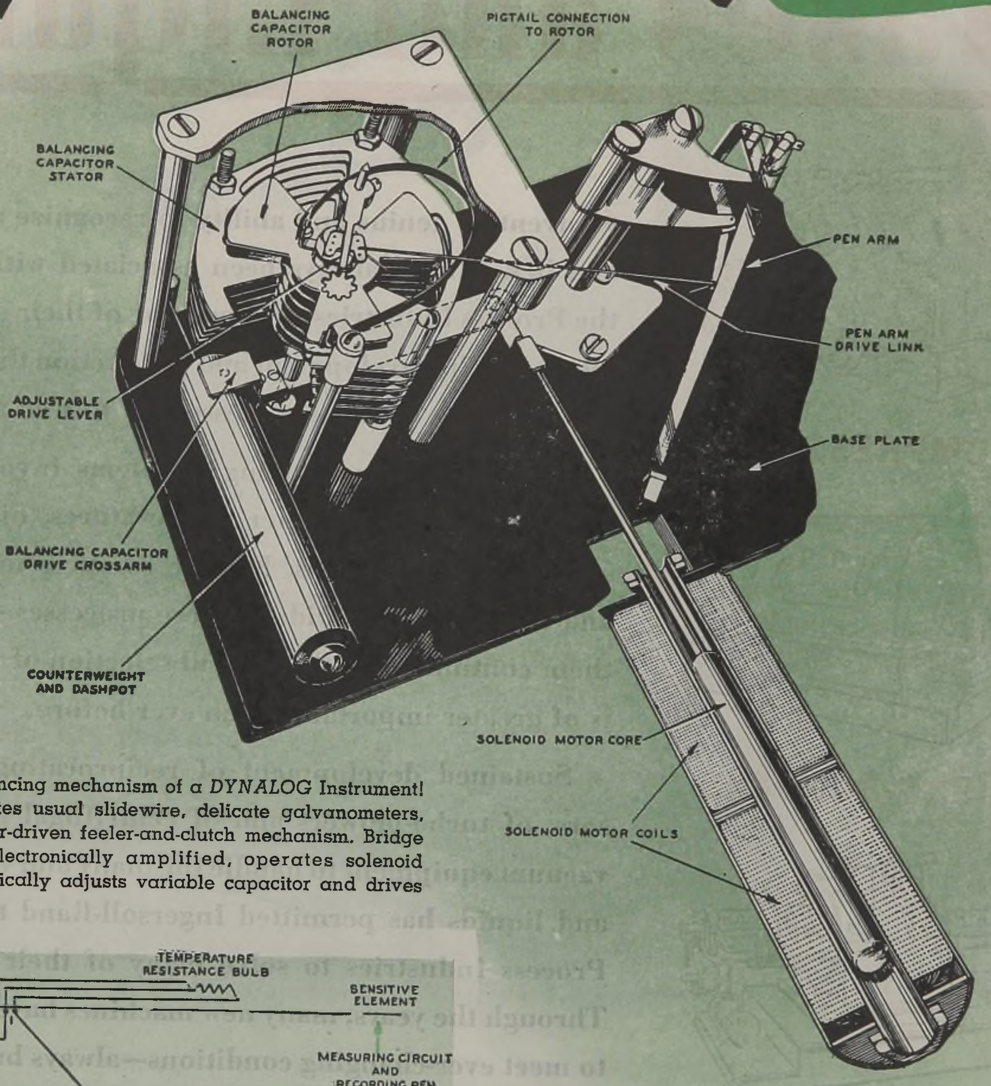
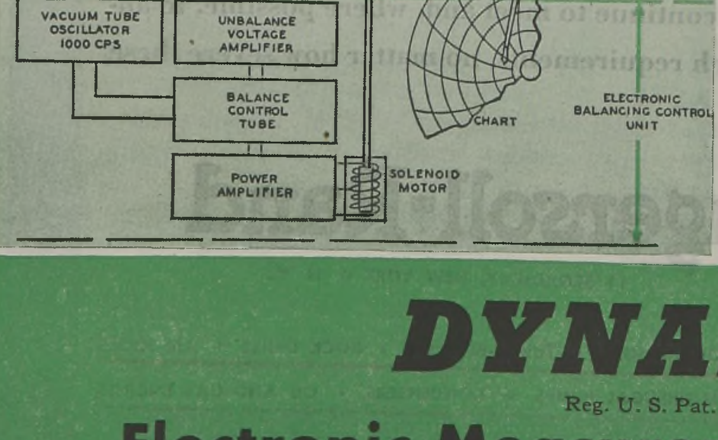

BALANCING CAPACITOR ROTOR
PIGTAIL CONNECTION TO ROTOR
BALANCING CAPACITOR STATOR
PEN ARM
PEN ARM DRIVE LINK
ADJUSTABLE DRIVE LEVER
BASE PLATE
BALANCING CAPACITOR DRIVE CROSSARM
COUNTERWEIGHT AND DASHPOT
SOLENOID MOTOR CORE
SOLENOID MOTOR COILS


TEMPERATURE RESISTANCE BULB
SENSITIVE ELEMENT
FIXED RESISTOR
1
2
4
3
MEASURING CIRCUIT AND RECORDING PEN
RECORDING PEN
VARIABLE BALANCING CAPACITOR
FIXED CAPACITOR
VACUUM TUBE OSCILLATOR 1000 CPS
UNBALANCE VOLTAGE AMPLIFIER
BALANCE CONTROL TUBE
CHART
ELECTRONIC BALANCING CONTROL UNIT
POWER AMPLIFIER
SOLENOID MOTOR

...from unique simplification of electronic instruments!

Advanced design, based entirely on electronic techniques, gives *DYNALOG* instruments unequalled combination of Sensitivity, Speed, and Accuracy

For the first time, the possibilities of high all-around performance plus mechanical simplicity through electronic design have been fully realized in Foxboro *DYNALOG* null-balance instruments.

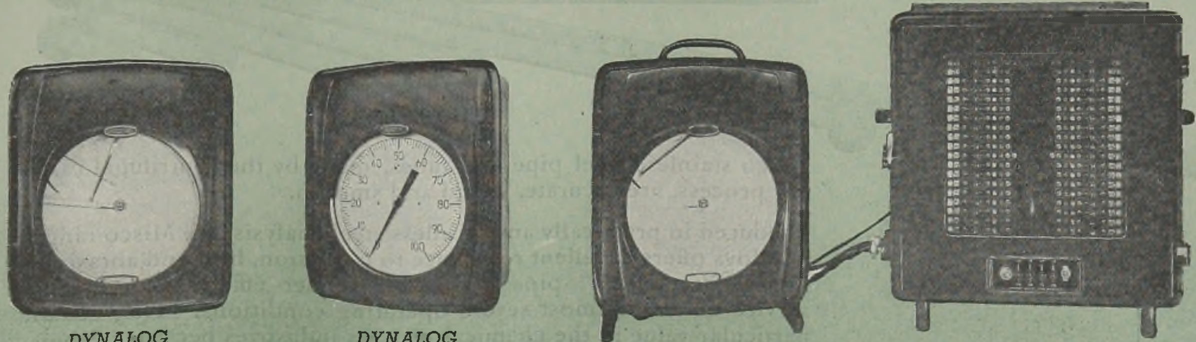
1. **High Sensitivity** – Definite balancing action on unbalance voltages of less than 15 microvolts. Bridge output voltages are amplified more than 1,000,000 in the electronic unit to control the balancing drive motor, yet performance is unaffected by any normal industrial plant fluctuations of power-supply voltage or frequency.

2. **High Balancing Speed** – 3 seconds for full-scale pen travel. Balancing drive motor with high power (at least 10 times as much as pressure-spring instruments). Lightweight and simple rigid-link drive system.

3. **High Calibration Accuracy** – ¼ of 1% of scale for all ranges. This results directly from the "live" balance drive with balancing capacitor and pen arm always power-positioned, even at balance point; and from the high balancing power developed by minute unbalances.

Greater Simplicity – Not only far more sensitive than previous null-type instruments, *DYNALOG* Instruments are also far simpler mechanically. The entire balancing mechanism contains only 5 moving parts! There is nothing to clean, lubricate, adjust, take up or replace in the measuring circuit or balancing system – *all mechanical maintenance has been eliminated.*

On any problem demanding the exceptional performance of these instruments, call in a Foxboro engineer. *DYNALOG* Temperature Recorders and Multiple-Point Indicators are available for 8-week delivery on AA1 rating. The Foxboro Company, 40 Neponset Ave., Foxboro, Massachusetts, U. S. A.



DYNALOG Temperature Recorder

DYNALOG Temperature Indicator

DYNALOG Multiple-Point Temperature Recorders, similar to this special strain gage instrument, are under development.

by FOXBORO

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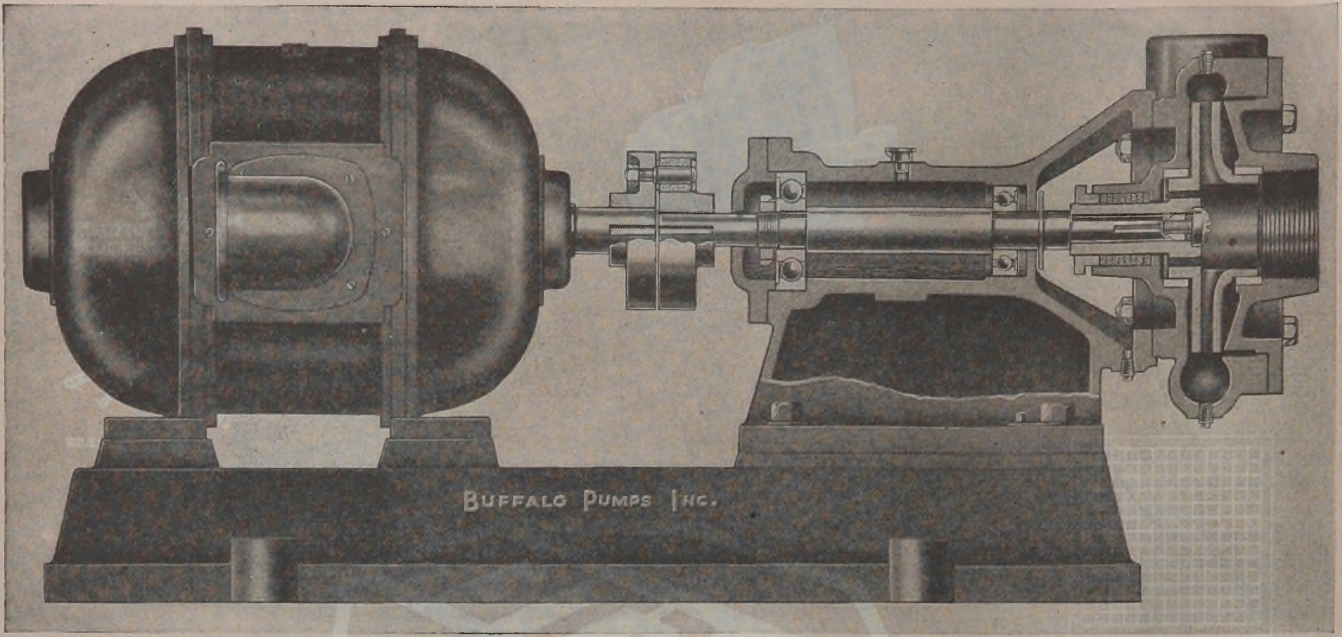
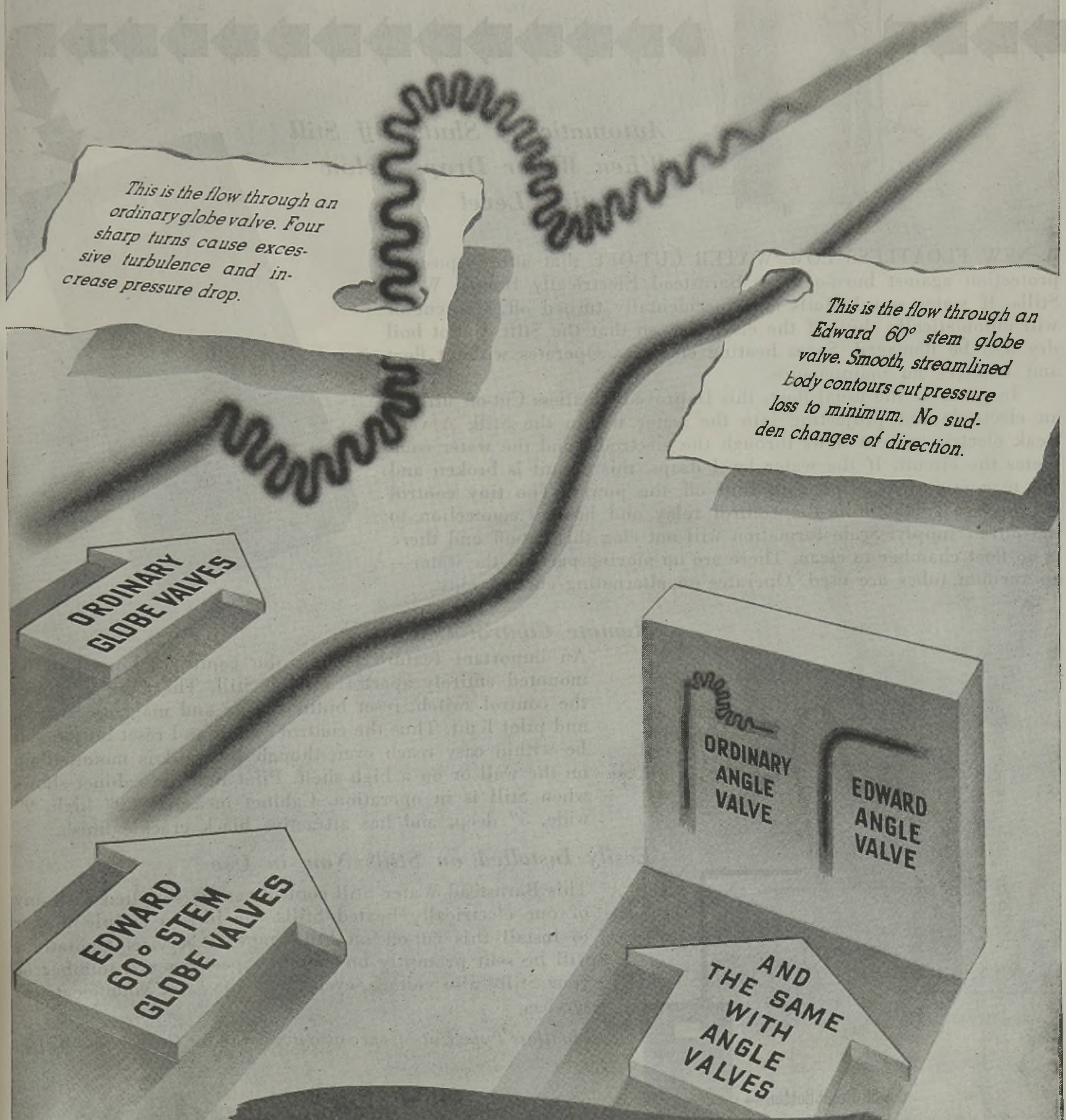
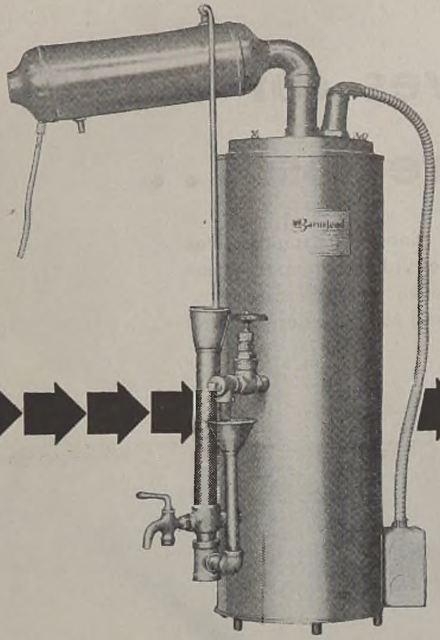
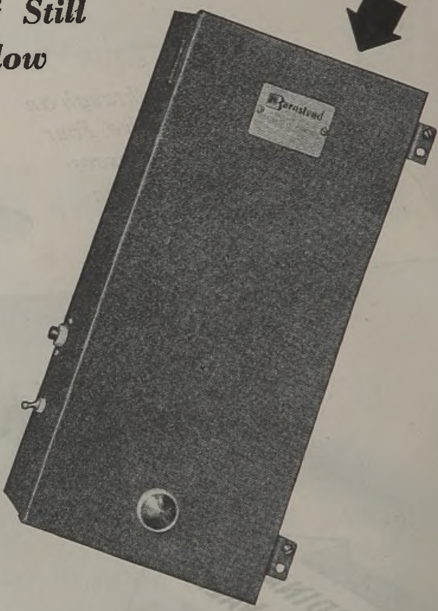
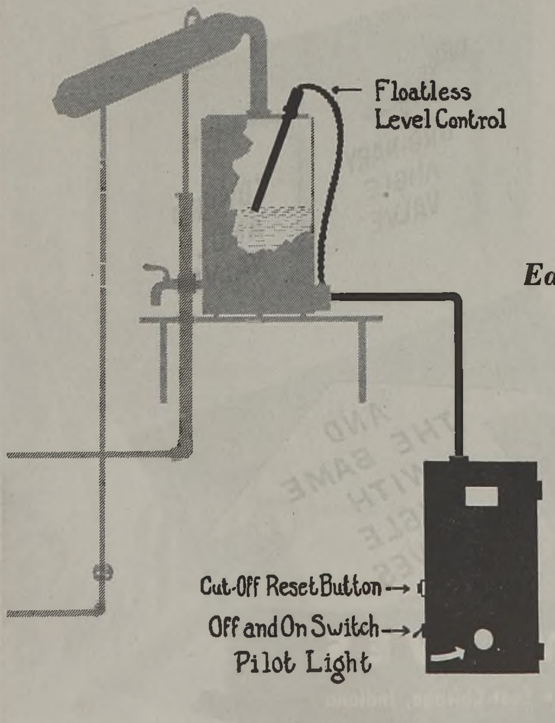

BUFFALO PUMPS INC.



ORDINARY GLOBE VALVES
EDWARD 60° STEM GLOBE VALVES
ORDINARY ANGLE VALVE
EDWARD ANGLE VALVE
AND THE SAME WITH ANGLE VALVES






Floatless Level Control
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Off and On Switch
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Your Guide to TRUSTWORTHY VALVES

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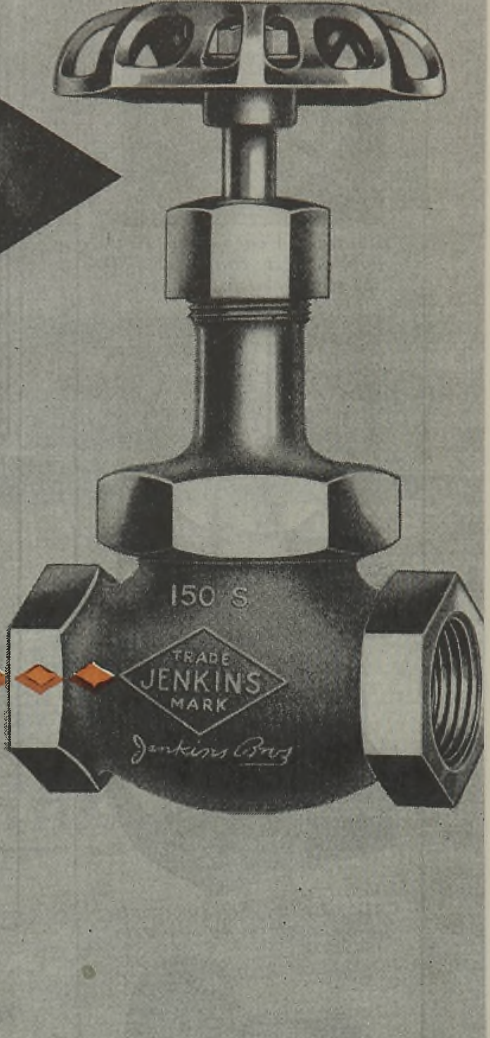

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Look for the famous JENKINS
DIAMOND-SIGNATURE TRADE MARK
and be sure of Extra Value in Valves

For more than 80 years, the familiar Jenkins Diamond Trade Mark has been the symbol of supreme quality in valves.

It is the mark that distinguishes valves of extra value . . . value assured by the superior materials that go into them, by the resourceful men who make them, by the integrity that has become synonymous with the name Jenkins.

Valves worthy of the universal trust the Jenkins Diamond has earned are the only valves that will ever bear this mark. It is our pledge to you of the finest quality it is possible to provide . . . now, and as long as Jenkins Valves are made.

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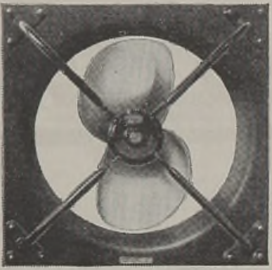
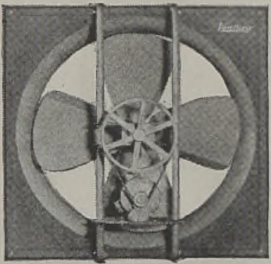
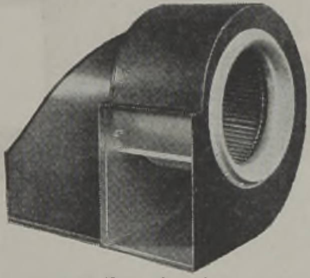
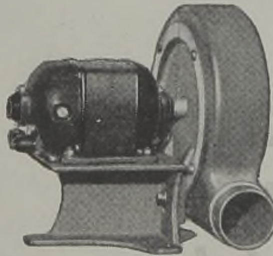
For every Industrial, Engineering, Marine and Commercial Service . . . In Bronze, Iron, Cast Steel and Corrosion-resisting Alloys . . 125 to 600 lbs. pressure

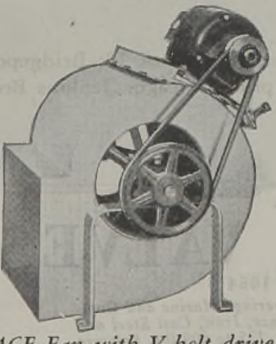
Sold Through Reliable Industrial Distributors Everywhere



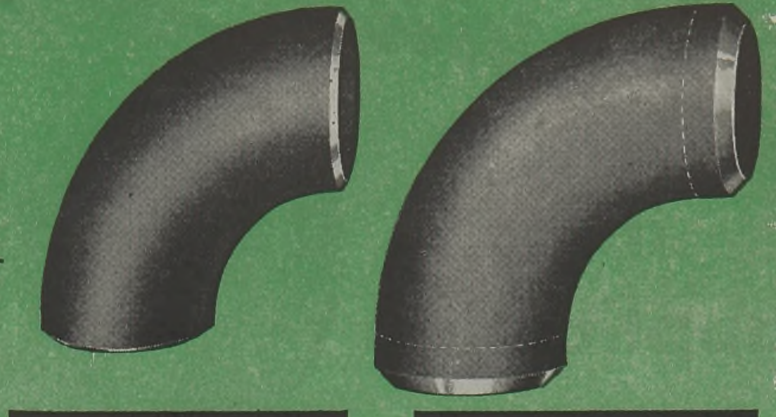








A
CHOICE
THAT CAN BE
IMPORTANT



MIDWEST "STANDARD" BUTT-WELDING ELBOW

MIDWEST "LONG TANGENT" BUTT-WELDING ELBOW

. . . . and ONLY MIDWEST offers THIS CHOICE

Before you select welding elbows to use on any given piping job, it will be worth your while to consider the relative values of the two elbows shown. On some jobs the correct selection can mean a real saving of time and money. Only Midwest offers you the choice of either type elbow . . . and there is no difference in price.

The "American Standard" elbow has a center-to-end dimension equal to one and one-half times the nominal pipe size. The Midwest "Long Tangent" elbow has a center-to-end dimension of one and three-quarters times the nominal pipe size; it has tangents (straight ends) equal to one-fourth of the nominal pipe size. These long tangents make it possible for pipe and fitting to be lined up more quickly and accurately. Less pipe is required, a short nipple and an extra circumferential weld are frequently eliminated, and slip-on welding flanges are more easily used.

Both elbows have all advantages of the unique Midwest manufacturing process: final working of the metal in compression (which means exceptional dimensional accuracy and uniformity), stress relieving, exact included angle, true circular section and uniform wall thickness.

MIDWEST
WELDING FITTINGS IMPROVE PIPING
DESIGN AND REDUCE COSTS

MIDWEST
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Sales Offices: New York—(Eastern Division) 30 Church Street
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Versatile in its application

. . . this Fairbanks-Morse Motor maintains its protective features in any position!

The reversible frame of this Fairbanks-Morse Motor provides for mounting the conduit box on either side. The lead-in can be from top or bottom. The bearing arms can be mounted in any one of four positions, 90 degrees apart. Thus, the motor may be installed in any convenient place—in any position, and still retain its protective features.

Other features listed below assure low-cost operation, greater dependability, and longer life. Yes, this is the motor of tomorrow, ready for you today.

OTHER PLUS FEATURES

Protected Frame—Dripping liquids and falling particles excluded in any mounting position.

Crossflow Ventilation—Another exclusive feature in frames 224 to 365 inclusive. Air moves in both directions, providing a motor of uniform temperature. No hot spots.

Recessed Conduit Box—An innovation for neat installations. Choice of conventional box or frame recess with cover flush with frame.

Balanced Characteristics—Motor rated 40° C., with high efficiency and power factor, and excellent starting and accelerating torques.

Ball Bearings—Sealed in and protected.

AND THE EXCLUSIVE *Copperspun* ROTOR

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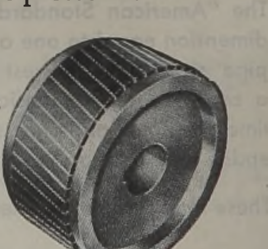

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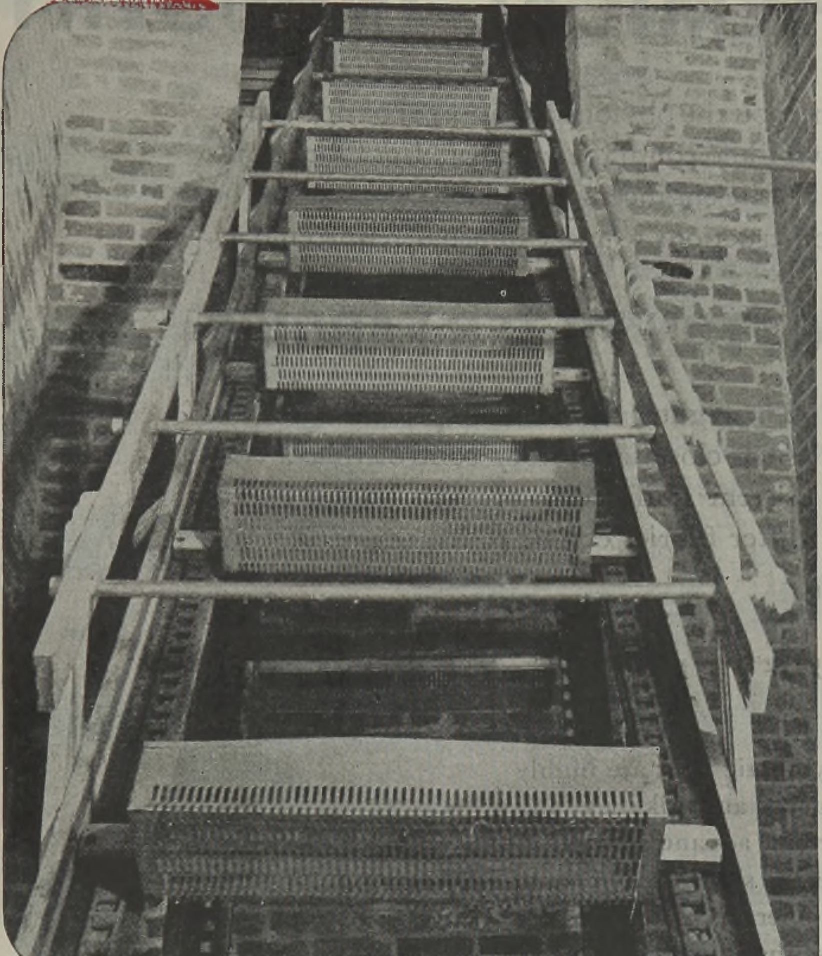

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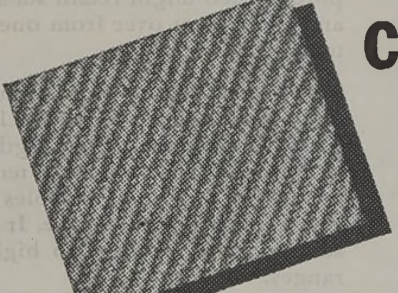

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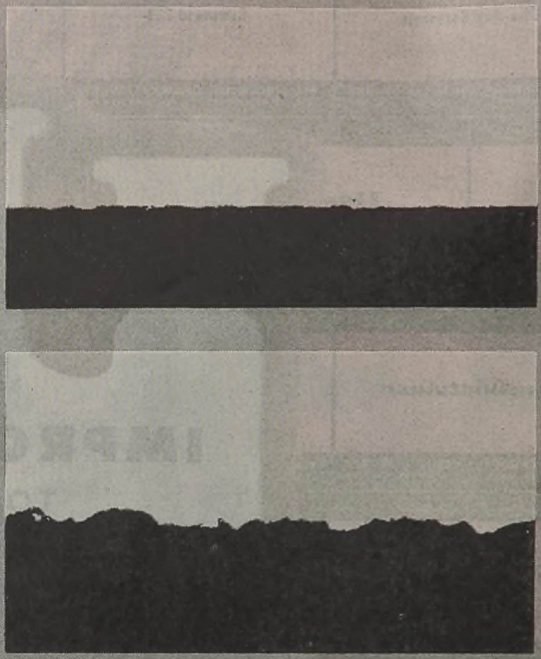

Photomicrographs, magnification 250:1. Above, unetched surface of SAE 1010 steel. Below, Ferrisul etched surface same steel. Etching by solution containing 10% Ferrisul, at 70°F. for 120 seconds. "Etch teeth" are shown to be .000375" high. Weight loss was .0104 lbs. per sq. ft. of area which corresponded to a calculated average penetration of .000258".

Those microscopic hills and valleys you see in the lower photomicrograph . . . etched there with Ferrisul . . . have functions important in three different handlings of steel:

1. Galvanizing. The light, evenly etched steel provided by Ferrisul treatment is preferable to a smooth, unetched surface because it gives the zinc coat a tooth to cling to . . . lessens the tendency of the coating to peel when the metal is bent or flexed.*

2. Drawing. A pre-etched surface provides space for the distribution and retention of lubricating agents during the draw. These lubricants, carried into the die, prevent scuffing of the finished surface, also reduce friction, lengthen the life of the die, and cut down the power required for the draw.

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Ferrisul, Monsanto's anhydrous ferric sulfate, is preferred for all three of these uses because: its action on steel is *rapid* (often 30 times faster than sulfuric acid), it does not liberate hydrogen and create consequent danger of embrittlement of steel; it has no acid fumes, and is easy and safe to use and store.

For full information on Ferrisul for metal treatments, write, wire or phone: MONSANTO CHEMICAL COMPANY, Merrimac Division, Everett Station, Boston 49, Massachusetts.

* * *

*Monsanto's research laboratories, working in close co-operation with industrial galvanizers, have developed valuable information on this work, especially on the optimum amounts of etch for ideal galvanizing . . . and are in a position to give assistance to galvanizers in adopting the use of Ferrisul.

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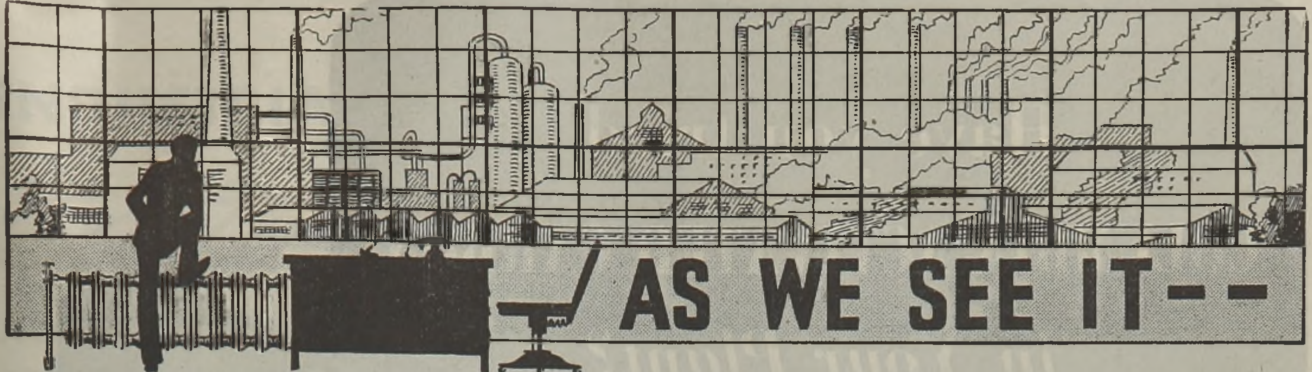

This Month

APRIL to Shakespeare may have meant uncertain glory but Ye Editors will back up the April issue with a vengeance, for there is no uncertainty about it. The issue will be known for years, we are sure, for its excellent papers on catalysis in the petroleum industry. There are seven articles, all written by experts on the subject, from the Symposium held by the A.C.S. Division of Petroleum Chemistry at the recent North Jersey meeting.

Three authors from the Sinclair Refining Company make a major report on the surface area of catalysts and the effect of sintering on area and structure. Voorhies, of Standard Oil Company of New Jersey, brings out several new facts concerning the rate of carbon formation in catalytic cracking. He states that carbon formation is, within limits, independent of the hydrocarbon flow rate. A third paper is on the use of aluminum chloride for making iso compounds from the straight-chain hydrocarbons of petroleum. Number 4 deals with silica-alumina gels and the effect on structure that variations in preparation of the gel would have. A brief paper on fluidizied fixed-bed catalytic cracking follows, and number 6 reports the catalytic isomerization of 1-hexene. The symposium winds up with a report on the catalysts used in synthetic liquid fuel processes—the Fischer-Tropsch process, the Bergius process, and the method of cracking petroleum fractions or fractions obtained in the hydrogenation of coal and coal tar. We hope that this line-up is impressive, and we reiterate its importance.

Keeping to the same subject, catalysis, we publish a paper by Archibald and Greensfelder on the catalysts behind the cyclization of *n*-heptane to toluene. The authors report that an 80% concentration of toluene is possible in the liquid product, using the technique described. In addition, the catalyst is said not only to be of value as a cyclization material, but also in dehydrogenation processes; it is therefore of great use in the dehydrogenation of methylcyclohexane to toluene.

Ipatieff, a great name in petroleum chemistry, and Schaad contribute a paper on the formation of heptenes and heptanes from propylenes and butylenes, via the catalytic route. This article describes a low-temperature process, and the heptenes obtained with a phosphoric acid catalyst were hydrogenated into heptanes having an octane number of about 90.

Canned orange juice is a fascinating subject, possibly because it would be so much easier, early in the morning, to unzip a can instead of patiently throttling the drops from the unwilling fruit. However, for the most part science has been unable, as yet, to capture the flavor of the juice as we usually know it fresh from nature's package. Oxygen, according to Boyd and Peterson, is one of the factors that destroys flavor, but length of processing and storage temperature are the two most important single items that rob the canned material of its tang.

Making ethyl alcohol from wood involves innumerable difficulties; Leonard and Hajny present a comprehensive investigation on the problems of fermentation connected with the process.

Rounding up the issue will be several additional important papers. One reports the compatibility of the new wonder insecticide, DDT, with materials with which it will probably come in contact during extensive civilian use; another is on a new potential raw material for resins, itaconic acid; and there is a study on still another resin material, cashew nutshell liquid.

WITH THE DEPARTMENTS. Brown discusses pumps and wartime developments, von Pechmann gives production executives a chart to help in the easy understanding of cost proposals, and Munch, among other items, clarifies some points on the use of hydraulic power in control instruments and a new mercury vapor detector.

Next Month

NEXT month we have a full quota of pages about the invention that Kettering claims the chemical industry made to prevent it from losing its shirt during the period between the laboratory and plant. We are speaking, of course, about the pilot plant, and the profession deserves great credit for the remarkable development that has enabled it accurately to transfer the war developments from small scale operation into commercial units without undue loss of operating time due to "bugs."

The A.C.S. Division of Industrial and Engineering Chemistry held a symposium on pilot plant phases of unit processes at its North Jersey meeting, and from that program we print ten papers. Subjects range from vapor-phase catalytic processes to ABC discussions on the utility of pilot plants and pilot plant equipment.

Barnacles cause the Navy plenty of trouble, slowing down the speed of ships and requiring their dry docking at frequent intervals. Therefore we are pleased to present two articles on the subject, one concerned with a method of evaluating antifouling paints, and the other on the mechanism of corrosion under antifouling paints.

We have recently received approval of a paper held up by the censor for over four years. It is on the properties of acrylonitrile, and is the first really authoritative article on the subject to appear. The country knows a lot about this substance and much has been done on its use since we entered the war, but this is as much as we can get through at this time.

Cellulose acetate will soon have no secrets, for the scientists are busy poking into its private life. Viscosities, osmotic molecular weights, and polymolecularity will make the May issue memorable to the textile chemists. Then, too, we will have the item promised last month on the use of sulfur and hydrocarbons to make hydrogen sulfide. Resinous plasticizers, hydrocarbon properties, soap manufacture, and acetylated castor oil will round out the May issue, and That Is How We See It.

F. S. Van Antwerpen

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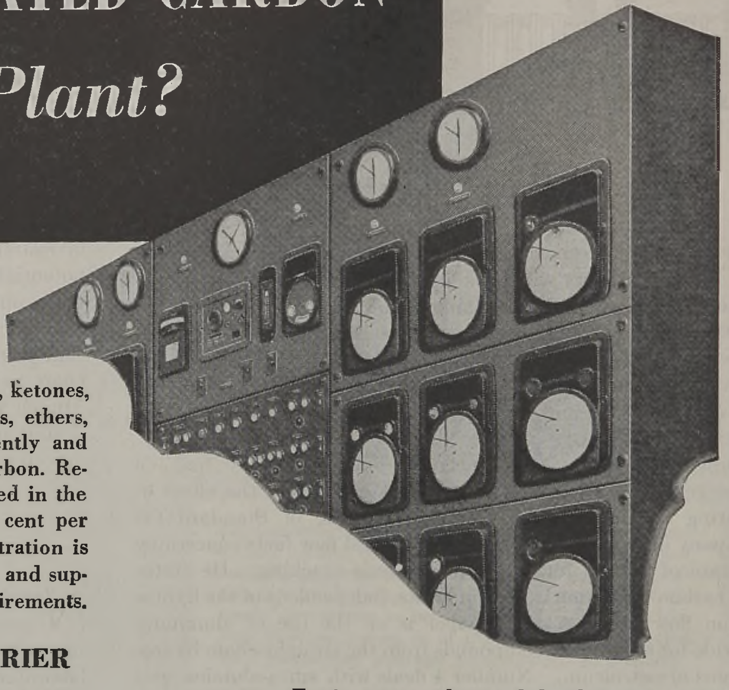

Equipment employing Columbia Activated Carbon for solvent recovery or gas purification is often automatically operated.

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INDUSTRIAL AND ENGINEERING CHEMISTRY

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY

Editorials

WALTER J. MURPHY, EDITOR

A Straw in the Wind?

WILLARD H. DOW, president of the Dow Chemical Company, last month presented some figures on magnesium productive capacity before a Senate Small Business Committee hearing that should be the cause for some very reflective thinking about disposal of surplus plants, not only for the manufacture of magnesium, but of many other materials.

Actually, we have a magnesium productive capacity of some 600,000,000 pounds. At one time the War Production Board suggested a goal of 727,000,000 pounds. Our peak consumption was 332,200,000 pounds in 1943, and only 316,000,000 pounds last year. Willard Dow, who certainly should know at least as much, if not more, about the postwar markets for magnesium than any one else, thinks five years hence we may consume as much as 63,000,000 pounds. Small wonder that 85 per cent of the capacity of our existing magnesium plants is now shut down, with a stock pile of 100,000,000 pounds and the immediate outlook on consumption none too bright in relation to our present facilities to produce.

That we far overshot the mark in magnesium is self-evident. Was it done purposely? Or was it just a poor guess on somebody's part?

There are those who feel that both magnesium and aluminum were singled out for special treatment; that the rabid "trust-busting antimonopolists" saw an opportunity to really go to town.

We should, however, think back to the year before Pearl Harbor and the uncertain desperate months that followed the Jap sneak attack on Hawaii. Who then could tell for a certainty what we would need in the way of magnesium; indeed, what we would need of everything vital to wage a modern technological war?

The illuminating figures presented by Dr. Dow on magnesium probably are but the forerunner of somewhat similar figures for many other products. His story should be cause for some sober thinking here in Washington when the subject of surplus plant capacity is up for discussion and ultimate decision as to final disposal. The stake the American public has in this question is great; how it is handled very likely will determine the future course of this country for years, if not for all time. Lincoln once said: "I believe this Government cannot endure permanently half free and half slave." Neither can we operate successfully with half of our industrial life government-owned and operated, and the other half in the hands of private enterprise. The decision is a momentous one to make. We hope the American public at least gets all the facts—not merely publicity or propaganda—before the pattern is cut for postwar America.

Meetings in Print

AS SPRING nears, we hope that most members of the American Chemical Society feel the same keen disappointment that we experience when we contemplate the lack of the traditional spring meeting, and this feeling is made doubly poignant by the announcement that an application for a permit to hold the fall meeting in Chicago has been denied. We have grown to look upon the national meetings as reunions, where we count noses and check up on the research and chemical achievements of the past months. This year the meetings would have been especially interesting, as censorship restrictions are beginning to lift, and there was always the hope in the back of our minds that the surrender of Germany would come during an ACS meeting. After all, we for one expect Germany's end this year, and the Society has been competing with Hitler for news space too long at our conventions to allow him to make his exit without the ACS members meeting together for an appropriate celebration. But we hope that these are the last meetings that must be cancelled because of the inclemency of the human spirit, and that soon we can meet to discuss the intricacies of peacetime chemistry and research.

But the fact remains that we are still a long way from the end of the war, and it may be possible that our hopes for peace will not materialize and still other meetings of the ACS may be cancelled. The loss caused by such cancellations cannot be estimated, for the progress of our profession and the whole chemical industry depends upon freely exchanged information. Therefore, it was with great enthusiasm that we read of the proposed "Meetings in Print" as published in the ACS News section of the February 25 issue of *Chemical and Engineering News*. The idea started in the New York Section, it now has the official endorsement of President Marvel, and all local secretaries have been advised of it in an official communication. Briefly the plan is to designate the final meeting of the spring season as a national meeting in miniature. Attendance and papers will be limited to the members of the section. The papers and speeches can be published in ACS journals and thus information can be spread to all. As Secretary Parsons said, in his letter to the sections suggesting that such local meetings be planned, a number of worthwhile papers are unquestionably available. The local sections should be able to plan outstanding programs, and possibly for the first time will recognize home talent.

We give it our hearty endorsement, and congratulate the New York Section and its active chairman, B. L. Clarke, for conceiving, during these trying times, such an outstanding and concise manner of aid to the chemical profession.

Getting the Story Over

WE HAVE been stressing recently the necessity of keeping the public reliably informed regarding the problems affecting scientists and technologists in general, and chemists and chemical engineers in particular.

For many years we have been content to emphasize only the scientific achievements of the professions, the contributions to the advancement of the physical welfare of our people, but now it is necessary to let the solid citizens of this country know about such matters as patents, cartels, deferments, maintenance of an adequate number of scientific trainees even in a war period, collective bargaining, disposal of surplus plant capacity, an adequate flow of risk money, etc. If we fail to do this effectively, the public will swallow, as gospel truth, the distorted half truths, innuendoes, and downright misrepresentations that are being fed them from every direction.

Obviously, we cannot expect the lay public to read our journals, but we can reach editors, science writers, and many others through the pages of the SOCIETY journals, and the activities of the AMERICAN CHEMICAL SOCIETY News Service. We should investigate the possibilities of both the radio and motion pictures as additional media for disseminating entertaining yet factual information about the problems which confront our profession and the chemical industry. We are not so presumptuous as to assume that the editors of *Collier's* obtained from ACS sources information upon which they based the following editorial, entitled "Back to Patent Fundamentals", which appeared in the March 24 issue. All we can say is that perhaps some of the sound thoughts expressed in this editorial were crystallized by an ACS news release, or, in some indirect manner, that we helped to stimulate the pen of the editor of *Collier's*. Whether or not we had anything to do with this particular editorial is beside the point. We welcome such aid as *Collier's* has given in this case, for in this way we will reach the public—millions of men and women who want the truth, not propaganda or pure fiction. And now for the *Collier's* editorial which says many things much better than we succeeded in doing in the past. Show it to your friends.

> The United States Supreme Court recently handed down a patent decision which we think deserves a round of applause. A patent is granted to an inventor or an owner of an invention to give him a monopoly on it for a long enough time to make some money out of it, as a reward for the ingenuity, research, expense, etc., that went into it. Our patent laws have been a strong stimulus to American inventive talent.
>
> Of late years, the Department of Justice has been ornamented with a lot of theorists who want to break up the patent laws' frank granting of monopolies to inventors for limited periods of time. A share-the-patent philosophy, so-called, has been rampant in the Department of Justice.
>
> In the case mentioned above, the Department of Justice wanted the Supreme Court to compel patent holders in the glass industry to license patented processes to all comers. Congress has long refused to pass any laws to that effect. The idea is a pretty one in the abstract; but the catch is that human nature just does not function so that the idea would work out in practice; meaning that if potential inventors could see no hope of generous rewards, they would remain mostly potential.
>
> The Supreme Court recognized all this in the glass industry case, and rebuffed the Department of Justice. It held that a patentee is "not in the position of a quasi trustee for the public, or under any obligation to see that the public acquires the free right to use his invention. He has no obligation either to use it or grant its use to others."
>
> Short of abusing his patent rights to the public injury, said the court, a patentee can tie just about any strings he desires to the use of his patent.
>
> The decision makes sense to us. We think it will help to keep American ingenuity alive and eager, to the benefit of all of us. And now if the Supreme Court at its next opportunity will kick out another Department of Justice notion—that a "flash of inventive genius", and only a "flash of inventive genius", brings forth a true invention, and that the discoveries of a cooperative group of scientists cannot be the result of a flash of genius, and so cannot be patented—the court will perform another public service. That notion would take away the key reason for the big, productive research departments maintained by many of our largest industrial concerns. Without organized research, our industries would be just about sunk.

H.R. 97

PATENTS are of great concern to those in the chemical profession. Much of the research progress of the Nation depends on the promise of the 17-year monopoly conferred by the patent right, and legislation affecting the status of patents is properly of interest to the chemical profession. A bill, H.R. 97, introduced by Representative Voorhis of California, is now before the House of Representatives. The bill, it is said, was sponsored by the Department of Justice and referred to the Judiciary Committee instead of the House Patent Committee because it was thought the action in the Judiciary Committee would be more favorable. The proposed law is dangerous, not only to the chemical fraternity but to the country as a whole, and for this reason we give a brief résumé of its major points.

The bill is a supplement to the antitrust law and is designed to bring the patent right as a potential monopoly within its scope. The amendment consists of five sections, numbered from 27 to 31. Section 27 requires the United States courts to notify the Attorney General whenever the validity, scope, or infringement of a patent is before them for trial. In addition, the Court must allow the Attorney General to intervene and become a party in the presentation of evidence.

Section 28 provides that "every sale, assignment, or other conveyance of any patent or patent application, or interference proceeding, and every transfer by license, agreement, or otherwise, of rights under a patent shall be embodied in a written instrument", and that every such written agreement be filed with the Attorney General within 30 days after it is made. When the bill has been a law for six months, all such instruments described above that are now in effect must be filed with the same official. Penalty for nonobservance is a fine of $500, plus $25 per day for each day over the time limit.

Section 29 makes it illegal to use or fail to use, or fail to grant licenses on a patent or patent application, if such action has the effect of limiting the article in commerce. The bill goes on to say that "The use or nonuse of any patent or patent application or of any interest therein in violation of the section shall render such patent or patent application null and void, and any court having jurisdiction of any action, civil or criminal, involving violation of this section shall adjudge that such patent or patent application is null and void". In addition, a $5000 fine, a year in jail, or both, may be imposed.

Section 30 says that if Section 29 is violated the violator will not be liable to criminal punishment provided he filed, in advance, with the Attorney General, a statement describing fully the proposed methods of doing business. It also states that if the Attorney General does not write him within 90 days after submission of said document that the agreement is illegal, he may proceed. If the Attorney General does not like what the patent holder proposes to do, an appeal may be made to the District Court of the United States. If the Court gives the patent holder a bill of health, the Court must, upon the petition of the Attorney General, give a reservation of jurisdiction which will enable the case to be reconsidered at a later date. Section 31 allows a party to show the invalidity of a patent in any litigation involving the antitrust laws. That, briefly, is the gist of the proposed law.

The Chairman of the House Patent Committee, the Honorable Frank Boykin, of Alabama, immediately protested the referral of the bill to the Judiciary Committee instead of to the Patent Committee. He claimed that because the bill profoundly affected the patent system, the House Committee should investigate, and he then appended to his letter seven pages of views, mostly objections to the bill.

Several possible corrections could be made in the present patent law. The Patent Planning Commission has studied this problem and made specific recommendations. As one instance, the commission wanted certain agreements concerning patents recorded with the Patent Office, obviously the proper place for them. In fact, a bill providing for the recording in the Patent Office of all agreements relating to patents is under consideration by the House Patent Committee. There is no reason to file them with the Attorney General. There is already in existence in the Patent Office a record of assignments and licenses affecting patents, fully indexed and readily available for public inspection. This backlog of information and experience should not be scrapped.

Perhaps the biggest objection to the bill is that it is based on the assumption that patents are inherently dangerous instrumentalities rather than grants in recognition of valuable contributions to the national economy. This viewpoint must be avoided for it is dangerous. Patent holders and inventors are not criminals seeking to do evil. They are almost invariably good American business men trying to live up to a democratic ideal of giving the public the benefit of inventive ability in exchange for the chance to make a profit under a monopoly granted and recognized by law.

Still Necessary to Button the Lips

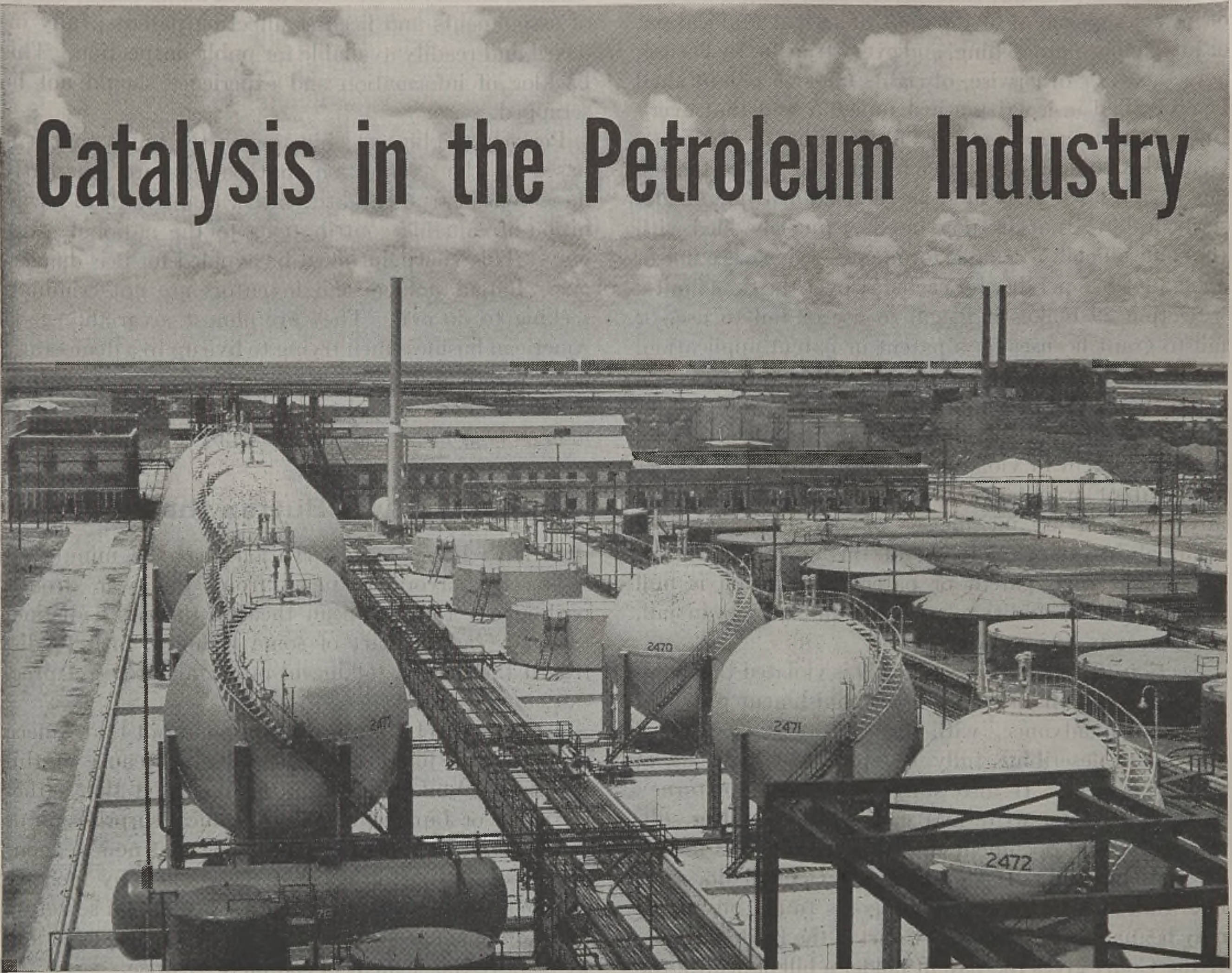
IT HAS been our observation that the minute we receive favorable news from the war fronts, particularly the European theatre, there is a distinct tendency on the part of some technical men to disregard the ban on talking in public about secret processes and products.

Again, we feel it is our duty to point out that American boys are likely to die needlessly because of this practice. While there is little likelihood that either Germany or Japan can spring technical surprises on us at this stage, it is certainly probable that new weapons developed by us can shorten the conflict by months, maybe even by years, provided we keep them secret up to the moment they are released on our enemies and we achieve the element of complete surprise.

Remember, if it is not your boy that is needlessly lost by idle talk, it may be your neighbor's. We who have been honored by being entrusted with some phase of developing America's secret weapons also have a grave responsibility to keep our secrets well guarded. Resist the impulse to talk about your work with those who can in no way contribute to its success, and be certain when you discuss it with collaborators that you do it out of earshot of others.

> THERE is a great voice in the world today, the voice of science and technology. It is a voice heard since ancient times but never until today has it spoken with such authority, have its words been so filled with promise, has it been listened to with such hope. And in no country in the world does the voice speak as eloquently as in our own.—ROBERT P. PATTERSON

Catalysis in the Petroleum Industry



COURTESY, CHICAGO BRIDGE AND IRON COMPANY

The seven papers which follow were part of a symposium presented before the Division of Petroleum Chemistry at the 108th meeting of the American Chemical Society in New York. C. L. Brown, Esso Laboratories, Standard Oil Co. of N. J. (Louisiana Division) presided

MEASUREMENTS of the surface areas of catalysts are important for several reasons. In the first place, they indicate the extent to which varying activity may be attributed to changes in surface area. Secondly, the area values provide a means for determining whether promoters and supports improve catalysts by increasing or maintaining area or by qualitative changes that increase catalyst activity per unit surface area.

For example, two catalysts of widely different areas may show the same activity per unit bulk or reactor volume or per unit mass. It is then essential to know the area difference because of the significance of the surface composition of the low-area catalyst. Provided the surfaces of the two catalysts have the same relative accessibility, the surface of the low-area catalyst is qualitatively superior, as demonstrated by its greater activity per unit area (specific activity). It is also important to study the catalyst of greater area with respect to the preparation techniques responsible for the high-area structure. It should thus be possible to combine this knowledge and incorporate the superior chemical or promoter composition in the structure of greater surface. The ultimate objective of such studies is to obtain a thermally stable catalyst of optimum specific activity and area.

The "relative accessibility" term used above includes all the factors in catalyst activity other than surface area and specific activity. The term, therefore, includes such factors as particle size and pore structure which have been discussed by Thiele (*18*) and more recently by Hougen and Watson (*13*).

"Accessible area" or "surface area" refers to the solid surface on which a reactant or any specified adsorbate is physically adsorbed under static equilibrium conditions. In certain cases of closely related catalysts, the accessible area alone may be sufficient for predicting catalyst activity.

Furthermore, area determinations provide a method for following changes in catalyst structure that occur at elevated temperatures. The temperature factor is important in the preparation and calcination of the catalyst and throughout the actual processing and regeneration treatments. For example, it is obviously important to ascertain the temperature at which a catalyst suffers a major loss in area. A portion of the following study concerns the area and adsorption properties of a supported catalyst after sintering at various temperatures. Such sintering studies may clarify the interpretation of the corresponding changes in catalytic activity.

SURFACE AREA OF CATALYSTS

Effect of Sintering on Area and Structure of a Supported Catalyst and Its Components

THE IMPORTANCE of surface area measurements in catalyst studies is discussed. Nitrogen adsorption isotherms are used to follow area changes of a supported catalyst after heating for various periods at 340°, 400°, 500°, 600°, and 650° C. Similarly, area values are obtained for the diatomaceous earth support after 340° and 650° C. heat treatments and for the unsupported catalyst after a 340° treatment. Areas calculated according to the Brunauer-Emmett-Teller equation show that the supported catalyst has a considerably greater area than either the unsupported material or the support. The supported catalyst loses 5% of its area at 500° C., 26% at 600°, and 75% at 650°; the support suffers a loss of 39% at 650° C. Fair agreement is found between the measured area of the support and the area of a model based on electron microscope pictures. An adsorption-desorption isotherm determination on the supported catalyst demonstrates a pronounced hysteresis effect which is discussed in relation to pore structure. Consideration is also given V_a/V_m isotherms as a means for studying specificity in nitrogen adsorption on the various solids.

HERMAN E. RIES, JR.,
ROBERT A. VAN NORDSTRAND,
AND JOHN W. TETER

SINCLAIR REFINING COMPANY, EAST CHICAGO, IND.

If the entire area of the catalyst is uniformly active and of the same relative accessibility, the relation between area and activity losses on heating is direct. If only active centers function, their extent in some cases may also be proportional to the total area. However, it is more likely that during the sintering process the fraction of such active centers that disappears is greater than the fraction of total area lost. A simple geometric relation may account in part for this if active centers exist in the form of edges and points and if sintering is considered to be the formation of larger particles or crystals. It has been pointed out (*17*) that for equal masses of geometrically similar particles the sum of the edge lengths is proportional to the square of the total surface, and the total number of points is proportional to the cube of the total area. Hence, if active centers are represented by edges and points, the activity of the catalyst may be very sensitive to area change on sintering.

Finally, area measurements may yield valuable information concerning the structure and function of supports. Careful investigation of the surface characteristics of the support should be accompanied by corresponding studies of the supported catalyst and the unsupported material.

The present paper deals principally with adsorption isotherm area measurements of a supported catalyst and its components. Included is a preliminary discussion of the high relative pressure region of the isotherms as related to hysteresis, average pore radii, and the number of adsorbate layers deposited at the saturation pressure.

DETERMINATION OF ADSORPTION ISOTHERMS

The apparatus and procedure are essentially the same as described by Emmett and Brunauer (*5, 6, 8*). Figure 1 is a general view of the two systems now in use. Each apparatus includes a 100-cc. bulb buret, a 5-cc. buret-manometer graduated in 0.01-cc. units, a mercury diffusion pump system, a McLeod gage, and a vapor pressure thermometer. Reservoirs and purification trains for nitrogen and helium are also incorporated.

An oxygen vapor pressure thermometer is used for low-temperature measurement in the following studies. The nitrogen vapor pressure values for relative pressure calculations are obtained from an experimentally determined curve of nitrogen vapor pressure *vs.* oxygen vapor pressure thermometer readings. The temperatures of the liquid nitrogen bath are then obtained from these data using the values determined by Keesom and Bijl (*14*).

During the portion of the isotherm determination used for calculating area by the Brunauer-Emmett-Teller (BET) method (*3*), the temperature of the liquid nitrogen bath rarely varies more than 0.03° C. as measured by the oxygen vapor pressure thermometer. The range of liquid nitrogen temperature variation for different experiments is somewhat greater, approximately 0.4° C. It was found experimentally that the use of relative pressures corrects satisfactorily for temperature variation in this range. In some of the long time-interval determinations necessary to obtain equilibrium data in the high relative pressure region, temperature variation is somewhat greater than in the BET portion. However, the frequent addition of liquid nitrogen somewhat richer in nitrogen than the original bath is effective in maintaining relative constancy over periods of several days.

The nitrogen and helium gases used in these experiments are obtained from the Ohio Chemical Company and are, respectively, 99.8 and 98.2% pure. The nitrogen is further purified by copper gauze at 500° C., a large drying tube containing barium oxide or phosphorus pentoxide, and a dry ice–acetone trap. The helium is further purified with activated charcoal packed in a trap at liquid nitrogen temperatures. The purifications are performed batchwise by allowing small volumes of the gas to remain in the purification system approximately 30 minutes.

The supported catalyst, A, is in the form of $^1/_8$-inch pellets. The unsupported catalyst, B, was prepared by L. E. Olson of these laboratories in a manner similar to that used for the supported catalyst. Catalyst B is in the powder form. The carrier, support C, is a finely divided diatomaceous earth.

Each isotherm determination is preceded by a thorough degassing of the catalyst and adsorption bulb in an overnight elevated-temperature evacuation. The catalyst sample is maintained at 340° C. and 10^{-6} mm. pressure for approximately 16 hours. Some of the sintering treatments are accomplished at higher temperatures during this evacuation, but in all other experiments the 340° C. evacuation is standard procedure. The sintering treatments are performed in vacuo for temperatures up to and including 500° C. At 600° and 650° C. the catalyst is heated in helium at atmospheric pressure in order to prevent distortion or collapse of the relatively thin-walled Pyrex adsorption bulb.

Dead-space volumes may be measured with helium at liquid nitrogen temperatures or with nitrogen or helium at room temperature. According to Emmett (*7*), nitrogen may be adsorbed at room temperature and atmospheric pressure to the extent of

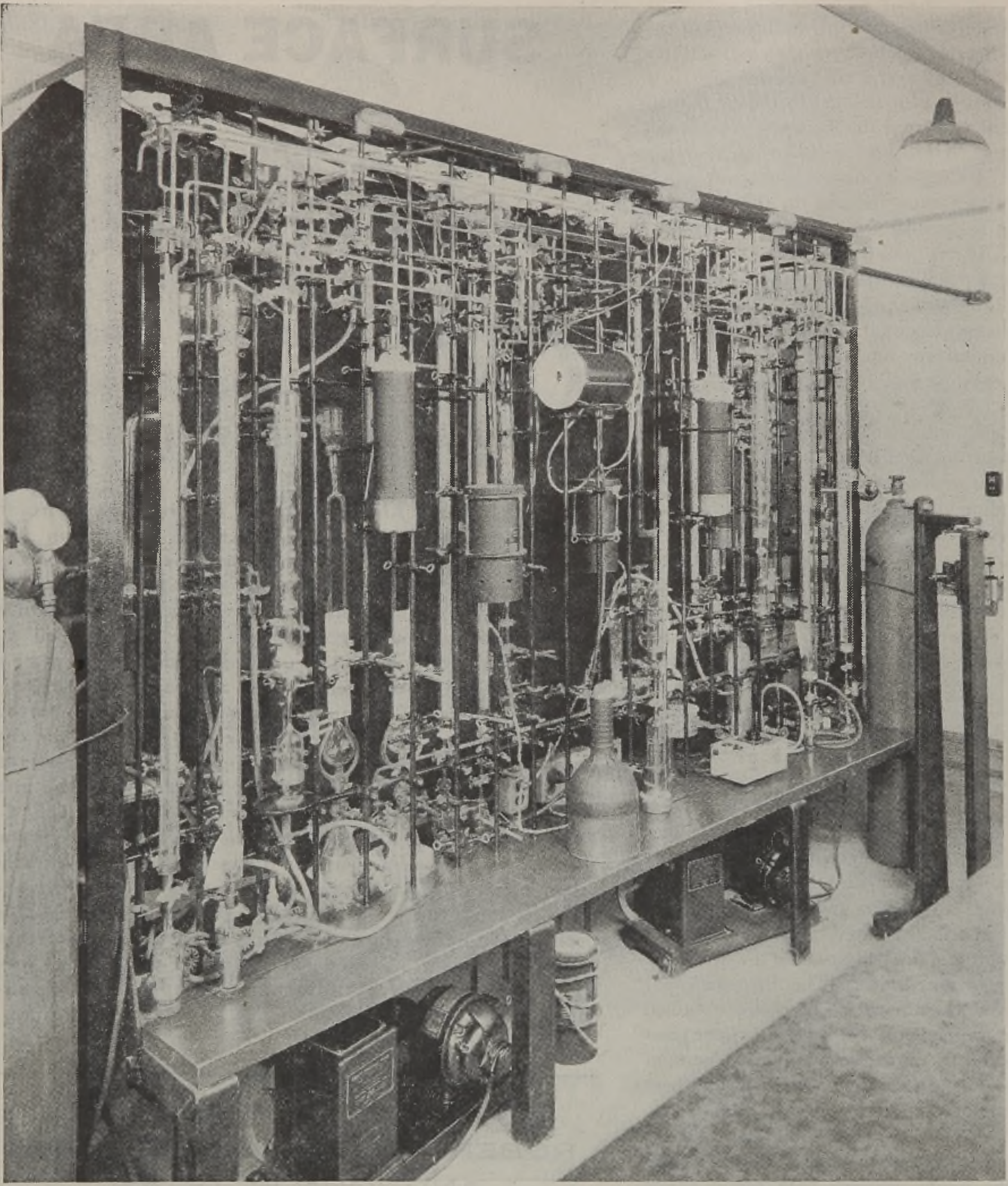


Figure 1. Adsorption Isotherm System for Catalyst Studies

0.02 fraction of a monolayer. Adsorption of nitrogen at room temperature thus introduces an error in the nitrogen dead-space measurement. The magnitude of the resulting inaccuracy in the adsorption data, however, varies throughout the isotherm since the amounts of gas adsorbed and held in the dead space are different functions of the pressure. Consequently the use of helium is generally preferable. The measurement with helium is conveniently performed under conditions corresponding to those of the isotherm experiments; that is, the catalyst bulb is immersed in liquid nitrogen during the determination. The volume of nitrogen adsorbate in the dead space is corrected for the deviation of nitrogen from the perfect gas law. The correction is based on a 5% deviation at −195.8° C. and 760 mm., with an assumed proportional variation with pressure as recommended by Emmett and Brunauer (*9*).

In the present study the dead-space volumes are obtained by means of nitrogen at room temperature, with the exception of experiments 33 and 34 in which helium is used at the temperature of the liquid nitrogen bath. Dead-space measurements, however, have been performed with both helium and nitrogen for solids of the type studied here. These experiments demonstrate that the error introduced in the area measurements may be as great as 1%. In all cases in which nitrogen is used for the dead-space measurement it remains in the system as the first addition of adsorbate gas, and therefore adsorption at room temperature does not enter as a double error (dead space and volume adsorbed). Another factor that must eventually be considered in a rigorous treatment of dead space is the reduction of the dead space by the volume of the adsorbed material.

A somewhat qualitative statement may be made at this point regarding the time required for adsorption equilibrium. In the relatively linear central portion of the common sigmoid isotherm, equilibrium is reached quite rapidly. For points on the steeply rising initial portion of the curve, equilibrium is achieved in a slightly longer period for similar pressure increments. Considerably greater time is required in the higher relative pressure portion of the isotherm. Near the saturation pressure in the following series of isotherms, time intervals of 2–4 hours may be required to establish equilibrium.

It may be that the equilibrium time is related to the time required for the dissipation of the heat liberated on adsorption and is, consequently, a function of the amount adsorbed and the heat of adsorption. Heat liberated at the catalyst surface is difficult to dissipate in the finely divided solid, low-pressure gas system, as pointed out by Beebe (*1*). Large amounts of gas are adsorbed for small pressure increments at the relatively low pressures. Similarly, large volumes are adsorbed or condensed in capillaries in the high-pressure region. However, in the linear central portion small volumes are adsorbed for corresponding pressure increments; also the heat of adsorption is less for the second layer than for the first. These relations are apparently in good agreement with the observations.

The extremely slow equilibration in the higher relative pressure region, requiring 2–4 hours near the saturation pressure, may be due, however, to several factors. For example, the decrease in the effective pore radii by the thick films deposited in this region will decrease the rate of gas diffusion to the interior and will retard the movement or distillation of condensed adsorbate into equilibrium positions in the capillaries. This factor combined with the thermal effects of adsorption-condensation phenomena may account for some of the equilibrium difficulties.

CALCULATION OF AREA

Area values are calculated from the adsorption isotherms by means of the Brunauer-Emmett-Teller (BET) equation (*3*):

$$\frac{p}{V_a(p_o - p)} = \frac{1}{V_m c} + \frac{(c - 1)p}{V_m c p_o}$$

where V_a = volume adsorbed at measured pressure, p; V_m = volume adsorbed in monolayer; p_o = saturation pressure of adsorbate gas; c = a constant related to heat of adsorption and heat of condensation of adsorbate.

Since the equation is linear, a plot of $p/V_a\ (p_o - p)$ against p/p_o will yield a value for V_m. The least squares method is applied to the following data.

Emmett and Brunauer suggest using the linear portion of such a plot between 0.05 and 0.35 relative pressure. The data of most of the following experiments fall on good straight lines over a slightly smaller range. Near 0.05 relative pressure the deviations are almost negligible, but at 0.30 relative pressure they become appreciable in a number of experiments. The deviations are always below the line at 0.05 and above at 0.35 relative pressure (Figure 5). Consequently, the data are used up to the point at which the expected trend in the deviations appears.

Each area value has been confirmed by at least one duplicate determination. It is convenient and practically necessary, particularly for the *in situ* sintering studies, to express area as area per gram of the original weight of the catalyst, although it is recognized that volatile matter may be lost during sintering treatments. Similarly V_a and V_m represent volumes adsorbed per gram of original weight.

The V_m values obtained by the BET method are translated into area units (square meters per gram) by using 16.2 sq. Å. as the area value for the nitrogen molecule (*9*). Harkins and Jura (*12*), however, suggest the use of 15.25 sq. Å. for porous solids and 16.2 sq. Å. for nonporous solids. The V_m values are included in Table I because they represent relative areas according to the BET equation without the assumption of a specific molecular area for nitrogen; or more correctly, they represent the relative numbers of molecules adsorbed.

Table I brings out the good agreement between the calculated V_m values and those obtained from estimates of the *B* point, the lower extremity of the central linear portion of the isotherm, as recommended in the earlier work of Emmett and Brunauer (*9*). Careful examination of the so-called central linear portions of these isotherms reveals irregularities similar to a few cases reported by Emmett and DeWitt (*10*). Perhaps these are related to the phase changes now being studied by Harkins and Jura.

The last column of Table I gives the relative pressures corresponding to the V_m values. These are quite different for the various adsorbents listed. This difference may indicate an appreciable specificity in the adsorption and will be discussed further in connection with the isotherms plotted as adsorption per unit surface.

SINTERING

Because of the war a considerable portion of the results obtained may not now be disclosed. This discussion therefore represents only a small part of a rather extensive study of catalysts subjected to various treatments. The nitrogen isotherms for the series of sintered samples of catalyst A are presented in Figure 2. The decrease in adsorbing surface with increase in sintering temperature is apparent. Table I gives the calculated area values. The area of the original material, evacuated at 340° C., is taken as that of experiment 15, 119.8 sq. meters per gram; this value nearly represents the average of four determinations, three of which were performed on different samples in the adsorption bulb. The sample used in experiment 15 is relatively large, 4.997 grams, for a material in this area range.

The high relative pressure points near p_o were determined in many of these experiments but are omitted in Figure 2. Figure 7 includes complete curves for those determinations in which special care was exercised in the high-pressure region. Figure 3 presents the isotherm data plotted according to the BET equation for the relative pressure range, 0.05 to 0.35.

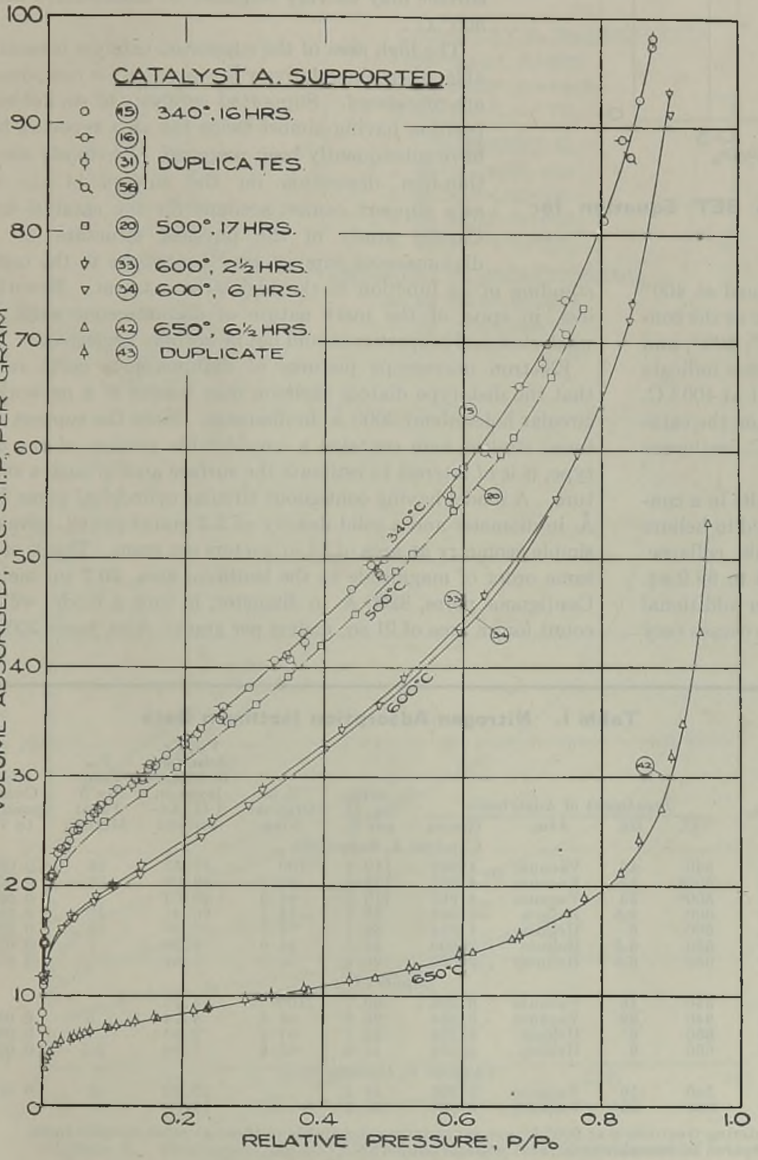


Figure 2. Nitrogen Adsorption Isotherms for Catalyst A, Supported

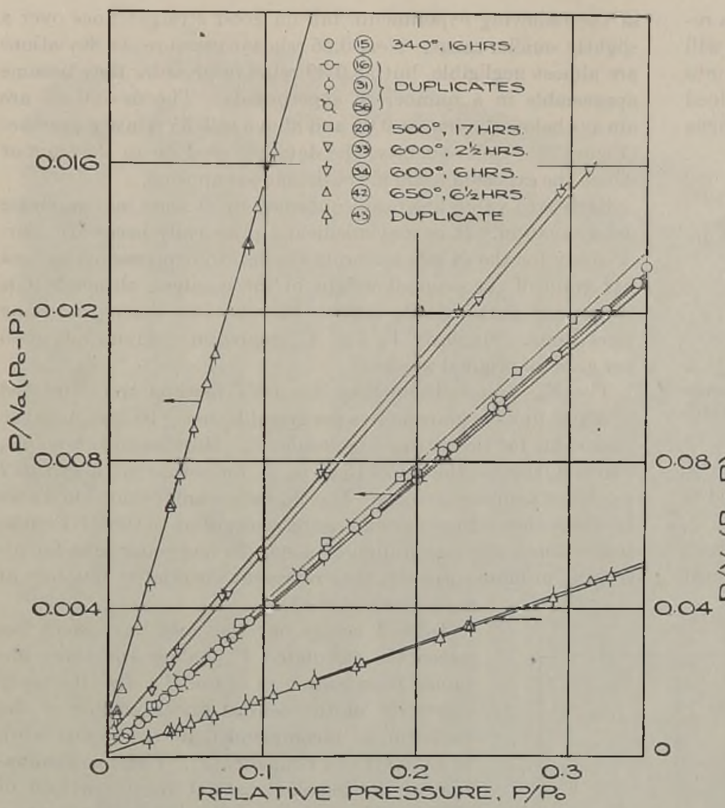


Figure 3. Nitrogen Adsorption According to BET Equation for Catalyst A, Supported

Although sintering experiments have been performed at 400° and 500° C., the detailed results are not included here as the conditions were not strictly comparable to those at 340°, 600°, and 650° C. Nevertheless, these closely related experiments indicate that no area loss occurs during the 20-hour treatment at 400° C. and that an area decrease of only 5% takes place when the catalyst is subjected to 500° C. for 17 hours. The 500° C. isotherms are the broken line curves in Figures 2 and 3.

At 600° C the first 2.5-hour period of heating results in a considerable loss in area. This treatment is accomplished in helium at atmospheric pressure to prevent adsorption bulb collapse. The area decreases from the original value of 119.8 to 88.9 sq. meters per gram, a loss of approximately 26%. An additional heat treatment for 3.5 hours at the same temperature causes very slight further sintering, the isotherm giving an area of 88.1 sq. meters per gram.

On heating the catalyst at 650° C. for 6.5 hours in helium, the area falls to 29.5 sq. meters per gram. This represents a loss of 75% of the original area. A major collapse of the high surface area structure has evidently taken place.

UNSUPPORTED CATALYST AND SUPPORT

It is of considerable interest that the area of the supported catalyst is much greater than that based on additivity of the areas of its components. Isotherms for catalyst B, the unsupported catalyst, and for support C after 340° C. evacuations are plotted in Figure 4. Included in addition are isotherms for the original and the 650° C. sintered samples of the supported catalyst and for the support sintered at 650° C. The data are plotted according to the BET equation in Figure 5. Deviations from the linear relation as described above are apparent.

Duplicate determinations of the unsupported catalyst area give 53.5 and 53.2 sq. meters per gram. These area values are considerably smaller than that of the supported catalyst, 119.8 sq. meters. The area of the support is 20.7 sq. meters per gram and decreases considerably on sintering at 650° C. for 6 hours, falling to 12.7 sq. meters, a loss of approximately 39%. Diatomaceous earth may contain a small amount of clay that contributes significantly to the support area. Sintering of the clay component may be responsible for some of the total area loss. Although this 39% loss is considerably less than the 75% loss in area suffered by the supported catalyst when subjected to the same treatment, it is recognized that such a change in the support surface structure may critically affect the catalyst superstructure. Preliminary sintering experiments with the unsupported material indicate that it loses approximately 60% of its area at 500° C. and that its surface may be very sensitive to temperature below 500° C.

The high area of the supported catalyst is remarkable when the relatively low areas of its components are considered. Supported catalysts of similar composition having almost twice the area reported here have subsequently been prepared. Obviously simple thin-film deposition on the surface of the low area support cannot account for the catalyst area. Careful study of the physical structure of the diatomaceous support may contribute to the understanding of its function in the high area catalyst. Nevertheless, in spite of the inert nature of diatomaceous earth, its weak chemical properties should not be entirely neglected.

Electron microscope pictures of diatomaceous earth reveal that the disk-type diatom skeleton may consist of a network of circular holes about 2000 Å. in diameter. Since the support material studied here contains a considerable portion of the disk type, it is of interest to estimate the surface area of such a structure. A model having contiguous circular cylindrical pores 2000 Å. in diameter and a solid density of 2.2 grams per cc., gives by simple geometry an area of 34 sq. meters per gram. This is of the same order of magnitude as the isotherm area, 20.7 sq. meters. Contiguous pores, 3200 Å. in diameter, in such a model will account for an area of 21 sq. meters per gram. Also, pores 2000 Å.

Table I. Nitrogen Adsorption Isotherm Data

Expt. No.	Treatment of Adsorbent ° C.	Hr.	Atm.	Grams	Area, Sq. M. per G.	% of Original Area	V_m, Cc. Adsorbed in Monolayer on 1 G. Adsorbent	V_m Estd. by B Point Method	p/p_0 Corresponding to V_m
				Catalyst A, Supported					
15	340	16	Vacuum	4.997	119.8	100	27.52	26	0.089
20	500[a]	17	Vacuum	4.997	113.5	94.7	26.08	25	0.094
22	500[a]	33	Vacuum	4.997	113.3	94.6	26.03	..	0.097
33	600	2.5	Helium	1.994	88.9	74.2	20.41	20	0.108
34	600	6	Helium	1.994	88.1	73.5	20.23	19	0.120
42	650	6.5	Helium	2.009	29.5	24.6	6.78	7	0.074
43	650	6.5	Helium	2.009	29.9	25.0	6.87	..	0.075
				Support C					
57	340	16	Vacuum	8.284	20.7	100	4.76	..	..
58	340	32	Vacuum	8.284	20.6	99.5	4.74	5	0.057
59	650	6	Helium	8.284	12.7	61.4	2.93	..	0.084
60	650	6	Helium	8.284	12.8	61.6	2.94	3.5	0.086
				Catalyst B, Unsupported[b]					
69	340	16	Vacuum	2.305	53.5	...	12.28	12	0.073
70	340	32	Vacuum	2.305	53.2	...	12.23	..	...

[a] Sintering treatments at 500° C. are not strictly comparable to those at other temperatures.
[b] Prepared to resemble catalyst A without support C.

in diameter, separated by approximately 120 Å., would give an area value of 21 sq. meters. If 2000 Å. represents the pore center-to-center distance, a pore diameter of 1860 Å. and a pore separation of 140 Å. will yield an area of 21 sq. meters per gram. The latter models are more acceptable as they satisfy the electron microscope data and the need for solid partitions between adjacent pores.

If such relatively large pores are an essential characteristic of a good support for high-area catalysts of certain types, then, contrary to many current concepts, the need for a comparatively low-area porous carrier follows directly. Perhaps the large pores of the support may be responsible for the stable high-area structure of the catalyst. Catalyst deposition from solution should take place readily within such pores whereas the poor accessibility of the smaller pores in high-area support materials may prevent the formation of high-area catalytically active structures. Thus for a given catalyst there may be a support of optimum pore size.

ADSORPTION PER UNIT SURFACE

Brief reference has been made to the apparent similarity of the ordinary isotherms for the different adsorbents studied. However, appreciable differences in the relative pressures corresponding to the V_m values for these adsorbents are evident in Table I. Similarities and differences in adsorption characteristics are demonstrated more clearly by reducing the adsorption isotherms to unit adsorbent surface. Figure 6 presents the V_a/V_m isotherms; the differences in nitrogen adsorption per unit surface indicate different adsorption forces or interaction energies, provided pores are sufficiently large so that their structure does not affect the isotherms in the low-pressure range considered.

According to these isotherm plots, considerable specificity is associated with the low-temperature van der Waals adsorption on the various solids. In the low-pressure range where pore structure probably exerts a minor effect, the V_a/V_m isotherm of the support appears quite different from that of the supported catalyst. Of interest also are the differences between the supported catalyst and the same material sintered at 600° and 650° C. Adsorption characteristics of the unsupported catalyst appear somewhat similar to those of the supported catalyst.

Detailed interpretation must await further work. It is conceivable, however, that isotherms reduced to unit surface may eventually provide a means for differentiating and classifying solid surface types and structures.

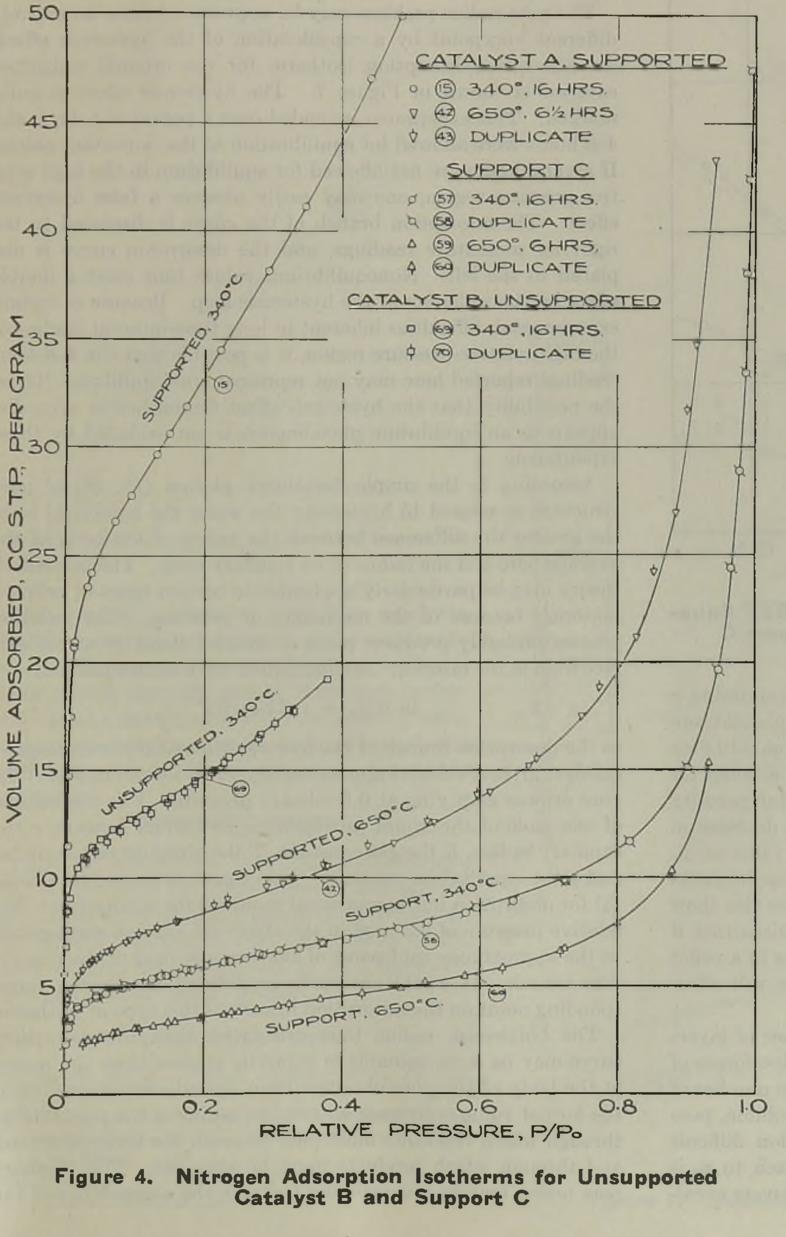


Figure 4. Nitrogen Adsorption Isotherms for Unsupported Catalyst B and Support C

HIGH RELATIVE-PRESSURE REGION AND PORE STRUCTURE

Careful study of the high relative-pressure region should yield additional valuable information concerning the surfaces of catalysts and supports. Considerable care has been exercised in obtaining equilibrium values for the higher pressure points plotted in Figure 7. Isotherms for three adsorbents are shown: the original supported catalyst, the 650° C. sintered sample, and the diatomaceous earth support. Two to four hours may be required for equilibrium readings in the upper portions of these isotherms.

The isotherms for the three adsorbents of Figure 7 approach p_o asymptotically. They are type II isotherms according to the classification of Brunauer, Deming, Deming, and Teller (*2*, *5*). The asymptotic approach, combined with the gradual curvature that precedes it, indicates a rather wide distribution of pore radii. The term "pore" as used here includes any internal space which may be in the form of cracks, crevices, or the interstitial space in a thin platelet structure. The three isotherms have no steeply rising portions followed by plateaus near p_o, such as are typical for those porous adsorbents which possess a certain uniformity of pore radii and which give type IV isotherms. Evidently the materials whose isotherms are shown in Figure 7 possess some large pores that do not fill completely below p_o. Adsorbents having extremely small pores of rather uniform radii might be expected to give the Langmuir type of flat isotherm, type I, since the pores fill almost completely at a relatively low pressure. Certain high-area carbons give this Langmuir type of isotherm.

An approximate thickness of the adsorbate film at p_o in terms of the number of adsorbed molecular layers may be obtained by dividing the volume adsorbed at the saturation pressure, V_s, by the volume of the monolayer, V_m. The V_s volume is, at best, an approximation for the type of isotherm obtained in these studies since the approach to p_o is asymptotic. Estimates of film thickness by this method give values quite different for the three materials whose upper isotherms were determined:

the supported catalyst, ten layers; the 650° C. sintered catalyst, thirty layers; and the support, about fifteen layers. The V_s/V_m values considered in making the above estimates are, respectively: 9.4, 10.8; 30.2, 33.6, 30.0, and 15.4, 17.2. For adsorbents having platelet structures of nonuniform wall separation, these values represent average adsorbate film thicknesses. Although it is clear that the number of layers on plane surfaces is represented by V_s/V_m, on concave (pore) surfaces the number of layers is greater and on convex surfaces the number of layers less than the V_s/V_m value. This variation with radius of curvature is due simply to the change in the volume of adsorbate required for a monolayer as the effective surface becomes greater or less with increasing adsorption.

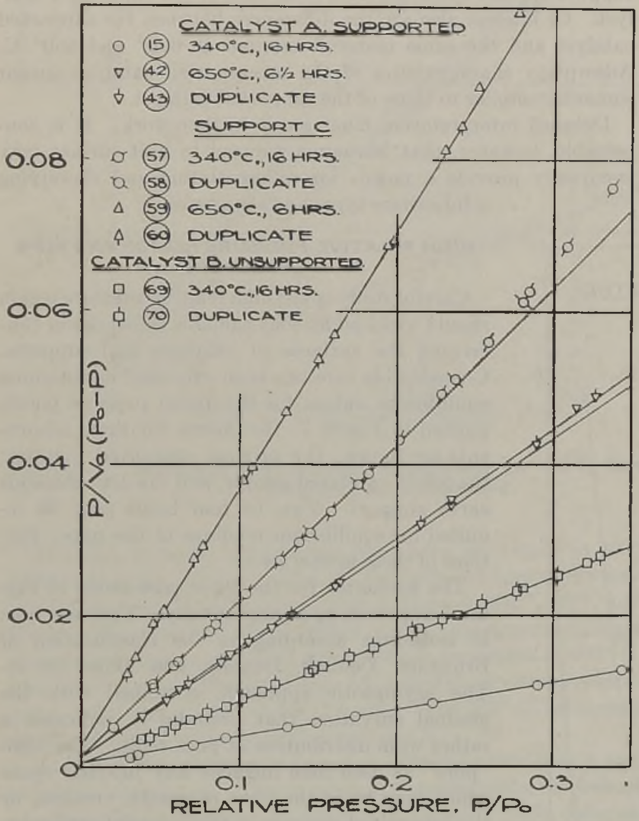


Figure 5. Nitrogen Adsorption According to BET Equation for Unsupported Catalyst B and Support C

The increase from ten to thirty adsorbate layers on sintering is probably associated with the increase in pore radii or platelet separation accompanying area loss. The area falls from 119.8 to 29.5 sq. meters per gram on sintering at 650° C. To account for the increased film thickness on the basis of a greater porosity would require a major porosity increase. Actually a decrease in porosity on sintering is indicated by the lower V_a value at p_0 (Figure 7). Direct helium-mercury displacement measurements of porosity by H. O. Bauermeister of these laboratories also show a decrease. Growth of average pore size is easily visualized if sintering is considered simply a crystal growth process in a pellet of constant volume and porosity. The pore spaces will effectively merge as do the solid particles or platelets.

One is tempted to attach significance to the number of layers deposited on an adsorbent as indicating the adsorptive forces of the solid; certainly thirty layers is an unusually large number of layers. However, the complicating factors of pore volume, pore radii, and capillary condensation make interpretation difficult for porous materials. Furthermore, since the approach to p_0 is asymptotic, the V_s value from which the number of layers is calculated in each case is necessarily of preliminary interest only. The development of a better method for obtaining V_s is now in progress.

Emmett and DeWitt (*11*) pointed out the following simple inverse relation between pore radius r and surface area A for a high-area material with constant pore volume, V, and uniform cylindrical pores:

$$V/A = r/2$$

The same relation obtains for thin platelet structures with r as the platelet separation. The threefold increase in film thickness on sintering may correspond approximately to an increase in pore radius or platelet separation and bears a somewhat similar relation to the fourfold decrease in area.

The supported catalyst on heating at sintering temperatures probably approaches the large pore structure of the support. If the pore radii of the active catalyst material increase, it may be that some interesting increases in catalyst activity on sintering should be attributed to the greater accessibility of the larger pores. The smaller pores of the higher-area material may not admit large reactant molecules.

HYSTERESIS

The pore radius problem may be approached from an entirely different viewpoint by a consideration of the hysteresis effect. An adsorption-desorption isotherm for the original supported catalyst is shown in Figure 7. The hysteresis effect is quite marked. This experiment extended over a period of 4 days, and 4–8 hours were allowed for equilibration at the important points. If several hours are not allowed for equilibrium in the high relative-pressure region, one may easily observe a false hysteresis effect. The adsorption branch of the curve is displaced to the right by premature readings, and the desorption curve is displaced to the left. Nonequilibrium values thus exert a double effect on the widening of the hysteresis loop. Because of certain experimental difficulties inherent in long time-interval studies of the high relative-pressure region, it is possible that the 4–8 hour readings reported here may not represent true equilibria. Thus, the possibility that the hysteresis effect diminishes or even disappears as an equilibrium phenomenon is not excluded by these experiments.

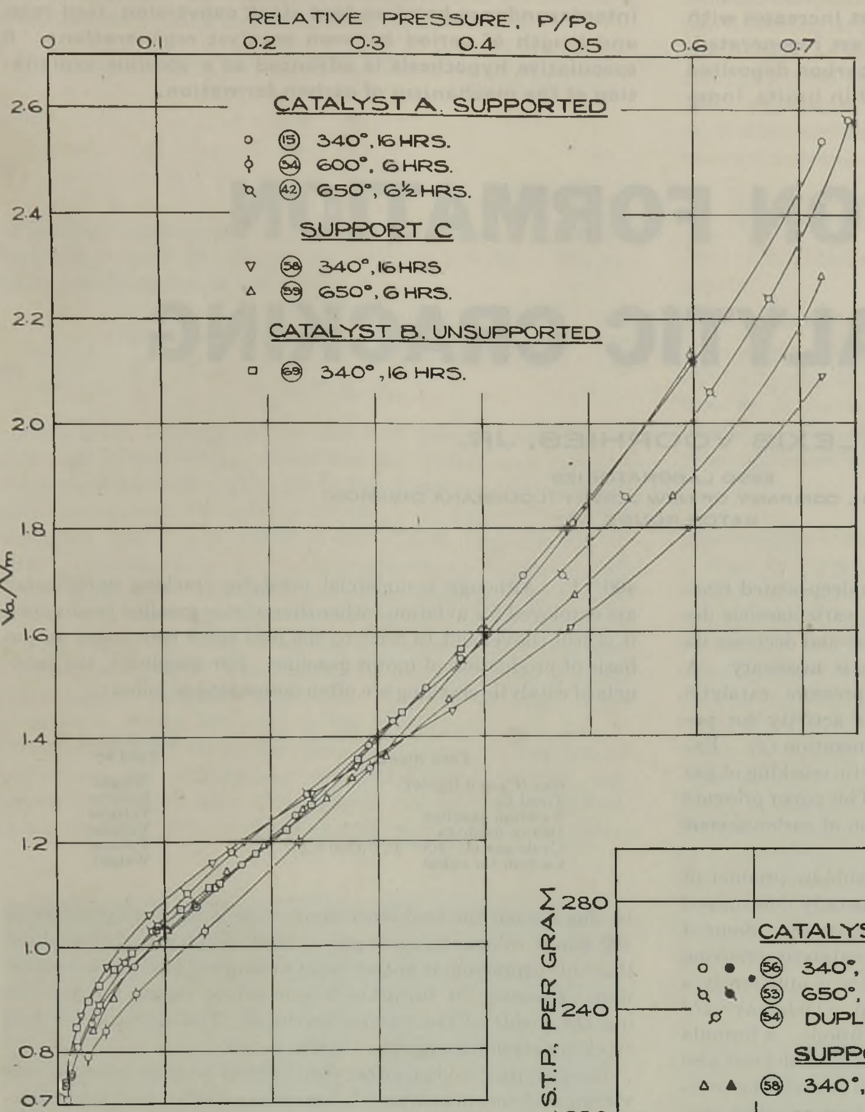
According to the simple bottleneck picture (*15*, *16*) of pore structure as related to hysteresis, the wider the hysteresis loop, the greater the difference between the radius of the body of the average pore and the radius of its capillary neck. The bottleneck theory may be particularly applicable to certain types of pelleted materials because of the mechanics of pelleting. The pelleting process probably produces pores of smaller diameter at the surface than in the interior. Application of the Kelvin equation,

$$\ln p/p_0 = -2V\sigma/rRT$$

to the desorption branch of the hysteresis loop for the unsintered catalyst gives a value of approximately 13 Å. for the radius of the pore orifices emptying at 0.5 relative pressure. V is the volume of one mole of the liquid (nitrogen), σ its surface tension, r the capillary radius, R the gas constant, T the absolute temperature, and p the equilibrium pressure. This equation is used by Cohan (*4*) for desorption but is somewhat modified for adsorption. The relative pressure of 0.5 used in the above calculation corresponds to the approximate mid-point of the steepest part of the desorption branch. It would obviously be difficult to select a corresponding point on the adsorption branch of this type of isotherm.

The bottleneck radius thus calculated from the desorption curve may be more valuable in catalytic studies than the radius of the body of the pore obtained from the adsorption branch, if the former value represents an average radius of the pore orifices through which reactants must pass to reach the internal surface and through which products must be removed. The capillary pore orifice may be a controlling factor in the accessibility of the

Figure 6. Isotherms of Nitrogen Adsorption per Unit Surface



large internal surface of high-area catalysts. Furthermore, the outer portion of the pore or the pore neck may be important, per se, in that it may provide the only portion of the pore surface effective in certain catalytic reactions. Fundamental studies along this and related lines should prove valuable in the investigation of catalytic processes.

ACKNOWLEDGMENT

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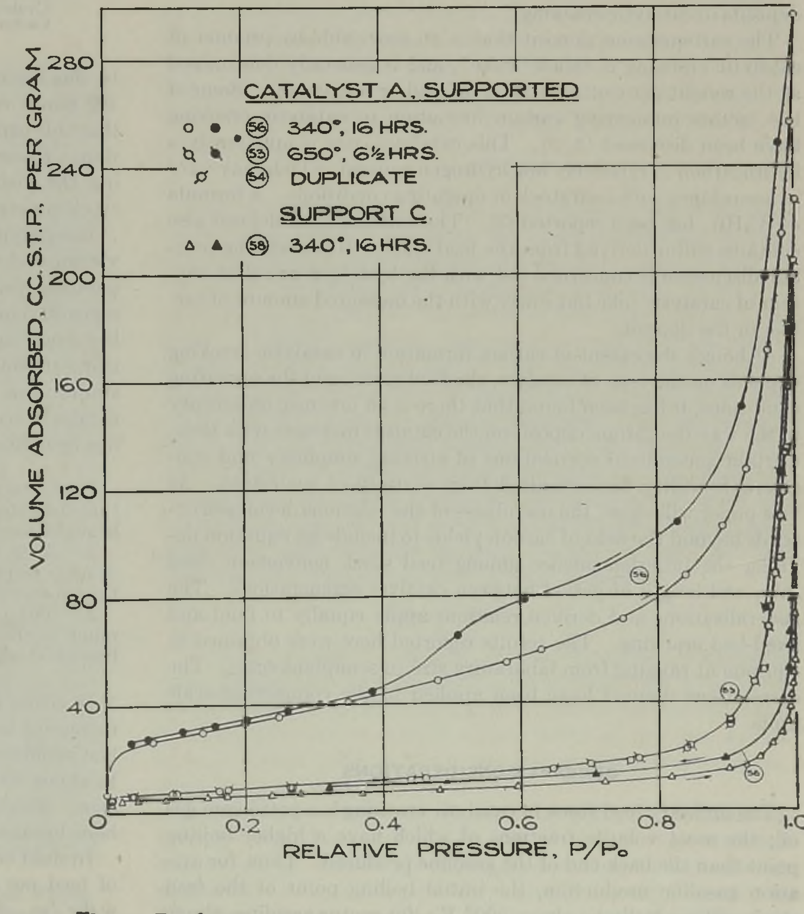

Figure 7. Isotherms for Nitrogen Adsorption and Desorption

IN CATALYTIC CRACKING, both fixed-bed and fluid, it has been found that there is an intrinsic uniformity in the way the carbon deposit on the catalyst increases with the time elapsed since the catalyst was last regenerated. For all the data examined, the amount of carbon deposited on the catalyst at given conditions is, within limits, independent of the hydrocarbon feed rate. From this study, correlations are derived that define mathematically the interdependence between feed stock conversion, feed rate, and length of period between catalyst regenerations. A speculative hypothesis is advanced as a possible explanation of the mechanism of carbon formation.

CARBON FORMATION IN CATALYTIC CRACKING

ALEXIS VOORHIES, JR.

ESSO LABORATORIES
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BATON ROUGE, LA.

WHEN petroleum hydrocarbons undergo deep-seated reactions in the presence of solid catalysts, carbonaceous deposits usually accumulate on the catalyst and decrease its activity, so that periodic regeneration is necessary. A conspicuous exception is the case of high-pressure catalytic hydrogenation where the catalyst retains its activity for periods up to a year and longer without any regeneration (*2*). Examples of regenerative processes are (*a*) catalytic cracking of gas oils and (*b*) catalytic reforming of naphthas. This paper presents a discussion of certain aspects of the formation of carbonaceous deposits in catalytic cracking.

The carbonaceous deposit that is an inevitable by-product of catalytic cracking is called "coke", and is generally determined as the weight per cent of carbon on feed or on catalyst. Some of the factors influencing carbon formation in catalytic cracking have been discussed (*1*, *3*). This catalytic coke is apparently a hydrocarbon of relatively low hydrogen content, which may vary in accordance with feed stock or operating conditions. A formula of $(C_3H_4)_n$ has been reported (*4*). The carbonaceous deposit also contains sulfur derived from the feed stock. However, the present discussion is concerned not with the hydrogen or sulfur content of catalytic coke but solely with the measured amount of carbon in the deposit.

Although the extent of carbon formation in catalytic cracking depends on the type of catalyst, the feed stock, and the operating conditions, it has been found that there is an intrinsic uniformity in the way the carbon deposit on the catalyst increases with time. Certain generalized correlations of striking simplicity and considerable utility have resulted from a study of such data. As this paper will show, the usefulness of the relations developed extends beyond the field of carbon yields to include an equation defining the interdependence among feed stock conversion, feed rate, and length of period between catalyst regenerations. The generalizations and derived relations apply equally to fluid and fixed-bed cracking. The results reported here were obtained in equipment ranging from laboratory size to semiplant scale. The correlations derived have been applied to the commercial-scale units.

GENERAL CONSIDERATIONS

The ordinary feed stock in catalytic cracking is a petroleum gas oil, the most volatile fractions of which have a higher boiling point than the back end of the gasoline produced. Thus, for aviation gasoline production, the initial boiling point of the feed stock will generally be above 300° F.; for motor gasoline, above 400° F. Although commercial catalytic cracking units today are employed for aviation rather than motor gasoline production, it is still convenient to refer to the feed stock conversion on the basis of production of motor gasoline. For simplicity, the products of catalytic cracking are often designated as follows:

Feed Stock	Per Cent of Feed by:
Gas (C_3 and lighter)	Weight
Total C_4	Volume
Aviation gasoline	Volume
Heavy naphtha	Volume
Cycle gas oil (400° F. initial b.p.)	Volume
Carbon (or coke)	Weight

In this system the feed stock conversion is arbitrarily taken as 100 minus volume % cycle gas oil (400° F. i.b.p.). It is realized that this expression is not an exact measure of feed stock destruction. However, it furnishes a convenient means for correlating the yields of the various products. This definition of feed stock conversion is employed in this paper.

In catalytic cracking, either fluid or fixed-bed, the extent of conversion is determined by such factors as catalyst, feed stock, temperature, pressure, feed rate, and length of time between catalyst regenerations (here called "catalyst residence time"). In fixed-bed cracking the conversion measured is the summation of the instantaneous conversions throughout the process period, the instantaneous conversions decreasing with time on stream as the catalyst becomes fouled with coke. Fluid catalytic cracking differs from fixed-bed as follows:

1. Catalyst is currently regenerated in a separate vessel, so that feed stock and freshly regenerated catalyst are continuously brought together in the reactor.
2. As a result of the above, a uniform conversion is maintained, rather than a continuously decreasing conversion as in the process cycle of fixed-bed cracking.
3. The catalyst residence time in fluid cracking is generally much shorter than the length of time between regenerations in fixed-bed work.

In either fluid or fixed-bed cracking, conversion increases with increasing temperature, decreasing feed rate, and decreasing catalyst residence time. The effect of increasing pressure, at least up to about 50 pounds per square inch gage, is to increase conversion. However, pressure was not a variable in the data presented here because substantially atmospheric pressure was employed.

