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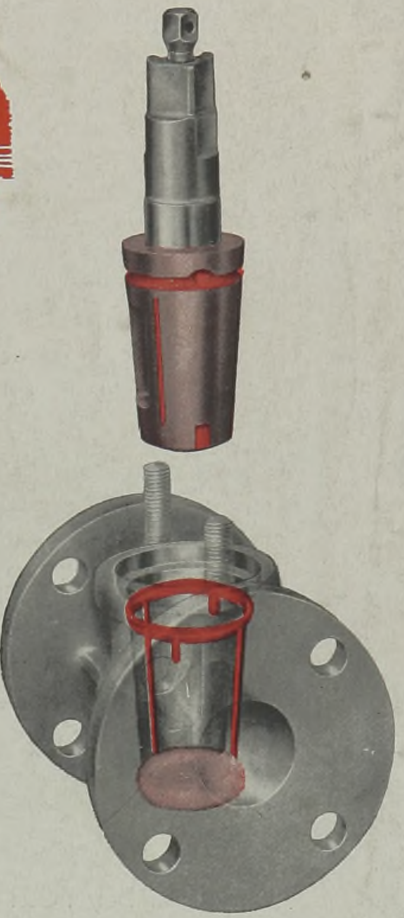

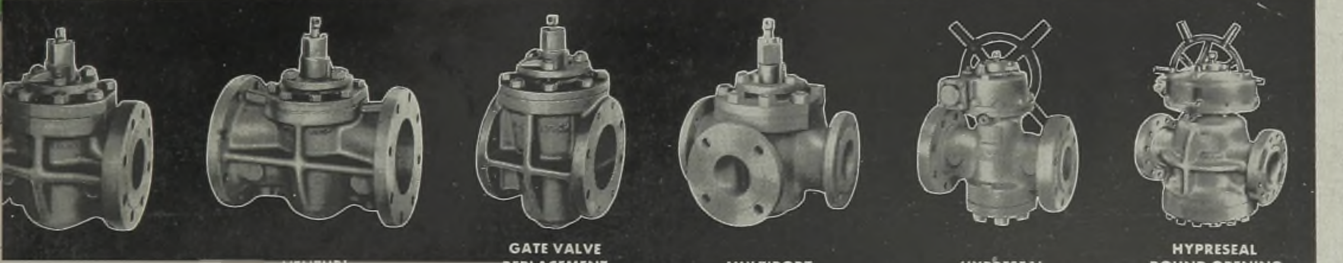

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DEPARTMENTS

TECHNICAL ARTICLES

UNIT PROCESSES

*** Indicates page number in the advertising section.**

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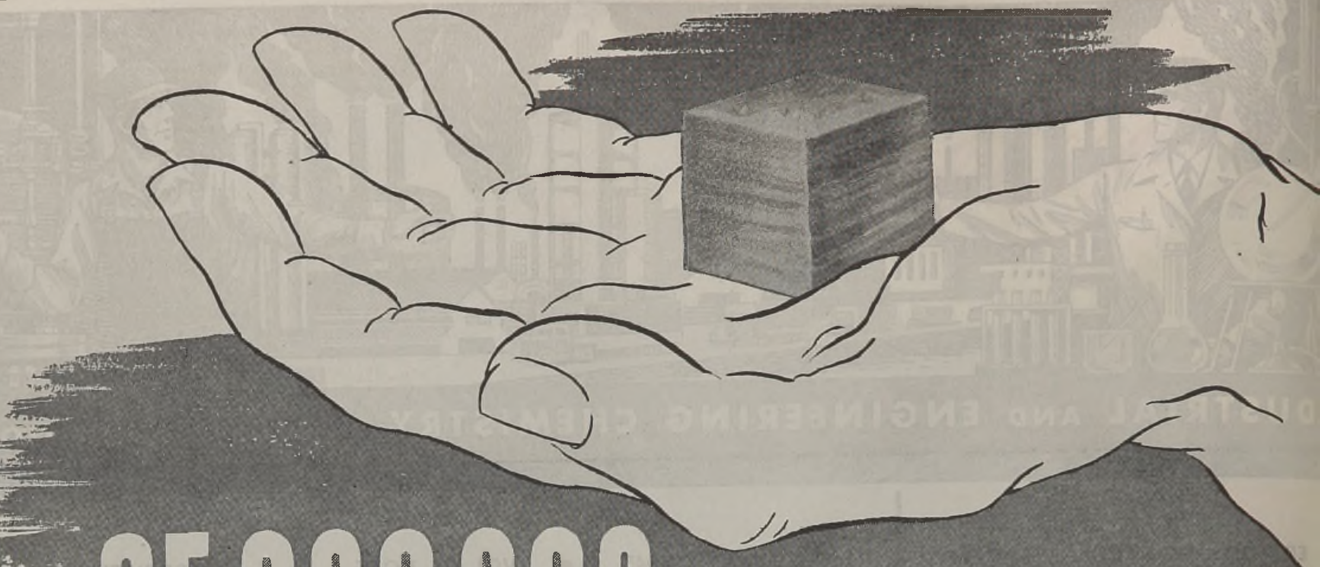

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INDUSTRIAL AND ENGINEERING CHEMISTRY
REPORTS
ON THE CHEMICAL WORLD TODAY

War and Postwar

War Research. Our war effort is becoming more efficient daily, thanks to the labors of various scientific boards. The National Advisory Committee on Aeronautics has given to the air forces many research developments of paramount importance. At a recent Army demonstration Colonel Faymonville gave credit to such research committees as OSRD, NRDC, and the Inventors Council for major assistance in perfecting the new weapons of war about to be shown.

Much of the display was a close-up of weapons already familiar to the public—long Toms, Pershing tanks (which are being outfitted with new and more powerful guns), the flame throwing tank, radar, automatic fuse cutting on antiaircraft units. However, several items deserve mention, especially one that may not see service in this war because it has just gone into production. This is a "snake" for destroying antipersonnel mines; it is made up of magnesium, powder, and rockets. At the fore end of a 100-foot section of an explosive-filled, elliptical, hollow magnesium sheet is a rocket shell. The section on which the rocket rests is turned up in front in the form of a ski to enable the section to clear obstacles. When a rocket is fired, the snake scurries over the ground. The elliptical section is filled with explosive; when the rocket comes to rest, the explosive charge is detonated and a 5-foot path, the length of the snake, is cleared through the mine field.

A telephone-line-laying coil for the Signal Corps is based on the principle of a ball of twine: The wire can be unraveled from the center of the ball. The usual spool is eliminated, weight is saved, more wire can be wound in a case, and the wire lies flat instead of kinking. Probably the most important advantage is that the operator can talk over the wire while he is laying it, by means of a telephone hooked to the end of the wire.

Chemical Warfare Service has an effective new phosphorus bomb. It is filled with steel wool pellets which give greater carrying range to the phosphorus and a better scattering effect. Lithium hydride is the basis of a new hydrogen generator; water only is needed to release the gas.

Cameras for combat photography are being made of magnesium. They have no bellows to deteriorate in the jungle, and the weight on the camera is considerably less. Optical theodolites were never made in the United States prior to the war, but now the Army has several of domestic make for artillery problems.

The latest use for nylon is crotch armor for engineers who are clearing mine areas. The nylon forms a thick unyielding pad, and this same material is the padding in new armor developed for bomber pilots. The plate used in the armor was formerly steel, but the job is being taken over by a steel-aluminum alloy. The new air armor has a trick release, and the airman can pop out of it in less than the twinkle of an eye.

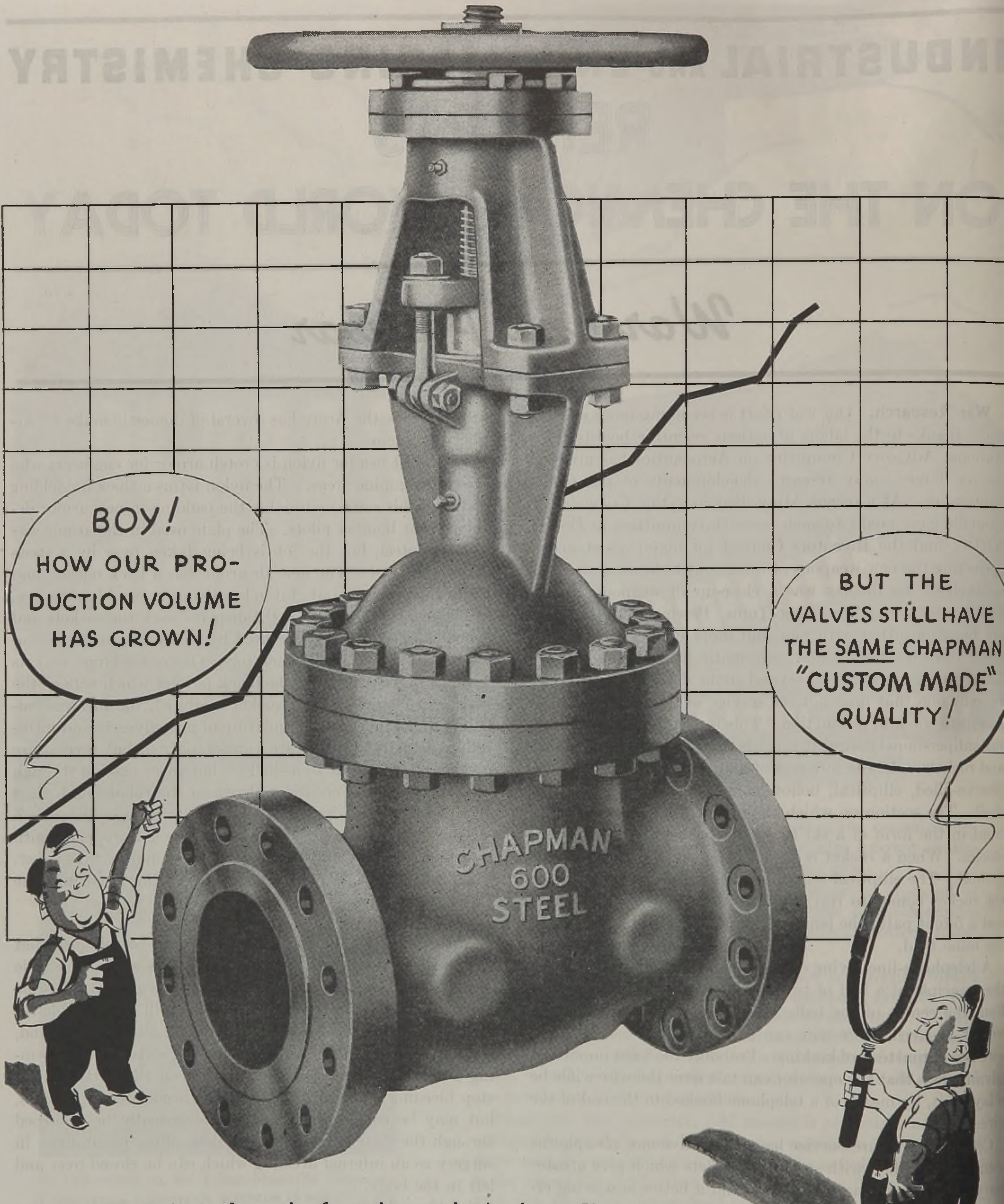
The most fascinating of the displays were the rockets and robot bombs. Rockets are fired by an electric current from either batteries or hand generators. One of the larger rockets requires 6 volts to ignite the black powder which acts as the fuel-firing charge. In the rocket exhibited, the fuel was ballisite (Nobel invention), a mixture of nitroglycerin and nitrocellulose. Most rockets are vane-stabilized, but several are given a whirl similar to a shell by hot gases passing through internal, angular Venturis. Shown in the robot bomb class was the JB2, containing a 1900-pound charge of tritonal, a mixture of TNT and aluminum. It is rocket-propelled until it gets in the air, and then a propulsion motor takes over. Final important fact disclosed is that gasoline used in flame throwers is thickened by means of a soap.

Absorbable Cellulose. A soluble form of cellulose that can be absorbed by the body and functions as a hemostatic agent is a new development which will soon go into full-scale production for military needs. When it will be available for civilian use cannot be predicted. Put on a bleeding wound, soluble cellulose stops the flow of blood by softening and forming a gelatinous clot. Gauzes applied on the battlefield to stop bleeding or to clean out wounds need not be removed, but may be covered over and will eventually be absorbed through the system. Soluble cellulose offers possibilities in surgery as an internal dressing which can be closed over and left in the body.

Soluble cellulose was announced at the St. Louis meeting of the AMERICAN CHEMICAL SOCIETY in the spring of 1941, where demonstrations of its solubility in dilute solutions of alkali and of salts aroused interest. It is formed by oxidation of cellulose with nitrogen dioxide. The reaction is specific, converting primary alcohol groups

(*Continued on page 8*)

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



BOY! HOW OUR PRODUCTION VOLUME HAS GROWN!
CHAPMAN 600 STEEL
BUT THE VALVES STILL HAVE THE SAME CHAPMAN "CUSTOM MADE" QUALITY!

How L-B drying process engineering helps YOU

Improve present drying – Select the right new method

●

THERE are many ways of drying materials. If your problem is degradation, dusting, case hardening, color, odor or uniformity, or appearance, we can help you. Let one of our experienced dryer engineers determine the right dryer, along with the proper speed and temperature to give you the most desirable product.

Link-Belt Company makes all kinds of equipment, and our engineers can give you unbiased advice on the right dryer to do your job. Take advantage of the broad experience of Link-Belt drying and process engineers to analyze your problem, to help you improve your drying or cooling, or select the right process for your product.

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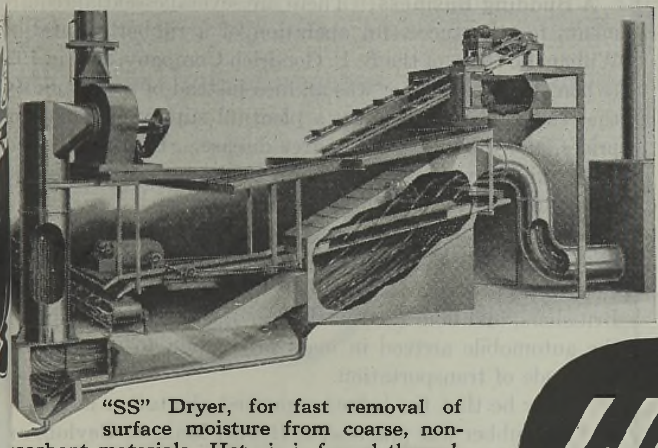

"SS" Dryer, for fast removal of
surface moisture from coarse, non-
sorbent materials. Hot air is forced through
e material as it moves forward along a shaker
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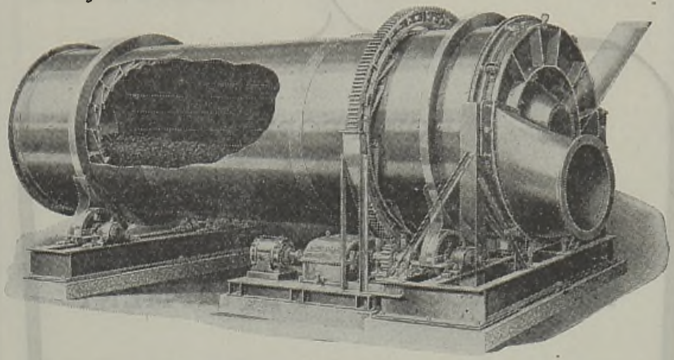
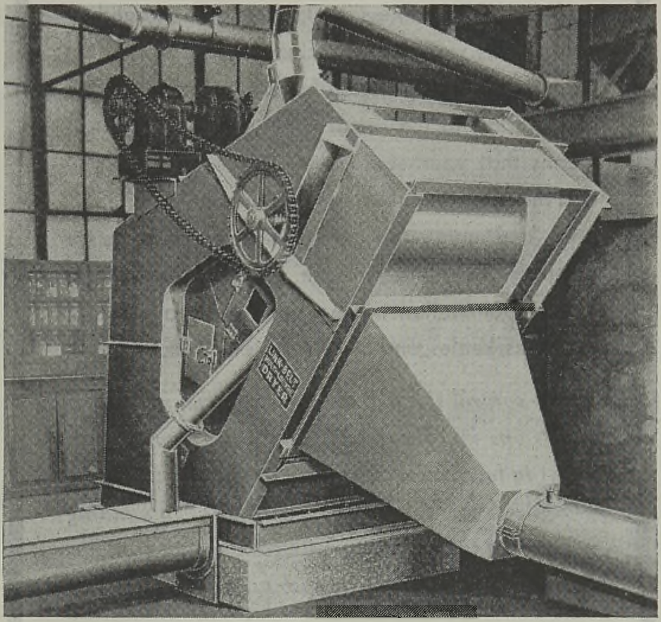
SOME LINK-BELT DRYERS

Link-Belt makes and installs a number of different dryers and coolers, which have been used successfully for a wide variety of materials.



L-B Roto-Louvre Dryer and Cooler, supreme where large volume, gentle handling, gradual drying, and accurate control are necessary. Available in a number of sizes, with equipment engineered to the job by Drying Process Engineers.



L-B Multi-Louvre Dryer applies the principle of forcing air through a constantly mixed bed of material. It is compact, economical to operate, and especially suited to materials which do not require long retention periods.

9842

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DRYERS AND COOLERS
DRYING PROCESS ENGINEERING

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

War and Postwar

to carboxyl. It was described by E. C. Yackel and W. O. Kenyon in the *Journal of the American Chemical Society* [64, 121–7 (1942)]. The physical form of the treated cellulose is not altered, and in the type now being produced it retains 85% of its original strength.

Absorbable cellulose has been critically studied at Columbia University and Parke, Davis research laboratories. Animal tests demonstrate its complete absorbability and lack of irritating properties without appreciable foreign-body reaction when left in body tissues. They also show that absorbable cellulose has definite hemostatic properties and may be used with or without thrombin or other clotting agents. Clinical investigation reveals the wide usefulness of oxidized gauze and cotton as a hemostatic dressing in all forms of surgery, war wounds, and civilian first aid. The most extensive clinical studies have been made at Columbia-Presbyterian Medical Center by V. K. Frantz, T. J. Putnam, and others, and at the Mayo Clinic by A. Uihlein *et al.* Experience with several hundred surgical cases shows oxidized cellulose to be a great convenience in surgical technique, not only as a hemostatic agent but also as an improvement on ordinary surgical gauze and cotton for all types of wounds. When it is used as a dressing or packing, absorbable cellulose can be removed later without any danger of secondary hemorrhage or pain to the patient.

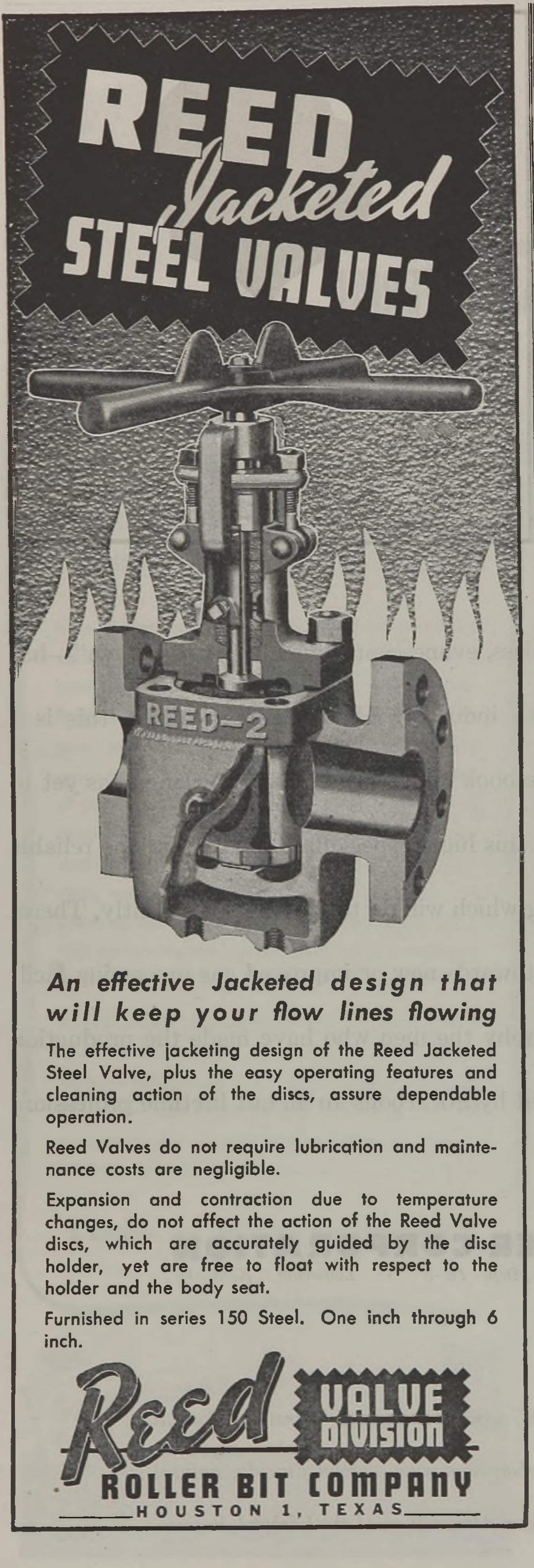
Absorbable cellulose will be packaged and distributed as a pharmaceutical because its use in the body demands the designation "drug". Incidentally, the handling of this important addition to the surgeon's armamentarium developed an unforeseen problem of great magnitude. Since the product is not stable under ordinary methods of sterilization, it was necessary to develop a new concept and technique of sterilization to ensure the safety of oxidized gauze and cotton for human use.

A Budding Business. There are several essential requirements for the successful operation of a rubber plantation. William C. Geer, of the B. F. Goodrich Company, said in 1922 (when synthetic rubber was an idea instead of a commodity) that these requirements are a plentiful supply of labor, low prices, and the treatment of tree disease. Brazil had been the leading supplier of rubber up to the turn of the century and could not meet all of these conditions.

Brazil probably lost an opportunity in trade which comes but once in the lifetime of a great nation when her rubber tree, *Hevea brasiliensis*, took root, with the aid of enterprising Britishers, and flourished in the Far East in 1900–10, just as the automobile arrived in mass production to revolutionize our mode of transportation.

It may be that the better organized plantation method of growing rubber was practical in British Malaya, Ceylon, and the Dutch East Indies, and that it was not practical in the dense and almost impenetrable jungles of South America. The Far East met the requirements set forth by Geer. It had a large native labor supply, which meant low tapping costs and reasonably cheap crude rubber, barring the periods of monopolistic control of both price and supply in late years.

(Continued on page 10



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

War and Postwar

Brazil lacked manpower for cultivating, tapping, weeding, and treating the rubber tree for blight known as South American leaf disease. That ruinous scourge has obliterated vast acreages of rubber-bearing trees; it is of interest to learn now that scientists of the U. S. Department of Agriculture, cooperating with the Ford Motor Company on the latter's plantation in Brazil, are apparently overcoming the leaf disease through an ingenious system called "double bud grafting".

This new technique goes beyond bud grafting as practiced by horticulturists and tree experts; it actually replaces roots, trunk, and the crown of the tree with healthier, disease-resistant growths. It is not easily carried out, and only the patience and diligence which characterize the agriculturist will finally yield results. Three grafting operations, one year apart, are necessary. First, a seedling selected from a disease-free tree is inserted into the root stock. During the second year cuts are made into the trunk proper, some 6 feet up, with buds from a healthy tree; in the third operation, grafting is effected above the branches. This latter bud transfer results in the growth of a new crown and involves an element of risk. The growing tree may now be resistant to blight infection but may turn out to be low in latex yield. The uncertainty arises from the necessity of waiting several years before the tree attains maturity as a rubber producer. Every effort is made to obtain the best specimen which is to serve as the mother tree for the bud grafting, but even this precaution is not always an assurance that it will run high in latex yield.

In general, however, the result of this work appears to point in the direction of more suitable strains for high-yield rubber production from South American trees and their future propagation. This may be significantly true in the instance of such scientifically operated projects as the Ford plantation. Four to five years more are needed to determine the value of double bud grafting; yet the experiment has advanced far enough to recommend itself to South American countries which wish to remain in the rubber picture.

Modern Miners. Small iron deposits are common throughout the eastern Appalachian area, and our pioneering forefathers sank many pits in this region in locations that seemed favorable. Had some of the delicate instruments now available to the modern geodesists been available then, these early miners would have had greater success in their production. During the spring of 1944, the U. S. Geological Survey, while conducting detailed magnetometer surveys near Boyertown, Pa., as part of the national effort to develop resources of iron ore near the eastern steel producing centers, found indications, through magnetic abberations, of a huge deposit of magnetite. Further research into the literature showed that several mines had, at one time, been sunk in this area, but unfortunately they had not gone deep enough and the main source of the ore was not tapped. Compared with the other deposits of ore known to exist throughout the East, this particular field is considerably nearer the surface; the rough measurements of the survey show the ore to be only 100 to 130 feet below the ground.

(Continued on page 14)

It's easier to insulate a streamlined job

NATURE found it comparatively simple to insulate a streamlined job like the seal, but did you ever try to wrap up a giraffe? Men who have to insulate flanged or threaded fittings in a piping system will readily understand the comparison. By the same token, Tube-Turn welding fittings give a streamlined silhouette which is easily insulated, with never a leak to cause insulation replacement.

Other Tube Turns advantages directly related to cost include lighter weight, greater strength, longer life, and the consequent lower maintenance. Smooth turns free from obstructions make for increased efficiency of flow. And Tube-Turn welding fittings permit installation of a piping system in less space, with greater flexibility of layout.

For complete information on the superiority of Tube Turns' exclusive manufacturing methods and data on successful installations in many industries, write for Catalog 111.

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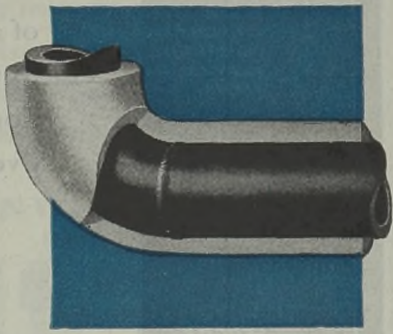

Smooth, permanent insulation

Because Tube-Turn welding fittings make smooth, leak-proof turns, insulation goes on easily, never needs to be removed because of leaks.

TUBE-TURN ***Welding Fittings and Flanges***

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SOUTH CELL RM
12 ROWS @ 17 CELLS EACH
NORTH CELL RM
12 ROWS @ 17 CELLS EACH
3"
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27" HG. VAC.
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SER. WATER HOSE
CONN. FOR WASHING
24"
2ND EFFECT
20" HG. VAC
161°F VAPOR
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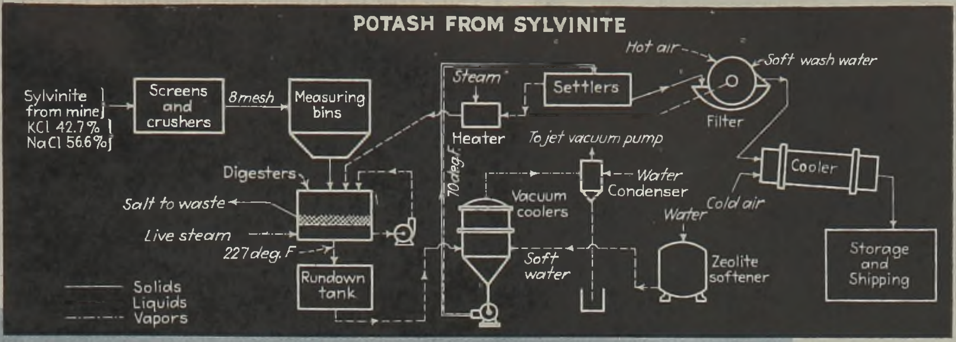
Sylvinite from mine KCl 42.7% NaCl 56.6%
Screens and crushers
8 mesh
Measuring bins
Digesters
Salt to waste
Live steam
227 deg. F
Rundown tank
Steam
Heater
70 deg. F
Settlers
To jet vacuum pump
Vacuum coolers
Water
Condenser
Soft water
Water
Zeolite softener
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Storage and Shipping
Solids
Liquids
Vapors


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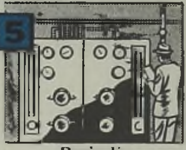
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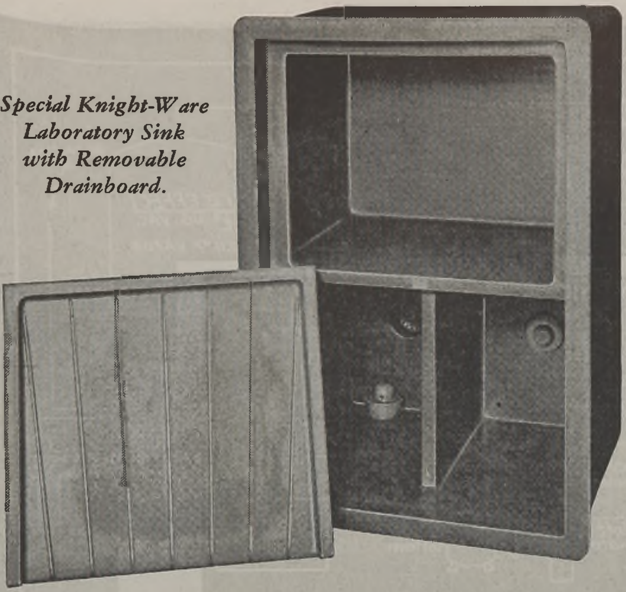

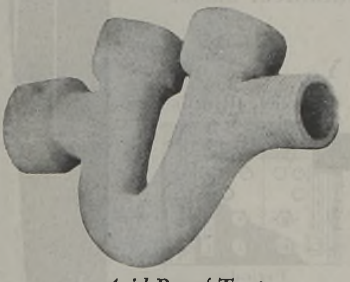

I. & E. C. Reports on the Chemical World Today
Technology

New Job for H_2SO_4. The experiment of subjecting the pine tree to sulfuric acid treatment to stimulate the production of rosin and turpentine evidently has encouraged a wider trial of the idea during the naval stores season which began April 1. Heretofore little has been known of the process outside of the experimental area in the South, but we now learn that sulfuric acid (40 and 60%) extends the flow of gum by retarding coagulation or hardening on the tree facing.

When the exudation of rosin gum is stopped by coagulation, it is necessary for workmen to chip a new "face" so that the flow can be resumed. Sulfuric acid, sprayed on the facing, delays that action to such an extent that chipping and acid treatment once every two or three weeks yields as much gum as chipping every week without the acid. This means that a woods worker in the naval stores belt need face only 7000 trees in three weeks instead of 7000 to 8000 per week.

The acid applied to long leaf pine is 60% strength, and that for slash pine, 40%. Propagation of the slash pine is favored in the South: (1) because it can be worked fifteen years after planting, and (2) because it is a good producer of gum and a valuable source of lumber. It was the slash pine which benefited industrially from the researches conducted by the late Charles H. Herty. During the 1945–46 naval stores season, experimental sulfuric treatment will be tried on at least five tree "crops" (10,000 trees each).

Much better chipping practices may result from the use of the sulfuric treatment in the belt. To obtain an effective facing, it is usually necessary to cut through the bark of the tree, down to and slightly below the surface of the wood. Chipping of this character is avoided if sulfuric is used, as it is necessary only to chip the bark, leaving the actual wood surface for the acid spray.

Some difficulty has been experienced in inducing certain workers to use spraying equipment. If precautions followed by industry in handling sulfuric acid are observed, however, the process can be applied with a minimum of danger to tree workers. The acid treatment idea may prove to be the greatest advance in the naval stores industry since Herty's cupping system replaced the ancient box method of gum collection.

Indicating Soap. Poisoning by nitro compounds was a serious menace during World War I. An answer was found when someone noticed in an aniline plant that the dark skinned workers were able to work longer than the fair skinned. Substitution of negroes for the work solved the problem. During this war strenuous efforts were made at the beginning of our expanding munitions program to prevent health hazards from becoming production menaces. One of the major techniques utilized was the removal of dust from the atmosphere. Toxic effects may arise from inhaling dust and vapors, but absorption of TNT, tetryl, and other nitro bodies through the skin causes dermatitis, sickness, and eventual degeneration of the liver. Removal of nitro compounds from the skin, therefore, also became a necessity. Washing with ordinary soap is inadequate.

A test for the presence of nitro bodies on the skin was available, and an agent was known

(*Continued on page 18*)

How to Select a Screw Conveyor

(If that's what you need)

Screw conveyors offer many advantages in handling bulk materials. They are efficient in power, space, and maintenance requirements; first cost is relatively low. They permit the use of dust and moisture-proof enclosures. They can be used alone or with other types of conveyors.

But to secure maximum efficiency, first be sure a *screw* conveyor is the type you should have; second, be sure you select the right *kind, design,* and *size* of screw conveyor.

To be sure on both points, consult a Link-Belt Materials Handling Engineer. His broad experience, and knowledge of all types of equipment will be helpful. And he can give you unbiased advice, because Link-Belt makes a wide variety of conveyors.

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A great deal of information on screw conveyors is available in Data Book 1289. Diagrams, tables, illustrations—128 pages. Send for a copy today.

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Continuous rolled flights, one piece, secured to shaft by welding and formed steel reinforcing lugs. Large pipe gives greater torque; no laps or rivets to catch dirt, or to wear out. Tapered cross section for greater strength.

SECTIONAL FLIGHT

Individual flights riveted together, secured to pipe or shaft with forged steel lugs. Easy to repair by renewing sections; costs less to make special sizes, types, materials.

RIBBON

For sticky materials such as molasses, raw sugar, hot tar, asphalt, etc. Available with beveled or straight edges, helicoid or sectional flights, single, or multiple ribbon for mixing action.

FOR ABRASIVE MATERIAL

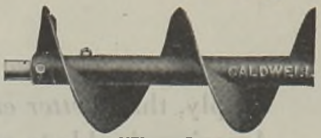
Conveyor flights of special abrasion resisting metals are available; or sectional flights cast in iron, alloys and steel. Case hardening or stellite treatment if needed.

CORROSION AND HEAT RESISTANCE

Corrosion resisting materials such as aluminum, bronze, copper, monel, stainless steel and others can be used when available and when justified. Heat resistant alloys or extra heavy flights are available for high temperature applications.

FOR MIXING

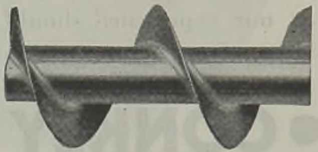
Multiple ribbons or paddles in various designs can be used as continuous or batch mixers for light or heavy materials, dry, damp, or wet.



HELICOID

SECTIONAL FLIGHT

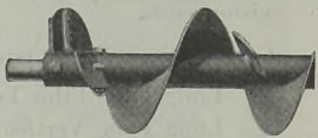
RIBBON



STAINLESS STEEL

CAST FLIGHTS

DOUBLE FLIGHT



MIXING PADDLES

FOR LIFTING

Helicoid Rotor Lift, with special flighting, hung from top thrust bearing, in dust-tight steel housing.

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GENERAL AMERICAN *for* BETTER

Nothing is easier to claim, or harder to supply, than *better engineering.* General American is able to offer better engineering because we have secured the services of *outstanding engineers,* and have furnished them with every facility for better, more constructive work. We would like to demonstrate what this can mean to you.

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For processes incorporating both evaporators and drum dryers our Technical Staff is available to help you lay out and connect these units. We have our equipment details and our experience should be helpful. Use our service wherever two or more different units of our manufacture are involved, be they filters, evaporators, agitators, dryers or other items marketed by us. Any special equipment is more efficient if the entire group used in the process is designed to work as a unit.

• CONKEY EVAPORATORS

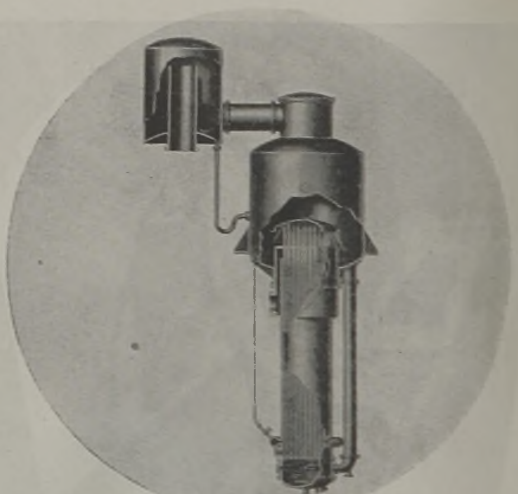
No type of equipment manufactured by General American better demonstrates the "Better Engineering" offered by this organization than Conkey Evaporator Equipment.

Every Conkey Evaporator design provides for maximum accessibility, minimum entrainment losses and high heat transfer. Each unit will give long-time, trouble-free operation with low maintenance and supervision costs.

Conkey evaporating equipment includes:

- Long Tube Film Type Evaporators
- Long Tube Vertical Recirculation Evaporators
- Vertical Tube Forced Circulation Evaporators
- Submerged Tube Forced Circulation Evaporators

The flexibility of General American designs makes them readily adaptable to efficiently meet special process requirements.

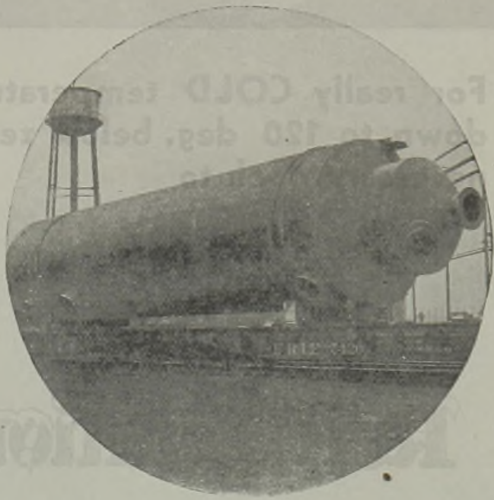


• GENERAL AMERICAN DRUM DRYERS

After many years of development, General American Drum Dryers are now widely accepted as a leader in the field of industrial drying equipment. For among many patented features are the "Air-Finger" blade bar which prevents sticking and fouling, cast-iron drums, finished under steam pressure and temperature to assure true cylindrical shape under working conditions, and steam joints that require no packing or lubrication other than the condensate itself. We would be happy to explain in detail how a General American Drum Dryer can increase your production capacity—lower your cost, because it is individually engineered to do a job—not just to meet a "spec."

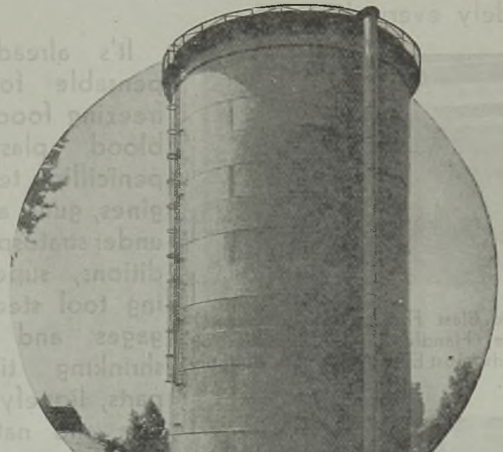
ENGINEERING!

•PLATE FABRICATION OF EVERY SORT



General American's Plate & Welding Division at Sharon, Pa. is *headquarters* for a diversified list of plate fabrication equipment.

If you are in the market for accumulators, crystalizers, dissolvers, heat exchangers, absorption towers, condensers, rotary kilns, digesters, storage tanks for oil, water, acid, etc., or any of the many types of plate fabrication—remember, General American is equipped to manufacture virtually anything made of carbon, stainless and alloy steels, Everdur, aluminum and other special alloys—either welded or riveted. General American offers, as well, complete X-ray facilities, heat-treating and stress-relieving furnaces and is in position to build and test all classes of welded vessels to API-ASME, ASME and other codes. Its unusually large manufacturing facilities are further supplemented by a staff of recognized engineers and scientists—complete research and development laboratories at both Sharon and Louisville, as well as a large field erection department for either foreign or domestic work. This all adds up to a combination which we believe to be unmatched elsewhere in America. Don't hesitate to call on us for any information that can be of assistance to you.



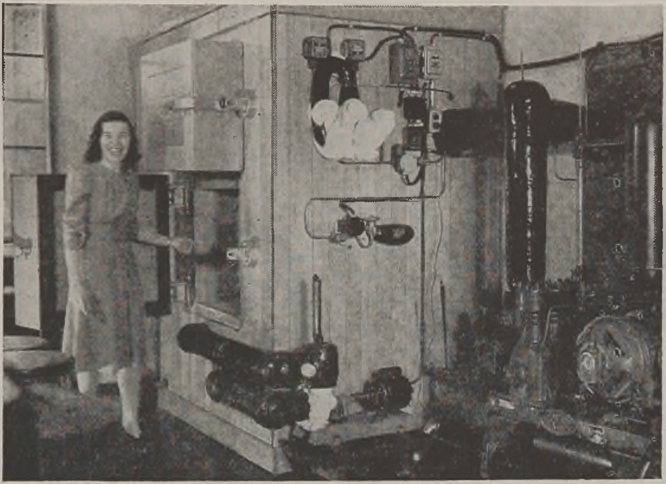
GENERAL AMERICAN

TRANSPORTATION GATX CORPORATION

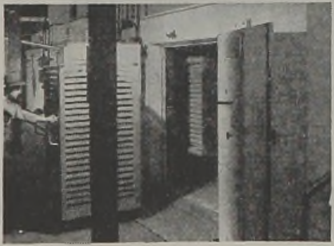
GENERAL AMERICAN

PROCESS EQUIPMENT DIVISION **PLATE & WELDING DIVISION**

General Sales Offices: **514 Graybar Bldg., New York 17, N. Y. •** ***Works:*** **Sharon, Pa., and Louisville, Ky.**
Sales Offices: **Louisville, Chicago, Sharon, Cleveland, Pittsburgh, St. Louis Salt Lake City,**
San Francisco, Tampa, Washington, D. C.



Frick Blast Freezers of the Tunnel Type, Handle Large Quantities of Foods Most Effectively. See Bulletin 147.



Smaller Producers Find Frick Blizzard Freezers the Answer to their Needs. See Bulletin 148.

that was partially effective in their removal. The Webster skin test, in which an alcoholic solution of sodium hydroxide is daubed on the skin after washing, gives a purple color in the presence of TNT, a blue color with DNT, and a dark brown color with tetryl. The test is useful in determining the effectiveness of preparations for the removal of nitro bodies, and it has had a psychological effect in impressing workers with the need for thorough washing, but it cannot be used for removal. For this purpose a 10% solution of sodium sulfite, followed by the usual soap and water bath, was recommended. Sodium sulfite turns deep red in the presence of nitro bodies. This method, however, was too tedious for the average worker since it often required repeated treatment, and a simpler method was desired, preferably a single product.

A bar soap was not suitable because a sufficiently high salt-soap ratio could not be obtained, because it presented an unsightly appearance after once being used (a deterrent to further use), and because it introduced a safety hazard in the showers. Furthermore, the addition of sodium sulfite to a liquid soap caused it to separate on standing. Potassium sulfite, however, which is compatible with liquid soaps, proved just as effective. Thus the worker is provided with visual evidence that he is removing TNT from his skin, and he is encouraged thereby to wash thoroughly and so safeguard his health. In fact a major problem of this safety program was to warn the worker, without scaring him, of the danger in not washing. A disagreeable odor, associated with the use of sulfite in early soaps, has since been eliminated.

One manufacturer considered that wetting agents in the soap might improve it. Several were found which removed nitro bodies so efficiently that potassium sulfite is now included in this soap simply as an indicator. It is the sulfite ion which produces red suds with TNT.

The Government now requires soap of this type to be used in all munition plants handling nitro bodies. Since this soap was introduced, the incidence of dermatitis and sickness has been markedly reduced, largely, it is thought, because of the 16-hour rest afforded the system every day by thorough washing. A small percentage of individuals are sensitive to the presence of salts in soap, and those to whom it is a skin irritant are removed to other jobs. While improvements in dust removal have been even more important in the over-all picture, these special soaps have played a significant part in improving health and safety in munition plants, and their value as a safeguard against possible long-range effects of nitro poisoning can only be imagined.

Plant Hormones. Naphthaleneacetic acid comes close to being the answer to an orchardist's prayer, for applied to fruit trees at different times in the season and in varying concentrations, it appears to accomplish whatever is needed at the moment. It has been in use for five years as an apple-set spray to reduce premature dropping of fruit and to permit the whole crop to be picked at the same time; recently it has been found effective in thinning blossoms, if applied early in the season. This artificial thinning at the blossom stage replaces the natural

(*Continued on page 22*)

advertisement.

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

U.S.I. CHEMICAL NEWS

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

SO_2 Household Fumigant Prepared with Acetone

In spite of its many desirable qualities as an insecticidal fumigant, sulfur dioxide has always been hard to handle because it is a gas at ordinary room temperatures. Mixed with acetone, sulfur dioxide becomes a definite liquid compound, whose vapor pressure is sufficiently low to allow it to be packaged in ordinary tin containers. Furthermore, a mixture of 1 part acetone with 1.9 parts sulfur dioxide, by volume, is non-inflammable in all concentrations in air. This liquid is stable while confined, but upon exposure to air decomposes and becomes progressively volatile.

In tests, the liquid was absorbed in diatomaceous earth pellets, and a quantity of these pellets was exposed in a room containing the test insects. The compound, when evaporated into the air, was lethal to the insects, which included bedbugs, flour beetles and carpet beetles. Treatment was harmless to wallpaper, white and colored fabrics, painted surfaces and metals.

Apparently the acetone-sulfur dioxide compound holds possibilities as a commercial fumigant, and will bear further investigation.

How to Make 2 = 3

This year, Washington reports, there will be *only two* War Loan drives, not three. But the total need is no less. For the Battle of Japan has just begun — and it's going to be a lot tougher and longer than many of us expect. So — let's stretch 2 into 3 by buying *bigger extra bonds* in this, America's Big Seventh War Loan drive.

Thermal Conductivity of Normal Alcohols

Recent studies at an eastern university have determined several new figures for the thermal conductivity of normal alcohols at 30 C. They are as follows:

Alcohol	*New figures*	*Others*
Methyl	0.00050	0.000503
Ethyl	0.00011	0.000433
n-Propyl	0.000380	0.000409
n-Butyl	0.000365	0.000400
n-Amyl	0.000365	0.000388

Pharmaceutical Lactones Yielded by New Process

Structurally complicated lactones, such as the cardiac poisons of the digitalis, strophanthus and squill series, may be prepared from easily-available products by a process discovered by a Swiss scientist. Basically, the process comprises condensing saturated or unsaturated lactones which are substituted by halogen with carbonyl compound. The condensing agents suggested include metallic alcoholates such as sodium ethoxide. Ether, acetone or both also enter into each of the four processes given as examples.

New U. S. I. Liquid Insulation Has Wide Range of Uses

Product Exhibits Remarkable Ability to Protect Electrical Systems from Moisture, Wet Weather and Many Acids

A unique insulating material which has won wide acceptance as a protector of electrical systems in automotive and amphibious combat equipment has been added to the list of products of U. S. Industrial Chemicals, Inc., according to a recent announcement. While the new product, trade-named PiB Liquid Insulation, will make an ideal companion product for the company's Super-Pyro Anti-Freeze in the automotive field, the company expects extensive expansion of PiB's market in the farm, marine and industrial fields.

This motor was removed from an oil burner in a flooded cellar where it had been "drowned out". PiB was sprayed into the motor and in a matter of minutes the motor was running smoothly. To test the "staying power" of PiB, the motor was then submerged in soapy water, where it has been running, intermittently, for two years without a hitch.

Long-Lasting Protection

The new product is described as a liquid with powerful penetrating action and high resistance to the action of water, ordinary acids, oils and greases. Its viscosity is low enough so that it flows freely into hard-to-get-at nooks and crannies and can be easily applied by brush or spray. Good water-repellent properties coupled with a strong "wetting" action enable PiB to undermine and displace water which may be present in the wiring system or on insulating surfaces. PiB has a dielectric strength of 4000 volts per mil; its protective qualities, under normal conditions, last for a minimum of six months.

War-Tested

Ignition systems on amphibious combat equipment are subjected to the severest kind of conditions. Salt spray and soggy climates all tend to break down insulation and cause corrosion. The most important current use of PiB is in protecting the ignition systems of American amphibious war machinery.

PiB is winning increasing popularity among operators of buses, trucks and passenger cars. It is used to waterproof ignition systems, to prevent corrosion and current losses in batteries, to re-insulate cracked and dried-out wiring. In the marine and farm fields, PiB is seen to have a particularly bright future. From yacht to modest outboard, marine equipment of every type will benefit from the protection PiB affords against starting failures and the ravages of salt air. Farm equipment that must stand up under hard usage and

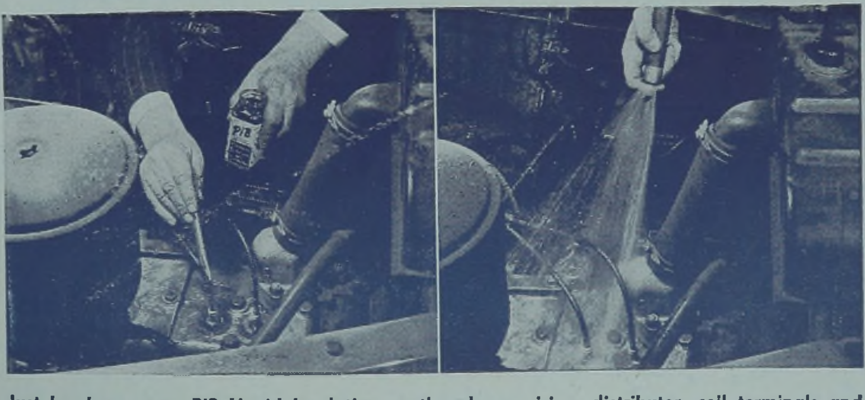
(*Continued on next page*)

New British Insecticide Exhibits High Potency

Efforts of a British concern to find an easily synthesizable replacement for scarce and costly derris have resulted in the development of a new insecticide which they report to be five times as potent as D D T.

The new substance is benzene hexachloride, briefly identified as "666" because of its formula $C_6H_6Cl_6$. Tests revealed that the gamma-isomer, present in the crude material in concentrations of from 10 to 12 per cent, was more toxic to weevils than any substance that this concern had ever tested. On the other hand, the alpha- and beta-isomers are virtually non-toxic.

If laboratory results are duplicated in commercial applications, new insecticide formulas will undergo drastic revisions.



Just brush or spray PiB Liquid Insulation on the plugs, wiring, distributor, coil terminals and battery of a water-stalled engine. Step on the starter and you're ready to roll! You can literally "hose down" an engine that has been properly treated with PiB and it won't even miss.

May ★ U.S.I. CHEMICAL NEWS ★ 1945

Patent Granted on All-Purpose Insectifuge

As previously described in Chemical News, a government-developed all-purpose insect repellent is doing a remarkable war job in protecting our fighting forces against the variety of insects they encounter on different parts of the globe. One of the vital ingredients of this repellent is U.S.I.'s Indalone.

Recently, a patent has been assigned to the United States, as represented by the Secretary of Agriculture, covering the composition of the product. The patent describes it as a ternary solution comprising by volume from 33½ per cent to 80 per cent of dimethyl phthalate, and complementary equal parts of 2-ethyl-1, 3 hexanediol and n-butyl mesityl oxide oxalate. (Indalone).

Bitter Soya Taste Yields to Alcohol

The bitter, beany flavor of present-day soya flour has seriously limited the use of this mineral- and protein-rich flour in bakery products. A new alcohol process for extracting the soyabean oil, however, gives promise of overcoming this handicap. According to a recent report, the new process leaves a sweet-eating bean for grinding into a flour which can be used in greater proportions for enriching bakery products.

Urethan May Play New Bactericidal Role

Experiments with urethan and other carbamates, such as butyl and prophyl, indicate that these compounds, when combined with sulfonamides, have unexploited possibilities as bactericidals and bacteriostatics, according to a recent report.

Indications are that, in addition, urea and urethane both antagonize slightly the sulfonamide inhibitors and that they increase the solubility and bacteriostatic activity of the sulfonamides. Both are effective mainly against Gram positive bacteria and to a lesser degree against Gram negative bacteria.

Tests indicate that urethan is superior to urea in all respects.

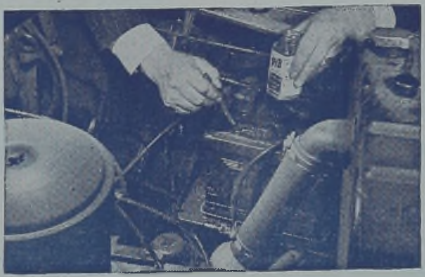
New Liquid Insulation

(Continued from preceding page)

exposure to weather also will give longer, more reliable service.

Industrial Uses

In industry, PiB appears to have limitless possibilities. Motors which operate in damp atmospheres can be protected simply by spraying with PiB. Open switchboards, control panels, automatic signaling systems and similar electric equipment can likewise be protected with PiB. The emergency uses of PiB—in treating drowned-out motors, leaking panel boards and other moisture-affected electrical equipment—should make it a "tool" every maintenance man will want to have in his kit.



Above, you see PiB being applied to a battery. Photo below shows test to determine current leakage. New battery shows no leakage. Used battery, prior to treatment with PiB, showed sufficient leakage to cause electrolysis and consequent corrosion of battery holders, cables and terminals. Same battery *after* PiB treatment showed no measurable leakage. It is estimated that periodic treatment with PiB can add 10 per cent to the life of a battery. However, PiB's biggest contribution to battery life is made indirectly — by assuring quick starting of motors even after long idleness in damp weather.

TECHNICAL DEVELOPMENTS

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

A new plastic material, which is claimed to transmit as much visible light as window glass, yet block all harmful ultra-violet radiation, is now on the market. **(No. 931)**

USI

A transparent new fabric is described as being as sheer as voile, but with exceptional strength and wind and water resistance. It is available for development work. Suggested uses include rain-proof garments, shower curtains, etc. **(No. 932)**

USI

Grease-proof cellophane packaging is offered in the form of a new cellophane-cloth-wax laminate, which is specially recommended for wrapping of grease-coated metal parts. **(No. 933)**

USI

A cleaner for plastic glass, such as plexiglass, is offered for sale in bulk at a new low price. It is applied by a new sprayer which is said to speed cleaning and improve results. **(No. 934)**

USI

A new chlorinated paraffin, resinous in nature, is claimed to be both flame and moisture resistant, and to be non-toxic. **(No. 935)**

USI

Corrosion proofing of metal surfaces is said to be facilitated by a new wax concentrate sold in solution with petroleum solvents. The liquid, which may be applied by brush, dipping or spray, dries in an hour, remains flexible at minus 20 F., and will stand heat up to 214 F. **(No. 936)**

USI

A new synthetic-rubber latex, reported to be a modified type of butadiene-styrene, is announced. Suggested postwar uses include impregnation of paper and fabrics used in shoes and binding of fibres and hair for upholstery. **(No. 937)**

USI

An abrasion-resistant plastic, said to be 250 times as resistant to abrasion as boiler plate, is offered. It is claimed to be useful for such tough jobs as protecting sand-blast equipment. **(No. 938)**

USI

An alternate for Carnauba wax, which is said to take its place in paste floor polishes, automobile polishes, carbon paper and water-wax emulsions, is on the market. **(No. 939)**

USI

Heat-indicating bands, used as bottle seals, are designed to give warning when the bottle has been subjected to a temperature harmful to the contents. Under these conditions, the color of the band changes permanently from green to bright orange. **(No. 940)**

USI

A new enamel-like paint, for use on concrete, brick or wood exposed to water or moisture, is offered. Maker states that new paint affords better coverage than its predecessor and is resistant to yellowing and the action of corrosive fumes. **(No. 941)**

U.S. INDUSTRIAL CHEMICALS, INC.

60 EAST 42ND ST., NEW YORK 17, N. Y.

BRANCHES IN ALL PRINCIPAL CITIES

ALCOHOLS
- Amyl Alcohol
- Butanol (Normal Butyl Alcohol)
- Fusel Oil—Refined

Ethanol (Ethyl Alcohol)
- Specially Denatured—all regular and anhydrous formulas
- Completely Denatured—all regular and anhydrous formulas
- Pure—190 proof, C.P. 96%, Absolute
- *Super Pyro Anti-freeze
- *Solox Proprietary Solvent

***ANSOLS**
- Ansol M
- Ansol PR

*Registered Trade Mark

ACETIC ESTERS
- Amyl Acetate
- Butyl Acetate
- Ethyl Acetate

OXALIC ESTERS
- Dibutyl Oxalate
- Diethyl Oxalate

PHTHALIC ESTERS
- Diamyl Phthalate
- Dibutyl Phthalate
- Diethyl Phthalate

OTHER ESTERS
- *Diatol
- Diethyl Carbonate
- Ethyl Choloroformate
- Ethyl Formate

INTERMEDIATES
- Acetoacetanilide
- Acetoacet-ortho-anisidide
- Acetoacet-ortho-chloranilide
- Acetoacet-ortho-toluidide
- Acetoacet-para-chloranilide
- Ethyl Acetoacetate
- Ethyl Benzoylacetate
- Ethyl Sodium Oxalacetate

ETHERS
- Ethyl Ether
- Ethyl Ether Absolute—A.C.S.

FEED CONCENTRATES
- *Curbay B-G
- *Curbay Special Liquid
- *Vacatone 40

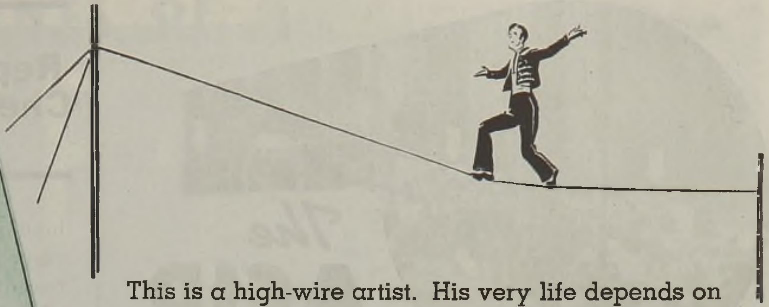
ACETONE
- Chemically Pure

RESINS
- S&W Ester Gums—all types
- S&W Congo Gums—raw, fused & esterified
- S&W *Aroplaz—alkyds and allied materials
- S&W *Arofene—pure phenolics
- S&W *Arochem—modified types
- S&W Natural Resins—all standard grades

OTHER PRODUCTS
- Collodions
- Ethylene Glycol
- Nitrocellulose Solutions
- Ethylene
- *Indalone
- Urethan

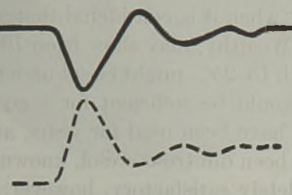
featuring HYPER-RESET

...industry's greatest "balancing act"!



This is a high-wire artist. His very life depends on hair-trigger response to the slightest disturbance of balance. The same principle applies to any industrial process in which conditions of temperature, pressure or flow are subject to frequent variation. A process disturbance that isn't detected and corrected soon enough passes along to other parts of the process, finally upsetting product uniformity.

You know how the usual automatic controller works. A disturbance in the process causes a deflection of the recording pen.

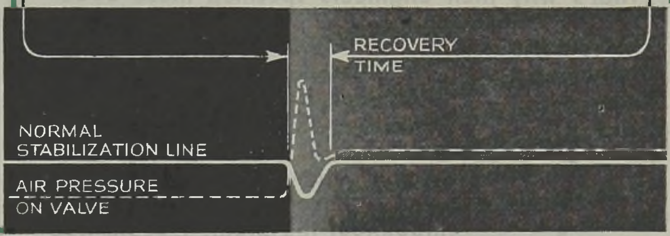


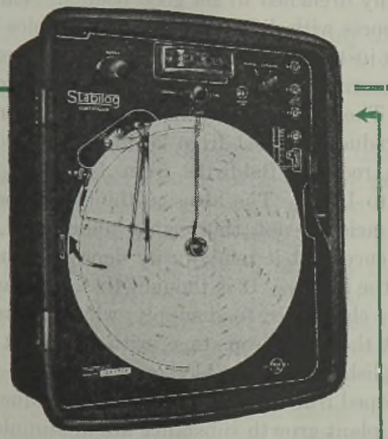
This initiates a corrective action immediately.

The length of time that elapses between the beginning of the disturbance and the completion of the corrective action is the

|← RECOVERY TIME →|

In the Foxboro Stabilog Controller this recovery time is reduced by the automatic, super-alert HYPER-RESET function to a point never approached before. By sensing the rate of disturbance at its very start, HYPER-RESET also radically reduces the amount of upset. This curve shows how fast recovery takes place. Both actions are simultaneous. Rate-sensitive action and reset function are combined. And both are smoothly coordinated with the proportional function for normal process stabilization. *All this in ¼ the usual time and with the amount of upset held to a minimum!*





ONLY 1 ADJUSTMENT

Since HYPER-RESET combines both the rate-sensitive and the reset functions, one adjustment is sufficient to establish both settings.

. . . and HYPER-RESET is only one precision feature of the Stabilog Controller

Obviously, the whole Stabilog Controller must be just as highly sensitive and readily responsive as any single part or function, such as HYPER-RESET. And those actions and functions must be perfectly coordinated in order to stabilize a process faster and wtih less upset. A good deal of this has been brought about by reducing friction, lost motion and inertia through the use of anti-friction bearings at critical points and by means of specially designed linkages. Stabilog Controllers reflect, in both design and operation, Foxboro's thirty years of process control engineering. Write today for your copy of Bulletin A330, describing HYPER-RESET Stabilog Control. The Foxboro Co., 40 Neponset Avenue, Foxboro, Mass., U. S. A.

FOXBORO
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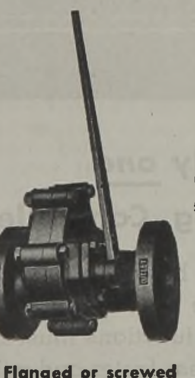
Stabilog Control
REG. U.S. PAT. OFF.



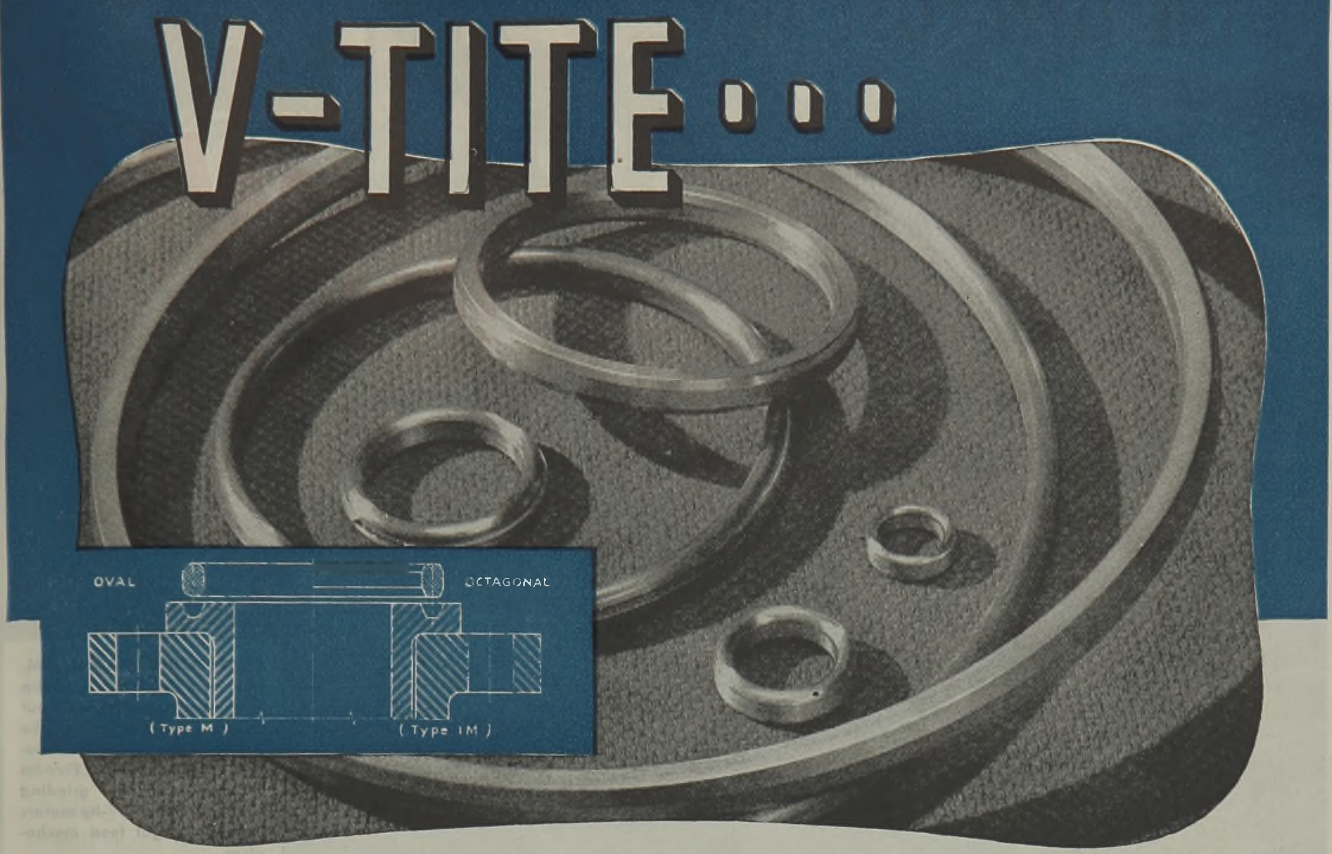
I. & E. C. Reports on the Chemical World Today

Technology

thinning which usually occurs after the fruit has partially developed and acts indirectly to increase the size of the fruit by concentrating all growth on the fruit which remains.

Naphthaleneacetic acid acts in its original function to delay the development of the abscission layer, a formation of large, weak cells at the base of the stem which causes the fruit to drop. One application of naphthaleneacetic acid near the end of the growing season holds the fruit on the tree for one or two weeks, and after two applications the apples can be pulled off only with difficulty. An interesting sidelight is that the only trees able to hold their fruit during the hurricane which swept the East Coast last fall were those which had been treated in this way. Other agents for setting fruit have been reported, and among them, 2,4-dichlorophenoxyacetic acid has been found notably effective.

The new function of naphthaleneacetic acid, that of thinning blossoms, is still in the experimental stage, but extensive field trials are being conducted. The need for thinning apple blossoms is evident when it is considered that a prolific tree, such as Baldwin or Wealthy, may show from 100,000 to 200,000 blossoms, of which 15–25% might be set under normal conditions when 2–5% would be sufficient for a good crop. Blossom-thinning sprays have been used for years, and most popular among them has been dinitro-*o*-cresol, known as DN. This has not been completely satisfactory, however, since it varies in effectiveness and frequently injures the tree. Naphthaleneacetic acid does not cause damage, and results with it have been better. The spray can be applied when the tree is in full bloom or later when it is in the petal-fall stage, but the tree must be literally drenched to get good results. Varying degrees of effectiveness with different varieties of apples have been observed; for instance, 10 p.p.m. in a spray reduced the set of Baldwin blossoms from 11% on untreated trees to 7% on sprayed trees. The same concentration applied to Grimes Golden blossoms reduced the set from 23 to 0.6%. Double this concentration reduced Baldwins from 14 to 5% and Wealthies from 8 to 1.4%. The blossom-thinning action of naphthaleneacetic acid is not thoroughly understood, but there is some evidence that it temporarily depresses physiological activity in the leaves. It is thought that this hastens competition for the elaborated food supply, which ordinarily occurs naturally at the June drop stage, with the result that thinning is accomplished with the blossoms instead of with the partially developed fruit at a later date. Other functions of this remarkable plant growth substance are in stimulating root growth and in producing artificial pollination. Sprayed on the blossoms of tomato and cucumber plants, it sets the fruit without pollination and produces seedless fruit. It also increases fruit set of partially pollinated flowers. Indolebutyric acid and substituted phenoxy acids are partially effective for the purpose. Both groups of substances are also useful for inducing root growth on cuttings and slips. Naphthaleneacetic acid has the opposite effect on potato eyes in that it prevents them from sprouting and will therefore be useful in treating potatoes for storage. As Zimmerman of Boyce Thompson Institute stated in a comprehensive article in 1943 (IND. ENG. CHEM., 35, 601): "The plant hormone field is still new and holds much for the future."


OVAL
OCTAGONAL
(Type M)
(Type IM)

PULVERIZING MAGNESIUM. Fourteen G-E Class II, Group E, motors operating right out in the open in one of the worst kinds of combustible-dust atmospheres. Five-hp motors drive the grinding wheels, while 7½-hp motors drive the ingot feed mechanism.

Air-break combination starter for Class I, Group D, locations. Combines air circuit breaker and magnetic starter in one compact unit. Made of cast, high-strength alloy, with accurately ground, tight-fitting flanges, these starters can withstand internal explosions and prevent the escape of hot gases.

Push-button station for corrosive and hazardous-gas locations. All contacts operate under oil. Entire unit is enclosed in a cast-iron case that is specially finished to withstand acid fumes, alkali dust, or exposed outdoor service.

Oil-immersed combination starter for Class I, Group D, locations. All contacts are at least 6 inches under oil. Easy-to-read indicator provides safety check on oil level. Extra-tough exterior finish provides extra protection from corrosion caused by chemical fumes or exposure to weather.

Buy all the BONDS you can—*and keep all you buy*

MOTORS AND CONTROL

for Hazardous Areas

EXPLOSION HAZARDS

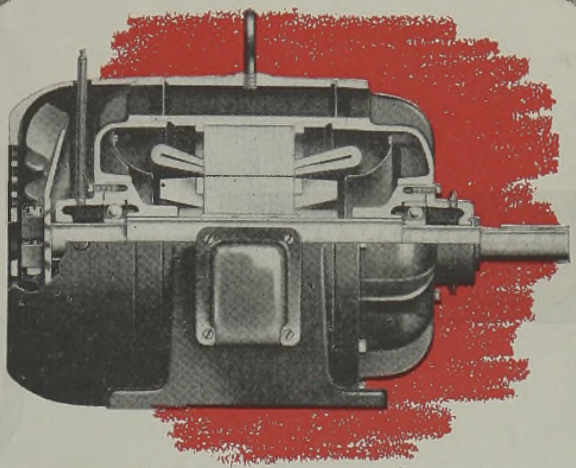
YOU SAVE ON ENGINEERING TIME, CONSTRUCTION COSTS, AND MAINTENANCE WHEN YOU LET G.E. HELP YOU APPLY THE *RIGHT* EXPLOSION-PROOF MOTORS AND CONTROLS.....

●In your plans to re-align your plant for competitive, peacetime production, have you considered how you can cut motor installation and operating cost in hazardous areas? Full utilization of G-E explosion-proof motors and control, wisely applied with the aid of G-E engineers, may well mean savings that will look big when competition gets keen.

It will mean savings in engineering time and construction costs because you eliminate the need for building special vaults to isolate motors and control. It will mean less maintenance because you get away from cumbersome remote drives, and because totally enclosed electric equipment is inherently less subject to trouble. It will mean lower insurance costs because your plant will have the very latest in electrical safety.

At G.E. you'll find a full line of motors and control specially designed for service in atmospheres containing gasoline, alcohols, acetone, and other Class I, Group D, hazards. You'll also find motors in a wide range of horsepower ratings for service in atmospheres containing magnesium dust and other Class II hazards. In fact, G.E., of all electrical manufacturers, builds the most complete line of motors and control for hazardous service.

Also, at General Electric you'll find expert assistance in selecting motors and control which best combine economy and safety on your jobs. Write for our new Bulletin, GEA-4131, "Motors and Control for Hazardous Locations," for complete information on G-E explosion-proof motors and control. *General Electric Company, Schenectady* 5, N. Y.



NEW...

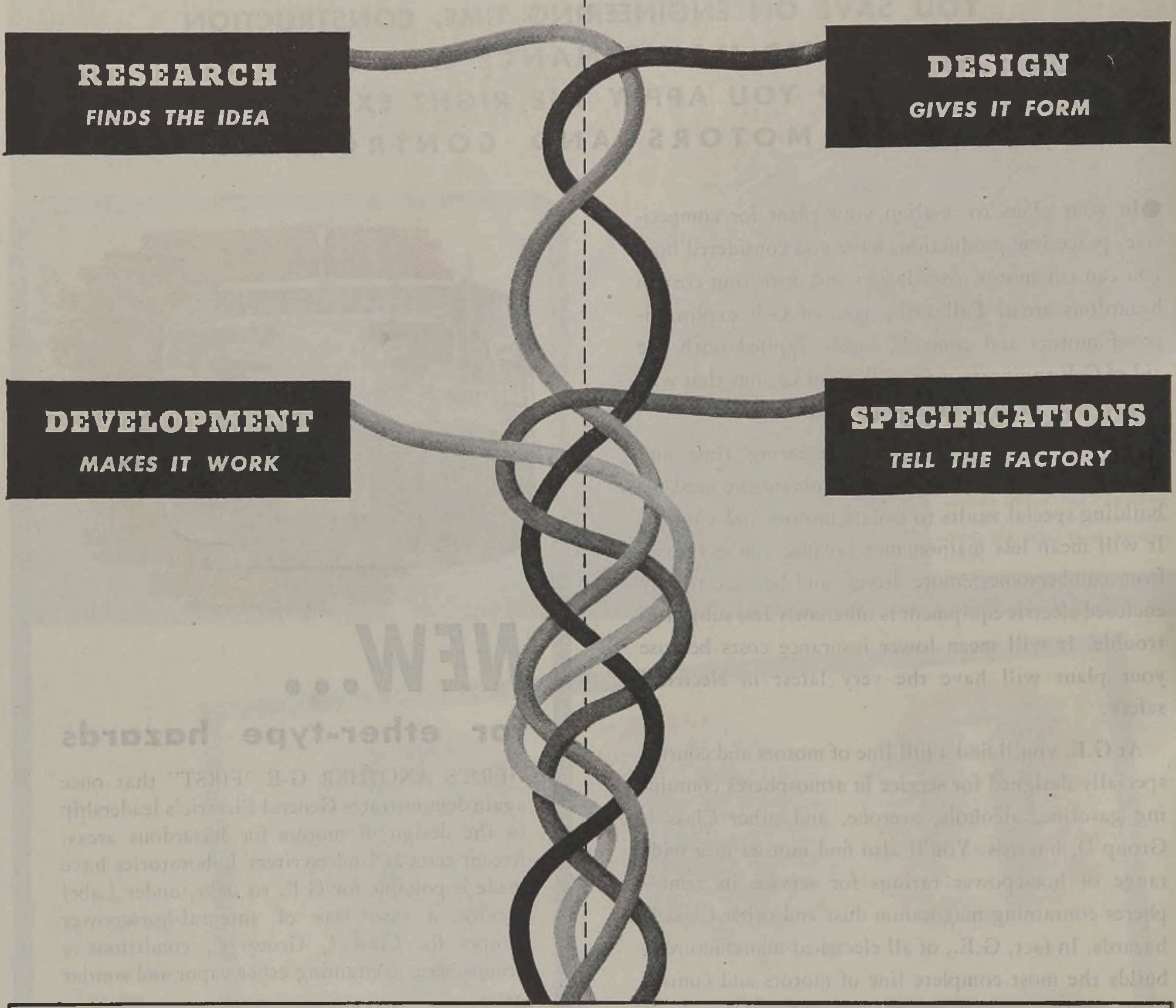
for ether-type hazards

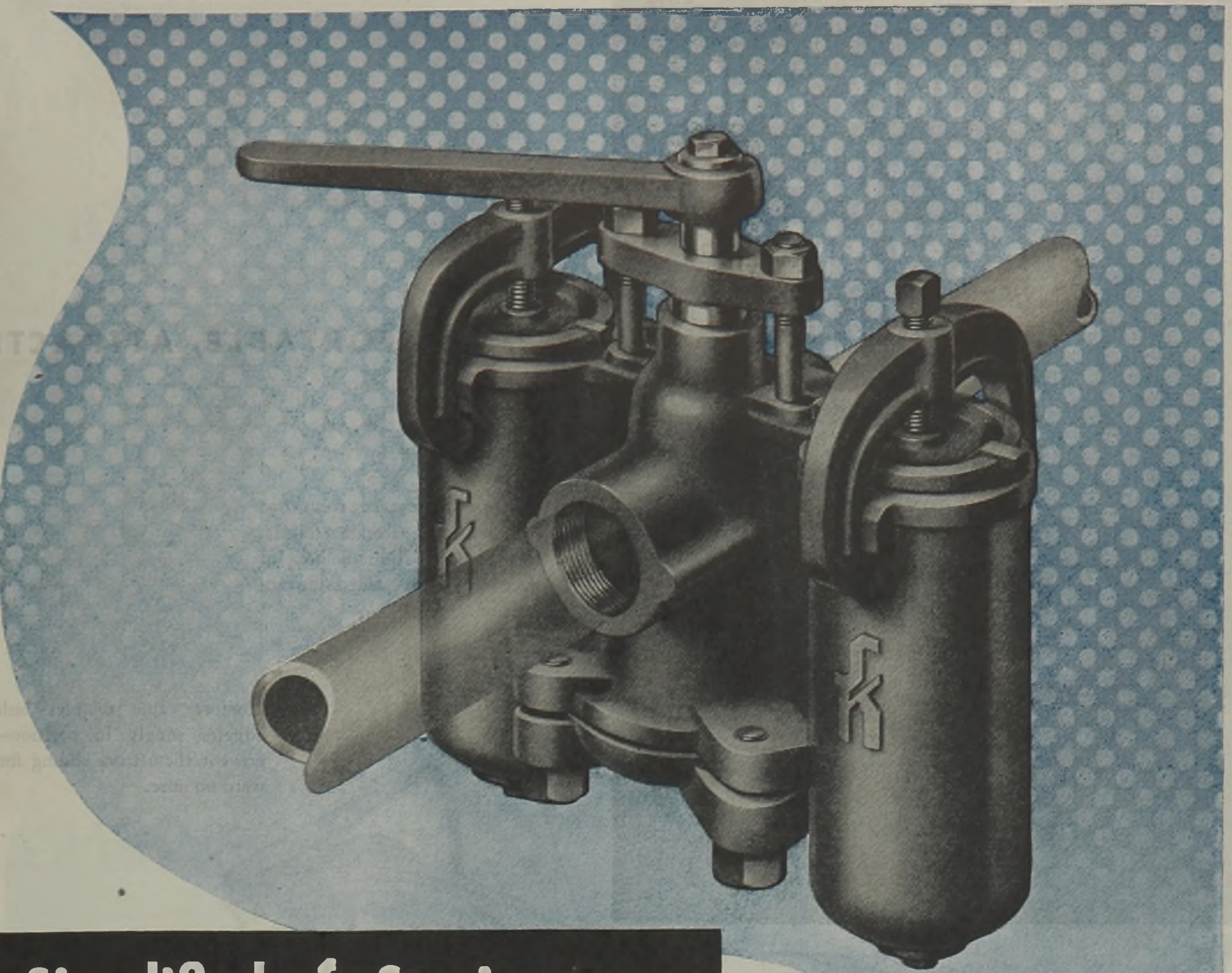
HERE'S ANOTHER G-E "FIRST" that once again demonstrates General Electric's leadership in the design of motors for hazardous areas. Recent tests at Underwriters' Laboratories have made it possible for G.E. to offer, under Label Service, a new line of integral-horsepower motors for Class I, Group C, conditions—atmospheres containing ether vapor and similar gases.

Construction of the new motor is essentially the same as that of Class I, Group D, motors, except that a special flame path is used at the shaft opening, and thermostats are mounted inside the motor. They operate in conjunction with a magnetic controller and disconnect the motor at a predetermined temperature. Ratings are from 1 to 15 hp.

GENERAL ELECTRIC

662-14-132


RESEARCH
FINDS THE IDEA
DESIGN
GIVES IT FORM
DEVELOPMENT
MAKES IT WORK
SPECIFICATIONS
TELL THE FACTORY



A Simplified SK Strainer . . .

designed to give you more for your money

Here is a duplex strainer which does a thorough job of removing dirt and other foreign matter from oil, water and other liquids, *yet is moderately priced.* Design simplifications, standardization and construction economies all contribute to making this new strainer outstanding in many ways.

Check These Features:

DUPLEX DESIGN—

permits each strainer to be cleaned without flow interruption.

ONLY 1 VALVE—

single shut off cock with double-port provides continuous flow during switch-over and is pressure balanced for easy operation. Steel spring takes up any plug wear and insures against leakage.

VERTICAL BASKETS—

allow continuous flow while cleaning. Dirt is collected in the basket which is easily removed without loss of fluid. Strainer free area is a minimum of 5 times pipe area.

SINGLE-SETSCREW CLAMPS—

quickly removable, yet seal basket chambers tightly.

PACKING GLANDS—

nut-and-stud type, easy to adjust and will not corrode and "freeze."

PLUG DRAINS—

on basket chambers for draining fluid from unit.

Made of cast bronze, these SK Duplex Strainers are designed for pressures up to 125 psi, in pipe sizes from ½ to 2 inches. Being light-weight, they need no support other than the pipe line.

Other SK Strainers are made in cast iron for pressures up to 250 psi or steel for pressures up to 600 psi and sizes up to 6 inches.

JET APPARATUS • CONDENSERS AND VACUUM PUMPS • HEAT TRANSFER EQUIPMENT
VALVES • ROTAMETERS • FLOW INDICATORS • GEAR PUMPS • STRAINERS
OIL BURNING EQUIPMENT • SPRAY NOZZLES AND ATOMIZERS • RADIAFIN TUBES

SCHUTTE & KOERTING CO.
Manufacturing Engineers
1160 Thompson Street, Philadelphia 22, Pa.

The light is always green at POWELL

At Powell, scientific study, research and experimentation *never* STOP. That's why Powell Engineering has always been able to solve the intricate flow control problems imposed by new products and processes.

Add to this our non-stop application of lessons learned through 99 years of practical experience and you have the Powell Line—a complete line of valves of every type and material needed to satisfy all flow-control requirements of industry today. And tomorrow, as new demands arise, there'll be Powell Valves to meet them.

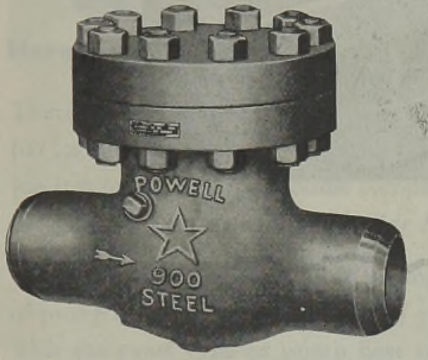


Fig. 9061 WE—Class 900-pound Cast Steel Swing Check Valve, with welding ends and bolted cap. Disc is hung on a 5-degree angle, and when wide open permits full, unobstructed flow through the valve body.

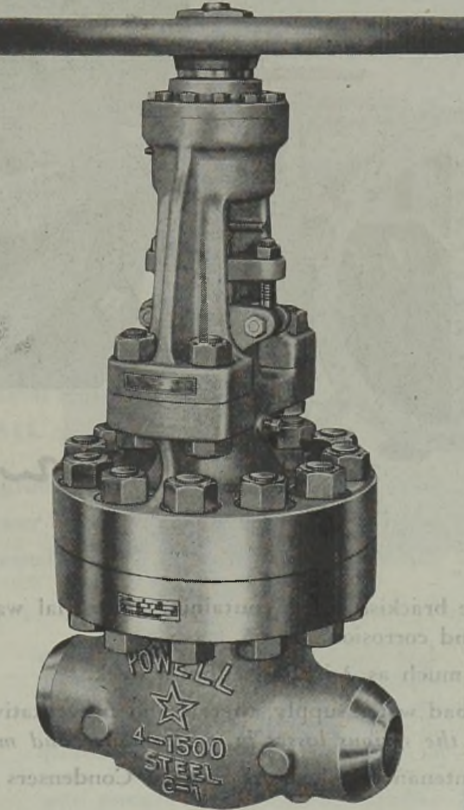


Fig. 1303 WE—Class 1500-pound Cast Steel Gate Valve, with welding ends, outside screw rising stem, bolted flanged yoke and taper solid wedge.

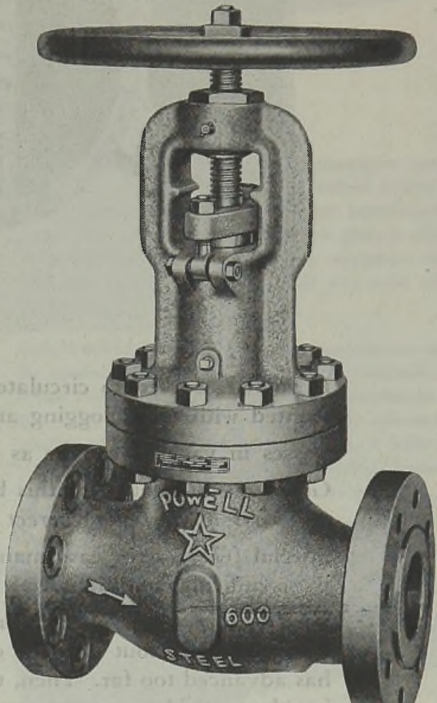


Fig. 6031—Class 600-pound Cast Steel Globe Valve, with flanged ends, outside screw rising stem and bolted flanged yoke.

The Wm. Powell Co.

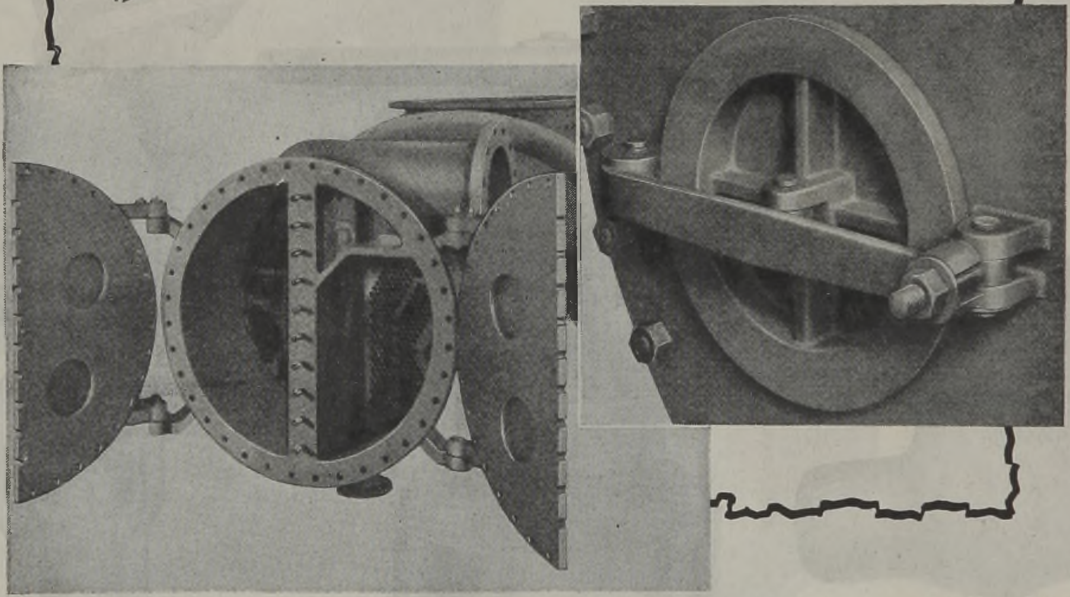
Dependable Valves Since 1846

Cincinnati 22, Ohio

POWELL VALVES

condenser tubes fouling from bad circulating water conditions?

SPECIAL FEATURES HELP YOU CUT TIME AND PERFORMANCE LOSSES



If you are forced to circulate brackish water containing industrial waste, you're going to be confronted with tube clogging and corrosion.

Losses in vacuum can be as much as 2 inches within a week.

Given no alternative to this bad water supply, there is no preventative for the fouling, *but there are ways to partially correct the serious losses in performance and manpower.*

Special features for easy maintenance make Ross Surface Condensers exceptionally well suited to these difficult conditions.

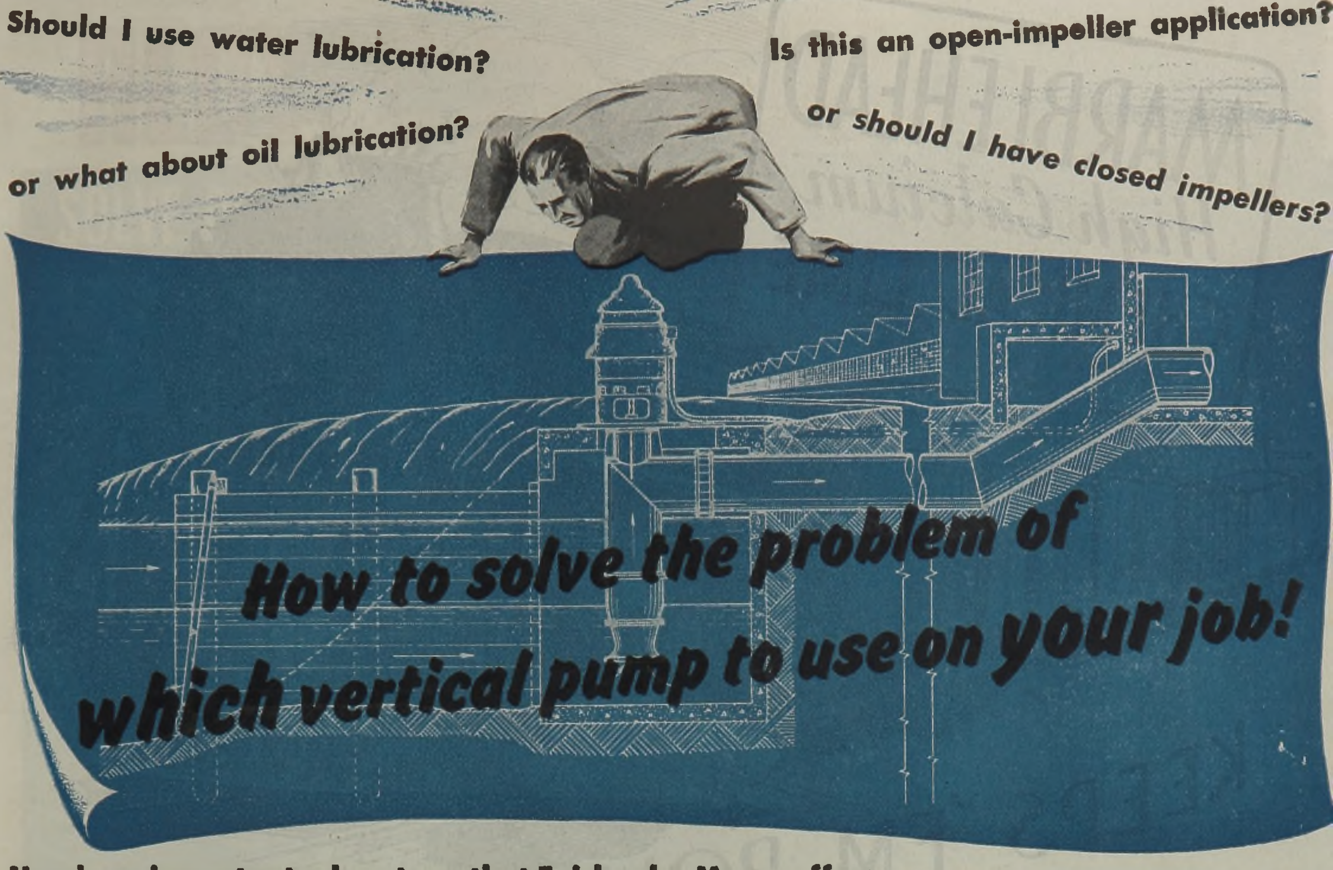
For instance, quick-opening inspection ports permit fast and frequent examination of tube sheets and tube ends (without need of opening entire cover). Fouling can, therefore, be detected before it has advanced too far. Then, when tube cleaning becomes necessary, the simplicity and ease of opening the water box covers materially reduce the service time. (Doors are self-aligning and mounted on hinges equipped with roller bearings. No special tools are needed to open or close—only a wrench.)

ROSS HEATER & MFG. CO., Inc.

Division of American Radiator & Standard Sanitary corporation

Full particulars in Ross Surface Condenser Manual No. 4017. Request only on your Company letterhead.

1423 WEST AVENUE BUFFALO 13, N. Y.



Here's an important advantage that Fairbanks-Morse offers

There are a number of different types and designs of vertical pumps. Each has its advantages or disadvantages, depending upon the exact nature of the job it is to be used upon. Some companies feature one design, others another design. *But Fairbanks-Morse builds* ALL *the major types of vertical pumps.*

This means that Fairbanks-Morse engineers are not limited in their choice of pump designs, but—*regardless of your water-moving job*—can supply you with the exact type of pump best suited to *your particular* requirements.

For example . . .

Water Or Oil Lubrication! If your job calls for uncontaminated water and simplified maintenance, a Pomona *Water-Lubricated* Pump—the pump that pioneered water lubrication—is the one to use. Or, for applications where the nature of the water or installation requirements make oil lubrication more practical, choose a Fairbanks-Morse Oil Lubricated Pump. Pomona, Fairbanks-Morse engineers supply BOTH types, assuring an absolutely unbiased recommendation on the pump best suited to *your* needs.

Open Or Closed Impellers! Pomona's semi-open impellers are famous for their ability to handle pulpy or grit-laden waters, and their ready adaptability to varying flow requirements with proportionate savings in power. But if your job calls for a closed impeller pump—a type also built by Fairbanks Morse—then Pomona, Fairbanks-Morse engineers are free to recommend it. As a result, *whatever your job*, you are assured of the best possible design to fit the requirements of *your* particular pump applications!

In Addition...

In the vertical pump field Fairbanks-Morse not only builds all the major types of vertical *turbine* pumps, but also manufactures vertical *centrifugal* pumps in a wide range of sizes. This gives a still wider selection of vertical pumping equipment to meet the specific requirements of any type of installation.

OUR TRAINED ENGINEERS, widely experienced in the application of the various types of Fairbanks-Morse Pumps, will be glad to make recommendations and work with you in the most efficient solution of your water-moving problem. A letter, wire or phone call places this engineering "know how" at your service. Fairbanks, Morse & Co., Chicago 5, Illinois.

For smaller-gallonage applications ask about Fairbanks-Morse WESTCO Pumps . . . the pumps that are simple to maintain, long-lasting and highly adaptable to varying types of work!

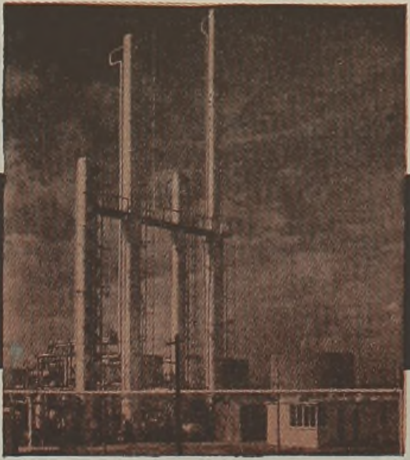
Fairbanks-Morse

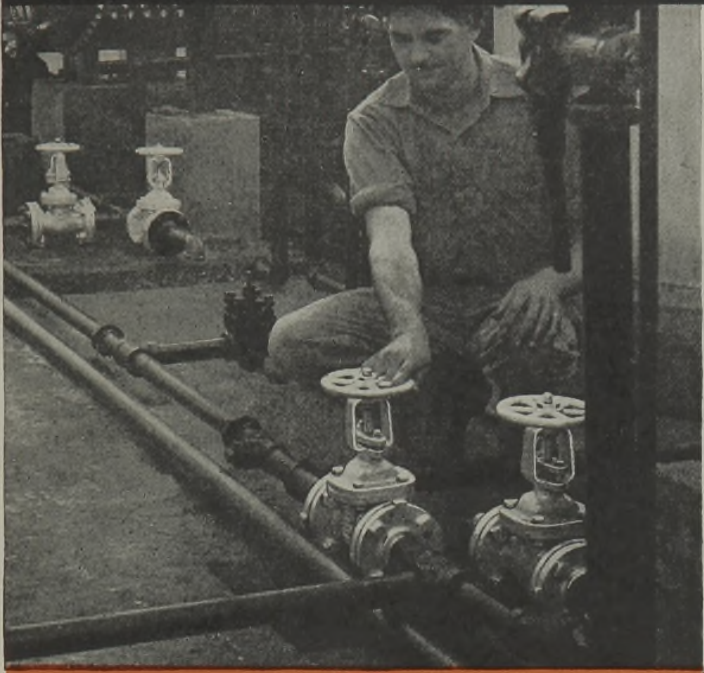
A name worth remembering

Diesel Locomotives • Diesel Engines • Generators • Motors • Pumps • Scales
Magnetos • Stokers • Railroad Motor Cars and Standpipes • Farm Equipment

ALOYCO STAINLESS STEEL VALVES

SOLVE DIFFICULT CORROSION PROBLEM AT COASTWISE PETROLEUM COMPANY





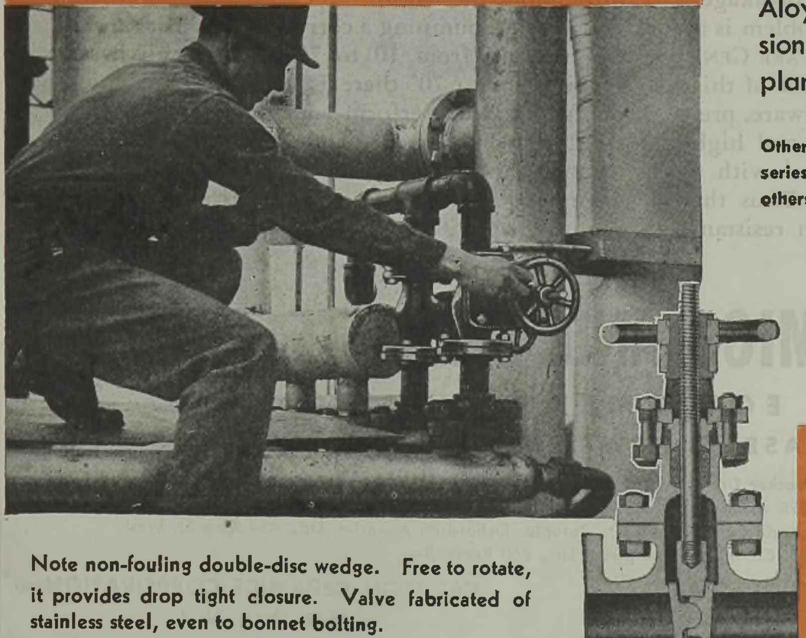
ALOYCO VALVES PREVENT STILL SHUTDOWN

To prevent shutdown of the distillation operation and avoid servicing in an inaccessible location, Aloyco Valves are installed in heat exchanger manifold since they are practically immune to acids encountered.

If you handle corrosive fluids, you can benefit from the experience of Coastwise Petroleum Company's Goodhope, Louisiana Plant. Before they began to use Aloyco Stainless Stee Valves, valve life on their Benzol Treaters was only a few months with acid, less with alkali—making repair charges high, causing frequent service interruptions. Finally, to withstand the effluent which varies from sodium sulphate, benzene sulphonic acid, sulphuric esters, etc. to soda and acids, they chose Aloyco Valves fabricated of Aloyco 20.

After one year of continuous service, these Aloyco Valves are still on the line and give promise of remaining there indefinitely This is but one of the many good records Aloyco Valves have made in resisting corrosion. Investigate what they can do in your plant. Write us today.

Other alloys available: 18-8S, 18-8SMo, the higher Chrome-Nicke series, Worthite, Hastelloy, Monel, Pure Nickel and others.



Note non-fouling double-disc wedge. Free to rotate, it provides drop tight closure. Valve fabricated of stainless steel, even to bonnet bolting.

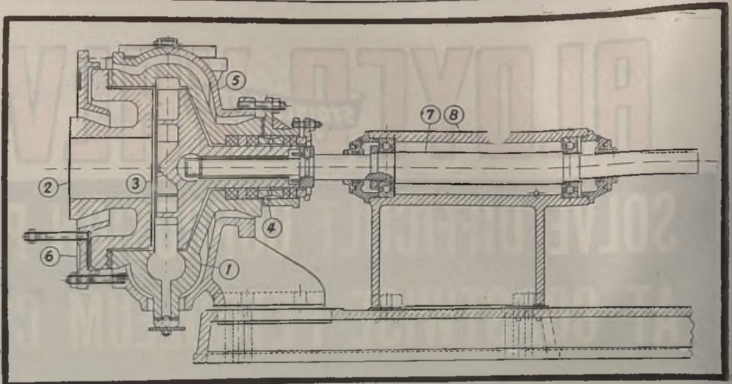
ALOYCO

Stainless Steel VALVES and FITTINGS

ATE VALVES • GLOBE VALVES
Y VALVES • CHECK VALVES
LEVER THROTTLE GATE VALVES
TANK VALVES • SCREWED FITTINGS
FLANGED FITTINGS
GAUGE GLASS FITTINGS

ALLOY STEEL PRODUCTS COMPANY, INC., 1310 West Elizabeth Avenue, Linden, N. J.

PRESCRIPTION FOR PROCESSING



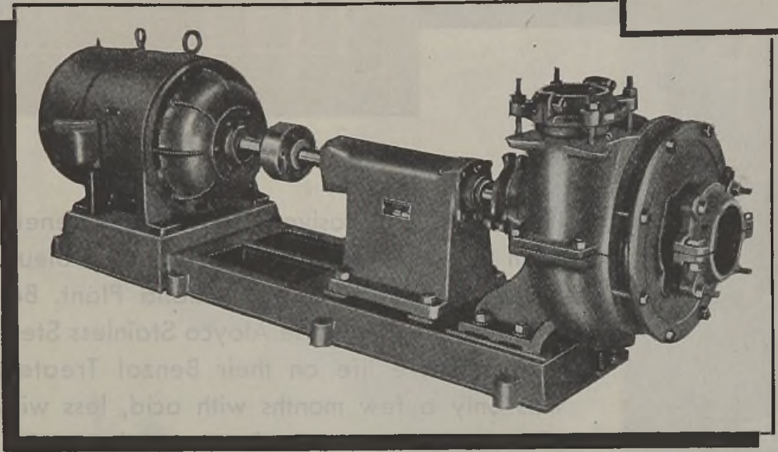


Fig. 423. *Direct Driven Long Coupled Centrifugal Pump.*

DESIGN FEATURES

- ❶ Stoneware Volute
- ❷ Stoneware Cover Plate
- ❸ Stoneware Impeller
- ❹ Water Sealed Stuffing Box
- ❺ Cast Iron Armor for Volute
- ❺ Cast Iron Armor for Cover Plate
- ❼ Steel Shaft
- ❽ Bearing Support

NOTE: Both direct motor drive and belt driven models are available.

Armored Stoneware Centrifugal Pumps

In specifying the equipment for a chemical plant one of the most important tasks facing the designing engineer is the choice of a pump which will withstand the ravages of the corrosive materials to be handled and will have the characteristics of good design which will insure trouble-free mechanical operation and freedom from breakage. Our prescription for this processing problem is a GENERAL CERAMIC'S ARMORED STONEWARE CENTRIFUGAL PUMP. The volute and impeller of this pump are constructed of chemical stoneware, precision ground to give close clearances and high efficiency. The stuffing box is equipped with a water seal to prevent excess leakage. Thus the entire "wet end" is not only corrosion resistant but corrosion "proof". To guard against mechanical shock and operating hazards the stoneware parts are encased in cast iron armor.

General Ceramic's pumps are successfully handling strong acids (except hydrofluoric), bleaching agents, and fine chemicals in processing plants throughout the world.

If you are pumping a corrosive liquid at capacities varying from 10 to 700 GPM with heads ranging up to 70′ there is a General Ceramic's pump that will perform your task with absolute freedom from corrosion and a minimum of maintenance expense. Send for Bulletin Number 211 describing and illustrating chemical stoneware pumps that will solve your pumping problems.

7197

GENERAL CERAMICS AND STEATITE CORP.

CHEMICAL EQUIPMENT DIVISION

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Tacoma: 702 Tacoma Bldg. • Montreal: Canada Cement Bldg. • Toronto: Richardson Agencies, Ltd., 454 King St. West
Vancouver, B. C.: Willard Equipment Ltd., 860 Beach Ave.

GENERAL CERAMICS and STEATITE CORPORATION
Keasbey, N. J.
Insulator Division

CARILLON CERAMICS CORPORATION
Metuchen, N. J.
Sanitary Ware Division

The manufacturing facilities of these affiliates of GENERAL CERAMICS & STEATITE CORP. are available for handling ceramic problems in all branches of industry. GENERAL CERAMICS & STEATITE CORP. is thus able to offer a service covering all industrial applications of ceramic products.

UNION CARBIDE *AGAIN* REPORTS

on the production of

BUTADIENE

for the Government's Synthetic Rubber Program

ONE OF THE MOST IMPORTANT factors in the Government's rubber program is the production of GR-S type synthetic rubber. The basic chemical in this rubber is Butadiene, which can be made from alcohol or hydrocarbon materials.

The Government's original plan provided that about one third of the required Butadiene would be made by CARBIDE AND CARBON CHEMICALS CORPORATION'S alcohol process.

In 1943, their first year of operation, however, the plants using this process produced over 75 per cent of all Butadiene made for GR-S type synthetic rubber.

In 1944, the second year, these plants produced about 64 per cent of all Butadiene necessary for military and essential civilian rubber. This was true despite the fact that good progress had been made in the production of Butadiene by other processes.

THE RECORD

The first tank-car load of Butadiene was shipped from the Government's Carbide-built, Carbide-operated plant at Institute, West Virginia a little over two years ago.

This was just five months after the famous Baruch Committee Report pointed out this nation's desperate need for rubber—and approved Carbide's butadiene alcohol process, originally selected by Rubber Reserve Company, as one of the solutions.

In its first year the Institute plant, with a rated capacity of 80,000 tons per year, produced enough Butadiene for more than 90,000 long tons of synthetic rubber.

Two more great plants using Carbide's alcohol process—and built from the blueprints of the Institute plant—are in full production. One of these, with an annual rated capacity of 80,000 tons of Butadiene is located at Kobuta, Pennsylvania and is operated for the Government by another important chemical company.

The second, with a rated capacity of 60,000 tons a year, is operated for the Government by Carbide at Louisville, Kentucky—making the total rated capacity of the two huge plants now operated by Carbide 140,000 tons a year.

In 1944, the production of Butadiene from the three plants using the alcohol process totaled 361,000 tons—representing operation at over 164 per cent of rated capacity. An even higher rate is expected in 1945.

* * * * *

Before Pearl Harbor, the United States was a "have not" nation with respect to rubber. Now, thanks to American research, engineering and production skill, our country can take its place as a dominant factor among the great rubber producing nations of the world.

▼

Business men, technicians, teachers, and others are invited to send for the book RU-8 "Butadiene and Styrene for Buna S Synthetic Rubber from Grain Alcohol," which explains what these plants do, and what their place is in the Government's rubber program.

SEPTEMBER 10, 1942

"Of all the critical and strategic materials, rubber is the one which presents the greatest threat to the safety of our nation, and to the Allied Cause . . . We find the situation to be so dangerous that unless corrective measures are taken immediately the country will face both a military and a civilian collapse."

—*Report of the Rubber Survey Committee (Baruch Committee).*

AUGUST 31, 1944

"Undoubtedly the outstanding achievement of your company has been the development of your process for the production of Butadiene from alcohol. With a rather meager background of experimental work, your engineers were able to design and construct commercial units for the production of Butadiene. In an exceedingly short time, the operation of this equipment at capacities up to 200 per cent of rating has been largely responsible for our present safe situation with respect to rubber supplies . . . "

—*Letter from Rubber Director Bradley Dewey to CARBIDE AND CARBON CHEMICALS CORPORATION*

The material herein has been reviewed and passed by the Rubber Reserve Company, the Defense Plant Corporation, and the War Department.

BUY UNITED STATES WAR BONDS AND STAMPS

UNION CARBIDE AND CARBON CORPORATION
30 East 42nd Street UCC New York 17, N. Y.

Principal Units in the United States and their Products

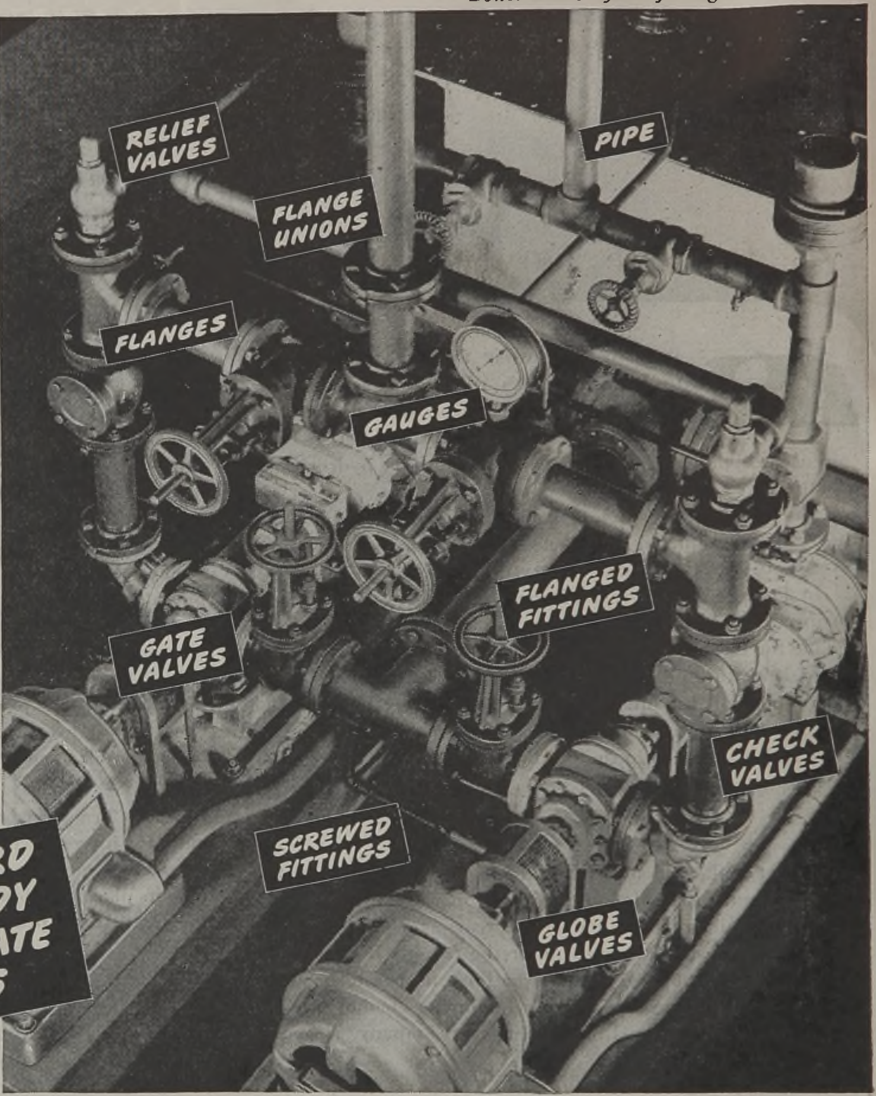
ALLOYS AND METALS—Electro Metallurgical Company, Haynes Stellite Company, Kemet Laboratories Company, Inc., United States Vanadium Corporation
CHEMICALS—Carbide and Carbon Chemicals Corporation PLASTICS—Bakelite Corporation ELECTRODES, CARBONS & BATTERIES—National Carbon Company, Inc.
INDUSTRIAL GASES AND CARBIDE—The Linde Air Products Company, The Oxweld Railroad Service Company, The Prest-O-Lite Company, Inc.

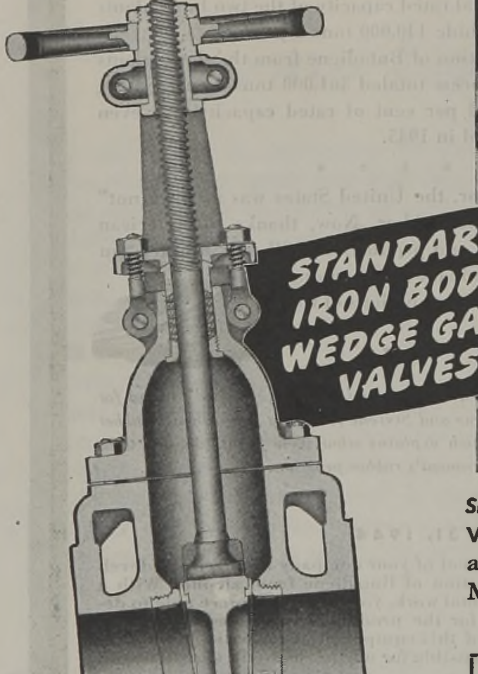
DEPEND ON CRANE . . . WHEN IT'S PIPING EQUIPMENT YOU NEED

ONE SOURCE OF SUPPLY • ONE RESPONSIBILITY FOR ALL PARTS • ONE STANDARD OF QUALITY

To keep piping at its best, to simplify and speed up deferred replacements—call on the Crane line. You choose from the world's greatest selection of piping materials—in brass, iron and steel. One source—your Crane Branch or Wholesaler—supplies on one order all your requirements. Every part is uniform in quality, backed by a single responsibility. Your whole task from ordering of parts to installing them is simplified—and at the same time you are benefiting by Crane Co.'s 90-year leadership in the field of piping materials. Below is an example of Crane complete lines—in Standard Iron Body Wedge Gate Valves.

Boiler control system for regulating dampers





***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 & 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

VALVES · FITTINGS · PIPE
PLUMBING · HEATING · PUMPS


WHEN SPECIFICATIONS SAY:
"The Charge must be dry"

Whatever his discovery may be—

GATX GENERAL AMERICAN

General American will build a tank car to carry it

Your future plans may include new liquids and gases never shipped before — and needing bulk transportation to be profitable. Call on General American engineers.

Specially designed General American cars today carry highly volatile liquids, gases requiring extreme pressures, *acids that corrode ordinary cars.*

The correct car to carry your "problem product" efficiently can be designed and built by General American — world's largest operators of specialized tank cars.

Planning Now with Tomorrow's Leaders

Even though your new product or problem commodity is still in the laboratory stage, General American engineers are ready to work with you now. Keeping pace with your progress, we will plan the new tank car with every feature needed for safe, economical transportation.

Call or write our general offices—135 South LaSalle St., Chicago 90, Ill.

GENERAL AMERICAN TRANSPORTATION

CORPORATION

Builders and Operators of Specialized Railroad Freight Cars ★ Bulk Liquid Storage Terminals ★ Pressure Vessels and other Welded Equipment ★ Aerocoach Motor Coaches ★ Process Equipment of all kinds ★ Fruit and Vegetable Precooling Service

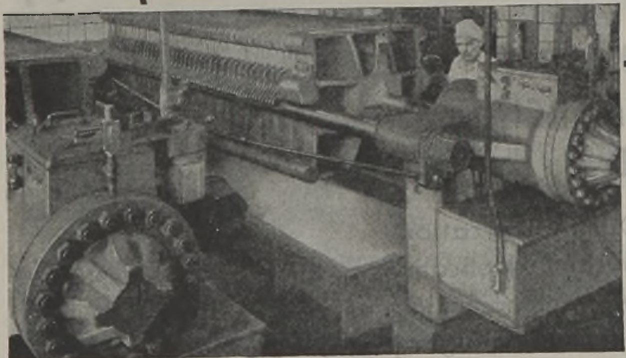

CATEX-ANEX
H_2O
$MgCO_3$
Na_2CO_3
$CaCl_2$
$MgCl_2$
Na_2SO_4
NaCl
$CaSO_4$
$CaCO_3$
$MgSO_4$

Integrity ...is basic with SPERRY!

Excerpts from letters acknowledging prompt delivery of Sperry Penicillin Filter Presses

"... we want to express our sincere appreciation for the excellent cooperation and punctual delivery which has been very gratifying."

"It has been a pleasure to work with your organization and it has also been a unique experience for us to deal with a firm that lives up to their promises."



Type of Sperry Filter Press used for Penicillin Production.

WHETHER it is an order for especially designed filter presses to help speed the production of life-saving Penicillin . . . or to meet the innumerable problems of industrial filtration which Sperry engineers are called upon to solve . . . you can be assured a Sperry built press will meet every reasonable requirement as to quality and delivery.

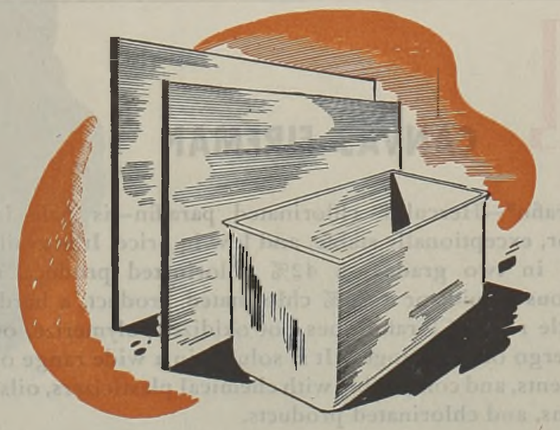
These are the reasons why Sperry . . . pioneer in the field of industrial filtration . . . is still a leader today in the design and manufacture of filter presses. If you have a filtration problem consult with Sperry . . . there is no obligation.

Eastern Sales Representative
Henry E. Jacoby, M.E.
205 E. 42nd Street
New York 17
Phone: MUrray Hill 4-3581

Western Sales Representative
B. M. Pilhashy
Merchants Exchange Bldg.
San Francisco 4, Calif.
Phone: Do 0375

D. R. SPERRY & COMPANY, BATAVIA, ILLINOIS
Filtration Engineers for over 50 Years

CANVAS FIREMAN. Coatings of Clorafin—Hercules' chlorinated paraffin—provide low-cost flame resistance for canvas awnings, tents, lawn furniture. Clorafin can be applied after weaving or after manufacture into finished products. See next page for details.

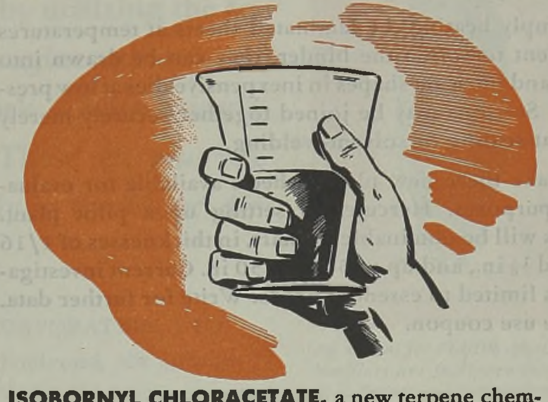


THERMOPLASTIC LAMINATES are unique. They are tough, resilient, readily drawn, permit low-cost forming of large shapes from flat laminated sheets. Outstanding are toughness, impact strength, light weight, unlimited color and design effects. See next page.

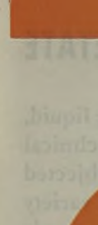
CUES AND CLUES

for improved products

PLASTIC DOLLS show how Vinsol Resin maintains production despite shortages of rosin, phenolics, shellac, other scarce plastic materials. Turn page for details on this non-critical thermoplastic.



ISOBORNYL CHLORACETATE, a new terpene chemical with interesting possibilities, is now available from Hercules in production quantities. For further details, please turn to next page.



Which of Hercules' hundreds of chemical materials can best improve the performance or processing of your present products, or speed your future developments to completion? Some timely suggestions are presented in this third edition of CUES AND CLUES. Future editions in this magazine will cover many others. For immediate attention on any material, write to Hercules Powder Company, 904 Delaware Trust Bldg., Wilmington, 99, Delaware.

HERCULES

SEE NEXT PAGE FOR DETAILS

1

CANVAS FIREMAN

Clorafin*—Hercules' chlorinated paraffin—is pale in color, exceptionally stable, and low in price. It is available in two grades—a 42% chlorinated product, a viscous liquid; or a 70% chlorinated product, a hard, brittle resin. Clorafin does not oxidize, polymerize, or undergo other changes. It is soluble in a wide range of solvents, and compatible with chemical plasticizers, oils, resins, and chlorinated products.

The outstanding use for Clorafin today is in the production of flame-resistant, water-resistant, and mildew-resistant coatings for canvas and other inflammable materials. It is also used for flameproof paints and adhesives.

Detailed properties, together with tables showing the compatibility of Clorafin with other materials, sent on request. Use coupon.

2

THERMOPLASTIC LAMINATES

Plastic laminates have been known for years. The field of thermoplastic laminates, however, has been largely undeveloped. In impact strength, deep-drawing properties, low temperature flexibility, electrical properties, and range of color, thermoplastic laminates based on cellulose acetate or ethyl cellulose are unexcelled. They are also light in weight.

By simply heating the laminated sheets at temperatures sufficient to soften the binder, they can be drawn into large and intricate shapes in inexpensive dies at low pressures. Sections may be joined together securely merely by heat-sealing or solvent-welding.

To make these new plastic sheets available for evaluation purposes, Hercules is setting up a pilot plant. Sheets will be obtainable, to start, in thicknesses of 1/16 in. and ⅛ in., and up to 50 in. x 50 in. Current investigation is limited to essential needs. Write for further data. Please use coupon.

3

PLASTIC DOLLS

Vinsol* Resin is currently available in quantity. Many manufacturers confronted with shortages of war-scarce resins are making use of this dark-colored, high-melting thermoplastic resin as an extender, modifier, or replacement. In the manufacture of children's dolls and similar plastic objects, for instance, Vinsol Resin serves as a binder. Under moderate heat and pressure, the Vinsol Resin melts and flows to give a composition with the necessary density, hardness, good surface, and easy removal from the mold.

Useful alike in plastics, special paints and sealers, and inks, Vinsol Resin may replace up to 35% phenolic resin without markedly impairing physical properties. Insoluble in petroleum derivatives, it promotes outstanding grease and oil resistance, hence its use in freight-car sealers and similar compositions. To many other applications, it brings excellent electrical characteristics, low water absorption, hardness, thermoplasticity at low cost.

Vinsol Resin is available in quantity at low price, in lump, flake, or pulverized form. You can best determine the material-stretching, money-saving advantages of Vinsol Resin by testing it yourself. Use coupon for further information.

4

ISOBORNYL CHLORACETATE

Hercules' isobornyl chloracetate is a high-boiling liquid, substantially water-white in color, available in technical grade with a purity of 85% or better. It can be subjected to a large number of organic reactions to yield a variety of compounds. Hercules' isobornyl chloracetate is saturated, and, therefore, stable in oxidation. It contains an extremely reactive halogen.

Hercules' isobornyl chloracetate is available now, in production quantity. Typical analysis and sample to facilitate your further investigation may be had on request.

*Reg. U. S. Pat. Off. by Hercules Powder Company

RETURN COUPON FOR FURTHER INFORMATION

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CELLULOSE PRODUCTS · TERPENE & ROSIN CHEMICALS · SYNTHETICS
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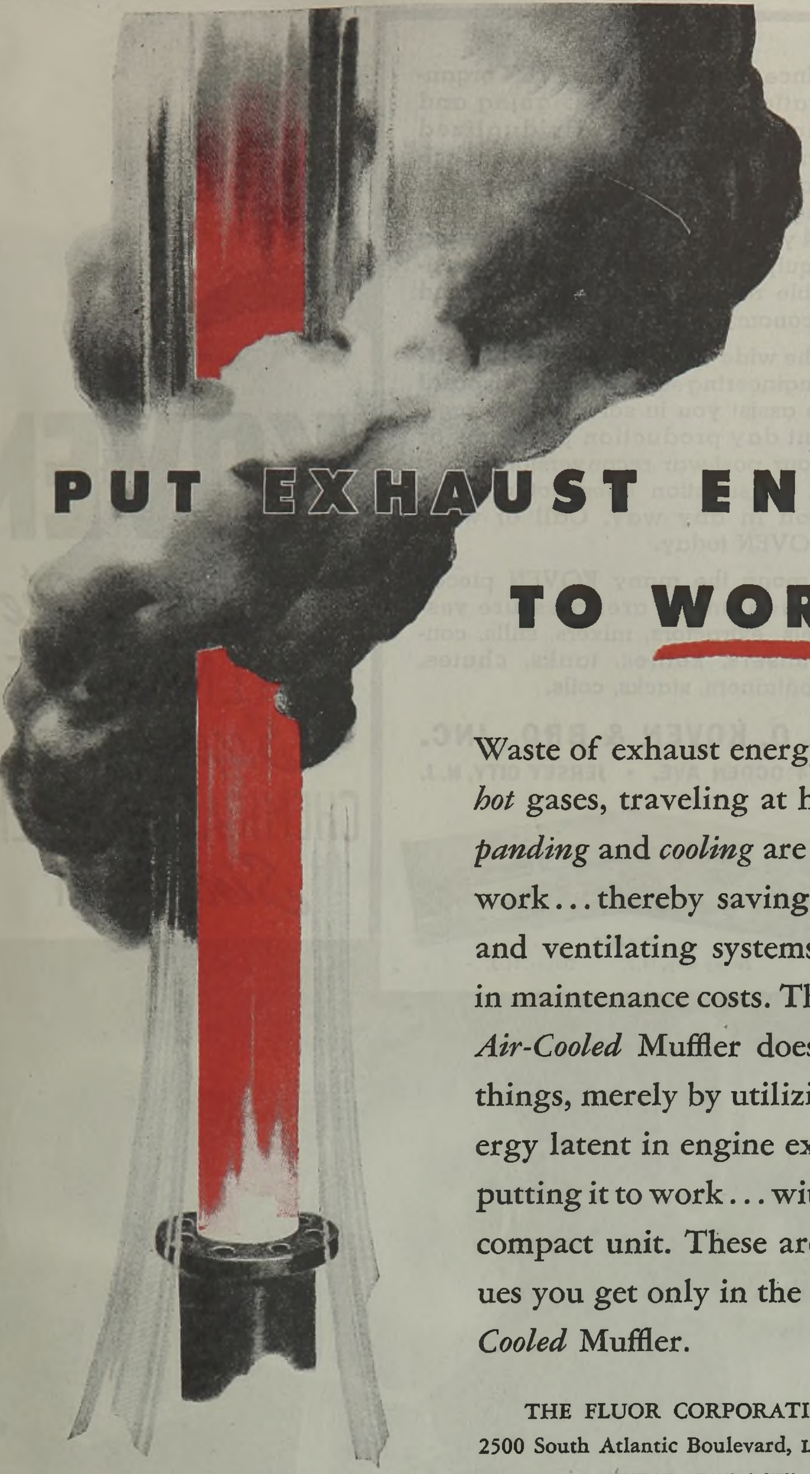
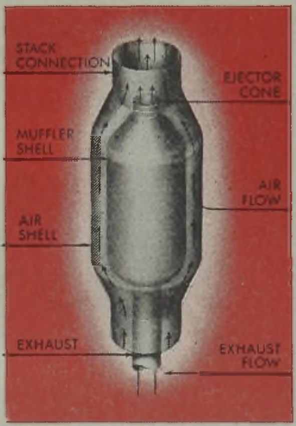
II-53



PUT EXHAUST ENERGY TO WORK

Waste of exhaust energy is a needless extravagance. The *hot* gases, traveling at high *velocity* and then rapidly *expanding* and *cooling* are a source of *energy* you can put to work... thereby saving thousands of dollars in heating and ventilating systems... in operating expenses... and in maintenance costs. The FLUOR *Air-Cooled* Muffler does all these things, merely by utilizing the energy latent in engine exhaust and putting it to work... with a single, compact unit. These are *plus* values you get only in the Fluor *Air-Cooled* Muffler.



All designs for FLUOR Air-Cooled Mufflers are fully protected by U. S. Patents and Patents Pending.

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SINCE 1890

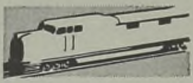
AUTOMOTIVE

STATIONARY ENGINES

MARINE

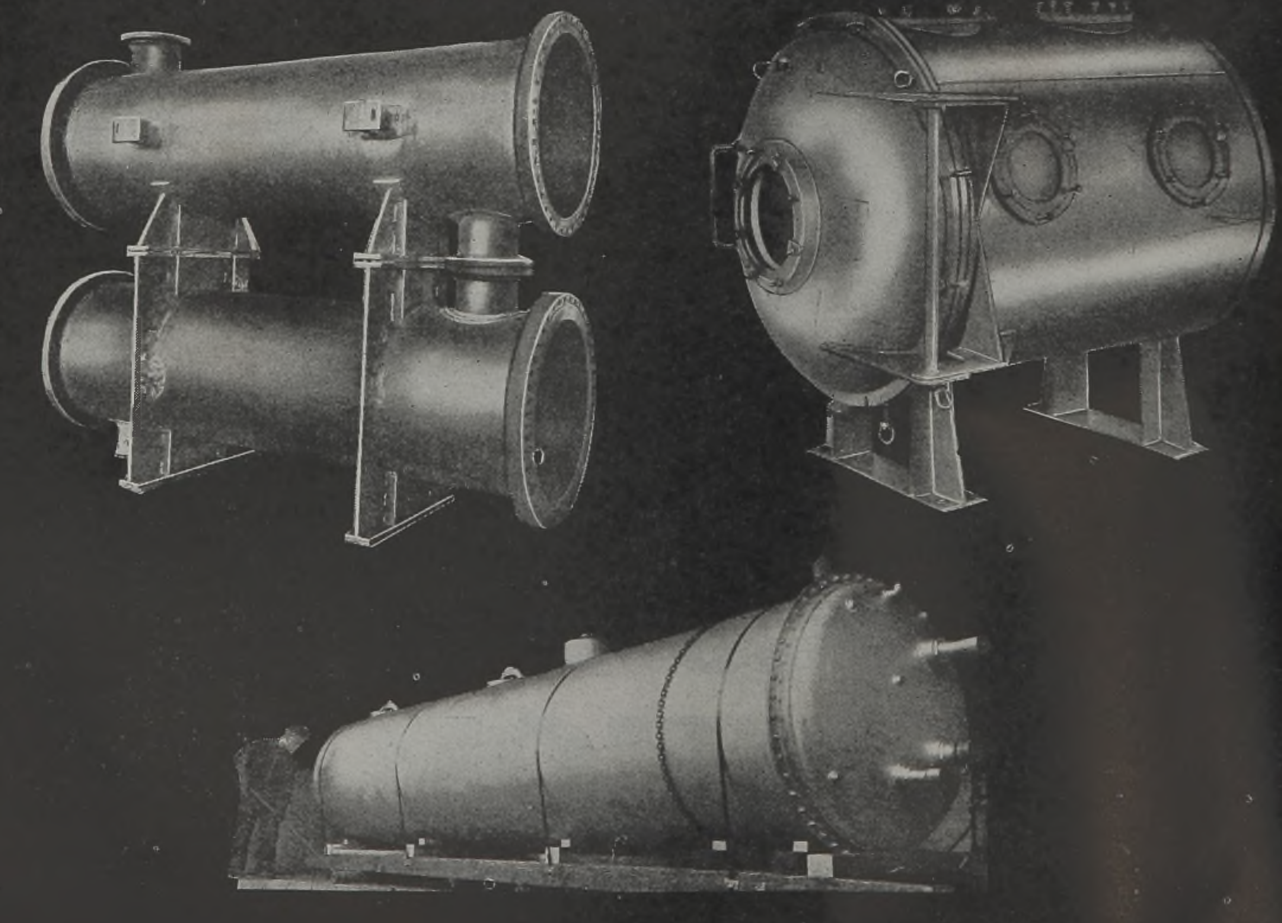
AIRCRAFT

RAILROAD

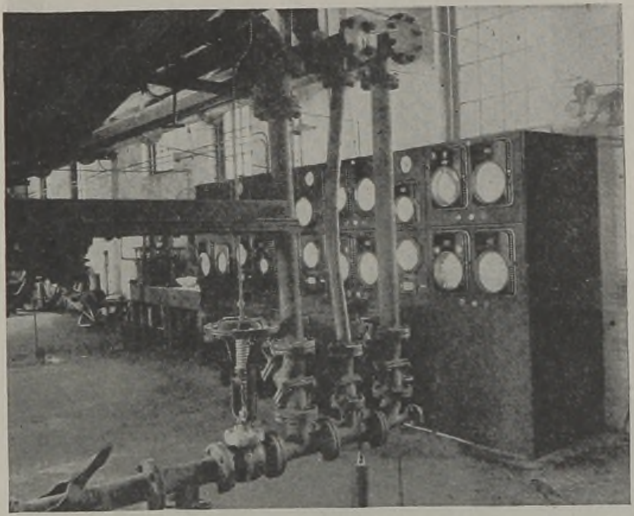


FLUOR

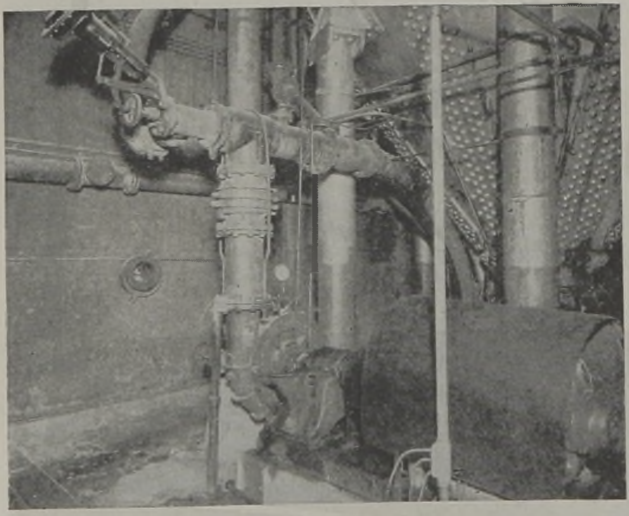
ENGINEERS • MANUFACTURERS • CONSTRUCTORS



Bristol Automatic Control Tones Up Sulphite Digestion



From this control panel, the entire operation is automatically controlled . . .



through synchro-air motors operating hydroheaters (above), and automatic valves.

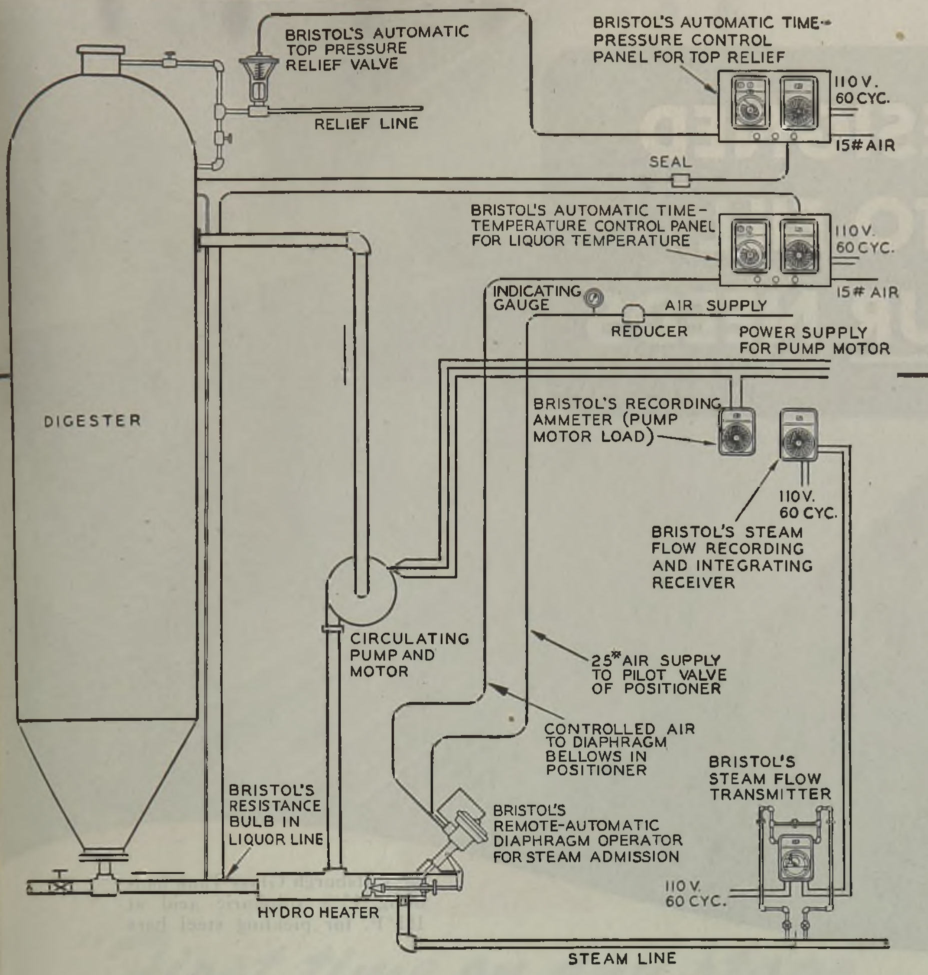
When temperature, pressure and flow are made to behave and acid strength stays where it belongs, uniform quality pulping is the result. Allowed to run loose, they cause both quality and costs to suffer.

The accompanying diagram of Bristol control instruments taking complete charge of a direct-heated circulating system for sulphite digesters will give you an idea of what can be done from a control panel.

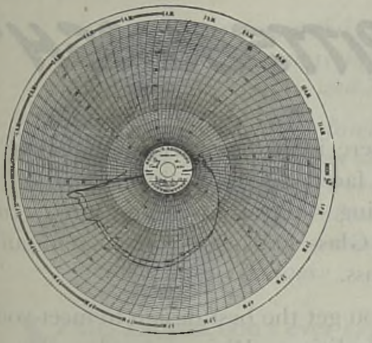
In this case, quality was greatly improved at the same time that important economies were being made.

Bristol's long and broad experience in instrumenting chemical processes suggests you can obtain valuable help from this source. When further instrumentation is taken up in your planning, have a Bristol engineer give you the benefit of his experience.

Address **THE BRISTOL COMPANY,**
110 Bristol Road, Waterbury 91, Conn.
(The Bristol Co. of Canada, Ltd., Toronto,
Ontario. Bristol's Instrument Co., Ltd.,
London N. W. 10, England).



Bristol instruments control temperatures of circulating liquor and digester . . . current input to pump motor . . . pressure in the digester . . . and steam flow to the digester.



Uniform temperature in different parts of the digester is important. This chart proves good chip distribution and circulation. The two record lines (top and bottom temperatures) stay together during heating-up, then never vary more than a few degrees.

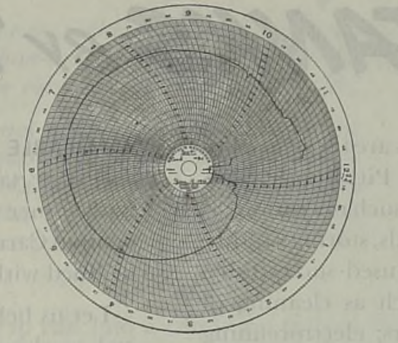
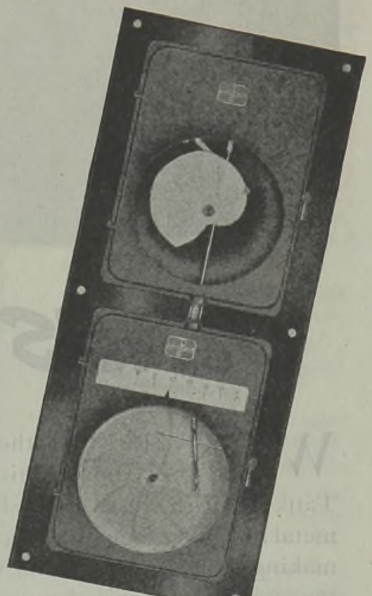
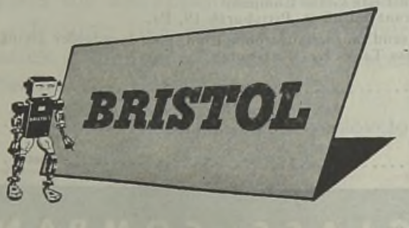


Chart record made by Pyromaster Time-Temperature Controller. Control instrument automatically brings temperature of circulating liquor up to 130°C. in six and one-quarter hours, then holds it for one and one-quarter hours.



Bristol Time-Temperature Controller, using potentiometer resistance thermometer measuring system and reset air-operated control mechanism. This instrument is described in detail in Bulletin P1200.



Engineers process control for better products and profits

AUTOMATIC CONTROLLING AND RECORDING INSTRUMENTS

28′ Pittsburgh Glass Tank handling 15% sulphuric acid at 185°F. for pickling steel bars

GLASS TANKS BY "PITTSBURGH"

WHATEVER the job, the chances are there's a glass tank to fit your requirements. Pittsburgh Glass Tanks have been used successfully for such operations as metal finishing, compounding chemicals, storing liquids, making cosmetics. And they've been used successfully, too, for many *unusual* purposes, such as cleaning of heavy engine parts; pickling steel bars; electrorefining of copper.

DURABLE Glass tanks are impervious to acids, alkalis, nearly all liquids (even hot chromic acid). They are non-porous, non-absorptive, and they don't contaminate their contents.

ECONOMICAL Because glass tanks are made of specially *tempered* glass, they have the strength and sturdiness for long service under hard usage. They are able to withstand the shock of sharp temperature changes. And glass tanks assure the absence of electric losses in processes such as electroplating.

AVAILABLE There is a wide variety of shapes, styles, and sizes: tanks faced with glass, inside and out; tanks with inner facing only; transparent tanks; colored, opaque Carrara Glass Tanks. Or your *present* tanks can be lined with glass.

Let us help you get the best design to meet your special working conditions. Write us today about your tank requirements. Pittsburgh Plate Glass Company, Grant Building, Pittsburgh 19, Pa.

"PITTSBURGH" stands for Quality Glass and Paint

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Please send me, without obligation, your free folder giving full details about Glass Tanks by "Pittsburgh."

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City.. State...........

PITTSBURGH PLATE GLASS COMPANY

★ Another example of Taylor Forge "know-how" that means extra value in WeldELLS

"First time on any stage"

★ As far as we know this is the only welding fitting of its kind. We forged it seamless in carbon-moly—10" pipe size in the run with .605" wall, and 7" in each branch with .429" walls.

It is neither "fish nor fowl"—not a side outlet tee because the included angle between the outlets is more than 90°, and it could hardly be called a cross. It's just one of the many once-in-a-life-time forging problems that have been assigned to us by engineers who have found that we do things with hot metal that no one else does.

YOU say you don't ever expect to run into a condition calling for a fitting like this? Probably not. But you do use standard welding fittings and this special fitting has a vital bearing on their selection. We have cited this and many other special forging problems because the "know-how" accumulated in solving them is the vital ingredient in every fitting in our regular production line of WeldELLS and other Taylor Forge fittings for pipe welding.

Every one of these many special problems has added something to our knowledge in a field where knowledge is all important. What else could explain the unduplicated combination of features found in WeldELLS . . . features like extra metal properly distributed where stresses are greatest . . . tangents . . . extremely accurate dimensions . . . and the many other features listed opposite?

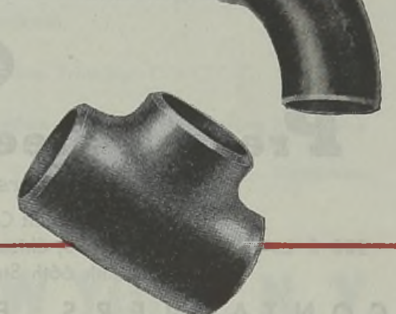
What else, indeed, could have developed fittings of which it can be said:

WeldELLS have everything

TAYLOR FORGE & PIPE WORKS, General Offices & Works: Chicago, P.O. Box 485
New York Office: 50 Church Street • Philadelphia Office: Broad Street Station Bldg.

WeldELLS alone combine these features:

- **Seamless** — greater strength and uniformity.
- **Tangents** — keep weld away from zone of highest stress—simplify lining up.
- **Precision quarter-marked ends**—simplify layout and help insure accuracy.
- **Selective reinforcement**—provides uniform strength.
- **Permanent and complete identification marking**—saves time and eliminates errors in shop and field.
- **Wall thickness never less than specification minimum** — assures full strength and long life.
- **Machine tool beveled ends** — provides best welding surface and accurate bevel and land.
- **The most complete line of Welding Fittings and Forged Steel Flanges in the World**—insures complete service and undivided responsibility.




DESIGNED
TO FILL
YOUR NEEDS

"First time on any stage"

★ As far as we know this is the only welding fitting of its kind. We forged it seamless in carbon-moly—10" pipe size in the run with .605" wall, and 7" in each branch with .429" walls.

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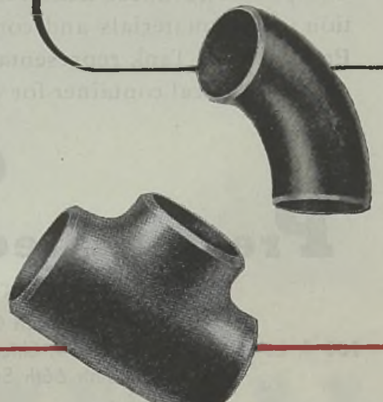

WeldELLS *have everything*

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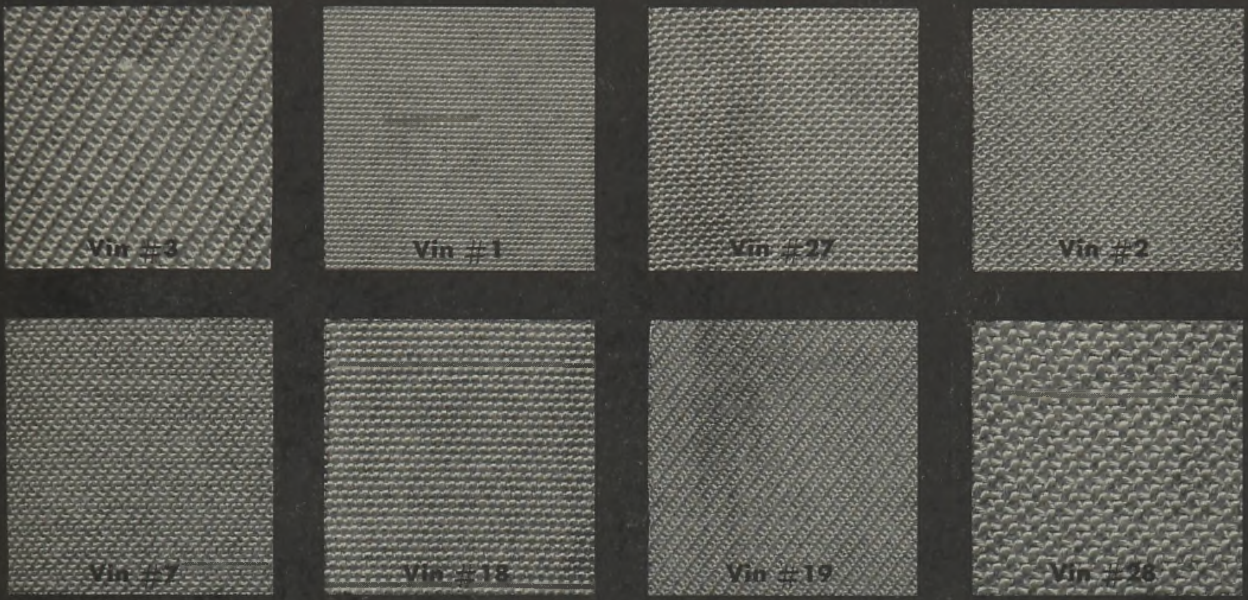
VINYON* FIBER



FOR FILTERING MINERAL ACIDS and ALKALIES

FILTER FABRICS

If you have a filter fabric problem in connection with any of the processes or products listed below, Vinyon fiber filter fabrics may be the solution. Subject always to certain heat limitations, Vinyon is highly resistant to corrosive fluids.

Perfected and developed through careful field studies, Vinyon fiber filter fabrics are now solving many problems in the filtration of mineral acid and alkali solutions.

Longer life, higher efficiency and therefore ultimate economy are characteristic of Vinyon fiber filter fabrics that will be of interest to you. The engineers on our staff are in a position to discuss with you the possible application of Vinyon fabric to your particular problems. When writing please include all information regarding your present filtration process.

*Reg. Trade Mark C. & C. C. C.

- **Pigments and Dry Colors**
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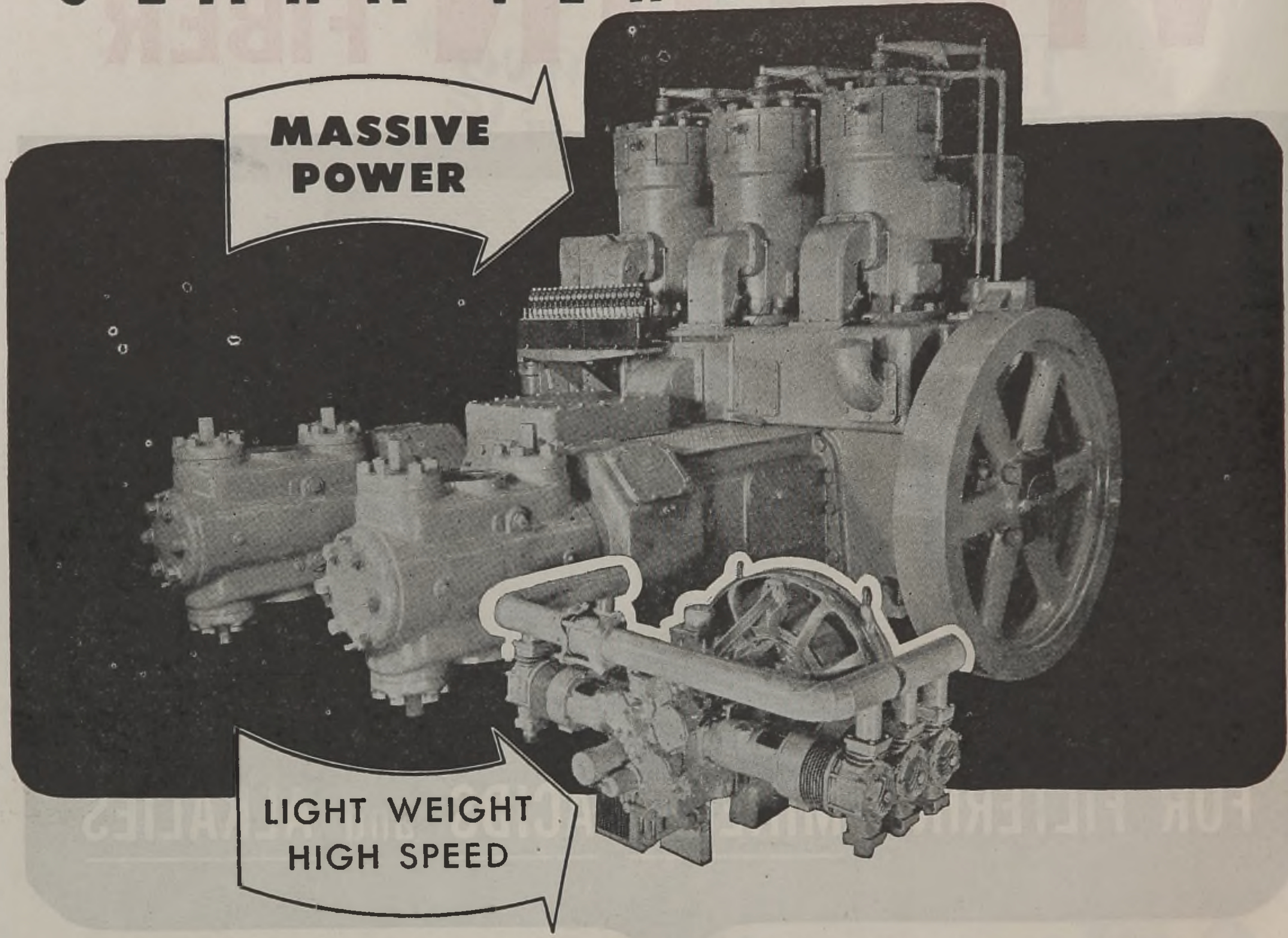

WHEN the Army needed a small, extremely light weight, nonlubricated, high-speed compressor, Clark undertook to design and build it. The speed required (1800 rpm) seemed at first to be beyond the practical limit, but like so many things that look impossible, "it had to be done and we did it".

We are not permitted to tell what this small compressor is used for, but it has proved highly successful. In contrast with one of our well-known standard models—a 3-cylinder gas engine driven "Angle" compressor—this little fellow looks and is a mere midget. But its 75 B.H.P. and 225 C.F.M. capacity are 25 per cent as great as its big brother's, over fifteen times its weight.

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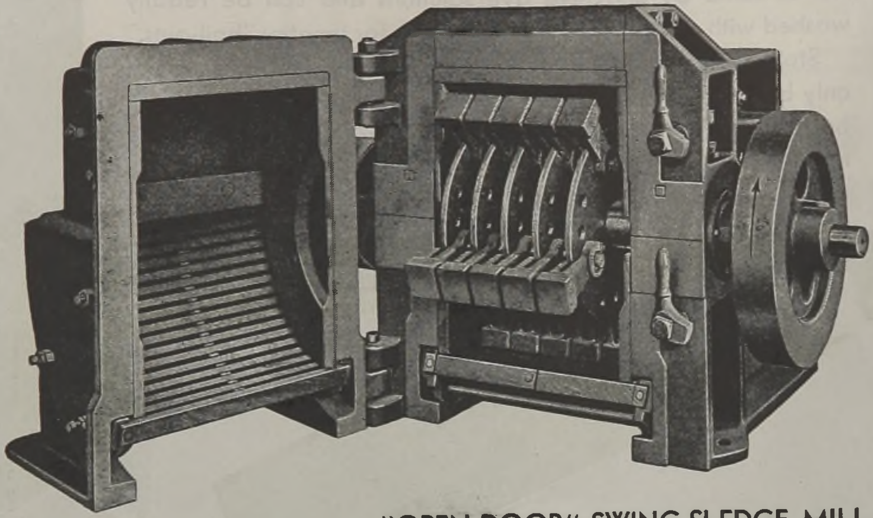
SETS THE PACE IN COMPRESSOR PROGRESS

Built for your HEAVY DUTY REDUCTION



"OPEN-DOOR" SWING-SLEDGE MILL

Sturtevant Mills and Pulverizers have the exclusive patented "Open-Door" feature.

Sturtevant Swing-Sledge Mills and Pulverizers are built for reduction of soft or hard materials to sizes ranging from 1 inch to 20 mesh and handle from ½ to 70 tons per hour.

The "Open-Door" feature of Sturtevant machines enables the interior to be exposed for examination. By simple removal of two bolts or latches, the entire front of the machine may be opened without disturbing feeder, spouting or discharge chute, as shown above.

Swing-Sledge Mills are for heavy duty reduction work on tough, hard materials. Lined with manganese steel, the Mills are furnished with steel hammers, manganese steel sledge hammers, hatchet hammers, or special equipment. Hinged-Hammer Pulverizers are for breaking down softer materials and may be furnished with grates for easier handling of sticky materials.

WRITE FOR FURTHER DETAILS AND SPECIFICATIONS

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SPECIALIZED EQUIPMENT

For Crushing and Grinding:

Rotary Crushers reduce moderately hard substances to quarter inch or finer with a minimum of dust.

Balanced Rolls reduce soft or hard material to 12–20 mesh with equalized pressure and less shock in operation.

All types have the exclusive Sturtevant Open-Door feature for easy care.

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Closed Circuit Air Separator is highly efficient in separating in a range of 40–400 mesh, with superior accuracy and capacity possible.

Moto-Vibro Screens come in 1, 2, or 3 sections, steel enclosed, with equally efficient vibration in all screens.

For Mixing:

Dry Batch Mixers with single opening for entrance and output of materials minimize dust escape.

Rotary Batch Blenders utilize four separate and distinct actions for complete and perfect blending.

For Elevating and Conveying:

Special equipment to fit your design requirements provide complete, easily accessible and compact superior construction.

For Fertilizer Manufacture:

A complete den and excavator unit with 2-man operation and capacity of 10–40 tons per batch makes a compact efficient production means.

For Laboratory Work:

Small size but powerful crushers, crushing rolls, sample grinders, and swing sledge mills incorporate the "Open-Door" feature with special design for laboratory operations.

Potash and Smoke

Asked how much smoke would be produced by the burning of 1,000 pounds of wood, Demonax, of Cyprus, answered: "Weigh the ashes! The missing weight has escaped as smoke." Ancient Greek writings reveal that this 2nd Century philosopher knew well the alkaline properties of wood and plant ashes (potash).

Alkaline plant ashes were included in the earliest Persian Pharmacopeia (975 A.D.) as well as the Arabian Canon of Medicine (about 1000 A.D.). But it was not until Sir Humphry Davy in 1807 isolated potassium that the true composition of potash became known. Later, with the exploitation of the Stassfurt salt mines, the door was opened to the vast commercial production of potassium salts for medicine, pharmacy and chemistry.

For 78 years MALLINCKRODT CHEMICAL WORKS have produced potassium salts of QUALITY IN QUANTITY. During this time more than 125 standardized and special salts, including the Acetate, Bicarbonate, Borate, Bromide, Citrate, Gluconate, Iodate, Iodide, Metabisulfite, Oxalate, Phosphate, Sulfate and Sulfite, have been of service to chemical users.

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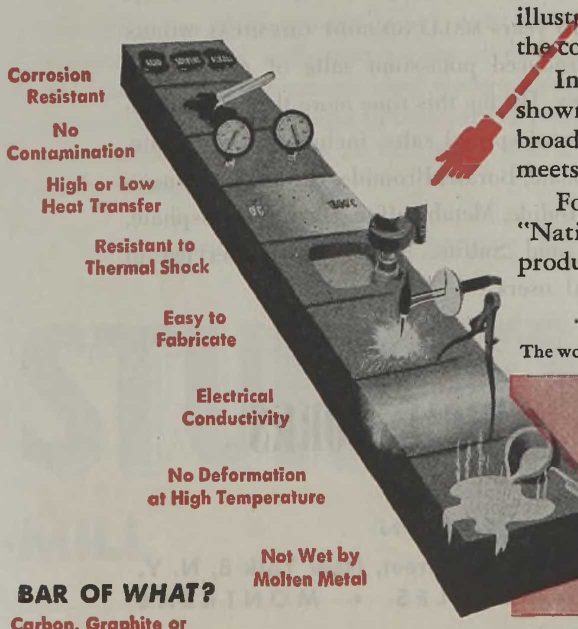
SINCE carbon and graphite and "Karbate" materials* are readily formed and machined into intricate shapes with precise dimensions, they are easily fabricated into equipment and structures of utmost utility for the metals, chemical, mechanical and other industries.

Examples are the injector-ejector, cooler-absorber, and five-way valve illustrated . . . each built of accurately finished pieces and each having the combination of properties for its job possessed by no other materials.

In the metals industries, applications run from the metallurgical tray shown to durable furnace linings easily built of fitted carbon blocks. A broad line of processing equipment—standardized or to your design—meets exacting demands of the chemical industries . . .

For detailed information on these and many other applications of "National" carbon and graphite and "Karbate" formed or fabricated products, write to our nearest division office for Catalog Section M-8000-A.

*Impervious carbon or graphite



BAR OF WHAT?
Carbon, Graphite or "Karbate" materials of course!

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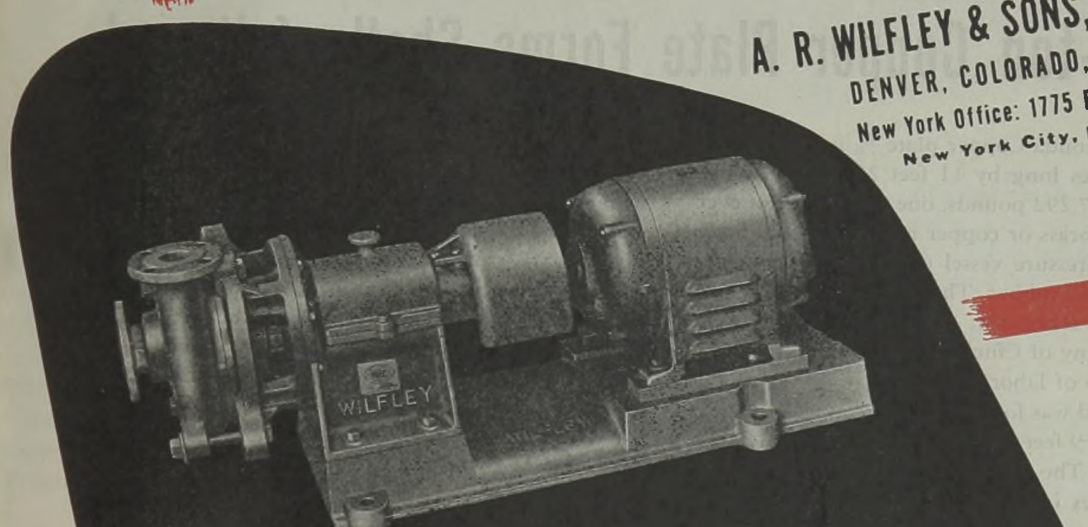
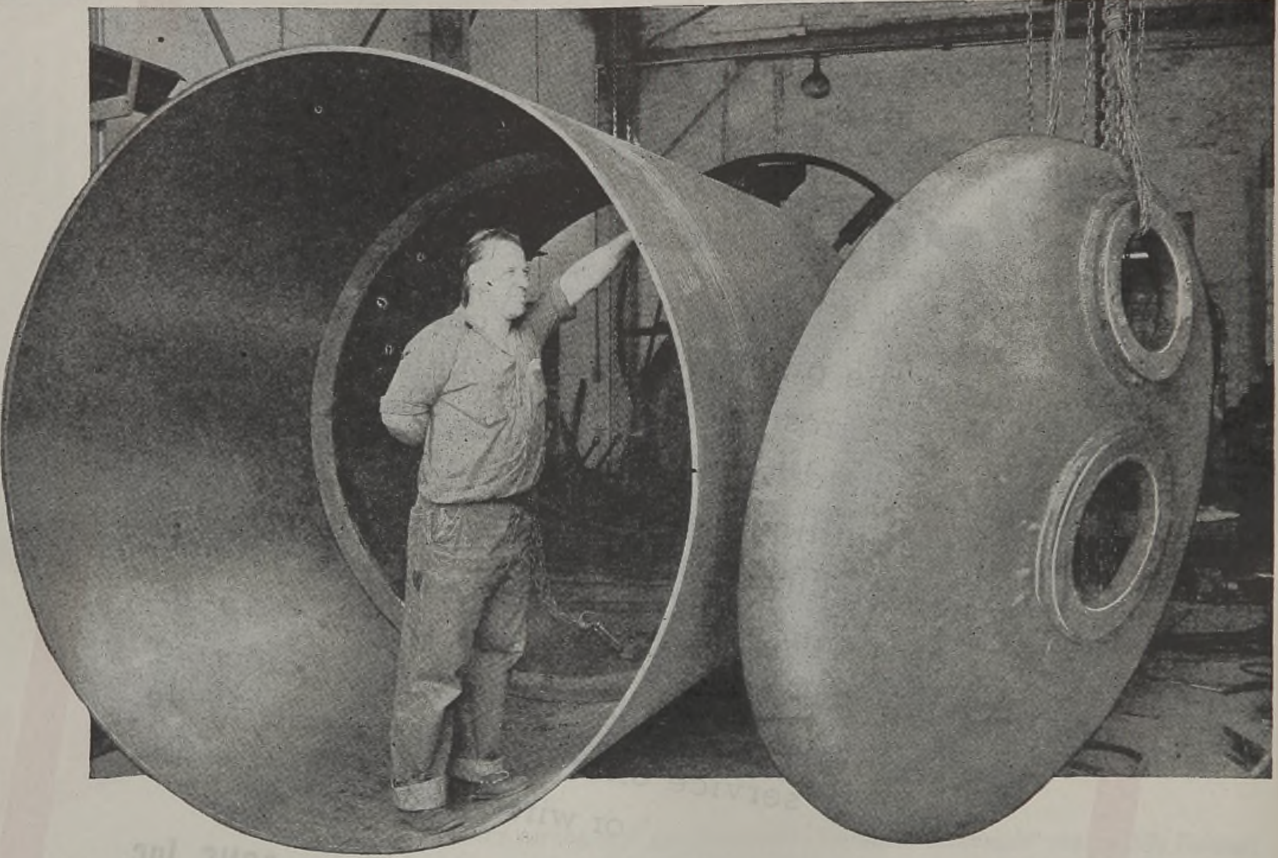

WILFLEY

FOR EASE OF WORKING...



Single 3½-ton Copper Plate Forms Shell of Vessel

A SINGLE Anaconda Copper plate ⅝ inch thick, 22 feet 10½ inches long by 11 feet 2⅝ inches wide, and weighing 7,292 pounds, one of the largest ever rolled by any brass or copper mill, forms the body of this large pressure vessel used for the manufacture of synthetic rubber. Through the use of a single plate, the fabricator, The Vulcan Copper & Supply Company of Cincinnati, saved an estimated 200 man-hours of labor.

The top head was formed from a copper circle ¾ inch thick and 9 feet ¾ inch in diameter, weighing 2,243 pounds. The circle for the bottom head was 8 feet 6 inches in diameter, ¾ inch thick, and weighed 1,964 pounds.

Both the longitudinal seam of the body and the top and bottom heads were oxy-acetylene welded with Anaconda Silver Bearing Copper 110 Rod.

Anaconda Metals . . . copper, brass, bronze . . . have always provided the chemical and process industries with materials high in corrosion resistance, ductility, strength and thermal conductivity. The availability of large plates and advancements in welding practice open new fields of usefulness for copper and copper-base alloys.

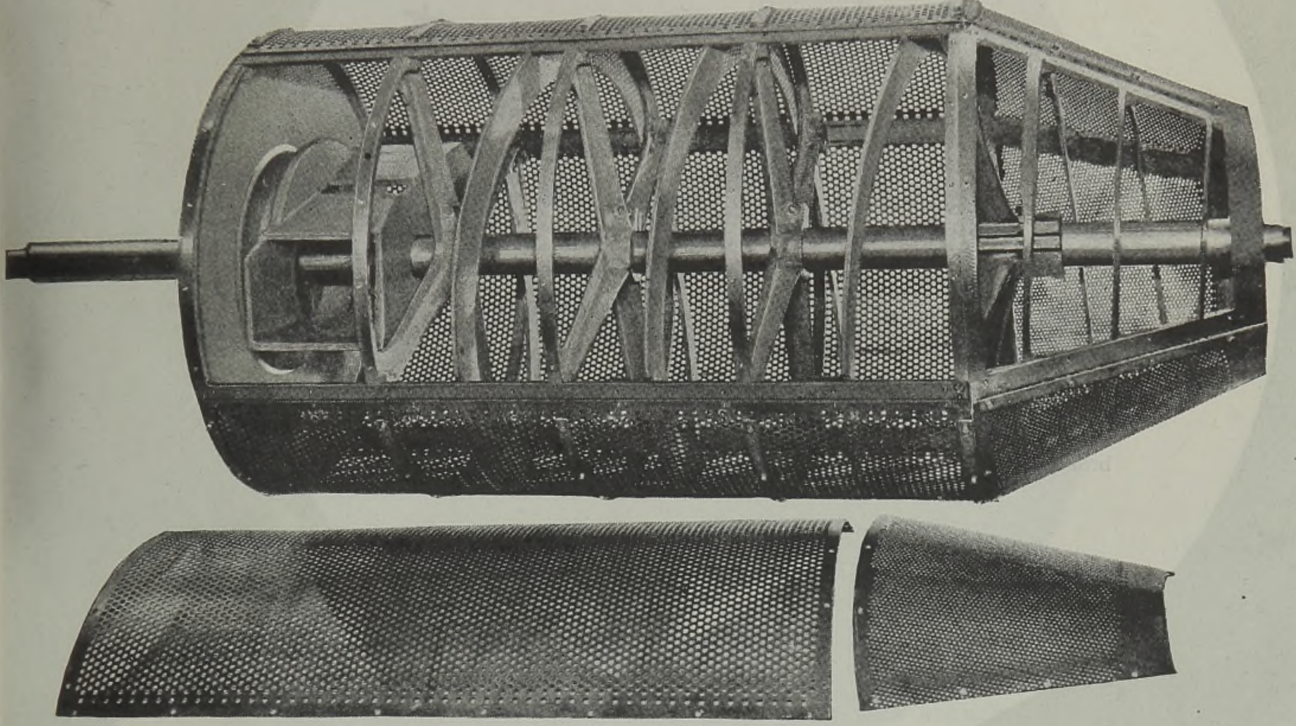
THE AMERICAN BRASS COMPANY
General Offices: Waterbury 88, Connecticut
Subsidiary of Anaconda Copper Mining Company
In Canada: ANACONDA AMERICAN BRASS LTD., *New Toronto, Ont.*

ANACONDA
from mine to consumer

Anaconda Copper & Copper Alloys

FOR RUGGED ENDURANCE...

Everdur* screens 60 tons of pulp per day...



THIS Pulp Knotter Cylinder made by Trimbey Machine Works of Glens Falls, New York, has a capacity of 60 tons of pulp a day and provides an excellent example of the strength, toughness and corrosion resistance of Everdur . . . and of its ability to stand up to severe conditions of service.

For, with the exception of the brass-encased shaft, every part is made of Everdur . . . perforated screens, framework, cast spiders, and even the bolts and nuts. So satisfactory has this manufacturer found Everdur, that this economical, long-lived metal is also used for direct acting float valves and water valve plungers in connection with the Trimbey Automatic Consistency Regulator; and for rotors and distributors in the Trimbey "Senior" Pulp Screens.

When designing equipment for handling, mixing, converting, storing or transporting corrosive or abrasive liquids, solids or gases, investigate the advantages offered by Everdur. It is available in rods, bars, plates and special shapes. Our Technical Department is available for assistance with special problems. 45166

*Reg. U. S. Pat. Off.

THE AMERICAN BRASS COMPANY
General Offices: Waterbury 88, Conn.
Subsidiary of Anaconda Copper Company
In Canada: ANACONDA AMERICAN BRASS LTD.,
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KEEP FAITH WITH YOUR FIGHTERS AND YOURSELF! BUY WAR BONDS FOR KEEPS

ANACONDA
from mine to consumer

Everdur Copper-Silicon Alloy

TO THESE MIGHTY WORLDS OF INDUSTRY

CHEMICAL

Industrial Ethyl Alcohol, Isopropanol and Higher Alcohols • Methanol, Synthetic and from Wood Distillation • Ethyl Acetate, Butyl Acetate and other Esters • Synthetic Acetic Acid and Acetic Anhydride • Nitrobenzene and other Nitro-Aromatics • Formic Acid and Higher Aliphatic Acids • Carbon Tetrachloride • Chloroform, etc. • Phenol, Cresols, etc., from Tar Acids • Aniline and other Amino-Aromatics • Beverage Alcohol and Spirits • Ethyl Ether and Isopropyl Ether • Acetone and other Ketones • Glycerine and Glycols • Phthalic Anhydride • Styrene • Ammonia • Butadiene • Fatty Acids • Ethyl Benzene • Formaldehyde • Nitroparaffines • Synthetic Phenol • Dibutyl Phthalate • Synthetic Camphor • Explosives and Smokeless Powder • Penicillin • And many others.

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On these pages are listed some of the many products Badger process engineering and construction services have helped to put into commercial production. *A Bulletin amplifying the scope of Badger activities is available for the asking.*

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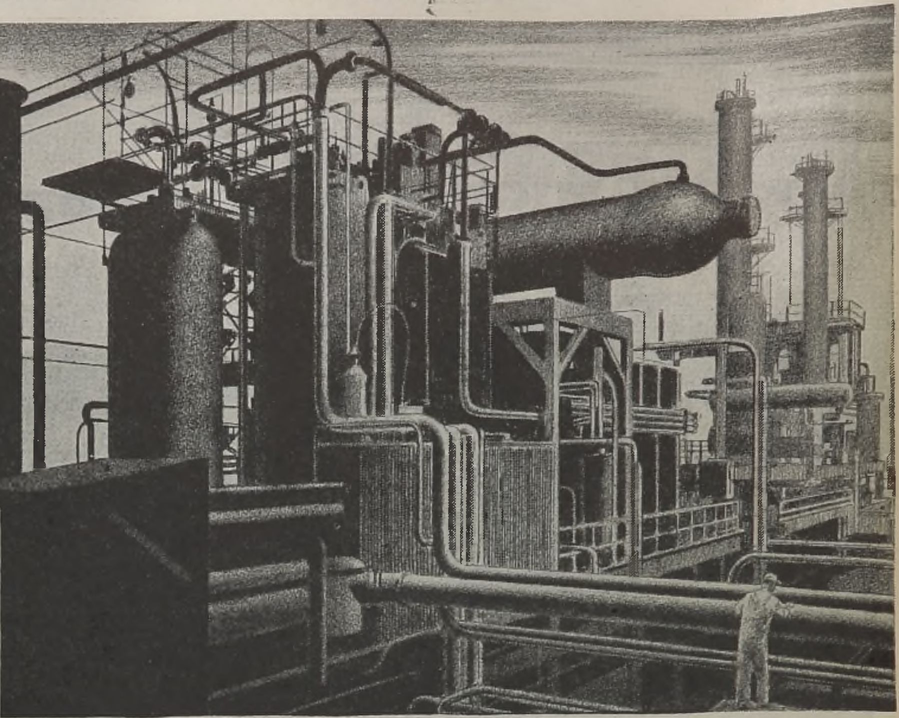

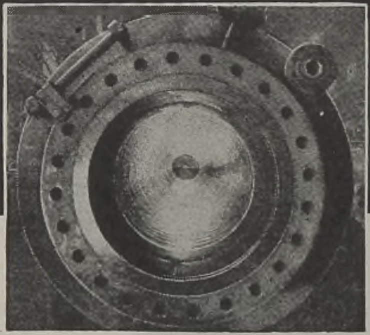

HASTELLOY Alloy lining of a large reaction vessel

HASTELLOY Alloys are used in Aviation Gasoline Isomerization Plants

- **Isomerization of light petroleum fractions with an aluminum chloride catalyst is an important part of the aviation gasoline program. But the highly corrosive hydrochloric acid and chlorides formed in the process attack most metals rapidly, so that the life of vessels, piping, pumps, and valves is short.**

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Offer All These Advantages:

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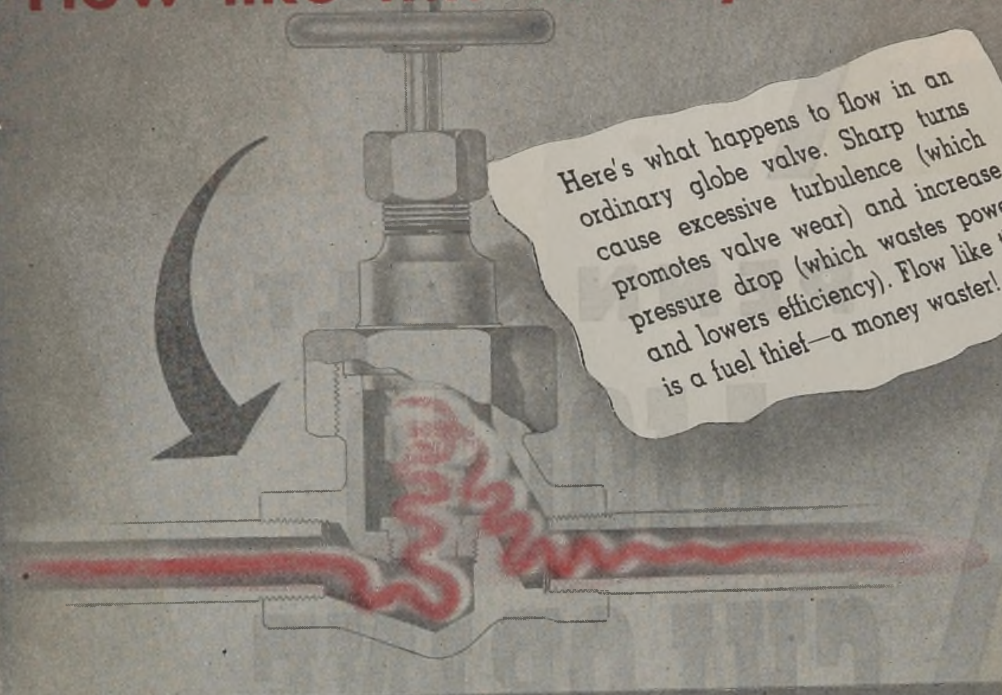

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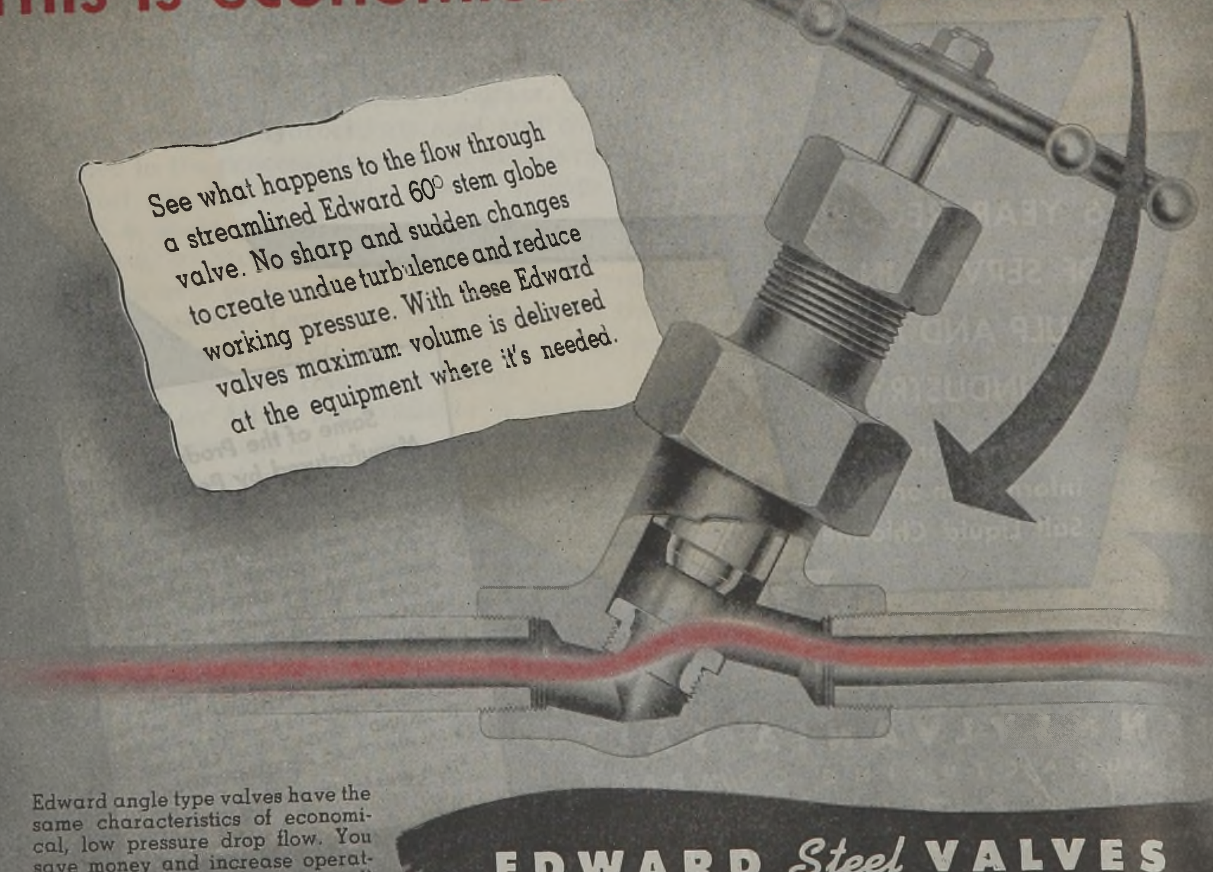

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This Month

PILOT PLANT PHASES is the title of the ninth unit processes symposium to be featured in an issue of INDUSTRIAL. The symposium is introduced by R. Norris Shreve who points out that pilot plants demonstrate the wisdom of the old saying concerning mistakes on a small scale and profits on a large scale. Each new development in the chemical field is dependent upon data and techniques worked out in the small scale plants, which are so particularly a part of the chemical engineer's heritage. Four papers are devoted expressly to pilot plants, and the remainder of the symposium deals with new developments in unit processes.

Barnebey, of Blaw-Knox Company, leads off with an article on the proper design, construction, and operation of chemical process pilot plants. He points out some of the stumbling blocks to designing efficient working units and emphasizes that good judgment must be exercised in adapting equipment to the needs of investigation.

Vilbrandt, of Virginia Polytechnic Institute, points out that a pilot plant has a definite purpose and that, to be successfully utilized, a specific program with the proper personnel is necessary. His article is concerned with a concrete example of how a pilot plant functions in solving manufacturing problems in the use of butane for making alcohols, aldehydes, and acids.

Mixer performance data from pilot plants by J. H. Rushton, of the University of Virginia, is not only an important contribution to the pilot plant symposium, but is an important addition to the symposium on agitation and mixing which was printed in the June, 1944, issue. Rushton has done considerable work on mixing and is well qualified to discuss this subject. He points out that the proper evaluation of equilibrium data and its translation to a large scale is dependent upon mixer performance; this, in turn, is dependent upon other factors. To him one of the critical items in proper design of pilot plant machinery is the determination of the best operating conditions for mixers.

Bissell, Miller, and Everett, of Mixing Equipment Company, also feel that one of the most important factors in pilot plant design is the correct application of the unit operation, mixing. They give general design data for vessel shapes, dimensions, and other important basic factors. This article is also an interesting adjunct to the agitation symposium published last year.

In quick order the other unit process articles concern the oxidation of chlorinated hydrocarbons to maleic and fumaric acids, catalytic vapor-phase oxidation of ethylene, oxidation of hexadecane, rosin ester development, oxidation of ferrous sulfate solutions with oxygen, and utilization of waste liquors from wood hydrolysis. All these papers are important in various ways to the industrial wellbeing of the nation and will undoubtedly have great effect on our chemical economics.

Tying in closely with the symposium is a paper by Carlsmith and Johnson which was part of the catalysis symposium published last month. This is a discussion of the pilot plant work which was carried out in the development of the fluid catalyst cracking processes. This technique of splitting oil fractions is one of the most important in operation during the war, and the trials and tribulations of the chemical engineer in bringing this to successful commercial operation makes worth-while reading.

Two extensive studies on antifouling mechanisms follow one another in this issue. The first is from the Woods Hole Oceanographic Institution and the Navy, and concerns a method for measuring the rate at which copper toxics dissolve from antifouling paints. The authors claim that, in order to prevent barnacles from growing, copper must leach from the surface at a rate of 10 micrograms per sq. cm. The second is from Mellon Institute and represents work done on a Stoner-Mudge fellowship. The authors investigated the mechanism of accelerated corrosion under antifouling coatings. They found that because of the concentration of copper in the antifouling paint, local couples and electrochemical effects are the main causes for accelerated corrosion.

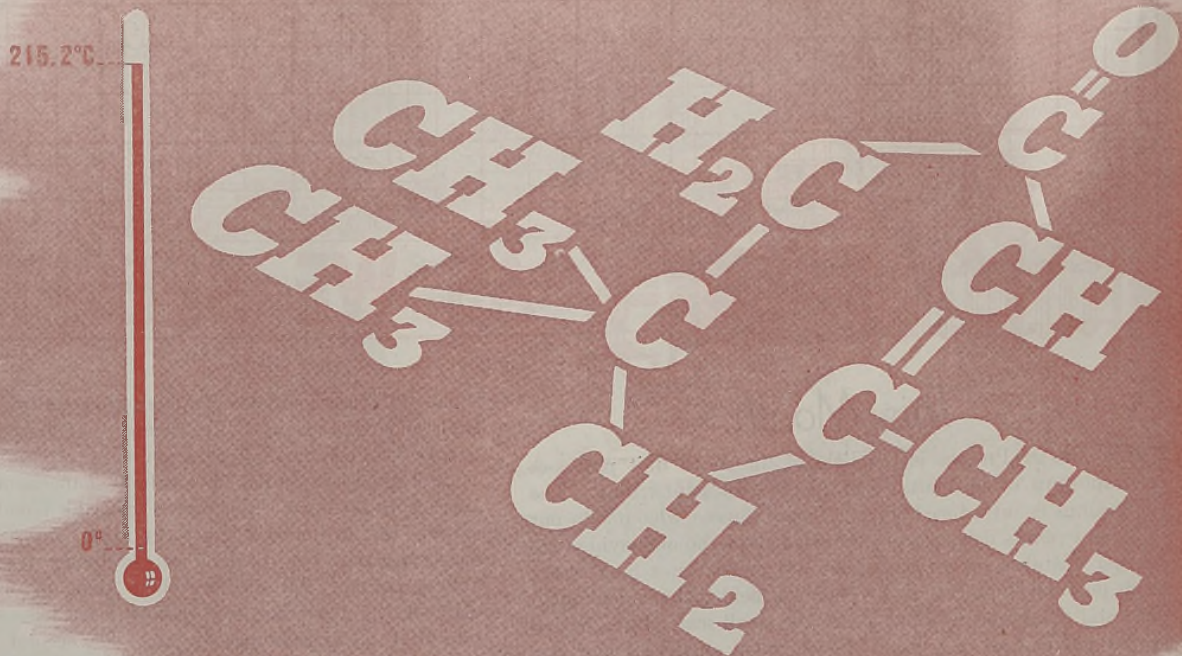
Bacon and Boe, of Texas Gulf Sulphur Company, have studied the production of hydrogen sulfide from sulfur and hydrocarbons. Because the market for hydrogen sulfide is now 20,000 to 25,000 tons annually, the authors have investigated carefully the possibilities of furnishing a portion of this demand by the reaction of sulfur with hydrocarbons. Depending on the sulfur used, yield of gas is about 75–80%, and purity is said to be high. They state that the material cost per pound of hydrogen sulfide is about 1.1 cents. Included also is a table of catalysts for the reaction of carbon disulfide with water to yield carbon dioxide and hydrogen sulfide.

Sookne and Harris present two papers on cellulose acetate, the first covering viscosities and osmotic molecular weights, and the second dealing with polymolecularity. Both are from the recent symposium on cellulose plastics held during the 108th Meeting of the AMERICAN CHEMICAL SOCIETY. The authors found that Staudinger's rule was followed, up to molecular weights of 130,000, inasmuch as the molecular weights were proportional to the intrinsic viscosities.

Physical properties of acrylonitrile are important to the chemical industry of the Nation since this organic material has become commercial in tank car commodities. Consequently the censor-delayed article of Davis and Wiedeman, of American Cyanamid Company, on this subject is important and the first authoritative information published.

With the Departments. Brown this month discusses the advisibility of setting up programs for the use of disabled veterans prior to their return to industry. Von Pechmann tackles the age-old problem of whether it is better to buy materials outside of the plant or whether they should be manufactured by readily available facilities. Munch recognizes the need for increasingly accurate temperature measurements and devotes his column to discussing the place that resistance thermometers have and will hold in the solution of this difficult problem.

F. S. Van Antwerpen



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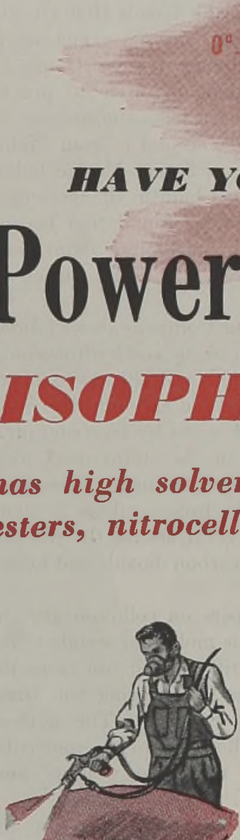

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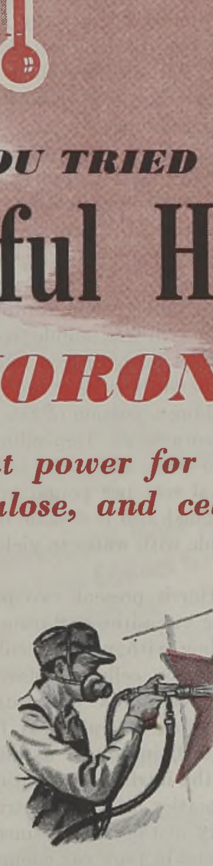

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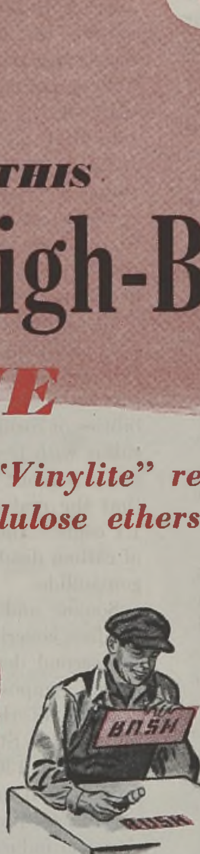

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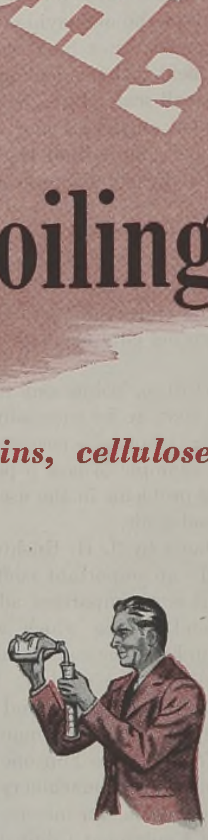

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INDUSTRIAL AND ENGINEERING CHEMISTRY

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY

Editorials

WALTER J. MURPHY, EDITOR

Now Is the Time for Action

A SPECIAL supplement on Scientific and Technological Manpower printed in the April 10 issue of *Chemical and Engineering News* marks a temporary culmination of several years of intensive labor on the part of the officers of the ACS. Manpower, with its problem of assuring the nation of an adequate supply of trained men, and with its problem of fighting for the deferment of necessary personnel, has received the attention of the American Chemical Society as no other problem has before it. Countless hours have been spent in studying and planning means of impressing upon the authorities the necessity of deferring chemists and chemical engineers, and the magnitude of this effort can be realized by a thorough study of the data presented in the special supplement. *But the time now has come when the Society can do no more as an entity. Now must the individuals that comprise the Society match the efforts of the officers in impressing upon the authorities the necessity of deferring trained men.*

That this is so is indicated by a message in the supplement from Secretary Parsons asking the members of the Society to express, to their Congressmen, their views on manpower matters, especially on H.R. 2827. This bill, which was introduced into the House by Representative McDonough of California, seeks "to authorize the release of persons from active military service, and the deferment of persons from military service, in order to aid in making possible the education and training and utilization of scientific and technological manpower to meet essential needs both in war and in peace". It is a short bill of little more than 300 words, but the implications and importance of those 300 words are of extreme and vital value to our nation. We urge the individual members of the ACS to read thoroughly all the material in the special supplement, and if more data are needed for transmittal to your government representatives, there is appended a bibliography of most of the important material that the ACS has published on the draft, Selective Service, and the manpower crisis.

Not only should our members, as individuals, become well versed in the facts about this situation, but they should acquaint others with the danger that is before the country if our scientific position is not strengthened. Our members must become missionaries in this cause, showing others where our true course lies.

But you, as a member of the ACS, must act now if anything is to be salvaged from a rapidly disintegrating situation. The war's finish in Europe will not give sufficient relief in this problem, for we must become still stronger technologically if Japan is to be finished quickly—and we cannot be strong technologically if the practice of inducting men and stripping our colleges continues. The postwar will require an inventive nation, and an inventive nation must be paced by research teams, which, in turn, are staffed by trained men.

The answer to the problem is in your hands, but only if your hand clasps a pen.

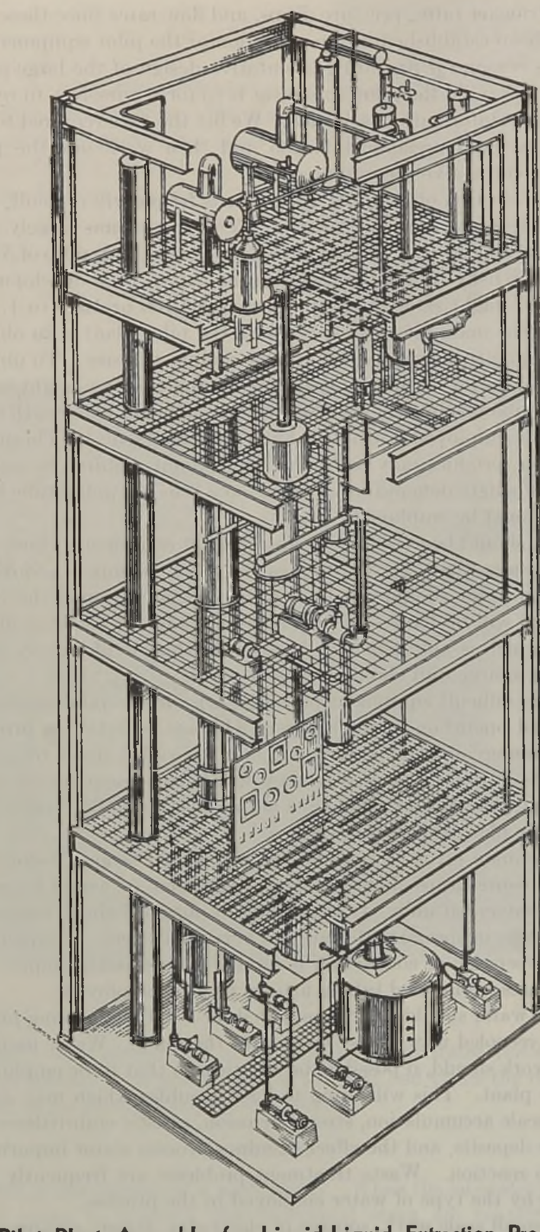
Illinois and the Scientist and Engineer

TWO months ago we called attention to the action of the United States Civil Service Commission in abandoning the long-established practice of requiring minimum educational requirements from those who seek positions as chemists, physicists, and engineers. A similar policy may be followed in the State of Illinois, for Senate Bill No. 55, an amendment to the Illinois Civil Service Act of 1905, reads as follows:

> No person shall be required to have completed any prescribed amount of school work or to have been graduated from any school as a prerequisite to the taking of any examination, or to being appointed to any position, but the holding of a valid license to engage in or practice a specialized trade or profession may be required of applicants for appointment to technical or professional positions.

This bill, which would eliminate all educational requirements prerequisite to the state examinations for chemical and all other nonlicensed technical positions, has passed the Illinois Senate and is now before the Lower House. The Illinois bill is open to the same severe condemnation that the Board of Directors of the American Chemical Society leveled at the action of the United States Civil Service Commission.

Legislators who vote for this measure possibly feel that they are assisting veterans to obtain employment, but no greater disservice could be done to our returning soldiers than to place them in positions that they are obviously unfit to hold because they lack the necessary educational background. The bill is a direct threat to the merit system in Illinois, it will place in jeopardy the health and welfare of the citizens of Illinois, and it is a direct challenge to the professional status of every chemist and chemical engineer in that state.