In fluid cracking the feed rate is generally expressed as weight of feed per hour per weight of catalyst held in the reactor or w/hr./w. Another term employed in fluid cracking is the catalyst-to-oil ratio, which is the ratio of the weight rates of flow of catalyst and oil. The catalyst residence time in the reactor is related to the w/hr./w and catalyst/oil ratio as follows:

$$\frac{(\text{w/hr./w})(\text{catalyst residence time, min.})}{60} = \frac{1}{\text{catalyst/oil ratio}}$$

$$\frac{W \cdot \theta}{60} = \frac{1}{Z}$$

or

$$W = 60/Z \cdot \theta$$

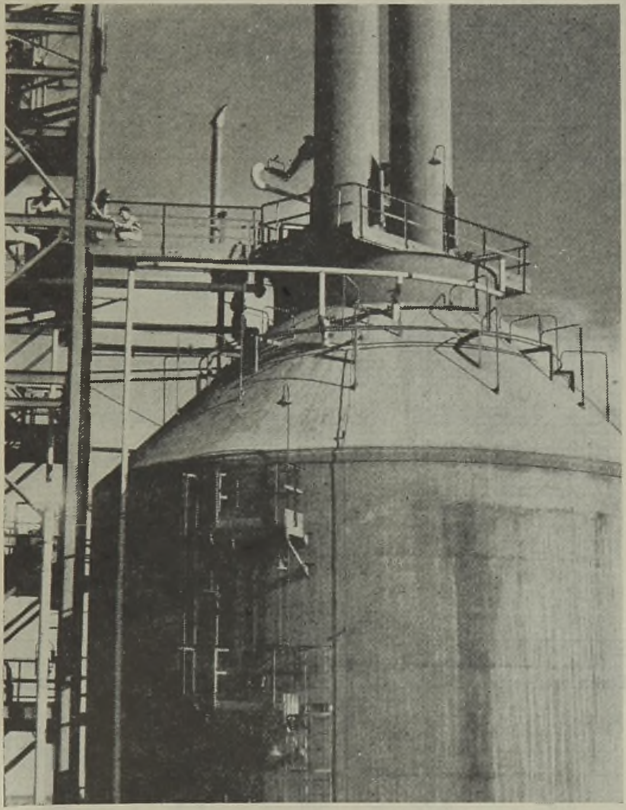
In fixed-bed cracking the feed rate is usually defined as volumes of feed per volume of catalyst per hour, or v/v/hr. The relation between w/hr./w and v/v/hr. is:

$$\text{w/hr./w} = (\text{v/v/hr.}) \left(\frac{\text{density of feed}}{\text{density of catalyst}}\right)$$

or

$$W = U \cdot D_o/D_c$$

At a given temperature the depth of catalytic cracking, as measured by conversion, determines the quality and yields of the various products. Thus the yields of gas and carbon invariably increase with increasing conversion. At a given conversion level, the quality and yields of the various products depend on the temperature, but are virtually independent of relative feed rate and catalyst residence time. Thus whether a given conversion is obtained by a high feed rate and a short residence time or vice versa, the yields of carbon and other products are substantially unaffected. The relation between carbon on feed and conversion is especially important. This carbon yield refers to catalytic carbon produced in the reaction and does not include the so-called strippable carbon, which represents adsorbed and interspersed hydrocarbon gas and liquid remaining with the spent catalyst after the cracking has been accomplished. It is common practice to purge off most of the strippable carbon before the catalyst is regenerated. For the cracking operations reported here, this increment of carbon yield was negligible compared to catalytic carbon.



Catalytic Regenerator at the Top of One of the Fluid Catalytic Cracking Units at the Baton Rouge Refinery

Although, as mentioned above, the yield of carbon on feed stock at a given temperature is a function of conversion, there is also a well-defined relation between the weight per cent of carbon on catalyst and the catalyst residence time. Important deductions are derivable from the following relations:

Wt. % carbon based on feed = function of feed conversion
Wt. % carbon on catalyst = function of catalyst residence time

Data in fixed-bed and in fluid catalytic cracking are treated separately.

CARBON FORMATION IN FIXED-BED CRACKING

A considerable amount of data shows that the weight per cent carbon formed on the catalyst is approximately a logarithmic function of the length of time elasped since the catalyst was freshly regenerated. For a given catalyst, feed stock, and temperature, the equation takes the form:

$$C_c = A \cdot \theta^n$$

Two examples of this relationship are discussed.

Example 1 is shown graphically in Figure 1, which depicts the relation between carbon on catalyst and residence time of catalyst for a West Texas gas oil and a natural (activated clay) cracking catalyst at 850° F. The experiments were conducted in a small fixed-bed unit. Each point on the plot represents a run, either on a fresh batch of catalyst or on one that had very few regenerations. In other words, the level of initial catalyst activity represented by the data was substantially constant. After the process period had lasted for the time indicated in Figure 1, the catalyst was purged to remove strippable carbon. Then the catalyst was discharged from the unit, and the carbon on it was determined by combustion of a representative sample. The cracking period lengths included much shorter residence times than are normally employed in fixed-bed cracking, because the experiments were designed to furnish fundamental information. The correlating line on the graph is represented by the equation:

$$C_c = 0.86\ \theta^{0.41} \tag{1}$$

A second example, also portrayed in Figure 1, shows the relation between carbon on catalyst and residence time for an East Texas gas oil and a synthetic (silica-alumina) catalyst at 850° F. The results were obtained in small fixed-bed units, on which a study was being made of the effect of feed rate (v/v/hr.) and length of process period (θ). The synthetic catalyst was of such inherent stability that its activity was completely restored after each successive regeneration. Hence the entire study was made on one batch of catalyst. After each process period the catalyst was purged and then regenerated *in situ* by air oxidation. The carbon formation was determined by measuring and analyzing the regeneration gases. Although the accuracy of these determinations was not of a particularly high order, a fairly good correlation was obtained between carbon on catalyst and residence time, represented by the following equation:

$$C_c = 0.65\ \theta^{0.44} \tag{2}$$

In the example just discussed for East Texas gas oil and synthetic catalyst, the implicit assumption is made that, within limits, the feed rate has no effect on the extent of carbon formation on catalyst for a given residence time. Although this may appear strange at first, there is a large amount of supporting evidence, some of which follows.

A rather extensive series of runs was made on a small-scale fixed-bed unit on an East Texas gas oil, both with natural and with synthetic catalyst, to determine the effect of feed rate on carbon formation at cracking temperatures from 800° to 950° F. The feed rate was varied from 0.6 to 1.2 v/v/hr., but the length

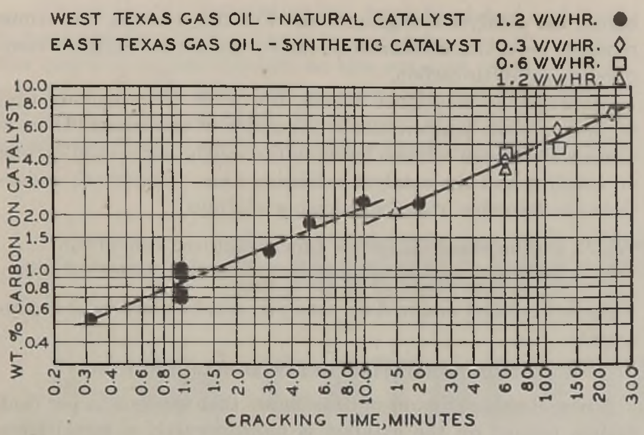


Figure 1. Carbon Formation *vs.* Cracking Time in Fixed-Bed Catalytic Cracking

of cracking period was uniformly maintained at 2 hours. After each run the catalyst was discharged from the unit and analyzed for carbon by combustion; and a fresh batch of catalyst was installed for the next run. The data are presented in Table I. It will be noted that, as the feed rate increases at a given temperature, the weight per cent carbon on feed decreases as might be expected, but the weight per cent carbon on catalyst remains substantially constant.

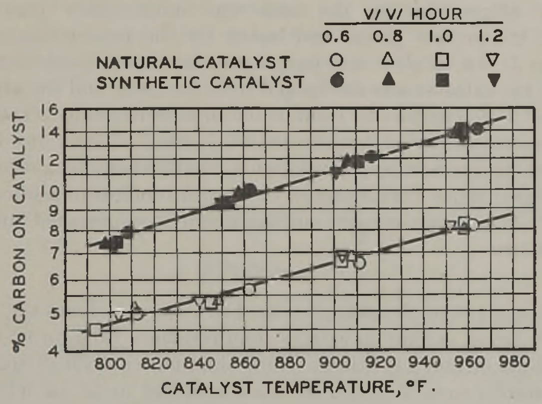


Figure 2. Carbon Formation *vs.* Cracking Temperature for 2-Hour Cracking Periods

Another example of the constancy of carbon formation on catalyst for a given residence time, regardless of feed rate, is furnished by data obtained on catalytic cracking of pure compounds. Both cetane and Decalin were cracked with natural catalyst in a small unit at 850° F. for a process period of 2 hours and at feed rates varying from 0.6 to 2.4 v/v/hr. After each period the catalyst was removed for carbon determination by combustion and was replaced by a fresh charge. The data are presented in Table II. Here again it is evident that the weight per cent carbon on catalyst is relatively independent of feed rate.

A practical demonstration that per cent carbon on catalyst is virtually unaffected by feed rate was furnished some years ago in the operation of a semiplant-scale, fixed-bed catalytic cracking unit. In each reactor there were four catalyst beds of equal height, vertically disposed one above the other. During the process period the flow of oil vapors was through the four beds in series. During regeneration, the flow of gases was through the four beds in parallel in order to minimize pressure drop. The individual temperature records for each bed during regeneration indicated that about the same amount of carbon was burned from each bed. This is equivalent to saying that the carbon on catalyst was independent of feed rate, because the feed-space-velocity (v/v/hr.) in the case of the first bed was four times that for the total reactor.

Much thought and speculation have been directed to answering the question as to why carbon on catalyst for a given residence time should be relatively independent of feed rate. The characteristics of the hydrocarbons in contact with the catalyst are continually changing as the feed stock progresses through the catalyst bed, and also different feed stocks differ in their carbon-forming tendencies. However, consider what happens as the feed stock passes through the bed of catalyst. It is converted to an increasing extent into (*a*) gasoline and gas which have less tendency to carbonize than the original feed and (*b*) cycle gas oil which has more tendency to carbonize than the original feed. To the degree that these two tendencies balance each other, the extent of carbon formation on catalyst will not differ at any level in the catalyst bed at any given time; this means that carbon on catalyst is independent of feed rate within limits. This phenomenon is thus ascribed to a fortuitous balance between the carbonizing tendencies of the unconverted feed and the total products of reaction. It is not proved or claimed that this observation will hold for all feed stocks, all catalysts, or an extreme variation in feed rates. In fact it seems remarkable that the generalization holds as broadly as indicated by the results presented in this paper.

The data in Table I permit a study of the effect of temperature on carbon formation. Figure 2 shows how carbon formation on catalyst increases with cracking temperature. The correlation is rather good, and indicates that the carbon formation doubles for approximately 190–200° F. increase in cracking temperature.

As indicated earlier, there is generally a good correlation between feed stock conversion and carbon yield based on feed for a given catalyst, feed stock, and temperature. As an example, the data obtained in a fixed-bed study on East Texas gas oil and synthetic catalyst at 850° and at various feed rates and cracking periods are portrayed in Figure 3. The runs involved are the same as those already discussed in connection with Figure 1. Figure 3 shows a fairly good linear correlation on log-log paper between conversion and carbon yield on feed. The one point consider-

Table I. Fixed-Bed Catalytic Cracking of East Texas Gas Oil for Process Periods of 2 Hours

Natural Catalyst				Synthetic Catalyst			
		Carbon wt.				Carbon wt.	
Feed rate, v/v/hr.	Temp., ° F.	% on feed	% on catalyst	Feed rate, v/v/hr.	Temp., ° F.	% on feed	% on catalyst
0.6	812	3.8	5.0	0.6	808	5.8	7.9
0.8	811	2.9	5.1	0.8	798	4.1	7.4
1.1	793	2.0	4.6	1.0	803	3.2	7.4
1.2	804	2.0	5.0	1.2	801	2.7	7.4
0.6	862	4.5	5.7	0.6	863	7.8	10.1
0.8	848	3.1	5.4	0.8	857	5.7	9.9
1.0	845	2.5	5.3	1.0	852	4.2	9.4
1.2	840	2.1	5.4	1.2	850	3.5	9.4
0.6	911	5.5	6.6	0.6	917	9.3	12.0
0.8	908	4.3	6.8	0.8	906	6.8	11.9
1.0	904	3.3	6.7	1.1	911	5.3	11.8
1.2	904	2.9	6.8	1.2	901	4.3	11.1
0.6	962	6.9	8.1	0.6	964	11.2	14.0
0.8	958	5.2	8.2	0.8	955	8.4	13.9
1.0	958	4.1	8.2	1.0	957	6.6	14.1
1.2	952	3.4	8.2	1.2	956	5.5	13.9

Table II. Fixed-Bed Catalytic Cracking of Cetane and Decalin with Natural Catalyst at 850° F. for Process Periods of 2 Hours

	Cetane		Decalin	
Feed rate, v/v/hr.	Wt. % C on feed	Wt. % C on catalyst	Wt. % C on feed	Wt. % C on catalyst
0.6	4.8	4.9	3.1	3.8
0.8	3.9	5.3	2.4	4.0
1.2	2.5	5.2	1.6	3.7
2.4	1.1	4.7	0.75	3.7

ably off the line, at about 36% conversion, may represent a faulty determination of conversion as discussed later. At this juncture it may be mentioned that numerous other data are available on other feeds, on other catalysts, and at other temperatures, which show that the logarithm of the conversion is approximately linear with the logarithm of the carbon yield (log-log), or that the conversion is linear with the logarithm of the carbon yield (semilog). The graph in Figure 3 is represented by the equation:

$$C_f = (3.55)(10^{-5})V^{2.93} \qquad (3)$$

It is interesting to consider simultaneously Equations 2 and 3, which refer to the same cracking runs. Since the carbon on catalyst is a logarithmic function of length of process period independently of feed rate, and since the carbon yield based on feed is a logarithmic function of conversion regardless of feed rate or cracking period length, certain significant deductions are possible. Specifically, an equation is developed below to show the interrelation of conversion, feed rate, and length of cracking period:

$$\%\text{ carbon on catalyst} = C_c = 0.65\cdot\theta^{0.44} \qquad (2)$$

$$\%\text{ carbon on feed} = C_f = (3.55)(10^{-5})\cdot V^{2.93} \qquad (3)$$

$$C_c = C_f \div (\text{catalyst-to-oil weight ratio}) \qquad (4)$$

$$= C_f\cdot U\cdot\frac{\theta}{60}\cdot\frac{D_o}{D_c}$$

$$\frac{D_o}{D_c} = \frac{1}{0.58}$$

$$\therefore\ 0.65\ \theta^{0.44} = (3.55)(10^{-5})\cdot V^{2.93}\ U\cdot\frac{\theta}{60}\cdot\frac{1}{0.58}$$

$$\text{whence } V = 96\cdot\frac{1}{U^{0.34}}\cdot\frac{1}{\theta^{0.19}} \qquad (5)$$

A graphical solution of Equation 5 is given in Figure 4 for feed rates of 0.3, 0.6, and 1.2 v/v/hr. For comparison, the actual data obtained in the runs are plotted. The concordance between actual and calculated values of conversion is generally good except for the point at about 36% conversion, in which case the predicted value would be 41%. If there had been an error in the determined conversion for this period, and if the predicted value were actually correct, the correlation shown in Figure 3 would also be considerably improved, as pointed out earlier.

The significance of the correlation among conversion, feed rate, and length of cracking period deserves further mention. First, it is possible from a relatively few runs, with accurate carbon determinations, to establish a good mathematical relation showing the relative effect of feed rate and length of process period in determining conversion. This correlation is readily amenable to linear graphical representation or to simple nomographic treatment, with a fair amount of extrapolation permissible beyond the actual confines of the data.

CARBON FORMATION IN FLUID CRACKING

Some of the differences between fluid and fixed-bed catalytic cracking have already been mentioned. However, the similarities far outweigh the differences; and it has been found that the same generalizations with respect to carbon formation, developed for fixed-bed cracking, are equally applicable to fluid operation.

An extensive study was made in fluid catalyst cracking on a semiplant scale both on natural catalyst and on synthetic. A number of different types of reactors were employed, many feed stocks were studied, and a wide range of operating conditions was covered. Two particular studies have been chosen to illustrate the relation between carbon formation on catalyst and residence time of catalyst. The first case is for an East Texas gas oil with natural catalyst at a cracking temperature of 900–925° F. The second is for a Tinsley gas oil with synthetic catalyst at 950°. In both cases the catalyst was continuously regenerated to a low residual carbon content, and good stripping of spent catalyst was obtained. The carbon formation thus represents substantially catalytic carbon only. The weight per cent carbon formed on catalyst is the difference in carbon content between spent and regenerated catalyst. Although samples of spent and regenerated catalysts are regularly withdrawn from fluid units for carbon determination by combustion, the absolute value of the carbon content even on spent catalyst is ordinarily so small that erratic results sometimes occur. A more reliable determination of the weight per cent carbon formed on the catalyst is obtained by dividing the weight of carbon burned in the regenerator in unit time by the weight rate of catalyst flow. This is the procedure regularly employed. The rate of carbon burning is determined from the quantity and analysis of the regeneration vent gas; and the rate of catalyst flow is determined by Venturi or other special meters. The catalyst residence time in the fluid cracking reactors is determined from the average catalyst concentration and the catalyst flow rate. The catalyst concentration is calculated by pressure drop measurements across various levels in the reactor.

The relation between carbon formation on catalyst and residence time of catalyst is illustrated in Figure 5, which also includes the previous correlations from fixed-bed cracking given in Figure 1. The study on the East Texas gas oil with natural cata-

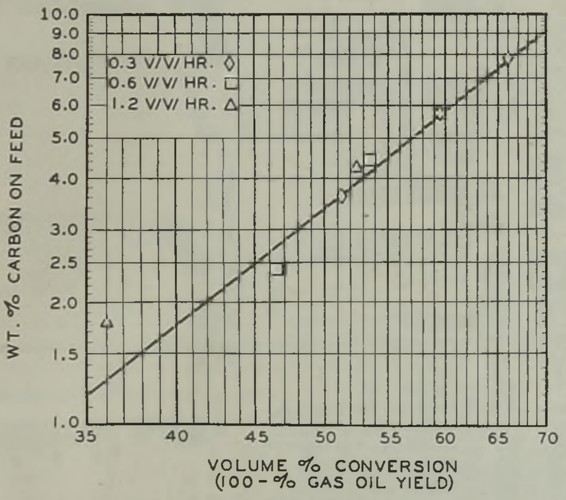


Figure 3. Carbon Yield *vs.* Feed Conversion for Fixed-Bed Catalytic Cracking of an East Texas Gas Oil with Synthetic Catalyst

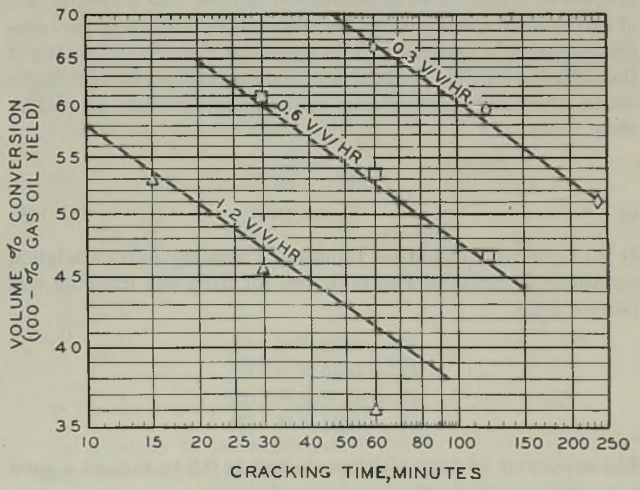


Figure 4. Feed Conversion *vs.* Cracking Time and Feed Rate for Fixed-Bed Catalytic Cracking of an East Texas Gas Oil with Synthetic Catalyst

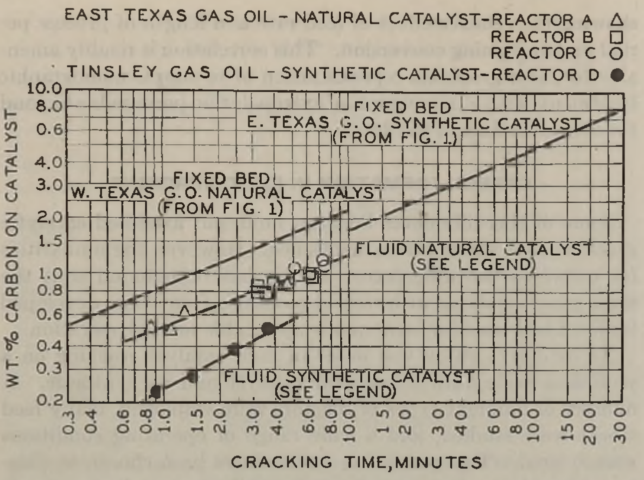


Figure 5. Carbon Formation *vs.* Cracking Time in Fluid Catalytic Cracking Compared to Fixed-Bed Cracking

lyst at 900-930° F. (Figure 5) was conducted in three reactors of different shape factors, employed in a special investigation of reactor type. The various points represent data at approximately the same level of catalyst activity. No difference is indicated for the various reactors. The equation for the correlating line is:

$$C_c = 0.52\,\theta^{0.38} \tag{6}$$

In the case of the Tinsley gas oil with synthetic catalyst at 950° F., the points in Figure 5 were corrected to a common activity level. The correlating line is represented by the equation:

$$C_c = 0.24\,\theta^{0.53} \tag{7}$$

In fluid catalyst cracking, as in fixed-bed, the carbon yield based on feed is a function of feed stock conversion. Hence it is possible to derive the same kind of equations relating conversion with feed rate (w/hr./w) and catalyst residence time or catalyst to oil ratio. Such equations have been used to construct graphical correlations that predict with satisfactory accuracy the conversions obtained at various feed rates (w/hr./w) and catalyst residence times or catalyst to oil ratios. These correlations have been particularly valuable in the analysis of data from the commercial units.

RELATION BETWEEN CARBON FORMATION AND RESIDENCE TIME

The very small temperature coefficient of carbon formation (Figure 2) is indicative of a diffusion control, and since the rate of carbonization drops off as the percentage of carbon on the catalyst increases, it is reasonable to postulate that the coke itself is the diffusion barrier. Indeed, if it is assumed that the rate of diffusion is inversely proportional to the weight per cent of carbon, then

$$\frac{dC_c}{d\theta} = \frac{K}{C_c}$$

or

$$C_c = A\cdot\theta^{0.5} \tag{8}$$

It is of interest to compare Equation 8 with the four correlation equations depicted in Figure 5, two for fixed-bed cracking and two for fluid:

$$C_c = 0.86\,\theta^{0.41} \quad (1)$$
$$C_c = 0.65\,\theta^{0.44} \quad (2)$$
$$C_c = 0.52\,\theta^{0.38} \quad (6)$$
$$C_c = 0.24\,\theta^{0.53} \quad (7)$$

The exponents of θ are all close enough to 0.5 to suggest a good concordance with the theory advanced above.

Just how the coke constitutes a diffusion barrier is not entirely clear, since the large specific surfaces of cracking catalysts require a large coke deposition to form even a monomolecular layer. Possibly the coke accumulates about active centers on the surface causing an effective diffusion choke while most of the surface is still bare.

NOMENCLATURE

A = constant, depending on catalyst, feed stock, and temperature
C_c = carbon, weight per cent on catalyst
C_f = carbon, weight per cent on feed
D_o = density of oil
D_c = density of catalyst
K = constant ($=A^2$)
V = volume per cent conversion of feed stock
U = feed rate, volumes/volume of catalyst/hour
W = feed rate, weight/hour/weight of catalyst in reactor
Z = weight ratio of catalyst to oil
θ = catalyst residence time, minutes
n = constant, depending only slightly on catalyst, feed stock, temperature

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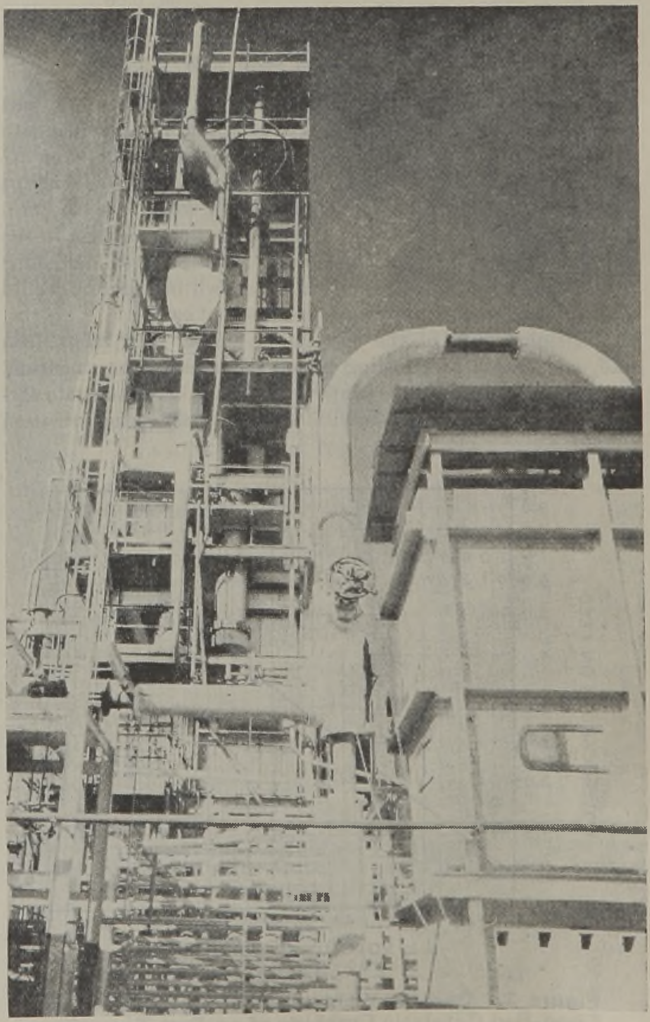

Semiplant Scale Fluid Catalyst Cracking Unit

PRODUCTION OF ISOPARAFFINS

Cracking of Petroleum Fractions in the Presence of Aluminum Chloride

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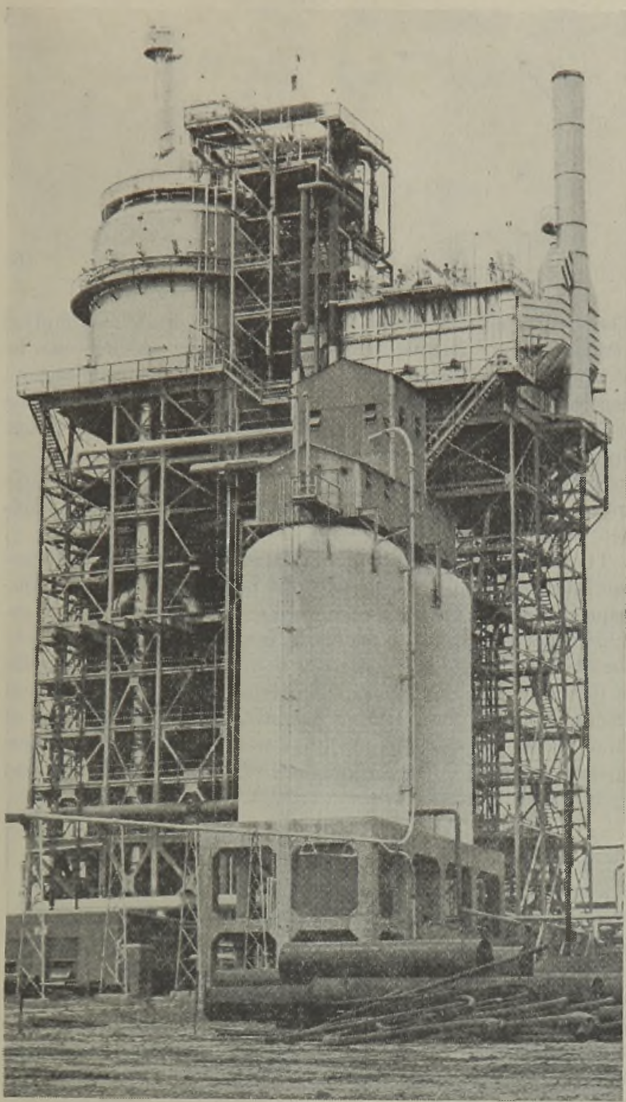

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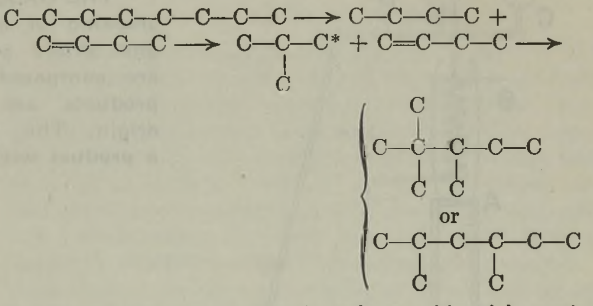
Modern Catalytic Cracking Unit

AS EARLY as 1878 Friedel and Crafts showed that hydrocarbons undergo decomposition in the presence of aluminum chloride to products of lower molecular weight. Of particular interest is the work of McAfee (*15*), who developed a cracking process for the production of gasoline from petroleum using anhydrous aluminum chloride as catalyst. An extensive literature, mostly patents (*2, 4, 6, 14*), has appeared on the subject. The McAfee process, however, did not find wide practical application. The action of anhydrous aluminum chloride on pure hydrocarbons has been extensively studied during the last decade (*1, 5, 17*). As a result of these studies, many interesting reactions have been discovered; of particular importance are: (*a*) the alkylation of paraffins by olefins (*9*), (*b*) the alkylation of cycloparaffins by olefins (*11*), (*c*) the phenomenon of destructive alkylation (*7*), (*d*) isomerization (*3, 13*), (*e*) intra- and intermolecular hydrogenation-dehydrogenation (*10*), and (*f*) conjunct polymerization (*8, 12*).

These reactions are usually accompanied by the formation of two layers. The upper layer contains hydrocarbons and the lower layer contains the so-called aluminum chloride–hydrocarbon complex. The lower layer on decomposition with water forms aluminum hydroxide, hydrogen chloride, and a highly unsaturated hydrocarbon layer. In cracking of natural hydrocarbon mixtures in the presence of aluminum chloride, two facts are apparent: The product in the upper layer is saturated, and isoparaffins are the principal upper-layer hydrocarbons. These products can readily be explained by the reactions mentioned above. Thus any hydrocarbon decomposing under the action of aluminum chloride and forming unsaturated fragments will form a saturated product by the processes of alkylation, intermolecular dehydrogenation-hydrogenation, and conjunct polymerization. For example,

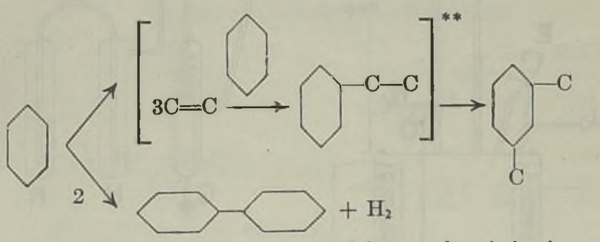
Paraffin Hydrocarbons:



$$\mathrm{C{-}C{-}C{-}C{-}C{-}C{-}C{-}C} \longrightarrow \mathrm{C{-}C{-}C{-}C} + \mathrm{C{=}C{-}C{-}C} \longrightarrow \mathrm{C{-}\underset{\mid \atop C}{C}{-}C^{*}} + \mathrm{C{=}C{-}C{-}C} \longrightarrow \left\{ \begin{array}{c} \mathrm{C{-}\overset{C \atop \mid}{\underset{\mid \atop C}{C}}{-}\underset{\mid \atop C}{C}{-}C{-}C} \\ \text{or} \\ \mathrm{C{-}C{-}\underset{\mid \atop C}{C}{-}\underset{\mid \atop C}{C}{-}C{-}C} \end{array} \right. \qquad (1)$$

* Isomerization can occur also prior to decomposition of the starting material.

Cycloparaffin Hydrocarbons:

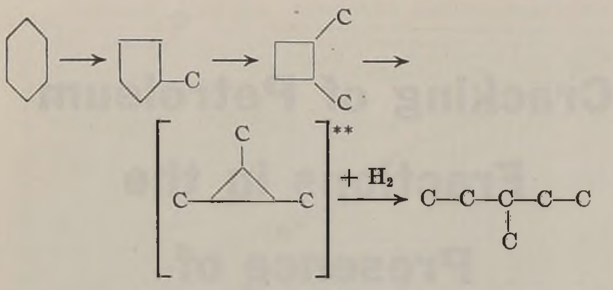


(2)

(3)

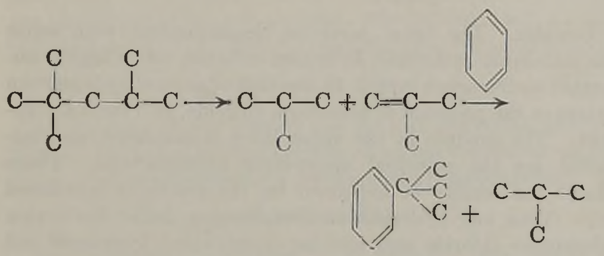
** Possible intermediate products which have not been isolated.

In addition to undergoing destructive alkylation and intermolecular dehydrogenation, cycloparaffin hydrocarbons have the tendency to isomerize with consequent degradation of the ring (*19, 20*) and thus of finally transforming into isoparaffins by the process of decyclization-hydrogenation. The necessary hydrogen is formed as in reaction 3.

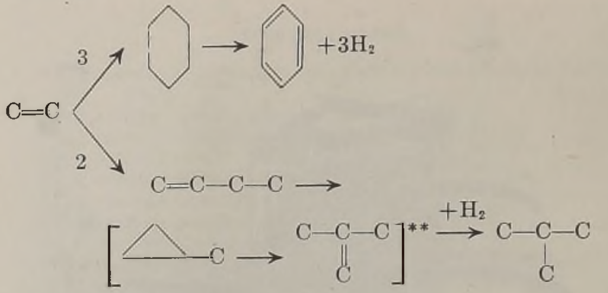

(4)

Aromatic Hydrocarbons. These hydrocarbons are the most stable under the conditions of aluminum chloride cracking. However, the similar reactions of destructive alkylation, intermolecular dehydrogenation, and dealkylation can take place. Because of the fact that they constitute a rather small part of straight-run petroleum products (*16*), their behavior does not change the over-all postulated results.

The unsaturated hydrocarbons formed as the result of cracking can also alkylate any other hydrocarbon present, and thus all classes of hydrocarbons can interact:


(5)

Part of the unsaturated hydrocarbons will form, with aluminum chloride, a lower layer and also undergo a conjunct polymerization with the formation of cycloparaffins, aromatics, and isoparaffins (*8, 12*):


(6)

These considerations point to the other important assumption verified by experiments; namely, similar final products can be obtained from stocks of various origin and chemical composition, depending on the conditions of operation and particularly on the time of contact with the catalyst. It was also to be expected that operating conditions could be found when the above reactions would be initiated and favored, with the result that only controlled changes with the maximum formation of the desired products would take place.

Thus the product of aluminum chloride cracking should contain a large amount of low-molecular isoparaffins and, as a consequence, should possess a high antiknock value and good tetraethyllead susceptibility. Therefore, it was of interest to restudy the aluminum chloride cracking of petroleum and the properties of the products obtained, using modern methods of analysis and fractional distillation. During this investigation the cracking of straight-run gas oils and naphthas was studied under various operating conditions in the presence of aluminum chloride and hydrogen chloride.

THE GASOLINE obtained as the result of aluminum chloride cracking of straight-run distillate has an 80 octane rating and shows good tetraethyllead susceptibility. The products are composed mainly of isoparaffin hydrocarbons. Similar products are obtained from charging stocks of various origin. The cracking reactions can be directed so that a product with the desired end point results.

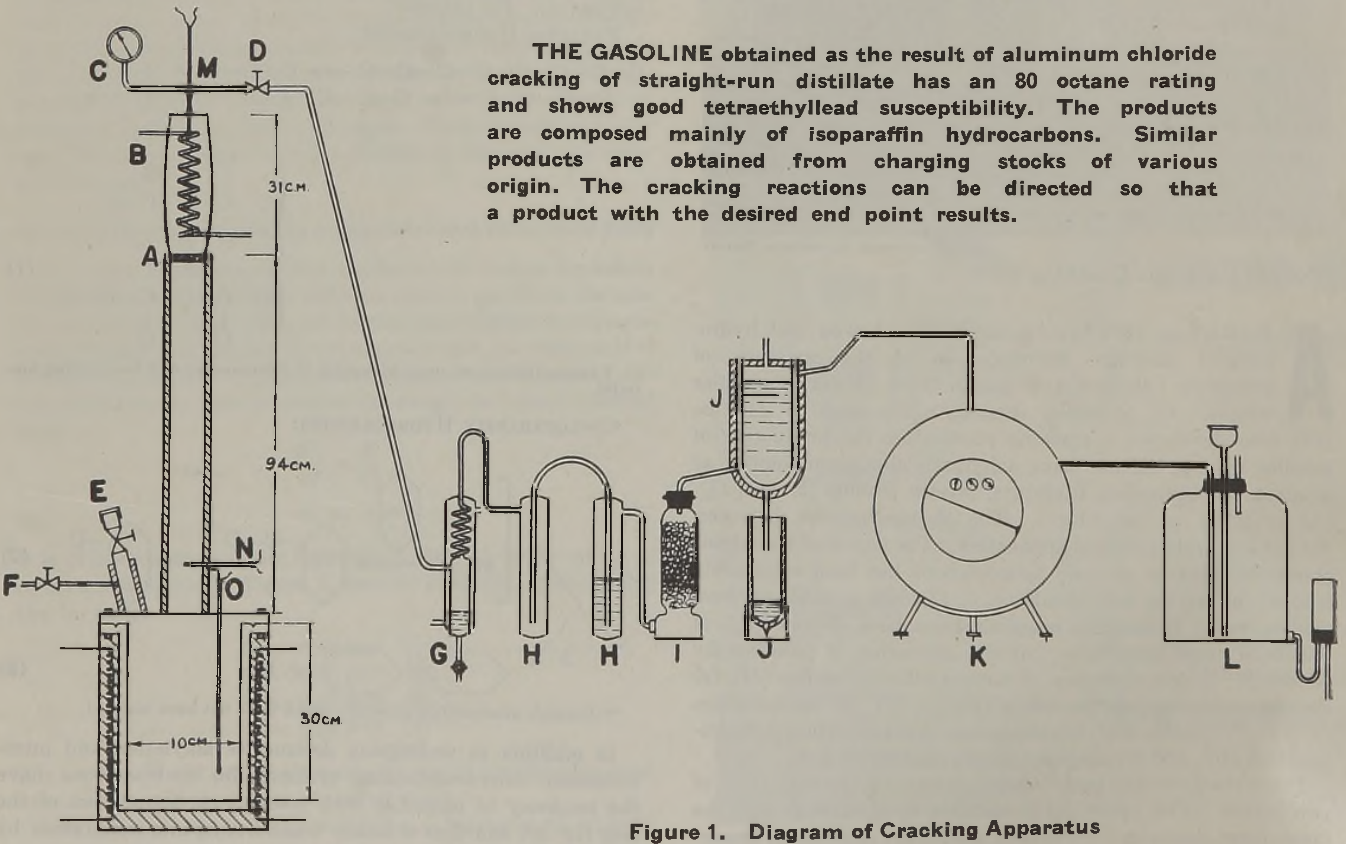


Figure 1. Diagram of Cracking Apparatus

Table I. Charging Stocks

	Calif. Kettleman Hills Gas Oil	Pa. Gas Oil	Trinidad Gas Oil	Calif. Gas Oil[a]	Mich. Naphtha[a]	Trinidad Naphtha[b]
Properties						
Gr., ° A.P.I. (15.56° C.)	33.4	38.0	31.2	22.1	54.0	41.4
Sp. gr. (15.56° C.)	0.8581	0.8348	0.8772	0.9212	0.7628	0.8184
Sulfur, %	0.24	0.07	....	3.72	....	....
Sediment and water,	0.0	0.0	0.0	Trace	....	....
Viscosity, Saybolt Universal sec. (37.78° C.)	40.5	44.4	43.1	91.3	....	....
100 cc. distillation, ° C.						
Initial b.p.	221	221	238	303	127	77
10% over	246	254	270	314	146	123
50% over	288	318	300	340	172	158
90% over	344	367	339	391	204	197
End point	367	399	367	404	221	221
% over	98.0	99.0	98.5	99.0	99.0	99.0
% at 300° C.	62.5	34.0	50.0	....	....	....
% bottoms	2.0	1.0	1.5	1.0	1.0	1.0

[a] Octane number below 0.
[b] Octane number 56.

Table II. Cracking of Pennsylvania Gas Oil (Charge 1500 Cc. or 1252 Grams)

Experiment No.	5	7
Catalyst wt., % on charge	10.0	10.0
Reaction time, hours	15	5
Products		
Noncondensable gas, liters	117.	3.3
Liquid, including condensable gas, vol. % on charge	94.5	88.0
Coke, wt. % on charge	20.3	10.0
Compn. of condensable gas and liquid, vol. % on charge		
Propane	13.0	2.0
Isobutane	34.0	5.8
Isopentane	21.1	3.9
Aviation gasoline (C_5 to 150° C. end point)	47.5	13.1
Motor gasoline (C_5 to 225° C. end point)	..	21.8
Higher-boiling (225° C. and up)	..	58.4
Octane No. of aviation gasoline	82[a]	53.5

[a] With 6 cc. of tetraethyllead, 100+ octane number.

EXPERIMENTAL PROCEDURE

Materials. The charging stocks were Pennsylvania, California, and Trinidad gas oils, and Trinidad and Michigan naphthas. Complete specifications of these materials are presented in Table I. The charging materials were dried with calcium chloride before the experiments. The catalysts were anhydrous aluminum chloride (Merck & Company) and hydrogen chloride (Harshaw Chemical Company).

Apparatus. The apparatus (Figure 1) consisted of a 5-liter, stainless steel, electrically heated reaction vessel and a condensing system for the products. A 94-cm. distilling column was connected to the reaction vessel. The column was supplied with a filter *A* for aluminum chloride vapors, a water-cooled coil *B*, a pressure gage *C*, and a needle valve *D*. The reaction vessel had a Nordstrom gate valve *E* for introduction of aluminum chloride and a hydrogen chloride inlet *F*. Temperature was measured by thermocouples *M*, *N*, and *Q*. The condensing system consisted of a water condenser *G*, hydrogen chloride absorbers *H*, a dryer *I*, dry ice condensers *J*, a wet test meter *K*, and a ample gas holder *L*.

The following procedure was used: After charging 1500 ml. of oil and the required amount of aluminum chloride the reaction vessel was closed and 10 atmospheres of hydrogen chloride were introduced into the vessel. (In the 15-hour experiments the catalyst was introduced by equal portions at 5-hour intervals.) The apparatus was gradually heated to 400° C. in experiments with gas oils and to 225° in experiments with naphthas. The pressure was maintained constant (13 atmospheres) by regulating exit valve *D*. The head temperature was maintained at 25–30° C. by adjusting the cooling at the head condenser. At the end of the experiments the pressure was released to atmospheric, and the total liquid reaction product was distilled from the vessel. The products of the reaction consisted of noncondensable and condensable (−80° C.) gas, liquid condensate and coke. The liquid condensate was submitted to Engler distillation (A.S.T.M. D86–30) in order to evaluate the content of aviation (end point 150° C.) and motor (end point 225° C.) gasolines and, in some cases, to fractionation in a Podbielniak column and hydrocarbon group (Pona) analysis (*18*). The condensable gas was fractionated in a Podbielniak column. All hydrocarbons boiling above C_4 were added to the gasoline fraction. Octane numbers were determined by the Motor method (A.S.T.M. D357–34j). Tables II to VI present the results of the experiments and the properties of the products.

DISCUSSION OF RESULTS

The cracking of straight-run gas oils and naphthas in the presence of aluminum chloride results in the production of gaseous and liquid hydrocarbons completely free from olefins. This fact differentiates these products from those obtained in thermal or catalytic cracking. The gaseous products contain large amounts of isobutane (30% by volume of charge). The liquid product boils entirely in the aviation gasoline range (end point 150° C.) and consists mainly of paraffin hydrocarbons (83–95%) as revealed by fractionation and hydrocarbon group analysis. The liquid product has an octane number of 80 and high tetraethyllead susceptibility. The similarity of the results obtained from

Table III. Cracking of Gas Oils

Expt. No.	8	9	10	11	11a
Charging stock (1500 cc.)	Calif. Kettleman Hills gas oil	Calif. gas oil rich in sulfur	—Trinidad gas oil—		
Catalyst, wt. % on charge	10.0	10.0	10.5	5.0	12.0
Reaction time, hr.	15.0	15.0	15.0	30.0	45.0
Products					
Noncondensable, liters	99.0	123.0	132.0	177.0	280.0
Liquid, including condensable gas, vol. % on charge	90.5	71.1	88.6	79.8	73.7
Coke, wt. % on charge	29.0	38.7	31.1	32.4	..
Compn. of condensable gas and liquid, vol. % on charge					
Propane	13.8	12.7	15.3	5.1	19.0
Isobutane	28.8	21.91	28.4	18.9	25.4
Isopentane	19.56	8.7	18.2	12.6	..
Aviation gasoline	47.9	35.2	44.9	50.2	29.3[b]
Motor gasoline	...	..	...	55.7	..
Higher-boiling	...	..	...	...	..
Octane No. of aviation gasoline	80[a]	76	80	75	..

[a] With 6 cc. tetraethyllead, 100+ octane number; with 3 cc., 94.
[b] This fraction contained 17.9% isopentane, 2.7% 2-methylpentane, and 8.7% 3-methylpentane.

Table IV. Cracking of Naphthas

Experiment No.	12	13	14	15
Charging stock (1500 cc.)	Michigan naphtha			Trinidad naphtha
Catalyst, wt. % on charge	4.8	5.0	4.8	3.0
Reaction time, hr.	5	6	7	12
Products				
Noncondensable gas, liters	..	180.0	..	120.0
Liquid, including condensable gas, vol. % on charge	90.9	93.0	99.1	83.2
Coke, wt. % on charge	12.0	18.4	21.5	27.8
Compn. of condensable gas and liquid, vol. % on charge				
Propane	9.6	17.1	15.0	11.64
Isobutane	21.7	42.1	37.3	27.5
Isopentane	13.0	15.9	18.7	13.8
Aviation gasoline	47.0	33.9	46.8	43.9
Motor gasoline	59.6	..	..	...
Higher-boiling	..	..	..	...
Octane No. of aviation gasoline	60.5	71	76.5	80

Table V. Properties of Products

Experiment No.	12	5	13	14	8	10	9	15	11	
Properties										
Gr. ° A.P.I. (15.56° C.)	...	81.9	81.7	78.3	77.7	77.5	69.2	68.6	66.3	60.7
Sp. gr. (15.56° C.)	...	0.6631	0.6637	0.6743	0.6764	0.6770	0.7050	0.7071	0.7132	0.7362
Bromine No.	0.5	....	....	0.5	....	....	1.0	0.5	0.5	0.5
Reid vapor pressure, lb.	9.3	12.0	11.9	10.7	10.9	10.4	7.4	8.6	7.2	6.0
100 cc. distn., ° C.										
Initial b.p.	33	32	35	38	36	35	38	38	47	41
10% over	43	42	48	47	46	46	56	58	61	63
50% over	57	56	72	63	61	61	83	76	92	137
90% over	97	112	127	105	104	104	123	116	132	202
End point	114	148	156	137	137	137	153	159	149	226
% over	...	97.5	97.5	98.0	98.5	98.0	99	98.5	98.5	98.5
% bottoms	...	1.0	1.0	1.0	1.0	1.2	0.2	1.0	1.2	1.1
% loss	...	1.5	1.5	1.0	0.5	0.8	0.8	0.5	0.3	0.4
Pona analysis										
Paraffin	...	95	....	....	87	83	....	....	....	....
Olefin	...	0	....	....	0	0	....	....	....	....
Naphthene	...	0	....	....	0	0	....	....	....	....
Aromatic	...	5	....	....	13	17	....	....	....	....

Table VI. Noncondensable Gas Analysis (Air-Free)

Experiment No.	5	7	8	9	10	11	13	15
Olefins, %	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen, %	46.4	49.0	33.2	55.7	59.5	45.1	39.0	45.2
Methane + ethane, %	53.6	51.0	66.8	44.3	40.5	54.9	61.0	54.8
Liters of gas/100 cc. oil charge	7.8	0.22	6.65	8.25	8.8	11.8	10.9	7.95
Wt. % of gas on oil charge	5.1	0.1	4.3	4.8	3.8	8.4	8.6	5.2

charging stocks of various origin, such as Pennsylvania (experiment 5), California (experiment 8), and Trinidad (experiment 10) gas oils indicates the similarity of the reactions taking place during aluminum chloride cracking.

A longer reacting time increased the formation of low-boiling paraffins and improved the octane number of the gasoline produced. This is particularly clear in the experiments with Pennsylvania gas oil (experiments 5 and 7). By increasing the reacting time from 5 to 15 hours, the yields of propane, isobutane, isopentane, and aviation gasoline increased from 2 to 13.8%, 5.8 to 34.0%, 3.9 to 21.1%, and 13.1 to 47.5%, respectively, with consequent increase of the octane value of aviation fraction from 53.5 to 82. The total yield of the low-boiling product (C_3 to 150° C. end point) increased from 20.8 to 94.5%. The same trend can be observed in the experiments with naphtha (12 to 14).

In experiment 11a with Trinidad gas oil a long reacting time (45 hours) resulted in a production of 100% paraffinic material with isohexane being the highest-boiling hydrocarbon produced.

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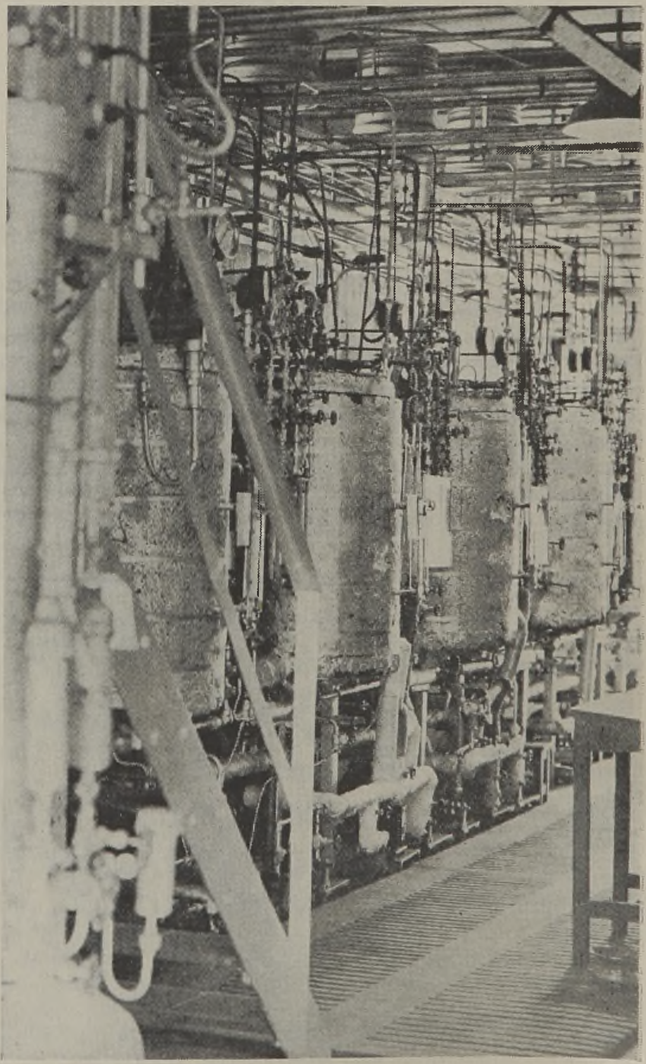

COURTESY, STANDARD OIL COMPANY OF N. J.

Small-Scale Pilot Plant Units for Catalytic Cracking

SILICA-ALUMINA GELS

Specific Surface and Particle Size Distribution

THREE SERIES of silica-alumina gels of various concentrations, made by (A) precipitation in sequence, (B) mixing wet gels, and (C) impregnation of partially dried silica gel, were examined by nitrogen adsorption, small angle x-ray scattering, and x-ray diffraction. Specific surfaces were smaller for A and larger for B than those expected for mixtures of the dried silica and alumina gels. Maxima in curves for specific surface *vs.* alumina content for B and C at about 5% by weight correlated with minima in average particle size. No alumina was detected by x-ray diffraction for gels containing as much as 26% by weight alumina.

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IN THE routine examination of commercial silica-alumina catalysts by x-ray diffraction, it was observed that no diffraction features characteristic of the alumina were obtained for catalysts containing appreciable amounts of alumina. When dried, pure silica gel gives a broad band indicating an amorphous structure, while dried alumina gel is crystalline. The nature of the crystalline alumina pattern depends on the temperature of drying.

The present investigation was planned in order to study the effect of the method of preparing silica-alumina gels on the physical structure of the gels. Three methods, representative of commercial preparations, were chosen: (A) precipitation in sequence, in which alumina is precipitated from an aluminum chloride solution in the presence of a dilute slurry of silica gel; (B) mixing of the two wet gels in a dilute slurry; and (C) impregnation of silica gel (dried at 120° C.) with aluminum nitrate and subsequent thermal decomposition to form alumina. Several samples of varying alumina content were made for each of these series.

To obtain additional information, the gel preparations were examined by low-temperature nitrogen adsorption and small-angle x-ray scattering in addition to the usual diffraction technique. From adsorption measurements the specific surface may be calculated, and from small-angle x-ray scattering the particle size distribution may be obtained. These examinations afforded a comparison of the specific surfaces calculated from particle size distribution data and from adsorption measurements.

PREPARATION OF GELS

Silica Gel I. A solution of 2000 grams of Philadelphia Quartz Company's N brand sodium silicate in 10 liters of water was precipitated by slow addition of dilute hydrochloric acid with good mixing until the system was just faintly pink to phenolphthalein. After stirring for 20 minutes, the solution was made slightly acid to Congo red by the addition of more hydrochloric acid. The mixture was stirred for 30 minutes, and dilute ammonium hydroxide was added, leaving the system just acid to litmus. After stirring for another half hour, the gel was filtered and washed five times by slurrying for one hour each time in 8 liters of water containing 8 cc. of concentrated hydrochloric acid. The gel was then washed by slurrying for one hour in 8 liters of water containing 80 grams of $AlCl_3 \cdot 6H_2O$. The gel was finally washed three times by slurrying in 8 liters of water for 30-minute periods. The gel was diluted to 8 liters, agitated for 8 hours, and allowed to stand for 2 days; then the gel was again stirred for an hour and allowed to settle for a half hour. The slurry was siphoned to another container, leaving behind about 3 liters containing the coarser particles of gel. The concentration of dry silica in the second container was found to be 2.4 grams per 100 cc. of slurry. This silica gel slurry was used in the preparation of six silica-alumina gels of series A. A portion was dried at 120° C. for x-ray diffraction, small-angle x-ray scattering, and adsorption measurement.

Silica Gel II. A solution of 2000 grams of the N brand sodium silicate in 10 liters of water was stirred for 30 minutes and acidified by the slow addition of 625 cc. of dilute hydrochloric acid, making the system just acid to phenolphthalein. After stirring for a half hour, 325 cc. more of the acid were added; leaving the system just basic to methyl red. After agitation for a half hour, the addition of 50 cc. of ammonium hydroxide left the system just acid to litmus. The gel was filtered and washed six times by slurrying in 5 liters of water containing 5 cc. of concentrated hydrochloric acid. After washing three times by slurrying with 5 liters of water, the gel was sucked dry on the filter. This wet gel was found to contain 92.9% water. Portions were used for the preparation of one silica-alumina sample in series A and all of the samples of series B. Another portion was dried at 120° C. and screened to 4–10 mesh for the preparation of silica-alumina samples of series C. The dried gel was found to contain 37.2% water.

Series A. Varying amounts of Baker's c.p. $AlCl_3 \cdot 6H_2O$ in solution were added to portions of silica gel I. Alumina was precipitated by the addition of dilute ammonium hydroxide until the system was just basic to litmus. The gel mixture was filtered and washed twice by slurrying for 30 minutes in 1 liter of water containing 1 cc. of concentrated ammonium hydroxide and once by slurrying in 1 liter of water. The washed gel was slurried in sufficient water to make a total of 1400 cc., filtered, and evaporated to dryness at 120° C. The quantities of materials used, together with the alumina contents found by analysis of the final dried gels, follow:

Wet Silica Gel I, Cc.	$AlCl_3 \cdot 6H_2O$, Grams	H_2O, Cc.	Al_2O_3 by Analysis, Wt. %
1340	7.1	160	5.2
1280	14.2	1720	10.0
1160	28.4	3840	19.8
1040	42.6	3960	26.5
680	85	4320	51.2
440	113	4560	69.5

One silica-alumina sample was made by this method from silica gel II. To 678 grams of silica gel II in 500 cc. water, a solution of 18.4 grams of Baker's c.p. $Al(NO_3)_3 \cdot 9H_2O$ in 50 cc. of water was added. After stirring for a half hour, the alumina was precipitated by dropwise addition of dilute ammonium hydroxide until the system was basic to litmus. The gel mixture was filtered and washed five times by slurrying in 500 cc. of water containing 1 cc. of dilute ammonium hydroxide. After final washing in 500 cc. of water, the gel was filtered and dried. Chemical analysis of this sample was not made. The theoretical alumina concentration was calculated to be 5% by weight.

Series B. An alumina gel was prepared by dissolving 1000 grams of Baker's c.p. $AlCl_3 \cdot 6H_2O$ in 10 liters of water and adding 1450 cc. of dilute ammonium hydroxide to make the system basic to litmus. The gel was washed five times by slurring with 5 liters of water containing 10 cc. of dilute ammonium hydroxide each time. A final wash with 5 liters of water peptized the gel and made filtration very slow. The water content of the gel was found to be 92.2%. Varying amounts of this wet gel were mixed with portions of wet silica gel II and stirred in 1 liter of water for an hour. The gels were then filtered, dried at 120° C. for 6 hours, and calcined for 6 hours at 540°. The quantities of materials and the percentages of alumina found by analysis of the final preparations are listed below:

Wet Alumina Gel, Grams	Wet Silica Gel II, Grams	Al_2O_3 by Analysis, Wt. %
16	332	5.2
32	314	12.0
64	280	17.5
96	245	31.0
192	140	59.5
256	70	77.5

Series C. Portions of silica gel II, which was dried at 120° C. (containing 37.2% water) and screened to 4–10 mesh, were added to varying amounts of a solution of Baker's c.p. $Al(NO_3)_3 \cdot 9H_2O$. One liter of this solution contained 367 grams of the salt which was equivalent to 0.05 gram of Al_2O_3 per cc. Four samples were prepared using amounts as listed below with the final chemical analysis. The samples were dried at 120° C. for 6 hours and calcined at 540° for 6 hours.

$Al(NO_3)_3$, Cc.	Silica Gel II, Grams	Al_2O_3 by Analysis, Wt. %
5	39	5.2
25	38	7.9
50	36	13.4
100	32	25.5

ANALYSES

Specific Surface Measurements. Low-temperature nitrogen adsorption isotherms were obtained by measuring the amount of nitrogen gas adsorbed at various pressures from a few millimeters of mercury up to the saturation pressure. The apparatus was of the volumetric type, similar to the one described by Emmett (*2*). The adsorbent was baked out under vacuum for 2 hours at 200° C. and, when cooled, immersed in a liquid nitro-

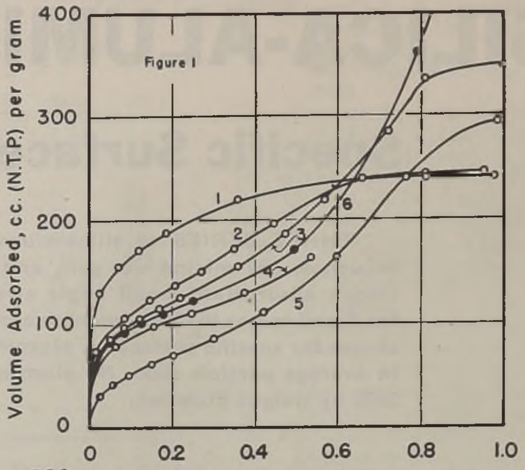

Figure 1. Nitrogen Adsorption Isotherms of Series A Gels, Made by Precipitation in Sequence on Silica Gel I

1, silica gel I; 2, 10% alumina; 3, 26.5% alumina; 4, 69.5% alumina; 5, 5% alumina on silica gel II; 6, silica gel II

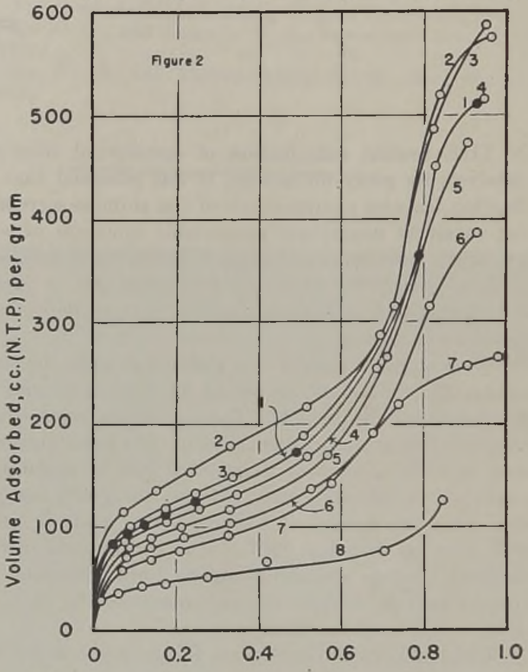

Figure 2. Nitrogen Adsorption Isotherms of Series B Gels, Made by Mixing Wet Silica Gel II with Alumina Gel

1, silica gel II; 2, 5.2% alumina; 3, 12% alumina; 4, 17.5% alumina; 5, 31% alumina; 6, 59.5% alumina; 7, 77.5% alumina; 8, alumina gel

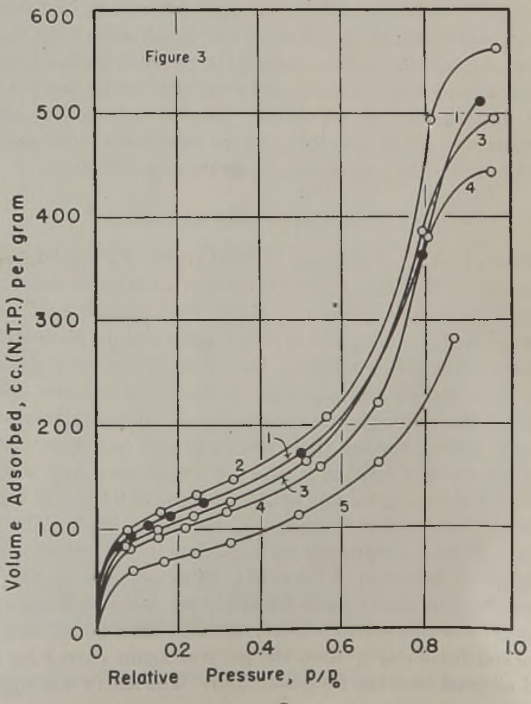

Figure 3. Nitrogen Adsorption Isotherms of Series C Gels, Made by Impregnation of Partially Dried Silica Gel II

1, silica gel II; 2, 5.2% alumina; 3, 7.9% alumina; 4, 13.4% alumina; 5, 25.5% alumina gen bath. The dead air space around the adsorbent was measured by the pressure produced by admitting a known amount of helium into the adsorption system. After the helium was pumped out, known volumes of nitrogen were added; when equilibrium was attained, the pressure of the adsorption system was recorded. The temperature of the liquid nitrogen bath, from which the saturation pressure may be calculated, was not measured; instead, the saturation pressure was measured directly at the end of each run by condensing nitrogen in the adsorption tube and reading the pressure.

The adsorption isotherms were interpreted according to the method of Brunauer, Emmett, and Teller (*1*). The experimental values for $p/V(p_o-p)$ were plotted as a function of p/p_o, where V is the amount of gas adsorbed per gram at pressure p, and p_o is the saturation pressure. Straight lines were drawn through these points; from the values of the slope and intercept, the amount of nitrogen, V_m, necessary to cover the surface of the adsorbent with a monomolecular layer was calculated. The specific surface, expressed as square meters per gram, was obtained by multiplying the V_m value, expressed as cc. of nitrogen (N.T.P.) per gram of adsorbent, by 4.38 square meters per cc. This constant is the value for the calculated area that the molecules of 1 cc. of nitrogen will cover if liquid density and close packing of spherical molecules in a monomolecular layer are assumed.

X-RAY DIFFRACTION. Photograms were obtained by the Debye-Scherrer powder method using filtered copper radiation. Compound identification was performed by comparison of the photograms with accepted or published diffraction patterns.

SMALL-ANGLE X-RAY SCATTERING. From a study of the intensity of x-ray scattering at small angles (from 0.1° to 2.2°), it is possible to obtain the particle size distribution in the scattering specimen. This technique has been described by Guinier (*3*) and Hosemann (*4, 5*).

Crystal monochromated CuKα radiation was used in an evacuated scattering camera for this study. X-ray intensities were recorded photographically and determined with a microphotometer. Additional details regarding the interpretation of the scattered x-ray intensities will be published elsewhere.

ADSORPTION ISOTHERMS

The nitrogen adsorption isotherms for the gel preparations dried at 540° C. from series A, B, and C are shown in Figures 1, 2, and 3, respectively. Figure 1 shows that, for the samples prepared with silica gel I by precipitation in sequence, the amount of nitrogen adsorbed at lower pressures decreases (curves 2, 3, and 4) as the concentration of alumina is increased. On the other hand, the amount adsorbed at the higher pressures does not vary uniformly with the alumina concentration. The adsorption isotherm of silica gel II (curve 6) has a different shape from that of silica gel I. The former is a typical S-shaped isotherm, whereas the latter is almost a Langmuir type of curve. The amount adsorbed near saturation pressure ($p/p_o = 1.0$) is much greater for silica gel II.

Table I. Results of Nitrogen Adsorption and X-Ray Diffraction Examination of Three Series of Silica-Alumina Preparations

Al_2O_3, Wt. %	Specific Surface, Sq. M./G.	X-Ray Diffraction Identification
Series A, Pptn. in Sequence on Silica Gel I		
0	750	....
5.2	...	Amorphous SiO_2[a]
10.0	523	Amorphous SiO_2[a]
19.8	...	Amorphous SiO_2[a]
26.5	448	Amorphous SiO_2[a, b]
51.2	...	Amorphous SiO_2, α-$Al_2O_3 \cdot H_2O$, α-$Al_2O_3 \cdot 3H_2O$[a]
69.5	285	Amorphous SiO_2, α-$Al_2O_3 \cdot H_2O$, α-$Al_2O_3 \cdot 3H_2O$[a]
Series A, Pptn. in Sequence on Silica Gel II		
5	373	....
Series B, Mixing Wet Gels (Silica Gel II)		
0	414	....
5.2	541	....
12.0	454	....
17.5	388	Amorphous SiO_2
31.0	377	Amorphous SiO_2[b]
59.5	345	Amorphous SiO_2, γ-Al_2O_3
77.5	276	Amorphous SiO_2, γ-Al_2O_3
100	173	....
Series C, Impregnation of Silica Gel II		
0	414	....
5.2	452	....
7.9	397	....
13.4	370	....
25.5	272	Amorphous SiO_2

[a] Samples dried at 120° C.; all others were dried at 540°.

[b] Faint pattern of crystalline alumina was obtained by electron diffraction.

Figure 2 gives adsorption isotherms for the series B samples prepared by mixing wet gels. In contrast with the behavior shown in Figure 1, the amount of adsorption at lower pressures does not decrease uniformly as the alumina concentration is increased but first increases (curves 2 and 3) to values higher than that for the pure silica gel (curve 1) and then decreases (curves 4 through 8). This initial increase shown by the samples containing 5.2 and 12.0% alumina was so unexpected that the results were checked by examination of another series prepared by the same method but using different silica and alumina gels. Exactly the same type of behavior was found. The data are not included here. Figure 2 also shows that the amount adsorbed at higher pressures for the samples is in about the same order as the amount adsorbed at lower pressures.

The curves for series C, made by impregnation of silica gel II with alumina formed by thermal decomposition of aluminum nitrate, are shown in Figure 3. The variation of amount adsorbed with alumina concentration is similar to that observed for series B. The sample containing 5.2% alumina adsorbs more at lower pressures than the pure silica gel.

To determine whether the uniform variation of amount adsorbed for series A was due to any unusual properties of the base silica gel I, a single sample containing about 5% alumina was

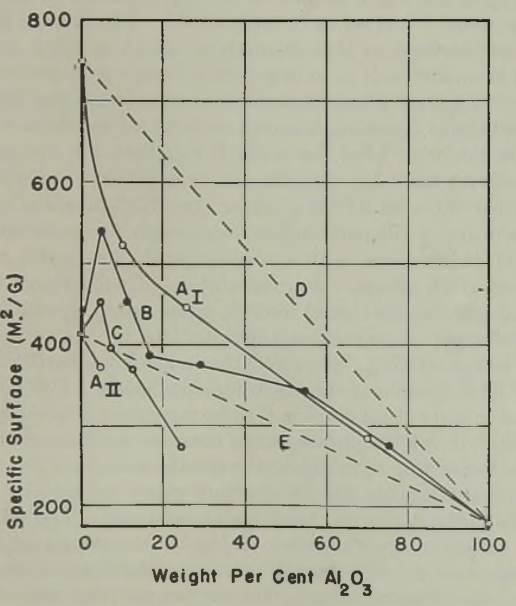

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Figure 4. Variation of Specific Surface with Alumina Concentration

Gels AI and AII prepared by precipitation in sequence on silica gels I and II; B, by mixing silica and alumina gels (wet); C, by impregnation of silica gel (partially dried) by alumina; D and E represent dry mechanical mixtures of alumina gel with silica gels I and II, respectively

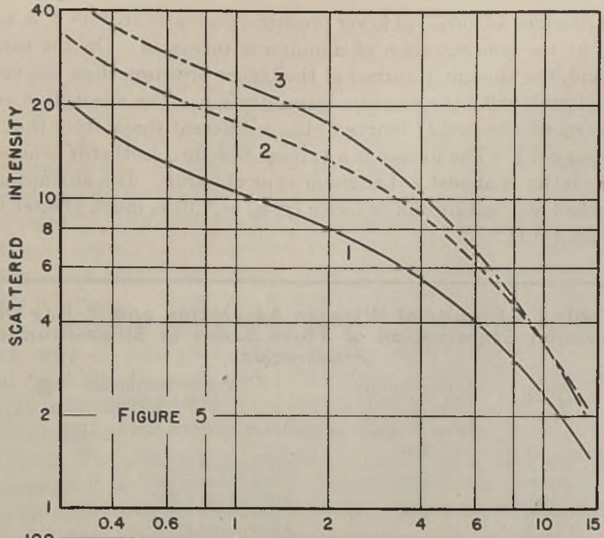

Figure 5. Small-Angle X-Ray Scattering for Series A Preparations

1, silica gel I; 2, 5.2% alumina; 3, 19.8% alumina

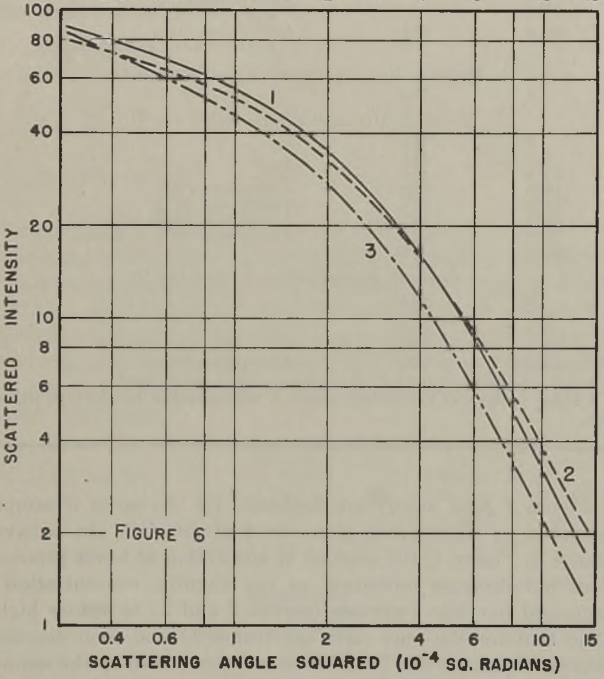

Figure 6. Small-Angle X-Ray Scattering for Series B Preparations

1, silica gel II; 2, 5.2% alumina; 3, 17.5% alumina

prepared by the precipitation in sequence of alumina on silica gel II. Curve 5 of Figure 1 is the isotherm for this sample; it lies below curve 6 for the base silica gel II, just as do the curves of series A. Hence it is concluded that the uniform variation is not specific to the base gel.

SPECIFIC SURFACE AND X-RAY DIFFRACTION

Specific surface values, calculated from the above adsorption data, are listed in Table I and plotted on Figure 4 as a function of alumina concentration. Dashed line D represents the expected variation of specific surface for mechanical mixtures of dried silica gel I and dried alumina gel, and curve E represents that expected for dried silica gel II and dried alumina gel. It is evident that the specific surfaces of the samples prepared by precipitation in sequence are less than would be expected for a mechanical mixture of the dried gels. The curve for series B (mixture of wet gels) lies above the expected curve for a mechanical mixture and shows a maximum at 5% alumina. A similar peak is observed for series C, made by the impregnation procedure. No attempt was made to measure the specific surface of the pure alumina so formed.

The results of x-ray diffraction examination are also listed in Table I. No diffraction pattern attributable to alumina is observed for samples containing as much as 26.5, 31.0, and 25.5% alumina for series A, B, and C, respectively. For comparison, a mechanical mixture of 5% dried alumina gel and 95% dried silica gel was prepared and examined by x-ray diffraction. A good pattern of crystalline α-$Al_2O_3 \cdot H_2O$ was obtained. Therefore, the failure of the diffraction method to detect alumina in these silica-alumina gels shows that less than 5% of crystalline alumina is present. These x-ray results were confirmed by electron diffraction examination, which might be expected to detect surface concentrations more readily.

For gels having higher alumina contents, patterns of α-$Al_2O_3 \cdot H_2O$ (boehmite) and α-$Al_2O_3 \cdot 3H_2O$ (hydrargillite) are obtained for samples dried at 120° and patterns of γ-Al_2O_3 for samples dried at 540° C. The diffraction lines of the aluminas are broad, indicating small crystals.

SMALL-ANGLE X-RAY SCATTERING

Three members of series A and three of series B were examined by the small-angle x-ray scattering technique. The scattering data for these two groups of preparations are given in Figures 5 and 6. Here the scattered intensity is plotted against the scattering angle squared, both on a logarithmic scale. Each of the curves on these figures is a composite of several experimental curves. Since it is impossible to measure reliably x-ray intensity changes larger than a factor of 5 on any one film, several exposures were taken of each material with different exposure times, and the data were combined into one curve. From these data it is possible to determine the particle size distribution in the specimen under examination if certain assumptions as to scattering theory and particle geometry are made. A complete discussion of these assumptions will be published elsewhere. In the absence of more precise information, the gel particles have been assumed to possess a symmetrical shape and to be defined in size by a particle diameter.

Figures 7 and 8 give the particle size distributions for the members of series A and series B, respectively. The average particle diameter (defined as that diameter at which as much material exists in smaller sizes as in larger sizes) is shown on each of these curves. Figure 7 shows that the average particle size increases regularly with increasing alumina content for members of series A. On the other hand, for series B members, the average particle size for the 5.2% alumina sample is definitely smaller than for either the original silica gel or the 17.5% alumina sample. This shifting of the particle size distribution curves for the various gel preparations is in agreement with the specific surface findings given above. A greater state of subdivision with a smaller particle size should result in an increased specific surface. The difference in particle size distributions for the two original silica gels is striking. Silica gel I has an average particle size of about 32 Å. as compared to 58 Å. for silica gel II. This large difference in state of subdivision is to be correlated with the marked difference in specific surface values obtained experimentally.

It is interesting to calculate the specific surfaces which should exist for the particle size distributions given in Figures 7 and 8. For simplicity, spherical particles are assumed. The results of these calculations are shown in Table II; the calculated specific surfaces show the same trends with increasing alumina content as do the experimental values. The surface anomaly with series B gels is thus confirmed; in addition, the surface variations are shown to be caused by changes in the particle size distribution existing in the gel microstructure.

The calculated values in Table II are all higher than the experimental values for the specific surface. Perhaps the simplest explanation for this is the shielding of particle surface from adsorbed gas at regions of particle-particle contact.

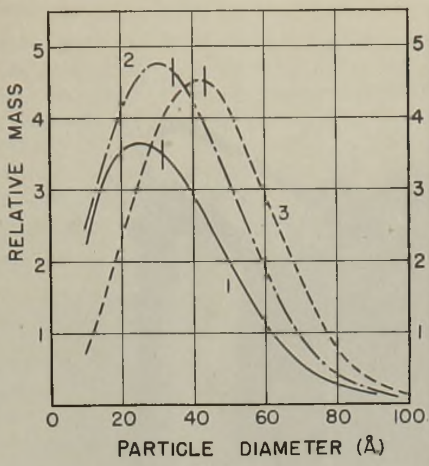

Figure 7. Particle Size Distributions for Series A Preparations

1, silica gel I; 2, 5.2% alumina; 3, 19.8% alumina

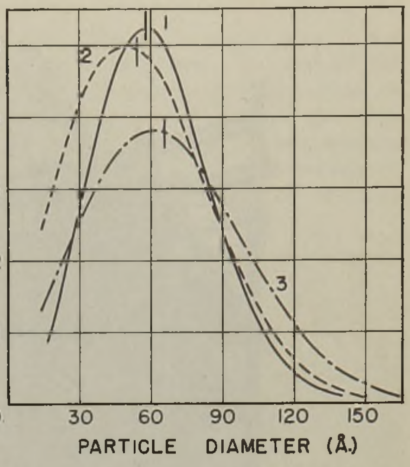

Figure 8. Particle Size Distributions for Series B Preparations

1, silica gel II; 2, 5.2% alumina; 3, 17.5% alumina

DISCUSSION OF RESULTS

The results show definitely that silica-alumina catalysts prepared by the three methods are not simple mixtures of silica particles and alumina particles such as would be expected from mixing fine powders of the two materials. Since there is no diffraction evidence of chemical compound formation between the silica and alumina, it seems reasonable to assume that the observed phenomena are due mainly to physical effects. The possibility of a solid solution of alumina in the silica gel is doubtful, particularly in the series prepared by the impregnation of partially dried silica gel. It may be postulated that the particle sizes of the wet gels and the partially dried silica gels are much smaller than the sizes observed for the dried gels. The addition of the alumina gel in the wet state may, therefore, prevent the formation of larger particles upon drying. Further investigation of particle size measurement of wet and partially dried gels is indicated.

Table II. Comparison of Specific Surfaces Measured by Nitrogen Adsorption and Calculated from Particle Size Distribution

Al_2O_3, Wt. %	Av. Particle Diam., Å.	Sp. Surface, Sq. M./G.		Ratio
		N_2 adsorption	Size distribution	
Series A, Pptn. in Sequence on Silica Gel I				
0[a]	31.5	829	1080	1.30
5.2[a]	34.5	675	1020	1.51
19.8[a]	43.5	580[b]	700	1.21
Series B, Mixing of Wet Gels (Silica Gel II)				
0	58.3	414	560	1.35
5.2	54.2	571	650	1.14
17.5	65.7	388	530	1.37

[a] Samples dried for 4 hours at 120° C. instead of 540°.
[b] Value obtained by interpolation on a graph of specific surface *vs.* composition.

The agreement between the results found by nitrogen adsorption and by small-angle x-ray scattering appears satisfactory, and promotes confidence in the usefulness of this relatively new x-ray technique. In all cases of specific surface variation, either in one preparation series or with members of both series, the changes are reflected in the particle size distribution curves in a manner to account for the observed surface phenomena. It must be admitted that the assumption of a spherical shape for the gel particles is not true in detail. Certainly the particles are irregular in size and shape, but when attention is centered on a large number of particles (as is done experimentally), it is believed that the size distributions obtained on the picture of spheres are representative of the true gel particles.

The differences between calculated and observed specific surfaces, shown in Table II, are believed to be indicative of the particle-particle packing. A simple calculation shows that nitrogen would be excluded from a small percentage of the particle surface at a particle-particle contact point. With irregularly shaped particles, this shielding effect will be more pronounced, and hence it is possible to explain the specific surface differences as being caused by a small number of contact regions for any one particle. There is no reason for expecting the magnitude of this shielding effect to remain constant from material to material since the particle packing need not remain constant.

SUMMARY

1. Silica-alumina gels precipitated in sequence were found to have lower specific surfaces than would be expected for mechanical mixtures of the dry gels.
2. Mixing of the wet gels gave specific surfaces greater than those expected for a mechanical mixture of the dry gels.
3. Specific surfaces of gels made by impregnation of partially dried silica were greater at small alumina concentrations and lower at large alumina concentrations than those expected for a mechanical mixture of the dried gels.
4. Crystalline alumina was not detected by x-ray or electron diffraction for gels with as much as 26% by weight of alumina, but was found in a sample containing 5% alumina made by mixing the dried gels.
5. Particle size distributions for the gels were determined by small-angle x-ray scattering technique. These showed maxima in particle size at from 30 to 65 Å.
6. A maximum was observed in the specific surface *vs.* concentration curve at about 5% alumina for the two series prepared by mixing the wet gels and impregnating the partially dried silica gel. The average particle sizes of these gels, as determined by small-angle x-ray scattering, had minima corresponding to the specific surface maxima.
7. Specific surfaces calculated from particle size distribution were found to change uniformly with experimental values but were always higher than the experimental values. This last effect is ascribed to a shielding of particle surface from adsorbed nitrogen at particle contact regions.

ACKNOWLEDGMENT

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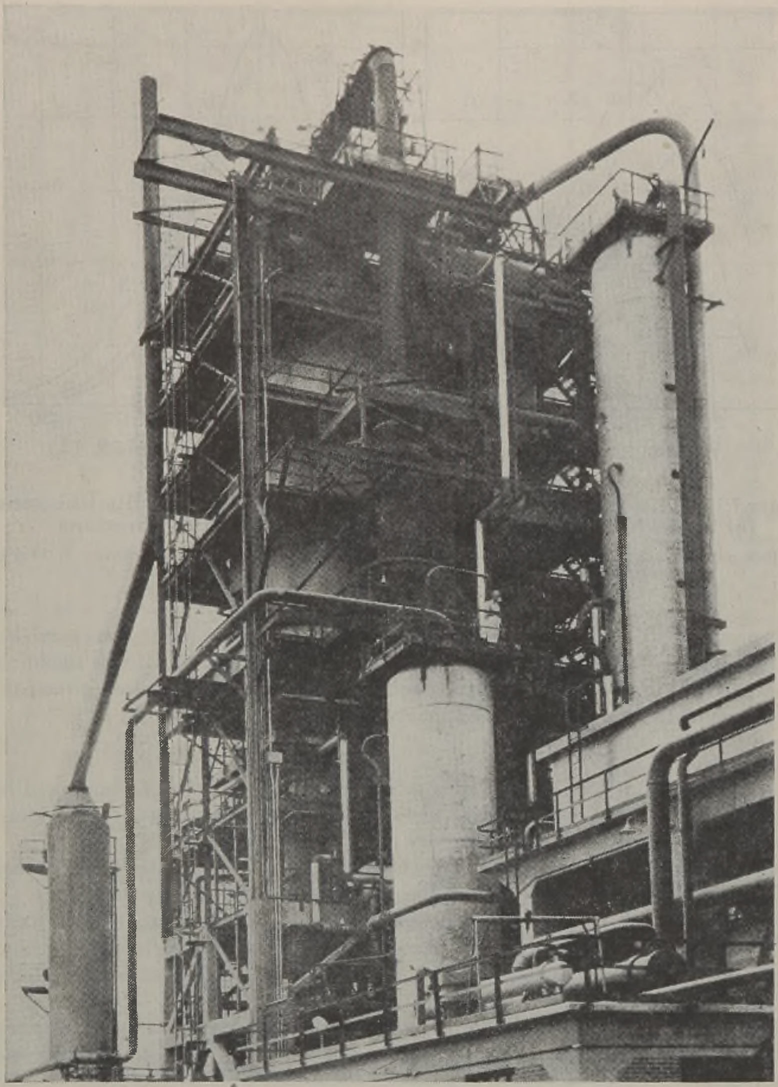

Cracking Unit Utilizing the Fluidized Fixed Bed

FLUIDIZED FIXED BED

Method for Contacting Solids with Gases and Vapors

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THE passage of gases or vapors upward (counter to gravity) through a mass of powdered solid produces the "fluidized fixed bed". The term "fluid" is used to convey the fact that the powdered solid becomes mobile or fluid in the presence of the flowing gases or vapors. In this respect it resembles the fluid catalyst systems that have become important in catalytic cracking (*1*).

All or most of the powdered solid remains in the reaction zone in the fluidized fixed bed. In this respect it resembles the fixed beds of immobile solid contact agents through which gases or vapors flow. Thus in the fluidized fixed bed both reaction and regeneration may take place in the same vessel as is usual with fixed beds of catalyst. Both in the fluidized catalyst system and in the compact moving-bed catalyst system it is customary for the catalyst to be regenerated in a vessel which is separated from the reaction zone.

If a column of powder is put in a vertical tube and air is passed slowly upward, a small flow of air can be obtained without any visible effect on the powder. If the air rate is increased beyond this rate, small channels are seen to form with a slight expansion of the powder. Further increase in the air rate results in a large expansion of the bed with violent agitation of the powder. This is the fluidized fixed bed condition. Still further increases in the air velocity result in further expansion of the bed, and finally the powder is blown out of the tube. This description indicates that a number of separable phenomena take place, and that the fluidized fixed bed condition obtains over only a part of the range of flow rates.

A number of factors determine the useful range of flow rates: (1) The diameter of the tube should be 2 inches or greater. At smaller diameters wall effects become sufficiently prominent to interfere with smooth operation. (2) The density of the powder is related to the air rate necessary to fluidize it; the greater the density, the greater the air rate needed. Most of our experience has been with powders having apparent bulk densities from 0.4 to 1.0 gram per cc. (3) For a given bulk density as the particle size of the powder increases, the air rate needed to fluidize the powder increases. A particle size range of 40 to 100 mesh was selected. With the above densities and sizes, the fluidized fixed bed air rate range was about 0.5 to 1.5 feet per second superficial linear velocity (the linear velocity that would obtain in the absence of the powder). (4) The shape of the particles of powder have an effect. Plate-shaped particles behave differently from rounded or spherelike particles.

The flow conditions necessary to obtain a desired operation were such that it was necessary to construct a full-scale glass model to determine the conditions for satisfactory operation and the limits of the desired type of operation. Based on data obtained with the glass model using air, metal units were constructed. The details of construction are given in Figure 1. Es-

THE PASSAGE of gases or vapors upward (counter to gravity) at controlled rates through a mass of powdered solid produces the "fluidized fixed bed". The passage of the gas or vapor causes the powdered solid to become mobile so that it moves about, resembling an agitated liquid. The particle size of the powder is regulated so that little of it is carried out of the reaction zone with the gas or vapor. The fluidized fixed bed is particularly adapted to catalytic reactions in which a reaction occurs that is accompanied by a large heat of reaction. The movement of the powdered solid tends to prevent the formation of localized high-temperature zones (called "hot spots"). Some examples are given which illustrate the application of the fluidized fixed bed to the catalytic cracking of gas oil and a hydrogen transfer treatment of an unsaturated gasoline.

sentially the unit is a piece of 2-inch standard pipe, 27 inches long. Attached to the lower end is a 20° (total angle) cone, 6 inches long. A small piece of 100-mesh screen is placed in the bottom of the cone to retain the powdered catalyst. Provisions for introducing reactants are made at the bottom of the cone. At the top a 100-mesh screen is used to retain catalyst, and provisions are made for removing reactants. A thermocouple well ($^1/_4$-inch, 18–8 chrome-nickel tubing) is inserted at the top. Junctions are located just above the screen in the cone at the bottom and every 7.5 inches upward to the top of the vessel (a total of five thermocouples). Connections for the thermocouples are indicated at the top of Figure 1.

The entire assembly is mounted in a thermostated metal block (*2*). With this arrangement no separate preheater has been necessary in our work; apparently the circulation of hot catalyst has served as a preheater.

Many successful tests have been made with the unit as described. An improvement in the degree of contact between solid and vapor was obtained by inserting baffles or distributor plates. These were plates $^1/_8$ inch thick, drilled with $^1/_8$-inch holes. Their diameter was such that they fitted snugly in the tube. They were spaced every 2 inches in the reactor. Apparently the $^1/_8$-inch holes in the baffles break up any large "bubbles" of vapor and any channels that form along the wall just as they would if the catalyst were a liquid. At the same time the $^1/_8$-inch holes are large enough to permit flow of catalyst.

Table I. Temperature Distribution during Regeneration with Air

Catalyst Level, In.	Temperature, ° F. 20 min.	40 min.	80 min.	120 min.
Bottom	1035	1054	978	923
7.5	1044	1065	1011	949
15	1000	1012	1045	975
22.5	975	981	1029	973
30[a]	892	890	898	892

[a] Above catalyst level.

Table II. Catalytic Cracking and Hydrogen Transfer in Fluidized Fixed Bed with 40–100 Mesh Silica-Alumina Catalyst

Catalyst vol., cc.	950	950	1020
Catalyst wt., grams	593	593	593
Charging stock type	Mid-continent gas oil		Gasoline[a]
Process period, hr.	0.5	1.0	1.0
Total time on test, hr.	96	16	36
Wt. oil/hr./wt. catalyst	0.51	1.00	0.52
Pressure, lb./sq.in. abs.	14.7	14.7	14.7
Block temp., ° F.	850	950	900
Regeneration period, hr.	2.17	2.67	2.67
Yields in vol. % charge			
Gasoline	46.1	45.1	67.5
Naphtha	3.2		14.1
Gas oil	14.6	21.6	
Liquid loss	36.1	33.3	18.4
Yields in wt. % charge			
Gasoline	37.8	38.4	65.3
Naphtha	3.2		16.8
Gas oil	16.0	23.3	
Gas	28.7	28.5	12.6
Carbon	14.3	9.8	5.3
Hydrogen	0.12	0.29	0.15
C_2H_4	0.63	1.05	0.70
C_3H_6	2.40	4.91	2.41
$C_1 + C_2 + C_3$ paraffins	8.74	9.09	4.31
Iso-C_4H_8	0.39	1.09	5.26
n-C_4H_8	0.95	1.92	0.50
Iso-C_4H_{10}	14.27	8.64	3.57
n-C_4H_{10}	1.23	1.45	0.68
Gasoline gravity, ° A.P.I.	66.5	58.9	60.9
Octane No., F-2	....	82.4	.....
Bromine No.	11	23	11
Analysis, %			
Olefins	6	14	6
Aromatics	32	33	32
Paraffins and naphthenes	62	53	62

[a] Bromine No. 51.

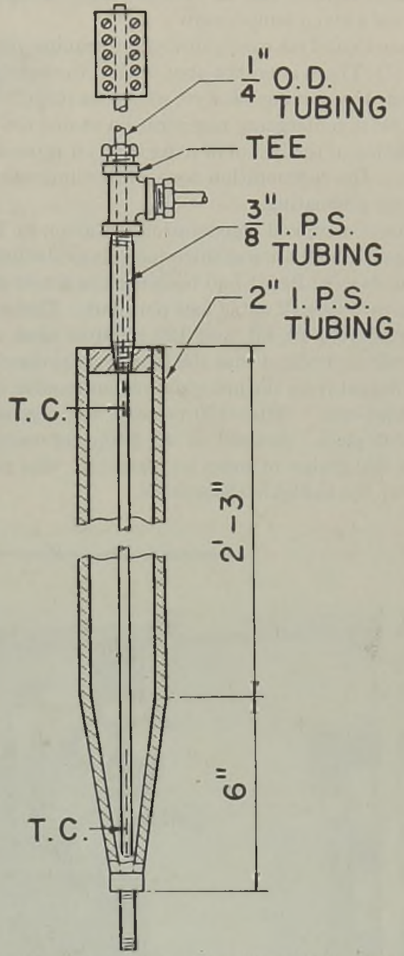

Figure 1. Fixed Fluidized Bed Unit

REGENERATION

Catalytic solids that have been contacted with hydrocarbons usually become contaminated with a carbonaceous deposit. It is customary to remove these desposits by oxidation with air or flue gas that contains oxygen. When a regeneration is carried out with air in the fluidized fixed bed, there is a rather uniform temperature rise throughout the catalyst zone. Burning seems to occur throughout the catalyst, and the motion of the catalyst seems to quench any hot spots that may form momentarily. This action is in distinct contrast to regenerations of true fixed beds of catalyst. The passage of air through a nonfluidized fixed bed of carbonized catalyst causes the formation of a relatively small high-temperature burning zone which is described aptly as a hot spot. This hot spot moves through the catalyst bed in the direction of air flow.

There are at least three undesirable characteristics of the nonfluidized fixed bed regeneration: (1) Careful control must be maintained to prevent the temperature of the hot spot from rising too high and damaging the catalyst. (2) Catalyst in the regeneration zone but outside the hot spot is idle—i.e., serving no useful purpose. (3) The gas for combustion must be preheated to some critical temperature to maintain combustion within the hot spot. This reduces the amount of heat that is removed by outgoing gas of a given temperature.

The fluidized catalyst overcomes the foregoing disadvantages as follows: (1) There is no hot spot within the catalyst. If one tends to form, the moving catalyst quenches it. (2) Essentially all the catalyst is undergoing regeneration at one time. (3) The lower hot portion of the bed of moving catalyst is used to heat the air as it enters the regeneration zone; this eliminates the necessity for outside preheating.

The results of a typical regeneration are given in Table I. In this regeneration, cold air was introduced into the bottom of the reactor immediately after it had been used in a test cracking gas oil. The air rate was 12 cubic feet per hour. Temperature surveys were made 20, 40, 80, and 120 minutes after the air was started. It will be noticed that the temperature distribution was distinctly different from the hot spots encountered in the regeneration of a fixed bed. After 120 minutes the regeneration was essentially complete. A total of 40 grams of carbon was removed from 600 grams of cracking catalyst; this regeneration was made with the baffles in the reactor.

RESULTS

Much of our experience with the fluidized fixed bed has been in catalytic cracking and hydrogen transfer. In these tests the unit has been used without any preheater. The cold oil is pumped directly into the bottom of the unit and is preheated by hot catalyst. This causes the temperature in the cone to be considerably lower than the rest of the catalyst in the unit. This practice has advantages and disadvantages. For our purpose the advantages outweighed the disadvantages.

A few of the results obtained with the unit are summarized in Table II. Two cracking runs are given, one at 850° and the other at 950° F.; both were made with baffles in the reactor. In addition, a hydrogen transfer run on a gasoline obtained by catalytic cracking is given; it was made without baffles in the reactor. These results are not given with the intention of comparing this method of contacting a solid with a vapor or gas with any other methods of contacting, but rather to demonstrate that useful results can be obtained by this method.

The fluidized fixed bed has certain desirable features that may be summarized as follows: (1) The catalyst (or solid) may be used in the form of a powder. (2) Localized thermal effects in the catalyst bed are eliminated by the moving catalyst. (3) The catalyst may be used and regenerated in the same vessel. (4) In most cases no separate preheater is necessary.

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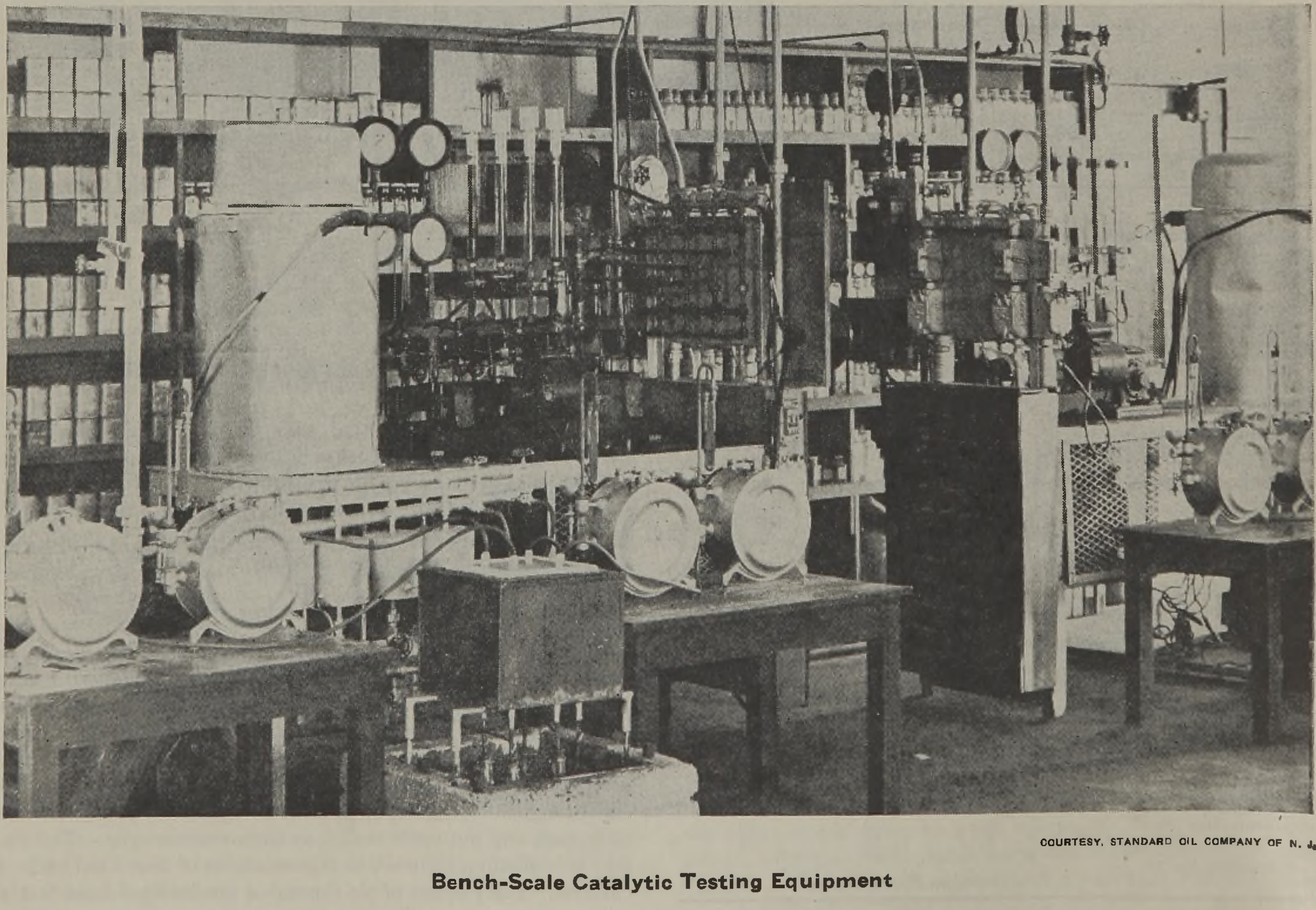

COURTESY, STANDARD OIL COMPANY OF N. J.

Bench-Scale Catalytic Testing Equipment

THE NORMAL OLEFINS can be catalytically isomerized to branched-chain olefins which frequently have more desirable properties, particularly for use as motor fuel. The skeletal isomerization of 1-hexene is investigated using several catalysts in the temperature range 285–500° C. and at space velocities of 0.1 to 1.9 reciprocal hours. The products obtained are chiefly methylpentenes with lesser amounts of dimethylbutenes and small amounts of higher- and lower-boiling hydrocarbons. The experimental results indicate that the catalysts must be acidic or have adsorbed hydrogen ions which are essential to the reaction. The isomerization appears to be stepwise: 1-hexene ⟶ methylpentenes ⟶ dimethylbutenes.

CATALYTIC ISOMERIZATION OF 1-HEXENE

THE normal 1-olefins, available from thermal cracking operations, can be catalytically isomerized to yield olefins having more desirable physical or chemical properties or more satisfactory characteristics as a motor fuel. As is generally known, olefin isomerization may be used to supply high-octane motor fuel for which the lower-boiling olefins are especially useful, or to supply branched-chain hydrocarbons for subsequent hydrogenation to yield high-octane paraffins for aviation gasoline. Further, as the demand for chemical derivatives from petroleum increases, it is possible that a certain structural arrangement of carbon atoms in a molecule may be desired and that olefin isomerization will provide a means for preparing needed raw material.

The products from the skeletal isomerization of the butenes and pentenes in the presence of various catalysts have been investigated, but little quantitative work on the skeletal isomerization of the higher olefins has been reported. The purpose of this investigation was to study the extent of isomerization of 1-hexene and the activity of several catalysts over the temperature range 285° to 500° C.

The catalytic skeletal isomerization of normal hexenes to the branched isomers has been reported using the following catalysts: alumina (*1*, *2*), zinc chloride on pumice (*4*), phosphoric acid on pumice (*5*), and thoria (*1*). The reported results of these experiments showed that no careful quantitative analyses of the products were made. In most instances only two or three of the possible isomers were reported to have been formed. No double-branched hexenes were reported.

ISOMERIZATION PROCEDURE

The isomerization system (Figure 1) consisted of an electrically heated Pyrex-lined furnace and preheater, a buret connected with a constant-pressure device, and a receiver equipped with a dry ice–acetone condenser to prevent loss of cracked products. The preheater section was packed with Pyrex chips, and the temperature of the preheater and of the reactor was measured by chromel-alumel thermocouples. The temperature was controlled manually by Variacs regulating the current to the preheater and to the furnace.

The 1-hexene was prepared by dehydrating technical *n*-hexanol over alumina at 400° C. The alumina was originally alkaline and was discarded after a throughput of 4 volumes of hexanol per volume of catalyst. This precaution was intended to avoid isomerization of the hexene as a result of an accumulation of acidic material on the catalyst surface. The hexene produced was largely 1-hexene and was purified by repeated fractionation. The final fractionation was made in a fifty-theoretical-plate column packed with a 4-foot section of $^3/_{32}$-inch stainless steel helices. The fraction boiling at 63.5 ± 0.1° C. at 760 mm. mercury and having a refractive index of 1.3876–1.3879 was used in these experiments. After the 1-hexene was hydrogenated the boiling point, refractive index, and density showed that the product was *n*-hexane with no detectable amount of branched isomers.

CATALYSTS

The catalysts used were phosphoric-acid-impregnated kieselguhr (U.O.P. catalyst) supplied by Universal Oil Products Company; activated alumina pellets, supplied by The Harshaw Chemical Company; Doucil [sodium permutite, $Na_2O.Al_2O_3.(SiO_2)_5$ + 50% excess water], supplied by American Doucil Company; 40–60 mesh Georgia clay, as used in the Gray tower clay-treating process; Houdry catalyst of 45 activity index (a synthetic aluminum hydrosilicate) supplied by the Houdry Corporation; Superfiltrol, supplied by Filtrol Corporation; anhydrous aluminum sulfate, prepared by dehydrating analytical-grade hydrated aluminum sulfate; superphosphate, prepared by pelleting commercial superphosphate fertilizer; silica gel, supplied by The Davison Chemical Corporation; activated carbon, supplied by Union Carbide & Carbon Company; sodium Zeocarb (a sulfonated coal), supplied by Permutit Company; and aluminum fluoride, supplied by Aluminum Ore Company.

Several of the inactive catalysts were treated with a dilute aqueous acid in an attempt to make them active. In this operation the material was kept covered with fresh 1 *N* hydrochloric acid while the solution was allowed to drain slowly from the bottom. The effluent solution was tested for hydrogen and other ions, and when the H^+ concentration reached the same value as that of the fresh acid, the catalyst was drained and oven-dried at 130° C. Relative values of the catalyst acidity before and after this treatment were obtained by titrating hot alcoholic and aqueous liquids containing weighed amounts of catalyst. Although the values were not absolute, they served to indicate whether hydrogen ions were adsorbed and held after drying at 130° C. or after use as a catalyst at higher temperatures.

Fresh catalyst was used for all runs. No attempt was made to determine catalyst life. Prior to the run the catalyst was heated overnight in a nitrogen stream at the reaction temperature. A weighed amount of 1-hexene was charged to the feed buret. The hexene was allowed to flow at a constant rate to the reactor. When all hexene

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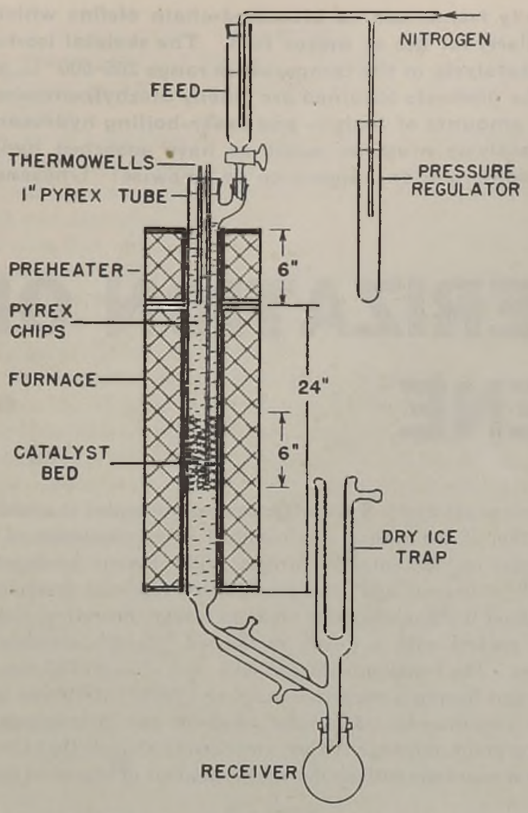

Figure 1. Isomerization System

had entered the reactor, the time was recorded and nitrogen was passed through the furnace for an additional 10 minutes so that all hydrocarbon vapors were swept out of the catalyst bed. The product, collected in a dry ice–acetone trap, was weighed and the percentage loss recorded. This loss included "carbon" or hydrocarbons deposited on the catalyst as well as mechanical losses. No significant amount of noncondensable gas passed the dry ice–acetone trap.

ANALYSES

The product consisted of isomeric hexenes and of hydrocarbons of higher and lower molecular weight. The hexenes and lower-boiling material were separated from the residue by distillation from a Claisen flask, equipped with a Vigreux column, to a vapor temperature of 83° C., which is 10° above the highest boiling hexene isomer. The distillate contained a small amount of higher boiling material while the residue was free of hexenes. The residue was weighed, and this value recorded as the amount of polymer formed in the reaction.

The small amount of residue obtained could not be accurately analyzed. It boiled over a wide range, chiefly above 100° C. up to a temperature greater than 300° C. The 50% boiling point was of the order of 150–175° C. The bromine number indicated 85 to 100% olefins, depending on the molecular weight estimated for the mixture. The residue probably consisted chiefly of polymer formed from hexene and the lower boiling hydrocarbons produced by cracking hexene.

With the equipment available, analysis of the hexenes was impractical because of the large number of isomers boiling in a narrow temperature range. It was found possible, however, to determine the amount of skeletal isomerization by hydrogenating the olefins and separating the isomeric paraffins by a precise fractionation. Hence, the product, freed from polymer, was hydrogenated over reduced nickel on alumina at 150° C. The conditions of hydrogenation were too mild to permit chain branching. The hydrogenation of *n*-hexene yielded only *n*-hexane, as shown by fractionation in the Stedman column, followed by density and refractive index determinations for the distillate.