Pilot Plant Assembly for Liquid-Liquid Extraction Process

correlate small scale and large scale operations. For example, with a jacketed kettle or a tank with an internal coil, the heating surface in two sizes of units should represent about the same number of square feet per gallon of liquid capacity. A small jacketed kettle does not look like a large one when the same ratio of heating surface to volume is maintained. When distillation or evaporation is part of a process, the vapor release area per gallon of liquid capacity or cubic feet of vapor per minute per square foot of surface should be as nearly the same ratio as can be conveniently obtained in both cases. It is always difficult to correlate agitated equipment. A particular type of agitator should have about the same peripheral speed (not r.p.m.) in the pilot and commercial equipment. The commercial plant should use approximately the same amount of power per gallon of liquid capacity or per square foot of wetted surface as does the pilot plant. It is convenient to consider both ratios and sometimes decide upon an intermediate figure. Another useful method of comparison where turbine agitators are used is to correlate them on the basis of the time required to turn over the liquid charge completely.

A pilot plant ought to be designed with engineering care, equal to that employed on commercial work. It should not be a tangled mass with wires, pipes, and levers running in all directions. The design should be neat, trim, and businesslike. It is preferable to use commercial equipment types wherever possible. Special provisions should be made for starting up and shutting down, because this will be done frequently. A well built pilot plant is usually an expensive toy and it is good policy to estimate the cost accurately before proceeding.

CONSTRUCTION

The pilot plant ought to be constructed with the same attention to safe operation as would be given in a large commercial plant. In fact, because of operating variations which will be introduced and because of frequent starting up and shutting down, there may be certain additional precautions to be taken with the small equipment. Also, since the process is being operated for the first time on long runs, unexpected conditions might arise. Whenever possible these should be anticipated so as not to cause danger to the equipment and its operators.

The pilot plant should be constructed by ordinary workmen, mechanics, and pipe fitters; if there are any unusual difficulties in the construction, they will report them. Each complete pilot plant is best set up by itself, not in close proximity to other operations. The pilot plant must operate very much like a commercial unit—that is, continuously 24 hours a day rather than just during the day shift. Working conditions must be favorable with no interference in the form of noise, fumes, or obstacles. A number of pilot plant operations should not be carried out in the same room.

It is good policy to employ the same type of housing for the pilot equipment that is anticipated for the final plant. If the large equipment is to be located out of doors, do the same with the pilot apparatus. In such cases, if time permits, the test runs should extend through a complete cycle of seasons so that the effect of hot weather and cold, sun, wind, rain, and snow can be observed.

The pilot equipment should be provided with suitable platforms and stairways so that access to the various portions of the equipment, either for observation or maintenance, is facilitated.

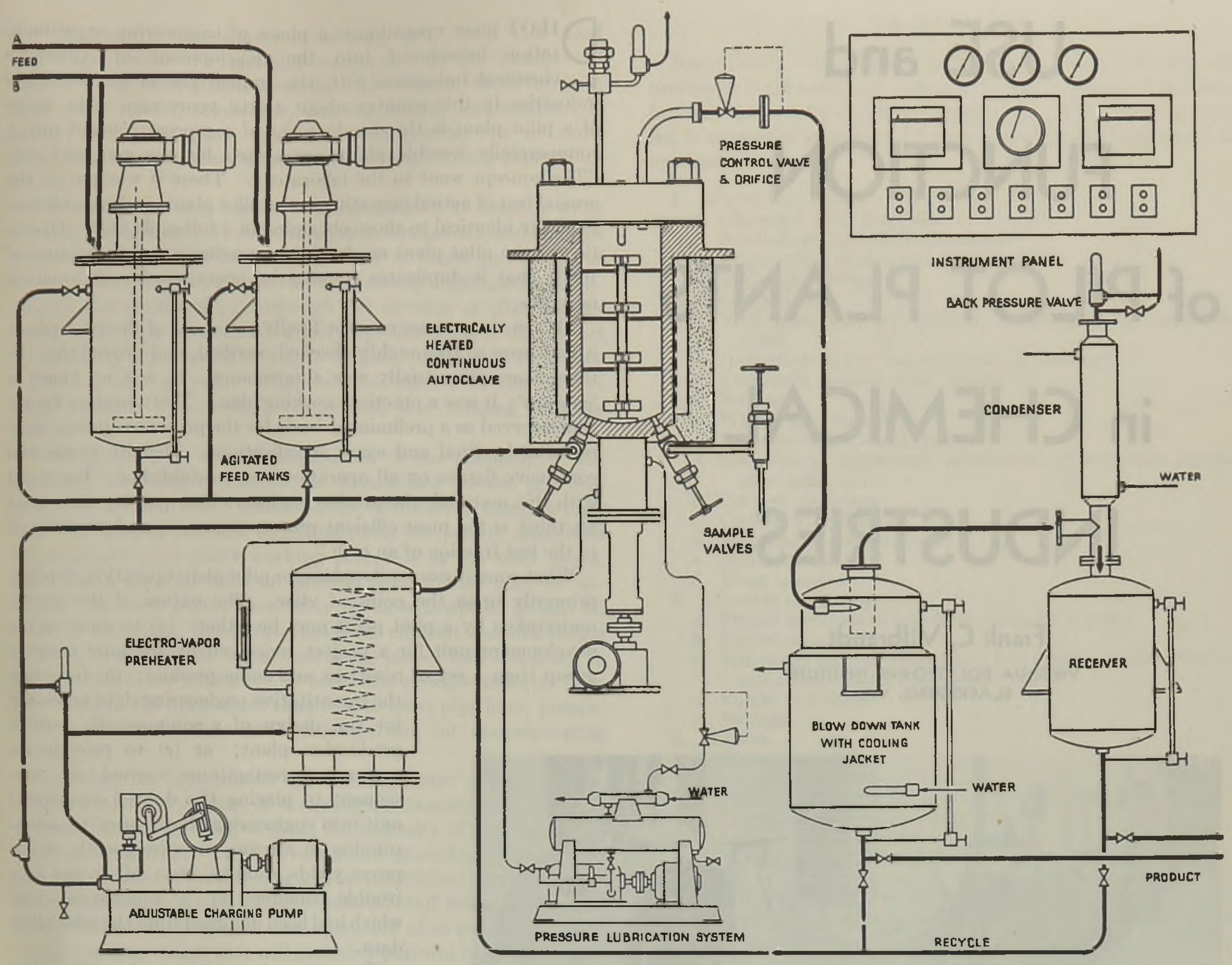
OPERATION

The pilot plant is operated by chemical engineers and regular process operators, not by research chemists. An excellent opportunity is here presented to train operators for the commercial plant.

Careful records should be kept of all runs, not just the good ones. A sufficiently large operating crew must be employed so that the process can be controlled and the required data taken simultaneously. The control tests to be employed in regular production should be determined and used at this stage.

A sufficient number of runs should be made to ensure that the data represent what can be expected in day after day operation. The tests ought to use exactly the same grades of raw materials as will be supplied to the plant. Tests should be run for a sufficiently long period to indicate any corrosion troubles. In addition to observing the effect on the equipment, small corrosion test samples may be placed at strategic points. Each sample should be made from commercially available material and contain a weld if fabrication is to be by welding. These can be removed from time to time for weighing and yield numerical results.

A complete detailed record should be kept of all the pilot plant work, including drawings, curves, tables of data, descriptions of runs, maintenance troubles, and photographs of the installation, since the design and construction of the commercial plant will probably be carried out by other personnel. Results of many months of work and many thousands of dollars expenditure must not be transmitted by word of mouth.



Flow Sheet of a Pilot Plant for Continuous Liquid-Phase Reaction at 4000 Pounds per Square Inch Pressure

During the course of the pilot work, meetings should be held at least once a week so that the engineers assigned to the job can discuss the progress and future plans with the department head, specialists who are working in a consulting capacity, a representative of the research department that carried the project through the laboratory stage, and a representative of the engineering department that will design the commercial plant.

The proper interpretation of the pilot plant data calls for care and experience. The more development work an engineer or a company does, the easier and more effective will be the utilization of the data. The results should be translated into usable form and commercial plant implications should be determined each day or each week, rather than at the end of a long series of runs; otherwise we may find that a month's work was aimed in the wrong direction.

The report on the pilot plant operation will be considered by management in the light of the cost involved. What did they get for the money spent? The general appearance of the report, the method of data presentation, goes a long way toward making the project appear worth while. Let us never become so involved in engineering that we forget to use salesmanship now and then.

A thorough knowledge of equipment design is essential to reproduce successful pilot operation with equally successful commercial machinery. Large companies frequently have sufficient experience within their own organization. Smaller concerns can often employ equipment specialists to advantage.

Good work can be done only by capable personnel. The best brains in the company should not be used for production, with development left to men just out of school as a training for production. A man should be trained for development as for any other important function. The development department should be organized with care and must be supervised by competent executives. Development is just as much a part of money making as production. The management must be just as efficient and practical.

The proper utilization of the pilot plant for the development of a chemical process calls for straight, logical thinking. In this connection we must be very critical of our own actions and be sure that every move is for a definite purpose. The pilot plant should always be considered a definite step in a program of chemical process development rather than as an isolated operation.

For one reason or another it is not always possible to do everything in the ideal way, but by considering the ideal before taking action, troubles are frequently avoided just because they have been considered. By having a set of rules, our thinking is clarified and we make departures from the rule with full knowledge of the consequences.

USE and FUNCTION of PILOT PLANTS in CHEMICAL INDUSTRIES

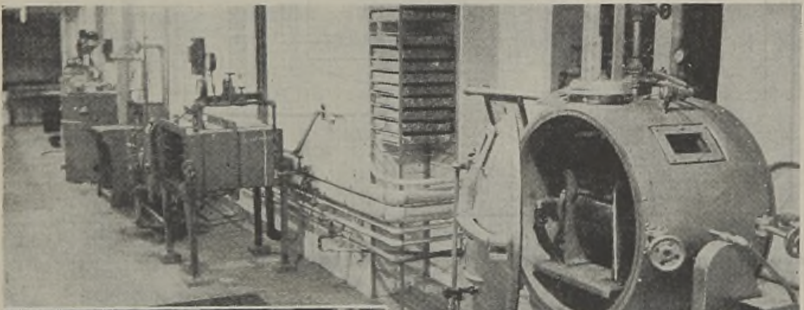
Frank C. Vilbrandt
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VA.

PILOT plant operation is a phase of engineering experimentation introduced into the development of America's chemical industries with the sudden rise of the chemical industries in this country about thirty years ago. The value of a pilot plant is the development of a process concept into a commercially feasible plant; as stated by one company (*3*): "The concept went to the laboratory. There it was put to the crucial test of actual operation in the pilot plant, under conditions virtually identical to those obtaining in a full-scale unit. Operation of the pilot plant so closely approaches a weight balance of 100% that it duplicates commercial operation for all practical purposes.

"When the process concept finally came out of the pilot plant, it had been so thoroughly checked, verified, and proved that the term 'concept' actually was a misnomer. It was no longer a 'concept'; it was a practical working plan. The tentative figures which served as a preliminary basis for the process engineers were replaced by final and exact specifications. Definite yields and conclusive figures on all operations were established. Equipped with this material, the process engineers then put together what we think is the most efficient process sequence, and yardsticked to the last fraction of an inch."

What constitutes a pilot plant, or pilot plant operation, depends primarily upon the point of view. The nature of the service undertaken by a pilot plant may be either: (*a*) to serve as the development unit for a project conceived by the pure research group from a set of reactions and some product; (*b*) to obtain the quantitative engineering data necessary for the design of a commercially feasible production plant; or (*c*) to provide for progress investigations carried on subsequent to placing the desired commercial unit into engineering, both prior to actual running in stream, or subsequently to improve yields, quality, etc.; (*d*) to act as a trouble shooter for a commercial unit which had been designed from the pilot plant data.

The pilot plant (*5*) may be either that phase of development embracing all the stages between the laboratory and the commercial unit, requiring the skill, technique, and mental approach of the process research group and the engineering experimental division, and requiring an attack based upon the application of chemical



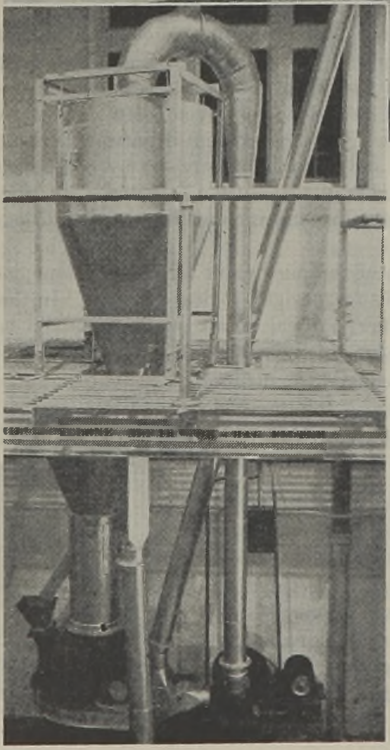


Figure 1 (*Above*). Pilot Plant Installation without Relation to Flow

Figure 2 (*Left*). Pilot Plant Size-Reduction Unit

The conversion of laboratory data handed down from the pure research group into plant design data is only one function of the pilot plant. Such a task requires the setting up of a definite program, including a thorough investigation of basic reactions and reactants, time, temperature, concentration and catalysis factors, a study of raw materials, operations needed, control specifications, safety and health hazards, etc.; it must be investigated with the thoroughness and zeal of a pure researcher, but with the viewpoint of a chemical engineer. The pilot plant in such cases is a research unit. The pilot plant also must provide the breakdown of a process into unit operations, selection of suitable equipment, savings of materials, equipment, time, labor, as well as a study of wastes and their recovery or disposal. After a new plant or process is designed, the pilot plant continues investigations of problems which require the elimination of the compromise acceptance of data, without which compromise a delay might be involved in plant construction. Operating processes use the pilot plant as the trouble-shooting division; when trouble shooting is not being carried on, the pilot plant is doing development work along lines of alternate raw materials, improvement of products and by-products, lower costs, safety, bringing the plant up to date, etc. The proper personnel in a pilot plant constitutes the most important feature of its success or failure.

and engineering principles, or it may deal only with that last stage before erection and completion of the commercial unit in which final quantitative data are sought. Such terms as large scale model, semiworks, halfway house, semicommercial plant, and pilot plant may be synonymous; or to some these may mean distinct subdivisions of engineering experimentation.

The pilot plant may consist of units as small as possible so as to permit operating flexibility, changes in equipment, and changes in arrangements, at a very small outlay of funds and time, yet be sufficiently large to give data which can be duplicated on commercial size equipment. Although the division of effort subsequent to the pure research laboratory's presentation of the project is essentially a matter of choice, it is quite possible to subdivide the effort into as many stages as the nature of the project may demand, if personnel, equipment, and housing facilities permit.

With increase in size of preparation of the commodity, the optimum operating conditions, as determined for the previous unit, may not hold true; consequently, flexibility in design is likewise desirable, so that the equipment may be quickly assembled to undertake pilot plant working processes as the need arises, from which detailed data on process performance may be obtained. In such a unit there may be no attempt to obtain all costs of operation, to operate upon an efficient manufacturing basis, or to arrange the apparatus in the proper flow relation. It is often much less expensive to carry the process material from one vessel to the next vessel than it is to erect pipe lines, pumps, etc., as would be done in flow production for manufacturing routine.

Emphasis has been placed upon the necessity of pilot plants; yet the practice does exist of designing the commercial unit from research laboratory data, without the necessity of making a pilot plant investigation. This is a reasonable procedure where a new process is similar in most respects to an established manufacturing process and one in which the experimental staff may be sufficient. The process may be placed into operation after passing through the unit process stage, as it will probably perform in the new commercial plant as it does in an established unit. In such cases the best method for materials handling, illumination, depreciation, maintenance, etc., can be fairly accurately predicted from experience and data obtained in the existing plant. Other information which may be needed, however, can be (*a*) the yield and quality of product from relatively large batches, and (*b*) the peculiar difficulties which did not show up in the old process and require solution before passing to the next stage. If the production of the large batch duplicates research laboratory data, it is assumed that similar results may be obtained on full scale units.

Where the process does not conform to past experience, the large scale process results are of great value in the design of the pilot plant, the semiworks, and/or the semicommercial unit. Information gained in the previous stages of experimentation through the unit process stages may concern themselves only with corrosion of the reaction vessel in a qualitative way, the best conditions for operation, yields and quality of product, and thermal considerations.

To obtain engineering data essential for the design of pilot plant in such an investigation, the following considerations may be important in the unit process, of large scale, experimentation:

1. Procedure essentials—i.e., proportions, temperatures, time
2. Raw material characteristics
3. Chemical flow diagram
4. Corrosion characteristics, precautions, safety, health hazards
5. Effect of impurities—catalysts
6. Heat consideration, temperature effects
7. Unit operations required, engineering flow sheet

THE PILOT PLANT

Immediately following the acquisition of data from the unit process or large scale unit experimentation, a review of pertinent facts on the process should be undertaken. The following check list is suggested as items to be considered in the pilot plant investigation:

1. FLOW RELATIONS
    - *a.* Chemical flow diagrams
    - *b.* Breakdown into unit operations
    - *c.* Engineering equipment flow diagrams
    - *d.* Material balance
2. MATERIALS
    - *a.* Raw materials, availability, substitute raw materials, costs
    - *b.* Impurities in raw materials and in products
    - *c.* Corrosion, erosion, dust, fumes
    - *d.* Solvents
    - *e.* Wastes and recovery
3. EQUIPMENT OR OPERATION
    - *a.* Selection of equipment, elimination of obviously unsuitable equipment
    - *b.* Cost of operation
    - *c.* Control specification
    - *d.* Material of construction
    - *e.* Heat transfer
    - *f.* Mass transfer
4. MATERIALS HANDLING
    - *a.* Proper methods of handling around the plant
    - *b.* Intermediate storage
    - *c.* Industrial hazards (corrosion, fire, erosion, safety, health, pollution, fumes, explosions)
    - *d.* Public nuisances
    - *e.* Storage
5. LABOR
    - *a.* Operators needed
    - *b.* Supervision
    - *c.* Control specifications from operator's viewpoint
    - *d.* Process simplification from operator's viewpoint
    - *e.* Safety from operator's viewpoint
    - *f.* Saving of time and labor

The ultimate desire is to operate the pilot plant with the assurance that all the risks, both technical and economic in the full scale commercial plant, have been minimized or, preferably, eliminated. The pilot plant must be capable of operating over relatively long periods under conditions which are not changed frequently, to obtain a fair approximation of labor costs and manufacturing expenses. In a pilot plant the pieces of equipment are selected specifically for the work to be performed. It should not be dismantled until such time as the full scale commercial plant is in successful operation, because it is the place where quality and manufactured improvements are worked out and checked before being put into full scale practice. Its product is salable, and the unit can serve as the source of supply for consumer testing; also, it should be available for some time to study certain suggestions as to changes in the process, without costly interference with production in the commercial unit, and for trouble shooting for the commercial work.

SIZE

Since there will be great variation in the size of pilot plants for different types of processes, the decision as to the proper size is based upon the principle that it should be the smallest unit that will actually duplicate working conditions of the commercial plant. If, after a period of pilot plant operation, the unit is found to be too small, the erection of a larger unit as a further precaution before proceeding to full scale is unhesitantly recommended by Weiss and Downs (*6*): "The acid test of a pilot plant is a smoothly and economically operating commercial plant designed therefrom."

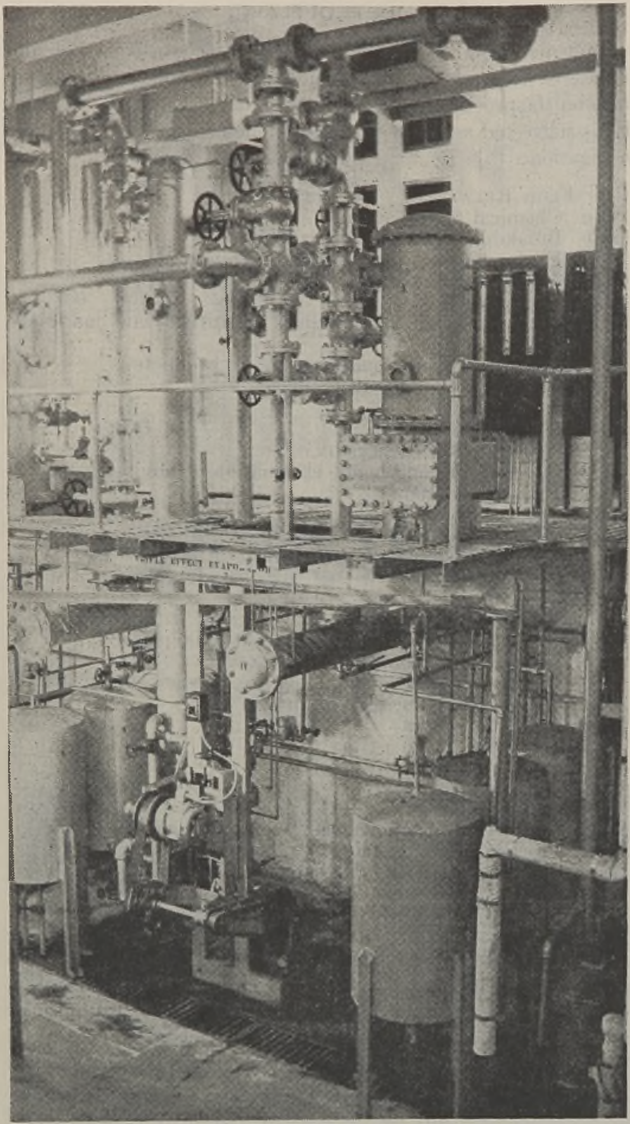


Figure 3. Pilot Plant Evaporator Assembly

The quantitative measure of the size of each step may vary; however, if a definite commercial production is sought, the process research laboratory should attempt to duplicate the laboratory reactions on a 0.05 to 0.10% basis; then the same group working with pilot plant scale should be adapted to a 5 or 10% basis; since 10% basis may be too large for economical study of variables, 5% seems to be a better limit; hence the usual steps might preferably be 0.05, 0.50, and 5.0%, respectively. A well established chemical plant may have developed its pilot plant to produce batches at some times on a 5-pound scale and at other times on a 2000-pound scale (*2*).

HOUSING

The housing of the pilot plant generally requires a different treatment from the large batch or unit process. Building, if required, may be temporary in character, cheaply erected and easily expandable to take care of inevitable alterations that generally are required. Frequently a process may be set up in the open with just those units covered where weather conditions might affect the equipment or make working conditions uncomfortable. If possible it should be set up near the manufacturing area so as to have available the large scale facilities for handling materials, disposal of products, heat supply, and similar services; but it should not be erected where a possible need for the space might require dismantling before all problems in connection with large scale production are solved.

For processes where stills, autoclaves, fusion pots, evaporators, cooling kettles, centrifugals, filters, dryers, etc., are required in the pilot plant, each piece of unit operation equipment should be installed individually and not necessarily erected in flow relation to apparatus or process. Such flexibility in available chemical engineering equipment permits of rearrangements and also the utilization of pilot plant equipment as the needs arise (Figure 1).

Many pilot plant establishments are housed in permanent structures and have definite status as a permanent unit in investigations by the companies (Figures 2 and 3). Such installations as the Dorr Company's Mill Pond Unit, at Westport, Conn., have permanent equipment designed to do specific jobs of a more or less standardized nature, but are sufficiently flexible to enable a rearrangement of functional units. The Jackson Laboratory of the Du Pont Company and the Hercules Powder Company's Experiment Station, in addition to specialized equipment pilot plants, have pilot plant area and space in which specially designed pilot plant equipment may be housed (*2*).

A practice which is quite prevalent during critical times is for the engineering department to by-pass the pilot plant in order to expedite the design of the commercial unit, and sometimes actually to build the commercial unit before the pilot plant is erected. The concept is held that a well trained engineering force, with experience and chemical engineering pilot plant data available from other processes, is able to translate laboratory data into plant practice and thus avoid the delay attendant upon the completion of a pilot plant study. Some measure of success has been obtained; many such units have already been built (such as the five pilot plants for synthetic rubber, *1*), or preparations are being made to build pilot plants to improve the process, the product, and the operations, to reduce the costs, and for subsequent trouble shooting when the commercial plant is in operation.

PERSONNEL

Pierce (*4*) presents the point of view that "the practice of handing over a process to someone else to work out a few engineering details destroys the enthusiasm and continuity of thought which should prevail from the initial experiment to the final plant". Some contact must be maintained with the originator of the idea while the process is undergoing engineering development; the research man should be carried along on the staff throughout the various stages of the development to give his assistance in the direction of the work, and also to ferret out impending difficulties and actively to carry on research that becomes evident with the progress of the process.

In many new projects the practice prevails today of moving the key men in each step, up with the project; these men then form the nucleus in the succeeding group. In this manner the time lag (usually present in the stepwise separate organizations) required to become acquainted with the problems is eliminated, and also the enthusiasm for the project increases as well as the responsibility assumed for carrying the project to a successful conclusion.

In addition to determining material ratios and conditions of time, temperature, and pressure, it is an important part of the research chemists' job to furnish data on materials of construction, on types of agitation, on thermodynamic studies, on possible hazards of operation, and on similar problems which will be encountered as soon as a larger scale production is started.

The research laboratory after due investigation, which consists not only in a study of the mechanism of the reactions involved, the order of procedure, and the conditions of preparation and yield, must sell the idea to the engineering experimental division. The latter must share in the responsibility for the success of the project; it must be ready to reject a project submitted to it on insufficient data or on a premature and unsound basis, and must direct the attention of the pure research group and its attendant process research laboratory to those phases upon which work should be done.

When a successful lot has been produced, the operation is then turned over to the pilot plant supervisor for future production, and from that point he carries the main responsibility. It is the job of the pilot plant chemical engineer to provide the cost estimates on the basis of whatever information the research laboratory can furnish. The pilot plant should have a chemical engineer in charge, a group of chemically trained supervisors, and a force of experienced foremen and operators. A force of maintenance mechanics and a group of control chemists should also be included in the organization.

Although the experimental units are looked after by technically trained and skilled men, it is necessary to consider that the major portion of the labor in the field commercial plant may be native labor. The types of labor under average conditions of plant operation should be discoverable from the pilot plant unit. A crew of technical men should go along with the project into the commercial unit in order to instruct the native labor in all the details of operation.

In the selection of men for pilot plants, and even for research work, when the policy is to carry men on through to a commercial unit, men should be sought who are cooperative, who have imagination and creative ability or knowledge, who are not afraid to get their hands dirty, who are observant and good recorders of data, who can analyze data, who can be hurried or driven at times, who have shown a tendency to be instructable and tractable by the acquisition of grades of B or better in college; and they must be human. It goes without saying that the ability to write a good report is also a valuable asset.

If the function of the pilot plant develops in its application as a trouble shooter for the commercial unit, the selection of personnel is also vitally important. The trouble-shooting personnel must have the complete confidence and cooperation of the factory operatives, must be fully conversant with factory processes, must be able to make accurate decisions quickly (to maintain the confidence of the operators), and also must have authority to go into the plant to get information. The trouble shooters must be diplomatic; they must keep aloof from petty bickerings between the operatives, between the operatives and supervisors, and between the operatives as labor and the administration as business or industry.

The success of the pilot plant or the success for carrying a concept through to commercial realization depends upon men and thought processes.

ILLUSTRATIVE EXAMPLE

Several years ago, before synthetic rubber created a critical use for butane, an independent oil company had available considerable quantities of commercial butane for which at that time there existed only a limited and unprofitable market. A research chemist presented his concept of partial oxidation of butane to alcohols, aldehydes, and acids, which seemed plausible enough, and a rough presentation directed the company toward the contacting of a consultant to investigate the process.

Small scale experimentation gave data which indicated that the process was feasible, and a review of the available cost data showed promise of commercial feasibility; therefore, the design was undertaken for a pilot plant, for handling 32,000 cubic feet of butane per day. The cost of materials, labor, heat, light, depreciation, thermal requirements, operating characteristics, by-products, etc., were to be sought.

This plant was designed for outdoor erection, with large scale compressor and recirculation units, large scale commercial condensers, and a specially designed multitubular reaction furnace (Figure 4). Most of the units were salvage units from other operations. The cost of erection was approximately $15,000. Three technically trained engineers were hired for specific operating duties. The originator of the process and a consultant also were on the ground.

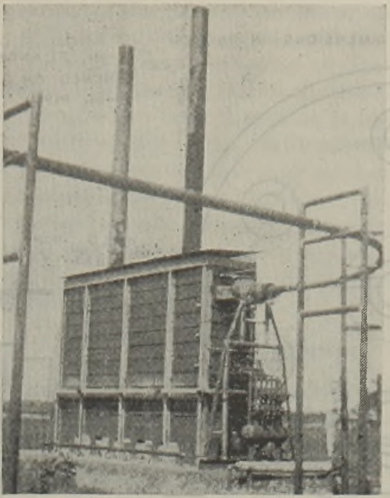


Figure 4. Pilot Plant Outdoor Reactor Furnace

A research chemical engineer, an analyst, and a young chemical engineer also maintained the small scale experimentation laboratory in full operation continuously, before and while the pilot plant was put into operation; it was available for answering questions which began to come from the pilot plant. The small scale unit was located over 500 miles away, and contact was made by telephone, telegraph, and letters. Many points in operation which were overlooked or were not apparent in the small scale operations began to indicate potential difficulties. Many questions were answered by the small batch laboratory before the results were available in the semicommercial plant. The furnace control had to be revised with a more accurate limitation to variation; a new condenser design became apparent; a change was required in the method of transportation of processed materials; a modification of recirculation design was introduced; a change in rectification equipment and processing was made; a new fractionating column was designed; additional gas cleaning devices had to be installed; a problem on waste disposal presented itself.

A previously unsolved slow resinification of one of the products became evident by clogging the condenser tubing, requiring a special study of conditions for operation in the small-scale experimentation laboratory to obviate this new difficulty. Only then did complete operating cost become available and a better flow relation obtain. A public nuisance hazard was unearthed which would have been a major factor in location of the commercial unit. Reclamation of valuable by-products were relegated back to the small scale experimentation.

The revised conditions obtained from the combined small scale and the pilot plant seemed to point to the correct commercial design for a feasible production of acetaldehyde, methanol, formaldehyde, and formic acid from butane. However, a change in market for butane has made further operations unlikely for some time to come.

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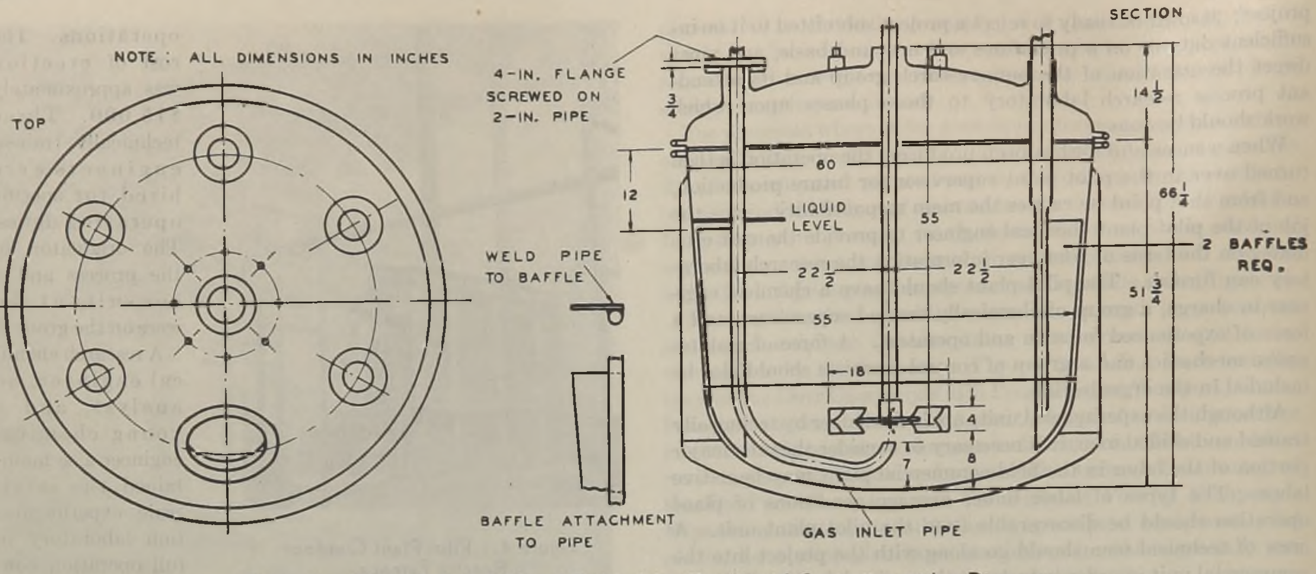

Figure 1. Water-Jacketed Vessel Refitted for Gas-Liquid Contacting with a Disperser

MIXER PERFORMANCE DATA from PILOT PLANTS

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MIXING is an operation that is utilized at some point in almost all chemical processes. Yet there is no well defined or universally accepted measure of mixing (*5*). The application of mechanical mixing devices is still an art and will remain so until sufficient performance data are accumulated to permit a clear understanding of the relations between the chemical reaction, the physical properties of the materials, the impeller, and the geometry of the system. The intent of this paper is to point out how mixing affects chemical reactions and, in view of present knowledge, what specific data should be obtained on pilot plant scale to give the most useful information for engineering design of unit process mixing equipment.

Pilot plant equipment is usually smaller than that used for manufacturing; it can also be modified so that control variables can be studied, and more temperature, pressure, and other physical measurements can be taken than would be practical in large scale operations. From pilot plant operations it should be possible to evaluate four important considerations: (1) the feasibility of the process with respect to yield of principal product; (2) the proper conditions of temperature, pressure, concentrations, etc., for optimum yield; (3) the operational costs in terms of heat, power, and life of equipment; and (4) the possibilities for scaling up the equipment for larger installations. Equilibrium and reaction rate data form the bases for evaluating all the considerations mentioned. Equilibrium data will enable one to estimate maximum yields and, together with rate data, will allow estimation of equipment size and operational costs. The evaluation of mixer performance in terms of the particular chemical reaction involved will then be of immediate usefulness. As data are accumulated from both pilot and full scale processes, it should be possible to develop means for correlating mixer performance with physical and chemical properties and geometric relations. Such correlations will then enable the pilot plant operator to estimate optimum mixing requirements before experiments are undertaken and thus reduce the number of experiments necessary to give the desired data.

THE PILOT PLANT

A piece of chemical equipment may be thought of as a container in which a proper environment can be maintained to allow a desired chemical reaction to take place. Since reactions take place of their own volition and are not compelled to do so by application of external influences, the objective in building a piece of unit process equipment for a pilot plant should be to discover how best to create an environment for large masses of molecules to react in a desired manner. One of the most important operations, when dealing with large masses of reacting particles, is to obtain the desired intimacy of contact. This is normally thought of as mixing. Mixing is an operation which heretofore has not been reduced to its elements in a quantitative fashion; yet mixing can play an important part in achieving the desired results in a chemical reaction taking place with large masses of material. Indeed it may often become the operation of prime importance. Many unit processes are carried out by batch or semicontinuous methods. This is partly because they are, for the most part, organic reactions that are not instantaneous (in fact often quite slow in reaction) and also because there is a lack of reaction rate data necessary for designing a continuous process. The length of time required for reaction is an important element in the evaluation of processes; time is correlated with other variables in terms of reaction rate.

THE CHEMICAL REACTION

The equilibrium constant of a reaction as determined in the laboratory is valid only for a given temperature and when sufficient time has been allowed for the reaction to reach equilibrium with respect to all molecules present. It may be exceedingly difficult to attain equilibrium between large masses of molecules if reliance is placed upon self-diffusion of molecules for considerable distances in order to get to a location favorable for reaction. Thus, when large masses of material are brought together for reaction, it is often difficult to reproduce true equilibrium conditions of a reaction as they may have been determined in the laboratory. If such masses of material are agitated, mixing will result and equilibrium will be approached more or less rapidly as the agitation varies. It follows that true equilibrium can be reached only at some given amount of mixing. It is sometimes impractical to reach this state, and the result is that an apparent equilibrium (in terms of equilibrium constant) can be attained which is different in value from the theoretical or laboratory measured equilibrium. Since equilibrium shifts with temperature, whenever the reaction is either exothermic or endothermic it becomes necessary to transfer heat so that constant temperature can be maintained. The mixing of reacting and unreacting molecules by an impeller will aid in the convection of heat, and thus indirectly the mixer will influence the equilibrium. If by mixing a very uniform temperature can be maintained, then the reaction can be controlled at a desired temperature. Maximum yields can be obtained only as true equilibrium is approached, and the use of the mixer as suggested plays an important role.

Side reactions often occur in organic processes, and close regulation of temperature and concentration is necessary to control their extent. If there is uniformity of opportunity for molecules to react in a desired fashion, the principal reaction should take place with a minimum of side reaction. In many cases a mixer may be employed to achieve this result. But to be properly used, quantitative data, showing how uniformity varies with mixer operation (i.e., location, speed, size, baffling, etc.), should be determined. Then the best design and operating conditions can be utilized.

The rate of a reaction may be evaluated as the ratio of driving force to resistance. A driving force may be thought of as the difference in activation energy of molecules, and the adjacency of unreacted molecules will result in the highest possible driving forces. With large masses of molecules a mixer can be applied to create the necessary intimacy in environment for rapid reaction. The top limit to driving force is a function of the molecular species involved. Therefore a mixer can only cause approach to maximum driving force at a given temperature. Resistance is directly proportional to length of path of travel and inversely proportional to the area through which flow or movement is occurring. Thus if a mixer will help to reduce the distance through which a particle must move to make reactive contact, the resistance is decreased and the rate of reaction increased. If the area of contact between reactive masses of molecules is increased, then resistance is decreased and reaction rate increased. It is not yet possible to correlate directly the quantitative effect of impeller discharge and turbulence to the rate of a reaction. But a mixer can be used effectively to accomplish increased area for reaction and decreased path for diffusion, and thus it lowers resistance and produces greater rate of reaction. If this effect can be achieved, rates of reaction similar to those obtained in the chemical laboratory under ideal and equilibrium conditions should be approached in the large scale process.

An indirect result of mixing on reaction rate is sometimes apparent when the temperature changes due to the disproportionate rates at which heat of reaction is liberated and heat is transferred to outside media. With increased agitation it frequently occurs that reaction rate is so increased that heat of reaction is liberated faster than it can be removed through cooling surfaces or evaporation. This results in temperature increase which, in turn, speeds up the reaction and may also result in a shift in equilibrium to a less desirable condition and in the stimulation of undesirable side reactions.

CONTROL

Control of a unit process consists in maintaining a steady environment for the reaction. With good automatic control, operating costs are held to a minimum. The maintenance of steady and uniform conditions within the body of reacting masses can often be achieved most easily by use of a mixer. While power applied to a mixer is not a true or complete measure of mixing (*7*), it is one index to economical mixer applications. When energy is applied to produce mixing, it should be possible to do so most economically by means of a mixer operating in the body of the fluid so that power is delivered at the most useful place. There are many examples in practice where external recirculating pumps have been replaced by mixers operating directly in blending tanks, quenching vats, and the like, and better control has resulted at less expenditure of energy.

Unit processes which require control of temperature, pressure, and contact time nearly always involve heat flow and the removal of one or more of the reactants. The control of a unit process can, therefore, be effected by controlling the component operations—heat transfer, fluid flow, crystallization, etc. These operations, which are necessary for continuous process operation and control, are subject to some quantitative analysis from data in the literature (*2*, *8*), but further study is needed for the operation of mixing and for specific processes by means of pilot plant operation.

ILLUSTRATION

One recent large scale installation for contacting a hydrocarbon oil with chlorine serves as an illustration of the effect of a mixer on a unit process. In this case a series of reaction vessels were refitted with dispersers and baffles. As is so often the case, the vessel shape and size were not the best and a compromise was made to achieve best impeller performance in the existing tank. Baffles were placed as dictated by available openings in the cover, and the impeller was sized and positioned from small scale pilot plant data. However, the impeller is closer to the bottom than it should be because the gas inlet pipe had been fixed previously. Figure 1 shows the glass-lined water-jacketed reactor as finally refitted with disperser and baffles. The complete power unit, shaft, and disperser are shown in Figure 2; Figure 3 is a photograph of the Hastelloy disperser used.

To obtain equilibrium and reaction rate data is, perhaps, the most important reason for operating pilot plants, since such data make possible the evaluation of: the feasibility of the process with respect to yield of principal product; the proper conditions of temperature, pressure, concentrations, etc., for optimum yield; the operational costs in terms of heat, power, and life of equipment; and the possibilities for scaling up the equipment for larger installations. Both equilibrium and reaction rate may be greatly affected by the mixing device used to control the agitation and heat transfer. For reactions involving the liquid phase where mechanical mixers are used, it is essential to employ a mixing device whose performance can be measured and properly interpreted. The data which are necessary for proper evaluation of performance and translation to a larger scale are outlined for the systems involving liquid-liquid, liquid-solid, liquid-gas, and liquid-gas-solid. Mixer performance is dependent on the container shape as well as upon its own characteristics; thus pilot plant equipment should be designed around the best possible operating conditions for the particular mixer involved.

The reaction had been carried out previously with an anchor-type paddle. The operation was batch and required approximately 8 hours for a 500-gallon charge of oil. Liquid level was 42 inches above bottom. It was desired to double the output of the reactors by reducing the time per batch. Operating data showed 70% utilization of chlorine with operating temperature of 110° F.

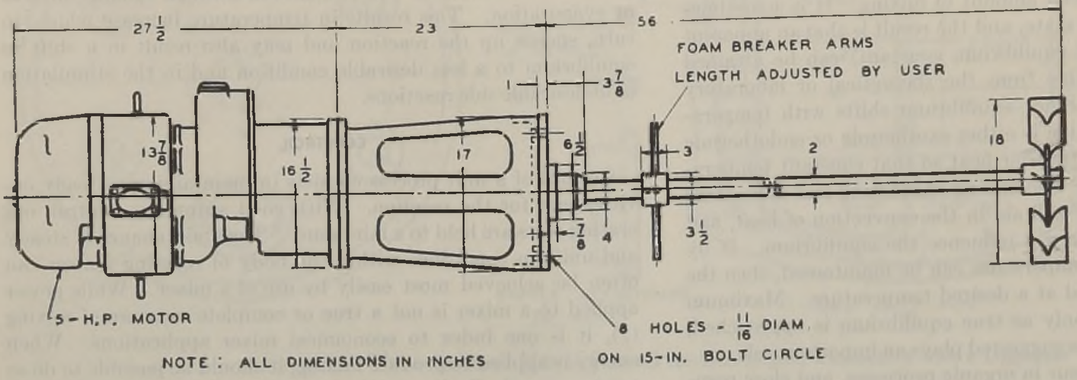

Figure 2. Power Unit, Shaft, and Disperser

With the disperser installed and operating at 175 r.p.m., the reaction time was reduced to less than 3 hours, the chlorine utilization was up to 98+% at an operating temperature of 130° F. Under these conditions the flow of cooling water had to be increased to hold the temperature, and side reactions were no greater than before when the temperature was 110° F. Not only was the capacity of the equipment increased more than twofold, but the saving in chlorine was approximately one third. Design of equipment of this sort can be made with reasonable accuracy when the necessary pilot plant data are available. Thus it is necessary to know the effect of the mixer at different operating conditions on the equilibrium, the reaction rate, and the heat transfer rate in order to make the proper economical design of the process equipment.

DATA

Because there is a lack of data regarding the effect of a mixing device upon the efficiency and controllability of a reaction, it is imperative that pilot plant equipment for unit process study be built so that mixing variables can be evaluated quantitatively. Mixing equipment manufacturers are in a position to supply equipment to produce desired fluid flow characteristics, but it is the function of the unit process pilot plant experimenter to determine the type of fluid flow characteristic which is desired, and how the magnitude or distribution of fluid flow affects the operation and controllability of the particular chemical process in question. Processes are normally operated in a pilot plant in such a way that temperatures, pressures, flows of material, and concentrations may be varied, sometimes over wide ranges, in order to establish optimum conditions for the reaction. When a mixing device is required in the equipment, it is essential that variation in its speed, position, and size be made so as to evaluate the mixing potentiality at the same time that other variables are studied. Too many pieces of pilot equipment are fitted with a mixer which will run at only one or two speeds and for which noncalibrated impellers are used, with the result that it is virtually impossible to find out how a different type of mixing would affect the course of the reaction. It is often the case that by changing the operating characteristics of the mixing device the process will have to be completely re-engineered with respect to heat transfer surface, rates of flow, and capacity of equipment. Mixing is often the most important operation; yet most unit process pilot equipment is notable for a lack of mixing facilities to enable wide variation in the degree of mixing and for studying it in terms of the reaction under development.

While mixing equipment manufacturers should know the hydraulic capacities of their equipment, fundamental data have not yet been developed which will allow computation of the speed and location of the proper mixing device required to produce a given suspension, or the effect upon rates of reaction for various chemical processes. The problem is complex, and at present it seems that the best solution can be attained through cooperation between equipment manufacturer and pilot plant experimenter. The characteristics of fluid flow in a tank, produced by an agitator, are gradually being studied and evaluated quantitatively. Unfortunately it is extremely difficult for the pilot plant experimenter to determine the type and quantitative magnitude of fluid flow or agitation which are required for a given reaction. Yet the pilot plant experimenter is the only one in a position to obtain data relating mixer operation to a particular process under development. It is suggested that over-all quantitative data on the relation between the mixer and the reaction be obtained in the pilot plant, and that such data be obtained in a manner and in terms that the equipment manufacturer can translate accurately to larger dimensions; in that way the identical pattern and velocity of fluid flow determined to be best in the small scale apparatus may be obtained in the large scale equipment.

The pilot plant data required by the equipment manufacturer for intelligent application to mixers on a large scale include the following physical characteristics of the mixing system: impeller type, speed, position; vessel size and shape; baffle size and position. Also, it is essential to know the physical properties of the fluids involved. Not only must the density and viscosity be known, but, in the case of gas-liquid contacting, it is often of prime importance to know the chemical content of the solution, its pH, and whether or not suspended solid particles are present. In the case of gas-liquid contacting, it is also important to determine the amount of gas entrained by the liquid (holdup at a given instant) and to relate this to impeller shape, speed, position, and rates of flow.

In descriptions of organic unit processes, one frequently sees such statements as "efficient agitation, by means of an agitator or recirculation by means of a pump, . . . markedly increases the rate of hydrolysis". This quotation is indicative of the state of our quantitative knowledge of the effect of agitation on chemical reactions. Agitation is frequently spoken of in terms of "mild agitation", "strong agitation", etc. These are meaningless terms, since they have no interrelation from one fluid system to another. The pilot plant is the place where quantitative terms can be applied to mixing and agitation. The applicable terms and the indices used are speed, size, shape, and horsepower of the impeller with relation to yield, rate of reaction, and rate of heat transfer. The data required and obtainable for pilot plant processes (to determine process feasibility, operation costs, and design scale-up) are as follows:

For Liquid-Liquid Mixing. Impeller position (i.e., location with respect to walls, bottom of container, and liquid surface), size, speed, and power required. The physical and chemical properties of the liquids or of different phases which may be present.

Liquid-Solid Mixing. Same as for liquid-liquid mixing.

Liquid-Gas Contacting. Same as for liquid-liquid mixing plus a determination of the amount of gas retained by the liquid at a given instant, and its relation to gas flow and chemical content of the liquid (*4*). In lieu of holdup, actual variation of absorption coefficient with impeller speed and size will serve the same purposes (*3*).

Liquid-Gas-Solid Contacting. Same as for liquid-gas contacting.

Elaboration of these types of data and their relation to performance, scale-up of equipment, and economic considerations is covered in the references given. They are merely summarized here to show what is essential for evaluating mixer performance and to point out the type of data which pilot plants design should make possible.

EQUIPMENT

To obtain uniformity of mixing and agitation, it is just as important to consider the size and shape of the containing vessel as those of the impeller (*1*). Therefore, the containing vessel should be designed to afford the best shape for operation of the mixer. This shape should be consistent with any requirements of heat transfer surface. Usually containers of depth approximately equal to diameter are most conducive to best mixer applications. However, when two or more impellers are placed upon the same shaft, liquid depths greater than liquid diameters may be used with success.

The impeller itself should be chosen with regard to the viscosities of the fluids involved, and baffles should be used with due attention to the viscosities or gas flows involved. The type of impeller—i.e., propeller, turbine, paddle, or disperser—should be chosen with regard to mechanical simplicity and the type of action desired. Certain types of impellers operate best for solid-liquid suspension, other impellers perform more effectively for gas-liquid dispersions. Regardless of the choice of impeller type, the impellers for pilot plant operation should be such that their fluid discharge and operating characteristics are known. One of the indices in impeller performance is the horsepower drawn by the impeller. If the pilot plant operator can determine the relation between horsepower, geometry, and reaction rates, it is then possible to scale-up the mixing device to large size. The variation of horsepower with reaction characteristics can be determined in either of two ways. The pilot plant equipment can be provided with a dynamometer and variable-speed control for the mixer, and thus the power used for any given set of conditions can be determined directly; or the pilot plant equipment can be supplied with impellers which are carefully calibrated. If the speed of calibrated impellers can be measured, the geometry of the container and baffles stated, and physical properties of the fluid known, then the power can be determined by data now available from the manufacturer. The horsepower characteristics of many types of impellers, operating in a wide variety of fluids and in definite geometrical relation to the container shape, are well known. Thus it seems reasonable to suggest that calibrated impellers be used for pilot plant work rather than a dynamometer for each setup. Dynamometers are costly luxuries for the process experimenter. They are inexpensive necessities for the equipment manufacturer. It is essential, however, that the mixer in a pilot plant be equipped with a variable-speed drive and a means for accurate measurement of the speeds obtained. Otherwise reliance cannot be placed upon speed variation measurements and thus upon power requirements. For any process there should be an optimum power consistent with the desired yield and rate of reaction.

Power measurements are not alone an index to scaling up of mixing equipment to large size vessels, but they are also an important item in evaluating the cost of operation of both pilot plant and large scale equipment. Cost data for large scale operation is often obtained through pilot plant operations. Operational costs for power required to drive a mixer and investment costs for the installation of the mixing device are both dependent upon the size of the mixer drive and its operating efficiency (*6*). The use of calibrated impellers in pilot plant equipment will allow determination of mixing costs and thus will allow proper evaluation of the process as a whole. The pilot plant setup should allow for sufficient power input variation to find the optimum condition for results at lowest over-all cost.

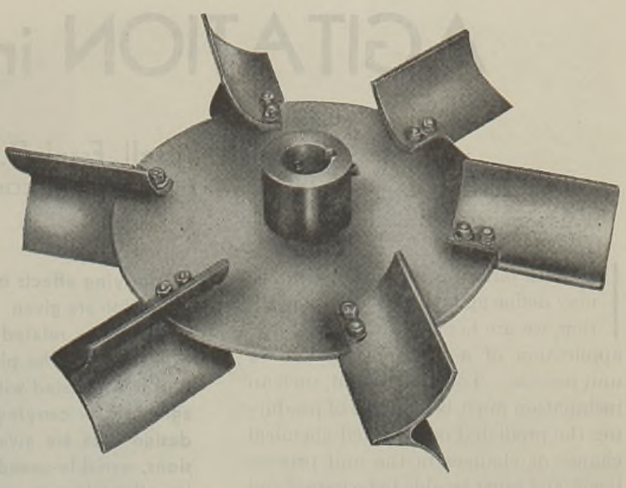
Figure 3. Hastelloy Disperser, 18 Inches in Diameter

UNIT PROCESSES

There are many unit organic processes such as nitration, sulfonation, esterification, hydrolysis, oxidation, and reduction which have been worked out in the laboratory. Many now carried out in batches could be converted to continuous operations when either large scale operation is desired and/or when better quantitative mixing data are available. Yield and rate data, as obtained in the research laboratory, can be achieved only when proper conditions and environment are created for large masses of molecules as must be handled in an economically sound process. One of the most important operations which will fix and control the environment for these reactions is mixing. The pilot plant equipment must be designed around the mixer or at least with due consideration for it, and data taken in pilot plant operations should include those which are essential to the proper evaluation of mixing performance consistent with reaction progress, not only to achieve most economical results but also to allow proper design scale-up to large scale or continuous plant operation.

ACKNOWLEDGMENT

Data and details for the illustration used were obtained from the files of the Mixing Equipment Company, Inc., and permission to use them is gratefully acknowledged.

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AGITATION in PILOT PLANTS

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Modifying effects of small containers on mixing action are given. Minimum dimensions are shown to be related to physical characteristics of materials. The pilot plant for studying agitation is contrasted with the pilot plant requiring agitation for carrying on the process. General design data are given for vessel shape, dimensions, variable-speed drive, horsepower range, impeller selection, method of supporting vessel. Photographs show several typical designs of pilot plant. Methods are also outlined for obtaining quantitative data and for extending pilot plant to commercial scale operation.

IF, FOR purposes of discussion, we may define agitation as a unit operation, we are here concerned with the application of a unit operation to a unit process. To be successful, such an installation must be capable of producing the predicted or expected chemical change or changes in the unit process itself, and must be able to be varied and controlled so as to enable the optimum points in the unit process to be achieved. The characteristics and performance of the agitation equipment must be capable of being recorded quantitatively so that larger scale equipment, for commercial size installations, can be designed from the data obtained from the pilot plant operation.

In certain cases, before the pilot plant for the unit process is set up, it will be desirable or necessary to provide a pilot plant for the study of agitation as a unit operation so as to reduce the number of variables which would otherwise be necessary in the unit process pilot plant.

VESSEL SIZE

While commercial plants for a given unit process will generally fall within relatively narrow limits of size, capacity, etc., this, unfortunately, is not true with pilot plants. The greatest variation in pilot plant design at present lies in the great range of physical size. The term "pilot plant" has acquired the connotation in some quarters of "miniature" so that any extremely small piece of equipment, made of metal, is apt to be considered pilot plant equipment. It is not rare to encounter autoclaves and reaction vessels as small as 4 inches in diameter and 6 inches in height. In the absence of any guide or data which illustrate the difficulties to be encountered in deriving information from results obtained in such small vessels, it is not surprising that the physical size of the reaction vessel is most frequently decided by other factors. Consideration of materials available, safety hazards involved, amount of room available, and disposal of end- and by-products play an important part in size determination of the vessel.

The purpose of this paper is to set forth a desirable minimum size of reaction vessel, together with the reasons involved in arriving at this size and the handicaps to be expected in dealing with smaller vessels. It will be shown that, while the function of mixing or agitation is primarily to produce physical changes, these physical changes are invariably associated with chemical changes inherent in a unit process; consequently, if the physical effect of agitation is impaired, reduced, or misapplied, the consequent chemical change will be affected accordingly.

For simplifying the discussion, the general physical effects of agitation can be divided into the six groups of Table I. However, in even a simple case, such as hydrogenation of a vegetable oil in the presence of a finely divided metallic catalyst, at least three of these functions of agitation are present—namely, gas dispersion, suspension of catalyst in a uniform manner, and the matter of heat transfer to be improved by the circulation of the liquid in the tank against the side walls or coils.

Let us assume that we are to consider a pilot plant for a study of this kind. Because of the use of hydrogen gas, it might be arbitrarily decided that the vessel was to be kept as small as possible. In considering the application of an agitator, however, it would be found that the dispersion of the hydrogen gas was the most difficult or controlling factor. A type of impeller would have to be used which would produce refinement of gas bubbles and also be capable of recirculation of the supernatant gas throughout the entire vessel—in other words, of providing the physical conditions necessary for the chemical change. Inadequate agitation at this point would result either in incomplete hydrogenation or prolonged time for hydrogenation, possibly concurrent with excessive amounts of catalyst required. Data derived from such results would lead to erroneous conclusions regarding the economic factors involved and, if translated to a large scale, would result in a totally inefficient commercial process.

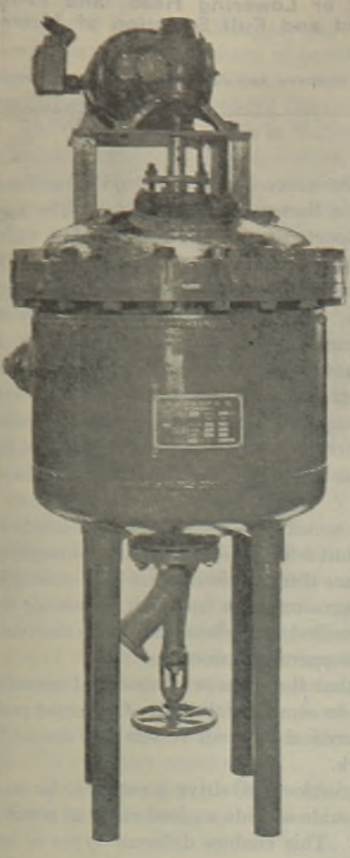
MINIMUM VESSEL AND IMPELLER SIZE

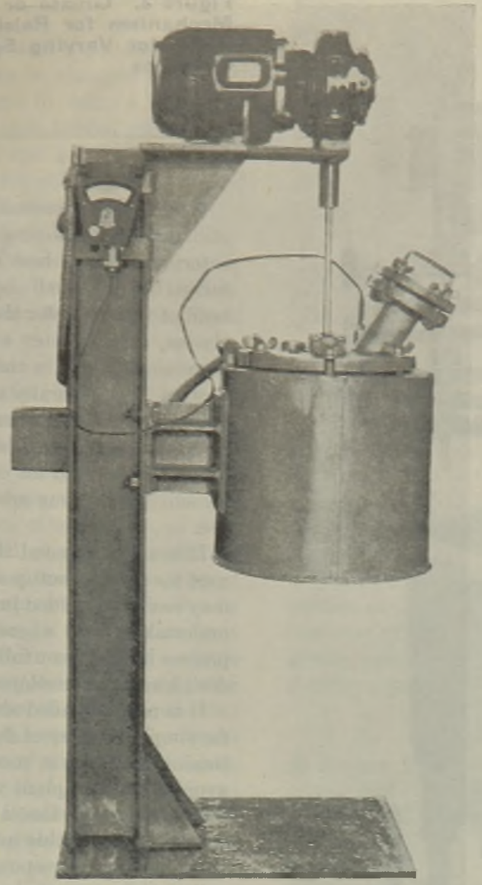
In the pilot plant unit, it is desirable to use an impeller which is geometrically similar to that of the full scale plant in order to scale-up the pilot plant results successfully. The considerations needed to be given an impeller are: (1) the circulation pattern in the vessel, (2) discharge velocity, (3) discharge capacity, and (4) a Reynolds number relation.

Experience has indicated that the ratio of tank diameter to impeller diameter should be between 3 and 4. This ratio leaves a clearance of approximately 1 to 1.5 impeller diameters between the impeller and tank wall. In the usual solutions (under 400 centipoises) a decreased clearance of impeller to tank wall would cause a large energy loss at the tank wall. More clearance would result in an insufficient velocity to create turbulence throughout the tank.

Table I. Grouping of Agitation Functions According to Physical Effect

Blending Miscible Liquids	Mixing Immiscible Liquids	Crystal Size Control	Gas Absorption and Dispersion	Suspension of Solids	Heat Transfer
Simple mixing of sol. liquids, as in reducing concn.	Washing of liquids Extraction Contacting Emulsifying	Precipitation Evaporation systems	Hydrogenation Aeration Gas scrubbing Chlorination Gas washing	Slurries Suspension of filter aid, activated C, fuller's earth, crystals while dissolving	Heating Cooling





COURTESY, PATTERSON-KELLEY COMPANY, INC.

Figure 1. Integral Unit for High-Pressure Pilot Plant Work, Equipped with Agitator and Special Valve

Figure 2. Pilot Plant Agitator Equipment with Counterbalanced Vessel Support and Agitating Device

This discussion leads into the selection of tank proportions. When tank proportions are selected with consideration for the agitator, the selection should be based on the stream paths that give the most uniform velocity distribution. For turbine impellers, the flow is radial from the impeller to the tank wall, then vertical along the tank wall to the liquid surface and the tank bottom, back to the tank center, and finally to the eye of the impeller. With this general flow pattern, circular patterns have the least flow resistance. Square patterns are a good compromise between the least flow resistance and the use of change of direction to create turbulence. The most desirable tank shape is indicated as one having liquid level height equal to the tank diameter.

There are few factual data on the discharge velocity of impellers. Using the centrifugal pump theory as a basis (*2*), the discharge velocities are proportional to the peripheral velocities. Thus, with the lack of positive velocity data, 700 feet per minute has been used as a desirable peripheral velocity applied to problems of mixing immiscible liquids, gas absorption and dispersion, suspension of solids, and heat transfer where turbulence is desired throughout the solution.

The tendency has often been to increase the peripheral velocities of impellers with increase of vessel size. This has been found unnecessary. By maintaining a fixed ratio of tank diameter to impeller diameter for similar radial flow turbines, the ratio of the discharge area to the flow area at the tank wall is constant for any size tank and impeller. By maintaining this ratio and fixing the peripheral velocity of the impeller, it has been found possible to scale-up mixing operations. It is therefore believed that a condition exists (analogous to that expressed by the law of continuity of flow) wherein the resulting fluid velocities at the tank walls are substantially the same for both the small pilot plant vessel and the selected commercial size, the ratio of impeller diameter to tank diameter being maintained as stated above.

The law of continuity of flow is generally stated in the following form for flow in nozzles and Venturis:

$$A_1V_1 = A_2V_2$$

where A = cross section area of stream
V = velocity of stream

Again borrowing from the hydraulics theory (*2*), we find that the discharge rate of similar pumps is proportional to the product of the discharge area and the discharge velocities. In other words, rate of discharge for similar impellers that operate at constant peripheral speed varies as the impeller diameter squared. Whereas the volume of the tank in which an impeller operates varies as the tank diameter cubed, then with fixed ratios of tank to impeller diameters, smaller tanks should have a decreased rate of circulation. For this reason it is necessary to set minimum tank and impeller diameters for pilot plant purposes. It has been difficult to obtain satisfactory "scale-up" results for impellers smaller than 4 inches in diameter. Using the 4-inch impeller as a minimum and allowing for a ratio of tank to impeller diameter of 3.5, a 14-inch-diameter vessel is found to be the minimum. For batch size convenience, a liquid level depth of 15 inches is selected to give a 10-gallon batch. The pilot plant vessel should have a space allowance for splashing, foaming, volume increase, and overflow connection. Three inches are allowed, which puts the minimum pilot plant vessel as 14 inches in diameter and 18 inches in depth.

Mechanical factors which also limit the impeller diameter are: (1) The shaft speed becomes a factor since impellers smaller than 4 inches would have a speed of 900 r.p.m. and above; the speed would be limited where stuffing boxes are involved and also where higher speeds introduce vibration problems. (2) It becomes difficult to produce a dimensionally similar impeller in sizes smaller than 4 inches.

Finally, in order to evaluate an impeller, we use the Reynolds number function SNd^2/μ, where S is specific gravity, N is impeller speed in r.p.m., d is impeller diameter in inches, and μ is viscosity in centipoises. SNd^2/μ is inconsistent as far as units of measure are concerned, but they do contain the necessary dimensions of the classical Reynolds number. This formula is useful inasmuch as it contains the dimensions usually measured. This function has been checked by plotting it as log SNd^2/μ against log of horsepower/SN^3d^5. The practicability of this function has been established by a large number of tests covering a wide range of impeller types, sizes

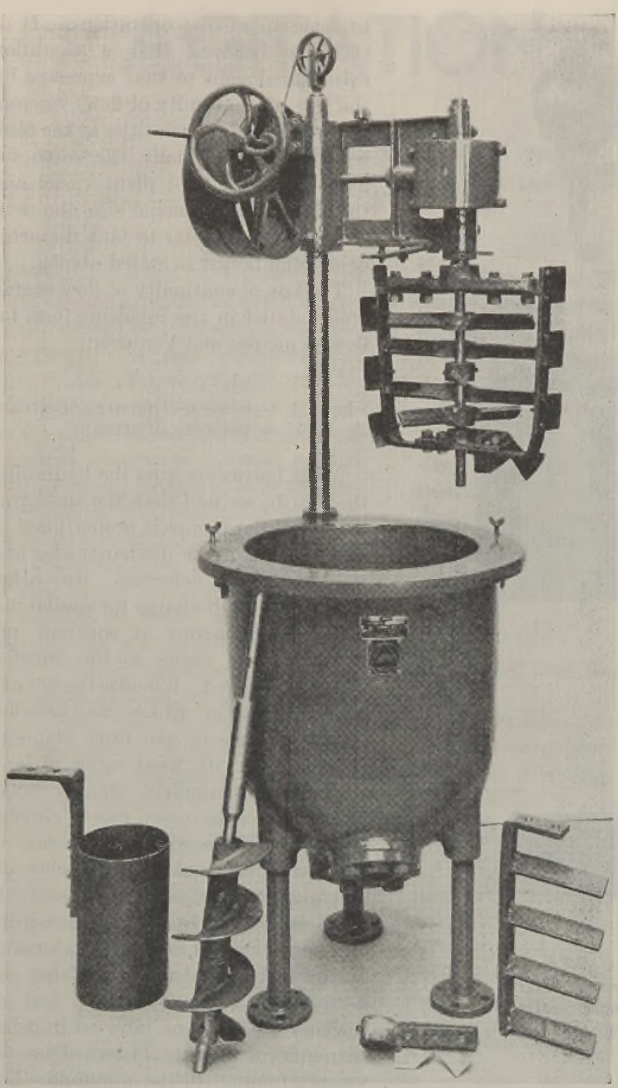


Figure 3. Grease or Paste Mixing Kettle with Crank Mechanism for Raising or Lowering Head, and Provision for Varying Speed and Full Selection of Mixer Elements

COURTESY, BUFFALO FOUNDRY & MACHINE COMPAN

and speeds, viscosity and density of fluid, and tank sizes and baffling. Our tests have shown that this Reynolds number function is relatively independent of the tank diameter and is remarkably consistent for changes of impeller diameter, speed, density, and viscosity.

This function indicates only the flow in the impeller, and is affected by factors such as tank dimensions and baffles only as they influence the flow through the impeller. For Reynolds number in agitation, laminar flow occurs in numbers up to 2, a transition between 2 and 20, and turbulent flow from 20 up. We have obtained numbers in turbulent range as high as 1,000,000. The Reynolds number alone is no more a measure of agitation than any other factor. It is used in the selection of a favorable diameter and speed to perform the mixing operation.

These minimum sizes of impellers and vessels should be closely adhered to. The reaction vessel need not, necessarily, have the same capacity of preceding or following equipment. Material may be accumulated or stored ordinarily so that smaller or larger equipment may precede or follow the reaction vessel.

GENERAL MECHANICAL REQUIREMENTS

The matter of access to the interior of the vessel is of prime importance. With the weight involved in the minimum size vessel recorded, mechanical aids should be provided. It is possible to design the vessel so that it may alternately: (1) be raised, lowered, or tipped for emptying or (2) support the vessel in a fixed position, and raise and lower the head.

Where pressure vessels are involved, there is also the option c utilizing a top-entering or a bottom-entering mixer. The top entering mixer is best supported in a cage construction whic carries the drive well above the operator's level and thus frees th head of the vessel for the installation of connecting nozzles, sigh glasses, thermometer wells, etc. Since there will normally b more connections in the head of the vessel than in the body c bottom, it is generally recommended that the head remain fixe and that the vessel be raised or lowered for access.

Where heated vessels are involved, flexible tubing or flexibl joints can be used for connections to the bottom or body of th vessel. Such items are commercially available and in commo use.

It is also suggested that metal equipment (not glass-lined) b used for the first setup so that additional nozzles and connection may easily be welded in place if found desirable. This should b undertaken even where corrosion rates are high, wherever th process has not been fully studied, and where changes in the vesse design must be developed as operation proceeds.

It is recommended also that the agitator be mounted centrall for simple transfer of data to commercial scale. Off-center positioning of mixers is most critical in small vessels and should b avoided in pilot plant work.

It is suggested that a variable-speed drive is essential for sucl work. It is desirable to provide as wide a speed range as possibl with constant horsepower. This enables different types of impellers to be operated at their optimum peripheral speeds, witl horsepower kept on a comparable basis. A satisfactory speec reducer of this type is produced by the Master Electric Company, which has a speed ratio of approximately 9 to 1. At present this must be used with a separate bevel gear reducer of 2 to ratio. With the vessel sizes recommended, a one-horsepowe motor is satisfactory for the drive, and will permit the handlin of a wide range of viscosities and specific gravities in the liquid to be agitated.

If the pilot plant is expected to produce actual studies of agitation, provision for accurate power consumption measurement must be made. This would normally involve either supportin the vessel so as to measure the torque transmitted (*1*) or use of differential dynamometer (*3*). Various speeds and consequen horsepowers may therefore be tested as affecting the unit proces itself, and the data thus obtained utilized in dimensioning th commercial vessel and selecting the type, characteristics, anc horsepower of the commercial size agitator.

For many operations, however, the same results can be observed by securing calibrated impellers from the manufacture who would be expected to provide speed *vs.* horsepower curves for the impellers in water, together with formulas for correction factors for viscosity and specific gravity. This would require only that the type of impeller and its diameter be recorded together with accurate measurement of actual r.p.m. which should be obtained by tachometer.

TYPICAL CONSTRUCTIONS

Figures 1, 2, and 3 are illustrations of pilot plant apparatus involving agitation.

Figure 1 is a high-pressure vessel with a fixed-speed stirrer. This is a self-contained and complete element, but does not provide facilities for variable speed or for raising or lowering either head or vessel, etc. A special valve which does not retain "dead pockets", as illustrated, is frequently a necessity in small vessels for ease in cleaning and preventing contamination of succeeding batches.

Figure 2 shows a self-supporting unit with counterbalance arrangement so that position of vessel can be changed if desired. Space has been gained in the vessel head by using a nozzle attached at an angle instead of the customary normal entry.

The design details shown in Figures 1 and 2 can, of course, be combined in an over-all design which would utilize structural steel cage support, swing joints, and flexible tubing so that the head may remain fixed while the vessel is lowered. The support of the vessel should be at the most comfortable height for the most difficult function involved, including the operations of loading, draining, cleaning, temperature measuring, sampling, and visual observation.

Figure 3 shows a complete assembly for handling materials similar to paste, greases, etc. Provision for raising and lowering the mixing head is built into the equipment, and extreme flexibility is obtained by interchanging mixing elements. Speed is apparently varied by changing flat belt pulleys. In connection with handling paste, greases, etc., the choice of the mixing elements themselves is very critical. A piece of equipment, as illustrated, is extremely valuable to anyone experimenting in the paste range of materials. In fluid mixing, however, the type of impeller is not critical, the choice most frequently being made on a mechanical limitations basis. Therefore, in fluid mixing it is generally possible to equip the pilot plant with only a single type of impeller, provided this impeller type is capable of being scaled up to the largest anticipated commercial size, and provided the pilot plant is designed to develop the optimum conditions for the impeller through proper selection of size, variable speed, and other factors noted above.

A single type or, at most, two types of impellers can be selected on the basis of final commercial size, physical characteristics of material to be handled, and over-all duty requirements of the agitator. Only when all of these factors are unknown at the time of designing the pilot plant is it necessary to make provision for trying out a wide variety of impellers.

It is suggested as important that the complete pilot plant for any unit process include, wherever possible, actual equipment representing each unit operation essential in the unit process itself. If a pilot plant is to produce complete results, both as to the chemical reactions involved and as to a study of the mechanical equipment and factors involved, greater attention must be placed on the mechanical equipment than appears to be common practice. For example, many times pumps are omitted from a pilot plant because the quantities handled are small enough to be transferred by buckets or by gravity. Consequently, no information is available for the engineers who design the commercial size plant.

It has also happened that mechanical methods for a unit operation are used in pilot plant work which are incapable of scaling up to commercial size. For example, a rocking tank producing agitation by shaking can hardly be scaled up beyond a relatively small batch size, owing to the massive equipment that would be involved.

The authors do not suggest complete standardization of that portion of the pilot plant involving agitation. They do believe, however, that the factors presented here are important in unit process pilot plant design, and it is hoped that these factors will provide a general guide for those approaching such problems.

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OXIDATION of FERROUS SULFATE SOLUTIONS with OXYGEN

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The factors controlling the oxidation of the ferrous iron in a solution of ferrous sulfate, ferric sulfate, and sulfuric acid have been studied, using both oxygen and air. The percentage oxidation of ferrous sulfate is shown here graphically on curves with respect to time, partial pressure of oxygen, temperature, acid concentration, and catalyst concentration. The oxidation of ferrous sulfate in acid solution by oxygen is a very difficult reaction, and good conversions to ferric sulfate occur only at quite high temperatures and pressures over a considerable time period.

The oxidation of ferrous sulfate solutions by atmospheric oxygen has been studied considerably by analytical chemists, who have expressed surprise at the slowness of the reaction (*6*). They report a variety of conflicting results, probably arising from the differences in experimental methods. In a physical-chemical study of the activation of the oxygen electrode, Lamb and Elder (*5*) studied a number of variables in this reaction and corrected many of the erroneous conclusions of earlier workers. In general, they determined the hours required for an oxidation of 1% of the ferrous ion at 30° C. Their results will be compared with those obtained in this work.

Industrial studies of this reaction were made by Reedy and Machin (*8*) who state that the initial concentration of ferrous sulfate makes little difference in the velocity of the reaction. They secured complete oxidation by circulating the solution five times over crushed pyrolusite. Posnjak (*7*) determined the hours required for oxidation of 0.1 and 0.5 *N* ferrous sulfate solutions at room temperature. Agde and Schimmel (*1*) bubbled air or oxygen through ferrous sulfate solutions at various temperatures and pressures.

As discussed by previous workers (*7*, *8*), the oxidation of ferrous sulfate is of importance in the "heap leaching" process in which cuprous and cupric sulfides in low-grade ores are oxidized by ferric sulfate and the copper sulfate is leached away and recovered. The ferrous sulfate must be reoxidized to ferric sulfate in order to cycle the leaching solution (*2*,*4*).

A totally different application is in the hydration of acetylene to acetaldehyde. In the low-acid process acetylene is bubbled through 6% sulfuric acid solution at 70° C. The catalyst for this hydration is mercuric oxide which is dissolved in the acid. This catalyst gradually decreases in activity, being transformed partially to free mercury and partially to a heavy organic sludge. The mercury is recovered from both, reoxidized to the oxide, and reintroduced into the process. The life of the mercuric oxide catalyst can be extended considerably by the addition of mild oxidizing agents, such as chromates and ferric salts (*3*). In another research project the ferric salt, as sulfate, was found to be preferable; but since it slowly reduced to ferrous sulfate by the acetaldehyde formed in the reaction, the reoxidation of the spent solution became an important phase of the hydration problem. The study of the initial phase of the oxidation (*5*) or the lengthy time reported (*7*), both at room temperature, made it desirable to secure data concerning the speed of this oxidation at highe temperatures and pressures.

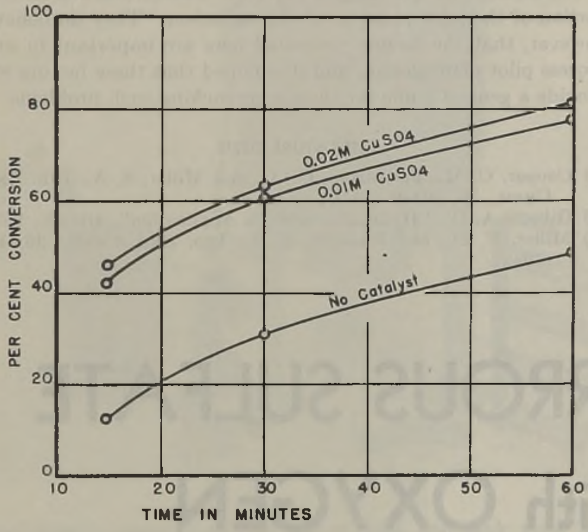

Figure 1. Effect of Time and Catalyst on Conversion at 100° C. and 275 Pounds per Square Inch Oxygen Pressure

OXIDATION PROCEDURE

The apparatus was a 4-inch-diameter steel autoclave, teste hydrostatically to 1500 pounds per square inch. Through packing gland in the cover came a quarter-inch shaft, the lowe portion of which was covered with a glass tube ending in glas stirrer. The solution (300 ml.) being treated was placed in a lip less beaker within the bomb. The beaker was surrounded b slightly alkaline water. Thus, the solution being treated did no come in contact with any metal. A mercury-in-glass thermometer passed through a packing gland in the cover and indicate the temperature of the solution. The total internal pressure wa indicated on a Bourdon spring type gage. The autoclave wa immersed to the top in a water bath heated by gas burners. Fo temperatures over 100° C. a salt bath (10 parts potassium nitrat to 8.5 parts sodium nitrite, melting point 135° C.) was used Oxygen or air was admitted from cylinders through a reducin valve and an inlet in the cover of the autoclave, through whic the pressure was relieved at the end of the experiment.

A synthetic solution of the same composition as the spen acetylene absorber liquor was used. It was made from analytica grade chemicals to the composition 0.0909 *M* $FeSO_4$, 0.0328 *M* $Fe_2(SO_4)_3$, 0.887 *M* H_2SO_4 (respectively, 13.8, 13.1, and 90.5 grams per liter). At the end of the experiment a sample of th solution was quickly cooled, and the ferrous ion remaining wa determined with standard permanganate. A duplicate sampl was reduced, and total iron determined to ensure that no change in concentration had occurred, or the results were calculated t the basis of the original solution using total iron as the tie element.

The experimental conditions, unless shown otherwise on the abscissa of the graphs, are for the composition of solution stated above: oxidized for 15 minutes at 100° C.; rate of stirring, 300 r.p.m.; copper sulfate concentration, 0.01 molar.

EXPERIMENTAL RESULTS

Catalyst Concentration. Previous work has shown copper sulfate to be the most satisfactory homogeneous catalyst (*5*, *7*). Figure 1 shows the percentage oxidation at 100° C. and partial pressure of oxygen of 275 pounds per square inch using no catalyst and 0.01 and 0.02 molar copper sulfate. Another experi-

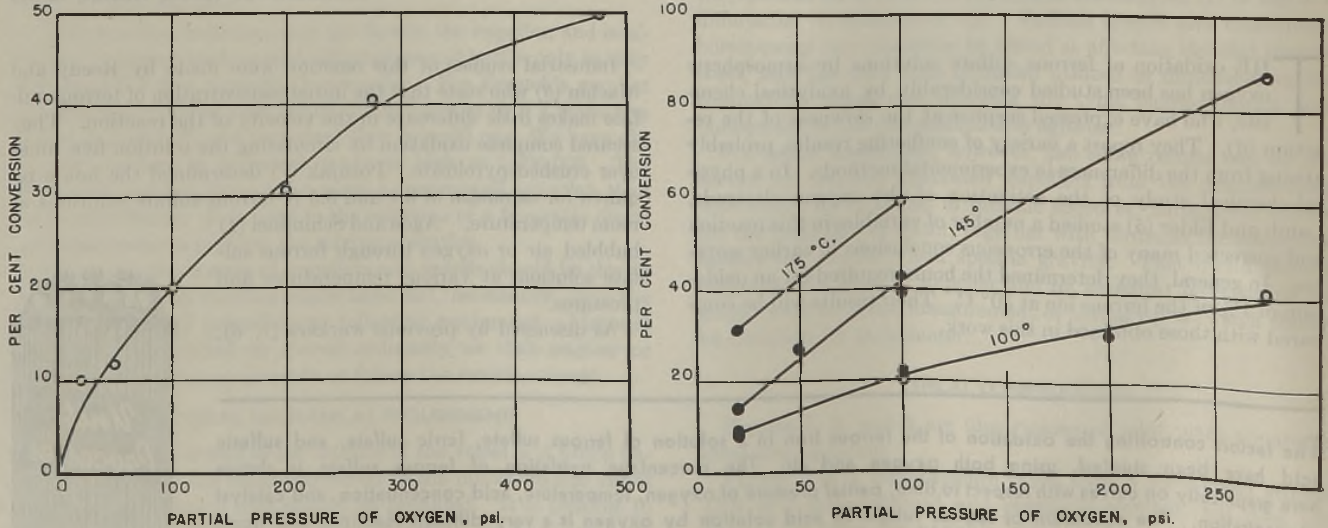

Figure 2. Effect of Partial Pressure of Oxygen on Conversion in 15 Minutes

● = air; ○ = oxygen

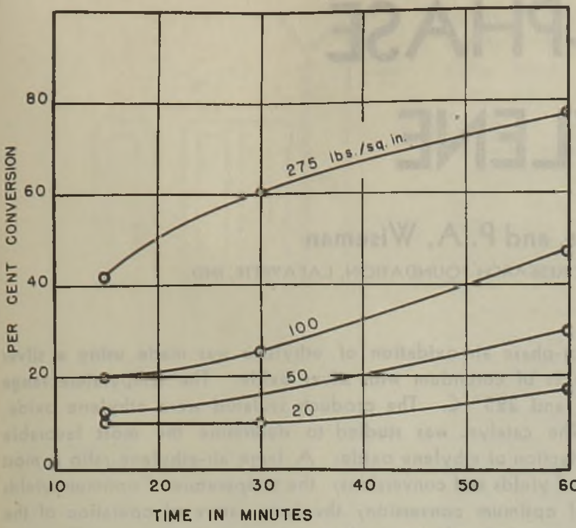

Figure 3. Effect of Time on Conversion at 100° C. and Various Pressures

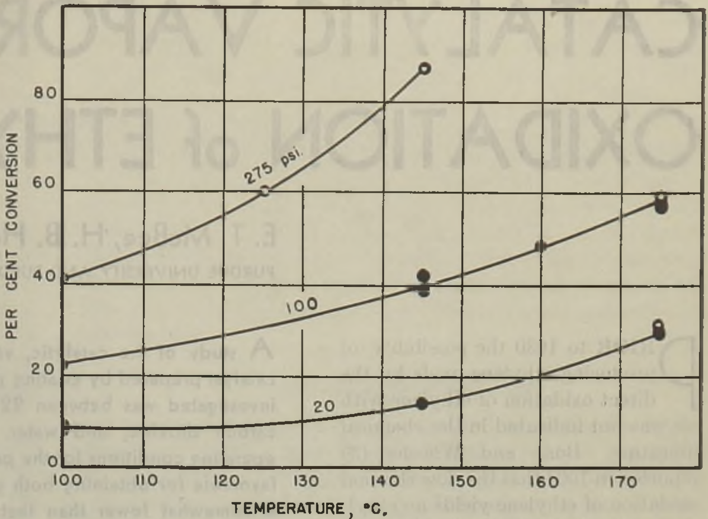

Figure 4. Effect of Temperature on Conversion in 15 Minutes at Various Pressures

● = air; ○ = oxygen

ment with 0.05 *M* copper sulfate showed results identical with 0.02 *M* solution. It appears that 0.01 *M* copper sulfate is the optimum concentration of catalyst, and this amount was used in all further experiments.

Time. Figure 1 also shows the effect of time on the conversion. All further experiments, unless otherwise indicated, were carried out for 15 minutes. Figure 3 shows conversions with respect to time at 100° C. and various partial pressures of oxygen.

Pressure. Figure 2 (left) shows the conversion at 100° C. in 15 minutes as a function of the partial pressure of oxygen above the solution. In Figure 2 (right) both air and oxygen are used as sources of oxygen at temperatures of 100°, 145°, and 175° C. Figure 3 gives the effect of time at various pressures and 100° C. It is immaterial whether the oxygen is supplied as pure oxygen or as air. This result was obtained by Lamb and Elder (*5*), but Agde and Schimmel (*1*) found greater oxidation with air which they attributed to the greater surface of the air bubbles in their solution.

Temperature. Figure 4 gives the conversion in 15 minutes as a function of the reaction temperature, using both oxygen and air at partial pressures of oxygen of 20, 100, and 275 pounds per square inch.

Acid Concentration. Previous work has shown the inhibiting effect of excess sulfuric acid. This has been checked, using the same concentration of ferrous and ferric sulfates but varying the molarity of the sulfuric acid. Figure 5 shows that the concentration used in this work has reached the minimum in the conversion curve.

Agitation and Dilution. Preliminary work had shown that the method of bubbling employed by Agde and Schimmel (*1*) gave greatly decreased conversions when compared to agitation by stirring. Conversion in an unstirred solution dropped to 9% from 20% at the normal rate. Increased stirring rate did not increase the conversion. When the original solution was diluted to one half and one quarter the original concentration, the conversions remained unchanged. The effect of concentration is reported differently by various workers; thus Reedy and Machin (*8*) state that the concentration of ferrous sulfate makes little difference in the velocity of reaction, Agde and Schimmel (*1*) report that the rate decreases, and Lamb and Elder (*5*) state that the initial velocity is proportional to the concentration.

Inhibitors. Addition of compounds present in the spent catalyst solution from hydration of acetylene to acetaldehyde gave decreased yields. Under conditions which gave 20% conversion with the synthetic solution, the addition of 10 grams per liter of mercuric oxide dropped the conversion to 18%, and the addition of six drops of acetaldehyde to the latter solution dropped the conversion to 7%. When this latter solution containing acetaldehyde was evaporated to half its original volume to distill off acetaldehyde and rediluted to its original volume, the conversion rose to 12%. The addition of manganese sulfate as a catalyst for the oxidation of acetaldehyde to acetic acid did not improve the conversion of ferrous sulfate.

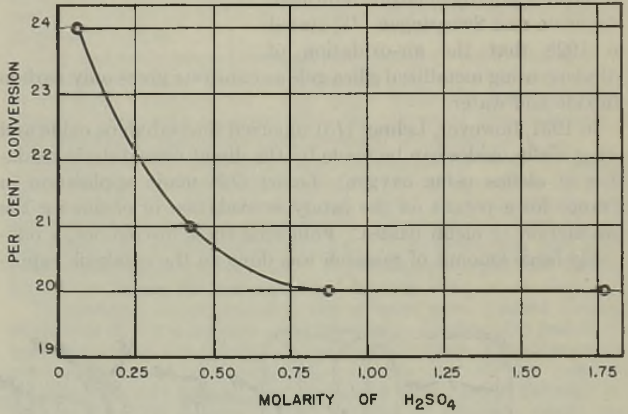

Figure 5. Effect of Sulfuric Acid on Conversion in 15 Minutes at 100° C.

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CATALYTIC VAPOR-PHASE OXIDATION of ETHYLENE

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A study of the catalytic, vapor-phase air oxidation of ethylene was made using a silv catalyst prepared by coating pieces of corundum with silver oxide. The temperature rang investigated was between 225° and 325° C. The products isolated were ethylene oxid carbon dioxide, and water. The catalyst was studied to determine the most favorab operating conditions for the production of ethylene oxide: A large air-ethylene ratio is mo favorable for obtaining both good yields and conversions; the temperature of optimum yiel is somewhat lower than that of optimum conversion; the temperature of operation of th catalyst must be raised as the contact time becomes shorter to maintain maximum efficienc small additions of ethylene dichloride to the reactants are desirable, large additions are d leterious; such a catalyst, when deactivated by excess ethylene dichloride, can be revived b raising the operating temperature and passing the reactants over the catalyst simultaneousl

PRIOR to 1930 the possibility of producing ethylene oxide by the direct oxidation of ethylene with air was not indicated in the chemical literature. Bone and Wheeler (*3*) reported in 1904 that the slow thermal oxidation of ethylene yields no ethylene oxide. In 1922 Blair and Wheeler (*2*) confirmed this report and stated that, although acetaldehyde can be produced in small quantities by such oxidations, no ethylene oxide is formed. Reyerson and Swearingen (*18*) stated in 1928 that the air-oxidation of ethylene using metallized silica gels as catalysts gives only carbon dioxide and water.

In 1931, however, Lehner (*13*) reported that ethylene oxide and other olefin oxides can be made by the direct noncatalytic oxidation of olefins using oxygen; Lefort (*12*) made application in France for a patent on the catalytic oxidation of olefins for the production of olefin oxides. Following these discoveries, a relatively large amount of research was done on the catalytic vapor-phase oxidation of ethylene to produce ethylene oxide. Durin the next ten years this chemical process developed rapidly, an ethylene oxide became one of our most important organic chem cals. Ethylene oxide is now being used in commercial quantiti for the production of such vital materials as plasticizers, plastic resins, insecticides, coolants, surface-active agents, solvents, an explosives.

The development of a suitable catalyst and the discovery the best method of ap plying such a catalys have been the aims many investigators. O the numerous materia tested and reported a least partially successfu (*4, 6, 9, 10, 12, 16, 18* silver and certain of it compounds seem to b the most desirable cata lysts yet found. Th metal may be used alon or in alloys. Mor commonly, however, silver compound such a the oxide, nitrate, car bonate, chloride, c cyanide is used to coat suitable inert carrier.

Almost any iner material which provide a large surface area ca be used as a catalys carrier. There is ev dence, however, tha both the chemical natur and the physical state the carrier may have a appreciable effect upo the activity of the cata lyst (*17*). Among th carriers which hav been tried are pumic

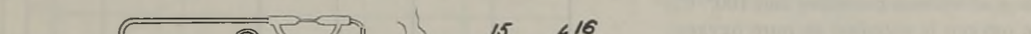

Figure 1. Apparatus Used in Studying the Reaction for Production of Ethylene Oxide by Catalytic Air Oxidation of Ethylene

1. Air cylinder
2. Ethylene cylinder
3, 4. T-tubes
5, 6. Glass tubes containing water
7. Drying towers
8. Air flowmeter
9. Ethylene flowmeter
10. Auxiliary inlet
11. Gases mixed here
12. Preheater
13. Catalyst chamber
14. Thermocouple (bath temperature)
15. Catalyst tube support
16. Thermocouple (catalyst bed temperature)
17. Salt bath
18. Stirrer
19. Direct reading pyrometer
20, 24. Stopcocks, three-way
21, 22. Ethylene oxide absorbers
23. Pinch clamp
25. Bubbler
26. Gas sampling tube
27. Mercury leveling bulb

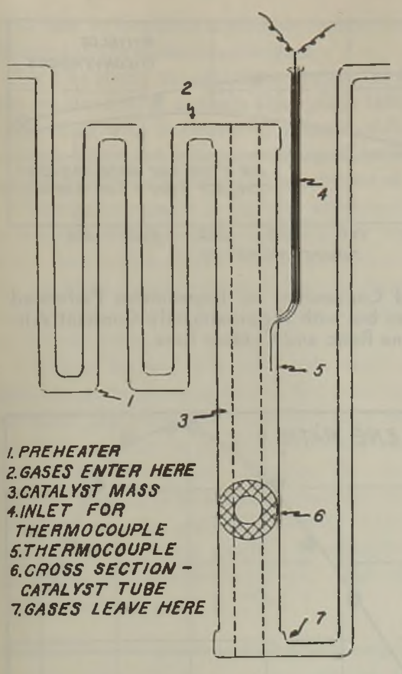

Figure 2. Reactor Used in Catalytic Oxidation of Ethylene

charcoal, activated carbon, silica gel, silica stone, alundum, and corundum (*4, 5, 10, 17, 18*). Of these materials, it appears that the most satisfactory ones consist of some form of aluminum oxide.

It has been shown that the addition of small quantities of modifying agents, called "promoters", often has a desirable effect on the silver-type catalysts (*4, 14, 16*). Such a promoter is usually an oxide or hydroxide of an alkaline earth metal. There seems to be little doubt but that catalysts so modified are more rugged and durable, and possess a more active and longer life than similar untreated ones.

During the oxidation of ethylene, the products which are obtained depend on the temperature and the manner in which the oxidation is performed. The products formed in the catalytic process are thought to be the result of two competing reactions:

$$2C_2H_4 + O_2 \rightarrow 2C_2H_4O; \quad \Delta H_{291} = -56 \text{ kg-cal.} \qquad (1)$$

$$2C_2H_4 + 6O_2 \rightarrow 4CO_2 + 4H_2O\,(g); \quad \Delta H_{291} = -631 \text{ kg-cal.} \qquad (2)$$

Reaction 2 is highly exothermic and must be brought under control. Since excessive temperatures favor the formation of carbon dioxide and water rather than ethylene oxide, it is essential that the catalyst be maintained within narrow temperature limits during operation. The more the formation of carbon dioxide and water can be suppressed, the more desirable the process becomes, both from the point of view of economy of operation and of materials.

A common method for controlling the temperature of an exothermic reaction is to surround the reactor with a material such as mercury or molten salt. By suitable regulation of this bath, it is possible to maintain the catalyst at the desired temperature level.

Another method widely reported as useful for controlling such a process is the introduction of a diluent along with the reactants. Many such diluents have been tried. Of these, nitrogen, carbon dioxide, air, and steam are the most common (*4, 6, 12, 16, 17*).

A third and interesting method of bringing the reaction under control is in the use of substances called "anticatalysts" (*1, 7, 11, 14*). An anticatalyst is a specific substance which, when added to the reacting gases in very small amounts, suppresses the formation of carbon dioxide and water and causes the catalyst to be more efficient in the production of the olefin oxide. Ethylene dichloride serves as a good example of such a material.

Of the vast amount of work which was performed in the development of the ethylene oxide industry, almost all of it was accomplished in industrial laboratories. No purely academic work seems to have been published on the subject. Although much valuable information is gained by studying the patents, they reveal little concerning the methods of approach to the problem; they tell nothing about the analyses used and give only the barest details concerning the nature of the reaction. Each new investigator in the field, consequently, finds that he must make an independent study of the reaction before any new phase of the problem can be attacked. Undoubtedly, this situation has led to repeated duplication of effort.

The purpose of this study was: first, to establish a definite method for the preparation of a silver catalyst which would be suitable for use in oxidizing ethylene to ethylene oxide with air; second, using the information already available in the patent literature, to learn as much as possible concerning the nature of this reaction; and third, to find a suitable method of testing rapidly any catalyst suspected of possessing desirable properties for this reaction.

OPERATION OF APPARATUS

Figure 1 is a drawing of the apparatus used during the experiments. The Pyrex catalyst tube which was found convenient for laboratory use is shown in more detail in Figure 2. The operations performed during a typical experiment were as follows:

By regulating carefully the valves attached to the air and ethylene cylinders, 1 and 2 (Figure 1), the gas flow was adjusted so that a small stream of gas issued from the ends of T-tubes 3 and 4. Air passed from the former, ethylene from the latter. The approximate desired flow of gases was established by adjusting the depth to which these T-tubes extended into the water contained in tubes 5 and 6.

The reactants passed through flowmeters 8 and 9, mixed at 11, were preheated to reaction temperature in tube 12, and reacted in catalyst chamber 13. The gases from the reactor passed through three-way stopcock 20. By means of this stopcock, it was possible to direct the gases through absorbers 21 or 22.

The first of the absorbing tubes, 22, contained 25 ml. of normal hydrochloric acid solution saturated with magnesium chloride. The second tube contained 25 ml. of 0.1 *N* hydrochloric acid saturated with magnesium chloride. Each of the three absorbing tubes (21) contained 25 ml. of 0.1 *N* hydrochloric acid saturated with magnesium chloride. The resistance to gas flow through absorbers 21 and 22 was equalized by adjusting pinch clamp 23.

To perform an experiment, the effluent gases passed through absorbers 21 for a definite time interval. During this period the temperature of the catalyst mass and the flows of reacting gases were determined and recorded. At the end of this interval, stopcock 20 was turned, and the gases were passed through absorbers 22. To determine the amount of ethylene oxide produced, it was necessary to remove the liquid from absorbers 21 and to titrate the unreacted acid with standard sodium hydroxide solution. The difference between the equivalents of base required for this titration and that required for a blank gave a direct measure of the ethylene oxide produced.

Since the time interval during which the ethylene oxide was absorbed in 21 for quantitative determination was so short, a second set of absorbers 22 was used to remove all of the ethylene oxide from the exit gases and to make sure the entire system was sufficiently purged so that a representative gas sample could be collected for analysis. After leaving absorbers 22 the gases normally passed through bubbler 25. By adjusting the stopcock at the top of gas sampling bulb 26, however, it was possible to collect a gas sample from this exit gas stream by the downward displacement of mercury in the bulb. When sufficient time had elapsed for the absorbing system to be swept out, a representative gas sample was taken in this manner.

The gas sample was analyzed on the Orsat apparatus for carbon dioxide, unreacted ethylene, oxygen, and carbon monoxide. No carbon monoxide was detected. Mercury, covered with a thin film of water, was used as the confining liquid in the Orsat so that the gas sample was always saturated with water vapor. Qualitative tests performed on the exit gases indicated that acetaldehyde was not produced in any appreciable quantity.

PREPARATION OF MATERIALS

Silver Catalyst. The catalyst was made by coating pieces of corundum of suitable size with silver oxide. This corundum

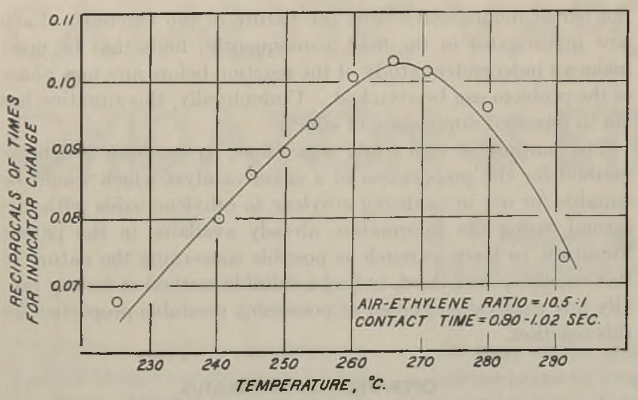

Figure 3. Temperature of Optimum Conversion at Constant Contact Time and Air-Ethylene Ratio for a New Silver Catalyst

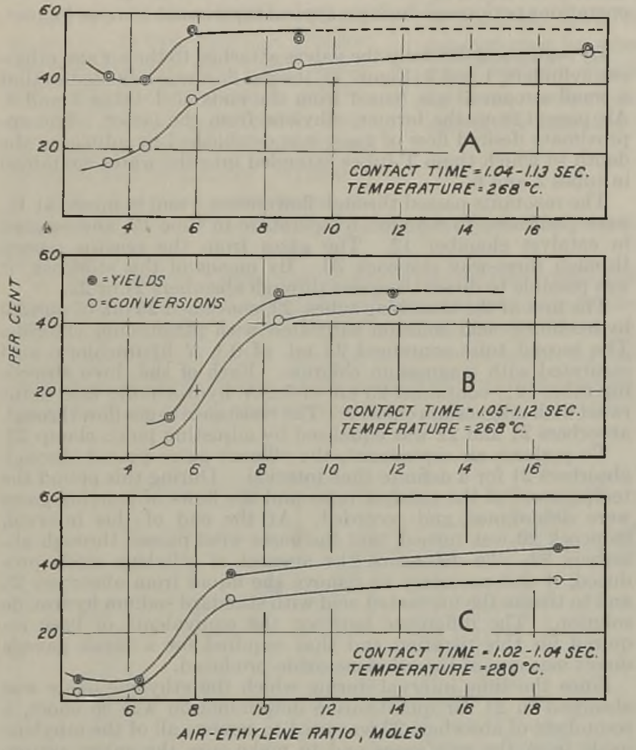

Figure 4. Yields and Conversions for Experiments with Varied Air-Ethylene Ratios but with Approximately Constant Temperature and Contact Time

A, new catalyst; *B*, 2-week-old catalyst; *C*, month-old catalyst

(No. T-61, Tabular alumina) was obtained from the Aluminum Company of America. Seventy grams of corundum of about 8-mesh, 21.98 grams of silver oxide, and 2.24 grams of barium peroxide were placed in a clean beaker. One hundred milliliters of distilled water were added to this mixture. The beaker containing these substances was placed on a steam cone. As the water evaporated, the mixture was stirred vigorously. By the time the water was completely removed, the corundum was well coated with silver oxide. The catalyst was then placed in an oven at 115° C. and allowed to dry for about 10 hours. This material was ready for immediate use.

Ethylene Oxide Absorbing Solution. The solution which was used for the absorption of ethylene oxide from the gaseous mixtures was prepared by dissolving 920 grams of magnesium chloride (hexahydrate) in 200 ml. of 0.5 *N* hydrochloric acid. The resulting solution was warmed to 50° C. with vigorous stirring. On cooling, the volume was made up to 1 liter. If solutions stronger than 0.1 *N* hydrochloric acid were desired, more acid was added in the proper proportions (*15*).

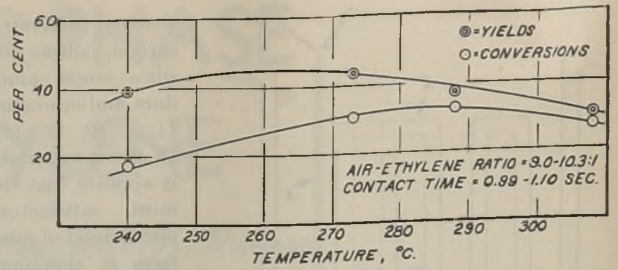

Figure 5. Yields and Conversions for Experiments Performed at Varied Temperatures but with Approximately Constant Air-Ethylene Ratio and Contact Time

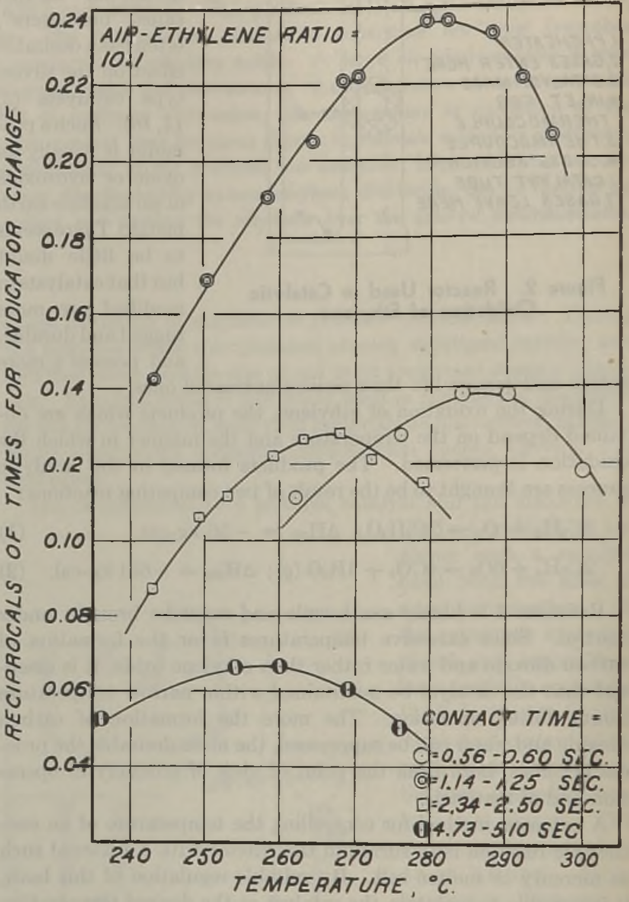

Figure 6. Temperatures of Optimum Conversion at Varied Contact Times, Using a Constant Air-Ethylene Ratio

Ethylene. During these experiments commercial ethylene was used. Samples from the cylinder were analyzed on the Orsat apparatus and were found to contain material, of which 97.5% was absorbed by fuming sulfuric acid.

Modified Methyl Orange Indicator. The modified methyl orange indicator used in these experiments was prepared by the method of Hickman and Linstead (*8*): 2 grams of methyl orange indicator were dissolved in 500 ml. of water, and this solution was added to an equal volume of 95% ethanol containing 2.8 grams of Xylene Cyanol FF.

CHECKING THE CATALYST

After the catalyst was prepared and placed in the catalyst tube, it was necessary to test its activity for the production of ethylene oxide and to establish a suitable temperature range for using this material in the initial experiments.

For this study the elaborate system for handling the exit gases was replaced with a single absorption tube. This tube was partially filled with a measured volume of 0.1 *N* hydrochloric acid solution saturated with magnesium chloride. A drop of modified methyl orange was added to the solution as an indicator.

The ethylene oxide in the exit gases and the hydrochloric acid in the absorbing solution combined to form ethylene chlorohydrin. As a result, the pH of the absorbing solution increased and the modified methyl orange indicator changed color from orange, to lavender, to colorless, to green. The colorless stage was taken as the end point.

A flow of air and ethylene in the ratio of 10.5 to 1 was established over the catalyst bed, which was initially at 225° C. The operator observed the time interval necessary for sufficient ethylene oxide to be produced to cause the indicator to undergo the changes mentioned. Keeping the air-ethylene ratio and the contact time approximately constant, the temperature of the catalyst mass was gradually raised. The time for a similar volume of the absorbing solution to become colorless was recorded at various temperature intervals. The observations from these experiments are given in Table I.

Table I. Determination of Suitable Operating Temperature for New Silver Catalyst

Temp., ° C.	Air, Liter/Min.	Ethylene, Liter/Min.	Time T, Min. to Decolorize 25 Ml. of Absorbing Soln.	$\frac{1}{T}$
225	0.445	0.0423	14.80	0.0676
240	0.445	0.0423	12.50	0.0800
245	0.445	0.0423	11.58	0.0865
250	0.445	0.0423	11.17	0.0895
254	0.445	0.0423	10.67	0.0937
260	0.445	0.0423	9.95	0.1005
266	0.445	0.0423	9.72	0.1028
271	0.445	0.0423	9.88	0.1012
280	0.445	0.0423	10.40	0.0962
291	0.445	0.0423	13.50	0.0740

The time necessary for the color change to occur in the indicator is a measure of the ethylene oxide being produced. By plotting the reciprocals of the times as ordinates and the temperatures as abscissas, the curve of Figure 3 was obtained. The temperature at which the maximum occurs in this curve (about 268° C.) was the temperature of optimum conversion for this particular air-ethylene ratio, catalyst, and contact time.

OPTIMUM AIR-ETHYLENE RATIO

A series of experiments was performed at approximately constant temperature (268° C.) and contact time (1.04 to 1.13 seconds). The air-ethylene ratios were varied, however, from 3.47:1 to 17.5:1. The purpose of this study was to determine the most favorable air-ethylene ratio for such oxidations. The data from these experiments are given in Table II.

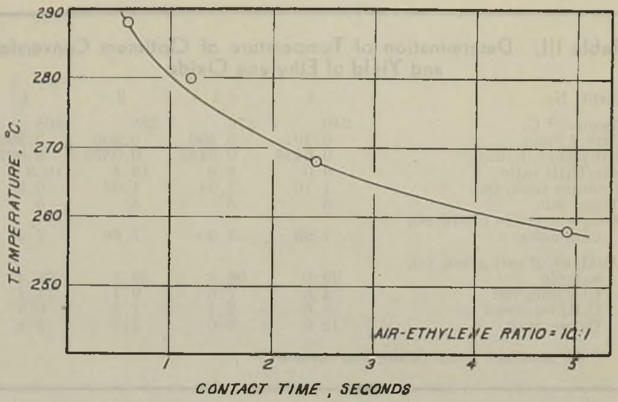

Figure 7. Relation between Temperature of Optimum Conversion and Contact Time in Experiments Performed with a Constant Air-Ethylene Ratio

Using the observations from these experiments, the yields and conversions were calculated. Yield represents the percentage of reacting ethylene converted to ethylene oxide. Conversion represents the percentage of total ethylene introduced which was converted to ethylene oxide. In Figure 4*A* the values for the yields and conversions are plotted against air-ethylene ratio.

The volumes of gases introduced as shown in the tables are the volumes measured at standard temperature and pressure. The contact times were calculated on the basis that the gases are at one atmosphere pressure and at the temperature shown for the reactor.

Similar quantitative experiments were performed about 2 weeks later to determine the effect of aging and continued use on the activity of the catalyst. The observations from these experiments are given in Table II, and Figure 4*B* is a graphic presentation of the calculated yields and conversions.

After approximately a month of almost daily use, the silver catalyst was rechecked to determine if 268° C. still represented a suitable reaction temperature. It was found that the temperature for optimum conversion had changed from around 268° C. to approximately 280° C. It now seemed desirable to know if the yields and conversions, obtained with the new catalyst at 268° C., could be duplicated by the month-old catalyst if it were operated at 280° C. A series of quantitative experiments was performed. Table II and Figure 4*C* show the results of these experiments.

From these various experiments, it may be concluded that: First, a high air-ethylene ratio is most favorable for obtaining both good yields and conversions, as shown by Figure 4. Second, as the catalyst ages, it becomes less and less efficient for the production of ethylene oxide. Third, on continued use, the temperature of operation of the catalyst must be raised if maximum efficiency for the production of ethylene oxide is to be maintained.

Table II. Effect of Air-Ethylene Ratio on Production of Ethylene Oxide

	New Catalyst (268° C.)					2-Week-Old Catalyst (268° C.)			Month-Old Catalyst (280° C.)			
Experiment No.	1	2	3	4	5	1	2	3	1	2	3	4
Air[a], liter/min.	0.414	0.362	0.371	0.346	0.314	0.400	0.365	0.340	0.410	0.393	0.371	0.358
Ethylene[a], liter/min.	0.0237	0.0405	0.0641	0.0784	0.0906	0.0340	0.0436	0.0657	0.0220	0.0436	0.0588	0.0794
Air/C_2H_4 ratio	17.5	8.95	5.80	4.41	3.47	11.8	8.37	5.18	18.7	9.02	6.32	4.51
Contact time, sec.	1.04	1.13	1.05	1.07	1.12	1.05	1.11	1.12	1.03	1.02	1.04	1.02
Time, min.	10	5	5	5	5	10	5	5	10	5	5	10
Ethylene oxide produced, millimoles	5.06	3.95	4.69	3.43	3.06	6.39	3.84	0.73	3.36	2.79	0.397	0.693
Analysis of exit gases, ml.												
Sample	97.5	100.2	99.2	99.6	99.0	96.6	99.4	98.0	99.0	100.0	97.2	97.4
Co_2 removed	3.6	8.0	9.6	11.8	10.7	6.2	9.3	13.0	4.6	12.4	13.4	12.6
C_2H_4 removed	0.1	2.0	6.4	10.2	15.3	0.8	1.9	9.9	1.0	2.2	6.8	12.6
O_2 removed	13.3	7.3	3.0	0.0	0.1	9.6	4.9	0.0	13.2	1.2	0.0	0.1

[a] At standard temperature and pressure.

Table III. Determination of Temperature of Optimum Conversion and Yield of Ethylene Oxide

Expt. No.	1	2	3	4
Temp., ° C.	240	273	288	308
Air[a], l./min.	0.391	0.390	0.390	0.390
Ethylene[a], l./min.	0.0435	0.0435	0.0379	0.0379
Air/C_2H_4 ratio	9.0	9.0	10.3	10.3
Contact time, sec.	1.10	1.04	1.03	0.99
Time, min.	5	5	5	5
Ethylene oxide produced, millimoles	1.63	2.90	2.66	2.25
Analysis of exit gases, ml.				
Sample	99.0	96.8	99.3	98.4
CO_2 removed	4.6	7.6	9.1	11.2
C_2H_4 removed	5.6	3.1	1.2	0.9
O_2 removed	12.0	7.0	5.7	3.4

[a] At standard temperature and pressure.

TEMPERATURE OF OPTIMUM CONVERSION

Optimum Yield of Ethylene Oxide. A series of quantitative experiments was performed with the air-ethylene ratio (9.0:1 to 10.3:1) and contact time (0.99 to 1.10 seconds) maintained approximately constant, but with the operating temperature varied. The purpose was to determine the relation between the temperature of optimum conversion and that of optimum yield.

The data are given in Table III. From these observations, the yields and conversions for the experiments were calculated and are shown in Figure 5. These data show that, for a definite air-ethylene ratio and contact time, the temperature of optimum yield is about 20° C. lower than the temperature of optimum conversion.

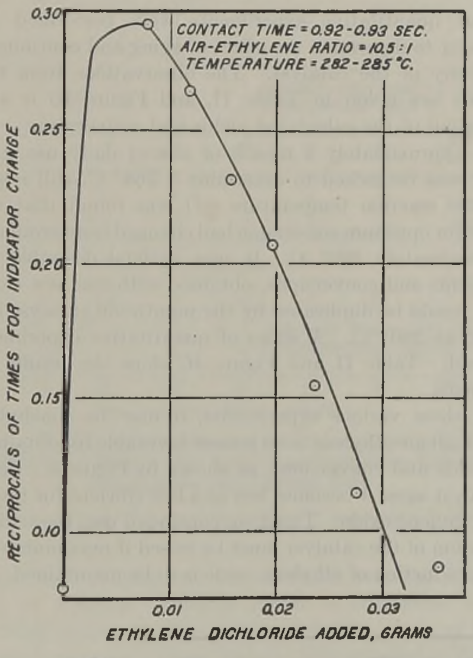

Figure 8. Effect of Small Additions of Ethylene Dichloride to Reactants, Air, and Ethylene

Values for ordinates are proportional to ethylene oxide produced per unit of time.

Effect of Contact Time. Ordinarily a great many quantitative experiments must be performed to establish the relation between contact time and the temperatures of optimum yields and conversions. In this particular process, however, a rapid and convenient method was available for determining the effect of contact time on the temperature of optimum conversion.

The experiments were performed with a constant air-ethylene ratio of 10 to 1. For each contact time, the time necessary to decolorize a definite volume of absorbing solution, containing modified methyl orange indicator, was determined at various temperature intervals. By plotting the reciprocals of these times against temperature, a curve showing the temperature of optimum conversion for this particular contact time was obtained. By plotting these optimum temperatures against contact times, a curve was obtained which shows the temperature of maximum conversion at any contact time. The contact times studied were 0.56 to 0.60, 1.14 to 1.25, 2.34 to 2.50, and 4.73 to 5.10 seconds.

The observations are given in Table IV. A graphical representation of the data is shown in Figures 6 and 7. The relation between the temperature of optimum yield and the temperature of optimum conversion is shown in Figure 5.

This study indicates that, for a definite air-ethylene ratio, as the contact time becomes shorter, the temperature of operation of the catalyst must be raised if maximum conversions are to be obtained.

THE CATALYST

Effect of Ethylene Dichloride. There are varying reports in the patent literature concerning the effect of certain "anticatalysts" such as ethylene dichloride on silver catalysts (*7*, *11*, *14*). It seemed worth while, therefore, to determine how the silver catalyst which was used in the previous experiments would respond to small quantities of ethylene dichloride. The catalyst tested was a little over a month old and had been used almost daily. It was relatively inactive when compared with its original state.

A small ethylene dichloride bubbler was attached to the oxidation apparatus. The equipment was arranged so that, when

Table IV. Determination of Effect of Contact Time on Optimum Conversion Temperature

Temp., ° C.	Contact Time, Sec.	Air, Liter/ Min.	Ethylene, Liter/ Min.	Time T, Min. to Decolorize 25 Ml. of Absorbing Soln.	$\frac{1}{T}$
262	0.60	0.693	0.0693	9.01	0.1110
276	0.59	0.693	0.0693	7.83	0.1276
284	0.58	0.693	0.0693	7.22	0.1386
290	0.57	0.693	0.0693	7.23	0.1384
300	0.56	0.693	0.0693	8.46	0.1181
243	1.25	0.346	0.0346	7.03	0.1425
250	1.23	0.346	0.0346	5.93	0.1689
258	1.22	0.346	0.0346	5.25	0.1905
264	1.20	0.346	0.0346	4.87	0.2055
268	1.19	0.346	0.0346	4.52	0.2215
270	1.19	0.346	0.0346	4.50	0.2222
279	1.17	0.346	0.0346	4.22	0.2372
282	1.16	0.346	0.0346	4.22	0.2372
288	1.15	0.346	0.0346	4.28	0.2335
292	1.14	0.346	0.0346	4.52	0.2215
296	1.14	0.346	0.0346	4.85	0.2063
243	2.50	0.174	0.0174	11.58	0.0864
249	2.47	0.174	0.0174	9.52	0.1052
253	2.45	0.174	0.0174	8.98	0.1113
259	2.43	0.174	0.0174	8.25	0.1212
263	2.41	0.174	0.0174	7.92	0.1264
268	2.39	0.174	0.0174	7.82	0.1280
272	2.37	0.174	0.0174	8.28	0.1208
279	2.34	0.174	0.0174	8.72	0.1148
236	5.10	0.086	0.0086	19.08	0.0525
254	4.92	0.086	0.0086	15.17	0.0660
260	4.87	0.086	0.0086	15.03	0.0666
269	4.79	0.086	0.0086	16.58	0.0604
276	4.73	0.086	0.0086	19.90	0.0502

Table V. Determination of Effect of Ethylene Dichloride on Catalyst

Temp., ° C.	$C_2H_4Cl_2$, Gram	Air Liter/Min.	Ethylene, Liter/ Min.	Time T, Min. to Decolorize 25 Ml. of Absorbing Soln.	$\frac{1}{T}$
285	....	0.436	0.0417	12.75	0.0785
285	0.0078	0.436	0.0417	3.45	0.2900
284	0.0117	0.436	0.0417	3.78	0.2650
282	0.0157	0.436	0.0417	4.32	0.2320
282	0.0196	0.436	0.0417	4.83	0.2070
282	0.0235	0.436	0.0417	6.50	0.1540
282	0.0274	0.436	0.0417	8.78	0.1140
282	0.0353	0.436	0.0417	11.58	0.0865

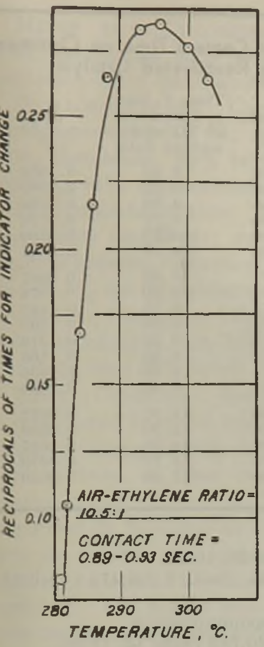

Figure 9. Effect of Simultaneously Raising the Temperature and Passing Air and Ethylene over a Catalyst Deactivated with Ethylene Dichloride

Values for ordinates are proportional to ethylene oxide produced per unit of time.

desired, nitrogen could be forced through this bubbler into the gaseous mixture of air and ethylene. A flow ratio of air and ethylene of 10.5 to 1 was established. Then ethylene dichloride was introduced intermittently into the gas stream. The changes which occurred in the catalyst were followed by determining, after each addition, the time required to decolorize a definite volume of 0.1 *N* hydrochloric acid saturated with magnesium chloride to which a drop of modified methyl orange had been added.

The data given in Table V and Figure 8 show that small additions of ethylene dichloride are desirable and increase the quantity of ethylene oxide produced by as much as fourfold. Too much ethylene dichloride, however, is deleterious.

Ethylene dichloride was introduced until the catalyst became more inactive than the original untreated material. The purpose of this deactivation was to determine if a catalyst, so treated, was permanently injured. This was not the case. It was found that the catalyst could be reactivated easily by raising the temperature and passing the reactants over the catalyst simultaneously (Table VI and Figure 9).

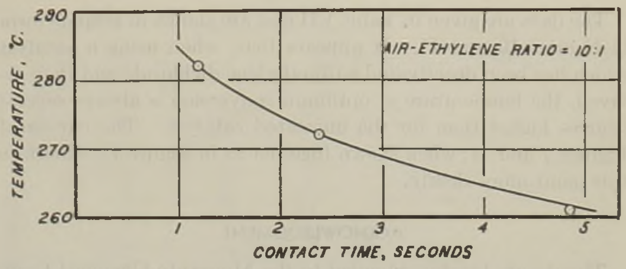

Figure 11. Relation between Temperature of Optimum Conversion and Contact Time in Experiments on a Reactivated Catalyst Using a Constant Air-Ethylene Ratio

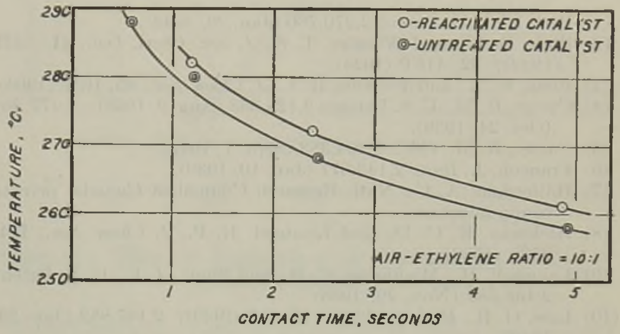

Figure 12. Relation between Temperatures of Optimum Conversion and Contact Times for a Catalyst before Deactivation and after Subsequent Revival

Table VI. Reactivation of Silver Catalyst Deactivated with Excess Ethylene Dichloride

Temp., ° C.	Air, Liter/Min.	Ethylene, Liter/Min.	Time T, Min. to Decolorize 25 Ml. of Absorbing Soln.	$\frac{1}{T}$
281	0.436	0.0417	12.92	0.0773
282	0.436	0.0417	9.47	0.1056
284	0.436	0.0417	5.90	0.1695
286	0.436	0.0417	4.60	0.2175
288	0.436	0.0417	3.77	0.2651
293	0.436	0.0417	3.52	0.2840
296	0.436	0.0417	3.50	0.2858
300	0.436	0.0417	3.60	0.2775
303	0.436	0.0417	3.78	0.2645

EFFECT OF CONTACT TIME ON OPTIMUM CONVERSION TEMPERATURE WITH REACTIVATED CATALYST. From the point of view of application, it was desirable to know how a catalyst, which was deactivated with ethylene dichloride and then revived, should be operated to obtain the best results. Therefore, a temperature–contact time study was made on the reactivated catalyst. The experiments were performed in the same manner as the study of the relation between contact time and temperature of optimum conversion for the untreated catalyst. The contact times were varied from 1.14 to 4.94 seconds and were studied at temperatures ranging from 252° to 293° C. A constant air-ethylene ratio of 10 to 1 was maintained.

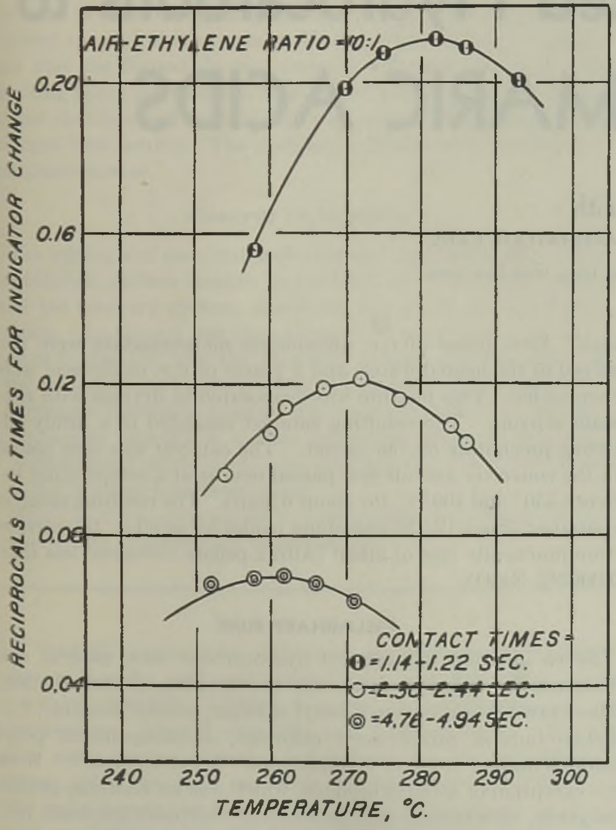

Figure 10. Temperatures of Optimum Conversion at Varied Contact Times for a Reactivated Silver Catalyst, Using a Constant Air-Ethylene Ratio

The data are given in Table VII and are shown in graphic form in Figures 10 and 11. It appears that, when using a catalyst which has been deactivated with ethylene dichloride and then revived, the temperature of optimum conversion is always several degrees higher than for the untreated catalyst. The curves of Figures 7 and 11, when shown together as in Figure 12, illustrate this point more clearly.

ACKNOWLEDGMENT

Thanks are hereby extended to the Monsanto Chemical Company for deferring the expenses of this investigation as Purdue Research Foundation Fellowship 198 and for their cooperation and interest.

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Table VII. Determination of Effect of Contact Time on Optimum Conversion Temperature with a Reactivated Catalyst

Temp., ° C.	Contact Time, Sec.	Air, Liter/Min.	Ethylene, Liter/Min.	Time T, Min. to Decolorize 25 Ml. of Absorbing Soln.	$\frac{1}{T}$
258	1.22	0.346	0.0346	6.40	0.1560
270	1.19	0.346	0.0346	5.02	0.1990
275	1.18	0.346	0.0346	4.80	0.2082
282	1.16	0.346	0.0346	4.72	0.2120
286	1.16	0.346	0.0346	4.77	0.2100
293	1.14	0.346	0.0346	4.97	0.2012
254	2.44	0.174	0.0174	10.35	0.0967
260	2.42	0.174	0.0174	9.30	0.1076
262	2.41	0.174	0.0174	8.75	0.1142
267	2.38	0.174	0.0174	8.38	0.1193
272	2.36	0.174	0.0174	8.22	0.1218
277	2.34	0.174	0.0174	8.58	0.1166
284	2.32	0.174	0.0174	9.13	0.1096
286	2.30	0.174	0.0174	9.53	0.1050
252	4.94	0.086	0.0086	14.92	0.0672
258	4.88	0.086	0.0086	14.50	0.0689
262	4.84	0.086	0.0086	14.37	0.0697
266	4.80	0.086	0.0086	14.72	0.0679
271	4.76	0.086	0.0086	15.88	0.0630

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Oxidation of Chlorinated Hydrocarbons to MALEIC and FUMARIC ACIDS

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IN CERTAIN instances polychlorinated aliphatic hydrocarbons are industrial by-products of comparatively low value. Accordingly such polychlorides may be available as cheap raw materials for chemical processes. This paper describes a process by which chlorinated hydrocarbons may be converted to more valuable products (i.e., maleic and fumaric acids) by simultaneous catalytic vapor-phase oxidation and dehydrochlorination. Hydrochloric acid is a by-product of the reaction.

Because of its widespread use, the catalyst chosen for this reaction was vanadium pentoxide deposited on various carriers. In order to determine the breadth of the reaction, numerous runs were made on various halogenated hydrocarbons in glass laboratory apparatus previously described by the author (*4*). This was followed by a series of runs on dichloropentane in larger-scale metal apparatus to obtain data on the effect of temperature and space velocity. This apparatus has also been described previously (*3*).

The vanadium pentoxide catalyst was prepared as follows: 80 ml. of aluminum pellets (made by compressing aluminum turnings to pellets approximately $^1/_4 \times {}^1/_8$ inch) or Alfrax pellets ($^3/_{16} \times {}^3/_{16}$ inch) were washed with strong oxalic acid solution, rinsed, and just covered with distilled water in an evaporating dish. Five grams of C.P. ammonium metavanadate were dissolved in the heated water, and 5 grams of C.P. oxalic acid were then added. This mixture was evaporated to dryness with constant stirring. The resulting catalyst consisted of a firmly adhering precipitate on the carrier. The catalyst was then placed in the converter and air was passed over it at a temperature between 350° and 400° C. for about 6 hours. The resulting catalyst contained about 12.4% vanadium oxides by weight; the carriers were practically free of alkali (Alfrax pellets contained less than 0.0002% Na_2O).

PRELIMINARY RUNS

Seven different halogenated hydrocarbons were used as raw materials in order to determine the breadth of the reaction. These raw materials were *n*-butyl chloride, *n*-butyl bromide, 1,2-dichlorobutane, mixed amyl chlorides, dichloropentane, polychloropentanes, *n*-hexyl chloride, and "keryl chloride". With the exception of *n*-butyl bromide, which was an Eastman practical grade, all materials were products of Sharples Chemicals, Inc. Of these, the 1,2-dichlorobutane and *n*-hexyl chloride were comparatively pure. The others were commercial grades with the following specifications:

Mixed Amyl Chlorides. Specific gravity at 20°/20° C., 0.88; distillation, 95% between 85° and 109° C.; amylene and pentane content, less than 3.0%; a mixture of monochlorides only.

Dichloropentane. Commercial product sold as Sharples dichloropentanes No. 14; specific gravity at 20°/20° C., 1.07 to 1.08; distillation, 95% between 130–200° C.; average chlorine content, 48% (approximate).

Polychloropentanes. Further chlorinated dichloropentanes (previously described); contain approximately 63.5% chlorine, which is between theoretical figures of 60.75 for trichloropentanes and 67.5% for tetrachloropentanes.

***n*-Butyl Chloride.** Specific gravity at 20°/20° C., 0.88 to 0.89; distillation, not less than 95% between 76.0–79.5° C.; not more than 25% below 77.5° C.

Keryl Chloride. Specific gravity at 20°/20° C., 0.899; a chlorinated kerosene fraction (12–14 carbon atoms per molecule) containing 13.85% chlorine.

Since most of these materials had relatively wide boiling ranges and, in the case of the glass laboratory equipment, were vaporized by bubbling air through the liquid, the vapors passed over the catalyst were higher in low-boiling constituents than the original material. For that reason fresh samples were used for each run. (As will be seen later, this was not necessary in the runs made in the larger metal apparatus, since complete vaporization was accomplished.)

Preliminary runs in glass apparatus were made on all the raw materials listed above with the exception of keryl chloride. These runs usually lasted 2 hours, during which time 5 to 12 grams of raw material were passed over the catalyst. Whenever a freshly prepared catalyst was used, the first run was about 8 hours in duration to eliminate the first period of abnormal catalyst activity usually exhibited. Data taken during this period were discarded.

The apparatus and experimental procedure were essentially the same as those described previously (*4*). Dry metered air was bubbled through the material to be vaporized at such a temperature that the desired air–raw material ratio was obtained. The resulting vapor mixture was then passed over the catalyst held in a glass chamber and maintained at the proper temperature by an external heat source. The reaction products were recovered in the usual manner.

ANALYSIS OF PRODUCTS

The products of each run were analyzed for maleic acid, hydrogen chloride, carbon dioxide, and aldehydes. They were washed from the recovery system, dissolved, and made up to a known volume. An aliquot was then titrated for total acid with 0.1 *N* sodium hydroxide, and the resulting neutral solution was analyzed for aldehydes by the neutral sodium sulfite method (*5*).

Hydrogen chloride in solution was determined by first neutralizing a sample with 0.1 *N* sodium hydroxide, adding a few drops of concentrated nitric acid, and titrating for the chloride ion with 0.1 *N* silver nitrate solution.

Maleic acid was determined by precipitation as barium maleate monohydrate as previously described (*4*).

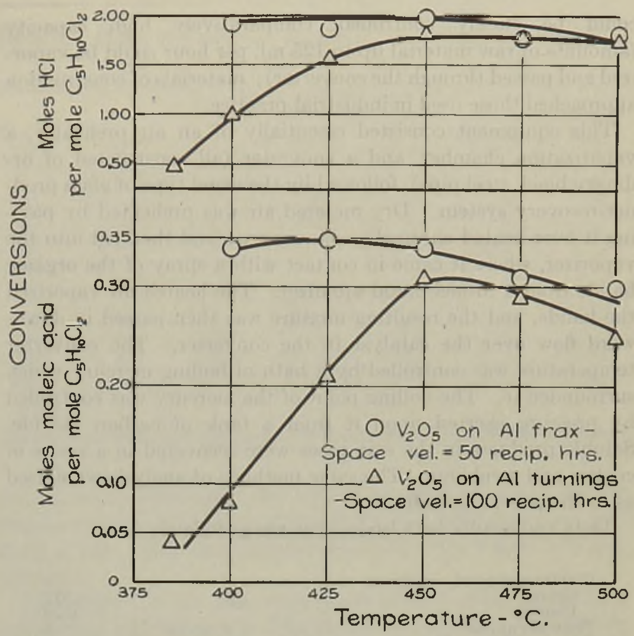

Figure 1. Effect of Temperature on Catalytic Oxidation of Dichloropentane

During the run a portion of the gases leaving the recovery system was analyzed for carbon dioxide and hydrogen chloride. In the carbon dioxide determination, the carbon dioxide was absorbed in a saturated barium hydroxide solution, the precipitate redissolved as barium chloride, and the barium determined by the usual precipitation as barium sulfate.

The gases were analyzed for hydrogen chloride by absorption in a potassium carbonate–glycerol solution consisting of equal parts of anhydrous potassium carbonate, water, and glycerol. This solution was analyzed for the chloride ion both before and after use by the usual titration with 0.1 *N* silver nitrate solution.

Typical results are shown in Table I. These runs were made using widely varying conditions; accordingly it is difficult to compare the results from one compound to another. On the other hand, the data show the catholicity of the general reaction.

CATALYTIC OXIDATION OF DICHLOROPENTANES

The action of specific variables on the oxidation of halogenated hydrocarbons was determined using commercial dichloropentanes only as a raw material. The variables studied were reaction temperature, space velocity, air–chlorinated hydrocarbon ratio, catalyst carriers, addition of diluents, and pressure.

The apparatus for this study was previously described (*3*). It was larger in size than that used in the general raw material study and was constructed of metal instead of glass. The advantages of the equipment of particular value in this investigation were: It allowed a material with a wide boiling range to be completely vaporized into the air stream; catalyst temperature

The catalytic vapor-phase oxidation of halogenated hydrocarbons over a vanadium pentoxide catalyst to maleic or fumaric acid and hydrochloric acid has been investigated. Data are presented for the oxidation of *n*-butyl chloride, *n*-butyl bromide, 1,2-dichlorobutane, mixed amyl chlorides, dichloropentane, polychloropentanes, *n*-hexyl chloride, and keryl chloride. The effect of temperature, space velocity, molar air-halide ratio, carrier, diluents, and pressure on the dichloropentane oxidation was determined. Optimum conversions, using vanadium pentoxide on Alfrax at 425–450° C. at a space velocity of 50 reciprocal hours, were 0.35 mole fumaric acid and 1.88 moles hydrochloric acid per mole commercial dichloropentanes. Whether maleic or fumaric acid was obtained depended upon the concentration of hydrochloric acid in the recovery system. The process appears to be a suitable means of utilizing the by-product polychlorinated hydrocarbons.

could be closely controlled; comparatively high capacity (amounts of raw material up to 125 ml. per hour could be vaporized and passed through the converter); materials of construction approached those used in industrial practice.

This equipment consisted essentially of an air preheater, a vaporization chamber, and a converter (all constructed of ordinary black steel pipe), followed by the usual type of glass product-recovery system. Dry metered air was preheated by passing it over heated chromel resistance wire and then led into the vaporizer, where it came in contact with a spray of the organic halide from a Monel metal atomizer. The heated air vaporized the halide, and the resulting mixture was then passed in downward flow over the catalyst in the converter. The converter temperature was controlled by a bath of boiling mercury which surrounded it. The boiling point of the mercury was controlled by pressure exerted upon it from a tank of carbon dioxide. Soluble products in the exit gases were recovered in a series of coolers and scrubbers. The same methods of analysis were used as in the previous studies.

Data and results for a typical run are as follows:

Dichloropentanes vaporized	
Grams	572
Pounds	1.26
Time of run, hr.	8
Temp. of boiling Hg in converter, ° C.	425
Flow of primary air, lb./hr.	5.1
Flow of secondary air, lb./hr.	1.05
Molar ratio, air to chloride	188
Weight ratio, air to chloride	39.0
Mixt. passed over catalyst (remainder by-passed), %	50
Dichloropentane passed over catalyst	
Grams	286
Pound	0.63
Length of catalyst, inches	20.3
Vol. of catalyst	
Cubic inches	6.08
Cubic foot	0.00352
Space velocity, cu. ft. organic vapor/hr./cu. ft. catalyst	57
Fumaric acid obtained (by analysis), grams	81.2
Hydrochloric acid recovered (by analysis), grams	139.5
CO_2 obtained (by analysis), grams	27.1
Aldehydes obtained (by analysis), gram mole	0.365

Conversion	Mole %[a]	Weight %
Fumaric acid	35.0	28.4
Hydrochloric acid	188.0	48.0
Carbon dioxide	30.0	9.4
Aldehydes	18.0	..

[a] Total moles products per mole dichloropentanes multiplied by 100.

EFFECT OF VARIABLES

TEMPERATURE. Figure 1 shows the effect of temperature on maleic acid and hydrochloric acid conversions at two different space velocities. Although different carriers were used for the V_2O_5 catalyst in the two cases, it is believed that they are comparable. The curves show that for any space velocity an optimum temperature exists. It is also interesting to note that the curves for both maleic acid and hydrochloric acid conversions have the same general shape. Optimum molar conversions for this series of runs were: at 50 reciprocal hours and 425° C., maleic acid 0.35, hydrochloric acid 1.88; at 100 reciprocal hours and 450° C., maleic acid 0.31, hydrochloric acid 1.80.

Actually the acid product recovered in this study using a metal converter was fumaric and not maleic acid. This was occasioned by a difference in the design of the recovery systems for the two pieces of equipment. In the glass apparatus referred to in the first part of this paper, most of the organic acid was collected at a temperature higher than the dew point of the exit gases, so that little or no hydrochloric acid came in contact with the maleic acid. In the case of the metal apparatus used in the runs now under discussion, the recovery system was such that both the organic acid and hydrochloric acid were collected together at a temperature below the dew point, with the result that the maleic acid was isomerized to the more stable fumaric acid. In a commercial plant the particular form of the organic acid obtained would be determined by the characteristics of the recovery system.

The other products of the reaction were determined as aldehydes and as carbon dioxide. Generally the aldehyde conversion curve had the same shape as the fumaric acid curve except that it was somewhat lower. Maximum molar conversions were 0.26 at 450° C. and 100 reciprocal hours and 0.22 at 50 reciprocal hours. No attempt was made to determine the actual composition of the aldehydes.

Carbon dioxide conversions varied considerably. Theoretically one mole of carbon dioxide is formed for each mole of fumaric acid produced. Carbon dioxide in excess of this amount averaged about 0.25 mole per mole dichloropentane.

SPACE VELOCITY. The variation of maleic acid and hydrochloric acid conversions with space velocity was studied in the small glass apparatus referred to above. Accordingly the absolute values are not comparable to those obtained in the larger metal apparatus. Values obtained with the small apparatus are not so representative of true values for the reaction for two reasons: (1) There was greater temperature variation in the catalyst bed, and (2) only the more volatile portion of the dichloropentane was vaporized. The general trend of the curves, however, is much the same as those obtained using the larger apparatus, and the values are presented in Figure 2 subject to these limitations.

These curves, like those of Figure 1, show that temperature and space velocity are so closely related that it is difficult to consider them separately. From a practical standpoint the curves show that long times of contact (low space velocities) at low temperatures may give the same conversions as short times of contact (high space velocities) at high temperatures. In commercial practice the final choice of conditions would depend upon cost of fuel, cost of compressor operation, catalyst life, space-time yield, limitations of materials of construction, and a number of other factors. These would probably vary from one plant to another so it is useless to pick out any one condition and state that it is optimum under all conditions.

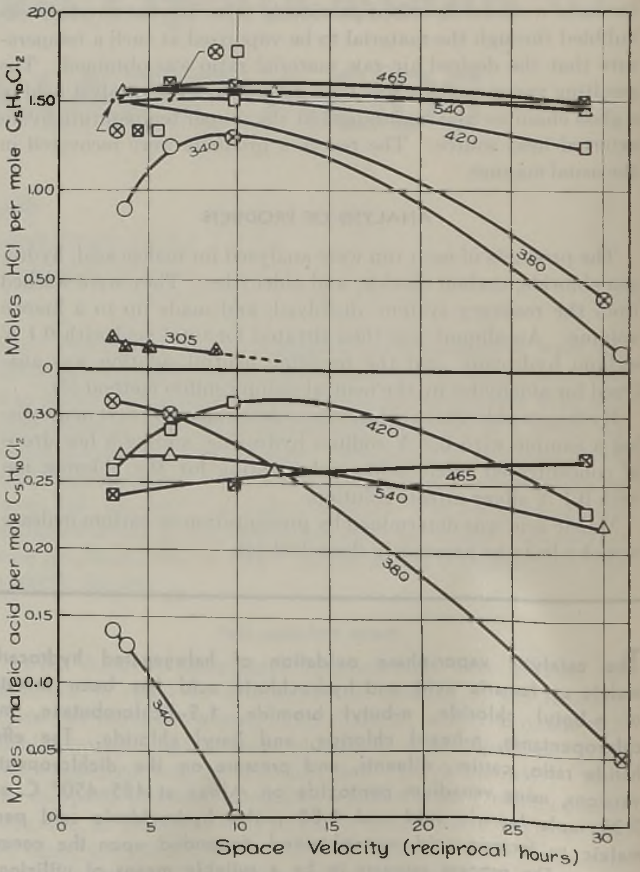

Figure 2. Effect of Space Velocity on Catalytic Oxidation of Dichloropentane

Table I. Catalytic Vapor-Phase Oxidation of Alkyl Halides

Catalyst Temp., ° C.	Space Velocity, Reciprocal Hours	Molar Air-Halide Ratio	Moles Product per Mole Sample: Maleic acid	HCl or HBr	CO_2[a]	Aldehydes
			n-Butyl Chloride			
350	21.4	182	0.01	0.10	0.00	0.03
450	22.8	171	0.09	0.55	0.19	0.19
550	21.7	179	0.12	0.83	0.39	0.21
			n-Butyl Bromide			
350	16.7	235	0.02	0.09	0.13	0.05
450	15.9	245	0.10	0.37	0.18	0.14
550	16.6	235	0.12	0.81	0.36	0.09
			1,2-Dichlorobutane			
350	12.8	310	0.04	0.28	0.00	0.04
450	14.1	280	0.23	1.33	0.17	0.17
550	12.5	320	0.18	1.56	0.14	0.17
			Mixed Amyl Chlorides			
350	30.7	128	0.00	0.41	0.00	0.03
450	30.1	127	0.17	0.75	0.13	0.16
550	33.6	110	0.23	0.88	0.41	0.20
			Polychloropentanes			
350	3.8	1065	Trace	0.53	0.00	0.27
450	5.6	775	0.34	2.36	0.28	0.35
550	5.8	760	0.33	2.60	0.28	0.28
			n-Hexyl Chloride			
350	6.1	580	0.01	0.12	0.00	0.08
450	6.5	550	0.17	0.55	0.12	0.22
550	8.2	440	0.19	0.81	0.36	0.32
			Dichloropentane			
420	28.0	650	0.23	1.25	0.10	0.25
465	28.0	660	0.27	1.50	0.40	0.28
505	28.0	680	0.25	1.50	0.50	0.26
			Keryl Chloride (Chlorinated Kerosene); Catalyst, V_2O_5 on Alfrax; Metallic Converter			
410	61	246	0.08	0.32	1.88	0.19
425	47	310	0.19	0.72	3.29	0.24
450	55	262	0.13	0.51	0.93	0.21

[a] With exception of keryl chloride figures, CO_2 is listed as amount in excess of that theoretically formed along with maleic acid.

Table II. Effect of Carrier on Conversions (Oxidation of Dichloropentane)

(Vanadium pentoxide catalyst; space velocity = 50 reciprocal hours, except aluminum = 100 reciprocal hours)

Temp., ° C.	Al	Alfrax	Activated Alumina	Carborundum	Infusorial Earth	Silica Aerogel (Santocel)
		Maleic Acid Conversions (Mole Per Cent)				
380	0.04	..	0.05	0.12[a]	0.14	0.08
425	0.21	0.35	0.02	0.28	0.24	..
450	0.31	0.34	..	0.31	0.33	0.07
475	0.29	0.31	..	0.31	0.31	..
500	0.25	0.30	..	..	0.31	0.04
		HCl Conversions (Mole Per Cent)				
380	0.47	..	2.01	1.08	1.25	1.15
425	1.56	1.88	1.95	1.75	1.82	..
450	1.82	1.99	..	1.72	1.97	1.26
475	1.79	1.79	..	1.79	1.90	..
500	1.80	1.82	..	..	1.99	1.01

[a] 370° C.

In the reaction under discussion, the fact that there are two main products, maleic or fumaric acid and hydrochloric acid, further complicates the choice of operating conditions. Under certain economic conditions it might be advisable to sacrifice a small percentage of hydrochloric acid conversion in order to obtain a higher maleic or fumaric acid conversion and vice versa. Fortunately the effect of different variables on the hydrochloric acid conversion is not so critical as on the organic acid conversions, so the latter may usually be chosen as the governing factor.

Catalyst Carrier. Vanadium pentoxide was deposited on six different carriers, and their action was studied in a series of runs using the larger apparatus. The various carriers studied were aluminum turnings, Alfrax, activated alumina, Carborundum, infusorial earth, and silica aerogel pellets. In the cases of the first four mentioned, the vanadium pentoxide was deposited on the pellets as described previously. The last two carriers were mixed in powdered form with ammonium metavanadate and oxalic acid, made into a thin paste, evaporated to dryness, and then pelleted in a suitable machine. Glucose was used as binder and a hydrogenated oil as lubricant. These were then burned out in preliminary runs.

Data on fumaric acid and hydrochloric acid conversions obtained by using these carriers are listed in Table II. No specific conclusions may be drawn from these data, since carrier activity is undoubtedly a complex function of many variables.

Air-Halide Ratio. Various molar air-halide ratios were used in this study, but their variation was not examined critically since such effects in highly exothermic oxidation reactions are well known. It is usually advantageous to work below the lower limit of the explosive range, and to have sufficient excess air to aid in heat removal from the catalyst bed. In the case of dichloropentane, molar air-halide ratios above 70 to 1 are sufficient to avoid explosion. Above that value the ratio has little effect on conversions. Generally, the ratio was approximately 500, although in isolated cases extremes of 100 and 1000 were used with little, if any, variation in fumaric acid and hydrochloric acid conversions.

Diluents. A few runs were made using varying amounts of both steam and nitrogen as diluents for the reaction. No definite conclusions were reached, although the use of steam appeared to have some merit. Nitrogen, on the other hand, offered no advantages commensurate with the added expense entailed by its use.

Pressure. Several runs were also made at superatmospheric pressure up to 45 pounds per square inch gage. Aside from a slight suppression of hydrochloric acid and carbon dioxide conversions, little variation from atmospheric pressure runs was noted. The economic aspects both of pressure and of diluent steam can be more accurately evaluated on a pilot plant scale.

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COMMERCIAL VALUE OF PROCESS

The industrial possibilities of maleic, fumaric, and other dibasic acids depend greatly upon their cost of manufacture. Accordingly any decrease in the cost of the raw material used is of commercial interest. Since no process has yet been found by means of which the paraffin hydrocarbons may be utilized directly, the two-step process involving intermediate chlorination is of interest. Indications are that the chlorination process would not have to be controlled so closely as a process directed toward a monochlorinated product, with consequent reduction in manufacturing cost.

Another source of cheap raw material is the polychlorinated by-product of alkyl monochloride manufacture. Various proposed processes for the manufacture of both chloroprene (*2*) and butadiene (*1*) also yield polychlorides as by-products. The process described could be a suitable economic outlet for these materials.

ACKNOWLEDGMENT

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WOOD HYDROLYSIS

Utilization of Waste Liquors

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Production of chemically converted products from wood and wood waste has increased for several decades, a further impetus being provided by wartime shortages of other materials. The continuous hydrolysis of wood and other plant fibers with dilute sulfuric acid produces lignocellulose for use in plastics. The waste liquors, in addition to the sulfuric acid, contain valuable constituents; yields, on the basis of dry wood processed, are: organic acids (as acetic), 5–6%; furfural, 2–3%; and wood sugars, 20–25%. The liquors may then be treated under pressure at a temperature which "rehydrolyzes" the sugars to give additional organic acids and furfural. Thus, a 15-minute treatment at 100 pounds per square inch was found to increase the furfural yield by 100–140% and the organic acids by as much as 14%. By-products have been separated subsequently by extraction with high-boiling solvents, such as octyl acetate, octyl alcohol, isophorone, and furfural. Batch and countercurrent extractions indicated that isophorone is the most practical solvent tested for extracting furfural and acetic acid from dilute hydrolysis liquors. A plant process utilizing isophorone is proposed.

An EARLIER paper (*3*) described a continuous process for the hydrolysis of wood. Although the lignocellulose residue was the main product (for utilization in plastics), by-product yields (organic acids as acetic, furfural, and reducing sugars) from maple sawdust were determined. It was noted that increased yields of organic acids and furfural were accompanied by a decrease in sugars with increased degree of hydrolysis.

Standard continuous wood hydrolysis runs (50% of cellulose hydrolyzed) yield approximately 10 pounds of liquor per pound of dry wood substance (d.w.s.). Average liquor analyses are: organic acids (as acetic), 0.5–0.6%; furfural, 0.2–0.3%; reducing sugars, 2.0–2.5%. On the basis of d.w.s., yields are: organic acids (as acetic), 5–6%; furfural, 2–3%; reducing sugars, 20–25%.

Acetic acid and furfural are the most valuable of the above by-products. Ethyl alcohol could be produced from the hexose sugars by fermentation, but concentrations seem to be on the borderline for economic operation except under present conditions. The possibility of conversion of the pentoses into furfural, and the pentoses and hexoses into organic acids such as acetic, was investigated. This operation is feasible, as the solutions already contain sulfuric acid to act as catalyst.

It is generally known that pentoses yield furfural by treatment with mineral acids (*4, 6, 10*). The conversion of xylose to furfural by dilute sulfuric acid depends on the concentration of acid, the temperature, and the duration of the operation (*2*). Other workers (*7*) hydrolyzed pentoses in birch wood with 0.25% hydrochloric acid or 0.5% sulfuric acid at 6 atmospheres pressure. Other investigators (*1, 12*) have studied production of pentoses and methylated pentoses from rye straw, cornstalks, etc., although current production is based on oat hulls and cottonseed hulls.

Three principal methods for concentrating aqueous solutions are used: chemical interaction, distillation, and extraction. If the chemical process were to be applied to wood hydrolysis liquors, the acids would have to be neutralized with lime before or after the recovery of furfural, and the solution evaporated to yield the salts. The organic acids can be recovered from their salts by redistillation with strong acids. This method requires the evaporation of large quantities of water; the steam cost, added to the cost of alkalies and acids used, makes it uneconomical.

Distillation of aqueous acetic acid to produce anhydrous acid is theoretically possible but expensive. Azeotropic distillation reduces costs (*8, 10*) which would, however, still be excessively high for these dilute solutions.

Mains (*5*) claimed a recovery of 95% of furfural present in four distillations of dilute solutions, but his heat costs are high.

The extraction method was decided upon as being the most practicable to avoid the high heat requirements of a straight distillation process.

METHOD OF ANALYSIS

ORGANIC ACIDS. Total acidity was titrated. Sulfuric acid was then obtained by precipitation as barium sulfate, and organic acids (as acetic) were calculated by difference. Unless otherwise indicated, amounts expressed as acetic include formic or other organic acids so determined. Solvent extracts seldom contained measurable amounts of sulfuric acid.

FURFURAL. Phloroglucinol was used for quantitative precipitation of furfural. The precipitate was filtered on a Gooch crucible and dried at 100° C. Furfural was calculated from the weight of the phloroglucide.

REDUCING SUGARS. Fehling solution was reacted with sugar solution to give a cuprous oxide precipitate. This was dissolved in ferric alum and titrated with a standard permanganate solution. Sugar values as glucose were then obtained from standard conversion tables.

REHYDROLYSIS OF BY-PRODUCT LIQUORS

METHOD AND EQUIPMENT. The apparatus was a specially constructed pressure vessel having a capacity of 2.8 liters. It was made of 4-inch copper pipe, 22 inches long, capped at the bottom, fitted with a flanged cover carrying pressure gage and feed connections, and tested to 250 pounds per square inch.

Approximately 2 liters of liquor, obtained by continuous hydrolysis of maple sawdust, were charged into the pressure vessel. The unit was then placed on an inclined stand, and the liquor brought to boiling by means of gas burners. All air was displaced through the vent by steam, the vent valve was closed, and heating was continued until the desired pressure was attained. This was maintained until it was desired to take one of the several samples required during a run. The bomb was then reversed on the stand, so that the flanged head was down and the feed or vent tube was connected to a water-cooled coil. Samples were removed slowly to prevent flashing. The vessel was then reversed on the stand to continue processing.

DATA TAKEN. Rehydrolysis runs were made at pressures of 50, 100, and 150 pounds per square inch; 250-cc. samples were

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withdrawn at intervals ranging from 3 to 60 minutes after operating pressure was attained. Results of these runs are listed in Table I and shown graphically in Figure 1.

Effect of Time. Acetic acid in the hydrolysis liquor increased with time of rehydrolysis at all three pressures studied, but the curves indicate that the increment decreases with prolonged time of treatment. The furfural curves, on the other hand, show a rapid initial rise in concentration, followed by a rapid decrease. As would be anticipated, the critical time of treatment for optimum yields decreased with increased operating temperature (or pressure).

Effect of Temperature. The elevation of the boiling point of the dilute hydrolysis liquors due to solute content was negligible, and values for water at the pressures concerned could be used. Operation at a temperature equivalent to 150 pounds per square inch gage yielded the greatest increase in organic acids, but best results for furfural were obtained at 100 pounds gage. Since the increment in furfural yield is so much greater than that for organic acids, it is obvious that the optimum temperature for formation of the former should govern. At this temperature the optimum operating time was about 15 minutes.

The rates of increase and decrease of furfural are greater at higher pressures, an indication that the reactions of hydrolysis of pentosans to furfural and of decomposition or polymerization and condensation of furfural are of the same order, and are affected in the same degree by temperature.

EXTRACTION STUDIES

Only a few solvents meet specifications for extraction of organic acids and furfural from the dilute liquors involved, and the following were selected for trial: octyl alcohol, octyl acetate, and isophorone. Furfural was also tested as a solvent for the organic acids.

Distribution Coefficients. Appropriate amounts of solvent, water, and acetic acid were shaken in a separatory funnel, both layers were titrated for acid, and the indicated terminals of tie lines were thus found.

Ternary Data. Solubility data for the ternary diagrams of the systems solvent–water–acetic acid were determined for the solvents listed above, using pure mixtures of acetic acid and water rather than hydrolysis liquor. The diagrams and corresponding data for octyl acetate and isophorone were presented by Othmer, White, and Trueger (*9*); those for octyl acetate, octyl alcohol, isophorone, and furfural are shown in Figure 2 and Table II. Tie lines, as determined from the distribution data, are shown for each ternary system. The ternary diagrams indicate desirable extraction characteristics for each of the solvents, although some shortcomings exist in each case.

Table I. Rehydrolysis Runs

% Concentration at 50 Lb./Sq. In.					
Time, Min.	0	9	23	43	60
Organic acids (as acetic)	0.50	0.50	0.52	0.55	0.56
Furfural	0.197	0.207	0.261	0.323	0.401
Reducing sugars	2.21	2.05	1.7	1.4	1.1
Sulfuric acid	2.57	2.60	2.61	2.58	2.57
% Concentration at 100 Lb./Sq. In.					
Time, min.	0	6	16	27	46
Organic acids (as acetic)	0.50	0.51	0.52	0.55	0.56
Furfural	0.197	0.344	0.489	0.451	0.366
Reducing sugars	2.21	1.28	1.08	0.90	0.90
Sulfuric acid	2.57	2.60	2.51	2.51	2.52
% Concentration at 150 Lb./Sq. In.					
Time, min.	0	3.5	6	12	21
Organic acids (as acetic)	0.50	0.52	0.52	0.55	0.57
Furfural	0.197	0.349	0.419	0.465	0.361
Reducing sugars	2.21	1.10	0.90	0.60	0.50
Sulfuric acid	2.57	2.52	2.50	2.50	2.50

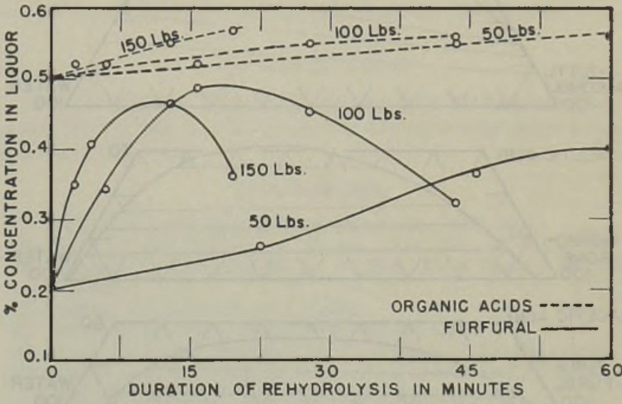

Figure 1. Effect of Rehydrolysis Time and Pressure (Temperature) on Organic Acid and Furfural Concentrations in Liquor

Octyl acetate and octyl alcohol have a low mutual solubility with water, which is not increased appreciably until high concentrations of acetic acid are reached. Distribution coefficients for acetic acid, as indicated by the slopes of the tie lines, are only fair.

Isophorone is soluble to a limited extent in water, with a greater solubility of water in solvent. The distribution coefficients for acetic acid are excellent, being about 1:1.

The high mutual solubility of furfural and water is an undesirable factor, especially in view of the large proportion of water present in the liquor. The use of furfural and octyl acetate as a mixed solvent has been found advantageous in reducing this mutual solubility (*11*).

Table II. Ternary Solubility Data

Wt. % at 24° ± 0.5° C.			Wt. % at 25° ± 0.5° C.			Wt. % at 24° ± 0.5° C.			Wt. % at 27° ± 0.5° C.		
Octyl acetate	Water	Acetic acid	Octyl alcohol	Water	Acetic acid	Isophorone	Water	Acetic acid	Furfural	Water	Acetic acid
0.1	95.0	4.9	0.8	62.0	37.2	7.5	65.1	27.4	8.3	91.8	0
0.1	88.5	11.4	1.5	55.6	42.9	13.7	56.6	29.7	9.9	85.0	5.1
0.1	79.1	20.8	5.2	42.4	52.4	19.2	50.8	30.0	13.2	76.1	10.7
0.1	65.5	34.4	9.2	36.3	54.5	23.6	41.7	34.7	19.0	67.0	14.0
0.7	48.6	50.7	11.3	32.7	56.0	24.2	45.6	30.2	21.5	62.9	15.6
0.9	46.8	52.3	21.0	25.8	53.2	25.9	42.9	31.2	74.8	14.5	10.7
1.8	44.2	54.0	25.1	23.6	51.3	30.0	38.8	31.2	78.6	12.2	9.2
2.4	36.8	60.8	29.5	21.4	49.1	30.9	37.8	31.3	83.5	10.1	6.4
5.4	29.9	64.7	33.6	19.2	47.2	31.7	37.8	30.5	86.2	8.9	4.9
7.8	26.9	65.3	36.1	18.0	45.9	39.2	30.8	30.0	88.4	7.6	4.0
10.9	24.6	64.5	38.3	16.8	44.9	48.8	23.6	27.6	91.0	6.5	2.5
13.4	22.8	63.8	43.3	14.1	42.6	55.9	19.1	25.0	92.5	5.8	1.7
18.1	20.4	61.5	50.2	11.3	38.5	66.6	14.0	19.4	94.0	5.1	0.9
25.1	17.8	57.1	56.9	9.9	33.2	69.3	13.1	17.6			
41.3	11.4	47.3	63.9	7.1	29.0	71.1	12.1	16.8			
59.8	6.2	34.0	69.3	4.2	26.5	77.4	10.8	11.8			
79.4	2.6	18.0	77.0	0.8	22.2	86.9	7.4	5.7			
			80.9	0.7	18.4	90.3	5.8	3.9			
			82.7	0.9	16.4						

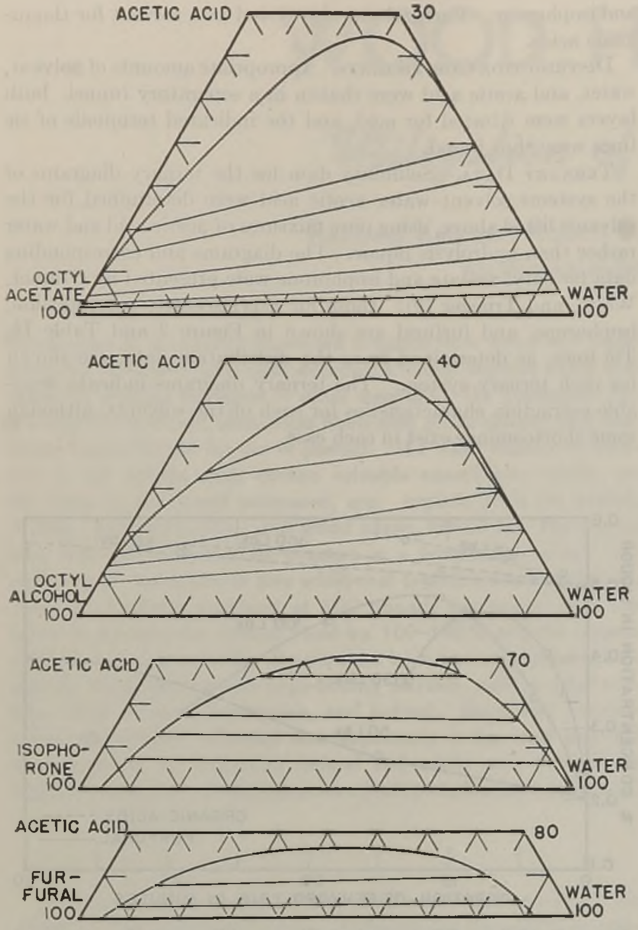

Figure 2. Ternary Solubility Diagram and Tie Lines for Four Systems of Solvent–Water–Acetic Acid

Batch Extraction. Preliminary tests on the efficacy of the solvents in extracting organic acids and furfural from hydrolysis liquors were carried out batchwise in separatory funnels. Initial tests were run on synthetic mixtures of water, sulfuric acid, furfural, and acetic acid, in order to minimize possibilities of interference with analyses due to sugars and extraneous materials present in wood hydrolysis liquors. Batch extractions were then carried out on hydrolysis liquor obtained from treatment of maple sawdust in the continuous hydrolysis process.

After elimination of the less desirable solvents, multiple batch extractions were carried out with isophorone and octyl alcohol in four steps. A fresh batch of solvent equal in volume to the original liquor was used in each step (Table III).

Since both solvents have rapidly decreasing coefficients for acetic acid and furfural with reduced concentration in the liquors, neither can extract efficiently batchwise more than about 85% of the organic acids; although octyl alcohol removed 90% of the furfural, isophorone removed only 50% due to the very large reduction in the coefficient.

Table III. Multiple Batch Extractions

Solvent	Stage No.	% Extd. in Each Stage: Organic acids	% Extd. in Each Stage: Furfural	% Extd. of Total Material: Organic acids	% Extd. of Total Material: Furfural	K (per Stage): Organic acids	K (per Stage): Furfural
Octyl alcohol	1	47.4	61.5	47.4	61.5	0.9	1.6
	2	34.3	53.7	18.1	20.7	0.52	1.16
	3	36.8	44.2	12.7	7.9	0.58	0.79
	4	25.6	1.1	5.6	0.1	0.34	0.01
Total				83.8	90.2		
Isophorone	1	74.5	47.7	74.5	47.7	2.92	0.91
	2	26.5	6.5	7.0	3.4	0.35	0.07
	3	16.9	[a]	3.1	[a]	0.20	[a]
	4	5.5	[a]	0.8	[a]	0.06	[a]
Total				85.4	51.1		

[a] Insufficient material for analysis.

Continuous Extraction. Further studies of the efficiency of extraction of organic acids and furfural were carried out in a continuous laboratory extraction column. This unit consisted essentially of a 1-inch Pyrex tube, 4 feet long and jacketed with a 2-inch tube to permit heating. Solvent and solution were fed by small centrifugal pumps through brass spargers which could be adjusted to vary the feed rate and droplet size of the liquid streams. Operations were controlled to give: fixed position of the interface, fixed ratio of solvent to liquor, and controlled rate of flow of solvent and liquor.

Extractions with equal solution-solvent rates of 500–2310 cc. per hour, made with octyl acetate and isophorone (Table IV), proved that only traces of sulfuric acid and no sugars were extracted by either solvent. Recovery of furfural and organic acid increased with liquor rate for both solvents, an indication that critical flow rates were not reached. Excessive acetic acid in the raffinate from the octyl acetate extractions was probably due to hydrolysis of the solvent.

Table IV. Continuous Extractions

Liquor Rate[a], Cc./Hr.	Component	Organic Acids, Wt. %	Furfural, Wt. %	Reducing Sugars, Wt. %	Sulfuric Acid, Wt. %
		Octyl Acetate			
660	Extract	0.076	0.066	0	Traces
	Raffinate	0.505	0.07	1.57	2.4
960	Extract	0.069	0.08	0	Traces
	Raffinate	0.57	0.062	1.57	2.4
1200	Extract	0.069	0.074	0	Traces
	Raffinate	0.518	0.063	1.58	2.4
2000	Extract	0.125	0.081	0	Traces
	Raffinate	0.525	0.051	1.57	2.4
		Isophorone			
500	Extract	0.16	0.04	0	0
	Raffinate	0.40	0.104	1.65	2.5
1000	Extract	0.13	0.039	0	0
	Raffinate	0.39	0.105	1.65	2.5
1760	Extract	0.25	0.064	0	0
	Raffinate	0.26	0.08	1.65	2.5
2310	Extract	0.27	0.089	0	0
	Raffinate	0.25	0.055	1.65	2.5

[a] Solvent: solution ratio = 1:1.

Octyl acetate was more efficient in extraction of furfural than organic acids but was eliminated due to excessive hydrolysis. Isophorone showed good solvent power for both components; especially notable is the fact that the efficiency of extraction of furfural was even greater than that of acetic acid. This is not in agreement with the low coefficients found for furfural in the multiple batch extractions, indicating some difficulty in analysis at low concentrations. The recoveries of 50–60% obtained in a 4-foot column are promising for design considerations for a large scale extractor.

CONCLUSIONS

Rehydrolysis of waste wood hydrolysis liquors yields 10–14% additional organic acids (as acetic) and 100–140% additional furfural, over and above the original yields obtained during the hydrolysis of the wood.

Optimum conditions for obtaining these yields are 15–20 minutes of treatment at 100 pounds per square inch gage in batch operation. Correlation with operations on batch and continuous wood hydrolysis (*3*) would indicate that the same result could be obtained in about 1–2 minutes at 200 pounds per square inch gage in a continuous hydrolysis unit.

The question also arises as to whether the same results could be obtained by recycling hydrolysis liquors to accomplish rehy-

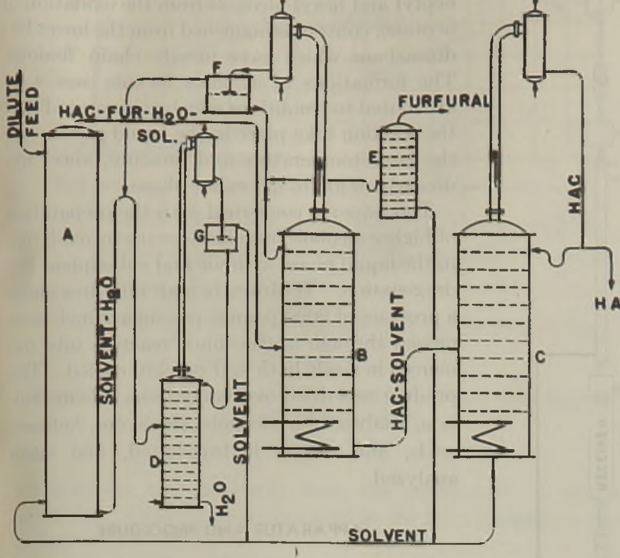

Figure 3. Proposed Flow Sheet for Recovery of Organic Acids and Furfural by Isophorone

A.	Extraction column	*D.*	Water column
B.	Azeotropic dehydrating column	*E.*	Furfural column
C.	Acetic acid column	*F, G.*	Decanters

drolysis (of pentosans) and hydrolysis of wood simultaneously. Initial work along this line has been promising.

Recovery of the by-products from the very dilute solutions encountered may be feasible in work with isophorone. Final cost analysis must await further research on stripping of solvent from water and determination of equipment sizes and costs to balance these values against heat economy.

Figure 3 is a proposed flow sheet of a process utilizing isophorone for the solvent recovery of organic acids (as acetic) and furfural from dilute solutions obtained by the hydrolysis of wood. The dilute solution is charged into extraction column *A* and is met by solvent passing up through the extractor countercurrent to the feed. The extract layer, with most of the furfural and organic acids and also a small amount of water, is then sent to azeotropic column *B* for separation of furfural and water from the acids and solvent. Crude furfural is drawn off from decanter *F* after adjusting the reflux to column *B*, so as to keep down the acids and solvent. The crude furfural is sent to furfural column *E* where it is stripped from the isophorone, preferably under vacuum. The water layer from decanter *F* goes to stripping column *D*. Acid column *C* is used for the separation of solvent and organic acids. The small amount of solvent dissolved in the deacidified water discharged from the extraction column is recovered in stripping column *D*. The solvent is returned to extractor *A*. The water layer is run to waste.

Suitable additions to this system may be employed to recover most of the sensible heat present in the solvent or water leaving each column. The most important heat exchanger would recover the sensible heat in the solvent discharged from the base of acid column *C* by preheating the liquid feed to column *B*. These exchangers are not shown in Figure 3. The necessary pumps, as well as storage tanks, are also omitted from the diagram.

ACKNOWLEDGMENT

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OXIDATION of HEXADECANE

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Hexadecane was oxidized with air under a pressure of 2000 pounds per square inch at temperatures from 190° to 300° C. The products were analyzed for alcohols, acids, esters, and carbonyl compounds. Hydrogenation of the oxidation products gave materials containing alcohols having average molecular weights as high as 165. Conversions for the two-step process were as high as 17%. Oxidations at 300° C. were characterized by the formation of sooty suspensions and products low in partial oxidation products.

ALCOHOLS possessing long aliphatic chains are commercially important in the production of detergents, synthetic waxes, insecticides, fungicides, and wetting, emulsifying, and foam-producing agents. Such alcohols are obtained industrially by catalytic hydrogenation of esters of the corresponding acids. The availability and low cost of raw materials has stimulated interest in the production of these higher alcohols by air oxidation of hydrocarbons.

Aliphatic hydrocarbons are easily oxidized. Bubbling air through hexadecane at 110° C. and atmospheric pressure will effect dehydrogenation, carbon-carbon fission, and the formation of alcohols, aldehydes, acids, ketones, peroxides, carbon dioxide, and water (*11*). The rate at which oxygen reacts with normal octane in the vapor phase at atmospheric pressure is greater than its rate of reaction with 3-methylheptane, 3-ethylhexane, 2-methyl-3-ethylpentane, or 2,2,4-trimethylpentane under similar experimental conditions (*15*). It has not been demonstrated that normal alkanes are more rapidly oxidized than their branched-chain isomers

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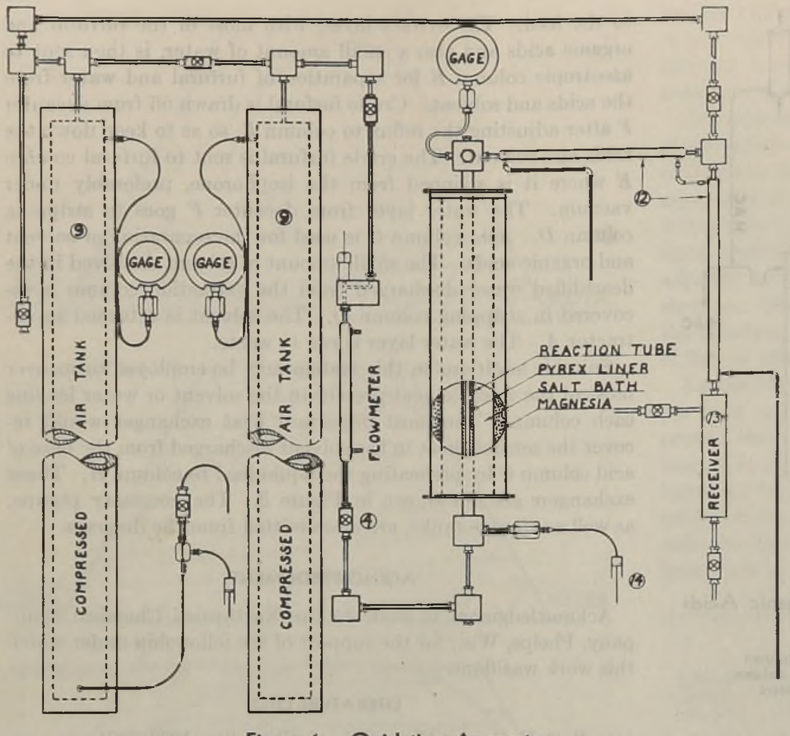

Figure 1. Oxidation Apparatus

when the reaction is carried out in the liquid phase. However, Burwell reports that more catalyst is required for the oxidation of petroleum fractions of highly branched compounds than for fractions rich in straight-chain materials (*5*). The ease of oxidation increases as homologous series are ascended (*17*). The stability to oxidation of various hydrocarbon types has been reported recently (*11*).

Chain reactions, peroxide formation, and successive hydroxylations have been advanced as possible mechanisms for the oxidation of aliphatic hydrocarbons. These have been adequately discussed (*6, 7*). The induction periods and retardation by surfaces and inhibitors exhibited by many oxidation reactions are characteristic of chain mechanisms. Peroxides possessing the formula $C_nH_{2n+2}O_2$ have been isolated from the oxidation products and are considered to be the compounds initially formed in the reaction. These have been shown to possess the structure ROOH, where R is an alkyl group (*2*). Peroxides are becoming increasingly important in attempts to elucidate the reaction mechanisms. No one of the theories thus far proposed is entirely satisfactory for explaining induction periods, the action of inhibitors, and the types of products obtained.

Early work was concerned with the preparation of acids from paraffin wax, fuel oil, and kerosene. The acids were used in the synthesis of fats, soaps, waxes, lubricants, solvents, and foam-producing agents. The general process for effecting the oxidation of hydrocarbons to acids by blowing with air was broadly covered by patents to Schaal (*16*) in 1884. Complex mixtures of acids, ketones, esters, aldehydes, and polyfunctional compounds were obtained. Industrial processes have been described by Bittler and James (*4*) and Burwell (*5*).

Three innovations for enriching the alcohol content of the oxidation products have been given in the literature. Hellthaler and Peter (*8*) prevented further oxidation of the alcohols by converting them to boric esters. The oxidation was carried out in the presence of boric acid, boric anhydride, and acetic acid or anhydride, alcohols being obtained by subsequent saponification. Hentrich, Lainau, and Kaiser (*9*) and Dietrich and Luther (*13*) proposed to increase the alcohol content by hydrogenation of the oxidation product. Wiezevich and Frolich (*17*) obtained mostly heptyl and hexyl alcohols from the oxidation of heptane, contradistinguished from the lower hydrocarbons which gave mostly chain fissions. The formations of alcohols in this case were attributed to conditions which necessitated that the reaction take place in the liquid phase. At the same temperature and pressure, lower hydrocarbons are in the vapor phase.

This paper is concerned with the preparation of higher alcohols from hexadecane by oxidation in the liquid phase with air and subsequent hydrogenation. Hydrocarbon-air mixtures under a pressure of 2000 pounds per square inch were passed through a glass-lined reaction tube immersed in a salt bath and quickly cooled. The product was dried over anhydrous calcium sulfate, analyzed for alcohols, aldehydes, ketones, acids, and esters, hydrogenated, and again analyzed.

APPARATUS AND PROCEDURE

The apparatus for the oxidation of hydrocarbons with compressed air is shown in Figures 1 and 2. Compressed air at 2500 pounds per square inch was obtained by filling storage tanks 9 (Figure 1) from commercial cylinders and intensifying the pressure by pumping water into the first tank, displacing the air into the second. The water saturating the air was not removed since its concentration was small. One half mole of oxygen as air was introduced into the reactor for each mole of hexadecane, the air flow being measured with a high-pressure flowmeter.

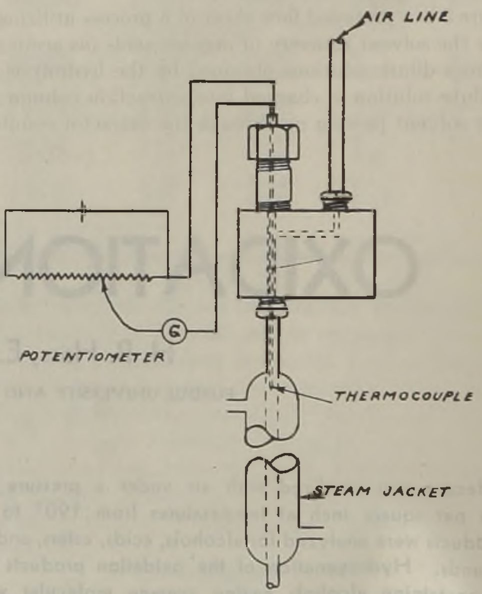

Figure 2. Flowmeter

The high-pressure flowmeter (Figure 2) is a modified form of the Thomas meter. Air from the reservoirs passes over a thermocouple in a section of the line heated with a steam jacket, cooling the thermocouple. The electromotive force of the thermocouple was read with the aid of a sensitive potentiometer. The flowmeter was calibrated by expanding the air to atmospheric pressure and measuring it with a wet-test meter. Calibration curves were obtained by plotting the drop in e.m.f. against flow rates. It was necessary to calibrate the meter before each run since constant

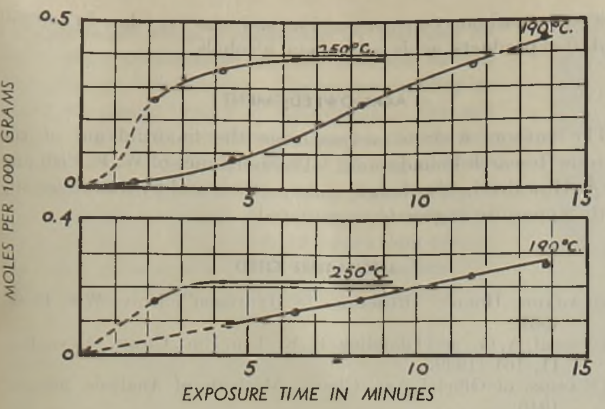

Figure 3. Acid Content of Oxidation Products (*above*) and Ester Content (*below*)

temperatures and pressures were not maintained in the air reservoirs. Air flows were regulated at the fine adjustment valve 4 (Figure 1).

Hexadecane was delivered to the reactor by a proportioning pump 14 (Figure 1). Flow rates were measured by timing the emptying of a 10-ml. pipet which was attached to the hydrocarbon reservoir. Adjustments in flow rates were provided for by a screw sleeve which allowed lengthening or shortening of the plunger stroke.

The reaction chamber consisted of a vertically mounted, stainless steel tube surrounded by an electrically heated salt bath. The tube was fitted on one end with connections for hydrocarbon and air lines, and on the other end with a block machined for a blowout safety valve, a thermocouple well, and connections for lines to a pressure gage and heat exchanger. The thermocouple well was removed after it was shown that the contents of the tube maintained a temperature which was approximately that of the salt bath. For studies on the oxidation of hexadecane, the reaction chamber was lined with a close-fitting Pyrex tube. The volume of the reaction space was varied by the insertion of glass rods.

The reaction chamber and receiver were filled with nitrogen at 2000 pounds per square inch before starting a run. Air and hydrocarbon met at the bottom of the reaction tube and passed concurrently up the tube. One half mole of oxygen as air was introduced per mole of hexadecane. Products and excess reactants passed from the reaction tube through two heat exchangers 12 to receiver 13 (Figure 1). Constant pressure was maintained in the reaction chamber by bleeding gases from the exhaust and removing product from the bottom of the receiver.

Hexadecane, purchased from the Du Pont Company, was washed with concentrated sulfuric acid until no color developed in the acid layer, shaken with sodium hydroxide solution, and dried over anhydrous calcium chloride. The chemically treated hydrocarbon was fractionated in a 3-foot Lecky column (*12*) at a pressure of 5 mm. of mercury, the cut boiling between 128° and 129° C. being taken.

ANALYSES AND DISCUSSION

Water was removed from the oxidation product by shaking with anhydrous calcium sulfate and filtering. The dried product was analyzed for acids, esters, active hydrogen, and compounds which react with methylmagnesium iodide without the evolution of methane. The volume of oxidation products was determined by extraction with concentrated sulfuric acid.

The acid content of an oxidation product was determined by dissolving a sample in alcohol neutralized to the phenolphthalein end point and titrating with standardized alcoholic sodium hydroxide. Refluxing a sample with a measured excess of alcoholic sodium hydroxide and back-titration with standard acid gave a measure of the total acid and ester contents. Subtraction of the acid value from the saponification value gives the ester content (*3*).

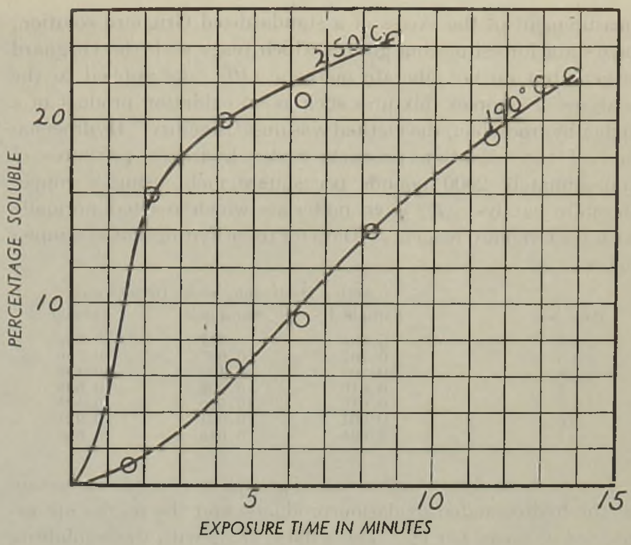

Figure 4. Solubility of Products in Sulfuric Acid

It was observed that extraction of the oxidation products with concentrated sulfuric acid at room temperature gave a raffinate which, when water-washed and dried, had a density of 0.7675 gram per cc. at 27° C. Distillation of this sulfuric-acid-insoluble material showed that it was essentially pure hexadecane, all the liquid except the pot and column holdup distilling in the range 128–129° C. at 5 mm. of mercury pressure. It was concluded from these observations that sulfuric acid treatment removes the oxygenated compounds and that the insoluble fraction is a measure of the unreacted paraffin.

For simple reactions the time required to effect a definite conversion is inversely proportional to the reaction rate constant, and the ratio of the contact times for equal conversions at two different temperatures is a constant. This is true also for complex reactions provided the temperature coefficients of the consecutive steps or simultaneous reactions are equal. As an approximation, assuming that the temperature coefficients of the various steps do not differ greatly from one another, we applied these principles in extrapolations of the various curves for the runs at 250° C., the correlations being made with the runs at 190° C. for which the data are more complete.

The curves expressing acid content, ester content, and sulfuric acid solubility as functions of the exposure time for two temperatures are shown in Figures 3 and 4. For a definite hydrocarbon conversion as shown by the solubility curves, the acid and ester contents are lower for the runs at 250° C. than for those at 190° C. This indicates a greater conversion to the partial oxidation products (alcohols, aldehydes, and ketones) at the higher temperature. The inflection shown by the sulfuric acid solubility curve is indicative of an induction period or a strongly autocatalytic reaction. Similar inflections in the acid content curves have no such significance since this is the normal type curve obtained in consecutive reactions.

Active hydrogen determinations, using a butoxybutane solution of methylmagnesium iodide, were used for estimating hydroxyl groups in the oxidation product. An apparatus and procedure similar to that described by Niederl and Niederl (*14*), allowing measurement of the excess of a standardized Grignard solution, gave data for estimating groups which react with the Grignard reagent but do not liberate methane (*10*). As applied to the analyses of complex mixtures such as an oxidation product of a higher hydrocarbon, the method was unsatisfactory. Hydrogenation of the oxidation products under hydrogen pressures of approximately 2000 pounds per square inch, using a copper chromite catalyst (*1*), gave materials which reacted normally with the Grignard reagent. Data for these hydrogenated samples follow:

Run No.	Active Hydrogen, Mole/1000 Grams Sample 1	 Sample 2	 Average
3	0.706	0.617	0.662
5	0.762	0.697	0.730
6	0.203	0.195	0.199
7	0.610	0.605	0.608
9	0.610	0.580	0.595
10	0.901	0.901	0.901
11	0.635	0.648	0.642

Gomplete analyses for functional groups were made on certain of the hydrogenated oxidation products, and the results are expressed as moles per kg. These data, along with the solubilities in concentrated sulfuric acid on a weight basis, allow calculation of the average molecular weight. The average molecular weights of alcohols in the hydrogenated oxidation products follow:

Run No.	Moles per Kg.	% by Wt. Sol. in Concd. H_2SO_4	Temp. of Oxidation, ° C.	Exposure Time, Min.	Mol. Wt. of Oxygen Compounds
3	0.896	14.7	250	4.21	165
5	1.258	17.2	250	6.36	137
7	0.648	9.9	190	8.29	153
9	0.627	9.5	250	2.19	152
10	1.081	14.0	194	13.8	129

We were unsuccessful in carrying out a smooth oxidation of hexadecane at 300° C. with air at 2000 pounds per square inch gage. The reaction under these conditions was characterized by minor explosions evidenced by "knocks" and oscillation of the pressure gage indicator. The product contained large amounts of a sooty carbonaceous suspension and was very low in partial oxidation products, acids, esters, and alcohols.

ACKNOWLEDGMENT

The authors wish to acknowledge the financial aid of the Purdue Research Foundation. The assistance of W. E. Fish and G. A. Hawkins in the design, construction, and hydraulic testing of the apparatus is greatly appreciated.

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This article contains material from the doctoral thesis of J. W. Churchill.

ROSIN ESTER DEVELOPMENT

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THE Synthetics Department of this company has specialized in the development of modified and unmodified esters of rosin, and in four plants it manufactures some fifty different materials. Most of these esters are made in the same type of equipment, a high-temperature reaction vessel. The maximum reaction temperature is usually about 300° C., which can be obtained by using a direct-fired or jacketed kettle, or a coil-containing vessel circulating hot oil or employing Dowtherm vapor heating. Different products require different amounts of agitation—mild, violent, or none at all; some are made under pressure and others under vacuum. Some modifying agents are very volatile liquids, others are fusible solids. The resin pilot plant, therefore, must be flexible in order to duplicate plant conditions and to study variations in process and product.

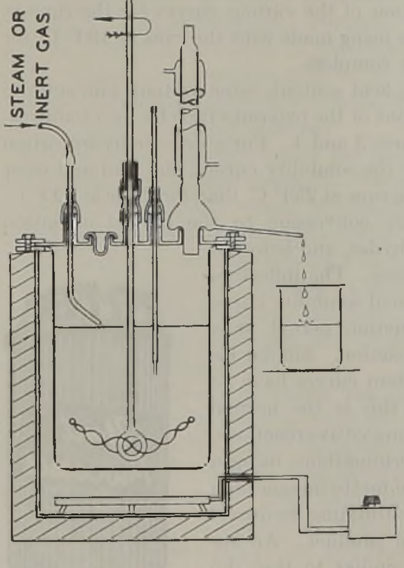

Figure 1. One-Gallon Stainless Steel Resin Reactor

LABORATORY REACTORS

A new rosin ester or modification is first investigated in the laboratory. The next step frequently is the preparation of the ester in a one-gallon stainless steel, or other metal, reactor (Figure 1). This is the first approach to pilot plant work, and here is chosen the metal of construction for larger pilot and final plant reaction vessels. Stirring and rate of heating can be varied at will. The reactor is heated by an air bath in an insulated container with a standard electrical ring heater at the bottom. The take-off condenser, as shown, can be made into a reflux condenser merely by putting a stopper in the take-off outlet.

Few engineering data can be had from a rosin esterification in the laboratory, but

A permanent setup is maintained by Hercules for pilot plant development of new products derived through rosin esterification. The reactor capacity for this work ranges from 1 to 400 gallons. The unit process of a rosin esterification can be closely followed at each stage by a method of plotting whereby a straight line represents accurately the progress of the reaction in laboratory, pilot plant, and commercial plant operations. The development of a rosin ester to a full-size plant process by these means is achieved in the shortest possible time and with maximum control.

much useful basic information on the reaction and the product will have been gained. The reaction rates at different temperatures can be determined under the most ideal conditions.

SMALL PILOT PLANT SCALE

A number of small pilot plant reaction vessels are available for the next step. The materials of construction are varied, consisting of stainless steel, aluminum, nickel, and glass-lined steel; capacities are about 25 to 50 gallons. These reactors approach in size the smaller commercial units, and from their operation engineering data can be obtained. Two of these reactors are shown in Figure 2. This equipment is flexible in respect to types and speeds of stirring. The pressure in the reactors can be either sub- or superatmospheric; inert gas can be applied to blanket the reaction mixture, or an inert gas sparge can be employed.

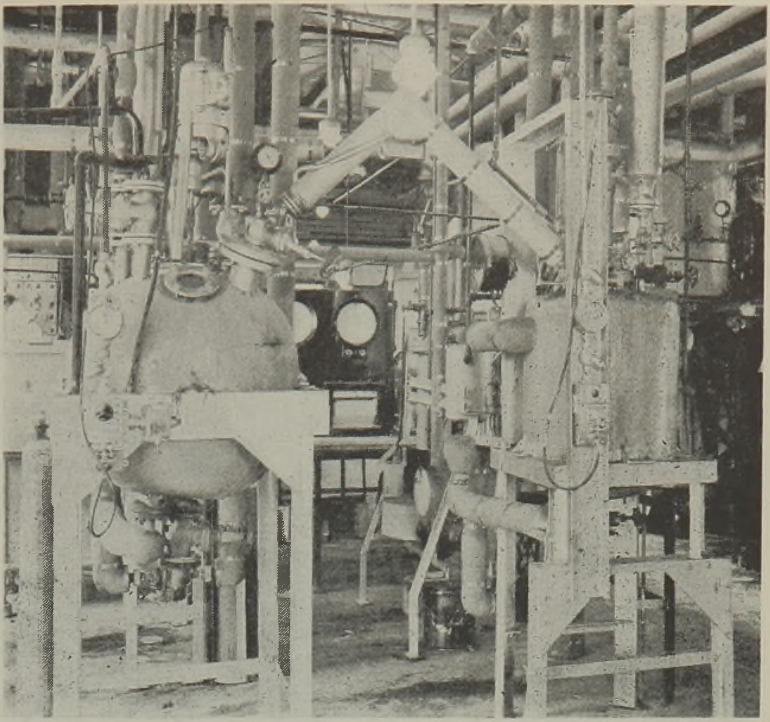

Figure 2. Small Pilot Plant Reactors

At this stage of the development a given rosin esterification is studied critically to determine the proper operating conditions for duplicating or improving upon the previously made laboratory product. It frequently happens, for instance, that in going up from laboratory-size equipment the color of the resin improves, primarily because of decreased ratio of surface to volume.

The rate of up-heat and the proper temperature at which modifying agents should be added to rosin esters are important and are determined as carefully as possible on equipment of this size. Heating by either electricity or circulating oil is automatically controlled. A portion of the control panel can be seen in the rear of the reactors of Figure 2. Any given heating rate, therefore, can be followed, and desired reaction temperatures can be closely duplicated. The reaction rate is studied, and if it is not up to the value which was predicted in the laboratory, conditions are investigated to effect an improvement.

After the new rosin ester has been made in the small pilot plant vessel, samples of the product may be sent to the trade for evaluation and recommendations, or may be tested for further uses by Hercules exclusively. If reports from this work are promising, the development is carried to the next step.

LARGE PILOT PLANT SCALE

The next stage involves the preparation of the resin in 400-gallon reactors. One of the units can be seen in the background

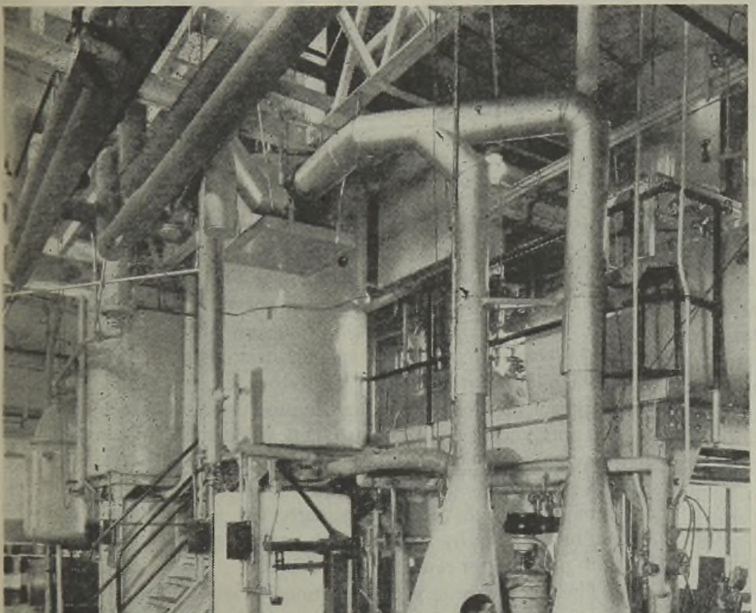

Figure 3. General View of Large Scale Pilot Plant

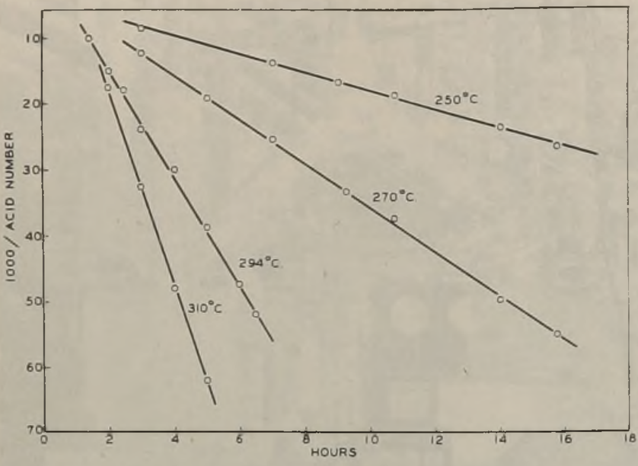

Figure 4. Effect of Temperature on Laboratory Preparation of a Rosin Ester

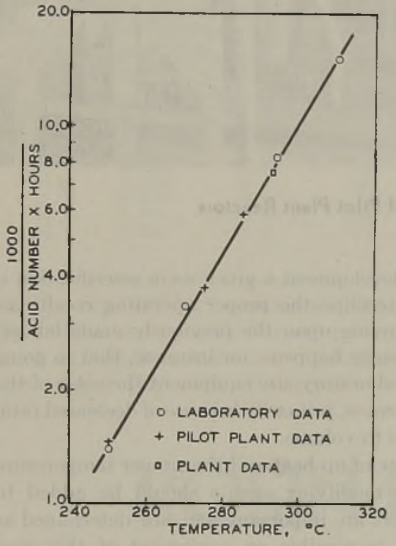

Figure 5. Esterification Rate of Rosin at Various Temperatures

in Figure 3. These vessels approach most closely our large-size equipment. Conditions obtained here can be duplicated very well in the plants. Figure 3 is a general view of the auxiliary equipment used in connection with the larger pilot plant reactors. In the background to the extreme left is a special vessel for producing resin solutions. In the center are several specially lagged tanks for accurately weighing and measuring the reactants or products. In the foreground are a supercentrifuge and equipment for clarifying molten resins.