The hydrogenated product was tested for the presence of olefins and, if completely hydrogenated, was transferred to a fractionating column packed with a 3-foot section of $^3/_8$-inch Stedman packing. The paraffin mixture was distilled slowly, about 60 hours being required to distill a 100-cc. charge. During the distillation the reflux ratio was maintained at about 50 to 1 when pure components were being taken off and at about 100 to 1 when mixtures were being recovered in the distillate. Fractions amounting to 1% of the charge were taken, and the refractive index was obtained for each of these.

The refractive indices of the close-boiling hexane isomers differ sufficiently so that the analysis can be checked by measuring this property. Further, alternately higher boiling isomers have lower refractive indices than the preceding isomers so that, when the refractive index of a fraction has the value of a pure isomer, it may be considered to be free of any significant amount of other isomers. A distillation curve and the refractive indices of the fractions are plotted in Figure 2.

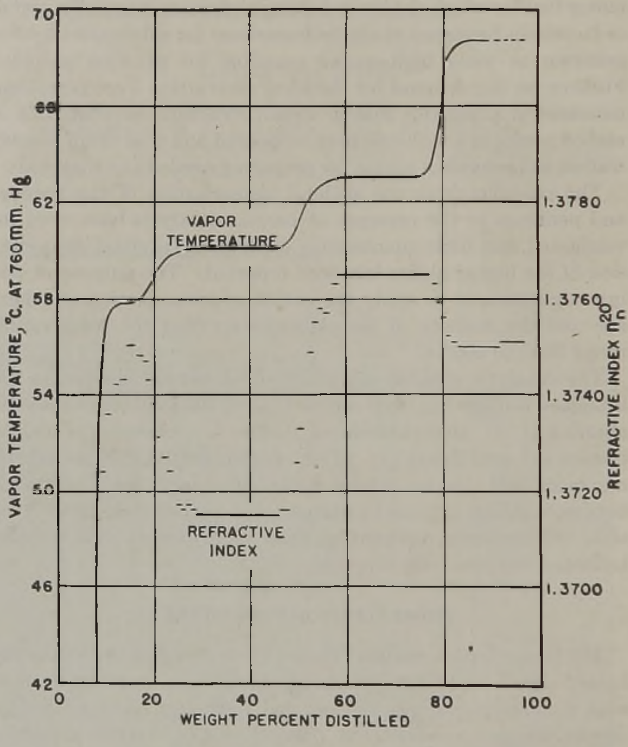

Figure 2. Distillation Curve with Refractive Indices of Fractions

The results from the fractionation were used to calculate the amount of hydrocarbons of molecular weight less than the hexenes, the amounts of straight- and branched-chain hexene isomers formed, and the relative amounts of the various skeletal isomers. No attempt was made to locate the positions of the double bond in either the normal or the branched isomers.

COMPARISON OF CATALYSTS

Eight catalysts were tested, and twenty runs in which skeletal isomerization occurred were made under various operating conditions. All catalysts were tested at 335–340° C. and a space velocity of 0.6 hour^{-1} (volumes of liquid hexene charged per gross volume of catalyst per hour), and the results of these runs are shown in Table I and Figure 3. The catalysts are compared on the basis of data obtained under these conditions, but it is not claimed that these are the optimum olefin isomerization conditions for any of the catalysts or equally near optimum conditions for all of the catalysts. The catalysts may be rated by analyzing the products from the point of view of the extent of skeletal isomerization—i.e., the amount of branched hexenes in the product as compared with the amount of unbranched hexenes. The catalysts listed in order of decreasing activity are: U.O.P., Superfiltrol, acid-treated Doucil, acid-treated alumina, clay, Houdry, anhydrous aluminum sulfate, and superphosphate. The U.O.P., Superfiltrol, and acid-treated Doucil catalysts were about equally active for olefin isomerization; alumina, clay, and the Houdry catalysts were somewhat less active. The aluminum sulfate showed relatively little activity and superphosphate virtually none. In addition to these catalysts, the untreated Doucil, activated alumina, silica gel, activated carbon, and sodium Zeocarb, as well as acid-treated silica gel, activated carbon, and sodium Zeocarb were tested and found to be inactive for skeletal isomerization under these conditions.

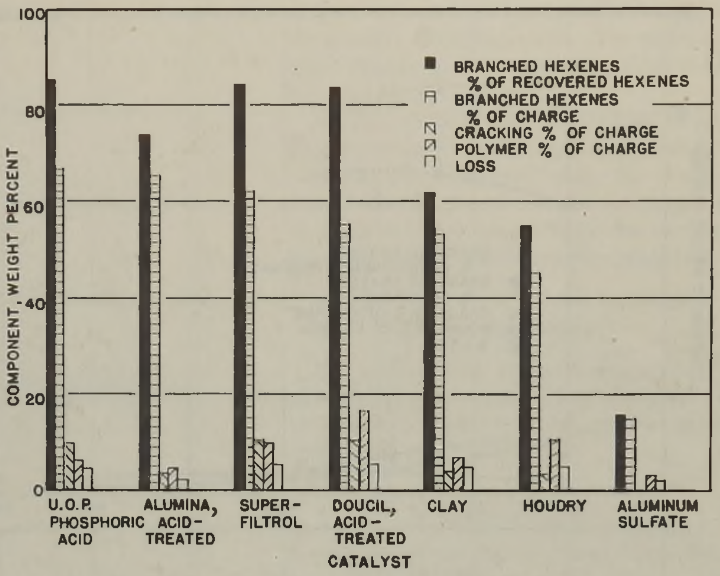

Figure 3. Comparison of the Various Catalysts Tested

Considering the yield of branched hexenes against the products of side reactions such as cracking, polymerization, and catalyst deposit, acid-treated alumina was the most efficient of the isomerization catalysts tested. Only 10% of the charge was consumed in side reactions as compared with 21, 26, and 35% for U.O.P., Superfiltrol, and Doucil catalysts, respectively.

EFFECT OF TEMPERATURE

Superfiltrol and U.O.P. catalysts were used in a series of runs in which 1-hexene was isomerized at temperatures varying from 285° to about 500° C. The results of these runs are given in Table I and shown graphically in Figure 4. All of these runs were made at a constant space velocity of 0.6 hour^{-1}, so that equilibrium was probably more nearly approached as the temperature was increased. The amount of chain branching decreases with increasing temperature over the range 335° to 500° C.

Table 1. Results of Runs with Different Catalysts

Catalyst	Temp., ° C.	Space Velocity, Hour^{-1}	Component as Per Cent of Charge: Branched hexenes	Loss	Cracking	Polymer	*n*-Hexenes	2,3-Dimethylbutenes	2-Methylpentenes	3-Methylpentenes	Branched Hexenes, % of Recovered Hexenes
U.O.P.	285	0.1	26.4	6.0	22.4	43.1	2.1	4.9	12.1	9.4	92.5
	283	0.6	61.5	3.0	8.9	11.3	15.3	9.9	26.8	24.7	80.1
	335	0.6	64.4	5.1	10.0	7.3	13.2	8.8	31.0	24.6	83.0
	335	0.6	67.0	4.8	10.1	6.6	11.5	10.3	29.0	27.8	85.4
	340	1.86	61.7	2.6	3.7	3.8	28.2	8.3	28.0	25.3	68.6
	381	0.6	67.2	4.6	5.6	4.1	18.4	10.2	29.7	27.4	78.5
	491	0.6	20.4	3.6	0.7	1.3	74.0	1.2	9.4	9.8	21.6
Superfiltrol	285	0.6	59.4	5.5	4.3	9.6	21.2	5.3	28.9	25.2	73.7
	285	0.1	46.9	15.8	12.0	19.0	6.3	7.3	23.0	16.6	88.1
	340	0.6	62.4	5.8	10.4	10.0	11.4	9.7	27.3	25.5	84.6
	433	0.6	56.3	8.9	13.0	10.0	11.8	7.1	27.9	21.3	82.6
	498	0.6	39.3	16.9	21.5	9.7	12.6	4.6	17.4	17.3	75.8
Georgia clay	335	0.35	59.2	5.2	3.2	8.7	23.7	6.1	29.5	23.6	71.4
	335	0.60	53.0	5.0	3.1	7.2	32.3	4.9	26.5	21.0	61.9
	335	1.90	38.1	2.5	2.0	5.0	52.9	2.0	18.6	18.0	42.2
Alumina, acid-treated	338	0.6	65.4	2.4	3.5	4.5	24.2	9.0	28.4	28.0	73.0
Doucil, acid-treated	338	0.6	56.1	5.8	10.6	16.8	10.8	8.4	25.2	22.4	83.9
Houdry	335	0.6	44.8	4.9	3.5	10.9	35.9	3.5	21.3	20.0	55.5
$Al_2(SO_4)_3$	335	0.6	15.3	2.2	0.0	3.3	79.2	0.2	8.4	6.7	16.2

At 335° C. the U.O.P. and Superfiltrol catalysts cause roughly equal amounts of isomerization, cracking, and polymerization. As the temperature is increased above 335° C., the amount of isomerization effected by the U.O.P. catalyst falls off more rapidly than that by the Superfiltrol catalyst. However, since in the former instance the amounts of cracking and polymerization decrease, while in the latter case there is an increase in the extent of these reactions, apparently there is a decreasing activity of the U.O.P. catalyst as the temperature increases. This decreasing activity probably results from loss by vaporization of phosphorus compounds or excessive dehydration of the catalyst.

Below 335° C. the amount of chain branching decreases with decreasing temperature, but this is probably due to a decrease in the reaction rate at the lower temperatures. This was confirmed by decreasing the space velocity from 0.6 to 0.1 hour^{-1} in runs in which 1-hexene was isomerized over the U.O.P. and Superfiltrol catalysts at 285° C. A larger fraction of the recovered hexenes is branched, the lower the temperature if equilibrium conditions are allowed to be more nearly approached. However, at the lower temperatures the reaction rate becomes the controlling factor. The optimum temperature at a space velocity of 0.6 hour^{-1}, both from the standpoint of extent of isomerization and of total yield of branched hexenes based on the charge, is about

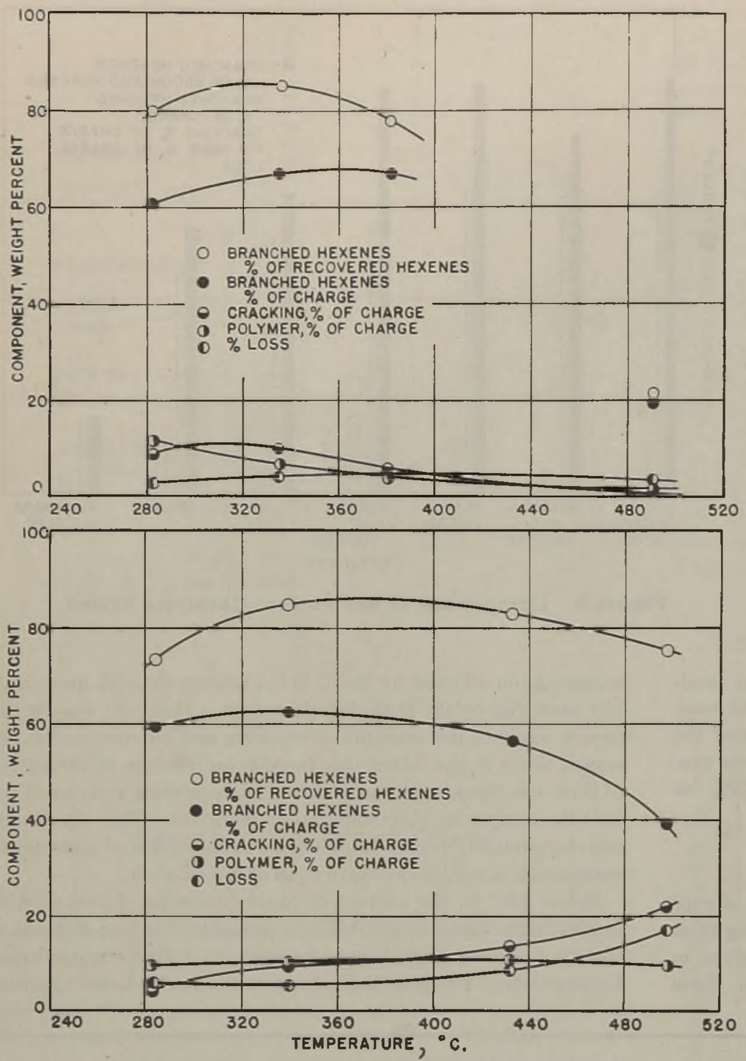

Figure 4. Effect of Temperature with U.O.P. (*above*) and Superfiltrol (*below*) Catalysts

335° C. Above this temperature the side reactions become more important and the amount of skeletal isomerization decreases. Below this temperature the rates of all reactions decrease, and the yield of branched hexenes decreases rapidly with decreasing temperature.

EFFECT OF SPACE VELOCITY

At 335° C. the U.O.P. catalyst and Georgia clay were evaluated at various space velocities. The results are given in Table I and shown graphically in Figure 5. As is to be expected, the amounts of all reactions decrease with increasing space velocity.

These experiments indicate that the lower space velocities favor a higher percentage conversion to branched hexenes. However, on the basis of the space-time yield, the optimum space velocity appears to be greater than 0.6 hour^{-1}. Very low space velocities tend to favor the side reactions more than the isomerization. Using the U.O.P. catalyst at 285° C. and at a space velocity of 0.1 hour^{-1} the amount of isomerization obtained was nearly equaled by the cracking and considerably exceeded by the amount of polymerization.

MECHANISM OF SKELETAL ISOMERIZATION

Considering 100 moles of the hexene charged, if the moles of each skeletal isomer per mole of hexene reacting to form branched hexenes are plotted against the total moles of branched hexenes formed, a Frolich-type plot (*6*) results (Figure 6). If the yields of 2,3-dimethylbutenes and 2- and 3-methylpentenes obtained with the various catalysts at 335–340° C. are plotted in this way and extrapolated to zero mole of branched-chain product, it is indicated that initially there were formed about 55% 2-methylpentenes, 45% 3-methylpentenes, and no 2,3-dimethylbutenes. This conclusion is based on analytical data which are less accurate than are desirable, and the points most affecting the extrapolated portion of the curve are the least accurate. Further, it is assumed that no catalyst has any selective action for the formation of any particular isomer. With the above reservations the results indicate that the isomerization probably occurs by a step-wise mechanism. The primary step appears to be the formation of the single-branched isomers, and these, in turn, may isomerize to double-branched isomers. For the higher olefins this process conceivably could continue forming the multibranched isomers.

Although neohexane has not been identified in any of the hydrogenated products, its absence may be explained since it has been reported (*3*, *7*, *8*) that the olefin corresponding to this isomer readily isomerizes under these conditions to an equilibrium mixture containing about 3% 3,3-dimethyl-1-butene and about 97% 2,3-dimethylbutenes. On the basis of these data, since the maximum yield of double-branched hexenes is less than 15%, the greatest amount of 2,2-dimethylbutane in the hydrogenated products should be of the order of magnitude of 0.5%. Since only 100-cc. portions were distilled in the Stedman column, this amount of any isomer could not be detected.

All of the catalysts found to be active were either acidic as originally prepared or capable of being made acidic by treatment with an acid. It is concluded that one of the requirements of an olefin skeletal isomerization catalyst is the ability to supply hydrogen ions. Supporting evidence is obtained from an investigation of the effect of acid treating various materials. Activated alumina and Doucil, both originally alkaline, were not effective as olefin skeletal isomerization catalysts but, after treatment with dilute acid, became quite active. The treated alumina was acidic and retained its acidic nature after use as a skeletal isomerization catalyst at 335° C. The acidity of each catalyst, both before and after treating, was determined by shaking in alcoholic and aqueous solutions and titrating with potassium hydroxide solutions. In contrast to the alumina, the silica gel and carbon catalysts, which were not active olefin skeletal isomerization catalysts, could not be activated by acid treating, and it was found that these materials did not selectively adsorb hydrogen ions which were retained after drying.

On the basis of these observations it may be suggested that olefin isomerization proceeds by adsorption involving interaction between the catalyst and the carbon atoms of the double bond, part of which interaction involves a hydrogen atom or ion supplied by the catalyst. Following the adsorption, a break occurs between two carbons in the chain followed by a recombination in a different structural arrangement. During this interval both fragments probably remain bound to the catalyst surface. Since more than one primary product is formed, either the carbon-carbon scission occurs at different positions relative to the double bond, or double bond isomerization may occur prior to scission.

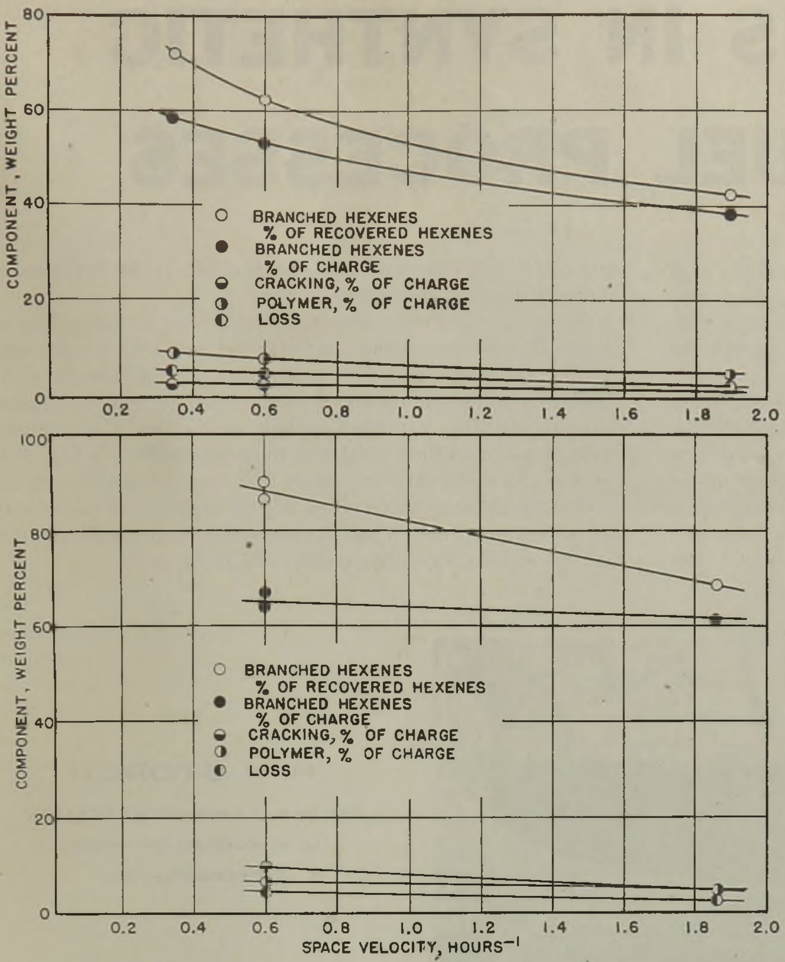

Figure 5. Effect of Space Velocity with Georgia Clay (*above*) and Superfiltrol (*below*) Catalysts

Under suitable conditions recombination of fragments chiefly results in isomerization, but under less favorable conditions the desorbed molecules may contain more or fewer atoms than the original; e.g., with the acid-treated alumina skeletal isomerization is the chief reaction, and the total of all side reactions is considerably less than with any of the other active catalysts. Also, the desorbed molecules may have been saturated by removing hydrogen from other molecules or from the catalyst surfaces; e.g., Superfiltrol causes the olefin to be saturated with the formation of a considerable amount of paraffinic hydrocarbon.

SUMMARY

1. The chain-branching isomerization of 1-hexene, using several catalysts under comparable conditions of 0.6 hour^{-1} space velocity, 335° C., and 6 to 1 ratio of catalyst bed height to diameter, was studied; the amounts of cracking, isomerization, polymerization, and loss for each of these were observed.
2. The catalysts tested may be listed in order of their relative effectiveness (per cent of charge converted to branched hexenes) as: U.O.P., acid-treated alumina, Superfiltrol, acid-treated Doucil, clay, Houdry, aluminum sulfate, and superphosphate.
3. The reaction rates increased with temperature while the extent of isomerization decreased with increasing temperature. The optimum isomerization temperature at 0.6 hour^{-1} space velocity was found to be about 335° C.
4. The extent of all reactions varied inversely as the space velocity, but at space velocities as low as 0.1 hour^{-1} the amounts of the side reactions considerably exceeded the amount of isomerization. The optimum space velocity at 335° C. was indicated to be less than 0.6 hour^{-1}.
5. The necessity for the presence of hydrogen ions on the catalyst was indicated.
6. It was suggested that the single-branched isomers were the primary products of skeletal isomerization while the double-branched isomers were secondary products.

ACKNOWLEDGMENT

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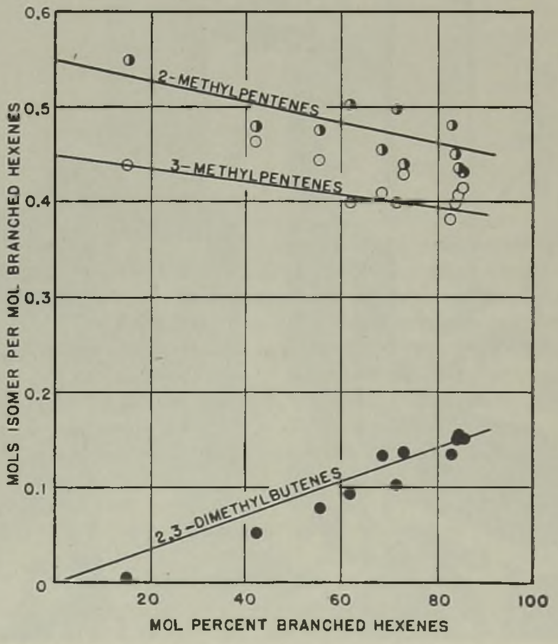

Figure 6. Frolich-Type Plot

CATALYSIS IN SYNTHETIC LIQUID-FUEL PROCESSES

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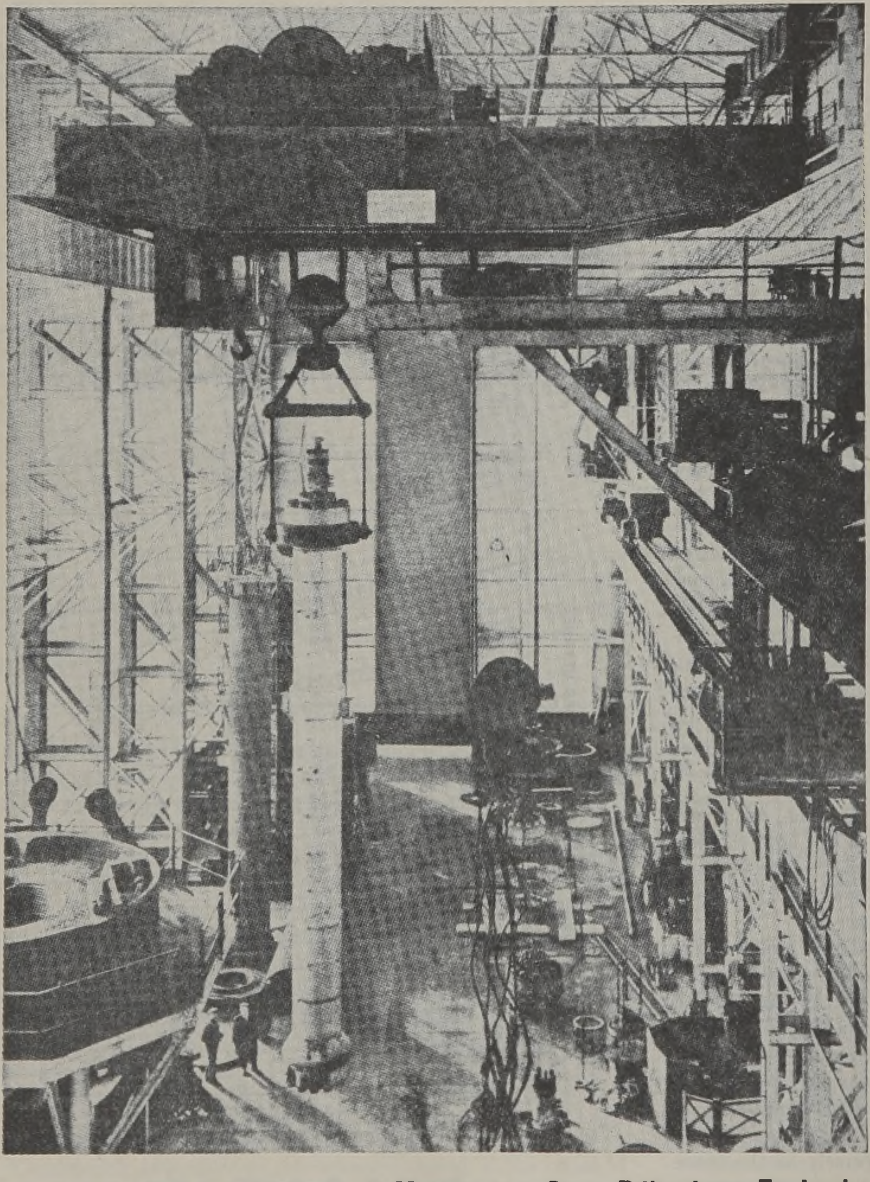
THE CATALYTIC phenomena of three synthetic liquid fuel processes are discussed. These are the synthesis of liquid hydrocarbons from a mixture of hydrogen and carbon monoxide, commonly entitled the Fischer-Tropsch process; the hydrogenolysis of carbonaceous materials such as coal and coal tar, usually termed the Bergius-I. G. process; and the catalytic cracking or re-forming of fractions from petroleum or from middle oils obtained by way of the hydrogenation of coal and coal tar. The catalytic reactions of the last two processes involve rupture of carbon to carbon, carbon to oxygen, carbon to nitrogen, and carbon to sulfur bonds.

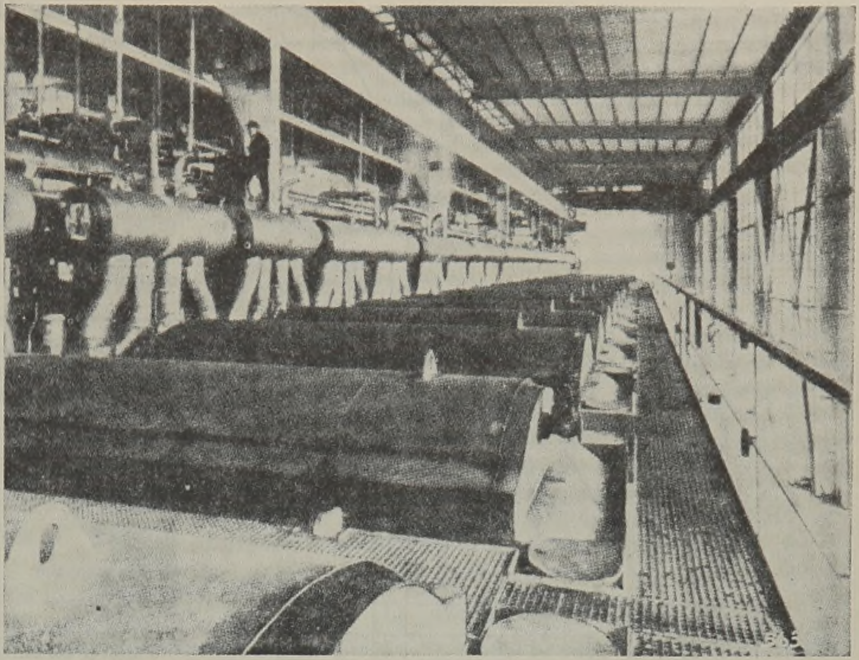
THE main components of the Fischer-Tropsch catalysts that are active in the synthesis of normally liquid hydrocarbons from hydrogen and carbon monoxide—namely, iron, cobalt, nickel, and ruthenium—form relatively unstable carbides of nonionic crystal structures upon exposure to carbon monoxide in the temperature range of the synthesis (*26*). These carbides react with hydrogen below about 350° C. whereby the carbide is quantitatively converted to methane plus a few per cent of ethane (*2–4*). Above 350° C. there is extensive decomposition of the carbides to carbon. It probably is significant that the optimum temperature ranges in this synthesis—185° to 215° C. for cobalt and 240° to 320° C. for iron catalysts—are below 350° C. Reaction of the carbides with dilute acids results in the formation of normally liquid hydrocarbons (*2, 22*).

The reaction between carbon monoxide and cobalt or iron or their oxides to form carbides is much too slow (*9, 10*) to account for the rate of synthesis of hydrocarbons when a mixture of hydrogen and carbon monoxide is used. In some fashion the presence of hydrogen catalyzes carbide production. Wagenheim (*51*), who studied the catalysis of the reaction $2CO \rightarrow CO_2 + C$ by iron at 350° to 500° C., found that the formation of carbon was markedly accelerated when a little hydrogen is mixed with the carbon monoxide. There is some evidence that carbon formation proceeds by way of the metal carbide (*14, 16, 29*).



Coal Hydrogenation Converter in Maintenance Shop, Billingham, England

It is conceivable that hydrogen acts as catalyst for metal carbide formation by forming an unstable metal hydride. This may result in sufficient distortion of the metal lattice so that, upon removal of the hydride hydrogen (by decomposition or by reaction with neighboring metal carbide or adsorbed carbon monoxide), penetration of the lattice by carbon monoxide is accelerated. At first consideration this mechanism appears to conflict with the fact, discovered by Craxford (*9*, *10*) that the transformation from para- to ortho-hydrogen proceeds to the extent of only about 5% when active synthesis of hydrocarbons other than methane occurs. When methane is the main product during the early stages of use of a freshly prepared catalyst, this transformation is virtually complete. However, the amount of hydride necessary to catalyze carbide formation effectively may be less than that needed for the conversion of 5% para- to ortho-hydrogen.



Top View of Fischer-Tropsch Converters

Craxford (*9*, *10*) states that the only alternate to the reaction

$$2Co + 2CO \rightarrow Co_2C + CO_2 \quad (1)$$

is

$$2Co + CO + H_2 \rightarrow Co_2C + H_2O \quad (2)$$

Since reaction 1 is too slow to account for the rate of hydrocarbon formation, reaction 2 is the main source of carbide. The mechanism suggested in the preceding paragraph is consistent with the fact that water is the main oxygenated product of the Fischer-Tropsch synthesis on cobalt catalysts. Reaction 2 is essentially a restatement of this fact and provides no information concerning the mechanism of the reaction.

Craxford's mechanism of carbide formation is difficult to apply to iron catalysts where the main oxygenated product is carbon dioxide rather than water, as on the cobalt catalysts. As cobalt is a much more active catalyst than iron for the water-gas shift reaction,

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

and because the most active iron catalysts catalyze this reaction to only a slight degree at temperatures below 300° C., it is probable that water and carbon dioxide are primary products on cobalt and iron catalysts, respectively. There is additional evidence that, although metal carbides are formed on both cobalt and iron, the mechanism of the synthesis on cobalt catalysts differs from that on iron catalysts. The ratio of the partial pressures of methane to ethane plus ethylene in the off-gases from the synthesis differs markedly for different catalysts, as shown in Table I. This ratio for cobalt is almost twenty times larger than that for iron-copper. This fact should be correlated with the discovery that, on cobalt catalysts, ethylene when mixed with synthesis gas participates in the synthesis to form normally liquid hydrocarbons, whereas on an iron-copper catalyst the added ethylene appears largely as ethane (*9*, *10*, *42*).

Fischer and co-workers (*21*, *33*, *48*, *49*) made an extensive examination of the products of the synthesis on an iron-copper and on a cobalt-thoria-kieselguhr catalyst. The product was largely olefins and saturated paraffins, but about 0.1% benzene, 0.4% toluene, and very small amounts of a solid aromatic oxygenated material identified as γ-pyrone were also found. Naphthenes and diolefins were not detected. Several per cent of branched-chain paraffins—3-methyloctane and 3,3-dimethylpentene—were found.

Koch and Hilberath (*33*) made a detailed analysis of the hydrocarbons boiling below 100° C., obtained by synthesis on a cobalt catalyst. Appreciable percentages of isoparaffins were found, including tertiary carbon but no quaternary carbon compounds. The production of tertiary hydrocarbons is particularly difficult to explain on the basis of Craxford's hypothesis (*9*, *10*) that during the synthesis molecular hydrogen and not atomic hydrogen is the reacting form of hydrogen.

Recent patents (*36*, *37*) disclose the use of iron catalysts "sintered" by reduction with hydrogen at 650–850° C. The hydrocarbons produced on these catalysts are reported to be largely branched-chain paraffins, whereas those formed on iron catalysts reduced at temperatures not greater than about 400° C. contain only a few per cent of isoparaffins. The sintered iron catalysts probably contain little if any iron oxide, whereas those reduced at lower temperatures contain some ferrous oxide. How far the reduction of ferrous oxide proceeds during the exposure of the latter catalysts to synthesis gas is not known, but it is apparent that a critical spacing of the metal atoms in the iron carbide lattice is essential for the production of isoparaffins. No data are available on the variation in the character of the products on cobalt catalysts with different conditions of preparation and reduction.

The fact that the iron catalysts, used to obtain the data of Table I, initially (before exposure to synthesis gas) contained ferrous oxide, whereas the cobalt catalyst was almost completely reduced to cobalt, may be the determining factor in the markedly different C_1/C_2 ratios observed. In iron catalysts reduced at 850° C. the spacing between some of the planes containing iron atoms must have been sufficiently altered to permit cross linkages to form, so as to produce a large proportion of isoparaffins.

EFFECT OF PRESSURE, DILUENTS, AND CONTACT TIME IN FISCHER-TROPSCH SYNTHESIS

The early work of Fischer and co-workers showed that pressures above 1 atmosphere favor the formation of oxygenated organic compounds and of high-molecular-weight hydrocarbons and reduce the yield of normally liquid hydrocarbons per cubic meter of synthesis gas (*17*). Pressures lower than atmospheric necessitated proportionately greater amounts of catalysts for

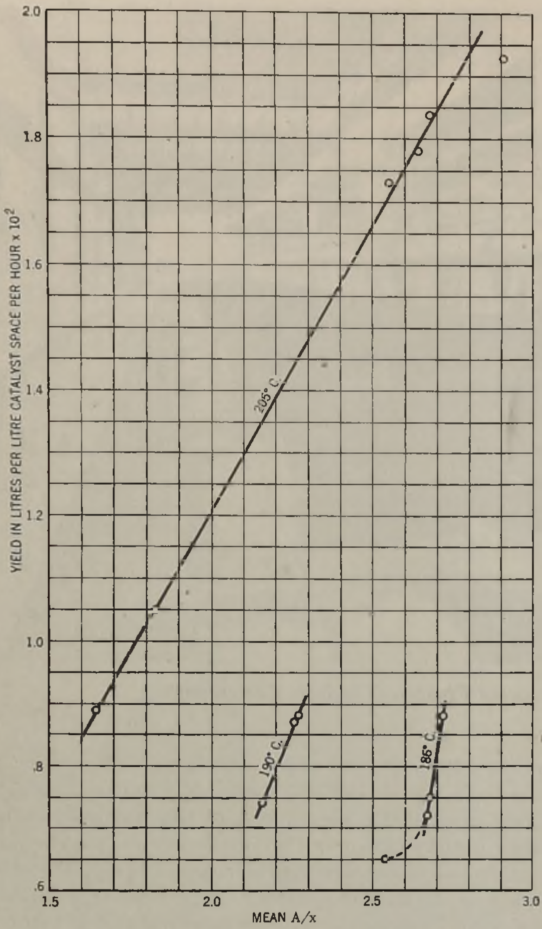


Figure 1. Space-Time Yield as Function of Partial Pressure *A* of Reactants and Partial Pressure *x* of Products at 1 Atmosphere Total Pressure

equal conversion to hydrocarbons, although the average molecular weight and chemical composition of the product were unaffected by the reduced pressure (*18*). In the absence of diluents, the reaction rate is approximately directly proportional to the pressure of $2H_2 + 1CO$ in the pressure range from 1 to 0.1 atmosphere.

For total pressure of about 1 atmosphere, dilution with nitrogen does not decrease the percentage of conversion. In fact, such dilution results in a percentage of conversion somewhat greater than would be calculated upon the basis of a first-order reaction. The following table contains results of recent work in the Bureau of Mines synthetic liquid-fuel research laboratories. Similar results have been reported by other investigators (*38, 50*).

	Yield, Grams of Oil/Cubic Meter	
Nitrogen, %	Observed	Calculated
1.0	101	....
16.3	88	84.5
28.8	90	72.3

The facts that in the absence of diluents the reaction is approximately first order and that in the presence of nitrogen the reaction rate is somewhat greater than corresponds to the partial pressure of the synthesis gas make it probable that the slow step in the reaction is the desorption of the products. If one assumes further that molecular bombardment by gaseous hydrogen is much more effective in desorption of the products than by nitrogen, the data in the two preceding paragraphs are readily explained.

The retarding effect of the reaction products is illustrated by the data of Aicher, Myddleton, and Walker (*1*), who used a nickel catalyst: "If adsorption (of the products) is an important retarding influence on the reaction, the rate of reaction should vary directly as the partial pressure of reactants and inversely as the partial pressure of the product. The yield of oil per unit time, per unit volume of catalyst, would then bear a linear relationship to *A*/*x*, where *A* is the concentration of the reacting gas and *x* the concentration of the product. By constructing graphs relating length of catalyst to yield, at various temperatures, and integrating these curves, we were able to estimate the average concentration of unchanged reactant in the experiments, over any catalyst layer."

Table I. Bureau of Mines Analyses of Residual Hydrocarbon Gas from Fischer-Tropsch Synthesis after one Pass through Catalysts (in Per Cent by Volume)

Catalyst	Co–ThO_2–Kieselguhr	Fe	Fe-Cu
Methane	45.7	38.3	14.8
Ethane	3.6	4.3	24.3
Ethylene	1.1	4.4	7.3
Propane	3.6	4.1	9.7
Propylene	5.4	6.6	16.4
Butanes	0.4	..	1.2
Butenes	0.8	0.9	3.0
Carbon monoxide	32.2	37.5	4.7
Hydrogen[a]	1.1	1.0	3.3
Carbon dioxide[a]	0.3	0.4	0.3
Nitrogen[a]	5.8	2.5	15.0
Ratio, C_1/C_2	9.8	4.4	0.5

[a] Most of the carbon dioxide was removed by absorption is caustic before condensing the gas, and most of the hydrogen and nitrogen were separated by condensation of the hydrocarbons.

Figure 1 is a reproduction of the data referred to in the quotation from Aicher *et al.* The straight line for 205° C. fits the data reasonably well, and one may conclude that the rate is retarded by the adsorbed products of the reaction. The data for 190° C. (Figure 1) are inadequate to determine a straight line, and those for 186° C. indicate that at low conversions there is some deviation from the rule of inverse proportionality to the partial pressure of the reactants. Some of the data of Aicher and co-workers (*1*, Figure 4) are suitable for calculating the temperature coefficient for relatively short contact times (that is, conversions of about 10 to 50%). The coefficient for the temperature ranges 197–207° C. and 191–207° C. are 1.4 and 1.67 per 10° C., respectively. These coefficients correspond to an activation energy per mole of about 20 kg.-cal. as calculated from the Arrhenius equation. This energy value is a reasonable one for a desorption process.

A study of the effect of pressures above atmospheric was made by Fischer and Pichler (*19*). As the pressure was increased above atmospheric, the yield at first increased and then (at about 15 atmospheres) decreased. Table II shows the results of their work. A cobalt-thoria-kieselguhr catalyst and a constant throughput of 1 liter (measured at atmospheric pressure) per hour of $2H_2 + 1CO$ gas per gram of cobalt metal were used. The data are averages for 4-week operation. Only a single pass of the gas through the catalyst was made, and there was no catalyst regeneration.

Because of the constancy of throughput, the contact time increased in direct proportion to the pressure. The yield of all hydrocarbons (column 2 plus column 6) increased from 155 grams per cubic meter at atmospheric pressure to 181 at 2.5 and 183 at 6 atmospheres, and then decreased with further pressure increase.

Table II. Effect of Pressures above Atmospheric

	Yields, Grams/Cu. Meter of Synthesis Gas				
Pressure, Atm.	Total solid and liquid hydrocarbons	Paraffin wax	Oil boiling above 200° C.	Gasoline boiling below 200° C.	Gaseous hydrocarbons C_1 to C_4
1.0	117	10	38	69	38
2.5	131	15	43	73	50
6.0	150	60	51	39	33
16.0	145	70	36	39	33
51.0	138	54	37	47	21
151.0	104	27	34	43	31

As the theoretical yield was about 208 grams per cubic meter, the maximum percentage of conversion to hydrocarbons was 88 to 89. The rapid decrease in yield of hydrocarbons for pressures above about 16 atmospheres was probably due to corrosion of active catalyst surface by carbonyl formation and by the stronger adsorption of the oxygenated organic compounds which were produced in larger amounts at the higher pressures.

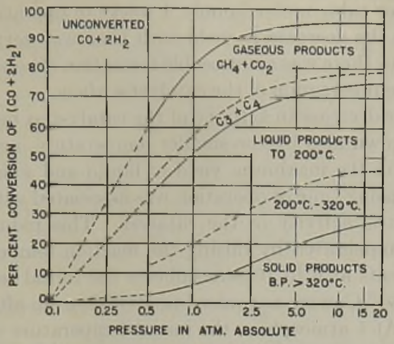


Figure 2. Effect of Pressure on Total Yield and Yield of Various Fractions (Cobalt-Thoria-Kieselguhr Catalyst)

Martin's curves (*34*), illustrating the effect of pressure, are reproduced in Figure 2 for comparison with data on the effect of pressure on a ruthenium catalyst by Pichler and Buffleb (*39*) at pressures from 15 to 1000 atmospheres. The results of the latter work are shown in Figure 3. Three grams of ruthenium catalyst were used, and the flow of synthesis gas was so adjusted that 1 liter (measured at 1 atmosphere pressure) of effluent gas was obtained per hour. The throughputs of $2H_2 + 1CO$ (calculated from the nitrogen contents of the ingoing and effluent gases) were 1.08, 1.16, 1.79, 2.57, 5.0, and 5.26 liters per hour per 3 grams of ruthenium for 15, 30, 50, 100, 180, and 1000 atmospheres, respectively. It must be remembered that the data of Figure 2 were obtained at a constant throughput per gram of catalyst, whereas those of Figure 3 were measured at varying throughput. If the throughput has been kept constant at, for example, 1 liter per hour per gram of ruthenium, then the yield and conversions would have been appreciably lower at 15, 30, and 50 atmospheres, only slightly lower at 100 atmospheres, and slightly higher at 180 and 1000 atmospheres. Therefore, the curves of Figure 3 on a constant throughput basis would have been steeper between 15 and 180 atmospheres. With this in mind, a comparison of Figures 2 and 3 shows that, for a cobalt catalyst, about 95% conversion is reached at 15 atmospheres, whereas for a ruthenium catalyst 95% conversion necessitates a pressure of about 300 atmospheres. It is interesting to note also that, whereas for a cobalt catalyst maximum life was obtained at 5 to 15 atmospheres pressure, only a few weeks of operation at 50–150 atmospheres sufficed to cause a large decrease in catalyst activity (Figure 6); for a ruthenium catalyst 6 months of operation at 100 to 1000 atmospheres did not result in any observable decrease in activity.

Table III. Effect of Varying the Throughput at 15 Atmospheres Pressure and 200° C., Using 4 Grams of Cobalt (in Cobalt-Thoria-Kieselguhr)

1	2	3	4	5	6
$2H_2$ + 1Co			Yield of Oil (Excluding Gasol)		
Liters/ hour at 1 atm.	Liters/ hr./g. of Co	Contraction, %	Grams/ cubic meter	G./1000 hr./g. Co (col. 4 × 2)	G./1000 hr./g. Co, calcd. from contraction[a]
4.6	1.15	74	101	106	106
9.0	2.25	60	85	192	131
14.5	3.6	48	60	216	164
40.5	10.0	16	16.5	165	490

[a] Assuming that the volume change upon reaction is constant for all throughputs and that yield is independent of the partial pressure of reactants and inversely proportional to partial pressure of products. Thus taking 106 grams per 1000 hours as the basis for comparison, the second row figure of column 6 is obtained from 106 × 0.74/0.6, the third row from 106 × 0.74/0.48, and the fourth from 106 × 0.74/0.16.

The retarding effect of the products of the action at pressures above atmospheric is demonstrated by the data of Table III calculated from the results of Fischer and Pichler's work (*19*).

The space-time yield (column 5) reaches a maximum at about 4 liters per hour per gram of cobalt. In column 6 the space-time yield was calculated as indicated in footnote [a]. The volume change upon reaction to form chiefly hydrocarbons with 5 to 16 carbon atoms is approximately constant over a wide range of variation of molecular weight distribution; therefore the partial pressure of the reaction products is directly proportional to the contraction. The figures in column 6 increase more slowly than those of column 5 with increasing throughput, but there is no maximum. It seems probable that the temperature of the catalyst surface increases with increasing throughput, despite the apparent constancy of the average temperature. At the higher temperatures a large proportion of the carbon monoxide used appears as gaseous hydrocarbons and as carbon dioxide.

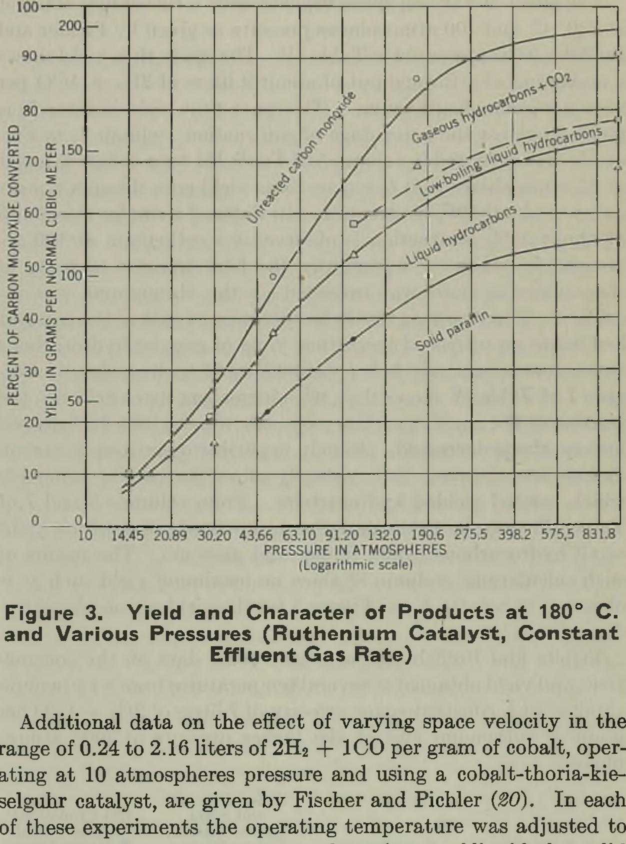


Figure 3. Yield and Character of Products at 180° C. and Various Pressures (Ruthenium Catalyst, Constant Effluent Gas Rate)

Additional data on the effect of varying space velocity in the range of 0.24 to 2.16 liters of $2H_2 + 1CO$ per gram of cobalt, operating at 10 atmospheres pressure and using a cobalt-thoria-kieselguhr catalyst, are given by Fischer and Pichler (*20*). In each of these experiments the operating temperature was adjusted to obtain a minimum of methane and maximum of liquid plus solid hydrocarbons. The results are presented in Figure 4, where the outstanding fact is the extraordinarily small amounts of C_2 hydrocarbon produced. This marked discontinuity in the quantitative composition of the product is of interest in connection with the data given in Table I and the discussion following it. Figure 4 shows that the yield of solid paraffin decreased with increasing space velocity, as did also the total yield of hydrocarbons other than methane. Because the data of Figure 4 were obtained by separation of the condensable (at room temperatures and 10 atmospheres pressure) hydrocarbons in two stages, and because only the total amount of condensed hydrocarbons for both stages is given, it is not possible to correlate partial pressure of the products with space-time yield.

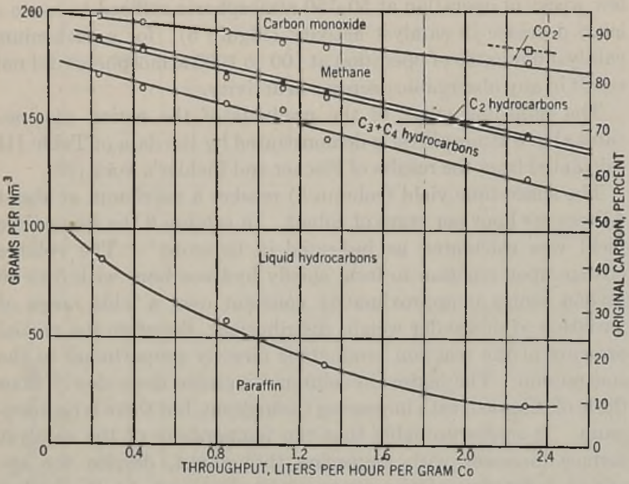


Figure 4. Intermediate Pressure Synthesis Yields and Carbon Balance *vs.* Throughput

The effect of varying space velocity over a ruthenium catalyst at 230° C. and 100 atmospheres pressure as given by Pichler and Buffleb (*40*) is presented in Table IV. The space-time yield shows a maximum at a throughput of about 9 liters of $2H_2 + 1CO$ per hour per gram of ruthenium. The space-time yield (column 5) is plotted against the percentage of contraction (column 2) in Figure 5. It was noted in column 5 of Table III for a cobalt catalyst at 15 atmospheres that the space-time yield goes through a maximum at about 50% contraction. In Figure 5 a similar maximum at about 55% contraction is observed for ruthenium at 100 atmospheres pressure. Apparently the heat transfer capacity of the apparatus used was exceeded as the throughput was increased. The resulting rise in temperature of part of the catalyst bed led to an increased space-time yield of gaseous hydrocarbons and a correspondingly lower yield of liquid hydrocarbons. Column 7 of Table IV shows that, with increasing space velocity, the fraction of the reacting carbon monoxide which yielded condensed hydrocarbons decreased. As only negligible quantities of carbon dioxide are obtained (*40*), virtually all of the carbon monoxide which reacted yielded hydrocarbons. From columns 5 and 7 of Table IV may be calculated the approximate space-time yield of all hydrocarbons (solid, liquid, and gaseous). The results of such calculations (column 8) show no maximum yield such as is observed in column 5 and Figure 5 for the yield of condensed hydrocarbons.

Pichler and Buffleb (*40*) also gave some data on the contractions and yield obtained at several temperatures from a ruthenium catalyst at a constant space velocity of 7 liters of $2H_2 + 1CO$ per gram of ruthenium and at the higher pressure of 1000 atmospheres:

Temperature, ° C.	Contraction, %	Yield of Liquid and Solid Hydrocarbons, Grams/Cubic Meter	CO Converted to Condensed Hydrocarbons, % of CO Used
164	49	72	41
180	55	79	44
190	62	89	51
200	65	95	55
210	69	104	60

The space-time yield of condensed hydrocarbons is plotted against contraction in Figure 5. Within the limits of heat transfer capacity of the apparatus, the yield is directly proportional to the contraction when the temperature is varied, because the temperature coefficient of the reaction rate apparently is large enough to overcome the increased retarding effect of the products with increasing conversion.

The effect of pressures above 1 atmosphere on the durability of a cobalt catalyst was investigated by Fischer and Pichler (*19*). Their results are graphically presented in Figure 6. The pressures given are gage readings, so that the 0 atmosphere curve shows the results at 1 atmosphere pressure. The yield of solid plus liquid hydrocarbons showed a minimum decrease with time for reaction pressures of 6 to 16 atmospheres. At these pressures the initial yield was more than 150 grams per cubic meter, and after 26 weeks of operation the yield was still above 100 grams per cubic meter. At 1 atmosphere pressure the yield dropped from 130 to 100 grams per cubic meter in only 4 weeks of operation. At 151 atmospheres the decrease in yield with time was very rapid. At such pressures there was a noticeable formation of cobalt carbonyl and consequent corrosion of the catalyst surface.

The slower decrease in activity of the catalyst at medium pressures was shown also by the smaller temperature increase necessary to obtain the maximum yield of liquid and solid hydrocarbons. Increasing time of operation was associated with a gradual lowering of the activity of the catalyst. This reduction could be partly compensated by raising the reaction temperature. In the experiments at 6 to 16 atmospheres the initial temperatures of 175° to 180° C. were not raised to 195° C. even after 6-month operation. At 1 atmosphere the initial temperature of 180° had to be increased to 195° C. after only 5 weeks of operation.

POISONING OF FISCHER-TROPSCH CATALYSTS BY SULFUR COMPOUNDS

Although Fischer-Tropsch catalysts are readily poisoned by sulfur compounds, they have a limited tolerance for hydrogen sulfide and carbon disulfide. Thus King (*32*) reports: "In our experiments, carbon bisulfide was added to the process gas over a period of 4 days to an extent corresponding to 33 mg. of sulfur per cc. of catalyst. The catalyst continued to synthesize oil at a high degree of conversion, but in order to maintain the efficiency it was necessary to raise the temperature progressively from 185° to 210° C. With the space velocity used (190 volumes per volume of catalyst per hour) the degree of fouling corresponds to about 10 years working at the concentration of sulfur (0.2 gram per 100 cubic meters) usually accepted as the highest permissible."

Table IV. Effect of Space Velocity on a Ruthenium Catalyst at 230° C. and 100 Atmospheres Pressure

1	2	3	4	5	6	7	8
		Yield, Grams of Liquid per:			CO Converted to Condensed Hydrocarbons		Total Hydrocarbons, G./L. of Catalyst Space/Hr
Liters[a]/Hour/Gram of Ru	Contraction, %	Cubic meter $2H_2$ + 1CO	Gram Ru/hr. × 100	Liter of catalyst space/hr.	% of CO used	% of CO reacted	
1.8	81	136	24	108	78	87	124
3.2	79	125	40	180	72	83	217
4.3	69	98	43	194	56	74	262
7.0	62	84	59	265	48	70	379
9.1	56	79	72	324	45	73	445
10.7	50	65	69	310	37	68	456
16.7	36	37	60	270	21	54	500

[a] Measured at 1 atmosphere pressure.

Herington and Woodward (*28*) conducted a similar determination of the tolerance of a cobalt-thoria-kieselguhr catalyst for hydrogen sulfide. The first additions of hydrogen sulfide caused a marked increase in the yield of liquid hydrocarbons at the same temperature employed before the hydrogen sulfide was added. There was, however, an immediate falling off in the yield of gaseous hydrocarbons. The total hydrocarbon yield increased until more than 8.0 mg. of sulfur had been added to each gram of catalyst. Further additions of hydrogen sulfide caused a drop in total hydrocarbon yield, but this could be offset by raising the reaction temperature more rapidly than would be normally necessary in the absence of hydrogen sulfide. After the addition of as much as 33 mg. of sulfur per gram of catalyst, the yield of liquid hydrocarbons was still 20% greater than before the addition of sulfur. Further additions of sulfur resulted in a continuous decrease in activity until complete poisoning occurred.

In Herington and Woodward's experiments (*28*) a sample of catalyst whose activity at 200° C. was lowered to 38% of its initial value by the addition of 19.4 mg. of sulfur per gram of catalyst was then treated with hydrogen at 375° C. for 14 hours. In the normal synthesis with virtually sulfur-free gas, this treatment restores the activity of the catalyst to a considerable extent. However, no hydrogen sulfide was observed to leave the tube, and the catalyst subsequently at 200° C. showed only 10% contraction of the synthesis gas passed over it. Herington and Woodward (*28*) explain this by saying: "In seeking an explanation of the marked effect in the case of the catalyst containing sulfur, it is to be borne in mind that the action at 375° C. will clear the catalyst surface of carbide or other protection. The observed toxicity may possibly be due to a redistribution of the sulfur, resulting in the poisoning of very active centers which were previously protected by carbide or in some other way. A similar effect has been reported by Fischer (*15*)."

CATALYSIS IN HYDROGENOLYSIS OF COAL AND TAR

In the first stage of the hydrogenolysis of coal, which yields a primary tar or pitch, the important factors are: (1) rank and type of coal, (2) nature of the catalyst used, and nature and amount of coal ash, (3) pressure of hydrogen, (4) character of the vehicle in which the coal is suspended, and (5) agitation. The first factor is virtually an independent variable, whereas the remaining four are dependent or "interlocked".

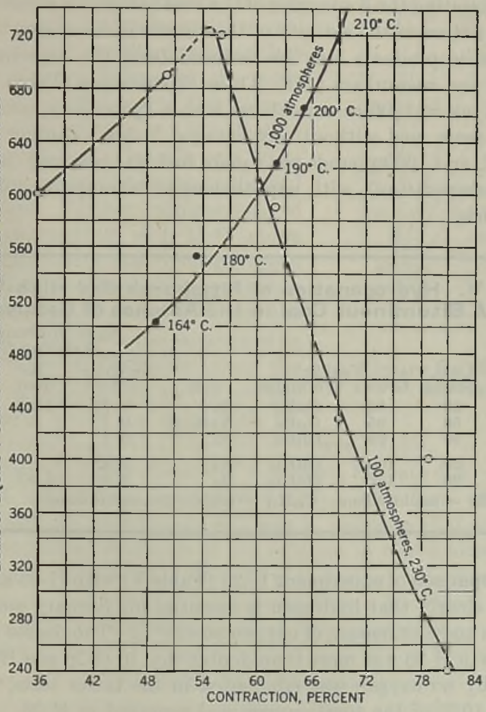


Figure 5. Relation of Space-Time Yield to Contraction (Ruthenium Catalyst)

As far as rank and type of coal are concerned, it is sufficient for the purposes of this paper to state that coals of rank higher than bituminous are difficult to hydrogenate and that the amount of highly carbonized constituents in coals of lower rank is important. These constituents such as fusain and durain which are present in appreciable quantities in splint coals and in minor amounts in most bituminous and subbituminous coals yield only small amounts of oil upon hydrogenation (*24*).

In the first stage of coal hydrogenation the crushed coal (to −80 mesh) is mixed with an equal weight of a recycle heavy oil containing aromatics, hydroaromatics, and some phenolic compounds. At temperatures of about 400° C. the coal dissolves rapidly and completely, except for the inorganic constituents, the fusain, and part of the durain. This solution remains optically clear for about 15 minutes, and subsequently, in the absence of catalysts and high-pressure hydrogen, an amorphous black powder precipitates. This precipitate hydrogenates more slowly than the original coal. During the solution process methane, carbon dioxide, and water are evolved. In the presence of a highly active catalyst and high-pressure hydrogen this reprecipitation can be avoided, and a stable heavy oil obtained.

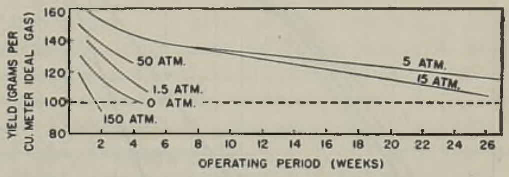


Figure 6. Variation of Yield with Time at Various Pressures

Most heavy metals and their oxides and sulfides are active as catalysts in primary liquefaction of coal. Alkali and alkaline earth oxides, carbonates, and some silicates, however, favor the repolymerization of the dissolved coal, and if present in the coal, they should be converted to chlorides by use of hydrochloric acid or ammonium chloride. The appreciable quantities of sulfur compounds and of organic substances of high molecular weight present in the coal solution rapidly foul most very active metal surfaces, such as that of reduced nickel. The metal sulfides, however, such as iron, nickel, and molybdenum sulfides, are active catalysts for the first stage of coal hydrogenation, arranged in the order of increasing activity. Tin added as massive metal or as any reactive compound is the most active catalyst known for converting coal to a heavy oil by hydrogenation. Thus, a few hundredths per cent of tin are equivalent to about ten times that amount of the next best catalyst—namely, molybdic acid. The outstanding activity of tin may be due in part to its versatility in distributing itself throughout the solid, liquid, and gas phases of the hydrogenation system. Thus it alloys with the steel of the pressure vessel; it is found adsorbed on the particles of fusain and durain and dissolved in the heavy oil, and there is some evidence that it enters the gas phase as volatile tin compounds.

A freshly machined stainless steel (18 chromium–8 nickel) surface enhances the activity of tin, but it is fouled after a short time by adsorption of organic polymers of high molecular weight. In the Bureau of Mines continuously operating experimental plant a converter, 3 inches i.d. and 96 inches high, was packed with stainless steel turnings. This packing approximately doubled the capacity of the plant for about 10 days, after which the enhanced activity due to the packing decreased until in a few days the maximum throughput was about the same as that of an unpacked converter. On the other hand, pumping hydrogen at 3500 pounds per square inch and coal-oil paste plus 0.05% of the weight of coal of tin sulfide or hydroxide, through an unpacked converter, may be continued for months without any observable change in yield. It is probable, therefore, that alloying the tin with the steel of the converter wall does not contribute to the catalysis under conditions of long runs where the steel walls are covered with a shellac-like layer of organic material of high molecular weight.

The catalysis by tin or tin alloys may be a form of homogeneous catalysis by minute amounts of tin hydride. As the tin is active in any form (other than metastannic acid), and because liquid tin would not present a large enough surface to assure an adequate rate of hydrogenation, Booth (*6*) concluded that an alloy of tin with the steel of the converter wall constituted the main catalytic surface. Although Booth observed no deterioration in the catalytic activity of acid-treated tin-iron alloys when used for thirteen consecutive small autoclave tests, each lasting about 30 minutes, the Bureau of Mines after 10 days of continuous operation noted rapid deterioration of the enhanced activity of small amounts of tin in the presence of a large alloy-steel surface. Tin is reported (*35*) to form tin hydride by the action of dilute solutions of organic acids on metallic tin in the presence of iron. Tin hydride formation is also accelerated by the presence of minute amounts of halogens such as iodine. This combination of tin and iodine is known to be superior to tin alone in the first stage of coal hydrogenolysis (*11*). Iodine is, per se, a fairly efficient catalyst when used in low concentrations (*11*), but the combination of tin and iodine is more active than either component by itself. A possible mechanism that can explain most of the observed phenomena is that tin hydride reacts with cyclic olefins to form $R = SnH_2$, which decomposes to give $RH_2 + Sn$. This reaction probably is facilitated by prior saturation of the olefin bond with iodine or hydrogen iodide:

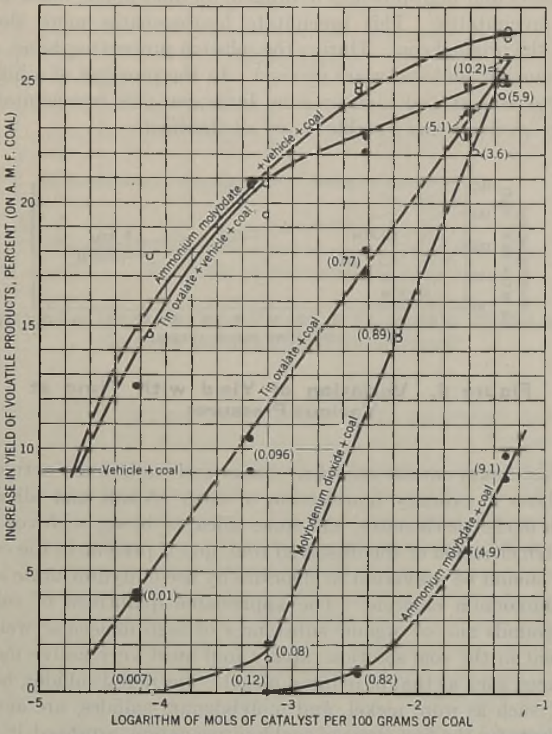


Figure 7. Increase in Yield of Volatile Products from High-Volatile A Bituminous Coal by Addition of Catalyst and Vehicle

Figures in parentheses are weight per cent of catalyst.

$$RI_2 + SnH_4 \rightarrow (RH)HSnI_2 + H_2 \rightarrow RH_2 + Sn + 2HI$$

In the absence of tin, the organic iodide is reduced by hydrogen dissolved in the vehicle.

Figure 7 illustrates the effects of varying amounts of stannous oxalate, molybdenum dioxide, and ammonium molybdate in the presence and absence of a vehicle. These data were obtained by Warren, Bowles, and Gilmore (*52*) in the hydrogenation of a high-volatile A bituminous coal for 5 hours at 445° C. and 204 atmospheres pressure. Small samples (0.6 to 1.0 gram) were placed in glass dishes, a number of which were supported inside a high-pressure vessel heated to reaction temperature. A slow stream of hydrogen moving about 0.8 cm. per second was passed through the vessel. The yield of volatile products was determined by measuring the loss in weight of the dishes corrected for any loss incurred by volatilization of the vehicle when present and for the loss of weight of the catalyst upon reduction. When tin oxalate was used as catalyst in the absence of a vehicle, the yield of volatile products is a linear function of the logarithm of the moles of catalyst used per 100 grams of coal. Under the same conditions, molybdenum dioxide in low concentrations is much less efficient and does not give a linear relation between the yield and logarithm of the catalyst concentration. In larger concentrations, molybdenum dioxide approaches stannous oxalate in catalytic activity, and a linear relation exists for concentrations above about 0.1% by weight of molybdenum dioxide. Ammonium molybdate in the absence of a vehicle is a much less active catalyst than either the tin oxalate or the molybdenum dioxide. In the presence of a vehicle, however, ammonium molybdate is as effective as tin oxalate. Probably the ammonium molybdate is more rapidly reduced to molybdenum dioxide by the vehicle than by gaseous hydrogen.

As Figure 7 indicates, the addition of a vehicle in the absence of catalyst yields 9.1% more volatile products than the yield (57%) obtained from the coal alone. The vehicle used was a distillate oil product from hydrogenation of a high-volatile A bituminous coal; about 50% distilled between 170° and 300° C. and the remainder above 300° C. This vehicle, although a distillate, contained 0.003% by weight of tin (or of the coal as about equal weights of coal and vehicle were used), which corresponds to 0.0056% of tin oxalate. Figure 7 shows that the increase in yield due to the vehicle alone is equal to that obtained when about seventeen times as much tin catalyst was used in the absence of a vehicle. It is apparent, therefore, that the vehicle itself is active in accelerating the conversion of the coal to volatile products.

The nature of the activity of the vehicle in increasing the yield of volatile products may be deduced from the experiments of Storch and co-workers (*44*). These experiments (Table V) were carried out in 1200-cc. autoclaves with a Pyrex liner, using Pittsburgh seam coal without any catalyst, 1-hour contact time at 400° C. and 1000 pounds per square inch gas pressure (initial, at room temperature), with naphthalene or tetrahydronaphthalene as vehicle.

Table V. Hydrogenation of Pittsburgh Bed High-Volatile A Bituminous Coal in the Absence of Catalyst

Series H Test No.	Coal, Grams	Vehicle Grams	Vehicle Formula[a]	Gas	% of Moisture- and Ash-Free Coal: O_2 eliminated	H_2 used	Liquefaction
26	50	65	$C_{10}H_8$	H_2	0.76	0.86	32.4
28	50	65	$C_{10}H_8$	Natural	0.1	..	13.8
29	50	65	$C_{10}H_8$	N_2	0.1	..	14.9
41	20	100	$C_{10}H_{12}$	N_2	2.45	..	67.2
40	20	100	$C_{10}H_{12}$	H_2	2.50	1.85	67.5

[a] $C_{10}H_8$ = naphthalene; $C_{10}H_{12}$ = tetrahydronaphthalene.

Comparison of experiment H-26 (Table V) with H-28 and H-29 shows clearly that hydrogen is essential for primary coal liquefaction and elimination of oxygen at 400° C. The degree of liquefaction in H-26 was more than double that in H-28 and H-29, and virtually no oxygen was eliminated in the latter tests, whereas about 10% of the total oxygen was removed in H-26. A comparison of H-26 with H-41, in which an excess of tetrahydronaphthalene was used and nitrogen replaced hydrogen, shows that the degree of liquefaction and oxygen elimination in H-41 was two to three times as great as in H-26. It is therefore probable that one of the slow steps in coal hydrogenation in the absence of a catalyst is the formation of hydroaromatic compounds which serve as hydrogen carriers. It is necessary in this argument to call attention to the fact that the amount of hydrogen present in H-26 (about 5.7 grams) greatly exceeded that necessary (about 2 grams) for complete liquefaction and oxygen elimination.

The comparison of H-26 with H-41 is of special interest in connection with the data of Pott and Broche (*41*) which show that

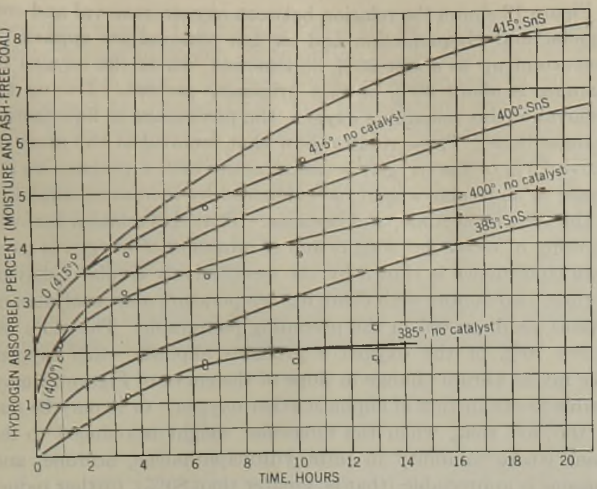


Figure 8. Influence of Catalyst on Rate of Hydrogen Absorption

Point of zero absorption is shifted on ordinate to make each pair of curves distinct.

virtually complete liquefaction of bituminous coals may be obtained when they are heated at 390° to 410° C. with an equal weight of tetrahydronaphthalene-phenol-naphthalene (2:1:2) solvent under the pressure of the solvent vapors—that is, with no added hydrogen or other gas. It is apparent from this discussion that tetrahydronaphthalene is the most essential constituent of this solvent and that its efficacy as a liquefaction agent is related, at least in part, to its ability to transfer hydrogen to the coal substance. Further comparison of experimental H-26 with H-41 shows that naphthalene plus hydrogen gas is a much poorer liquefaction agent than tetrahydronaphthalene without hydrogen. Indeed, in the presence of an excess of tetrahydronaphthalene the degree of liquefaction and of oxygen removal is about the same with nitrogen (experiment H-41) as with hydrogen (H-40).

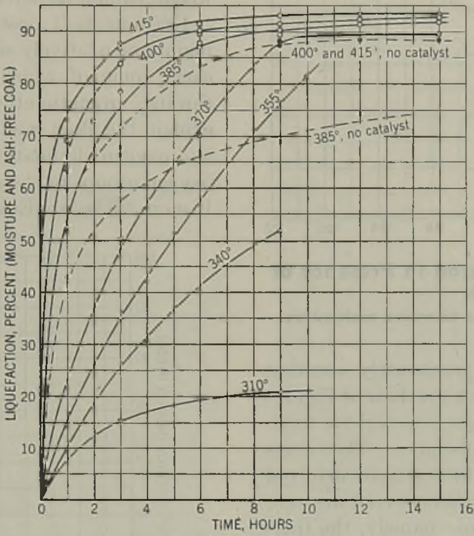


Figure 9. Effect of Catalyst (Tin Sulfide) on Rate of Oxygen Elimination

At 400° C., in the absence of a catalyst, the rate of hydrogenation of naphthalene is very slow (*27*). This fact, considered along with the experiments of Table V, indicates that one of the most important functions of the catalyst in coal-hydrogenation reactions is to accelerate the rate of formation of hydroaromatic compounds that served as hydrogen carriers. Additional information on this postulated function of the catalyst is provided in Figures 8, 9, and 10. These data were obtained by Storch and coworkers (*44*) on Pittsburgh seam coal plus an equal weight of tetrahydronaphthalene as vehicle in 1200-cc. rotating autoclaves. The curves show that the catalytic effect of tin sulfide is considerably greater at 385° C. than at higher temperatures. This is probably due to the slow rate of noncatalytic regeneration of the hydrogen carrier (*27*) at 385° C., whereas at 400° C. and higher temperatures this rate is of the same order of magnitude as that of the reaction between the hydrogen carrier with the primary decomposition products of the coal.

Further information about the kinetics of the hydrogenolysis of coal is obtained from Figures 8 to 15, containing data obtained by Storch and co-workers (*44*). Figure 11 illustrates the rates of hydrogen absorption at different temperatures; three peculiarities should be noted: (1) The temperature coefficient for the first hour at reaction temperatures increases sharply between 370° and 385° C. from a value of about 1.0 per 15° below 370° to about 3.0 per 15°. Above 385° C. this coefficient again decreases markedly to a value of about 1.0 per 15°. The large coefficient in the 370° to 385° C. region is of the same order of magnitude (about 3.0 per 15°) as those given in a later section of this paper for oxygen elimination and coal liquefaction during the first hour of the reaction. (2) The change in the temperature coefficients with temperature for reaction times beyond the first hour for temperatures below 385° C. indicates a diffusion process as the rate-determining step between 300° and 385°. (3) Temperature coefficients for temperatures above 385° C. are low (about 1.25 per 15°), although higher than those for the 300° to 385° region. The shape of the curves above 385° also differs from those below this temperature. The latter, after the first hour of reaction, are approximately straight lines, indicating zero order with respect to the material reacting with the hydrogen (the concentration of hydrogen is approximately constant because of the periodic refilling). The shape of the curves above 385° indicates that an opposing (dehydrogenation) reaction is gaining in speed or that the hydrogenation reaction is first or second order.

These peculiarities may be explained if one assumes that the following processes occur during coal hydrogenation: (1) Diffusion of hydrogen through liquid films on the surface of the catalyst and on the surface of the coal. The latter surface probably persists for several hours at temperatures below about 370° C. but has only a short life (minutes) at temperatures above 385°. Alternatively, the slow step in the temperature range 300° to 370° may be the diffusion of hydrogenated, solvated coal from the solid coal into the liquid phase. (2) Primary decomposition of the coal. (3) Hydrogenation of unsaturated groups in the primary decomposition products. (4) Secondary decomposition of the coal, involving reaction between oxygen groups in the coal substance and a hydrogen carrier. (5) Dehydrogenation of the products of (4) due to thermal instability.

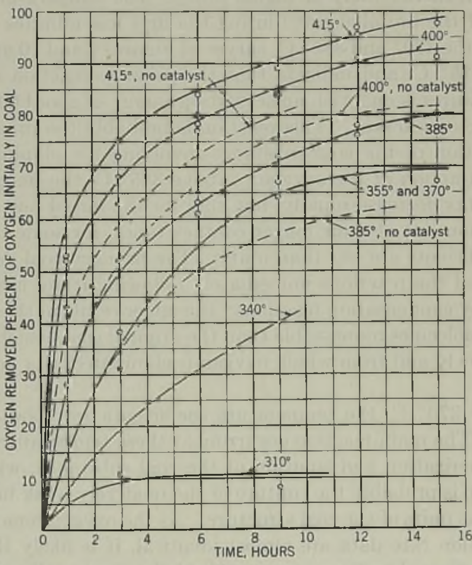


Figure 10. Effect of Catalyst (Tin Sulfide) on Rate of Liquefaction

Data on oxygen removal and rates of coal liquefaction are presented in Figures 9 and 10. The degree of liquefaction was measured by determining the amount of residue obtained upon centrifuging the tetrahydronaphthalene solution of the product and subsequently washing the centrifuge residue with acetone and benzene. It is apparent, therefore, that the term "liquefaction" means decrease in molecular weight until the products are gaseous under normal conditions or dissolved by the treatment just described. Eliminated oxygen is defined as that appearing in water, carbon dioxide, carbon monoxide, and oxygenated organic compounds boiling below 215° C.

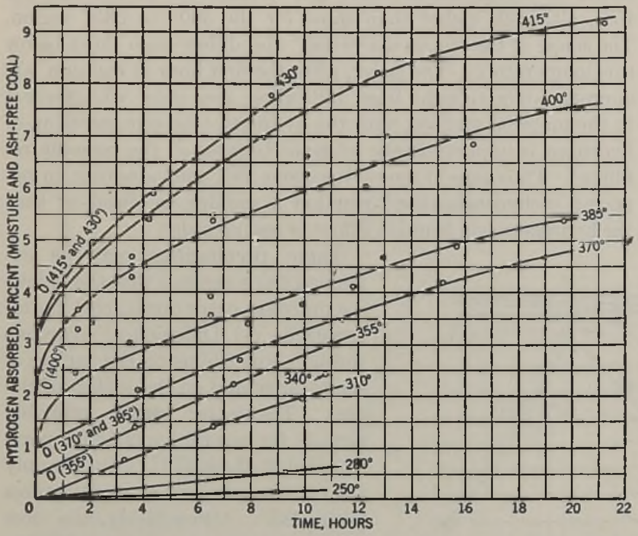


Figure 11. Rate of Hydrogen Absorption in Presence of Tin Sulfide Catalyst

Point of zero absorption is shifted on ordinate to make each curve distinct.

As the hydrogen pressure was kept approximately constant in all of the experiments performed to obtain the data of Figures 9 and 10, the rates of liquefaction and oxygen removal are functions only of the concentration of the coal substance. The curves obtained when the data are plotted as if the reactions involved were first order with respect to the concentration of coal are not, however, straight lines. The initial reaction—namely, the thermal decomposition of the coal, probably is first order, although subsequent reaction of the primary decomposition products with hydrogen carriers may be higher order. The temperature coefficients of the initial slopes (during the first few minutes of reaction) of the 370° and 385° C. curves of Figures 9 and 10 are 2.5 to 3.0 per 15° C. and indicate that the primary reaction at these temperatures is one with an activation energy of about 60 kg.-cal. per mole of reactant. This reaction is probably the primary decomposition of the coal substance involving the elimination of a large fraction of the oxygen. Above 385° C. the temperature coefficients decrease rapidly, not only for the initial few minutes of reaction but also for longer contact times, for some of which the coefficients are less than unity. The primary coal decomposition and the reactions immediately following it are largely obscured by condensation reactions; the latter result in the production of molecules more stable than the original coal, which liquefy more slowly and from which oxygen is eliminated at a very slow rate.

Below 370° C. the temperature coefficients are about 1.3 per 15° C. The main reaction occurring at these temperatures is the depolymerization and solution of the coal substance, where the slow step is probably the rupture of the relatively weak bonds between the units of the coal structure. As the oxygen removal and liquefaction rate data are almost identical, it is likely that carbon-to-oxygen bonds are ruptured and the oxygen eliminated as water by transfer of hydrogen within the unit of the coal structure.

Figure 12 shows the relation between oxygen removal and coal liquefaction. Liquefaction and oxygen removal are apparently concurrent up to about 90% liquefaction, where the oxygen remaining is about 30% of that originally present. During the removal of this remaining oxygen, the percentage of liquefaction changes little. These results show that removal of the more reactive 70% of the oxygen is concomitant with a progressive decrease in molecular weight, as evidenced by increasing solubility in the vehicle, acetone, and benzene. That this relation between lowering of molecular weight and elimination of oxygen is more than coincidence is shown by the qualitatively similar behavior of these two factors with changing temperature and catalyst conditions, as discussed in the preceding paragraph. The more reactive 70% of the oxygen is probably aliphatic ether oxygen. The rather abrupt change in slope of the curve of Figure 12 may be due to exhaustion of aliphatic ether oxygen; or it may be due to the fact that, when the molecular weight is reduced to the point where solubility in tetrahydronaphthalene, acetone, and benzene is appreciable (that is, greater than 80%), further reduction does not appreciably increase the liquefaction as measured by such solubility. Whether removal of the less reactive 30% of the oxygen is also to be associated with a lowering of molecular weight cannot be determined from the data presently available.

Erasmus (*13*) postulated that coal is a polymer consisting mainly of relatively small cyclic units of about 10 carbon atoms each, some of which are linked through aliphatic and some through aromatic ether oxygen bonds. Such a structure would explain the close relation between reduction of molecular weight and oxygen elimination, as well as the existence of two types of oxygen groups in the coal structure, as postulated by Fisher and Eisner (*23*) before Erasmus' book was published.

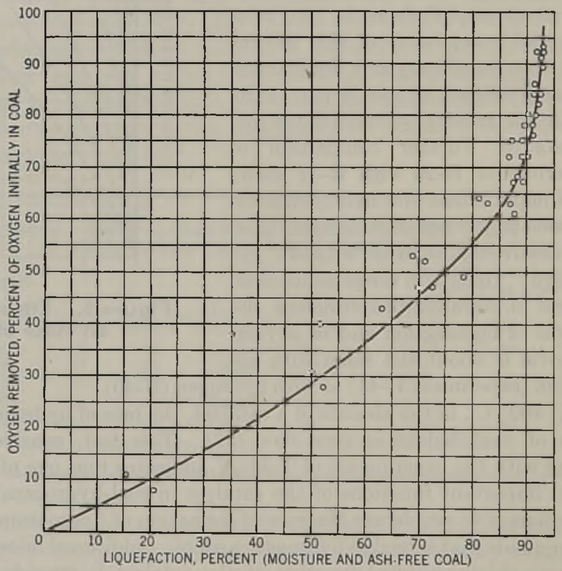


Figure 12. Relation between Coal Liquefaction and Fraction of Coal Oxygen Removed

Figure 13 shows that there is no direct or simple relation between the hydrogen consumption rate and the rates of oxygen removal and of coal liquefaction. The curves of Figure 13 for less than 80% liquefaction indicate large changes in the extent of coal liquefaction, with only relatively small changes in the amounts of hydrogen used. For the 10-hour curve, in going from 20 to about 80% liquefaction, the hydrogen used increases by only about 0.5 gram per 100 grams of coal. This 20–80% portion of the 10-hour curve involves temperatures not higher than 355° C. The similar portion of the 4-hour curve is much steeper, for the increase in hydrogen used is about 1.0 gram per 100 grams of coal. However, the temperatures involved range up to 385° C. Beyond 385° C., for all contact times studied, the rise in hydrogen consumption becomes very steep. It is apparent that the most important factor in determining hydrogen consumption is the temperature, and that if enough time is allowed, almost complete liquefaction can be obtained at comparatively low temperatures and with relatively little utilization of hydrogen. The rate determining factors in the coal liquefaction process, therefore, differ from those that regulate the rate of hydrogen consumption. It should be recalled, however, that the reactions under discussion are occurring in a vehicle containing a relatively high concentration of hydroaromatic compounds, which function as hydrogen donors. Although hydrogen is not directly involved in the oxygen elimination and coal liquefaction reactions, high pressures of hydrogen are necessary to maintain this excess of hydroaromatics.

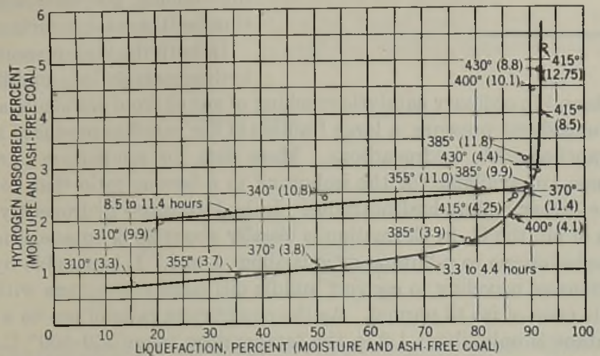


Figure 13. Relation between Hydrogen Used and Conversion of Coal to Oil, Gas, and Water

Figures in parentheses are contact times, in hours; those in front of parentheses are centigrade temperatures.

The rapid change in slope of the curves of Figure 13 for temperatures above about 370° C. is probably connected with the shift from diffusion to chemical reaction as the slowest step limiting the hydrogen-absorption rate. Above 370° C. the rate of hydrogen consumption is controlled by the rate of regeneration of hydroaromatic compounds which serve as a hydrogen reservoir, whereas, the rates of liquefaction and oxygen removal depend largely upon the rate of decomposition of the coal substance. Between 370° and 415° C. subsequent reaction of the products of this decomposition with hydrogen carriers does not directly influence the rate of hydrogen consumption when a sufficient reserve of such carriers is available. Above 415° C., however, the elimination of alkyl groups during decomposition of the coal substance increases rapidly, and hence the hydrogen transfer from the carriers increases to such proportions that the over-all rate of hydrogen consumption is increased markedly.

The rate of hydrocarbon gas formation (methane, ethane, propane, butane, and corresponding olefins) is presented in Figure 14. These curves are similar in many respects to those of Figure 11 for the rate of hydrogen consumption. Thus, the temperature coefficient for the first hour increases sharply from about 1.0 per 15° C. for temperatures below 355° C. to about 4 per 15° for temperatures between 370° and 385° C. For all reaction times the 310° and 355° C. rates are virtually identical, an indication that a diffusion process is the rate-determining step at these temperatures. For reaction times between the second and eighth hours, the temperature coefficient is about 3, 2, 1.2, and 1.4 per 15° for the 355–370°, 370–385°, 385–400°, and 400–415° C. intervals, respectively. A similar trend in the temperature coefficients of hydrogen consumption rates was noted in discussing the curves of Figure 11. The curves of Figure 14 confirm some of the conclusions of that discussion: Diffusion processes control the rate of hydrogen consumption and hydrocarbon formation between 310° and 355° C. Between 355° and 370° C. the diffusion rate surpasses that of the primary thermal decomposition of the coal substance, and the latter becomes the rate controlling process. Above 385° the rate of the primary decomposition of the coal substance surpasses that of the secondary decomposition, which is probably a reaction between the oxygen groups of the primary decomposition products of the coal and a reactive hydroaromatic such as tetrahydronaphthalene. This secondary reaction results in several smaller fragments per molecule of the primary products, and the proportion of gaseous hydrocarbons will be determined largely by the probabilities of rupture of the various bonds in the primary product molecule. All of the reactions mentioned thus far in connection with the formation of gaseous hydrocarbons are noncatalytic processes. Points *H* on Figure 14 indicate experiments carried out in the absence of catalyst; in those marked *HC*, 1% of stannous sulfide was added. There is little or no observable effect of the catalyst on the rate of hydrocarbon gas formation. However, the increase of the temperature coefficient from 1.2 per 15° at 385–400° C. to 1.4 per 15° at 400–415° suggests the possibility of autocatalysis by solids of highly condensed structure, which are formed in small but increasing quantity as the temperature is increased beyond 400° C.

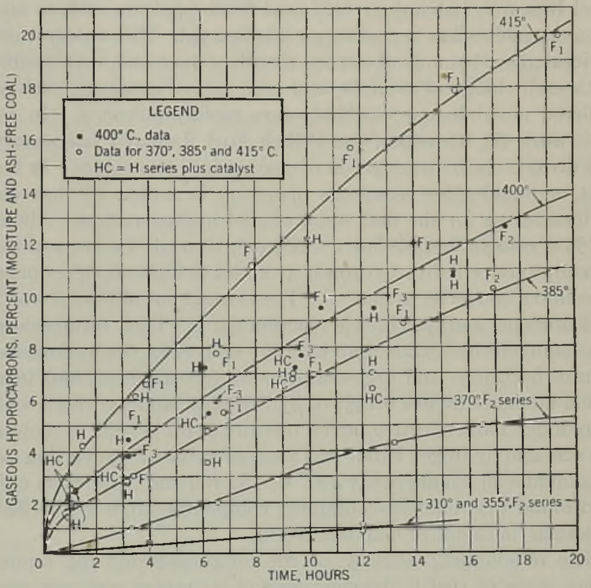


Figure 14. Rates of Hydrocarbon Gas Formation at Different Temperatures

***HC*, *F*₁, *F*₂, *F*₃ series were carried out in presence of 1% of stannous sulfide; no catalyst was used in *H* series.**

Data on rates of ammonia formation at various temperatures are presented in Figure 15. These curves are outstandingly different from those for the rates of any of the other coal hydrogenation reactions. The rates of ammonia formation during the first 2 hours are very small and virtually the same at all temperatures. After the second hour these rates increase rapidly for temperatures above 370° C., and the temperature coefficients are 3.0, 2.2, and 1.5 for 15° in the temperature intervals 370–385°, 385–400°, and 400–415° C., respectively. There are two possible explanations of the characteristics of Figure 15: The rate determining step in the ammonia formation may be an autocatalytic reaction; or the nitrogen atoms are centrally located in the units of the coal structure, so that rupture of many carbon-to-carbon bonds precedes rupture of carbon-to-nitrogen bonds. If the latter explanation is correct, then one should expect the curves of Figure 13 to decrease in slope after an appreciable fraction of the nitrogen had been converted to ammonia. At 415° C., with about one fifth of the total nitrogen converted, there is no sign of any flattening of the curve. However, further data corresponding to the conversion of more than half of the nitrogen should be obtained to assist in further determination of the mechanism of ammonia formation.

Table VI. Isobutane Production in Catalytic Cracking

Reactant	Catalyst	Temperature, ° C.	Volumes of Oil/ Vol. of Catalyst	Gaseous Products, Weight % of Feed	Moles of C_4/ 100 Moles Gas		Ratio, Moles Iso to n-C_4		Cyclic Hydrocarbons in Liquid Product, Wt. %
					Satd.	Unsatd.	Satd.	Unsatd.	
Cyclohexane	Al_2O_3	575	0.4	17.0	31.0	..	2.5	...	...
Iso-octene	Al_2O_3-SiO_2-ZrO_2	375	1.0	12.9	53.2	17.2	4.0	0.5	18
Cetane	Al_2O_3-SiO_2	455	0.6	20.1	15.1	14.3	3.4	0.5	25^a
Decalin	Al_2O_3-SiO_2	455	0.6	16.8	36.4	3.2	7.2	0.3	70^a
	Al_2O_3-SiO_2-ZrO_2	400	1.0	9.1	65.1	5.9	2.9	0.3	82
	Al_2O_3-SiO_2-ZrO_2	500	3.8	13.8	42.1	8.8	2.2	0.4	87
Gas oil	Al_2O_3-SiO_2	400	FF^b	15.8	47.7	9.7	7.2	0.2	42^a
		455	FF^b	17.5	31.6	12.4	6.2	0.3	42^a
		510	FF^b	18.9	19.8	14.3	4.8	0.7	42^a
Gas oil	Clay-MoS_2	385	1.5^c	15.0	80.0	..	4.0	..	30

^{a} Gasoline fraction only.
^{b} Fluid flow.
^{c} High-pressure hydrogenolysis.

LIQUID-PHASE HYDROGENATION OF TAR

In their early work on the hydrogenation of coal tar the British Fuel Research Laboratory (*12*) used fixed catalysts such as ammonium molybdate deposited on alumina gel. This catalyst deteriorated so that only about one month of operation was feasible with each charge of catalyst, and more active catalysts, such as pelleted molybdenum disulfide, were rapidly poisoned. In recent work (*7*), therefore, the British Fuel Research Laboratory has divided the hydrogenation of coal tar into two stages. In the first or liquid-phase stage the operation is similar to that described above for the first stage of coal hydrogenation. About 0.2% of catalyst is distributed uniformly through the tar, and the mixture pumped with hydrogen at about 200 atmospheres pressure into a converter at 450° C. The throughput of the tar was 2 to 3 liters per hour per liter of reaction space. Their results show that stannous hydroxide is an inferior catalyst for the hydrogenation of both low- and high-temperature (of carbonization) tars. Small amounts (about 0.1%) of hydrochloric and hydriodic acid were much more effective, and a mixture of 0.1% each of molybdic acid and hydrogen iodide was most effective for converting tar to a middle oil boiling below 300° C. Storch and co-workers (*45*) also found that halogen-containing compounds were more effective than tin sulfide or molybdic acid.

The outstanding activity of tin compounds for the liquid-phase stage of coal hydrogenation and its rather mediocre performance with coal tar indicate that reactive groups are present in coal which form addition compounds with tin hydride or iodide, whereas such groups are not present to any large extent in coal tar.

HYDROGENATION AND CRACKING OF MIDDLE OILS

For the hydrogenation cracking of middle oils boiling below 300° C., catalysts such as pelleted molybdenum or tungsten disulfides are very active at comparatively low temperatures (375° to 400° C.). Combinations of FeS (85%) and WS_2 (15%) are more desirable than either alone, because less of the cyclic hydrocarbons are converted to naphthenes and paraffins. Thus the products from pure WS_2 using coal hydrogenation middle oil at 400° C. contained only 3% of aromatics and that from FeS alone, 27%; whereas that from 85% FeS + 15% SW_2 contained 66% aromatics (*30*). Recently activated clays plus about 10% of a hydrogenating catalyst such as WS_2, MoS_2, or FeS have been preferred for vapor-phase hydrogenation.

For efficient operation of these catalysts, it is desirable to remove all oxygen and nitrogen containing compounds by a relatively mild hydrogenation with WS_2 or MoS_2 catalysts before introduction over the "splitting" catalysts such as activated clay plus metal sulfides. It is also essential to introduce 1 to 2% (of the oil feed) of hydrogen sulfide to maintain the activity of these metal sulfide catalysts. It was thought that the presence of hydrogen sulfide prevented reduction of the catalyst to a lower sulfide or to the metal. Ferrous sulfide is thermodynamically stable, however, under the conditions of operation in the absence of hydrogen sulfide, and in this case at least it is likely that the beneficial action of hydrogen sulfide is of kinetic origin. It is conceivable that hydrogen sulfide acts as a hydrogen carrier and saturates cyclic olefins which might otherwise form high-boiling polymers and thus foul the catalyst surface.

In both the high-pressure hydrogenolysis of middle oils and in ordinary catalytic cracking of gas oil from petroleum at atmospheric pressure, a large fraction of the paraffins produced is branched-chain hydrocarbons. More data for comparison purposes are available for the isobutane to n-butane ratio than for the higher boiling hydrocarbons. In high-pressure hydrogenolysis of oil, the C_1 to C_4 fraction is usually about 80% butane, and the isobutane to n-butane ratio is about 4 to 1. It is possible by extensive recycling to convert middle oils largely to butane with this ratio of iso to normal. As the equilibrium ratio of iso- to n-butane is only about 1.0 in the temperature range 350–500° C., it is apparent that higher ratios must be of kinetic origin. Table VI summarizes available data for the catalytic cracking of pure compounds and of gas oil. The data for cyclohexane were obtained by Haensel and Ipatieff (*25*), for iso-octene by Thomas (*46*), for cetane and Decalin using an alumina-silica catalyst by the Standard Oil Company of Louisiana (*43*), for Decalin using an alumina-silica-zirconia catalyst by Block and Thomas (*5*), for gas oil in "fluid flow" catalytic cracking by Thomas and co-workers (*47*), and for gas oil in high-pressure hydrogenolysis by Imperial Chemical Industries (*31*).

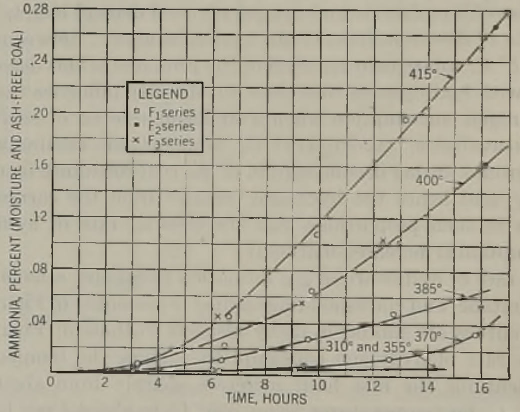
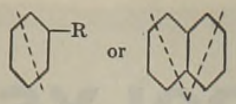


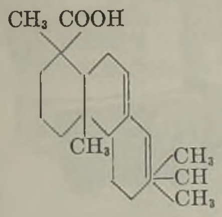
Figure 15. Rates of Ammonia Formation at Different Temperatures

Ratios of iso- to n-butane obtained from both cyclic and aliphatic hydrocarbons (compare iso-octene and cetane results with cyclohexane and Decalin results in Table VI) are higher than the equilibrium ratio, whereas most of the iso- to n-butene ratios are, with one exception, somewhat lower than the equilibrium values. In all the experiments of Table VI a considerable fraction of the liquid product was cyclic. It is apparent that cyclization reactions were prevalent. A possible explanation of the high iso- to n-butane ratios is that isoparaffins are formed during the cracking of any single ring structure having an alkyl group attached to it, or by the simultaneous rupture of two condensed rings:



In most of these decompositions the branched-chain olefin must be rapidly saturated by hydrogen transfer within the reaction complex on the catalyst surface. It is possible that complete cyclization is not essential. It may suffice to have adsorption on active patches on the catalyst surface in such fashion as to form a complex whose resonance with the final products will facilitate the production of the saturated paraffin and an aromatic in one step upon decomposition of the reaction complex. This mechanism helps to explain the fact that only a few per cent of naphthenes are found in the cyclic fraction of the products.

It is also of interest to note some recent results obtained by Charmbury and Wright (*8*) in studying the high-pressure hydrogenolysis of abietic acid:



The experiments were carried out in an alloy-steel rotating autoclave with no added catalyst. The iso- to *n*-butane ratios were 2.3, 4.2, and 6.3 at 400°, 425°, and 450° C., respectively. In Table VI the iso- to *n*-butane ratios decreased with increasing reaction temperature. In the decomposition of abietic acid the increase of this ratio with reaction temperature is probably associated with different temperature coefficients of the many possible modes of rupture of the condensed structure, higher temperatures favoring the rupture of the ring with the isopropyl group attached.

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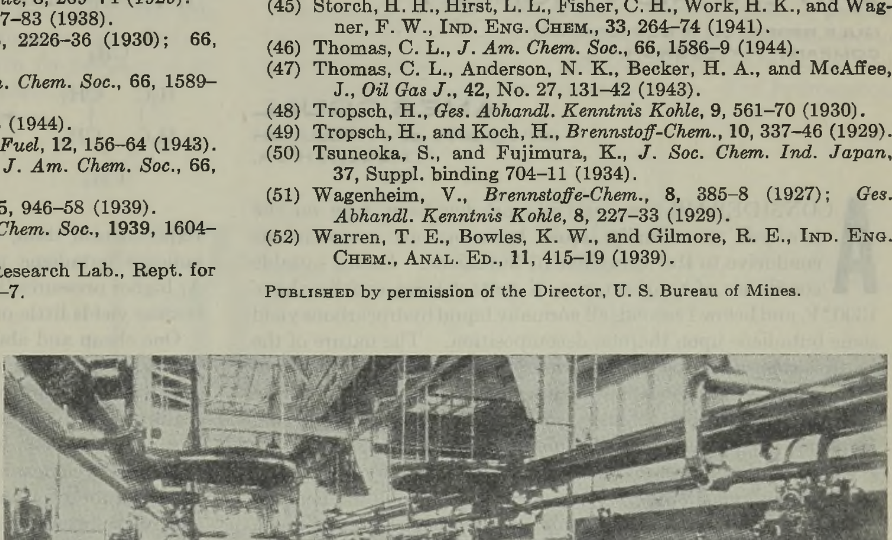
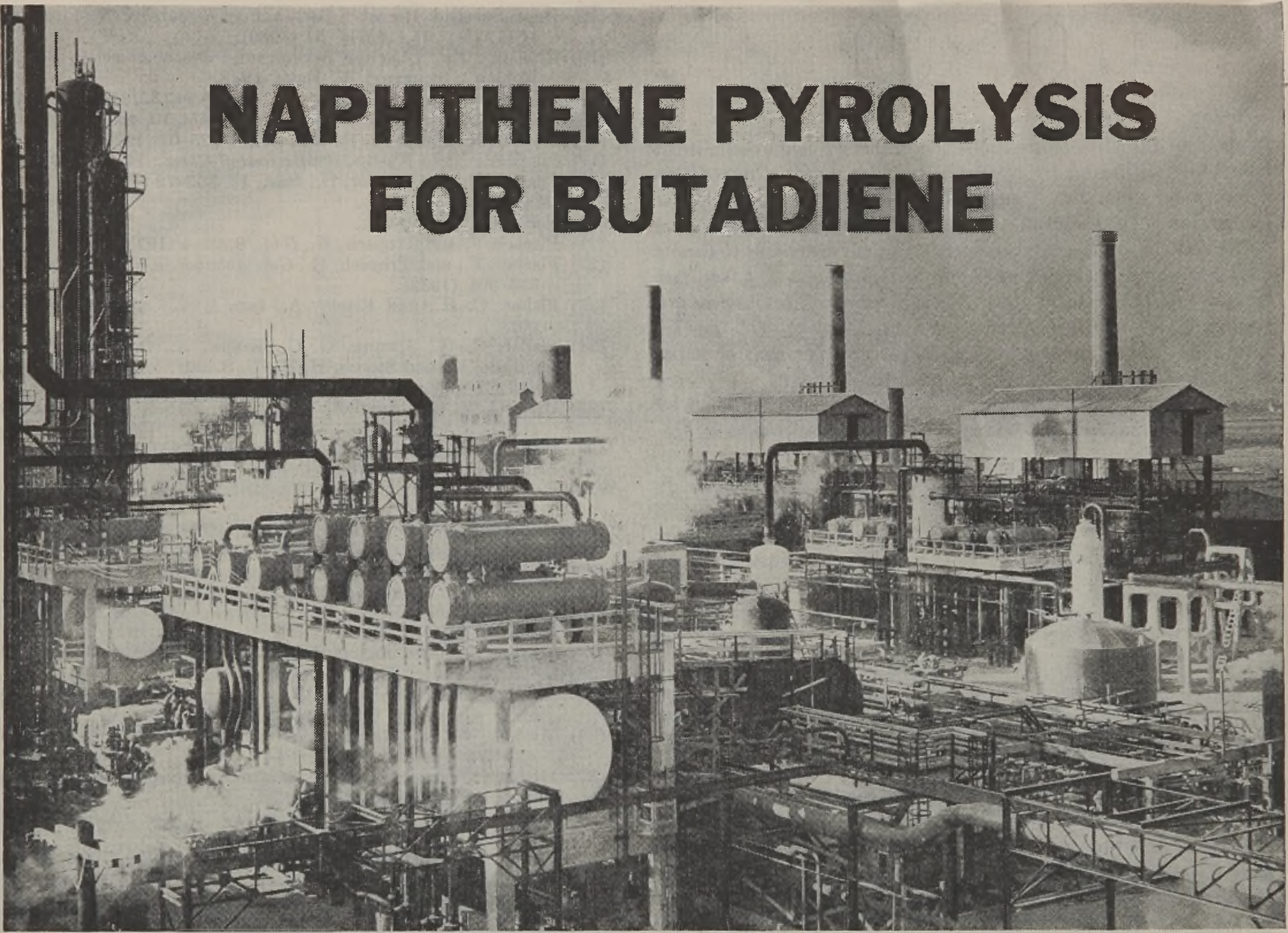


View of Fischer-Tropsch Plant Control Floor

[End of Symposium]

NAPHTHENE PYROLYSIS FOR BUTADIENE



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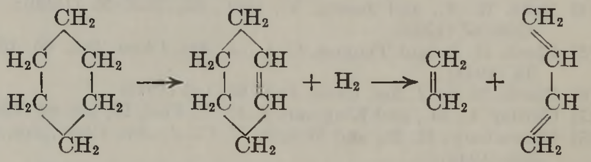
A CONSIDERABLE amount of work has been done on the pyrolysis of normally liquid hydrocarbons at conditions conducive to the formation of butadiene. Under suitable conditions of temperature and contact time, usually above 1300° F. and below 1 second, all normally liquid hydrocarbons yield some butadiene upon thermal decomposition. The nature of the hydrocarbon decomposed has a marked effect upon the yield of butadiene. Other conditions being equal, the yield of butadiene increases for different charge stocks in the order: aromatics, paraffins, olefins, naphthenes, unsaturated naphthenes. Considering the decomposition of normally liquid pure hydrocarbons, cyclohexene appears to give the highest yield of butadiene on thermal decomposition. Following in decreasing order of yield, other normally liquid pure hydrocarbons which give high yields of butadiene upon thermal cracking are: 3-methylcyclohexene, cyclohexane, ethylcyclohexane, methylcyclohexane, 1,4-, 1,2-, and 1,3-dimethylcyclohexanes, and decalin. If the compounds not readily available are eliminated from this list, cyclohexane appears to be the best of the normally liquid hydrocarbons for the production of butadiene by thermal cracking.

Considerable work has been done on the thermal decomposition of cyclohexane, and under proper conditions the reaction is reasonably clean-cut to yield hydrogen, ethylene, and butadiene (*1, 3, 4, 5*), presumably by the reaction:



Experimental data, as well as thermodynamic considerations, indicate butadiene production to be favored by low pressure. At higher pressures it has been shown that the pyrolysis of cyclohexane yields little or no butadiene (*2*).

One cheap and abundant source of cyclohexane is the C_6 fraction of a naphthenic petroleum. Such a fraction from a properly selected petroleum often contains more than 50% naphthenes. Unfortunately the naphthenes in this fraction are seldom cyclohexane exclusively, but invariably comprise methylcyclopentane as well as cyclohexane. Figure 1 shows the results of a precision fractionation of a naphthenic gasoline, and the large amount of methylcyclopentane as well as cyclohexane in the C_6 fraction can be seen from the refractive index curve. The boiling point and the refractive index at 20° C. are: for cyclohexane, 80.8° C. and 1.4262; for methylcyclopentane, 71.8° C. and 1.4098.

Little previous work has been reported on the pyrolysis of methylcyclopentane. Kazanskiĭ and Plate reported that at 650° C. the gaseous products consisted chiefly of propylene and some isobutylene (*3*). The two principal reactions appeared

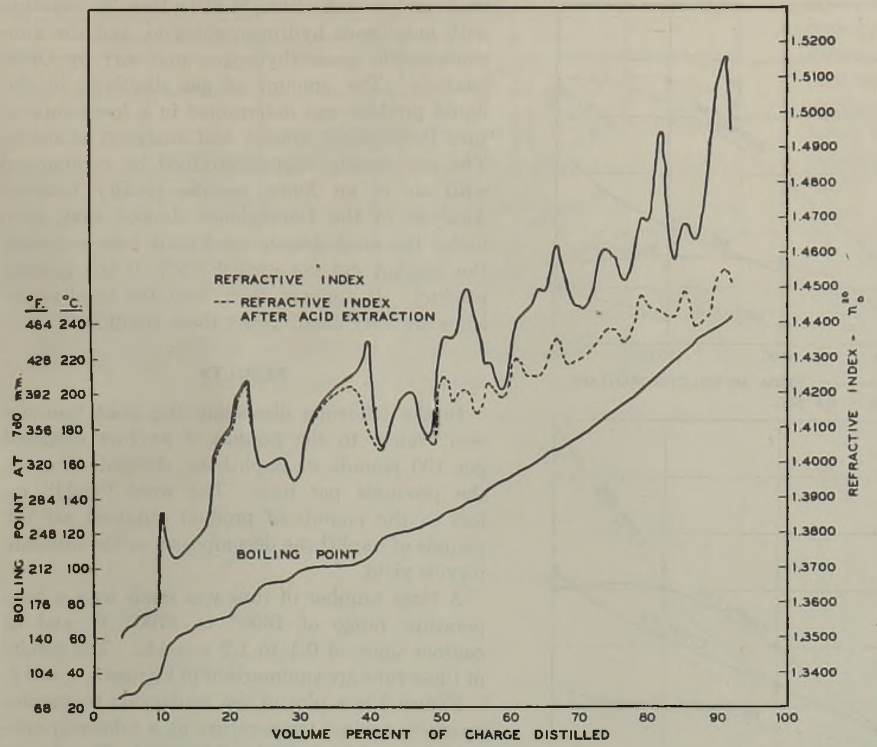


Figure 1. Precision Fractionation of a Naphthenic Straight-Run Gasoline

to be, first, splitting into two molecules of propylene and, second, splitting into a molecule of ethylene and a molecule of isobutylene.

This paper is concerned with a laboratory-scale investigation of the thermal noncatalytic decomposition of the common six-carbon naphthenes under conditions conducive to the formation of butadiene. The work was confined to ranges of temperature and contact time which give a maximum yield of butadiene. Each of these variables was studied independently so that peak yields of butadiene were obtained and optimum conditions thus established. The effect of a diluent was investigated by carrying out a series of thermal decompositions in the presence of approximately 4 moles of steam per mole of naphthene.

THE PYROLYSIS of the naphthenes, cyclohexane, and methylcyclopentane, has been studied over a range of temperature and contact times favorable to the formation of butadiene. Cyclohexane gives a good yield of butadiene, while methylcyclopentane is a relatively poor source. Maximum yields of butadiene from cyclohexane were obtained when temperature and contact time were regulated to give 35 pounds of 3-carbon and lighter compounds per 100 pounds of cyclohexane charged. . . . The picture shows the northwest portion of Neches Butane Products Company at Port Neches, Texas (courtesy, The Lummus Company)

OPERATION OF EQUIPMENT

Figure 2 is a diagram of the equi ment. Naphthene and water, when diluent was used, were fed from gradu ated separatory funnels into slurr pumps equipped with neoprene tube Slurry pumps normally deliver the fee with a pulsating flow. To eliminat this pulsation, which might have cause unevenness of flow through the reacto a valve was introduced into the lin beyond the pump, and a back pressur of about 5 pounds was maintained o the pump. The naphthene (and wate if used) was discharged into a Pyre glass vaporizer. The vaporizer was fille with 1/2-inch Berl saddles and sur rounded by an electrical heater. Th vapors passed out through an electri cally heated Pyrex tube, which acted a a preheater, to a Vitreosil quartz reac tion tube, 70 cm. long and 1.3 cm. insid diameter and having a volume of 93 c Three indentations, evenly spaced, wer made in the quartz tube and chromel alumel thermocouples inserted in them The quartz reaction tube was fitte into a 1-inch i.d. refractory combustio tube which was heated with a 2000 watt Nichrome winding. The tem perature was maintained so that, whe plotted against reaction tube length, the areas above an below the average temperature balanced. The highest tem perature which occurred near the middle of the tube was abou 15–30° C. above the average. The apparatus may yield som error in the absolute value of temperature; however, the tem perature differentials, from which the conclusions were drawn, ar accurate. At the exit end of the reaction tube, distilled wate was supplied at a constant rate of 70 ml. per minute by means o another slurry pump to act as a quench for the hot gases emitte from the reaction tube. The products were condensed by passin through Liebig condensers. The liquid product was collected i a cooled, jacketed receiver where the water was separated an continuously recycled to the quench pump. The hydrocarbo

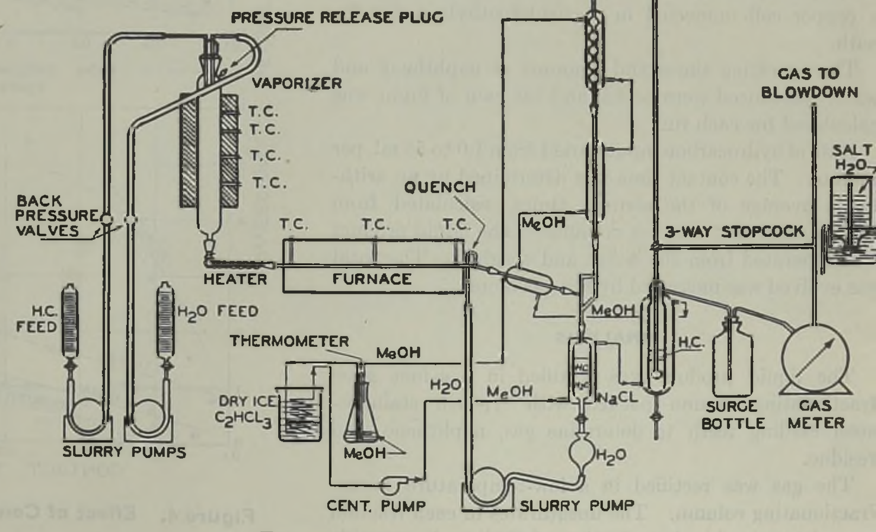


Figure 2. Diagram of Equipment

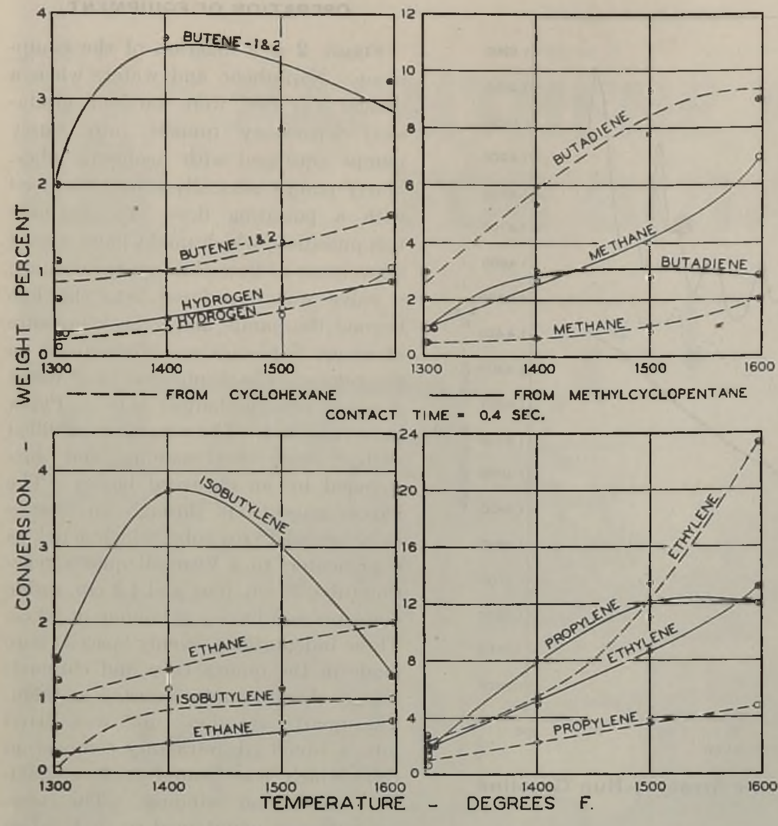


Figure 3. Effect of Temperature on Conversion to Gaseous Products

gases passed through a saturated salt water trap in a cooled jacketed receiver where, at higher reaction temperature or high flow rate, some hydrocarbon liquid condensed. The uncondensed gases passed through a gallon surge bottle into a wet-test gas meter for measurement. From there they either passed out the blowdown line or were switched to a gas bottle and collected over saturated salt water for analysis. The system was put together with ground-glass joints. A ground-glass joint with a sealed tube on the vaporizer held by rubber bands acted as a pressure release. The condensing system, cold trap, and jacketed receivers were connected in series, and cold methanol was circulated by means of a small centrifugal pump. The methanol was kept at 0–15° C. by circulation through a copper coil immersed in a trichloroethylene–dry ice bath.

The operating times and amounts of naphthene and water introduced were noted, and the rate of input was calculated for each run.

Rate of hydrocarbon input varied from 1.0 to 55 ml. per minute. The contact time was determined by an arithmetic average of the contact times, calculated from the entrance and exit gas volumes. The liquid product was separated from the water and weighed. The total gas evolved was measured by the gas meter.

ANALYSIS

The liquid product was rectified in a 4-foot glass fractionating column packed with $^1/_4$-inch stainless-steel carding teeth to determine gas, naphthene, and residue.

The gas was rectified in a low-temperature micro-fractionating column. The unsaturates in each fraction were determined by bromination—butadiene by reaction with maleic anhydride, isobutylene by reaction with anhydrous hydrogen chloride, and the non-condensable gases (hydrogen and air) by Orsat analysis. The amount of gas dissolved in the liquid product was determined in a low-temperature Podbielniak column and analyzed as above. The gas density was determined by comparison with air in an Acme specific gravity balance. Analysis of the 1-acetylenes showed that, even under the most drastic conditions here reported, the amount did not exceed 0.5% of the gaseous product. It appears, then, that the total acetylenes are very small under these conditions.

RESULTS

In the following discussion the word "conversion" refers to the pounds of product obtained per 100 pounds of naphthene charged—that is, the products per pass. The word "yield" refers to the pounds of product obtained per 100 pounds of naphthene decomposed, or the ultimate recycle yield.

A large number of runs was made over a temperature range of 1300° to 1700° F. and at contact times of 0.1 to 1.2 seconds. The results of these runs are summarized in Figures 3, 4, and 5.

Figure 3 is a plot of the conversion to gaseous products against temperature at a relatively constant contact time of 0.4 ± 0.1 second. The gaseous products from both cyclohexane and methylcyclopentane are presented on the same plot to emphasize the difference in decomposition of the two naphthenes. Under these conditions the pyrolysis products of both naphthenes were highly olefinic. Methane and a small amount of ethane were the only paraffins formed. The 3-carbon and 4-carbon fractions

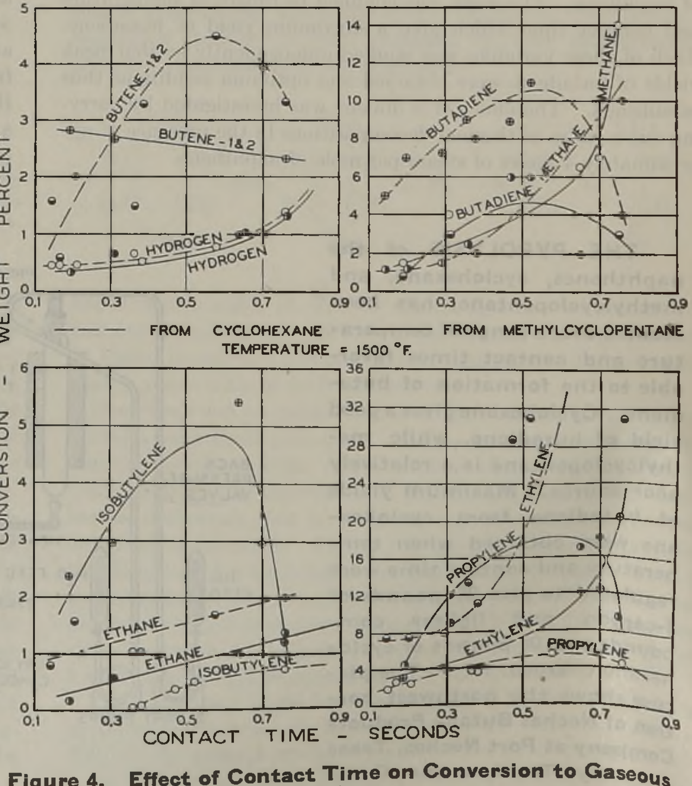


Figure 4. Effect of Contact Time on Conversion to Gaseous Products

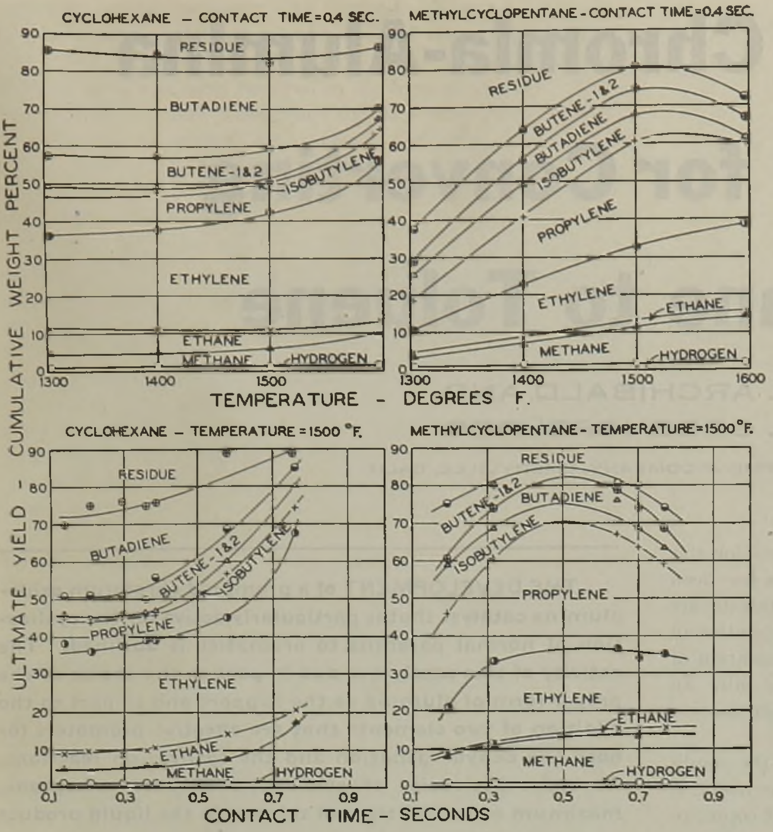


Figure 5. Ultimate Yield of Gaseous Products on a Cumulative Basis

were always 100% olefinic over this range of conditions. Figure 3 shows that cyclohexane cracks predominantly to hydrogen, ethylene, and butadiene. From methylcyclopentane, however, no such simple cracking reaction appears to take place. Propylene is the most abundant product except at the highest temperature, where the C_3 and C_4 products as well as the methylcyclopentane appear to be decomposing. This would indicate considerable cracking of the methylcyclopentane molecule into two C_3 molecules. The C_4 products are about equally divided among 1- and 2-butenes, butadiene, and isobutylene, an indication that carbon-carbon fission takes place anywhere in the methylcyclopentane molecule. The fact that 1- and 2-butenes plus butadiene exceed isobutylene is in accord, since methylcyclopentane can be split in several ways to yield a normal 4-carbon chain, but in only one way to form isobutylene. The considerable quantity of methane produced from methylcyclopentane even at relatively mild conditions indicates cracking to C_1 fragments as well.

At 1600° F. the gaseous product appears to be resolving into hydrogen, methane, and ethylene only; the other gaseous products tend to diminish. At longer contact times this is even more pronounced, as Figure 4 shows. Figure 4 is analogous to Figure 3 except that the conversion to gaseous products is plotted against contact time, the temperature being held constant at about 1500°F. The similarity in the shape and trends of the curves of Figure 4 and Figure 3 shows that increased temperature and lengthened contact time have essentially the same effect upon the pyrolysis products.

Figure 5 shows the ultimate yield of gaseous products *vs.* temperature and contact time plotted on a cumulative basis. Thus, the distance from the abscissa to the upper butadiene or 1- and 2-butene line represents the total gaseous product. Since the curves are plotted on a weight rather than a volume or molar basis, the amount of hydrogen is not readily apparent. The data show, however, that hydrogen comprises 15 to 30 mole per cent of the gaseous product. The residue shown on Figure 5 represents all the liquid or solid products except the original naphthene. It includes all products from the light liquids to the heavy tars and coke. Thus, in methylcyclopentane pyrolysis, the minimum residue observed at about 1500° F. or 0.5-second contact time merely denotes maximum gasification at those conditions. At the more drastic conditions methylcyclopentane showed an increase in the amount of tar and coke formation, whereas cyclohexane tended toward more complete gasification. For both naphthenes above 1500° F. the coke lay-down became appreciable; below that temperature, except at the longest contact times, coke formation was not an important factor.

The use of diluent was investigated by cracking the hydrocarbon in the presence of 4 moles of steam. Little difference in results was observed between the runs with and without steam. A small increase in the optimum amount of butadiene from cyclohexane was noted. The yield was about 12 pounds per 100 pounds of charge with steam and about 9 pounds in the absence of a diluent. The optimum conditions are the same, either with or without steam, a maximum conversion to butadiene being obtained at 1500–1600° F. and 0.3–0.5 second contact time. The advantage of using a diluent appears to be principally as a means of attaining the high temperature quickly and the desired short contact time.

A relation between contact time and temperature may be obtained by considering the depth of cracking—namely, the pounds of C_3 and lighter products per 100 pounds of charge. The data show that a maximum amount of butadiene is produced from cyclohexane when the conditions of temperature and contact time are so regulated as to produce about 35 pounds of C_3 and lighter per 100 pounds of cyclohexane charged, regardless of whether a diluent is used.

The results of the pyrolysis of cyclohexane indicate that shorter contact times favor a higher percentage of butadiene in the C_4 fraction. They also show that, at constant contact time in the temperature range 1400–1600° F., lower temperatures yield higher percentages of butadiene in this fraction. These statements apply only to the quality of the C_4 fraction, not to the quantity of this fraction or actual amount of butadiene produced.

ACKNOWLEDGMENT

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Presented in two parts (entitled "Pyrolysis of Cyclohexane" and "Pyrolysis of Methylcyclopentane") before the Division of Industrial and Engineer ing Chemistry at the 107th and 108th Meetings of the American Chemica Society in Cleveland, Ohio, and New York, N. Y., respectively. Base upon a thesis submitted by George L. Sumner, Jr., to the faculty of the Uni versity of Pittsburgh, in partial fulfillment of the requirements for th degree of Master of Science in Chemical Engineering.

Promoted Chromia-Alumina Catalyst for Converting *n*-Heptane to Toluene

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THE DEVELOPMENT of a promoted chromium oxide-alumina catalyst that is particularly active for the cyclization of normal paraffins to aromatics is outlined. The activity of this catalyst is due in part to the choice of the proper form of alumina as the support and in part to the addition of two elements that are effective promoters for both the dehydrogenation and the cyclization reactions. At high efficiencies of conversion of pure *n*-heptane, maximum concentrations of toluene in the liquid product exceeding 80% can be attained with the catalyst; the average is about 75% over a period of 10 hours.

THE activity of chromium oxide–alumina catalysts for the dehydrogenation and cyclization of hydrocarbons has been treated extensively in the literature. Such catalysts are ordinarily made by one of two methods: coprecipitation of the hydroxides of chromium and aluminum or impregnation of alumina with a solution of chromic acid or a chromic salt. In both cases the material is subjected to subsequent calcination for expulsion of water and volatile acids.

The impregnation method is simpler; and under the conditions of preparation and with the promoters to be discussed, it results in catalysts equaling or exceeding in activity the coprecipitated chromia-alumina catalysts. All catalysts reported here were made by the impregnation method.

Chromia-alumina catalysts are particularly active for cyclization of paraffins to aromatics [first reported by Moldavskiĭ and Kamusher (*3*) and sometimes called "dehydrocyclization" or "aromatization"], as well as the simple dehydrogenation of naphthenes of the cyclohexane type to the corresponding aromatics, at substantially atmospheric pressure. In general, any catalyst that has high cyclizing activity is also an active catalyst for naphthene dehydrogenation, although the reverse is not always true. It has been found, however, that the paraffin cyclization reaction is much more sensitive to catalyst composition and that side reactions or intermediate products have a more harmful effect on the cyclization activity than on the dehydrogenation activity of a catalyst. In the development of the promoted chromia-alumina catalyst, the cyclization activity was therefore chosen as the criterion by which catalyst preparations were judged, although the activity of some preparations for dehydrogenation of naphthenes was also tested.

For these tests the following two commercially obtainable hydrocarbons were used. Further purification was unnecessary.

n-HEPTANE (A.S.T.M. primary knock-testing standard; California Chemical Company):

Boiling point (760 mm.), ° C.	98.41
Freezing point, ° C.	−90.68
Specific gravity, d_4^{20}	0.6836
Refractive index, n_D^{20}	1.38769

METHYLCYCLOHEXANE (Barrett Company):

Boiling point	2% below 100° C., none above 101°
Specific gravity, d_4^{20}	0.7688
Refractive index, n_D^{20}	1.4232
Specific dispersion	97.5
Aromatics, olefins	Nil

Activity tests were ordinarily made under the following conditions. In the presentation of test results, any deviations from these standard conditions are indicated: 490° C.; atmospheric pressure; catalyst bed, 16 inches long, $^5/_8$ inch in diameter, with axial thermowell; catalyst volume, 69 cc.; liquid feed rate, 25 ml. per hour; liquid hourly space velocity (L.H.S.V.), 0.36 volume per volume of catalyst space per hour.

The apparatus for the cyclization and dehydrogenation tests consisted of a reactor tube about 2 feet long, of $^1/_2$-inch iron pipe size, 18–8 chrome–nickel steel tubing with an axial thermowell. Surrounding the reactor was a heavy Meehanite block for heat distribution. Heat was supplied by a cylindrical electric furnace around the block. The furnace was controlled in sections so that the temperature profile through the catalyst bed did not deviate from the average temperature by more than ±1° C. Accessory apparatus included condenser, receiver, outlet gas meter, purge gas flow indicator, and temperature controlling and recording instruments.

CATALYST SUPPORT

The literature demonstrates that porous alumina is a good support for chromic oxide and certain other dehydrogenation or cyclization catalysts. The present work has confirmed this, and while no exhaustive investigation of possible supporting media has been made, alumina is by far the best of those tried. Silica in several forms and in combination with alumina has also frequently been recommended as support for various catalytic materials. However, chromia catalysts prepared from such supports were of low activity. The present work was therefore largely confined to the use of alumina supports.

Alorco Grade A activated alumina (from Aluminum Ore Company) had been known to be one of the better supports for chromia-alumina catalysts of the impregnated type. It was found in the course of this investigation, however, that if this alumina was calcined under suitable conditions prior to impregnation (*1*), a considerable increase in the activity of the resulting chromia-alumina catalysts was realized. X-ray investigation showed that the calcination had converted the Alorco alumina[1], which was largely α-$Al_2O_3.H_2O$, to γ-Al_2O_3. Catalysts prepared directly upon a support received in the form of gamma alumina pellets from Harshaw Chemical Company were about equal to those made from calcined Alorco Grade A alumina, and were not further improved by calcination.

Both α-$Al_2O_3.H_2O$ and γ-Al_2O_3 alone were tested as cyclization catalysts, but were found to have no activity.

The conversions[2] of *n*-heptane to toluene with chromia-alumina catalysts on calcined and uncalcined Harshaw and Alorco aluminas are compared in Figure 1. The experimental points for these catalysts, with the exception of the one made from uncalcined Alorco alumina, lie virtually on a single curve. Since the upper curve corresponds to catalyst supported on γ-Al_2O_3 and the lower curve to one on α-$Al_2O_3.H_2O$, a clear distinction between the two types is evident. The differentiation shown in Figure 1 is magnified when promoters are added; for example, Figure 2 compares cyclization tests on two promoted catalysts differing only in the form of alumina. The calcining process has increased the maximum percentage concentration of toluene in the liquid product by about twenty units. The experimental points are omitted from these and other curves of this type. However, the agreement between the points and the curves drawn is at least as good as that shown in Figure 1. It is interesting to note in Figure 1 the disappearance of the initial "induction period" when γ-Al_2O_3 is the catalyst support. Figure 2 shows that the use of cerium and potassium as promoters for such a catalyst causes the induction period to reappear. The importance of the structural form of the alumina in chromia-alumina catalysts for dehydrogenation of cyclohexane-type naphthenes is demonstrated by Figure 3 for the unpromoted catalysts and methylcyclohexane. The effect of the promoters is not nearly so marked as in the cyclization reaction but is still evident.

Continued calcination of γ-Al_2O_3 results in the conversion of some of it to the α-modification (corundum, not to be confused with the α-monohydrate) which reduces the activity of the finished catalyst. When pure corundum was used as the support for a promoted chromia-alumina catalyst, virtually no *n*-heptane was converted to toluene.

The influence of time and temperature of calcination of Alorco alumina on the activities of the finished catalysts is shown in an approximate way by Figure 4. The plotted points indicate whether the maximum concentration of toluene in the liquid product is more or less than 80% by weight and whether the deficiency is caused by over- or undercalcination of the alumina. From this definition, the curves drawn between the plotted points to delimit approximately the optimum conditions for calcination are shown primarily as useful guides to preparation of the alumina support.

To obtain the full effect of the γ-alumina, it is imperative that the alumina be in this crystalline form prior to impregnation. It appears that the particular crystalline structure of the alumina at the time of impregnation influences the ultimate physical nature and disposition of the chromic compound with which it is impregnated, which in turn determine the activity of the finished catalyst. The exact catalyst structure remains obscure, however, since it is not susceptible to resolution by methods now available.

X-ray and electron diffraction studies (made by A. E. Smith of these laboratories) indicate that γ-Al_2O_3 in thin films is slowly hydrated in the presence of water vapor, even at room temperature. The hydration is slow at ordinary temperatures, but at higher temperatures it might become appreciable. A similar change might also be expected in the extensive surface of larger particles of porous γ-alumina. Therefore, it is desirable that precautions be taken to minimize this possibility.

While the work with Harshaw and Alorco aluminas is exemplified here, other commercial porous aluminas have proved satisfactory as long as they were in the gamma form when impregnated with chromium.

CHROMIUM

The active ingredient in the cyclization catalyst is ordinarily considered to be Cr_2O_3. However, small proportions of other

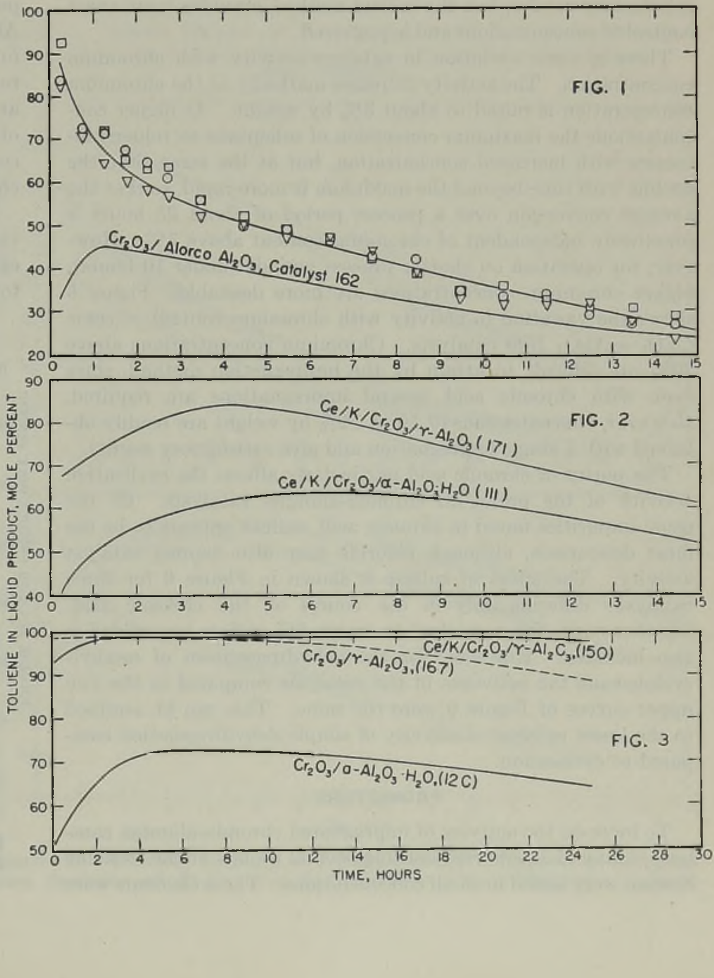

Figure 1. Effect of Calcining Alumina for 6 Hours at 700° C. on Cyclization Activity of Catalysts with *n*-Heptane as Feed

○ Cr_2O_3–Harshaw Al_2O_3 (catalyst 163)
▽ Cr_2O_3–calcined Harshaw Al_2O_3 (catalyst 168)
☐ Cr_2O_3–calcined Alorco Al_2O_3 (catalyst 167)

Figure 2. Comparison of Two Forms of Alumina as Supports for Cerium-Potassium-Chromia-Alumina Catalysts with *n*-Heptane as Feed

Figure 3. Comparison of Catalysts for Dehydrogenation of Methylcyclohexane

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[1] Because of the confused state of the nomenclature on oxides of aluminum and their hydrates, the forms discussed in this paper are identified as follows: α-$Al_2O_3.H_2O$ is böhmite; γ-Al_2O_3, the anhydrous form obtained by moderate heating of böhmite, gibbsite, or bayerite; α-Al_2O_3, corundum, the natural or synthetic high-temperature form.

[2] As discussed later, weight losses to side reactions are rather constant. Hence, true conversion of heptane to toluene is parallel to per cent toluene in liquid product, which is informally called "conversion" in the text for brevity and then only in a relative sense.

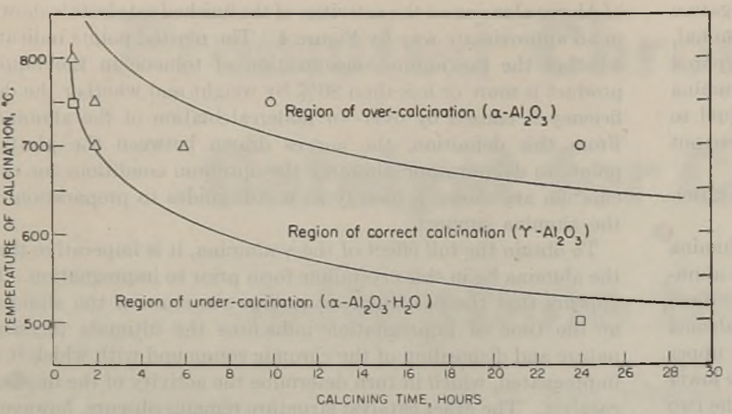


Figure 4. Calcining Conditions for Alorco Grade A Activated Alumina Used in Cerium-Potassium-Chromia-Alumina Catalysts for Cyclization of *n*-Heptane

△ Correctly calcined, maximum conversion more than 80%.
☐ Undercalcined, maximum conversion less than 80%.
○ Overcalcined, maximum conversion less than 80%.

chromium oxides may contribute to the activity, and we refer to the chromium component simply as Cr_2O_3 (or chromia) for lack of knowledge of its exact nature and crystalline form.

Equally active catalysts have been obtained by impregnating alumina with either chromic acid or chromic nitrate solutions. Less active catalysts have been obtained when ammonium dichromate was used. Chromic nitrate has the disadvantage of being insufficiently soluble in water to produce the desired concentration on the catalyst with a single impregnation. Chromic acid can be applied either by soaking the alumina in an excess of solution or by adding the desired quantity of chromic acid in just enough water to be completely absorbed. Either method gives satisfactory results, but the second method provides more exact control of concentrations and is preferred.

There is some variation in catalyst activity with chromium concentration. The activity increases markedly as the chromium concentration is raised to about 3% by weight. At higher concentrations the maximum conversion of *n*-heptane to toluene increases with increased concentration, but at the same time the decline with time beyond the maximum is more rapid, so that the average conversion over a process period of about 25 hours is practically independent of chromium content above 3%. However, for operation on shorter process periods (under 10 hours), higher chromium concentrations are more desirable. Figure 5 shows the variation in activity with chromium content of some Cr_2O_3-α-$Al_2O_3 \cdot H_2O$ catalysts. Chromium concentrations above 20% are difficult to attain by the impregnation method, since even with chromic acid several impregnations are required. However, concentrations of 10 to 14% by weight are readily obtained with a single impregnation and give satisfactory results.

The purity of chromic acid particularly affects the cyclization activity of the promoted chromia-alumina catalysts. Of the usual impurities found in chromic acid, sulfate appears to be the most deleterious, although chloride may also depress catalyst activity. The effect of sulfate is shown in Figure 6 for three catalysts differing only in the source of the chromic acid. Another curve for a catalyst to which 5% sulfate was added is also included. However, for the dehydrogenation of methylcyclohexane the activities of the catalysts compared in the two upper curves of Figure 6 were the same. This can be ascribed to the lesser catalyst sensitivity of simple dehydrogenation compared to cyclization.

PROMOTERS

To increase the activity of impregnated chromia-alumina catalysts, many elements representing several groups of the Periodic System were added in small concentrations. These elements were added in the form of water-soluble salts and were subsequently converted to the oxide or elemental form, depending on the behavior of the compound when first dried in air and then exposed to the pretreating and testing conditions. Of the elements tested, palladium and platinum in concentrations of about 0.1% by weight had the greatest initial effect on Cr_2O_3-α-$Al_2O_3 \cdot H_2O$ catalysts. There was no induction period, and the initial product contained about 85% toluene; both results were similar to those obtained with the unpromoted Cr_2O_3-γ-Al_2O_3 catalyst. The conversion dropped rapidly, however, until after about 5 hours no further advantage of the promoter was apparent. Tests with platinum-promoted catalysts indicated that the concentration chosen, 0.1% by weight, was about the optimum. Cerium, cobalt, and ruthenium, in concentrations of 0.5% by weight, eliminated the induction period found for the unpromoted Cr_2O_3-α-$Al_2O_3 \cdot H_2O$ catalyst, but gave an initial toluene concentration of only 50%. Columbium, gold, iron, nickel, thorium, uranium, zinc, and zirconium in concentrations of 0.5% by weight had no apparent effect on the shape or position of the conversion curve.

The first group of the Periodic System was considered separately, and significant results were obtained with the alkali metals (as oxides) in the order of their atomic weights. Lithium was a definite depressor. Sodium was either a weak depressor or a weak promoter, depending on its concentration. Potassium was a strong promoter within a certain molal concentration range. Cerium in the same range was even better than potassium. Rubidium was not tested. Curves showing the results of cyclization runs with promoted Cr_2O_3-γ-Al_2O_3 are given in Figure 7. Sodium was tested with Cr_2O_3-α-$Al_2O_3 \cdot H_2O$, so that results are not directly comparable. Figure 8 shows the effect of adding about 1% potassium by weight on the cyclization activity of Cr_2O_3-γ-Al_2O_3 catalyst (167 and 118). Promoter concentrations were found to have more significance when expressed in their molal ratio to chromium, since the highest conversions were obtained at a constant molal ratio of promoter to chromium. The data of Figure 9 for the variation in conversion with the potassium content of the catalyst are given on this basis, although the chromium concentration was about 11% by weight in every case.

Of the useful promoters in the other periodic groups, cerium (as oxide) had the characteristic, along with a few of the other elements tested, of eliminating the induction period ordinarily found with Cr_2O_3-α-$Al_2O_3 \cdot H_2O$ catalysts. On the other hand,

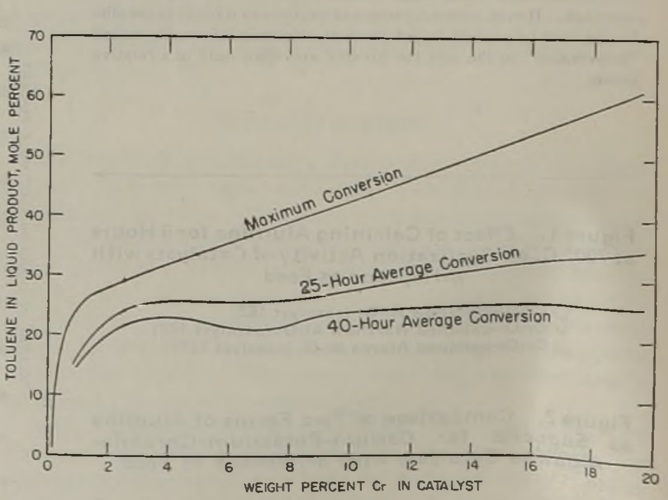


Figure 5. Influence of Chromium Content on Cyclization Activity of Cr_2O_3-α-$Al_2O_3 \cdot H_2O$ Catalysts with *n*-Heptane as Feed

when cerium is added to a potassium–Cr_2O_3–α-$Al_2O_3.H_2O$ catalyst, it does not have this effect but does increase the over-all catalyst activity appreciably (Figure 10). Finally, the same general improvement is observed when cerium is added to the highly active potassium–Cr_2O_3–γ-Al_2O_3 catalyst, as the two upper curves of Figure 8 show. These results led to the selection of catalyst 171 as the best cyclization agent available. Cerium, like potassium, also has an optimum concentration which is between about 0.5 and 1%, although it is not very critical.

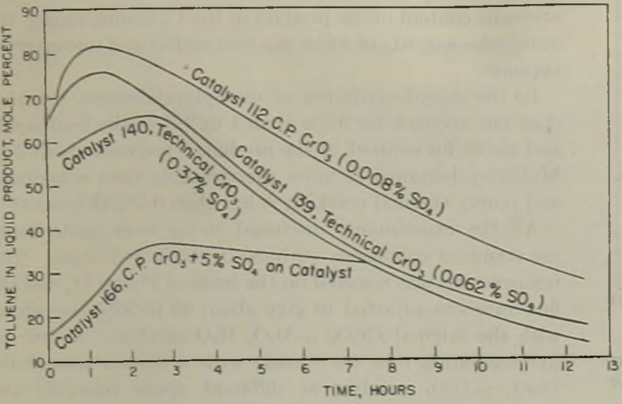


Figure 6. Effect of Sulfate on Cyclization Activity of Cerium–Potassium–Cr_2O_3–γ-Al_2O_3 Catalysts with *n*-Heptane as Feed

Technical grades of cerium oxide have been tested and found to be equal to the C.P. cerium nitrate used, although the concentration of other rare earths amounts to some 20% of the mixed oxides. It may be mentioned that, while platinum has shown some desirable characteristics as a promoter for Cr_2O_3–α-$Al_2O_3.H_2O$ catalysts, it has no apparent value when added to potassium–Cr_2O_3–α-$Al_2O_3.H_2O$ catalysts or as a component of Cr_2O_3–γ-Al_2O_3 catalysts. Although not tested in a potassium–Cr_2O_3–γ-Al_2O_3 catalyst, the same negative result is anticipated.

The foregoing has summarized the development of a rugged and inexpensive catalyst designed particularly for the cyclization of suitable aliphatic hydrocarbons to aromatics (*2*). In respect to percentage conversion of *n*-heptane to toluene over process periods of several hours, we believe it surpasses any catalyst described in the literature. The cerium–potassium–Cr_2O_3–γ-Al_2O_3 catalyst is very effective for the simple dehydrogenation of cyclohexane homologs and can be regenerated (removal of carbon deposit) by controlled combustion with air.

Compositions of the catalysts discussed are summarized in Table I. Their compositions were determined as follows: Alumina, as specified in Table I, was impregnated with a solution of chromic acid or salt and dried. A sample was analyzed for chromium and for loss on ignition to constant weight at 1000° C. The concentration of element Cr in the ignited material was then accurately known. Weighed quantities of the promoters were added to the dried material, and their concentrations calculated to an ignited basis by using the value for the loss on ignition determined on the original chromia-alumina, and computing the alkali metals as M_2O and cerium as CeO_2. The sulfate in catalyst 166 was added to material of the composition specified; that shown for other catalysts was present as impurity in the chromic acid and is accounted for in the stated metal percentages.

PREPARATION OF CATALYST

The activity of the promoted catalyst is not affected by small changes in concentration of components or by minor alterations in the preparative procedure. The following can therefore be considered as a representative method capable of variation within reasonable limits.

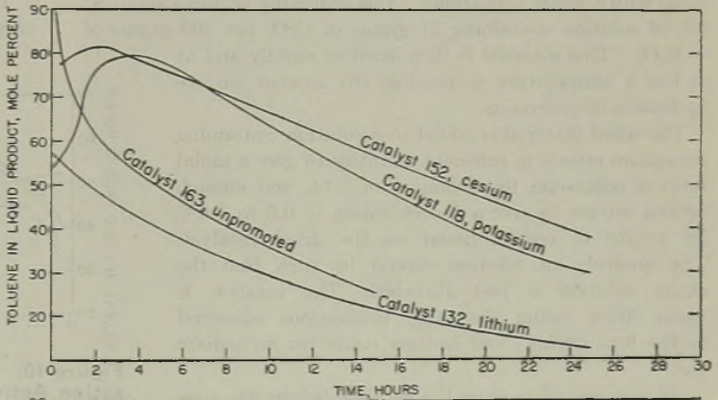
MATERIALS. Alumina must be in the gamma form, at least until the added CrO_3 (or soluble chromium salt) has been converted to an insoluble state. α-$Al_2O_3.H_2O$ can be converted to γ-Al_2O_3 by calcining as previously described (3 hours at 750° C.

Table I. Compositions of Catalysts

Catalyst No.	Composition (Wt. % of Elements)
12C	13.7 Cr–α-$Al_2O_3.H_2O$
44	0.59 Ce–10.6 Cr–α-$Al_2O_3.H_2O$
61	1.0 K–10.6 Cr–α-$Al_2O_3.H_2O$
111	0.78 Ce–1.56 K–13.7 Cr–α-$Al_2O_3.H_2O$
112	0.57 Ce–1.14 K–11.1 Cr–γ-Al_2O_3 (sulfate, 0.008% of CrO_3)
118	1.14 K–11.1 Cr–γ-Al_2O_3
132	0.217 Li–12.5 Cr–γ-Al_2O_3
139	0.56 Ce–1.11 K–10.8 Cr–γ-Al_2O_3 (sulfate, 0.062% of CrO_3)
140	0.57 Ce–1.14 K–12.0 Cr–γ-Al_2O_3 (sulfate, 0.37% of CrO_3)
150	0.71 Ce–1.18 K–11.3 Cr–γ-Al_2O_3
152	3.4 Cs–11.3 Cr–γ-Al_2O_3
162	12.2 Cr–Alorco Al_2O_3 (α-$Al_2O_3.H_2O$)
163	10.7 Cr–Harshaw Al_2O_3 (γ-Al_2O_3)
166	0.71 Ce–1.18 K–11.3 Cr–γ-Al_2O_3 (sulfate, 5.0% of catalyst)
167	10.6 Cr–calcined Alorco Al_2O_3 (γ-Al_2O_3)
168	11.0 Cr–calcined Harshaw Al_2O_3 (γ-Al_2O_3)
171	0.67 Ce–1.11 K–10.6 Cr–γ-Al_2O_3

Figure 7. Alkali Metals as Promoters on Cr_2O_3–γ-Al_2O_3 Catalyst

12% Cr on γ-Al_2O_3 plus 0.028 mole of alkali metal per 100 grams catalyst; feed, *n*-heptane.



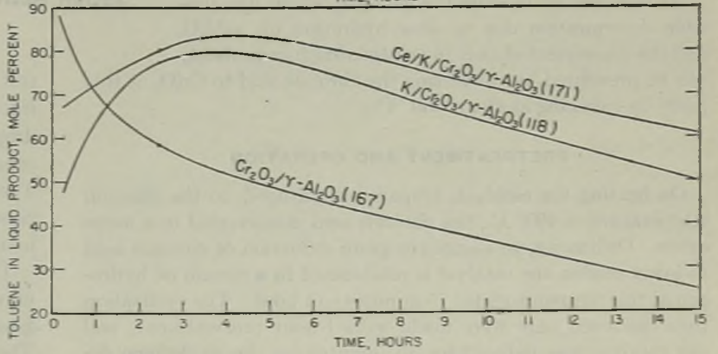


Figure 8. Effect of Cerium and Potassium Promoters on Cyclization Activity of Cr_2O_3–γ-Al_2O_3 Catalysts with *n*-Heptane as Feed

is satisfactory). α-$Al_2O_3.3H_2O$ can be used in the same fashion after conversion to α-$Al_2O_3.H_2O$.

Chromic acid (CrO_3) is the most satisfactory source of chromium. For use in cyclization catalysts, a C.P. grade or high-quality technical grade containing less than about 0.01% sulfate should be used. For dehydrogenation of naphthenes, more sulfate can be tolerated, although the upper limit has not been determined.

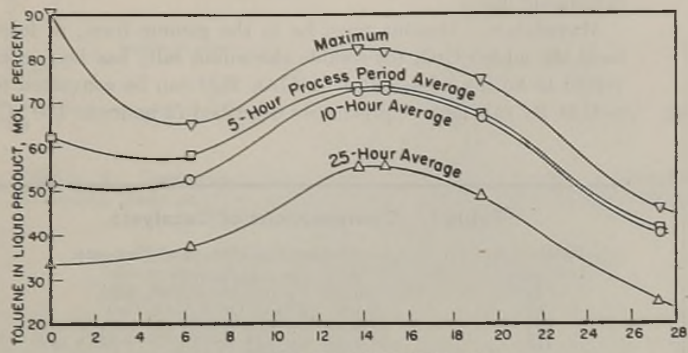


Figure 9. Effect of Potassium Concentration on Cyclization Activity of Potassium–Cr_2O_3–γ-Al_2O_3 Catalysts with *n*-Heptane as Feed

Potassium nitrate of C.P. grade has been used in most of the promoted catalysts. Potassium hydroxide can also be used as promoter but has not proved so effective as the nitrate. Cerium has been employed with equal effectiveness, both as C.P. cerium nitrate and as a nitric acid solution of technical cerium oxide (80% CeO_2).

METHOD. A weighed quantity of γ-Al_2O_3 is added at room temperature to chromic acid solution containing about 11% of the weight of the alumina as chromium and sufficient water so that the entire solution is absorbed, leaving the alumina particles with a moist appearance; this ordinarily requires about 42 ml. of solution containing 21 grams of CrO_3 per 100 grams of γ-Al_2O_3. This material is then dried as rapidly and at as low a temperature as possible (to prevent surface hydration of γ-alumina).

The dried material is added to a solution containing potassium nitrate in sufficient quantity to give a molal ratio of potassium to chromium of 0.14, and enough cerium nitrate to give a concentration of 0.5 to 1.0% by weight of cerium based on the dried catalyst. The quantity of solution should be such that the entire solution is just absorbed. The catalyst is again dried (using the same precautions observed in the first drying) and is then ready for immediate use.

(If it is desired to store the catalyst before use, possible deterioration due to slow hydration of γ-Al_2O_3 and the consequent change in crystal structure probably can be prevented by converting the chromic acid to Cr_2O_3 at this point by calcining at about 500° C.)

PRETREATMENT AND OPERATION

On heating the catalyst, prepared as outlined, to the reaction temperature of 490° C., the chromic acid is converted to a lower oxide. Ordinarily, to assure complete reduction of chromic acid to lower oxides, the catalyst is maintained in a stream of hydrogen at this temperature for 15 minutes to 1 hour. The cyclization runs discussed here were made with 1-hour pretreatment, and the catalyst was reduced for 15 minutes for the naphthene dehydrogenation runs.

There is invariably a small amount of cracking when *n*-heptane is cyclized over Cr_2O_3–Al_2O_3 type catalysts at 490° C. and 1 atmosphere. This cracking is ordinarily sufficient to account for a loss of about 2% of the feed as hydrocarbons below C_3, and an additional 5 to 10% from C_3 to C_6 as well as 1 or 2% as carbon deposited on the catalyst. (Purely thermal cracking at 490° C. has been found to account for a loss of about 3.5% of the *n*-heptane fed, as shown in Figure 11.) The efficiency of the cyclization will, in general, fall in the range 80 to 90% for toluene concentrations in the liquid product above about 40%. The curves already discussed (Figures 1, 2, 5–10) indicate the aromatic content of the product in the C_7 boiling range; the remainder consists of a few per cent olefins and unconverted heptane.

In the dehydrogenation of methylcyclohexane, cracking does not account for more than 1 or 2% of the feed stock, and the olefin content of the product is not over about 1%. Methylcyclohexane is more thermostable than *n*-heptane, and purely thermal cracking is less than 0.5% (Figure 11).

All the experiments discussed so far were made under the standard conditions outlined in the introduction. The temperature was selected on the basis of Figure 11, and the flow rate was adjusted to give about 40 to 50% conversion with the original Cr_2O_3–α-$Al_2O_3.H_2O$ catalyst. A few dehydrogenation runs were made with a cerium–potassium–Cr_2O_3–γ-Al_2O_3 catalyst at different space velocities and temperatures to show their effect on conversion and rate of decline of activity. The results are given in Figure 12. Increasing the temperature above 490° C. increases the cracking and, consequently, the rate of decline due to coke deposition. With higher space velocities, conversions are lower unless the temperature is raised to increase the reaction rate. Temperature and space velocity can, therefore, be adjusted to produce the most satisfactory balance between conversion, process period, and conversion efficiency.

REGENERATION

The cerium–potassium–Cr_2O_3–γ-Al_2O_3 catalyst can be regenerated with air diluted with inert gas at about 550° C. In a life test made on this type of catalyst with a crude methylcyclohexane fraction from petroleum, the aromatic content of the product dropped from 88 to 74% after sixty-seven regenerations (400 processing hours), an average drop of 0.21% per regeneration. The rate of decline decreased thereafter so that the average decline per regeneration after 200 regenerations (1200 processing hours) was 0.12%.

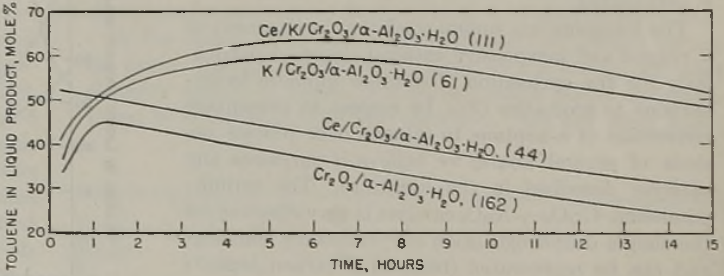


Figure 10. Effect of Cerium and Potassium Promoters on Cyclization Activity of Cr_2O_3–α-$Al_2O_3.H_2O$ Catalysts with *n*-Heptane as Feed

The ratio of processing time to time for complete carbon removal is about 6 to 1 for cyclization of *n*-heptane; for dehydrogenation of methylcyclohexane this ratio is more nearly 20 to 1. The following data, obtained by direct analyses for carbon of typical promoted and unpromoted catalysts, show both the effect of the promoters and the effect of the feed stock on carbon formation:

Catalyst			Length of Run, Hours	Carbon, % by Wt.	
No.	Type	Feed Stock		On catalyst	Of total feed
167	Cr_2O_3–γ-Al_2O_3	Methylcyclohexane	25	1.9	0.29
150	Ce–K–Cr_2O_3–γ-Al_2O_3	Methylcyclohexane	25	1.1	0.17
167	Cr_2O_3–γ-Al_2O_3	*n*-Heptane	15	5.1	1.46
171	Ce–K–Cr_2O_3–γ-Al_2O_3	*n*-Heptane	15	3.1	0.88

CYCLIZATION OF PETROLEUM FRACTIONS

Poisoning by Nonaromatizable Hydrocarbons. Petroleum fractions in the gasoline range ordinarily contain some hydrocarbons that cannot be converted directly to aromatics by either dehydrogenation or cyclization. Such hydrocarbons are those containing fewer than six carbon atoms, paraffins and olefins containing fewer than six carbon atoms in a straight chain, cyclopentane naphthenes, and a few geminate dialkyl paraffins, olefins, and cyclohexane naphthenes. The low-boiling hydrocarbons can be removed easily by distillation, whereas the proportion of highly branched nonaromatizable paraffins and olefins in a gasoline is usually small. Cyclopentane naphthenes may be fairly abundant, however, and their effect on a dehydrogenation or cyclization catalyst must be considered in particular.

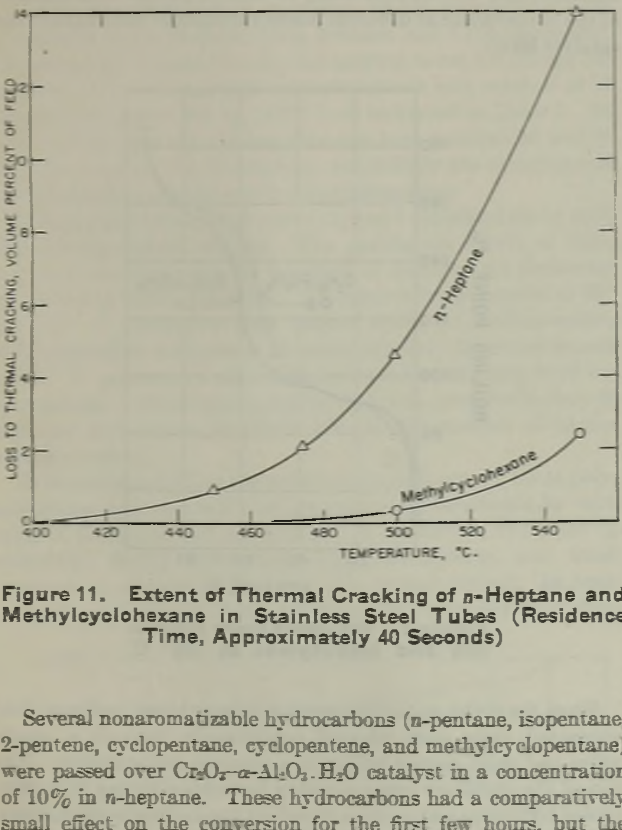


Figure 11. Extent of Thermal Cracking of *n*-Heptane and Methylcyclohexane in Stainless Steel Tubes (Residence Time, Approximately 40 Seconds)

Several nonaromatizable hydrocarbons (*n*-pentane, isopentane, 2-pentene, cyclopentane, cyclopentene, and methylcyclopentane) were passed over Cr_2O_3–α-$Al_2O_3.H_2O$ catalyst in a concentration of 10% in *n*-heptane. These hydrocarbons had a comparatively small effect on the conversion for the first few hours, but the poisoning increased considerably as the runs progressed beyond the point of maximum conversion, so that after 25 hours the average conversion of *n*-heptane containing 10% of any one of the nonaromatizable compounds tested was only about half as great as that of pure *n*-heptane. While the experimental runs have usually been continued for 25 hours, practical process periods would probably not exceed 6 or 8 hours, and consequently the poisoning effect of the nonaromatizable hydrocarbons would not be so serious.

Effect of Aromatics in Feed. For certain applications where it might be desirable to recirculate the product over the catalyst for higher conversion to aromatics, or where the feed stock contains an appreciable proportion of aromatics, the influence of aromatic compounds on the catalyst was examined. Tests have been made in which toluene in an equivolume mixture with *n*-heptane was passed over a cerium-potassium–Cr_2O_3–γ-Al_2O_3 catalyst at 490° C., and also the product of a cyclization run has been used as the feed for another run. In both these cases the effect of the aromatic has been simply that of an inert diluent.

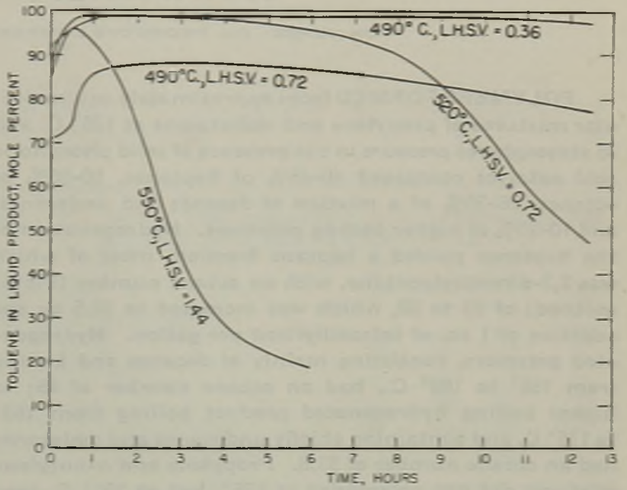


Figure 12. Influence of Temperature and Space Velocity on Catalyst Life and Dehydrogenation Activity (Catalyst 150 and Methylcyclohexane as Feed)

When pure aromatics were passed over a Cr_2O_3–α-$Al_2O_3.H_2O$ catalyst at 525° C., considerable amounts of carbon were deposited on the catalyst. The use of 3 moles of hydrogen per mole of aromatic almost entirely eliminated this carbon formation. Ordinarily, sufficient hydrogen is evolved in the production of aromatics to counteract their tendency to decompose on the catalyst.

Induction Period. The maximum activity of the catalyst is ordinarily not reached until the hydrocarbon feed has been passed over it for a few hours. Under certain conditions, however, this induction period does not exist, and the maximum activity of the catalyst occurs at the beginning of the run.

The structure of the alumina affects the induction period. A Cr_2O_3–γ-Al_2O_3 catalyst has no induction period and a high initial conversion, while Cr_2O_3–α-$Al_2O_3.H_2O$ catalysts do not reach their maximum activity until *n*-heptane has been passed over them for about 1.5 hours (Figure 1).

In the presence of potassium or both potassium and cerium, the induction period invariably exists in spite of the use of γ-Al_2O_3 (Figure 8). Cerium appears to be of considerable benefit here in raising the initial conversion.

The induction period also varies with the type and extent of pretreatment given the catalyst; insufficient data are available to permit satisfactory prediction of the behavior of a particular catalyst under varying conditions of pretreatment. However, the differences are not of critical importance as a rule.

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HEPTENES and HEPTANES from PROPYLENE and BUTYLENES

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POLYMERS FORMED from approximately equimolecular mixtures of propylene and isobutylene at 135° C. and 38 atmospheres pressure in the presence of solid phosphoric acid catalyst contained 40–45% of heptenes, 10–15% of octenes, 25–30% of a mixture of decenes and undecenes, and 10–25% of higher boiling polymers. Hydrogenation of the heptenes yielded a heptane fraction, most of which was 2,3-dimethylpentane, with an octane number (Motor method) of 89 to 90, which was increased to 98.5 by the addition of 1 cc. of tetraethyllead per gallon. Hydrogenated polymers, consisting mainly of decanes and boiling from 155° to 163° C., had an octane number of 89; a higher boiling hydrogenated product boiling from 163° to 175° C. and containing chiefly undecanes and dodecanes had an octane number of 93.6. Propylene and *n*-butylene mixtures did not polymerize at 135°, but at 191° C. they formed mono-olefinic polymers which on hydrogenation yielded paraffinic mixtures; the 150° C. end-point fraction had an octane number of 56 to 62.

HEPTENES and other polymers (*2*) can be obtained by polymerizing olefins from a C_3–C_4 fraction of refinery gases in the presence of solid phosphoric acid catalyst (*3, 6, 8*). The present paper describes a process (*7, 9*) for producing branched-chain heptenes by polymerizing mixtures of propylene and isobutylene in the presence of solid phosphoric acid catalyst at relatively low temperatures. These branched-chain heptenes were hydrogenated into a heptane fraction of 89.4–90.4 octane number (Motor method) which was increased to 98.5 octane number by the addition of 1.0 cc. of tetraethyllead per gallon. This heptane fraction contained a high percentage of 2,3-dimethylpentane. This hydrocarbon was identified by its physical constants and Raman spectrum.

In the presence of 50% butane, equimolecular mixtures of propylene and isobutylene polymerized under conditions of selective polymerization (*5*) in contact with standard solid phosphoric acid catalyst; approximately the same yields and types of polymers resulted as were produced similarly from the olefin mixture not diluted by butane. Polymers formed at 191° C. in the presence of solid phosphoric acid from mixtures of propylene and *n*-butylene, present in the approximate molar proportions of 3 to 1, yielded hydrogenated fractions of 150° C. end point and 56–62 octane numbers. These octane numbers were about the same as those of fractions of similar boiling range obtained by hydrogenation of propylene polymers produced at 205° C.

The pressure tube apparatus and the procedure were essentially the same as were employed previously in the polymerization of butylenes (*5*). In the present work the charging stock, contained in a steel charger under a nitrogen pressure of 45 atmospheres, was passed through 5-mm. copper tubing to the upper end of the vertical steel catalyst tube (14 mm. inside diameter) containing 45.4 grams (0.10 pound) of extruded solid phosphoric acid polymerization catalyst in the form of 5 × 5 mm. cylindrical pieces. The catalyst was held in place in the catalyst tube by plugs of steel wool so that it occupied the central portion of the heating section surrounded by an aluminum bronze block furnace, the latter being heated electrically and provided with an automatic temperature regulator. The temperature measured was that of the aluminum bronze block surrounding the catalyst tube. Some runs were also made at 38 atmospheres pressure in the presence of 500 grams (1.1 pound, occupying a volume of 570 cc.) of 4–10 mesh granular solid phosphoric acid catalyst; the catalyst was in a vertical tower of 4.7 cm. inside diameter, provided with a thermocouple well located along its axis to permit measurement of the temperature at different places throughout the length of the catalyst layer.

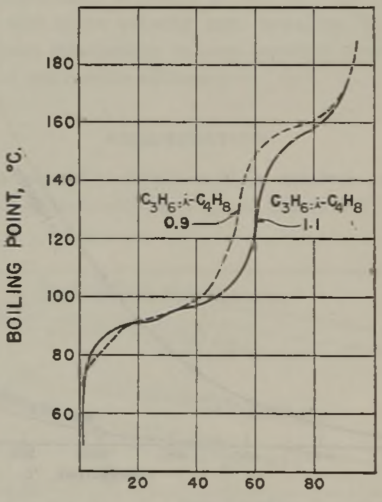

Figure 1. Polymers from Propylene and Isobutylene at 135° C.

From the outlet end of the catalyst tube or tower, polymers and unreacted gases were released continuously through a needle valve and short copper tubing to a receiver and stabilizer. The top of the stabilizer was connected by rubber tubing to a trap, cooled by dry ice and acetone, to collect low-boiling hydrocarbons.

The polymers were distilled through a column packed with glass rings and separated into fractions corresponding to heptenes, octenes, and higher-boiling hydrocarbons. Some of these fractions were hydrogenated catalytically in an Ipatieff high-pressure autoclave to the corresponding paraffins, upon which octane number determinations were made. Other of these liquid olefin fractions were subjected to precise distillation through a hundred-plate Bruun bubble-cap column (*1*), followed by measurement of the physical constants of the different fractions.

Table I. Mixed Polymerization of Propylene and Isobutylene at 38 Atmospheres

Run No.	1	2	3
Temperature, ° C.	93	125	162
Hourly gaseous space velocity			
Charge	211	245	640
Exit gas	43	49	38
% polymerization of:			
Propylene	62	60	89
Isobutylene	93	98	99
Total olefins	79	80	95
Molar polymerization ratio, C_3H_6: Iso-C_4H_8	0.5	0.5	0.7
Polymer			
Fraction boiling below 150° C., %	66	66	68
150–225° C., %	26	27	28
Bottoms and loss, %	8	7	4
Hydrogenated fraction, boiling below 150° C.			
Octane No. (Motor method)	93	93	90
A.P.I. gr. at 15.5° C.	72.3	71.5	70.3
Sp. gr. at 15.5° C.	0.6943	0.6970	0.7012
A.S.T.M. distn.			
Initial b.p., ° C.	82	85	85
10% over, ° C.	89	90	90
20%	90	91	92
50%	93	95	95
90%	97	108	116
End point, ° C.	108	145	162
% over	99	99	98.5
Bottoms	1	1	1.0
Loss	0	0	0.5
Vol. % over at 100° C. based on:			
i. b. p. −150° C. hydrogenated fraction	95	75	70
Total polymer	68	49	47
% by wt. of charge converted into hydrogenated fraction with end point of:			
100° C.	51	39	43
150° C.	54	52	62

MIXED POLYMERIZATION OF PROPYLENE AND ISOBUTYLENE

A mixture of 40.9 mole % propylene, 51.6% isobutylene, 1.7% *n*-butylenes, 0.8% propane, 0.9% butanes, and 4.1% uncondensable gases was charged through the catalyst tower containing 500 grams of 4–10 mesh granular solid phosphoric acid catalyst at 38 atmospheres and at 93° to 162° C., as indicated in Table I. In each of these runs the exit gas rate was kept between 38 and 49 liters per hour per liter of catalyst; accordingly the charging rate was dependent upon the speed of polymerization.

The polymers obtained in runs 1, 2, and 3 contained about 60% of a heptene-octene mixture. The distillation curves of these polymers also indicated the presence of decenes and undecenes in the higher boiling fractions. At catalyst temperatures of 93° and 125° C., polymers were formed which on hydrogenation yielded paraffinic mixtures of 93 octane number; polymers formed at 162° C. produced a saturated hydrocrabon mixture of 90 octane number. These hydrogenated mixtures consisted mainly of heptanes and octanes, together with small amounts of higher boiling paraffins.

To investigate further the nature of these heptanes, other polymerization runs were made on approximately equimolecular mixtures of propylene and isobutylene. A mixture of 47.0 mole % propylene, 46.9% isobutylene, 3.8% *n*-butylenes, and small amounts of propane and butane were passed through the pressure tube apparatus containing 45.4 grams of extruded solid phosphoric acid catalyst maintained at 135° C. Results on these polymerization runs appear in Table II. During a similar run of 116 hours at 135° C., 88% of the propylene and 99% of the isobutylene polymerized to liquid hydrocarbons. The mole ratio of propylene to isobutylene polymerized was 0.9 to 1.0. Several short runs (4 to 6, Table II) at 100° to 121° C. showed less polymerization of propylene and gave polymers corresponding to 0.5 mole of propylene per mole of isobutylene polymerized.

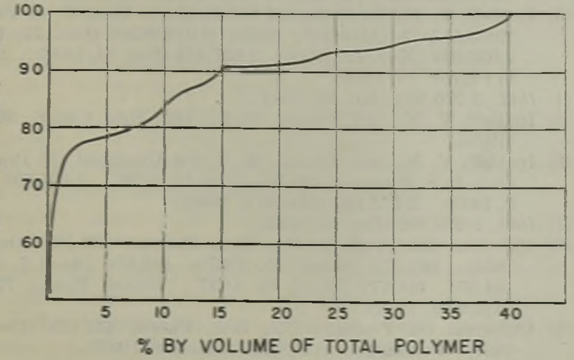

Figure 2. Heptene Fraction of Polymers Formed from Propylene and Isobutylene at 135° C.

The results in Table II show that polymerization of isobutylene in presence of propylene was more selective at 100° to 121° C. than at 135° C.; at the latter temperature both isobutylene and propylene polymerized with ease. The rate of polymer formation decreased rapidly as lower catalyst temperatures were used.

Similar runs were made at a catalyst temperature of 135° C. on a mixture containing 50.0 mole % propylene, 41.4% isobutylene, 3.8% *n*-butylene, and small amounts of propane and butane. In these runs propylene and isobutylene were polymerized in the molar ratio of 1.1 to 1.0. Typical polymer products had the compositions shown in Table III.

Table II. Mixed Polymerization of Propylene and Isobutylene at 45 Atmospheres Pressure

Run No.	4	5	6	7
Temperature, ° C.	100	107	121	135
Hours on test	22	8	14	24
Hourly gaseous space velocity				
Charging rate	71	87	163	375
Exit gas	43	43	43	27
% polymerization of:				
Propylene	25	46	52	87
Isobutylene	47	89	96	99
Total olefins	33	55	77	93
Polymer, cc./hr./liter catalyst	62	135	370	1040
Polymerization ratio, moles propylene per mole isobutylene	0.5	0.5	0.5	0.9

Table III. Polymers from Propylene and Isobutylene at 135° C. and 38 Atmospheres Pressure

Run No.	8	9
Mole ratio of propylene to isobutylene polymerized	1.1	0.9
Fraction, vol. %		
Initial b.p. to 100° C.	48.8	41.0
100–125° C.	11.1	10.6
125–150° C.	8.2	10.0
Above 150° C.	30.5	38.4
Loss	1.4	0

These polymers of propylene and isobutylene, which had been separated by the preliminary distillation (through a 152-cm. column packed with glass rings, about nineteen theoretical plates) into fractions boiling up to 91°, 91–100°, and 100–125° C., were later subjected to precise distillations through the hundred-plate Bruun column. This preliminary distillation of the polymers gave the curves shown in Figure 1. The Bruun distillation curve of the heptene-octene fraction (5705 cc.) of these polymers is given in Figure 2, in which the distillate is expressed on the basis of the total polymer.

HYDROGENATION OF HEPTENE FRACTIONS. Half of the total polymer boiling up to 100° C. was hydrogenated in the presence of 5% by weight of nickel-kieselguhr catalyst (4) by heating with hydrogen at 100° C. for 6 to 10 hours at 100 atmospheres initial pressure. After this hydrogenation treatment, the product was completely saturated as evidenced by its stability to nitrating mixture. This paraffin fraction, consisting mainly of heptanes and some octanes, was distilled through the hundred-plate Bruun column and separated into narrow-boiling fractions. The distillation curve of these heptanes and the refractive indices of the different heptane fractions are given in Figure 3.

Determinations were made of the boiling points of these fractions by the Cottrell method, of density by the Westphal balance, and of refractive index by the Abbe refractometer. Comparison of these physical properties with published data on pure heptanes indicated that this heptane fraction contained high

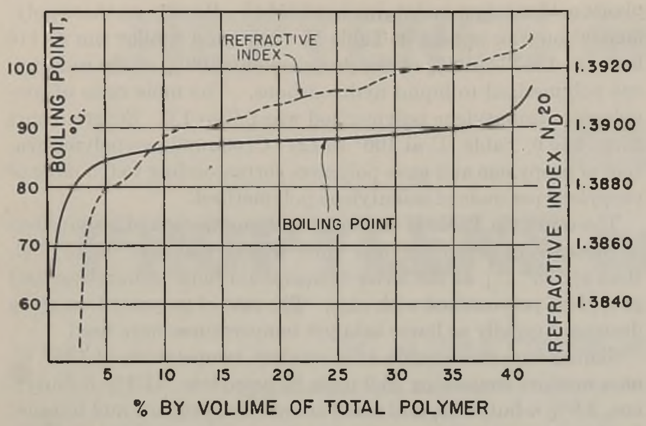

Figure 3. Heptane Fraction Produced by Hydrogenating Polymers Formed from Propylene and Isobutylene

percentages of 2,3-dimethylpentane, together with relatively small proportions of lower boiling heptanes.

Raman Spectra of Heptane Fractions. Additional evidence of the presence of 2,3-dimethylpentane was obtained by Raman spectra determinations on several of these heptane fractions:

Fraction No.	Cottrell Boiling Range at 754 Mm., ° C.	d_4^{20}	n_D^{20}	% Composition of Fraction
4	77.0–79.4	0.6745	1.3823	55–60 2,2-dimethylpentane, 45–40 2,4-dimethylpentane
10	85.8–86.0	0.6890	1.3893	5–10 2,4-dimethylpentane, 95–90 2,3-dimethylpentane
32	89.4–89.6	0.6938	1.3921	100 2,3-dimethylpentane

Octane Numbers of Heptane Fractions. Octane numbers were determined on composites of some of the heptane fractions of the hydrogenated polymers referred to in Figure 3. The following results show that these heptane fractions, consisting mainly of 2,3-dimethylpentane, had octane numbers of 89.4 to 90.4 by the C.F.R. Motor method. A composite of these three heptane samples was increased in octane number to 98.5 by the addition of 1.0 cc. tetraethyllead per gallon.

Fraction No.	Boiling Point at 754 Mm., ° C.	d_4^{20}	n_D^{20}	Obsvd. Octane No.
10	85.8	0.6890	1.3893	89.7
14	86.8	0.6898	1.3900	
26	88.3	0.6925	1.3913	89.4
31	89.4	0.6938	1.3921	
33	89.6	0.6942	1.3922	90.4
41	96.6	0.6944	1.3931	

MIXED POLYMERIZATION OF PROPYLENE AND ISOBUTYLENE IN PRESENCE OF *n*-BUTANE

A mixture of 25.3 mole % propylene, 25.5% isobutylene, 1.9% *n*-butylenes, and 47.3% *n*-butane was passed through the pressure tube containing extruded solid phosphoric acid catalyst maintained at 135° C. The charging rate, expressed as gas volume, of the propylene–isobutylene–*n*-butane mixture was from 520 to 620 liters per hour per liter of catalyst. During a time of 116 hours, 65 to 68% of the olefins polymerized; that is, 99% of the isobutylene and 59% of the propylene were converted into liquid polymers. The mole ratio of propylene to isobutylene polymerized was 0.6. About the same type of polymer product resulted as was obtained in the absence of the butane diluent.

The polymer fraction boiling from 150° to 175° C. was hydrogenated and distilled. The lower boiling portion of the hydrogenated polymer, consisting mainly of decanes, had a boiling range of 155.5–163.0° C., n_D^{20} 1.4190–1.4219, and an octane number of 89; the higher boiling fraction, consisting mainly of undecanes and dodecanes, had a boiling range of 163.0–174.8° C., n_D^{20} 1.4219–1.4231, and an octane number of 93.6.

MIXED POLYMERIZATION OF PROPYLENE AND *n*-BUTYLENES

A mixture containing 57.0 mole % propylene, 1.9% isobutylene, 17.0% *n*-butylenes, 21.3% butane, and 2.8% propane was contacted with extruded solid phosphoric acid polymerization catalyst at 191° C. In this run, which extended over a period of 200 hours, the propylene–*n*-butylene mixture was charged at an average rate of 125 liters per hour per liter of catalyst. The polymer formed was equivalent to 59% by weight of the mixture charged. The average polymerizations of propylene and *n*-butylenes were 89 and 74%, respectively, based upon the amount of these olefins present in the charging stock. Properties of different fractions of these polymers follow:

Fraction No.	Boiling Point, ° C.	Dist., % by Vol. Per fraction	Total	n_D^{20}	Br No.
1	59–95	4.2	4.2	1.4060	153
2	95–125	7.2	11.4	1.4158	141
3	125–150	39.7	51.1	1.4240	116
4	150–175	16.4	67.5	1.4284	114
Residue	Above 175	30.5	98.0	1.4360	...
Dissolved gas	.....	0.9	98.9	....	...

Hydrogenated Mixed Polymers. Catalytic hydrogenation of the 125–150°, 150–175°, and 59–175° C. fractions of the above polymers produced paraffin hydrocarbon fractions of relatively low octane number, as indicated by the following results:

Hydrogenated fraction No.	3	4	Comp.[a]
Boiling range, ° C.	125–150	150–175	59–150
Octane No.	59.8	55.9	61.7
A.P.I. gr. at 15.5° C.	62.3	58.5	64.6
Sp. gr. at 15.5° C.	0.7301	0.7447	0.7216
Initial b.p., ° C.	132	152	104
End point, ° C.	153	180	151
10% over, ° C.	134	155	119
20%	135	156	122
30%	136	158	127
40%	137	159	129
50%	138	160	132
60%	139	161	134
70%	140	163	137
80%	142	166	139
90%	144	169	142
99%	153	180	151
Total % over	99	99	99
Bottoms, %	1.0	1.0	1.0

[a] Composite of fractions 1 to 3, inclusive, blended in the same proportions as they occurred in the polymer.

The octane numbers of these hydrogenated mixed polymers of propylene and *n*-butylenes were about the same as those of hydrogenated propylene polymer, the latter produced at a polymerization catalyst temperature of 205° C.

ACKNOWLEDGMENT

The authors are indebted to E. J. Rosenbaum (then of the University of Chicago) for Raman spectra determinations and to G. L. Hervert for assistance with experimental work described here.

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EMULSION POLYMERIZATION OF ACRYLIC ESTERS

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Effects of various agents on the emulsion polymerization of acrylic esters are described, and directions are given for preparing several types of resin emulsions. When emulsion polymerization is used merely to convert monomeric acrylic esters into polymers or copolymers of relatively high molecular weight, Tergitol Penetrant No. 4 and ammonium persulfate can be used satisfactorily as emulsifier and polymerization catalyst, respectively. The resulting emulsion is only moderately stable and can be coagulated readily by the addition of aqueous solutions of sodium chloride, acetic acid, or mixtures of the two. Triton K60 and hydrogen peroxide also can be used conveniently to produce emulsions of only moderate stability. Emulsions remarkably stable to electrolytes (but not to mechanical agitation or solvents such as acetone and ethanol) can be made with Triton 720 as the emulsifier. Triton 720 and Tergitol Penetrant No. 4 can be used together in various proportions to produce emulsions of almost any desired stability to electrolytes. Stable emulsions suitable for brushing and spraying can be prepared with several combinations of agents. The combination used frequently for this purpose is E. F. Houghton No. 1, ammonium alginate, ammonium hydroxide, and ammonium persulfate. The viscosity of acrylic resin emulsions can be controlled over a wide range by using various quantities of ammonium alginate, modified casein, and Tergitol Penetrant No. 4. Films obtained from these emulsions adhere well to smooth surfaces.

BECAUSE of several inherent advantages, aqueous dispersions of resins, including the acrylic resins (*12*), are being used to an increasing extent for coating cloth, leather, and other materials. Advantages of aqueous dispersions include ease of application, rapid drying, and freedom from the fire and toxicity hazards that ordinarily accompany the use of resins dissolved in organic solvents.

During investigations in this laboratory concerned with the polymerization and copolymerization of acrylic esters and the production of stable resin emulsions, considerable information was obtained on the use of various emulsifiers and auxiliary agents in the emulsion polymerization of acrylic esters. Some of the results are given in the present paper. The first part of the paper describes various combinations of emulsifiers and polymerization catalysts for preparing acrylic resin emulsions of moderate or high stability; the latter part gives methods for preparing emulsions of almost any desired viscosity. The general properties, advantages, and applications of resin emulsions have been discussed at length elsewhere (*2, 4, 9, 10, 11, 13*).

The emulsions were prepared in a round-bottom, three-neck Pyrex flask fitted with glass-ground joints for a condenser, water-sealed glass stirrer, and thermometer well. Water and emulsifier were stirred and heated (below 85° C.) in the flask until a smooth dispersion or solution was obtained. The monomer or monomers were then added, and polymerization was induced by heat and catalysts. Hydrogen peroxide (30%) and ammonium persulfate were used as catalysts in many of the experiments. The emulsions were refluxed during the polymerization, and at refluxing temperature a period of 30 minutes to several hours was usually required. With half-moon or paddle-type stirrers operated at 100 to 150 revolutions per minute, emulsions with particle size as small as 0.05 micron in diameter were made without incorporation of air. The yield of polymer was almost quantitative. In some cases steam was blown through the emulsion at the end of the polymerization to remove unchanged monomer. The temperature rose during the polymerization from about 72° to 82° C. and from 82° to 92° C. when methyl acrylate and ethyl acrylate, respectively, were the monomers. Hence the course of the polymerization could be followed roughly by noting the temperature. The polymerizations were followed in some instances by observing changes in the refractive index, density, and solids content.

Emulsion polymerization can be carried out more satisfactorily if, in addition to suitable emulsifiers and catalysts, pure monomers and critical conditions of temperature and catalyst concentration are used. The monomer should be free of inhibitors or regulators or their amount and effect should be known. The monomer should be freshly distilled (under vacuum if high boiling) or, when storage is unavoidable, kept under conditions unfavorable for peroxide formation. Removal of inhibitor with dilute sodium hydroxide (1 or 2%) should be followed by several washings with distilled water, dilute sulfuric acid (0.01%), and twice again with distilled water. Removal of inhibitor from methyl and ethyl acrylate in this manner causes a considerable loss of monomer.

The amount of ammonium persulfate required to initiate polymerization depends largely on the temperature. Only traces of catalyst are needed under refluxing conditions (approximately 72° for methyl acylate and 82° for ethyl acrylate), but much larger quantities are needed at somewhat lower temperatures. Polymerization may not occur in several hours with the same amount of catalyst if the temperature is as little as 0.5° below refluxing. Too much catalyst causes a vigorous reaction, violent refluxing, and, in some instances, coagulation of the emulsion. When only traces of catalyst are used at gentle refluxing temperature, polymerization proceeds smoothly, yielding a polymer of high molecular weight; little or no additional heating is required; and the polymerization can be controlled by the rate of addition of the catalyst. A steam bath is more satisfactory than a water bath for this type of polymerization.

The benefits of carrying out the emulsion polymerization of monomers and monomer mixtures at refluxing temperature are so outstanding that some feature of refluxing other than temperature seems important. If it is assumed that most of the polymerization occurs in the aqueous phase, refluxing might be beneficial because of increased solubilization of the monomer or the increased rate at which the monomer is transported from the oil phase into and throughout the aqueous phase.

Fryling (*5*) described suitable laboratory methods for preparing resin emulsions from small quantities of monomers and for following the course of the polymerization.

EMULSIONS OF MODERATE STABILITY

The emulsifiers listed in Table I formed dispersions of moderate stability without auxiliary agents or other emulsifiers. Hydrogen peroxide (30%), which has the advantage of being essentially neutral and decomposing into water, was used conveniently as a catalyst in these initial experiments. In a few instances, when it

Table I. Polymerization of Methyl Acrylate with One Emulsifier[a]

Expt. No.	Emulsifier						
	Trade Name	Type (*9*, *15*)	Grams	Water, Ml.	Methyl Acrylate, Ml.	H_2O_2, Ml.	Time, Min.
1[b]	Triton W-30	Sulfated aromatic ether alcohol	.9	50	45	0.5	60
2[c]	Triton K-60-S	Quaternary ammonium salt	4.5	250	250	2	50
3[c]	Nacconol NRSF	Sodium alkyl aryl sulfonate	.9	50	45	0.5	60
4[b]	Gardinol LS	Fatty alcohol sulfate	.9	50	45	0.5	45
5[c]	Aquasol AR-75%	Sulfonated castor oil	.9	50	45	0.5	60
6[c]	Tergitol Penetrant No. 4	Sodium salt of higher secondary alkyl sulfate	.9	50	45	0.5	45
7[b]	....	Glyceryl monostearate	.9	50	50	0.5	...
8[c]	E. F. Houghton No. 1	....	.9	60	40	0.25	30
9[b]	E. F. Houghton No. 3	....	1.8	60	40	0.5	60
10[c]	E. F. Houghton No. 4	....	.9	60	40	0.5[d]	60
11[c]	Daxad No. 11	Polymerized Na salts of alkyl naphthalene sulfonic acids	1.0	50	45	2	...
12[b]	Daxad No. 23	Polymerized Na salts of substituted benzoic alkyl sulfonic acids	1.0	50	45	3[d]	...
13	Atlas Span 85	Sorbitan trioleate	3.0	50	40	1	...
	Atlas Tween 85	Sorbitan trioleate polyoxyalkylene derivative	2.0				
14	Atlas Span 20	Sorbitan monolaurate	2.0	50	40	1	...
	Atlas Tween 20	Sorbitan monolaurate polyoxyalkylene derivative	2.0				
15	Emulphor ELA[e]	Ethylene oxide condensate with fatty acids	2.0	70	50	4.5	150
16	Emulphor ON[f]	....	2.0	70	50	4.5	105
17[f]	Igepon T	$C_{17}H_{33}CON—CH_3C_2H_4SO_3Na$	2.0	70	50	1	10
18	Igepon AP extra	Na sulfonate of oleic acid ester of aliphatic compound	2.0	70	50	1	240
19[f]	Nekal BX	Sodium alkyl naphthalene sulfonate	2.0	70	50	1	30
20[f]	Nekal BX	Sodium alkyl naphthalene sulfonate	2.0	70	50	2	35
21	NH_4 Alginate	Ammonium alginate	1.0	50	40	1	20
22	Pectinate H-69	Acid-demethylated pectin	1.4	70	50	0.5	20
23	Protovac 8979	Modified casein	5.0	70	50	0.5	11
24	Nekal A	Sodium alkyl naphthalene sulfonate	1.0	70	50	0.3	6

[a] The mixture was refluxed (temperature of mixture, 75° C.) until polymerization was virtually complete

[b] A large amount of polymer separated during the polymerization.

[c] Emulsions were satisfactory except for brushing or spraying.

[d] 0.5 gram benzoyl peroxide was also used.

[e] Heating reduced emulsifying action.

[f] A small amount of polymer separated during polymerization.

appeared that hydrogen peroxide alone was not sufficiently effective, a small amount of benzoyl peroxide was added. Ammonium hydroxide, Houghton No. 2[1], Triton NE, Emulphor AG, and Nekal RU appeared to inhibit the polymerization of methyl acrylate under conditions similar to those shown in Table I.

The emulsions obtained with single emulsifiers (Table I) were not stable enough for brushing or spraying. Optimum conditions for each emulsifier were not determined, and it is possible that different concentrations and conditions would have given improved emulsions. Emulsions of only moderate stability are desirable for some purposes, and some of the formulas of Table I could be used to advantage under such circumstances. Triton K60S (experiment 2) has been used conveniently in this laboratory many times in converting acrylic esters into resins of relatively high molecular weight; in these experiments the emulsions were coagulated by the addition of dilute solutions of sodium chloride, acetic acid, or mixtures of the two.

When used under the conditions shown in Table I, the following materials appeared unsuitable as emulsifiers in the polymerization of methyl acrylate: Triton W-30, Gardinol LS, glyceryl monostearate, Houghton No. 3, Daxad No. 11, Atlas Span 85 + Atlas Tween 85, Atlas Span 20 + Atlas Tween 20, Igepon AP extra, ammonium alginate, Pectinate H-69, Protovac 8979, and Nekal A. These agents were not studied thoroughly, however, and excellent results might have been obtained with other monomers under other conditions, or when used in conjunction with other emulsifiers.

STABLE EMULSIONS

Some of the emulsifiers that had given promising results in the earlier experiments (Table I) were used in later experiments with other agents. Emulsions stable enough for brushing and spraying were obtained with certain combinations of agents (Table II). It was not demonstrated that these combinations would function satisfactorily with all monomers, but stable emulsions were obtained when methyl acrylate was polymerized alone or copolymerized with acrylonitrile or bis-(carballyloxyethyl)maleate (prepared from 2 moles of allyl lactate and 1 mole of maleic anhydride). The combination used most often consisted of Houghton No. 1, ammonium alginate, and ammonium hydroxide (experiments 1 to 5 and 18 to 23, Table II, and experiment 6, Table IV). Ammonium hydroxide had little or no inhibiting effect, possibly because it was partly or totally neutralized by Houghton No. 1.

Triton 720 (sodium salt of aryl alkyl polyether sulfonate) formed emulsions that were remarkably stable to electrolytes (Table III). Although stable when treated with sodium chloride, acetic acid, or hydrochloric acid, the Triton 720 emulsions could be coagulated by mechanical treatment or by the addition of alcohol or acetone. With mixtures of Triton 720 and Tergitol Penetrant No. 4, emulsions of almost any desired stability to electrolytes were prepared (Table III).

SELECTION OF POLYMERIZATION CATALYST

Although hydrogen peroxide has certain advantages and was used satisfactorily in many experiments, the ammonium persulfate is preferable as catalyst. With this agent the polymerizations proceeded smoothly, and it was effective in exceedingly low concentrations; polymers of high molecular weight could be prepared easily with traces of it. Presumably potassium and certain other persulfates could be used. Sodium perborate appeared to have no particular advantage. Benzoyl peroxide was active and was used in conjunction with hydrogen peroxide when the latter seemed ineffective.

Ammonium persulfate was not employed with all the emulsifiers shown in Tables I and II, but it was used satisfactorily with Tergitol Penetrant No. 4 and a mixture of Houghton No. 1, ammonium alginate, and ammonium hydroxide. Other examples of the preparation of satisfactory emulsions with ammonium persulfate are given in Tables III and IV. Unlike hydrogen peroxide, ammonium persulfate was unsatisfactory with Triton K60, owing to the formation of a precipitate.

MISCELLANEOUS OBSERVATIONS

Of the several agents tried (mineral oil, *n*-octanol, lauryl alcohol, *n*-hexanol, castor oil, and ethanol), *n*-octanol and *n*-hexanol seemed most suitable for preventing foaming. A small amount was added during the polymerization when foaming became excessive.

Dodecyl mercaptan appeared to facilitate control of the rate of polymerization, particularly when hydrogen peroxide was used as catalyst.

The effect of pH was not studied thoroughly, and few conclusions were reached regarding the desirability of controlling this

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[1] Obtained through the courtesy of J. T. Eaton of E. F. Houghton & Company.

variable. Fryling (*6*) made interesting observations regarding changes in pH during emulsion polymerization.

Use of extremely small quantities of emulsifiers was not studied, but polymerization occurred less readily when Triton K60 was used in low concentration with hydrogen peroxide as catalyst. This is in agreement with the observations of Fryling (*6*).

Unless monomers (usually about 2% of the quantity used in the experiment) were removed, the emulsions had an objectionable odor. In many instances, steam was passed through the emulsions at the end of polymerization to remove residual monomers and improve the odor.

CONTROL OF VISCOSITY

Viscosity influences the ease with which both resin emulsions and solutions can be applied. The viscosity of resin solutions increases so rapidly with increase in resin concentration that the resin content must be kept low enough for convenient application. On the other hand, aqueous resin dispersions usually are fluid, even when the resin content is 50% or even higher. Data supplied by Jackson (*8*) illustrate the differences between the viscosities of aqueous dispersions and ethyl acetate solutions of an acrylic resin (Table V).

The viscosity of resin solutions can be controlled easily by changing the resin concentration (Table V) or the solvent, but the viscosity of resin emulsions cannot be controlled by these methods. Since resin emulsions are ordinarily fluid, several agents, including methylcellulose (*1*), have been added to increase the viscosity and facilitate brushing, spraying, or calendering (*7*). Although these agents are useful for some purposes, some of them have distinct disadvantages. Methylcellulose, for example, cannot be added before polymerization because its solutions are coagulated by elevated temperatures. Moreover, it is moderately soluble in cold water, and films containing methylcellulose would be expected to have decreased water resistance.

During this study a simple and effective method for preparing acrylic resin emulsions of almost any desired viscosity was found. This consists in adding a casein preparation and a water-soluble alginate before polymerization. The casein and alginate have a synergistic effect on

TABLE II. PREPARATION OF STABLE ACRYLIC RESIN EMULSIONS[a]

Expt. No.	Emulsifier			Other Agents, Grams				Water, Ml.	Monomers, Ml.		Catalyst, Ml.	Time, Min.	Films
	Designation	Type	Grams						Methyl acrylate	Acrylonitrile			
1	E. F. Houghton No. 1		0.9	NH_4 Alg.[b]	0.9	NH_4OH	0.9	60	50		H_2O_2, 1	150	Smooth, flexible, clear
2	E. F. Houghton No. 1		4.0	NH_4 Alg.	4.0	NH_4OH	3.0	250	200	50	H_2O_2, 3	200	Same
3	E. F. Houghton No. 1		4.0	NH_4 Alg.	4.0	NH_4OH	3.0	250	225	25	H_2O_2, 2	135	Same
4	E. F. Houghton No. 1		0.5	NH_4 Alg.	0.7	NH_4OH	1.2	55	45		H_2O_2, 0.5 cc.	65	Same
5	E. F. Houghton No. 1		0.5	NH_4 Alg.	0.7	NH_4OH	0.3	55					
6	Nacconol NRSF	Sodium alkyl aryl sulfonate	0.9	NH_4 Alg.	0.7	NH_4OH	0.3	55	40	5.0[c]	H_2O_2, 1	90	Same[d]
7	Aquasol-AR-75%	Sulfonated castor oil	0.9	NH_4 Alg.	0.7	NH_4OH	0.3	55	45		H_2O_2, 1	105	Cloudy; re-emulsifies in water
8	Tergitol Penetrant No. 4	Na salt of higher *sec* alkyl sulfate	0.9	NH_4 Alg.	0.7	NH_4OH	0.3	55	45		H_2O_2, 1	75	Clear; becomes soapy in water
9	Aquasol-AR-75%		0.9	NH_4 Alg.	0.5	NH_4OH	0.18	53	45		H_2O_2, 0.5	110	Clear and colorless
10	Aquasol-AR-75%		0.9	NH_4 Alg.	0.5			50	45		H_2O_2, 0.5	135	Same; turns white
11	Aquasol-AR-75%		0.5	NH_4 Alg.	0.3	NaOH	0.03		45		H_2O_2, 1	150	Same
				Buffer (pH 8.95) 5 cc.				50					
12	Daktose	Deacetylated chitin	0.8	Acetic acid 1.0				50	40	1.0[e]	H_2O_2, 3	125	Same
13	Daktose		0.4	Acetic acid 0.5				50	45		H_2O_2, 0.75	45	Opaque, nontacky
14	Aquasol-AR-75%		5.0	NH_4 Alg.	6.5	NaOH	0.2	500	30		H_2O_2, 0.5	30	Same
				Buffer 8 cc.					500		H_2O_2, 2.5	45	Smooth, clear
15	Aquasol-AR-75%		5.0	NH_4 Alg.	5.0	NaOH	0.14	500	450	50	H_2O_2, 4, Lucidol, 0.5 g.	95	Colorless, nontacky, tough
16	Aquasol-AR-75%		5.0	NH_4 Alg.	5.0	NaOH	0.14	500					
17	Aquasol-AR-75%		5.0	NH_4 Alg.	5.0	NaOH	0.087	500					
18	E. F. Houghton No. 1		5.0	NH_4 Alg.	7.0	NH_4OH	3.0	500	400	100	H_2O, 4	155	Hard, brittle
19	E. F. Houghton No. 1		5.0	NH_4 Alg.	7.0	NH_4OH	3.0	500	400	100	H_2O, 2	210	Same
20	E. F. Houghton No. 1		5.0	NH_4 Alg.	7.0	NH_4OH	3.0	500	440	110	H_2O_2, 2	195	Hard and tough, not brittle
21	E. F. Houghton No. 1		0.9	NH_4 Alg.	0.9	NH_4OH	1.4	60	450	50	H_2O_2, 1	180	Smooth, clear, tough, nontacky
22	E. F. Houghton No. 1		0.9	NH_4 Alg.	0.9	NH_4OH	1.4	60	500		H_2O_2, 2.5	60	Smooth, clear
23	E. F. Houghton No. 1		0.7	NH_4 Alg.	0.5	NH_4OH	0.42	60	40		H_2O_2, 0.5	150	Same
24	Triton-K60-S	Quaternary ammonium salt	0.7	NH_4 Alg.	0.5			50	50		H_2O_2, 1	150	Same
25	Triton-K60-S		0.9	NH_4 Alg.	0.8			50	45		H_2O_2, 0.25	150	Same
26	Daktose		0.4	Acetic acid 0.5				60	20		Lucidol, 0.5 g.	90	Smooth
	Aquasol-AR-75%		0.5										
27	E. F. Houghton No. 1		8.0	NH_4 Alg.	8.0	NH_4OH	6.0	500	45		Lucidol, 1.5 g.	45	Smooth
28	E. F. Houghton No. 1		1.0	Pectinate H-69[f]	1.0	NH_4OH	0.72	82					
29	Aquasol-AR-75%		1.0	Protovac 8979[g]	5.0			70	40		H_2O_2, 2	30	Opaque, nontacky
30	Nekal-BX	Sodium alkyl naphthalene sulfonate	1.0	Pectinate H-69[f]	1.4	NH_4OH	0.12	70					
31	Tergitol Penetrant No. 4		1.0	Protovac 8979[g]	2.5			70	450	50	H_2O_2, 1.5	90	Smooth, clear
32	Tergitol Penetrant No. 4		4.0	Protovac 8979[g]	12.0			280	50		H_2O_2, 0.5	60	
33	Aerosol-OT	Dioctyl ester of sodium sulfosuccinic acid	1.0	Protovac 8979[g]	2.5			70	50		H_2O_2, 0.5	95	Adheres to glass; slightly cloudy
									50		H_2O_2, 0.2	13	Rough, irregular
34	E. F. Houghton No. 1		0.5	NH_4 Alg.	0.7	Morpholine	2.5	50	50		H_2O_2, 0.1	35	Adheres to glass; slightly cloudy
									225		H_2O_2, 0.2	30	Same
35	E. F. Houghton No. 4		1.0	NH_4 Alg.	1.0			50	50		H_2O_2, 0.05	26	Adheres to glass; slightly cloudy and brittle
									45		H_2O_2, 2	150	Gummy, soft, tacky
									45		H_2O_2, 2	90	Soft and tacky

[a] Refluxed during polymerization; temperature of mixture was approximately 75° C.; films were prepared by pouring a sample of emulsion onto a glass plate and allowing the water to evaporate.

[b] Ammonium alginate (Superloid).

[c] Plus 0.2 ml. of allyl acrylate.

[d] Insoluble in acetone or toluene.

[e] Allyl lactate maleate.

[f] Apple pectin after demethylation with acid.

[g] Modified casein.

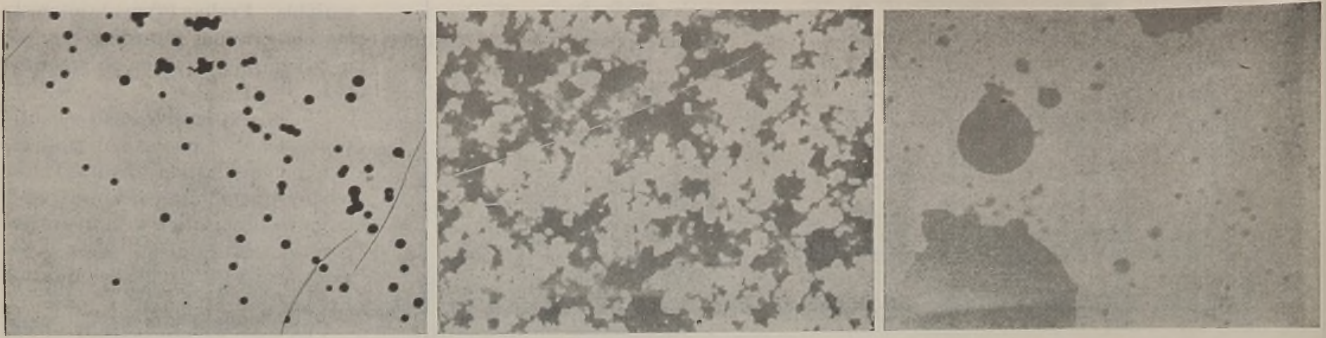

Figure 1. Electron Micrographs of Methyl Acrylate Polymer Emulsions

viscosity, and small amounts of these two agents, when used together, produce highly viscous emulsions.

The emulsions were made with the equipment and technique described early in the paper. After polymerization was completed, the emulsions were allowed to cool to room temperature with stirring and were then poured into glass bottles to stand overnight before the viscosity was measured. The samples were shaken gently, and the viscosity was determined with a Brookfield Synchro-lectric viscometer at 6, 12, 30, and 60 revolutions per minute. The emulsions were thixotropic and, in some instances, considerably thinned by agitation. The accuracy of the viscometer was checked periodically with oils of known viscosity supplied by the National Bureau of Standards. No attempt was made to maintain an accuracy higher than 10% of the scale value of the instrument.

It has been claimed (*4*) that casein retards the polymerization of some monomers. Results of the present work indicate that this effect causes no real difficulty. Of the various casein preparations studied—Protovac 8979, rennet casein, and acid casein—satisfactory results were obtained only with Protovac 8979.

Although emulsifiers other than Tergitol Penetrant No. 4 were given little attention, Triton K60 and Daxad No. 11 were used satisfactorily (in combination with ammonium alginate and modified casein) to produce viscous, acrylic resin emulsions. Nacconol seemed less suitable.

The few observations made of the pH value indicated that the emulsions were never highly acidic or basic. This might have been partly due to a bufferlike action of the casein. In some instances a mixture of sodium borate and sodium hydroxide was added before polymerization without any important noticeable effect.

The size of resin particles in several methyl acrylate polymer emulsions was determined by examination of electron micrographs. Representative fields are shown in Figure 1. The particle size in some emulsions was rather uniform, most diameters lying in the range 0.1 to 0.4 micron (Figure 1*A*). *B* illustrates the aggregation of spherical particles of the same emulsion to form chains, clusters, and networks. In many cases coalescence was incomplete, as evidenced by density variation over the image of aggregates and especially by the circular outline of particles near the periphery. *C* shows the tremendous variability in particle size in one of the resin emulsions. Particles ranged from less than 0.1 to more than 7 microns in diameter.

Films were prepared from some of the emulsions (casein and ammonium alginate type) by spreading the emulsion on a pane of glass and allowing the water to evaporate. The films prepared from foamy emulsions had bubbles, but this difficulty could be avoided by adding a small amount of *n*-hexanol or *n*-octanol, either before or after the emulsion polymerization. Because of

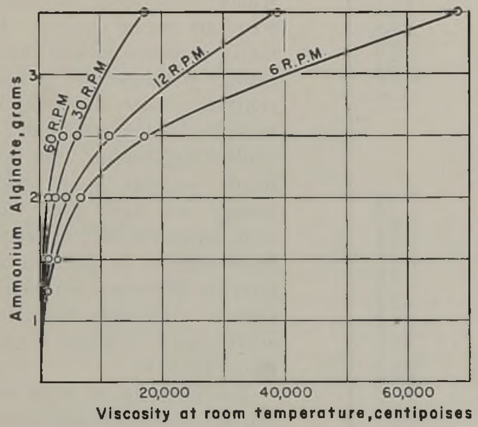

Figure 2. Effect of Ammonium Alginate on Viscosity

TABLE III. EMULSION POLYMERIZATION OF ETHYL ACRYLATE[a]

Expt. No.	Emulsifier	Grams	Water, Ml.	Ethyl Acrylate, Grams	Ammonium Persulfate, Mg.	Time, Min.
1	Tergitol Penetrant No. 4	3	300	200	3.0	80
2	Tergitol Penetrant No. 4 paste	4	400	200	5.0	50
3	Triton 720	2.5	400	130	5.0	50
4	Triton 720 Tergitol Penetrant No. 4	1.0 2.0	400	200	5.0	50
5	Triton 720 Tergitol Penetrant No. 4	4.0 14.0	1600	800	5.0	100
6	Triton 720 Tergitol Penetrant No. 4 paste	30.0 60.0	6000	3000	40.0	180

[a] Refluxed; temperature 82–91° C.

TABLE IV. EMULSION POLYMERIZATION OF METHYL ACRYLATE

Expt. No.	Ammonium Alginate, Grams	Protovac 8979, Grams	Other Agents, Grams	Water, Ml.	Methyl Acrylate, Grams	Ammonium Hydroxide, G.	Ammonium Persulfate, G.	Time, Hr.
1	1.25	10.0	Tergitol Penetrant No. 4, 5.0	300	150	0.9	0.125	2 1/2
2[a]	6.25	35.0	Tergitol Penetrant No. 4, 23.5	1500	750	10 0	0.112	2 1/2
3[b]	0.4	3.0	Tergitol Penetrant No. 4, 3.2	140	73	0.9	0.290	8 1/2
4	1.5	..	*l*-Ascorbopalmitate[c], 1.0	175	125	1.0	0.120	4 1/2
5	..	..	Ursolic acid, 1.5; Pectinate H-69[e], 1.0	200	150	1.5	[d]	5
6	4.0	..	E. F. Houghton No. 1, 4.0	250	250	3.0	0.800	2 1/4

[a] 15 ml. *n*-hexyl alcohol also used.

[b] 0.3 g. Sudan Red BBA dissolved in monomer.

[c] Palmitate of ascorbic acid (*14*).

[d] 13 ml. H_2O_2.

[e] Apple pectin after demethylation with acid.

TABLE V. VISCOSITIES OF COMPARABLE SOLUTIONS AND EMULSIONS OF POLYMERIZED ETHYL ACRYLATE[a]

Concn. of Polymer, %	Viscosity, Minutes Ethyl acetate soln.	 Aqueous dispersion
5	17.2	12.2
10	64.6	12.4
20	No longer measurable	12.7
25	Ditto	12.8
50	Ditto	20.3

[a] Viscosities were determined at 20° C. in the No. 4 Ford cup.

TABLE VI. EFFECT OF AMMONIUM ALGINATE ON VISCOSITY OF METHYL ACRYLATE EMULSIONS[a]

Expt. No.	Ammonium Alginate[b], Grams	Brookfield Viscosity, Centipoises 6 r.p.m.	 12 r.p.m.	 30 r.p.m.	 60 r.p.m.
1	0.25	Too low	3	6	8
2	0.75	40	40	35	32
3	1.25	910	615	370	260
4	1.75	3,500	2,250	1,200	780
5	2.00	6,400	4,150	2,200	1,440
6	2.50	17,000	10,800	5,800	3,750
7	3.50	68,000	39,000	17,280	Above range of spindle

[a] Ingredients other than ammonium alginate: water, 350 ml.; Protovac 8979, 7 g.; Tergitol Penetrant No. 4, 5 g.; methyl acrylate, 250 ml.; dodecyl mercaptan, 1 ml., and hydrogen peroxide. Viscosity of water at 20° C. is 1.0050 centipoises.

[b] Superloid.

excellent adherence, it was difficult to remove some of the films from the glass surface. The films could be removed easily, however, after soaking in hot water.

Water resistance of some of the films was determined by suspending a strip of the film in water for several days, noting the increase in weight, and observing the effect of the water on the appearance and strength of the specimen. Resistance to water was not satisfactory, but the methyl acrylate and methyl acrylate–acrylonitrile films were little affected by hydrocarbons containing less than 50% aromatics.

EFFECT OF AMMONIUM ALGINATE. As mentioned above, the greatest increase in viscosity resulted when both the alginate (Superloid) and casein preparation (Protovac 8979) were used. Increasing the proportion of alginate, however, was more effective in increasing the viscosity than using larger amounts of the modified casein (Table VI and Figure 2). When the quantity of ammonium alginate was increased from 0.25 to 3.5 grams, the viscosity of the resulting emulsions was raised from approximately 2 to 68,000 centipoises, a 34,000-fold increase. This remarkable increase in viscosity, however, depended on the modified casein, since fluid emulsions (2 to 5 centipoises) resulted when the casein preparation was omitted. It is apparent from Figure 2 that the greatest effect on the viscosity was caused by increasing the quantity of ammonium alginate from 2 to 3.5 grams (0.84 to 1.47% by weight of the methyl acrylate polymerized).

EFFECT OF MODIFIED CASEIN. The modified casein (Protovac 8979) also increased the viscosity of the emulsions (Figure 3). Less than approximately 3 grams had little effect on the viscosity, but the viscosity increased greatly when the quantity was increased from 3.5 to 14 grams (1.47 to 5.9% by weight of the methyl acrylate polymerized).

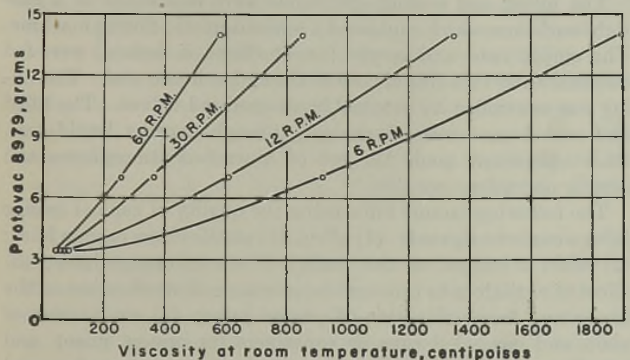

Figure 3. Effect of Protovac 8979 on Viscosity

The quantity of the casein preparation required to produce viscous emulsions was appreciable; hence the influence of the casein on the properties of the resin films deposited from the emulsions merits consideration. The films obtained from the resin emulsions contained approximately 1.5 to 6.0% of the modified casein. The casein decreased tack and increased the water resistance of the films, but the most noticeable effect was the increased tenacity with which these films adhered to smooth surfaces. Hence, the over-all effect of the casein preparation in the resin film appears beneficial. Butler (*3*) stated that as much as 10% of Protovac 8979 in films of ester resin does not affect water resistance or durability.