REACTION CONTROL

Some information on the preparation of one of our larger-volume standard resins will show the kind of data obtained in the units of various sizes. The ester was first made in the laboratory, and the rate of reaction was followed by taking the acid number at constant temperatures. The reciprocals of the acid numbers were plotted against time (Figure 4). A straight line resulted because of the following conditions: (*a*) One of the products is removed from the reaction mixture, and thus a reverse reaction is prevented. Rosin esterifications are conducted at such high temperatures that water is liberated with ease during the reaction. (*b*) The rate of reaction is proportional to the square of the acid number because here we are dealing with a typical esterification (second-order reaction) and because the equivalents of the reactants (i.e., the number of hydroxyl and carboxyl groups present) are about equal.

Figure 4 shows a few of these straight lines, the slopes of which represent the relative reaction rates at the different temperatures. When the logarithms of these slopes (reciprocal of the product of acid number and time) are plotted against temperature, a straight line results (Figure 5). This straight line indicates that the reaction rate approximately doubles for each 17° C. rise in temperature.

The reaction rate was then determined on a run in the 400-gallon vessel under proper conditions for equipment of this size, the acid number being taken every hour after the temperature reached 250° C. (Figure 6). It was found that, when the temperature (curve with solid dots) reached the desired point and was leveled off, the reciprocal acid number–temperature curve (open circles) became a straight line. Furthermore, the slope of the straight portion of the reciprocal acid number curve and the slope of the tangents to this curve at lower temperatures (shown by points marked + in Figure 5) fell on the reaction rate curve as previously determined in the laboratory. This agreement showed that optimum conditions for the 400-gallon reactor had been obtained. If too little alcohol had been used, the curve would have bent upward; if too much, it would have bent downward. If the water of reaction had not been properly freed, the slope would have been less, an indication that the reaction rate was slower.

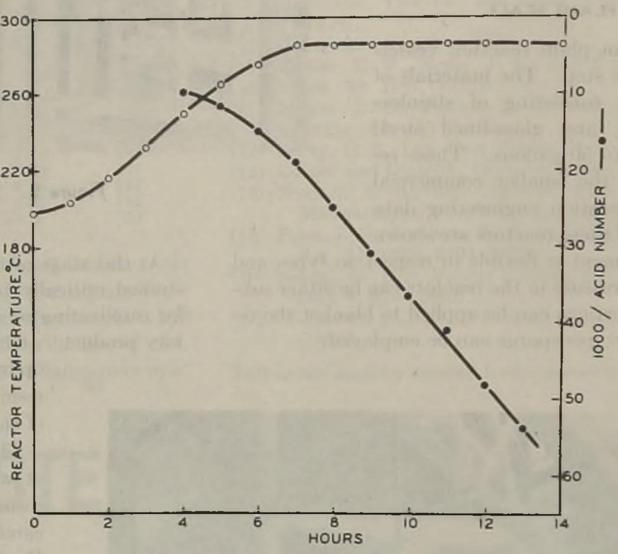

Figure 6. Pilot Plant Preparation of a Rosin Ester

Operation in the plant reactor was found to follow the same rate as that shown in the reaction curve; this is shown by the point marked □ in Figure 5. This showed that plant conditions at the chosen temperature of operation were the same as those in the pilot plant and in the laboratory.

By this method of plotting the progress of a rosin esterification reaction, very accurate control is possible at all times and in each stage of the development. The theoretical reaction gives a straight line when so located on a graph (Figure 4). Deviations from the straight line can be corrected, or the slope of the line can be changed by altering such variables as temperature, agitation, pressure, or reactant proportions.

Thus, a new resin is carried from the laboratory to commercial production in a minimum of time with the assurance that the plant product is uniform and duplicates closely the properties of the desired resin. Synthetic resins derived from rosin find use in a vast number of varied applications. A new resin may be required to satisfy a critical war shortage, and in the shortest time it becomes a commercial reality—a laboratory sample expanded to carload quantities.

[*End of Symposium*]

The Fluid Catalyst cracking process was developed by intensive pilot plant work to successful commercial usage. The pilot plant equipment comprised a variety of sizes from small laboratory units to a semiplant scale unit of nominal 100-barrel-per-day feed capacity. This 100-barrel plant was relied on for the major part of the process data and engineering and equipment studies required for the commercial designs. A description of this unit is given, as well as that of a smaller unit of 2-barrel-per-day capacity. The various engineering studies made are discussed and type of results obtained indicated. The original 100-barrel plant, which was used to pilot the first model of the commercial units, was later modified to a simpler design which has been incorporated in more recent full-scale plants. The results obtained on both designs have been translated to the commercial scale with singular accuracy.

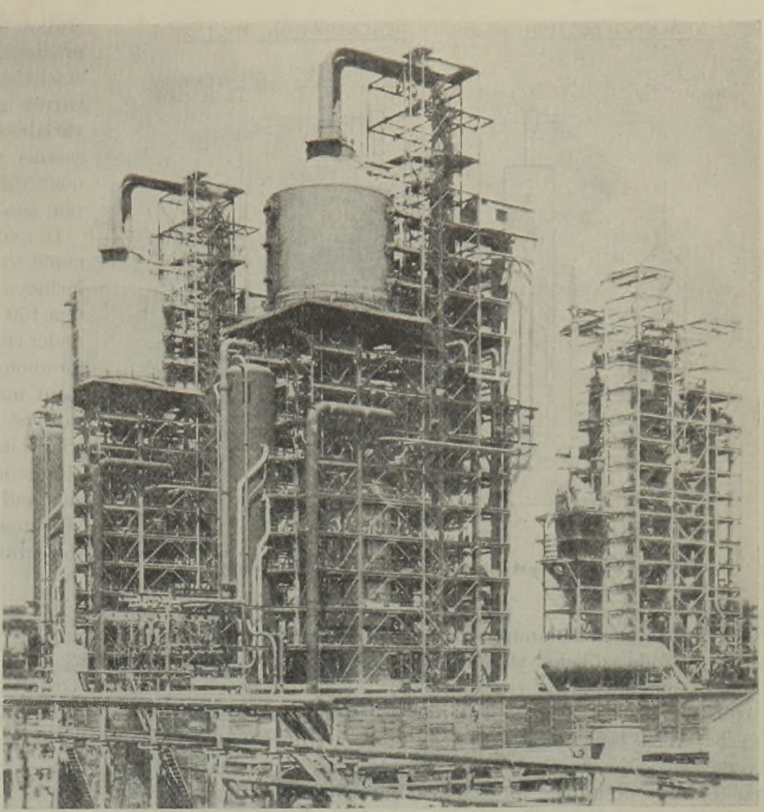

Figure 1. First Fluid Catalyst Plant at Right, Two Newer Simplified Units at Left

PILOT PLANT DEVELOPMENT OF FLUID CATALYTIC CRACKING

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THE Fluid Catalyst process has been developed from a laboratory scale to wide commercial usage during the past few years. According to recent figures (*3*), a total of thirty-four Fluid Catalyst cracking units have been built or are under construction. These plants are presently being used exclusively to produce aviation gasoline and raw materials for the war program. After the war these units may be used to produce high-quality motor gasolines with a considerable increase in feed capacity.

Previous articles (*1*, *2*) have discussed the Fluid process in considerable detail. These papers described the first commercial plant which was designed before the entrance of the United States into the war and was planned for peacetime production of premium motor fuels. Engineering and design data were based on a background of experimental and semiplant experience in continuous Fluid Cracking as well as in intermittent fixed-bed operations. The first commercial plant was designed by the Standard Oil Development Company and placed in operation at the Baton Rouge refinery of the Standard Oil Company of New Jersey in the early part of 1942. This installation was followed by the design and construction of a simplified type of plant which offered greater flexibility in operation. Figure 1 shows a plant of the original design and two of the improved, simplified type.

The purpose of this paper is to trace the development of the Fluid process through the laboratory, pilot plant, and semiplant stages, and to describe the equipment used in this development. The 100-barrel-per-day Fluid Catalyst unit has contributed a large amount of the process and engineering data required for this development.

DEVELOPMENT OF COMMERCIAL SCALE UNITS

The Fluid Catalyst operation represents a new industrial method of handling solids and controlling the temperature of gaseous or vapor reactions. Figure 2 presents the principle of the process as applied in catalytic cracking. Catalyst from a standpipe on the regeneration section is mixed with oil vapors which carry it up into the reaction vessel of rather large cross section. The catalyst leaving the reaction vessel is separated from the cracked vapors in conventional cyclone separators, and the cracked vapors pass on to fractionation equipment. The separated catalyst is collected in a hopper and allowed to flow by grav-

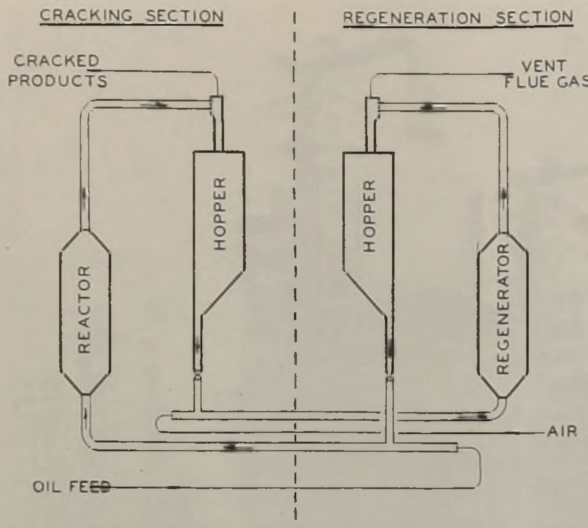

Figure 2. Catalyst Flow in Fluid Catalyst Cracking

ity down through a standpipe and slide valve at controlled rates. Air is introduced below the slide valve, and the air-catalyst mixture is contacted in the regenerator for the desired time to effect oxidation of the carbonaceous material formed in the reaction cycle. It has been found possible by suitable adjustment of gas or vapor velocities to build up relatively high concentrations of solids where desirable—for example, in the reactor or regenerator or in the standpipes. The densities which can be attained in vessels are functions of catalyst feed rate, composition, and particle size as well as of vapor or gas velocity. The quantity of catalyst remaining in the vessel as well as the catalyst passed through the vessel may, therefore, be adjusted independently. This type of contacting gives a solid-gas mixture which is very turbulent and resembles in many aspects a boiling liquid. In addition to excellent mixing, this process allows for adjustment of time of contact of both catalyst and vapor in the vessel, both of which are important in obtaining the desired results. The pressures required to effect the flow of catalyst through the system are obtained in the standpipes where the density of the catalyst is relatively high due to the small amount of aeration vapor present.

Prior to the development of the above principles as applied in Fluid Catalyst cracking, several other processes were tried for transferring and contacting the catalyst in the reaction and regeneration cycles. The choice of the principles described was based mainly on ease of operation and on elimination of moving mechanical parts. Other methods investigated for transferring the catalyst included the use of screw pumps and lock hopper systems. Although operable, these devices were not so satisfactory as the standpipe system, either as to mechanical repairs or ease of operation. The use of other types of reactors was studied also, including smaller pipes and coils, but these did not allow so much flexibility and required more materials than the type of equipment chosen. The choice of the design has been justified in that operation of several of the Fluid units have extended over six-month periods and then have been taken off stream voluntarily for routine mechanical inspection.

Design factors involved in the development of this process included items such as type of catalyst, feed stocks, operating conditions, and yields and quality of products. Engineering and equipment studies included the mechanics of catalyst flow, catalyst recovery, methods of avoiding erosion and attrition, heat transfer data, control and capacity of the regenerator and reactor, stripping of spent catalyst, and the general know-how in any new process.

The choice of pilot plant equipment to study the process involved first a study in small equipment of the reaction and regeneration stages separately. Later, a small pilot unit feeding approximately 2 barrels per day of gas oil was used to study feed stocks and catalysts. A larger unit with a feed capacity of 100 barrels per day was built to study engineering and equipment variables and to confirm process and catalyst data observed in the smaller units. This larger unit was also used to supply large quantities of gasoline for full scale evaluation, particularly in aviation gasoline blends.

In addition to the pilot unit equipment, numerous tests were made to study particular phases of the process. These studies included the temporary installation of a catalyst circulating system 150 feet high, on the side of a fractionation tower which was under construction for other purposes. This equipment was used for about one month to obtain the necessary data. Other equipment included a circulator system where visual observation of catalyst flow could be made through a window equipped with a windshield wiper and illumination on the inside of the vessel. Numerous glass models were made and used for visual observation and demonstration of the principles involved. These pieces of equipment were especially useful in demonstrating the process to operating personnel and in training new workers.

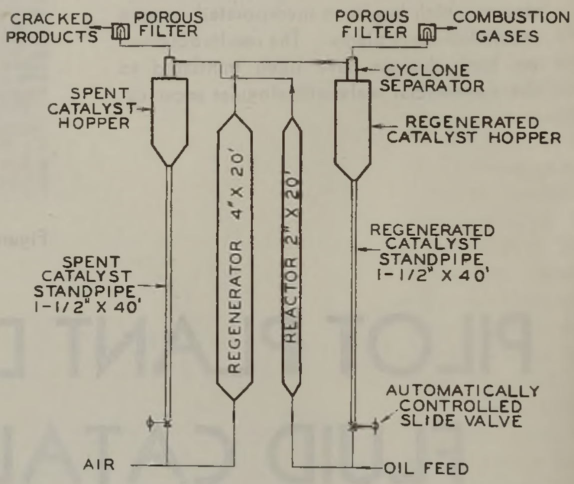

Figure 3. Fluid Catalyst Pilot Unit, with a Capacity of 2 Barrels per Day

In addition to the tests on the pilot units, numerous tests were made on smaller equipment to develop catalysts and test the catalysts used in the larger units for contamination and activity.

Among the first pilot units which included both reaction and regeneration sections was the so-called 2-barrel-per-day unit; this comprised the general principles used in the plant design (Figure 3). The unit included a 2 inch × 20 foot reactor, and a 4 inch × 20 foot regenerator. Oil was pumped through a vaporizing coil contained in a lead bath (not shown) and then mixed with regenerated catalyst. The mixture flowed into the reactor where the cracking reaction was controlled by the vapor throughput, catalyst rate, and temperature. The cracked products plus catalyst leaving the top of the reactor were passed through a cyclone separator where catalyst was separated. The cracked oil vapors were then passed through a porous filter to remove the last traces of catalyst; the oil was then condensed and separated from the noncondensable gases. The catalyst from the filter was returned to the system. The liquid and gases were separated, pressured to 80 pounds by a small pump and a compressor, and then separated again. The final liquid, which contained most of the gasoline components, was stabilized and fractionated to the desired specifications.

The spent catalyst collected in the hopper was allowed to flow downward through the 1.5 inch × 40 foot spent catalyst stand-

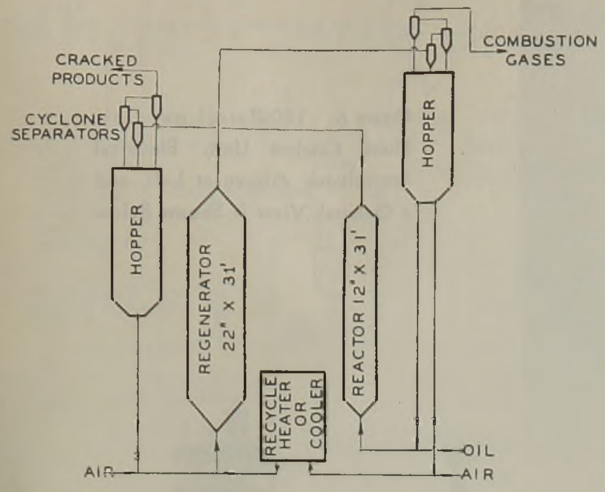

Figure 4. Fluid Catalyst Unit with a Nominal Capacity of 100 Barrels per Day

pipe. Steam or inert gas introduced at points in the standpipe displaced any hydrocarbons accompanying the catalyst. The "stripped" catalyst flowed through an automatically controlled slide valve, was mixed with regeneration air, and flowed into the regenerator where, under proper time and temperature conditions, the carbonaceous materials were removed. The combustion gases plus regenerated catalyst were separated in a cyclone separator; final traces of catalyst were removed in a porous filter. The regenerated catalyst was collected in a hopper, flowed down a 1.5 inch × 40 foot standpipe, and was picked up by the oil vapors as previously described.

The entire unit was electrically heated to provide for the heat losses attendant to the use of this size equipment. The various circuits were controlled through the use of small transformers and resistors. The quantities of feed stock, catalyst, and air normally used for this unit varied, depending on the severity of cracking desired. Nominal oil feed rates of approximately 2 barrels per day were employed, and air rates of 150–200 cubic feet per hour could be used. The yields of products from the unit were obtained with good accuracy throughout the complete range of hydrocarbons from hydrogen in the gas to carbon burned. Material balances of 99–100% were normally obtained. The yields of products have correlated well with large plant performance, and consequently this unit has been useful in predicting the utility of various feed stocks, catalysts, and operating conditions proposed for commercial operations. This unit has been limited in usefulness in obtaining engineering data because of its small size and comparatively large heat losses. Catalyst flow control and dust recovery were the factors influencing operability during the initial stages of operation of the 2-barrel-per-day unit, but difficulties with both of them were satisfactorily overcome.

The 100-barrel-per-day unit was constructed primarily to obtain engineering and process data for designing commercial units. This unit is of sufficient size and is instrumented to allow for complete coverage of process and engineering data. This unit has had an important part in the development of the commercial units, and has operated successfully from the beginning. Catalyst flow and control are smoother than in the smaller units. The feed rate may be varied considerably, but 100 barrels per day is the nominal capacity. The unit is completely equipped with feed preparation, product recovery, fractionation, and storage facilities. Figure 4 is a flow diagram of the reactor and regenerator section. The flow is essentially the same as in the 2-barrel unit except that an additional circuit has been added whereby regenerated catalyst may be recirculated to the regenerator through a heat exchanger. This allows an additional control of the temperature in the regenerator. Various sizes of reactor and regenerator have been tried in studies of process variables. Catalyst flows are maintained by pressure built up in the standpipes, the rates being controlled by the slide valves.

The plant was equipped with facilities for feed preparation as well as for product recovery. Figure 5 shows some of the equipment available. A heater, flash tower, and superheater are available for the feed stock. Any one or all of these items may be bypassed as desired. The product recovery system includes a cooler, low-pressure separator, pumps and compressor, high-pressure separator, stabilizer, and fractionation tower. A tank farm consisting of fourteen tanks with a total capacity of 400,000 gallons is available for storage of feed and product. An electrical precipitator is used to recover fines leaving the regenerated catalyst cyclones. This material is returned to the unit through the recycle line to the regenerator. An oil scrubber, not shown, is used to recover fines leaving the reactor cyclones. This material may be returned to the unit with the feed. The reactor, regenerator, and standpipes are enclosed in a flue gas jacket to take care of heat losses. The remainder of the unit outside the jacket is heavily insulated.

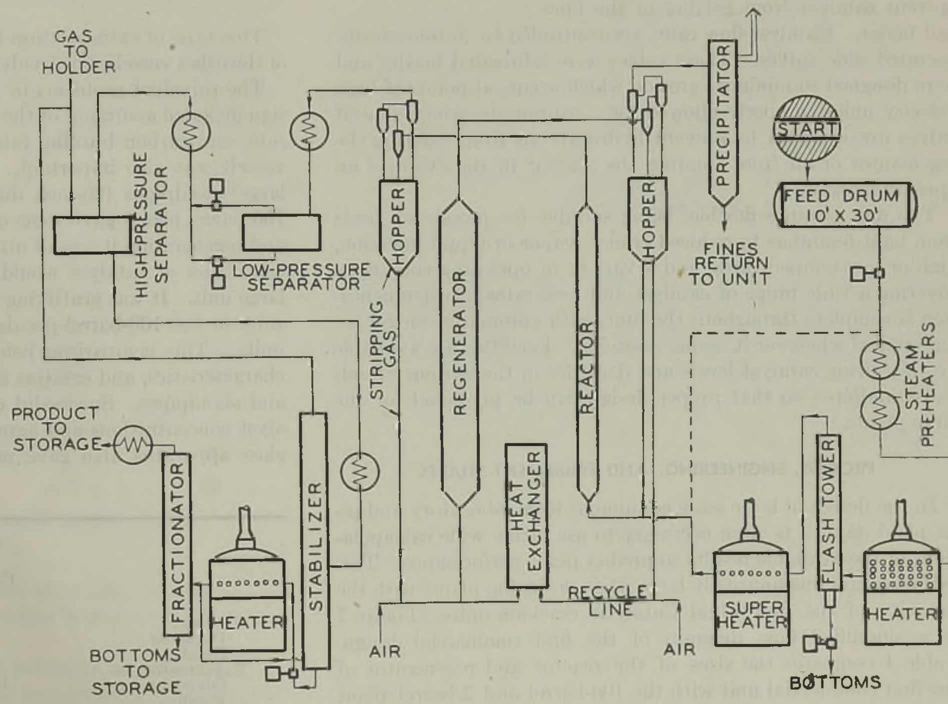

Figure 5. 100-Barrel Fluid Catalyst Unit with Auxiliary Equipment

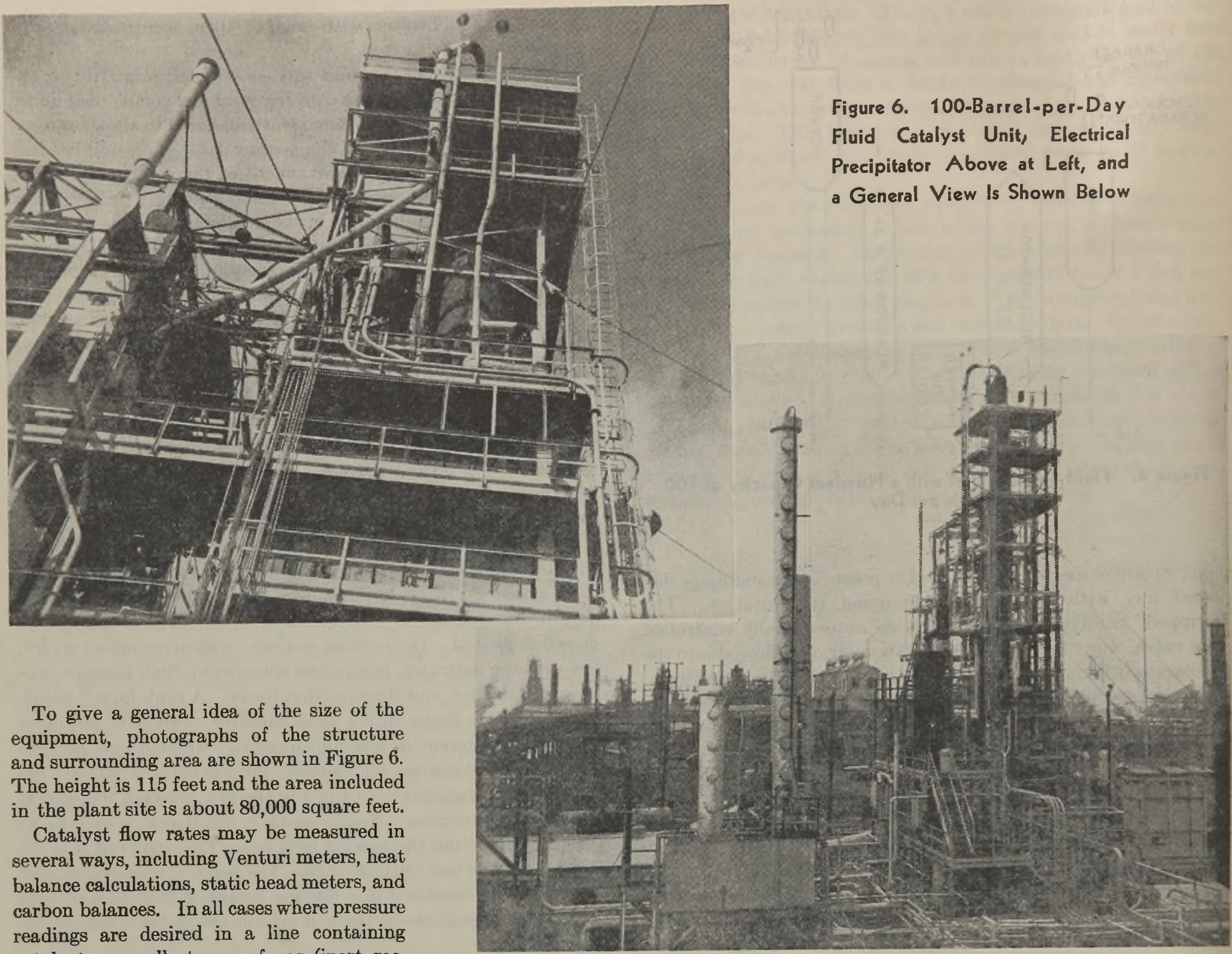

Figure 6. 100-Barrel-per-Day Fluid Catalyst Unit, Electrical Precipitator Above at Left, and a General View Is Shown Below

To give a general idea of the size of the equipment, photographs of the structure and surrounding area are shown in Figure 6. The height is 115 feet and the area included in the plant site is about 80,000 square feet.

Catalyst flow rates may be measured in several ways, including Venturi meters, heat balance calculations, static head meters, and carbon balances. In all cases where pressure readings are desired in a line containing catalyst, a small stream of gas (inert gas, air, or steam as desired) is injected to prevent catalyst from getting in the lines and meter. Catalyst flow rates are controlled by automatically operated slide valves. These valves were fabricated locally and were designed to minimize erosion which occurs at points of high velocity unless properly allowed for. Automatic safety shutoff valves are included to prevent hydrocarbons from entering the regenerator or air from entering the reactor in the event of an upset in the unit.

The unit is quite flexible, being suitable for processing feeds from light naphthas to reduced crudes, vapor or liquid injection, high or low temperatures, and a variety of operating conditions covering a wide range of catalyst and feed rates. Instrumentation is complete throughout the unit, with automatic control being applied wherever it seems desirable. Facilities are available for measuring catalyst levels and densities in the various vessels and standpipes so that proper design can be predicted for the large plants.

PROCESS, ENGINEERING, AND EQUIPMENT STUDIES

In the design of large scale equipment from laboratory and pilot plant data, it is often necessary to use rather wide extrapolations of the available results to predict plant performance. This extrapolation was unusually large when designing plants with the capacity of the first Fluid Catalytic cracking units. Figure 7 is a simplified flow diagram of the first commercial design. Table I compares the sizes of the reactor and regenerator of the first commercial unit with the 100-barrel and 2-barrel plant vessels.

This type of extrapolation may be carried through to the sizes of the other vessels, lines, valves, etc., in the units.

The principal problems in the extrapolation to large scale design included assurance of the same product distribution, cracking rate, and carbon burning rate. The proper mixing in the large vessels was also important. The type of catalyst flow in the large standpipes (26-inch diameter compared to 4-inch in the 100-barrel plant) gave some concern. To assure proper cracking and regeneration it was of utmost importance to know what concentration of catalyst would be obtained in the vessels of the large unit. It was gratifying to find good agreement between results in the 100-barrel-per-day plant and results in the smaller units. This comparison held for process results, catalyst flow characteristics, and catalyst concentrations in the various vessels and standpipes. Successful correlation of factors involving catalyst concentrations and agreement with visual results in an all-glass apparatus also gave more confidence in extrapolation of

Table I

	Commercial Plant	100-Barrel/ Day Unit	2-Barrel/ Day Unit
Reactor			
Diameter	15 ft.	12 in.	2 in.
Height	28 ft.	31 ft.	20 ft.
Regenerator			
Diameter	19.5 ft.	22 in.	4 in.
Height	37 ft.	31 ft.	20 ft.

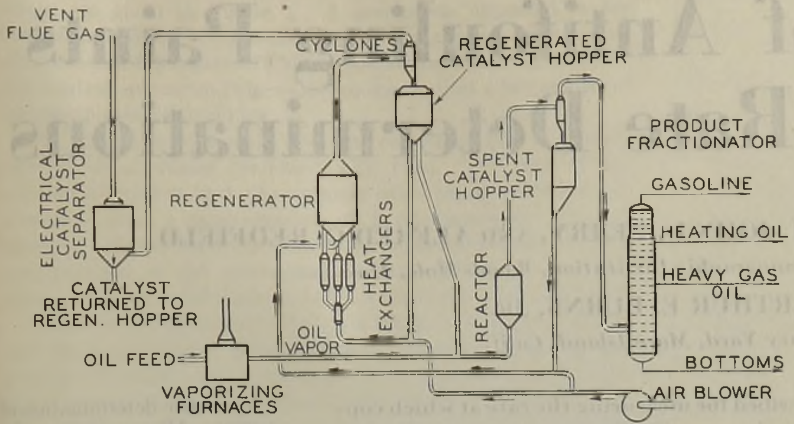

Figure 7. Fluid Catalyst Cracking Plant

results to commercial scale. This glass apparatus which was constructed of 6-inch glass tubing was used to study aeration and mixing of various types of powders. It was found that particle size and particle size distribution both affected the aeration characteristics of catalysts. The effects of particle size, absolute density, and gas velocity on Fluid density were studied. Tests were also made to determine settling rates of the various powders to aid in the design of hopper sizes.

To check further the process data and hindered settling catalyst concentrations, four reactors having various shape factors were studied in the 100-barrel plant (Figure 8). Comparison of results with these various reactors gave further assurance that the extrapolation of results on the 100-barrel unit to plant design was sound.

The product distribution and quality obtained in the commercial unit have been compared (*3*) with that of the 100-barrel plant; it was shown that good agreement existed. This comparison may be extended to include the 2-barrel-per-day unit also as shown in Table II.

Table II

	Commercial Plant	100-Barrel Unit	2-Barrel Unit
Reactor size	15 ft. × 28 ft.	15 in. × 20 ft.	2 in. × 20 ft.
Feed stock, ° A.P.I.	30.5	31.7	31.0
50% point, ° F.	690	680	680
Yields on feed			
Gasoline (10 lb. Reid vapor pressure), vol. %	42.0	45.0	45.0
Excess butane, vol. %	7.5	4.7	5.2
Gasoline (100% C_4), vol. %	49.5	49.7	50.2
Gas oil, vol. %	50.0	50.0	50.0
Dry gas, wt. %	6.2	5.0	4.2
Carbon, wt. %	2.8	2.8	3.2
Motor gasoline properties			
Gravity, ° A.P.I.	60.3	60.4	59.6
Per cent at 212° F.	45.0	46.0	45.0
Aniline point, ° F.	85	87	84
Bromine No.	93	75	77
Octane No.			
A.S.T.M. (clear)	79.2	79.7	79.5
CFR-R (1939) (clear)	92.9	92.0	92.4
CFR-R (1939) + 1.5 ml. tetraethyllead/gal.	97.3	97.0	97.6

These results show excellent agreement among the three units, indicating that interpolation of the results between units is justifiable.

Other equipment studies included extensive determinations of factors influencing the following: (*a*) heat transfer coefficients in fluid systems, (*b*) pressure drop data, (*c*) erosion of lines and equipment, (*d*) determination of catalyst rates, (*e*) catalyst losses and attrition, (*f*) rates of burning in the regenerator, (*g*) oxygen requirements and heat of combustion in regeneration, (*h*) stripping of spent catalyst, (*i*) recovery of catalyst by oil scrubbing, and (*j*) cyclone and electrical precipitator efficiencies. These and numerous other problems were studied, and the necessary data for plant design determined in the 100-barrel plant prior to operation of the large unit. Many of these problems were new in the field of petroleum refining.

As mentioned previously, the newer commercial units employ a simplified principle of design. The 100-barrel plant was modified to the new principle soon after the design data for the first plant were obtained. It became apparent that further catalytic cracking units were necessary and simplifications in design could be made. It was necessary at that time, however, that engineering and process data for design changes be obtained in a short time to allow for inclusion in the new plants.

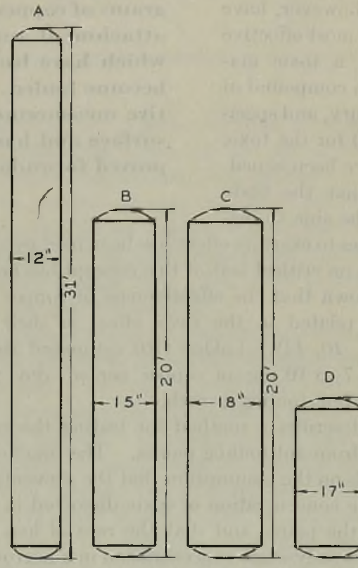

Figure 8. Reactors Used in 100-Barrel Fluid Catalyst Unit

The new design offered considerably more flexibility, and successful operation was observed from the start. Both the general mechanical performance and the product distribution were satisfactory. The basic catalyst flow data obtained on the original system were found to be applicable with only minor modifications. Process data were in agreement with the original type results, and catalyst requirements to maintain a given severity of cracking were also similar.

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Evaluation of Antifouling Paints by Leaching Rate Determinations

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A method is described for measuring the rate at which copper toxics dissolve from antifouling paints, and conditions are given under which a significant value for the copper leaching rate will be obtained. It has been found that the leaching rates of antifouling paints change upon immersion in the sea. It is therefore necessary to determine leaching rates after various times of immersion to interpret adequately the antifouling properties of a paint. Evidence is presented which shows that the copper antifouling paints must leach at the rate of about 10 micrograms of copper per sq. cm. per day in order to prevent the attachment and growth of fouling organisms. All paints which have leaching rates consistently below this value become fouled. The leaching rate test permits quantitative measurement of the toxicity of an antifouling paint surface and has been useful in the study of new and improved formulations.

MANY theories have been proposed to explain the action of antifouling paints (*16*), but the development of such paints has been handicapped for lack of a clear understanding of the properties essential to satisfactory antifouling performance. Many investigators (*1, 9, 17, 20*), however, have noted that the most effective paints contain a toxic material, usually a compound of copper or mercury, and specifications (*2, 12*) for the toxic ingredients have been issued. The concept that the toxic material must be able to dissolve in sea water to exert its effect has been held by some workers (*9, 15, 20*), but no critical test of this concept has been available. It has been shown that the effectiveness of copper and copper-base alloys is related to the toxic effect of their products of corrosion (*5, 7, 10, 14*). LaQue (*10*) estimated that the average solution of 7 to 10 mg. of copper per sq. dm. per day was sufficient to prevent fouling growth.

This paper describes a method for testing the rate at which copper leaches from antifouling paints. The practical interest in the test depends on the assumption that the prevention of fouling is related to the concentration of toxic dissolved in the water at the surface of the paint, and that the rate of loss of toxic is a measure of the steady-state concentration in a narrow zone at the paint surface. Experience gained in three years of study at the Woods Hole Oceanographic Institution and the Mare Island Navy Yard indicates that the prevention of fouling by the paint is directly related to the leaching rate as determined by the method described in this paper.

Previous attempts have been made to measure the loss of toxics from antifouling paints. Orton (*13*) and Edmondson and Ingram (*8*) measured the loss of copper and other toxics from painted surfaces by determining their content in the paint before and after soaking in the sea. Bray (*3*), Edmondson and Ingram (*8*), Whedon and collaborators (*18*), and Miller and Cupp (*11*) have determined the toxicity of solutions in which painted panels had been soaked for a definite period. None of these tests have proved practical as a guide for the formulation of paints.

When a glass or metal panel coated with a copper paint is soaked in a beaker of sea water, copper is liberated and accumulates in the water. The initial rate of solution is defined as the leaching rate of the paint. The following conditions have been found convenient:

PANELS. Sandblasted glass panels, 3 × 4 inches, are painted on both sides. Similar results are obtained if primed steel panels are used, but the presence of iron in solution interferes with the colorimetric determination of copper. After painting, the panels are allowed to dry for 1–4 days. Prolonged drying times change the results obtained with some paints.

LEACHING SOLUTION. Clean aerated sea water is used as the leaching solution. The pH of the solution should be between 8.0 and 8.2, and the chlorinity of the sea water should be 17 parts per thousand. The ratio of the area of paint exposed (in square centimeters) to the volume of leaching solution (in cubic centimeters) is 1:5. Thus, one 3 × 4 inch (150 sq. cm.) panel is leached in 750 cc. of sea water, two panels in 1500 cc., etc. If panels of a different size are to be used, the volume of solution should be selected to maintain this ratio.

AGITATION. The solution is agitated by a rapid stream of air bubbles delivered at the base of the beaker by a 7–8 mm. i.d. glass tube.

TIME OF SAMPLING. The sample should be taken before the concentration of copper in solution exceeds 0.5 microgram per cc. Above this concentration the rate of solution from the paint decreases and insoluble compounds of copper are precipitated. For routine determinations a specific sampling time may be selected. A leaching rate measured after 2 hours will give accurate results if the value is 30 micrograms per sq. cm. per day or less, a 4-hour sample if the value is 15 or less, etc.

ANALYTICAL METHOD. Copper analyses were made by the diethyl dithiocarbamate colorimetric method described by Callan and Henderson (*4*) and Coulson (*6*). A 50-cc. sample of the leaching bath is treated with citric acid, ammonium hydroxide, and sodium diethyl dithiocarbamate, as described by Coulson. Amyl acetate is used to extract the yellow copper salt of diethyl dithiocarbamic acid from the sea water. The quantity of copper present is determined with a properly calibrated Klett-Summerson photoelectric colorimeter, using a green filter (No. 54, approximate spectral range 500–590 millimicrons) for solutions containing between 0.3 and 2.0 micrograms per cc. and a blue filter (No. 42, approximate spectral range 400–465 millimicrons) for solutions containing less than 0.4 microgram per cc.

CALCULATIONS. The leaching rate is defined as the number of micrograms of copper liberated from a square centimeter of paint surface per day. It is calculated according to the equation:

$$\text{leaching rate} = \mu\text{g./cc.}\left[\frac{\text{volume (cc.)} \times 24}{\text{area of paint (sq. cm.)} \times \text{time (hr.)}}\right]$$
$$= \mu\text{g./sq. cm./day}$$

(This unit is numerically equivalent to mg. per 1000 sq. cm. per day, which is currently used by the Navy paint laboratories. The results obtained in these units must be divided by 10 to convert to mg. per sq. dm. per day, the unit frequently used in corrosion studies.)

SOLUTION OF COPPER FROM TYPICAL PAINTS

Typical data for the total amount of copper dissolved by 750 cc. of sea water from 3 × 4 inch panels painted with a metallic copper, a red copper, and a green copper paint of commercial origin are given in Figure 1. A precipitate appeared in the beakers containing the metallic copper and cuprous oxide paints after the first few hours. When a sample was taken for analysis, the solution was stirred vigorously to ensure that a fair sample of the precipitate was included.

The metallic copper paint liberated copper initially at a rapid rate which gradually decreased with time. The rate of dissolution of copper from the cuprous oxide paint decreased appreciably after a concentration of 1 microgram per cc. was reached. No further copper leached from the green paint after a concentration of 0.5 microgram per cc. was reached. These relations appear to be characteristic for the types of paint studied.

Under service conditions a paint is being bathed continuously with fresh sea water. This condition is represented in the test only by the initial rate of leaching. The accumulation of copper which occurs as the test proceeds, and which ultimately slows down the rate of dissolution of copper, has no counterpart under service conditions. Consequently, only the initial slope of each curve in Figure 1 gives the "leaching rate" of the paint.

FACTORS INFLUENCING LEACHING RATE

The concentration of copper dissolved from an antifouling paint in any period of time depends upon the rate of agitation, the temperature, the volume of the solution, and the area of the panel used. The pH and chloride ion concentration of the leaching bath also have a pronounced effect. The latter are sufficiently constant if clean aerated sea water is used for the determination. Some of the observations are summarized here to aid in defining the conditions under which accurate results may be obtained.

It is necessary to agitate the leaching bath adequately to ensure that the leaching rate measured is characteristic of the paint and not limited by the diffusion of dissolved copper away from the surface. The results of an experiment to determine the rate of stirring necessary to give maximum values for the leaching rate are given in Table I. Results obtained when a painted microscope slide, sealed to the bottom of a cylindrical flask, was rotated at 30 r.p.m. about its own axis are included as an example of mechanical stirring. The results show that the agitation is most critical at short times when rapid dissolution of copper is occurring—i.e., during the period on which the leaching rate calculations are based. As the rate of dissolution diminishes, the rate of stirring becomes less important.

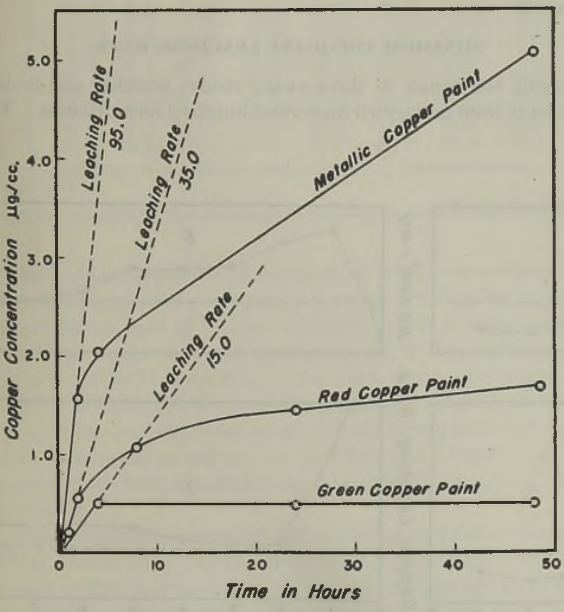

Figure 1. Dissolution of Copper from Copper Paints

Panels were freshly painted, and one panel of 150 sq. cm. area was leached in 750 cc. of sea water. Leaching rates in micrograms per sq. cm. per day.

Table I. Effect of Stirring Rate on Leaching of Copper from a Cold Plastic Cuprous Oxide Paint

(Conditions: stirring, one 3 × 4 inch painted panel in 750 cc. of sea water; rotation, one 1 × 3 inch painted panel in 190 cc. of sea water)

Stirring	Copper Concn., µg./cc., after: 1 hr.	2 hr.	$4^1/_2$ hr.	8 hr.
Violent bubbling	0.29	0.56	1.00	1.07
10 bubbles/sec.	0.21	0.43	0.88	1.02
2 bubbles/sec.	0.16	0.33	0.76	0.96
No stirring	0.11	0.20	0.49	0.58
Rotation 30 r.p.m.	..	0.53	..	1.12

Table II. Leaching of a Cold Plastic Cuprous Oxide Paint in 1500 Cc. of Sea Water (Vigorous Agitation)

No. of Panels	Area *A*, Sq. Cm.	Time *t*, Hours	Area × Time, *At*	Copper Concn., µg./cc.
1	155	$^1/_2$	78	0.16
1	155	1	155	0.26
2	310	$^1/_2$	155	0.29
1	155	2	310	0.44
2	310	1	310	0.54
4	620	$^1/_2$	310	0.53
1	155	4	620	0.81
2	310	2	620	0.76
4	620	1	620	0.87
1	155	8	1240	1.15
2	310	4	1240	1.17
4	620	2	1240	1.17
2	310	8	2480	1.34
4	620	4	2480	1.31
4	620	8	4960	1.46

It should be pointed out that the higher the leaching rate, the more violent is the stirring required to keep pace with dissolution. Even violent bubbling may give inadequate agitation with paints having a high leaching rate. For such paints a mechanical means of stirring may be necessary.

The concentration of copper dissolved in the leaching bath in a given time will depend on the area of the panel and on the volume of sea water used. The curves in Figure 1 are, therefore, characteristic of the paint area and volume of solution as well as of the paint being studied. Data in Table II show that, in a given volume of solution, an approximately constant amount of copper is dissolved from the paint for equal values of the product, area × time. Table III shows that the effect of changing the volume of the leaching bath is the opposite of changing the paint area, and that approximately equal concentrations are obtained when the quantity (area × time)/volume is maintained constant. In the large-volume leaching baths vigorous bubbling was used to ensure adequate agitation.

The copper concentrations from Tables II and III are plotted in Figure 2 against At/V. The initial slope of the line in this figure is the leaching rate of the paint. It is clear from this figure that accurate results will be obtained only if the time for sampling the leaching bath is selected so that the concentration of copper is less than 0.5 microgram per cc. If the concentra-

Table III. Leaching of a Cold Plastic Cuprous Oxide Paint at a Constant Value of 0.21 for (Area × Time)/Volume (Vigorous Agitation)

No. of Panels	Size of Panels, Inches	Area, Sq. Cm.	Time, Hours	Volume, Cc.	Copper, µg./cc.
1	8 × 10	1030	2	10,000	0.55
2	8 × 10	2060	1	10,000	0.43
1	3 × 4	155	2	1,500	0.41
2	3 × 4	310	1	1,500	0.43
4	3 × 4	620	$^1/_2$	1,500	0.41
1	1 × 3	39	1	190	0.41
2	1 × 3	78	$^1/_2$	190	0.43

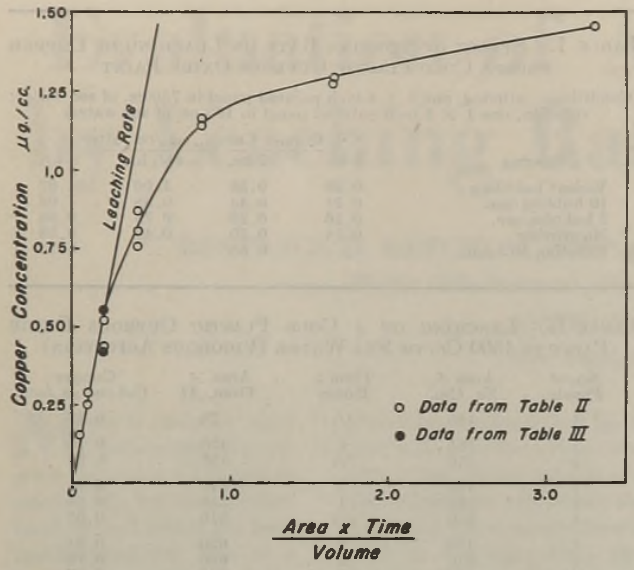

Figure 2. Relation of Copper Concentration in Leaching Bath to Area of Panel × Time of Leaching ÷ Volume of Leaching Bath

tion is allowed to exceed this value, the leaching rates calculated will be low.

The temperature of the water in the leaching bath has a considerable influence on the initial leaching rate of a cuprous oxide paint. The data in Table IV show that during the period of rapid dissolution a fourfold increase in concentration is observed as the temperature is increased from 1° to 40° C. For practical purposes it has been found adequate to determine leaching rates at room temperature (20° C.). In the neighborhood of this temperature there is a variation in the leaching rate of about 3% per ° C.

LEACHING RATE FOR CHARACTERIZING ANTIFOULING PAINTS

It has been found that all paints change in leaching characteristics on immersion in the sea. The changes in leaching rates of several typical paints are shown in Figure 3. In this experiment a painted, 3 × 4 inch, ground-glass panel was leached in 750 cc. of sea water with vigorous bubbling, and a sample withdrawn for analysis after 4 hours ($At/V = 0.81$ hr. cm.$^{-1}$). The leaching rates with a value of 15 micrograms per sq. cm. per day or less are accurate under these conditions. All of the higher rates resulted from a copper concentration of more than 0.5 microgram per cc. and are consequently lower than would be obtained if the leaching bath had been sampled at shorter times. After the leaching test, the panels were placed in wooden racks and immersed in the sea. At monthly intervals they were removed from the racks, and the leaching rate determination was repeated under the same conditions. Each curve in Figure 1 represents the history of an individual paint panel. The dashed line is drawn at the minimum leaching rate essential for the prevention of fouling which, as will be shown in the next section, is 10 micrograms of copper per sq. cm. per day.

Table IV. Effect of the Temperature of Leaching Bath on Solution of Copper from a Cold Plastic Cuprous Oxide Paint

(Conditions: one 3 × 4 inch panel in 750 cc. of sea water, vigorous bubbling)

Temp., ° C.	Time, Hr.	Copper Concn., μg./cc.
1	1	0.26
18	1	0.48
22	1	0.57
26	1	0.65
40	1	1.04

Four different responses to sea immersion are given in Figure 3. Curve *A* shows a moderately high initial leaching rate which, after two-month immersion, dropped to an inadequate value. At this time the paint became fouled. Curve *B* shows a leaching rate which never exceeded the essential value. Paints such as this become fouled immediately upon exposure to intense fouling conditions. Curve *C* shows a low initial leaching rate which had increased to an adequate value by the end of one month. This was maintained for six or seven months. Such paints may foul when initially immersed in the sea. If they survive the initial period, however, they remain free of fouling until the leaching rate again falls to low values. Curve *D* shows a high initial leaching rate which decreased, although adequate values were maintained for the duration of the exposure. This is the most satisfactory type of paint since it is always safe from fouling attachment, and it is capable of maintaining an adequate leaching rate as long as the paint lasts. The life of the paint is determined by the thickness of the film. This particular paint, exposed at Point Reyes, Calif., for 24 months, is still free from fouling. A panel exposed at Miami Beach, Fla., was free from fouling for twenty months, and is still only slightly fouled after twenty-seven months of exposure.

It is obvious from these data that the leaching rate determination is characteristic of the paint only at the time the measurement is made. It is not possible to predict the future behavior of a paint from any single leaching rate determination.

Young, Schneider, and Seagren (*21*) presented hypothetical curves to describe the changes which might be expected in the concentration of toxic at the interface after various times of immersion. Some of their curves are very similar to the data in Figure 3.

MINIMUM ADEQUATE LEACHING RATE

During the course of three years' study, leaching and fouling tests have been performed on several hundred formulations. The

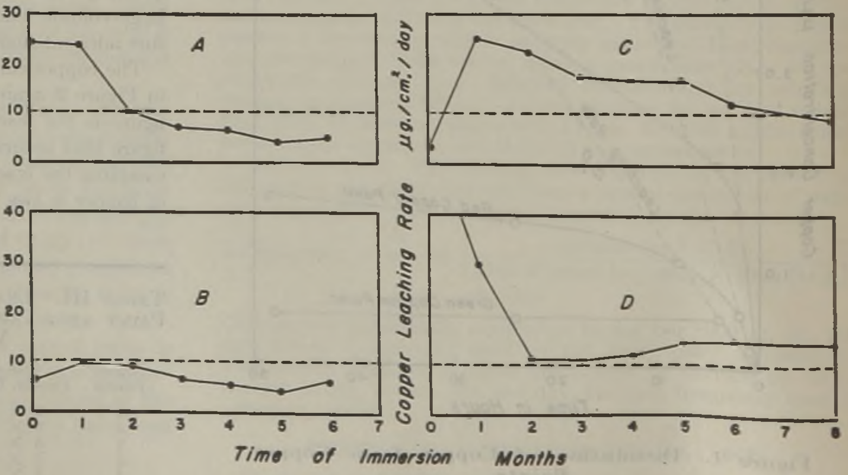

Figure 3. Changes of Leaching Rate of Four Typical Paints after Various Periods of Immersion in the Sea

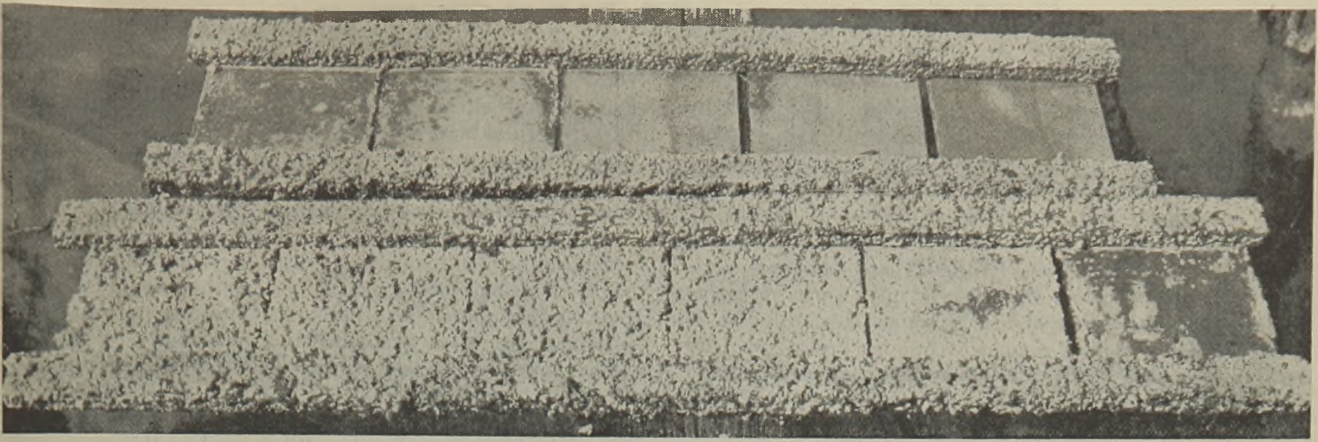

Figure 4. Fouling on Paints Described in Table V, Containing Graded Amounts of Cuprous Oxide, After Four-Month Immersion at Tahiti Beach, Fla.

Paints in the bottom row are Nos. 1–6, in the top row Nos. 7–11, reading from left to right.

fouling characteristics of practically all these paints are accurately portrayed by their leaching rates. Some examples of the correlations obtained are given in this section.

A series of paints, all of which had the same matrix, were made up to contain graded amounts of cuprous oxide. The pigment volume content was maintained constant in all paints by substitution of magnesium silicate for cuprous oxide. Leaching rates during the first eight months of sea immersion were measured on panels at Woods Hole (Table V). Steel panels painted with the same paints were exposed at Tahiti Beach for tests of antifouling performance.

Table V. Leaching Rates of Cold Plastic Paints Containing Graded Amounts of Cuprous Oxide

Paint No.	% Cu_2O in Dry Paint	Leaching Rate, µg. Cu/Sq. Cm./Day, after: 0	1 mo.	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.	8 mo.
1	0.4	1.1	1.0[a]	0.6[a]	1.3[a]	0.3[a]	0.6[a]	0.1[a]	0.6[a]
2	1.23	2.9	1.2[a]	0.9[a]	1.7[a]	0.6[a]	0.6[a]	0.3[a]	0.9[a]
3	2.23	5.0	1.3[a]	0.9[a]	3.1[a]	0.9[a]	0.9[a]	1.2[a]	...
4	4.64	17.8	3.9[a]	1.6[a]	2.4[a]	1.9[a]	2.8[a]	2.5[a]	1.2[a]
5	9.3	25.0	7.5	4.7[a]	4.4[a]	1.9[a]	3.7[a]	7.1[a]	3.3[a]
6	13.8	27.4	14.1	11.3	10.0	10.5	Lost	...	...
7	19.2	40.6	19.3	11.3	8.8	8.1	10.1	8.0	8.1
8	24.8	51.5	27.7	12.5	9.5	12.2	12.3	9.8	9.0
9	30.0	55.1	28.5	13.4	9.7	10.3	13.8	14.4	13.8
10	36.0	57.4	30.2	11.6	10.9	12.0	14.4	14.7	14.1
11	50.7	47.2	44.3	21.0	14.2	15.6	20.2	18.7	17.7

[a] Formulations which fouled when exposed at Tahiti Beach for the indicated time.

By the fourth month of exposure at Tahiti the surfaces of the first five paints were completely covered with fouling (Figure 4). The total amount of fouling increased as the cuprous oxide content decreased. No fouling attachment of any kind was found on paints 6 to 11, inclusive, at any time during the course of the experiment although a heavy slime appeared on paints 6, 7, and 8. The copper leaching rates of all the effective paints were greater than 8 micrograms per sq. cm. per day at all times. All of the paints which fouled had leaching rates lower than this at the time of fouling.

Leaching rates were measured on the same paints immersed at Point Reyes for a six-month period. The paints were also exposed at this location on 10 × 12 inch steel panels to determine antifouling performance. The results of these tests were in close agreement with those of Table V. Paints 6–10 were entirely free from fouling growth during the period of test, and at all times maintained a leaching rate greater than 8.2 micrograms of copper per sq. cm. per day. Paints 1–5 fouled badly after one to two months of exposure and had leaching rates lower than 7.5 micrograms per sq. cm. per day at the time fouling occurred.

A series of paints was formulated by substituting various resins on an equal weight basis for the rosin content of the antifouling paint made according to Navy Department Specification 52-P-61. All other components of the specification formula were maintained constant. The unesterified Albertol resins used in these paints were prepared in the laboratory. The WW rosin and ester gum were procured under applicable government specifications; the esterified Albertol (Amberol F-7) and coumarone-indene resin (Neville G) were procured from commercial sources. All paints were prepared on a laboratory three-roll mill.

Leaching rate results on these paints immersed at Woods Hole are listed in Table VI. Paints 4, 5, and 6 became heavily fouled upon exposure at Tahiti Beach, Fla., and Point Reyes. These same paints had low and inadequate leaching rates. Paints 1, 2, and 3 were free from fouling throughout exposure at both locations and had leaching rates in excess of 9.6 micrograms per sq. cm. per day at all times. The adequate amount of cuprous oxide in paints 4, 5, and 6 apparently is not free to dissolve and has no repellent effect on the fouling organisms.

Table VI. Leaching Rates of Specification 52-P-61 Type Paints Formulated with Various Resins Substituted for Rosin

Paint No.	Resin	Leaching Rate, µg. Cu/Sq. Cm./Day, after: 0	1 mo.	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.
1	WW rosin	30.0	18.0	16.2	13.5	14.1	16.2	15.8
2	Unesterified Albertol 1	33.3	20.4	17.1	13.8	16.5	18.0	18.8
3	Unesterified Albertol 2	32.1	11.1	10.5	...	9.6	10.8	9.8
4	Ester gum	30.3	3.4[a]	5.5[a]	4.2[a]	2.7[a]	0.9[a]	0.9[a]
5	Esterified Albertol	5.7	0.9[a]	0.0[a]	...	3.3[a]	0.0[a]	...
6	Coumarone-indene	25.6	4.0[a]	2.1[a]	2.1[a]	4.2[a]	...	1.5[a]

[a] Paints which fouled when exposed the indicated time.

A series of paints was formulated by substituting various amounts of Navy Department Specification 52-V-17 phenolic varnish solids for the standard rosin-hydrogenated methyl abietate matrix of Navy Department Specification 52-P-61 antifouling paint. Other components of the specification formula were maintained constant. The paints were prepared on a laboratory three-roll mill.

Leaching rate results on the varnish modified Specification 52-P-61 type paints immersed at Point Reyes are given in Table VII. Paints 1, 2, and 3 maintained leaching rates in excess of 12.1 micrograms per sq. cm. per day at all times and were completely free from fouling throughout the test period at Point Reyes. Paints 4 and 5 had low leaching rates and fouled heavily during the same period.

As a result of these observations and many others, we have concluded that a paint must liberate copper at a rate of about 10 micrograms per sq. cm. per day in order to prevent fouling attachment. Some paints may be effective with leaching rates which occasionally fall slightly below this value (Table V). All paints so far tested which have had leaching rates consistently below this value have become fouled. These statements, however, are limited to paints which depend upon copper or copper compounds as the toxic agent. They are not meant to apply to paints containing mercury compounds or other toxics. Mercury leaching rates have also been measured and have been found to correlate with the effectiveness of mercury-containing paints.

Table VII. Leaching Rates of Specification 52-P-61 Type Antifouling Paints Containing Various Proportions of Phenolic Varnish Solids

Paint No.	Varnish Solids in Matrix, %	Leaching Rate, μg. Cu/Sq. Cm./Day, after: 0	1 mo.	2 mo.	3 mo.	4 mo.	5 mo.	6 mo.
1	0	38.4	21.2	19.3	...	18.6	14.1	15.0
2	10	35.0	18.5	13.1	15.7	16.3	12.9	...
3	20	33.7	15.8	16.3	14.6	13.2	12.1	11.6
4	50	9.0	3.0[a]	5.3[a]	4.2[a]	7.0[a]	4.2[a]	3.1[a]
5	100	2.2	1.3[a]	2.5[a]	0.7[a]	...	...	...

[a] Paints which fouled when exposed the indicated time.

Some paints having poor film characteristics may lose copper in particulate form to the leaching bath. This can result in a high apparent leaching rate which is not a true measure of the effectiveness of the paint, since undissolved copper does not contribute to the toxicity of the surface.

DISCUSSION

It has been shown that the solution of 10 micrograms of copper per sq. cm. of paint surface per day will prevent attachment of all marine growths which normally present a serious ship-bottom fouling problem. Any of these organisms, which include barnacles, annelids, mollusks, hydroids, bryozoa, tunicates, and some species of algae, will attach to paints which consistently maintain lower copper leaching rates. The growth of many microbiological species and some types of algae does not appear to be inhibited by a leaching rate of 10 micrograms per sq. cm. per day, but these organisms are seldom of practical importance in ship-bottom fouling.

The value of 10 micrograms per sq. cm. per day for the minimum adequate leaching rate is lower than that determined by LaQue (*10*) from weight loss measurements of nickel-copper alloy panels. Leaching rate determinations on copper alloys also indicate that some of them may require a higher leaching rate than paints to prevent fouling.

Failure of ineffective copper-base ship-bottom paints to develop adequate leaching rates is usually the result of fundamental errors in formulation. The most common of these are the use of insufficient toxic, as illustrated by the data of Table V, or selection of an unsuitable vehicle, as illustrated by the data of Tables VI and VII. Of course the compound used as the toxic must have an appropriate solubility in sea water in order to leach.

As there are practical limits to the amount of toxic which can be incorporated in a paint film, it is necessary to have an accurately controlled leaching rate to avoid premature exhaustion of the toxic reserve. Young (*19*) first stated the dilemma that the toxic must be soluble and, if soluble, will be washed away, which has discouraged many investigators of the problem ever since. Determination of the rate at which toxic must be liberated permits a more accurate appraisal of the situation. Thus, to maintain a uniform adequate copper leaching rate for one year, a paint film must contain at least 3.6 mg. of copper per sq. cm. of surface area. At a spreading rate of 300 square feet per gallon, this corresponds to a copper content of 2.2 pounds per gallon of paint, a figure well within the limits of practical paint formulation. However, since most effective paints leach at an excessive rate when first exposed and maintain steady-state leaching rates somewhat greater than the minimum adequate value, a fairly large factor of safety as to toxic content must be allowed.

The leaching rate method has proved to be a valuable tool which can be used by the paint technologist in the formulation and testing of antifouling paints. By judicious use of this test a great deal of information upon the characteristics and behavior of antifouling paints can be obtained in the laboratory. It must be stated, however, that the leaching rate test is not presented as a substitute for panel exposures or fouling tests. It is a supplementary tool and has its greatest value when used in conjunction with ship or panel tests. When used in this manner, it serves to eliminate many poor paints in the initial stages, to aid in formulation, and to give insight into the reasons for the failure of various paints. The ultimate evaluation of the effectiveness of antifouling paints will continue to be based on the performance of the formulations on ships in service.

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ANTIFOULING PAINTS

Mechanism of Accelerated Corrosion under Antifouling Compositions Applied to Steel

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Accelerated attack on steel coated with heavy metal antifouling paints is localized at holidays and bare areas if efficient undercoats are employed. The intensity of attack is directly proportional to the concentration of dissolvable copper toxicant in the immediately adjacent antifouling film, and inversely proportional to the area of exposed steel. The experimental evidence suggests that electrochemical deposition of copper at gross breaks, discontinuities, and areas where the undercoat is unduly attenuated, with accompanying acceleration of corrosion under the influence of these secondarily established local couples, is the major causative factor. None of the antifouling paint films examined appears capable of functioning as a gross cathode.

EARLIER papers in this series presented data showing the essential equivalency in antifouling efficiency of metallic copper and cuprous oxide pigments (*3*). It seems conclusively established that these efficiencies are a direct function of the amount of copper available for solution; that from cuprous oxide and similar copper compounds probably is derived by simple solution, whereas metallic copper dissolves by a corrosion process which can be profoundly influenced by the nature of the corroding medium, extraneous electrochemical effects, accidental coupling, etc. Once in solution, the copper, from whatever source derived, functions to protect against permanent attachment and growth of fouling organisms unless and until it is precipitated or otherwise removed from the critical paint-water interface layer. It has already been demonstrated that direct and intimate contact with steel can result in materially decreased efficiency of cupriferous antifouling paints, with accompanying accelerated corrosion of the steel substrate. The attack is particularly severe wherever the steel is exposed, as at a scratch or mechanical break in the paint film (*4*).

The present paper presents the results of studies of such accelerated corrosion at gross breaks and unpainted areas, where opportunity for possible stifling by accumulated corrosion products is limited.

ACCELERATED CORROSION AS A FUNCTION OF AREA EXPOSED

In actual ship-bottom painting, it frequently happens—either through inadvertence or because of reasons of inaccessibility—that small but finite areas of bare plate are missed by the priming coat; the final antifouling coat may or may not cover these bare spots. In an effort, therefore, to determine the possible danger due to accelerated corrosion at such gross discontinuities, a series of experimental panels was prepared and exposed for five months totally immersed at Kure Beach, N.C. These panels were diliberately left uncoated at predetermined spots; duplicates were prepared in which the antifouling coat actually contacted the steel at a point approximately 4 inches from the "unpainted" area. The preparation schedule follows:

Freshly sandblasted and weighed 6 × 12 × 3/32 inch, medium carbon steel panels were fitted with squares of masking tape in the center of each face, of areas equivalent to 0.1, 1, and 5% of the total area, respectively. A duplicate set of panels carried an additional 1 square inch of masking tape applied on one face only, 2 inches from one end. All the panels were then brush-coated with one coat of a chromate type primer (Navy Specification 52-P-18), and one coat of a 33-gallon phenolic varnish pigmented with blue lead as anticorrosive coat. At this stage the single inch-square patches on half the panels were removed, so that the over-all coat of antifouling paint next applied contacted the bare panel face at this previously masked square-inch area. When the final coat of antifouling paint was dry, the central patches were carefully traced with a sharp knife and peeled away, leaving a range of symmetrical bare spots exposed.

For control purposes additional panels were prepared having: (*a*) no bare areas and no deliberate contact with the antifouling paint, (*b*) no bare areas but with the antifouling paint contacting the steel at the fixed inch-square area, and (*c*) no finite bare areas but with the faces cross-scribed in the manner described in earlier experiments (*4*), both with and without direct contact to steel at the fixed inch-square area. A complete set of panels on which the top (antifouling) coat was replaced by another coat of the anticorrosive was also included.

Two experimental antifouling paints were employed in this study; the first had given evidence of considerable accelerated attack in the earlier studies (*4*); the second simulates an orthodox copper bottom paint:

	A. F. PAINT 1	A. F. PAINT 2
Binder	3 gal. tung oil 3 gal. linseed oil 100 lb. Cumar V-3	3 gal. tung oil 3 gal. linseed oil 100 lb. Cumar V-3
Pigment	60% metallic copper 40% barytes	50% cuprous oxide 50% zinc oxide
P/B ratio	2:1 by weight	3:1 by weight

Following the five-month immersion at Kure Beach, the panels were removed and returned for detailed study. The paint was removed by light sandblasting (a procedure previously demonstrated to result in less than 1 gram weight loss on a panel weighing approximately 900 grams), and the gross loss in weight was determined for each panel. The average depth of attack on the originally exposed bare areas was determined with a Starrett No. 640 E depth gage accurate to 0.25 mil; each recorded value is the average of twenty to twenty-five individual readings at random points on the test area. The data obtained for both total weight loss and depth of attack are summarized in Table I.

The first and most important finding is that accelerated attack at a gross discontinuity (larger than about 1/4 inch in diameter) can take place; actual perforation occurred in several instances. This accelerated attack is an inverse function of the area of metal originally exposed down to a limiting value where stifling by nonremovable corrosion products can take place, and is also dependent on the composition of the antifouling paint employed. It should be noted, however, that severe accelerated attack can also occur at gross discontinuities in paint films where no antifouling paint is involved. The data for the control paint system in Table I demonstrate this point. This is in accord with earlier

Table I. Weight Loss and Depth of Attack on Panels Immersed Five Months

		No A. F. Paint		A. F. Paint 1		A. F. Paint 2	
% of Area Left Bare	A. F. Paint Contacting Steel	Wt. loss, g./sq. ft.	Av. depth, mils	Wt. loss, g./sq. ft.	Av. depth, mils	Wt. loss, g./sq. ft.	Av. depth, mils
0.0	No	4	..	6	..	4	..
0.1	No	3	20.0	6	P[a]	5	P[a]
1.0	No	4	4.5	11	37.5	9	19.0
5.0	No	5	2.5	13	8.5	9	5.5
Scribed	No	5	5.0	13	19.0	6	7.5
0.0	Yes	.	..	5	..	17	..
0.1	Yes	.	..	21	P[a,b]	15	P[a]
1.0	Yes	.	..	12	P[a]	13	P[a]
5.0	Yes	.	..	12	8.5	10	6.5
Scribed	Yes	.	..	30	33.0	4	4.5

[a] P = perforated the $^{3}/_{32}$-inch panel.

[b] This panel also perforated the inch-square area directly contacting the bare steel.

Table II. Ratio of Depth to Weight Loss

	No Deliberate Contact			Deliberate Contact		
% Area Exposed	Control	A.F. 1	A.F. 2	Control	A.F. 1	A.F. 2
0.1	6.7	8.0[a]	9.6[a]	...	2.3[a]	3.2[a]
1.0	1.1	3.4	2.1	...	4.0[a]	3.7[a]
5.0	0.5	0.6	0.6	...	0.7	0.6

[a] Depth when "perforated" is 48 mils.

experiments by Hudson (*1*) which demonstrated that preferential sacrifice at bare areas on steel panels painted with red lead took place at a doubled rate when compared with unpainted controls. The conclusion seems obvious that the steel beneath the paint film immediately adjacent to the break is cathodic for an area at least equivalent to the bare area.

The data in Table I show no clear-cut relation between exposed area and total weight loss. As a matter of interest the ratio of depth of attack at the bare areas to the total weight loss is shown as a function of the area exposed in Table II. The figures indicate that there is inherent danger in leaving small but finite uncoated areas on steel exposed to immersion in sea water, whether or not a copper antifouling paint is employed in the paint system. This danger has perhaps been insufficiently emphasized to users of marine paint.

ACCELERATED CORROSION AS FUNCTION OF SHAPE OF HOLIDAY

It is obvious from the earlier published data (*4*) and from those presented in Table I that markedly different penetration rates resulted with the symmetrical bare areas, compared with the cross-scribed series where the discontinuity was a long narrow scratch. Accordingly, in another series of experiments the influence of the shape of the gross discontinuity on corrosion acceleration was investigated. The average penetrations at bare spots of various dimensions, left on steel panels coated with two coats of chromate type primer (Specification 52-P-18), an inert barrier coat, and a top coat of antifouling paint formula 1, are summarized in Table III.

Table III. Effect of Shape on Corrosion Attack

Total Area Exposed on 6 × 12 In. Panel, Sq. In.	Dimensions, Inches	Av. Penetration after 5 Mo., Mils
$^{1}/_{16}$	$^{1}/_{16}$ × 1	13
	$^{1}/_{8}$ × $^{1}/_{2}$	9
	$^{1}/_{4}$ × $^{1}/_{4}$	13
$^{1}/_{8}$	$^{1}/_{64}$ × 8	2
1	$^{1}/_{8}$ × 8	6.5
2	$^{1}/_{4}$ × 8	5
3	$^{3}/_{8}$ × 8	7
4	$^{1}/_{2}$ × 8	4.5

These panels were immersed at Daytona Beach, Fla., for 5 months; the data may not, therefore, be directly compared with those in Table I which were obtained at Kure Beach, N.C. It appears, however, that the most severe penetration takes place at holidays roughly $^{1}/_{16}$ to $^{1}/_{8}$ square inch in size. The attack is apparently independent of the shape of the area exposed except when one dimension becomes small enough to allow entrapment of corrosion products, with accompanying stifling action. It will be noted that the previously established inverse ratio of area to depth of attack is qualitatively confirmed.

EFFECT OF COPPER DEPOSITION ON CORROSION

One mechanism which can account for accelerated pitting beneath a heavy metal antifouling paint insufficiently insulated from the base steel by the barrier coat, as well as for accelerated attack at film breaks and gross holidays, postulates that soluble copper complexes or ions migrate inward by diffusion through the water-saturated paint film. If the barrier film is sufficiently thin or is imperfect, appreciable concentrations of copper could thus reach the paint-steel interface and be deposited there by familiar electrochemical displacement. The local cells resulting from such deposition would give positive corrosion acceleration at these sites.

In an effort to demonstrate qualitatively the effect of such copper deposition beneath intact paint films, a number of 6 × 12 × $^{3}/_{32}$ inch medium carbon steel panels were carefully cleaned and then immersed in acidulated copper sulfate for (*a*) 6 seconds and (*b*) 60 seconds; they were then rinsed thoroughly and dried. A $^{1}/_{4}$ × $^{1}/_{4}$ inch area was masked off on each face, and the following paint systems were applied: system A, one coat of chromate primer (Specification 52-P-18), two coats of a blue lead–phenolic anticorrosive paint; system B, three coats of the blue lead–phenolic anticorrosive paint. After drying, the small masking patches were removed to expose bare metal. No antifouling paint as such was employed in either of these systems.

These panels, together with controls, were immersed for three months at Daytona Beach, then returned, and the paint was removed. Data on accelerated penetration at the predetermined bare area are summarized in Table IV; they prove that severe acceleration, with actual perforation, can result from even slight deposition of copper on the steel. (The 6-second treatment, for example, gave an almost invisible flash deposit.)

Table IV. Corrosion Acceleration by Copper Deposition

Panel Preparation	Area Pre-exposed, In.	Paint System	Av. Depth of Attack, Mils[a]
6 sec. Cu flash	None	A	....
6 sec. Cu flash	None	B	....
6 sec. Cu flash	$^{1}/_{4}$ × $^{1}/_{4}$	A	P (>45)
6 sec. Cu flash	$^{1}/_{4}$ × $^{1}/_{4}$	B	P (>45)
60 sec. Cu flash	$^{1}/_{4}$ × $^{1}/_{4}$	A	P (>45)
60 sec. Cu flash	$^{1}/_{4}$ × $^{1}/_{4}$	B	P (>45)
None	$^{1}/_{4}$ × $^{1}/_{4}$	A	21
None	$^{1}/_{4}$ × $^{1}/_{4}$	B	14.5

[a] P = perforated $^{3}/_{32}$-in. panel in 3 months.

CONDUCTIVITY OF ANTIFOULING PAINTS

An alternative mechanism has frequently been suggested to account for accelerated corrosion beneath antifouling paints, particularly those employing metallic copper as toxic agent. That is, a multiplicity of tiny local cells are formed by direct contact of pigment agglomerates with steel; this is certainly a possibility where the pigment volume is sufficiently great to prevent the binder from being the continuous phase. Such a random distribution of local cells on the steel surface would satisfactorily account for the severe pitting known to take place under antifouling paints in direct contact with steel (*4*), but would not explain the almost equally severe pitting observed when a highly attenuated or imperfect barrier coat is employed beneath the antifouling layer; nor will it account for pitting when the pigment is cuprous oxide or other nonmetallic source of copper. It is possible that the pitting mechanisms are different for the two cases—namely, metallic copper paints *vs.* cuprous oxide paints; this possibility seems remote, however, because of the consistency

Table V. Trans-Film Resistance of Selected Paint Systems

Paint System	Pigments	Film Thickness, Mils	Film Resistance, Ohms
A.F. Paint 1	Copper, barytes	1.5	1
		3.0	6
		4.0	150
A.F. Paint 2	Cuprous oxide, zinc oxide	1.5	>1000 × 10^6
Navy Formula 16	(*2*)	1.5	>1000 × 10^6
Navy Formula 15RC	(*2*)	1.5	>1000 × 10^6
Commercial sample 1	Copper	1.5	1
Commercial sample 2	Cu, HgO, inert	1.5	2.5
Commercial sample 3	Copper	1.5	5
Commercial sample 4	Treated Cu	1.5	>1000 × 10^6
Bronzing lacquer	Aluminum	1.0	0.5

of the relation between accelerated attack and copper content of the paint as such, from whatever source derived (*4*).

These and other considerations, therefore, led us to explore the actual magnitude of the resistance of films made from a variety of antifouling paints, both dry and after prolonged exposure to synthetic sea water. For this purpose we used a conventional RCA electronic volt-ohmmeter, of total range 0.2 ohm to 1000 megohms. The selected paints were applied (*a*) direct to clean steel coupons and (*b*) over one or more intermediate barrier coats of the chromate or blue lead type employed in the immersion studies. Contact to the underlying metal was easily effected through a standard battery clip; contact to the outer surface of the paint film was more difficult to establish. For some of the paints a mere brush contact sufficed to yield consistent readings; where there was appreciable skinning or blooming, it was necessary to break through this superficial skin to get finite readings. The use of a mercury contact was early abandoned for this reason. Further, we found that the through-film (trans-film) resistance was a function of the pressure applied on the contacting electrode—an inverse function, as would be expected. Accordingly, we standardized on use of a 1-kg. brass weight to establish primary contact, giving a contact area of 3.14 square inches; before the reading was taken, the weight was given a half turn with mild pressure to disrupt any insulating skin on the paint film.

A few resistance values obtained in this way are summarized in Table V. It is apparent that there is considerable spread in values, varying from an ohm to immeasurably high values. It is important to note that only the copper oxide paints as a class show high dry-film resistivities. There would thus appear to be a definite possibility of contact-accelerated corrosion under the usual racing bronzes and similar metallic-base paints if these low film resistivities persist in the water-saturated paint films and if no barrier coats are employed.

Whether these observed differences between metallic and cuprous oxide paints are to be attributed solely to the difference in specific conductivity of metallic copper *vs.* cuprous oxide (itself a conductor), or are associated with the fact that cuprous oxide is ordinarily admixed with a high proportion of nonconductive pigments such as iron oxide, zinc oxide, and the like, we cannot say.

Having established the low film resistance values characterizing certain types of antifouling paints, we then explored the conductivities of paint systems involving the usual primers and barrier coats under the antifouling finishes. As was expected, application over even a single coat of primer eliminated any measurable current flow through the resulting two-coat systems. Contact couples can thus be completely eliminated by interposition of the usual barrier coats.

All attempts to measure a resistance in the plane of the film of even the most conductive metallic antifouling paints were unsuccessful. It was necessary to devise a different experimental setup, where the test film is deposited on a nonconductive support; otherwise the current path would be through the film to the base and out through the film at the second contact point. Accordingly, we applied the paints to chemically cleaned and dried glass U-tubes; the ends were immersed in individual mercury wells after the dried paint film was abraded with emory paper to disrupt any skin. Using this and a number of alternative means of obtaining positive electrical contact, we nevertheless were unable to measure any current flow in any of the paints. These findings appear to eliminate definitely the possibility of any antifouling paint film being able to act as a gross cathode through accidental contact with bare steel at some few points.

MEASUREMENTS WITH SATURATED PAINT FILMS

Accurate resistivity values are not easy to measure on immersed paint films; since the resistance of the electrolyte is low, it is imperative that completely continuous films be employed and that all extraneous current paths be eliminated. In order to eliminate self-generated potentials and capacitance effects in the setup, a Scheering bridge circuit employing high-frequency alternating current would best serve. Such an instrument was not available; accordingly, we used the RCA direct-current meter previously described; the values recorded for water-saturated films are thus significant only for comparison within the test group and do not necessarily represent the true resistance of the immersed paints.

For the supporting metal surface we used thermally deposited silver on Pyrex test tubes; the external electrode was constructed of pure silver foil. The silvered test tubes were adopted as support for two reasons: (*a*) They enabled deposition of uniform and pore-free films by dipping, free from any edges or sharp projections where the film might be weak or strained. (*b*) The paint films were uniformly exposed to penetration by the electrolyte, and the tubes extended out of the electrolyte far enough to enable positive clip contact to the metal.

The electrolyte employed was a 3.5% solution of Turks Island sea salt in aerated distilled water, adjusted to a pH of 8–8.5 with sodium hydroxide, and readjusted at weekly intervals throughout the test period. Each paint system was exposed in a separate beaker containing 75 ml. of electrolyte, the painted test tube being immersed to a depth of 1 inch and supported in a split rubber stopper. Under these conditions the cell constant, obtained on a bare silvered test tube with the silver foil electrode $^1/_4$ inch removed, was 22 ohms; dry contact direct to the silver (mirror) gave a lead resistance of 0.5–2.0 ohms.

The paint coats were applied by dipping to a depth of 3 inches Sixteen hours of drying time were allowed between coats of paint, and 6 hours were allowed before immersing the specimens. Re-

Table VI. Wet Film Resistances of Selected Paint Systems

Antifouling Paint	No. of Coats	Primer	No. of Coats	Resistance, Ohms: 30 min.	10 days	40 days	60 days
A.F. 1	1	None	.	2.8 × 10	5.9 × 10^3	1.6 × 10^3	1.7 × 10^3
	2	None	.	3.0 × 10^3	7.6 × 10^3	6.6 × 10^3	12.6 × 10^3
	3	None	.	1.3 × 10^5	8.8 × 10^3	6.4 × 10^6	100 × 10^6
Navy 16	1	None	.	2.0 × 10^3	2.2 × 10^6	34 × 10^6	130 × 10^6
	2	None	.	3.9 × 10^6	10.4 × 10^6	50 × 10^3	29.6 × 10^3
	3	None	.	3.9 × 10^6	4.0 × 10^6	1.9 × 10^6	9.4 × 10^6
Navy 15RC	1	None	.	3.9 × 10^6	4.7 × 10^6	13.1 × 10^3	6.4 × 10^6
	2	None	.	6.9 × 10^6	2.5 × 10^6	11.1 × 10^3	11.1 × 10^3
	3	None	.	1.9 × 10^6	15.4 × 10^6	50.0 × 10^3	100 × 10^3
A.F. 1	1	52-P-18	1	3.9 × 10^8	175 × 10^3	2.5 × 10^6	2.6 × 10^6
	1	52-P-18	2	3.0 × 10^8	11.4 × 10^6	5.4 × 10^6	17.4 × 10^6
	1	52-P-18	3	4.0 × 10^8	24.9 × 10^6	9.4 × 10^6	7.9 × 10^6
Navy 15RC	1	52-P-18	1	7.5 × 10^8	9.4 × 10^6	4.9 × 10^6	39.6 × 10^3
	1	52-P-18	2	1.0 × 10^9	14.4 × 10^6	13.9 × 10^6	17.7 × 10^6
	1	52-P-18	3	1.6 × 10^8	110 × 10^6	7.1 × 10^6	9.9 × 10^6

sistance readings were taken 30 minutes after immersion and thereafter at regular intervals for 60 days.

Comparison values for a selected number of these systems are summarized in Table VI. It will be noted that there is no clear-cut distinction among any of the three widely differing antifouling paints, nor among the multiple-coat systems involving them. The resistances after 10-day immersion are very high, in the megohm range for all but the metallic copper formula; and when this paint is applied over a primer, it is indistinguishable from the others.

There is no evidence of any extremely low resistances such as would be demanded if the antifouling paints are to act as cathodes in galvanic couples with the substrate metal. It thus appears that, even if a metallic antifouling paint has initially conductive characteristics, within a relatively short time following immersion it is so swollen and permeated by water as to break the low-resistance paths between pigment aggregates; this undoubtedly arises from the highly specific nature of the vehicles normally employed in antifouling compositions (*3*, *5*).

CONCLUSION

The most probable mechanism for accelerated corrosion in the presence of heavy metal antifouling paints involves actual deposition of copper from aqueous solution in and under the paint film, and at breaks and similar discontinuities. The acceleration probably results from the couple action of these copper deposits rather than from the metal pigment as such; the possibility of direct coupling at localized spots where pigment aggregates accidentally contact bare steel is not eliminated, but this appears to be a minor factor in the over-all phenomenon.

ACKNOWLEDGMENT

We gratefully acknowledge the cooperation of F. L. LaQue, The International Nickel Company, who extended the privilege of using his marine exposure facilities at Kure Beach, N. C., for certain of these studies. The silvered test tubes employed in the resistance studies were prepared by the Liberty Mirror Works, for whose assistance we are grateful.

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PHYSICAL PROPERTIES of BUTANES and BUTENES

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DURING the last decade or so there have been outstanding contributions to knowledge in the branches of hydrocarbon chemistry which have to do with alkylation, dehydrogenation, isomerization, and polymerization. All these reactions are now being utilized commercially, and the respective processes are of fundamental importance in the production of aviation gasoline. In this development the butanes and butenes have had an important role, both from the scientific and practical standpoint. Furthermore, some of them have occupied an important position in work on kinetics (*15*), in studies of the mechanism of isomerization (*13*) and dehydration (*19*), in Ziegler's stereochemical studies (*27*) in Hückel's rearrangement studies (*10*), etc. In all exact work involving the determination and separation of the butanes and butenes, an accurate knowledge of their physical properties is indispensable.

A survey of the literature has disclosed that no data are available on any indices of refraction of the butanes or butenes or on the densities of *cis*- and *trans*-2-butene; in other cases the data on densities, boiling points, vapor pressures, and melting points of different authors are in disagreement with one another.

In this work the physical properties of *n*-butane, isobutane, 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutylene (2-methylpropene) were determined or redetermined wherever the literature values were lacking or inadequate. The values finally selected represent the best values available to date.

MATERIALS AND PROCEDURE

SOURCE OF MATERIAL. The butenes were the original purified samples used by Kistiakowsky and co-workers (*15*) in their precision work on the heats of hydrogenation of olefins. With the exception of 1-butene, the purity of the butenes was checked (*24*) by determining freezing point curves, and is likely to be around 99.9% or at least appreciably better than 99.5%.

The butanes were Pure Grade samples of Phillips Petroleum Company (over 99% pure). Each hydrocarbon was further purified by low-pressure fractionation in a Stock high-vacuum all-glass apparatus (*22*) equipped with mercury seal valves, and the middle cuts were used. The purity of the original samples may be judged from the fact that in all cases the vapor pressures of the different cuts of each compound did not vary more than 0.5% from their absolute value. These samples were distilled directly into the vapor pressure apparatus and dilatometer which were sealed to the high vacuum apparatus.

TEMPERATURE. Temperatures below −30° C. were determined by Stock vapor pressure thermometer (*22*) containing ammonia. A sample of pure ammonia was further fractionated in a high vacuum apparatus at a low temperature, and the best fraction, as determined by its vapor pressure, was used. This thermometer checked within 0.1° C. at the standard reference points of subliming carbon dioxide (−78.5°) and melting mercury (−38.87°), when compared with the accurate vapor pressure of ammonia as determined by Stock.

Above −35° C. a calibrated mercury thermometer graduated in 0.1° was used. The mercury and ammonia thermometers checked within 0.05° at −35° C.

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The literature data on physical properties of *n*-butane, isobutane, 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutylene are briefly surveyed. The data have been redetermined where discrepancies occur and, when absent, have been measured. These properties include refractive indices, liquid densities, boiling points, vapor pressures, and melting points. Refractive indices, from −10° to −50° C., on pure samples of these C_4 hydrocarbons are presented. Measured also are the liquid densities, from 0° to −70° C., of *cis*- and *trans*-2-butene. New data on liquid densities below 0° C. are presented for isobutane, isobutylene, and 1-butene. The vapor pressures from 20 to 800 mm. have been measured on *n*- and isobutane, and are presented as substantiating evidence of the latest literature data.

INDEX OF REFRACTION. The procedure was identical with the one described (*8*) and used for the C_3 hydrocarbons (*9*).

LIQUID DENSITY. A dilatometer of approximately 3.5-cc. capacity was employed. Volumes were determined over a considerable range of temperature. Densities were calculated after the weight of the contents had been determined. The weighings were corrected to vacuum and for the hydrocarbon vapor present.

VAPOR PRESSURE. Vapor pressures were determined from approximately 30 to 800 mm. by the static method described by Stock (*22*). These values, in millimeters of mercury, were corrected to 0° C. and 45° latitude.

INDEX OF REFRACTION AND MOLECULAR REFRACTION

There are no available data on refractive indices of the liquid butanes and butenes except the previous measurements (*8*) on less pure samples. (Data on $n_{\rm D}$ and polarization of gaseous C_4 hydrocarbons are given by Watson and Ramaswaney, *25*.) Experimental values on the present samples are given in Table I and shown graphically in Figure 1. Within the experimental error (±0.0001) of reading the refractometer, $n_{\rm D}$ values are found to be linear functions of temperature. Constants in the equation,

$$n_{\rm D}^t = A - B_t$$

which may be used for computing $n_{\rm D}$ in the temperature range −10° to −50° C., are as follows:

	A	*B*
n-Butane	1.3466	0.00061
Isobutane	1.3364	0.00065
1-Butene	1.3628	0.00065
cis-2-Butene	1.3786	0.00064
trans-2-Butene	1.3698	0.00064
Isobutylene	1.3641	0.00067

The significant difference observed in the refractive indices of the butanes and butenes and also between *n*- and isobutane may be well utilized in the quantitative estimation of binary mixtures of these hydrocarbons, such as are obtained, for example, in isomerization or dehydrogenation studies. The marked similarity observed between isobutylene and 1-butene is also borne out by their densities, boiling points, and vapor pressures.

The Lorenz-Lorentz molecular refractions, MR^{LL} were calculated at 20° C. by extrapolation of the $n_{\rm D}$ curves of Figure 1 and the density curves of Figure 2, and are given in Table II. The refractions of these hydrocarbons are of interest since they together with the previously reported C_3 hydrocarbons, are the lowest members of the respective series so far studied in the liquid state. Included in Table II for comparison are the molecular refractions computed from Eisenlohr's atomic refractions of carbon and hydrogen, the experimental values at the normal boiling point and at −50°, and the temperature coefficient. The close agreement between theory and experiment is apparent. This agreement is much better than in the case of the C_3 hydrocarbons.

DENSITY

The only literature data available on the liquid densities of these hydrocarbons are those of Coffin and Maass on *n*-butane (*4*), isobutane (*4*), 1-butene (*4*), and isobutylene (*5*), Dana's approximate results on isobutane (*6*), and the measurements of the Natural Gasoline Association of America on *n*-butane, isobutane, and 1-butene (*17*).

In view of discrepancies between Coffin and Maass and more recent data by other authors on boiling points of these compounds, as brought out in the following section, and the relatively short temperature range covered by the N.G.A.A. measurements on 1-butene, we determined the densities of Kistiakowsky's four butenes and of isobutane in the range of about 0° to −70° C. The experimental data are given in Table III.

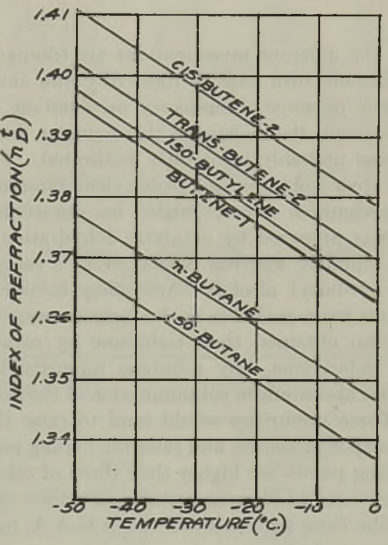

Figure 1. Refractive Indices of Butanes and Butenes

TABLE I. REFRACTIVE INDICES OF LIQUID BUTANES AND BUTENES (EXPERIMENTAL)

t° C.	$n_{\rm D}$	*t*° C.	$n_{\rm D}$	*t*° C.	$n_{\rm D}$
n-Butane		Isobutane		1-Butene	
−12.8	1.3543	−12.8	1.3447	−12.7	1.3711
−24.3	1.3613	−24.3	1.3524	−25.5	1.3792
−45.6	1.3745	−44.5	1.3653	−42.4	1.3905
cis-2-Butene		*trans*-2-Butene		Isobutylene	
−12.7	1.3868	−12.7	1.3778	−12.7	1.3727
−25.5	1.3946	−25.5	1.3862	−25.5	1.3811
−42.4	1.4060	−42.4	1.3969	−42.4	1.3926

TABLE II. MOLECULAR REFRACTION, $MR_{\rm D}^{LL}$

	Calcd. (Eisenlohr at 20° C.)	Extrapolated, 20° C.	Experimental		$\Delta MR_{\rm D}^{LL}/\Delta t$	Mol. Vol. at N.B.P.
			N.B.P.	−50° C.		
n-Butane	20.67	20.69	20.60	20.54	0.0020	96.57_0
Isobutane	20.67	20.85	20.71	20.64	0.0030	97.71_0
1-Butene	20.21	20.21	20.13	19.98	0.0034	89.66_5
trans-2-Butene	20.21	20.30	20.24	20.04	0.0038	89.64_4
cis-2-Butene	20.21	20.17	20.10	19.91	0.0036	87.55_2
Isobutylene	20.21	20.29	20.22	20.11	0.0026	89.65_1

TABLE III. EXPERIMENTAL DENSITY DETERMINATIONS

Isobutane			1-Butene			*cis*-2-Butene			*trans*-2-Butene			Isobutylene		
Temp., ° C.	Exptl.	Calcd.	Temp., ° C.	Exptl.	Calcd.	Temp., ° C.	Exptl.	Calcd.	Temp., ° C.	Exptl.	Calcd.	Temp., ° C.	Exptl.	Calcd.
0.0	0.58096	0.58096	0.0	0.6188	0.6188	10.3	0.6337	0.6336	9.4	0.6169	0.6167	0.0	0.6181	0.6181
−9.5	0.59199	0.59204	−15.1	0.6356	0.6354	0.0	0.6448	0.6448	0.0	0.6269	0.6269	−17.0	0.6365	0.6367
−19.5	0.60344	0.60333	−31.1	0.6527	0.6530	−12.8	0.6590	0.6587	−16.6	0.6451	0.6450	−30.9	0.6517	0.6519
−29.5	0.61415	0.61423	−49.8	0.6736	0.6736	−21.7	0.6688	0.6685	−30.8	0.6603	0.6605	−51.4	0.6745	0.6744
−39.5	0.62471	0.62473	−78.1	0.7048	0.7047	−31.2	0.6786	0.6788	−50.0	0.6814	0.6814	−70.0	0.6948	0.6948
−49.5	0.63486	0.63484												

TABLE IV. COMPARISON OF DENSITY VALUES

	n-Butane		Isobutane		
Temp., ° C.	N.G.A.A. (*17*)	Coffin & Maass (*4*)	Present data	N.G.A.A. (*17*)	Coffin & Maass (*4*)
10	0.5901	0.5905	0.5689	0.5692	0.5711
0	0.6011	0.6012	0.5810	0.5808	0.5830
−20	0.6219	0.6218	0.6039	0.6033	0.6047
−40	0.6416	0.6415	0.6252	0.6244	....
	Isobutylene		1-Butene		
	Present data	Coffin & Maass (*5*)	Present data	Coffin & Maass (*4*)	N.G.A.A. (*17*)
10	0.6071	0.6075	0.6078	0.6064	0.6065
0	0.6181	0.6190	0.6188	0.6179	0.6183
−20	0.6400	0.6416	0.6408	0.6405	....
−40	0.6619	0.6639	0.6628	0.6626	....

Results of the different investigations are compared in Table IV. We prefer our own data to those of Coffin and Maass, although there is no great discrepancy on 1-butene, because, as Dana (*6*) disclosed, the resistance thermometer used by Coffin and Maass was probably incorrectly calibrated. Furthermore, the purity of their isobutane and isobutylene samples, where the greatest discrepancies occur, might be questionable. Their isobutylene was prepared by catalytic dehydration of isobutyl alcohol over alumina, whereas Kistiakowsky's sample was prepared from *tert*-butyl alcohol. According to our experience, isomerization is more probable in the former case. Since Coffin and Maass also obtained their isobutane by catalytic hydrogenation of isobutylene, any *n*-butene impurity in their isobutylene would also result in contamination of the isobutane with *n*-butane. These impurities would tend to raise the densities, decrease the vapor pressures, and raise the boiling points. Their recorded boiling points are higher then those of other investigators, as shown in the following section. Further evidence may be noted in the close agreement of the N.G.A.A. measurements and our own on isobutane.

TABLE V. SUMMARY OF BEST DENSITY VALUES

	d_4^t (Vacuum)	(±) Deviation	Exptl. Range, ° C.
n-Butane (*4*)	$0.601164–0001057t–0.051241t^2$	0.00015	−35 to 20
Isobutane	$0.58096–0001185t–0051955t^2$	0.00005	−50 to 0
Isobutylene	$0.6181–0.001096t$	0.0001	−70 to 0
1-Butene	$0.6188–0.00110t$	0.0001	−80 to 0
cis-2-Butene (high-boiling)	$0.6449–0.00109t$	0.0002	−50 to 10
trans-2-Butene (low-boiling)	$0.6269–0.00109t$	0.0001	−50 to 10

The data of Coffin and Maass and those of the N.G.A.A. on *n*-butane are in close agreement. Coffin and Maass' data are given in the summary below mainly because they prepared *n*-butane by hydrogenation of 1-butene; their data and ours are in reasonable agreement on the latter compound and cover a greater temperature range than the N.G.A.A. data. There is good agreement, however, between all the data. The data on *cis*- and *trans*-2-butene were the first recorded in the literature.

The best values for the butanes and butenes are summarized in Table V. To represent their interrelation more clearly, these equations are presented graphically in Figure 2.