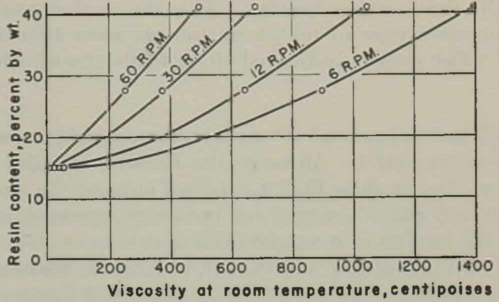

Figure 4. Effect of Resin Content on Viscosity of Polymethyl Acrylate Emulsions (Brookfield)

EFFECT OF RESIN CONCENTRATION. Unlike the acrylic resin emulsion (Table V) described by Jackson (*8*), the viscosity of the emulsions prepared with peptized casein and ammonium alginate was dependent on the resin content, particularly when the resin content was higher than 15% (Figure 4). This fact may be attributed to the alginate and modified casein, since emulsions containing as much as 55% of acrylic resins were fluid in the absence of these agents. Other ingredients used in the experiments shown in Figure 4 were 150 ml. water, 0.4 gram ammonium alginate, 3.0 grams Protovac 8979, 3.2 grams Tergitol Penetrant No. 4, and hydrogen peroxide.

ACKNOWLEDGMENT

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Quality of Canned Orange Juice

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Some factors affecting the flavor of canned orange juice have been studied. The influence of oxygen, volatile oil, and heat treatment during sterilization and cooling was determined on a large number of samples packed with specially designed equipment. The effects of storage temperature and type of metal containers were also investigated. The results indicated that, while the elimination of oxygen during preparation and canning of orange juice is highly desirable, its substantially complete elimination through the use of inert atmospheres did not entirely prevent flavor deterioration. The length of heat treatment for sterilization was a more important factor in flavor loss than temperature. Low storage temperatures were found to be most favorable for flavor retention.

THE first commercial attempts to can orange juice were far from successful. Although the research recorded in the literature, largely since 1927, has helped improve the quality of commercially canned orange juice, further improvement is necessary if this product is to compete with fresh juice or other canned juices. During canning and storage, undesirable flavor changes are encountered. The characteristic flavor and flavor changes are, in the main, due to trace constituents such as esters, alcohols, volatile and nonvolatile oils, proteins and other nitrogenous substances, pectinous materials, vitamins, etc. Such changes occurring in orange juice after canning and upon subsequent storage may be divided into two types: (1) loss of original flavor and (2) development of flavors foreign to the fresh juice.

Some of the factors influencing the destruction of flavor may also be responsible for the development of off-flavors. Changes in canning practice that may greatly reduce or prevent the development of off-flavors may not necessarily prevent the loss of original flavor. Consequently, efforts toward preservation of orange juice should take both types of change into consideration.

Analyses have shown that the original oxygen content in a can of orange juice is reduced to practically zero in a short time. Oxidative changes in orange juice are marked by a loss in the reducing substances as measured by the reaction with iodine or 2,6-dichlorophenol indophenol. Eddy (*2*) found, however, that a greater amount of oxygen was absorbed than was indicated by potential reducing substances as determined by the dye titrations of the fresh juice.

There is an increase in the carbon dioxide content of canned orange juice during storage. This change has been observed by Wilson (*12*) and Loeffler (*3*). The increase in carbon dioxide content is greater than can be accounted for by the oxygen consumed. Loeffler (*4*) reported a correlation between carbon dioxide increase, storage, and flavor changes, and ascorbic acid loss, an indication that the carbon dioxide may be one of the end products of reactions that may contribute to off-flavor development.

Von Loesecke, Mottern, and Pulley (*10*) found an increase in invert sugar from 5.54 to 9.14% and a decrease in sucrose from 6.36 to 1.21% and a drop in pH from 4.02 to 3.62 without any change in titratable acidity in canned orange juice stored for nine months at 80° to 100° F. Nolte and Von Loesecke (*6*) endeavored to trace some of the off-flavors in canned orange juice to the oxidation of the fatty material in the juice. This work indicated that in aged canned orange juice, the fatty material had undergone oxidative change, with the creation of hydroxy acids and other products associated with rancidity development.

Extensive investigations have been made by the authors to determine the changes occurring in orange juice during preparation, canning, and storage, and to find means of preventing these changes. These have included studies of the effect of antioxidants, chemical preservatives and other additions, as well as preparation and processing operations. However, this discussion is limited to those studies which can be broadly classed as canning practices.

In order to conduct a number of these investigations, special equipment had to be constructed. A number of the experiments were also carried out in commercial size equipment with the exception of the filling and closing unit. A brief description of this equipment follows:

For pretreatment of the oranges to reduce the amount of oil liberated from the peel during juice extraction, and to reduce the bacterial contamination, an enclosed 20-foot roller conveyor was used. This was equipped for either liquid spray or steam treatment.

A rotary press type extractor was used; it was enclosed in a gastight sheet metal housing with liquid seals through which the fruit entered and the waste discharged. The finisher was completely enclosed with a liquid seal for discharge of seed, rags, etc. The deaerator was of the spray type, equipped with a float-controlled inlet valve.

The pasteurizer was a commercial, small-tube heat exchanger with a constant rate of flow. The juice entered the pasteurizer under high pressure, so that boiling was prevented regardless of temperature used. The heating period was approximately 2 seconds, with a cooling period of approximately 5 seconds. It was generally operated without any holding time at the top temperature.

The filling and sealing operations were conducted in a gastight enclosure which contained a semiautomatic closing machine. The empty cans and covers (pre-sterilized if desired) were fed automatically into this enclosure through a liquid seal. The filling was controlled by external hand-operated valves. The filled and sealed cans were discharged through another liquid seal. Such equipment made the use of controlled atmospheres and aseptic operations possible.

The following factors influencing the quality of canned orange juice were investigated: (1) effect of volatile oil on orange juice; (2) effect of oxygen on the quality of canned orange juice; (3) effect of variations in time and temperature of sterilization on the flavor and flavor retention of orange juice; (4) comparison of plain and enameled cans as containers for orange juice; and (5) effect of storage temperatures on flavor retention of canned orange juice.

Since it was impossible to make all the experiments using one lot of oranges, sufficient replication of packs was made with different lots of oranges so that variations in fruit could be discounted and samples prepared by different procedures from different lots evaluated on a relative scale. More than one hundred experimental packs, totaling many thousands of individual samples, were put up during these investigations. Periodic examinations of samples from these packs and commercial samples packed at approximately the same time were made over a period of 18 months. It is to be expected that, in such large number of samples, anomalous findings would occasionally occur. For these reasons the results of individual examinations are omitted, and only the over-all findings and conclusions are discussed.

VOLATILE OIL CONTENT

The presence of volatile oil in fresh orange juice gives it a pleasant aroma and adds to the flavor. However, under certain conditions, the presence of even small amounts of oil in canned orange juice on prolonged storage may give rise to objectionable off-flavors. It has been found that objectionable flavors due to volatile oil may develop on prolonged storage with an oil content as low as 0.01%. Numerous experimental packs in which the volatile oil content was below 0.007% (some as low as 0.001%) after 18-month storage, even at room temperature, did not develop the off-flavors produced by the presence of higher oil contents. However, orange juice prepared in the laboratory eliminating all peel oil was lacking in aroma and tasted somewhat "flat".

Volatile oil from the peel is incorporated with the juice at the time of extraction. The amount incorporated depends to some extent on the method used in preparing the juice. Some of the early mechanical extractors gave a much higher oil content than hand reaming. Commercial mechanical extractors are now in use which, when properly operated, will produce a juice having a very low oil content. To take advantage of the capabilities of these machines, the fruit must be accurately sized to fit the cups or pockets and the machine adjusted to use no more pressure on the fruit than is necessary to extract the juice. The oil is not readily expressed from the peel by pressure against a smooth surface, but any bending or tearing of the peel will release a relatively large amount of oil. The amount of oil from the peel entering the juice during extraction can be greatly reduced by giving the oranges a short steam or hot water treatment. While the steam treatment had been used earlier to reduce bacterial contamination, so far as is known, it was first tried out in Florida in 1940 for lowering the oil content of the juice. At the suggestion of V. C. Guse of this company, this method was put into practice by some canners experiencing difficulties with peel oil in their citrus juices following the freeze in February, 1940. Since the authors were conducting experiments on orange juice canning at that time, the effect of steaming of the fruit on the reduction of peel oil entering the juice was further investigated. For this study an enclosed roller conveyor was used, the steam being admitted through jets above the fruit. The same type of extractor, previously mentioned, was used for extraction of the juice. In these tests, fruit showing no frost damage, moderate damage, and severe damage was used. The results are given in Table I.

The method of analysis of the volatile oil content was an adaptation of the Clevenger method employing an oil separatory tube and direct distillation of 1000 ml. of orange juice (*1*). This was not an official method but actually gave slightly higher percentages of volatile oil than the official steam distillation procedure.

Another series of tests using samples from the same lot of fruit, using steam periods of 0, 1, $1\frac{1}{2}$, 2, 3, 4, and 5 minutes, were made. These tests showed a steaming time of 1 minute to be satisfactory, with $1\frac{1}{2}$ and 2 minutes only slightly more effective. Steaming for periods of more than 2 minutes did not give any further decrease in the amount of oil entering the juice. Immersing the fruit in hot water (185° F.+) for $\frac{1}{2}$ to 3 minutes was found to be as effective in reducing peel oil as steaming. Scott (*9*) reported similar results using grapefruit.

Table I. Effect of Steam Treatment of Oranges before Extraction of Juice on Volatile Oil Content of Juice

	Oil Content of Juice, %	
Variety of Orange	Washed but not steamed	Washed and steamed 5 min.
Valencia and Pineapple (severe freeze damage)	0.04	0.029
Valencia (no freeze damage)	0.022	0.007
Pineapple (low in juice due to freeze damage)	0.04	0.015
Exptl. packs (Valencias showing no freeze damage)	...	0.002
		0.001
		0.007
		0.009

The steam or hot water treatment volatilizes any peel oil that has been released by mechanical damaging of the surface. However, contrary to popular belief, this is only a small fraction of the oil that would normally enter the juice. The chief beneficial action of the treatment is in the softening or wilting of the peel, making it more pliable so that few of the oil cells are broken during the extraction treatment.

For commercial operation the hot water method is preferable as it is simpler to control, and uniform treatment of fruit is assured. The water should be maintained at 180° F. or higher and the treating period should be for at least 1 minute. The fruit should pass first through a brush washer and over the sorting belt prior to the heat treatment. This ensures against possible rupturing of the oil cells following heat treatment and minimizes collecting of dirt in the treating bath.

EFFECT OF OXYGEN

Numerous experiments were made to determine the effects of oxygen on flavor retention of canned orange juice. Using equipment previously described, orange juice was extracted in inert atmospheres[1] (nitrogen and carbon dioxide), screened, pasteurized, cooled, and canned under aseptic conditions in inert atmospheres. Orange juice was also prepared and handled in a similar manner with the additional treatment of deaeration (degassing) between screening and pasteurization. Orange juice was also extracted in air, deaerated, pasteurized, cooled, and canned in a nitrogen atmosphere. Juice similarly prepared was canned in air. Other cans were vacuum-closed, and some were closed with oxygen in the head space. Other packs were made using commercial methods except that the air was replaced in the head space just prior to closure with nitrogen using a special machine, other cans closed in the usual manner being taken as controls. In most of the above experiments the pasteurization consisted of heating the juice to 225° F. in 2 seconds and immediately cooling, the temperature being reduced to around 100° F. in 5 seconds. For comparative purposes a number of samples of commercially canned orange juice, both deaerated and nondeaerated, packed at approximately the same time as the experimental packs were obtained.

The over-all results, obtained on periodic examinations over a period of 14–18 months, indicated that the use of a nitrogen atmosphere in the extraction and canning chambers gave slightly better retention of flavor. However, juice extracted in air and immediately deaerated, pasteurized, cooled, and canned under aseptic conditions in nitrogen, was very close to that handled entirely under nitrogen. In fact, no difference was detected in a few packs. Carbon dioxide was found to be slightly less satisfactory than nitrogen for use as an oxygen-free atmosphere. The juice handled under carbon dioxide often had a slight foreign flavor which for lack of a better description was called "musty".

Large amounts of oxygen will cause a rapid loss of flavor and the development of foreign flavors as well as darkening of the juice. While similar changes probably occur with small quanti-

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[1] A number of patents cover parts of these procedures.

ties of oxygen but to a correspondingly lesser degree, other factors than oxygen that cause flavor change may completely overshadow the oxygen effect.

Oranges contain small amounts of oxygen which, according to Roberts and Gaddum (*8*), ranges from 0.18 to 0.20 per cent (calculated basis). In extracting orange juice in inert atmospheres, the juice is therefore exposed to relatively small amounts of oxygen. Samples of canned juice that have been extracted in a nitrogen atmosphere and degassed to remove this oxygen also gradually changed in flavor upon storage. The change was largely a loss of flavor rather than the development of foreign flavors. It is thus evident that substantially complete elimination of oxygen will largely prevent the development of foreign flavors but will not prevent ultimate loss in flavor.

Theoretically, juice that has not been deaerated even though filled hot may contain more oxygen than is normally present in the head space of properly filled cans. For this reason the removal of air from the head space with an inert gas alone may be of little benefit unless the oxygen content of the juice is low. Samples of commercially canned orange juice, which had the air in the head space removed with nitrogen just prior to closure, had slightly better flavor than controls from the same run closed without air removed. This difference, however, usually disappeared after about six weeks of storage. No flavor differences were then perceptible on periodic examination for one year.

Oxygen in the can may also cause some loss of ascorbic acid. However, this loss may become a relatively large proportion of the total under some conditions. To illustrate, an experimental pack of deaerated sweetened orange juice was made very late in the season in Florida (June, 1944) using both plain and enameled cans. In some cans the head-space air was replaced with nitrogen just prior to closure; others were closed in the usual manner. Since this was very late season juice, the ascorbic acid content was low. Direct titration, with dichlorophenol-indophenol, of samples to which had been added an equal volume of buffered 3% metaphosphoric acid gave the following results three weeks after canning:

Type of Can	Ascorbic Acid
Enameled, head-space air removed	26.4 mg./100 ml.
Enameled, control	21.8
Plain, head-space air removed	28.3
Plain, control	27.0

In addition to accelerating the rate of flavor change in the juice, and the loss of ascorbic acid, excessive oxygen in canned orange juice often causes loss of adhesion and peeling of the enamel in enamel lined cans and promotes corrosion of the tin plate in plain cans. This corrosion may, if excessive, impart undesirable metallic flavors to the juice. It is evident that there are several reasons why, in canning orange juice, the oxygen (air) content of the cans should be held to a minimum. To keep the oxygen content to a minimum, the juice should be thoroughly deaerated before pasteurization and canned with the least amount of reaeration possible. The use of nonaerating filling equipment is highly desirable. Deaeration has been discussed by Pulley and Von Loesecke (*7*). For adequate deaeration the temperature of the liquid determines the vacuum required. This relation for substantially complete removal of dissolved gases is shown in Figure 1. Slightly lower vacuums (1 to 2 inches) than those shown on the curve will give satisfactory results with some types of deaerators, provided the deaerator is not overloaded. Where proper vacuum is used, the juice must be exposed in thin films or as a fine spray, otherwise the dissolved gases will not have time to diffuse out of the juice. Best results are obtained when the vacuum liquid temperature relation is such that slight boiling of the liquid occurs.

EFFECT OF STERILIZING METHODS

Improper heat treatment during pasteurization and canning often causes the development of undesirable cooked flavors. Considerable information can be found in the literature (*5, 11*) on the proper sterilization temperatures for orange juice in ranges below 212° F. In the work reported in this paper, temperatures ranging from 175–240° F. were investigated for the purpose of determining the effect of a wider range of temperatures than was previously reported.

Orange juice free from spoilage bacteria was prepared by surface sterilization of stemless oranges free from breaks in the skin, and extracting under aseptic conditions in inert atmospheres. Both chemical and steam sterilization methods for surface sterilization were tried. The steam treatment reduced the amount of peel oil as well as destroying the surface bacteria. The use of sterile juice, prepared in this manner, made possible the canning of unprocessed juice under aseptic conditions, and a study of mild heat treatments that were known to be inadequate for preservation under normal conditions.

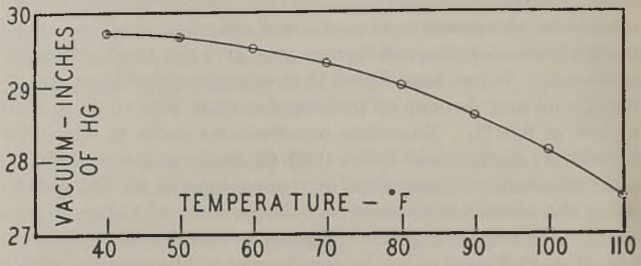

Figure 1. Vacuum Required for Complete Removal of Dissolved Gases in Flash Deaeration at 40° to 110° F. at 30-Inch Barometer

Using orange juice prepared as described above, packs were made with no further heat treatment. Other packs using juice from fruit similarly treated but without precautions to ensure complete sterility were heated to various top temperatures in 2 seconds and immediately cooled, so that the filling temperatures were reached in 5 seconds. Top sterilizing temperatures of 175° to 240° F. in 5° steps, and filling temperatures with the rapidly cooled juice of approximately 135°, 110°, and below 100° F. were studied. In those packs where the closing temperature was above 100° F., the cans were water-cooled to approximately room temperature. In some instances a few samples were allowed to air-cool. Other packs were made in which the orange juice was heated to 180–185° F. and filled hot with the closed cans being water-cooled to below 100° F. after holding for approximately 30 seconds. A few small packs were made in which the juice was canned cold and processed in the can in boiling water, both still and agitating cooks being used. The cans were similarly water-cooled after processing.

The results obtained in these experiments indicate that the temperature to which the juice is heated during processing is a minor factor in the cause of cooked and other off-flavors. The length of time the juice is at elevated temperatures is the major factor in determining the amount of cooked flavor in the final product and, to some extent, the rate of flavor change during storage under normal conditions. Orange juice which was heated to 240° F. in 2 seconds and then rapidly cooled to 100° F. and canned under aseptic conditions was initially better flavored and deteriorated at a slower rate than the best commercially canned juice packed in the same area at about the same time. Inoculated packs included in this study required a top temperature of 225° F. for sterilization when immediate cooling was employed.

Samples from none of the packs where the juice was rapidly heated and cooled to 100° F. or lower, prior to canning, had any detectable cooked or other foreign flavor immediately after packing. Those similarly treated but filled at 135° F. had a very slight cooked flavor (odor). Samples from those packs where the juice was filled hot (180° F.) usually had some cooked flavor shortly after packing, being less in those that were completely water-cooled than in those that were only partially water-cooled and then allowed to air-cool. The following example illustrates the desirability of adequate cooling of the juice before storing. Two consecutive cans of orange juice coming from the cooler in a commercial cannery were taken. The temperature was approximately 110° F.; one of these was immediately water-cooled to room temperature (75° F.), while the other was allowed to air-cool. Eighteen hours later the two samples were flavor-tested. The one that had been completely water-cooled had an excellent flavor. The one that was allowed to air-cool in the usual manner had developed a more pronounced cooked flavor and was so changed in flavor that the two samples would not be recognized as being from the same pack.

The results obtained in these tests indicate that for best results orange juice should be pasteurized using a high-temperature short-time method with complete cooling (at least to 100° F.) in the shortest practical time.

The exclusion of oxygen from the specially prepared nonheated and/or mildly heated juice by the use of inert atmospheres should minimize any activity of oxidative enzymes. It was expected that some enzymes might not be inhibited with some of the milder heat treatments used. Taking the separation and clarification of the juice as an index, it was found that even the mildest heat treatment greatly reduced the enzyme activity. The juice that was not given any heat treatment showed rapid settling with clarification in a few days. In those packs where rapid heating and cooling were used, the rate of separation decreased as the processing temperature increased. In those packs where the top temperature was 225° F. and higher and in those where hot closure or long processing times were used, complete clarification did not occur during one-year storage at room temperature.

The packs of juice that had not been heat-sterilized[2] lost flavor more rapidly than sterilized juice when stored at room temperature and higher, but under refrigeration (32–40° F.) for one year it appeared that the processed samples deteriorated slightly more in flavor as compared to the unprocessed juice. These differences may be due to enzymatic action in the case of room-temperature storage and the effect of heat treatment in the case of samples stored under refrigeration. However, the flavor differences of the refrigerated samples, although slightly in favor of the unprocessed juice, have little practical significance since conditions for preparing such juice are not considered commercially practical.

STORAGE

The storage temperature of canned orange juice is a very important factor in the prevention of the loss in flavor. Storage temperatures ranging from 32° to 98° F. were investigated. In all cases there was some loss in flavor when samples were stored up to 12 months or more. Canned orange juice stored at room temperature, when the maximum temperature was slightly below 70° F., showed little flavor change after nearly 4 months. In fact, less change occurred under these conditions than was noted in samples from the same pack after about two weeks at 90° to 100° F. Samples from a number of separate test packs that had been stored at 40° F. for 14 to 18 months were found, on direct comparison, to have a better flavor than a number of commercial samples that had been canned less than four months and kept at the prevailing room temperature (65–85° F.).

The results obtained from these storage tests lead to but one conclusion, namely: Canned orange juice should be kept at the lowest temperature (above freezing) that is economically practicable. These results confirm those of several other investigators.

CONTAINERS

The tin can is the common container used for canned orange juice, two types of cans—plain and enamel lined—being employed. In Florida the plain can is used almost exclusively; in California the enamel lined can is used. Plain cans cause some bleaching of the color of orange juice and impart a characteristic flavor, which are apparently due to the reducing action of the tin. The corrosion of the tin is, to some extent, dependent on the oxygen in the can. This slight change in color and flavor is not seriously objectionable, but is at least undesirable in a product that must compete, to some extent, with fresh juice. The use of enameled cans prevents the loss of color and the development of flavors due to metallic contact; with some enamels, the terpene flavor may be less due, apparently, to some absorption of the terpene in the enamel. With a given oxygen content, more oxidation of the juice constituents occurs in enameled cans than in plain cans.

RECOMMENDATIONS

Commercial equipment is not available for some of the operations found to give the best canned orange juice. For this reason the following general recommendations, made for available equipment, will lead to a substantially improved quality of canned orange juice:

1. The best fruit available from a juice standpoint should be used, with blending of fruit from several sources when necessary for the desired juice characteristics.
2. After washing and sorting, the fruit should be given a hot water treatment of 1–2 minutes (180–185° F.) to wilt the peel and thereby reduce the amount of oil extracted.
3. An extractor should be used which can be operated so that little oil (0.010% or less is most desirable) from the peel enters the juice. Fruit should be properly sized to fit the cups or pockets of those extractors that hold the cut fruit in cups during the extraction operation.
4. The juice should be screened to remove rag, seeds, etc., as soon as possible after extraction.
5. The juice should be immediately deaerated under suitable vacuum as determined by the juice temperature.
6. The juice should be flash-sterilized using high-temperature short-time pasteurizers, heating to 225–240° F. in a few seconds, and immediate cooling to approximately 185° F.
7. After flash sterilization, the juice should be filled into cans with the minimum amount of reaeration during filling and closed with as complete exclusion of head-space air as possible.
8. The filled cans should be held only long enough to ensure sterility of the can and then rapidly water-cooled to 100° F. or lower.
9. The canned juice should be stored at the lowest temperature economically practical until consumed.

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[2] The unsterilized juice was prepared in a manner to ensure freedom from spoilage organisms and with substantially no exposure to oxygen at any time.

Separation of Cholesterol from Degras

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Wool fat (degras) was saponified in 52.5-pound batches by sodium hydroxide, and the unsaponifiable material was extracted from the wet soaps by gravity separation with ethylene dichloride. Cholesterol of 97% digitonin precipitability was prepared from the unsaponifiable extract in 4-pound yields per batch by a pilot process based on the formation of the oxalic acid addition product insoluble in ethylene dichloride solutions. By-products obtained per batch were 37 pounds of fatty acids, 14 pounds of oily unsaponifiable material, and 9 pounds of isocholesterol wax.

THE development of a process for the production of cholesterol from wool fat was undertaken to find a new source of cholesterol for a prospective and rather extensive use in the vitamin field (*10*). Supplies were limited and high in price while millions of pounds of low-priced wool fat (degras of commerce) rich in cholesterol were available in the United States. This raw material contains about 15% cholesterol. The supply is sufficiently constant and large, and should continue to be so as long as wool is prepared for spinning.

The main difficulties encountered in the use of wool fat unsaponifiable extract as a source of cholesterol are due to the large variety of similar organic products of which it is composed. The unsaponifiable portion composes about 40% of the degras. It contains isocholesterol, which consists largely of lanosterol and a small amount of agnosterol. While present in about half of the percentage of cholesterol, isocholesterol has properties so similar to those of cholesterol that the two have been separable in quantities only with difficulty by mixing solvents in lengthy and involved fractionation procedures. A sharp separation in small quantities can, however, be effected through the digitonide. Other less expensive addition compounds are known, but are lacking generally in specificity or insolubility in appropriate solvents. Other methods of separation involving fractional crystallization procedures with various solvents have been proposed (*2, 5, 8*).

Oxalic acid was first used for the separation of cholesterol from the almost inseparable isocholesterol of wool fat products by Madinaveitia and Gonzalez (*4*) in 1916. They treated the wool fat unsaponifiable extract, dissolved in ether, with an ether solution of oxalic acid; the addition compound of cholesterol gradually crystallized in a relatively pure condition. This method has not been utilized to any extent because of the low yields obtainable from the kind of unsaponifiable that can be produced on a large scale. Also the extensive use of ether in such operations is hazardous. It has been found, however, that the cholesterol addition product separates first, with minimum amounts of oxalic acid, from certain solvents; but with an excess of the acid the isocholesterol also forms an insoluble addition compound, and the two products separate together from the solvent solution at room temperature. Furthermore, other sterol derivatives have been found by Meischer and Kägi (*6*) to form insoluble oxalic acid addition compounds. Stronger acids such as the halogen (*11*) and sulfuric acids (*3, 8*) also form addition compounds with sterols, which are insoluble in certain solvents. Of these, halogen acid gases only were found adaptable to the recovery of cholesterol from wool fat (*11*). However, oxalic acid as a precipitant of sterols from wool fat unsaponifiable extract has these advantages: It is less corrosive, an excess is less destructive to sterols, the addition compound is more stable at higher temperatures, and it can be readily recovered.

In preliminary experiments with oxalic acid to find a solvent more suitable than ether, cholesterol oxalic acid separated most completely in those solvents which contained no oxygen. In this group the chlorinated solvents were more suitable because of low cost and resistance to fire. It was found that the cholesterol oxalic acid was the least soluble in the unsaponifiable extract of wool fat, dissolved in ethylene dichloride (*12*).

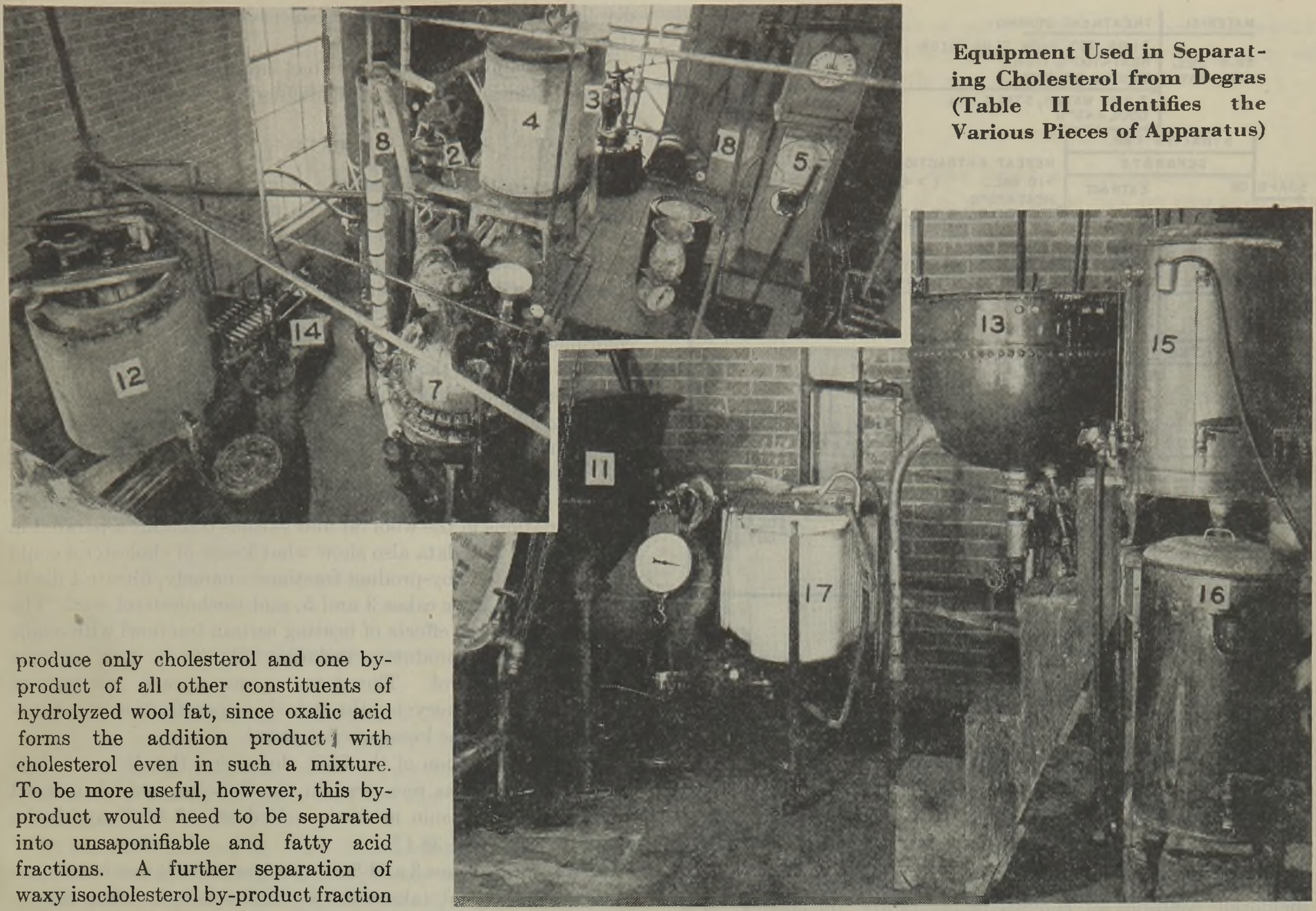
Preliminary experimental data in Table I demonstrated that anhydrous oxalic acid is sufficiently soluble in ethylene dichloride solutions of wool fat unsaponifiable extract at 60° C. to react and separate the cholesterol rather completely. In solutions of pure cholesterol (experiment 13) the acid is so little soluble, however, that the precipitation must be repeated on the filtrates to recover the cholesterol completely as the addition product. The latter contains, when pure, 89.5% cholesterol or two molecules to one of oxalic acid. In experiment 19 it was found that purification of the cholesterol in the first filter cake was possible by recrystallization of the addition product from excess of hot solvent with an over-all yield of 70%. Furthermore, the oxalic acid could be removed with hot water to leave a relatively pure cholesterol.

Table I. Preliminary Separations of Cholesterol with Oxalic Acid

Expt. No.	Unsap., Grams	Cholesterol %[a]	Cholesterol Grams	$(CH_2)_2Cl_2$, Ml.	$(COOH)_2$, Grams	*T*, ° C.	Cake, Grams	Cholesterol, %	Recovery, %
8	2	25	0.5	9	0.11[b]	25	0.55	68.0	75
11	10	25	2.5	50	0.57[b]	25	3.4	57.8	79
14	10	25	2.5	50	0.6	60	3.55	59.2	85
18	56.5 ml.		2.0	...	0.5	60	2.35	69.0	81
13	...	99	1.93	50	0.45	70	1.04 0.5 0.4	89.0	89
19	40	23.5	9.4	120	2.4	55	8.4	79.2	70

[a] By digitonin procedure.
[b] Dissolved in a minimum of acetone.

Although the primary objective in this work was the production of cholesterol from wool fat, the separation of the by-products in a useful form necessarily had to be kept in mind. Thus a process could probably have been developed to



Equipment Used in Separating Cholesterol from Degras (Table II Identifies the Various Pieces of Apparatus)

produce only cholesterol and one by-product of all other constituents of hydrolyzed wool fat, since oxalic acid forms the addition product with cholesterol even in such a mixture. To be more useful, however, this by-product would need to be separated into unsaponifiable and fatty acid fractions. A further separation of waxy isocholesterol by-product fraction without much additional complication of the process was also found possible due to the effect of oxalic acid at lower temperatures.

PILOT SCALE PROCEDURE

Preliminary experiments were carried on with unsaponifiable extracts of wool fat saponified at 100° C. with an excess of 45% caustic. Ethylene dichloride was stirred into the soaps at 70° C., and enough water added to separate the soaps in the aqueous layer. On cooling sufficiently, the solvent solution could be filtered from the soaps to make an unsaponifiable extract in ethylene dichloride relatively free of soaps. Filtration of this material had to be repeated with each succeeding extraction, and on a large scale this operation was impractical. Therefore, a method of separation by stratification was developed which could be completed in the saponification kettle without transfer of the soap fraction. Some features of this separation have since appeared in a patent issued to Buxton and Colman (*1*). Better than 90% of the cholesterol can be thus extracted and is in a form, after concentration, which is suitable for further processing.

The process shown in Figure 1 was developed for the separation of cholesterol and three by-product fractions from 52.5-pound batches of wool fat. Intermediate fractions containing cholesterol were recycled at two points in the process without building up interfering impurities. The separation is based upon the difference in solubility of the isocholesterol fraction in the presence of excess anhydrous oxalic acid and the cholesterol addition product at a temperature of 40–45° C. in ethylene dichloride solvent. By removing the isocholesterol from the chilled filtrate 2, a recrystallization of filter cake 2 in filtrate 3 then removed practically all impurities from the cholesterol oxalic acid cake 2 without much loss of cholesterol.

To obtain oxalic-acid-free cholesterol from filter cake 4, it was necessary only to stir it with sufficient water and solvent at 60° C. and allow the aqueous solution of oxalic acid to separate in the upper layer, draw off the clear solution of cholesterol in the solvent from the bottom, and distill it until free of water. On cooling, the cholesterol then crystallized in large relatively pure crystals.

In developing this procedure, however, a hitherto unrecognized property of cholesterol caused considerable difficulty and delay. In the presence of small amounts of water, concentrated ethylene

Table II. Description of Equipment

No.	Item	Description	Capacity, Gal.
1	Autoclave	Jacketed, lead-lined, 10-in. propeller stirrer, top and bottom vents, with slight glass in bottom vent	50
2	Autoclave	Jacketed, top and bottom vents, rake stirrer; connected to coil condenser	50
3, 4	Settling tanks	Chlorinated solvent drums	55 each
5	Pump	Gasoline, with dial register; operating to 15 lb. pressure	6 per min.
6	Storage tank	Copper, for solvent	100
7	Still 1	Pfaudler glass-lined, with stirrer, distilling head, and gage	40
8	Condenser	Tubular, copper and copper adapter	......
9	Still 2	Pfaudler glass-lined	20
10	Condenser	Glass-lined; sectional cast iron and glass-lined adapter	......
11	Vat	Jacketed, cast iron, for degras supply	100
12	Vat	Jacketed, stainless steel, for pptn. of cholesterol oxalic acid	50
13	Vat	Jacketed, copper, for crystallizing cholesterol	20
14	Filter press	Schriver, 12-in., plate and frame	......
15, 16	Separators	Jacketed, stainless steel urns	6 each
17	Centrifuge	Basket, aluminum, 18 × 10 in.; washer spinner dryer with copper tub	......
18	Dryer	Shelf, with air connections	......
19	Blower	Ventilator, with air suction lines	......

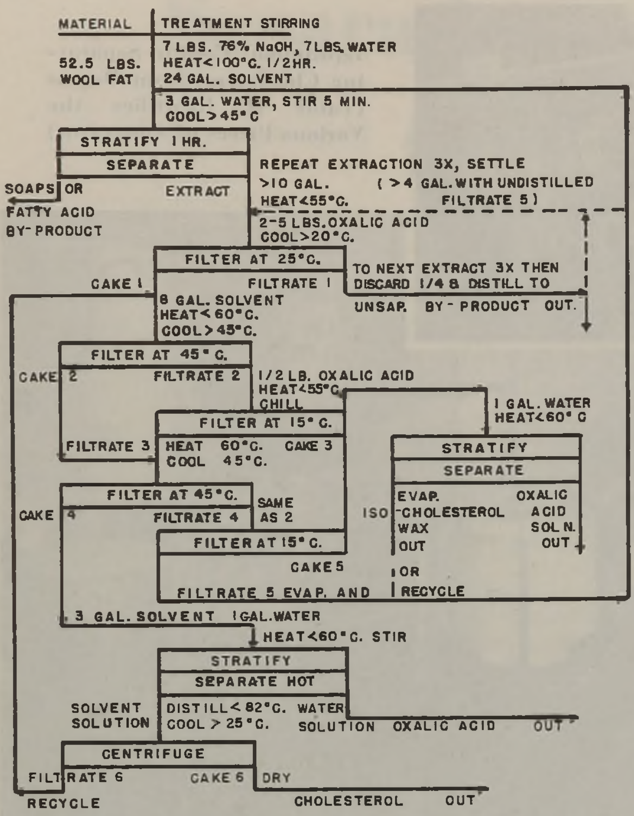


Figure 1. Steps in Process for Separating Cholesterol from Degras

dichloride solutions of cholesterol crystallize, on cooling, to a gelatinous mass which cannot be sufficiently freed of the mother liquor to dry pure. When the solution was distilled up to a vapor temperature of 83° C., the interfering traces of water were removed with the solvent; the cholesterol crystallized and could be centrifuged sharply from mother liquor filtrate 6 (Figure 1).

Further purification of cake 4 can be ensured by a third recrystallization. However, the two recrystallizations of cake 1 have produced purities of 75 to 80% by the colorimetric assay (*7*) which, with the excess oxalic acid present, indicates sufficient purity for subsequent successful separation.

EQUIPMENT. Figure 2 is a flow sheet indicating the equipment used. The arrangement proved very adaptable to numerous trials with changes in procedure. Since more suitable apparatus was not available because of the war, the miscellaneous equipment described in Table II was set up.

In lieu of suitable soap drying equipment, the extracted soap layer by-product (Figure 1) was converted with an equivalent of sulfuric acid to free fatty acids. The dense sulfate solution layer was drawn off from the bottom, and the solvent solution of fatty acids remaining was run into autoclave 2. This was equipped with a power rake stirrer and connected to a coil condenser to recover residual solvent from the fatty acid by-product by distillation. The hot fatty acid residue was then run out through the bottom vent.

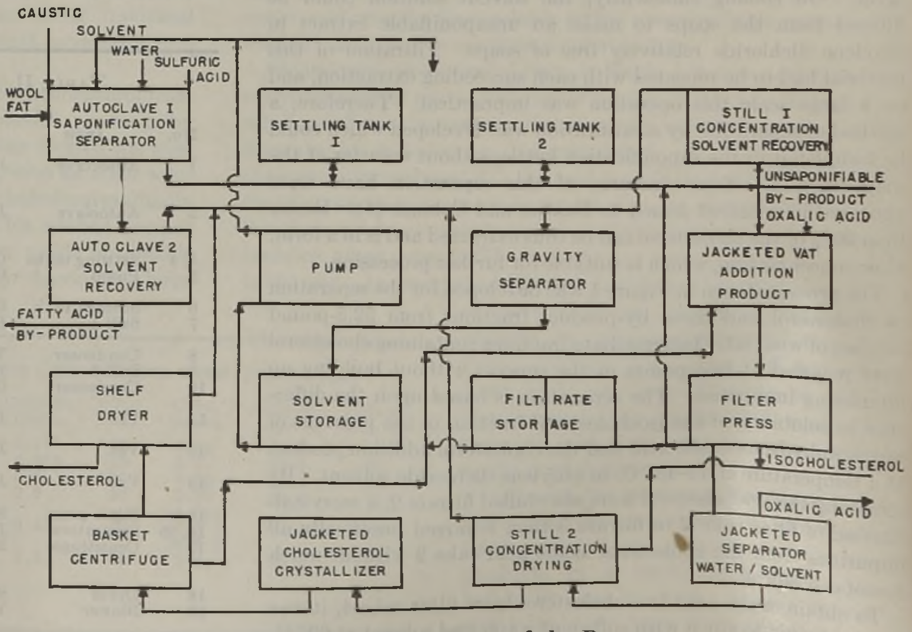


Figure 2. Flow Sheet of the Process

Neither copper nor stainless steel equipment was attacked by the hot oxalic acid and ethylene dichloride mixtures.

DATA

Because of the interference of esters in the crystallization of cholesterol, it was necessary to control the ester content. Since the alcohol-insoluble cholesterol digitonide is not formed from cholesterol esters which do develop the Liebermann-Burchard assay color with sulfuric acid and acetic anhydride, the difference in cholesterol content determined by both the digitonin and colorimetric assay techniques indicated the ester content. The methods used were the original gravimetric digitonin procedure of Windaus (*9*), modified for semimicrodeterminations by potash weighing filter tubes, and the colorimetric procedure of Meyers and Wardell (*7*), modified by a red Wratten light filter in the colorimeter.

Table III lists cholesterol determinations by the two methods to show variations in the wool fat and various fractions separated in the process. The data also show what losses of cholesterol could be expected in the by-product fractions—namely, filtrate 1 distillation residue, filter cakes 3 and 5, and isocholesterol wax. The data also show the effects of heating certain fractions with oxalic acid. These by-products, including filtrate 5, may contain esterified cholesterol. Therefore, as many such fractions as possible should be recycled through the saponification step to reduce still further the losses of cholesterol.

On recrystallization of the 98% cholesterol (lot 4) in ethylene dichloride, 76% was recovered in the first crop, which assayed 100% by the digitonin method, melted at 146–8° C. and had a rotation, $[\alpha]^{25}_{D}$, of −38.1°.

By reworking cakes 3 and 5 of experiment 143 it was found that purification did not take place by the usual procedure for recrystallization of cake 1 when the impurities were esterified. The analysis of this fraction shows that the cholesterol was not esterified. However, when the recrystallized cake was resaponified, extracted, and reprecipitated like the original ethylene dichloride extract with oxalic acid, cake 1 of 70% purity was obtained. Therefore, the unsaponified constituents other than cholesterol of cakes 3 and 5 had interfered with the separation of the cholesterol, and resaponification of the isocholesterol wax frac-

TABLE III. AMOUNT OF CHOLESTEROL IN PROCESS FRACTIONS OF WOOL FAT

Expt. No.	Material	Amount, Lb.	Cholesterol[a] % D	Lb. D	% C	Lb. C
1143	Degras *Z*	...	16.1	....	..	..
3844	Degras *Z*	...	16.8	....	20.5	..
5443	Degras *Z*	428	17.0A	72	..	..
5443	Degras *Z*, unsap. 1st & 2nd extn.	130	41.5	60	..	..
5443	Degras *Z*, unsap. 3rd & 4th extn.	43	36.0	15	..	..
139	$(CH_2)_2Cl_2$ ext.	53	13.1	6.9	19.1	10.1
139	$(CH_2)_2Cl_2$ ext., unsap.	26	29.1	7.7	..	..
139	$(CH_2)_2Cl_2$ ext. fatty acids	1	1.4	....	..	..
133	Filtrate 1	170	1.4B 2.6A	2.4B 3.5A	4.0	6.8
133–6	Filtrate 1, unsap. by-product	71	15.0A	10.7A	..	..
136	Cakes 3 & 5	38	.....	....	4.8	1.8
143	Cakes 3 & 5	68	7.6	5.1	6.3	4.3
	Cakes 3 & 5 reworked as cake 1					
143	To cake 2	9.1	.....	....	27.5	2.5
143	To cake 4	6.5	.....	....	26.6	1.7
143	To cake 4A[a] + oxalic acid	2.1	.....	....	70.4	1.5
135–9	Cakes 3 & 5 distn. residue	41	7.5	3.1	..	..
135–9	Cakes 3 & 5 distn. unsap.	31	34.0	10.5	..	..
135–9	Cakes 3 & 5 distn. fatty acids	5	6.8	0.3	..	..
140	Washed cakes 3 & 5 distn. residue	6	27.9	1.7	32.5	1.9
133	Filtrate 5	105	1.5	1.6	..	..
134	Filtrate 5 distn. residue	10	15.5	1.5	31.0	3.1
134	Filtrate 5 distn. residue unsap.	...	31.5	3.1	..	..
142	Filtrate 5 residue	9.5	21.1	2.0	24.2	2.3
136	Filtrate 6	20	.....	....	6.7	1.3
142	Isocholesterol wax	2.2	53.0	1.2	44.7	1.0
...	Cholesterol lot 3	50	97	....	..	..
...	Cholesterol lot 4	50	98	....	..	..
...	Cholesterol lot 4 recrystallized	...	100	....	..	..

[a] A denotes after saponification; B, before saponification; C, colorimetric assay; D, digitonin assay.

tion was necessary for the maximum recovery of its cholesterol content by this process. The yields of cholesterol listed in Table IV could probably be increased by recycling the isocholesterol wax fraction through the saponification step when the cholesterol content rises.

It should be pointed out that the data listed in Table IV were obtained through operation of the process as shown by Figure 1 except as indicated for the recycled filtrate 5. Returning filtrate 1 to the succeeding extract for precipitation of the addition product increased the recovery of cholesterol in cake 1 by about 2 pounds. However, no increase in the final product (cake 6) occurred until filtrate 5 was recycled into the saponifier.

The amount of anhydrous oxalic acid was varied from time to time without any consistent effect except that separation of the addition compound was completed sooner with the larger additions. Any presence of water prevented the separation of the addition product. The final aqueous oxalic acid washings of cake 4 were of such concentration and temperature that the acid which separated on cooling was sufficiently pure for re-use.

CONCLUSION

The data presented demonstrate that cholesterol of a useful grade can be separated from degras on a semicommercial scale. By-products of the process which also may be useful in commerce are fatty acids and two grades of unsaponifiable material.

ACKNOWLEDGMENT

Credit is due Frank D. Kodras for the collection, arrangement, installation, and first operation of the equipment used. Thanks are also due R. M. Hixon and W. F. Coover of the Chemistry Department and C. A. Iverson of the Dairy Industry Department, Iowa State College, for the transfer of important equipment to this project. The advice of B. H. Thomas of the Animal Chemistry and Nutrition Subsection during the progress of this project is appreciated.

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JOURNAL Paper J-1245 of the Iowa Agricultural Experiment Station, Project 772.

TABLE IV. OPERATIONAL DATA

Expt. No.	Degras, Lb.	Cholesterol[a] % D	Cholesterol[a] Lb. D	Filtrate 5 Residue, Lb.	Ext., Lb.	Cholesterol %	Cholesterol Lb.	$(COOH)_2$, Lb.	Cake 1, Lb.	Cholesterol %	Cholesterol Lb.	Cake 6, Lb.	By-Products, Lb. Acids	Unsap.	Wax
128	52.5	16.0	8.4	...	92	8.4	7.7	2.0	26	16.0	4.2	3.0	..	..	..
129	52.5	16.0	8.4	...	94	8.2	7.7	2.0	31	17.6	5.4	2.5	36	..	..
130	52.5	16.0	8.4	...	79	9.6	7.5	2.5	40	15.3	6.2	3.0	40	..	..
131	52.5	16.0	8.4	...	97	7.7	7.5	3.5	47	13.0	6.1	3.0	33	..	..
132	52.5	16.0	8.4	...	43	17.7	7.6	3.25	36	15.0	5.4	3.3	40	..	..
133	52.5	16.0	8.4	...	52	14.4	7.5	2.5	46	13.3	6.1	3.0	32	12	..
134	52.5	16.0	8.4	7	56	15.3	8.5	2.6	47	15.5	7.3	3.0	36	12	..
135	52.5	16.0	8.4	10	92	11.2	10.3	3.5	45	17.1	7.7	3.8	35	7.5	9
136	18.0 34.5	16.0 16.8	2.9 5.8	7	84	12.1	10.1	3.0	64	13.8	9.0	4.0	37	7.5	9
137[b]	52.5	16.8	8.8	7.6	64	16.5	9.7	3.0	29	16.0	5.1[b]	3.7[b]	31	16	10
138	52.5	16.8	8.8	5.7	204	4.5 4.0D	9.3 8.2D	3.0	43	16.4	7.1	2.5[b]	29	16	5
139	52.5	16.8	8.8	6.5	53	19.1 13.1D	10.1 6.9D	3.0	41	16.6	6.8	3.0[b]	37	15	7
140	52.5	16.8	8.8	6.5	91	9.8 9.4D	8.9 8.5D	3.0	51	14.9 12.4D	7.6 6.3D	3.8	33	15	6
141	52.5	16.8	8.8	6.0	86	11.0 9.3D	9.5 8.0D	4.0	56	14.1 13.5D	7.9 7.6D	4.0	30	12	8
142	52.5	16.8	8.8	8.0	103	10.2 7.7D	10.5 7.9D	3.0	49	16.4 14.7D	8.1 7.3D	3.9	45	12	10
143	52.5	16.8	8.8	4.4	90	9.0 9.0D	8.1 8.1D	5.0	71	11.0 10.9D	7.8 7.7D	4.1	40	16	12
Av. 140–43	52.5	16.8	8.8	6.2	92	8.8D	8.1D	..	57	12.9D	7.2D	3.9	37	14	9

[a] D denotes digitonin assay; all others are by colorimetric assay.
[b] Poor saponification and yields due to water leak into saponification reaction.

Effect of Atmospheric Humidity on GR-S

The variability of the curing rate of GR-S compositions has presented a serious problem, both to the factory compounder and to the laboratory charged with establishing and maintaining specifications. Moisture content of the raw polymer has been found to have a definite effect on the curing rate. Using the GR-S specification recipe, a study of the effect upon the physical characteristics of vulcanizates due to exposure of the mixed stocks to various relative humidities has shown good correlation between moisture content of the mixed stock and the curing rate. Little effect on the other physical properties has been observed. The rate of moisture absorption of three samples of raw polymer and their compounds has been determined. These data show that the presence of only a trace of soap has a marked influence on the rate of moisture absorption.

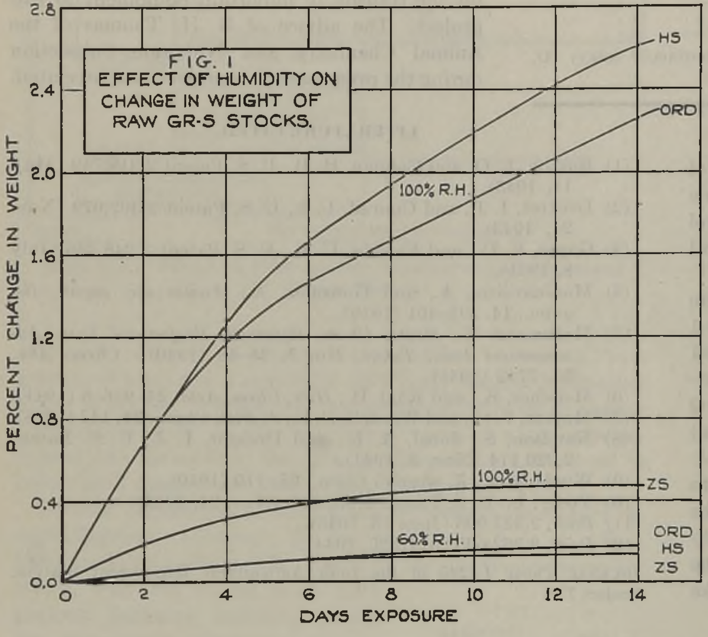
FIG. 1
EFFECT OF HUMIDITY ON CHANGE IN WEIGHT OF RAW GR-S STOCKS.

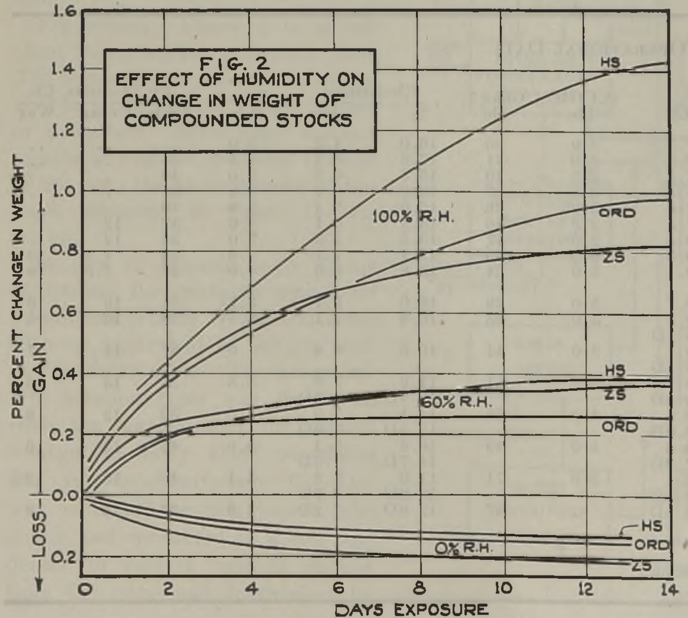
FIG. 2
EFFECT OF HUMIDITY ON CHANGE IN WEIGHT OF COMPOUNDED STOCKS

A RECENT publication by Braendle and Wiegand (*1*) demonstrated that the moisture content of GR-S stocks has a marked effect on the rate of cure and, to a lesser degree, on the physical properties of the vulcanizates. Other unpublished data of The B. F. Goodrich Company and The Goodyear Tire and Rubber Company show clearly that moisture has a definite effect on the plasticity of raw GR-S as well as on the rate of cure of its compounds. Hall and Hall (*2*) in England found, independently, the same effect of moisture on the rate of cure and processing. Natural rubber compositions show a similar effect due to moisture (*3*).

It has been observed that, in testing a large master batch of GR-S at intervals, variations in rate of cure and modulus values beyond experimental error occurred without any apparent relation to time of standing. The humidity of the storage room was one of the uncontrolled variables. Therefore, at the request of the Committee on Specifications for Synthetic Rubber, an investigation of the effect of atmospheric humidity during storage of uncured stock on the stress-strain relations and the rate of cure of GR-S was undertaken.

RAW MATERIALS AND MOISTURE DETERMINATION

Three samples of GR-S were chosen because of their variation in soap content. They were supplied by the Office of the Rubber Director and designated by the following code:

GR-S	Soap Content
ORD	0.18%
High soap (HS)	0.70
Zero soap (ZS)	0.0

The other ingredients used and their source were as follows: carbon black, E. P. black; BRT No. 7, zinc oxide, sulfur, and mercaptobenzothiazole, Office of Rubber Director.

CRUDE GR-S. Moisture was determined by the hot mill method. A sample of at least 200 grams was weighed to 0.1 gram. The volatile matter (moisture

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and/or styrene) was driven off by passing this sample repeatedly through a mill with the rolls at a temperature of 210° to 230° F. At the start a mill opening of approximately 0.1 inch was used, and this was reduced as rapidly as possible without converting the GR-S to crumb. When the opening had been reduced to about 0.01 inch, the rubber was weighed at intervals until constant weight was obtained. This usually required about 20 minutes. The following data were obtained: ORD GR-S, 0.14% volatile matter; ZS GR-S, 0.18%; HS GR-S, 0.63%.

Carbon Black. The moisture content in the black was determined, by heating at 105° C. for 24 hours, to be 1.30%. These determinations were made on the material as received without conditioning.

Mixed Stock. The hot mill method as described above was used on a sample of about 25 grams. In this case constant weight was attained in about 12 minutes. The following results were obtained: ORD GR-S, 0.09% volatile matter; ZS GR-S, 0.10%; HS GR-S, 0.13%.

MILLING PRACTICE

Weighing of Ingredients. All ingredients were weighed to within 1.0% of the weights specified. The final weight of the mixed batch was in each case less than the sum of the ingredients. The data obtained follow: Sum of weights of all ingredients in each case was 2616 grams except that the GR-S was increased by 10 grams in the case of the high soap GR-S. This allowance was made because of the relatively high moisture content of the original crude GR-S:

GR-S	Original Wt.	Final Wt.	Loss in Mixing
ORD	2616 g.	2605 g.	0.42%
ZS	2616	2604	0.46
HS	2626	2607	0.72

Milling Equipment. The mill used for the mixing of the three stocks had rolls 8 inches in diameter and 16 inches in length with a working distance between the guides of 15.25 inches. The speed of the slow roll was 23 r.p.m., and the speed of the fast (back) roll was 30 r.p.m.

Two batches were mixed from each of the GR-S samples and were thoroughly blended to give a theoretical batch weight of 2616 grams. The actual weight of each batch mixed was 1308 grams according to the following formula:

GR-S	100.0	800
E. P. black	50.0	400
BRT No. 7	5.0	40
Zinc oxide	5.0	40
Sulfur	2.0	16
Mercaptobenzothiazole	1.5	12
	163.5	1308

During the mixing, the temperature of the rolls was determined at various times by a Cambridge surface pyrometer. The temperature varied between 123° and 130° F.

Mixing and Milling Procedure. The following schedule was observed during the mixing of each batch. Whenever a $^3/_4$ cut is mentioned, it was made by cutting three quarters of the way across the roll and holding until the bank just disappeared. When cuts each way are mentioned, they were made from alternate directions. Various steps in the mixing operation follow:

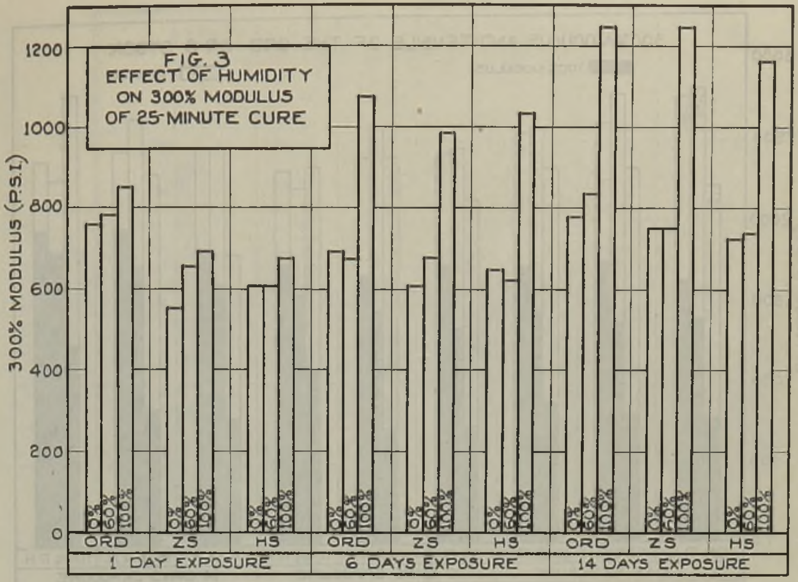

FIG. 3
EFFECT OF HUMIDITY ON 300% MODULUS OF 25-MINUTE CURE

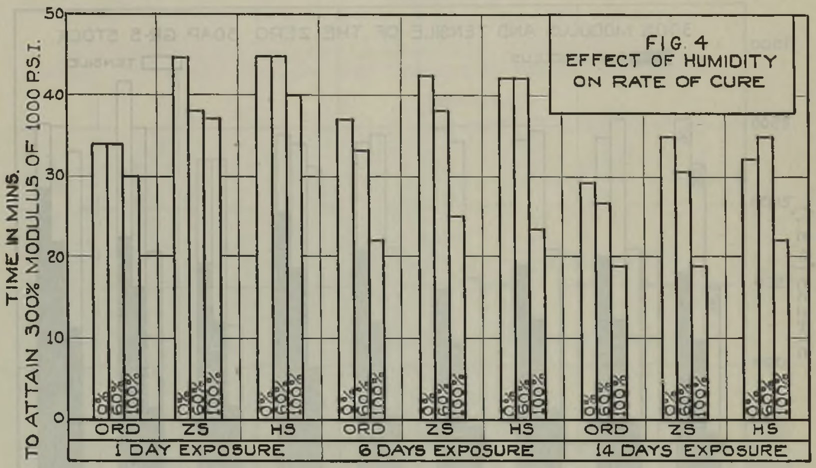

FIG. 4
EFFECT OF HUMIDITY ON RATE OF CURE

GR-S was passed through the rolls twice, without banding, at a mill setting of 0.008 (±0.002) inch. Total time elapsed, 1 minute.

GR-S was banded on the front roll with mill set at 0.055 (±0.005) inch, and $^3/_4$ cuts were made from alternate sides every 30 seconds. Total time elapsed, 11 minutes.

Carbon black was added slowly and evenly across the mill; the mill was opened at intervals to maintain a constant bank. A $^3/_4$ cut was made from each side when half of the black was added, and another from each side when all the black had been added except that which had fallen through the mill rolls. Then the black in the pan was added. Total time elapsed, 23 minutes.

Melted softener was added. Softener had been kept at about 210° F. for 30 minutes. Zinc oxide, sulfur, and accelerator were added carefully. Total time elapsed, 29 minutes.

Three $^3/_4$ cuts were made from each side. Total time elapsed, 31 minutes.

Batch was cut from mill, and with mill setting of approximately 0.030 inch, the rolled stock was passed endwise through the mill six times. Total time elapsed, 33 minutes.

The batch weight was checked at this point. After a second batch was prepared by this procedure, the two were blended. The stock was passed through the rolls twice without banding at a mill setting of 0.008 inch. The stock was banded, and three $^3/_4$ cuts were made from each direction and sheeted to approximately 0.085 inch. The batch was cooled to room temperature on a

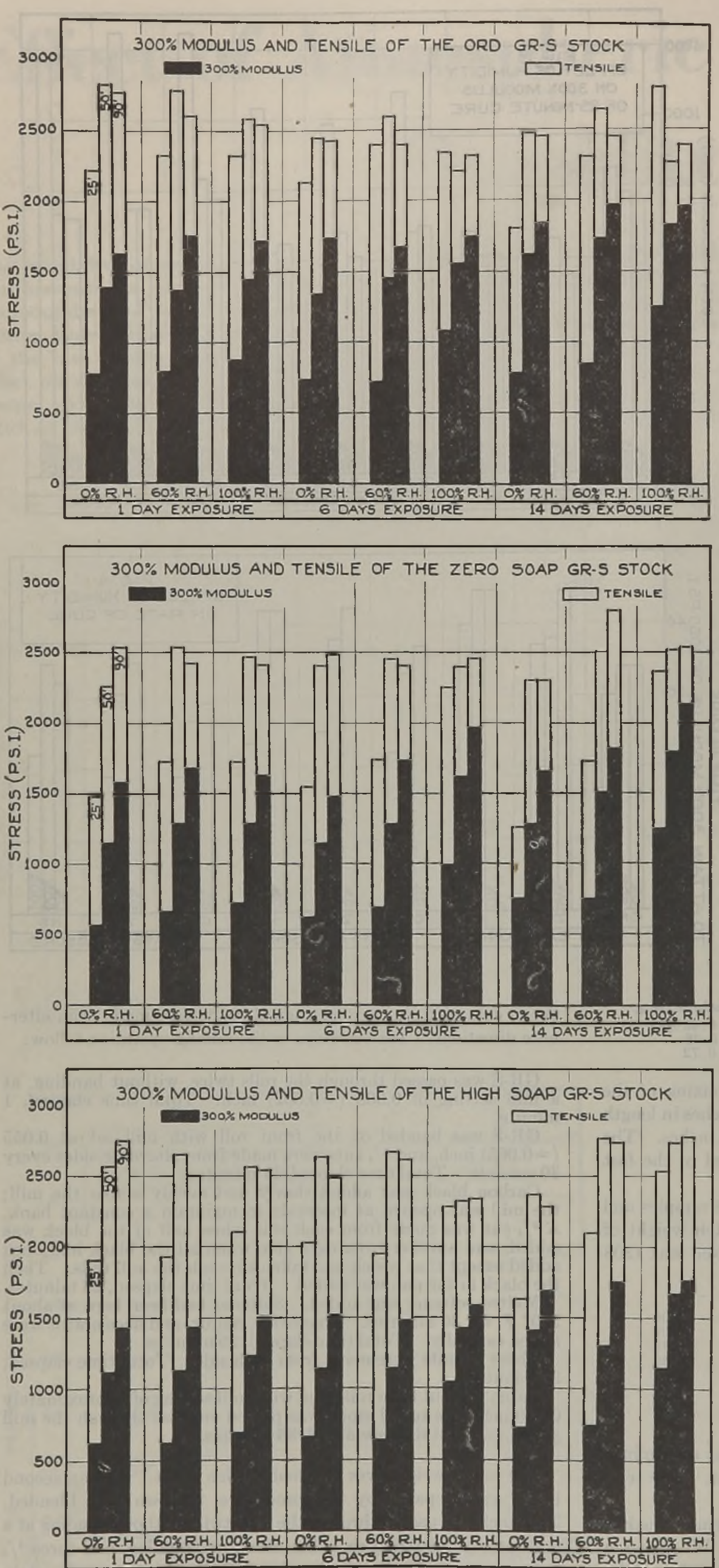

Figure 5

zinc-covered surface and cut into $5^3/_4 \times 5^3/_4$ inch slabs. When the batch had reached room temperature, the moisture in the mixed batch was determined by the hot mill method.

CONDITIONING, CURING, AND TESTING

Unvulcanized slabs of each batch and of each type of GR-S were placed in desiccators to give constant relative humidities as follows:

Relative Humidity	Content of Desiccator
0%	Anhydrous $CaCl_2$
60%	38.7% H_2SO_4
100%	Water

While conditioning in the desiccators, the compounded slabs were placed on galvanized screens ($^1/_4$-inch mesh) which were separated by slabs of wood, $^1/_4$-inch thick. By this method practically the entire surface of each slab was exposed to the desired relative humidity. Slabs of each crude GR-S and of each of the compounded stocks were weighed accurately before being placed in the desiccators, and then weighed every 24 hours to determine the moisture pickup or loss.

It should be noted that slabs exposed for 14 days at 100% relative humidity showed signs of bloom, the nature of which was not determined. This was slightly in evidence with those slabs exposed for 14 days to 60% relative humidity. Conditioning was done at 25° (±2.0°) C.

CURING. After exposure periods of 24 hours, 6 days, and 14 days, three sheets of each stock from each humidity condition were cured, one each at 25, 50, and 90 minutes at 292° F. A mold similar to that shown in Figure 1 of A.S.T.M. (specification D15-41) was used, and all curing was done according to procedure described in the specification.

TESTING. Only three strips were pulled in each case unless good agreement was not obtained. In such instances more dumbbells were tested until satisfactory agreement was reached.

The weight pickup of slabs during the 24 hours of elapsed time between curing and testing was determined for the 25-minute cures since these should show the greatest pickup. It was found to be negligible and so was made only for the 1- and 6-day exposures. Constant humidity control during this period was not available, so relative humidity during these resting periods is recorded (Table I).

RESULTS AND DISCUSSION

The GR-S samples were selected to demonstrate a wide range of moisture absorption rates. While it was realized that there are several constituents of GR-S which might influence the rate of moisture absorption, it was assumed that the soap content would be a satisfactory index of this property and selection was made on this basis. The rates of moisture absorption of the three GR-S samples are illustrated in Figure 1. It is observed that the rate of absorption of moisture by raw GR-S is roughly proportional to the humidity of the atmosphere in which it is conditioned. However, the presence of only a trace of soap has a marked influence on moisture absorption. The ORD sample contains 25% of the soap content of the high soap sample; yet under conditions of 100% relative humidity its moisture pickup, over and above that of the sample with 0% soap content, is 85% of that of the high soap sample. On the other hand, the absorption of moisture by the compounded stocks shows a more direct relation with the soap content. This is illustrated in Figure 2.

The object of this investigation was to determine the effect of this absorbed moisture on the rate of cure as indicated by the stress-strain characteristics of the vulcanizates. To illustrate this effect, the 300% modulus values of the 25-minute cured stocks were selected since these stocks are definitely undercured and naturally show greater variations than those stocks nearer the optimum cure. This use of modulus seems justified since all sheets of each base polymer were from one blend of laboratory-mixed stocks. Figure 3 presents graphically the 300% modulus figures of the 25-minute cured stocks of the three compounds after various conditions of exposure. This chart demonstrates that the rate of cure increases with increased humidity and increased length of exposure It has been shown that moisture absorption of the compounded stocks is roughly proportional to the soap content of the GR-S, but a study of the effect of this absorbed moisture on the rate of cure fails to reveal that the changes in rate of cure can be traced entirely to the variation in soap content. The changes in rate of cure appear to be more directly a function of relative humidity and time of exposure. By soap content is meant, not the effect of the soap as such, but the effect it exerts through its influence on moisture pickup.

Figure 4 presents the same data in modified form by plotting the time required to attain a 300% modulus of 1000 pounds per square inch. Here again the marked effect of both humidity and time of exposure on rate of cure are illustrated, without much correlation between soap content and rate of cure.

Figure 5 gives both 300% modulus and tensile figures for the three stocks for all cures, humidities, and exposures. It appears that the optimum physical properties vary but little as a result of exposure to high humidities for relatively long periods of time. However, the increase in rate of cure is illustrated by the progressively higher tensiles of the undercured stocks as the humidity and time of exposure increase.

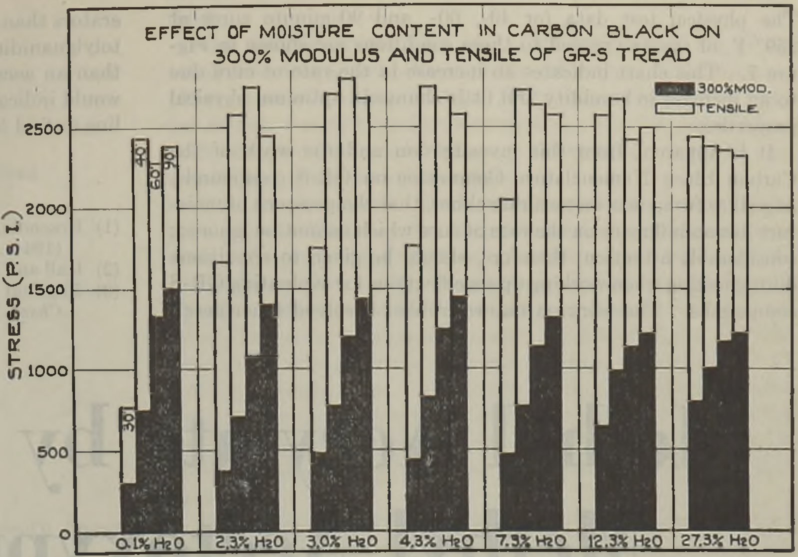

Figure 6

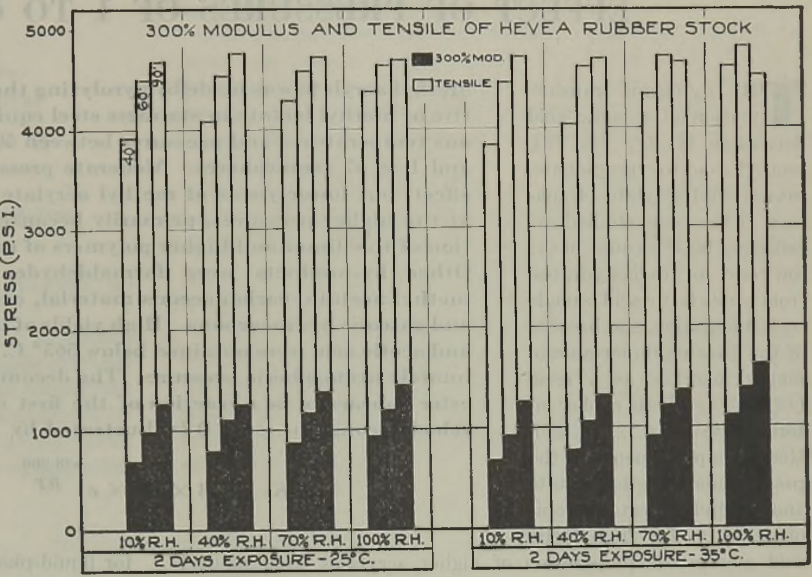

Figure 7

The results of this investigation are substantiated by the data obtained by the Carbon Black Nomenclature Committee in a study of the influence of moisture in carbon black upon rate of cure. Figure 6 illustrates changes in modulus and tensile figures due to increasing moisture content of the carbon black. Little change in the optimum physical properties is observed, but there is a decided increase in the modulus and tensile values of the undercured vulcanizates with increasing moisture content.

To compare the results of this investigation with similar results obtained on natural rubber, data were taken from a report of the A.C.S. Physical Testing Committee (*3*). Using the following formula, data were obtained for stocks exposed to 10, 40, 70, and 100% relative humidities at 25° and 35° C. for 2 days between milling and curing:

Smoked sheet	100.0	Mercaptobenzothiazole	1.0
Zinc oxide	5.0	Stearic acid	3.0
Sulfur	3.5	Pine tar	2.0
Carbon black	40.0		154.5

Table I. Weight Pickup of Cured Slabs[a] during 24-Hour Period between Curing and Testing

Conditions of Storage				
% Rel. hum.	Temp., ° C.	GR-S	% Wt. Change	Days of Exposure before Cure
22	24	ORD	−0.06%	1
		ZS	<0.01	1
		HS	−0.12	1
17	23	ORD	+0.03	6
		ZS	+0.04	6
		HS	+0.13	6

[a] Cured for 25 minutes at 292° F.

The physical test data for 40-, 60-, and 90-minute cures at 259° F. of stocks exposed to these conditions are shown in Figure 7. This chart indicates an increase in the rate of cure due to an increase in humidity, but little change in optimum physical properties.

It is apparent from this investigation and the work of the Carbon Black Nomenclature Committee on GR-S compounds, as well as from data on natural rubber, that the presence of moisture has an influence on the rate of cure which cannot be ignored; considerable attention, therefore, should be given to conditions during testing when working up specifications for evaluating GR-S compounds. The work on natural rubber involved other accelerators than thiazoles, however, and data with stocks using di-*o*-tolylguanidine as accelerator showed a retardation of cure rather than an acceleration due to increase in moisture content. This would indicate that further work should be done along this same line to find the effect of other types of acceleration.

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Methyl Acrylate by Pyrolysis of Methyl Acetoxypropionate

EFFECT OF PRESSURES OF 1 TO 67 ATMOSPHERES

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Methyl acrylate was made by pyrolyzing the acetyl derivative of methyl lactate in stainless steel equipment at various temperatures and pressures between 500° and 625° C. and 1 to 67 atmospheres. Moderate pressures had little effect, but lower yields of methyl acrylate were obtained at the higher pressures, primarily because of the formation of the dimer and higher polymers of methyl acrylate. Other by-products were formaldehyde, acetaldehyde, methyl acetate, carbonaceous material, oxides of carbon, and gaseous hydrocarbons. High yields of methyl acrylate and acetic acid were obtained below 565° C. under approximately atmospheric pressure. The decomposition of the ester appears to be a reaction of the first order. Specific velocity constant (sec.$^{-1}$) is illustrated by the equation:

$$K_1 = 7.8 \times 10^9 \times e^{\frac{-38{,}200}{RT}}$$

THE pyrogenic transformation of a lactic acid derivative (*4, 17, 18, 19*), methyl α-acetoxypropionate, into methyl acrylate (Equation 1) has been studied extensively both because of the low cost of carbohydrates, from which lactic acid is made by fermentation, and because of the growing importance of methyl acrylate as a resin (*13*) and synthetic rubber intermediate (*2, 6, 7, 20, 22*). Recent improvements in the preparation of methyl lactate and methyl α-acetoxypropionate (*8, 9, 10*) from lactic acid and in the preparation of higher acrylates from methyl acrylate (*15*) have lent added interest to the process.

$$CH_3COOCH(CH_3)COOCH_3 \xrightarrow{550^\circ\ C.} CH_3COOH + CH_2{:}CHCOOCH_3 \quad (1)$$

Previous papers (*11, 19*) described the effects of temperature, contact time, and contact materials on the thermal decomposition represented by Equation 1. This paper presents results obtained in a study of the pyrolysis of methyl acetoxypropionate in stainless steel equipment at pressures from atmospheric to 1000 pounds per square inch (66.7 atmospheres). The scale of operation was considerably larger than any hitherto reported for this pyrolysis.

Possibly the most conspicuous advantage of high pressure is that it increases the throughput of a given pyrolysis unit. Throughput at 67 atmospheres, for example, is 67 times that obtained at 1 atmosphere. In addition, if the reaction is kinetically of order higher than one, increased pressure would be expected to increase the reaction rate more than proportionally. Heat transfer is also more efficient at increased pressures.

On the other hand, increased pressure may have some deleterious effects. It expedites side reactions if they are kinetically of a higher order than one. High pressure also raises the boiling points of reagent and products, and hence these exist in the liquid phase at higher temperatures, making it easier for liquid-phase side reactions to occur. Such liquid-phase reactions might be (*a*) formation of methyl acetate by ester interchange, (*b*) production of acrylic acid, acetoxypropionic acid, and methyl acetate by acidolysis, and (*c*) polymerization of methyl acrylate. One other conceivable effect is the reversal of the desired reaction, according to the principle of Le Chatelier (*16*). It was estimated by the method of Bruins and Czarnecki (*3*) that the magnitude of this effect might be appreciable, but the applicability of this method can be questioned because the thermal decomposition is not necessarily reversible; methyl β-acetoxypropionate might be formed instead of the alpha isomer.

PREPARATION AND PROPERTIES OF METHYL ACETOXYPROPIONATE

The reagent was prepared from methyl lactate and acetic anhydride (*5, 8*), and that used in most of the experiments was redistilled through efficient columns. When the methyl acetoxy-

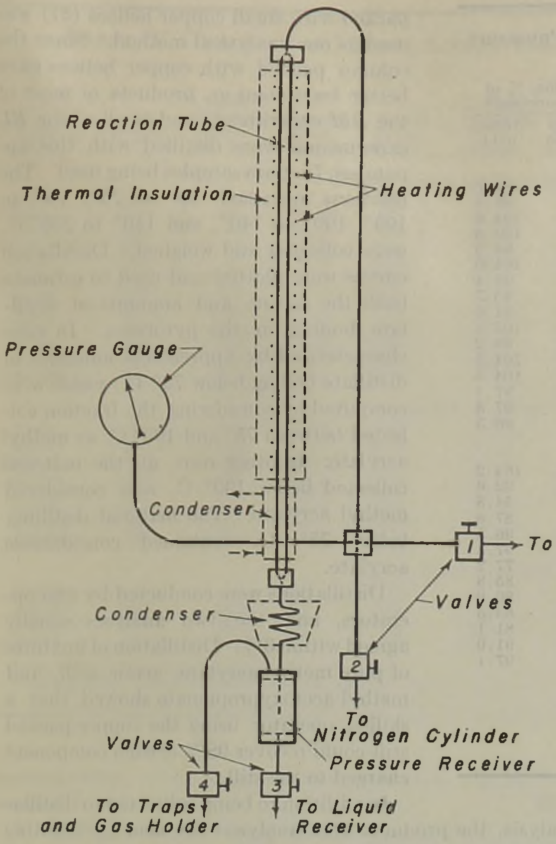

Figure 1. Diagram of *EL* Pyrolysis Apparatus

propionate was not carefully redistilled prior to pyrolysis, no appreciably different results were observed.

One large sample was carefully distilled through a column packed with stainless steel rings (*21*), and the specific gravities and refractive indices of several middle fractions were determined at various temperatures. The refractive index was measured by an Abbe refractometer and the specific gravities by a hydrometer 25 cm. long. Values for these physical constants were plotted against temperature, and a smooth curve was drawn among the points. Values from this curve are presented in the following table. The molecular refraction calculated from the physical constants determined at 20° C. was 33.26 (theoretical, 33.22).

Temp., ° C.	Refractive Index	Specific Gravity Determined	Specific Gravity From literature (*14*)
17	1.4110	1.0907	1.091
20	1.4095	1.0875	1.088
25	1.4070	1.0823	1.082
30	1.4045	1.0770	1.076

PYROLYSIS

EQUIPMENT. The earlier experiments, designated by the prefix *BM*, were carried out in equipment of the Central Experiment Station of the U. S. Bureau of Mines at Pittsburgh. The pyrolysis equipment at this laboratory, employed for the later *EL* experiments, was generally similar to that used at the Bureau of Mines. The reaction tube was a 4.3-meter length of 18-8 stainless steel tubing, having a diameter of 14 mm. outside and 8 mm. inside, heated electrically over a length of 3.5 meters. It was insulated with asbestos pipe covering 2 inches thick.

Four heating sections were used; one (covering 40 cm. of the tube) served as a preheater, and the other three (each covering 105 cm.) served as main heaters. The temperature of each heating section was independently controlled; for this purpose two millivoltmeter-type controllers and a two-point recording and controlling potentiometer were used.

Nine chromel-alumel thermocouples were employed. They were spaced with one at the center of each heating section, one at each of the junctions of the heating sections, and one at each end of the heated zone. They were attached by silver solder to the outside of the tube wall. The leads were brought to a selector switch connected to a potentiometer. In a typical run the temperature of any control couple did not vary more than 10° C. from its average value. At certain points along the tube, however, the average temperature deviated as much as 50° C. from the average of the control couples. The control average for the three main heaters is reported in the tables as the pyrolysis temperature.

The connecting pressure tubing of the *EL* system was 18-8 stainless steel having a diameter of 6 mm. outside and 3 mm. inside. The pressure receiver, which was a modified hydrogenation bomb, and the valves and fittings were cold-rolled steel. Joints were made by the high-pressure closure technique of the American Instrument Company (*1*).

The *EL* pyrolysis tube was mounted vertically, and the reagent was pumped to the top of the pyrolysis tube, whence it flowed downward. At the bottom of the reactor the condensers were installed; these included a water jacket at the lower end of the reactor and a coil of smaller-diameter tubing immersed in a vessel filled with water.

The reagent was delivered by the pump through valve 1 (Figure 1) to the cross, whence it traveled to the top of the reactor at the pressure shown by the gage. Before starting an experiment, nitrogen gas was admitted from a tank through valve 2 until the reaction pressure was reached.

The products were condensed at the lower end of the reactor and traveled to the bottom of the receiver through a drip tube. The liquid products were released intermittently through valve 3 and the overhead gases through valve 4, which was connected to a wet test meter and gas holder through two traps cooled with solid carbon dioxide.

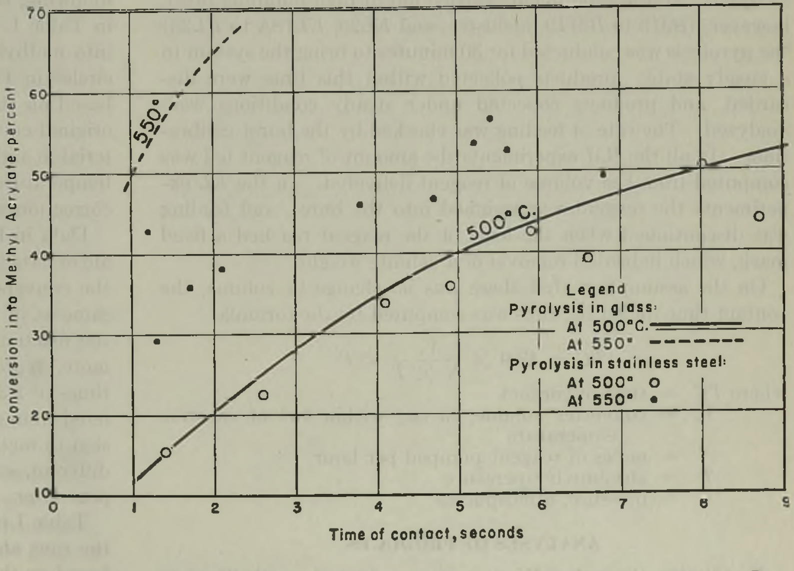

Figure 2. Relation between Conversion into Methyl Acrylate and Time of Contact

Table I. Pyrolysis of Methyl Acetoxypropionate at Atmospheric Pressure

Expt. No.	Av. Temp., ° C.	Contact Time, Sec.	Total Grams Pyrolyzed	Liquid Products, % of Charge	Methyl Acetoxypropionate Decomposed, %	Conversion, %		Yields, % of Theoretical[a]	
						To methyl acrylate	To acetic acid	Methyl acrylate	Acetic acid
				First Series					
*EL*1	498	8.7	219	90[b]	55.4	42.6	45.2	76.8	81.7
*EL*2	494	6.6	376.0	95.3	42.1	34.8	36.5	83.0	86.8
*EL*3	494	8.0	390.0	98.5	48.8	46.0	50.4	94.8	104.6
*EL*4	499	5.9	608.0	99.4	46.1	41.8	47.0	90.6	102.0
*EL*5	497	4.1	963.7	97.2	38.0	31.5	35.4	83.0	93.5
*EL*6	500	4.9	803.0	100.3	39.5	35.7	40.9	89.9	104.0
*EL*7	501	2.6	828.8	98.6	26.9	22.7	25.9	84.6	98.4
*EL*8	497	1.4	1626.7	99.0	15.2	13.5	14.3	88.4	95.7
*BM*2[c]	546	20.4	194	90.0	90.2	74.5	84.5	80.8	91.6
*EL*9	548	1.3	1624.8	99.7	30.7	27.9	31.4	90.8	103.2
*EL*10	548	1.7	1610	100.0	39.2	34.4	38.8	87.8	98.2
*EL*11	553	2.1	1590	100.5	44.2	40.1	45.9	90.9	104.3
*EL*12	555	3.8	1065	99.5	55.3	49.6	57.7	89.7	104.5
*EL*13	552	4.7	1090	97.2	57.1	48.1	55.1	84.2	97.1
*EL*14	550	5.6	910	96.8	61.0	52.4	59.2	86.0	97.8
*EL*15	550	5.2	660	93.5	66.2	53.3	63.8	80.5	96.3
				Second Series					
*EL*27	600	4.7	590	96.7	87.2	69.6	90.1	79.8	104.2
*EL*28	629	4.1	606.1	84.2	69.2	40.8	64.5	59.0	92.6
*EL*29[d]	625	4.1	506.6	76.1	66.5	39.4	36.0	59.3	54.8
*EL*32[d]	598	1.1	1851	91.2	63.1	48.3	54.7	76.6	87.8
*EL*33	551	1.2	1778	97.4	50.0	43.9	47.4	87.9	96.5
*EL*34	566	1.1	1968	97.1	65.8	56.1	62.9	85.4	97.3
*EL*35	602	2.0	595.1	87.5	64.0	47.2	48.7	73.2	77.2
*EL*36	576	2.8	1043	87.4	92.8	74.1	78.6	80.8	85.8
*EL*37[d]	574	2.8	974	88.2	86.1	66.7	73.5	77.6	86.0
*EL*38[e]	628	2.2	766	84.3	78.6	51.0	64.7	64.3	83.3
*EL*39[d]	552	6.8	510.6	81.5	81.0	51.2	64.9	63.3	81.1
*EL*40[d]	554	5.4	415.5	94.5	75.1	60.4	67.5	80.3	91.0
*EL*41	565	1.0	1439	97.6	59.4	48.9	56.0	82.6	97.1

[a] On basis of starting material not recovered.
[b] Estimated.
[c] Conducted at 5 pounds per square inch gage pressure.
[d] Before this run, the tube was cleaned with water vapor at high temperature.
[e] The reagent contained 1.94% distilled water.

Reagent was delivered to the pump from a buret assembly consisting of two one-liter burets connected to a two-way stopcock. The latter was sealed to a 10/30 ground-glass joint, which fitted in a joint ground into a length of copper tubing attached to the pump.

A Milton Roy pump (type MD-1, with $^5/_{16}$-inch piston, rated at 1.5 gallons per hour maximum at a discharge pressure of 1500 pounds per square inch) was used in some of the experiments. The pumping chamber, valves, and pistons were of 18-8 stainless steel. The pump used in other experiments was a Wilson chemical pump (DES-1 diaphragm type) with a stainless-steel pumping chamber.

Procedure. In most of the experiments, products resulting from pyrolysis of all the material pumped were collected and analyzed. In the experiments carried out at high pumping rates, however, (*BM*9 to *BM*19, inclusive, and *EL*26, *EL*18A to *EL*23) the pyrolysis was conducted for 30 minutes to bring the system to a steady state; products collected within this time were discarded, and products collected under steady conditions were analyzed. The rate of feeding was checked by the buret calibrations. In all the *BM* experiments the amount of reagent fed was computed from the volume of reagent delivered. In the *EL* experiments the reagent was weighed into the buret, and feeding was discontinued when the level of the reagent reached a fixed mark, which indicated removal of a definite weight.

On the assumption that there was no change in volume, the contact time for all the runs was computed by the formula

$$TC = 43.9 \times \frac{V_c}{N \times T} \times P$$

where TC = time of contact
V_c = converter volume, in cc., within 15° of reaction temperature
N = moles of reagent pumped per hour
T = absolute temperature
P = pressure, atmospheres

ANALYSES OF PRODUCTS

Distillation through a Weston column (usually with 25-gram samples) or a column (30.5 cm. long and 1 cm. in diameter) packed with small copper helices (*21*) was used as one analytical method. Since the column packed with copper helices gave better fractionation, products of most of the *BM* experiments and of all of the *EL* experiments were distilled with this apparatus, 75-gram samples being used. The fractions obtained up to 75°, 75° to 100°, 100° to 140°, and 140° to 200° C. were collected and weighed. Distillation curves were plotted and used to estimate both the nature and amounts of distillate boiling in the pyrolyses. In runs characterized by appreciable amounts of distillate boiling below 75° C., yields were computed by considering the fraction collected between 75° and 100° C. as methyl acrylate. In other runs, all the material collected below 100° C. was considered methyl acrylate. The material distilling below 75° C. contained considerable acrylate.

Distillations were conducted by two operators, and the two analyses usually agreed within 3%. Distillation of mixtures of pure methyl acrylate, acetic acid, and methyl acetoxypropionate showed that a skilled operator using the copper-packed still could recover 98% of each component charged to the still.

In addition to being subjected to distillation analysis, the products were analyzed for acid by titrating aliquots with standard alkali; the acid content was computed as acetic acid.

In the examination of products from experiment *EL*26 and later ones, the distillation analyses were supplemented by saponification and titration of the distillate fractions. In almost every case the amounts of both esters as determined by this method were lower than those determined by distillation. Nevertheless, results by the two methods usually agreed within 4%. The values reported in the tables are averages of the various determinations.

PYROLYSIS AT ATMOSPHERIC PRESSURE

The runs were made in two series, one preceding, the other following, the *EL* high-pressure runs. The data are summarized in Table I. The relation between contact time and conversion into methyl acrylate is shown by the positions of the dots and circles in Figure 2. For comparison, Figure 2 includes curves based on the same contact times from the literature (*19*). The original curve was plotted on the basis of 30 cc. of packing material in a glass tube, and since the volume within 15° of reaction temperature in the glass tube was also approximately 30 cc., no correction was necessary.

Data in Figure 2 were corrected to 500° and 550° C. with the aid of data from the literature (*19*). It is apparent that at 500° C. the conversion in the stainless steel equipment was almost the same as in the glass tube. However, it appears that at 550° C. the reaction went much more slowly in the steel tube; furthermore, reproducibility was not especially good. With contact times of 1.3 and 1.2 seconds, one experiment (*EL*9, Table I) differed from another (*EL*33, Table I) by about 16% in the conversion to methyl acrylate. The fact that these results occurred in different series may partly explain this discrepancy, as will appear later.

Table I indicates that the yields of methyl acrylate in most of the runs at 500° and 550° C. were satisfactory. The yields are based on the methyl acetoxypropionate not recovered, and hence any mechanical, distillation, and other losses would result in

Table II. Pyrolysis of Methyl Acetoxypropionate at Increased Pressures

Expt. No.	Av. Temp., ° C.	Gage Pressure, Lb./Sq. In.	Contact Time, Sec.	Grams Pyrolyzed	Liquid Products, % of Charge	Methyl Acetoxypropionate Decomposed, %	% Conversion to: Methyl acrylate	% Conversion to: Acetic acid	Yields, % of Theoretical[a]: Methyl acrylate	Yields, % of Theoretical[a]: Acetic acid
					Experiments at About 550° C.					
*BM*3	540	45	20.4	196.5	87.5	100	63.1	92.2	63.1[b]	92.2
*BM*4	547	45	27.0	231.6	81.4	100	57.4	92.2	57.4[b]	92.2
*BM*5	550	45	20.8	315.5	85.4	100	65.6	98.9	65.6[b]	98.9
*BM*6	544	45	9.2	532.8	92.6	100	76.2	98.3	76.2[b]	98.3
*BM*7	547	45	4.5	1060	95.5	91.2	72.7	94.2	79.7[b]	103.1
*EL*24	547	50	3.3	2150	93.2	70.0	55.8	66.9	79.7[b]	96.3
*EL*25	547	100	3.1	3590	96.4	68.6	58.4	67.3	85.2[b]	98.4
*BM*8	544	135	26.8	616	78.5	100	45.7	92.6	45.7	92.6
*BM*9	547	135	14.6	858	88.9	100	61.1	100.0	61.1	100.0
*EL*26	547	150	2.9	4760	95.0	70.9	54.0	68.3	76.1	96.0
*EL*23	549	300	4.2	4850	96.0	81.9	63.7	82.7	77.7	100.8
*EL*22A	547	500	7.1	6470	89.5	93.1	54.6	90.9	58.6	94.8
					Experiments at 500° C.					
*EL*16	498	50	3.9	2120	96.7	33.2	27.1	31.6	79.7	94.3
*EL*17	498	100	3.9	4370	99.3	34.9	26.2	31.9	75.8	93.3
*BM*14	502	135	14.3	1110	92.8	79.6	56.5	76.5	72.0	96.3
*BM*15	498	135	31.1	502	93.1	93.4	60.8	96.6	65.2	103.4
*BM*16	500	360	16.4	1318	91.7	80.9	52.4	72.3	64.8	90.6
*BM*17	493	735	18.5	4675	91.6	84.4	48.4	72.2	56.7	85.9
*BM*18A	488	900	12.3	1580	98.5	42.9	27.8	36.5	66.1	88.7
*BM*19	497	1000	22.5	3725	100.5	87.5	56.2	75.8	64.3	86.5
					Experiments at 450° C.					
*BM*10	448	45	26	168	100.5	93.1	34.4	40.4	86.6	101.5
*BM*11	450	135	65	298	95.3	73.3	52.4	71.7	71.4	97.8
*BM*12	449	135	27	521	98.9	43.4	27.7	45.9	63.9	106.0
*BM*13	452	360	28	1560	100	45.4	28.9	49.2	61.7	107.5

[a] On basis of starting material not recovered.
[b] All distillate collected below 100° C. was considered methyl acrylate.

lowered yields. On a plant scale the yields could probably be increased.

To ascertain whether complete conversion could be obtained in one pass, experiments in the second series were conducted at higher temperatures. Table I shows that higher temperatures did not cause complete conversion and that the results depended largely on the previous use and treatment of the pyrolysis tube. In experiment *EL*27, for example, the yield of methyl acrylate was about normal; yet in certain later experiments (*EL*32 and 35) yields, as well as conversions, were lower in spite of the shorter contact times. Destruction of acetic acid increased in some of the later runs even with short contact times. Table I shows that high temperatures drastically reduced the yields of both methyl acrylate and acetic acid. At 625° C. the yields were poor for both. Even 550° gave reduced yields if the contact time was long (experiment *EL*39). That a similar run in the first series (*EL*14, Table I) gave good yields is further evidence that the history of the tube is important. On the basis of the data in Table I, it appears that 565° C. is about the highest temperature at which good yields can be obtained in the equipment used. This tentative conclusion was made on the assumption that aging would not improve the behavior of the tube.

In the runs characterized by low acrylate yields, the recovery of liquid products was low, and large quantities of gas were formed. Gas formation was invariably accompanied by formation of coke in small hard particles that occasionally choked the outlet of the pyrolysis tube. A hard film of coke was also formed on the tube wall. This was removed by scraping the tube with a stiff wire, by pumping steam through the tube at 500° or drilling from the outlet end with a small cutter head at the end of a flexible shaft. The runs preceded by such cleansing are indicated in Table I by [d]. An initially clean tube, however, was not always satisfactory, as shown by runs *EL*29, *EL*32, and *EL*39. In fact, if there was any difference, a coated tube was better than a clean one. The methyl acrylate yield in run *EL*33 was satisfactory, although it followed a run marked by a low acrylate yield.

In view of the behavior of stainless steel at high temperatures, it seems probable that the lack of reproducibility at 550° and 1.2 seconds was due largely to a change in the condition of the tube wall.

The similarity in behavior of stainless steel at high temperatures to that of iron at lower temperatures (*11*) suggested the use of water to inhibit side reactions. Accordingly, run *EL*38 was carried out at 628° C. with a reagent containing 1.94% distilled water. The yield was still unsatisfactory, but the fact that it was possible to operate at all was evidence that the water inhibited carbonization, for after *EL*29, two attempts were made to operate at 625° C. and each time the pyrolysis tube blocked up within a few minutes. Inhibition of the desired reaction by water (*11*) was not observed here.

Summarizing, the stainless steel equipment was satisfactory for preparing methyl acrylate at 500° C. At 550° C. the reaction proceeded more slowly in stainless steel than in glass, but yields were still satisfactory. Above 565° C. yields decreased because of carbonization. At 550° C., with long contact times, carbonization occurred in some experiments.

PYROLYSIS AT INCREASED PRESSURES

In general, yields of methyl acrylate obtained at increased pressures were not so high as those at atmospheric pressure (Tables I and II). Yields of acetic acid apparently were little affected by increasing the pressure. The lower yields of acrylate were due mainly to the formation of less volatile substances (distilling above 200° C. and 760 mm.), which were probably dimers, trimers, and higher polymers of methyl acrylate. As mentioned later, one fraction of the distillation residue was tentatively identified as methyl acrylate dimer; polymethyl acrylate was also isolated.

The amount of less volatile substances in the pyrolysis product appeared to be mainly dependent on the pyrolysis pressure

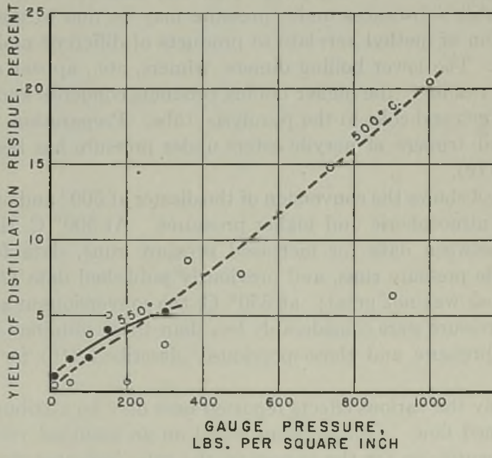

Figure 3. Relation between Yield of Distillation Residue and Pyrolysis Pressure

(Figure 3). While the points in Figure 3 are rather widely scattered, the trend is unmistakable.

Several times, especially at higher pressures, the pyrolysis tubes were entirely blocked by a plug of carbonaceous material. It was usually possible to anticipate coking, for it was preceded by a sudden increase in the rate of gas formation. Formation of residue appeared also to be related to the condition of the tube wall; the run at 900 pounds per square inch, in which there was a relatively small amount of residue (Figure 3), followed a lengthy application of steam to remove a coke plug.

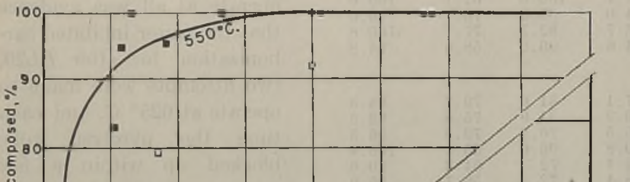

Figure 4. Effect of Contact Time on the Decomposition of Methyl Acetoxypropionate

These facts suggest that carbonization (described in the section on pyrolysis at atmospheric pressure) and the formation of less volatile substances under pressure may be due to the polymerization of methyl acrylate to products of different molecular weights. The lower boiling dimers, trimers, etc., appear as distillation residue; the higher boiling products condense and char, forming gas and coke in the pyrolysis tube. Preparation of dimers and trimers of acrylic esters under pressure has been described (*12*).

Figure 4 shows the conversion of the diester at 500° and 550° C. at both atmospheric and higher pressures. At 500° C. the disparity between data for increased pressure runs, data for atmospheric pressure runs, and previously published data (*19*) for glass tubes was not great; at 550° C. the conversions at atmospheric pressure were considerably less than those obtained at increased pressure and those previously described (*19*) for glass tubes.

Possibly the various effects reported here may be attributed to streamlined flow. Computation based on an assumed viscosity of 0.02 centipoise for the vapors in the tube indicates that the critical Reynolds number would be reached in the increased pressure experiments but not at atmospheric pressure. Hence coke formation at atmospheric pressure might be relatively high because of long contact of some of the vapor at the tube wall.

The effect of turbulence on the pyrolysis at atmospheric pressure is being investigated in a No. 446 steel tube. Preliminary results indicate that with turbulent flow pyrolysis may be carried out satisfactorily above 565° C.

PYROLYSIS BY-PRODUCTS

The large amounts of reaction products processed to recover methyl acrylate and unconverted methyl acetoxypropionate made it possible to investigate some of the by-products formed in the reaction. In the normal runs by-products occurred in minute amounts. In the high-temperature experiments in which carbonization occurred, however, the methyl acrylate fraction did not distill within a narrow temperature range; instead, the distilling temperature increased gradually from about 70° to 80° C. The boiling points of the acetic acid and methyl acetoxypropionate fractions were not affected. The fact that methyl acrylate forms several azeotropes (*15*) made identification of by-products difficult, since the lower boiling material consisted mainly of methyl acrylate. One impurity appeared to be water, collected as the methyl acrylate–water azeotrope. After a number of analytical distillations, a white solid collected in the reflux condenser of the analytical still. When removed, it had a pronounced odor of formaldehyde, an indication that it was probably a formaldehyde polymer. To verify the purity of the methyl acrylate obtained by pyrolysis, the acrylate fractions of two experiments (*EL*32 and *EL*36) were combined and redistilled, and saponification equivalents were determined on two fractions. The first fraction, collected over the range 69–80° C. and amounting to 30% of the charge, had an indicated purity of 94%. The second cut, taken at 80° C., had an indicated purity of 99%.

From the pyrolyses conducted under increased pressure, more by-products were identified; these were found to include both low-boiling and high-boiling substances. Three of the former were identified as acetaldehyde (as the 2,4-dinitrophenylhydrazone derivative), formaldehyde (by its odor), and methyl acetate. (The ester was hydrolyzed; methanol was identified as the 3,5-dinitrobenzoate and α-naphthyl urethan; and acetic acid was identified as the *p*-bromophenacyl derivative.) One high-boiling by-product was tentatively identified as methyl acrylate dimer by its boiling range (113–123° C. at 18 mm.), its saponification equivalent of 86.3, and its unsaturation. In addition, a soft resin, presumably polymethyl acrylate, was isolated from the distillation residues by precipitation with methanol. As mentioned above, gases were formed as reaction by-products. Even under the best conditions, a small amount of gas was formed; this consisted mainly of carbon monoxide, carbon dioxide, and unsaturated hydrocarbons. When gas evolution was pronounced, the gas consisted of carbon monoxide, carbon dioxide, saturated hydrocarbons, and unsaturated hydrocarbons in descending order of quantity.

Rapid cooling of the vapors and condensate leaving the pyrolysis tube probably would decrease the side reactions in the liquid phase.

KINETICS OF THE REACTION

A preliminary investigation of the kinetics of the reaction was made, based on the following assumptions: (1) The methyl acetoxypropionate disappears only via the decomposition into methyl acrylate and acetic acid; (2) the time of contact (reaction time) is equal to the free volume of the reactor divided by the average volume of the vapors entering and leaving per second. The first assumption led to the exclusion of any experiment in which the recovery of liquid products was less than 90%. The contact time was found by multiplying the contact time in the tables by $2/(2 + x)$, where x is the fraction of the diester converted.

In a first-order reaction the rate of disappearance of the reactant is proportional to the first power of the reactant concentration, and the specific velocity constant is given by the formula:

$$K = \frac{2.3}{t} \log \frac{C_o}{C} \qquad (2)$$

where C_o = initial concentration
C = concentration after time t

When the reaction is carried out at constant pressure as in these experiments, the term C_o/C is replaced by $1/\alpha$, where α represents the fraction of starting material not used.

For a second-order decomposition the rate of disappearance of the reactant at any instant is proportional to its concentration squared, and the specific velocity constant is given by the formula:

$$K_2 = \frac{1}{t} \times \left(\frac{1}{C} - \frac{1}{C_o}\right) \qquad (3)$$

The first-order and second-order constants, computed from Equations 2 and 3, indicate that while neither "constant" is truly constant, the first-order values fit the data far better than do the second-order values. Thus, at 550° C. an increase of more than eightfold in the initial concentration (comparing *BM*7 and *EL*22A) was accompanied by a variation of about 10% in the first-order constants, but about 900% in the second-order constants. (Extreme variation of constants within the same range of concentrations was about 60% for first-order and 1600% for second-order.) At 500° C. an increase of more than sixty-seven fold in C_o (comparing *EL*6 and *BM*19) was accompanied by a variation of 9% in the first-order constants, but 2300% in the second-order constants. (The extreme variation in first-order constants for the same range of concentrations was 37%.) It appears likely, therefore, that the reaction in this stainless steel system was approximately first-order with respect to methyl acetoxypropionate. The data do not permit an evaluation of any wall effect on the reaction.

Evaluation of first-order constants made it possible to estimate the activation energy for the reaction and, hence, to predict the conditions under which most of the ester would be decomposed in the absence of inhibition or side reactions. Constants corrected to 450°, 500°, and 550° C. follow:

Temp., ° C.	K_1, Sec. $^{-1}$	Experiments Fixing K_1	Average Deviation, %
550	0.634	6	12.5
500	0.134	8	9
450	0.0263	3	4

Computation of these constants made it possible to find the energy of activation and the frequency factor for the reaction from the Arrhenius reaction:

$$\log K_1 = \frac{E}{2.3\,RT} + \log s$$

where E = activation energy
R = gas constant
T = absolute temperature
s = frequency factor

To find E and s, log K_1 was plotted against $1/T$, and the slope and intercept of the resulting straight line were found by the method of least squares. The activation energy computed in this way was 38,200 calories per mole. Since the frequency factor was 7.4 × 10⁹ per second, the specific velocity constant of the reaction can be expressed by the equation:

$$K_1 = 7.8 \times 10^9 \times e^{\frac{-38,200}{RT}}$$

Computation of this factor makes possible the estimation of the temperature and contact time necessary to bring about any desired degree of decomposition. It appears probable that industrially the conversion desired would be as high as possible. If this conversion is arbitrarily taken as 98%, then at 550° C. the reaction would be 98% complete at a contact time of 9.9 seconds, based on the assumption of no change in volume. As already reported, the reaction did not go this far at atmospheric pressure and 550° C., presumably owing to inhibition by the steel or lack of turbulence.

Figure 5 shows a graph of the feed rate of reagent against the desired conversion at three pyrolysis temperatures. The curves are based on the constants for the normal uninhibited decomposition.