BOILING POINT AND VAPOR PRESSURE

Correlation of the best data recorded in the literature on the boiling points and vapor pressures in the range 10 to 1000 mm. reveals discrepancies between different authors, particularly in the cases of isobutane and isobutylene. (Data on very low pressure in the range −180° to −130° C. on *n*- and isobutane, 1-butene, and isobutylene are given by Delaplace, *7*.) These data, together with our results on *n*- and isobutane are shown in Table VI. Experimental data are expressed in terms of the Rankine equation,

$$\log_{10}P_{\text{mm.}} = \frac{-A}{T} - B\log_{10}T + C$$

in the belief that it is adequate for most purposes and is more easily handled than four-constant equations. In each case the authors' data were used to calculate the constants of the equations by the method of least squares. Various derived constants from the empirical equations are included for comparison. The molecular heats of vaporization neglect the volume of the liquid phase and assume the saturated vapor to behave as a

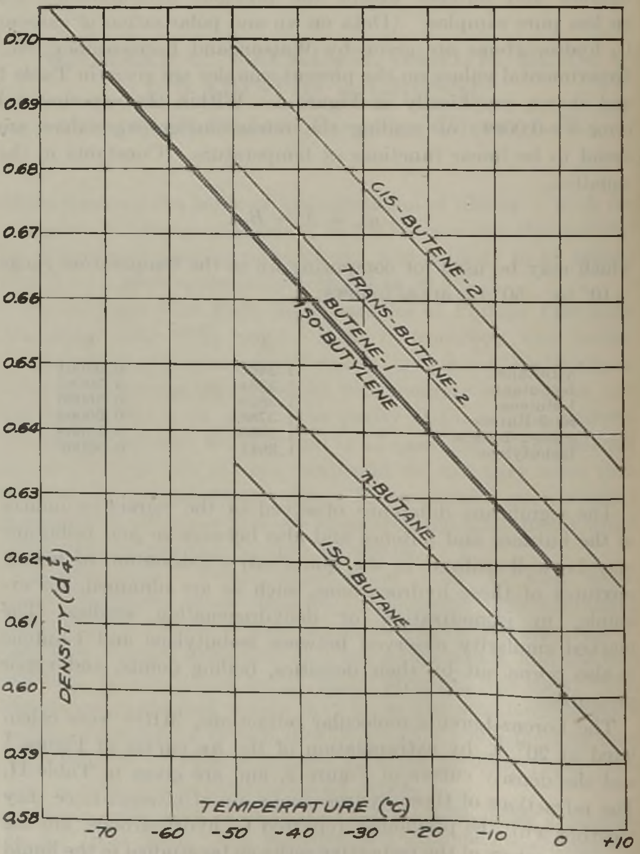

Figure 2. Densities of Butanes and Butenes

TABLE VI. BOILING POINT DATA

Hydrocarbon	B.P., ° C. at 760 Mm. Selected value	B.P., ° C. at 760 Mm. Calcd. from equation	Constants of Rankine Equation (0° C. = 273.2° K.) *A*	*B*	*C*	Mean Deviation of Calcd. from Obsvd., ±%	Exptl. Range of Equation, Mm.	Δ H or Heat of Vaporization at N.B.P., KCal./Mol.	*dt/dp* at N.B.P.	Trouton's Constants	Reference
n-Butane	− 0.5	− 0.5	1744.65	4.8193	21.01654	0.7	20 to 1000	5.376	0.0362	19.7	Authors
		− 0.7	1487.74	2.5986	14.6688	0.5	10 to 1000	5.404	0.0359	19.8	*(26)*
		− 0.3	2247.75	10.2426	36.0698	1.5	7 to 760	4.737	0.0411	17.4	*(3)*[m]
		− 0.3	See Equation M[a]			1	1 to 760	4.714	0.0413	17.3	*(3)*
		− 0.5	1202.98	−0.21387	6.77130	0.5	370 to 1130	5.625	0.0346	20.9	*(6)*[m]
		− 0.7	See Equation N[b]			0.1	370 to 4500	5.691	0.0342	20.9	*(6)*
		− 0.49	1692.96	3.9876	18.80151	0.08	10 to 800	5.590	0.0348	20.5	*(2)*[m]
		− 0.50	See Equation S[g]			0.01	10 to 800	5.565	0.0355	19.6	*(2)*
Isobutane	−11.7	−11.7	1608.61	4.3084	19.44755	0.3	30 to 800	5.126	0.0349	19.6	Authors
		−12.1	1515.55	3.1263	16.24147	0.1	400 to 1100	5.317	0.0335	20.4	*(6)*[m]
		−12.2	See Equation O[c]			0.1	400 to 10000	5.308	0.0336	20.3	*(6)*
		−12.3	1529.50	3.2408	16.57494	0.3	220 to 740	5.323	0.0335	20.5	*(11)*
		−13.5	See Equation P[d]			1	1 to 760	3.500	0.0237	13.5	*(3)*
		−11.71	1600.84	3.9392	18.52561	0.05	10 to 800	5.283	0.0339	20.2	*(1)*[m]
		−11.72	See Equation T[h]			0.01	10 to 800	5.268	0.0342	19.5	*(1)*
		− 6.1	1762.84	5.1190	21.90232	0.2	60 to 820	5.354	0.0349	20.0	*(4)*
1-Butene-1	− 6.3	− 6.3	1507.64	2.6596	14.98239	0.2	60 to 1000	5.492	0.0339	20.6	*(16)*[m]
		− 6.3	See Equation U[i]			0.1	60 to 1000	5.520	0.0338	20.7	*(16)*
cis-2-Butene	3.6	3.6	1754.29	4.0361	19.07542	0.1	5 to 1580	5.811	0.0345	21.0	*(14)*[m]
		3.73	See Equation Q[e]			0.1	5 to 1580	5.810	0.0345	21.0	*(14)*
		3.45	1408.00	0.90605	10.18293	0.7	5 to 1000	5.949	0.0337	21.5	*(16)*[m]
		3.53	See Equation V[j]			0.5	5 to 1000	5.900	0.0339	21.3	*(16)*
trans-2-Butene	0.9	0.9	1664.99	5.5069	17.50541	0.3	8 to 1500	5.713	0.0340	20.8	*(14)*[m]
		0.96	See Equation R[f]			0.1	8 to 1730	5.695	0.0345	20.8	*(14)*
		0.87	1755.55	4.3841	19.97416	0.2	15 to 1100	5.650	0.0348	20.6	*(16)*[m]
		0.91	See Equation W[k]			0.2	15 to 1100	5.620	0.0350	20.6	*(16)*
Isobutylene	− 7.0	− 6.4	1990.81	7.1752	27.75109	0.6	65 to 780	5.310	0.0351	19.9	*(5)*
		− 7.12	1814.06	5.5574	23.17522	0.2	65 to 1000	5.367	0.0345	20.2	*(16)*[m]
		− 7.12	See Equation X[l]			0.1	65 to 1000	5.370	0.0345	20.2	*(16)*

[a] Equation M: $\log_{10}P_{\text{mm.}} = -1633.3/T + 1.75 \log_{10}T - 0.0109T + 7.589$

[b] Equation N: $\log_{10}P_{\text{atm.}} = -1337.8/T + 1.75 \log_{10}T - 0.00407T + 1.75680$

[c] Equation O: $\log_{10}P_{\text{atm.}} = -1164.4/T + 1.75 \log_{10}T - 0.00299T + 1.00856$

[d] Equation P: $\log_{10}P_{\text{mm.}} = -1632.6/T + 1.75 \log_{10}T - 0.0158T + 9.068$

[e] Equation Q: $\log_{10}P_{\text{mm.}} = -2379.264/T - 15.4405 \log_{10}T + 0.0097519T + 46.48442$

[f] Equation R: $\log_{10}P_{\text{mm.}} = -2505.74/T - 18.78681 \log_{10}T + 0.012991T + 54.2623$

[g] Equation S: $\log_{10}P_{\text{mm.}} = -2352.90/T - 16.4923T \log_{10}T + 0.011111869T + 48.64763$

[h] Equation T: $\log_{10}P_{\text{mm.}} = -1716.69/T - 6.3887T \log_{10}T + 0.0024182T + 24.26032$

[i] Equation U: $\log_{10}P_{\text{mm.}} = -1330.977/T - 0.0017607T + 8.33816$

[j] Equation V: $\log_{10}P_{\text{mm.}} = -1375.857/T - 0.0011167T + 8.16234$

[k] Equation W: $\log_{10}P_{\text{mm.}} = -1532.745/T - 0.0040597T + 9.58593$

[l] Equation X: $\log_{10}P_{\text{mm.}} = -1503.866/T - 0.0046649T + 9.77465$

[m] Data recalculated to Rankine equation

perfect gas. Equations of other types given by other authors are included at the bottom of Table VI.

The latest data by Aston and co-workers on normal (*2*) and isobutane (*1*) and by Lamb and Roper (*16*) on the butenes have done much to clarify the previously existing differences.

Aston and Messerly's precision data (*2*) on *n*-butane, substantiated by our measurements and those of Dana (*6*), definitely establish the boiling point of *n*-butane at −0.5° C. Coffin and Maass (*4*) also obtained −0.5° experimentally as the normal boiling point of their sample used in density measurements. Further weight might be given this value since it was obtained on samples prepared by several different methods.

Our experimental data on the vapor pressure of *n*-butane, obtained prior to Aston and Messerly's publication, are given in Table VII, primarily as substantiating evidence. They are to be in reasonable agreement with the data of Aston and Messerly.

The precision measurements of Aston, Kennedy, and Schumann (*1*) on isobutane are in accord with our data, which were originally made because of lack of satisfactory literature data. Previously the only trustworthy data were those of Dana (*6*), and Hückel (*11*), which were obtained over the respective ranges 400–1100 and 220–740 mm. Burrell's data (*3,21*) are probably in error because of incorrect temperature measurements (*10*). Our data are compared in Table VIII with Dana's and Aston's data. Aston's results and ours were obtained on samples prepared by different methods, and equations representing both sets of data give a normal boiling point of −11.7° C.

The boiling point of −10.2° C. for isobutane given by Coffin and Maass (*4*) is definitely out of line. This was obtained on the sample used by them in their density measurements and, as previously mentioned, may be in error because of erroneous thermometric calibration and possible impurities.

TABLE VII. VAPOR PRESSURE OF *n*-BUTANE

Temp., ° C.	Vapor Pressure, Mm. of Hg: Exptl.	Calcd. from our equation (Table VI)	Calcd. from Aston's equation (Table VI)
5.6	955.0	942.3	...
0.0	775.4	773.4	774.5
−7.1	589.3	593.1	...
−11.3	498.0	502.7	495.2
−17.7	384.5	385.7	...
−22.7	310.9	309.9	300.4
−31.3	207.4	207.3	...
−45.0	99.6	100.1	95.2
−60.0	42.5	40.8	...
−67.7	23.5	24.0	21.9

The boiling point given by Coffin and Maass (*5*) for isobutylene is also high when compared with the latest measurements of Lamb and Roper (*16*). Inasmuch as Coffin and Maass' sample was used to prepare their isobutane, their result on isobutylene may be in error for the same reason given for their doubtful results on isobutane. Therefore preference is given Lamb and Roper's data. The value of −7.0° C. is selected as most probable. This is in complete agreement with the experimental value determined by Kistiakowsky (*14*).

Measurements (*4*) on *cis*- and *trans*-2-butene, previous to those of Kistiakowsky and co-workers (*14*) and of Lamb and Roper (*16*), were made on mixtures of the geometrical isomers[2]. Lamb and Roper's data on both isomers were obtained on samples from the same source as Kistiakowsky's. Since both sets of data are in good agreement and the high purity of the samples is

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[2] Attention is called to the data on vapor pressure and melting point by Scott, Ferguson, and Brickwedde (*20*) which became available too late for inclusion in Table VI.

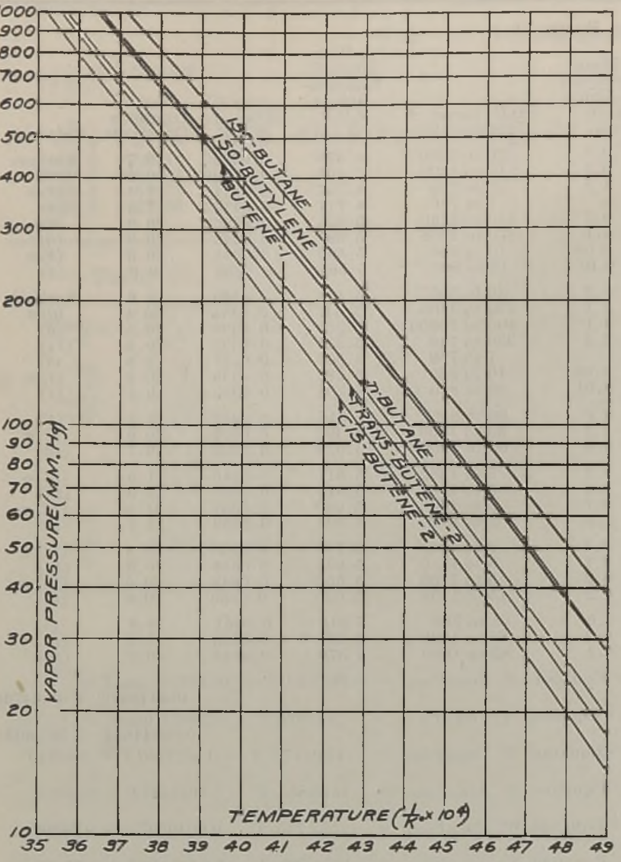

Figure 3. Vapor Pressures of Butanes and Butenes

known, they may be accepted without reservation. The values of 3.6° and 0.9° C. for *cis-* and *trans*, respectively, are selected as the most probable normal boiling points.

The only vapor pressure data available on 1-butene are those of Coffin and Maass (*4*) and Lamb and Roper (*16*). The data of Coffin and Maass were obtained on a pure sample prepared by the action of excess alcoholic potash on *n*-butyl iodide. Lamb's data were obtained from the pure samples prepared by Kistiakowsky for his studies of the heats of hydrogenation. These were made (*a*) by Ipatieff's method from *n*-butyl alcohol over alumina (boiling point −6.49°), and (*b*) by action of zinc granules on 1,2-dibromobutenes (boiling point −6.52° C.). Since Lamb's boiling point at 760 mm. (−6.3° C.) is the average of Maass' and Kistiakowsky's values (*14*), and since other calculated values check reasonably well, his vapor pressure data and normal boiling point were selected as the most probable.

The final results for all six hydrocarbons are plotted in Figure 3. The decrease in volatility is of the order to be expected from considerations of molecular structure. The most spherelike, isobutane, is also the most volatile. Also, unsaturation causes greater attractive forces, which result in olefins that boil higher than the corresponding paraffin. Other constants, such as the boiling points and vapor pressures, lie within a narrow range: the heats of vaporization between 5.1 and 5.8 kg.-cal./mole, the dt/dp values between 0.0339 and 0.0348, and Trouton's constants between 19.5 and 21.0. The marked similarity between isobutylene and 1-butene which was noted in the densities and refractive indices is also borne out by the vapor pressures.

TABLE VIII. VAPOR PRESSURE (MM. OF Hg) OF ISOBUTANE

Temp., ° C.	Exptl. Value	Calcd. from Equations in Table VI: Ours	Dana's	Aston's
−10.4	799.1	797.8	812.9	799.3
−11.9	758.0	754.1	...	...
−15.0	666.7	669.6	678.1	667.5
−22.7	491.2	490.9	...	...
−31.0	342.0	341.9	339.2	334.4
−35.8	271.3	273.7	...	...
−44.4	178.9	178.4	...	171.6
−58.0	83.8	83.5	...	...
−66.7	48.3	48.3	...	45.1

MELTING POINTS

The available literature data on the melting points of butanes and butenes are given in Table IX. The best values are underscored. These values, based on the determinations of Aston and co-workers (*1*, *2*), Kistiakowsky (*14*), and Todd and Parks (*24*) are selected because of the known purity of their samples.

TABLE IX. MELTING POINTS OF BUTANES AND BUTENES

Hydrocarbon	Melting Point, ° C.
n-Butane	−138.29 (*2*); 134.1° K. (*12*); −135.0 (*23*)
Isobutane	−159.42 (*1*); −160.0 (*18*); −145.0 (*23*)
Isobutylene	−140.7 (*14*, *24*); −146.8 (*5*)
cis-2-Butene	−139.3 (*14*, *24*)
trans-2-Butene	−105.8 (*14*, *24*)
1-Butene	<−195 (*24*); <−190 (*4*)

ACKNOWLEDGMENT

We wish to thank G. B. Kistiakowsky of Harvard University for the loan of his pure samples of butenes.

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HYDROGEN SULFIDE PRODUCTION from SULFUR AND HYDROCARBONS

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Hydrogen sulfide can be produced commercially from sulfur and various hydrocarbons. At temperatures of 250° C. heavy fuel oils will react with sulfur to give high yields of hydrogen sulfide. At 600–650° C., using various catalysts, sulfur will react quantitatively with methane and water vapor to form hydrogen sulfide and carbon dioxide. To prevent the formation of sulfur dioxide, the reaction can be carried out in two steps: (1) the reaction of sulfur with methane at 600–650° C. to form hydrogen sulfide and carbon disulfide, and (2) the conversion of the carbon disulfide at 300–350° C. to hydrogen sulfide and carbon dioxide by means of water vapor.

APPROXIMATELY 20,000 to 25,000 tons of hydrogen sulfide are now recovered or produced annually in this country. Since there are indications that the demand for this substance may increase, it seems desirable to study additional methods for the commercial production of this gas. Two common laboratory methods for preparing this compound which may be made the basis for industrial production are (1) the reaction of iron sulfides with dilute sulfuric acid and (2) the reaction of sulfur with hydrocarbons. The first produces a gas which is wet and contaminated by volatile hydrides of arsenic, phosphorus, selenium, etc., and for large-scale operation poses the difficult problem of disposing of the ferrous sulfate solution. The second furnishes a gas which may be contaminated by volatile hydrocarbons, depending upon the hydrocarbon material initially used and the reaction temperatures. Economic and physical considerations indicate that the reaction of sulfur with hydrocarbons is better suited to large-scale production of hydrogen sulfide.

REACTION OF SULFUR WITH OIL

This reaction was studied to determine which of the cheaper petroleum oils would be suitable, the amount of oil required, the optimum temperatures and time for the reaction, and the yield and purity of the hydrogen sulfide.

A series of small-scale experiments indicated that about 250° C. was a good working temperature. At 200° the reaction was too slow and incomplete. At 300° the rate of reaction was somewhat greater than at 250°, but the yields were not increased. At this temperature there were indications of some reactions which might contaminate the hydrogen sulfide with organic sulfides and light petroleum products.

Any petroleum oil which does not contain fractions boiling below 250° C. may be used. In this work an oil with these characteristics was employed:

Gravity, ° A.P.I.	20.5
Flash point, ° F.	175
Saybolt Furol viscosity, sec. at 100° F.	193
Bottom settlings plus water, %	0.3
Pour point, ° F.	50+

Based on the sulfur used, the yield of hydrogen sulfide is about 75–80% for a 3-hour heating period with about 50–65% of the theoretical amount of the gas being evolved in the first hour. The hydrogen sulfide gas is of high purity and free of carbon disulfide, thiophene, and hydrolyzable organic sulfides.

Inspection of an arbitrary equation for a reaction of this type

$$C_{10}H_{20} + 10S \longrightarrow 10H_2S + 10C$$

shows that less than 0.5 pound of oil is required per pound of sulfur. It was found, however, that this value could not be approached because the material cooks up to such an extent in the early stages of the reaction that it is very difficult to heat it uniformly in order to complete the action. The minimum amount of oil required to give satisfactory heating was a weight equal to that of the sulfur used. After approximately 80% of the theoretical amount of hydrogen sulfide was evolved, further liberation of the gas was so slow as to be negligible.

The hydrogen sulfide was determined by loss in weight and was checked in certain cases by absorbing it in a sodium hydroxide solution and determining the sulfur by weighing as barium sulfate. The results showed hydrogen sulfide (by loss of weight) as 63.9 grams, and by analysis 64.1 grams, after heating 100 grams of oil with 100 grams of sulfur for one hour at 250° C.

These experiments were repeated on a larger scale in a cylindrical stainless steel pot, 12 inches in diameter and 19 inches deep, with a lid carrying a vertical water-cooled reflux condenser for returning to the pot any light distillate which might form. The condenser was 4.5 feet long and 4 inches in diameter. The temperature was measured by a thermocouple set in a well 2 inches from the side wall and sealed 2.5 inches from the bottom of the pot. The pot, set in a brick oven with its upper 3 inches above the edge, was evenly heated with gas by so designing the oven that direct flames did not impinge on the pot. The pot and charge were heated gradually and as uniformly as possible to the reaction temperature in 30 to 50 minutes and were kept at the desired temperature for different time periods.

Periodic sampling of the issuing gas in some of the runs showed 99.9 to 100% absorption in iodine solutions. The gas was colorless and free of contaminating sulfur compounds as in the small scale experiments. The loss in weight after heating was taken as the amount of hydrogen sulfide evolved. This value was also checked by analysis of the residues. For example, in one run heating 15 pounds of oil with the same weight of sulfur at 240–250° C. for 3 hours gave a loss in weight of 11.31 pounds. Analysis of the residue was as follows:

Free sulfur (CCl_4 soluble)	1.99%
Combined sulfur (CCl_4 insoluble)	21.04
Oil, etc., soluble in CCl_4	20.43
Carbon, etc., insoluble in CCl_4	56.54

Table I. Experimental Data on Heating Petroleum Oil with 15 Pounds of Sulfur

Wt. of Oil, Lb.	Heating Time, Hours	Temp., ° C.	Loss of Wt., Lb.	% Loss Based on Wt. of S
10	7	220–251	8.31	55.4
15	1	240–244	6.19	41.2
15	3	240–251	11.31	75.4
15	5	240–255	12.06	80.4

By calculation these values show a total weight of sulfur left in the residue as 4.29 pounds, or 10.71 pounds evolved in combination with 0.67 pound of hydrogen to give 11.38 pounds of hydrogen sulfide against a loss of weight of 11.31 pounds.

Typical runs summarized in Table I verify the small scale experiments and show that, with equal weights of sulfur and oil at approximately 250° C., about 80% of the sulfur is converted within a reasonable time into hydrogen sulfide of sufficient purity for many purposes. It is noteworthy that with heavy fuel oil of the type used at $1.00 per barrel, the cost of raw materials per pound of hydrogen sulfide produced is approximately 1²/₃ cents. At the temperatures employed, the stainless steel pot showed no signs of corrosion.

SULFUR REACTIONS

With Hydrogen. Sulfur reacts rapidly with hydrogen at temperatures above 350° C. giving a very pure hydrogen sulfide. While pressure appears to favor the reaction (*1*), hydrogen sulfide can be produced from sulfur and hydrogen at atmospheric pressure through the use of catalysts (*6*). In certain natural gas regions hydrogen can be made cheaply. Synthetic ammonia plants after the war may have excess hydrogen capacity thus providing another cheap source of this gas. These potential sources of cheap hydrogen will favor the production of hydrogen sulfide by direct union of the elements.

With Methane. Natural gas is available in tremendous quantities in the sulfur-producing regions of this country. It offers an excellent source of cheap hydrogen for producing hydrogen sulfide by direct reaction between methane and sulfur. Our object was to carry out the reaction directly,

$$CH_4 + 4S + 2H_2O \longrightarrow 4H_2S + CO_2 \qquad (1)$$

or in two stages according to the following reactions:

$$CH_4 + 4S \longrightarrow 2H_2S + CS_2 \qquad (2)$$

$$CS_2 + 2H_2O \longrightarrow 2H_2S + CO_2 \qquad (3)$$

As our work approached completion, a study of reaction 2 by Thacker and Miller (*7*) appeared. Therefore, with respect to this reaction, there is some overlapping.

With natural gas available at 10 to 15 cents per thousand cubic feet, inspection of reaction 1 shows that from the standpoint of cost it is only of minor importance to obtain a high yield of hydrogen sulfide based on the natural gas used.

The free energies (*2*, *4*) for reactions 2 and 3 are favorable at all temperatures under consideration—500–800° C. for reaction 2 and 127–700° C. for 3. At equilibrium these reactions should be almost complete. The side reactions likely to occur are:

$$CH_4 + 2S \longrightarrow CS_2 + 2H_2$$

$$CH_4 \longrightarrow C + 2H_2$$

$$CS_2 \longrightarrow C + 2S$$

$$CS_2 + H_2O \longrightarrow H_2S + COS$$

$$3S + 2H_2O \longrightarrow 2H_2S + SO_2$$

These will be taken up later.

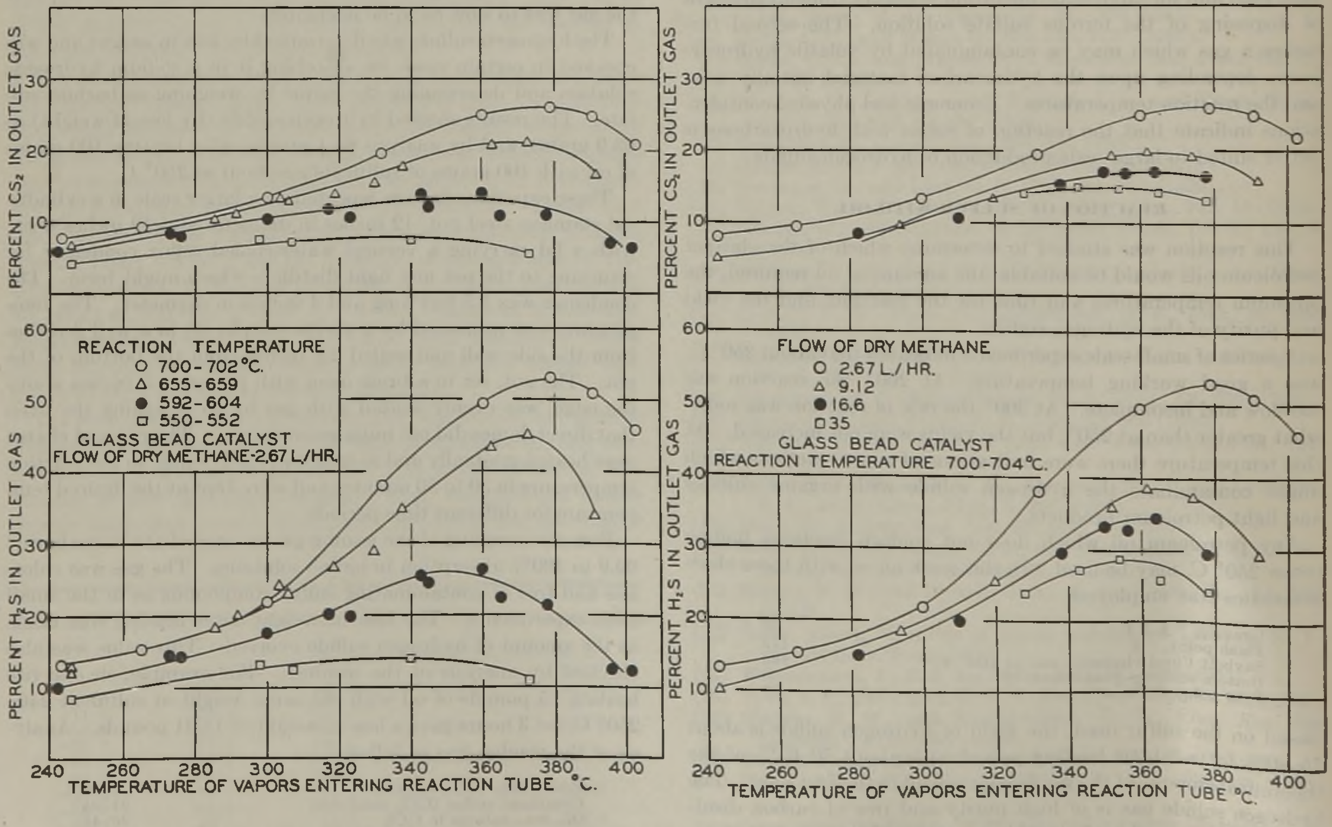

Figure 1. Effect of Sulfur Concentration on Yield of Hydrogen Sulfide and Carbon Disulfide

PROCEDURE FOR REACTION 2

The natural gas used was from a South Texas field with the following percentage composition: 97.1 methane, 1.91 ethane, 0.66 propane, and 0.33 isobutane. The sulfur was a crude commercial grade, free of arsenic, selenium, and tellurium, and containing better than 99.5% sulfur.

A cylindrical stainless steel pot, 4 inches in diameter and 8 inches deep with removable lid, was used to hold the molten sulfur. A stainless steel pipe, 1 inch in diameter and 23 inches long, was welded horizontally to the side wall just below the top. This pipe, heated electrically, served as the reaction tube. Preliminary runs indicated that for consistent results this tube had to slope downward a few degrees in order to drain off condensed sulfur vapor. The sulfur pot was also electrically heated and around the thinly insulated winding was coiled small-bore copper tubing for preheating the methane. This heavily insulated coil was connected at the top of the pot to a small steel pipe which extended 3 inches below the surface of the molten sulfur.

Table II. Experimental Data on Reaction of Sulfur with Methane

Flow of Dry Methane, Liters/Hr.	Reaction Temp., ° C.	Vapor Temp., ° C.	Vol. % in Outlet Gas		Volume Ratio, H_2S/CS_2
			H_2S	CS_2	
Catalyst 1, Empty Reaction Tube					
2.67	601	343	37.0	19.8	1.87
2.67	704	373	67.1	27.7	2.42
9.12	704	369	50.5	23.5	2.15
16.60	702	350	40.8	19.5	2.09
35.00	705	340	35.7	18.7	1.91
Catalyst 2, Glass Beads					
2.67	550	340	13.9	7.4	1.88
2.67	602	360	26.3	14.0	1.88
2.67	659	373	45.1	21.5	2.10
2.67	700	379	53.0	26.1	2.03
2.67	752	380	59.5	29.1	2.04
2.67	804	385	63.4	30.2	2.10
4.74	602	356	15.1	7.7	1.96
4.74	754	373	50.2	24.5	2.05
9.12	602	342	9.9	5.8	1.71
9.12	704	362	38.6	19.8	1.95
9.12	752	362	45.4	22.7	2.00
16.60	600	336	7.4	4.1	1.80
16.60	704	364	34.5	17.2	2.01
35.00	704	354	28.7	14.6	1.97
Catalyst 3, Nickel on Pumice Stone[a] (6–8 Mesh)					
2.67	605	355	26.6	14.1	1.89
2.67	705	376	60.4	29.5	2.05
9.12	705	370	44.7	23.0	1.94
16.60	705	372	39.0	20.3	1.92
35.00	705	362	33.9	17.3	1.96
Catalyst 4, Pumice Stone (6–8 Mesh)					
2.67	606	355	26.8	14.4	1.86
2.67	703	382	60.0	29.2	2.05
9.12	705	379	43.5	22.3	1.95
16.60	705	368	35.6	18.7	1.90
35.00	703	361	28.4	14.8	1.92
Catalyst 5, Pumice Stone (10–20 Mesh)					
2.67	702	383	61.4	29.6	2.07
9.12	703	380	45.4	22.9	1.98
16.60	705	375	36.6	18.7	1.96
35.00	705	364	30.0	15.5	1.94
Catalyst 6, Roasted Pyrites (8–10 Mesh)					
2.67	603	352	26.1	14.0	1.86
2.67	705	375	61.8	28.9	2.14
9.12	702	362	45.2	22.4	2.02
16.60	705	360	37.2	18.7	1.99
35.00	705	358	29.6	15.7	1.88
Catalyst 7, Alumina of Lenander Type (6–8 Mesh)					
2.67	602	363	39.5	20.0	1.98
2.67	706	373	65.5	31.1	2.11
9.12	604	348	24.4	12.9	1.89
9.12	703	367	51.2	25.9	1.98
16.60	703	354	40.5	20.6	1.96
35.00	705	348	33.0	17.35	1.90
Catalyst 8, Molybdenum on Pumice Stone[b] (6–8 Mesh)					
2.67	602	352	31.8	16.6	1.92
2.67	702	375	62.7	31.1	2.02
9.12	702	367	52.0	25.9	2.01
16.60	700	353	41.5	21.4	1.94
35.00	702	345	30.2	15.5	1.95
Catalyst 9, Silica Gel (6–8 Mesh)					
2.67	553	392	53.8	25.0	2.15
16.60	554	371	29.4	15.1	1.95
16.60	653	377	51.7	26.2	1.97
Catalyst 10, Activated Alumina (Alorco) (6–8 Mesh)					
2.67	556	360	52.9	25.9	2.04
2.67	607	373	65.6	28.1	2.33
2.67	657	382	66.6	31.9	2.09
9.12	556	340	32.4	16.4	1.98
9.12	603	365	50.2	24.6	2.04
9.12	657	373	59.5	29.7	2.00
9.12	708	375	63.7	30.9	2.06
16.60	554	332	24.3	13.0	1.87
16.60	605	372	41.2	20.2	2.04
16.60	658	367	55.0	26.7	2.06
16.60	703	370	59.1	29.8	1.98
35.00	606	346	37.6	19.0	1.98
35.00	653	360	46.2	23.2	1.99

[a] Pumice stone soaked in a solution of nickelous nitrate and dried. heated to form oxide, and reduced with hydrogen at 400–450° C.

[b] Pumice stone soaked in ammonium molybdate solution, heated to form oxide, and reduced with hydrogen at 450° C.

All temperatures were measured by shielded iron-constantan thermocouples. The temperature of the sulfur and methane vapors (here called "vapor temperature") was determined in the pot at a point just below the entrance to the reaction tube. The catalyst beds (5 inches long with a volume of 71.6 cc.) were centered in the heated portion of the reaction tube. The center of the beds gave maximum temperatures while at other points the temperatures averaged 20° C. lower. All reaction temperatures given are maximum values.

The pot was filled to a depth of about 4 inches with liquid sulfur, and the temperature of the reaction zone was adjusted to and held constant at the desired value. Natural gas, measured by a flowmeter after drying by anhydrone, was preheated as described and passed at a constant rate through the molten sulfur. The vapor temperatures were then varied by adjusting the temperature of the sulfur pot. The exit gases, after passing through glass wool to condense and remove sulfur vapors, were analyzed for hydrogen sulfide and carbon disulfide by passing a measured amount through iodine solution to absorb the hydrogen sulfide and then through 10% potassium hydroxide in ethyl alcohol which converts the carbon disulfide to xanthate. Back-titration of the iodine solution with thiosulfate solution, etc., gives the hydrogen sulfide content while titration of the xanthate solution with iodine, etc., gives the carbon disulfide value.

EXPERIMENTAL RESULTS

As the metering of small amounts of liquid or gaseous sulfur is difficult and uncertain, a method for obtaining the maximum reaction at a given reaction temperature and flow of methane was devised. Starting with a low vapor temperature such as 260° C., after maintaining this temperature constant for a time sufficient to ensure fairly constant results, the outlet gas was analyzed for hydrogen sulfide and carbon disulfide. The vapor temperature was then raised, and the procedure was repeated. This was continued up to vapor temperatures around 400° C.

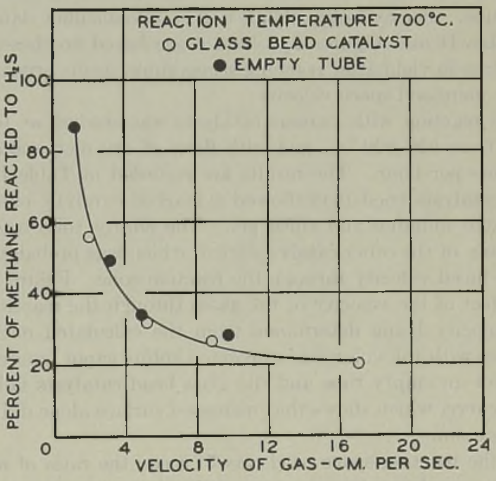

Figure 2. Effect of Velocity of Gas on Reaction $CH_4 + 4S \rightarrow CS_2 + 2H_2S$

Table III. Conversion of Carbon Disulfide Formed in First Reaction to Hydrogen Sulfide and Carbon Dioxide by Water Vapor

(Volume ratio of water vapor to calculated flow of dry inlet gas, 1.33)

Reaction Temp., ° C.	Inlet Gas: H_2S, % by vol.	Inlet Gas: CS_2, % by vol.	Inlet Gas: Calcd. flow, l./hr. (dry basis)	Outlet Gas, % by Vol.: H_2S	CS_2	COS	CO_2	CH_4, H_2	% Conversion
Catalyst, 5-Inch-Long Bed of Activated Alumina (6–8 Mesh)									
309	66.0	30.1	7.3	78.0	0.3	Trace	20.6	1.1	98.6
401	65.5	30.7	7.3	78.6	0.3	Trace	19.3	1.8	98.5
505	66.1	31.6	7.5	79.2	0.3	Trace	18.4	2.1	98.4
307	49.3	24.1	17.8	64.8	0.3	Trace	16.7	18.2	98.2
413	49.3	24.3	17.9	63.9	0.3	None	16.8	19.0	98.2
490	47.4	24.3	17.5	64.1	0.3	Trace	16.1	19.5	98.2
127	32.0	16.7	24.7	32.4	16.0	Trace			
172	32.0	16.7	24.7	44.3	4.2	Trace	18.9	42.6	68.0
200	31.5	16.7	24.6	52.2	0.3	Trace	12.4	35.1	97.6
245	31.6	16.7	24.6	51.9	0.2	Trace	14.3	33.6	98.6
310	27.9	14.8	23.3	50.3	0.3	Trace	13.8	35.6	97.9
508	40.8	20.4	28.0	55.9	0.2	None	14.9	29.0	98.7
702	37.2	18.9	26.6	52.6	0.3	None	11.9	35.2	97.5
Catalyst, 2-Inch-Long Bed of Activated Alumina (6–8 Mesh)									
195	68.4	29.1	7.3	79.4	0.2	None	18.9	1.5	99.6
210	58.5	26.3	20.4	76.5	0.4	None	11.5	11.6	96.6
260	43.3	21.9	16.1	62.2	0.3	None	13.8	23.7	97.9
200	38.0	19.1	26.8	58.5	0.9	None	18.7	31.9	90.6
260	37.8	19.0	26.7	55.5	0.7	None	12.7	31.1	94.8
300	37.6	18.8	26.6	54.7	0.3	Trace	13.7	31.3	97.9
500	36.1	18.5	27.6	52.2	0.3	None	13.7	33.8	97.9

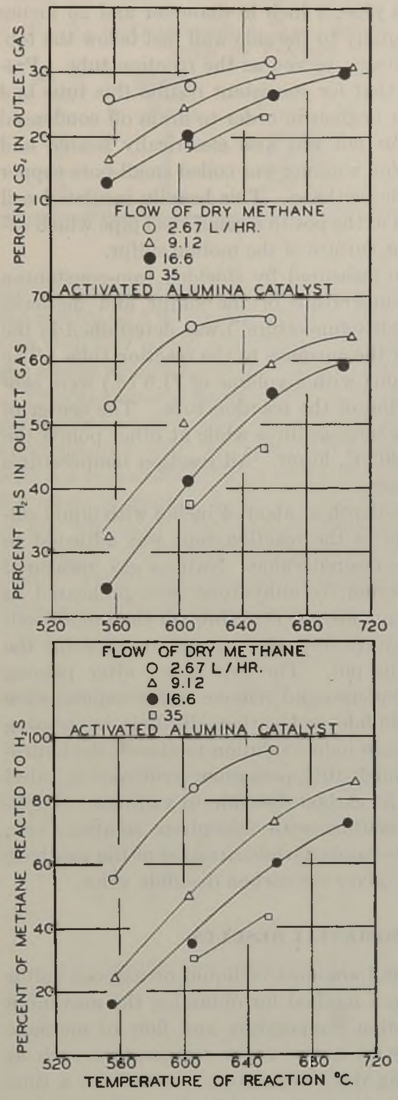

Figure 3. Effect of Temperature on Reaction $CH_4 + 4S \rightarrow CS_2 + 2H_2S$

By plotting the increasing vapor temperatures against per cent hydrogen sulfide and carbon disulfide in the outlet gas, curves similar to those of Figure 1 were obtained for each catalyst at each reaction temperature and flow. As Figure 1 shows, the hydrogen sulfide and carbon disulfide content of the issuing gas passes through a maximum. These maxima are accepted as the best yields possible for each set of conditions prevailing in the reaction tube. The hydrogen sulfide and carbon disulfide data shown in Table II and Figures 2, 3, and 4 are based on these values. The drop in yield after reaching a maximum seems primarily due to the increased space velocity.

The reaction with various catalysts was studied at temperatures from 550–800° C. and with flows of dry methane of 2.67–35 liters per hour. The results are recorded in Table II. The only catalysts tried that showed a marked catalytic effect were activated alumina and silica gel. The empty tube was better than any of the other catalysts tried, which was probably due to the reduced velocity through the reaction zone. Figure 2 shows the effect of the velocity of the gases through the reaction zone, the velocity being determined from the calculated outlet flow of gases with the volume of unreacted sulfur vapor ignored. Results for an empty tube and the glass bead catalysts fall on the same curve, which shows that increased surface alone did not aid the reaction.

As the reaction space used was 71.6 cc., the ratio of methane volume per hour (standard conditions) to reaction space for methane flows of 2.67, 4.74, 9.12, 16.6, and 35 liters per hour was, respectively, 37.3, 66.2, 127, 232, and 489. The total gas flow through the catalyst bed includes the volume of sulfur vapor present as well as that of the methane. An accurate determination of the volume of sulfur vapor is difficult, but from an examination of the vapor temperatures needed for maximum yields of hydrogen sulfide, it appears that a ratio of slightly less than four atoms of sulfur to one molecule of methane gave best results. Hence for maximum yields at temperatures of 700° C. and higher, where primarily S_2 gas is present, the total flow of gases will be slightly less than three times the methane flow. At lower temperatures, due to the presence of S_6 and S_8 gases, the total flow compared to methane flow will be further decreased. If space velocity is defined as total volume of gases passed per hour through unit volume of reaction space, and all the sulfur vapor is assumed as S_2, then these space velocities become, respectively, 112, 199, 381, 696, and 1467.

The upper graphs of Figures 3 and 4 indicate the range of yields of hydrogen sulfide and carbon disulfide obtainable with activated alumina catalyst as the reaction temperature is varied from 550° to 700° C. and the flow of methane from 2.67 to 35 liters per hour. It was found that, as a general rule, increasing the temperature of reaction increases the ratio of hydrogen sulfide to carbon disulfide, and that increasing the flow decreases the ratio. Likewise the ratio increases with increase in sulfur content of the vapors up to the point of maximum yield. Under all conditions tried, the ratio varied from 1.7 to 2.4, the higher and lower values being obtained only under conditions not commercially practical such as very low sulfur content and slow rates of flow. At maximum yield conditions and practical rates of flow the variation was between 1.9 and 2.0 with few exceptions. Since the methane gas used was natural gas containing 97% methane, the other 3% being mostly ethane, the theoretical ratio of hydrogen sulfide to carbon disulfide is slightly less than 2. This checks with the ratio experimentally obtained, and hence the reaction proceeds under maximum yield conditions according to Equation 2 without appreciable side reaction.

Under conditions which gave results slightly below maximum yields of hydrogen sulfide and carbon disulfide due to insufficient sulfur vapor, the ratio of hydrogen sulfide to carbon disulfide is low. Analysis of the exit gases showed the presence of 2.3–3.0% of hydrogen, an indication of some dissociation of hydrogen sulfide into hydrogen and sulfur.

When the rate of flow is very slow with reaction temperatures 700° C. and above, the ratio of hydrogen sulfide to carbon disulfide is above 2. This is probably due to the thermal decomposition of a small amount of methane into carbon and hydrogen with the latter uniting with sulfur to form hydrogen sulfide.

Calculations were made, based on reaction 2, of the percentage of methane reacted under various conditions by the following expression:

$$\%\text{ methane reacted} = \frac{0.5a}{0.5a + (100 - a - b)} \times 100$$

where $a = \%H_2S$, $b = \%CS_2$ in outlet gas

The results for activated alumina showing the marked effect of temperature and of slow rates of flow upon the percentage of methane reacted are given below and are illustrated in the lower graphs of Figures 3 and 4:

Flow, L./Hr.	Space Velocity	% Methane Reacted[a] to H_2S at: 550° C.	600° C.	650° C.	700° C.
2.67	112	52	81	94	..
9.12	381	22	48	71	84
16.60	696	13	36	57	72
35.00	1467		27	43	..

[a] Read from Figures 3 and 4.

REACTION OF CARBON DISULFIDE WITH WATER VAPOR

The gas leaving the first reaction tube contains hydrogen sulfide, carbon disulfide, methane, and small amounts of hydrogen. The sulfur is removed. The gas is then saturated with moisture at 65–85° C. to give definite volume ratios of water vapor to carbon disulfide, and is passed under varying conditions of temperature and space velocity through a second stainless steel reaction tube. This tube, 1 inch in diameter with a thermocouple in the center of its catalyst bed, was heated electrically. The flow of gas leaving the first reaction tube before saturation with moisture varied from 7 to 28 liters per hour.

The gas issuing from the second reaction tube was analyzed for hydrogen sulfide, carbon oxysulfide, carbon disulfide, and carbon dioxide. The hydrogen sulfide and carbon disulfide were determined, as already described with the intermediate removal of the carbonyl sulfide, by passing the gas after absorption in iodine solution through a 7.5% calcium chloride solution containing 1% ammonium hydroxide and finally through the alcoholic potassium hydroxide. Conversion of the sulfur in the calcium chloride solution to barium sulfate, etc., gave the amount of carbon oxysulfide. The carbon dioxide was determined by absorption in concentrated potassium hydroxide and correcting the absorbed volume by the amounts of hydrogen sulfide and carbonyl sulfide found in the first determination. All gas concentrations are reported in per cent by volume on a dry basis.

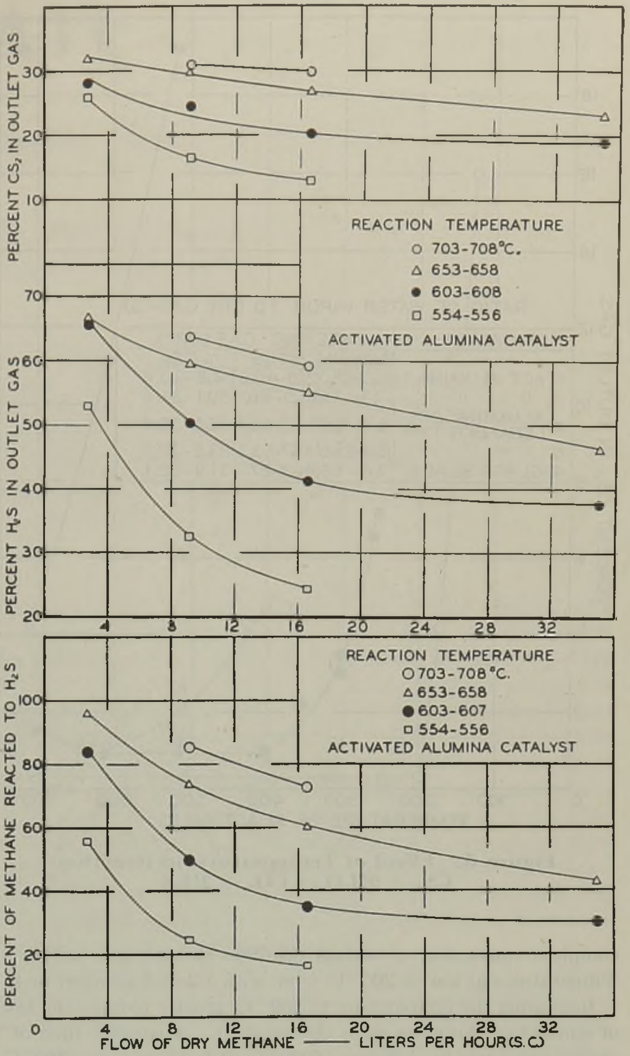

Figure 4. Effect of Flow of Methane on Reaction $CH_4 + 4S \rightarrow CS_2 + 2H_2S$

This reaction was studied using a large number of catalysts at various temperatures. Activated alumina was the best. The data for this catalyst, shown in Table III, indicate practically

TABLE IV. RELATIVE EFFICIENCY OF CATALYSTS[a] FOR REACTION $CS_2 + 2H_2O \longrightarrow CO_2 + 2H_2S$

Catalyst Used	Temp., ° C.	% Converted	Temp., ° C.	% Converted	Temp., ° C.	% Converted	Temp., ° C.	% Converted	Temp., ° C.	% Converted
Activated alumina	245	98.6	310	97.9	...	....	508	98.7	...	....
Uranium oxide on activated alumina	260	97.5	307	98.5	408	98.6	510	97.9	...	....
Thoria on pumice stone	251	64.7	310	96.5	413	95.0	...	....	...	....
Uranium oxide on pumice stone	...	....	320	87.7	415	92.2	513	94.9	600	97.3
Chromia on alumina	...	....	310	89.7	405	96.8	510	96.5	600	96.1
Magnesia on pumice stone	253	58.0	314	87.5	412	97.3	...	....	...	....
Porocel	265	77.7	334	79.6	415	93.4	520	95.5	615	93.8
Activated charcoal	...	....	325	53.4	418	83.0	513	85.0	603	85.9
Bauxite	...	....	306	64.2	400	67.8	504	71.7	600	76.5
Potassium oxide on pumice stone	...	....	300	3.9	410	83.1	502	81.9	...	....
Calcium oxide on pumice stone	...	....	310	12.4	402	61.0	508	93.2	...	....
Sodium oxide on pumice stone	...	....	307	4.4	405	22.0	503	80.0	...	....
Alumina of Lenander type	...	....	...	...	...	....	...	....	605	92.0
Bismuth oxide on pumice stone	...	....	302 300	8.9 2.7	...	....	503	41.3	602	90.9
Silica gel (2-in. bed)	...	....	...	...	405	9.2	...	....	602	56.1
Chromia on pumice stone	...	....	302	0	...	....	503	30.3	635	87.7
Nickel oxide on pumice stone	...	....	300	3.6	...	....	510	12.1	645	77.6
Manganese oxide on pumice stone	...	....	300	0	...	....	502	31.9	620	42.3
Tungstic oxide on pumice stone	...	....	302	4.6	...	....	508	10.7	...	....
Pumice stone	...	....	300	0	...	....	503	3.6	633	33.5
Lead oxide on pumice stone	...	....	300	0	...	....	506	7.5	605	12.6

[a] Empty reaction chamber gives very little reaction up to 700° C.

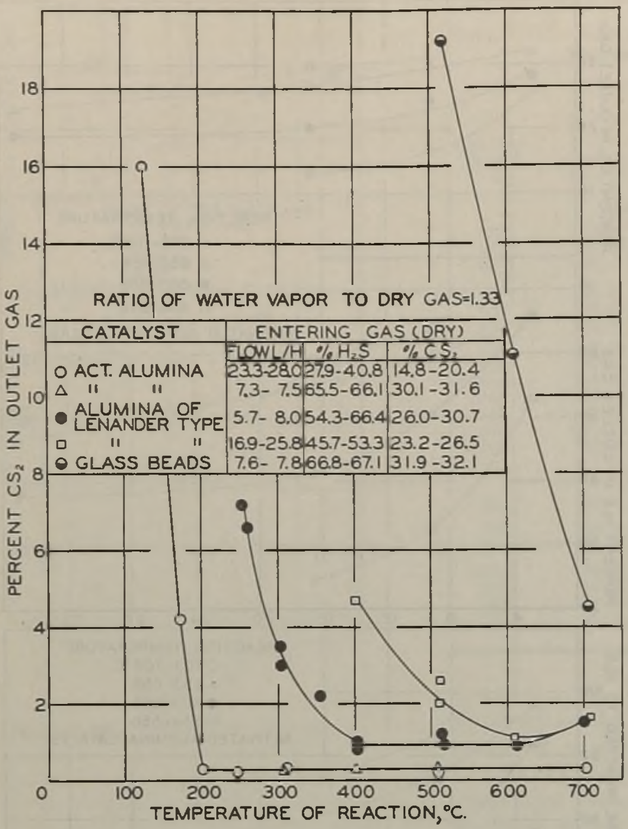

Figure 5. Effect of Temperature on Reaction $CS_4 + 2H_2O \rightarrow CO_2 + 2H_2S$

complete conversion of carbon disulfide to hydrogen sulfide at temperatures as low as 200° C. even with a 2-inch catalyst bed.

Increasing the temperature to 300° C. greatly reduces the time of contact of the gases with the catalyst. A contact time of 1 second appears to be sufficient at 200° C., 0.4–0.7 second at 260° C., and less than 0.4 second at 300° C. Further reduction of contact time should be possible at higher temperatures.

Comparative data given by other catalysts are shown in Table IV. No reaction takes place between carbon disulfide and water vapor in an empty tube at temperatures up to 700° C. With glass beads, at slow rates of flow, there is some reaction at 500–700° C. With alumina of the Lenander type (*5*) of catalyst, the reaction rate becomes appreciable and reaches its maximum value at 400–600° C., depending upon rates of flow. With silica gel the conversion is incomplete even with slow rates of flow and at temperatures as high as 600° C. Pumice stone shows very little reaction until temperatures well above 600° C. are reached. Oxides of uranium, thorium, and magnesium give good conversion at temperatures of 300° C. Activated charcoal, Porocel, and bauxite also show considerable reaction at 300° C.; oxides of potassium and calcium give appreciable reaction in the temperature range 400–500° C. Oxides of such metals as bismuth, chromium, nickel, manganese, tungsten, and lead are decidedly poor as catalysts for this reaction. Figure 5 shows the conversion of carbon disulfide to hydrogen sulfide by water vapor in the presence of some of these catalysts.

TABLE V. EFFECT OF VARYING THE CONCENTRATION OF WATER VAPOR ON CONVERSION OF CARBON DISULFIDE AT REACTION TEMPERATURE OF 303–316° C.

(Gases leaving first reaction before saturating with moisture: flow 28.7–30.7 liters/hour, 42.7–45.8% H_2S, 21.3–23.0% CS_2)

Volume Ratio of Water Vapor Added to Gases Leaving First Reaction	Theoretical Volume Ratio of Water Vapor of Gases Leaving First Reaction	CS_2 in Outlet Gas, %
5-In.-Long Bed of Activated Alumina (6–8 Mesh)		
0.44	0.444	0.8
0.61	0.430	0.3
0.88	0.426	0.2
2-In.-Long Bed of Activated Alumina (6–8 Mesh)		
0.33	0.436	5.1
0.44	0.456	0.8
0.61	0.460	0.3

The amount of water vapor necessary to give maximum conversion in the presence of activated alumina need be only slightly above the theoretical amount. Table V shows the effect of varying the water vapor concentration.

Some work was done on the direct reaction 1 by mixing water vapor, methane, and sulfur vapor, and passing the mixture through the catalyst bed. With glass beads at 700° C. the reaction was very incomplete. With activated alumina at 600° C. only 0.2–0.3% of carbon disulfide was found in the outlet gases with a small amount of sulfur dioxide due to the side reaction.

$$3\ S + 2\ H_2O \longrightarrow 2\ H_2S + SO_2 \qquad (A)$$

These results indicate that the direct reaction can be made to go to practical completion in the same temperature range required for reaction 2.

Addition of sulfur vapor to the inlet gases containing hydrogen sulfide, carbon disulfide, and water vapor, in the second reaction stage, using activated alumina at 300–500° C., produced no sulfur dioxide in the exit gases. This is due to the fact that the low temperatures and the high initial concentration of hydrogen sulfide favors the reverse of reaction A.

The final gases from the two-step process contain 0.2–0.3% carbon disulfide with hydrogen sulfide and carbon dioxide in the approximate volume ratio of 4 to 1, together with varying amounts of methane, occasional traces of carbonyl sulfide, and slight amounts of hydrogen. No sulfur dioxide, carbon monoxide, oxygen, or mercaptans are present.

CONCLUSION

A number of factors indicate that this process should be an economical method of making hydrogen sulfide. The material cost per pound of hydrogen sulfide is about 1.1 cents. The reaction temperatures, to obtain good yields at practical flows, are reasonably low—600–650° C. for the first reaction and 200–300° C. for the second reaction. Although two reaction zones may be needed, the process is a continuous one, requiring only the addition of low-pressure steam to the gases leaving the first zone. This steam cools the gases to a temperature satisfactory for the reaction in the second zone. Undesirable gases such as sulfur dioxide, carbon oxysulfide, and carbon disulfide are either absent or present in only small amounts. Moreover, it should be possible to remove the carbon dioxide by methods already suggested (*3*, *4*).

ACKNOWLEDGMENT

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CELLULOSE ACETATE FRACTIONS

Intrinsic Viscosity and Osmotic Molecular Weight

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The intrinsic viscosities and osmotically estimated number-average molecular weights of a series of cellulose acetate fractions have been measured. It was found that, within the range of chain lengths investigated (number-average molecular weight up to 130,000), the number-average molecular weights are proportional to the intrinsic viscosities in acetone solutions, in agreement with Staudinger's rule and the results of Kraemer. An estimate is provided of the relative homogeneity with respect to molecular size of the fractions and the starting material from which they were prepared.

According to Staudinger's rule, the molecular weight, M, of a linear high polymer is related to its intrinsic viscosity, $[\eta]$, by the expression (*9*):

$$[\eta] = KM$$

where $[\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c} \right)$
K = a constant
c = concentration, grams/100 ml. of solution

The validity of this relation has often been questioned, and it has recently been demonstrated (*3*, *5*) that several unbranched polymers do not conform to this rule, but rather to the more general relation:

$$[\eta] = KM^a$$

where a = a constant with a value between 0.5 and 2

Some time ago a series of cellulose acetate fractions was prepared in this laboratory, in connection with a study of the mechanical properties of this material (*8*). The starting material from which the fractions were prepared had an acetyl content of 38.6%, an ash content of 0.06%, a melting point of 250° C., and a char point of 301°.

The intrinsic viscosities and the osmotically estimated molecular weights of these fractions and the starting material have now been determined in acetone solutions. This paper, which presents the results of these measurements, shows that for this type of acetate and within the range of chain length investigated, the system cellulose acetate in acetone does conform to Staudinger's rule; i.e., for this system the constant a has the value unity in the relation cited above.

MEASUREMENTS

Viscosity. The viscosity measurements were made in an Ostwald viscometer at 25° ± 0.03° C. Since the time of efflux of the acetone was approximately only 30 seconds, kinetic energy corrections were applied (*1*). These were determined by calibrating the viscometer with oils of known viscosity, obtained at the National Bureau of Standards. (Failure to apply kinetic energy corrections leads to errors of several per cent in the values of the intrinsic viscosities of the fractions of higher molecular weight.)

Osmotic Pressure. The osmotic pressure values for all the fractions, except the one of lowest molecular weight, were determined by the dynamic method of Fuoss and Mead (*4*). The denitrated cellulose nitrate membranes recommended by these authors were used. The measurements were made at room temperature (approximately 28° C.). The cell was placed in a box insulated with cotton waste, and the entire assembly was then covered with a wooden hood in order to minimize drifts caused by changes in temperature. Measurements of the osmotic pressures were made by means of a cathetometer sighted through a window in the hood. It was found practical to use the same membrane for a series of measurements by using increasing concentrations of the same sample in successive measurements, as recommended by Fuoss and Mead (*4*). The membrane was then rinsed thoroughly with acetone, soaked overnight in this solvent, and rinsed thoroughly again, all without taking the membrane from the cell. This treatment sufficed to remove adhering cellulose acetate so that the membrane could be used again.

With the fraction of lowest molecular weight (No. 15), and to a lesser extent with the starting material, appreciable diffusion of the solute through the denitrated cellulose nitrate membranes occurred. For these two samples, cellophane membranes swollen with ammonium hydroxide, according to the directions of Flory (*3*), were therefore used. These measurements were made by the static method in a constant-temperature room. Equilibrium was reached overnight, after which no appreciable change in osmotic pressure occurred for several days.

Since the osmotic pressure measurements were made at slightly different temperatures, the number-average molecular weights, $\overline{M}_n$, were calculated as follows: The apparent value of $\overline{M}_n$ at each concentration (and corresponding temperature) was first calculated, using the van't Hoff relation, and the value of $\overline{M}_n$ at zero concentration was then obtained algebraically, assuming that the apparent value of $\overline{M}_n$ is a linear function of concentration.

RESULTS AND DISCUSSION

The results of the viscosity measurements are presented in Table I and shown graphically in Figure 1, where the values of η_{sp}/c are plotted on a logarithmic scale. When this procedure is followed, the results fall on straight lines suitable for extrapolation to zero concentration for obtaining the intrinsic viscosity. (When the values of η_{sp}/c and c are both plotted on a linear scale, the results do not fall on straight lines except at very low concentrations, where the experimental errors are largest. The use of the semilogarithmic plot gives weight to the more precisely determined values obtained in the range of higher concentration.)

The results of the viscosity measurements conform quite closely to Martin's equation (*7*):

$$\log \frac{\eta_{sp}}{c} = \log[\eta] + k[\eta]c \qquad (1)$$

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Table I. Viscosities of Cellulose Acetate Samples in Acetone Solutions at 25° C.

Sample[a]	Concn. Grams/ 100 Ml.	η_{sp}	η_{sp}/c	$[\eta]$
Starting material	0.126	0.218	1.73	1.59
	0.268	0.50_1	1.87	
	0.537	1.21_0	2.25	
Fraction 2	0.094	0.289	3.08	2.75
	0.273	0.99_9	3.66	
	0.546	2.77	5.08	
Fraction 3	0.096	0.278	2.89	2.59
	0.345	1.27_8	3.71	
	0.690	3.78	5.48	
Fraction 4	0.114	0.286	2.52	2.25
	0.351	1.10_1	3.13	
	0.703	3.12	4.43	
Fraction 5	0.110	0.251	2.28	2.06
	0.384	1.10_7	2.88	
	0.769	3.14	4.08	
Fraction 6	0.118	0.247	2.09	1.91
	0.353	0.89_1	2.52	
	0.775	2.70	3.48	
Fraction 7	0.119	0.224	1.88	1.72
	0.358	0.79_5	2.22	
	0.877	2.81	3.21	
Fraction 8	0.138	0.239	1.74	1.60
	0.275	0.52_1	1.89	
	0.428	0.88_5	2.07	
Fraction 9	0.152	0.226	1.49	1.37
	0.271	0.42_5	1.57	
	0.541	0.98_3	1.82	
Fraction 10	0.152	0.209	1.38	1.28
	0.303	0.45_0	1.49	
	0.684	1.23_6	1.81	
Fraction 11	0.149	0.179	1.20	1.13
	0.297	0.385	1.30	
	0.625	0.94_0	1.50	
Fraction 12	0.147	0.159	1.08	1.02
	0.294	0.338	1.15	
	0.533	0.67_1	1.26	
Fraction 13	0.149	0.108	0.72	0.70
	0.269	0.199	0.74	
	0.403	0.305	0.76	
Fraction 14	0.147	0.089	0.61	0.59
	0.335	0.210	0.63	
	0.587	0.390	0.66	
Fraction 15	0.273	0.063	0.23_1	0.23
	0.411	0.097	0.23_6	

[a] The samples are numbered in the order of molecular weight to conform with their designations in a previous publication (*4*). The lowest number represents the sample of highest molecular weight.

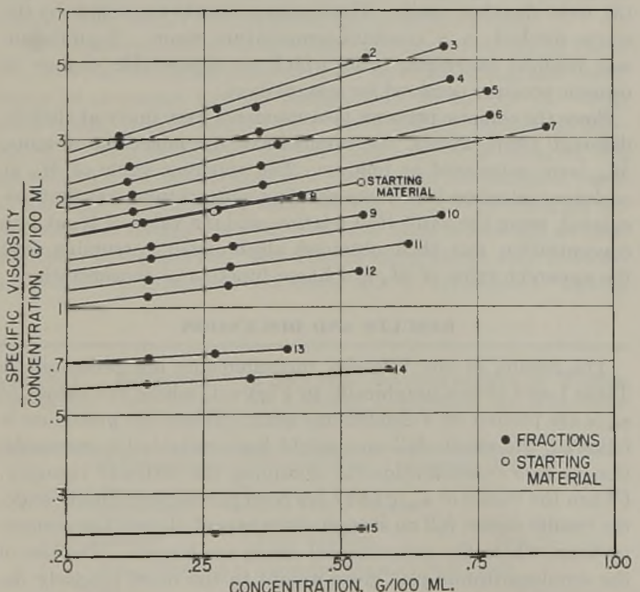

Figure 1. Viscosity-Concentration Relation in Acetone Solutions for Cellulose Acetate Samples

The samples are numbered in the order of molecular weight to conform with their designations in a previous publication (*4*). The lowest number represents the sample of highest molecular weight.

where c is the concentration and k is a constant characteristic of a given polymeric series in a given solvent. It should be noted that the concentration is expressed in grams per 100 ml. of solution in the data presented here, whereas it is given as weight per cent in the reference (*7*). The values of $[\eta]$ in Table I were obtained by algebraic extrapolation, using the method of least squares.

The results of the osmotic pressure measurements are given in Table II. Since it has been shown that a plot of the reduced osmotic pressure (π/c) against c gives straight lines for samples of cellulose acetate in acetone (*2*), the osmotic pressure values were measured at only two concentrations for most of the samples. The slopes of the lines obtained by plotting π/c against c are nearly identical for all of the samples except the two fractions of lowest molecular weight (14 and 15) which give larger slopes. Fraction 15 diffused through the denitrated cellulose nitrate membranes of Fuoss and Mead (*4*). When measurements were made by the dynamic method with these membranes and the results extrapolated back to zero time, the apparent value of $\overline{M}_n$ for fraction 15 was 16,000. The value of $\overline{M}_n$ when the less permeable swollen cellophane membranes were used was 11,000 (Table II).

Figure 2 shows the relation between the intrinsic viscosities and number-average molecular weights of the acetate fractions. The results appear to fall on a straight line passing through the origin, although the points for the two fractions of highest molecular weight appear to deviate somewhat from a line drawn through the remaining data. This deviation may be real, which would suggest that at higher values of molecular weight, the value of $[\eta]$ may increase less rapidly than $\overline{M}_n$ (i.e., the value of a is less than unity in the equation $[\eta] = KM^a$). Results of this type have been obtained by Gralen and Svedberg for cellulose in cuprammonium (*5*). It should be noted, however, that these fractions cover the usual molecular weight range of commercial cellulose acetates. If the data are treated as though they conform with the relation $[\eta] = KM^a$, a value for a of 1.03 is obtained by the method of least squares. It should be noted that the value of a

Table II. Osmotic Pressures of Cellulose Acetate Samples in Acetone Solutions

Sample	Concn., Gram/ 100 Ml.	Osmotic Pressure, Cm. Acetone	Temp., ° C.	Apparent $\overline{M}_n$	$\overline{M}_n$
Starting material	0.240	1.96	26	40,000	42,000
	0.449	3.71	26	39,000	
	0.837	7.19	21	37,000	
	0.899	8.03	26	36,000	
Fraction 2	0.259	0.67	26	126,000	130,000
	0.547	1.47	24	121,000	
Fraction 3	0.345	1.10	28	102,000	110,000
	0.690	2.37	28	95,000	
Fraction 4	0.351	1.37	27	84,000	86,000
	0.703	2.83	27	81,000	
Fraction 5	0.384	1.71	30	74,000	78,000
	0.769	3.59	30	71,000	
Fraction 6	0.388	1.82	30	70,000	76,000
	0.775	3.98	31	64,000	
Fraction 7	0.439	2.49	32	59,000	62,000
	0.877	5.33	33	55,000	
Fraction 8	0.428	2.44	24	57,000	61,000
	0.855	5.27	25	53,000	
Fraction 9	0.136	0.85	28	52,000	53,000
	0.182	1.15	28	52,000	
	0.271	1.75	30	51,000	
Fraction 10	0.342	2.42	24	46,000	48,000
	0.684	5.14	25	43,000	
Fraction 11	0.312	2.59	30	40,000	42,000
	0.625	5.44	31	38,000	
Fraction 12	0.266	2.68	30	33,000	34,000
	0.533	5.49	31	32,000	
Fraction 13	0.135	1.34	30	33,000	33,000
	0.269	2.67	30	33,000	
Fraction 14	0.168	2.41	25	23,000	24,000
	0.335	5.15	26	21,000	
Fraction 15	0.146	4.52	25	10,400	11,000
	0.291	9.75	25	9,700	

is very sensitive to the results obtained for the fractions of lower molecular weight. Moderately small errors in the results for these fractions might change the value for *a* appreciably.

From the best straight line drawn through results shown in Figure 2, the following average relation is obtained:

$$\overline{DP}_n = 150[\eta]$$

where $\overline{DP}_n$ = number-average degree of polymerization

(The weight per glucose residue of cellulose acetate of this degree of acetylation is 260.) The corresponding result obtained by Staudinger (*9*), who also used osmotic pressure measurements to calibrate his viscosity method, is $\overline{DP}_n = 110\ [\eta]$. It should be noted that this relation holds only for fractions of this particular degree of homogeneity. Viscosity results should properly be related to weight-average or viscosity-average molecular weights, rather than to number-average values. No estimate of $\overline{DPn}$ can be obtained by viscosity measurements made on an unfractionated sample, or a fractionated sample of unknown degree of homogeneity.

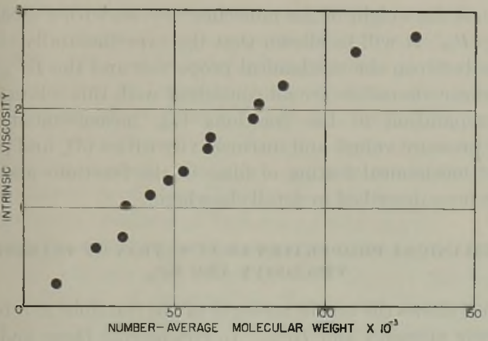

Figure 2. Relation between Intrinsic Viscosity and Osmotically Estimated Molecular Weight for Cellulose Acetate Fractions

Kraemer measured the molecular weights of a series of secondary cellulose acetates by sedimentation equilibrium in the ultracentrifuge, and obtained the relation (*6*):

$$\overline{DP}_w = 230[\eta]$$

where $\overline{DP}_w$ = weight-average degree of polymerization

These results suggest that the cellulose acetate fractions used in this study are more homogeneous than those employed by Staudinger, but that they are not sufficiently homogeneous so that their weight- and number-average *DP* values are equal. This is shown by the results in Table III.

Column 2 gives the number-average *DP* values of the fractions and starting material as obtained from the osmotic pressure measurements. Column 3 lists the intrinsic viscosities, and column 4 the product 230 $[\eta]$ which, according to Kraemer's results, should approximate $\overline{DP}_w$. Since the ratio $\overline{DP}_w/\overline{DP}_n$ is unity for a perfectly homogeneous polymer, and increases with the heterogeneity with respect to molecular size, the value of the ratio may be taken as a measure of this heterogeneity. Because of the uncertainty involved in applying Kraemer's constant to these samples, the ratios $\overline{DP}_w/\overline{DP}_n$ should not be taken as absolute values. (Measurements of $\overline{DP}_w$ for several of these samples by ultracentrifugal and light-scattering methods are in progress.) The values of this ratio for the several samples are shown in column 5. The starting material, with a ratio $\overline{DP}_w/\overline{DP}_n$ of 2.3, is manifestly less homogeneous than any of the fractions, the ratios for which range between 1.2 and 1.8. The fact that the lowest value obtained for this ratio is slightly higher than unity is entirely consistent with Kraemer's results. However, the heterogeneity of all the samples may be somewhat different from that indicated by these ratios, since the value of Kraemer's constant is subject to some uncertainty (*6*). The results indicate that the samples have not all been fractionated to the same degree.

TABLE III. COMPARATIVE $\overline{DP}_n$ AND INTRINSIC VISCOSITY RESULTS FOR CELLULOSE ACETATE SAMPLES

Sample	$\overline{DP}_n$	$[\eta]$	$230[\eta]$	$\frac{230[\eta]}{\overline{DP}_n}$
Starting material	160	1.59	366	2.3
Fraction 2	502	2.75	633	1.3
Fraction 3	422	2.59	596	1.4
Fraction 4	331	2.25	518	1.6
Fraction 5	298	2.06	474	1.6
Fraction 6	291	1.91	439	1.5
Fraction 7	240	1.72	396	1.7
Fraction 8	234	1.60	368	1.6
Fraction 9	204	1.37	315	1.5
Fraction 10	186	1.28	294	1.6
Fraction 11	160	1.13	260	1.6
Fraction 12	131	1.02	234	1.8
Fraction 13	127	.70	161	1.3
Fraction 14	92	.59	136	1.5
Fraction 15	43	.23	53	1.2

From the values in Table III and the yields of the fractions, summated values of $[\eta]$ and $\overline{DP}_n$ can be calculated. These calculated values are $[\eta] = 1.50$ and $\overline{DP}_n = 175$, compared with experimental values for the starting material of 1.59 and 160, respectively. Since the results do not include fraction 1, which was not completely soluble in acetone, and since a certain amount of loss is inevitable in a long fractionation procedure, these results represent reasonably good agreement between the calculated and observed values.

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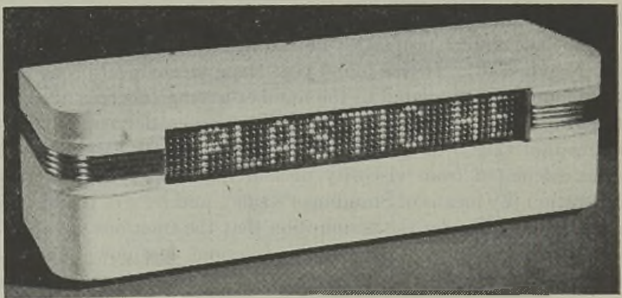
THIS paper (and the one which follows) were presented under the title "Mechanical Properties of Cellulose Acetate as Related to Molecular Chain Length", in the Symposium on Cellulose and Cellulose Plastics before a joint session of the Divisions of Cellulose Chemistry and of Paint, Varnish, and Plastics Chemistry at the 108th Meeting of the AMERICAN CHEMICAL SOCIETY in New York, N. Y. The authors were Research Associates at the National Bureau of Standards representing the Textile Foundation.



Illuminated Motion Display Sign of Transparent Cellulose Acetate (Courtesy, Monsanto Chemical Company)

Polymolecularity and Mechanical Properties of Cellulose Acetate

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The tensile strength, ultimate elongation, and folding endurance of films prepared from a series of cellulose acetate fractions and blends were studied. When the mechanical properties are plotted against the intrinsic viscosities (or relative weight-average degrees of polymerization), the results for the fractions and different blends fall on separate curves. In contrast, when the mechanical properties are plotted against the number-average degrees of polymerization, the results for the fractions and all of the blends fall approximately on a single curve for each property. The results are shown to be qualitatively consistent with the hypothesis that the mechanical properties of blends are the weight averages of the properties of their components:

$$\text{Property}_{\text{blend}} = \Sigma w_i P_i / \Sigma w_i$$

where w_i is the weight of the molecular species with a mechanical property P_i. The results emphasize the importance of the determinations of the number-average degree of polymerization in studying commercial polymolecular materials.

HIGH polymers are, in general, polymolecular—that is, heterogeneous with respect to molecular size. The problem of the influence of the degree of polymolecularity on the mechanical properties of such materials is important, and it has received considerable study in recent years. The detailed results of these investigations are reviewed elsewhere (*2*, *8*, *9*). The procedure generally followed in these studies was to fractionate a polymer with respect to molecular size and compare the mechanical properties of the fractions with those of blends. There has been substantial agreement among the more recent investigators that fractionated cellulosic materials are superior in mechanical properties to blends of the same intrinsic viscosity—i.e., the same weight-average molecular weight (*4*, *6*, *8*). In particular, it has been found that the presence of material of low molecular weight exerts a harmful influence on the mechanical properties of blends. These results appear to be unambiguous only for unoriented or slightly oriented specimens; it is possible that other conclusions may be reached when oriented or crystallized materials are considered.

In an approach to this problem a large quantity of commercial cellulose acetate was fractionated in this laboratory (*7*), and some of the mechanical properties of the fractions and their blends were studied (*6*). It was found that these mechanical properties were more closely related to the number-average degrees of polymerization ($\overline{DP}_n$) than to the weight-average degrees of polymerization ($\overline{DP}_w$) of the samples. However, $\overline{DP}_w$ was at that time calculated from viscosity measurements at only one concentration (by means of Staudinger's rule), and $\overline{DP}_n$ of the blends was calculated under the assumption that the fractions were perfectly homogeneous. $\overline{DP}_n$ of the fractions has now been determined experimentally by osmotic pressure measurements in acetone solution, and their intrinsic viscosities have been determined in the same solvent (*5*). The purpose of this discussion is to re-examine the data for the mechanical properties of the fractions and blends in the light of these new measurements of $\overline{DP}_n$ and intrinsic viscosity. In addition, examination of the data shows that, to a first approximation, the mechanical properties of the blends are the weight averages of the properties of their components:

$$\text{Property}_{\text{blend}} = \Sigma w_i P_i / \Sigma w_i \tag{1}$$

where w_i is the weight of the molecular species with a mechanical property P_i. It will be shown that the experimentally obtained relations between the mechanical properties and the $\overline{DP}_n$ values and intrinsic viscosities are all consistent with this relation.

The separation of the fractions (*7*), measurement of the osmotic pressure values and intrinsic viscosities (*5*), and preparation and mechanical testing of films of the fractions and blends (*6*) have been described in detail elsewhere.

MECHANICAL PROPERTIES AS FUNCTION OF INTRINSIC VISCOSITY AND $\overline{DP}_n$

Figure 1 shows the tensile strength of the fractions as a function of intrinsic viscosity and $\overline{DP}_n$. In considering these and subsequent data (Figures 1 to 6), the intrinsic viscosity may be taken as a direct measure of $\overline{DP}_w$ on the basis of Kraemer's results (*1*), and because of the linear relation between $\overline{DP}_n$ and $[\eta]$ (intrinsic

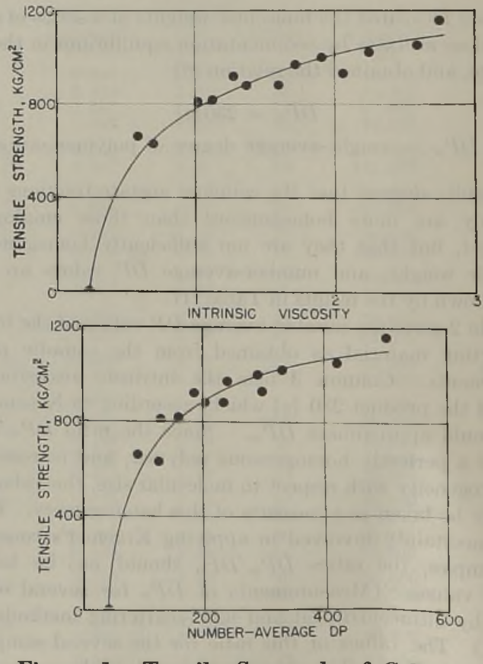

Figure 1. Tensile Strength of Cellulose Acetate Fractions as a Function of Intrinsic Viscosity (Upper Graph) and $\overline{DP}_n$ (Lower)

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viscosity) found for the fractions (*5*). Because of the uncertainty in the value of Kraemer's constant, the data are plotted as a function of $[\eta]$ rather than of $\overline{DP}_w$. (The scale of the axis of abscissas in each upper graph of Figures 1 to 6 has, however, been so adjusted that it compares directly with the *DP* axis of the lower graph, assuming Kraemer's relation: $\overline{DP}_w = 230\ [\eta]$.)

The curves have a large slope in the region of small chain length, followed by a gradually decreasing slope which may represent an approach to an asymptotic value for very high *DP* values. Similarly shaped curves have been observed for numerous polymers (*3*). The fraction of lowest chain length ($\overline{DP}_n = 43$) was so brittle that it would not form a coherent film of sufficient size to be tested by ordinary techniques, and it has therefore been assigned a strength of zero. Small fragments of this sample were tested by special techniques, however, and a strength as high as 250 kg. per sq. cm. was obtained. This result suggests that the failure to obtain measurable strengths for this and other samples of very low *DP* results from the inadequacy of the film casting and testing techniques, rather than from the weakness of the sample. Although it is true that such materials have zero strength as far as their practical utilization is concerned, the possibility exists that the curve relating strength to *DP* would pass through the origin if suitable testing techniques were used.

Figure 2 shows the ultimate elongations of the fractions, plotted in the same manner as the tensile strength results. The shapes of the latter curves are generally similar to those for the tensile strength data, except that the approach to a limiting value is completed at a lower *DP* for the ultimate elongation results. As Figure 3 shows, entirely analogous results were obtained for the measurements of the folding endurances of the fractions (made on a Massachusetts Institute of Technology fold tester).

To study the effect of distribution of chain length on mechanical properties, blends were prepared from pairs of the fractions. The major portion of the work on blends was done with three series, made by mixing in various proportions pairs of fractions of the following $\overline{DP}_n$: 502 + 43, 502 + 127, and 502 + 204. (These same pairs of fractions are identified by their intrinsic viscosities of 2.75 + 0.23, 2.75 + 0.70, and 2.75 + 1.37, respectively.) A number of miscellaneous blends and the starting material were also studied. The intrinsic viscosity and $\overline{DP}_n$ of the blends were calculated from their known weight composition and the intrinsic viscosity and $\overline{DP}_n$ of the fractions.

The intrinsic viscosities of the blends were calculated from the formula

$$[\eta]_{\text{blend}} = f_1[\eta]_1 + f_2[\eta]_2$$

where f_1 and f_2 are the weight fractions in the blend of the components of intrinsic viscosities $[\eta]_1$ and $[\eta]_2$, respectively. The values of $\overline{DP}_n$ for the blends were obtained from the relation:

$$\overline{DP}_{n\text{blend}} = \frac{1}{\dfrac{f_1}{\overline{DP}_{n_1}} + \dfrac{f_2}{\overline{DP}_{n_2}}}$$

where f_1 and f_2 are the weight fractions in the blend of the components of $\overline{DP}_{n_1}$ and $\overline{DP}_{n_2}$, respectively.

Calculated rather than experimental values of $[\eta]$ and $\overline{DP}_n$ for the blends were used because of the unquestioned validity of the calculation procedure, and because samples of the original blends sufficient for the experimental measurements were not available.

Figure 4 shows the tensile strength of the blends as a function of both intrinsic viscosity (upper graph) and $\overline{DP}_n$ (lower). The respective curves for the fractions, traced from the smooth curves of Figure 1, are included for comparison. As the upper graph of Figure 4 shows, the strengths of the blends are in general lower than those of the fractions when the results are plotted against intrinsic viscosity (or relative $\overline{DP}_w$). Further, the discrepancy between the curve for the fractions and that for a series of blends appears to increase with increasing difference in chain length between the components in a given series. Thus, the open circles, which represent blends of the longest and shortest chain lengths, fall farthest below the curve for the fractions. In contrast, when the tensile strengths are plotted against $\overline{DP}_n$ (lower graph, Figure 4), the results for the blends, including the starting material and a number of miscellaneous blends not shown in the upper graph, in general fall closer to the smooth curve for the fractions. However, the open circles (which represent blends of the longest and shortest chain lengths) fall consistently somewhat above the smooth curve. The possible cause for this will be discussed below.

The results of the ultimate elongation measurements on blends (Figure 5) are qualitatively similar to the tensile strength data, but the differences between the upper and lower graphs are more clearly defined. In the upper graph, the curves for the blends of

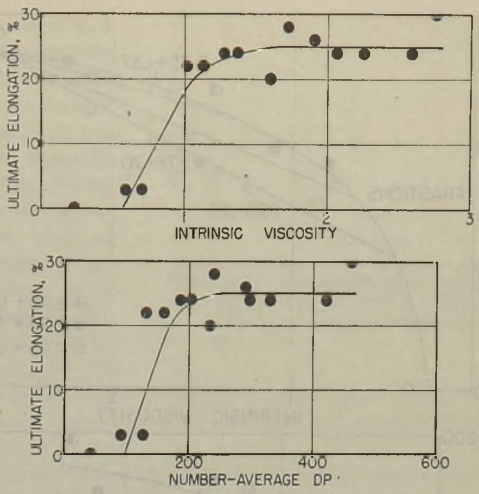

Figure 2. Ultimate Elongation of Cellulose Acetate Fractions as a Function of Intrinsic Viscosity (Upper Graph) and $\overline{DP}_n$ (Lower)

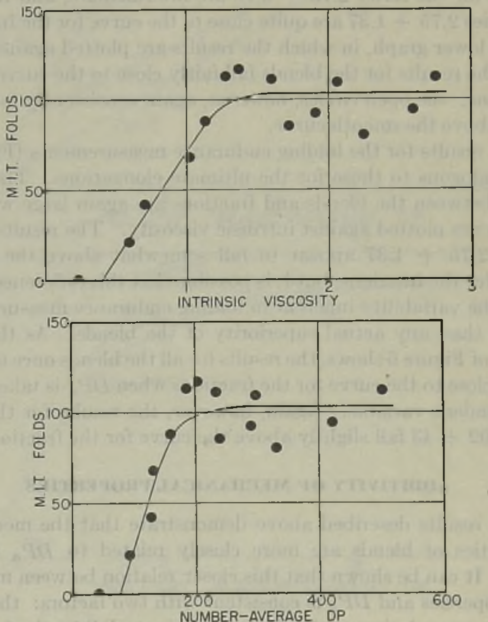

Figure 3. Folding Endurance of Cellulose Acetate Fractions as a Function of Intrinsic Viscosity (Upper Graph) and $\overline{DP}_n$ (Lower)

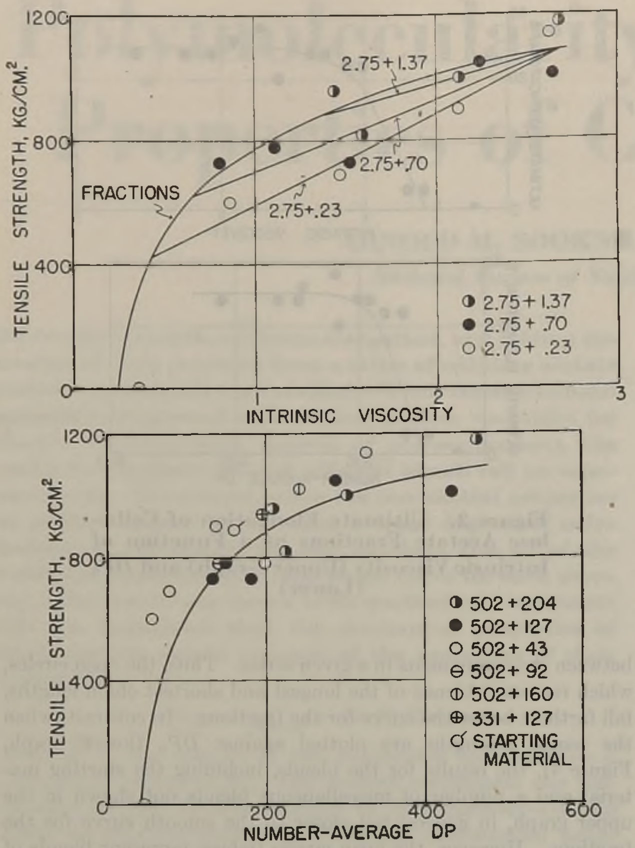

Figure 4. **Tensile Strength of Blends of Cellulose Acetate Fractions as a Function of Intrinsic Viscosity (Upper Graph) and $\overline{DP}_n$ (Lower)**

The curve for the fractions (traced from Figure 1) is included for comparison.

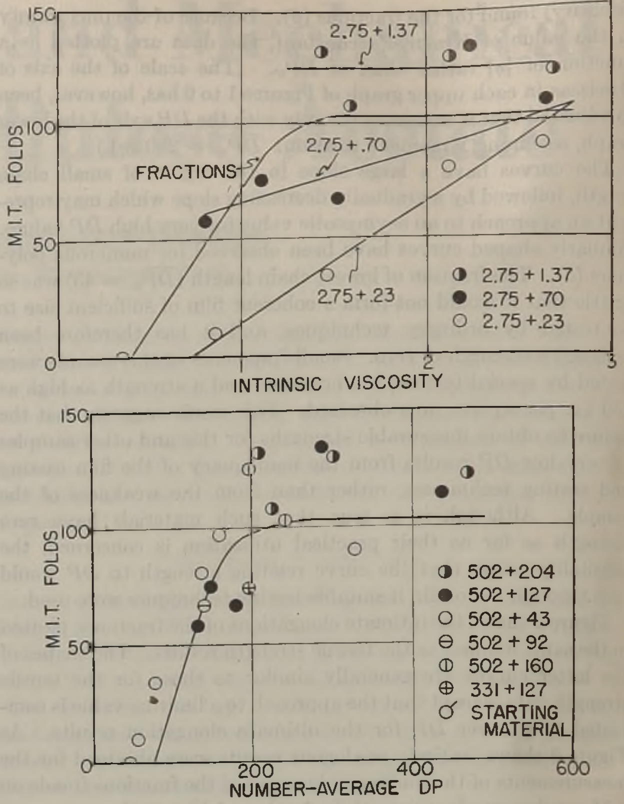

Figure 5. **Ultimate Elongation of Blends of Cellulose Acetate Fractions as a Function of Intrinsic Viscosity (Upper Graph) and $\overline{DP}_n$ (Lower)**

The curve for the fractions (traced from Figure 2) is included for comparison.

fractions of intrinsic viscosity 2.75 + 0.23 fall markedly below the smooth curve for the fractions (traced from Figure 2); the results for the series 2.75 + 0.70 are intermediate, and those for the series 2.75 + 1.37 are quite close to the curve for the fractions. In the lower graph, in which the results are plotted against $\overline{DP}_n$, all of the results for the blends fall fairly close to the curve for the fractions; the open circles, however, again consistently fall somewhat above the smooth curve.

The results for the folding endurance measurements (Figure 6) are analogous to those for the ultimate elongations. The differences between the blends and fractions are again large when the results are plotted against intrinsic viscosity. The results for the series 2.75 + 1.37 appear to fall somewhat above the smooth curve for the fractions, but it is possible that this difference results from the variability inherent in folding endurance measurements, rather than any actual superiority of the blends. As the lower graph of Figure 6 shows, the results for all the blends once more fall fairly close to the curve for the fractions when $\overline{DP}_n$ is taken as the independent variable. Again, however, the results for the series $\overline{DP}_n$ 502 + 43 fall slightly above the curve for the fractions.

ADDITIVITY OF MECHANICAL PROPERTIES

The results described above demonstrate that the mechanical properties of blends are more closely related to $\overline{DP}_n$ than to $\overline{DP}_w$. It can be shown that this closer relation between mechanical properties and $\overline{DP}_n$ is consistent with two factors: the shape of the curve relating mechanical properties to DP for the fractions, and the fact that the mechanical properties of a blend are the weight averages of the properties of their components (Equation 1). The second point will be considered first.

Examination of the tensile strength data for the blends reveals that if a strength of approximately 260 kg. per sq. cm. is assigned to the fraction of lowest DP, for which no precise experimental value could be obtained, the strength of each blend is the weight average of the strengths of its components. This is shown in Figure 7, where the observed strength of each blend is plotted against the value calculated (according to Equation 1) from the weight percentages and strengths of the fractions of which it is composed. A line of 45° slope passing through the origin is included for comparison. The one blend which departs seriously from the line (observed strength 0, calculated strength 310) was a 95:5 mixture by weight of the fractions of shortest and longest chain lengths, respectively. This blend, like the fraction of lowest DP, was too brittle to give a film suitable for testing.

A similar relation between the observed and calculated ultimate elongations of the blends can also be demonstrated; but because of the lower precision of these results, the agreement between the observed and calculated values is not so good as for the tensile strength measurements. The folding endurances of all the blends except those containing the fraction of smallest chain length ($\overline{DP}_n$ = 43) are also approximately additive. For the latter blends, the folding endurance values are additive only if the fraction of $\overline{DP}_n$ 43 is assumed to have a negative folding endurance. This somewhat unreasonable result is, however, consistent with the shape of the curve relating folding endurance to $\overline{DP}_n$ for the fractions (Figure 3), since extrapolation of this curve to a $\overline{DP}_n$ of 43 would lead to a negative folding endurance.

It is now of interest to examine the consequences of applying the concept of additivity of mechanical properties to curves relating such properties to chain length for fractionated materials. For this purpose the curve shown in Figure 8 was chosen. It should

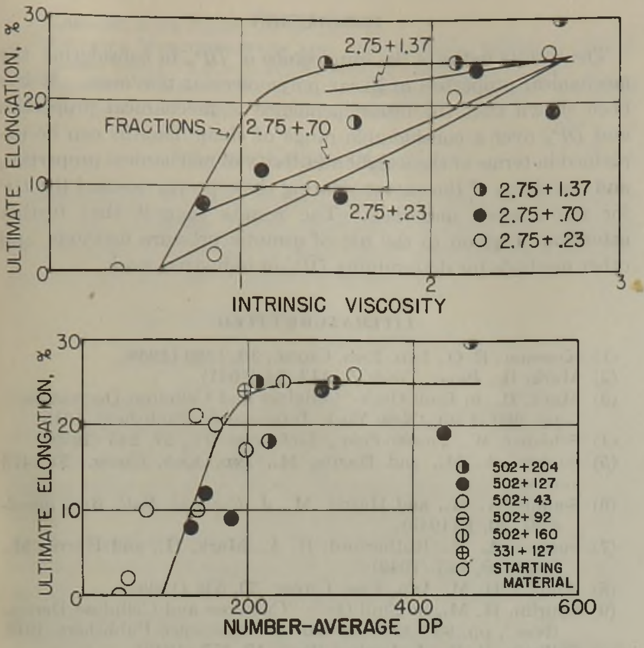

Figure 6. Folding Endurances of Blends of Cellulose Acetate Fractions as a Function of Intrinsic Viscosity (Upper Graph) and $\overline{DP}_n$ (Lower)

The curve for the fractions (traced from Figure 3) is included for comparison.

be emphasized, however, that the results described below would be qualitatively similar if any of the experimental curves of Figures 1 to 3 were used in this discussion. Figure 8 is a theoretical curve calculated from the equations of Sullivan (*10*), relating strength and fiber length of yarns which are perfectly homogeneous with respect to fiber length. According to Sullivan's analysis (*10*), to the left of the broken line in Figure 8, yarn breakage occurs solely by slippage of the fibers. Since the strength is contributed solely by frictional forces in this range, it is directly proportional to fiber length. To the right of the broken line the frictional forces are sufficiently large to cause some fiber breakage, and the strength approaches asymptotically to a maximum value at which all fibers break. The analogy between frictional forces between fibers in a yarn and interchain forces in a film or filament is fairly close, but it is not suggested that the breaking in tension of a film can be explained in terms of this analysis. Thus, the breaking of a film includes a complex process of flow and crystallization, for which there is no counterpart in a yarn. The two processes do, however, contain a number of interesting points of similarity.

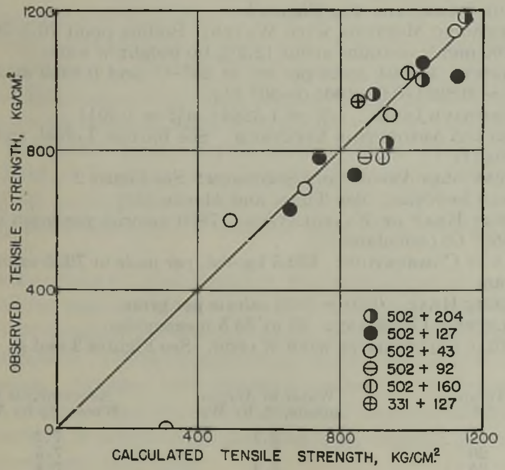

Figure 7. Observed Tensile Strength of Blends of Cellulose Acetate Fractions as a Function of Strength Calculated According to the Assumption That Strengths of Fractions Are Additive (Equation 1)

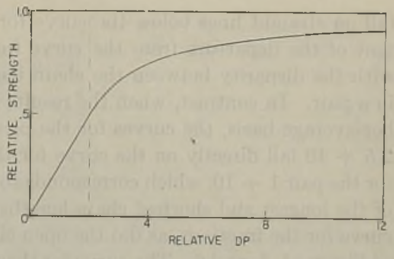

Figure 8. Theoretical Curve Relating Strength to *DP* for Perfectly Homogeneous Polymers

Figure 8 differs qualitatively from typical experimental curves only in that it passes through the origin. As suggested above, however, the failure of the experimental strength–*DP* curves to pass through the origin may well result from technical difficulties in film preparation and testing. In any case, this difference does not seriously affect the conclusions drawn below.