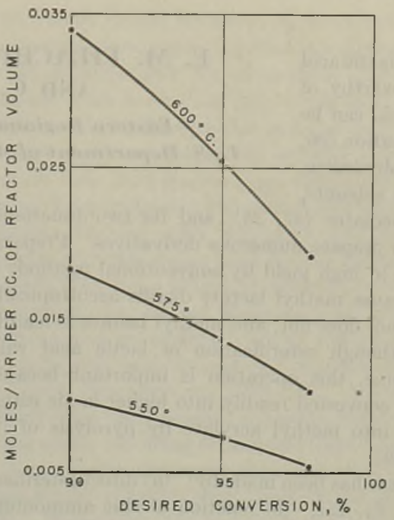

Figure 5. Relation between Feed Rate and Conversion of Methyl Acetoxypropionate

ACKNOWLEDGMENT

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Preparation of Methyl Lactate

CONTINUOUS ALCOHOLYSIS OF LACTIC ACID POLYMERS

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THE conversion of lactic acid into its esters is worthy of study because lactic acid can be made easily by fermentation (*20, 21*) from several carbohydrates, its esters are useful as solvents, plasticizers, or intermediates (*27, 28*), and its two functional groups can be used to prepare numerous derivatives. Preparation of methyl lactate in high yield by conventional methods is unusually difficult because methyl lactate distills azeotropically with water but methanol does not, and methyl lactate is readily hydrolyzed (*25*). Although esterification of lactic acid with methanol is troublesome, this operation is important because methyl lactate can be converted readily into higher lactic esters by alcoholysis (*5*) or into methyl acrylate by pyrolysis of its acetyl derivative (*5, 29*).

Methyl or ethyl lactate has been made by: (*a*) direct esterification (*1, 2, 3, 7, 8, 11, 24, 34*); (*b*) reaction of zinc ammonium lactate (*12, 19, 22, 32, 35*) with methanol in the presence of sufficient mineral acid to liberate lactic acid; (*c*) reaction of calcium magnesium, or sodium lactate (*6, 15, 20, 26, 27, 33*) with methanol in the presence of adequate quantities of mineral acid; (*d*) reaction of silver lactate (*22, 23, 24, 31*) with methyl iodide; (*e*) reaction of anhydrides or polymers (*3, 4, 6, 9, 10, 13, 14*) of lactic acid with methanol; (*f*) treating ethyl lactyl lactate with ethanol (*16*); and (*g*) heating calcium or sodium lactate with potassium ethyl sulfate or with ethyl toluene sulfonate (*17, 30*).

The present paper describes the preparation (both batch and continuous) of methyl lactate by alcoholysis of lactic acid polymers, a method that for the most part avoids the difficulties encountered when water is present.

PREPARATION OF LACTIC ACID POLYMERS

Polylactic acid used for the production of methyl lactate was prepared by batch or continuous methods (*10*). The batch method comprised distilling water from lactic acid under reduced pressures. The continuous method consisted in passing 82% lactic acid of edible grade (containing a small amount of sulfuric acid) down a heated column (Pyrex tube, 1 inch in diameter and 4 feet long) packed with small Berl porcelain saddles, withdrawing water vapor from the top, and removing the lactic acid polymers from the bottom of the column.

The extent of the dehydration and self-esterification of the lactic acid was usually estimated by the amount of water removed and by titration and saponification of the condensation polymers. At room temperature the polymers ranged from amber semisolids to brown firm masses, depending upon the degree of dehydration. All the polymers were fluid at about 90° C.

METHYL LACTATE FROM LACTIC ACID POLYMERS

CLOSED-VESSEL EXPERIMENTS. In experiments not described here it was found that methyl lactate can be produced in 50 to 65% yields by refluxing polylactic acid with methanol for about 10 hours in the presence of mineral acid catalyst. Higher yields, however, were obtained at somewhat higher temperatures in a closed vessel, and less reaction time was required (Table I). The results of several closed-vessel experiments indicated, however, that 100° C. for 1 hour is approximately as effective as 150° for the same period of time. High yields were obtained even when the mole ratio of methanol to available lactic acid was as low as 2.5.

The experimental procedure was as follows: The mixture of polylactic acid, methanol, and catalyst was placed in the reaction vessel ("magnesia" bottle for 100° C. and glass-lined bomb for 150° C. experiments) and heated for several hours. The catalyst was neutralized with sodium acetate; methanol and a small amount of water were distilled at atmospheric pressure; and methyl lactate was distilled under diminished pressure (Table I). No correction was made for the small amounts of methyl lactate that distilled azeotropically with water.

CONTINUOUS METHOD. In other experiments it was found that methyl lactate can be made continuously and in high yields by passing methanol vapor through polylactic acid, withdrawing methanol and methyl lactate vapors from the reaction vessel, and passing the mixed vapors into continuous distillation equipment.

In one series of experiments (Table II), the reaction vessel was a cylindrical chamber 8.5 inches high and 2.75 inches in diameter. A fritted-glass plate at the bottom, through which methanol vapor was passed, dispersed it as small bubbles over the entire cross section of the reaction vessel. Polylactic acid containing esterification and alcoholysis catalysts, such as sulfuric or toluenesulfonic acids, was introduced into the reaction vessel through a separatory funnel. The vessel was immersed in an oil bath maintained at reaction temperature. The vapors withdrawn from the top consisted mainly of methanol and methyl lactate. The condensed mixture was distilled at atmospheric pressure to remove methanol and under reduced pressure to recover the methyl lactate. Virtually all the material placed in the reaction vessel was volatilized; the principal by-product was distillation residues.

In another series of experiments, methyl lactate was prepared by treating lactic acid polymers with methanol vapor in a tower (1 inch in diameter and 4 feet long) packed with small Berl porcelain saddles. Condensation polymers, as such or dissolved

TABLE I. METHYL LACTATE FROM POLYLACTIC ACID (CLOSED-VESSEL EXPERIMENTS)

	Polylactic Acid						
Expt. No.	Lactic acid equivalent, mole	Equivalent wt.[a]	Ratio, Methanol/ Lactic Acid	Concd. H_2SO_4, Ml.	Temp., ° C.	Time, Hr.	Conversion to Methyl Lactate, %
130	0.5	..	2.5	0.25	150 ± 5	4	75–8
132–7	0.5	..	2.5	0.5	150 ± 5	4	78–83
157	0.5	79	1.0	0.5	150 ± 5	4	33
164	0.5	79	2.5	0.5	150 ± 5	2	73
165	0.5	79	2.5	0.5	150 ± 5	1	76
166	0.5	79	1.0	0.5	100	4	51
167	0.5	79	2.5	0.5	100	4	76
168	0.5	79	5.0	0.5	100	4	75
169	0.5	79	10.0	0.5	100	4	78
170	0.5	79	5.0	0.5	100	2	78
173	0.5	79	5.0	0.5	100	1	84
181	1.0	77	2.5	1.0	100	4	76
182	1.0	77	5.0	1.0	100	4	75
184	1.0	77	2.5	0.5	100	4	79
185	1.0	77	2.5	0.25	100	4	80
195	0.5	77	5.0	1.0	100	4	81
199	0.5	77	5.0	0.5	100	4	84
196	0.5	76	5.0	0.5	100	4	88

[a] Ultimate neutralizing capacity expressed as weight in grams of polylactic acid capable of reacting with 40 g. sodium hydroxide (calculated from total amount of standard sodium hydroxide solution required to neutralize and saponify a known quantity of sample). Completely polymerized lactic acid and monomeric lactic acid have equivalent weights of 72 and 90, respectively.

Table II. Preparation of Methyl Lactate by Passing Methanol Vapor through Polylactic Acid (Cylindrical Vessel with Fritted-Glass Plate)

Expt. No.	Polylactic Acid as Lactic Acid Equivalent, Mole	Temp., ° C.	Methanol Introduced, Moles	Rate of Adding Methanol, Millimoles per Min.	Conversion to Methyl Lactate, %
1[a]	0.5	140–150	7.5	15–18	77
2[a]	0.47	140–150	5.0	11.1	72
3[a]	0.5	135–148	5.0	16.0	70
4[a]	0.5	140–150	6.0	26.0	70
5[a]	0.5	120–126	5.0	20.0	73
6[a]	0.5	110–112	6.25	11.0	89
7[a]	0.5	110–112	6.85	23.6	90
8[a]	0.5	98–102	8.75	20.0	87
9[a]	1.0	110–120	12.5	30.5	86
10[b]	1.0	110–118	13.3	56.0	82
11[c]	1.0	110–118	39.0	43.0	79
12[d]	0.5	125–130	13.2	67.0	81

[a] Toluenesulfonic acid (1 g. per mole of lactic acid) was used as catalyst.
[b] Sulfuric acid (1 ml. per mole of lactic acid) was used.
[c] Phosphoric acid (2 ml. of 85%) was used.
[d] Anhydrous zinc chloride (4 g.) was used.

in methanol (usually 70 grams polymer in 30 ml. of methanol), were fed continuously into the top of the tower. If not already present, the catalyst was dissolved in the polylactic acid prior to introduction into the tower. Methanol vapor was passed continuously (from a flask containing boiling methanol) into the tower near the bottom, and vapors of methanol and methyl lactate were withdrawn continuously from the top and passed into a continuous still. The methanol vapor from the top of the continuous still was recycled—that is, passed into the flask of boiling methanol and then as vapor into the bottom of the esterification or alcoholysis tower. The methyl lactate withdrawn from the bottom of the continuous still contained approximately 30% methanol and small quantities of water. Probably methyl lactate containing only traces of methanol would have been obtained with a more efficient column. The methyl lactate–methanol mixtures were redistilled, and the data thus obtained were used to calculate the yields given in Table III.

In some instances (experiments 221 and 222, Table III) the amount of methyl lactate recovered by distillation was small, and appreciable yields of distillation residue were obtained. It is believed that acidic material, such as sulfur dioxide, was carried over with the methanol and methyl lactate vapors and that this catalyzed the conversion of methyl lactate into compounds which were left as a residue in distillation. It was found advantageous to add basic material, such as sodium acetate, prior to distillation, especially when sulfuric acid had been used as catalyst. The advantages of neutralizing acidic constituents and distilling under reduced pressures were discussed in a previous paper (*25*).

ETHYL LACTATE

The reaction of polylactic acid with the higher alcohols was not studied extensively, but ethyl lactate was prepared by the interaction of polylactic acid and ethanol. In the first preparation, 77 grams of polylactic acid (equivalent to 1 mole of lactic acid), 115 grams of ethanol (2.5 moles), and 1 ml. of concentrated sulfuric acid were heated at 100° C. for 4 hours in a closed bottle. The mixture was treated with 4 grams of anhydrous sodium acetate and distilled. The conversion into ethyl lactate distilling at 65° (28 mm.) was 57%; the distillation residue amounted to 39 grams.

In the second preparation, an ethanol solution containing 73.5 grams of polylactic acid (equivalent to 1 mole of lactic acid) and 0.5 ml. of concentrated sulfuric acid was passed into the top of the packed tower while ethanol vapor was passed into the bottom. The temperature was 120° to 126° C., and the operation lasted 2.9 hours. The conversion into ethyl lactate was 77%. On the basis of starting material not recovered as distillation residue, the yield was 86.5% of theoretical.

CRUDE LACTIC ACID AS STARTING MATERIAL

As Tables II and III show, lactic acid of moderate purity can be converted into methyl lactate continuously and in high yields by dehydration and polymerization followed by methanolysis. Because of its lower cost (*18*), crude lactic acid is preferable to edible or other refined grades as a raw material. Several samples of crude lactic acid were less suitable experimentally, however, because their dehydration rates were lower, and solids separated during the dehydration and subsequent treatment with methanol. Results obtained with polylactic acid prepared from several samples of crude lactic acid by the batch distillation of water (usually after the addition of concentrated sulfuric acid) under a pressure of 10 to 20 mm. of mercury are given in Table IV. The methanolyses were carried out by passing methanol solutions of the polylactic acid through the reaction tower used for the experiments described in Table III. Although solids had been filtered from the methanol solutions, some precipitation occurred in the tower, requiring occasional cleaning by washing with water.

It was found advantageous to use more sulfuric acid than was required for catalysis with some of the samples of crude lactic acid. Presumably the larger quantities of sulfuric acid were required because of the sodium chloride, organic nitrogen compounds, or other materials capable of reacting with sulfuric acid. Considerable quantities of hydrogen chloride were volatilized with the methyl lactate when sodium chloride was present in the crude lactic acid. Hydrogen chloride in the distillate facilitated the hydrolysis of methyl lactate and made analysis for chloride necessary when the lactic acid content of the distillate was determined by titration and saponification.

Table III. Methyl Lactate from Polylactic Acid and Methanol Vapor (Packed Tower Experiments)

Expt. No.	Polylactic Acid as Lactic Acid Equivalent, Moles	Catalyst (H_2SO_4), Ml.	Temp., ° C.	Addition of Polylactic Acid: Total time, hr.	Addition of Polylactic Acid: Millimoles per min.	Conversion to Methyl Lactate, %
221	1.0	1	110–125	1.5	11.0	53
222	1.0	[a]	110–125	2.5	6.7	55
228	1.0	1	110–125	1.0	16.7	85
230	2.0	2	110–125	2.0	16.7	83
232	4.0	4	110–125	3.6	18.0	82
238	1.0	1	100–105	2.0	8.3	92
239	2.0	2	125	3–3.5	9.5–11	88
240	2.0	2	98–105	4–4.25	7.8–8.3	89

[a] Toluene sulfonic acid, 1 gram.

Table IV. Alcoholysis of Polylactic Acid Prepared from Crude Lactic Acid

Expt. No.	Polylactic Acid: Lactic acid equivalent, moles	Polylactic Acid: Concn. as lactic acid, %	Concd. H_2SO_4, Ml.	Temp., ° C.[a]	Time, Hr.	Lactic Acid Volatilized[b], %	Methyl Lactate Yield, %: A[c]	Methyl Lactate Yield, %: B[d]
1[e]	2	116	2	98–106	12	..	67	73
2[e]	5	115	5.1	100–112	10.5	..	57	74
3[f]	1	91	1	101–109	4	73	29	55
4[f]	2	89	8	88–105	3.2	92	64[g]	74[g]
5[f]	1	84	14	87–109	2.5	85	79[h]	80[h]
6[i]	2	117	2	98–103	5.5	..	78	85

[a] Temperature at a point midway between the bottom and top of the reaction tower.
[b] Determined by titration and saponification of the distillate.
[c] Based on polylactic acid passed into the tower.
[d] Based on polylactic acid not recovered as distillation residue (90 g. residue taken as 1 mole).
[e] Crude material contained 26% lactic acid prior to concentration (supplied by Sheffield Farms, Inc.).
[f] Crude material contained 23% lactic acid prior to concentration (supplied by the Clinton Company).
[g] Distillation residue recycled once.
[h] Distillation residue recycled twice.
[i] Crude material contained 81.3% lactic acid prior to concentration (supplied by the Clinton Company).

Although the use of crude lactic acid is more troublesome, it gives moderately high yields of methyl lactate (Table IV) under suitable conditions. The present work indicates that addition of sulfuric acid in quantities greater than used for catalysis is helpful, that filtration of solids from the methanol solution of the polylactic acid may be required, that treatment with sodium acetate or similar agent prior to distillation is beneficial, that entraining agents such as benzene may be used advantageously to distill water from methyl lactate, and that distillation of methyl lactate under reduced pressure is preferable.

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Fermentation of Wood Sugars to Ethyl Alcohol

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IN THE preparation and fermentation of wood sugars in the Fullerton, La., and Georgetown, S. C., plants (*6, 27*), the acid hydrolyzate was aerated and neutralized to a pH slightly higher than is ordinarily used for modern yeast fermentations. A nitrogen source and growth factor source were supplied, and a slow feed technique was used to fill the fermenters. When the wort started fermenting, there was a change in color to a lighter shade (*26*), indicating a reduction of the medium. Frequently 96 hours were required to form only 2% alcohol by weight.

Patents on processes for preparing wood sugars for fermentation admit these difficulties of fermentation (*10, 39, 47*), and laboratory procedures have employed various means of inducing more rapid fermentation (*13, 28, 32, 41, 49, 61*). Previous investigators have determined the major constituents (*18A, 24, 27*) of the wood hydrolyzate, but the minor constituents have not yet been found. It has been assumed that the difficulty of fermentation was due to toxic constituents.

Four potential sources of toxic substances have been pointed out: equipment, carbohydrate decomposition (*2, 21, 32*), lignin decomposition (*38*), and wood extractives and their decomposition products (*22*).

Toxic concentrations of metals resulting from the corrosion of the equipment have been encountered frequently in experimental work (*25, 54*).

The potentially toxic materials arising from the organic substances have been divided into three classes—terpenes, aldehydes, and polyhydroxy aromatics. Generally, terpenes have been shown to be the most active physiologically toward yeast, aldehydes next, and polyhydroxy aromatics least (*9, 23, 31, 32, 35*). The action of these organic substances was dependent on temperature, pH of the media, presence of oxygen, concentration and type of toxic substance, ratio of yeast cells to toxic substance, and physiological condition of the cells. There was also wide variation in the toxicity of various substances on the metabolism of yeast (*44, 60*). For example, formic acid is more toxic than acetic acid (*23*).

An unfavorable oxidation-reduction potential has also been cited as a cause of poor fermentability. Three methods have

Fermentation of neutralized wood-sugar liquors was difficult except under special conditions. Acid sugar liquors, which had been treated with lime to a pH of 5 and then heated to 138° C. for a short time before filtering, gave a preparation that fermented anaerobically in 14 to 20 hours with 2% by volume of distiller's yeast. The addition of reducing agents was useful for production of easily fermented wood-sugar preparations.

been proposed for overcoming unfavorable potentials in fermentation media—phytochemical reduction by large amounts of yeast, use of reducing agents, and production of reducing substances from sugars either by caramelization or alkali degradation. The effect of phytochemical reduction on fermentation of media containing furfural (*29*, *30*) and of inocula size on this reduction (*45*) were noted. Collingsworth and Reid (*4*) found that the addition of reducing agents to media with high oxidation-reduction potentials improves their fermentability. Reducing substances produced by the caramelization of sugars by heat (*11*, *15*, *45*) and those formed by the action of alkali on sugars (*8*) also affect the fermentation.

Aerobic production of inoculum has been employed for alcoholic fermentations with success (*1*, *34*, *56*). Recovery and preservation of yeast for succeeding fermentations has been used in many modifications (*12*, *14*, *43*, *46*).

TABLE I. EFFECT OF HEATING WOOD SUGAR MEDIA FOR VARIOUS PERIODS AT 121° C.

Heating Period, Min.	Fermentation pH		Initial Sugar Concn.[a], G./100 Ml.	% Sugar Fermented at:		Alcohol	
	Initial	Final		146 hr.	215 hr.	Concn.[b], g./100 ml.	Conversion[c], %
5	5.75	5.80	5.18	..	6	0.08	..
15	5.80	5.10	5.34	27	31	0.76	46
45	5.80	4.90	5.41	60	70	1.68	44
120	5.80	4.90	5.41	58	71	1.69	44

[a] Expressed as apparent glucose (*48*).
[b] Determined gravimetrically.
[c] Per cent of sugar fermented.

The rate of fermentation is largely dependent on the concentration of active yeast (*19*, *36*, *43*, *50*, *51*). Agitation is necessary when high yeast concentrations are used (*1*, *43*) and perhaps for aerobic cultures (*58*). The use of large amounts of yeast for fermentation, however, does not guarantee good results, for both low and high yields of alcohol have been obtained by this method (*16*, *18*, *33*, *55*).

GENERAL FACTORS INFLUENCING FERMENTATION

Most research on wood hydrolysis for sugar production has been conducted with the purpose of obtaining maximum economic sugar yields and not easily fermentable worts (*17*, *27*, *42*). Research at the Forest Products Laboratory was conducted in an effort to develop both a preparatory treatment to yield a more easily fermentable wort and a fermentation process to give a more rapid sugar conversion.

Effect of Metals. To determine the effect of small quantities of metal, hydrolyzates were prepared in glass vessels and small quantities of copper, iron, and nickel were added. There was no resultant inhibitory action.

Effect of Method of Neutralization. Neutralization of the acid hydrolyzates to pH 4.5 or 5.0 customarily used in yeast fermentation did not result in satisfactory fermentation of otherwise untreated and undiluted hydrolyzates when a standard fermentation procedure was used. Fermentations were more easily obtained at a pH of 6.0 or 6.5. If a reducing agent was added, improved fermentations were usually obtained as low as pH 5.6 to 6.0.

A simple but not commercially practical method of preparing hydrolyzates for fermentations is to adjust the pH to 9 or 10 and then acidify to a pH suitable for fermentation (*39*, *49*). It was not found necessary to hold the solutions for more than a few minutes at the high pH in order to obtain favorable action. The original reason for this step was to remove metals (*49*) which were known to be present, and to accomplish this filtration at the high pH would be helpful. Better fermentation was obtained by liming the hydrolyzate to a high pH, but the filtration had a negligible effect. Since the filtration did not improve the action, it was believed that, instead of removing metals, the alkali treatment caused some type of irreversible change of the toxic substances, or perhaps reduction by means of alkali degradation products of sugars. No decrease and sometimes a slight increase in reducing sugar value of the solutions was found.

Barium, calcium, sodium, and ammonium hydroxides were determined to be of equal quality for neutralization and alkaline treatment of the hydrolyzates. Addition of lead and mercury salts to precipitate potentially toxic compounds did not improve or injure the fermentations.

In the Fullerton plant hydrolyzates were neutralized at 80° or 90° C. (*26*), whereas in current laboratory work the hydrolyzate has been neutralized near room temperature. Hydrolyzates neutralized near 100° C. were appreciably easier to ferment than those neutralized at 25° C. It was also noted that heat-sterilized solutions were more readily fermented than those not heated. An example of the length of the heating period upon the fermentation is illustrated in Table I, where a slow-feed fermentation of Douglas-fir sugar solutions was used. These were neutralized to pH 5.8 and then heated for various periods at 121° C.

The sugar solutions used in this work were those produced in the laboratory investigations of hydrolysis procedures (*17*, *42*).

For industrial operation it was suggested that the acid hydrolyzate be neutralized at an elevated temperature and filtered immediately to remove calcium sulfate. The solubility of calcium sulfate was suppressed when the solutions were filtered at temperatures above 100° C. Sugar decomposition was found at a pH above 5.2. Table II gives data for a single neutralization and filtration of hydrolyzate at 138° C. Soluble sulfate was determined gravimetrically as $BaSO_4$.

TABLE II. NEUTRALIZATION OF ACID HYDROLYZATE AT 138° C

Operating Time, Min.	pH	Sugar Concn., Grams/100 Ml.	Sol. Sulfate, P.P.M. of $CaSO_4$
0	1.20	5.23	10,600
32	4.70	5.35	800
43	5.30	5.29	850
47	5.30	5.27	880
59	5.20	4.90	880

The fermentability of solutions neutralized at 138° C. was better than that of solutions neutralized at lower temperatures. Comparison was made between worts neutralized hot and agitated with air, as in the Fullerton, La., plant, and worts neutralized hot and then heated (Table III). The hydrolyzate obtained during 1910 to 1923 differed from present hydrolyzate in that now it is separated from the residue at a temperature 60° to 100° C. higher. The absorptive power of lignin at the lower temperature may be sufficient to remove substances inhibiting fermentation. It was found that the action of heat on neutral solutions, and not the act of neutralizing hydrolyzates at high temperature, was responsible for the beneficial effect.

TABLE III. COMPARISON OF WORTS NEUTRALIZED BY EARLY AMERICAN PROCESS WITH WORTS PREPARED BY HEAT TREATMENT PROCESS[a]

Process	Initial Sugar Concn., G./100 Ml.	Optical Rotation, Degrees (+) in 4-Dm. Tube	Alcohol Concn., G./100 Ml.
Air agitation	4.20	4.82	0.91
Without air agitation	4.30	4.71	0.82
Heated 5 min. at 138° C.	5.00	3.43	1.78

[a] All neutralized at 90° C.; additions, 0.015 gram urea and 0.003 gram $Ca(H_2PO_4)_2$ per 100 ml.; pH of wort, 5.8; inoculum, 1.1% by volume of *Candida tropicalis*.

Improved Fermentability by Reducing Substances. Before experiments involving neutralization of hot hydrolyzates and heat treating, a series of tests was made upon the assumption that the worts were at an oxidation-reduction potential unfavora-

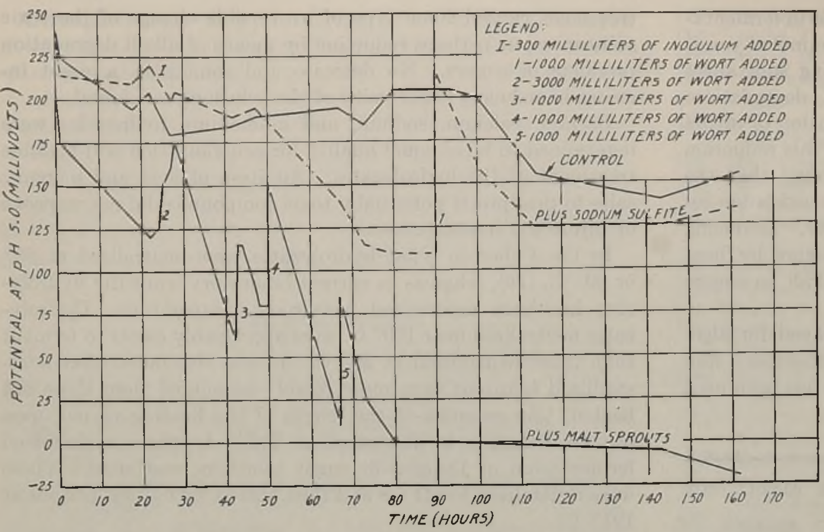

Figure 1. Changes in Oxidation-Reduction Potential during Fermentation of Wood Sugar Worts with Sodium Sulfite and Malt Sprouts Added as Compared with the Control

ble to yeast. Potentials were taken on various worts and were found to be between +200 and +250 millivolts when the values were adjusted to pH 5.0. Figure 1 shows changes in potential during the course of three typical fermentations. They were made by the convention sallow-feed technique used in laboratory experiments. Further data are given in Table IV.

Improved fermentation, obtained by the addition of Na_2SO_3, $NaHSO_3$, $Na_2S_2O_2.5H_2O$, $Na_2S_2O_5$, $Na_2S_2O_4$, $KHSO_3$, Na_2S, sulfite waste liquor, alkali-decomposed sugar, ascorbic acid, cysteine, and reduced iron filings, was further evidence of a high potential existing in the worts. Diethanolamine, triethanolamine, pyridine, aniline, dimethylaniline, and similar substances showed favorable action under some conditions. The use of organic aldehyde precipitating reagents gave no improvement.

Table IV. Yield of Alcohol Resulting from Fermentations of Various Media of Figure 1

Medium	Amount Added, G./100 Ml.	Inoculum, Ml.	Wort, Ml.	Alcohol Produced, Grams
Control	..	800	2000	25
Plus sodium sulfite	0.05	800	2000	34
Plus malt sprouts	0.5	500	7000	135

Table V. Effect of Adding a Reducing Agent upon Amount of Sugar Fermented[a]

$Na_2S_2O_4$ Added, as % of Sugar	% of Sugar Fermented	
	With heat (121° C.) sterilization	Without heat sterilization
0.00	0	..
0.03	59	..
0.30	77	0
0.91	..	12
1.36	..	76
2.28	..	76
11.40	..	7

[a] Medium: 4.4 grams southern pine sugars, 0.1 gram $(NH_4)_2SO_4$, 0.02 gram $(NH_4)_2HPO_4$, 0.5 gram malt sprouts per 100 ml.; pH at 4.8. Inoculum: 50 ml. molasses beer with *S. cereviseae Hungarian* into 500 ml. of wort.

The amount of reducing agent required is dependent upon the length and temperature of heat treatment period as indicated in Table V. Heating neutral hydrolyzates at higher temperatures, such as 138° C., appreciably decreases the demand for added reducing materials. A decrease in optical rotation was observed when neutral sugar solutions were heated at 138° C. (Table III). As would be expected, the extent of the change in optical activity is a function of pH, temperature, and time. The favorable action obtained by heating neutral wood-sugar solutions may be due to a small amount of alkaline type of sugar decomposition, which yields reducing substances.

Nutrients. Information on yeast nutrients required for wood-sugar media is meager. Wood-sugar worts and sulfite waste liquor contain inositol and para-aminobenzoic acid, but biotin has been found only in sulfite waste liquor. In only two other cases have microorganism growth factors from wood been reported (*5*, *7*). It was assumed for these experiments that, with the exception of inositol and *p*-aminobenzoic acid, all other growth factors were lacking or present in very small amounts.

It was found that small additions of nitrogen compounds were necessary; a few hundredths per cent of urea based on the weight of wort was satisfactory. There is still some doubt as to whether it is necessary to add phosphorus for the alcohol fermentation. Between 0.005 and 0.010% of a phosphate salt was used. Malt sprouts proved to be the best source of growth factors with small amounts of inoculum; but with large amounts of inoculum, such as 2% by volume of yeast, it was found that 0.02% cane blackstrap molasses gave a satisfactory increase in alcohol production. In addition, yeast extract, liver, corn steep, Curbay BG, Vacatone, distiller's solubles, and malt extract sirup were tried and found to give slight stimulation.

Microorganism Types. Existing knowledge concerning strains desirable for wood sugars is also slight. Since the German literature emphasizes the use of *Torula* sp., a number of these yeasts were tested in comparison with *Saccharomyces* sp. It was found that comparable amounts of alcohol were produced, but that a much longer fermentation time was required when *Torula* sp. were used. *Torula* sp. and *S. ellipsoideus* were found to be slower fermenters than *S. cereviseae*, *Candida tropicalis*, and *S. anamensis*. In the present investigation no yeasts were found to produce alcohol from pentoses in anaerobic fermentations. *Fusarium lini* were found, in confirmation (*59*), to produce alcohol both from hexose and pentose sugars, but the fermentations were slow. One strain of *F. lini* formed 1.6% alcohol from glucose in 7 days with a 45% conversion, which indicates that good possibilities exist for further investigation.

Investigation of several strains of distillery yeasts indicated that the first selection, *S. cereviseae* No. 49, University of Wisconsin collection, was among the most favorable. Since nothing developed to require changing to another strain, this was used throughout these experiments. Ability of a strain to produce cells on wood sugar (*41*) was not related to its ability to form alcohol in more concentrated wood sugar solutions. Subculturing yeast thirty to fifty times on wood sugars did not produce any favorable effects due to acclimatization. Instead, the cultures usually became progressively weaker in fermentation power.

Fermentation Procedures. Whereas grain and molasses fermentations give a ten to twenty fold increase in number of cells, wood sugar worts give only a two- to fourfold increase during the course of fermentation under similar conditions. The rate of fermentation of wood sugars is correspondingly low. Although 500 or 1000 cells per ml. are sufficient to initiate a slow fermentation in a grain wort, untreated wood sugar worts require as many as 100 million cells per ml. to initiate fermentation. Carefully controlled slow feeding is needed to ferment wood sugars with smaller inocula than this.

Table VI. Effect of Large Amounts of Inoculum on Alcohol Production[a]

Vol. % Yeast Added[b]	Vol. of Fermentation, Ml.	Sugar Fermented, %	Time, Hr.	Alcohol Concn., g./100 ml.	Alcohol Conversion, %
1.6	250	77	...	1.46	36
2.5	7000	80	8.5	1.78	42
3.1	250	87	...	1.80	38
5.0	7000	80	4.0	1.90	45
5.2	250	90	...	1.83	39

[a] Medium: 5.26 grams of Douglas fir heat-treated (138° C.) sugars, 0.015 gram urea, 0.006 gram NaH_2PO_4 per 100 ml.; pH, 5.8. Inoculum: *S. cereviseae No. 49.*

[b] Volume of yeast added is per cent wet yeast determined by centrifuging.

Table VII. Repeated Transfer of Yeast on Heat-Treated Wood Sugar Worts[a]

Transfer Nos.	Feed, Hr.	pH Initial	pH Final	Sugar Initial, g./100 ml.	Sugar % fermented	Alcohol Concn., g./100 ml.	Alcohol Conversion, %	Alcohol Yield, %[b]	Yeast Vol., %	Yeast Count, 10^6/ml.	Yeast Viable, %	Bacteria Count 10^6/Ml.
1 to 8	24, slow	5.9	5.4	5.54	86	2.18	46	40	2.3	190	..	...
9 to 17	24, slow	6.0	5.1	5.39	83	1.94	44	36	2.8	220	45	160
9 to 17	24, slow	5.4	4.9	5.39	77	1.83	44	34	2.7	220	45	150
18 to 26	24, batch	5.7	5.3	5.74	70	1.81	45	31	2.1	130	45	37
18 to 30	12, batch	5.7	5.5	5.84	67	1.77	45	30	3.1	210	40	50

[a] Media: Douglas-fir sugars neutralized at 138° C. with $Ca(OH)_2$ to pH of 4.8 or 5.0 and held at that temperature for 15–20 minutes; further adjusted with NaOH to the fermentation pH after cooling; for nutrients 0.015 gram urea and 0.0066 gram NaH_2PO_4 per 100 ml. were added. Inoculum: *S. cereviseae No. 49* produced aerobically.

[b] Per cent of total sugar.

The slow feed technique (*27, 34, 37*) is a means of using indirectly a large initial cell count for inocula and overcoming an unfavorable oxidation-reduction potential (*45*). As a laboratory procedure the use of alkaline treatment combined with slow feeding was found to decrease the time of fermentation from the 96 hours common in the early American plants to 30 hours or less. It is significant that in many hundreds of fermentations without sterilization, little contamination was obtained in wood sugar worts. For industrial operation, however, it would be desirable to eliminate the use of the alkaline treatment and to increase further the rate of sugar utilization.

To accomplish this, several procedures were available. Proper pretreatment of the worts by use of the heat reaction and by the addition of small amounts of reducing agents was considered industrially practical. In order to increase the rate of sugar utilization, a slow feed procedure was possible, but the growth of yeast was still too slow for practical operation. Since information was available on aerobic yeast production (*41*), and since so little contamination was encountered, it was decided to revive the old brewery and bakery yeast practice to produce a large initial inoculum and to recover the yeast after fermentation. Gravity sedimentation of the yeast was considered, but the fact that yeast was less active after standing in the beer and the necessity of a large tank capacity were sufficient reasons to abandon the procedure. Rapid sedimentation in a centrifuge or rapid filtration provided a practical means of recovery.

Within reasonable limits, the rate of sugar utilization is dependent upon the quantity of yeast. With large volumes of yeast in filtered wood sugar worts, however, agitation is necessary to keep the yeast suspended. Laboratory agitation by shaking and by stirrers was used. Without means to exclude air, shake flasks gave low conversion yields, as shown by the 250-ml. fermentations in Table VI. With larger volumes and stirring, the conversion was higher (*20*). The rate of fermentation was appreciably increased by the use of preformed inoculum (Table VI).

Recovery of the yeast and transfer to a succeeding batch of wort was tried with considerable success. With about 2% by volume of yeast and pretreated wood sugar worts, the fermentation was usually completed in less than 20 hours with a rate of sugar utilization of 0.20 to 0.30 gram of sugar per 100 ml. converted per hour. This rate is slower than grain or molasses fermentations. Yeast was recovered from more than thirty successive batches of wort, but in each successive batch the viability as determined by methylene blue decreased, and the conversion rate decreased accordingly. About fifteen or twenty transfers may be made successfully from the initial inoculum before it becomes necessary to start from a fresh culture. Yeast growth takes place, but it is slow and barely produces sufficient new cells to balance the mechanical and biological loss. Morphological examination and staining of the yeast indicated that, in addition to the toxic substances that are reduced, there may be other toxic substances in wood sugar hydrolyzates that cannot be overcome by the yeast. As the unreduced toxic substances accumulate from successive batches of fresh wort, they finally kill the cell.

Table VII records some average data on the repeated transfer of yeast. In many aspects these data are typical of those usually obtained—rather low conversion of sugar to alcohol, decreasing amount of sugar fermented, decreasing amount of alcohol yield contrary to some claims (*3*), and increase in volume percentage of yeast due to accumulation of tar. Bacterial contamination was obtained in one case and then lost to some extent on repeated transfer.

Discussion. These studies of the experimental development of wood sugar fermentation have by no means exhausted the possibilities of improvement. It has been necessary to have methods for demonstration and quantitative comparison of the various factors influencing fermentation. Many factors may be responsible for the difficulties encountered, but the major portion of the information available from the foregoing experiments indicates that much of the difficulty must be due to slightly oxidized substances that may be reduced chemically or biologically. It appears that for industrial fermentations, it will be necessary only to apply a combination of treatments, such as heating at 138° C. for a short time plus the addition of reducing substances, in order to obtain an easily fermentable preparation.

PRETREATMENT OF HYDROLYZATES FOR INDUSTRIAL FERMENTATION

Satisfactory methods of counteracting the toxic character of wood hydrolyzates are essential for a successful fermentation of wood sugars to ethyl alcohol. The collection of acid hydrolyzate at an elevated temperature, neutralization at that temperature, and a reaction time before filtration and cooling are practical industrial procedures. It is desirable to suppress the calcium sulfate content to about 750 parts per million (*57*). Since the period at which the sugar solutions are held at an elevated temperature affects their fermentability, it was first necessary to determine conditions that permit the removal of sufficient calcium sulfate and then to determine the effect of heat on the fermentability of the solutions.

Crystallization Period for Calcium Sulfate. The solubility of calcium sulfate is at the desired concentration in saturated solu-

Table VIII. Crystallization of Calcium Sulfate in Wood Hydrolyzates at Various Temperatures

130° C.[a] Time, min.	130° C.[a] pH	130° C.[a] $CaSO_4$, p.p.m.	140° C.[b] Time, min.	140° C.[b] pH	140° C.[b] $CaSO_4$, p.p.m.	150° C.[c] Time, min.	150° C.[c] pH	150° C.[c] $CaSO_4$, p.p.m.
0.0	1.2	7980	0.0	1.2	7700	0.0	1.2	7720
5.5	5.4	1006	6.0	4.7	6800	4.0	5.5	690
11.0	5.5	950	11.0	...	710	11.0	5.1	670
18.0	5.4	930	21.0	...	690	19.0	5.0	670
28.0	5.3	960	30.0	...	690	30.0	4.9	650
39.0	5.2	980	43.0	...	680	39.0	4.8	630
50.5	...	980	56.0	...	650	62.0	...	590

[a] Reported solubility, 830. [b] Reported solubility, 665. [c] Reported solubility, 530.

TABLE IX. OBSERVED CHANGES IN OPTICAL ROTATION AND SUGAR CONCENTRATION OF HEAT-TREATED HYDROLYZATES

Variable pH (Heated 5 Min. at 141.5° C.)		Variable Temp. (Heated 5 Min. at pH 5.2)			Variable Time, (Heated at pH 5.5 and 140° C.)		
pH	Rotation[a], degrees	Temp., ° C.	Rotation[a], degrees	Sugar, g./100 ml.	Time, min.	Rotation[a], degrees	Sugar, g./100 ml.
3.5	9.9	25	9.8	4.82	1	6.6	4.82
4.0	9.3	110	9.1	..	5	5.6	..
4.5	8.3	120	8.5	..	10	4.9	4.70
5.1	6.2	130	7.7	4.88	20	3.7	4.77
5.8	5.1	140	5.3	4.70	30	2.5	..
...	...	150	1.5	4.62	40	...	4.65
...	...	...	...	..	60	...	4.49

[a] Optical rotation is measured in circular degrees for a 4-dm. tube.

TABLE X. FERMENTATION OF HEAT-TREATED GLUCOSE, CALCIUM ACETATE, AND CALCIUM SULFATE MIXTURES[a]

Mixture	Temp., ° C.	$[\alpha]_D$	Sugar: Initial, g./100 ml.	Sugar: Fermented, %
Glucose	25	52.9	4.39	99.5
Glucose, $Ca(OAc)_2$	130	47.1	4.44	99.2
	140	41.1	4.47	98.8
	150	26.5	4.35	96.5
Glucose, $CaSO_4$	130	52.7	4.54	99.3
	140	50.7	4.47	99.3
	150	49.6	4.35	99.0
Glucose, $Ca(OAc)_2$, $CaSO_4$	130	48.3	4.52	99.1
	140	40.6	4.56	98.9
	150	28.6	4.25	96.5

[a] Mixtures: 0.015 gram urea, 0.006 gram KH_2PO_4, 0.1 gram Difco yeast extract per 100 ml.; inoculated with 0.9% by volume *S. cereviseae No. 49;* heat treatment for 15 minutes at pH 5.0 ± 0.1.

tions at the temperatures corresponding to 30–40 pounds (gage) steam pressure (*40*). Calcium sulfate has a transition point in its solubility curve at 97° C. at which the crystalline form of the salt changes. Because of this, seed crystal formation below 97° C. required heating periods over 1 hour to reach the solubility corresponding to 141.5° C. (40 pounds steam pressure). With seed formation above 97° C., however, the desired suppression of calcium sulfate was obtained in about 30 minutes. To obtain a zero time for crystallization studies, a rotary digester (*42*) was used. Neutralization was made by injection of a predetermined amount of base. Less than 700 p.p.m. of calcium sulfate remained in solution after 20 to 30 minutes at 140° C. With this information it was possible to perform heat treatment studies under conditions comparable to expected industrial conditions. Results of experiments performed at three neutralization temperatures are given in Table VIII.

Effect of Heat on Neutral Hydrolyzates. The favorable effect of heat on neutral hydrolyzates may conceivably arise from three sources: change in sugar structure to a more easily fermented form, polymerization or change of toxic substances to inactive forms, and formation of reducing substances. The possibility of more easily fermented sugars has little support, although information is available on the behavior of yeast toward different sugars which indicates that such action might take place (*19, 52, 53*). It is possible that furfural could be disposed of by heat treatment, but too little was present to account for the differences found. The idea of reducing substance formation was followed because the addition of reducing substances gave more easily fermented solutions. Previous work had shown that the change in optical activity constituted a rapid method of observing the results of different heat treatments. The decrease in optical activity was proportional to increase in pH, increase in temperature, and increase in time. There was some loss of sugar during the treatments. Data are given in Table IX on the effect of pH, temperature, and time on rotation.

It was thought that calcium acetate was the cause of the changes observed. To check this theory and to determine whether a decrease in fermentable sugar resulted from heat treatment, a glucose solution containing 0.5% calcium acetate, 0.5% calcium sulfate, or both, was heat-treated and fermented. Only a slight loss in fermentable sugar was found. The data for three temperatures are given in Table X.

The effect of heat treatments on fermentation and alcohol yield was determined for worts prepared from neutral hydrolyzates heated at pH 4.5 and 5.2. Data are given in Table XI. The loss in total sugar was appreciable in some treatments, but alcohol production was best for heat treatments of 15 minutes at 140° C. with a pH of 5.2. The pH usually decreased slightly during heat treatments. To obtain good alcohol yields and avoid sugar loss, heat treatment is limited to a rather small operating range of 20 to 30 minutes at 140° C. with a pH of 5.0 ± 0.2.

Effect of Steam Distillation. Some preliminary experiments (*28*) showed that, when more than 0.1% furfural was present, steam distillation or steam stripping was beneficial to the fermentation. Some evidence indicated that other volatile constituents were also removed. Hydrolyzates were steam-distilled both before and after neutralization and heat treatment. The favorable effect of steam distillation of hydrolyzates containing less than 0.1% furfural was demonstrated. Data on the comparative effect of steam distillation at constant volume are presented in Table XII. Less distillation was required after neutralization and heat treatment.

TABLE XI. EFFECT OF HEAT TREATMENT AT 140° C. ON AMOUNT OF ALCOHOL PRODUCED[a]

Heat Treatment		Sugar Concn., G./100 Ml.		Alcohol Concn., G./100 Ml.
pH	Time, min.	Initial	Fermented	
4.5	5	7.1	0.1	0.0
4.5	15	6.7	3.9	1.8
4.5	30	6.5	3.8	1.7
5.2	5	6.9	4.4	2.1
5.2	15	6.7	4.7	2.3
5.2	30	5.7	3.5	1.8

[a] Media: pH 5.8, 0.001 gram urea and 0.006 gram KH_2PO_4 added per 100 ml.; inoculated with 2.0% by volume *S. cereviseae No. 49.*

TABLE XII. EFFECT OF STEAM DISTILLATION ON THE FERMENTATION[a]

Treatment	Sugar: Initial, g./100 ml.	Sugar: Fermented, %	Time of Fermentation, Hr.	Alcohol Concn., G./100 Ml.
None	4.82	2	48	0.0
Heat	4.77	2	48	0.0
SO_2 + heat	5.03	2	48	0.0
SO_2 + heat + dist. 1	4.70	79	10	1.72
SO_2 + heat + dist. 5	4.92	80	10	1.76
Dist. 1 + SO_2	4.93	2	48	0.0
Dist. 1 + SO_2 + heat	4.75	79	48	1.33
Dist. 5 + SO_2	4.61	80	9	1.68
Dist. 5 + SO_2 + heat	4.66	81	10	1.67

[a] Heat treatment at 140° C. for 20 minutes at pH 5.0. SO_2 added as $Na_2S_2O_5$ at 0.02% of hydrolyzate weight. Dist. 1 equals 1 volume distillate; dist. 5 equals 5 volumes of distillate per volume of hydrolyzate. Fermentation nutrients were 0.015 gram urea and 0.006 gram NaH_2PO_4 per 100 ml.; pH 5.8. Inoculated with 1.0% by volume *S. cereviseae No. 49.*

Laboratory Fermentations with High Conversion. Small fermentations were made in 250-ml. volumes in 500-ml., round-bottom, long-necked flasks plugged tightly with cotton. Flasks were shaken one hundred 2-inch strokes per minute. With this method, alcohol formed seldom exceeded 47.0% of the sugar consumed and frequently was less. Table XIII gives a comparison of this type of fermentation with some in which the air was excluded with carbon dioxide and the escaping gas was evolved through a Bunsen valve. Larger amounts of alcohol are formed when the larger volumes of inoculum are used. Better conversion is obtained under a carbon dioxide atmosphere.

Method of Fermenting Wood Sugars. One method of fermenting wood sugars that was successful is as follows: Neutralize the acid hydrolyzate with calcium hydroxide slurry to a pH 5.0 ± 0.2 at room temperature; filter and add the equivalent of 0.03% by weight of sulfur dioxide in the form of Na_2SO_3, $Na_2S_2O_5$, or other similar salt; heat the mixture in a bomb for 15 minutes at 135° to 140° C.; draw and cool the mixtures to fermentation temperature, 30° C.; adjust the pH to 5.8 with sodium hydroxide and add 0.02% urea and 0.006% NaH_2PO_4 by weight. Inoculation with 2.0% by volume of fresh yeast and agitation by means of shaking or stirring should give a fermentation complete in less than 20 hours if the sugar concentration as glucose is initially 5.0 to 7.0 grams per 100 ml. The inoculum can be produced in an aerobic fermentation of 1.5% wood sugars. Aeration at the rate of 1 or 2 volumes of air per minute per volume of medium is suitable.

Table XIII. Effect of Excluding Air from Alcohol Fermentations with Large Amounts of Inoculum[a]

Inoculum, % by Vol.	Alcohol Formed under CO_2 Atm. Concn., g./100 ml.	Conversion, %[b]	Yield, %[c]	Alcohol Formed under Air Atm. Concn., g./100 ml.	Conversion, %[b]	Yield, %[c]
1.0	..	..	..	1.17	45.8	24.4
1.2	..	..	6.8	..	..	..
1.6	1.92	47.9	38.7	..	..	..
2.0	..	..	..	1.74	46.4	36.1
3.0	..	..	..	1.83	47.1	38.0
4.0	1.89	49.2	39.3	1.86	47.4	38.6
5.0	1.93	50.2	40.1	1.84	47.6	38.3
6.0	1.94	50.5	40.4	1.87	47.8	38.9

[a] Douglas fir sugars heat-treated 20 minutes at 138° C. with 0.02% SO_2 as $Na_2S_2O_5$ added. Fermentations at pH 5.8 with 0.015 gram urea and 0.006 gram NaH_2PO_4 added per 100 ml. *S. ceréviseae No. 49.*

[b] Per cent alcohol based on sugar consumed.

[c] Per cent alcohol based on total sugar.

CONCLUSIONS

1. The favorable pH for fermentation of wood sugars by yeast was 5.6 to 5.8.
2. The most successful method of improving the fermentability of wood hydrolyzates was the addition of reducing agents. The amount required and the method of their use was affected by many other factors.
3. Heating the neutral solutions gave the same effect as the addition of reducing agents.
4. Successful batch fermentations were possible when a large initial inoculum was used in a heat-treated reduced medium.
5. The amount of dissolved calcium sulfate was decreased by neutralization at 140° C., crystallizing, and filtering at that temperature. Slight sugar loss resulted from this procedure.
6. Heat treatment to give a favorable effect on fermentation was limited to a pH range between 4.5 and 5.2 for 15 to 30 minutes at 140° C.
7. Steam distillation removed toxic constituents from the hydrolyzates.
8. Laboratory fermentations gave better yields when they were initiated under a carbon dioxide atmosphere.

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It has been found that the heat treatment used in the manufacture of raw commercial cashew nutshell liquid does not change the carbon skeleton of the main monophenolic component. The structure of the phenol is established as 3-pentadecadienylphenol which is in agreement with the results obtained by earlier workers using a solvent-extracted shell oil. In the manufacture of Cardanol from the raw commercial shell liquid, almost complete reduction of one of the double bonds in the side chain of the monophenol occurs, but it takes place without alteration in the length, the position, or the configuration of the fifteen-carbon side chain.

CASHEW NUTSHELL LIQUID

Comparison of the Monophenol Isolated from Commercial Raw Cashew Nutshell Liquid and from Commercial Cardanol

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THE oily liquid in the shell of the cashew nut appears to be almost completely phenolic in character; its major component is anacardic acid, which is present to the extent of about 90%, and the remainder is mainly cardol (*8*). Smit (*7*) working with a solvent extract from the husk of the fruit of *Anacardium occidentale* (cashew tree), showed that anacardic acid was a hydroxybenzoic acid carrying a normal fifteen-carbon side chain containing two double bonds. He believed it to be a homolog of salicylic acid but did not establish the position of the side chain. More recently Backer and Haack (*1*), working with a solvent-extracted oil from the shell of the cashew nut, showed that anacardic acid is 2-carboxy-3-pentadecadienylphenol, and that cardol is 5-pentadecadienylresorcinol. The positions of the two double bonds in the normal fifteen-carbon side chains have not yet been determined.

Anacardic acid readily loses carbon dioxide on heating (*1*, *7*) to yield a monophenol, which has found considerable industrial application (*3*). For commercial usage the liquid is obtained from the cashew nutshell by a process that involves heating the shells to a high temperature for several minutes in a vat of previously obtained shell liquid. During this process the shell liquid is held at the high temperature for several hours. Considerable decarboxylation of the anacardic acid takes place, as well as some polymerization of the phenolic bodies to yield a commercial raw cashew nutshell liquid which is mainly monophenolic in character, but contains a small amount (approximately 16%) of anacardic acid (*5*), cardol, and polymerized material. To obtain the monophenolic portion of the oil, known commercially as Cardanol, the raw cashew nutshell liquid is first treated with small amounts of alkyl sulfates and sulfuric acid, filtered, and then distilled at relatively high temperatures with the aid of steam (*3*), as Figure 1 shows.

Smit (*7*) was among the first to investigate the chemical nature of the monophenol resulting from the decarboxylation of anacardic acid obtained from a solvent-extracted oil. Although he did not locate the position of the side chain, he showed that it contained two double bonds in a fifteen-carbon side chain arranged in a normal configuration.

These results were recently confirmed by Backer and Haack (*1*) who, in addition, located the side chain in the 3-position and named the monophenol "anacardol". Harvey and Caplan (*3*), investigating the same problem, except that they worked with Cardanol, concluded that its main constituent was a monophenol substituted in the 3-position with a normal fourteen-carbon side chain containing one double bond.

In comparing the results of Harvey and Caplan with those of Smit and of Backer and Haack with reference to the length and degree of unsaturation of the monophenol side chain, it seemed probable that the disagreements might be due to the difference in the method of isolation of Cardanol and Anacardol. With this in mind it seemed advisable to determine whether structural changes, outside of decarboxylation, occur during the commercial preparation of raw cashew nutshell oil and Cardanol.

The purpose of this communication is to report that the monophenol obtained by direct vacuum distillation of the commercial raw cashew nutshell liquid is identical with that isolated by Backer and Haack from solvent-extracted oil. In other words, the heat treatment during the preparation of the commercial raw cashew nutshell liquid apparently does not lead to any serious structural change in the side chain of the phenol.

It has likewise been found, as previously reported by Harvey and Caplan, that the side chain of Cardanol has approximately one double bond. However, the side chain contains fifteen carbon atoms instead of fourteen as they reported (*3*). Thus in the commercial preparation of Cardanol from commercial cashew nutshell liquid, almost complete reduction of one of the double bonds in the side chain occurs.

MONOPHENOL FROM COMMERCIAL RAW LIQUID

The series of reactions used to establish the identity of the monophenol obtainable from commercial raw cashew nutshell liquid are shown in Figure 1. The phenol (I) was obtained from the commercial liquid by direct vacuum distillation after decarboxylation for a period of 2 hours at 130–200° C. under vacuum. About 50% of the liquid distilled over as a light yellow oil and left a black elastic solid in the flask. After two fractionations of the light yellow oil in vacuo, a clear colorless oil was obtained that analyzed correctly for $C_{21}H_{32}O$. Quantitative hydrogenation, with palladium oxide catalyst, resulted in the absorption of two moles of hydrogen; the presence of two double bonds in the side chain was thereby confirmed. The white crystalline tetrahydrophenol (II) obtained melted at 51.0–51.5° C. and analyzed correctly for $C_{21}H_{36}O$. [Backer and Haack (*1*) report a melting point of 51.5–52.5° C. for tetrahydroanacardol.] To establish the length of the side chain, the tetrahydrophenol (II) was oxidized with potassium permanganate in wet acetone to yield an aliphatic carboxylic acid melting at 61–2° C. The identity of this acid with palmitic acid (melting at 61.5–62.5° C.) was proved by mixed melting point. Mixtures of the acid with stearic and myristic acids gave depressions of the melting point of 5–11° C. The isolation of palmitic acid thereby established the side chain as a normal configuration of fifteen carbon atoms, since Furukawa (*2*) showed previously that a fifteen-carbon side chain yields palmitic acid under these conditions of oxidation. The methyl ether of the tetrahydrophenol (III) analyzed correctly for $C_{22}H_{38}O$ (tetrahydroanacardol methyl ether).

To locate the position of the side chain of the monophenol, the methyl ether of the unsaturated phenol (IV) was prepared by methylating the decarboxylated cashew nutshell liquid just prior to distillation. A pure sample of the ether which analyzed correctly for $C_{22}H_{34}O$ was obtained. On oxidation with alkaline potassium permanganate, a white solid (melting point 105–106° C.) resulted; by mixed melting point it was found to be identical with *m*-methoxybenzoic acid (melting point 106–107° C.). The position of the pentadecadienyl side chain was thereby established as meta to the phenolic hydroxyl group. Quantitative hydrogenation of the methyl ether (IV) resulted in the absorption of two moles of hydrogen, to yield 3-pentadecylanisole (melting point 29–30° C., *1*) which proved to be identical with tetrahydroanacardol methyl ether (III), obtained previously by methylation of tetrahydroanacardol (II).

MONOPHENOL FROM CARDANOL

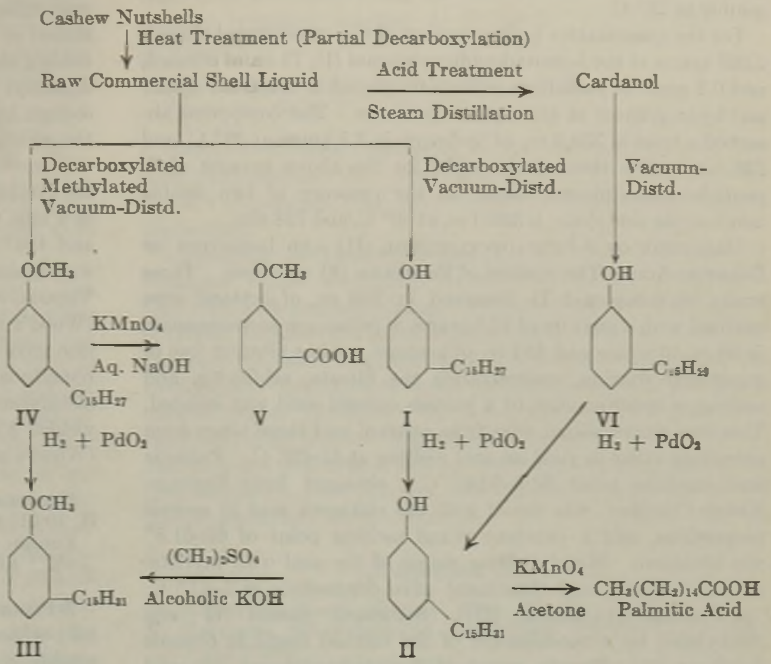
Upon direct vacuum distillation of commercial Cardanol it was found that about 70% by weight came over as a yellow oil which darkened on standing. The residue in the flask set to a black viscous semi-liquid. After two fractionations of the yellow oil in vacuo, a clear light yellow monophenol (VI) was obtained. Catalytic quantitative hydrogenation of this oil resulted in absorption of 1.15 molar equivalents of hydrogen, calculated on the basis of the molecular weight of anacardol. The hydrogenation experiment was repeated with several samples of distilled phenol. Although fresh catalyst was added in several of the experiments after the absorption of hydrogen had ceased, in no case were more than 1.15 moles of hydrogen absorbed; this was the hydrogen absorption obtained with the sample of phenol purified for analysis. The purified sample of phenol upon analysis gave carbon and hydrogen values that were in accordance with the quantitative hydrogenation data. That is, they agreed with values calculated for a phenol having a fifteen-carbon side chain containing an average of 1.15 double bonds.

The hydrogenated phenol was found to be identical with the tetrahydroanacardol (II) prepared from raw cashew nutshell liquid as previously described. This was established by carbon and hydrogen analysis, mixed melting point, and the fact that oxidation with potassium permanganate in wet acetone yielded palmitic acid as in the case of tetrahydroanacardol.

EXPERIMENTAL

The raw commercial cashew nutshell liquid and the commercial Cardanol used in this investigation were provided by the Irvington Varnish and Insulator Company. Melting and boiling points were obtained with a thermometer calibrated against a Bureau of Standards thermometer, and are otherwise uncorrected. Solubility data are based on the solubility of one drop of material in ten drops of solvent.

Figure 1. Flow Sheet



3-Pentadecadienylphenol (I). About 750 grams of raw commercial cashew nutshell liquid were placed in a one-liter round-bottom flask and decarboxylated by heating on a Wood's metal bath at 130–200° C. for 2 hours under 4 mm. pressure. The ground-glass jointed flask was equipped with an electrically heated Vigreux column, condenser, and multiple receiver, and the brown oil distilled at 1.5 mm. The main fraction boiling at 205–219° (Wood's metal bath at 260–292° C.) amounted to 393 grams of a yellow oil which darkened on standing. Upon redistillation at 1.4 mm., a pale yellow middle fraction was cut at 204–204.5° (Wood's metal bath at 250–259° C.). A small sample of clear colorless oil was obtained for analysis by another fractionation at 1.0 mm. with a boiling range of 186–187° (Wood's metal bath at 260–264° C.).

Calculated for $C_{21}H_{32}O$: molecular weight, 300.5; C, 83.94; H, 10.76.
Found: C, 83.89; H, 10.91.
$n_D^{27.2}$ 1.5060.

The water-insoluble colorless phenol was found to be soluble in acetone, benzene, ethyl acetate, ethanol, methanol, and petroleum ether at room temperature.

3-Pentadecylphenol (II). Seventy grams of the 3-pentadecadienylphenol (I) in 150 cc. of ethanol were hydrogenated in the presence of 1.2 grams of palladium oxide catalyst at room temperature under 1–3 atmospheres of hydrogen. After filtering the solution free of catalyst and removing the alcohol by distillation, the residue was distilled at 1.5 mm. and cut at 195–200° (Wood's metal bath at 241–245° C.), yielding 66.5 grams (95% of theory) of a colorless oil which crystallized as white needles. A middle fraction boiling at 197° and 1.5 mm. (Wood's metal bath at 244° C.) was collected for analysis; its melting point was 51–51.5° C. [Backer and Haack (*1*) reported a melting point of 51.5–52.5° for this compound, and Furukawa (*2*) reported 50° C.]

Calculated for $C_{21}H_{36}O$: molecular weight 304.5; C, 82.80; H, 11.95.
Found: C, 82.51; H, 11.80.

3-Pentadecylphenol was found to be water-insoluble, but was soluble in acetone, benzene, ethyl acetate, ethanol and methanol at 0° and 25° C. It was insoluble in petroleum ether at 0° but soluble at 25° C.

For the quantitative hydrogenation of the unsaturated phenol, 2.037 grams of the 3-pentadecadienylphenol (I), 75 cc. of ethanol, and 0.2 gram of palladium oxide were placed in a 250-cc. shaker and hydrogenated at atmospheric pressure. The compound absorbed a total of 334.3 cc. of hydrogen in 3.5 hours at 30° C. and 758 mm. The theoretical uptake for the above amount of 3-pentadecadienylphenol, based on the presence of two double bonds in the side chain, is 335.0 cc. at 30° C. and 758 mm.

OXIDATION OF 3-PENTADECYLPHENOL (II) AND ISOLATION OF PALMITIC ACID. The method of Furukawa (*2*) was used. Three grams of compound II dissolved in 150 cc. of acetone were oxidized with a mixture of 10.5 grams of potassium permanganate in 60 cc. of water and 450 cc. of acetone. After filtering free of manganese dioxide, concentrating the filtrate, acidifying, and cooling, a small amount of a reddish colored solid was isolated. This was recrystallized once from ethanol and three times from petroleum ether to yield an acid melting at 61–62° C. Palmitic acid (melting point 61.5–62.5° C.), obtained from Eastman Kodak Company, was mixed with the unknown acid in several proportions, and a constant mixed melting point of 61–61.5° was obtained. Mixed melting points of the acid with myristic acid and stearic acid (Eastman) gave depressions of 5–11° C.

3-PENTADECYLANISOLE (III). Saturated phenol II was methylated by a modification of the method found in *Organic Syntheses* (*4*). Twenty grams of 3-pentadecylphenol (II) and 60 cc. of absolute methanol were placed in a 200-cc. three-neck round-bottom flask, equipped with stirrer, condenser, and dropping funnel. An alcoholic solution of potassium hydroxide was prepared by dissolving 15.7 grams of potassium hydroxide in 15 cc. of water and diluting with methanol to a total volume of 60 cc.; 19.3 cc. of this solution were added to the flask. The flask was heated on the steam bath, and 10.4 grams of dimethyl sulfate were added at a rate to maintain an ebullition of the reaction mixture. After the above portion of dimethyl sulfate had been added, the flask was heated for 15 minutes; then 2.2 grams of dimethyl sulfate were added, and the flask was again heated. At this point the acid reaction mixture was made basic by the addition of 3.2 cc. of the alkali solution and then more of the sulfate (2.2 grams) added. This procedure of adding the alkali solution and sulfate portionwise and heating was repeated twice more; after the remainder of the alkali had been added, the entire mixture was refluxed for 15 minutes. Because of its low solubility in dilute methanol the methylated phenol separated as an oil early in the reaction. The reaction mixture was cooled and diluted with water, and the substituted anisole layer was separated, dried by distillation of benzene from the mixture, and distilled in a 25-cc. Vigreux conical-bottom flask under vacuum. A middle fraction, boiling at 175–177° and 1.5 mm. (Wood's metal bath at 223–231° C.) which solidified on cooling (melting point 29–30° C.) was cut for analysis. Backer and Haack (*1*) also reported the melting point of this compound to be 29–30° C.

CALCULATED FOR $C_{22}H_{38}O$: C, 82.95; H, 12.03.
FOUND: C, 82.95; H, 11.86.

3-Pentadecylanisole was found to be soluble in acetone, benzene, ethyl acetate, hot ethanol and methanol, and petroleum ether, but insoluble in water and cold ethanol and methanol.

3-PENTADECADIENYLANISOLE (IV). The methyl ether of unsaturated phenol IV was obtained directly from the raw commercial shell liquid by decarboxylating the liquid and then methylating it before distilling. The decarboxylation was carried out by heating the liquid at 3 mm. for 45 minutes on a Wood's metal bath maintained at 150–210° C. The oil was then methylated according to the method of Perkin and Weizmann (*6*) by adding 252 grams (2 moles) of dimethyl sulfate to 308 grams of the decarboxylated oil dissolved in 600 cc. of methanol. The reaction was carried out in a 2-liter three-neck flask equipped with stirrer, reflux condenser, and dropping funnel. After the flask was chilled, the reaction was initiated by adding 100 grams (2.5 moles) of sodium hydroxide in 180 cc. of water, with continuous cooling and stirring. After refluxing for about 30 minutes, more dimethyl sulfate (120 grams) was added and then 30 grams of sodium hydroxide in 60 cc. of water. After refluxing one hour, the mixture was diluted with water; the oily layer separated and was dried by the addition and distillation of benzene from the residue. Vacuum distillation of the dark brown oily residue at 1 mm. yielded 244 grams of yellow liquid boiling between 186° and 198° (Wood's metal bath at 262–270° C.). This fraction was again distilled at 1–1.5 mm. in a 30-cm. electrically heated Vigreux column, and a middle fraction boiling at 195–195.5° (Wood's metal bath at 247° C.) was taken. Because this fraction gave a slight positive sodium test, a portion (20 grams) was remethylated as described above. The remethylated oil, on distillation at 1.0 mm. in a 25-cc. Vigreux conical-bottom flask, yielded 5 grams of clear colorless middle fraction boiling at 188.5° (Wood's metal bath at 242–251° C.) which was used for analysis.

CALCULATED FOR $C_{22}H_{34}O$: molecular weight, 314.5; C, 84.01; H, 10.91; OCH_3, 9.86.
FOUND: C, 84.10; H, 11.13; OCH_3, 10.02.
$n_D^{25.5}$ 1.5008.

3-Pentadecadienylanisole was found to be insoluble in water, cold ethanol and methanol, slightly soluble in hot methanol and soluble in acetone, benzene, ethyl acetate, petroleum ether, and hot ethanol.

OXIDATION OF 3-PENTADECADIENYLANISOLE (IV) AND ISOLATION OF *m*-METHOXYBENZOIC ACID. In a 500-cc. round-bottom flask equipped with a reflux condenser were placed 5 grams of compound IV, 500 cc. of water, 2.0 grams of potassium permanganate, and 3 cc. of 0.2 *N* sodium hydroxide, and the mixture was refluxed overnight. The manganese dioxide was filtered off, and the filtrate was concentrated, acidified with hydrochloric acid, and cooled in the refrigerator. The milky mixture yielded white crystals (melting at 105–106° C.) that were isolated and recrystallized twice with petroleum ether. Mixtures of this product with several proportions of a known sample of *m*-methoxybenzoic acid (melting at 106–7°; Beilstein melting point, 105–106.6° C.) gave constant mixed melting points of 105–107°; the identity of the product was thereby established as *m*-methoxybenzoic acid.

CONVERSION OF 3-PENTADECADIENYLANISOLE (IV) TO 3-PENTADECYLANISOLE (III). Eight grams of compound IV in 75 cc. of glass-distilled ethanol and 25 cc. of acetone were hydrogenated at atmospheric pressure and room temperature in the presence of 0.4 gram of palladium oxide catalyst. After the absorption of 2 moles of hydrogen, the reaction ceased and the catalyst was removed by filtration. After removal of the solvent by evaporation, the oil was washed three times with Claisen's solution (an equivolume mixture of 50% potassium hydroxide and methanol) to remove free phenol and once with water, and was then dried by the addition and distillation of benzene. Final purification was achieved by two distillations at 2 mm., using in the last distillation a 25-cc. Vigreux conical-bottom flask. A middle fraction of clear colorless oil boiling at 196–8° (Wood's metal bath at 237° C.) which solidified to a white solid, melting at 29–30°, was taken for analysis:

CALCULATED FOR $C_{22}H_{38}O$: C, 82.95; H, 12.03.
FOUND: C, 82.80; H, 11.80.

MONOPHENOL (VI) FROM COMMERCIAL CARDANOL. Commercial Cardanol was redistilled three times under vacuum. In the first distillation about 85% of the oil was found to distill between 42° and 245° at 1.5–4.0 mm. (Wood's metal bath at 178–305° C.), leaving a black semi-liquid residue in the flask. About 65–70% of the oil was collected between 204° and 236° (Wood's metal bath at 258–290° C.). Two more distillations of this fraction yielded a light yellow oil, the major portion of which distilled at 198–205° and 1.0 mm. (Wood's metal bath at 233–236° C.). This oil darkened slightly on standing to a reddish orange color. A fraction boiling constantly at 205° at 1.0 mm. (Wood's metal bath at 233–236° C.) was taken for analysis:

CALCD. FOR $C_{21}H_{32}O$ (ANACARDOL)	CALCD. FOR $C_{21}H_{34}O$	FOUND
Mol. wt. 300.5	Mol. wt. 302.5	......
C_{15} side chain with 2 double bonds	C_{15} side chain with 1 double bond	......
C, 83.94	C, 83.37	C, 83.32
H, 10.76	H, 11.34	H, 11.23
$n_D^{25.2}$ 1.5070	......	......

DIHYDRO-CARDANOL (II) OR TETRAHYDROANACARDOL. The presence of one double bond in the fifteen-carbon side chain of the above purified monophenol (VI) from Cardanol was verified by quantitative hydrogenation; 1.688 grams of (VI) in 60 cc. of ethanol were reduced with hydrogen at 30° C. and 763 mm. pressure, using 0.3 gram of palladium on carbon as a catalyst. A total volume of 161.4 cc. of hydrogen was absorbed. The theoretical absorption for this amount of the phenol, based on one double bond in the side chain, is 140.5 cc. Thus an equivalent of 1.15 double bonds was indicated in the purified phenol (VI).

To prepare a larger amount of the dihydro-Cardanol for preparative purposes, 100 grams of (VI) dissolved in 160 cc. of ethanol were reduced under a pressure of 2 atmospheres of hydrogen, using 2.0 grams of palladium on carbon as catalyst. After the absorption of hydrogen had ceased with an uptake of 1.1 equivalents, an additional gram of catalyst was added but no more hydrogen was absorbed. After filtering off the catalyst, the solvent was removed by distillation and the residue was vacuum-distilled at 1.0 mm. in a 250-cc. flask equipped with an electrically heated Vigreux column. The fraction taken at 202.5–205.0° (Wood's metal bath at 232.4° C.) solidified on cooling to yield a light yellow solid melting at 47–48° C. After four recrystallizations from petroleum ether, the melting point of the pure white crystals remained constant at 51.0–51.5° C. The yield was 21.5 grams.

CALCULATED FOR $C_{21}H_{36}O$: C, 82.80; H, 11.95.
FOUND: C, 82.74; H, 11.98.

Mixtures of these crystals with varying proportions of pure 3-pentadecylphenol (II) obtained as previously described from the raw commercial shell liquid melted at 51.0–51.5° C. with no depression.

OXIDATION OF DIHYDRO-CARDANOL (II) AND ISOLATION OF PALMITIC ACID. To verify further the identity of dihydro-Cardanol as 3-pentadecylphenol, the length of the side chain of dihydro-Cardanol was established by the method used with the 3-pentadecylphenol that was obtained from the raw commercial shell liquid. Oxidation of the dihydro-Cardanol with permanganate in acetone yielded a white crystalline product which, after three recrystallizations from ethanol, melted at 61.5–62.0° C. Just as in the former case, mixtures of these crystals with varying proportions of pure palmitic acid (melting point 61.5–62.5°) melted constantly at 61.0–62.0° C.

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Red Lead-Alkyd Resin Reactions

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RED lead–alkyd resin paints have been used for the protection of structural iron and steel for approximately fifteen years. Many specifications (*7, 13, 14, 15*) have been written to cover paints of this type. Red lead is a pigment of basic character. It is known that all basic pigments react to some degree with oleoresinous vehicles. The presence of limited amounts of reaction compounds formed from red lead and oleoresinous vehicles has been found to impart beneficial properties to the paint film. This investigation concerns the factors influencing the reaction between red lead and alkyd (phthalic) resin vehicles. In order to study these factors, the following points were considered: variations in degree of reactivity of red leads of varying true red lead (Pb_3O_4) content; effect of time and temperature on the formation of these reaction compounds; degree of reaction between red lead and the alkyd resin vehicles; solubility of the reaction compounds in the vehicle.

Analytical methods for determining phthalates in such paint systems presented a problem; therefore special attention was given to the methods involved. The important steps in determining phthalic reaction products are the centrifugal separation of the pigment from the vehicle and the determination of the phthalic anhydride content of the pigment and vehicle portions. The extent to which reaction products formed was determined by analysis of pigments and vehicles extracted from paints of known composition and history.

Several methods have been described for the quantitative determination of phthalic anhydride in alkyd resin varnishes. The two in general use are the Kappelmeier (*3*) and the U. S. Navy method (*8*), which were discussed by Sanderson (*9*). The Kappelmeier method has been modified (*5, 6*), but the original method (*3*) was used in this investigation for the analysis of extracted vehicles. It was necessary to determine the volatile portion since the phthalic anhydride in the vehicle should be reported on the solids basis. Here, again, various methods were used. They include the A.S.T.M. standard method (*1*), a vacuum method (*10*), and a method using castor oil (*4*).

The determination of the phthalate in the pigment portion presented a still different problem. The Kappelmeier (*3*) and Navy (*8*) methods were modified by the authors; the Kappelmeier modified method was found to be more satisfactory.

A qualitative method for phthalic anhydride in extracted pigments has been reported (*12*). Reference has been made to the reaction between red lead and alkyd resin vehicles (*11*). No quantitative method for determining phthalate was given.

For simplicity, paints were made according to the formulation given under "Experimental Work". Six samples of each

Red lead–alkyd resin paints have come to be widely used for protecting steel from corrosion. Red lead is known to be reactive with drying oils and the older types of oleoresinous vehicles, but the reaction between red lead and the alkyd resin vehicle in these paints has not been thoroughly studied. In this investigation the degree of reaction, the effects of varying true red lead (Pb_3O_4) content of the pigment, time, temperature, and moisture, as well as the solubility of the reaction products in the vehicle were considered. Various grades of red lead were made into paints with a linseed-oil-modified glycerol phthalate vehicle. A portion of each paint was centrifuged at varying time intervals, and the separated pigment and vehicle were analyzed. Physical tests were made on some of the paints as well as a study of the reactions of red lead and phthalic acid in an aqueous medium. This investigation indicates that: (*a*) The true red lead (Pb_3O_4) portion of the pigment does not react with the alkyd resin, while (*b*) the free PbO portion reacts with the free fatty acids present in the vehicle, and (*c*) on aging paints made with 97% Pb_3O_4 grade red lead, they do not change in film flexibility. A quantitative method for phthalates is given.

paint were stored in suitable airtight containers. Freshly opened samples were therefore used at various time intervals, so that the effect of time and storage on the reaction could be studied. In the first stages of the investigation, each sample was extracted with four portions of hot benzene and centrifuged. The clear vehicle portions from the extractions were combined, the volatile matter driven off, and the residue analyzed. This method was abandoned as being inaccurate; instead, the paint itself was centrifuged. The pigment was extracted to remove residual vehicle and air-dried. The pigment portion was analyzed for phthalic anhydride and examined petrographically for lead phthalate. Two analytical methods for phthalic anhydride were tried on the pigment portion. The Navy method (*8*) was employed first, and the results obtained on samples extracted from the paints and on known mixtures of red lead and potassium acid phthalates, are shown in Table I. In all tables portions *A* and *B* are duplicate parts of the same sample.

The modification of the Navy method was discarded, and the following revised Kappelmeier method was used: A weighed amount of the extracted pigment, varying from 1 to 8 grams, was treated in a 250-ml. glass-stoppered soil digestion flask with 150 ml. of 0.5 *N* anhydrous alcoholic potassium hydroxide. An air-cooled condenser was attached, and the mixture was refluxed for 3–4 hours on a steam bath with intermittent agitation. After refluxing, the samples were allowed to cool, and the condenser was washed with absolute ether. The red lead containing precipitated potassium phthalate was filtered on a fritted-glass Gooch crucible, washed with a 50–50 mixture of absolute ether and absolute alcohol, and dried at 60° C. for 10 minutes. The crucibles were allowed to stand overnight in an evacuated sulfuric acid desiccator and weighed the next morning. The red lead and potassium phthalate on the crucibles were washed thoroughly with distilled water, dried at 105° C., and then reweighed. The difference in weight represented potassium phthalate containing one molecule of alcohol of crystallization and was calculated to per cent phthalic anhydride. A determination for lead was made on the filtrate from the water washings to ascertain whether any water-soluble lead products were washed out. No trace of lead was found. The accuracy of the method was checked by analyzing mixtures containing known amounts of lead phthalate and red lead. The results obtained with such mixtures containing 0.3 to 34% phthalic anhydride are shown in Table II.

The extracted pigments were analyzed for true red lead content as follows: A one-gram sample of the dry pigment was wet with a small amount of ethanol and distilled water, and the "red lead solution" of sodium acetate, potassium iodide, and acetic acid was added. The free iodine was then titrated with standard sodium thiosulfate, using starch solution as indicator.

The presence of phthalate was found to interfere slightly with the end point of the red lead titration. Therefore, true red lead was subsequently determined on the residue from which the phthalate had been removed by washing in the phthalic anhydride determination. Total lead content of the extracted vehicles was also determined.

MATERIALS USED. The pigments were three red leads varying in true red lead content as follows: 85% grade, 92% grade, and 97% grade. In addition, two experimental pigments were prepared from the 97% grade. The free litharge had been removed from one pigment by treatment with acetic acid, and the second was treated with phthalic acid to convert the free litharge to lead phthalate. This was done to determine the effect of any free PbO.

The alkyd resin solution contained 50.1% mineral spirits and 49.9% resin. The nonvolatile vehicle was a linseed-oil-modified glyceryl phthalate resin, analyzing 34.5% phthalic anhydride and having an acid number of 6.5.

The volatile thinner for the paints was high-solvency petroleum spirits. This was used also wherever a thinner was needed in the subsequent centrifuging. The drier in the red lead paints was a cobalt naphthenate solution (6% cobalt). The extraction mixture (*4*) was composed of 10 volumes ethyl ether, 6 volumes benzene, 4 volumes methanol, and 1 volume acetone.

EXPERIMENTAL WORK

The red lead paints were made according to the following formulation:

Pigment 68%		Vehicle 32%	
Red lead 100%		Alkyd resin solution	79.2%
		Volatile thinner	19.8
		Cobalt naphthenate (6% Co)[a]	1.0

[a] In the paints containing the two treated pigments, the drier consisted of 0.4% cobalt naphthenate (6% Co) and 1.43% lead naphthenate (24% Pb).

The paints were mixed in a laboratory mixer and given one pass over a three-roll laboratory mill (0.002-inch clearance). They

TABLE I. PER CENT PHTHALIC ANHYDRIDE EXTRACTED FROM PIGMENTS BY NAVY METHOD

Sample No.	1	2	3	4
Portion *A*	1.84	3.04	2.05	3.52
Portion *B*	3.76	2.76	1.86	2.07
Known Mixt. No.	1	2	3	
Calcd.	3.60	3.60	0.80	
Found	2.54	2.94	0.93	

TABLE II. PER CENT PHTHALIC ANHYDRIDE EXTRACTED FROM PIGMENTS BY MODIFIED KAPPELMEIER METHOD

Sample No.	5	6	7	8	9	10
Portion *A*	1.39	0.30	0.27	1.43	0.33	0.61
Portion *B*	1.38	0.32	0.30	1.49	0.33	0.57
Known Mixt. No.	5	6	7	8		
Portion *A*	1.66	34.03	19.61	30.12		
Portion *B*	1.69	34.17	19.63	30.95		
Calcd.	1.4	33.87	19.0	30.18		

were put in 4-ounce glass containers, filled to the top, tightly sealed, and stored at room temperature until analyzed.

At the time of analysis, the samples were thoroughly mixed and two 50-gram portions were centrifuged. The clear vehicles from the two portions were combined for analysis. The pigment was extracted with five 50-ml. portions of the extraction mixture and air-dried overnight. In determining the phthalic anhydride in the vehicles, the per cent volatile was determined by two different methods (Table III). The phthalic anhydride in the vehicle was run by the Kappelmeier method (Table IV). The anhydride and the true red lead in the pigment were determined as previously described.

TABLE III. PHTHALIC ANHYDRIDE CONTENT OF EXTRACTED VEHICLES ON SOLIDS BASIS

Portion	% Volatile (Castor Oil Method) A	% Volatile (Castor Oil Method) B	% Phthalic Anhydride A	% Phthalic Anhydride B	% Volatile[a] (Castor Oil Method) C	% Volatile[a] (Castor Oil Method) D	% Phthalic Anhydride[a] C	% Phthalic Anhydride[a] D
Sample 1	70.12	70.01	34.21	34.04	71.71	71.77	29.63	28.96
Sample 2	72.91	72.63	37.49	37.32	67.60	67.83	36.17	36.55
Sample 3	77.79	78.01	34.50	34.61	61.64	61.66	32.07	32.01
	(A.S.T.M. Method)				(A.S.T.M. Method)			
Sample 4	71.48	71.08	34.08	34.13	70.90	71.98		
Sample 5	66.71	...	36.28	36.03	67.51	61.41		
Sample 6	80.09	...	33.16	32.76	79.86	80.59		

[a] Portions *C* and *D* are duplicates of the same sample.

TABLE IV. PER CENT PHTHALIC ANHYDRIDE IN EXTRACTED VEHICLES BY KAPPELMEIER METHOD

First tests	Calcd. Amount	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11
Portion *A*	34.5	30.64	24.77	28.44	21.67	23.08
Portion *B*	34.5	30.48	24.31	28.30	22.96	23.99
Repeat tests						
Portion *A*	34.5	31.06	30.37	31.47		
Portion *B*	34.5	31.49	29.98	33.32		

The first series of paints included the phthalic-acid-treated red lead, the acetic-acid-treated red lead, and commercial 97% grade red lead, aged at various intervals (Table V).

Film flexibility tests were also conducted. Films of uniform thickness were spread with a doctor blade on $^1/_{32}$-inch rolled steel, immediately baked at 160° F. for 6 hours, chilled in a mixture of ice and water, and bent over a conical mandrel (*2*). The results are shown in Table VI.

A second set of paints was prepared with commercial grades of red lead. They were made, stored, and examined in the same way as those of the first series except for the time intervals. Results are shown in Table VII.

On aging, the pigments in the paints settled with the clear vehicle above them. In between these two portions a layer of white flocculent precipitate settled out. Although the precipitate seems very voluminous, it is only a small percentage of the total paint by weight. To obtain more information on this precipitate, the clear supernatant vehicle was carefully removed. The white precipitate was then removed, mixed with benzene, and centrifuged. The precipitate which was insoluble in benzene was dried and analyzed. Analysis showed 0.8% lead and 18% phthalic anhydride. The remainder was complex glycerides. A microscopic examination of this precipitate showed it to have a waxlike character. It was definitely not lead phthalate.

A 31-month-old commercial sample of red lead–alkyd resin paint of similar composition was obtained. This sample was divided into three parts. The first part was analyzed, as received, to determine the extent of any reaction which might occur on long storage. The second portion was maintained at 90° C. for 5 hours to ascertain the effect of temperature on any reaction which might occur. To evaluate the effect of water, the third portion was intimately mixed with 1% of its weight of water and allowed to stand for 3 weeks at room temperature. The three portions were then analyzed with the results shown in Table VIII.

It was decided that an investigation of the reactions of red lead and phthalic acid in an aqueous medium as well as in paint would give a more complete picture. A 97% grade red lead was treated, in water, with varying amounts of powdered phthalic anhydride. The solid residues were washed thoroughly, dried at 80° C., and analyzed for total lead monoxide (PbO), lead dioxide (PbO_2), and phthalic anhydride. From the analytical data the compositions of the residues were computed in terms of unchanged red lead, *n*-lead phthalate, and free lead dioxide. The results are shown in Table IX.

The product from experiment 1 had about the same color as the original red lead. The products obtained in the other three experiments were dark brown, due to the presence of free lead dioxide. The products of experiments 2 to 4 also had a lustrous sheen imparted by free *n*-lead phthalate. It follows from these data that true red lead, in contrast to its behavior in alkyd resin vehicles, reacts in water containing appreciable amounts of free phthalic acid.

The results of these experiments lead to the belief that the following reactions take place:

$$Pb_3O_4 + 2C_6H_4(COOH)_2 \xrightarrow{H_2O} PbO_2 + 2PbC_6H_4(COO)_2 + 2H_2O \quad (1)$$

$$Pb_3O_4 + 3C_6H_4(COOH)_2 \xrightarrow{H_2O\ +\ \Delta} 3PbC_6H_4(COO)_2 + 3H_2O + {}^1/_2\ O_2 \quad (2)$$

Reaction 1 may occur to some extent at room temperature. Reaction 2 takes place appreciably only at elevated temperatures. Gas evolved during reaction 2 was identified as oxygen. A small percentage of carbon dioxide, which was present in the original red lead as basic lead carbonate, was also evolved.

DISCUSSION OF DATA

The phthalic anhydride in the extracted pigments of the 92 and 97% grades of red lead was low (0.45 to 0.55%) on the day made (Table VII) and showed no appreciable increase during 19-week storage. However, the 85% grade started with 1.47% phthalic anhydride and showed an increase to 2.02% during the same period.

The phthalate in the 85% grade pigment on the day made and in the 92 and 97% grade pigments after storage was not lead phthalate but unextractable resinous material. This material is present in two forms: (*a*) vehicle retained by the pigment and

TABLE V. CHANGES IN COMPOSITION OF FIRST SERIES OF RED LEAD–ALKYD RESIN PAINTS ON STORAGE

	Original Material	Age of Paint Samples 1 wk.	2 wk.	3 wk.	8 wk.
Phthalic-acid-treated, 97% grade red lead					
% Pb_3O_4 in extd. pigment	97.3	96.7	...	96.7	95.7
% pigment	68.0	68.6	67.6	68.2	67.9
% P.A.[a] in nonvolatile vehicle	34.5	30.6	34.9	31.3	32.4
% P.A. in red lead	1.4	...	...	1.3	1.4
Acetic-acid-treated, 97% grade red lead					
% Pb_3O_4 in extd. pigment	99.4	99.3	...	98.7	98.0
% pigment	68.0	67.4	66.9	68.0	67.6
% P.A. in nonvolatile vehicle	34.5	24.5	33.6	28.0	30.1
% P.A. in red lead	None	...	...	0.18	0.22
Untreated commercial 97% grade red lead					
% Pb_3O_4 in extd. pigment	98.2	98.3	...	97.9	97.5
% pigment	68.3	68.1	68.3	70.0	66.9
% P.A. in nonvolatile vehicle	34.5	28.4	33.6	32.4	27.6
% P.A. in red lead	None	...	...	0.28	0.31

[a] P.A. = phthalic anhydride.

TABLE VI. PER CENT ELONGATION AT CRACKING POINT OF PAINT FILM

Red Lead Pigment	Age of Paint Sample			
	2 days	3 days	7 days	23.5 wk.
Phthalic-acid-treated	6.0	6.8	7.0	7.0
Acetic-acid-treated	6.5	6.8	6.5	6.2
Commercial 97% grade	6.5	6.5	6.8	7.0

TABLE VII. CHANGES IN COMPOSITION OF SECOND SERIES OF RED LEAD–ALKYD RESIN PAINTS ON STORAGE

	Original Material	Age of Paint Samples			
		Same day	2 wk.	8 wk.	19 wk.
85% grade red lead					
% Pb_3O_4 in extd. pigment	85.5	85.0	85.9	87.6	89.5
% Pb_3O_4 in treated pigment	...	..	...	93.3	95.4
% P.A.[a] in red lead pigment	None	1.47	1.30	1.46	2.02
% total lead as Pb in nonvolatile vehicle	.....	1.2	5.2	...	17.5
92% grade red lead					
% Pb_3O_4 in extd. pigment	92.1	92.1	92.8	93.3	95.0
% Pb_3O_4 in treated pigment	.....	....	...	95.4	97.0
% P.A. in red lead pigment	None	0.55	0.39	0.37	0.51
% total lead as Pb in nonvolatile vehicle	.....	2.0	3.3	...	8.2
97% grade red lead					
% Pb_3O_4 in extd. pigment	98.9	98.2	97.5	98.0	98.3
% Pb_3O_4 in treated pigment	.....	....	97.9	98.6	97.7
% P.A. in red lead pigment	None	0.45	0.32	0.33	0.59
% total lead as Pb in nonvolatile vehicle	.....	0.34	...	...	1.6

[a] P.A. = phthalic anhydride.

not extractable for this reason and (*b*) the small amount of white flocculent precipitate thrown down with the pigment.

The retention of resinous vehicle (*a*) seems to be a function of the litharge content of the pigments, as shown by the relatively high phthalic anhydride figure for the 85% red lead sample the same day the paint was made. The small amount of flocculent precipitate (*b*) forms as the paints age. This material is not lead phthalate. The analyses show that it contains only 0.8% lead and about 18% phthalic anhydride. The remainder consists of complex glycerides. During the separation of the pigment and vehicle by centrifuging, this flocculent precipitate is thrown down with the pigment portion. The amount of this precipitate formed is also a function of the litharge or free PbO content of the red lead. A theory advanced for the formation of this insoluble material is that, as the soluble lead soaps form in the vehicle, this product precipitates, as explained above.

That the per cent phthalate in Table VII is unextractable material and not lead phthalate has been shown by microscopical examination of the pigments at 1000 magnifications. Only on the 19-week sample of 85% grade red lead was it possible to isolate any crystals which remotely resembled lead phthalate. The number of crystals found was few and could not be positively identified as belonging to the family of known lead phthalates. On the other pigments none of these crystals could be detected at 1000 magnifications. However, on all pigments identification was made of particles of red lead coated with dried resinous materials.

Considering the entire system, the only possible reactions between pigment and vehicles are the formation of soluble lead soaps by free PbO with the fatty acids and other components of the vehicle, and the reaction of free PbO with the alkyd resin vehicle to form lead phthalate. The first of these two possible reactions is substantiated by a chemical examination of the paints. The second reaction does not take place in paints of low free-PbO content. The data from this investigation make its occurrence appear improbable even in red leads of high PbO content in the absence of water.

The total lead content of the extracted vehicle is sufficient evidence of the occurrence of the first reaction, which proceeds until the major portion of the free PbO is formed into lead soaps. The appreciable increase in the percentage of phthalic anhydride in the extracted 85% Pb_3O_4 pigment during 19-week storage, and the findings upon microscopic examination of the same pigment, provide the only evidence of the possible occurrence of the second reaction. However, even with high free-PbO (85% Pb_3O_4) red leads there is no conclusive evidence of the formation of lead phthalate, and the occurrence of the reaction under the test conditions is highly improbable.

Table V substantiates the discussion of the data of Table VII. Table V refers to a duplicate 97% grade red lead paint; yet at 8 weeks the results are the same as those indicated in Table VII. The treated red leads, from which the free PbO has been removed, behave in the same manner as the commercial 97% grade red leads and show no increase in phthalic anhydride content.

According to the data, the "per cent pigment" value is not sufficiently accurate to form the basis for any conclusions regarding the extent of reaction. The data which show a worthwhile picture are the "per cent elongation" values (Table VI). With 97% grade red lead paint there is no loss of flexibility, even after 23.5 weeks of storage. This indicates that changes in paint on storage do not adversely affect the flexibility of the paint film.

TABLE VIII. EFFECT OF TIME, TEMPERATURE, AND MOISTURE ON COMPOSITION OF A COMMERCIAL RED LEAD–ALKYD RESIN PAINT

Paint	% P.A. in Extd. in Pigment	% Pb_3O_4 Extd. Pigment	% Pb_3O_4 in Treated Pigment	% Total Pb in Nonvolatile Vehicle
1. After 31 mo. in container	0.37	97.5	98.8	...
2. Same as 1, refluxed 5 hr. at 90° C.	0.56	97.3	98.6	...
3. Same as 1, with 1% H_2O added	0.54	97.2	99.0	2.7

TABLE IX. DATA ON AQUEOUS RED LEAD–PHTHALIC ACID SYSTEMS

Expt. No.	Reactants, Grams[a]		Heating		Compn. of Residue, %		
	Phthalic anhydride	Water	Time, hr.	Temp., ° C.	Pb_3O_4	Lead phthalate	PbO_2
1	1.42	200	48	80	95.5	4.3	0.00
2	22.3	600	3	85	42.0	48.0	10.0
3	43.5	600	3	85	6.6	76.5	16.9
4	64.7	600	3	95	0.0	85.0	15.0

[a] 100 grams of red lead in each experiment.

Table VIII is a compilation of results on a commercial paint sample which was almost three years old. Even after storage for this length of time the phthalic anhydride content of the pigment has not increased beyond the amount shown by the laboratory-prepared 97% grade red lead paint the day it was made. Together with the other data, this shows that in 97% grade red lead paint no lead phthalate is formed during storage. Other data in Table VIII indicate the effect of heat and moisture on the reaction. Even at elevated temperatures and with moisture present in the paint, the reaction to form lead phthalate does not take place with the true red lead.

Tables I and II compare the Navy and the modified Kappelmeier methods of analysis. By the Navy method, duplicate samples of the same pigment do not check. With the Kappelmeier method, duplicate samples gave checks within a few hundredths per cent. The range of amounts of phthalic anhydride which can be determined accurately by the modified Kappelmeier method varies from 0.3 to 35%.

The data of Tables III and IV show the difficulties that arise in an attempt to determine the phthalic anhydride in an extracted vehicle. The Kappelmeier method is precise in that check results on duplicate determinations are easily obtained.

The difficulty lies in the determination of volatile and the subsequent translation of the phthalic anhydride values to a nonvolatile basis. Various methods of test for percentage of volatile were tried, but they were not sufficiently accurate to use as the basis for determination of the phthalic anhydride content of the extracted vehicle solids. On a straight alkyd resin varnish, which had not been made into a paint and to which no drier had been added, two different operators, working some 5 months apart, obtained the same value for the phthalic anhydride content.

With the methods of analysis now available, no definite conclusion can be drawn from the change in the phthalic anhydride content of the extracted vehicle. In other words, a change of a few tenths per cent in the phthalate content of the extracted vehicle cannot be determined, and therefore a study of the vehicle does not show the possible formation of lead phthalate or other phthalate reaction products.

CONCLUSIONS

1. No reaction takes place between true red lead (Pb_3O_4) and alkyd resin. Reaction takes place only between the free litharge (PbO) and the alkyd resin vehicle. Red lead pigments containing 92% or more Pb_3O_4 do not react with alkyd resin vehicles to form lead phthalate. The evidence of formation of lead phthalate in the case of red lead of 85% true red lead content is not conclusive.
2. The phthalate found in the extracted red lead pigments was present as unextracted alkyd resin retained on the pigment.
3. After long storage, red lead–alkyd resin paints, in which the pigment is 97% true red lead, show no change in paint film flexibility.
4. The phthalate content of the vehicle extracted from red lead paints cannot be determined accurately with present methods of analysis.
5. The method established for determining the phthalate content of the extracted pigment, as set forth, is quantitative and reliable.

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Compatibility of DDT with Insecticides, Fungicides, and Fertilizers

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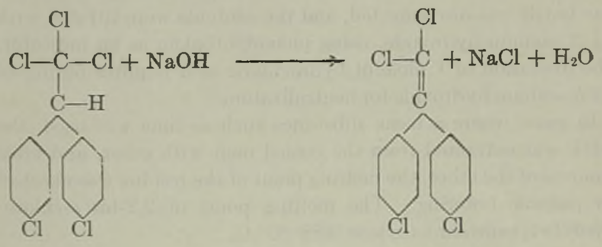
THE indicated widespread use of DDT as an insecticide (*1, 4*) and its known instability in the presence of certain catalysts (*2*) make it desirable to have information as to the possible catalytic effect of other insecticides, fungicides, fertilizer materials, and accessories with which it may be applied. DDT is a rather stable compound by itself. Long periods of exposure to the air have caused no appreciable change. Irradiation of the solid material, spread in a thin layer, for 35 hours with a 100-watt General Electric mercury vapor lamp, type AH-4, caused the melting point of DDT to be lowered by only 2° C. Similarly, an alcoholic solution of pure DDT showed no change after exposure to sunlight for over a year.

In contrast to this stability in the neutral state, it has been shown that DDT in alcoholic solution readily reacts with alkalies in accordance with the following reaction (*3*):



Some of the more common insecticides, fungicides, and fertilizers have been tested for catalytic action in the dehydrochlorination of DDT. Materials used for diluents have been shown to vary in their activity as catalysts for the decomposition of DDT. The anhydrous chlorides of iron, aluminum, and chromium are active dehydrohalogenation catalysts for DDT. The catalytic action of anhydrous ferric chloride has been shown to be promoted by solution in naphthalene, chloronaphthalene, chlorobenzene, *o*- and *p*-dichlorobenzenes, and nitrobenzene, and inhibited by various hydrocarbon and fatty oils, alcohols, ketones, acids, and anhydrides.

TABLE I. CATALYTIC ACTIVITY OF ACCESSORY MATERIALS IN PRESENCE OF DDT

Material	Moles HCl Evolved per Mole DDT
Alumina	None
Aluminum chloride	1.00
Aluminum powder	None
Kaolin	1.03
Bentonite	0.32
Calcium oxide	None[a]
Hydrated lime	None[a]
Chromic chloride, $CrCl_3.6H_2O$	0.05
Chromic chloride, anhydrous (0.01%)	0.98
Chromic oxide	None[a]
Chromium	1.02
Stainless steel (18-8)	0.98
Copper powder	None
Cupric chloride	0.12
Frianite	0.04
Fuller's earth	1.00
Iron powder (U.S.P., hydrogen reduced)	None
Iron powder (alcoholized)	1.00
Iron filings	0.98
Iron oxide (red)	0.32
Iron oxide, magnetic (black)	0.79
Iron rust	0.73
Ferric sulfate	None
Ferric chloride, $FeCl_3.6H_2O$	0.86
$FeCl_3.6H_2O$ (alone)	0.34
Ferric chloride, anhydrous (0.01%)	1.02
Ferrous carbonate (Blaud's mass)	None
Lead	None
Lead chloride	0.09
Lead sulfate	0.09
Magnesium oxide	0.07[a]
Nickel powder	0.07
Pyrax ABB (sample 1)	0.04
Pyrax ABB (sample 2)	0.91
Sericite	None
Talc (U.S.P.)	None
Talc (West Coast)	1.03
Talc (Vermont)	None
Talc, off-color (Maryland)	1.05
Tin	None
Zinc dust	None
Zinc chloride	None
DDT alone	None

[a] DDT was isolated unchanged from the melt.

It has been shown (*2*) that certain catalysts also will decompose DDT, with the formation of hydrochloric acid and 2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethylene. The latter compound, formed either by catalytic action or by reaction of DDT with an alkali, is markedly inferior to DDT as an insecticide.

Procedure. The apparatus used to test for catalytic activity was the same as that described previously (*2*). Into a 6-inch Pyrex U-tube were placed 2 grams of recrystallized DDT (melting at 104–106° C.) and 2 grams of the material to be tested. The U-tube was connected to a gas-washing bottle which contained 50 ml. of water to absorb any hydrochloric acid that might be liberated. A gentle current of dry air was drawn through the apparatus. The U-tube was placed in an oil bath at 115–120° C. to a depth of about 3 inches. After heating for 1 hour, the absorption bottle was disconnected, and the contents were titrated with 0.1 *N* sodium hydroxide, using phenolphthalein as an indicator. The liberation of 1 mole of hydrochloric acid requires 56 ml. of 0.1 *N* sodium hydroxide for neutralization.

In cases where a basic substance such as lime was used, the DDT was extracted from the cooled melt with ether, and after removal of the ether, the melting point of the residue was checked for possible lowering. The melting point of 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene is 88–89° C.

Insecticides. Commercial grades of sodium fluoride, sodium fluosilicate, cryolite, Paris green, calcium arsenate, and lead arsenate showed no catalytic activity in decomposing DDT. Likewise, pure rotenone and pyrethrum were found to be inactive.

When pure nicotine was used, the DDT decomposed and the product was isolated by means of ether extraction, washing with dilute acid and then with water, and evaporation of the ether. The decomposition product melted at 70–79° C. By recrystallization from alcohol the melting point was raised, and the product was identified as 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene by a mixed melting point determination. Since basic nitrogen-containing compounds react with DDT, this action with nicotine should be regarded as the type obtained with alcoholic caustics rather than as a catalytic decomposition. Tests to determine whether this reaction occurs under field conditions would seem to be in order.

Fungicides. Commercial lime-sulfur and 2,3-dichloro-1,4-naphthoquinone showed no catalytic action. With mixtures of DDT and ferric dimethyl dithiocarbamate 0.05 mole of hydrochloric acid was evolved. With Bordeaux mixture 0.04 mole, and with sulfur 0.07 mole, were obtained.

Fertilizers. The following fertilizers showed no catalytic activity: ammonium sulfate, monoammonium phosphate, ammoniated superphosphate, ammonium nitrate, Cyanamid, manure salts, potassium sulfate, Uramon, dicalcium phosphate, double superphosphate, sulfate of potash-magnesia, potassium chloride, sodium nitrate, steamed bonemeal, Milorganite, and mixed fertilizers No. 1 (8-8-8), No. 2 (8-12-16), No. 3 (5-10-5), No. 4 (4-12-4), No. 5 (4-10-6), and No. 6 (3-9-6).

Dolomitic limestone was the only fertilizer tested which showed catalytic activity. One-hour heating of the mixture produced 0.89 mole of hydrochloric acid. The catalytic action persisted after the limestone had been slurried with water and then dried at 110° C. This treatment would destroy the catalytic action if it were due to small traces of anhydrous ferric, aluminum, or chromic chlorides.

Accessory Materials. Accessory material that may be used in the preparation of DDT dusts, as well as other compounds encountered in the manufacture and use of DDT, were tested. The results are recorded in Table I. The wide difference in the catalytic activity of various samples of the same mineral indicates the presence of small amounts of active catalysts unevenly distributed in the mineral. Of these catalysts known at present, iron and iron oxides, chromium, and anhydrous ferric, aluminum, and chromic chlorides are indicated. Of this group the anhydrous chlorides are most active. Ferric and chromic chlorides may be formed by the action of DDT on the metals themselves. It is therefore indicated that the catalytic action of the various accessory materials of mineral origin is due to small amounts of catalytic impurities apt to be found in minerals. Hence the content of catalytic substance may vary with the source of the mineral.

In diluted dusts the action of these catalysts is not rapid until temperatures are reached that are above the melting point of

TABLE II. CATALYTIC ACTIVITY OF SOLVENTS IN PRESENCE OF DDT AND ANHYDROUS FERRIC CHLORIDE

Solvent	Moles HCl Evolved per Mole DDT
Acetic anhydride	None[1]
Chlorobenzene	1.07
α-Chloronaphthalene	1.07
Cyclohexanone	0.18
p-Dichlorobenzene	1.00
o-Dichlorobenzene	1.05
o-Dichlorobenzene (bath temp. 50–55° C.)	0.80
o-Dichlorobenzene (bath temp. 27–30° C. for 4 hr.)	0.11
Dioxane	None[a]
Ethylene chloride (80° C.)	1.10
Fuel oil (No. 2)	0.02
Kerosene	0.02
Motor oil (S.A.E. 30)	None
Naphthalene	1.05
Nitrobenzene	1.13
Octadecyl alcohol	0.02
Oleyl alcohol	0.02
Refrigeration oil (unsaturation-free)	0.43
Soybean oil	None
Stearic acid	0.05
Tetrahydronaphthalene	0.02
p-Toluenesulfonic acid	0.02
Velsicol AR-60	None
Xylene	0.16

[a] DDT was isolated unchanged from the melt.

DDT. Since this temperature is above that ordinarily encountered under normal outdoor conditions, decomposition effected by an accessory material under the accelerated test should be viewed as indicating storage tests at working temperatures.

Solutions of DDT. For this series of tests 2 grams of recrystallized DDT and 2 grams of the solvent were placed in the U-tube. After the temperature of the tube and its contents had come up to that of the oil bath, 2-3 mg. of anhydrous ferric chloride were dropped down the inlet arm of the U-tube. The tube was then shaken gently to ensure good mixing with the catalyst. The results (Table II) show that most of the solvents used with DDT have a marked inhibiting action toward the catalytic decomposition reaction. The notable exceptions are the nitro- and chlorobenzenes. With *o*-dichlorobenzene the catalytic action was shown to occur even at room temperature.

ACKNOWLEDGMENT

The fertilizer materials were supplied by the Bureau of Plant Industry, Soils, and Agricultural Engineering, through the courtesy of J. O. Hardesty.

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FERMENTATION PROCESS FOR ITACONIC ACID

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A fermentation process for the production of itaconic acid, based on the cultivation of a superior strain of *Aspergillus terreus* (NRRL 1960) on the surface of glucose nutrient media, has been developed and operated on a semipilot plant scale. Itaconic acid yields in excess of 30 grams per 100 grams of glucose supplied are obtained in 12 days. The major portion of itaconic acid produced can be recovered by crystallization after concentrating and cooling the filtered liquors. The fermentation is resistant to contamination, since the nutrient medium is maintained at a low pH level throughout the culture period.

RESEARCH on the production of itaconic acid (methylene succinic acid), a potential raw material for resins of the methacrylate type, was undertaken as a means of increasing the industrial utilization of agricultural products. Itaconic acid was first reported as a product of mold metabolism by Kinoshita (*3*) who obtained it from cultures of *Aspergillus itaconicus*. Calam, Oxford, and Raistrick (*1*) reported obtaining small quantities of this acid from one strain of *Aspergillus terreus*, and preliminary investigations conducted by Moyer and Coghill (*5*) confirmed the suitability of *Aspergillus terreus* for bringing about this reaction. The present paper describes the production of itaconic acid from glucose on a semipilot plant scale, using the organism and conditions found best in this Laboratory.

The organism was a strain of *Aspergillus terreus* isolated by Kenneth B. Raper from a soil sample obtained from San Antonio, Texas. It was one of the best itaconic acid-producing strains found in preliminary investigations. The organism is carried in this Laboratory's culture collection as *Aspergillus terreus* (NRRL 1960) and is maintained in stock culture on Czapek-Dox solution agar as cited by Thom and Church (*7*). To obtain frangible spore-bearing material from *Aspergillus terreus* to be used for the inoculation of production cultures, a medium of the following composition was employed:

Glucose monohydrate (commercial), grams	275
$NaNO_3$, grams	5
$MgSO_4.7H_2O$, gram	0.024
KCl, gram	0.005
H_3PO_4, gram	0.003
Concd. corn steep liquor[a], ml.	0.5

[a] A commercial by-product of the corn wet-milling industries. It contains approximately 50% total solids, and is a rich source of mineral nutrients and protein degradation products.