Figure 9 shows the strengths of blends, calculated from the curve of Figure 8, assuming additivity of strength. As in the experimental curves, the strengths are plotted on both weight- and number-average bases. Results for four series of blends are plotted, representing varying proportions of the following pairs: 4 + 10, 2.5 + 10, 1 + 10, and 0.01 + 10. The numbers were so chosen that the first three of these approximately represent the three series of blends studied experimentally, and the last is roughly equivalent to blends of the fraction of highest *DP* and a monomer. As the upper graph shows, when the results are plotted on a weight-average basis, the calculated strengths of the blends

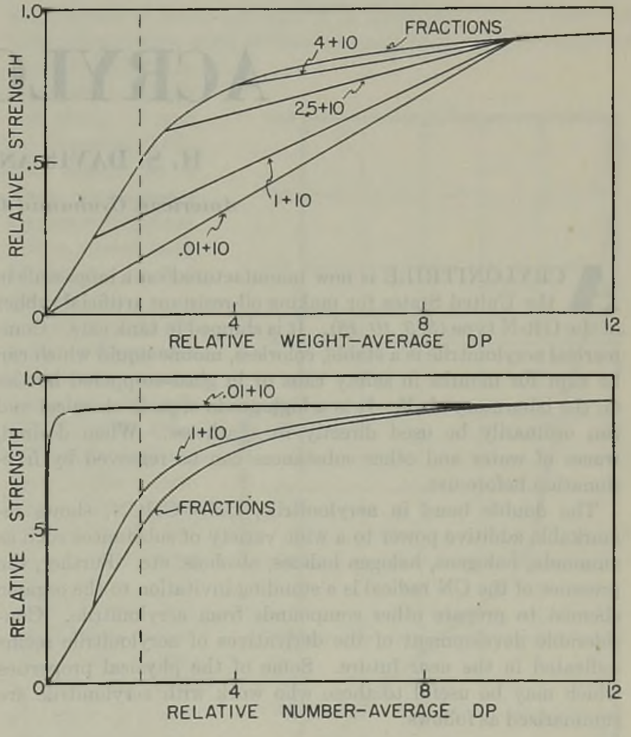

Figure 9. Theoretical Curves Relating Strength to $\overline{DP}_w$ (Upper Graph) and $\overline{DP}_n$ (Lower) for Blends of Homogeneous Polymers

The curve for the fractions is identical with that given in Figure 8.

fall on straight lines below the curve for the fractions. The extent of the departure from the curve for the fractions increases with the disparity between the chain lengths of the components in a pair. In contrast, when the results are plotted on the number-average basis, the curves for the blends of pairs 4 + 10 and 2.5 + 10 fall directly on the curve for the fractions. The curve for the pair 1 + 10, which corresponds to the experimental blends of the longest and shortest chain lengths, falls slightly above the curve for the fractions, as did the open circles in the lower graphs of Figures 4, 5, and 6. The curve for the pair 0.01 + 10, however, falls far above the curve for the fractions; this result is also in accord with experience (*9*). Thus these curves, which merely represent a statement of the weight additivity of the strength, reproduce all the features of the experimental data. It is perhaps worth noting that the series 1 + 10 (and the corresponding experimental series as well) contains blends considerably more heterogeneous than the common, unplasticized, commercial polymers. Thus, some of the blends in this series have a ratio of $\overline{DP}_w/\overline{DP}_n$ higher than 3, as compared with a value of about 2 for most ordinary polymers. Even for this series, however, the mechanical properties are much more closely related to $\overline{DP}_n$ than to $\overline{DP}_w$.

The discussion above provides only a limited and qualitative approach to the problem of the mechanical properties of blends as related to the properties of their components. Further, the conclusions should be taken as applying principally to strength properties rather than to the more complicated properties such as ultimate elongation and folding endurance. It is felt, however, that the concept of additivity of mechanical properties should prove helpful in some types of practical work and may provide a basis for a more detailed analysis of the problem.

CONCLUSION

The results indicate the importance of $\overline{DP}_n$ in considering the mechanical properties of linear polymolecular polymers. It has been shown that the interdependence of mechanical properties and $\overline{DP}_n$ over a considerable range of chain lengths can be explained in terms of the weight additivity of mechanical properties, and the shape of the curves relating these properties and the DP for fractionated materials. The results suggest that further attention be given to the use of osmotic pressure methods, and other methods for determining $\overline{DP}_n$ in industrial work.

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This paper (and the one which precedes) were presented under the title "Mechanical Properties of Cellulose Acetate as Related to Molecular Chain Length", in the Symposium on Cellulose and Cellulose Plastics before a joint session of the Divisions of Cellulose Chemistry and of Paint, Varnish, and Plastics Chemistry at the 108th Meeting of the American Chemical Society in New York, N. Y. The authors were Research Associates at the National Bureau of Standards, representing the Textile Foundation.

PHYSICAL PROPERTIES OF ACRYLONITRILE

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ACRYLONITRILE is now manufactured on a large scale in the United States for making oil-resistant artificial rubber of the GR-N type (*3, 9, 10, 13*). It is shipped in tank cars. Commercial acrylonitrile is a stable, colorless, mobile liquid which can be kept for months in safety cans or in glass-stoppered bottles on the laboratory shelf. It is a high-grade organic chemical and can ordinarily be used directly in syntheses. When desired, traces of water and other substances can be removed by fractionation before use.

The double bond in acrylonitrile, $CH_2{=}CHCN$, shows remarkable additive power to a wide variety of substances such as ammonia, halogens, halogen halides, alcohols, etc. Further, the presence of the CN radical is a standing invitation to the organic chemist to prepare other compounds from acrylonitrile. Considerable development of the derivatives of acrylonitrile seems indicated in the near future. Some of the physical properties which may be useful to those who work with acrylonitrile are summarized as follows:

Molecular Weight: 53.03
Freezing Point: −83° to −84° C.
Boiling Point. 77.3° C. (760 mm.)
Change of Boiling Point: 0.043° C. per mm. change in atmospheric pressure
Vapor Pressure: See Figure 1
Azeotropic Mixture with Water: Boiling point 70.5–70.7° C. (760 mm.); contains about 12.5% by weight of water
Density: 0.8004 gram per cc. at 25° C. and 0.8060 at 20° C.; $d = 0.8281 - 0.001106t$ (0–30° C.)
Refractive Index: $n_D^{25} = 1.3884$; $n_D^{20} = 1.3911$
Infrared Absorption Spectrum: See Barnes, Liddel, and Williams (*1*)
Ultraviolet Absorption Spectrum: See Figure 2
Raman Spectra: See Timm and Mecke (*20*)
Latent Heat of Evaporation: 7800 calories per gram mole at 0–80° C. (calculated)
Heat of Combustion: 420.5 kg.-cal. per mole or 7925 calories per gram
Specific Heat: 0.50 ± 0.03 calorie per gram
Dielectric Constant: 38 at 33.5 megacycles
Mutual Solubilities with Water: See Figures 3 and 4

Temp., ° C.	Water in Acrylonitrile, % by Wt.	Acrylonitrile in Water, % by Wt.
0	2.1	7.2
20	3.1	7.3
25	3.4	7.4

Solubility: Soluble in all proportions in acetone, benzene, carbon tetrachloride, ether, ethanol, ethyl acetate, ethylene cyanohydrin, methanol, petroleum ether, toluene, xylene, and some kerosenes

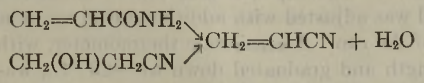
Flash and Fire Point: 0° ± 2.5° C.

Explosive Mixtures with Air: Acrylonitrile, 3.05% by volume (lower limit), 17.0 ± 0.5% by volume (upper limit) (*12*)

Toxicity: Acrylonitrile is somewhat poisonous, and sustained exposure to its vapors should be avoided (*5, 7, 8, 14, 15*)

MATERIALS AND METHODS

Acrylonitrile was first prepared and identified by Moureu in 1893 (*16*). He made it from acrylamide and also from ethylene cyanohydrin, in each case by the removal of the elements of water through reaction with phosphoric anhydride:



$$\left.\begin{array}{l}CH_2{=}CHCONH_2\\CH_2(OH)CH_2CN\end{array}\right\rangle CH_2{=}CHCN + H_2O$$

The samples used for determining the constants recorded here were prepared from commercial acrylonitrile. It was fractionated in efficient glass-packed columns, only the intermediate fraction boiling within less than 0.1° C. being retained. It is easy to overestimate the purity of organic substances. Nevertheless, this close-cut material seemed to be 99–100% pure. This conclusion is based largely on analyses for total and saponifiable nitrogen, and also on the fact that we were not able to find more than traces of other substances.

Freezing Point. This property was measured on a toluene-in-glass thermometer which was standardized by determining its reading at the freezing point of ethyl acetate under the same conditions. The freezing point tube was of thick Pyrex, 2 cm. in diameter and 20 cm. high, and had a side tube at the top for passing in dry air which emerged around the loose-fitting stopper. It was cooled in a bath of solid carbon dioxide plus acetone contained in a wide-mouth Dewar flask of one quart capacity. Although the temperature of such a mixture ordinarily reaches only about −78° C., it can readily be brought to −90° C. or lower by passing in dry air through a tube reaching to the bottom of the Dewar flask, provided the latter is kept well filled with solid carbon dioxide.

Eastman's "anhydrous" ethyl acetate was used for standardizing the thermometer. It was freshly distilled, and the two main middle fractions gave identical freezing point readings. Skau (*19*) found −83.6° C. for the freezing point of ethyl acetate.

The freezing point of acrylonitrile in the same apparatus turned out to be identical with that of ethyl acetate, within the limits of accuracy of the measurements which we estimate at ±0.5° C. That would place it at −83.6° ± 0.5° C. or, say, −83° to −84° C., which is a little lower than the value found by Timmermans, −82° ± 1° C. (*21*), for a sample of acrylonitrile obtained from Moureu with a boiling range of 77.5° to 79° C.

It may be of interest to note that dissolved water has little effect on the absolute value of the freezing point of acrylonitrile. At that temperature the liquid dissolves less than 0.1% of water. If the sample contains more than this amount at room temperature, the excess freezes out on cooling before the acrylonitrile itself freezes. Indeed, an approximate test of the dryness of a sample of acrylonitrile can be quickly made by cooling it and finding the temperature at which a cloud of ice crystals precipitates.

Boiling Point. This property was determined in a distilling flask of the type described by Richards and Barry (*18*) in which the whole thread of the thermometer is heated to the temperature of distillation. The thermometer had been standardized for total immersion. Moureu (*16*) originally placed the boiling point at 78° C. Moureu and Brown (*17*) gave the following boiling points for fractions of acrylonitrile prepared from ethylene cyanohydrin and phosphoric anhydride:

Fraction	% by Weight	Boiling Point, ° C.
I	29	75–77.5
II	47	77.5–79
III	19	79–80

They considered fraction II to be the purest. However, the true boiling point seems to lie a little under its lower limit and is near 77.3° C. at 760 mm.

Vapor Pressure. Measurements were made by the static method using a small flask attached to an open mercury manometer. The acrylonitrile was first boiled under reduced pressure in the flask until all air had been expelled.

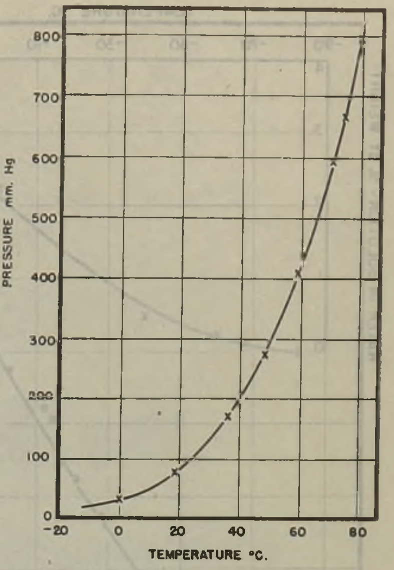


Figure 1. Vapor Pressures of Acrylonitrile

Density. Pycnometers were constructed of the type described by Baxter and Wallace (*2*); they consisted of volumetric flasks of the ordinary shape except that they are constricted at the point of graduation. They have two advantages over other forms commonly used. First, the stoppered surface is not wet by liquid and hence there is no difficulty from evaporation. Second, when determining densities below room temperature, the upper part of the neck serves as a reservoir to hold the overflow of liquid as it expands when allowed to warm up for weighing. We prefer that the constricted part of the neck be made from tubing of narrow diameter sealed to the other parts rather than that it be formed by drawing down a wider neck in the flame. Mobile liquids like acrylonitrile or water can readily be introduced into or removed from pycnometers with orifices as small as 2 mm. by means of capillary pipets as described by Davis and Davis (*4*) and by Jermstad (*11*). The liquid in a 10-cc. pycnometer reaches equilibrium with a stirred bath of water in 3–5 minutes.

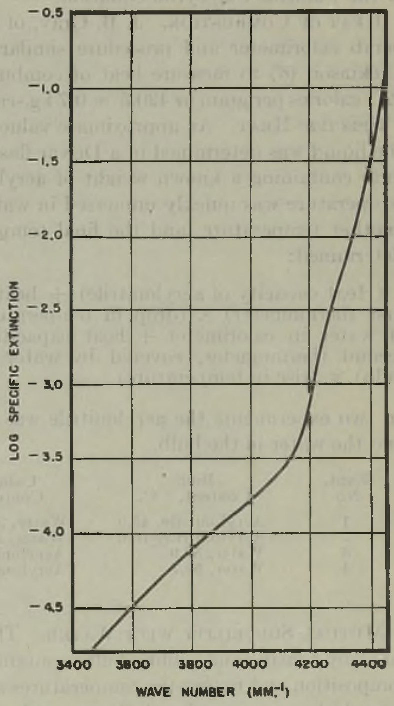


Figure 2. Ultraviolet Absorption Spectrum of Acrylonitrile

Refractive Index. The measurements were taken on a Bausch & Lomb Abbe type refractometer, using sodium vapor light. The same values were obtained with white light.

Ultraviolet Absorption Spectrum. The values in Figure 2 were measured on a medium Hilger spectograph with a Spekker photometer. The acrylonitrile was examined un-

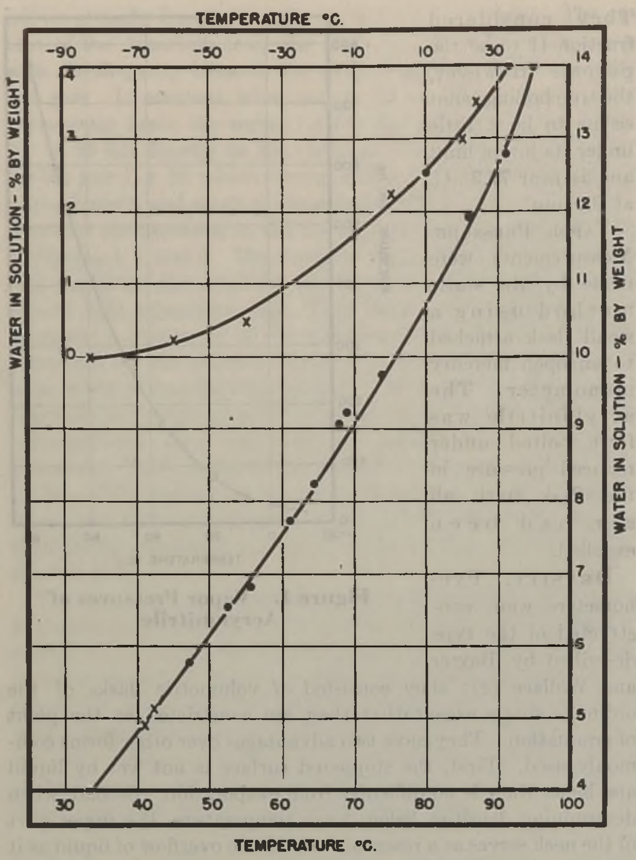


Figure 3. Solubility of Water in Acrylonitrile

diluted in an adjustable micrometer absorption cell with quartz end plates. It should be noted that mere traces of some impurities can cause marked changes in the absorption spectrum.

Latent Heat of Evaporation. This property was calculated from the slope of the vapor pressure–temperature curve by means of the Clausius-Clapeyron equation.

Heat of Combustion. J. B. Gray, of this laboratory, used a bomb calorimeter and procedure similar to that described by Dickinson (*6*) to measure heat of combustion. It is 7925.2 ± 12.7 calories per gram or 420.5 ± 0.7 kg.-cal. per mole.

Specific Heat. An approximate value for the specific heat of the liquid was determined in a Dewar flask calorimeter. A glass bulb containing a known weight of acrylonitrile at a measured temperature was quickly immersed in water in a Dewar flask at another temperature, and the final temperature of equilibrium determined:

(Heat capacity of acrylonitrile) + heat capacity of bulb and first thermometer) × (drop in temperature) = (heat capacity of water in calorimeter + heat capacities of glass, including second thermometer, covered by water after introduction of bulb) × (rise in temperature)

In two experiments the acrylonitrile was put in the calorimeter and the water in the bulb.

Expt. No.	Bulb Content, ° C.	Calorimeter Content, ° C.	Sp. Heat, Cal./Gram
1	Acrylonitrile, 45.9	Water, 29.9	0.52
2	Acrylonitrile, 10.0	Water, 29.6	0.52
3	Water, 59.9	Acrylonitrile, 27.0	0.50
4	Water, 59.7	Acrylonitrile, 21.5	0.47
		Average	0.50

Mutual Solubility with Water. The measurements were made by heating and cooling bulbs containing mixtures of known composition and noting the temperatures at which the cloud of a second phase appeared and disappeared. The thermometer was immersed in the liquid itself inside the bulb and not in the bath liquid. Figures 3 and 4 are based on results obtained in two separate investigations.

Flash Point and Fire Point. A Tagliabue open-cup tester was used for these determinations. The directions which accompany this tester are brief and, moreover, are written for materials flashing at 100 ° F. (37.8° C.) or higher. When working with substances such as acrylonitrile which flash well below room temperature, the operator must use his own discretion on certain details.

The procedure was as follows: The sample of acrylonitrile was put into the cup of the tester and cooled in solid carbon dioxide to about −25° C. The cup was then placed in the tester and the liquid level was adjusted with additional cold material to within 3–4 mm. of the rim. A centigrade thermometer, with a bulb 12 mm. in length and graduated down to −20° C., was placed in such a position that the bulb was just immersed in the liquid. The temperature of the acrylonitrile was then allowed to rise without the application of heat, and the test flame, 3–4 mm. in length, was moved over its surface at intervals of 2.5° C. In the vicinity of the flash point the rate of rise in temperature did not exceed 1° C. per minute, although it was more rapid at the start. Throughout the test the apparatus was shielded from draughts. The flash point and fire points were identical.

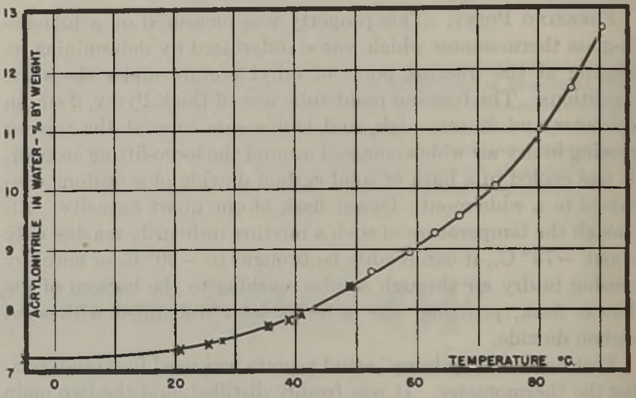


Figure 4. Solubility of Acrylonitrile in Water

Explosive Mixture with Air. The values given in the summary are taken from a Bureau of Mines investigation (*12*). Prior to that publication, we had obtained results of the same order—namely, 3.6% by volume of acrylonitrile as the lower limit and 14.0% (saturation with acrylonitrile vapor at 25° C.) as still explosive. It was difficult in our apparatus to make determinations above room temperature.

ANALYTICAL METHODS

Total Nitrogen. Standard Kjeldahl procedure was used. It is convenient to break a bulb containing a weighed quantity of the acrylonitrile under the sulfuric acid.

Nitrile Nitrogen. The nitrile group is hydrolyzed by boiling with an excess of dilute sodium hydroxide, and the evolved ammonia is titrated with standard acid. This simple method works well for high-boiling nitriles, but not for the more volatile acrylonitrile. A modified procedure has proved satisfactory. A small piece of sodium is reacted with 100 cc. of ethanol in a flask. The weighed sample of acrylonitrile is then added, preferably in a small glass bulb, and the flask is stoppered and allowed to stand for one hour. A considerable proportion, perhaps all, of the acrylonitrile reacts to form the higher-boiling ethoxypropionitrile, and the entire contents of the flask are then analyzed by hydrolysis as usual.

ACKNOWLEDGMENT

The authors are indebted to members of the Stamford Laboratories for suggestions and aid in determinations of the data reported above.

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ACETYLATED CASTOR OIL

Preparation and Thermal Decomposition

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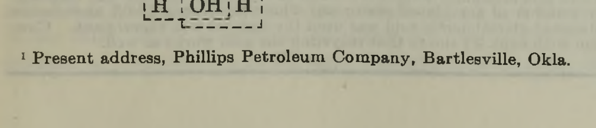
Castor oil is easily and quantitatively acetylated by acetic anhydride. Acetic acid, in the presence of *p*-toluenesulfonic acid as catalyst, leads to hydrolytic splitting of the glycerides unless the water of esterification is immediately removed. With continuous fractional distillation during esterification, castor oil can be acetylated with acetic acid. Acetylated castor oil slowly decomposes at 250° C. to form acetic acid and an oil of greater unsaturation than castor oil. The rate of decomposition has been measured at 295°, 300°, 306°, 312°, 320°, 330°, and 340° C. The process is first order with an energy of activation of 44.5 kg.-cal. The thermal polymerization which occurs during the reaction can be minimized by high temperatures (320–340° C.) and short reaction times. The product is a light yellow oil having about 30% of molecules containing a pair of conjugated double bonds and suitable for use as a drying oil in protective coatings.

THE thermal decomposition of esters to form the corresponding acid and the olefin of the corresponding alcohol has been known since the work of Krafft (*17*) on cetyl palmitate:

$$C_{15}H_{31}COOC_{16}H_{33} \rightarrow C_{15}H_{31}COOH + C_{16}H_{32} \qquad (1)$$

Only recently, however, has this reaction found application in the preparation of certain unsaturated hydrocarbons and their derivatives. Among these applications may be noted the synthesis of various olefin hydrocarbons from acetate esters (*39*), butadiene from 2,3-butylene glycol diacetate (*11*), methyl acrylate from acetoxy methyl propionate (*6*, *7*), and dehydrated castor oil from acetylated castor oil (*3*). In some instances the thermal decomposition of esters, especially the acetate esters, gives better yields of olefinic products with less likelihood of rearrangement of the carbon skeleton than the parallel dehydration of alcohols.

The problem of converting castor oil to a drying oil is essentially one of dehydrating the secondary alcohol groups of the ricinoleic acid radicals, which castor oil contains to the extent of about 85% (*10*), to double bonds at either the 11,12 or 12,13 carbon atoms:



$$CH_3-(CH_2)_4-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CH=CH-(CH_2)_7-\overset{O}{\overset{\|}{C}}-O-\underset{|}{CH_2} \qquad (2)$$

Various methods have been developed to effect this dehydration, and their success is evidenced by the several commercial dehydrated castor oils now marketed and their wide acceptance in the protective coating industry (*21*). Briefly, these methods fall into three groups: (*a*) thermal dehydration of ricinoleic acid by distillation and esterification of the product with glycerol (*32*); (*b*) catalyzed thermal dehydration of castor oil by such catalysts as sulfuric and persulfuric acids (*25*, *29*), phosphorus pentoxide (*35*), metallic oxides (*22*), and alkali metal bisulfates (*8*); and (*c*) thermal decomposition of castor oil esters such as the acetate (*3*), phthalate (*37*), and octadecadienoate (*23*).

The purpose of the present investigation was to study the preparation of acetylated castor oil, the kinetics of its thermal decomposition, and the properties of the resulting product.

ACETYLATION OF CASTOR OIL

By the use of excess acetic anhydride, castor oil is easily and quantitatively acetylated. Acetyl chloride cannot be used because the acetylated oil was found to contain combined chlorine, possibly as a result of the addition of hydrogen chloride to ethylenic linkages. Presumably ketene would be a suitable acetylating agent, since it has been used successfully on other secondary alcohol esters (*6*, *34*). From the economic standpoint, acetic acid would be the cheapest acetylating agent because its original cost is relatively low, and it is reformed on thermal decomposition of the acetylated oil. On the other hand, acetic anhydride forms one molecule of acetic acid during acetylation, and this

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Table I. Reaction of Castor Oil (100 Grams)[a] with Acetic Acid at Reflux (130–145° C.)

Expt. No.	HOAc, Grams	Reaction Time, Hr.	Acid No.	Saponification No.[b]
1	60[c]	16	17	254
3		24	27	276
5		36	32	289
6		50	45	305
7		60	47	308
8	120	12	11	256
9		16	16	268
11		24	24	284
12		40	39	304
13		60	49	319

[a] 0.107 mole or about 0.27 equivalent of hydroxyl.

[b] Calculated for completely acetylated castor oil, 300. These values are not corrected for the free acid content.

[c] 1.0 mole.

Table II. Reaction of Castor Oil (100 Grams) with Acetic Acid (60 Grams) at 130–145° C. and 0.1% p-$CH_3C_6H_4$-$SO_3H \cdot H_2O$

Expt. No.	Time, Hr.	Acid No.	Saponification No.
15	5	37	279
16	11	68	307
17	15	82	319
18	40	80	316

acid, along with that obtained from thermal decomposition, would have to be converted to the anhydride. If ketene were used, the by-product acetic acid would have to be cracked to reform ketene (*5*). These considerations led to a study of the esterification of castor oil with acetic acid.

Preliminary experiments were run by allowing castor oil and excess glacial acetic acid to react at reflux (130–145° C.) for various periods of time. When the excess acid and water of esterification were removed by distillation, the partially acetylated oil was unexpectedly found to contain a considerable amount of free acids (Table I).

The free acids present must be of higher molecular weight than acetic since they were not removed by distillation up to 240° C. or by washing with water. These experiments indicate that an equilibrium is being approached at which the acid number is about 50 at the end of a 60-hour reaction time.

To determine if the reactions occurring between castor oil and acetic acid were susceptible to the usual esterification catalysts, several experiments were run in the presence of 0.1% of *p*-toluenesulfonic acid (Table II).

Again acetylation was accompanied by the formation of large amounts of free acids. The acid catalyst greatly accelerated the reactions, as shown by experiments 7 and 16 in which the reaction times were 60 and 11 hours, respectively. To make certain that the free acid content of these partially acetylated oils was due entirely to higher fatty acids, 70 grams of a product of acid number 47 and saponification number 313 was vacuum-distilled at 1 mm. pressure. The distillate collected up to 215° C. weighed 14 grams, had an acid number of 150 and saponification number of 311. Assuming the distillate to be pure acetylated ricinoleic acid, the yield should have been 16.2 grams with acid number 165 and saponification number 330. The discrepancy in these constants is probably due to the presence of other 18-carbon-atom acids.

Table III. Reaction of Linseed Oil (50 Grams) with Acetic Acid (25 Grams) and 0.1% p-$CH_3C_6H_4SO_3H \cdot H_2O$ at 135–145° C. for 10 Hours

Expt. No.	Ac_2O, Grams	Water, Gram	Acid No.	Saponification No.
21	1	....	1.0	189
25[a]	50	....	1.0	189
22	...	0.075	13.2	196
23	...	0.38	27.3	206
24	...	0.75	43.0	214

[a] No acetic acid used.

The presence of free higher acids in these esterification products showed that acid interchange or displacement was occurring. It seemed likely that the water of esterification was a key factor in this process because the acetylated castor oil made with acetic anhydride as the acetylating reagent, with or without *p*-toluenesulfonic acid, contained practically no free acid. No water is formed in this reaction as long as at least one mole of anhydride is taken for each equivalent of alcoholic hydroxyl. To show that water is a requisite for the acid interchange, several model experiments were run with linseed oil, which contains only traces of hydroxy acids, acetic acid, and known amounts of water.

In experiment 21 one gram of acetic anhydride was added to remove any traces of water. In this anhydrous mixture practically no free acids were formed. The results parallel those of experiment 25 where acetic anhydride without acetic acid was used; but when small quantities of water were added in the following experiments, the amount of free acids increased with increasing amounts of water. Therefore the acid interchange is not a direct process but rather an indirect one in which the intermediate reaction is hydrolysis of the glyceride. Conditions are actually favorable for hydrolysis because the acetic acid serves as a coupling solvent for the oil and water and the *p*-toluenesulfonic acid acts as a hydrolysis catalyst. The interaction of castor oil and acetic acid at reflux must lead to a complex group of equilibria involving, in addition to acetic acid and water, 16- and 18-carbon-atom saturated and unsaturated acids, ricinoleic acid, acetylated ricinoleic acid, and various glycerides based on all of these acids.

REMOVAL OF WATER

These results clearly indicated that, if acetic acid were to be used successfully, the water of esterification had to be removed immediately. Two experimental approaches to this condition were investigated. The first consisted of passing acetic acid vapor through castor oil heated at 160–240° C. As Table IV shows, acetylation with little acid interchange was achieved in this way, but the rate of reaction was very slow. Even in 12 hours (experiment 33) only 56% of the oil was esterified.

Experiments 30–32 show that a temperature increase of 160 to 240° C. has little effect on the rate of acetylation. A possible

Table IV. Reaction of Castor Oil (100 Grams) with Acetic Acid (100 Grams per Hour)[a]

Expt. No.	Temp., ° C.	Time, Hr.	Acid No.	Saponification No.	% Acetylated[b]
30	160	3	2.2	200	19
31	200	3	2.0	202	20
32	240	3	4.8	206	21
33	200	12	3.2	248	56
34[c]	200	3	2.4	202	20

[a] After passage through the oil, the acid along with any water formed was condensed and recycled.

[b] Calculated on the basis of 177 and 300 as the saponification numbers for castor and acetylated castor oil, respectively. These are experimental values determined on the castor oil used in this work and on the acetylated oil made by acetic anhydride acetylation. The acid value of the latter was 2.0. If the acid value of the sample is not greater than 2.0, the per cent acetylated is:

$$\frac{\text{Saponification No.} - 177}{300 - 177} \times 100$$

For acid numbers greater than 2.0, the ester number—i.e., saponification number − (acid number −2.0)—is used in place of the saponification number. A more accurate calculation would use the saponification number of the ester portion of the sample. While this is readily calculated, it is not useful since the actual molecular weight of the ester is not known exactly, due to hydrolysis to form acids and possibly some esterification with acetic acid, and this molecular weight is needed to revise the value of 300 (saponification number of acetylated castor oil) which represents 100% acetylation.

[c] Reagent glacial acetic acid was used throughout this experiment. Comparison with expt. 31 shows that recycling the acid works as well.

explanation for this unusual result is that the amount of acid dissolved in the oil—i.e., its effective concentration—decreased with increasing temperature and thus offset the effect of temperature increase.

To increase the rate of acetylation under these conditions, *p*-toluenesulfonic acid was tried as a catalyst. Because of the possibility that a portion of the hydroxyl groups of castor oil might be destroyed either through etherification or dehydration, the partially acetylated oils were further treated with acetic anhydride and the saponification numbers measured. If these values are lower than 300, there has been a loss of hydroxyl groups (Table V).

TABLE V. REACTION OF CASTOR OIL (100 GRAMS) WITH ACETIC ACID (100 GRAMS PER HOUR) AND *p*-$CH_3C_6H_4SO_3H \cdot H_2O$ AT 200° C.

Expt. No.	Catalyst, Gram	Time, Hr.	Acid No.	Saponification No.	% Acetylated	Sap. No. after Acetylation
36	0.1	3	3	245	56	296
37	0.16	6	6	284	84	288
38	0.16	9	10	286	82	289

Experiment 37 represents the most favorable conditions: 84% of the oil was acetylated in 6 hours, but there was a simultaneous loss of hydroxyl groups to the extent of about 10%. If this were due entirely to dehydration, it should not affect adversely the drying properties of the final dehydrated oil. On the other hand, etherification would lead to a final product having somewhat less unsaturation and possibly slower drying power.

The second experimental technique designed to remove the water of esterification before it caused hydrolysis depended on continuous fractional distillation during the acetylation reaction. The column used had a glass-helix-packed section 152 cm. in length and an efficiency of forty-two theoretical plates, measured at total reflux on a *n*-heptane–methylcyclohexane mixture (*18*). Two hundred grams of castor oil, 70–170 grams of acetic acid, and 0.0–0.6 gram of *p*-toluenesulfonic acid were allowed to react in the experiments summarized in Table VI. The rate of distillation was adjusted so that the temperature at the head of the column was 100–101° C. and the distillate consisted of 12–14 ml. of acetic acid–water (about 8 ml. was water) if approximately 90% acetylation were obtained. Unless otherwise indicated, the catalyst was added at the start of the reaction (Table VI)

TABLE VI. REACTION OF CASTOR OIL (200 GRAMS) AND ACETIC ACID WITH CONTINUOUS FRACTIONAL DISTILLATION

Expt. No.	HOAc, Grams	Catalyst, Gram	Time, Hours	Acid No.	Saponification No.	% Acetylated
47	120	...	6	2.0	234	46
56	120	0.25	3	6.3	283	83
58	120	0.4	3	7.8	295	91
59	120	0.5	3	11.8	302	94
60	120	0.6	2	11.5	299	92
61	120	0.6[a]	3	10.4	303	96
62	120	0.6[b]	3	9.1	301	95
54	90	0.5[c]	3	13.8	305	94
51	170	0.4	3	8.7	291	87

[a] 0.3 at start, 0.2 at 1 hour, 0.1 at 2 hours.
[b] 0.2 at start, 0.2 at 1 hour, 0.2 at 2 hours.
[c] 0.3 at start, 0.2 at 1 hour.

As experiments 56–62 show, a weight ratio of acid: oil of 1.2:2.0 is most suitable in terms of time, acid content of product, and degree of acetylation. In 62 the oil was substantially completely acetylated in 3 hours at 130–140° C., and its acid number was only 9.1. Portionwise addition of the catalyst has the advantage of bringing the catalyst concentration to a maximum in the later stages of acetylation where the rate normally falls because of consumption of the acid and hydroxyl groups; also, the lower catalyst concentration at the start does not produce water of esterification at such a high rate that it cannot be removed by distillation. Experiments 54 and 51 of Table VI used smaller and larger relative quantities of acetic acid. It would be expected that the greater concentration of acid would lead to more rapid acetylation; that this is not the case must be due to a lower temperature of reaction—i.e., refluxing temperature. When 170 grams of acid were used as in experiment 5 (Table I), the temperature ranged from 124° to 130° C.; with 120 grams of acid the temperature was 130–140°; and with only 90 grams of acid the temperature was 138–160°.

From these results it was concluded that castor oil could be satisfactorily acetylated with excess acetic acid in the presence of *p*-toluenesulfonic acid as catalyst by fractionally distilling water and some acetic acid continuously from the reaction mixture. Obviously this process has a considerable economic advantage over the acetic anhydride acetylation.

To substantiate the selection of *p*-toluenesulfonic acid as the best catalyst, several other substances were tried at a reaction time of 2 hours, using the fractional distillation procedure (Table VII). Benzene and *p*-toluenesulfonic acids have about the same activity but the former causes some discoloration of the oil. The other substances tried were all much less effective.

TABLE VII. REACTION OF CASTOR OIL (200 GRAMS) WITH ACETIC ACID (120 GRAMS) AND VARIOUS CATALYSTS (0.1%)

Expt. No.	Catalyst	Acid No.	Saponification No.	% Acetylation
39	Trichloroacetic acid	2.0	221	36
42	Phosphoric acid (85%)	3.0	230	43
45	Litharge	1.5	207	24
46	Zinc oxide	1.7	207	24
40	*p*-Toluenesulfonic acid	7.0	273	74
41	Benzenesulfonic acid	6.6	275	76
43	Camphorsulfonic acid	3.0	254	63
44	3,5-Naphthalenedisulfonic acid	3.4	239	50

ACETYLATION PROCEDURE

CHEMICALS. A commercial grade of castor oil was furnished by the Sherwin-Williams Company. It showed the following constants: acid number 1.5, saponification number 177, n_D^{25} 1.4770, and viscosity 8.4 poises at 23.9° C. Technical-grade glacial acetic acid was distilled for use in the acetylations. Technical-grade acetic anhydride (Dow Chemical) was also distilled before using. *p*-Toluenesulfonic acid monohydrate was Eastman Kodak's best grade.

APPARATUS. The acetylations with acetic acid vapor were carried out in a cylindrical reaction flask of about 35-mm. diameter fitted with a side arm, sintered glass bubbler, and thermometer. One hundred grams of oil with the bubbler and thermometer immersed made a column about 12.5 cm. high. The acetic acid was distilled from a distilling flask whose side arm was wrapped with wire gauze so that the vapor could be superheated with a wing-top flame. After this preheater and before the ground-glass connection to the bubbler, a T-tube held a thermometer to measure the vapor temperature. During an acetylation a slow current of dry nitrogen was passed through the acetic acid flask, the reaction flask was heated to the desired temperature, and the off-vapor of acetic acid and water escaped through the side arm of the reaction flask into a water condenser.

The fractionating column was a standard model purchased from the Ace Glass Company. Its over-all length was 193 cm., the packed section was 152 cm. long and 14 mm. in diameter, and the packing consisted of single-turn glass helices about $^1/_8$ inch in diameter. A silvered vacuum jacket and an automatic take-off on a total condensing head completed the assembly. The efficiency was determined at total reflux with a mixture of

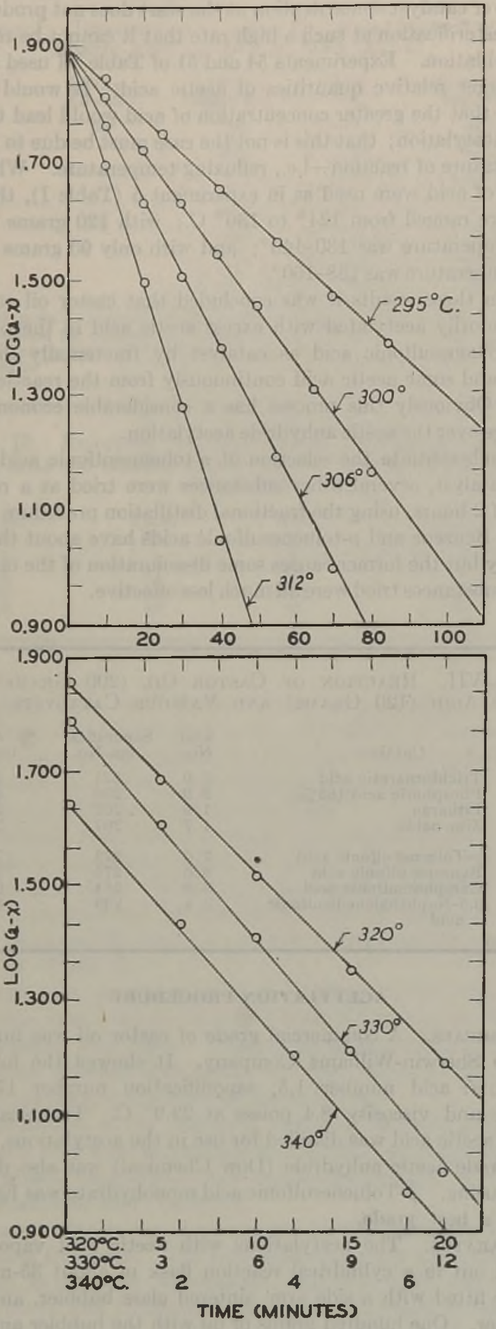


Figure 1. Rate Measurements at 295° to 340° C.

1 part of pure *n*-heptane and 2 parts of pure methylcyclohexane (*18*). The average of several determinations was forty-two theoretical plates.

Constants. Saponification, acid, and hydroxyl numbers, refractive index, and viscosities were determined in the usual way.

Acetylation with Acetic Anhydride. 1000 grams (1.07 moles) of castor oil and 500 grams (4.9 moles) of acetic anhydride were carefully brought to reflux in a 3-liter round-bottom flask. This must be done cautiously because of the exothermic reaction. After refluxing 2 hours the product was transferred to a 5-liter, three-neck flask fitted with a nitrogen inlet tube, thermometer, efficient mercury-seal stirrer, and glass delivery tube connected to a water condenser set for distillation. With a stream of nitrogen passing beneath the surface of the oil and with vigorous stirring the mixture was heated to 240° C. until no more distillate came over. The yield was 1130 grams, 99-100%, based on the hydroxyl number of the castor oil (159). The product had an acid number of 2.0, saponification number of 300, n_D^{25} of 1.4680, and viscosity at 23.9° C. of 3.2 poises.

KINETICS OF THERMAL DECOMPOSITION

Preliminary experiments showed that acetylated castor oil slowly decomposed with the formation of acetic acid at about 250° C. By measuring the rate of acetic acid formation at various times, the rate of thermal decomposition could be determined. Two experimental procedures appeared to be practicable: In the first the evolved acid was collected in excess standard alkali, and aliquot portions of this solution were titrated at various time intervals. Alternatively, the distillate could be collected and weighed. The second procedure was found to give more reproducible results, if fairly large samples of oil (500 grams) were taken. Rate measurements were made at 295°, 300°, 306°, 312°, 320°, 330°, and 340° C., and a typical set of data is given in Table VIII.

In Figure 1 log $(a-x)$ is plotted against time for each of the rate experiments. The straight-line curves obtained show that the thermal decomposition of acetylated castor oil is a first-order reaction in the temperature range 295-340° C. From the slopes of these lines the specific reaction rate constants k were calculated:

$$-\log (a - x) = \frac{k}{2.303} t + \text{constant} \qquad (3)$$

The energy of activation was calculated to be 44.5 kg.-cal. by plotting log k against $1/T$ in Figure 2 and determining the slope from this graph. From the foregoing data constant k can be evaluated:

$$\log k = \frac{-44{,}500}{2.303\ R} \frac{1}{T} + 15.286 \qquad (4)$$

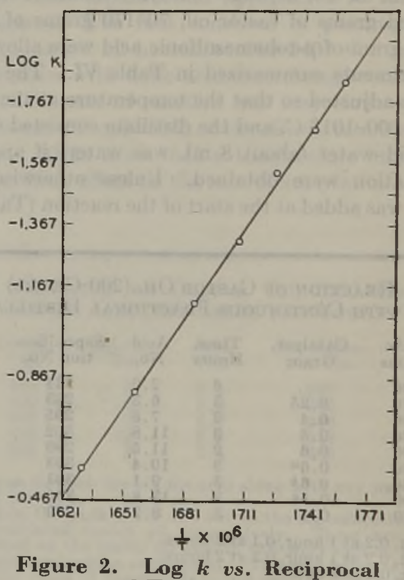


Figure 2. Log k vs. Reciprocal of Temperature

From this equation the rate of decomposition can be estimated at any temperature. For example, at 250° C. k equals 0.00049, which means that about 0.05% of a sample of acetylated castor oil will decompose per minute at 250° C.

Although a number of acetate esters have been thermally decomposed for purposes of synthesis, the literature contains relatively little kinetic data on this process. Rudy and Fugassi (*30*) and Warrick and Fugassi (*38*) investigated the vapor-phase decomposition of *tert*-butyl acetate at 242–302° C. and *tert*-butyl propionate at 240–296° C. The observed energies of activation were 40.3 and 39.16 kg.-cal, respectively. In the case of *tert*-butyl propionate no change in velocity constant with pressure was observed at pressures down to 17 mm. The fact that these are esters of a tertiary alcohol may account for the lower energies of activation compared to the acetylated castor oil, which has secondary alcohol groups. There is evidence that the ease of thermal decomposition of esters varies with the parent alcohol and increases in the order: primary, secondary, tertiary (*14, 19*); it thus resembles the dehydration of alcohols.

Table VIII. Decomposition of Acetylated Castor Oil[a] at 295° ± 1° C.

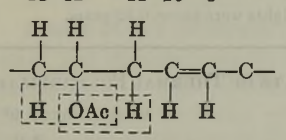
Time, Min.	x	$(a - x)$	Log $(a - x)$
0	0	78.1	1.893
10	8.4	69.7	1.843
25	22.3	55.8	1.747
40	33.2	44.9	1.652
55	41.8	36.3	1.560
70	48.6	29.5	1.470
85	53.8	24.3	1.386

[a] x represents grams of acetic acid collected in time t; $(a - x)$, grams of acetic acid remaining at time t. The theoretical yield of acetic acid from 500 grams of acetylated castor oil is 78.1 grams.

Table IX. Rate Constants at Various Temperatures

Temp., ° C.	$k \times 10^2$	log k
295°	1.45	−1.839
300	2.08	−1.682
306	2.90	−1.538
312	4.77	−1.322
320	7.74	−1.111
330	15.1	−0.821
340	27.1	−0.567

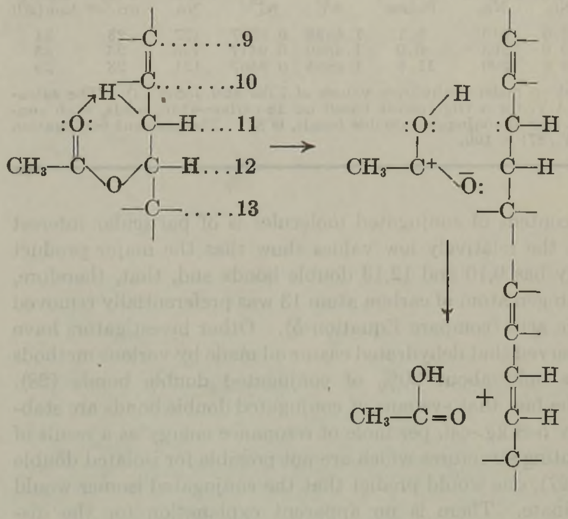
Closely related to the decomposition of acetylated castor oil is the decomposition of acetylated methyl ricinoleate. Recent measurements on this substance at 290–320° C. have given 42.6 kg.-cal. as the energy of activation (*33*). In a glyceride containing one or more acetylated ricinoleic acid radicals, it seems likely that the splitting out of the units to form acetic acid from each carbon chain would proceed independently; i.e., from the kinetic standpoint the decomposition of one molecule of acetylated ricinolein should not differ materially from the decomposition of three molecules of acetylated methyl ricinoleate. This assumption is not unreasonable if one notes the many atoms which separate the acetate ester groups in the glyceride molecule. On the basis of this assumption the observed reaction rates and energy of activation correspond to the elimination of a single molecule of acetic acid and formation of a new double bond. A more exact definition of the reaction in terms of the structurally isomeric and stereoisomeric products formed cannot be formulated. Examination of the products has shown the presence of both conjugated and nonconjugated double bonds. These products form because the atom of hydrogen which pairs with the acetate group may come from either carbon atom 11 or 13:



(5)

Therefore two reactions have occurred simultaneously which may not be kinetically identical. Furthermore, the presence of two double bonds in each chain theoretically permits the formation of four geometrical isomeric forms, and here again the reactions leading to these isomers may not be identical in rate or energy of activation. From a practical standpoint the kinetic measurements reported here are useful, but the complexity of the system prevents a complete analysis of all the simultaneous reactions which may take place.

The reaction mechanism for the decomposition of esters and of similar compounds has been discussed by Ingold (*13*), Hurd (*14*), and Stevens (*36*). According to their view, the initial step is chelation through an intramolecular hydrogen bond. Then the proton from the beta-carbon atom with respect to the oxygen atom is transferred to the carbonyl oxygen, the other carbon-oxygen bond is split, and rearrangement of the resulting fragments gives acetic acid and a molecule with a new double bond:



(6)

This proposed mechanism has been carefully considered, but no new evidence either for or against it has been found.

OILS FROM THERMAL DECOMPOSITION

Table X summarizes several decompositions run on 500-gram samples of acetylated castor oil at various temperatures and reaction times. In most cases the yield was about 415 grams, which is 99% of the theoretical yield of 422 grams.

These data show that the products vary considerably in viscosity, a property which depends on the extent of thermal polymerization or "bodying". This polymerization is favored by longer reaction times at a given temperature (compare experiments III-VI) and by higher reaction temperatures (experiments III and VII). In all cases the product contains some free acid, which must be formed by cracking because all uncombined acetic acid is distilled. By the proper choice of temperature and time, the viscosity and acid number of the oil can be controlled to some extent. The least polymerization (as measured by viscosity) is obtained by the use of a high temperature and a short reaction time; for example, the product from experiment 12 had a vis-

Table X. Thermal Decomposition under Various Conditions

Expt. No.	Temp., ° C.	Time, Min.	Wt. Loss,[a] Grams	Acid No.	Viscosity at 23.9° C., Poises
I	295	145	79	9.5	7.5
II	300	125	78	9.8	11.0
III	306	55	71	12.2	3.6
IV	306	70	82	8.3	6.0
V	306	80	79	8.3	7.8
VI	306	90	86	7.0	11.6
VII	312	55	82	11.0	6.7
VIII	312	65	80	12.1	9.6
IX	320	35	88	7.8	6.9
X	320	45	90	9.2	15.7
XII	340	6	81	12.7	3.1
XIII	340	21	100	8.9	51.0

[a] Theoretically, 78.1 grams of acetic acid. Some cracking to form other volatile products probably occurs in all of the experiments and certainly in those whose loss of weight exceeds 78.1 grams.

cosity of only 3.1 poises. Other significant properties of three of these oils are given in Table XI.

As is generally true of polymerized oils, those of higher viscosity have higher indices and densities and lower iodine values. The high saponification number in experiment XII is probably due to some undecomposed acetate groups.

Table XI. Constants of Dehydrated Castor Oils

Expt. No.	Acid No.	Saponification No.	Viscosity at 23.9° C., Poises	n_D^{25}	n_4^{25}	Iodine No.	% Conjugation: Maleic anhydride[a]	% Conjugation: Ultraviolet absorption (*20*)
XII	12.0	210	3.1	1.4838	0.9347	127	23	34
IV	9.0	203	6.0	1.4860	0.9417	125	25	33
VI	9.0	200	11.6	1.4865	0.9467	121	23	29

[a] Based on maleic anhydride values of Ellis and Jones (*4*). The calculated M.A.V. for a triglyceride based on 18-carbon-atom acids, each containing a pair of conjugated double bonds, is 87. The per cent conjugation is (M.A.V./87) × 100.

The content of conjugated molecules is of particular interest because the relatively low values show that the major product probably has 9,10 and 12,13 double bonds and, that, therefore, the hydrogen atom of carbon atom 13 was preferentially removed as acetic acid (compare Equation 5). Other investigators have also observed that dehydrated castor oil made by various methods contains only about 30% of conjugated double bonds (*28*). From the fact that systems of conjugated double bonds are stabilized by 5–8 kg.-cal. per mole of resonance energy as a result of contributing structures which are not possible for isolated double bonds (*27*), one would predict that the conjugated isomer would predominate. There is no apparent explanation for the distribution of products observed.

Examination of the film-forming properties of this product showed that it dried rapidly to a hard, nontacky film of good water, alkali, and soap resistance. These properties were also apparent when the oil was formulated into varnishes and paints. As Tables XII and XIII show, the oil film rapidly absorbs oxygen in the absence of driers, and its rate of thermal polymerization at 305° C. is high.

DECOMPOSITION PROCEDURE

Rate Measurements. The acetylated castor oil used in these experiments was made by the acetic anhydride method. The product prepared by acetic acid esterification with fractional distillation can also be used, if the *p*-toluenesulfonic acid catalyst is first removed. This is readily done by treating the crude ester with 1% of Magnesol clay with vigorous stirring at 100° C. for 2 hours and then filtering. The apparatus for the rate measurements consisted of a 2-liter three-neck round-bottom flask; the upper two thirds was insulated with a 1/4 inch layer of asbestos cement. The flask was fitted with a nitrogen inlet tube reaching to the surface of the oil, a calibrated thermometer, an efficient mercury seal stirrer, and a condenser set for distillation. Five hundred grams of acetylated oil were placed in the flask, and the nitrogen flow was adjusted to 120 bubbles per minute at a small bubble counter. The sample was brought to 240° C. by direct heating with a Mekker flame, and then brought to the desired reaction temperature as rapidly as possible. This heat-up time to the desired temperature varied from 5 to 9 minutes. The acetic acid formed in that interval was discarded and "zero time" taken when the reaction temperature was reached. This temperature was maintained manually to ±1° C. The acetic acid was collected in tared flasks and weighed to the nearest 0.1 gram.

Constants. Iodine numbers were found by the Wijs 60-minute procedure (*12*). These values probably do not measure total unsaturation because of the conjugated double bonds present (*9*).

Although maleic anhydride values for conjugation (*4*) are considered less reliable than the ultraviolet absorption measurements (*20*), they were determined here for the sake of comparison. As Table XI shows, the absorption measurements give results which are somewhat higher than those obtained with maleic anhydride (*24*). The following modified Ellis and Jones procedure gave reproducible results: Sixty grams of redistilled maleic anhydride are dissolved in 500 ml. of warm reagent-grade toluene; solution is cooled, diluted to 1 liter with additional toluene, and filtered after standing overnight. Approximately 1.0 *N* aqueous sodium hydroxide is standardized against 1.0-gram samples of pure maleic acid dissolved in 100 ml. of water. Phenolphthalein indicator is used, and the maleic acid acts as a dibasic acid. Approximately 3.0 grams of oil, weighed to the nearest milligram, is weighed in a 250-ml. round-bottom flask with a ground-glass joint, 25.0 ml. of maleic anhydride solution are added by a pipet, and the mixture is refluxed for 5 hours. Duplicate samples and duplicate blanks are run. At the end of the refluxing the mixture is allowed to cool, 5.0 ml. of water are added, and refluxing is continued for 15 minutes. After cooling, the condenser is rinsed with 5 ml. of ether, and the solution is transferred to a 100-ml. separatory funnel, using three 10-ml. portions of water for rinsing. After vigorous shaking the aqueous layer is drawn into a 250-ml. Erlenmeyer flask, and the toluene solution extracted again with 25 ml. of water, then with 10 ml. The combined aqueous extracts are titrated with standard base:

$$\text{Maleic anhydride value} = \frac{(A - B)\text{ ml. NaOH} \times \text{normality} \times 12.69}{\text{weight of sample}}$$

where

A = average ml. NaOH for blank
B = ml. NaOH for sample

CATALYZED THERMAL DECOMPOSITIONS

A variety of substances was tried as catalysts for the thermal decomposition of acetylated castor oil to determine (*a*) the general nature of the active catalysts for this reaction, (*b*) the possibility of operating the process at lower temperatures and/or shorter reaction times, and (*c*) the effect of catalysts on the distribution of conjugated and nonconjugated products. Fifty-gram samples of acetylated castor oil and 2% by weight of catalyst were heated to 300° C. in the same way as the rate measurements were made. With no catalyst, 3.0 grams of acetic acid were formed in 20 minutes. If a catalyst caused the formation of 4.0 grams of acid in this time, the rate of decomposition was

Table XII. Rate of Oxygen Absorption for 0.003-Inch Films on 3 × 5 Inch Tin Panels

Time, Hours	Wt. Increase, Mg.[a]: Dehydrated castor oil	Wt. Increase, Mg.[a]: Alkali-refined linseed oil	Wt. Increase, Mg.[a]: Tung oil
0	0	0	0
32	3.7	...	2.4
60	9.8	2.4	5.0
85	15.5	10.2	15.0
109	19.5	15.0	22.5
130	22.6	20.0	32.5

[a] The initial film weights were about 0.32 gram.

Table XIII. Rate of Thermal Polymerization at 305° C.[a]

Time, Min.[b]	Viscosity at 23.9° C., Poises
0	3.0
60	7.0
85	9.5
95	16.1
105	27.0
115	41.2
125	56.6

[a] One liter of oil was heated and mechanically stirred in an open stainless-steel kettle.
[b] The temperature reached 305° C. after 75 minutes.

Table XIV. Catalytic Thermal Decompositions at 300° C.

Catalyst[a]	Effect on Rate of HOAc Formation
Acids	
Phosphoric (65%)	Decompn. temp. lowered to 270° C.
Sulfuric (96%)	Decompn. temp. lowered to 280°
p-Toluenesulfonic	Decompn. temp. lowered to 250°
Trichloroacetic	None
Anhydrous metallic acetates	
Lead acetate	None
Zinc acetate	Increased rate 30%
Anhydrous metallic chlorides	
Ferric chloride	Decompn. temp. lowered to 270°
Mercuric chloride	None
Zinc chloride	Decompn. temp. lowered to 230°
Metallic oxides	
Alumina (Alcora)	None
Litharge	None
Titania (pigment grade)	None
Titania gel (from $TiCl_4$), (*16*)	Slight increase
Metals	
Aluminum	None
Iron	None
Nickel	None
Raney nickel (*26*)	None
Miscellaneous	
Pumice	None
p-Toluenesulfonyl chloride	Decompn. temp. lowered to 280°
Zinc sulfate	None

[a] The acids and salts used were reagent grade. Aluminum, iron, and nickel were approximately 100-mesh powders.

considered to be increased 33%. In some instances a very active catalyst accelerated the decomposition so that all of the acetic acid (7.8 grams) was collected before 300° C. was reached. The results of the catalyzed experiments are summarized in Table XIV.

The activity of the strong acids and the metallic chlorides in this reaction resembles the catalytic dehydration of alcohols (*2*). The titania gel was tested in several experiments because of its reported activity for the decomposition of ethyl acetate (*31*), and was found to have some activity at the start of the reaction but this activity was quickly lost. The catalyst became black, probably because of the deposition of carbon. After regenerating by heating to 400° C. in air, the original light brown color appeared, and the catalyst was again active for a short time.

Most of the catalysts which appreciably accelerated the decomposition rate also caused discoloration of the oil and were therefore of no practical value. An exception was *p*-toluenesulfonyl chloride which gave an oil of very light color and with no appreciably greater viscosity than a similar sample made with no catalyst.

Ultraviolet absorption measurements were made on samples prepared in the presence of 2% of *p*-toluenesulfonic acid, activated alumina, and Raney nickel. The first two substances did not alter the amount of conjugated molecules, but the nickel catalyst yielded a product having 40% of two double-bond conjugation, an increase of 6% over an oil prepared without nickel. Since metallic hydrogenation catalysts are capable of catalyzing the partial isomerization of the double bonds in linseed and soybean oils to conjugated positions (*1*, *15*), the action of nickel in this case is probably on the dehydrated castor oil itself rather than on the acetylated oil by way of a directive effect during decomposition.

LARGE SCALE OPERATION

If the preparation and thermal decomposition of acetylated castor oil were carried out on a large scale, the esterification with acetic acid using continuous fractional distillation and the purification of the recovered acetic acid should offer no difficulty. The thermal decomposition step, however, could undoubtedly be best done by means of a vertical, heated, packed column through which the acetylated castor oil would flow. By controlling the rate of flow in the column and its temperature, dehydrated oils of any desired viscosity could be made. Operation of the column under reduced pressure would permit the acid number of the oil to be held to low values, although presumably this would not affect the rate of decomposition (*38*). If the use of high temperatures and short reaction times to make oils of low viscosity led to appreciable quantities of volatile decomposition products, those products, after recovery of the acetic acid, might serve to suppress the cracking reactions if they were recycled in the column with the acetylated oil.

ACKNOWLEDGMENT

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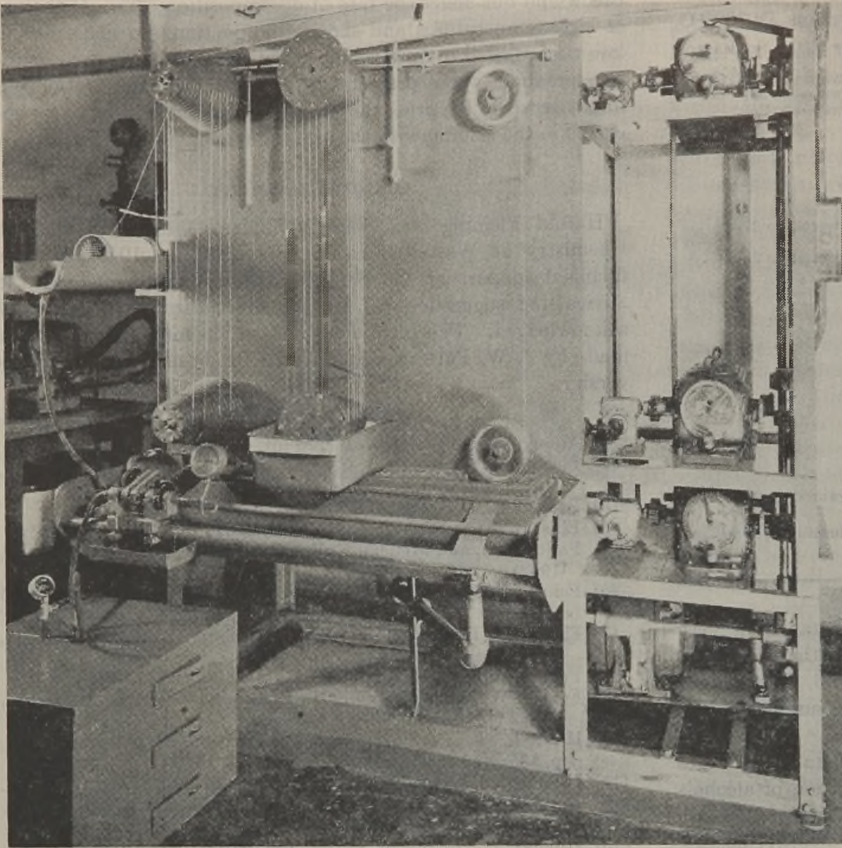

Figure 1. Spinning Apparatus

TEXTILE FIBER from CASEIN

Factors Affecting the Tensile Strength

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THE casein fiber, Aralac, is being manufactured in the United States at the rate of several million pounds a year. The material is used as a textile fiber and is also blended with imported rabbit fur in making hats (*3*, *22*). Despite the fluctuation of the market price of casein from 15 to 30 cents a pound, quotations on the manufactured textile fiber have not varied from 64 cents a pound in recent years. The economic position of casein fiber in various countries has been favorably discussed by several authors (*2*, *11*, *15*). Artificial protein fibers have been made from soybean, peanut, and other proteins by essentially the same process employed for casein: solution of the protein in alkali, extrusion of the solution into a precipitating bath containing acid and salt, and hardening of the fiber with formaldehyde (*6*, *9*). Expansion of the casein fiber industry and large-scale production of similar fibers from other proteins will depend in a postwar economy on relative price and relative quality. Further development of the wet and dry strengths will enhance the competitive position of this class of fibers.

Although large-scale commercial development of casein fiber started in Italy in 1936, processes were invented for manufacturing casein fiber prior to that date. In 1899 two patents (*21*) were issued to Millar covering manufacture of a casein fiber by spinning into air. A 50% solution of casein in glacial acetic acid was used. Shortly afterward, Todtenhaupt was granted a series of four German patents (*28*). Present-day methods for spinning alkaline solutions of proteins represent refinements of this early work. In 1936 the manufacture of casein fiber, known as Lanital, was begun by Snia Viscosa in Italy, under the Ferretti patents (*10*). Working independently in this country, Whittier and Gould obtained eight public service patents (*29*) on the production of casein fibers.

Todtenhaupt's fibers tended to stick together and were hard and brittle (*17*, *26*). Ferretti's patents emphasized the use of a special "textile" casein in overcoming these difficulties. Ferretti also incorporates aluminum salts in the spinning bath as well as salt in the formaldehyde hardening bath. Certainly improvements in machinery for spinning fiber achieved by the rayon industry between 1904 and 1936 were an important factor in the development and production of Lanital fiber. Ferretti's British Patent 483,731 covers in detail a process for manufacturing casein fiber. The special textile casein is prepared from skim milk by precipitation with sulfuric acid in 56% excess of the amount ordinarily employed to coagulate the casein. The casein is heated with the acid whey at a pH of 2.9 to 3.0 for one hour at 45° C. The curd is separated and pressed to remove the serum content and dried without washing. This special casein is made into solution, using a quantity of sodium hydroxide equal to 9.76 grams per 100 grams of moisture-free casein. As the viscosity increases with age, the solution is diluted to keep the viscosity within manageable limits. The final concentration in terms of moisture-free casein is 16 to 18%. After being aged for 48 hours, the solution is spun into a precipitating bath of sodium sulfate, sulfuric acid, and aluminum sulfate. The fiber is hardened in a series of solutions containing sodium chloride and formaldehyde, washed, and dried.

Küntzel and Doehner (*18*) reported the only extensive quantitative data dealing with the effect of spinning conditions and materials on filament strength. These authors spun casein solutions with a viscosity of 4 to 6 poises through single-hole spinnerettes into a bath held at 52° C. In our experience these conditions of temperature and viscosity are satisfactory with a single-hole spinnerette, but owing to formation of blebs they are not satisfactory with multihole spinnerettes. However, their conclusions are of considerable interest especially in regard to a salient point of the Ferretti patents. According to them, the only advantage in use of excess sulfuric acid in precipitating the "textile" casein is the subsequent introduction of sodium sulfate into the spinning solution. Better results are claimed for the direct addition of sodium sulfate to a solution of casein precipitated at the isoelectric point. Their casein fibers gave an x-ray diagram which showed no orientation, even when the fibers were stretched.

The patents issued to Whittier and Gould (*29*) are concerned mainly with the additions of various agents to the casein solution or to the precipitating bath for the purpose of modifying the resulting fiber. For example, in the first patent sodium aluminate is employed in the spinning solution to increase strength and water resistance, and fat acids, to improve flexibility and softness. Another patent describes the spinning of fibers from concentrated skim milk. They used a ratio of sodium hydroxide to casein lower than Ferretti's to minimize hydrolysis of the casein. The solutions, prepared from any acid-precipitated casein of good quality, are spun without aging.

Patents recently issued to Atwood (*5*) reveal in detail processes for the production of casein fiber. Some features are (*a*) very low alkalinity of spinning solution, corresponding to a pH of 7 and about 2 grams of sodium hydroxide per 100 grams of casein, (*b*) a short procedure for dispersing acid or rennet casein with the aid of heat, (*c*) a continuous method for treating with formaldehyde, and (*d*) acetylation with ketene or acetic anhydride.

It is obvious that, whereas a great deal has been accomplished in the development of artificial protein fiber, much remains to be done. Acetylation has provided a means for making such fiber resistant to boiling aqueous solution. Eventual enhancement of all the basic properties within limits of compatibility is desired. These properties are, of course, considerably interdependent. It is generally agreed, however, that the current need is for higher wet and dry strengths. This study was undertaken to evaluate some of the factors contributing to the strength of casein fiber. The principal factors investigated were pH and viscosity of the spinning solution, composition of the precipitating bath, effects of drawoff and godet stretch, and progressive stretch during hardening.

APPARATUS AND METHODS

A substantial spinning machine was constructed with a steel frame approximately 6 × 6 × 2 feet to hold the various reduction gears and drives (Figure 1). The metering gear pump assembly and spinning bath are located on the front of the frame. Glass godet wheels (wheels for guiding or stretching the yarn) are mounted on shaft extensions above the precipitating bath. A large panel coated with acid-resisting paint serves as a splash shield. A two-horsepower, 1725 r.p.m. motor is coupled to a vertical countershaft through a worm and pinion reduction gear. By means of spiral miter gears this shaft energizes three variable-ratio (nonslip) chain drives, placed vertically above one another in the frame. Three reduction units couple the variable drives to three drive shafts on the machine. The lowest variable drive thus controls the gear pump for the casein solution; the middle variable drive controls the speed of the first godet (take-off wheel); and the upper variable drive controls the speed of the other godet wheels and the traversing reel which collects the fiber. This reel has a unique feature, in that the fiber tow remains in the same relative position while the bobbin is moved back and forth by the traversing mechanism. By changing chains and sprockets, any set of godet wheels may be run from any variable drive.

The spinning solution is contained in a converted 27-quart pressure cooker enclosed in a wooden cover. Air pressure lifts the viscous material to the metering pump, which forces it at a uniform rate through a standard viscose candle filter and thence through the glass gooseneck to the spinnerette. A gage registers the pressure in the line between the gear pump and the filter. The pressure ordinarily stood at 150 pounds per square inch for a viscosity of 200 poises at 25° C. A multihole spinnerette was used so that moderate amounts of fiber could be spun and the results would be applicable to commercial practice. The same spinnerette, a platinum-gold alloy cup with a 1.5-inch diameter face containing two hundred and fifty 0.003-inch holes arranged in concentric circles, was used in the experiments reported here. The precipitating bath was contained in a rubber-lined trough, 8 inches wide, 8 inches deep, and 40 inches long. Two precipitating baths differing with regard to the incorporation of aluminum salt were employed:

PRECIPITATING BATH I	PRECIPITATING BATH II
5500 cc. H_2O	5500 cc. H_2O
1200 grams Na_2SO_4	1800 grams Na_2SO_4
600 grams $Al_2(SO_4)_3.18H_2O$	810 grams concd. H_2SO_4
810 grams concd. H_2SO_4	

Studies on the preparation of fibers from acid-precipitated casein with a laboratory spinning machine are reported. Attention was directed to the major operations of fiber production—namely, dissolving the casein, spinning, stretching, and hardening. A spinning solution containing 20% protein and having a pH of 9.2 was employed in most of the experiments. All fibers were given a final hardening treatment with formaldehyde. Stretching the tow issuing from the spinnerette, either in the precipitating bath or between godet wheels in air, gave a tensile strength of about 0.7 gram per denier. Under these conditions of stretching, the addition of aluminum sulfate to the precipitating bath containing sulfuric acid and sodium sulfate did not affect the strength of the fiber. However, such incorporation of aluminum sulfate had a marked effect in a subsequent operation involving simultaneous stretching and partial hardening with formaldehyde. When the latter process was operated at 85° C., a dry strength of 1 gram per denier and a wet strength of 0.5 gram per denier were obtained. Comparative measurements of tensile strength of artificial protein fibers which will be exposed to moisture are best made after the fibers have been swollen in water and dried.

The baths as well as the spinning solutions were at room temperature, 25° to 28° C. The concentration of acid in the bath was not permitted to decrease more than 5% of the total during an experiment.

After traveling about 20 inches in the spinning bath, the tow of filaments from the spinnerette is gathered by the first godet wheel on the lower right, passes over the second wheel mounted immediately above it, and then proceeds to the bobbin. (When a skein is required, the tow is passed in an endless loop around two godet wheels until sufficient fiber has been accumulated.) Early experiments indicated that stretching treatments were much more effective if the fiber was under tension during the formaldehyde hardening. Consequently the fiber was hardened on bobbins. To neutralize the acid carried over from the highly acid precipitating baths, a strongly buffered hardening bath was used. It consisted of 30% sodium acetate and 5% formaldehyde, adjusted to pH 5.8 by addition of acetic acid. For convenience, hardening was done overnight (16 hours), but less time would suffice. The fiber was finally washed for 8 hours in running water, dried for 24 hours at room temperature, cut from the bobbins, treated to remove stresses, and then tested.

TABLE I. EFFECT OF pH OF CASEIN SOLUTION ON TENSILE STRENGTH OF FIBER

(Solutions held at 25° C. for 24 hours; pump rates varied to give fiber of same denier; precipitating bath I at 25–28° C.; drawoff rate, 17.9 meters per min., godet stretch, 41%)

pH of Casein Soln.	NaOH, G./100 G. Casein	Casein, %	Viscosity, Poises (25° C.)	Tensile Strength, G./Denier		
				70° F., 65% r.h.	Wet	Ratio, wet to dry
10.40	6.64	24.8	144	0.51	0.11	0.22
9.21	4.00	19.6	200	0.65	0.24	0.37
6.65	2.66	20.0	200	0.62	0.29	0.47

When the fiber was dried on bobbins, it tended to contract with considerable force. Cutting across the fibers sometimes released the tension with an audible snap. The cut, dry fiber was still subject to residual strains, as shown by contraction in length upon immersion in water. Heim (*13*) has shown that stretched casein fiber contracts to its original length rapidly in water but very slowly when dry. These and other observations led to the suspicion that unrelaxed fibers would evince excess tensile strength, and this was found to be the case. For example, the tensile strength of one sample of highly stretched fiber, dried on the bobbin, was 1 gram per denier. However, when the fiber was cut from the bobbin, wet, and dried before testing, the tensile strength dropped to 0.85 gram per denier and remained at that figure even after another wetting and drying. One factor involved in the higher tensile value is its calculation on the basis of a transiently reduced cross section. The higher strength is dissipated rapidly by water but slowly by the moisture of the atmosphere. Therefore, a practical basis for evaluation of the tensile strength is the value obtained after the fiber is swelled in water and dried without tension. All the results reported here were obtained by this procedure.

Tensile strength was measured with a Scott I P-2 serigraph. Determinations were first made with the spark-recording attachment on single fibers, but the large spread in the values required forty to fifty tests to yield an average of sufficient accuracy. In addition, the circulating air of the testing room dried out wet single fibers so rapidly that erroneous figures for wet strength resulted. For these reasons, a modified bundle test was adopted. As expected, results obtained with the bundle test were less than the averages of single fiber tests, usually about 15% lower. The procedure was based on the A.S.T.M. method for rayon staple (*1*). The needle combs and general technique of handling the fiber specified under D540-41T are employed, but smaller bundles are broken on a machine of smaller capacity.

The test bundles are prepared as follows: About a 2-inch section of tow material is cut. Held in the fingers, this is passed through the fine comb ten times, starting near the ends of the fibers, and proceeding by stages to the center of the bundle. The bundle is then shifted, and the other half combed in the same fashion. The parallel fibers are laid on a cutting block and held down by a brass template 22.5 mm. wide; a razor blade is used to sever the protruding ends. The fiber bundle is now weighed to 0.01 mg. on a microtorsion balance with a capacity of 0 to 10 mg. Only bundles falling in the range 2.00 to 2.75 mg. are used. Two pieces of masking tape, 1 inch long and 1/2 inch wide, are laid with their adhesive faces up and their long sides parallel. They are held about 1/16 inch apart by temporary attachment to a card. The fiber bundle is laid on the strips and the fiber is carefully pressed into the adhesive. The ends of the tape are brought over to cover the adhesive surface, and the bundle is marked with its weight.

The flat bundles described above are broken on the testing machine with the jaws set 1 mm. apart. Since an extension is necessary to place the jaws at this distance, a small correction factor is applied for the increase in weight of the carriage. Load is applied at the rate of 1.0 to 1.4 grams per denier per minute, depending on variations in the weight of the bundle. The bundles are broken at 70° F. and 65% relative humidity in the testing room after the fiber has been equilibrated at these conditions overnight (16 hours). The results of ten bundle tests are averaged in each evaluation. Statistical appraisal of several such series of ten from different fiber preparations showed the following characteristics: Standard deviation, 0.03 gram per denier; standard deviation of the mean (of ten bundle tests), 0.0096; standard deviation of the difference of two such means, 0.0133. Therefore, differences in strength amounting to 0.03 gram per denier may be regarded as significant. Wet strengths are obtained by the same procedure except that the taped bundles are placed in distilled water for 30 minutes before they are broken. The film of water retained by the bundle prevents drying of the fibers while they are tested.

TABLE II. COMPOSITION OF CASEIN[a] AND CASEIN FIBER

(Casein solution at pH 9.2; held at 55° C. for 16 hours and spun into bath I)

	Casein, %[b]	Fiber, %[b]
Carbon	49.13	51.00
Hydrogen	7.48	7.68
Nitrogen	14.80	14.02
Ash	1.88	2.10
Ash, $Ca(Ac)_2$ method	2.70	4.97
Phosphorus	0.86	0.74
Sulfur	0.79	1.14
Aluminum	Trace	0.50
Formaldehyde	None	2.03

[a] This analysis is representative of the commercial product, a low-ash casein precipitated with hydrochloric acid, which was used in all the experiments.
[b] Moisture-free basis.

EFFECT OF ALKALI

It appeared important first to investigate the influence on fiber strength of spinning solutions having a lower alkali content than that proposed by Ferretti. As already pointed out (*5, 29*), such solutions of lower pH have been employed and have been claimed to yield increased strength (*14*). We attempted to spin a series of solutions with a uniform 20% concentration but with pH ranging from 7 to 10.5. However, the solution of highest pH was too low in viscosity to spin from a multihole spinnerette. In this instance it was necessary to increase the concentration of casein. Three solutions of different pH were deaerated by letting them stand for 24 hours, spun into bath I containing aluminum salt, and hardened with formaldehyde as described. As Table I shows, dry and wet strengths of the fiber prepared from the spinning solution at pH 10.4 are definitely lower than the strengths of the fibers prepared from solutions at pH 9.2 and 6.7 A reasonable assumption is that cleavage of protein chains at the higher pH was responsible for the decrease in fiber strength. It is conceivable that harmful degradation of this kind could result from scission of some peptide bonds with only small liberation of amino nitrogen. Losses of ammonia, sulfur, and phosphoric acid occur at pH 10.4 but are not necessarily associated with chain splitting.

Table II illustrates some composition changes which occur when casein is converted to fiber by the general procedure described here. In this case the pH of the spinning solution was 9.2. There is little, if any, loss of organic phosphorus. The increase in the ash reflects the uptake of 0.5% aluminum from the spinning bath. Any change in the organic sulfur of the casein is masked by the sulfate-sulfur picked up from the precipitating bath. The amount of formaldehyde introduced into the fiber by the hardening process employed in these experiments is about 2%.

TABLE III. EFFECT OF VISCOSITY OF CASEIN SOLUTION ON TENSILE STRENGTH OF FIBER

(Solutions at pH 10.8, held at 25° C. for 24 hours; pump rate constant at 21.1 cc. per min.; precipitating bath I at 25–28° C.; drawoff rate, 17.9 meters per min.; godet stretch, 41%)

Casein Solution		Tensile Strength, G./Denier		
Concn., %	Viscosity, poises (25° C.)	70° F., 65% r.h.	Wet	Ratio, wet to dry
25.5	299	0.54	0.11	0.19
24.3	170	0.57	0.11	0.19
23.0	121	0.59	0.12	0.20
22.0	67	0.57	0.11	0.19

Since it is difficult to attain exact control of viscosity in preparing spinning solutions, experiments were undertaken to determine whether viscosity of the casein solution influenced the tensile strength of the fiber. The change of viscosity with concentration is so great that we were able to attain a fourfold increase in viscosity with only a 15% increase in protein concentration. The data in Table III do not indicate any appreciable effect over the viscosity range 67 to 299 poises. The pH of the casein solutions was 10.8. The same result was secured with solutions having viscosities from 53 to 252 at pH 9.2 and from 45 to 157 at pH 7.1. The dry strength values in Table III are higher than that in Table I for the corresponding pH. This was due to the fact that different lots of casein were employed in the two sets of experiments.

EFFECT OF STRETCHING

Attention was next directed to evaluating the relative effects of the various stretching treatments on the strength of the finished fiber. The results are presented in Tables IV and V. For this series of experiments the spinning solution contained 20% casein and 4.5 grams of sodium hydroxide per 100 grams of dry casein. The pH was 9.2. Candle filtration alone did not ensure stable operation of the spinnerette for production of the number of samples required. Hence, the solution was supercentrifuged at 55° C. and then held at this temperature for 16 hours to dissipate the entrained air. The viscosity was 200 poises at 25° C., the temperature of the precipitating bath. The metering gear pump was set to feed 20.3 cc. of casein solution to the spinnerette per minute. The same lot of casein was employed throughout.

The first stretching operation ordinarily takes place in the precipitating bath, where the sodium caseinate solution is converted to insoluble casein by action of the acid and the newly formed filament is partially dehydrated by the action of the salts. The stretch given the fiber at this stage is dependent upon the speed at which the fiber is removed from the precipitating bath relative to the speed of extrusion. The flow of spinning solution through the spinnerette was held constant while the drawoff rate was increased tenfold by steps to 47 meters per minute. Strength progressively improved with drawoff rate until the latter reached the range of 20 to 30 meters per minute (Table IV*A*). Further stretch was of no benefit. The maximum strength of about 0.69 gram per denier showed no significant dependence on aluminum salt in the precipitating bath. The next step was to determine whether godet stretch superimposed on a moderate drawoff stretch would further increase tensile strength. The results of applying godet stretch combined with a drawoff rate of 17.9 meters per minute are reported in Table IV*B*. The figures show that the maximum strength thus secured with the bath containing aluminum salt is slightly greater than the corresponding maximum strength obtained by maximum drawoff stretch alone (Table IV*A*). Under the experimental conditions, strength from both types of stretch appeared to approach the same limit.

Application of stretch in the manner described above entails drawing of a weak and water-laden fiber, which is only subsequently hardened with formaldehyde. A more promising method is to stretch the fiber in the presence of hardening agents (*16, 20, 23, 30*). For this purpose two conical stepped pulleys were installed (vertical pair in middle of panel, Figure 1). The lower conical pulley was partly immersed in a bath containing a heated solution of 30% sodium acetate and 5% formaldehyde, buffered to pH 5.8 with acetic acid (bath III, the same as that used throughout for final hardening of the fiber on the bobbin). With fifteen loops of the casein tow around the two conical pulleys, the fiber was simultaneously stretched and hardened by passage through the heated bath for approximately 2 minutes. This mechanism contributed 100% stretch, which absorbed some tendency of the fiber to sag under the heat treatment. A second stretching operation was imposed between the upper cone pulley and an adjacent godet wheel before the fiber was collected on the bobbin. (The set of conical pulleys on the left in Figure 1 was not used in these experiments.)

Table V*A* shows that these procedures increased the strength of the fiber containing aluminum salt from about 0.71 to 0.85 gram per denier. Other experiments showed that stretching the fiber in hot 20% sodium chloride increased the strength only slightly, while stretching in hot acetate buffer at pH 5.8 increased the strength moderately but not to the values obtained when formaldehyde was also present in the stretching bath. Contrary results were secured with fiber precipitated in the absence of aluminum salt (bath II). Stretching this fiber in a heated bath of acetate buffer and formaldehyde (Table V*A*), sodium chloride, or acetate buffer alone gave a weaker fiber.

TABLE IV. EFFECT OF DRAWOFF RATE AND GODET STRETCH ON FIBER STRENGTH

A. No Godet Stretch			*B.* With Godet Stretch[a]		
Drawoff rate, m./min.	Tensile strength (70° F., 65% r.h.), g./denier		Godet stretch, %	Tensile strength (70° F., 65% r.h.), g./denier	
	Bath I	Bath II		Bath I	Bath II
4.8	0.45	0.18	20	0.69	0.60
9.9	0.54	0.43	41	0.72	0.58
13.6	0.62	0.61	64	0.75	0.68
17.9	0.67	0.64	89	0.73	0.71
22.4	0.68	0.65	119	0.71	0.71
27.4	0.69	0.69	134	0.70	0.61
34.2	0.69	0.67	150	Tow breaks	
43.6	0.70	0.69			
47.0	Tow breaks				

[a] Drawoff rate was 17.9 meters per min.

Since the presence of aluminum salt in the fiber proved so advantageous, fiber was stretched in a heated solution of 10% aluminum sulfate, 10% sodium sulfate, and 2% formaldehyde (bath IV). Fiber of even higher strength was obtained (Table V*B*). The best fiber of this series had a dry strength of 0.98 and wet strength of 0.46 gram per denier. Both the dry and wet breaking elongations were 52%. Immersed in water, the fiber increased in length by 6% but receded to its original length upon being dried and reconditioned. Boiling in water for 10 minutes produced a shrinkage of 19% measured on the wet fiber. It was not resistant to boiling in water for an hour unless it was acetylated (*5*, *7*) or treated with quinone (*12*, *19*). This fiber did not show arcing of the rings in the Debye-Scherrer x-ray photograph. However, when it was given a 50% stretch in clamps, a slight arcing of the inner ring was observed. The birefringence was positive and of magnitude 5×10^{-3}.

Table V. Effect of Stretch with Partial Hardening on Fiber Strength

Godet Stretch[a], %	Stretched in:	Tensile Strength[b], G./Denier Bath I	Bath II
A. Effect of Aluminum Salt in Precipitating Bath[c]			
107	Air, 27° C.	0.72	0.74
127	Bath III, 27° C.	0.71	0.56
136	Bath III, 40° C.	0.77	0.69
173	Bath III, 50° C.	0.80	0.68
206	Bath III, 60° C.	0.85	0.65
B. Effect of Aluminum Salt in Both Precipitating and Stretching Bath[d]		Bath I	Bath I Wet tensile
255	Bath IV, 25° C.	0.77	0.24
349	Bath IV, 55° C.	0.81	0.28
349	Bath IV, 65° C.	0.92	0.34
472[e]	Bath IV, 85° C.	0.98	0.46

[a] Maximum without breaking tow; the initial 100% of this stretch was obtained with the conical stepped pulleys.
[b] At 70° F. and 65% relative humidity.
[c] Drawoff rate, 17.9 meters per min.
[d] Drawoff rate, 16.6 meters per min.
[e] Pump rate was increased to 48 cc. and drawoff rate decreased to 15.2 meters per minute for this bobbin to make the higher stretch possible.

DISCUSSION

In spinning casein fiber, it appears desirable within practical limits to seek mild conditions of alkalinity in the spinning solution and of acidity in the precipitating bath. Even if exposure to extreme conditions of pH does not entail injurious hydrolysis of the protein, excess acid or alkali in the fiber must eventually be neutralized and washed out. Otherwise the hydrophilic nature of salt groups formed in the protein or of inorganic salt present in the fiber heightens the absorption of water and its generally weakening effect. The spinning baths employed in the experiments described here resemble those used in the viscose rayon industry in their high acid and salt contents. While they operate acceptably, precipitation at higher pH values is possible (*16*).

The experiments on stretching are presented only to show the relative values of the particular procedures in producing stronger casein fibers. Any continuous process not involving final hardening of the fiber on the bobbin would doubtless yield different strength values. A marked increment in strength is induced by the stretching of fiber containing aluminum salt in hot buffered formaldehyde baths. The results suggest the trial of other combinations of mechanical and physical factors and of other salts such as those of chromium (*10*) and beryllium (*27*) in place of aluminum.

The properties of our best fiber do not provide a basis for anticipating the upper limits of dry and wet strengths, since the combined stretching and hardening treatment applied to this fiber was brief. Nevertheless, it is of interest to give some theoretical consideration to this point. The most plausible mechanism by which stretch becomes effective in increasing tensile strength is by orientation of micelles or of individual chains in the fiber. Maximum strength would appear to depend on chains of sufficient length, extension of chains parallel with the fiber axis, and packing of these chains. Casein of commerce is a globular protein with a low axial ratio, as shown by various properties including relatively low viscosity in dilute solution. If we assume a molecular weight for casein of 33,600 as determined by Burk and Greenberg (*8*), an average residue weight of 115, and a continuous chain of the amino acids present, there would be about 300 peptide links per molecule. Since the repeating peptide unit occupies a space of 3.5 Å., a fully extended chain would have a length of about 1000 Å. and a width of 10 Å. In a fiber the proper orientation of chains with an axial ratio of 100 should markedly increase the tensile strength. In view of these considerations the denaturation of casein and its treatment to obtain oriented protein chains is a promising line of research. Some common denaturing agents, such as urea, have been patented in this connection (*4*). However, our spinning experiments with urea solutions of casein have not thus far produced a fiber with any orientation detectable by x-ray diffraction or with an appreciably higher strength than is secured in fibers spun from sodium hydroxide solution. A number of procedures for the orientation of the peptide chains of casein have recently been investigated in this laboratory. It has been found that large extruded filaments of casein and other proteins can be converted by moisture, heat or a variety of chemical agents, and mechanical treatment to an oriented structure with chains extended along the fiber axis characteristic of silk and stretched wool (*24*, *25*). The application of these findings to the production of oriented textile fiber by a continuous spinning process is now under investigation.

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YIELD VALUE OF COMMERCIAL SOAPS

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The yield values of typical framed, milled, and the new converter soaps have been measured as a function of temperature with a cutting wire plastometer. The yield value is determined partly by the number and nature of the phases present and partly by mechanical factors. Changes in slope in the curves of yield value *vs.* temperature for framed soap appear to be independent of the rate at which the bar was cooled in manufacture even though the actual magnitude of the yield value may vary greatly. They are, therefore, indicative of phase changes. Rapid cooling results in increased hardness. This result is explicable in terms of increased randomness of orientation of the crystallites but is difficult to reconcile with recently proposed phase theories for these systems. Most converter soaps appear to undergo transitions at 43–46° C. and 63–66° C., irrespective of water content or soap stock, contrary to all published phase diagrams for aqueous soap systems. Several samples also showed transitions at about 52° C.

THIS paper presents the first results obtained in a systematic study of the rheological properties of soap systems. This study attempts to determine the phase relations in these complicated systems, and investigates the effect of thermal history and processing conditions on the properties of the final product. Data were obtained on framed, aerated, and milled soaps, covering a range of composition from 8 to 45 weight % water.

The hardness of soaps has sometimes been measured as a routine test (*10*). However, little use can be made of such data for studying phase behavior and phase structure because of the empirical nature of the tests and the irreproducibility of the results, the latter being due to inadequate control of experimental conditions. Bowen and Thomas (*2*) took measurements based on the force required to move a wire at constant velocity through a cake of soap, and succeeded in demonstrating the effect of chemical composition and of rate of cooling on the hardness of the bar. McBain and Watts (*18*) investigated liquid crystalline soap phases by an extrusion plastometer and a centrifugal falling-ball technique but did not extend their study to solid systems. Recent work by Ferguson *et al.* (*6*) shows that rheological measurements may be useful for determination of phase diagrams, since these authors detect considerable difference in arbitrary firmness at room temperature between beta, gamma (omega), and delta soap phases.

In this work yield values of soaps at room temperature were determined as a function of the thermal history of the sample, the general result being an increase in hardness after heating. These data bear on questions concerning the internal nature of the phases, the development of secondary structure (*5*), and the effects of induced orientation of crystallites in the soap bar. As is the case with other colloidal systems, such as asphalt, rubber, and natural and synthetic fibers, time, temperature, and mechanical working during soap processing affect the rheological properties of the final product. In the case of soap the effects appear to be due partly to effects of these variables on the forms or phases produced and partly on the secondary structure.

Yield values of soap systems have also been determined as a function of temperature. The curves obtained show several sharp changes of slope at temperatures of phase change or other significant alterations in the samples. The method appears most satisfactory in precisely the region of temperature and concentration—above 70% soap and below 100° C.—where previous methods have been inadequate. Thus the method assists in the completion of phase diagrams already established in part by previous work (*13, 25*). The present data suffice to show that all phase diagrams published so far require revision in this important region of concentration and temperature.

APPARATUS AND TECHNIQUE

The cutting wire plastometer consists essentially of a steel wire stretched across a U-bar which is attached to one arm of a torsion balance. Thus a means is provided for measuring the force required to push the wire through the samples, which are contained in a slitted, stainless steel box. Both cutting wire and samples are housed in a constant-temperature constant-humidity air oven. The position of the wire is determined by reading a wall scale on which a spot of light is thrown by a mirror attached to the pointer of the balance. Details of this instrument are given in another publication (*11*).

Samples for most experiments were obtained by cutting slabs of appropriate size out of ordinary commercial bars obtained on the open market. The temperature of the soap was determined by a thermometer embedded in the bar and could easily be kept constant within ±0.02° C. The humidity control was such that a bar, containing 35% water–65% soap and left 24 hours at 40° C., underwent a change of only 0.5% in concentration near the surface and was unchanged near the center. Even at higher temperatures the change in composition was never greater than ±1%; water content of all samples was determined before and after each run by drying to constant weight at 105° C.

The practical yield value (*8*)—the force at which flow becomes observable practically under the usual conditions of the test (10^{-4} cm. per second in this apparatus)—was determined as follows: The wire was first pushed gently 2 to 3 mm. into the sample to eliminate the effects of any surface skin. Counterbalancing weights were then removed until the wire began to move with a velocity not greater than 1 mm. in 5 minutes. This weight, expressed in grams per cm. of cutting wire of 0.0206-cm. radius, was taken as the yield value, provided the motion could be stopped and started again by adding and withdrawing a 10-gram weight.

In obtaining yield value–temperature data, the soap was first placed in the plastometer and the yield value determined at room temperature. The regulator was then set for a temperature 3–4° C. higher, which was reached by the soap after 30 to 45 minutes. At first the soap was allowed to stand at the new temperature for an additional half hour before measurement, but in most of the runs this time was standardized at 5 minutes. This process was repeated until the soap became so soft that accurate yield values could no longer be obtained.

To permit preparation of samples of known and controllable thermal history, a pressure tank was designed and constructed. It was made of $^1/_{16}$-inch stainless steel pipe, 2 inches in diameter and $5^1/_2$ inches long. The end plates were $^1/_2$-inch steel plate and were bolted to the flanges of the tank by eight $^1/_2$-inch bolts, and were seated on an asbestos-filled sheet-iron washer. Heating and cooling at a controlled rate were effected by placing the soap in the tank which was then placed in a double-walled as-

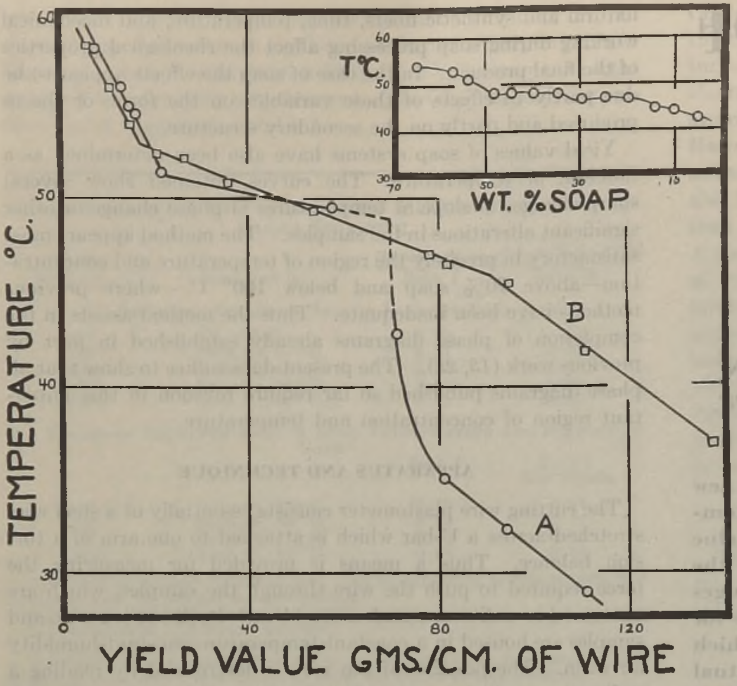

Figure 1. Yield Values of Framed Soap Q

Curve *A* on untreated bar, *B* after cooling from 185° C. Insert shows T_c, the temperatures above which all solid phases have disappeared in this system.

bestos-lined air oven. Soap of 35% water content could be heated to 300° C. in this apparatus with only a slight amount of leakage.

MATERIALS USED

Examples were studied of each of the three chief types of soap; framed, milled, and the new converter soaps (*1*) as represented by Swan and New Ivory. Framed soaps usually contain around 30% water and are obtained by crutching, followed by undisturbed cooling of soap boiler's neat soap over a period of 4 days to a week. Milled soaps as made usually contain around 15% water and result from drying of soap boiler's neat soap, followed by milling, plodding, and extrusion as a continuous bar. Converter soaps are prepared by intense mechanical agitation with incorporation of air into the soap at about 20% water content at temperatures such that it is in a plastic semifluid condition during the working.

Milled and converter soaps for the present work were obtained by purchase of cakes of various brands at local stores. Framed soap Q was a special sample furnished through the courtesy of Lever Brothers Company, and prepared to match as closely as possible the sodium soap A of McBain, Vold, and Porter (*16*). Framed soap R, another typical kettle soap, was obtained through the courtesy of Procter & Gamble Company.

Identifying characteristics of the soaps investigated are assembled in Table I, all compositions being expressed in weight per cent of the original sample. Water was determined by drying to constant weight at 105° C. Fatty acids were obtained by splitting the soap in hot aqueous solution with normal sulfuric acid, removing the fatty acids by ether extraction, followed by evaporation of the ether and of any traces of water. Iodine values on the fatty acids were determined by the method of Fryer and Weston (*7*), and average equivalent weight was found by titration in hot neutral alcohol solution to phenolphthalein with 0.5 *N* sodium hydroxide. Chloride was determined by analysis of the aqueous layers from the fatty acid extraction by the Volhard method. Potassium was determined by the chloroplatinate method as used in the presence of interfering ions (*23*). Free acid or base was determined by titration of a hot alcohol solution of the soap with 0.1 *N* sulfuric acid or sodium hydroxide as required.

The T_c curve (temperatures at which all traces of solid white curd disappear from systems of known composition on slow heating in sealed tubes) was determined for framed soap Q for comparison with that of sodium soap A of McBain, Vold, and Porter (*16*), and is shown in Figure 1. Since the two are very similar over the whole range of compositions (48° C. for soap Q and 49° for soap A, both at 33.5% soap content), it seems permissible to use the other phase data determined for sodium soap A in attempting to interpret the rheological data obtained with framed soap Q. Curiously, the T_c curve for soap Q is slightly lower (1° to 4° C.) than that for soap A in spite of the greater salt content of the former; this result is opposite to the effect of salt on the T_c curve of sodium oleate and water (*14*).

The phase behavior of the potash-containing converter soaps of the present investigation (E, F, G, L) should be intermediate between that of sodium soap A and potassium soap B of McBain, Vold, and Porter (*16*), the present soaps containing somewhat less than half as much potash as potassium soap B.

The data consist of yield value–temperature curves and derived values; a few, typical of the many determined, are shown in Figures 1, 2, and 3. The relatively high precision of the data is evident from Figures 3*a* and 3*e;* these graphs show that, with two different sections of the same composition from each of two different bars, studied under somewhat different conditions, identical yield values were obtained within about 3%.

Table II gives typical yield values for a framed soap at a series of temperatures, both before and after heating to an elevated temperature. Table III lists the temperatures, important for deductions concerning phase behavior, at which there are changes of slope in the yield value–temperature curves of converter soaps. Table IV gives typical yield values of converter soaps at a series of temperatures while similar data for milled soaps are presented in Table V.