Distilled water was added to bring the medium to 1000 ml. Sterile 50-ml. portions in 200-ml. Erlenmeyer flasks were heavily seeded with spores obtained from a 10-day-old slant culture. On the liquid medium, a good crop of spores was obtained after 5-day incubation at 30° C. One flask culture is sufficient to inoculate 100 liters of nutrient solution; appropriate portions were used to inoculate the 12-liter quantities of medium used in each of the seven fermentation pans.

The fermentation was conducted in shallow aluminum pans, 22 × 36 × 2 inches, in a cabinet described by Ward, Lockwood, May, and Herrick (*8*) for the cultivation of molds on the surface of solutions. The pans were sterilized with flowing steam for 3 hours, then cooled under a slight pressure of sterile air. The inoculated solutions then were blown into the pans through sterile glass tubes inserted through the front of the cabinet. Twelve liters of medium were placed in each pan. The fermentation solution had the following composition:

Glucose monohydrate (commercial), grams	165
$MgSO_4.7H_2O$, grams	4.4
NH_4NO_3, grams	2.5
NaCl, gram	0.4
$ZnSO_4.7H_2O$, gram	0.0044
Nitric acid (sp. gr. 1.42), ml.	1.60
Concd. corn steep liquor, ml.	4.0

and distilled water was added to bring the volume to 1000 ml. The initial pH was approximately 2.0.

Throughout the 12-day fermentation period the tier of cultures was aerated at the rate of 5 liters of humidified air per minute. The entering air was sterilized by passage through a cotton filter. The considerable heat evolved during the course of the fermentation was dissipated by the circulation of cold water through coils installed in the cabinet. The temperature was maintained at 30° to 32° C. by a thermostatically operated solenoid valve controlling the flow of water to the coils.

At harvest the solutions were drained from the pans, and the pans and mycelia were washed with small quantities of cold water. Main filtrates and washings from each pan were combined, and appropriate samples were taken for analysis. Glucose determinations were made by the method of Shaffer and Hartmann (*6*). Itaconic acid was determined by the bromination method of Koppeschaar (*4*), as modified in this Laboratory by Friedkin (*2*).

The combined liquors from each pan were evaporated on a steam bath, with constant stirring, to a volume of approximately one liter; a slurry of fine crystals of itaconic acid resulted. The agitated mass was cooled to room temperature, and the crystals were separated in a perforated basket centrifuge and washed with cold water. The resultant product, consisting of almost pure itaconic acid, was very light in color. In some cases it was possible to obtain a second crop of itaconic acid crystals after further evaporation of the supernatant liquor, which was dark brown and low in viscosity.

RESULTS OF FERMENTATIONS

Data from two groups of fermentations are presented to illustrate typical results. Table IA shows data obtained when the fermentation is conducted under the most favorable conditions yet found. It is apparent that analytical yields representing approximately 50% of theory, based on glucose consumed, and in excess of 25% on a weight basis, are obtained. The theoretical yield is assumed to be one mole of itaconic acid per mole of glucose consumed, although there is no proof of this relation as yet.

Table I. Production of Itaconic Acid from Glucose

	A. Typical Pan Fermentations		*B.* Duplicate Pan Fermentations at Initial Glucose Concns. of:			
	Pan 1	Pan 2	10%	15%	20%	25%
Initial glucose, grams (calcd. to anhydrous basis)	1800	1800	1200	1800	2400	3000
Glucose consumed, grams	1583	1539	1128	1565	1617	1810
Itaconic acid produced, grams	569	602	242	561	577	568
Yield of itaconic acid based on glucose consumed[a], %	49.9	54.3	29.8	49.7	49.5	43.5
Itaconic acid recovered by crystallization, grams	453	490	192	436	457	429
Recovery efficiency, %	79.7	81.4	79.4	77.8	79.2	75.2
Recovery weight yield[b], %	25.2	27.2	16.0	24.2	19.0	14.3
Mycelial weight, grams	222	144	223	233	245	277

[a] Based on assumption that 1 mole of glucose should yield 1 mole of itaconic acid.

[b] Ratio of grams itaconic acid recovered to grams glucose supplied (anhydrous basis).

Data obtained in similar experiments have indicated the presence of appreciable quantities of neutral nonreducing materials in the fermented liquor. Also, in numerous experiments a small quantity of acidic material other than itaconic acid has been found. Analyses of the exhaust gases have shown a carbon dioxide content of about 1% and an oxygen content of 20.5% which indicates that the oxygen supply has been in excess of the requirements of the cultures.

In recovery studies approximately 20% of the itaconic acid produced was left in the mother liquors after the crystallized itaconic acid had been removed. Preliminary experiments have indicated that much of this acid can be recovered from the residual sirup by extraction with organic solvents, such as *n*-butanol. Using a 1% aqueous solution of itaconic acid at 28° C., a water/butanol distribution ratio of 0.469 was obtained. Some variation from this value was observed when residual fermentation sirups were extracted. The itaconic acid crystallized readily from the butanol upon concentration.

Analysis by alkali titration and by bromination methods of the first crop of itaconic acid crystals obtained from the evaporated liquors usually indicated purities of more than 97%; analysis of the second crop of crystals generally indicated purities greater than 90%.

Table I*B* presents the results of the fermentation of solutions of different initial glucose concentrations. It is apparent that yields of itaconic acid and fermentation efficiencies are low when the initial glucose concentration is 10%. The efficiency of conversion of glucose to itaconic acid is considerably higher in solutions of 15% initial glucose concentration, but no significant improvement is found at the 20 or 25% concentration levels. At the latter concentrations the residual glucose content of the solutions, after fermentation, is disproportionately large. This residual sugar represents a loss in over-all operating efficiency and also interferes with the recovery of the product, since it has not been found possible to obtain a second crop of crystals by further evaporating the mother liquor obtained from the initial crystallization. These and similar data suggest that glucose solutions of approximately 15% concentration are most desirable for itaconic acid production.

The process described here is believed to offer a practical means of producing itaconic acid from cheap abundant materials. This compound has heretofore been produced from the more expensive raw material, citric acid. The quality of the crude product obtained by the fermentation process suggests that further purification may be unnecessary prior to the esterification step in resin manufacture.

The raw materials cost would be about 22 cents per pound of itaconic acid recovered; this estimate is based on the assumption of a 25% recovery yield and a cost of 5.3 cents per pound of glucose (anhydrous basis), 2.5 cents per pound of corn steep liquor, and 0.4 cent for other nutrient salts required to produce one pound of itaconic acid.

The fermentation process is readily conducted, and is not easily susceptible to contamination, since the nutrient medium is maintained throughout the culture period at a pH level too low for the growth of most organisms.

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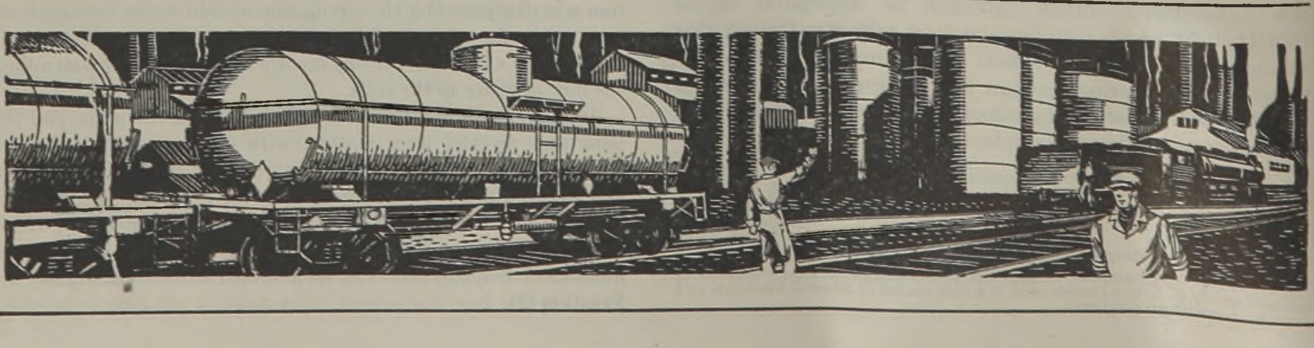
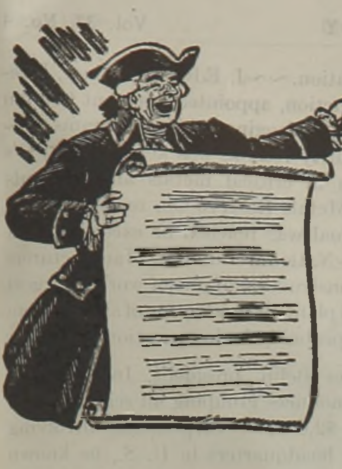
Presented by title before the Division of Agricultural and Food Chemistry at the 108th Meeting of the American Chemical Society in New York, N. Y.





MARCH'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ MARCH 1. Senate confirms appointment of Henry Wallace as Secretary of Commerce but shorn of lending agencies.∼∼American Farm Bureau Federation asks for legislation empowering Federal Government to set up plants for producing potash, nitrogen, and phosphate fertilizers.∼∼Firestone[1] completes $2,000,000 research laboratory for development of improved tires and other rubber and plastic products.

¶ MARCH 2. Sugar Research Foundation announces establishment of a series of sugar prizes totaling $45,000 to stimulate scientific research for discovery of new uses for sugar.

¶ MARCH 3. Ira Mosher, president, National Association of Manufacturers, says privately owned American manufacturing industry will provide employment for between 3,400,000 and 4,400,000 more workers after reconversion to peacetime production than it did in 1939.

¶ MARCH 4. Du Pont[1] announces plans for the construction of $20 million nylon plant near Orange, Tex., at government request. ∼∼National Research Council's Division of Medical Sciences says new drugs to combat malaria are being tested in three large penal institutions, where several hundred prisoners have volunteered to serve as living test tubes.

¶ MARCH 5. U.S. Rubber reveals that it waterproofs tanks so they can roll off a landing barge into 6 feet of water and go ashore fighting.∼∼Willard H. Dow, president, Dow Chemical, tells Senate's Small Business Committee[2] magnesium production has exceeded wartime consumption demands and that 10 plants with 85% of yearly capacity are now shut down. He suggests that 50% of capacity be leased to private business after war as standby units.∼∼U.S. Supreme Court tentatively grants review of Justice Department's antitrust case against U.S. Alkali and California Alkali Export Association[2].∼∼Peter Honig, director of Netherlands Indies Rubber Research Institute, discloses that new government-controlled organization will be put in temporary control of rubber production and trade in that area to speed exportation of rubber from Netherlands Indies when it is liberated.

¶ MARCH 6. President appoints Fred M. Vinson Federal Labor Administrator.∼∼Marion C. Joswick, 17, of Brooklyn, and Edward Malcolm Kosower, of New York, win scholarships valued at $2400 each in the Fourth Westinghouse Science Talent Institute. Thirty others received one-year scholarships valued at $100 each[3].

¶ MARCH 7. President appoints William H. Davis, chairman of War Labor Board, director of Economic Stabilization.∼∼WPB and Army jointly release tire makers from operating on 7-day week for remainder of month owing to lag in production of carbon black[4].∼∼WPB warns that over-all lead situation is getting increasingly tighter and that available stock piles of natural resins are rapidly diminishing.

¶ MARCH 8. WPB places further restrictions on use of tin because reserves hit low levels.∼∼Nicholas Murray Butler, president, Columbia University, announces 20 cash gifts to the university aggregating $50,428.84. Corn Industries Research Foundation gave $9500 for research on starch[5].

¶ MARCH 9. State Department spokesman says that department will assist Arabian American Oil Co. in negotiating for right of way for Near East pipe line.∼∼Vincent du Vigneaud, Cornell University Medical College, accepts William H. Nichols Medal of N. Y. Section, ACS.

¶ MARCH 11. Rubber Reserve Co. says output of synthetic rubber must be increased 31% in 1945 and 58% in 1946 to meet essential military and civilian transport requirements[1].∼∼American Telephone & Telegraph awards fellowships carrying a stipend of $3000 each to five scientists.∼∼Foreign Economic Administration announces that U.S. Commercial Co. will assist in getting commercial imports of pharmaceuticals from France. ∼∼Shell Oil officials disclose that a laboratory for the study of fuels and lubricants for jet propulsion aircraft is in operation at Wood River, Ill.∼∼WPB places further restrictions on civilian uses of copper because of increased demand by Armed Forces.∼∼Estimated industrial alcohol requirements for 1945 have been revised downward owing to small cutbacks in estimated direct military and Lend-Lease needs.

¶ MARCH 12. U.S. Supreme Court denies Government a review of lower court decision holding invalid its seizure of Montgomery Ward properties. Holds that Circuit Court of Appeals must first rule on lower bench decision.∼∼U.S. Circuit Court of Appeals reverses Federal Court decision that Aluminum Co. of America and its subsidiaries are not violating antitrust laws and returns case to lower tribunal.

¶ MARCH 13. Government asks Circuit Court to deny motion filed yesterday by Montgomery Ward for dismissal of its appeal from ruling in Federal District Court that Army's seizure of war properties was illegal.

¶ MARCH 15. WPB's Rubber Bureau adds two projects to the heavy tire expansion program for which DPC has authorized funds to Goodrich and Pharis Tire & Rubber Co.∼∼Rohm & Haas make commercially available new fungicide, Dithane, said to increase potato yield by 60 to 100 bushels an acre.

¶ MARCH 16. National Foreign Trade Council reports that more than 1300 Chinese technicians will be involved in International Administration's programs initiated by Foreign Economic Administration and Office of Defense Transportation to give the technicians intensive "on-the-job" training in specific activities. ∼∼M. L. Jacobs, president, Iron Mines Co. of Venezuela, a subsidiary of Bethlehem Steel, says company will ship 2,000,000 tons of iron ore to U.S. for smelting purposes when operations get underway.∼∼Aluminum Co. of America issues statement

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[1] *Chem. Eng. News*, **23**, 544 (March 25, 1945).
[2] *Ibid.*, 558 (March 25, 1945).
[3] *Ibid.*, 546 (March 25, 1945).
[4] *Ibid.*, 552 (March 25, 1945).
[5] *Ibid.*, 599 (March 25, 1945).

interpreting March 12 decision by U.S. Circuit Court of Appeals of Government's antitrust action against Alcoa and points out that it does not have monopoly now and has kept out of cartels. ∼∼Winkler-Koch Engineering Co. files antitrust damage suit against 11 oil companies.

¶ March 17. Paul N. Gross, head, Chemistry Department, Duke University, is 1945 winner of Herty Medal for tobacco research work.∼∼Worthington Pump & Machinery strikers by overwhelming majority vote to return to work after 3-day strike. ∼∼Regional War Labor Board orders 4000 employees of U.S. Rubber to end 3-day strike.

¶ March 18. Justice Department says it will resume prosecution of antitrust cases as soon as they will no longer interfere with war production.∼∼WPB announces that it will dip into Nation's stockpile of lead to bolster essential civilian requirements. ∼∼Zay Jeffries, a vice president of General Electric, selected to receive Francis J. Clamer silver medal of Franklin Institute for "achievements in the field of metallurgy" and for his "meritorious contributions to the science of metals".∼∼Attorney General Biddle in annual report outlines postwar antitrust policy designed to reduce concentration of business made necessary by war.

¶ March 19. Anglo-American oil agreement, readied for President's Committee by State Department, retains antitrust protective provision requested by industry.∼∼Attorney General Biddle asks Supreme Court to reconsider its refusal to take immediate jurisdiction of Montgomery Ward case.∼∼Pressed Metal Institute holds annual meeting by mail and sends complete agenda to members.∼∼J. Howard Pew, president, Sun Oil, in vigorous attack against private, government controlled, and superstate cartels, suggests that surplus Lend-Lease materials at war's end and Bretton Woods monetary agreements be used as protective devices if there is an attempt to "strong arm" the United States into cartel arrangements.

¶ March 20. President asks Congress for $4,480,000 appropriation to plan TVA for Missouri River Valley.∼∼Chemical and pharmaceutical industries initiate campaign to raise $500,000 for expansion of library of N.Y. Academy of Medicine.∼∼WPB warns that United States crude rubber supply will fall 40% below estimated danger line by year's end and that synthetic rubber plant must undergo $22 million expansion.∼∼U.S. Department of Agriculture says its scientists have developed method whereby chemicals introduced into sap stream of wood increase length of service of fence posts, garden stakes, etc.

¶ March 21. WPB Chairman Krug announces appointment of John L. Collyer, Goodrich president, as Special Director of Rubber Programs. Nation's rubber supply said to be "more critical than at any time since Pearl Harbor".∼∼Alien Property Custodian Markham authorizes General Aniline & Film Corp. to sell 6150 shares of Class B common stock of Winthrop Chemical at public auction.∼∼Howard W. Blakeslee, science editor for The Associated Press, honored at Waldorf-Astoria dinner on 65th birthday and completion of 40 years' service with A.P.

¶ March 22. Alien Property Custodian's Office begins registration of patents and contracts involving enemy nationals or citizens of enemy-occupied territories which will be available for public inspection.∼∼Monsanto announces that it will sell DDT under the name "Santobane".∼∼Firestone discloses electronic rubber curing process as much as 17 times faster than conventional steam method.∼∼Rubber Bureau, WPB, says DPC has authorized funds for 40th rubber project.∼∼WPB shifts control of potash salts to general chemicals order M-300.

¶ March 25. WPB reduces amount of wood pulp for nine civilian uses for second quarter.

¶ March 26. President Roosevelt asks Congress for authority to reduce tariff rates 50% below present rates in reciprocal trade agreements.∼∼Supreme Court again refuses to take immediate jurisdiction of Montgomery Ward case, thus denying government's petition for reconsideration.∼∼J. Edward Trainer, Firestone's vice president for production, appointed assistant to John L. Collyer to assist in speeding up lagging rubber programs.∼∼Veil of secrecy which for security reasons was kept over RFC's efforts to build up stockpiles in critical metals and minerals has been partially lifted and Metals Reserve Co. reveals that of a total of 51 programs the goal was reached or exceeded with 23 metals and minerals.∼∼National Lumber Manufacturers Association announces that construction of one of world's largest and America's first commercial plant for production of alcohol from sawdust and waste wood will probably be in operation July 1.

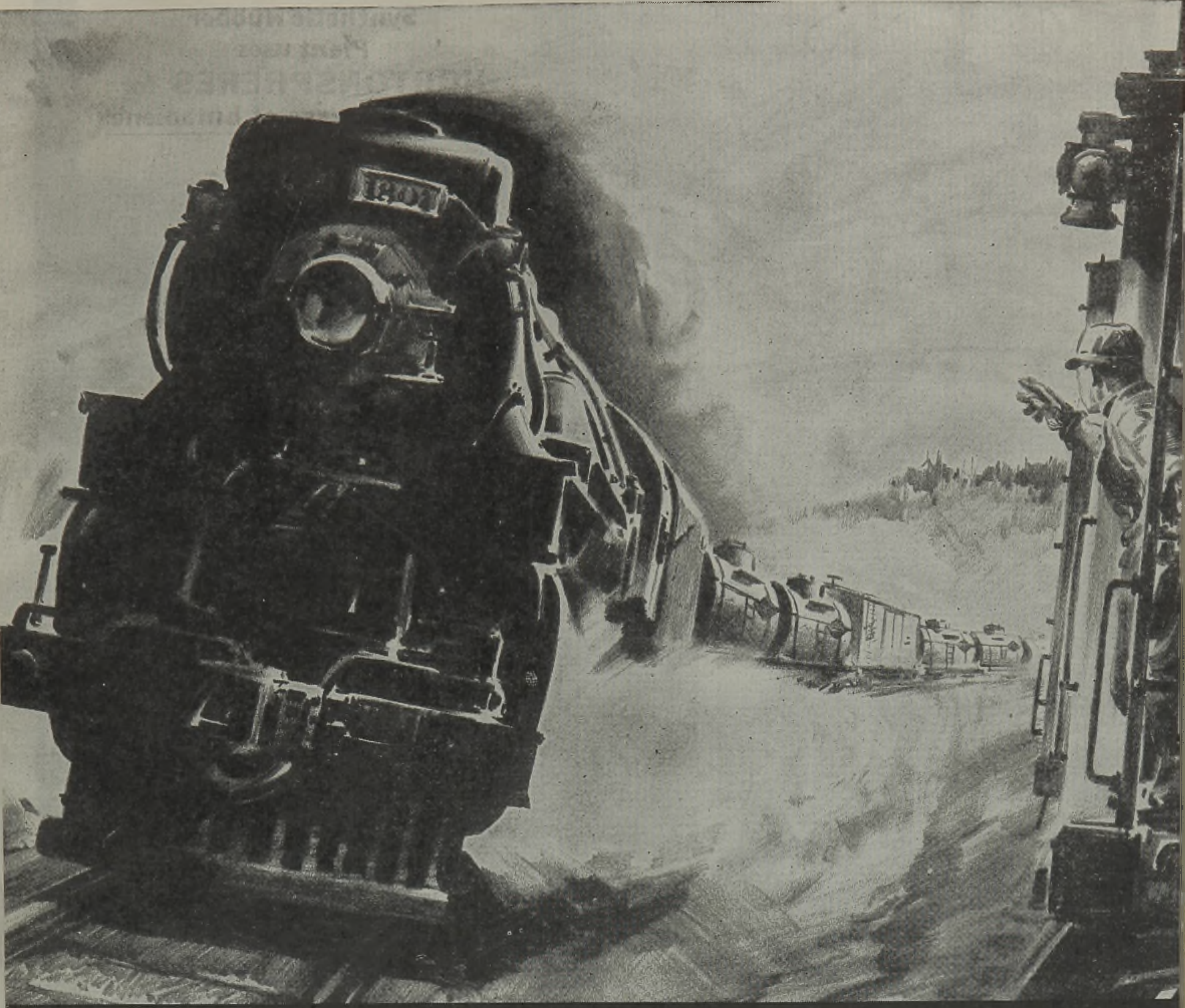
¶ March 27. Col. Sosthenes Behn, president, International Telephone and Telegraph, announces grouping all scientific and research activities in a new $2,000,000 corporation, involving world-wide organization with headquarters in U. S., be known as International Telecommunication Laboratories, Inc., with Col. Behn as chairman and E. M. Deloraine, general director of Federal Telephone and Radio Laboratories, New York, as president.∼∼WPB cuts allotments on steel drums and shipping pails because of critical shortage of sheet steel.∼∼Du Pont's fabrics division reports a new type of oil-resistant hospital sheeting coated with neoprene which withstands oils and sterilization much better than sheeting coated with natural rubber.∼∼Calco Chemical Division, American Cyanamid, announces commercial production for civilian use of a melamine resin for control of wool shrinkage.

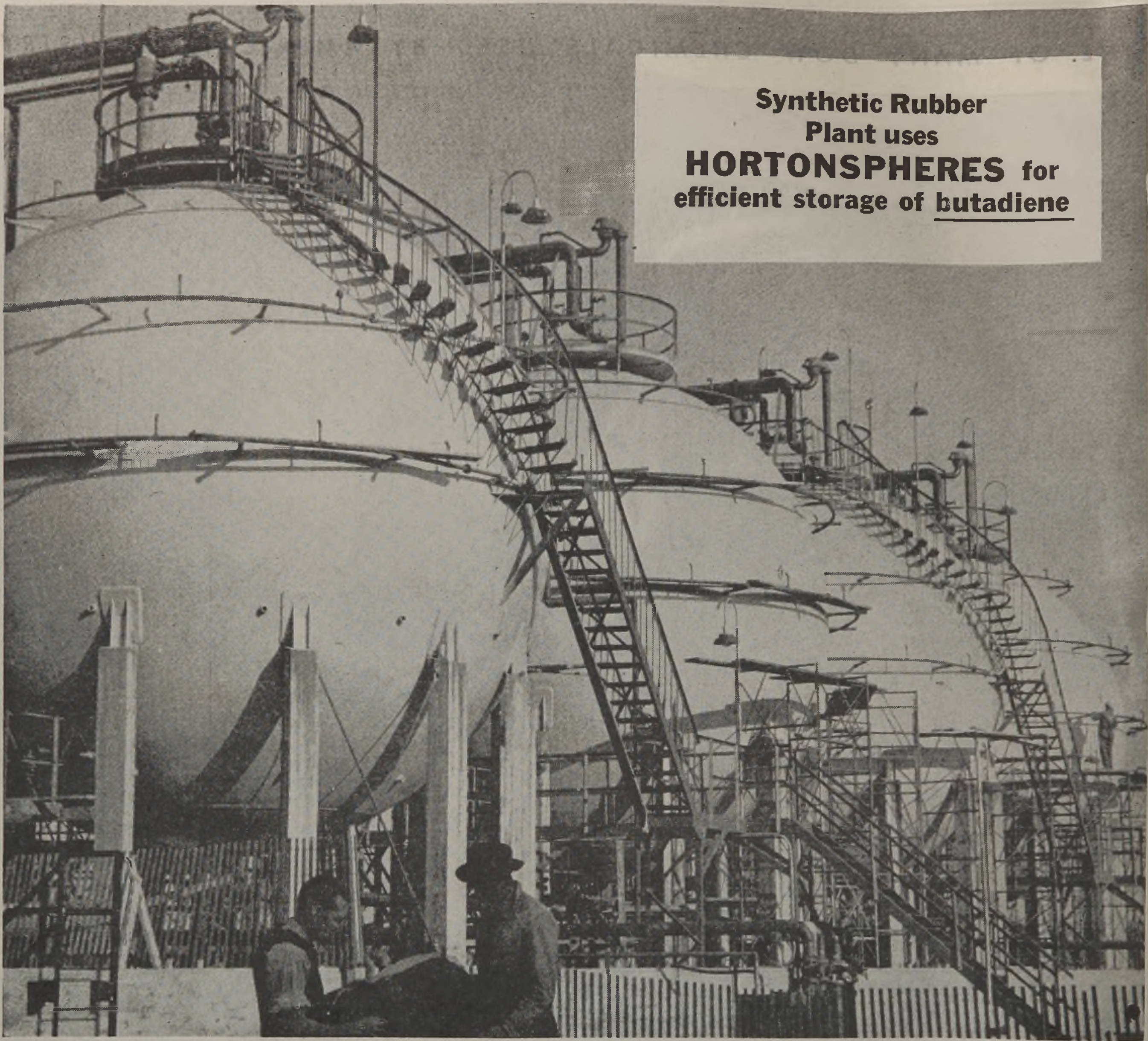
¶ March 28. Katharine B. Blodgett, researcher in molecular films at G. E.'s research laboratory, Schenectady, N. Y., wins $2500 Achievement Award of the American Association of University Women.∼∼Fred M. Vinson, Federal Loan Administrator, says U.S. will buy an additional 250 million pounds of aluminum in Canada for delivery before December 31, 1945.∼∼Brigadier General F. M. Hopkins, member Army-Navy Munitions Board, suggests at Small Business Committee hearing that to conserve limited bauxite deposits against future national emergency, stockpiles be acquired from foreign sources.∼∼War Food Administration amends WFO 42A to reduce from 50 to 40% quantity of fats and oils available, effective April 1, 1945, for manufacture of protective coatings, coated fabrics, and floor coverings for civilian use.∼∼Nutrition Foundation approves grants totaling $258,100 for nutritional research covering 6 new research projects and 24 renewals of grants.

¶ March 29. WPB assigns top priority to carbon black projects in order to increase production.∼∼S. DeWitt Clough, president, Abbott Laboratories, tells stockholders company has appropriated $50,000 for research fellowships in 10 universities.∼∼House Agriculture Committee in legislation introduced by Representative Page recommends government sponsorship of 10-year program for domestic rubber and urges increase plantings of guayule and additional experimentation.

¶ March 30. National Research Council announces grant of $335,000 from Rockefeller Foundation for establishment of temporary nation-wide program of predoctoral fellowships for graduate study in natural sciences.∼∼Franklin Institute announces Sanford Lockwood Cluett, vice president Cluett Peabody & Co., is winner of Longstreth Medal for development of process for preshrinking of woven fabrics known as Sanforizing.∼∼Senate Small Business Committee announces public hearings to inquire into government financing of big aluminum Shipshaw plant in Arvida, Quebec.∼∼Heyden Chemical assembles largest single shipment of penicillin—19.5 billion units—since discovery of the drug for use in Army hospitals.

¶ March 31. Justice Department files brief with U. S. Circuit Court of Appeals in defense of government seizure Dec. 28, 1944, of Montgomery Ward properties in 7 cities.∼∼Twenty-six million units of penicillin hidden beneath groceries seized from bus on way to Mexico at International Bridge, Laredo, Texas.





Synthetic Rubber Plant uses HORTONSPHERES for efficient storage of butadiene

PRESSURE storage tanks provide chemical and process plants with the most efficient means of storing volatile liquids. Pressure storage is one of the most effective means of preventing evaporation loss. This is accomplished by using a tank that permits pressure to build up on the inside when temperature changes cause the contents to expand or when additional liquid is pumped into the tank. As long as vapor is not allowed to escape through the vents, no evaporation loss will occur.

Hortonspheres, spherical pressure vessels, are being fabricated in our plants for chemical and process industries for pressures as high as 100 lbs. per sq. in. up to 45 ft. diam.; 150 lbs. up to 30 ft. diam.; 200 lbs. up to 22½ ft. diam.; 250 lbs. up to 18 ft. diam. and 300 lbs. up to 15 ft. diam. If you need efficient and economical storage for volatile liquids, write our nearest office for quotations on Hortonspheres to meet your requirements.

The group of five Hortonspheres shown above is located at a synthetic rubber plant. Each sphere is 29½ ft. in diam., holds 2400 bbls. and is designed to operate at 100 lbs. per sq. in. pressure. At this plant light hydrocarbons from a nearby refinery are converted into butane—butylene fractions and is used in making butadiene.

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Current Developments in EQUIPMENT AND DESIGN

Excellent designs of pumps developed to meet wartime demands will be ready for the needs of postwar industries.

Discussed by Charles Owen Brown

Before World War I, the writer was engaged in a research program, part time at Mellon Institute and part time with the Magma Copper Company. The problem then being investigated is now known as floth flotation, and the ore contained almost all of the known copper minerals plus native copper. The problem was difficult and results came slowly. At that early stage of the art, flotation of an ore was somewhat like developing a successful horse machine, except that the ore did not die; there was always an abundance left. So we reasoned as convincingly as possible that modifications were justified, because when completed the experiments could be run at twice the speed.

We were out at the Magma Works when J. M. Callow, president of General Engineering Corporation, suggested operating this miniature laboratory bench flotation mill continuously. To do this required a small pump capable of circulating the "pulp" or finely ground ore, suspended in water, smoothly and uniformly. There seemed no other solution than to do what the General Engineering Company did, using bronze. The machine, while inconveniently large, was speedily ruined by the abrasive action of the ore. This disappointment quickened the creative mood. A faint memory came to mind of a toy pump, seen at least fifteen years before in the *Youth's Companion*, with directions to enable any boy to build it. The masterpeice is shown in Figure 1 as reconstructed by the writer. While the laboratory rubber tubing did not last indefinitely, it was cheaply and quickly replaced. Crude as it seems, several of these pumps were used for many years at Mellon Institute and served the purpose admirably. Because of the unusual construction and materials required, this pump has not been widely accepted.

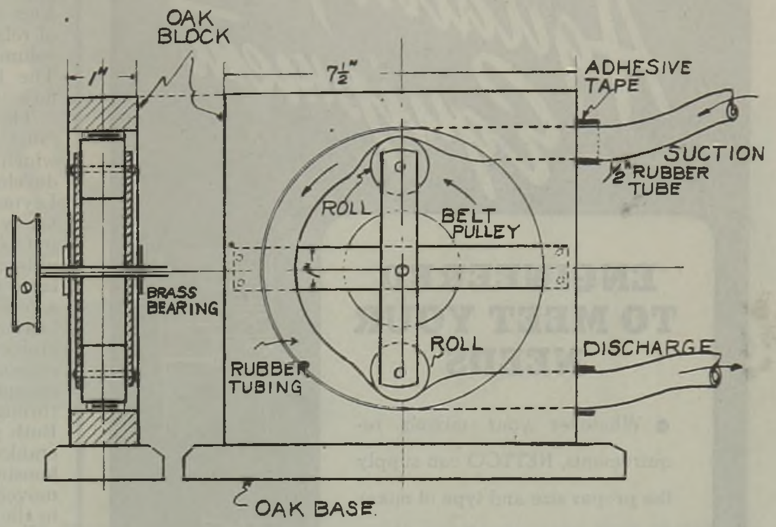


Figure 1. Laboratory Ore-Water Pump

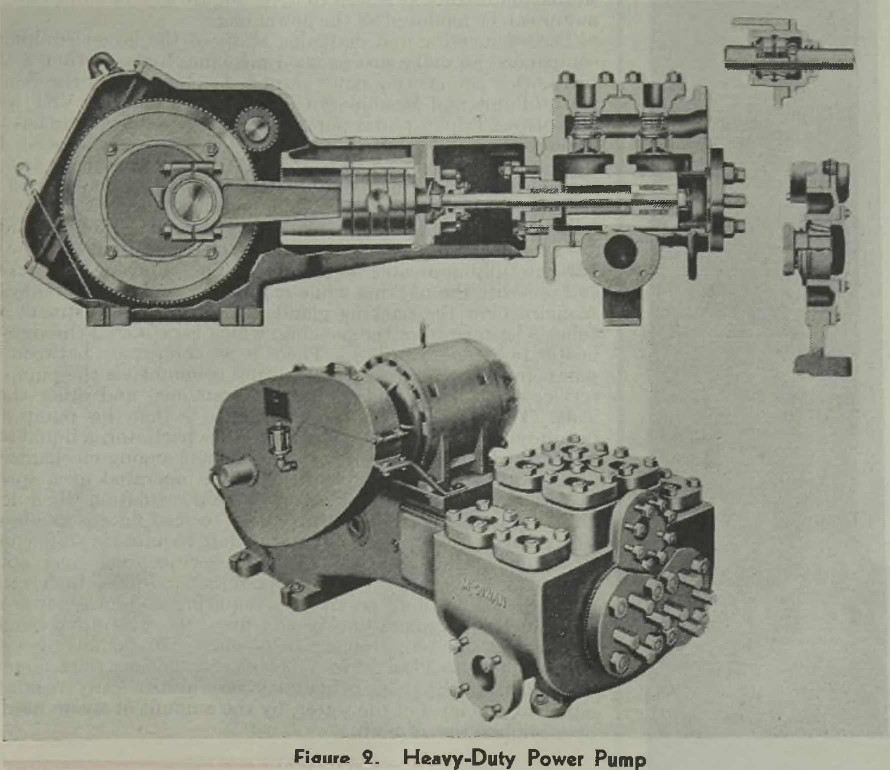
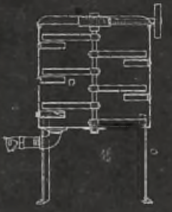
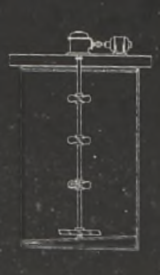


Figure 2. Heavy-Duty Power Pump

As recently as 1939 a metal-rubber pump of the same design was placed in production, using a molded rubber tube with anchoring lugs attached, and mounted in a metal case. The principle and design are covered by a recent patent, in spite of the pump's eighteenth century ancestors. The principles of flexing an elastic material to change the enclosed volume continues to appeal to inventors. About 1926 a manufacturer in France offered a pump in small sizes which had a single metallic disk, 10–11 cm. in diameter, supported at the outer edge between two flanges. On one side of this disk the casing included an inlet pipe with a valve and a discharge pipe with a valve. The center of the disk was pushed in and then pulled out, moving about $^{1}/_{8}$ to $^{5}/_{32}$ inch at the rate of 2000 to 3000 times per minute. The disk was said to last a surprisingly

(*Continued on page 72*)





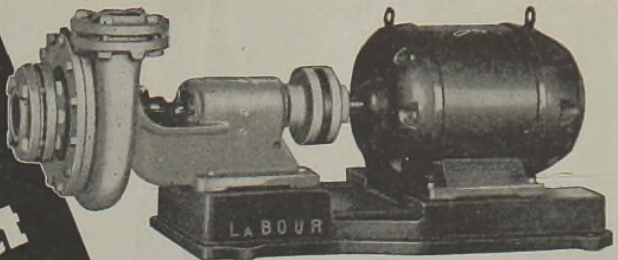
Equipment and Design

long time before failure, and the cost of a new disk was very small. It is easy to visualize that the flow of liquid from this pump would be practically as steady and uniform as from a centrifugal pump. The designer of this pump apparently was willing to substitute for a packed rotating shaft and vane impeller, a highly stressed steel disk and two valves operating 2000 to 3000 times each minute. This decision is not easy to understand. We believe the prompt failure of the tortured metal in the disk and valve seats sealed the fate of this pump. The way was paved, however, for saving the principle and improving the application to a satisfactory degree. A material better than steel is now used for the disk, and the high speed decreased to a larger, slower movement. One design for perfecting these points is shown in a page advertisement of Wilson Chemical Feeders, Inc. [*Chem. Eng. News*, 22, 2163 (1944)]. This is a flexing diaphragm pump of relatively slow movement, but this fact is placed in the credit column by the manufacturer in naming his device "Pulsafeeder". The liquid is moved positively without slippage in measured flow. Capacities of 10 gallons per minute are available.

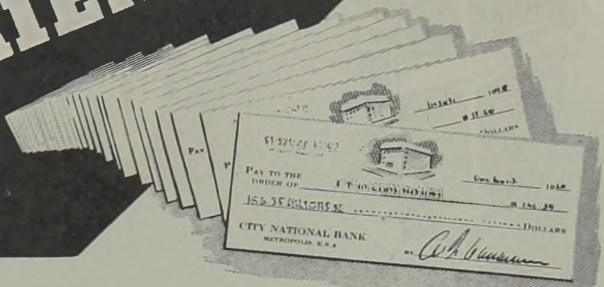
The above sketchy design philosophy deals with somewhat fancy types of pumps. There are heavier, standard machines which also have had some "face-lifting" improvements. A recent development of the John H. McGowan Company Division of Leyman Manufacturing Corporation deserves mention. A heavy-duty power pump is shown in Figure 2; the design of this pump, over and above the essential features needed to move liquids against a pressure, is the separation of the parts so that a large number of pumps may be operated constantly by keeping a few essential parts in the storeroom. The power frame is a heavily ribbed, special iron casting; the liquid end is of fine grained, controlled cast iron, or it may be changed to any one of several other metals. Gears are continuous tooth herringbone, engaging a pinion forged integral with the shaft which extends through the casting on both sides for connection to the driver. Both pinion and crankshaft have Timken roller bearings. The crankshaft, bearings, and gear are supported in a large separate housing by simple insertion. The liquid piston rod can be removed from the crosshead by removing a cover and stuffing box in the power frame. The liquid end was given critical study before a duplex side-pot type with a suction on either side was selected. The ample valve areas are covered with pot caps, sealed with metal-covered gaskets, the same construction used in cylinder heads. The removable liners may be made from several desirable materials. It is well to note (Figure 2) how shipshape the motor can be mounted on the power end.

The engineering and designing staffs of the larger equipment companies can make just as good machines for peacetime activities as they are making now. A new development of the Worthington Pump and Machinery Corporation is its Type VST, variable-stroke Triplex power pump. This heavy-duty pump has two important characteristics: Operation is at constant speed, but the liquid delivered may be controlled from zero to full capacity in a uniform, stepless increase. Mechanically the pump is well arranged; the driving parts and volume control gear are enclosed in a tight, splash- and pressure-lubricated case. The pump cylinders are attached to the crankcase in a reversed position, with the rod packing fully accessible at the rear. The plungers work on the end opposite the packing while moving in toward the crankcase. A guard over the packing glands protects the adjustment and collects leakage from the packing, which is delivered through the heater to a pipe overflow. There is no connection between the pump and the crankcase; this feature recommends the pump for service with caustic soda solutions, ammonia, and other chemicals. The most important improvement is that this pump ma be automatically controlled by a pressure regulator, a liquid leve indicator, or a gas analyzer. The stroke-changing mechanism actuated by oil under pressure, which is operated by a spring loaded regulator with pilot air or by hand regulation when desi able. This pump is admirably suited to feed liquids in absorption processes, where the volume of liquid required is proportiona to the gas being absorbed. In this service one may obtai pumps for pressures up to 5900 pounds per square inch with volume of 5.72 gallons per minute, requiring a 25-horsepower m tor. In the complete line twenty-five capacities are availabl the largest pumping 150 g.p.m. against 570 pounds pressur These pumps are ideal for feeding boiler water since the amount water delivered to the boiler may be automatically regulated either by the level of the water, by the amount of steam used, by a combination of both.

These Pumps Help YOU Collect DIVIDENDS ON EXPERIENCE



LaBour Type Q:—Compact and highly efficient, this pump, although non-priming, has a remarkably large air capacity.



Whenever you encounter a pumping problem that may be new to you, remember that LaBour's broad experience probably has solved that very problem somewhere else.

LaBour centrifugal pumps—both self-priming and non-priming—are of the open impeller type. Their high initial efficiencies are developed without the use of close-fitting parts. Consequently, they retain those efficiencies for surprisingly long periods. That's just one of the many reasons why LaBour pumps have drawn industry's toughest assignments ever since 1923.

It will pay you to get the complete story on LaBour pumps suited to your particular applications. Write us about your needs today. We'll furnish details to show how LaBour chemical pumps can pay you dividends in the form of lower costs and improved operations.

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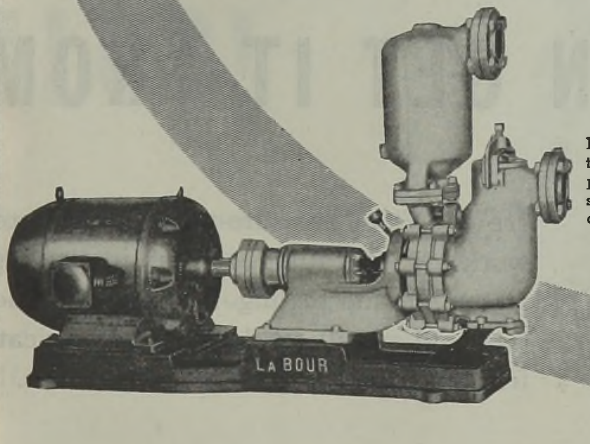

LaBour Type DPL:—One of the genuinely self-priming pumps that have made possible better, safer handling of dangerous liquids.

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CENTRIFUGAL PUMPS

YOU CAN GET IT FROM

ALCO has ample shop space and equipment... specially designed for plate-work, welded, annealed, X-rayed.

ALCO has an ample force of engineers, metallurgists and shopmen... men who are expert in pressure-vessel and plate-work layout, rolling, assembly, welding, annealing and testing. Men who can design and specify, if desired; or fabricate from your drawings and specifications.

Work Quickly?

ALCO!

When you order pressure vessels or other plate-work from ALCO and you want it *rush,* you will get it rush. And what is more, you will get it RIGHT . . . every time, from ALCO!

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Instrument Air *must be* CLEAN AIR!

Remember! Only a Nash Compressor can supply Clean Air!

Because Nash Compressors have no internal lubrication and because delivered air is thoroughly washed within the pump, the Nash delivers only clean air, free from dust, heat, or oil. Therefore, instrument air supplied by a Nash assures immediate instrument response and eliminates all troubles resulting from fouled instrument lines, gummed orifices, and rotting instrument diaphragms. Also avoided are trouble and expense of the usual oil filters, dust filters, and after coolers, as none are used. Nash means dependable, low cost instrument operation.

Nash Compressors produce 75 lbs. pressure in a single stage, capacities to 6 million cubic feet a day in a single structure. No valves, gears, pistons, sliding vanes, or other enemies of long life complicate a Nash. Original capacity is maintained throughout a long life. Investigate the Nash Compressor now.

No internal lubrication to contaminate air handled.

No internal wearing parts.

No valves, pistons, or vanes.

75 lbs. pressure or 26 in. mercury vacuum in one stage.

Non-pulsating pressure.

Original performance constant over a long pump life.

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Current Developments in INSTRUMENTATION

Hydraulic power unit, electrostatic voltmeter, tramp metal detector, and mercury vapor detector are considered.

Discussed by Ralph H. Munch

Instruments for automatic control commonly employ electrical, pneumatic, or hydraulic means to transmit and apply power. Air-operated instruments combining the indicating, recording, and controlling functions are widely used where the force to be applied is not too great. They are simple and trustworthy. Hydraulic controllers have found their most extensive use where heavy loads have to be handled at high speeds without loss of sensitivity or accuracy, or where the inertia of the hydraulic system is desirable. The Askania Regulator Company, Chicago, Ill., has designed a hydraulic power unit which can be used with a standard air-operated recorder-controller in place of the usual diaphragm-type motor. This system is said to retain the advantages of both the pneumatic and hydraulic classes of instruments while eliminating their disadvantages, and to extend greatly the range of air-operated instruments. The hydraulic power unit enables a pneumatic controller to handle erratic or shock loads because it applies power instantly and has the self-locking action inherent in a hydraulic system. It can handle heavy loads. Since the cylinder is double acting, it can position a load having high inertia smoothly, without overshooting. The unit permits greater stroke than air-operated diaphragm motors.

The operation of the power unit can be understood from Figure 1. Air pressure from a controller is applied to bellows (*A*) which, acting through jet pipe relay (*B*), sets the piston in motion. The follow-up cam operated by the piston controls the action of the jet pipe relay so that the position of the piston is a function of the air pressure applied to the bellows.

Figure 2 shows the unit and its dimensions. Power is transmitted from the piston to the mechanism to be operated by means of a crank arrangement which makes it possible to enclose the piston rod entirely and to take advantage of the toggle action of the crank when it is nearly parallel to the connecting rod. Maximum recommended torque for the unit is 2000 inch pounds, and maximum permissible pull on the connecting rod is 1550 pounds.

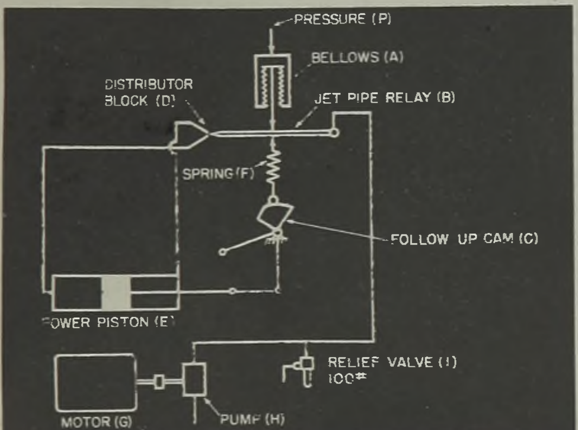


Figure 1. Operation of Hydraulic Power Unit

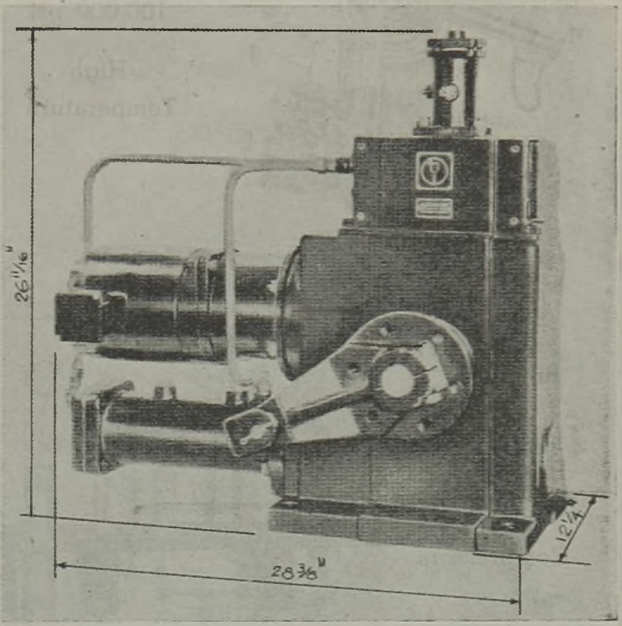
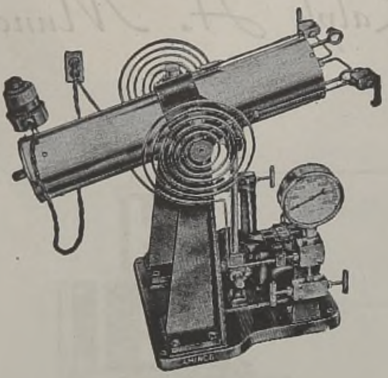


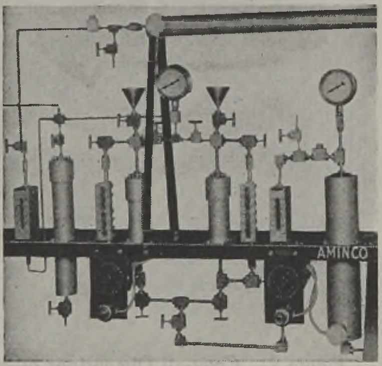
Figure 2. Over-all Dimensions of Hydraulic Power Unit

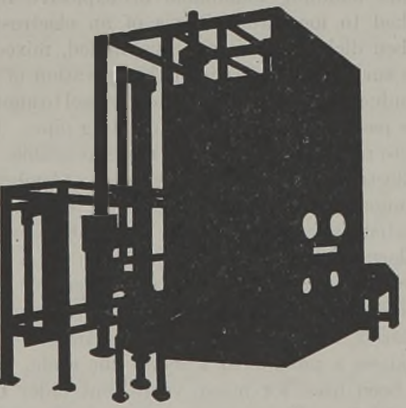
Electrostatic Voltmeters. Instrument engineers and physicists who work in plants handling flammable or explosive materials are often asked to measure voltages of an electrostatic nature built up when dielectric materials are milled, mixed, or sifted. Sometimes such voltages occur in the operation of sublimers, when nonconducting liquids flow from one vessel to another, or even when a gas passes through a nonconducting pipe. Usually no instrument to make such measurements is available.

The Rawson Electrical Instrument Company, Cambridge, Mass., recently announced an improved line of electrostatic voltmeters, designated as type 518, which is suitable for such measurements. Electrostatic voltmeters consist of a fixed element and a movable element to which the potentials to be measured are applied. Since the charges on these two elements are of opposite polarity, the moving element is attracted to the stator and thus causes a pointer to traverse the scale. Such instruments have been used for many years, but older types were lacking in sensitivity. Electrostatic meters can be used for either direct or alternating current voltages. One of their valuable features is the very small amount of power which they draw from the circuit being measured. This feature makes them suitable for measuring static potentials on plant equipment.

The Rawson type 518 meters are supplied in portable cases with hinged cover and Bakelite panel. They are provided with an internal shield to protect the meter element from stray fields. This also serves to protect the user from high voltages in case of overloads. The moving system, which is rugged but light in weight, is air-damped. Both pivots (*Continued on page 78*)



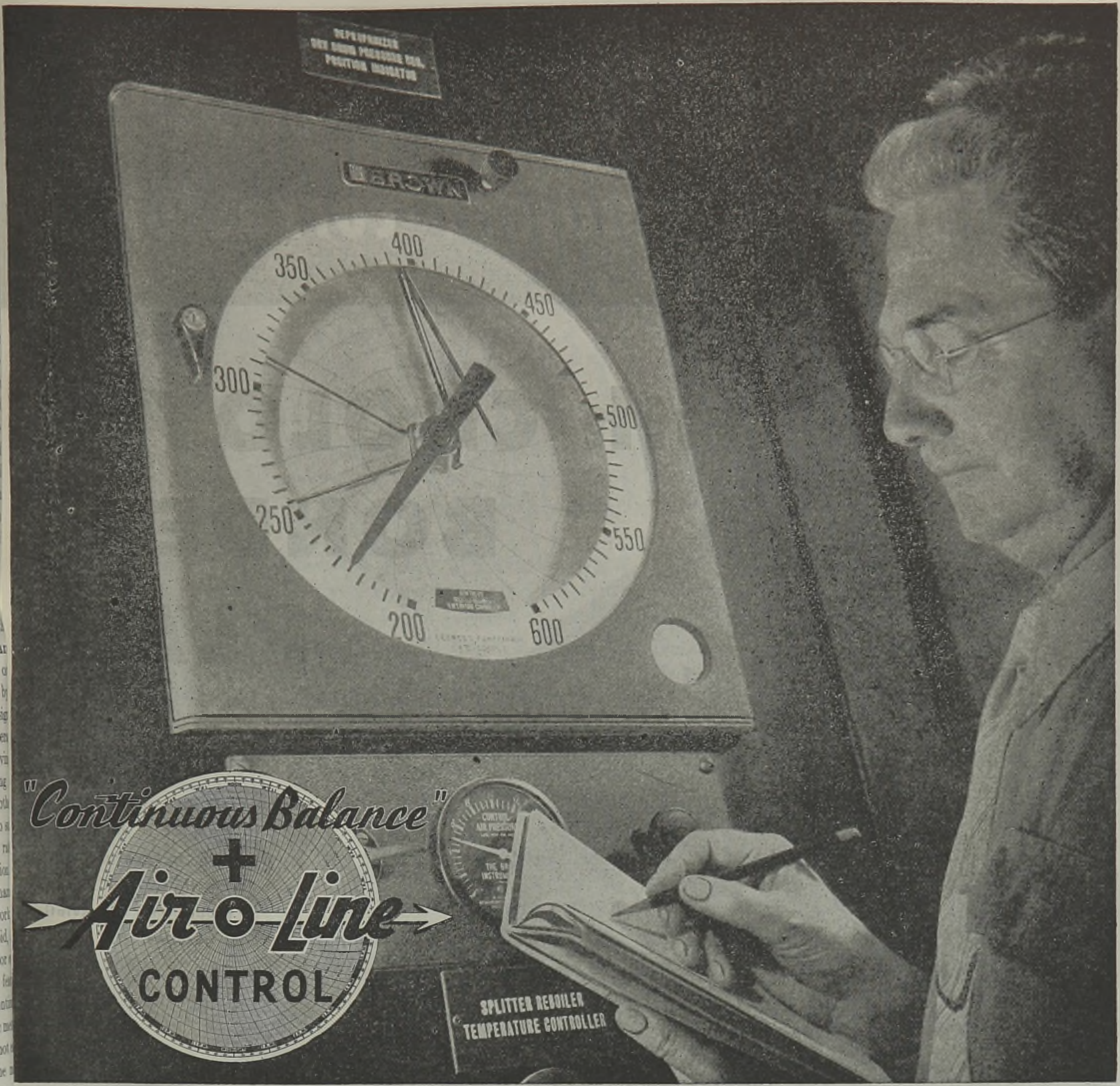




point down and rest in highly polished sapphire jewels. This construction makes possible a mechanical clamp to protect the system from damage when the meter is not being used. These meters can be supplied with ranges of 1, 2, 3, 5, and 10 kilovolts full scale. All are guaranteed to have insulation resistance higher than 10^{12} ohms under normal conditions. The 5.5-inch mirror scale and knife-edge pointer are calibrated with an accuracy of 1.0% or better.

Metal Detectors. In many cases pieces of tramp metal accidentally introduced along with material being processed can damage equipment and cause serious expense and delay or injury to personnel. The type YE-6 metal detector was developed by the Electronics Department of General Electric Company, Schenectady, N. Y., to indicate the presence of dangerous metal in nonmetallic material. This electronic device has proved its ability to spot hidden metallic materials and warn of their presence. The equipment consists of a hollow coil assembly through which material to be processed passes and an a.c.-operated amplifier arranged to operate an alarm or a relay to stop the processing equipment automatically. The coil assembly has four coaxial windings grouped in pairs on a hollow cylindrical mount to form two adjacent air core transformers. The coils are balanced and connected to give zero input to the amplifier. Passage of metal through the coil mount destroys the balance between the two transformers and thus provides an input voltage to the amplifier which then operates alarms or relays. Reliable operation is obtained at high sensitivity by careful design of both coil assembly and amplifier. The design used was chosen to minimize the effect of variations in temperature, vibration, line voltage, frequency, wave form, and moving metal equipment. The equipment can detect iron having a minimum dimension 0.01 times the coil inside diameter, or other metals three times that size. Coil assemblies are made to suit the application. Material can move through the coil at rates from 20 to 600 feet per minute, depending on the application.

Mercury Vapor Detectors. Mercury poisoning is a hazard encountered by chemists and physicists in laboratory work as well as by various industrial workers. Because no rapid, accurate means has been available to measure mercury vapor concentrations, many workers have been unnecessarily fearful about handling mercury. Since the toxic limit for continual breathing is considered to be 1 mg. of mercury in 10 cubic meters of air (1.3 parts of mercury vapor in 10^8 parts of air), it is not easy to make measurements by chemical means. One of the most widely used methods has been the selenium sulfide mercury vapor detector distributed by the Special Products Section of General Electric Company. This device, while simple to use, is slow and has limited sensitivity and accuracy. For these reasons its makers have introduced a photoelectric photometer which measures mercury vapor concentration by measuring the absorption of light of wave length 2537 Å. The General Electric instantaneous mercury vapor detector is a portable instrument containing a 12-inch absorption cell with a low-pressure mercury vapor lamp at one end and an ultraviolet sensitive photoelectric cell at the other end. By means of a bridge type amplifier, a decrease in light intensity reaching the photoelectric cell is translated into an increased reading on the indicating meter of the detector. Thus, when air contaminated with mercury is drawn through the absorption cell by the built-in blower, the meter reading increases. The sample can be drawn from any desired point by using the 5-foot rubber inlet tube as a sampling probe. This detector will measure directly from 0.03 to 3.0 mg. of mercury per cubic meter with an accuracy of approximately 5%. It has made possible much more accurate study of factors affecting the likelihood of mercury poisoning than could be made before.


BROWN
350
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250
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"Continuous Balance"
+
Air-o-Line
CONTROL
SPLITTER REBOILER
TEMPERATURE CONTROLLER

Typical of the many alloy-clad pressure vessels fabricated by Babcock & Wilcox is a huge Reactor Tower—85 ft. high, 27 ft. diameter and weighing 360,000 lb.—recently completed for a refinery producing aviation gasoline. For long life and high resistance to corrosion at 30 lb. per square inch and 1000° F., it was fabricated from B&W Croloy-Bonded Plate.

Developed and used exclusively by B&W, this plate consists of a base metal clad with a corrosion-resisting chromium alloy over *the complete surface without unbonded areas.*

The alloy is electrically resistance-welded to the base metal with a complete thermal and mechanical bond by means of an original B&W process.

In the case of this reactor tower, base metal was carbon molybdenum steel, to which a B&W Croloy #13 Bond 7/64" thick was applied, plus a nickel insert layer.

The Croloy #13 stainless alloy used on this job is gaining wide acceptance in oil cracking, hydrogenation, reforming, polymerization, alkylation and gas cracking or wherever high strength and corrosion resistance are factors. This is one of several B&W Croloy alloys used for types of process work in the chemical industry where their properties are indispensable.

We believe that the experience and skill, which we have demonstrated by many "firsts" in development and design of pressure vessels for the process industry, may be helpful to you.

If you have a similar problem now, drop us a line and we will gladly offer advice and provide data.

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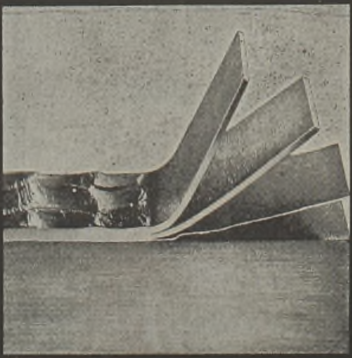
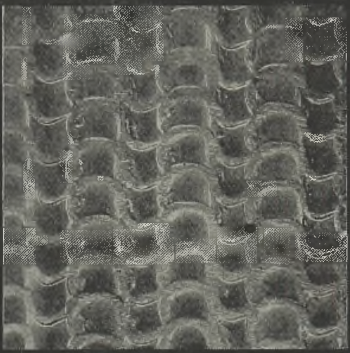


LAYER CONSTRUCTION

Layer construction makes possible the bonding process by increasing the resistance to the flow of welding current, and by reducing the required pressure on the sheets to complete the bond.

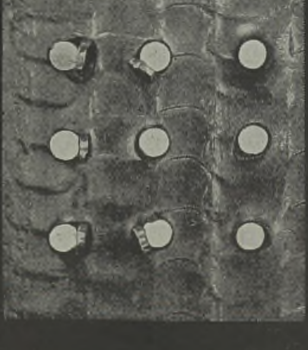


COMPLETE BOND OVER ENTIRE SURFACE

High thermal-conduction efficiency, with the complete over-all bond, minimizes temperature differentials between alloy and base metal that might cause bulging of the lining and its consequent failure. The complete bond also has high resistance to failure that might otherwise result from repeated heating and cooling — and eliminates the possibility of liquid flow between base metal and alloy.

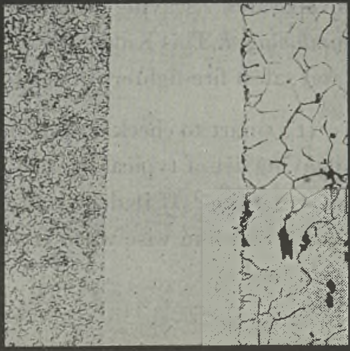
PUNCH TEST SHOWS STRENGTH OF BOND

loles were drilled with a lat-bottom drill through he base metal of a onded plate to, but not eyond, the junction line etween the alloy layers nd the steel plate. The onded alloy was punched vith a square-nose punch lightly smaller than the oles in the plate. With nly ½-inch and ¾-inch igaments between holes, he alloy did not pull way from the plate, but roke clean around the oles.



NICKEL SHEET STOPS CARBON MIGRATION

The importance of the nickel sheet between the base metal and the Croloy lining is illustrated by this micrograph. Note the absence of carbon migration from the base metal to the alloy, due to the lack of affinity of nickel for carbon. Thus, interface precipitation of carbon is prevented when the materials are subjected to high temperatures during bonding.



KILL TOUGH FIRES BEFORE THEY GROW—WITH KIDDE EQUIPMENT

When tough fires spring up—the fast-moving ones that break out in flammable liquids (Class B); the hard-to-get-at kind that start in electrical equipment (Class C)—the Kidde portable or hose reel system acts fast to knock them down—and *out*!

Ordinary water-type extinguishers can't control these tough fires. But the Kidde portable shoots out a cloud of carbon dioxide gas, forming a heavy blanket that smothers the flames. Then the dry, inert, non-toxic gas merely evaporates...leaving valuable liquids *uncontaminated*, electrical equipment *undamaged*. This Kidde method is recognized as one of the speediest, cleanest and safest fire-fighters in use today.

It's smart to check on tough fire areas in your own plant. Does the accompanying list of typical hazards suggest places that still need safeguarding? If it does, call in a Kidde representative—you'll find him wise when it comes to fire protection. Drop us a line.

Kidde Kills Tough Fires

- PROCESS ROOMS
- MIXING TANKS
- AGITATORS
- PUMP ROOMS
- STORAGE AREAS
- DRUM-FILLING ROOMS
- MOTORS
- TRANSFORMERS
- ELECTRICAL CONTROL PANELS

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Current Developments in
PLANT MANAGEMENT

Production executives should insist that cost proposals be submitted in a form readily understandable by personnel not trained in cost accounting.

Discussed by Walter von Pechmann

THE advantages of the process type of cost system in the chemical industry are generally recognized. This method of costing not only gives a process cost per pound, gallon, etc., but also makes it possible to analyze the cost of major operations. It would therefore be assumed that production executives favor the installation of such a system. This is not always the fact. Their reluctance to accept process costing, however, should not be taken as unwillingness to approve a method which has been specially designed to measure the efficiency of operations. Investigation usually will reveal that the person responsible for the installation has not taken sufficient pains to explain the system properly. This may be due to the common assumption on the part of accountants that the lack of specialized training in cost work disqualifies the production executive from passing judgment upon the merit of a new cost system. Therefore, they would rather force production to accept a method than try to sell it to production. The fact that detailed cost descriptions which are submitted to production are often not favorably received is frequently cited as proof that production personnel should not be asked to give their opinion on matters pertaining to accounting. This point of view is subject to criticism. If method descriptions were written in an easily understood manner and did not contain information of no concern to production people, it is believed that they would participate enthusiastically in working out new cost systems. It is not unreasonable for production to insist that cost system proposals be presented in a clear manner which can be easily understood by nonaccountants.

The writer once worked out such a proposal, the principle of which follows: The problem was approached by attempting to show the process cost system in graph form and by furnishing production with a short description of the important phases which could not be covered on the graph. The description explained the basic difference between the present system and the proposed process cost system. The advantages gained by production in accepting this method of costing were outlined, as well as the additional statistical material which could be obtained. Necessary eliminations or additions of production recordings were cited. Furthermore, the method description, intended for accounting purposes, was condensed drastically before being submitted to production. As an example the accounting procedure may have read as follows: "Actual quantities of materials A and B will be distributed to the various products passing through this center on the basis of standard quantities established by production formulas. The cost of raw materials

(*Continued on page 84*)

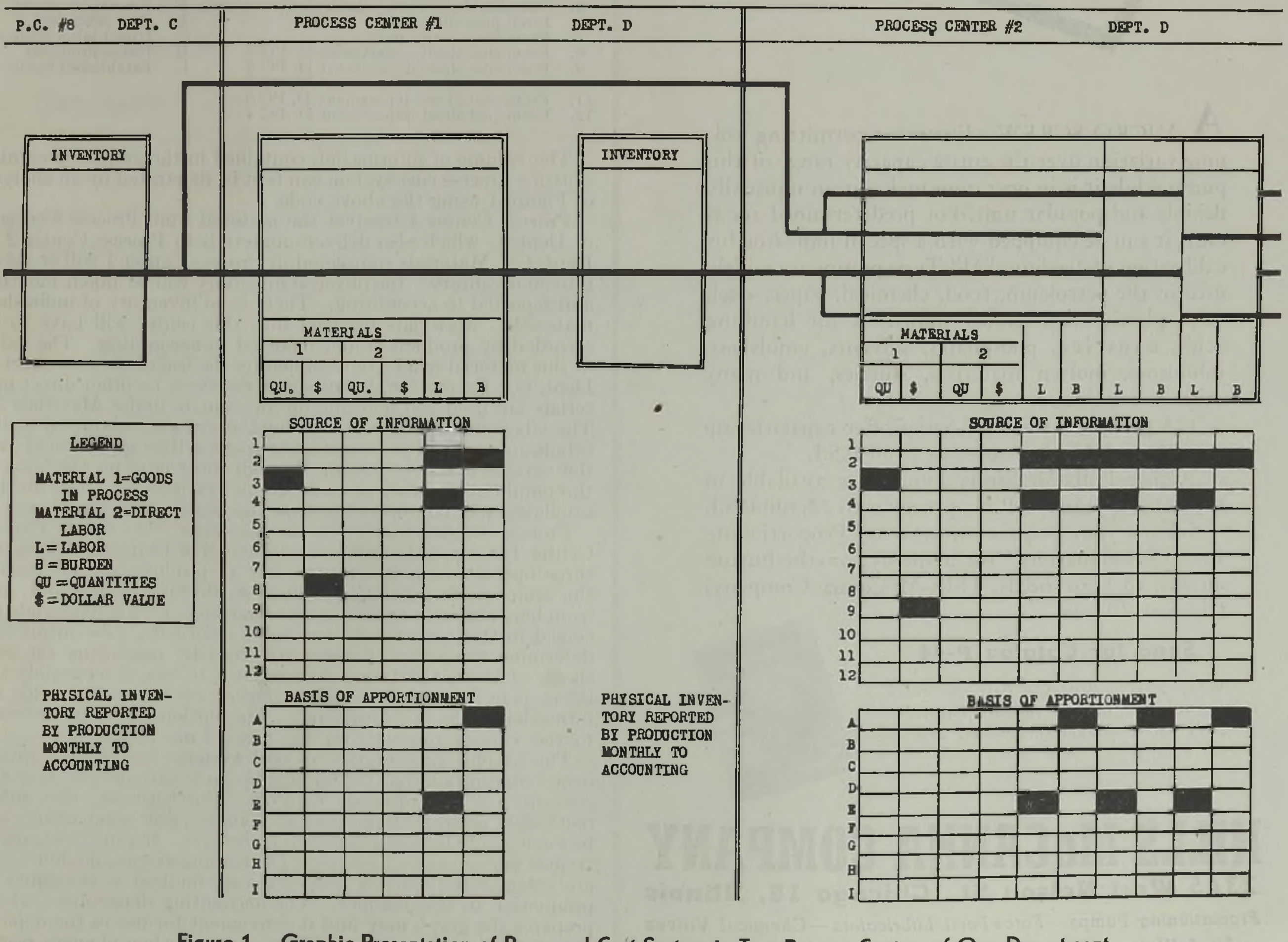
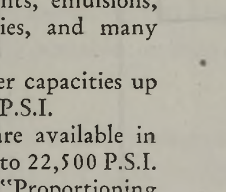


Figure 1. Graphic Presentation of Proposed Cost System in Two Process Centers of One Department



Plant Management

used will be secured through the raw material consumption report and will be distributed to the products on the basis of the materials used, as apportioned by the formula." This paragraph was changed to read: "Formulas will be used to apportion the consumption of materials A and B to the products." Approval of this statement assures the accountant that production is in agreement with cost distribution on a formula basis and that actual consumption recordings are not necessary.

To develop the graph properly, it was necessary to anticipate the questions production executives would ask. The following questions are illustrative of the queries in a production executive's mind when a new cost system is proposed:

1. How many process centers have been selected and how many operations, within each center, will be recognized for costing purposes?
2. At what points will inventories be evaluated and how should the inventory be taken?
3. What is the accountant's conception of the flow of materials through the various process centers?
4. How does the accounting department intend to arrive at the quantities used?
5. How will direct and indirect labor and direct materials be accumulated and how will the cost be distributed to the products?

Figure 1 is intended to give the answer to these questions. This graph can be elaborated upon, either by the insertion of additional factors such as waste, etc., into the square of each process center, or by the replacement of the shaded areas by symbols. An example of a code which might be used to shade the squares below each center follows:

SOURCE OF INFORMATION

1. From apportionment unit
2. From tabulation
3. From production recordings
4. Accumulated by timekeepers
5. Calculated (inventory difference)
6. From payroll
7. From fixed assets unit
8. From cost sheet department C, PC 1
9. From cost sheet department D, PC 1
10. From cost sheet department D, PC 2
11. From cost sheet department D, PC 3
12. From cost sheet department D, PC 4

BASIS OF APPORTIONMENT

A. Machine hours
B. Total labor dollars
C. Incentive rates
D. Number of employees
E. Pounds produced
F. Feet produced
G. Direct labor dollars
H. Pieces produced
I. Established factor

The volume of information contained in the graphic presentation of a process cost system can best be illustrated by an analysis of Figure 1 using the above code.

Process Center 1 receives the material from Process Center 8 of Dept. C which also delivers materials to Process Center 2 of Dept. C. Materials completed in Process Center 1 will be taken into an inventory; the physical inventory will be taken monthly and reported to accounting. There is no inventory of unfinished materials. Materials received into this center will have to be recorded by production and reported to accounting. The value of this material will be determined by the use of the cost sheet of Dept. C. Except for the materials received, no other direct materials are used (no marking on any square under Materials 2). The labor will be recorded by timekeepers and submitted to the tabulation unit. The cost of labor spent will be apportioned over the various products passing through this center on the basis of the number of pounds of each product turned out. The burden tabulated will be apportioned on the basis of machine hours.

Process Center 2 receives the materials from either Process Center 1 of Dept. D or Process Center 8 of Dept. C. There are three operations in this center, but all products do not receive the same treatment. All products go through operation 1, and from here either to operation 2 or operation 3. The materials received in this center will have to be recorded. Accounting will determine the value of these materials by consulting the cost sheets of Dept. C. It will be necessary to record separately the labor spent for each operation; timekeepers will submit this information to the tabulation unit. The burden will be apportioned to the various products on the basis of machine hours.

The graphic presentation of cost systems has the advantage over a description that the highlights can be obtained without the necessity of considerable reading. Furthermore, the entire method of costing can be seen at a glance, and comparisons can be made easily between two or more centers. Because technically trained personnel are accustomed to reading graphs, no difficulties are encountered when a proposed cost method is presented to production in this manner. The accounting department which prepares the graph may find it convenient for use in the department and for discussions with production when changes occur.

The Case of the Oyster Shells

the Dolomite

and the Coke

It is bad enough to have one difficult materials handling problem. But when you have three, then it really becomes serious. That is the fix in which a certain chemical company found itself.

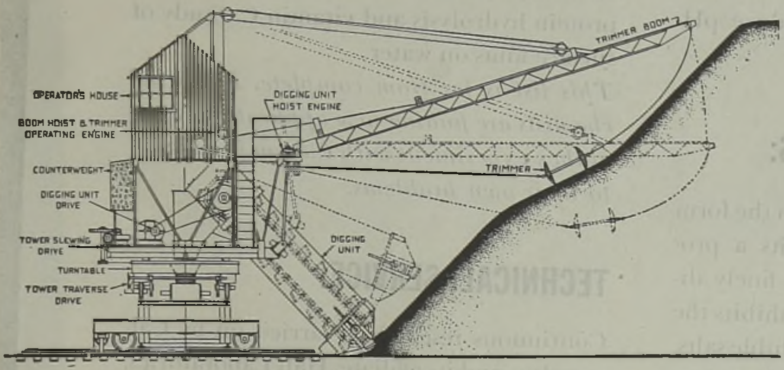
There were oyster shells and dolomite and coke—all to be unloaded, stocked in storage piles and reclaimed for use. The oyster shells tended to arch and pack; the dolomite was crystalline in form; the coke was frangible and friable. Each presented its own peculiar difficulties in handling, yet all would have to be handled on the same unified system.

The problem was put up to Robins. Some parts of it were easy—the unloading, storing and conveying; the answers were drawn from our long and varied experience. But the reclaiming was something else again. Because the oyster shells tended to arch and pack, because the coke was so easily broken, traditional reclaiming methods were not adequate; the shells would not flow and the coke would break.

Nothing in existence up to then was able to do the job properly. So Robins engineers had to invent something. We call it a "Digging Reclaimer." It under-mines the material—working along the bottom of the pile instead of the top. It reduces degradation and breakage to an absolute minimum. It reduces the cost per ton of material reclaimed to a figure never before reached.

Thus another difficult problem was solved. Thus another innovation was added to an already imposing list of Robins "firsts." Thus another company was able to obtain celerity, efficiency and economy in the handling of its materials.

Solving difficult bulk-materials handling problems has been a Robins habit since 1896. Perhaps you face one now. If so, you are invited to submit the facts to Robins for unbiased, non-obligating analysis. When writing, please address Dept. IEC-4.



Cross-section view of Robins Digging Reclaimer

ENGINEERS, MANUFACTURERS AND ERECTORS OF MATERIALS HANDLING MACHINERY

ROBINS ***makes:*** BELT CONVEYORS · COAL AND ORE BRIDGES · BUCKET ELEVATORS · CAR AND BARGE HAULS · CAR DUMPERS · CAR RETARDERS · CASTINGS · CHUTES · CONVEYOR IDLERS AND PULLEYS · CRUSHERS · FEEDERS · FOUNDRY SHAKEOUTS · GATES · GEARS · GRAB BUCKETS · PIVOTED BUCKET CONVEYORS · VIBRATING SCREENS · SCREEN CLOTH · SELF-UNLOADING BOAT MECHANISMS · SKIP HOISTS · STORAGE AND RECLAIMING MACHINES AND SYSTEMS · TAKEUPS · LOADING AND UNLOADING TOWERS · TRIPPERS · WEIGH LARRIES · WINCHES · WINDLASSES

ROBINS
CONVEYORS
INCORPORATED
Founded in 1896 as Robins Conveying Belt Co.
PASSAIC • NEW JERSEY

FOR MATERIAL AID IN MATERIALS HANDLING . . . . It's ROBINS

Data for the chemist on calgon

CALGON:

Registered trade mark for the *Glassy Sodium Phosphate* products of Calgon, Inc., Pittsburgh, Pa. Produced by a thermal process from soda ash and food-grade phosphoric acid. Available as Glass (adjusted or unadjusted); powdered (unadjusted); flakes (adjusted or unadjusted); agglomerated flakes (adjusted).

CHARACTERISTICS:

Composition: Unadjusted Calgon glass contains not less than 67 per cent of P_2O_5. In the adjusted form a small amount of alkali is admixed to control the pH value of the solution. Impurities total less than 0.2 per cent: moisture less than 0.6 per cent.

Solubility: Miscible with water in all proportions; solutions containing 50 per cent by weight may be readily prepared. Insoluble in other liquids.

pH Value: Substantially neutral. In 0.25 per cent solution, various forms produce pH values ranging from 6.0 to 8.3.

FUNDAMENTAL PROPERTIES:

1. Sequesters many metallic ions in the form of soluble complexes. **2.** Exhibits a pronounced dispersive action upon finely divided metal oxides and salts. **3.** Inhibits the crystallization of many slightly soluble salts, stabilizing a condition of supersaturation. **4.** Is distinguished from orthophosphates and pyrophosphates by its ability to coagulate albumen. **5.** Essentially neutral when first dissolved; reverts slowly to orthophosphate with a decrease in pH value.

TYPICAL APPLICATIONS:

From sequestration property: Cheese processing; Leather processing (dyeing, fat liquoring); Paper processing (felt washing, pulp washing); Textile processing (boiling, scouring, dyeing, rinsing); Water softening.

From dispersion property: Beneficiation of clay; Casein dispersion; Flotation of minerals; Paper processing (sizing and coating); Pigment dispersion.

From stabilization property: Industrial and municipal water treatment (corrosion control, preventing precipitation of dissolved iron, preventing scale formation).

From coagulation property: Leather processing (tanning).

Special applications: Drying and dehydrating agent; food preservation; reagent for phosphate test in milk, for determination of lead, mold in cream and butter, for protein hydrolysis and vitamin C; Study of surface films on water.

This list is far from complete. Industrial chemists are finding new applications daily as they experiment with Calgon in relation to their own problems.

TECHNICAL SERVICE:

Continuous research is carried on by Calgon, Inc. and its affiliate, Hall Laboratories, Inc. Their technical facilities are at the service of industrial chemists. Data concerning specific problems furnished on request.

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Cyclohexylamine has applications in the fields of corrosion inhibitors, paint film solvents, emulsifying agents, petroleum, dyestuffs and chemical manufacture. It has possible uses in the manufacture of plasticizers, as a curing agent for soya bean molding powders, as a color stabilizing agent in vinyl resins, in dry-cleaning soaps, as a blending agent for alcohol-gasoline mixtures and in the manufacture of insecticides.

Dicyclohexylamine is used in extreme-pressure lubricants, in the manufacture of cutting oils and in the production of chemicals. Some derivatives have special application as insecticides.

For technical data, and samples of these low-priced alicyclic amines, contact the nearest Monsanto office or mail the coupon to MONSANTO CHEMICAL COMPANY, Organic Chemicals Division, 1700 South Second Street, St. Louis 4, Missouri. District Offices: New York, Chicago, Boston, Detroit, Charlotte, Birmingham, Los Angeles, San Francisco, Seattle, Montreal, Toronto.

(These suggested uses are for illustration and are not to be construed as recommending violation of any patent.)

CYCLOHEXYLAMINE

(Also known as hexahydroaniline)

Clear, practically colorless liquid.

Distilling Range	132.0 to 137.5°C
Sp. Gr. at 15.5/15.5°C	0.870 to 0.874
Flash Point (by "Tag" open cup)	90°F
Fire Point (by "Tag" open cup)	90°F

Cyclohexylamine is a primary amine, being more aliphatic than it is aromatic in nature.

DICYCLOHEXYLAMINE

Clear, practically colorless liquid.

Distilling Range	252.0 to 258.0°C
Sp. Gr. at 15.5/15.5°C	0.916 to 0.920
Flash Point (by "Tag" open cup)	Above 200°F
Fire Point (by "Tag" open cup)	Above 200°F

Dicyclohexylamine, a strong base, is only slightly soluble in water. It is soluble in all common organic solvents.

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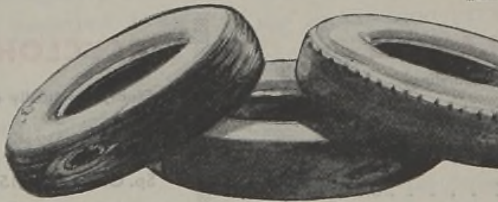

reclaim

DUAL PURPOSE SOFTENERS AND EXTENDERS
SPECIFICATIONS

	B.R.T. No. 3	B.R.T. No. 4	B.R.T. No. 7
Specific Gravity 25°C/25°C	1.15 to 1.20	1.15 to 1.20	1.20 to 1.25
Specific Viscosity, Engler			
50 ml at 40°C	13 to 18		
50 ml at 50°C		15 to 30	
50 ml at 100°C			6 to 9
Insoluble in Carbon Disulfide % by weight	4 to 10	4 to 10	15 to 20
Water % by volume (maximum)	3	3	0.1
Distillation			
to 170°C % by weight (maximum)	5	2	1
to 270°C % by weight (maximum)	25	20	13
to 300°C % by weight (maximum)	35	30	25
Softening Point Ring and Ball Distillation Residue at 300°C Degrees Centigrade	30 to 60	35 to 65	35 to 65

Through his selection of B.R.T. softeners, the rubber compounder is offered a choice of refined coal-tar plasticizers with different viscosities, distillation ranges and carbon disulfide insoluble contents. Serving both as softeners and extenders, the value of these products is indicated by their use throughout the rubber industry for mechanicals, footwear and reclaiming.

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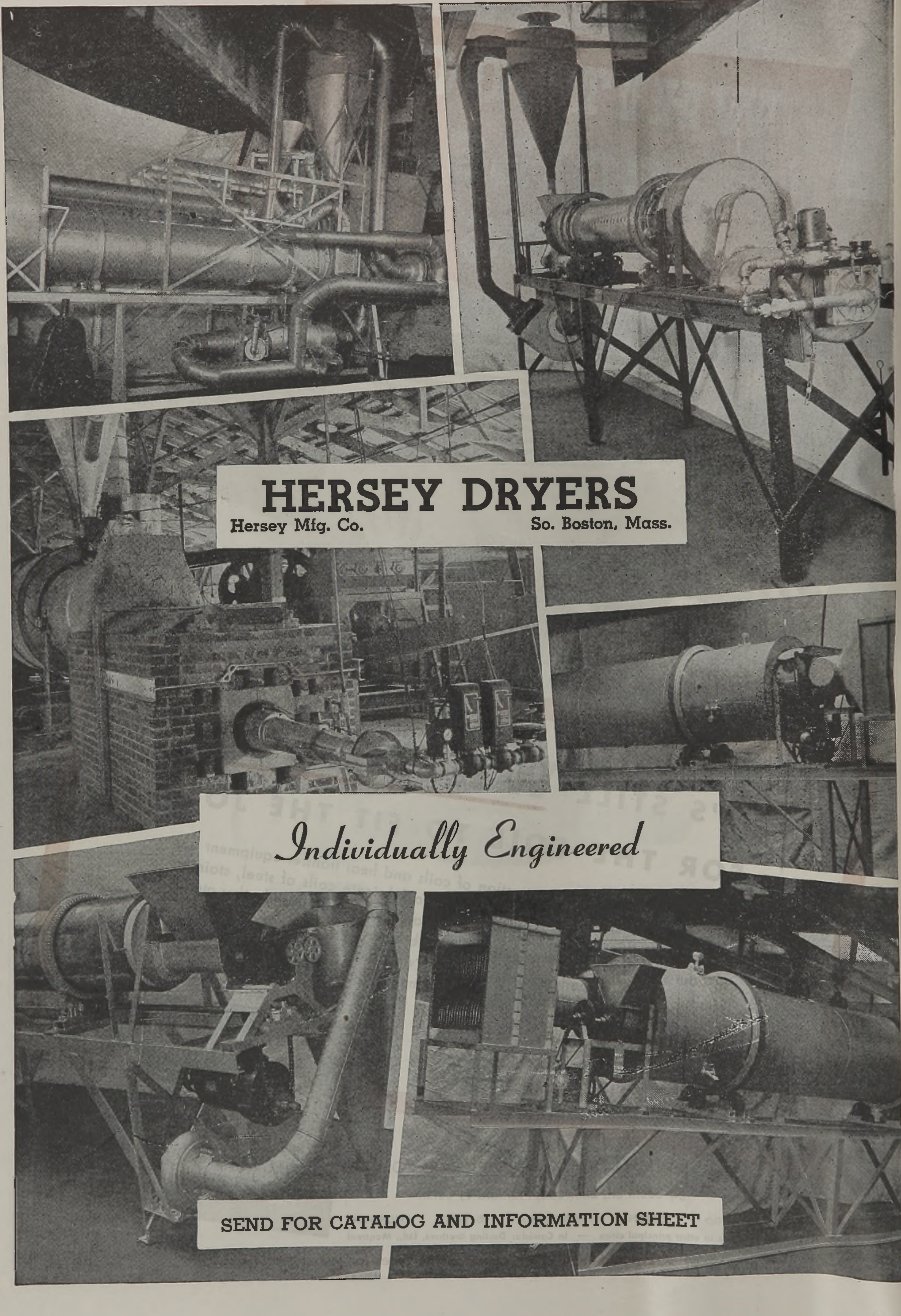
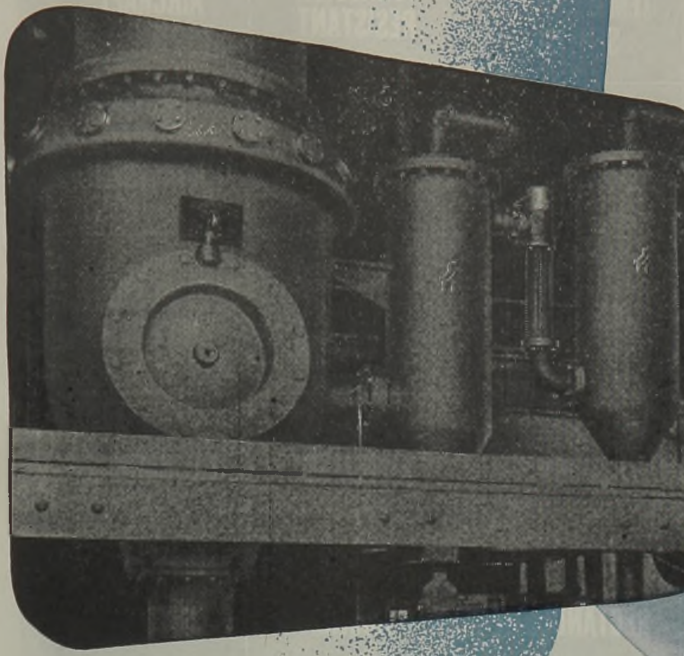
ONE OF AMERICA'S GREAT BASIC BUSINESSES



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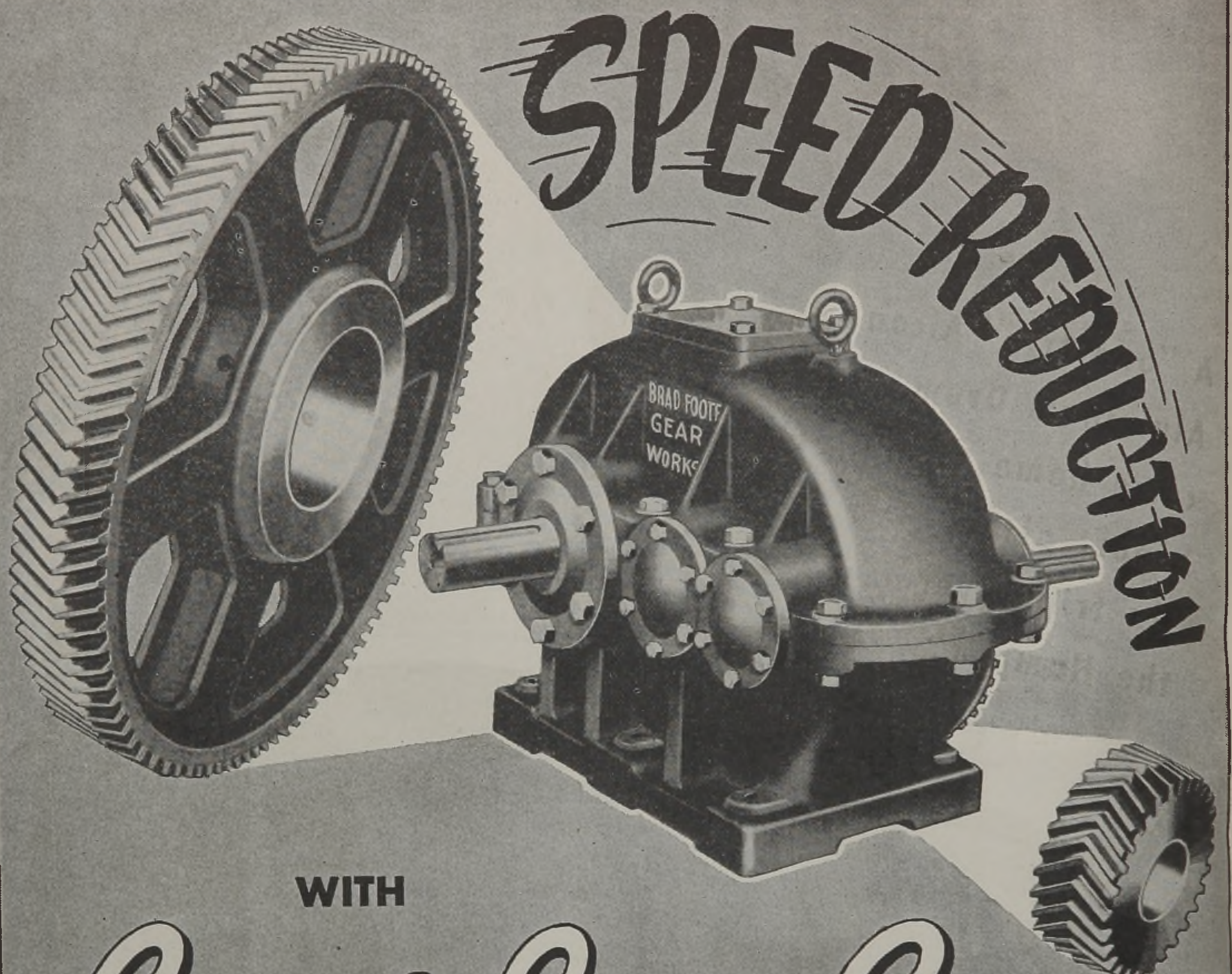
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. . . are bland, water-soluble, chemically stable compounds with applications similar to those of Diethylene Glycol. The Polyethylene Glycols of molecular weights up to 1,000 are liquids; the "Carbowax" Compounds, Polyethylene Glycols above 1,000 in molecular weight, are wax-like solids. Of special interest are the uses of these materials as water-soluble lubricants for rubber molds, textile fibers, and metal-forming operations.

Diethylene Glycol is a practically colorless, odorless liquid, that boils at 244° C. It is widely used as a hygroscopic agent to remove moisture from natural gas. Since it forms both mono- and di-esters, it may be used in the preparation of such compounds as diglycol phthalate and similar esters of the dicarboxylic acids. With the higher fatty acids it forms good emulsifying agents.

Further information on Diethylene Glycol is contained in the booklet "Glycols" (Form 4763). A copy will be sent on request.

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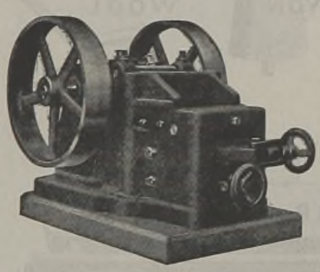
Sturdy Sturtevant Laboratory Machines have the rugged strength and all the features of full size machines combined with an even wider range of adjustment. Of superior design and construction, with all parts readily accessible for cleaning, these miniature machines are capable of continuously efficient performance 24 hours a day.

Besides those illustrated the Sturtevant line also includes Screens, Air Separators, Vibrating Test Sieves and Coal Crushers and Sampler. Write for full details.



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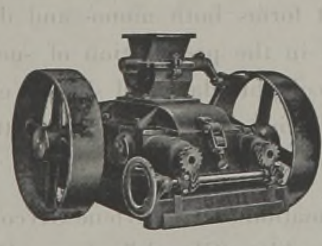
Special Roll Jaw action simplifies close regulation of the product with capacities varying from 300 or 400 lbs. per hour at finest settings, to 1000 or 2000 lbs. when opened for coarser work. Each part of the crusher is accessible for quick and easy cleaning.

These crushers weigh from 900 to 1000 lbs. and are fitted with Manganese Steel jaw plates, reversible shields, and steel pitman. The driving shaft is equipped with anti-friction bearings. The bronze toggles work in tool-steel seats, and all shafts, bearings, and working parts are of ample proportions.



LABORATORY CRUSHING ROLLS . . . .

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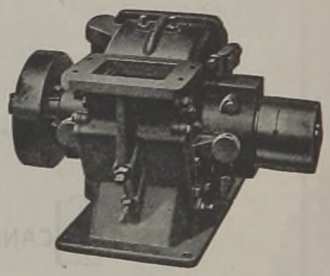
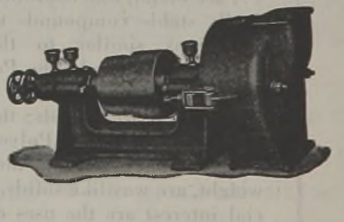


LABORATORY SWING-SLEDGE MILLS . . . .

Capable of reducing soft, moderately hard and tough orfibrous materials to any degree of fineness between 1 in. and 20 mesh — the Laboratory Swing Sledge Mill is strong, rugged and built on the same principles as full size Swing Sledge Mills.

The full feed opening of 5 x 6 in. may be utilized for soft substances. On harder materials the machine should be fed with pieces not larger than 2 to 3 in. The patented "Open Door" feature permits ready accessibility for cleaning.



LABORATORY SAMPLE GRINDER . . . .

Laboratory Sample Grinders are of the "Open-Door" disc type and are capable of very fine work, producing products as fine as 100 mesh (coarser if desired) when working on dry, friable, soft or moderately hard materials. On many hard rocks and ores, they will operate with somewhat reduced capacities.

Feed may be ¼" and finer material. Every part is accessible for quick and easy cleaning and by the simple turning of a hand wheel the product may be regulated from 10 to 100 mesh.

STURTEVANT MILL COMPANY, 2 HARRISON SQUARE, BOSTON 22, MASSACHUSETTS

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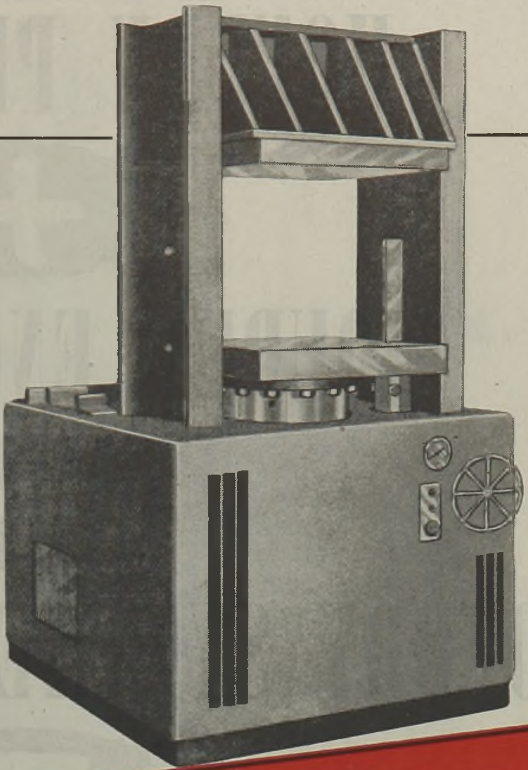

THE FIN•FAN HEAT EXCHANGER actually solves two problems: 1. It provides an efficient cooling unit where water is scarce or expensive and where minimum temperature required is approximately dry bulb temperature. 2. Where gases, liquids or vapors at high temperatures and pressures must be cooled or condensed.

The many exclusive features of the Fin•Fan Heat Exchanger make it ideal as a steam condenser, jacket-water cooler or hot oil cooler for all services under pressures to 5000 P.S.I. and temperatures to 1500° F.

The Fin•Fan Heat Exchanger consists of finned tubes, cooled by air circulated through the unit by fans. Vertical air flow prevents recycling of hot air by prevailing winds.

Maintenance cost is negligible. Expense of cleaning, descaling and replacement of parts corroded by the use of water is eliminated.

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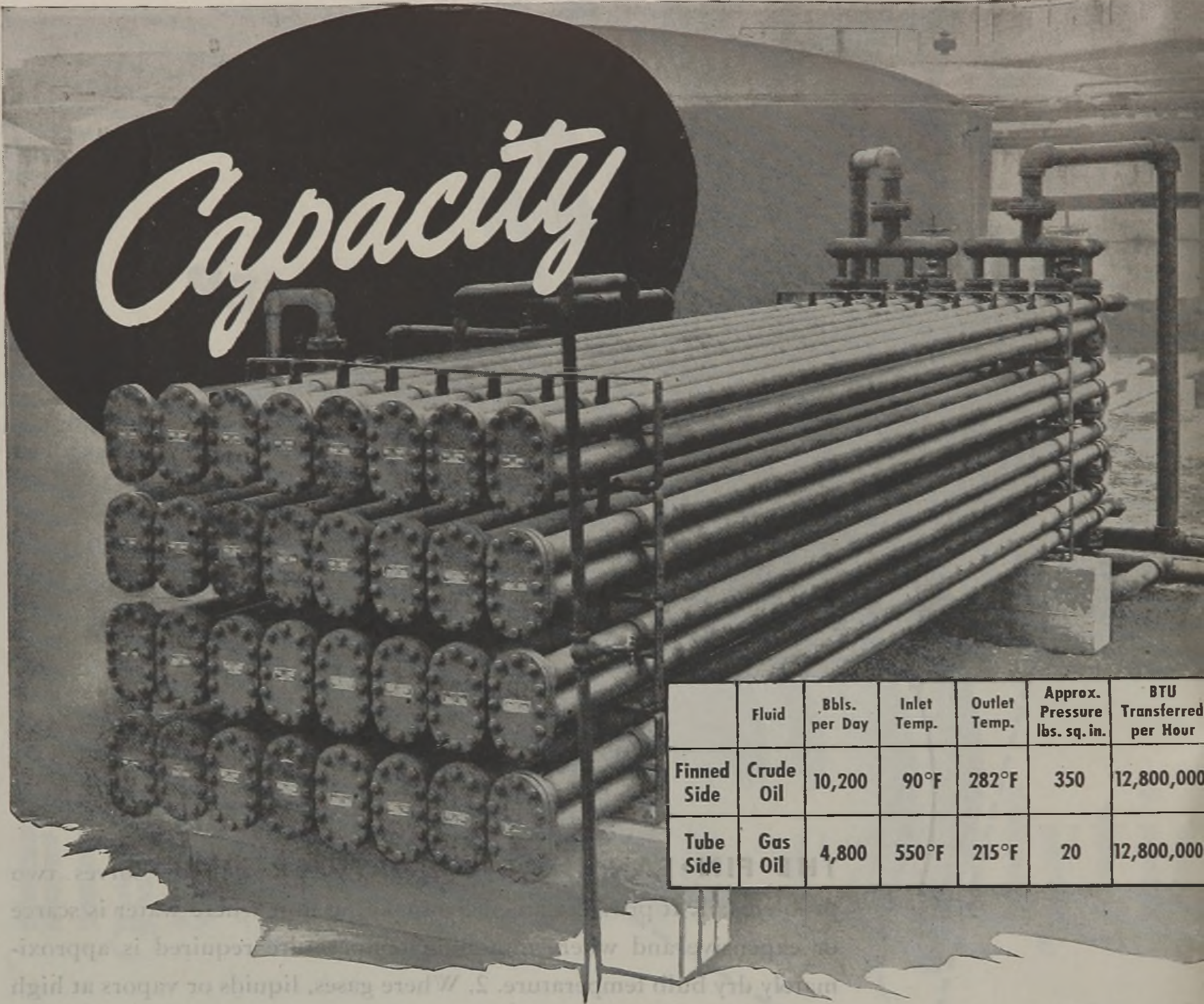
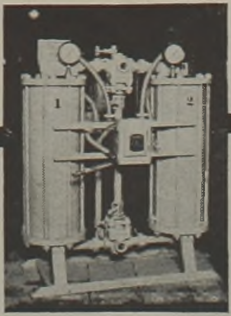
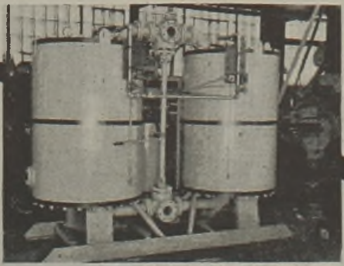

Capacity

¼ Std. CFM



20 Std. CFM



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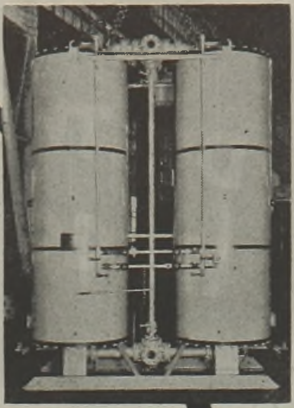
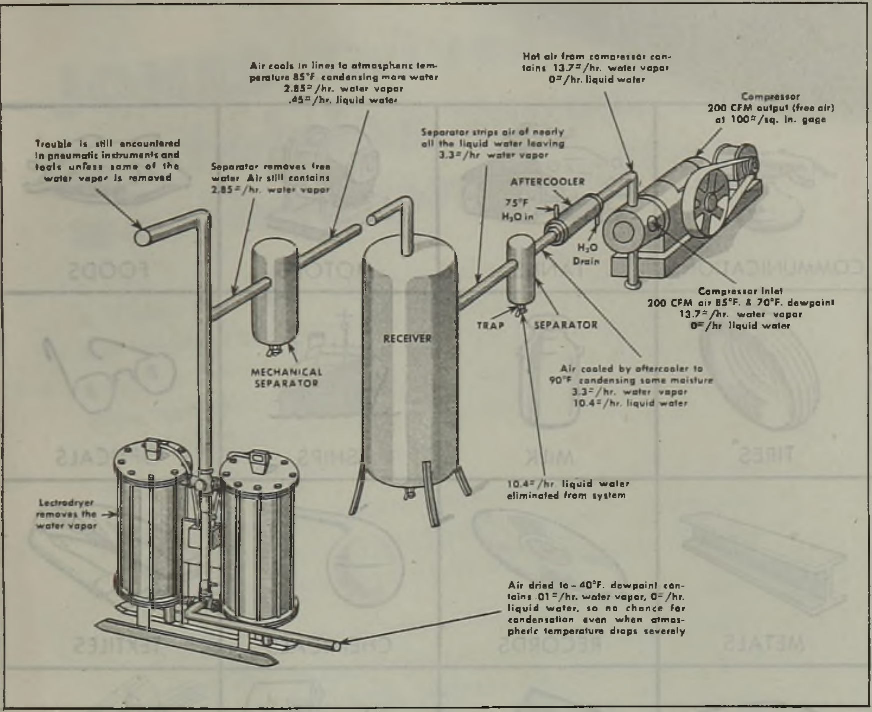
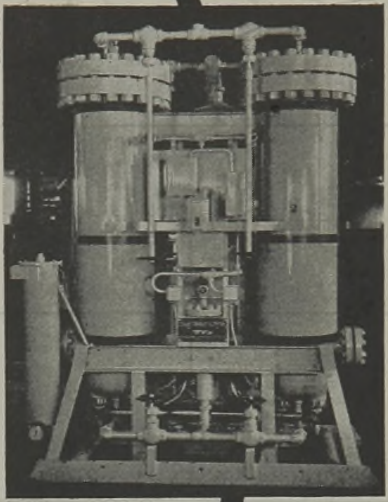
350 Std. CFM







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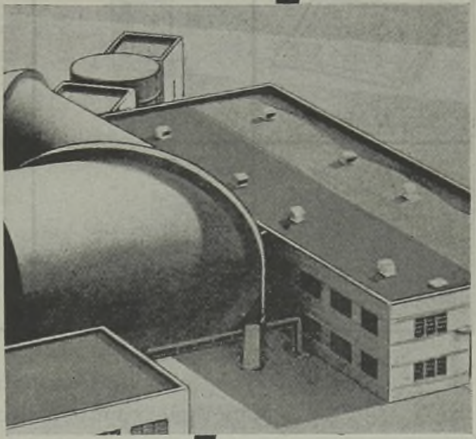

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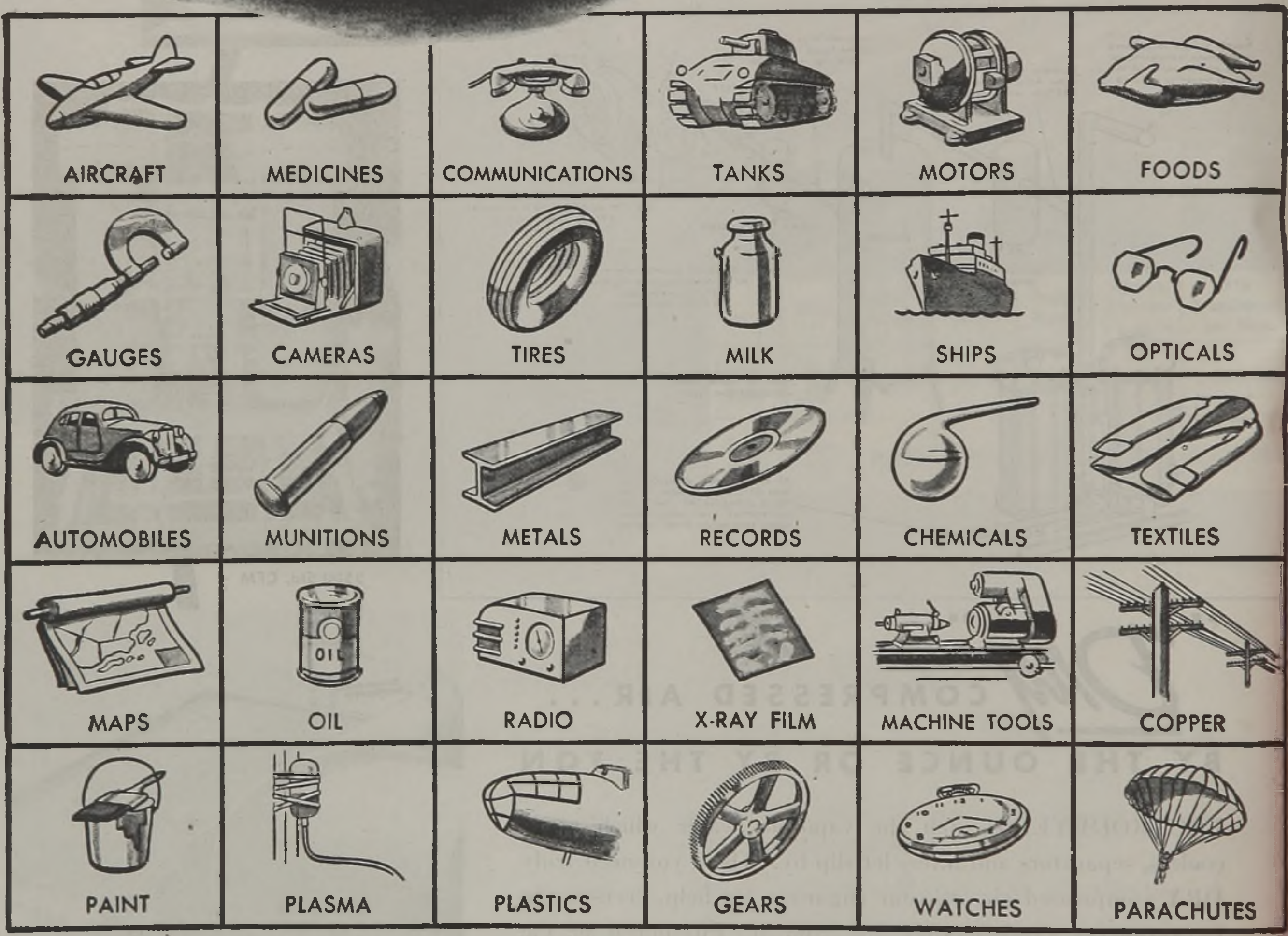
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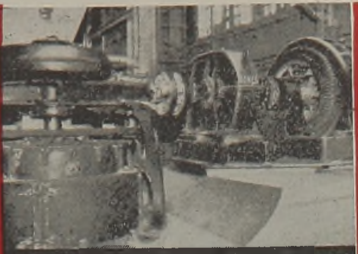
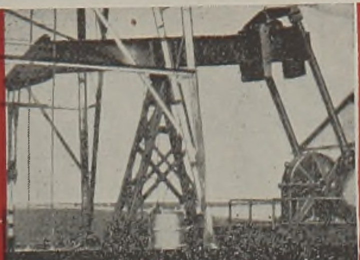


Bradley Hercules mill driven by Jones herringbone speed increaser from synchronous motor.



Oil field pumping unit using single type herringbone reducer driven by belt from gas engine.

JONES Drives that are helping speed up wartime production

• Today every phase of war work calls for drives that will stay on the job. Jones Speed Reducers have been built for long, trouble-free service. And the records established by these speed reducers in 24 hour a day service show that they have the ruggedness and stamina for which all Jones Transmission Products are known.

The accompanying illustrations are presented to give a general idea of the services the Jones organization is prepared to render on drive problems where speed reducers are required.

If you would like to have a condensed picture of the Jones products and engineering services, that are being widely used by industry, just ask for Bulletin No. 80, "Jones Drives for Industry".

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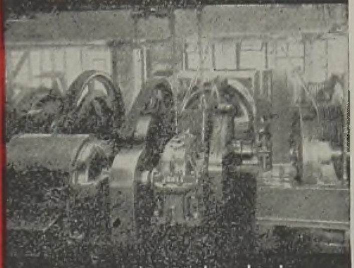
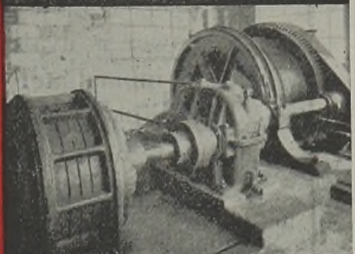
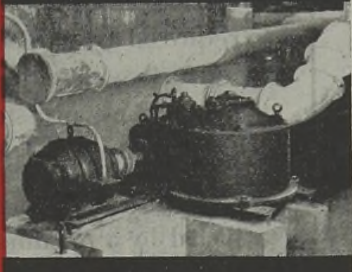
Hydraulic dredge which was equipped with Jones reducers as shown in view below.



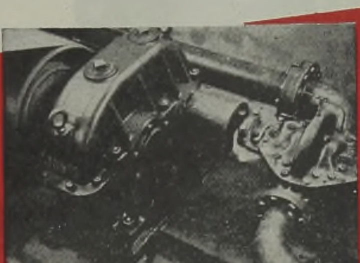
Drums and control mechanism of hydraulic dredge driven through Jones reducers.



A hoist for a coal mine driven by a Jones herringbone speed reducer.

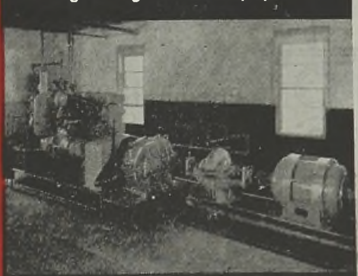


Jones worm-helical speed reducer driving an agitator in a paper mill.



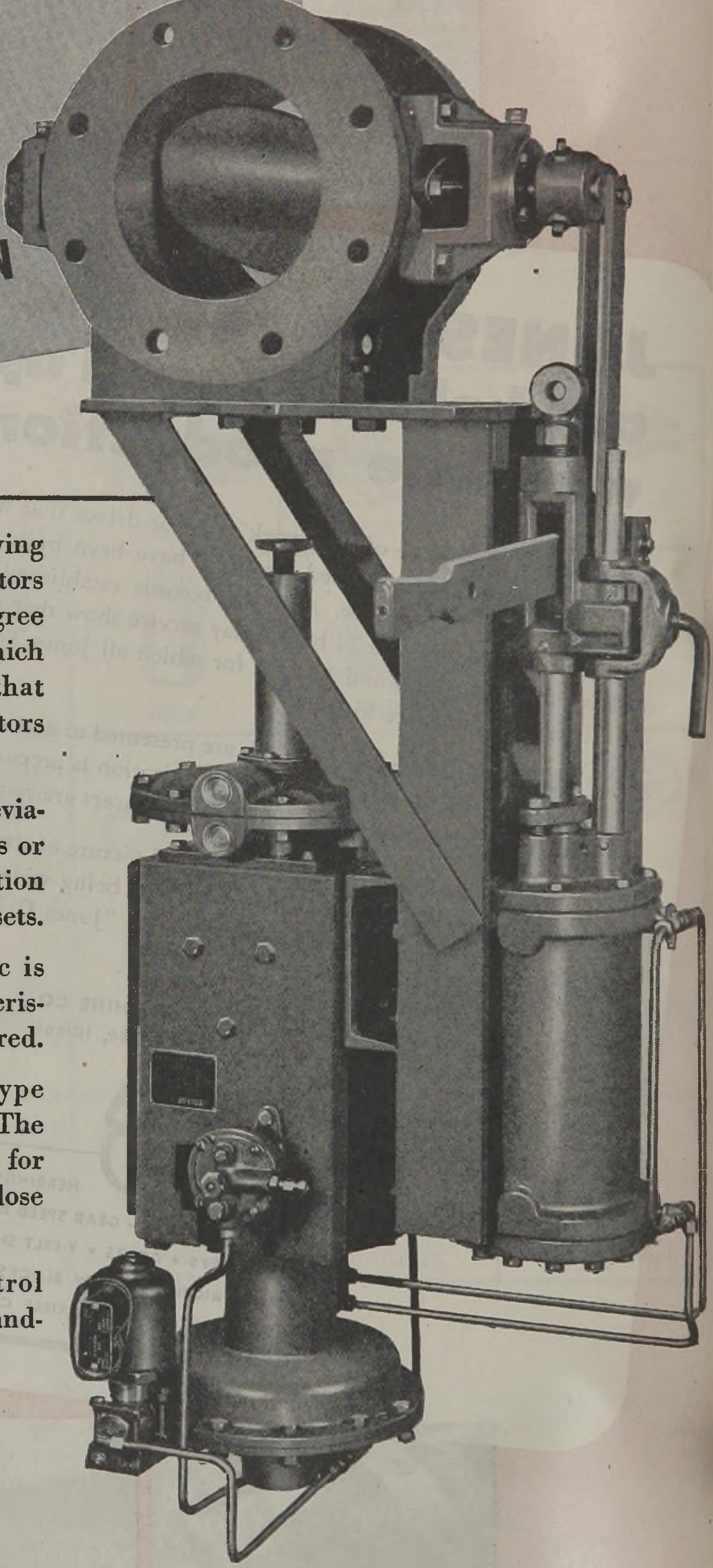
Centrifugal pump driven by a Jones speed increaser from belt drive to single cylinder gas engine.

A rotary kiln in a cement plant driven by Jones herringbone speed reducer.



Jones speed increaser driving a centrifugal pump from a Diesel engine.

PRECISION PRESSURE CONTROL for SUPERFRACTIONATION



● Republic regulators, employing pneumatic or hydraulic piston operators as the power elements, offer a degree of precision in pressure control which is a considerable advance over that obtained from conventional regulators or controllers.

Power is available to correct deviations immediately without overruns or instability. Available speed of operation insures handling of even bad upsets.

The basic control characteristic is floating, with proportional characteristic easily added in the field if required.

Valve bodies may be of any type required by operating conditions. The butterfly valve illustrated is suitable for many back pressure services on close fractionation.

Remote setting from the control board by a pneumatic loader is a standard feature.

Write for complete data!

Pneumatic loader for remote hand setting available.

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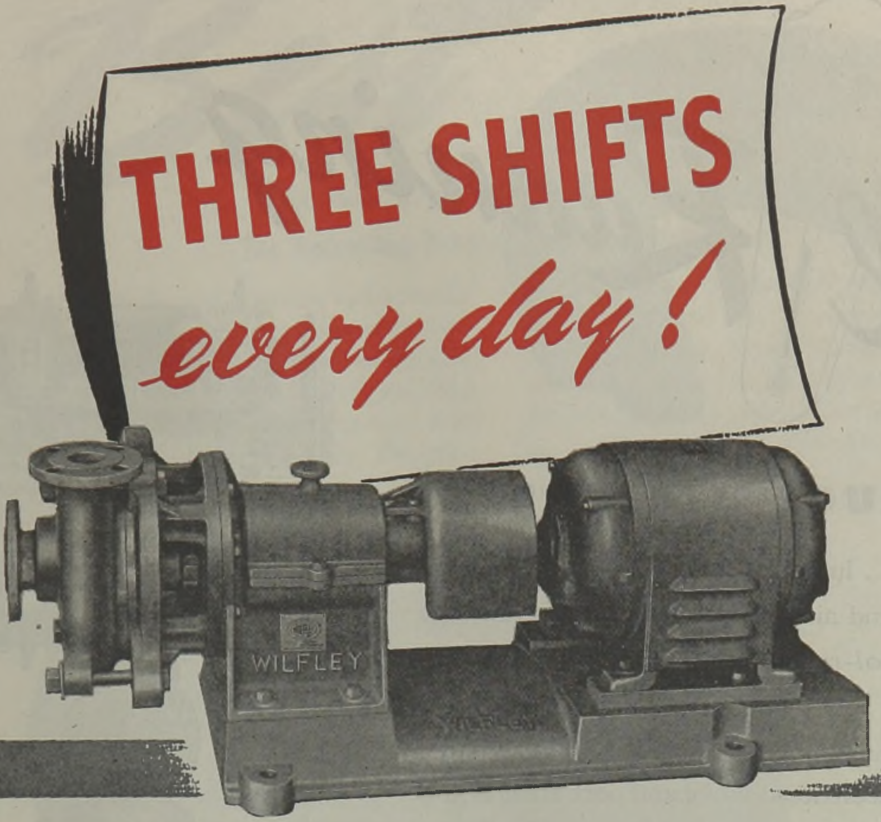

Where acids, corrosives, hot liquids, mild abrasives or any other hard-to-handle solution, must be kept on the move every hour of the twenty-four, WILFLEY Acid Pumps do a cost-saving job. This is the pump without a stuffing box, therefore the pump that's free from stuffing box troubles. For intermittent or continuous pumping jobs. 10- to 1,000-G.P.M. capacities. 15- to 125-ft. heads or higher. Individual engineering service on every application.

Write or wire for complete details.

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centrifugal PUMPS

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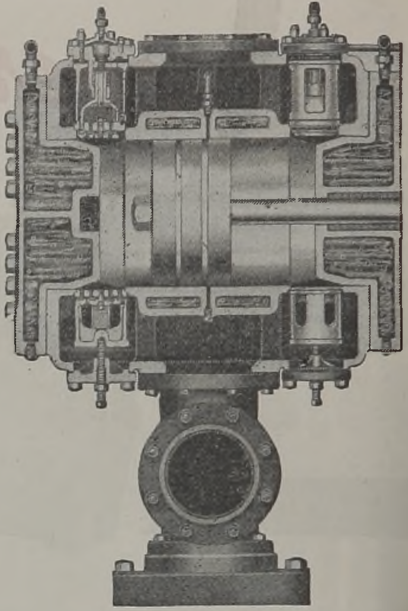
DENVER, COLORADO, U.S.A.
New York Office: 1775 BROADWAY, NEW YORK CITY

...TO REDUCE AIR COSTS!

Horsepower savings . . . lubrication economy . . . less wear and tear on air hoses and air tools . . . all these advantages are yours with the *cool-running* Gardner-Denver "RX" compressor.

Complete jacketing of all valves, air passages and cylinder heads plus large and unrestricted valve and port areas of this Single-Stage Horizontal Compressor reduce the heat of compression, insure minimum oil consumption and increase compression efficiency.



Cross-section of cylinder showing jacketing and large port areas.

OTHER "RX" ADVANTAGES

1. **Additional horsepower savings because air is automatically regulated to fit your needs.**
2. **Rugged dirt-free main frame assures long life . . . minimum maintenance.**
3. **Positive flood-type lubrication assures ample lubrication of all moving parts.**
4. **Duo-Plate "cushioned" valves are simple, durable, and quiet in operation.**
5. **Smooth, vibration-free operation assured by counterweighted crankshaft and Timken tapered roller bearings.**

For complete information on Gardner-Denver "RX" Single-Stage Horizontal Compressors, write Gardner-Denver Company, Quincy, Illinois.

USE COMPRESSED AIR FOR SAFETY CONVENIENCE FLEXIBILITY

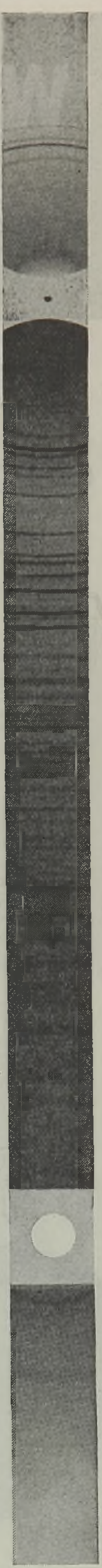
GARDNER-DENVER *Since 1859*

Best BY DESIGN

The New G-E XRD Powder Camera
For Recording X-Ray Diffraction Patterns

Skilled Mechanical ingenuity and scientific knowledge gained from years of specialized research are incorporated in the G-E XRD Powder Camera—recently modified to include new developments that assure even greater efficiency. Designed in optimum proportions—fundamentally based on x-ray diffraction data of the ASTM-ASXRED Card Index—it permits much faster exposures without an attendant sacrifice in final result quality. There is no finer instrument available for qualitative and rough quantitative analysis of solid materials.

An example of the speedier, yet more informative patterns produced by the G-E XRD Powder Camera—an annealed copper wire pattern. Similar patterns can be produced in as little as 5 minutes. Every diffraction line characteristic is clearly revealed—resolution is sufficiently high to permit accurate interpretation in lattice parameter of one part in ten thousand.

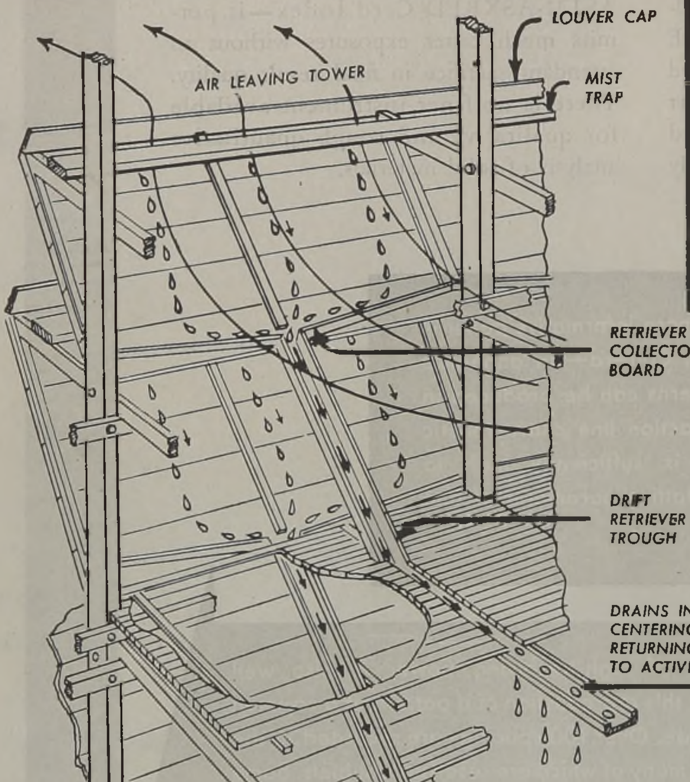


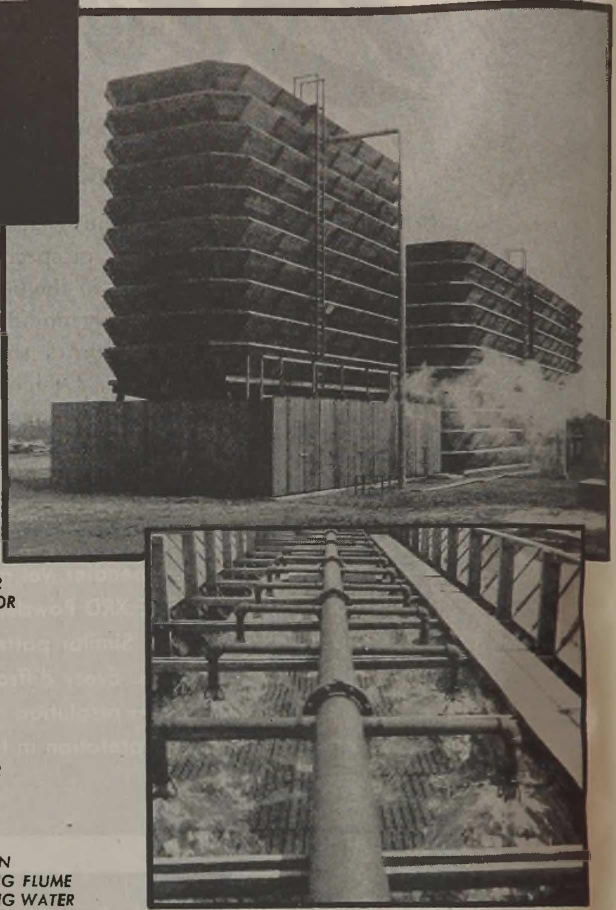
The importance of high resolving power is also well demonstrated in this reproduction of a pattern of a common form of lead oxide. Over 100 spacings are recorded in the original pattern, many of which are resolved doublets. Some of these lines are, of course, lost in this reproduction, but it is obvious that—were this substance to occur in mixture with others—employing a small camera would intolerably heighten the probability of maximal coincidence.

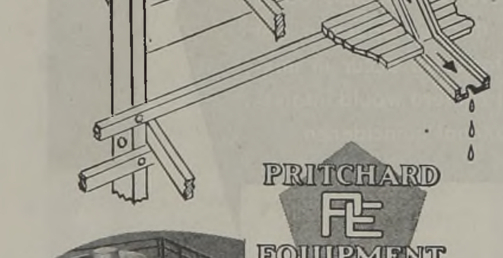
There is a host of outstanding design and construction features exclusive to the G-E XRD Powder Camera, all of which combine to insure maximum convenience, precision, and practically foolproof simplicity. Engineered to provide for many variations in technic, it embodies—as does all G-E X-Ray Diffraction Equipment—the newest and best developments in this increasingly important field. For full information about the G-E XRD Powder Camera and other units included in the G-E X-Ray complete line of x-ray diffraction apparatus—or to request the services of the G-E X-Ray Diffraction Laboratory in applying diffraction to your industrial problems—write or wire, today, to Department NN44.

1895 OUR FIFTIETH YEAR OF SERVICE 1945

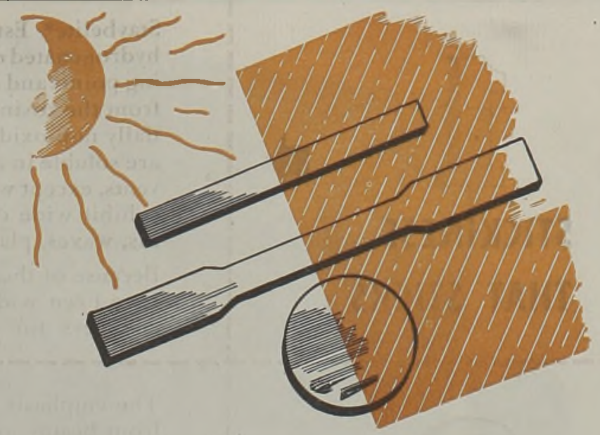
GENERAL ELECTRIC X-RAY CORPORATION
2012 JACKSON BOULEVARD CHICAGO (12), ILLINOIS, U. S. A.


LOUVER CAP
AIR LEAVING TOWER
MIST TRAP
RETRIEVER COLLECTOR BOARD
DRIFT RETRIEVER TROUGH
DRAINS IN CENTERING FLUME RETURNING WATER TO ACTIVE COOLING





STICKINESS THAT STICKS. With Hercules' Staybelite Esters as tackifiers in the synthetic rubber used, wartime adhesives stay "alive" even longer than those of pre-war rubber. These tackifiers are non-reactive with both synthetic elastomers and pigments. Details on next page.



THERMOPLASTICS STAY PUT. Accelerated plastics research, demanded by war needs, has meant marked improvements in the dimensional stability of the cellulosics. Tests show how these improvements produce plastics that withstand high temperatures and humidities. See next page.

CUES AND CLUES

for improved products

ROSIN-RESIN SAVER. From the wood of the Southern long-leaf pine comes still another Hercules product to help beat wartime material shortages. Its name is Vinsol Resin—a low-cost extender, modifier, or replacement for many natural and synthetic resins. Turn page for details.

LENS PROTECTOR. Lacquer's toughness and durability is serving in many ways to keep existing equipment in service. Unique is a transparent coating on welders' goggles, to protect glass lenses from scratch burns. New coatings are easily applied on the spot. Please see next page.

TO help expedite your development of new and better products, or the improvement of existing ones, Hercules presents the second edition of CUES AND CLUES. If these timely reports on Hercules' materials and their uses suggest a solution to one of *your* problems why not get in touch with us today? Immediate attention will be given to your inquiry on any material. Write Hercules Powder Company, 904 King Street, Wilmington 99, Dela.

HERCULES

SEE NEXT PAGE FOR DETAILS ➡

1

STICKINESS THAT STICKS

Staybelite* Esters are the esters of hydrogenated rosin, with graded melting points and hardnesses. They differ from the rosin esters in being essentially non-oxidizing. Staybelite Esters are soluble in all commonly used solvents, except water and alcohol. They exhibit wide compatibility with resins, waxes, plasticizers, film-formers.

Because of these characteristics, they have been widely accepted as stable tackifiers for pressure-sensitive adhesives made with synthetic rubber. Such adhesives, for surgical tapes, have long shelf-life, non-toxicity, do not discolor. Masking and wrapping tapes made with them are easily removed without leaving a mark. Synthetic rubber cement, tackified with Staybelite Esters, meets all requirements in shoe manufacture, contributes to waterproofness.

When requesting information please describe your adhesive problems.

2

THERMOPLASTICS STAY PUT

The emphasis in plastics has shifted from beauty and glamor to strength and endurance. This new approach has brought about the development of properties which will make for better postwar plastics.

Hercules has prepared a new technical booklet, which lists and describes the results of dimensional stability tests on cellulosic plastics at high temperatures and high humidities—simulating tropical conditions.

The data indicate that cellulose acetate (regular or high acetyl, as conditions may warrant) is satisfactory for most uses, and that ethyl cellulose is outstanding for toughness and stability under more severe conditions.

Color sketches, photographs, four comprehensive tables, an explanation of test conditions, and a discussion of data contained in the sketches, make this booklet a comprehensive source of engineering data.

3

ROSIN-RESIN SAVER

Vinsol* Resin is dark-colored, has a high melting point (234° F. to 239° F. Hercules Drop Method). It is largely insoluble in petroleum solvents, but is soluble in alcohols, ketones, and esters. Vinsol Resin is available in lump, flake, or pulverized form, or as a stable emulsion.

Because of its compatibility with many natural and synthetic resins, and its extremely low cost, Vinsol Resin offers the plastics industry a valuable extender or replacement for critical materials. To such compositions it brings excellent electrical properties, oil resistance, hardness, good finish.

Vinsol Ester Gums, for use with lacquers, varnishes, floor tile, etc., are available at comparably low cost.

Other diversified uses include air entraining agents for Portland cement, stains, adhesives, paper impregnants, asphalt emulsions.

4

LENS PROTECTOR

Hercules produces high-quality nitrocellulose for manufacturers who make lacquers for industrial consumers. Among the latest developments, born of long research by Hercules and the protective-coatings industry, are new-type high-solids lacquers. They carry more film per coat, thus appreciably reducing spraying costs. And they air-dry quickly without expensive baking equipment.

High-solids lacquers will be available in lustrous colors and effects to meet every finishing need . . . beautiful pastels; rich, deep shades; shimmering iridescents; transparent. And with revival of color will come excellent protection against moisture, oils, acids, abrasion.

Descriptive literature will be supplied on request.

*Reg. U. S. Pat. Off. by Hercules Powder Company

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CHEMICAL COTTON • EXPLOSIVES • PAPER MAKERS CHEMICALS


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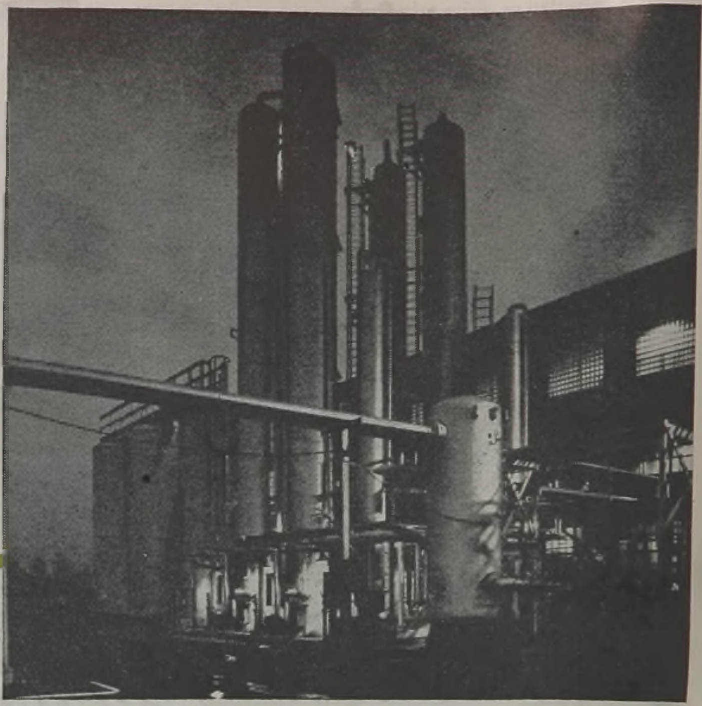

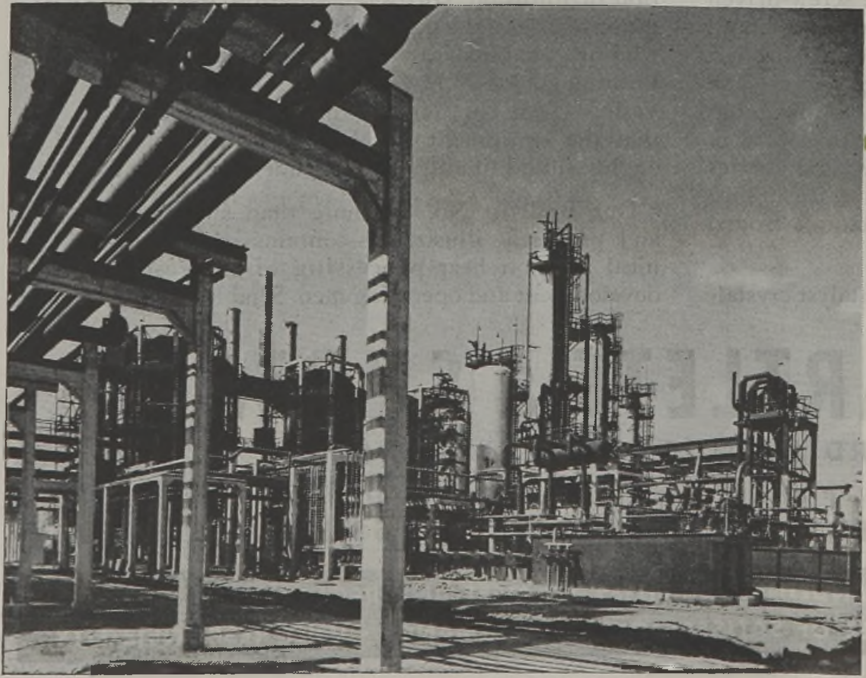

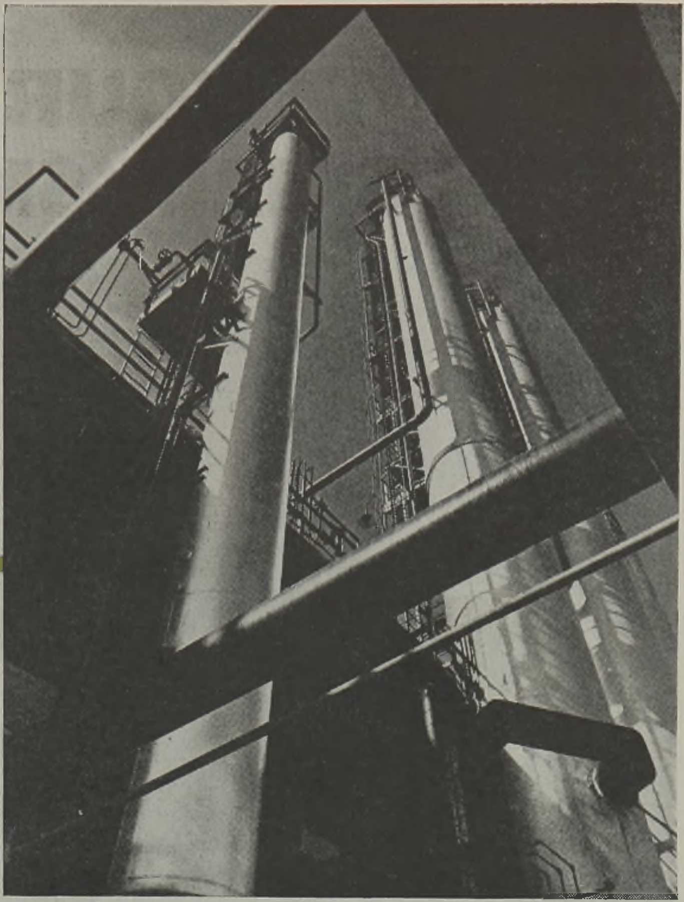

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Score a *BULLS-EYE* in Low-cost, LASTING IDENTIFICATION

Your postwar product deserves a fine trademark...a lasting form of identification that continuously tells "who made it" for the life of the product. Meyercord Decals, combat-tested on world battle fronts, provide the ideal trademark or nameplate. They're durable, washable, and resistant to acid, vibration and temperature extremes. They can be produced in any size, colors or design and applied at fast production line speeds. No rivets, bolts or screws required. Easy-to-use methods of adhesion permit fast, lasting application to any known *commercial surface.* Investigate the better "Trademarksmanship" of Meyercord Decals. Free designing and technical service is at your disposal. Write for literature. Address all inquiries to Department 90-4.

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SOLID STAINLESS
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HEAT-RESISTING

Maintenance time reduced to a minimum

Every day, Powell Valves are piling up records for continuous operation without requiring maintenance. And when they finally need attention, Powell design and construction is such that the time spent in maintenance is reduced to a minimum. The gate valves shown here are examples of the complete Powell Line in which ease of maintenance is always a feature.

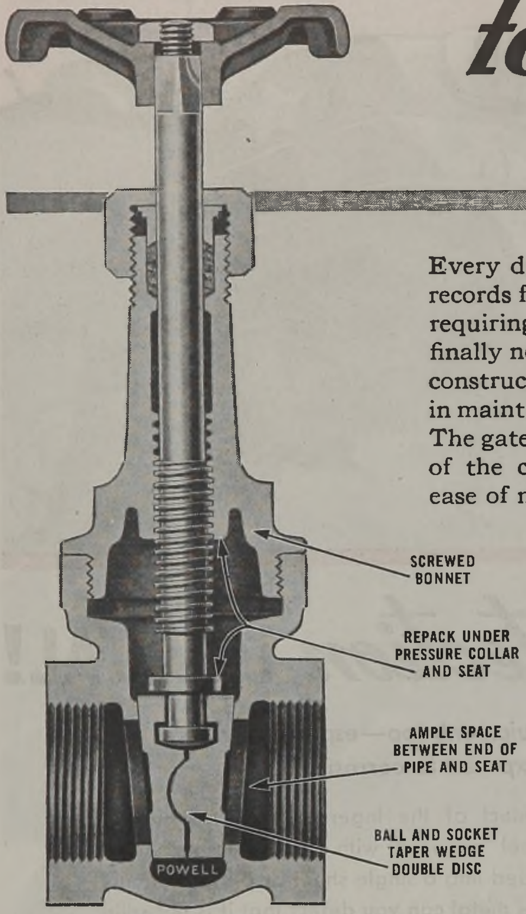

Fig. 500
BRONZE "U. S." GATE VALVE

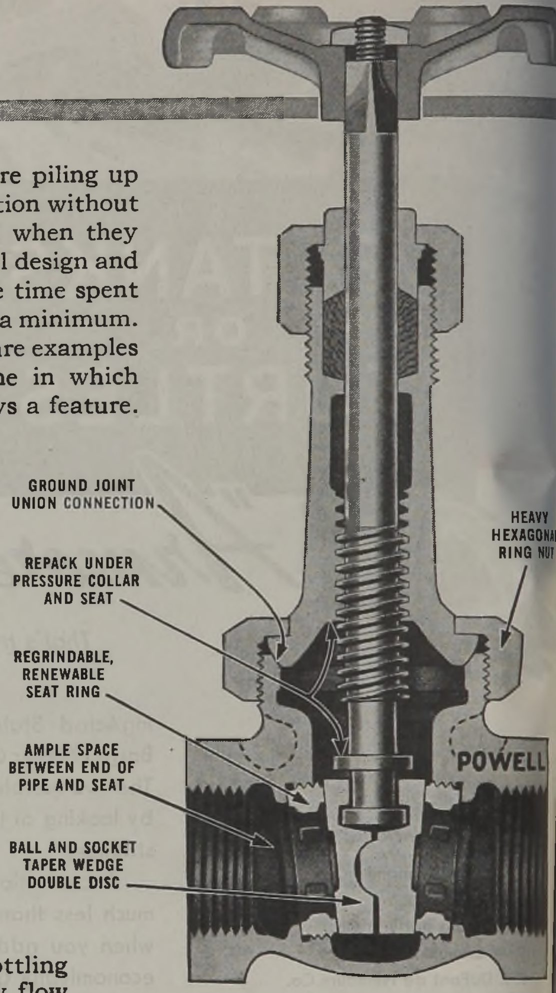

Fig. 1375
BRONZE "WHITE STAR" GATE VALVE

In all installations where pressure drop is undesirable and throttling is unnecessary, the gate type of valve, with its full straightway flow area through the body, should be used.

Fig. 500 is Powell's answer to the widespread demand for a sturdy small bronze gate valve where initial cost is a consideration. With its readily removable screwed-in bonnet it is easy to reface the seats and disc or replace the disc if necessary. The taper wedge double disc, with its Powell-designed ball and socket action, readily adjusts itself to any inclination of the seat faces caused by refacing, thus effecting a tight closure. Since the seats are cast integral with the body, this valve will give dependable service as long as sufficient metal remains in the seats to permit refacing.

For *extra long life*, Fig. 1375 is recommended. The ground joint union connection makes it especially easy to remove the bonnet assembly from the body to reface or, if necessary, to replace the disc and renewable seats. This may be done any number of times without any distortion of the body neck, such as might occur with a screwed-in bonnet. Both disc and seats are made from a special hard nickel-bronze alloy which resists wear over a long period of time. When these parts will not take further refacing, they can be readily replaced with new ones, thus greatly prolonging the life of this valve.

All Powell Valves that require repacking are provided with a specially machined cut-off to permit repacking under pressure when wide open.

The Wm. Powell Co
Dependable Valves Since 1846
Cincinnati 22, Ohio

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SW Struthers Wells CORPORATION

One of America's important sources for *Advanced Engineering* and designing of PROCESSING EQUIPMENT . . .

. . . from STAINLESS STEEL, NICKEL, MONEL, HASTELLOY and other CORROSION RESISTANT ALLOYS

Accumulators, Hydraulic and Steam
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Circulating Heating Systems, Hot Oil and Dowtherm
Components, Ordnance
Condensers, Barometric
Condensers, Gas, Oil and Chemicals
Cookers, Cereal
Coolers, Ammonia
Coolers, Gas, Oil and Chemicals
Coolers, Rotary
Crankshafts, Rough and Finished Machined
Crystallizers
Cylinders, Air and Hydraulic
Cylinders, Arresting Engine and Elevator
Cylinders, Creosoting
Cylinders, Steering Engine
Deck Auxiliary Equipment
Deodorizers, (Edible Oils)
Devulcanizers, Rubber
Die Blocks
Digesters, Pulp and Paper, Stationary and Rotary
Distillation and Extraction Equipment
Dryers, Rotary, Direct and Indirect Heat
Dryers, Drum
Dryers, Vacuum
Engines, Gas and Oil
Equipment, Corrosion Resisting Alloys
Evaporators, Inclined High Velocity
Evaporators, Single and Multiple Effect
Evaporators, Water Distilling
Exchangers, Heat
Extraction Plants, Solvent
Extractors, Rotary and Stationary
Flame Cutters
Forgings, Hollow or Solid, of Carbon or Alloy Steels Rough or Finished Machined
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Fractionating Towers, Pressure, Atmospheric, Vacuum
Furnaces, Rotary Drying and Carbonizing
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Hammer Rams
Heat Exchangers
Heaters, Air, Gas, Liquid
Heaters, High Pressure Feed Water
Heaters, Suction for Oil Storage Tanks
Impregnating Equipment
Kneading Machines
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Kettles, Food Cooking
Kettles, Grease and Oil Blending
Kettles, Lead Melting
Kilns, Lime
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Masts
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Mixers, Electrically Heated
Mixers, Revolving Drum
Mixers, Vacuum and Pressure
Nitrators
Oil Coolers
Oil Country Boilers
Oil Country Gas and Oil Engines
Ordnance, Compounds
Pans, Crystallizing, Drying, Evaporating, Etc.
Pipe, Corrosion Resisting Alloy
Pipe Moulds, Finished Machined
Pipe, Steam Jacketed
Piston Rods Rough or Finished Machined
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—at lower costs

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solids in liquids, solids in solids, or liquids in liquids, PREMIER insures immediate chemical reaction—more finely divided colloidal suspensions.

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every particle of fiber or cellulose in animal or vegetable tissue . . . instantly exposes these particles to the extractive action of the suspending liquid.

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achieving non-separating emulsions with plumit ratings as low as ½.

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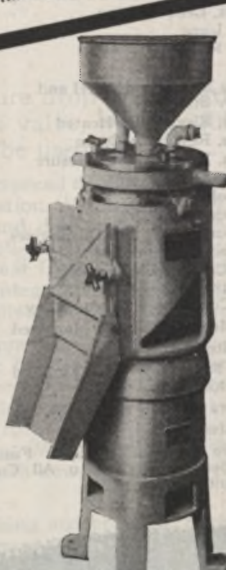
assuring superior homogenized products by compelling uniform distribution of fat globules throughout the mix.

SIMPLEST ROTOR-STATOR

Easy to { CLEAN OPERATE ADJUST



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Write for this important brochure on superior processing describing the complete line of PREMIER COLLOID MILLS. Hourly capacities from 10 to 3000 gallons.

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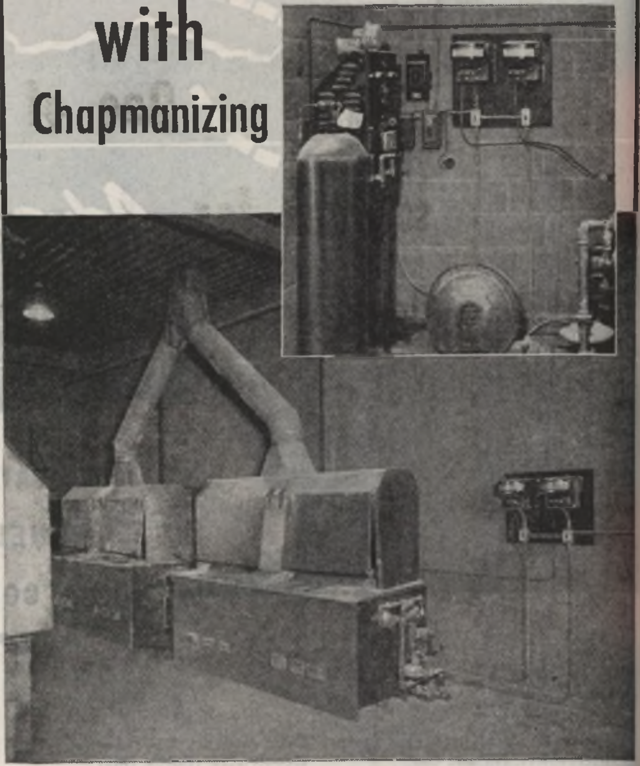
Capacitrols insure precise control with Chapmanizing



As with other top flight heat treating plants over the country, Ipsen Industries, Rockford, Illinois, chose Wheelco Capacitrols to maintain precise control on their Chapmanizing furnaces and on other equipment, because of their simplicity of operation . . . dependability . . . and long life under all operating conditions.

Both gas-fired and electric heat treating furnaces in this plant are temperature-controlled by Wheelco Capacitrols, Model 221 indicating control Pyrometers. For a complete description of these electronic instruments ask for Bulletin D2-3.

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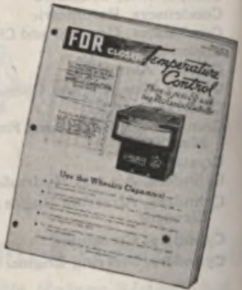
A complete line, including Flame-otrol combustion safeguards . . . Capacitrol pyrometer controllers . . . Indicating pyrometers . . . Proportioning controls . . . Program controls . . . and a wide range of accessories.



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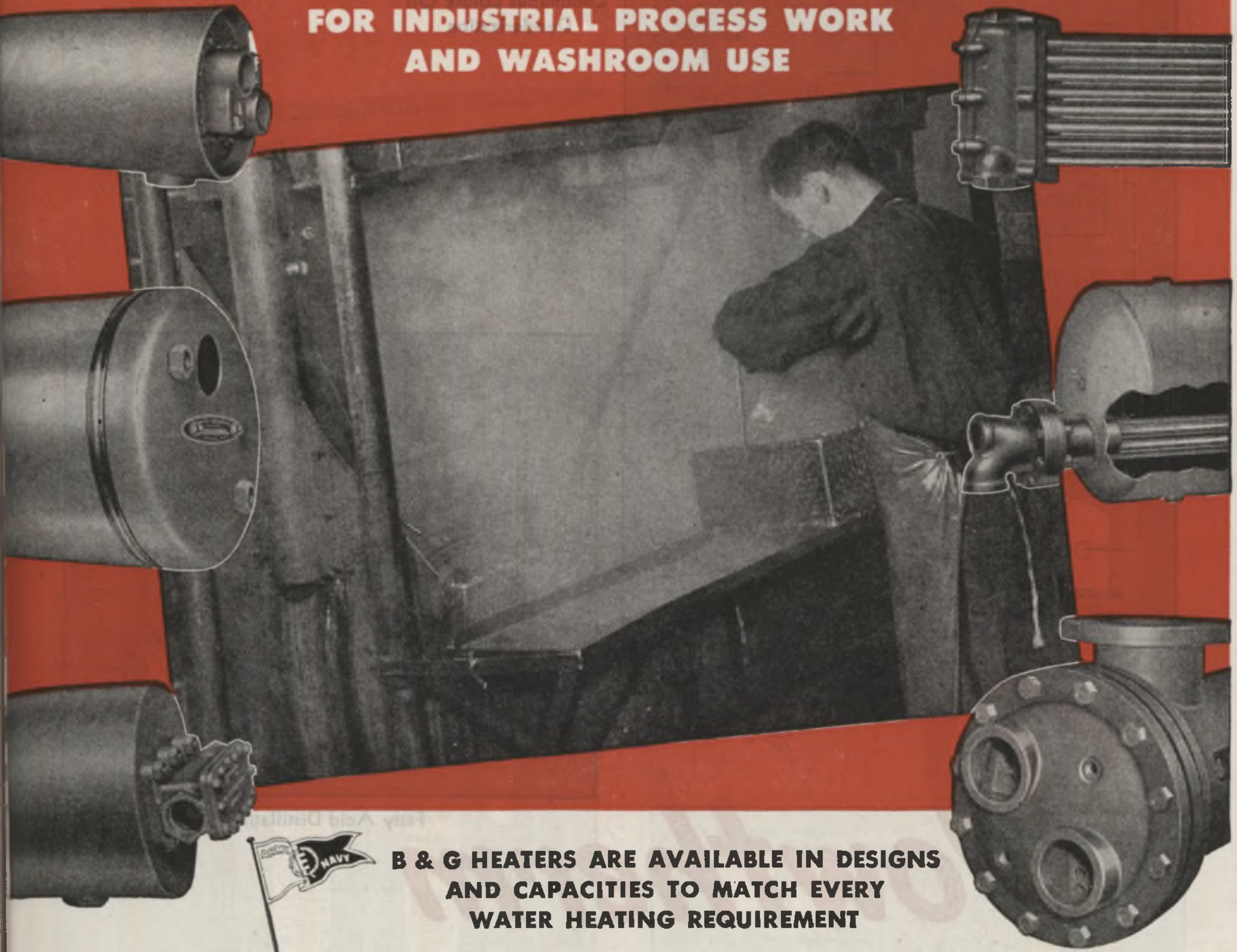
FOR INDUSTRIAL PROCESS WORK AND WASHROOM USE



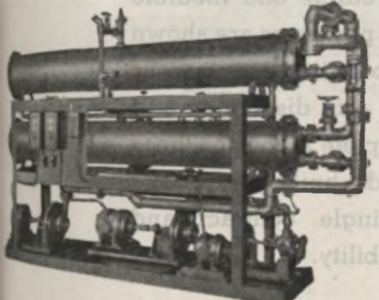
B & G HEATERS ARE AVAILABLE IN DESIGNS AND CAPACITIES TO MATCH EVERY WATER HEATING REQUIREMENT

Better check your water heating facilities now—long service may have reduced efficiency or brought equipment to the breakdown point. Then look over the B & G line for a suitable replacement—you'll find it offers the last word in money-saving water heating apparatus.

Whether you want a Water Heater for tankless operation or for use with a storage tank . . . for installation on a steam boiler or hot water boiler . . . for furnishing hot water for process work or washroom use, B & G has just the unit to economically meet your requirements.

B & G Water Heaters are known the country over for design which assures a maximum amount of hot water from a minimum size unit and with the least tax on the boiler. They give genuine satisfaction to the engineer who demands top efficiency from all his equipment.

Water heating costs go down and volume goes up where B & G Water Heaters are installed.



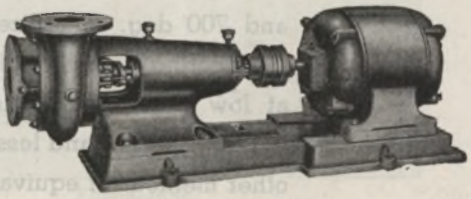
Typical example of a B&G Self-Contained Heat Exchanger Unit for oil cooling, fully equipped and ready for quick, easy installation.

B & G HEAT EXCHANGERS

. . . engineered to your requirements

The Bell & Gossett Company offers a helpful engineering service on all heat transfer problems. Whether you are planning to modernize present equipment or are experimenting with new ideas for faster production and better quality, there is no obligation involved by a preliminary consultation with B & G engineers.

B & G Heat Transfer Products can be furnished either as separate items or as self-contained units, complete with Heat Exchangers, Pumps, Controls and other necessary auxiliary equipment. Your request for information will receive prompt attention.



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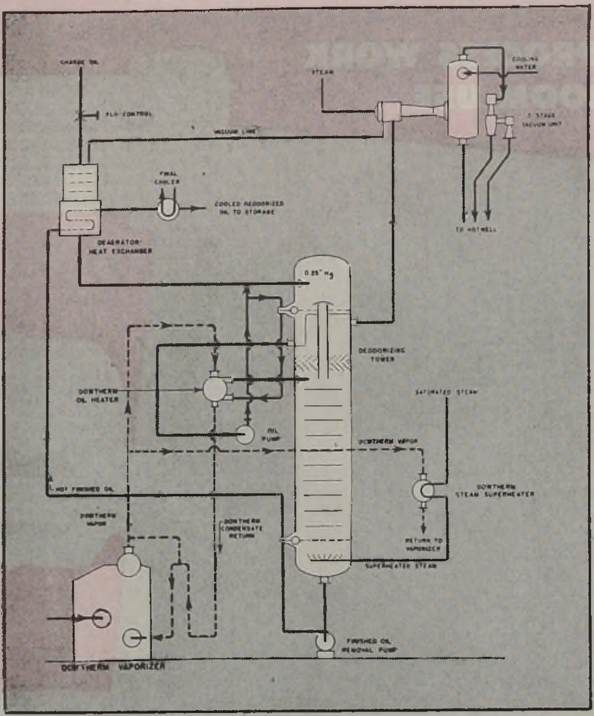
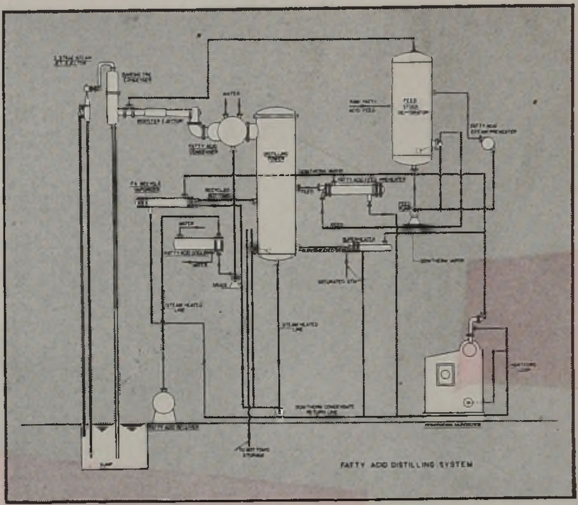
Rugged, compact units, built to stand up under the strain of continuous operation. Available with semi-open or enclosed impellers—motors flexible coupled or integral with pump. Send for catalog.

B&G HEAT TRANSFER EQUIPMENT

BELL & GOSSETT COMPANY • MORTON GROVE, ILLINOIS



Continuous Edible Oil Deodorization



Fatty Acid Distillation

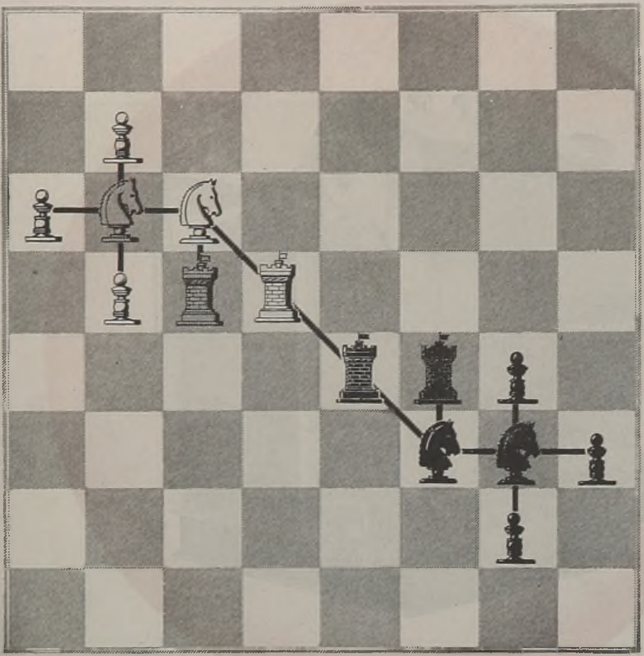
Dowtherm

PROCESSING OF FATS AND OILS

The ideal processing system for the temperature range between 500 deg. F. and 700 deg. F. utilizes Dowtherm as the heating vehicle. High temperature at low pressure, precision of heating control, simpler and less expensive than other methods of equivalent capacity.

For instance, Dowtherm is the accepted heating medium for the industrial processing of edible and inedible oils and fats. Four processes are shown here: batch deodorization, continuous deodorization, fatty acid distillation and esterification. Complete plants for these are designed and built by Foster Wheeler under single contract and undivided responsibility.

FW FOSTER



This is not a game of skill ...IT'S BECCO ACETYL PEROXIDE

Perhaps chess was played before Brodie first began his investigations of Acetyl Peroxide in 1863; and certainly prior to a continuation of his studies by Vanino, Clover, Richmond, Gambarjan and Kharash. But its use was more risky than playing chess, for Kharash said of Acetyl Peroxide in the Journal of the American Chemical Society: "An outstanding peroxide of great usefulness but must be used on the spot (of manufacture) because of its sensitivity."

Chemists of the Buffalo Electro-Chemical Company, Inc., have developed a process for making solutions of acetyl peroxide which are perfectly safe to handle. It can, at present, be furnished in laboratory size samples only. It is a 30 percent solution of acetyl peroxide in dimethylphthalate, water white, non-explosive and immune to shock and impact.

Besides its value as a polymerization agent, other interesting applications include its use as a germicide, a bleaching and oxidizing agent, and in vulcanization. It has great possibilities in organic syntheses as it is very reactive and offers a source of active oxygen in a non-aqueous medium.

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BUFFALO ELECTRO-CHEMICAL COMPANY, INC.

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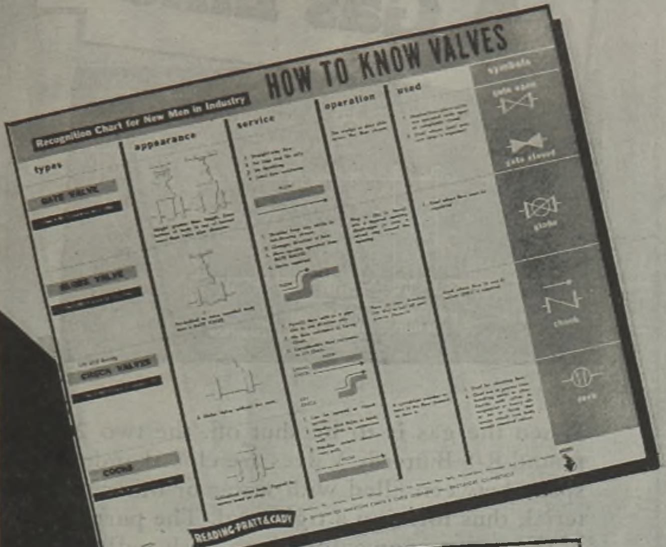
NOT only good valves, but best possible valve service—that's the R-P & C idea. A valve can do its best only on the job for which it was designed—and then only if correctly installed and properly used.

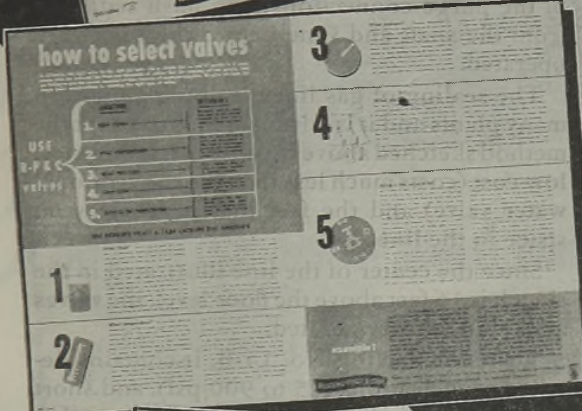
There is a good R-P & C valve for practically any job. And there is an R-P & C expert ready to advise on any valve question. However, if your problems are simple ones, perhaps the answers may be found on one or another of the charts shown on this page.

Thousands of these charts have been requested and received by valve users. If you do not have them, we will send you one or a complete set. Apart from their practical everyday use, they will remind you of a source for good valves and expert valve information.


HOW TO KNOW VALVES
Recognition Chart for New Men in Industry

types	appearance	service	operation	used	symbols
GATE VALVE					
GLOBE VALVE					
CHECK VALVES					
COCKS					

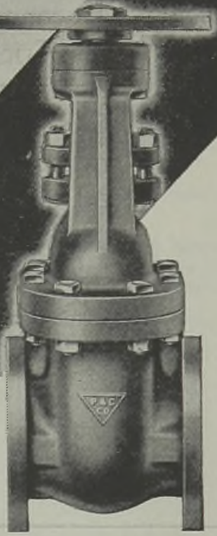
READING-PRATT & CADY


how to select valves

USE R-P & C valves

1
2
3
4
5


how to protect your valves



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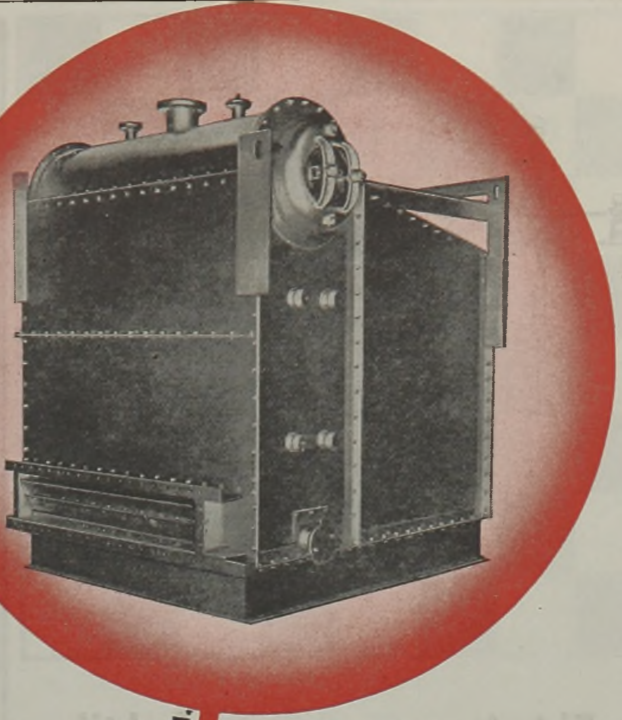
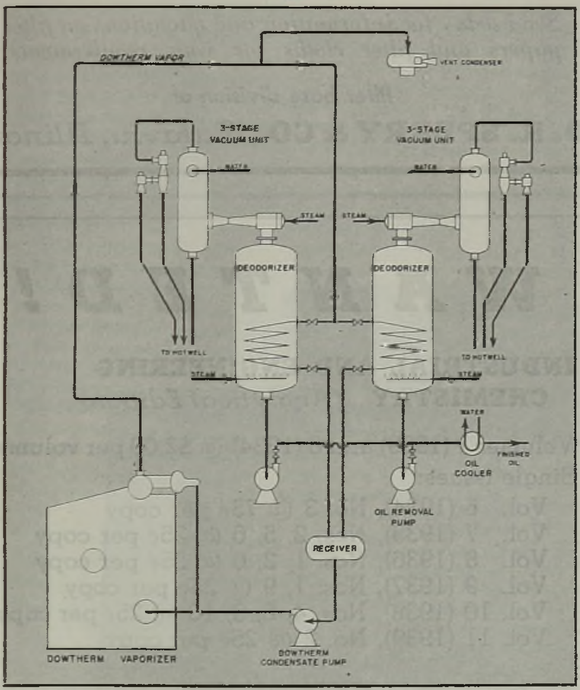
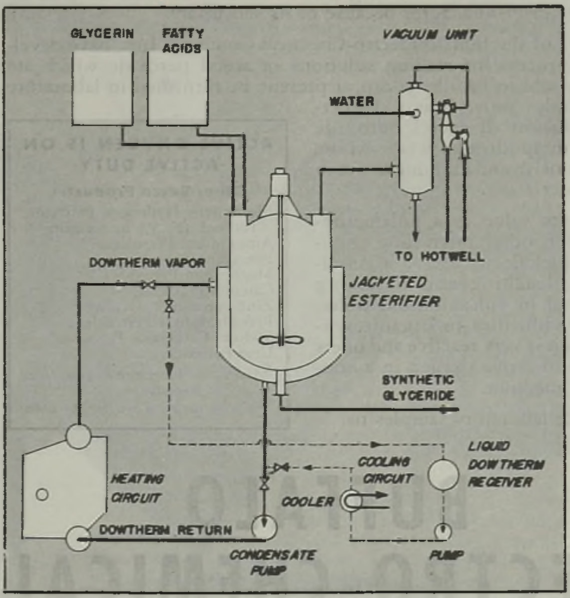




Batch Edible Oil Deodorization



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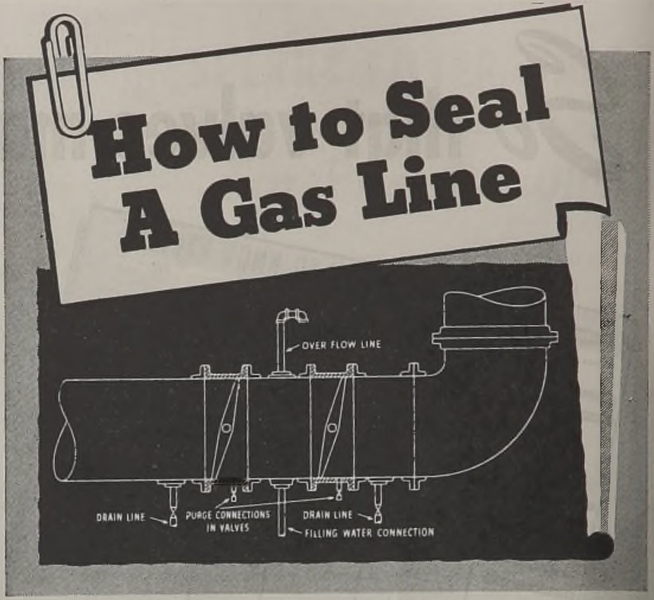

When the gas is to be shut off, the two 25-pound R-S Butterfly Valves are closed and the space between filled with water or other material, thus forming a tight seal. The purpose of the purge connections is to flush sediment from the shaft and vane before the valves are operated.

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Since the center of the line illustrated in the sketch is 16 feet above the floor level, the valves are chain wheel operated.

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No. 495

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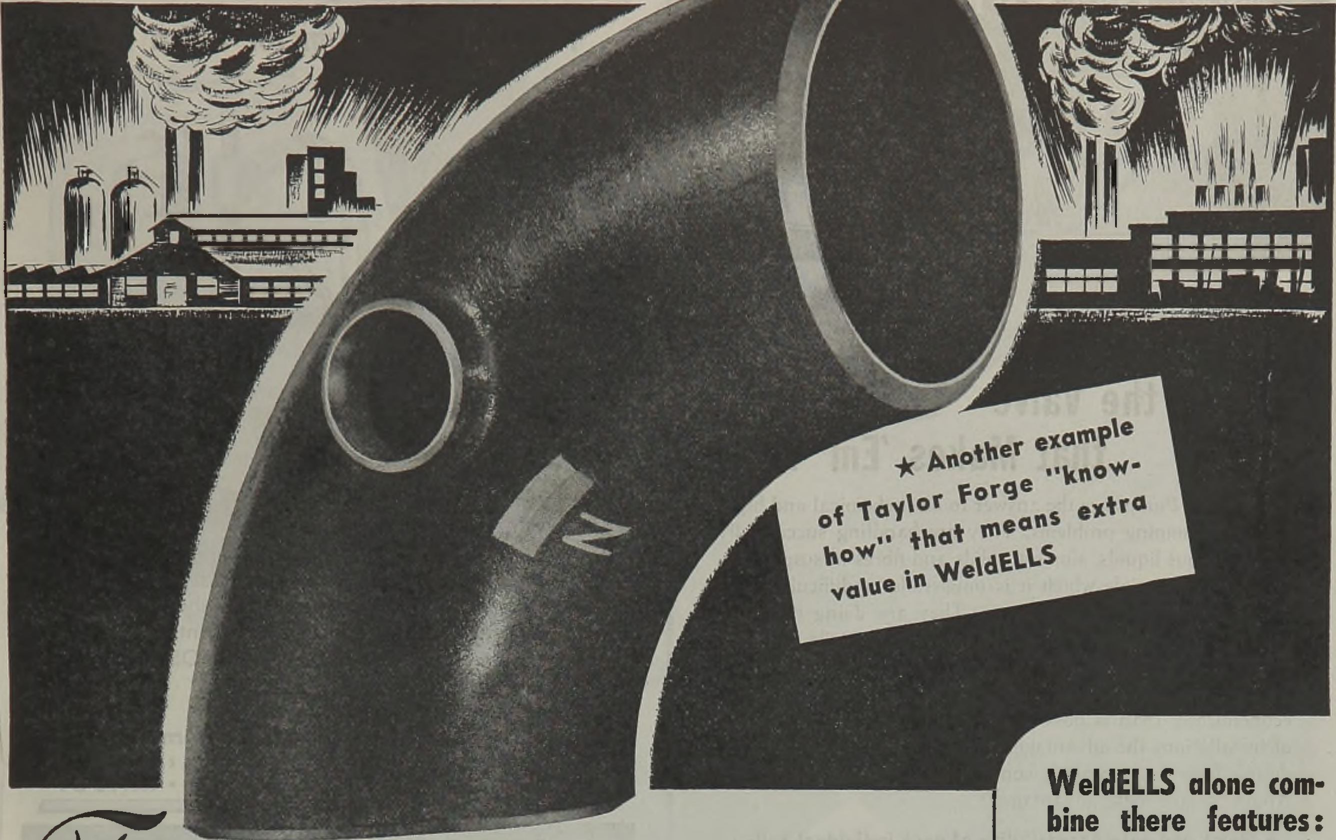
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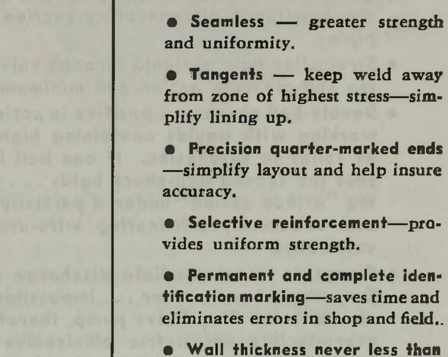
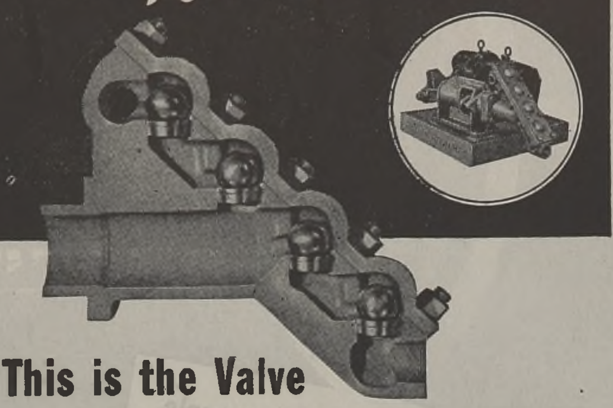


MILTON Roy Step-Valve PUMPS



This is the Valve that Makes 'Em "Tick"

Milton Roy Pumps are the answer to *most* chemical and high-pressure pumping problems. They are handling successfully many viscous liquids, slurries, solids and fibres in suspension, and other materials which it is impossible or difficult or too costly to pump by other means. They are doing the more common-place jobs of pumping acids, alkalies, oils, solvents, etc., in exactly controlled volumes, at pressures up to 20 thousand pounds per sq. inch, more efficiently and more economically than is possible by other means. In hundreds of installations the advantages of the Milton Roy Step-Valve design have been proved, conclusively, in years of service. And what are these advantages?

- **Quick and easy accessibility of each individual ball-check *without disconnecting suction or discharge piping.***
- **Streamline flow of liquid through valve with resulting *self-cleaning action and minimum slippage.***
- **Double-ball checks . . . positive in action, even when working with liquids containing high percentages of solids in suspension. If one ball is held off its seat the second ball-check holds . . . thus eliminating "orifice action" under a partially closed valve and effectively *eliminating wire-drawing of the valve seat.***
- **Complete and immediate discharge of air or gas from the valve chamber . . . impossible to "pocket" air. With the Step-Valve pump, therefore, high and reproducible volumetric efficiencies are assured *. . . exactly the same volume of material is delivered* at a given stroke setting with every stroke of the pump.**
- **The Milton Roy Step-Valve with single cover plate (illustrated) is particularly well adapted for handling VISCOUS MATERIALS, CRYSTALS IN SUSPENSION, FIBRES IN SUSPENSION, SLURRIES, FOOD PRODUCTS.**
- **Flow resistance in this type Step-Valve is at a minimum because the ball-checks *lift completely out* of the stream of flow . . . the flow passes *under the ball-checks,* not around them.**
- **Removal of the single cover plate provides complete and quick accessibility . . . ball-checks and pump chamber may be thoroughly cleaned whenever required, as in handling foods for example.**

These are only a few of the principal advantages of Step-Valve design. Write for Bulletin 426 with the complete story. Ask also for the Milton Roy Pump Catalog if you do not have one in your files.

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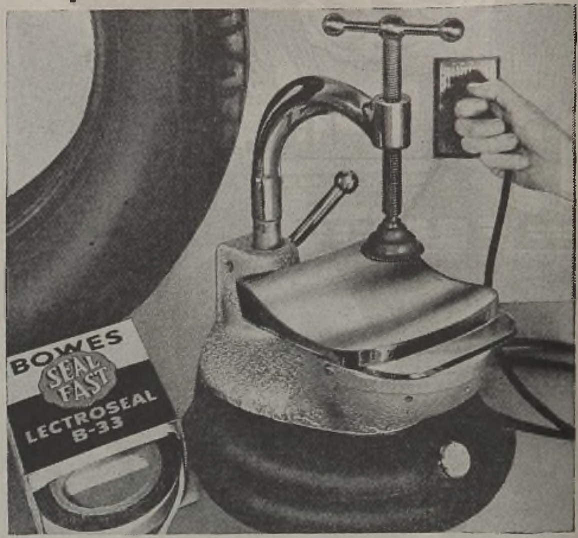

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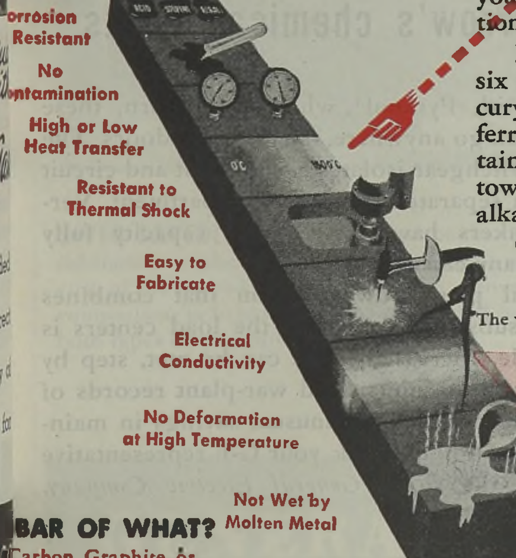

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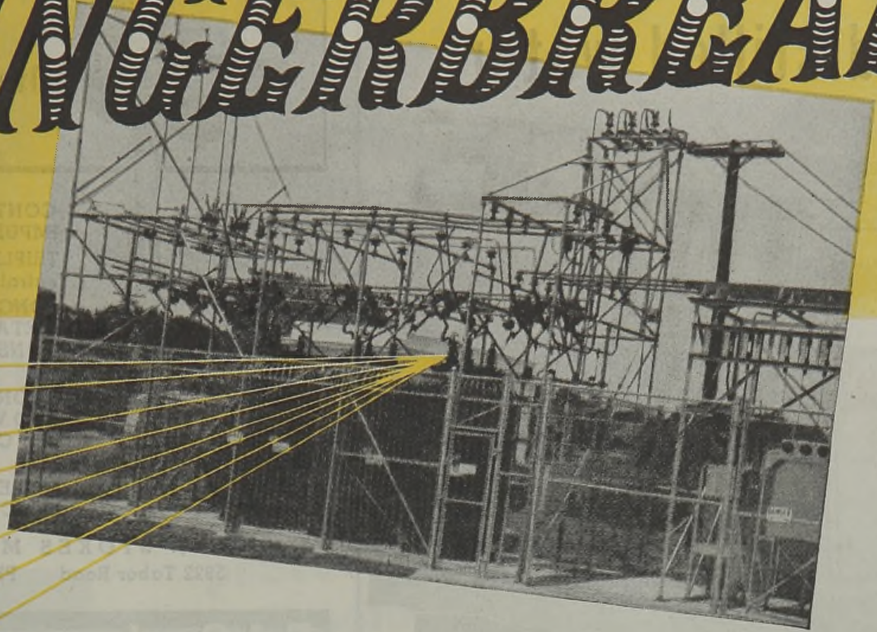

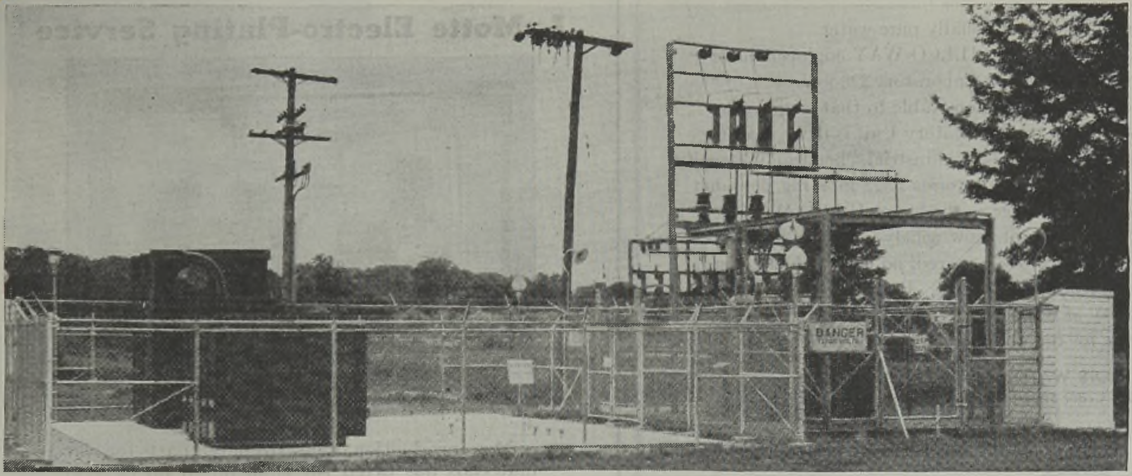

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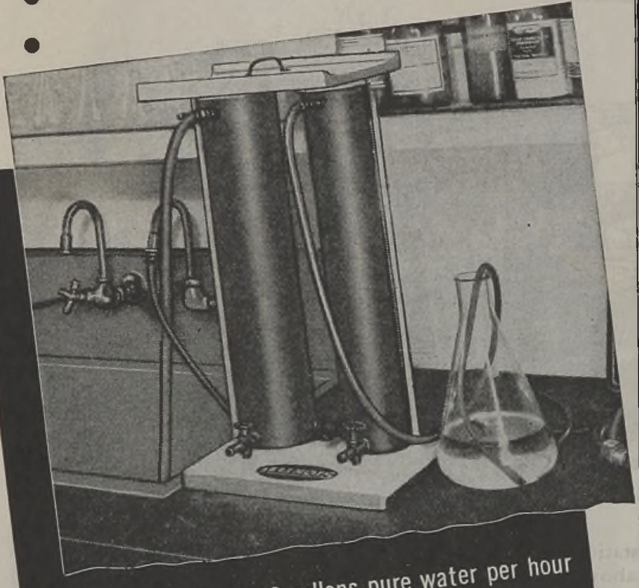

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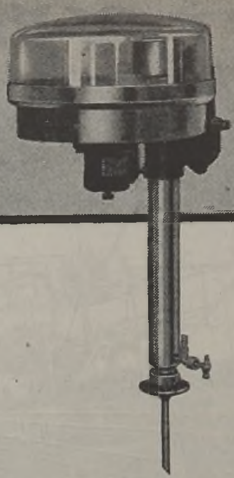

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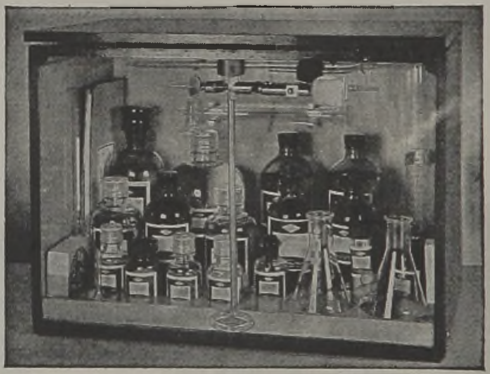

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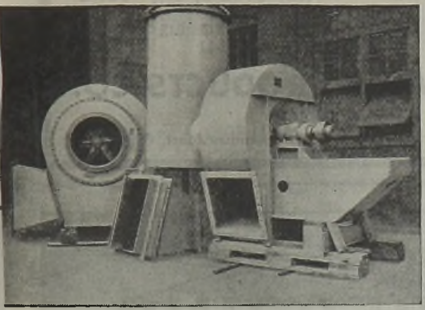

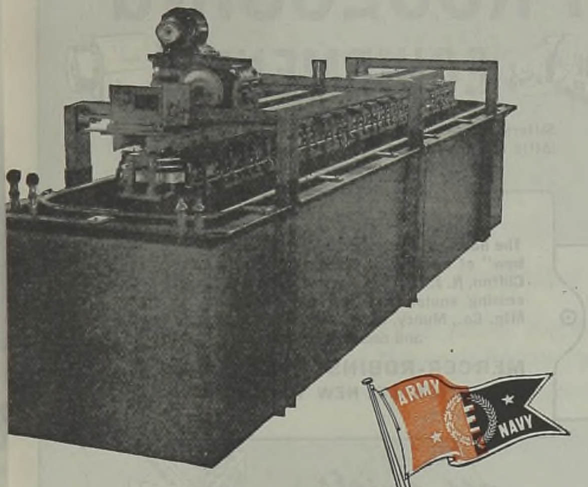

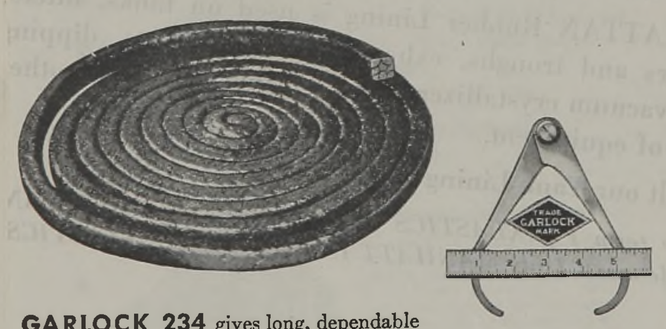
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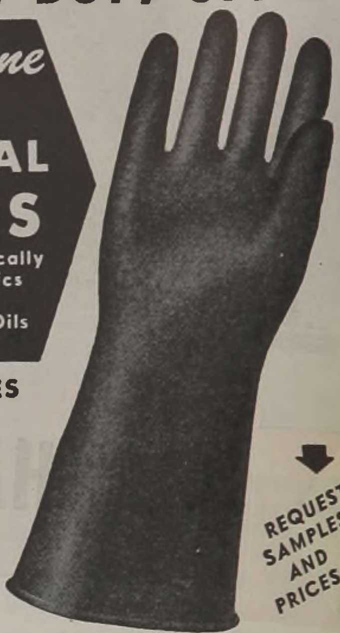

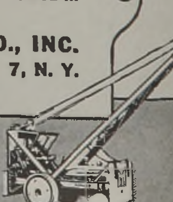

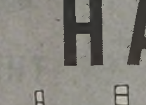

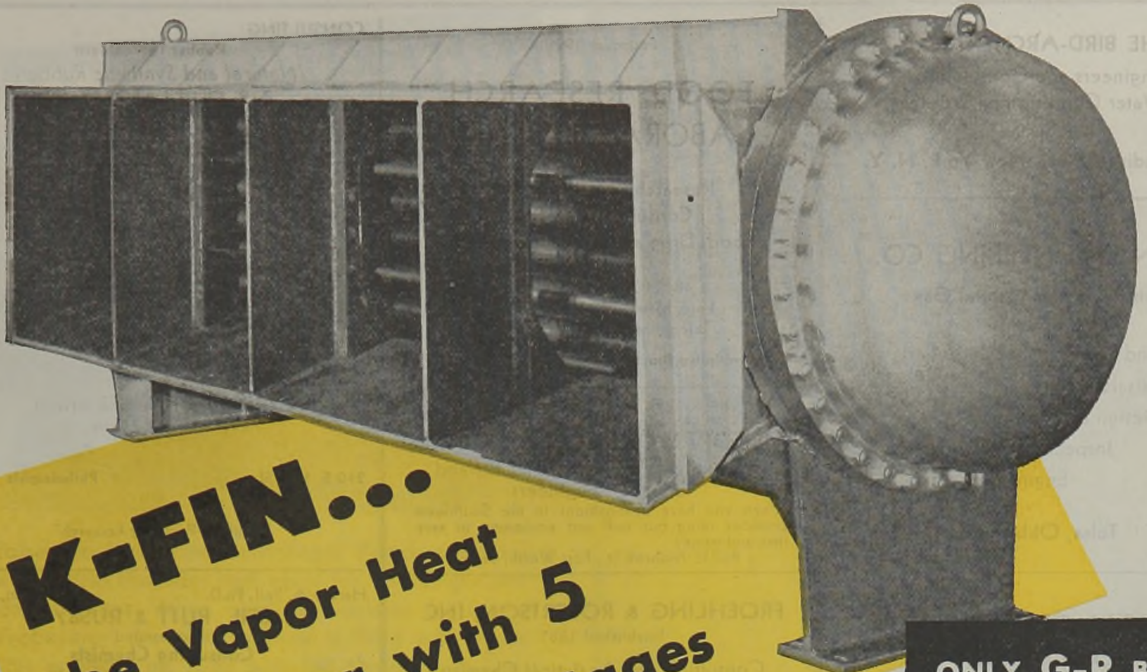

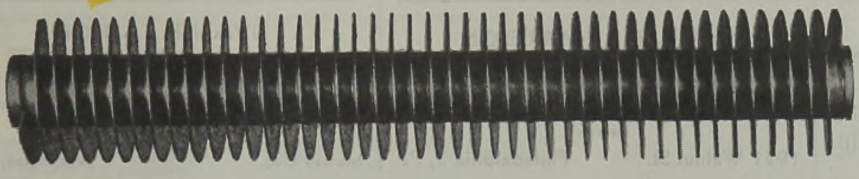

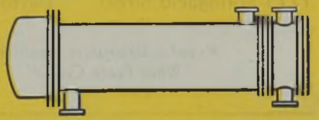

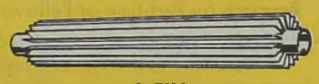

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STUFFING BOX
For Processing and
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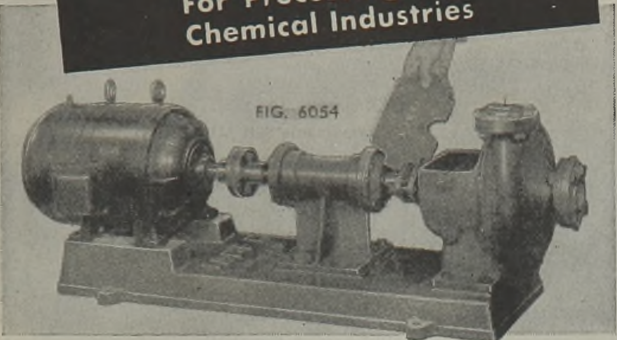

Taber single suction Centrifugal Pump, equipped with a drip chamber and cover for handling chemical solutions. When used for vacuum service on evaporators the drip chamber is filled with water. This prevents air from entering through packing. The stuffing box is thereby water-sealed.

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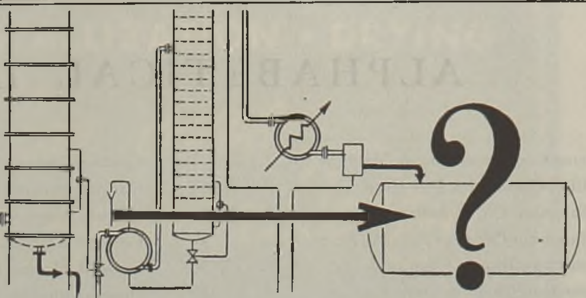
Taber Pumps for Higher Practical Performance



If you know what you want as an end-product, or what you can start with, Hicks engineers can solve your process and/or equipment problems.

- By-products
- New processes
- Yield increases
- Improved products
- Syntheses
- Recovery

may be possible in your process work. *Investigate* and *engineer now* — build now or later.

Here as in China, "To go anywhere, you must take the first step." Write

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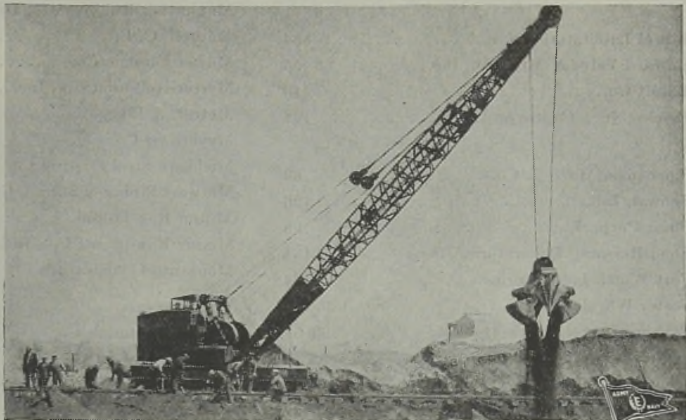
Today's accelerated production pace calls for speedy material handling. In tomorrow's period of rebuilding, the demand may be even greater. For swift, low cost operation Industrial Brownhoist equipment is unsurpassed. Write for full particulars.



Above: An electrically operated I.B. Tower Crane (20 ton capacity at 60 foot radius) helps set production records at an eastern shipyard. Right: Note the patented Monitor-type cab which allows the operator 360° visibility on I.B. gas or Diesel locomotive cranes.

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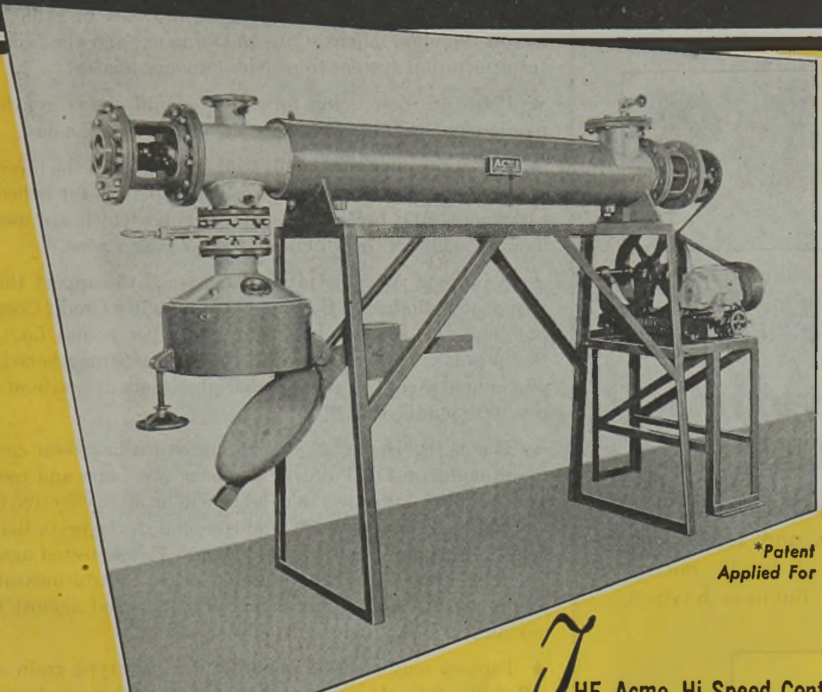

PILOT INSTALLATION

continuously producing 50 lbs. of dry chemical salt per hour from a solution, while evaporating and recovering 170 lbs. per hour of organic solvent.

*Patent Applied For

THE Acme Hi-Speed Continuous Rotary Film-Type Dryer is a stationary, jacketed cylinder having internal removable-type conveyor flights rotating at 300 R.P.M. At this speed, centrifugal force throws the material being handled against the heating surface in the form of a thin film or layer, utilizing the jacketed surface of the cylinder for heat transfer.

The Acme Hi-Speed Continuous Rotary Film-Type Dryer is operated under pressure or vacuum and may be used for the recovery of solvents. It can be used for cooling as well as heating. Inert gases may be introduced if desired, thereby producing a deodorized, dry product.

This unit is designed in single and multi-stage arrangements, fabricated of ferrous or non-ferrous metal, and in sizes to suit individual requirements. This apparatus can be adapted to many processes, resulting in elimination of separate unit operations by combining them in one machine—one operation. Thus we reduce both initial cost and cost of production.

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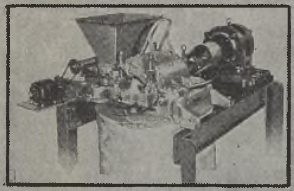


Last-Minute Flashes

FROM THE EDITOR'S DESK

The news about penicillin continues to grow more favorable. It is now generally available to hospitals and drug stores of the nation. Recently experiments were reported on the use of penicillin to cure a Gram-negative disease in a plant, and this development is being investigated with intensity. This is the first report that penicillin is effective in Gram-negative-type ailments.

★ It is reported that only 9% of the blast furnaces in France are operating. Reasons are said to be the lack of skilled workers lost in the mass deportations to Germany, and the failure of the transportation system to provide raw materials.

★ Plans are now going forward to build a new synthetic ammonia plant in India, of about 300 tons capacity a day.

★ Forest fires may be fought with helicopters if the present plans of the Forest Service materalize. The plan is for helicopters to supplement the present transport planes which are used to deliver fire fighters by parachute to the danger zone.

★ War Food Administration has agreed to support the Puerto Rican sugar industry by having Commodity Credit Corporation purchase the 1945 crop at 3.46 cents per pound f.o.b. Puerto Rican ports. The program will be further strengthened by supporting payments to growers and processors at a rate of 55 cents per 100 pounds of sugar.

★ The U. S. Department of Agriculture has been conducting experiments on DDT during the past two years and recently issued a report. It shows that DDT will be more effective than any heretofore used insecticide against some thirty pests that attack field crops, man, livestock, and trees. It was tested against 170 different species. Of this number, other control measures were just as effective against nineteen insects; and against fourteen insects DDT had little or no effect.

★ Tapioca may soon be made from a new type grain sorghum called "Cody". It is a cross between two other sorghums.

★ Electronics has entered the rubber field. Firestone Tire and Rubber Company has announced the application of an electronic rubber-curing process that is seventeen times faster than the older process. The reason for the speed in curing is inherent in electronic heating. The mass is heated throughout, and time is not lost while heat seeps through.

★ Control over potash salts has been placed under the WPB General Chemicals Order. This is in line with an announced policy of placing all chemicals under one control.

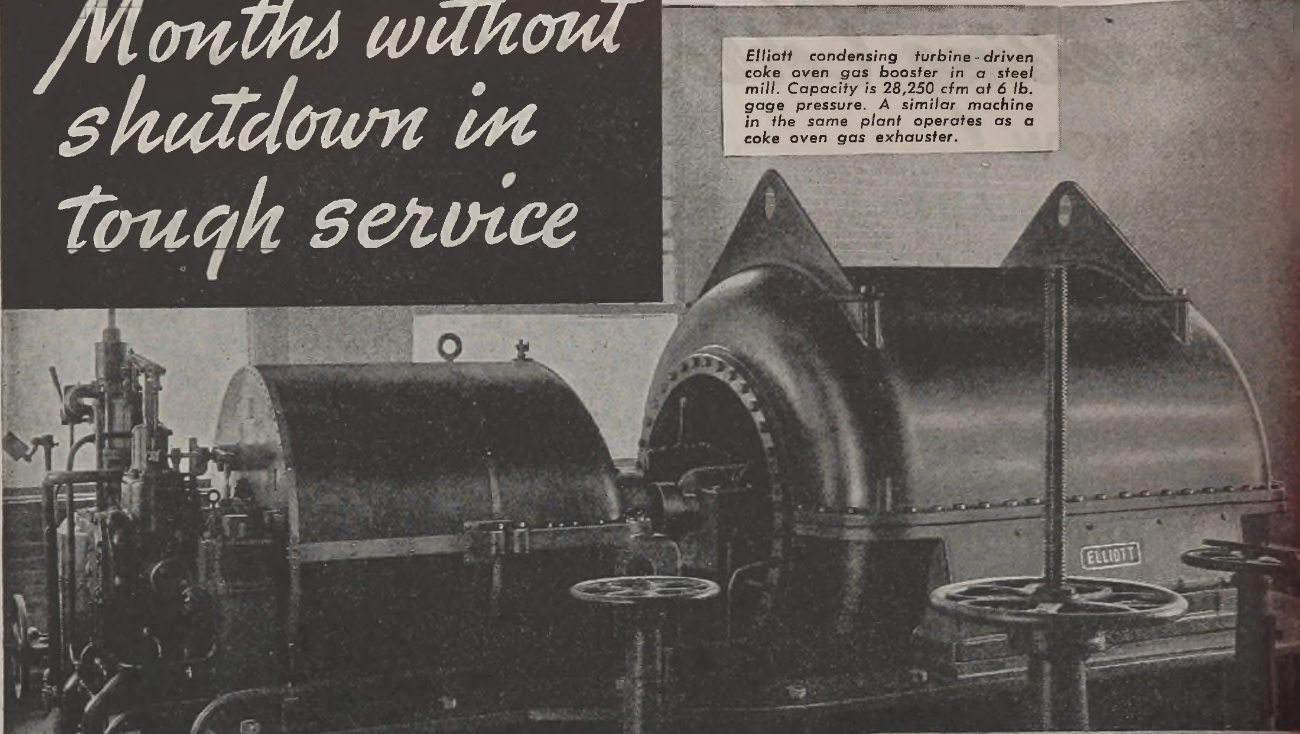
★ WPB has asked the Army to cut its demands for textiles. Civilian supplies are said to be extremely low, and the industry accuses the Army of huge stock piles. The Army claims this is untrue, stating that it is living on a hand-to-mouth basis.

★ Patents and patent contracts held by the Alien Property Custodian are to be made public for the first time under an executive order requiring their registration with the Patent Office.

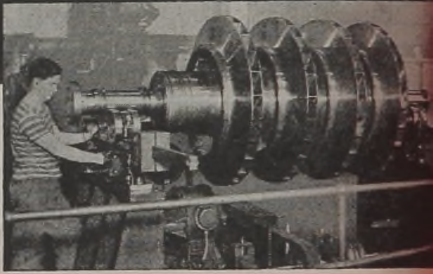
★ A record amount of oil was shipped to the East Coast during a recent week when the total reached over two million barrels a day.


FLUSH VALVE
SAFETY VALVE
PORCELAIN PIPE
ARMY
E
NAVY

Months without shutdown in tough service



Elliott condensing turbine-driven coke oven gas booster in a steel mill. Capacity is 28,250 cfm at 6 lb. gage pressure. A similar machine in the same plant operates as a coke oven gas exhauster.



At right: Typical Elliott four-stage closed type impeller rotating element on balancing machine. The rotor is balanced statically and dynamically, with extremely close accuracy, as required by Elliott standards.

This Elliott coke oven gas booster is subject to the usual operating problems encountered in such service, such as the tendency for a carbonaceous deposit gradually to reduce capacity and unbalance the rotating element. Boosters previously installed in this plant have required frequent shutdown for cleaning. But the Elliott booster has operated for months at a time without cleaning—several times the longest run ever obtained with the other boosters.

The reasons? Each Elliott blower is engineered for the job, incorporating those refinements which mean the difference between mere satisfaction and outstanding performance. Elliott welded impellers have streamlined passages and no corners where dirt can collect unevenly and ultimately cause unbalance of the rotating element.

Consult your nearest Elliott field engineer on your next blower job. Elliott builds the driver as well as the blower, making possible a more intelligent analysis of your problem and combined responsibility for the complete machine.

ELLIOTT COMPANY
Centrifugal Blower Dept., JEANNETTE, PA.
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ELLIOTT BLOWERS

THEIR RUGGEDNESS *plus* REFINEMENT *equals* RELIABILITY

3000 to 5000 square feet

OF SURFACE AREA IN ONE POUND OF

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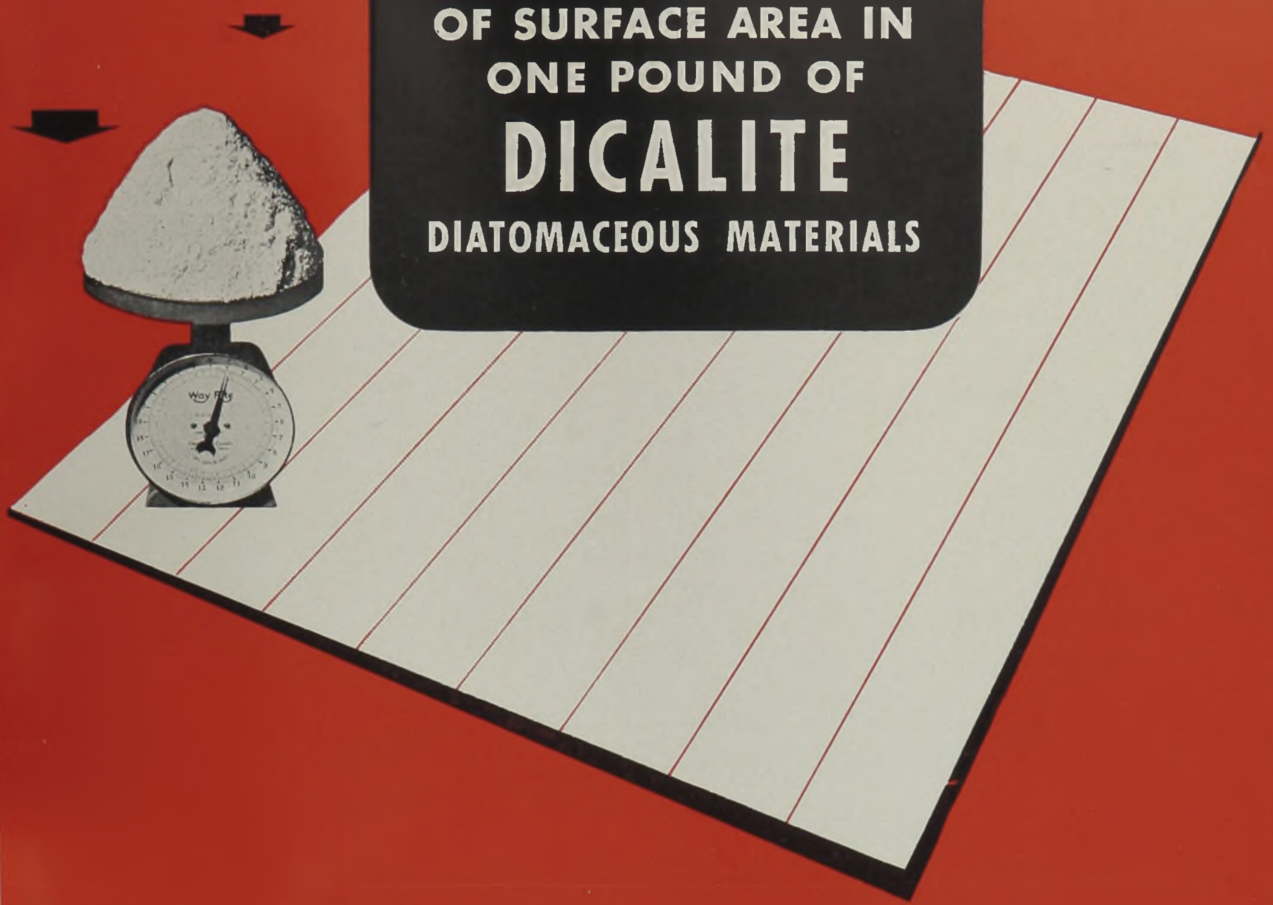
DIATOMACEOUS MATERIALS



Sounds like—and is—a tremendous surface area. It is one of the advantages Dicalite has as a filler in many products, as a carrier for catalysts, as a carrier or diluent for insecticides, as a pigment in paint, to give a few examples. Other properties are a loose weight of only 7 to 13 lbs. per cubic foot, high absorptiveness, low refractive index, fine particle size—all stemming from the unique diatom structure. Investigate Dicalite fillers to give a product bulk with small weight increase, give added strength toughness and resistance to abrasion, reduce brittleness, decrease heat conductivity, or add mild polishing qualities. Many products have been improved and their cost reduced by use of Dicalite materials. Any Dicalite office will furnish further data.

THE DICALITE COMPANY

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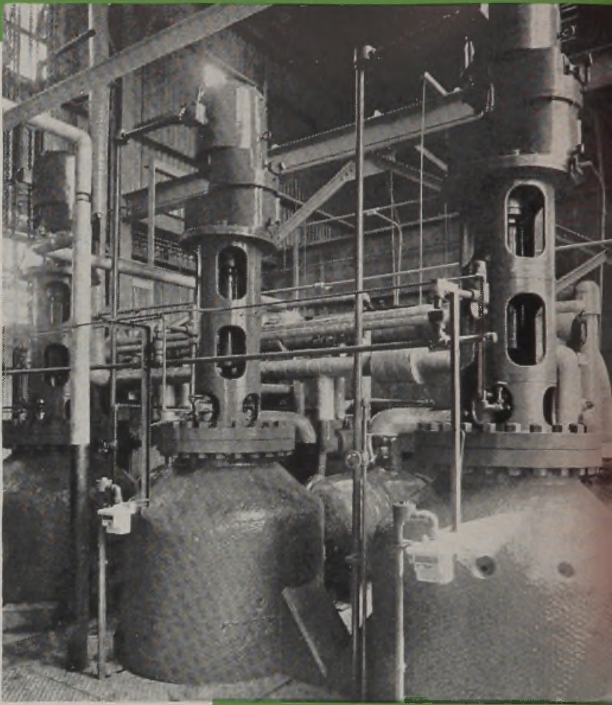
HOW SHELL OIL USES

Process Adapted Agitation



An Installation of Mixers
the Shell Oil Company P

MIXING PROBLEMS

To disperse completely and uniformly on a continuous basis a heavy, molten salt catalyst with hydrocarbon, to combine metals of construction for economy and protection and to provide special step bearing and stuffing box details to meet drastic conditions of high pressure and pressure of corrosive gases.

HOW YOU CAN SOLVE THEM

Shell Oil Company solved the problem with the *"MIXCO"* Agitator (shown above), which is just one of a complete line of *"LIGHTNIN"* and *"MIXCO"* Mixers and Agitators. Mechanical details were worked out on a cooperative basis.

"LIGHTNIN" TOP ENTERING UNITS

(*Propeller and Turbine Types.*) The extended line of Mixco Heavy Duty Agitators (up to 50 H.P.) for open and closed tanks, find wide application in the newer catalytic processes, providing intimate dispersion, fine particle size and high rates of recirculation within tank. This insures high yield and uniform results for properly designed systems. Newer types of impellers designed according to proven hydraulic principles, decrease weight and diameter of impellers. Selection of drives to meet any operating conditions.

Watch These MECHANICAL DETAILS

The following are a few of the mechanical details which Mixing Equipment engineers take into account when designing equipment to handle immiscible liquids:

Use a liquid depth at least one to one and a half times the diameter of the vessel;

Use a jacketed vessel instead of coils for heating or cooling;

Use a dish-bottom tank whenever possible;

Avoid square and rectangular tanks;

Correct placement of incoming feed lines is supremely important to the efficiency of continuous operations;

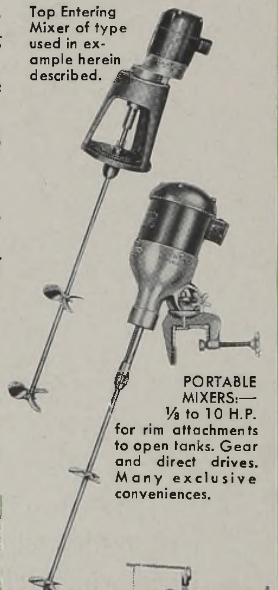
If at all possible, manifold all lines together on suction side of pump before entering tank, to provide a rough pre-mixing.

The BASIS of Our Recommendations

Twenty-three years of experience has resulted in an organization, research facilities and skill which qualify Mixing Equipment Company as a leading authority in the whole broad field of agitation.

Mixing Equipment Company offers its service in the solution of any problem involving controlled recirculation of liquids to produce physical and chemical changes, as included in the following table.

Blending Miscible Liquids	Mixing Immiscible Liquids	Crystal Size Control	Gas Absorption & Dispersion	Suspension of Solids	Heat Transfer
Simple Mixing of soluble liquids as in reducing concentration.	Washing of Liquids Extraction Contacting Caustic Treating Emulsions	Precipitation Evaporation Systems	Hydrogenation Aeration Gas Scrubbing Chlorination Gas Washing	Slurries Slaking Lime Suspension of: filter aid, activated carbon, Fullers Earth, Crystals while dissolving.	Stills Evaporators Reactor Vessels Heating Cooling



Top Entering Mixer of type used in example herein described.

PORTABLE MIXERS:—⅛ to 10 H.P. for rim attachments to open tanks. Gear and direct drives. Many exclusive conveniences.

SIDE ENTERING MIXERS:—1 to 25 H.P for horizontal use. Any size tank. Propeller type only Many models and drives.

Showing blade types and method of attachment. Number of blades is variable. Blades may be cast or fabricated.

Straight blade Radial
Turbine Simplified
for general agitation,
ferred for lead and r
covering.

Curved blade Radial Flow Turbine Simplified form for blending and general agitation.

Disperser type Radial
Turbine for gas-l
liquid-liquid, solid-l
dispersion.

• TOP-ENTERING • LIGHTNIN TRADE MARK REG. U.S. PAT. OFF. MIXCO PORTABLE • SIDE-ENTERING •

There is a Process Adapted Agitator for every size and shape of tank; for batch or continuous operation. Your savings will quickly repay the necessary modest investment. Because Mixing Equipment Co. products include *all* types of fluid agitators, you can obtain from them an impartial recommendation for the most economical solution of any problem involving fluid agitation. Mixing Equipment Company engineers will gladly assist.

MIXING EQUIPMENT COMPANY, Inc.

GARSON AVENUE, ROCHESTER 9, N. Y.

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☐ B-78—Top Entering Mixers
☐ B-75—Portable Mixers (*Electric and Air D*
☐ B-77—Laboratory Mixers
☐ Mi-11—Operating Data Sheet

Name..