FRAMED SOAPS

Phase Diagrams. Typical yield value–temperature curves for framed soaps are shown in Figure 1. Samples from the same large chunk of settled soap showed different yield values at room temperature, depending on whether they came from the exterior or the interior of the piece; those from the outer portions were

Table I. Characteristics of Soaps[a]

Soap	Water Content, %	Chloride, %	Equiv. Wt. of Fatty Acids	Iodine Value of Fatty Acids	Free Base as % Na_2O	Free Acid as % HOl	Potassium, %
Framed Q	33.5	1.89	263.1	43.1	...	0.13	Absent
Framed R	28.5	0.49	269.0	44.9	...	0.05	Absent
Milled O	11.7	0.49	271.0	45.5	...	0.42	Absent
Milled N	7.7	0.75	269.0	46.5	...	0.46	Absent
Milled M	6.5	0.94	258.0	45.4	...	0.30	Absent
Milled P	10.3	1.10	273.0	49.7	...	0.12	Absent
Converter A	21.1	0.92	260.8	40.9	0.02	..	Absent
Converter E	18.3	0.25	250.0	37.7	0.02	..	0.78
Converter F	18.3	0.38	261.5	42.4	0.008	..	1.11
Converter G	17.0	0.38	249.7	37.6	0.007	..	0.97
Converter H	20.0	..	...	..	...	..	Absent
Converter J	18.6	..	...	..	...	..	Absent
Converter K	14.7	0.87	261.9	39.5	0.02	..	Absent
Converter L	20.3	0.22	265.8	45.5	...	0.22	0.74

[a] % refers to weight per cent on a wet basis except potassium which is on a dry basis.

Table II. Yield Values of Framed Soap Q

(Fresh Cake Water Content 35.5%)			After Storage (Water Content 31.6%)			
Temp., ° C.	As received	After cooling from 185° C.	Temp., ° C.	Original bar	Cooled from 105° C. over 3 hr.	Quenched from 105° C.
39	107	189(?)	22	92	129	220
40	73	121	29	59	77	166
50	50	44	43	59	77	96
55	17	12	52	7	15	26

Table III. Temperatures of Marked Slope Changes in Yield Value–Temperature Curves of Converter Soaps

Temp., ° C.	Yield Value	Temp., ° C.	Yield Value	Temp., ° C.	Yield Value
Soap A		Soap J		Soap E	
43	155	43–44	101	43	216
47	95	Not studied above 58° C.		66	18
57	33				
63	32			Soap F	
66	16	Soap K		45	155
		51–52	280	52	150
Soap H		65	78	64–65	45
45–46	105				
52	58	Soap L		Soap G	
62–63	19	40	177	61	88
		64	55	67–68	47

about twice as hard as those from the center. This is not surprising since the interior must have cooled more slowly than the outside, and rate of cooling has been shown to have an effect on hardness. The difference in yield value diminishes as the samples are heated, exterior and interior samples giving substantially identical results above about 45° C.

With all samples of framed soap Q, there was a marked change of slope in the yield value–temperature curve at 46–48° C.; the yield value decreased rapidly above this temperature. At 53° C. there was another marked change of slope; the soap was then very soft, and the yield value changed only slightly with further increase in temperature.

The temperature of the second change in slope corresponds to the visual value of T_c, 54° C. and, according to the phase diagram of McBain, *et al.* (*16*), is due to the final disappearance of all "solid" phases from the system. This interpretation is in accord with the observed softness of the material. The continued existence of a finite yield value proves that soap boiler's neat soap itself is a plastic rather than a viscous material.

In view of the great decrease in hardness which begins at 46–48° C. and is complete at T_c, it seems most probable that the change in slope of the yield value–temperature curve at this point represents the temperature of initial formation of soap boiler's neat soap in the system. According to earlier phase diagrams (*16*), as the temperature is raised above 47° C., isotropic solution should disappear from the system leaving a mixture of middle soap and a more concentrated phase. At 49° C. soap boiler's neat soap should make its initial appearance, middle soap should disappear at this temperature, and the proportion of neat soap should continually increase at the expense of the more concentrated phase until at T_c only neat soap remains. It is significant in this connection that dilatometric experiments (*16*) showed a change, in the sense of a gradual increase of specific volume over a temperature range, occurring at this moisture content at about 45° C. (*16*, Figure 7). Whether the failure of the rheological method to detect two distinct changes is due to the closeness of the two eutectoid temperatures or whether it points to the need of some revision of the phase diagram is not yet clear.

Another mechanism by which soap boiler's neat soap may be produced gradually over a range of temperature is through fractionation of the solid into either pure phases or solid solutions; the unsaturated soaps in the cake possibly undergo transition to neat soap at lower temperatures than the unsaturated soaps. This possibility cannot be excluded until results have been obtained on a single salt of a pure fatty acid, work which is now in progress.

The results on framed soap R (Figure 2) are similar, although the soap is harder and the two transitions have been shifted to somewhat higher temperatures. These differences are in accord with the fact that soap R was drier than soap Q.

Effect of Thermal History on Hardness. The data in Figure 1 and Table II are typical of numerous results on unbuilt settled soaps, showing that the yield values of such samples which have been heated and recooled are greater than those of the original material. At higher temperatures approaching T_c, differences resulting from different thermal treatments become much smaller, as would be expected due to gradual disappearance of the solid phase or phases and the appearance in all comparable samples of soap boiler's neat soap of the same composition.

Curve *A*, Figure 1, represents untreated framed soap Q; curve *B* for the same material after holding at 185° C. for one hour in the presssure tank, followed by cooling to room temperature over a 2-hour period (180° to 87° C. in the first half hour, 87° to 55° C. in the second half hour). The greater yield value of the heated and recooled cake must be due to the presence of different phases at room temperature or to varying degrees of orientation or to different crystal sizes induced by the different rates of cooling or by the maximum temperature to which the samples had been heated.

To investigate these questions further, several experiments were made in which the yield value was determined in immediate succession on three samples processed simultaneously in the plastometer box: One was a bar of the original framed soap Q (cooled from soap boiler's neat soap over a 3–4 day period); the other two were bars prepared by holding between 90° and 105° C. for an hour in the pressure tank, followed in the one case by cooling to room temperature over a period of 3–4 hours and in the other by quenching the tank for 30 minutes in ice water. Samples were kept 24 hours in closed containers at room temperature before determination of yield values. As always, moisture determinations were made before and after the run to exclude the possibility of changes of composition during the experiment. The results (Table II) show the original bars to be the softest, the slow-cooled bars of intermediate hardness, and the quenched bars the hardest.

These results are best interpreted in terms of differences in orientation and crystal size in the different samples. It is well known (*3*, *12*, *20*) that the mechanical properties of fibrous materials (cellulose, nylon, etc.) are greatly influenced by the degree of orientation of the micellar units, and shear hardening of metals due to change in orientation of crystallites is likewise a familiar

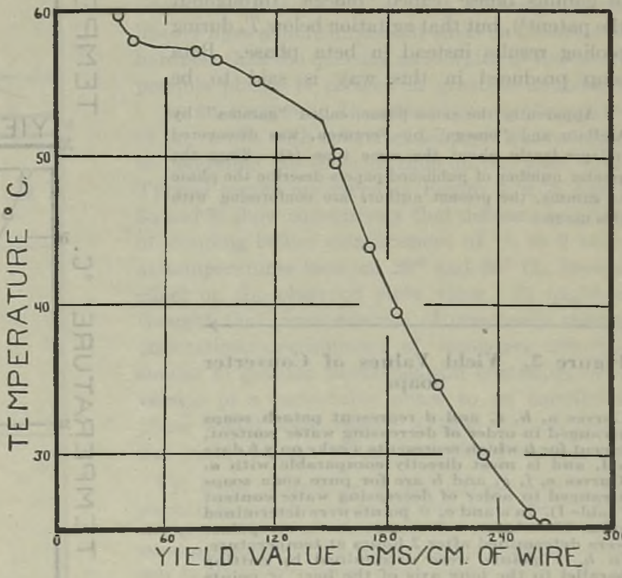

Figure 2. Yield Values of Framed Soap R

phenomenon (*9*). With most materials the strength increases, the greater the degree of orientation. If a cake of soap consists primarily of an interlocked mesh of fibers, as in dilute systems (*21*), but is not yet established for concentrated systems, then a similar dependence on orientation might be expected.

However, in soaps the molecules are perpendicular to the fiber axis (*24*) whereas in cellulose, etc., the main valence chains are parallel to the fiber axis. Consequently, if a perfectly oriented soap sample is cut at right angles to the fiber axis, the break is primarily between relatively weak-linked hydrocarbon chains without breaking primary valence chains. This leads to the prediction that in the case of soaps the yield value would become less, the greater the degree of orientation of the sample.

The present data are in accord with this hypothesis. The degree of orientation obtained in a solid soap is greater, the slower the rate of cooling from a molten or liquid crystalline state (*19*). Correspondingly we find the slowest cooled soap to be the softest and the quenched sample the hardest. This result is also in qualitative accord with Bowen and Thomas (*2*) who showed that the quick-cooled soap is harder than that cooled more slowly.

There is little correlation between the observed yield values and present theories as to the nature of the phases present in these systems. Even if phases of different hardness are present in the different samples as a result of varying thermal history, their thermodynamic properties must be very similar. This conclusion follows from the fact that the general shape of the yield value–temperature curve is unaltered by the previous thermal treatment of the sample, all curves showing only two changes of slope, the transition temperatures likewise being substantially independent of the history of the sample.

The patent literature (*22*) maintains that undisturbed cooling of soap boiler's neat soap usually results predominantly in the formation of gamma phase (called "omega" throughout the patent[1]), but that agitation below T_c during cooling results instead in beta phase. Beta soap produced in this way is said to be

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[1] Apparently the same phase, called "gamma" by McBain and "omega" by Ferguson, was discovered independently about the same time (*5*). Since the greater number of published papers describe the phase as gamma, the present authors are conforming with this usage.

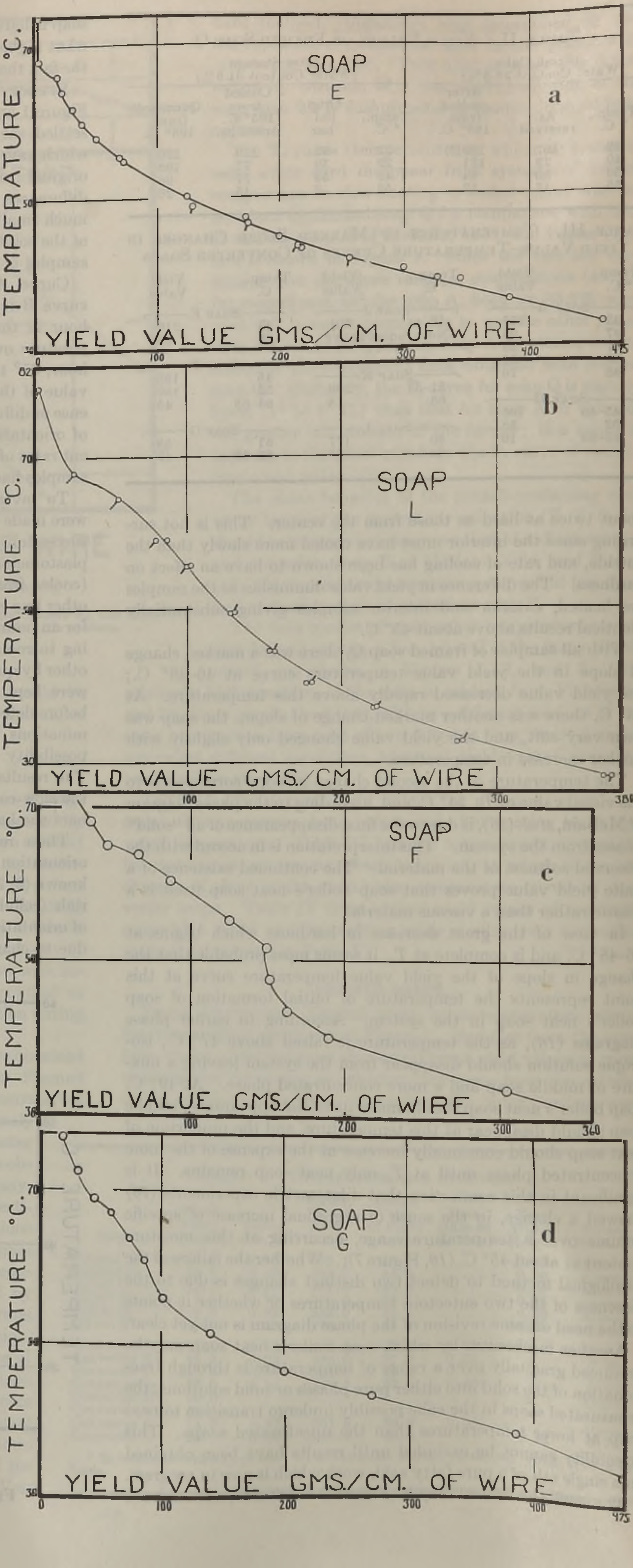
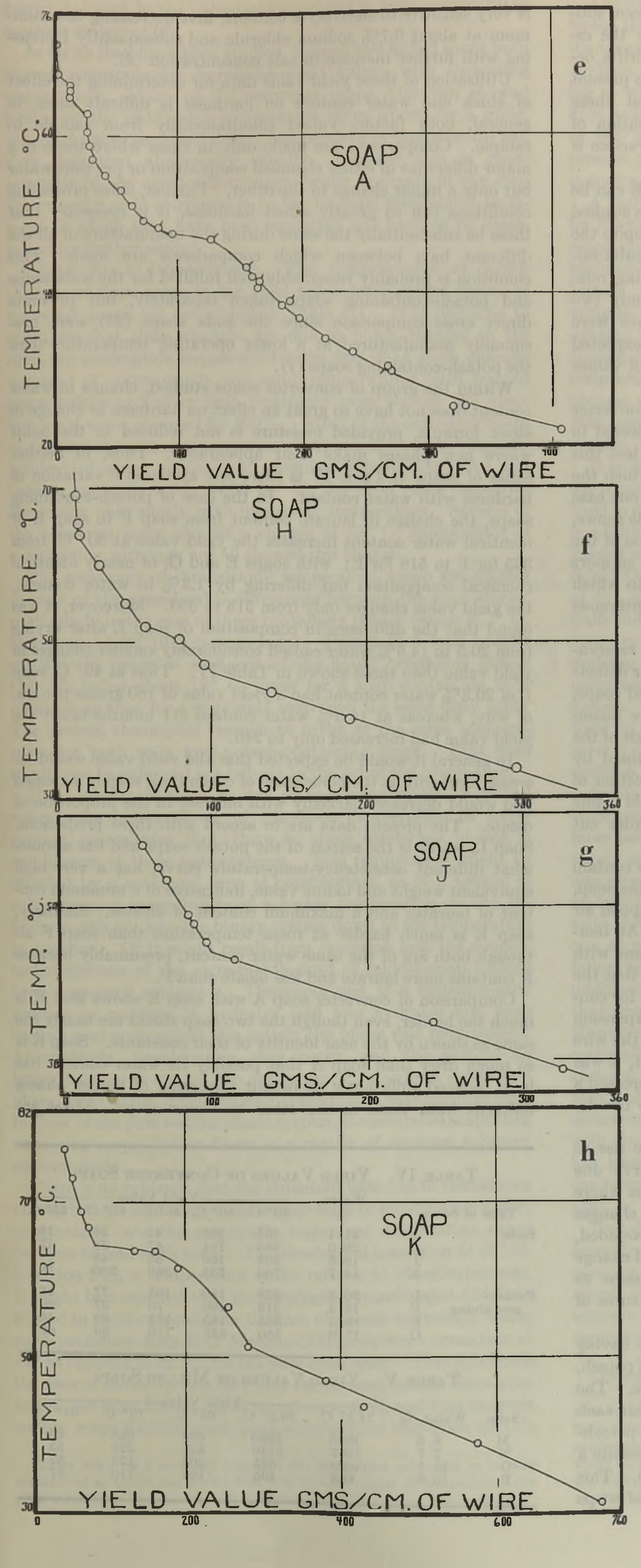


Figure 3. Yield Values of Converter Soaps

Curves *a*, *b*, *c*, and *d* represent potash soaps arranged in order of decreasing water content, except for *b* which represents a cake only 6 days old, and is most directly comparable with *a*. Curves *e*, *f*, *g*, and *h* are for pure soda soaps arranged in order of decreasing water content (Table I). In *a* and *e*, ○ points were determined after 30 minutes at temperature; σ points were determined after 2 hours at temperature. In *b*, Q points were determined by cutting parallel to the long axis of the bar; σ points were determined by cutting perpendicular across the long axis of the bar.



much softer than "omega" soap. Subsequent work (*6*) recognizes more explicitly that degree of orientation, size, and coherence of crystals may have as great an effect on the firmness as the nature of the phase present. Differences of this type due to different processing must be the explanation for the fact that the beta soap studied in the later investigation was found to be harder than the gamma (omega) soap.

Still more recent work (*5*) from the same laboratory suggests that quick chilling of soap boiler's neat soap favors formation of gamma phase, while slow cooling increases the proportion of beta which can, therefore, be formed spontaneously as well as by mechanical agitation. On the average, T_c for beta and gamma phases[2] of the same composition is reported to be the same within 2–3° C. Although it is suggested that delta phase may be the most stable modification at room temperature, it appears to be formed on cooling, chiefly, only in systems more dilute than those currently under consideration.

It is not possible to draw any clear relation from this work between the hardness of the bar and the phases present since (*a*) which phase is formed has not been precisely evaluated in terms of the method of preparation of the sample and (*b*) the dependence of the hardness of a given phase on the processing of the sample has not been clearly specified. The yield values of soaps prepared by cooling soap boiler's neat soap at different rates cannot be explained exclusively in terms of any phase theory heretofore proposed. Undisturbed cooling might be expected to form chiefly gamma phase in all samples, in which case, contrary to fact, all might be expected to have about the same yield value. If slower cooling increases the proportion of beta in the bar, then the initial bar should be the hardest, according to Ferguson *et al.* (*5*, *6*) since it should contain the largest proportion of beta which was shown to be harder than gamma, even though beta formed as specified by Mills (*22*) is softer than gamma. Contrariwise, the observed hardness is seen from Table II to decrease rather than increase as the soap is cooled more slowly. It thus appears that, at least with framed soaps, in this range of composition orientation factors arising from differing thermal history have a more important effect on the observed hardness than the question as to which of the several possible phases is present in greatest abundance.

Aging Effects. In order to assess the validity of the results with converter soaps, it was necessary to determine the effect of time on the yield value. Typical results are given in Figure 3, *a*, *b*, and *e*; 3*a* and 3*e* show conclusively that differences in time of standing before measurement of 1/2 to 2 hours, at temperatures between 20° and 60° C., have no effect on the observed yield value. It might be thought that disappearance of previously induced orientation, development of secondary structure similar to gelation phenomena in bentonite, or reversion of a metastable phase to an equilibrium phase would have caused a time dependence of the yield value. That no changes were ob-

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[2] T_c is the temperature of final disappearance of solid phases (whatever their nature) on heating with the formation of nigre, middle soap, or soap boiler's neat soap according to the composition. It is a temperature of complete melting only in composition ranges where nigre is formed. In the range of most commercial soaps complete melting usually does not occur until a temperature some 200° C. above T_c.

served indicates that all such processes must have been substantially complete within less than half an hour after the establishment of each new temperature, although slow drifts occurring over long periods of time are not excluded by the present experiments. It must be remembered, however, that these experiments refer to small samples and that extrapolation of these conclusions to the large batches of commercial practice is not necessarily valid.

Some information on the effect of longer aging periods can be obtained by comparison of Figure 3, *a* and *b*; soap E was studied 11 months, and soap L, 6 days after manufacture. Despite the differences in chemical composition and in age, the results obtained with the two soaps were very similar, both giving relatively smooth yield value–temperature curves with only two marked changes of slope. The transition temperatures were slightly lower for soap L than for soap E, as would be expected from the greater content of unsaturated acid; the pair of values was, respectively, 40°, 43°, and 64°, 66° C.

Effect of Macroscopic Orientation. Since converter soap is formed by an extrusion process, it might be expected to have a grain structure due to orientation of flow. To test this hypothesis, measurements were carried out on bars in which the wire cut perpendicular to the long axis of the bar in the one case and at right angles to this axis in the other. As Figure 3*b* shows, the yield value was essentially independent of the position of the bar in the case of converter soaps. This would seem to support the contention (*1*) that the intense mechanical agitation to which these soaps have been subjected results in a uniform continuous structure.

However, this conclusion cannot be accepted without reservation since the plastometer may not be very well suited for detecting differences of this sort. Thus, experiments on milled soaps, where macroscopic orientation is known to exist, were inconclusive; values obtained on cutting parallel to the long axis of the bar did not differ by more than 5% from those obtained by cutting across the bar. No regular dependence on direction of orientation was found; one brand gave the same yield value measured in either direction, a second brand was harder cut across the bar, and a third was harder cut along the bar.

Effect of Incorporated Air. Since converter soaps contain large amounts of air distributed throughout the bulk of the soap, it becomes important to consider the effect of this entrapped air on the course of the yield value–temperature curve. At temperatures such that the soap is soft, it can be seen to expand with rising temperature. Consequently it might be predicted that the change of yield value with temperature would be greater for converter soaps than for milled and framed soaps, since expansion of the air might result in a decrease in the proportion of the wire actually cutting solid soap. In accord with this concept, it was found that the yield value of converter soaps usually decreased a little more than 50% between 30° and 40° C., whereas the decrease with the other soaps was not so great.

It might be feared that the entrapped air would give rise to changes in the slope of the yield value–temperature curve due to changes in rate of expansion of the air at temperatures where the soap becomes softer, and independent of any phase changes in the sample. Although this possibility cannot be excluded, it seems plausible that ordinarily such air expansion would change the size of the voids in the bar at temperatures the same as those at which transitions occur to softer phases or mixtures of phases.

Effect of Composition. Among chemical variables having an important effect on the yield value are the proportion of potash, coconut oil, oleate, water, and electrolyte in the soap stock. The differences in electrolyte content between the samples within each group, the pure soda soaps (A, H, J, and K) and the potash-containing soaps (E, F, G, and L), are relatively small despite a considerable difference between the two classes (Table I). This is fortunate since it has been shown that the hardness of soaps is very sensitive to electrolyte content, first decreasing to a minimum at about 0.7% sodium chloride and subsequently increasing with further increase in salt concentration (*2*).

Utilization of these yield value data for determining the effect of stock and water content on hardness is difficult since, in general, both factors varied simultaneously from sample to sample. Comparisons are made only in cases where there is a major difference in either chemical composition or per cent water but only a minor change in the other. Further, since processing conditions can so greatly affect hardness, it is necessary that these be substantially the same during the manufacture of all the different bars between which comparisons are made. This condition is probably reasonably well fulfilled for the soda soaps and potash-containing soaps taken separately, but prevents direct cross comparison since the soda soaps (*22*) were presumably manufactured at a lower operating temperature than the potash-containing soaps (*1*).

Within the group of converter soaps studied, change in water content does not have so great an effect on hardness as change in stock formula, provided moisture is not reduced to the point where new phases make their appearance. Thus, in neither series of soaps of Table IV is there any systematic variation of hardness with water content. In the case of potash-containing soaps, the change in laurate content from soap F to soap E of identical water content increases the yield value at 30° C. from 365 for F to 518 for E; with soaps E and G, of nearly identical chemical composition but differing by 1.3% in water content, the yield value changes only from 518 to 550. Moreover, it was found that the difference in composition of soap L after drying from 20.3 to 14.6% water caused considerably smaller changes in yield value than those shown in Table IV. Thus at 40° C. soap L of 20.3% water content had a yield value of 180 grams per cm. of wire, whereas at 14.6% water content (11 months later) the yield value had increased only to 240.

In general it would be expected that the yield value would increase markedly as the percentage of coconut oil soap is increased and would decrease markedly with increase in the proportion of oleate. The present data are in accord with these predictions. Soap L, which is the softest of the potash soaps and has a somewhat different consistency-temperature curve, has a very high equivalent weight and iodine value, indicative of a minimum content of laurates and a maximum content of oleates. Similarly, soap E is much harder at room temperature than soap F although both are of the same water content, presumably because E contains more laurate and less oleate than F.

Comparison of converter soap A with soap K shows that K is much the harder, even though the two soap stocks are nearly the same as shown by the near identity of their constants. Soap K is so much drier than soap A that possibly its water content has been reduced sufficiently to permit formation of harder phases different from those in the other converter soaps. These are

Table IV. Yield Values of Converter Soaps

Type of Soap		Water, %	Yield Value 30° C.	40° C.	55° C.	60° C.	65° C.
Soda	A	21.1	265	168	41	26	18
	H	20.0	355	194	47	28	17
	J	18.6	305	160	65	48	..
	K	14.7	760	535	260	200	78
Potash-containing	L	20.3	328	180	103	77	48
	E	18.3	518	290	70	37	20
	F	18.3	365	195	125	90	44
	G	17.0	550	355	110	89	66

Table V. Yield Values of Milled Soaps

Soap	Water, %	Yield Value 24.3° C.	39.5° C.	62° C.	73° C.	91° C.
M	6.5	1885	1680	663	368	63
N	7.7	1367	1140	331	220	52
O	11.7	1020	625	202	129	52
P	10.3	663	405	184	110	37

known to occur in the anhydrous soap and in very concentrated aqueous systems (*16*).

As far as they have been studied, framed and milled soaps both showed continuously decreasing yield values with increasing temperature. Many of the converter soaps, however, showed humps on the yield value–temperature curve where, for a while, the yield value remained nearly independent of temperature and then decreased abnormally rapidly. Whether this is characteristic of the composition range (water content) of the converter soaps or is attributable to the unusual mechanical treatment to which they have been subjected will have to be determined by further study[3].

PHASE RULE IMPLICATIONS. The temperatures at which changes of slope occur in the yield value–temperature curves of converter soaps are assembled in Table III. It is plausible to speculate that these changes are due to phase changes in the soap, an assumption supported by the fact that slope changes occurred at substantially the same temperatures with framed soaps before and after heat treatment even though the absolute yield value changed by 100%. Most of the converter soaps underwent changes at temperatures between 43° and 46° C. independent of water content and chemical composition. All also became markedly softer at 63–66° C., the yield value thereafter decreasing only slowly with increasing temperature. Several of the converter soaps showed a change at 52° C. independent of composition, although not all showed this change.

The constancy of "transition" temperature seems remarkable in view of the considerable differences between the soap stocks, particularly in the case of those containing potash (soaps E, F, G, and L are about 10% potash soap). Potash in a soap usually extends the range of existence of the liquid crystalline phases (*16*), T_c being about 12° C. lower for a soap containing 25% potash soap than for a pure soda soap from the same fatty acids. The present rheological transitions occur at the same temperatures for both soda and potash-containing soaps. That such results can be achieved is a tribute to the art of the soapmaker.

If the system behaves as one of two components (soap and water), the independence of transition temperature of water content necessitates that there be three condensed phases in equilibrium at these temperatures. This requirement might be satisfied by a eutectoid type of construction, as of a tongue of subwaxy soap extending from a higher temperature on the anhydrous axis out into the binary system down to the temperature in question. Or it might result from extension into the concentrated systems of the nigre-middle-curd or middle–soap boiler's neat soap–curd eutectoids. Decomposition of a stoichiometric hydrate or mixture of hydrates into two hydrates and soap boiler's neat soap would also satisfy the phase rule requirement. Alternatively, fractionation may occur, and the system no longer behave as one of two components; a sodium oleate-rich phase, for example, might undergo transition at temperatures close to those of the pure sodium oleate system, the saturated soaps then remaining suspended as fibers in a matrix of aqueous subwaxy sodium oleate.

There is no evidence that the eutectoid flats due to coexistence of soap boiler's neat soap–middle soap–curd or middle soap–nigre–curd extend into the practically important composition range between 65 and 85% soap. The rheological transition at 66° C. is at too high a temperature to be related to these eutectoids. It might be suspected that the rheological transition at 43° C. is related to these eutectoids in the case of potash-containing soaps, since potassium soap B of McBain (*16*) underwent transition at 40° as opposed to 52° C. for the pure soda soap. That this is not the case is shown by the fact that the present potash soaps contained less than half as much potash as soap B, and that the pure sodium soaps likewise underwent a rheological transition at 43°.

The data obtained here are not sufficient to permit a choice between the other alternative explanations but do demonstrate the inadequacy of previously proposed phase diagrams. Thus, McBain and Lee (*13*) present a tentative phase diagram according to which there should be no change in a system containing 85% soap on heating from 60° to 80° C. except a gradual shift in the relative amounts of two phases in equilibrium. The present data, however, indicate an important change occurring in such a system at 66° C.

A rather different picture of the phase relations is suggested by Ferguson (*5*). According to this concept, ordinary converter soaps should consist predominantly of either gamma (omega) or hydrous beta[4] phases, depending on their thermal and mechanical history. These phases are both believed to have continuously variable composition, not to be hydrates, and to be capable of existing either singly or in equilibrium with each other. Although the evidence is not entirely clear from the published description, the inference is that a phase diagram based on this picture would show a homogeneous single-phase region in just that composition and temperature region where the present data require there should be transitions.

It is difficult to find other phase data with which to correlate the present work. The dilatometer curves used by McBain and Vold in deducing the phase diagram (*16*) showed many inflections in addition to the reported values of T_1 and T_2, but these were regarded at the time as being too indefinitive to warrant publication. One group of such points occurred at about 65°, another at 45°, and a third at 30° C., all these temperatures being essentially independent of composition. There are, then, some supplementary data tending to show that solid commercial soaps undergo several transitions, the temperature of each of these being essentially independent of the water content of the total system. In addition, unpublished calorimetric data of R. D. Vold on the system sodium oleate–water indicate that here, too, several transitions occur at temperatures independent of composition.

In his most recent paper (*5*) Ferguson advocates abandoning the classical concept (*4*) of bar soap as consisting of "fibers of the more insoluble soaps enmeshing a gel or sol of the more soluble soap", and prefers to regard them as "made up solely of crystalline phase without any apparent separation of liquid crystalline or liquid phases", the crystalline phase being in the form of a solid solution of the various constituent soaps, and existing in one or more of several possible crystalline modifications. The failure to find rheological transitions at the middle-neat-curd and middle-curd-nigre eutectoid temperatures supports the view that there is no free liquid phase in concentrated soap systems. However, this idea is by no means new. It was shown dilatometrically (*15*) for both sodium oleate and sodium palmitate systems that the water in solid aqueous soap systems froze near zero only in dilute systems, and a set of compositions was determined at which the tightness of combination of the water with the soap changed markedly. Moreover, McBain (*13*, *17*) has long distinguished between wet curd and dry curd, only the former having any free soap solution enmeshed in the soled cake.

The data obtained on milled soaps (Table V) are not sufficiently extensive to permit construction of yield value–temperature curves. With the exception of soap P, which contained cresol, the order of hardness agrees with the order of water content. The chemical composition of the four brands is rather similar except that soap M has a somewhat greater content of

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[3] Later work on a specially prepared set of samples subjected to intense mechanical agitation has shown that over certain ranges of temperature the yield value may increase instead of decrease with increasing temperature.

[4] Ferguson recognizes (*5*, footnote on page 7) that his usage of the name "beta" to describe the phase resulting from crystallization of soap boiler's neat soap is contrary to Thiessen's earlier usage of "beta" to describe the form which results on heating "alpha"; the latter phase is probably thermodynamically different from both "alpha" and Ferguson's "beta". To avoid confusion this difference must be clearly recognized. Although realizing its limitations, the present author proposes to call the two phases, respectively, "Thiessen's beta" and "hydrous beta".

laurate (Table I) which causes it to be by far the hardest of the group.

It should be pointed out that milled soaps as manufactured contain considerably more water than the present samples and, hence, might give somewhat different results.

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Resinous Plasticizers from Sebacic Acid

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THE development of plasticizers has closely paralleled the growth of both the plastic and the rubber industries. The use of camphor in nitrocellulose is an early example of a plasticized composition in the plastic industry; the use of modifiers, such as mineral and vegetable oils, waxes, resins, and tars in natural rubber is probably as old as the industry itself. In recent years the tremendous expansion of the plastic and synthetic rubber industries has increased many fold the volume usage of plasticizers over that of only a few years ago. In many present-day plastics and synthetic rubbers the function of the plasticizer is second in importance only to that of the base material.

The increasingly important role played by plasticizers has imposed more exacting and severe serviceability requirements on them. These demands could not always be met by available materials. This condition stimulated plasticizer research rather generally, until today there are on the market materials with resistance toward heat, chemicals, and other deteriorating influences that would have been thought impossible several years ago.

Plasticizers are used in many plastics and in natural and synthetic rubbers chiefly for two reasons: (1) to aid processing and (2) to impart desirable and specific properties to the finished products.

As processing aids, plasticizers reduce power consumption on mills, calenders, extruders, and other equipment, as well as cutting down the time necessary for such operations. Higher-quality products result from the greater smoothness and good definition of the formed surfaces of compounds containing plasticizers. In the case of many plastics the use of plasticizing agents is mandatory in order to reduce processing temperatures to a practical level. With synthetic rubbers, the contribution of the property of building tack by plasticizers is invaluable. The inherent toughness and resistance to breakdown of some synthetics is largely overcome by the use of plasticizers.

Plasticizers impart to plastics and to synthetic rubbers properties that are generally desirable in the finished product such as appearance, smoothness, and feel, but in addition, certain other specific properties may be obtained by the proper choice of plasticizing agent. Flexible, rubberlike compositions are produced when plasticizers are incorporated in certain rigid plastic materials. The degree of hardness and flexibility obtained is a function of the concentration and type of plasticizer employed. Such compound designing involves a knowledge of the functions of the various classes of plasticizers, as well as those of the individual members of these classes. Some specific properties that may be designed into a compound by means of plasticizers are low-temperature flexibility, resilience, varying degrees of room-temperature flexibility or modulus, and resistance to hardness gain on aging at elevated temperatures.

GENERAL REQUIREMENTS OF A PLASTICIZER

PLASTICIZING EFFICIENCY. This term refers to the ability of a material to plasticize the rubber or plastic to produce softness for easier processing or flexibility in the case of the elastomeric plastics. The nature of the plasticizer must be such that this is accomplished at no sacrifice of other general requirements. This property is the first and most important requirement of a plasticizer.

COMPATIBILITY. In order to be generally useful, a plasticizing material must be completely compatible under all conditions (especially of temperature) likely to be encountered in service.

PERMANENCE (LOW VOLATILITY). This property is desirable in order that the beneficial effect of the plasticizer may persist throughout the useful life of the base material.

WATER RESISTANCE. Since most plasticized compositions come in contact with water more or less frequently during their

A sebacic acid polyester plasticizer has been developed which shows good compatibility with polyvinyl chloride, vinyl chloride–acetate copolymer, Buna N (oil-resistant type), GR-S, GR-M, and nitrocellulose. When compounded in typical formulations, this plasticizer exhibits outstanding qualities of permanence, heat stability, oil and gasoline resistance, nonflammability, water resistance, and nonmigration to adjacent plastics, combined with plasticizing efficiency and low-temperature properties equal in some cases to those of the monomeric-type plasticizers. Since the polyester chosen for this work is only representative of a large class of materials, proper choice and combination of suitable raw materials, molecular weight, and polymer modification should yield other polymers whih may have other desirable properties.

serviceable life, this property is also important. A plasticizer must be stable toward, and essentially nonextractable by water.

Chemical Inertness. A plasticizer must be chemically stable at room, processing, and service temperatures, must be inert toward materials with which it is likely to come in contact in service, and must be inert toward the base material in which it is used, so as not to accelerate the decomposition of the latter.

Ease of Incorporation. In factory practice there is a practical limit to the time and temperature needed to incorporate a plasticizer, and for this reason ease of incorporation is important.

Freedom from Odor. An obnoxious odor in a plasticizer would be objectionable in most applications.

Resistance to extraction by oil and solvents is desirable, but this requirement is specific for given applications.

Many specific requirements, such as light stability, good electrical characteristics, and nonflammability, may become necessary or of paramount importance in special applications, and most of them can be met by judicious choice of plasticizer or combination of plasticizers.

CLASSIFICATION OF PLASTICIZERS

Plasticizers in general fall into one or the other of the two following classifications, although there may be some borderline cases: (1) monomeric, exemplified by the esters, amides, and others; (2) polymeric or resinous, exemplified by some alkyd resins, urea-formaldehyde alkyd combinations, and linear polyesters.

The monomeric types are characterized by their good efficiency—i.e., low plasticity imparted to synthetic rubbers and low modulus imparted to vinyl plastics, good resilience, low-temperature flexibility, and low hardness of the compounds containing them. They suffer in varying degrees from the disadvantage of being nonpermanent (volatile), having characteristic odors, poor resistance to solvents, oil, and gasoline, and of being inflammable; the latter property carries over into the compounds containing them, to a greater or less degree.

The properties of the polymeric types are, to some extent, complementary to those of the monomeric type. Thus, many of the former are permanent (nonvolatile), oil, solvent, and gasoline resistant, nonflammable, heat stable, nonmigratory from a compounded stock, and water resistant.

Certain of the polyesters however, combine to a remarkable degree the good qualities of the plasticizers of both broad classifications. Thus, they impart low-temperature flexibility (bend-brittle point) and plasticizing efficiency equal to those of some monomeric types. An additional advantage is the possibility of their being "tailor-made" to meet predetermined requirements by adjusting the molecular weight level and by proper choice of raw materials. The effect of molecular weight on the properties of certain polyesters is known. The effect of various polyhydric alcohols and polybasic acids on the properties of the polyesters is also known, and this approach offers wide latitude in the choice of raw materials from which to make a polyester with desired properties.

Of the polyester plasticizers prepared to date, those derived from sebacic acid have shown most promise, and one has been found to have more general utility as a plasticizer than most of the others. The data presented in this paper have been collected principally on this plasticizer (Paraplex G-25). The use of the sebacic acid polyesters as plasticizers and rubbery materials has recently assumed great importance with the advent of the synthetic rubbers and some of the newer plastics.

MATERIALS AND FORMULATIONS

The sebacic acid polyester, as well as several other typical widely used plasticizers, was evaluated in the following three types of commercial polyvinyl chloride: copolymer of 95% chloride and 5% acetate, copolymer of 90% chloride and 10% acetate, and 100% polyvinyl chloride. Most of the work reported here was carried out on the 95–5 copolymer.

The formulation used for the copolymer batches was as follows:

Polyvinyl chloride-acetate copolymer	63.5%
Basic lead carbonate	1.0
Stearic acid	0.5
Plasticizer	35.0
	100.0

With 100% polyvinyl chloride the amount of plasticizer was increased from 35% to 40%, based on the compound. Basic lead carbonate was used as a stabilizer, and stearic acid as a milling aid. The amount of plasticizer in this formulation was chosen as being fairly typical of that used in commercial practice. Pigments were purposely omitted so that the modifications effected in the properties of the finished compound would be due only to the plasticizer. Samples for evaluation were prepared by methods to be described later.

For the evaluation of the plasticizers in synthetic rubber, a typical oil-resistant Buna N was used in the following formulation:

Buna N (oil-resistant type)	100 parts
Zinc oxide	5
Stearic acid	1
Benzothiazyl disulfide	1.5
Sulfur	1.5
Medium-processing channel black	50.0
Plasticizer	30.0

The batch was milled and vulcanized by methods to be described later. Tests were carried out on both cured and uncured samples. Tests on the cured stock were made on specimens from the optimum cure.

Plasticizer compatibility was the only study made with GR-S, GR-M, and Thiokol FA. These elastomers were milled in the following typical formulations:

GR-S, 100 parts; semireinforcing furnace black, 50; zinc oxide, 5.0; mercaptobenzothiazole, 1.5; diphenylguanidine, 0.2; sulfur, 2.0; plasticizer, 10, 20, or 30.

GR-M, 100 parts; fine thermal black, 100; zinc oxide, 5.0; neozone A, 2.0; stearic acid, 0.5; extra light-calcined magnesia, 4.0; plasticizer, 25.0.

Thiokol FA (master batch), 100 parts; zinc oxide, 10; stearic acid, 0.5; plasticizer, 10, 20, or 30; SRF black, 60.

Thiokol FA master batch: Thiokol FA, 700 parts; benzothiazyl disulfide, 2.1; diphenylguanidine, 0.7.

These batches were milled and vulcanized by standard methods, and compatibility tests were run.

Compatibility studies were also made with the plasticizer, and lacquer grades of nitrocellulose, cellulose acetate, cellulose acetate-propionate, cellulose acetate-butyrate, ethylcellulose,

Table I. Data on Various Plasticizers in 95% Vinyl Chloride–5% Vinyl Acetate Copolymer

Plasticizer	100% Modulus, Lb. per Sq. In.	Heat Stability, Hr. at 150° C.	Bend-Brittle Temp., ° C.	% Extraction Loss in: Water	Oil	Aromatic gasoline	Volatile Loss at 60° C.	Flammability, % Burned	Heat Deformation, %
Sebacic acid polyester	1650	6	−50	0.1	0.1	19.0	+1.0	7	15
Tricresyl phosphate	1440	3	−30	0.1	1.8	28.0	+1.0	0	23.4
Dioctyl phthalate	1060	3.5	−50	0.1	8.4	..	+1.2	100	24.3
Trioctyl phosphate	820	2	−70	0.2	22.4	..	+0.2	12.5	..
Dibutyl sebacate	540	5	−70	0.3	24.6	..	−9.8	100	37

Table II. Data on Three Plasticizers in Vinyl Polymer

Plasticizer	100% Modulus, Lb. per Sq. In.	Heat Stability, Hr. at 150° C.	Bend Brittle Temp., ° C.	% Extraction Loss in: Water	Oil	Volatile Loss at 60° C.	Flammability, % Burned
In 90% Vinyl Chloride–10% Vinyl Acetate Copolymer							
Sebacic acid polyester	1560	2.5	−20	...	0.1	+0.8	7.5
Dicapryl phthalate	665	3	−40[a]	0.3	5.0	+1.5	58
Dibutyl sebacate	222	3.5	−60	0.5	24.3	−10.5	47
In 100% Polyvinyl Chloride							
Sebacic acid polyester[b]	1050	8+	−40	...	−0.2	+0.6	31
Dicapryl phthalate	1210	8	−40[a]	0.1	18	+1.5	100
Dibutyl sebacate	550	5–8	−60	0.5	24	−11.6	100

[a] Approximately.
[b] This batch contained the polyester plasticizer in a concentration of 40%, based on the compound.

and chlorinated rubber. These tests were run in solvents common to the plasticizer and the plastic. Several proportions of plasticizer were used in each case.

METHODS FOR POLYVINYL COMPOUNDS

Preparation of Polyvinyl Chloride and Chloride-Acetate Batches for Milling. The ingredients were weighed out and dry-blended by hand. The batch (400 grams) was then charged to a 6 × 12 inch laboratory rubber mill heated with steam to about 300° F. After the powder was fluxed, it was allowed to mill with a rolling bank for 5 minutes with frequent cutting. It was then sheeted off at about 0.060-inch thickness. A portion of the batch was placed back on the mill and sheeted off at 0.010-inch thickness for use in extraction and volatility tests.

Molding. This operation was carried out in a standard A.S.T.M. four-cavity mold, yielding slabs 6 × 6 × 0.075 inch. The molding cycle was 10 minutes at minimum ram pressure at 300° F., then 10 minutes at 900 pounds per square inch at 300° F. The stock was charged to a cold mold. The samples were cooled under pressure in the mold.

Compatibility. This property was observed on samples from 0.010-inch milled sheets after 24 hours at 0° C. in air and also after 24 hours at room temperature in water. Incompatibility was manifested by surface exudation of plasticizer. Plasticizers which would not allow the batch to flux to a sheet on the mill were also reported to be incompatible. Additional evidence of incompatibility was low tear strength and whitening of the sheet when bent double.

100% Modulus. This test was run at 70° F. using dumbbell-shaped specimens (A.S.T.M. D412–41, die C) on an autographic inclined plane tensile tester which applied load at the constant rate of 167 pounds per minute. The load recorded at 100% elongation was computed to unit stress and called "100% modulus". The dumbbell specimens were cut from A.S.T.M. molded sheets.

Heat Stability was judged by the time required to produce significant discoloration of the compound at 150° C.

Bend-Brittle Temperature was the temperature below which specimens from the molded stocks could not be flexed without shattering when bent through 180° over a rod $^3/_8$ inch in diameter. The samples were preconditioned by storing in air at −30° C. for 24 hours before testing. After preconditioning, the samples were quickly transferred to a dry ice–methanol bath at −40° C. The bath temperature was changed 5° C. at a time and the samples tested until break occurred, after being stored for 5 minutes at each temperature. The bend-brittle point was taken as that temperature 5° above the maximum at which the sample broke.

Extraction Tests. The methods were essentially those of Reed[1] except that samples 0.010 inch thick and 30 square inches in area were used.

Volatility Test. The method used was also that of Reed[1] except that samples 0.010 inch thick and 24 square inches in area were used in a simpler oven.

Flammability was determined by A.S.T.M. method D568–434.

Heat Deformation was measured by a Randall Stickney gage loaded to 30 pounds per square inch on a 13/32-inch-diameter foot. The time of test was 30 minutes at 120° C.

Electrical Properties. A.S.T.M. method D150–42T (4-inch-diameter electrodes) was used for measurement of dielectric constant and power factor. A.S.T.M. method D149–36T for dielectric strength was used under the following conditions: temperature, 25° C.; electrodes, 2-inch diameter under oil; rate of rise of voltage, one kilovolt per second.

METHODS FOR BUNA N COMPOUNDS

Milling. The 6 × 12 inch laboratory mill was used. The standard procedure recommended by the manufacturer of the Buna N was followed. The batches were refined on cold tight

Table III. Milling Properties Plasticized Polyvinyl Chloride

Resin	Plasticizer	Roll Temp., ° F.	Speed of Fluxing	Smoothness of Sheet	Texture of Blend
95 chloride–5 acetate	Polyester	290–300	2–3 passes	Smooth	Lumpy[a]
	Dicapryl phthalate	290–300	Fast	Smooth	Uniform
	Dibutyl sebacate	290–300	Very fast	Smooth	Uniform
90 chloride–10 acetate	Polyester	235–240	Fast	Sheet very soft	Lumpy[a]
	Dicapryl phthalate	290–300	Very fast	Sheet very soft	Uniform
	Dibutyl sebacate	290–300	Very fast	Sheet very soft	Uniform
100% polyvinyl chloride	Polyester	310–320	5 min.	Smooth	Lumpy[a]
	Dicapryl phthalate	290–300	2–3 passes	Smooth	Uniform
	Dibutyl sebacate	290–300	2–3 passes	Smooth	Uniform

[a] Indicates some aggregates of plasticizer were present in the blend after the hand-mixing operation.

Table IV. Electrical Properties of Plasticized 95 Chloride–5 Acetate Copolymer

Plasticizer	Frequency, Cycles	Dielectric Strength, Volts/Mil	Power Factor	Dielectric Constant
Polyester	60	370	0.110	6.8
	1000		0.105	5.6
Tricresyl phosphate	60	395	0.153	7.6
	1000		0.145	5.5
Dicapryl phthalate	60	450	0.084	6.3
	1000		0.092	5.2

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[1] Reed, M. C., Ind. Eng. Chem., 35, 896 (1943).

Table V. Plasticizers in Buna N Stock

Plasticizer	Incorporation Time, Min.	Compatibility[a]		Williams Plasticity after 15 Min., In.	Optimum Cure, Min. at 65 Lb. Steam Pressure	Tensile, Lb./Sq. In.	Elongation, %	Permanent Set, %	Shore Hardness	Hardness Gain, %	Heat Loss, % at 150° C.	Bend-Brittle Temp., 0° C.	Water Absorption Mg./Sq. In.	Oil Resistance (SR-10)			Aromatic Gasoline Resistance (SR-6)		
		Room temp.	0° C.											Weight change, %	Temporary vol. swell, %	Permanent vol. swell, %	Weight change, %	Temporary vol. swell, %	Permanent vol. swell, %
Polyester	13	C	C	0.1310	40	2670	520	15	60	45	1.6	−40	31	− 0.5	19	0.6	− 0.4	50	0.2
50–50 mixt. of plasticizer SC & tributoxy ethyl phosphate	28	C	C	0.0940	40	3090	580	15	50	...	12	−55	18	−16	−10	−17	−14	10	−16
P1 35 (dimethyl amide of a fatty acid)	22	Slight S	S	0.1015	40	2580	734	19	42	104	13.6	−40	18	....	− 8.9	−15.5	....	19.9	−14.2
Dibenzyl sebacate	17	C	C	0.1212	50	2632	510	11	56	51.8	5.4	−35	18.3	−14.4	− 9.2	−16.1	−14.1	12.3	−14.7
Dibutyl sebacate	32	C	C	0.0900	40	2740	603	17	48	102	16	−55	16	−15	− 8	−16	−14	11	−17

[a] C = complete; S = sweat out.

rolls 24 hours after milling. A small portion was sheeted out about $^3/_8$ inch thick for Williams plasticity tests, and the remainder $^1/_4$ inch thick for slab cures.

Molding was done at 65 pounds per square inch steam pressure in a four-cavity, 6 × 6 × 0.075 inch A.S.T.M. mold.

Compatibility procedure was the same as with polyvinyl chloride compounds, except that the water immersion test was not run.

Williams Plasticity. The standard test was used (5000-gram load, 2-cc. sample, 70° C.). The 15-minute reading in inches was recorded as the plasticity value. The details of this test are described in the literature of the manufacturer (Henry L. Scott Company).

Tensile Strength and Ultimate Elongation were obtained on a standard, vertical, Scott rubber tester.

Permanent Set was determined by measuring the distance between the 1-inch bench marks on the broken tensile specimens 30 minutes after break.

Optimum Curing Time was that time of cure which gave the maximum tensile strength.

Nonaromatic Gasoline Resistance was measured with standard nonaromatic gasoline (SR-10 fluid) as the medium. The samples were immersed for 3 days at 100° C. The temporary swell was the per cent increase in volume as measured by specific gravity on the Jolly balance, immediately after the samples were removed from the medium. The permanent swell was the per cent increase in volume after the gasoline had been dried out of the samples for 3.5 hours at 125° C.

Aromatic Gasoline Resistance. SR-6 fluid, a standardized aromatic fuel, was used. The tests were carried out for 3 days at 25° C. and the same measurements made as in the oil resistance tests.

Water Absorption tests were carried out at 70° C. for 7 days on test specimens measuring 0.5 × 1.5 × 0.075 inch. Results were reported as increase in weight in milligrams per square inch.

Heat Loss at 150° C. was the loss in weight of a disk $^1/_8$ inch thick and 1$^3/_4$ inches in diameter after 48-hour exposure to the elevated temperature.

Shore A Durometer Hardness was taken on the disk samples before and after heat loss test. The increase was calculated as per cent of the original hardness.

Bend-Brittle Test was the same for both polyvinyl chloride and Buna N samples.

METHODS FOR OTHER SYNTHETIC RUBBERS AND CELLULOSE DERIVATIVES

Compatibility studies with GR-S, GR-M, and Thiokol FA were carried out by observing behavior of the batch during milling, immediately after curing, after 24 hours at room temperature, and after 24 hours at 0° C. (cured stocks).

With the GR-S stock, 10, 20, and 30 parts of plasticizer were used per 100 parts of rubber; all were cured 40 minutes at 55 pounds per square inch steam pressure. In the GR-M stock, 10 and 25 parts of plasticizer for 100 parts of rubber were used; all were cured for 15 minutes at 65 pounds steam pressure. In the Thiokol FA stock, 10, 20, and 30 parts of plasticizer per 100 parts of rubber were used; all were cured 60 minutes at 55 pounds steam pressure. Milling of the compounds was carried out in each case according to the method recommended by the manufacturer of the synthetic rubber.

The compatibility studies of the plasticizer in the cellulose derivatives (lacquer grade) and in chlorinated rubber (20 centipoises) were carried out as follows: Solutions of each of the materials were made, using solvents which were completely miscible with the solvent in which the plasticizer was dissolved. The solutions were mixed in such a way that the ratio of plastic to plasticizer (solids) in the resulting solutions was, respectively, 9/1, 3/1, 1/1, and 1/3. Each of the latter was flowed out on a glass plate and allowed to dry, and the film examined for clarity. Clear films indicated complete compatibility. Haziness in a film was evidence of incompatibility.

RESULTS WITH POLYVINYL COMPOUNDS

Table I gives data on sebacic acid polyester and on other plasticizers for comparison. All of the plasticizers were completely compatible under the test conditions.

The sample containing the sebacic acid polyester was still flexible after the heat stability test at 150° C., whereas the other plasticized compounds had stiffened considerably. The bend-brittle temperatures are lower than would be obtained in an apparatus like the Kemp tester but serve to rate the plasticizers qualitatively. The oil extraction values show the extreme resistance to extraction by oil of the sebacic acid polyester. The positive volatile losses indicate either that the samples absorbed plasticizer from adjacent samples, or that the filter on the air inlet was not 100% efficient in removing oil from the incoming air.

Table II gives data on the sebacic acid polyester and on two other plasticizers in 90–10 chloride-acetate copolymer, and in 100% polyvinyl chloride. All three plasticizers were compatible in both resins.

Table III compares milling properties of polyester plasticized batches with those of two batches using ester type plasticizers, in the three kinds of polyvinyl chloride.

Table IV summarizes electrical properties of the plasticized 95 chloride–5 acetate copolymer; data collected on the Buna N stock plasticized with sebacic acid polyester appear in Table V. Results on several other representative plasticizers are included for comparison.

Table VI gives a summary of compatibility data compiled for the polyester plasticizer and several others in some well-known synthetic rubbers. The values represent complete compatibility under all conditions of the tests—that is, during milling, after 24 hours at room temperature, and after 24 hours at 0° C.

TABLE VI. COMPATIBILITY DATA[a]

Plasticizer	GR-S	Thiokol FA	GR-M
Polyester	30%	10%	25%
Dibutyl sebacate	30	Incompatible on mill	25
Dibenzyl sebacate	10[b]	10[b]	25
Dibenzyl phthalate	10[b]	30	25
Dicapryl phthalate	30	Incompatible in cured slab	25
Plasticizer 36	30	Incompatible in cured slab	25

[a] The values are the percentages of plasticizer based on the rubbers.

[b] These values should be interpreted as meaning that compatibility was complete at 10%, but not at 20%. In GR-S and Thiokol FA compatibility tests were run at 10, 20, and 30% levels, and in GR-M at one level only, 25%. Thus, with the exception of the 10% values, the results do not necessarily represent the limits of compatibility. It was thought impractical to go to higher amounts of plasticizer.

Table VII gives compatibility data for the sebacic acid polyester in various cellulose derivatives (lacquer grades) and in chlorinated rubber (20 centipoises). Compatibility was decided on the basis of clarity of the dried film.

TABLE VII. COMPATIBILITY DATA FOR CELLULOSE DERIVATIVES

Plastic/Plasticizer[a]	9/1	3/1	1/1	1/3
Nitrocellulose	C	C	C	C
Cellulose acetate	I	I	I	I
Cellulose acetate-propionate	C	C	I	I
Cellulose acetate-butyrate	I	I	I	I
Ethylcellulose	I	I	I	I
Chlorinated rubber	C	C	C	I

[a] The ratios are those of plastic to plasticizer (solids) in the solutions. C = compatible, I = incompatible.

DISCUSSION OF RESULTS

The data in Tables I and II show that the sebacic acid polyester is an outstanding plasticizer for polyvinyl chloride and chloride-acetate copolymer. Its extreme oil resistance is especially noteworthy. Its flammability and plasticizing efficiency are not quite equal to those of the widely used tricresyl phosphate, but it is better for oil resistance, heat stability, bend-brittle point, aromatic gasoline resistance, and heat deformation. Dioctyl phthalate exceeds the polyester only in its better plasticizing efficiency.

The low heat deformation of polyester-plasticized polyvinyl chloride or copolymer is evidence of the wider temperature range of usefulness of such a composition. This is especially important in applications at slightly elevated temperatures, such as cable coverings, which must not deform under their own weight more than a minimum amount.

The reason for the positive volatility values has already been given. In those cases where positive values were obtained, it is certain that actual losses were either negligible or too small to come within the accuracy of the test. Small differences in weight before and after testing were difficult to measure accurately because of the relatively large samples used. Nevertheless the test served to bring out the differences between permanent and fugitive plasticizers.

Two valuable properties of polyester-plasticized compositions that do not appear in the tables are (1) their good processing and (2) the nonmigrating character of the plasticizer in such a composition. As a result of field trials it has been reported that polyester-plasticized compounds, both polyvinyl chloride and Buna N synthetic rubber, process satisfactorily. This is especially true in extrusion operations, in which surface uniformity of the extruded article is of first importance.

The nonmigrating character of the polyester, particularly in polyvinyl chloride or copolymer compositions, makes it unique among plasticizers. Field tests indicate that when such a composition is in direct contact with another plastic composition, there is no appreciable migration of the polyester to the second plastic. Many fabricated articles consist of two or more plastic compositions; it is of great importance in some of these applications that the plasticizer be permanent, in the sense that it should show no tendency to migrate and thus adversely affect the properties (such as electrical characteristics) of the other plastics.

Table III shows that the speed of fluxing of the polyester-plasticized batches was not so great as with those containing the ester plasticizers, but fluxing was complete under the conditions of time and temperature specified. A mechanical mixer such as a Banbury can also be used.

The data in Table IV indicate that the polyester plasticizer is qualified electrically for many of the insulation applications, which account for a large portion of present-day vinyl plastics production.

Table V shows that the sebacic acid polyester plasticizer exhibits the same desirable properties in Buna N as in polyvinyl chloride or copolymer. Low heat loss and hardness gain indicated plasticizer permanence, and oil and gasoline resistance were outstanding. The hardness gain test was designed to measure the increase in hardness due to loss of plasticizer by volatilization, but it was somewhat too severe and some of the hardness gain was due to increase in hardness of the rubber itself. The values obtained were comparative, however, and serve to show that the polyester was the least volatile of the plasticizers tested. The very low weight change values, in contrast to those for the other plasticizers, show that little or no polyester was extracted out by the solvents. The incorporation time required for the polyester in Buna N was less than for any of the other plasticizers tested. A short incorporation time usually indicates good compatibility, because those plasticizers which are on the verge of being incompatible or have a tendency to exude from a cured slab invariably require an excessively long incorporation time.

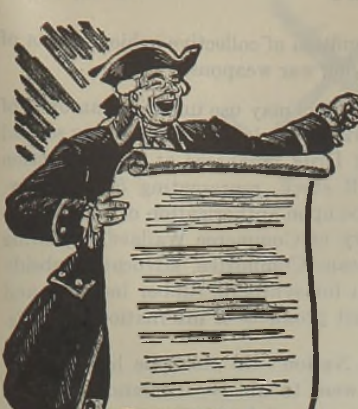
The compatibility data in Table VI for other synthetics supplement the good results previously found for the polyester in Buna N. As shown by Table VII, however, compatibility of the polyester in cellulose derivatives is not good but is complete in all proportions in nitrocellulose.

The low plasticizing efficiency of the sebacic acid polyester can be compensated for by using somewhat greater quantities (10 to 15%) than would be necessary with a monomeric type. The problem of increasing the efficiency of the polyester plasticizer is being actively pursued, and it is already known that change in molecular weight, change in one or more of the raw materials, or modification of the polymer all have an effect on the plasticizing efficiency. It is expected that suitable adjustments by one of those means will yield a material of improved efficiency, without at the same time impairing the unique qualities of the polyester.

ACKNOWLEDGMENT

The authors wish to thank C. F. Moculeski for compatibility data in GR-S, GR-M, and Thiokol FA; H. L. Tuthill for compatibility data in cellulose derivatives and in chlorinated rubber; and R. J. Myers for many helpful suggestions during the course of the work.

PRESENTED before the Division of Paint, Varnish, and Plastics Chemistry at the 108th Meeting of the AMERICAN CHEMICAL SOCIETY in New York, N. Y.



APRIL'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ April 1. Congressman McDonough introduces H. R. 2827, authorizing release and deferment from military service of technologically trained men, and providing that President prescribe rules and regulations to aid in making possible their education, training, and utilization to meet essential needs, both in war and peace[1].∼∼War Department stops operation of most of Canol oil project[2].∼∼War Mobilization Director Byrnes recommends vigorous steps to prevent formation of private international cartels after Japan's defeat.

¶ April 2. War Production Board's Chemicals Bureau authorizes unlimited use of corn of certain grades for industrial alcohol production.∼∼Office of Price Administration authorizes price increases to encourage output of rubber grades of carbon black.∼∼Supreme Court rejects Government's suggestion that federal courts retain power to dissolve Hartford-Empire Co. in enforcing Court's decision in glass antitrust case but modifies opinion rendered in February.∼∼WPB places additional restrictions on use of collapsible tubes owing to "extremely short supply" of lead.∼∼President Roosevelt accepts resignation of James F. Byrnes as director of Office of War Mobilization and Reconversion and names Fred M. Vinson to succeed him.∼∼WPB increases reserve production of paperboard from 40 to 50% of a manufacturer's average monthly output.∼∼WPB revises L-197 to provide more equitable distribution for steel drums.∼∼Senate Small Business Committee defers hearings on Canadian aluminum contract until April 10.∼∼WPB removes restrictions on delivery and use of Freon-12 for air conditioning and certain types of refrigerating systems.

¶ April 3. Construction changes involving use of more synthetic and less natural rubber will save 3000 tons of natural rubber a year, according to WPB.∼∼Glass Containers Manufacturers Institute, a nonprofit organization, incorporated by nondefendants in recent glass antitrust cases.∼∼Senate rejects compromise manpower control bill.

¶ April 4. Senator Harry Byrd introduces bill for establishing research board for national security to keep military inventions abreast of the times.∼∼WPB rules that magazines and most commercial printers must take a 13% reduction in deliveries of paper in April, May, and June.∼∼State Department reveals that Government has promised Chile it does not expect to continue operation of synthetic nitrogen plants after the war, except to keep them in stand-by operating condition and for continuing scientific research and technological experiment, and that it would consult Chilean Government if cession or sale of such plants to private interests seriously affected Chilean economy.∼∼WPB takes drastic action to force compliance with container order owing to continuing shortages of fiberboard shipping containers; takes steps to conserve low supply of phthalic alkyd resins by amending Schedule 59; and places hydroquinone under allocation to meet higher demands for synthetic rubber program.∼∼Goodrich establishes B. F. Goodrich Chemical Co. with offices and laboratories in Cleveland, and manufacturing plants in Niagara Falls, N. Y., and Louisville.∼∼Four rayon plants ask WPB for 860 workers, saying that otherwise a 12% deficit in second-quarter tire fabric production will result.

¶ April 5. WPB Chairman Krug announces appointment of Henry P. Nelson as coordinator of reconversion for automotive industry.∼∼Spokesmen for aviation fuel suppliers, airline operators, and engine manufacturers, at meeting of Society of Automotive Engineers in New York, agree that superfuels of 100-octane rating and higher will play minor role in postwar civilian aviation, that 91-octane gasoline will dominate in commercial flying, and 80-octane should prove sufficient for light or medium aircraft for private use.

¶ April 6. Petroleum Administration for War extends indefinitely restrictions against use of butane and propane-butane mixture for drilling oil and gas wells where natural gas is available[3].∼∼U. S. Engineer's Office announces production of new portable aluminum bridge, weighing 54 tons, which can span a river up to 436 feet in width.∼∼WPB again restricts use of tungsten in high-speed tool steels.∼∼Goodyear develops adhesive cement, Pliobond, which L. B. Sebrell, director of laboratory, says may replace needle and thread in garment trades.∼∼New waterproofing chemical being sold by U. S. Industrial Chemicals is said to make car motors waterproof.

¶ April 7. Special Senate committee on petroleum resources announces it will investigate cartels in relation to world oil trade in hearings to start about May 1[4].∼∼F. L. Martin, Sunray Oil's vice president, says $500,000 addition to refinery at Allen, Okla., will go on stream this week, and increase plant's cracking capacity to 5500 barrels.

¶ April 8. Krug appoints committee to handle problems relating to easing controls for smooth reconversion by industry.∼∼National Association of Manufacturers, in weekly *NAM News*, urges planning now for contract ending and warns against bottleneck for war industries after war.∼∼Monsanto announces new series of casting sealants now used on B-29 bombers.∼∼Army says Lt. Gen. W. S. Knudsen will resume duties as War Department director of production May 1.∼∼Guy M. Gillette, chairman, Surplus Property Board, announces appointment of Col. Alfred E. House, former Air Corps procurement officer, as administrator of Surplus Property Board.

¶ April 10. American Viscose sponsors rayon launderability research fellowship at American Institute of Laundering.∼∼Du Pont absorbs Defender Photo Supply Co.∼∼Senator Capehart introduces S. 840 to extend life of unexpired patents for periods equal to time patents have been in force during war.∼∼

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[1] *Chem. Eng. News*, **23**, 645 (April 10, 1945).

[2] *Ibid.*, 640 (April 10, 1945).

[3] *Ibid.*, 729 (April 25, 1945).

[4] *Ibid.*, 730 (April 25, 1945).

W. L. Batt, WPB vice chairman of international supply, appearing before Senate Small Business Committee, strongly defends 1941 contract between this country and Aluminum Co. of Canada for expansion of Canadian power and aluminum production facilities; says cost was secondary when we needed metal.∼∼Corn Industries Research Foundation says loss of workers at corn refineries seriously reduces output of starch for war industry.

¶ April 11. Senator Magnuson, speaking before Senate Small Business Committee, advocates Congressional review of government aluminum contracts to determine whether they tend to foster monopolies.∼∼Army halts work on plant at Pine Bluff, Ark., which was to have been operated by American Can for production of fiber containers.∼∼WPB amends aluminum copper orders banning blanket permission to sell under CMP-4.

¶ April 12. Krug says unless war demand for aluminum decreases, Government's stock will run out before end of year.∼∼Machine developed by Food Machinery Corp. applies law of gravity to sorting food.∼∼President Roosevelt dies at home in Warm Springs, Ga.; Harry S. Truman takes oath of office as President of the United States.∼∼Department of Justice files antitrust suit charging Westinghouse with entering into agreements with two German concerns to divide world markets for manufacture and sale of electrical equipment[5].

¶ April 13. WPB places further restrictions on use of cadmium.∼∼Western New York Section, ACS, announces award of Jacob F. Schoellkopf Medal for 1945 to Alexander Schwarcman[6], of Spencer, Kellogg & Sons.

¶ April 14. PAW says it is assisting British interests in construction of 100-octane refinery on Curaçao.∼∼Du Pont announces postwar program for scientifically color conditioning industrial interiors.∼∼Edwin J. Cohn, professor of biochemistry, Harvard University, chosen as first winner of Passano Foundation Award of $5000[7] as result of nationwide poll among leaders in medical sciences.

¶ April 15. Federal Government takes over strike-bound 100-octane gasoline refinery and butadiene plant of Cities Service Refining Corp.

¶ April 16. WPB, by amendments to L-340 and L-289, fixes paper inventories at 50-day supply.∼∼Benton R. Cancell, of WPB Forest Products Bureau, tells House Committee investigating newsprint shortage that agency fears serious reconversion bottleneck because of lack of containers from pulp and waste paper.∼∼Ethyl Corp. announces new method for making ethyl chloride and construction of $750,000 unit employing this process at Baton Rouge, La.

¶ April 17. Senators Bankhead and Hill of Alabama introduce S. 882 providing $46,000,000 fertilizer program for government construction of three plants, purchase of fertilizer resources, 75 demonstration farms in each county, and other educational work.∼∼First government-financed channel-type carbon black plant starts operations, Robert I. Wishnick, president, Continental Carbon, states.∼∼WPB eases control on lactic acid.

¶ April 18. Dun & Bradstreet report that manufacturers of chemicals, electrical machinery, transportation equipment, and rubber items will offer greatest percentage of new products. ∼∼Franklin Institute presents Zay Jeffries, vice president of General Electric, with Francis J. Clamer Medal for "meritorious contributions to science of metals"; Sanford L. Cluett, president, Cluett Peabody & Co., with Edward Longstreth Medal for "mechanical ingenuity in development of process for preshrinking woven fabrics"[8].

¶ April 19. American Cyanamid announces formation of new textile resin department.∼∼National Academy of Sciences receives $25,000 award in recognition of collective achievements of American scientists in supplying war weapons.

¶ April 23. WPB says distillers may use unlimited amount of corn graded No. 3 for industrial alcohol production during second quarter of 1945.∼∼Sterling Drug purchases at public auction Winthrop Chemical Class B stock, representing 50% equity. Stock sold by General Aniline upon authorization of Alien Property Custodian.∼∼Secretary of Commerce Wallace, appearing before House Ways and Means Committee, advocates subsidy rather than tariff protection for synthetic rubber industry and special tariff measures against products of international cartels.

¶ April 24. WPB reports Nation's tin stockpile has dropped to lowest point since U. S. went to war.∼∼Secretary of Commerce, testifying at trade agreement hearing, says export controls may have to be continued some 2 years after end of war.∼∼Attorney General Biddle in report to Congress advocates lease rather than immediate sale of surplus government plants.

¶ April 25. WPB says solid or corrugated fiber containers, reformed, reshaped, repaired, or reconditioned, are not subject to restrictions of Limitation Order L-317.∼∼WPB sees Navy's need of alkyd resins in Pacific area much heavier. Krug predicts that nearly one third of WPB's industry controls will be released in next 4 months.

¶ April 26. Tariff Commission Chairman Ryder discloses U. S. plans to insert provision in future reciprocal trade agreements whereby imports of any commodity can be limited to safeguard domestic producers.∼∼WPB outlines adjustment in production schedules from two- to one-front war and establishes tentative output goal for first year after V-E day of $48,000,000,000.∼∼Secretary of Commerce appoints committee to study patent structure, consisting of William H. Davis, director of Economic Stabilization, as chairman, Attorney General Francis Biddle, Vannevar Bush, director of Office of Scientific Research and Development, and Charles F. Kettering, vice president of General Motors.∼∼WPB further amends rubber order to limit inventories of crude, latex, synthetic, reclaimed, and chlorinated rubber.∼∼Raymond B. Fosdick, president, Rockefeller Foundation, in an indictment of government policy toward training of scientific men in wartime, says U. S. has lost so much technical strength that it may be unable "to meet the needs of the next generation".

¶ April 27. WPB says manufacturers of Class A chrome pigments in May will receive approximately 60% of their requirements of sodium bichromate controlled by Order M-370.∼∼Zinc industry spokesmen appearing before House Ways and Means Committee protest broadening of reciprocal trade law and state that it would mean destruction of U. S. zinc industry.

¶ April 28. NAM'S board of directors passes resolution urging U. S. to take the lead to outlaw international cartels.∼∼WPB bans after May 7 use of imported cane alcohol for blending beverage spirits and other nonessential uses.∼∼Montgomery Ward files brief in seizure case in reply to Government's appeal from ruling of Jan. 27 which held Presidential order had neither statutory nor constitutional authority.

¶ April 29. WPB Chairman Krug names John P. Small executive officer of WPB.∼∼E. W. Thompson, plant manager, says completion of new unit at Du Pont-operated neoprene plant in Louisville will step up production by approximately 26%.

¶ April 30. Supreme Court establishes right of patent applicants to a review by Lower Court of Claims rejected by Patent Office and Board of Patent Appeals.∼∼R. E. Wilson, chairman of board, and A. W. Peake, president Standard Oil (Ind.), say company plans $100,000,000 modernization program.

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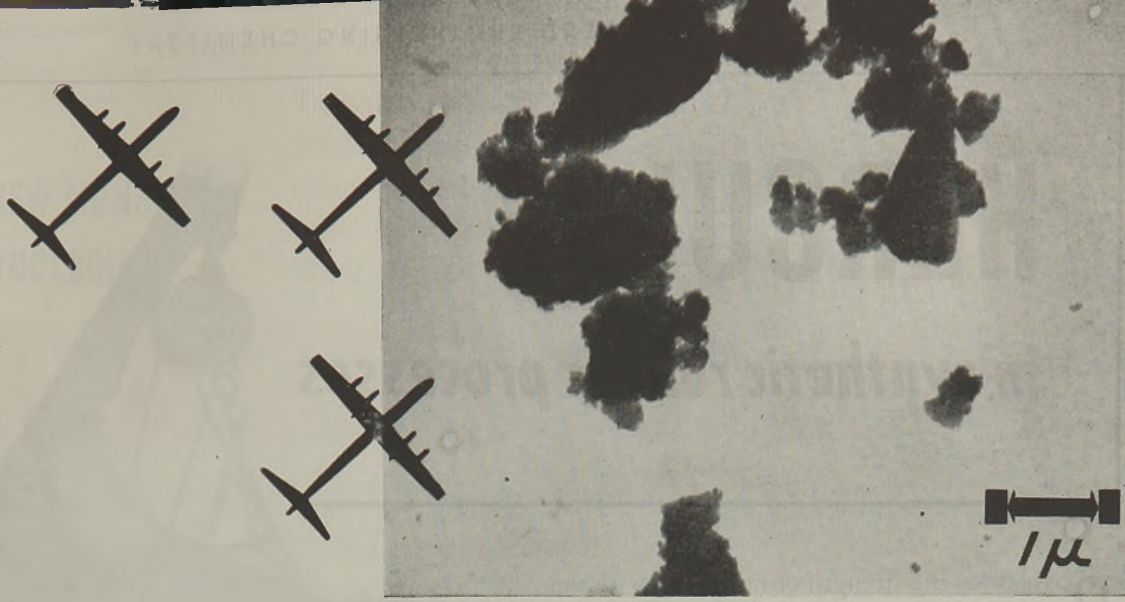
[5] *Chem. Eng. News*, 23, 735 (April 25, 1945).

[6] *Ibid.*, 704 (April 25, 1945).

[7] *Ibid.*, 728 (April 25, 1945).

[8] *Ibid.*, 636 (April 10, 1945).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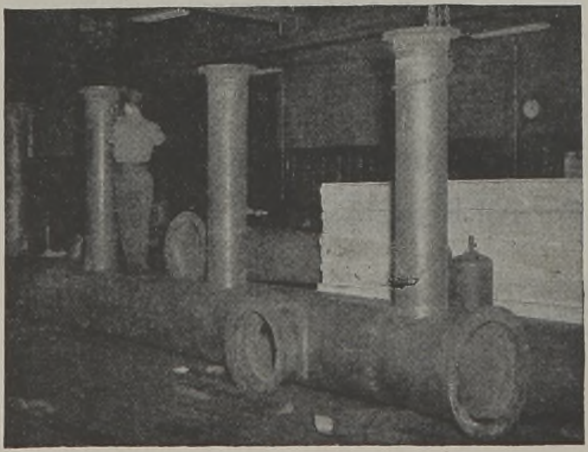

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Current Developments in EQUIPMENT AND DESIGN

C. O. Brown, now consulting in Mexico City, tackles the knotty but moral and humane problem of fitting our disabled veterans into the industrial picture.

Discussed by Charles Owen Brown

For a long time the author of this column has wanted to present an earnest message about jobs for disabled veterans. This is a theme of encouragement, of new hope for disabled veterans wishing to become operators of plants, rather than of plants and equipment. Here in the sunshine of Mexico City, there seems to be time and mood to do the subject justice. We believe that in management will be found fairness, ability, and a dignified consideration of the problem of creating jobs for disabled veterans. These suggestions are therefore respectfully directed to the able leaders of the chemical industry.

It is certain that if a maimed veteran approaches any company within the chemical industry to ask for a position, he will be given every consideration. What we are suggesting, however, is a more systematic policy for the employment of disabled veterans, a plan which will have been fully considered and perfected before the applicant seeks employment.

Making a new connection is important, sometimes embarrassing, and always serious for the average individual. To a crippled or disabled person it is far more difficult, mentally and actually. Let us have the machinery for employing disabled veterans skillfully organized, well thought out, ready for use, before the handicapped man makes his application. This is not an easy problem. Considerable study from new angles must be given to the various operations and positions in plants, and research made on the ability of disabled men to accomplish these duties and operations safely. There will be discussions with the plant safety committee which should approve and pass upon any new policy of this sort. This will not be completed quickly or easily. Let us get at it now.

With these matters standardized, it will be more cheerful for the disabled veteran appearing at the employment window or gate to be told in a friendly, helpful manner just how he may obtain a suitable place for his talents. There are many operations which a disabled veteran can perform, but much depends on his type of disability. As this matter is studied further, one will be surprised at the number of positions and jobs which can successfully be made available to handicapped men.

Several of the large chemical companies and most of the oil companies have already remodeled policies for giving jobs to former employees. The rules are on the record. The annual report of The Texas Company contains a statement of policy, regarding the re-employment of former employees, which is generous and encouraging. We propose, however, that this matter be carried much farther, and that a policy be adopted which materially increases the number of jobs available to the disabled. If managements are permitted to manage to the capacity of their talents, we have every confidence that sufficient jobs will be opened up, not only to all disabled men, but to all returning veterans. That is a laudable objective.

First, a list should be made of the types of disability most likely to be encountered. For this preliminary discussion, let us consider handicaps of the following types:

1. Amputation of one arm
2. Amputation of one leg
3. Amputation of one hand
4. Deafness in one ear or difficulty in hearing
5. Complete deafness
6. Blindness in one eye
7. Total blindness
8. Loss of speech or serious speech impediment
9. Loss of toes or fingers

The number of jobs available for some types of disability in this list will be larger than for others. On the other hand, we must face the fact that relatively few jobs exist which can be successfully performed with other types of disablement, particularly total blindness. Careful study may reveal the fact that more than half the unit operations in the average chemical manufacturing plant can be carried out, with perhaps slight preparation, by men with serious handicaps. Study will develop a greater than expected number of jobs for the totally blind, for the speechless, or for those who have lost both legs or both arms. The proper approach to this problem may well be to pose the question, "What jobs cannot be done by a man disabled by each of the above classifications?" Then we can chart the jobs resulting from that study.

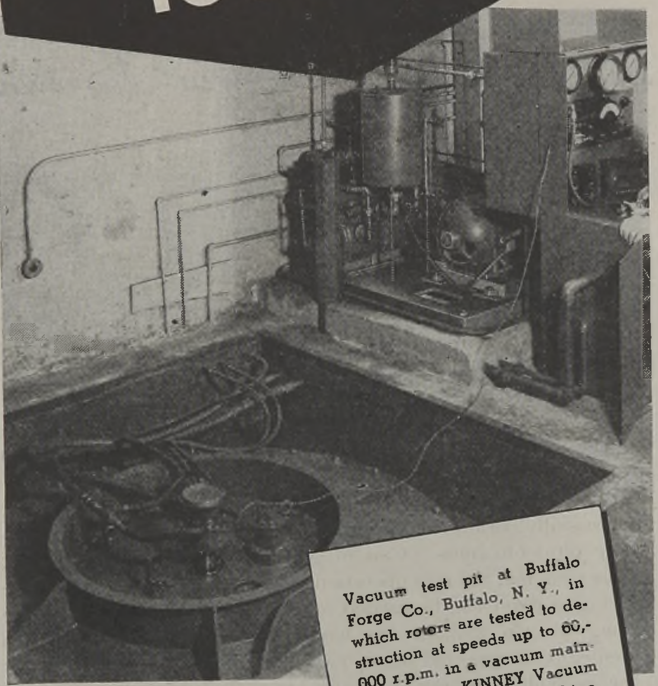
Since this is an age of labor-saving machinery, body disablements in general are not so crippling and certainly not so serious as those same handicaps were in operations regularly performed some fifteen or twenty years ago. Many of the automatic devices and mechanized operations now being carried out need only supervision and slight adjustment to make sure nothing gets out of order; the operation itself is completed mechanically.

In studying the various jobs which disabled men may perform, one should not forget the enormous improvements which have been made in the efficiency of artificial limbs. Part of the job of management, in this problem, is to study the efficiency of artificial limbs, and then specify what disabled veterans can perform when wearing these limbs. The amputation of one hand is not serious for many tasks, and we may be able to put more than 50% of all operating jobs in this class where a man with one modern, artificial substitute hand can be efficient. In like manner, a man who has lost one arm, which is replaced by a modern artificial arm, can exert considerable strength of shoulders and back in simple operations requiring a good pull or lift.

The amputation of one leg can be overcome not only by an artificial leg, but by one crutch. The only effect of the crutch is to slow up the man and make his movements seem more awkward. The number of things he will do in the course of a day is almost as varied as if he had two good legs.

Deafness is not so much of a handicap as it would have been several years ago. At present, unless the case is serious, hearing aids may correct the trouble, or at least make the man almost as efficient as a worker with perfect hearing. Even uncorrected, total deafness is not so serious as it

(*Continued on page 74*)



might appear at first. There are at least twenty-two types of jobs in chemical and general industrial plants which may be undertaken by the totally deaf.

Since I have studied this matter, I have come to the conclusion that a man blind in one eye should not be classified as disabled. One eye will see as clearly and accurately, and will permit as distant vision as two eyes. Perhaps the second eye has been included by Nature as a spare. In any event, the loss of one eye requires only more care to avoid overworking it. I have a lifelong friend who lost one eye as a youth. It has not prevented him from obtaining scientific and technical fame and the development of a billard game which is consistently better than my own.

Total blindness is a serious defect. The number of jobs which the blind may carry out safely and efficiently is undoubtedly limited. However, blind people are now quite mobile compared to those of former years. Perhaps younger members of the family who have not attained employment age can take them to and from work. The Seeing Eye dog is widely used. Once at work a totally blind man can carry out tasks where feeling or hearing is the important function—for example, inspecting production parts with go and no-go gages, and gas making with automatic controls.

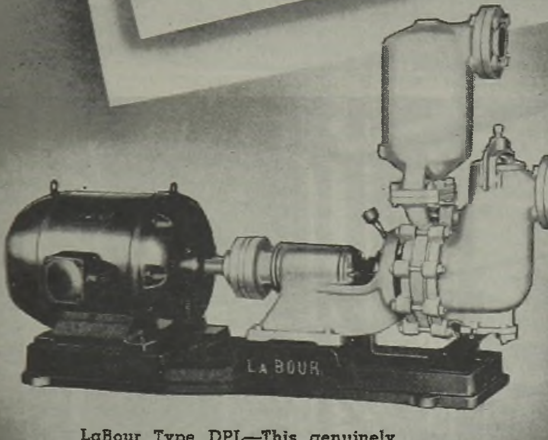
The loss of toes or fingers presents minor problems from the employment standpoint. Probably many men are doing important jobs in every plant where the loss or crippling of one toe is hidden in a strong, safety type of shoe.

One of the first to make a careful report on this problem was George Trundle, Jr., president of Trundle Engineering Corporation of Cleveland. His report stated that only a few of many hundreds of executives had given recent thought to the problem. Trundle has done an excellent piece of work, covering 171 separate job classifications and plotting the possibilities of each. His jobs were mostly those of the mechanical production and construction field. I have made a hasty study of the chemical field and increased the number of job classifications to 200. The following tabulation gives the percentage of jobs studied which can be filled by men with a single type of disablement. The first column gives data from Trundle's report, and the second column gives data for both studies, to include the chemical industry. This list is only a start, based on too little research and upon a single viewpoint, for the most part. It will not be surprising if some cases must be removed by more careful consideration, some surely can be added; barbers, hairdressers, and mail clerks, among many others, have not been studied:

No. of Classifications	171	200
Loss of one arm	14.6%	13.5%
Loss of one hand	26.9	24.5
Loss of one leg	35.0	32.6
Hard of hearing or deaf in one ear	26.3	27.0
Completely deaf	12.3	13.2
Loss of one eye	23.4	30.0
Loss of both eyes	2.9	3.0
Serious defect in speech	11.7	12.0
Loss of toes or fingers	32.1	34.6

The important point is that consideration be given by plant management to the establishment of suitable rules before the veteran returns. Let us not delay but have everything ready when he reaches the gate. The embarrassing moment is when a disabled person arrives at the employment window which is symbolic of authority, orderliness, and other intangibles he may feel unable to cope with. Let us do everything possible to wipe out any unfortunate inferiority attitude and welcome the man as though we had been waiting for him. This is easily done if we are really ready and, therefore, are actually waiting for him.


WHICH WOULD YOU CHOOSE?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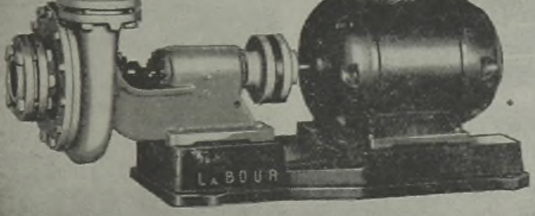
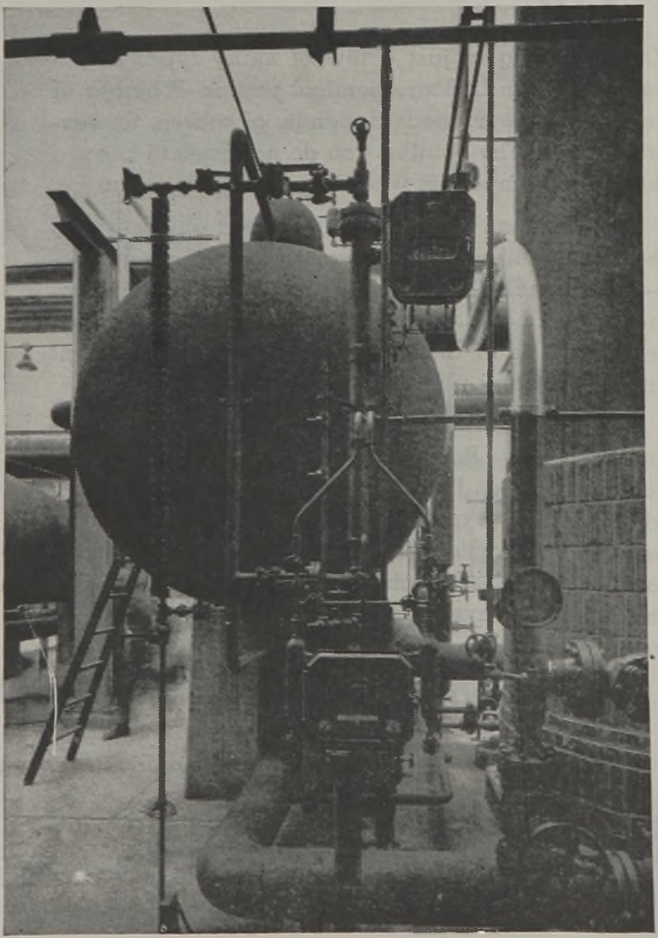
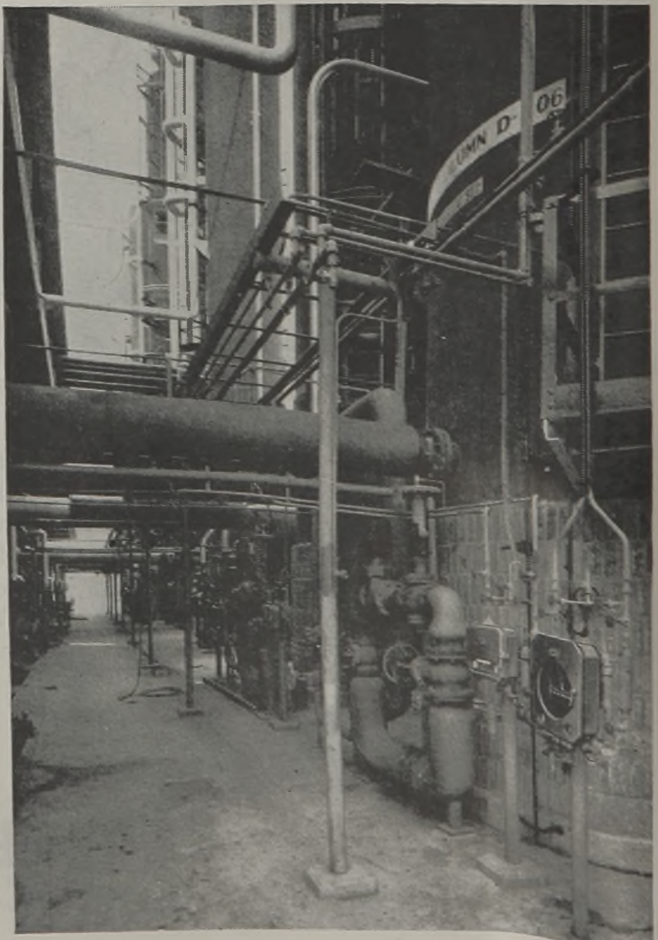

LaBOUR

LATEST FASHIONS IN





INSTRUMENTATION

Photos from new Union Oil Plant show latest Taylor developments

THESE pictures from the Union Oil Company's new plant, built by The Lummus Company and C. F. Braun & Co., show some of the latest developments in instrument control of aviation gasoline production.

Here's a partial list of the many varieties of Flow, Liquid Level, Pressure and Temperature instruments supplied. It's an interesting demonstration of the breadth of Taylor's services and the versatility of the Fulscope Controller mechanism:

REMOTE PNEUMATIC TRANSMISSION SYSTEMS —utilizing both Mercury—and Aneroid—manometer Flow transmitters; Internal-float and "Levelbuoy" Buoyancy type Level transmitters; and Pressure transmitters . . . For some Pressure and Level applications *both* Transmission and Control were incorporated in the same instrument at the point of measurement (see upper instrument in lower left photo).

Receivers are Recording Controller with Automatic Reset, and plain Recorders with 1 or 2 pens.

FLOW CONTROLLERS—Mercury type with Automatic Reset.

PRESSURE CONTROLLERS AND RECORDERS in Compressor Plant (see photo at left below).

PNEUMATIC-SET CONTROLLERS—Liquid level resetting Flow.

LIQUID LEVEL CONTROLLERS—both Internal-float and "Levelbuoy" Buoyancy types.

TEMPERATURE CONTROLLERS—with "Accuratus" (temperature compensated) mercury tube systems and "Thermospeed" Separable Well constructions.

AUTOMATIC-MANUAL BY-PASS—in both Internal and External forms.

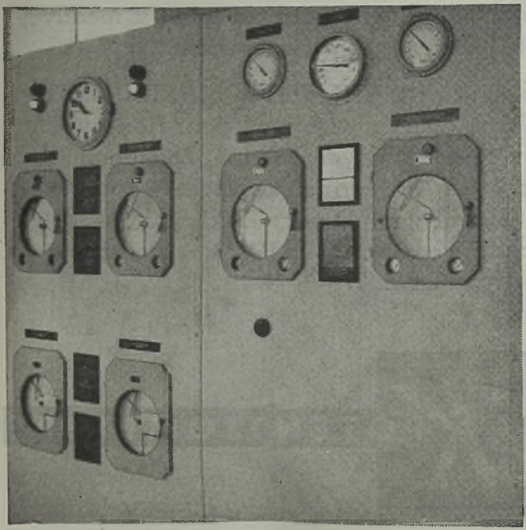
"PRECISOR" VALVE POSITIONERS.

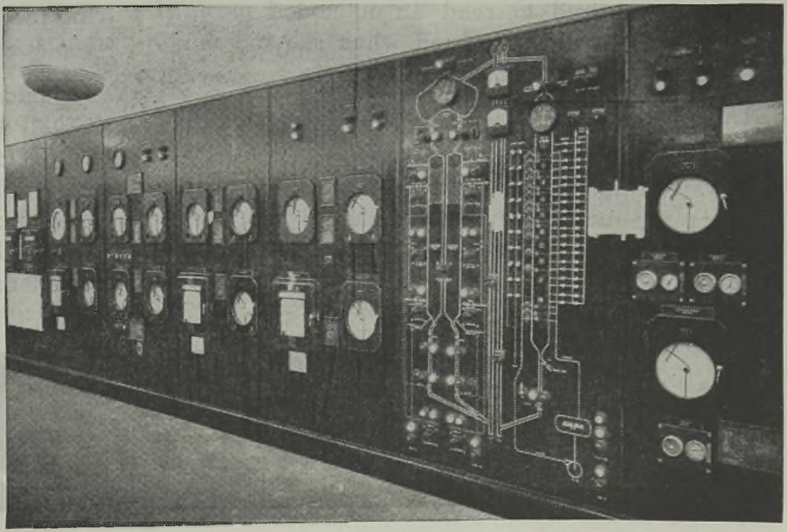
SELF-ACTING TEMPERATURE CONTROLLERS.

The moral is obvious: *We want to work with you on your new and modernization projects, too!* Call your nearest Taylor Field Engineer. Taylor Instrument Companies, Rochester, N. Y., and Toronto, Canada. *Instruments for indicating, recording and controlling temperature, pressure, humidity, flow and liquid level.*

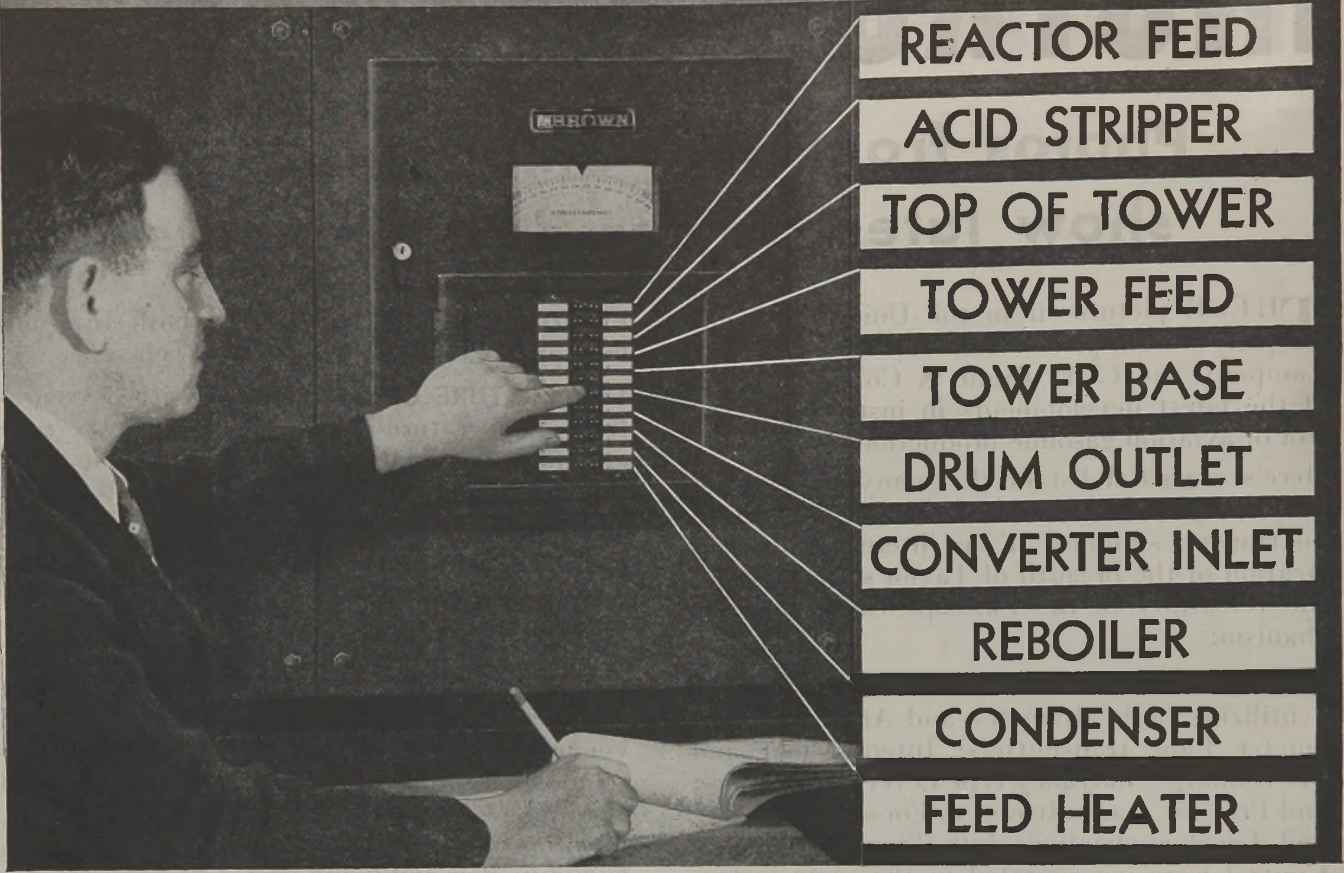
ARMY E NAVY

Taylor Instruments
MEAN
ACCURACY FIRST
IN HOME AND INDUSTRY





Check these Temperatures in a SPLIT SECOND.



Eliminates Manual Balancing

The self-balancing Centralized Reading Indicator pictured above is as modern as jet propulsion.

The operator merely touches the desired switch. The instrument does the rest, leaving his hands free to log readings.

Time between readings is limited *ONLY* by human ability to pick off a reading. Compare this time to that required to read an outmoded *manual* balance indicator, designed when shaving mugs were on every barber shop shelf.

The Brown Centralized Reading Indicator is unique for other reasons, too.

The electronic "Continuous Balance" principle delivers sensitivity previously unheard of. Fancy being able to read one part in twenty-four hundred!

The ElectroniK is totally unaffected by vibration — mount it on a drill rig if it suits your purpose.

The ElectroniK utilizes circular instead of reciprocating motion. Components move only when the scale is changing position. Specify the Brown Precision Indicator for that post-war cracking unit.

Specify it, too, for your present processes. Utilizing the same wiring and thermocouples, it readily replaces old-fashioned instrumentation.

For information write THE BROWN INSTRUMENT COMPANY, a division of Minneapolis-Honeywell Regulator Co., 4480 Wayne Avenue, Philadelphia, Pa. Offices in all principal cities. Toronto, Canada: 117 Peter Street — England: Wadsworth Road, Perivale, Middlesex — Stockholm, Sweden: Nybrokajen 7.

BROWN *ElectroniK* POTENTIOMETERS

Current Developments in INSTRUMENTATION

Demands for increasingly accurate temperature measurements focus our attention on resistance thermometers.

Discussed by Ralph H. Munch

Resistance thermometers were first suggested by C. W. Siemens in 1871. Those which he made proved to be inaccurate. This appears to have been caused by contamination of the platinum resistance element with iron from the sheath which covered it, when the thermometers were heated to high temperatures. In 1887 H. L. Callendar described improved forms of this instrument. His work is the foundation of modern resistance thermometry. When he started his research, resistance thermometers were in poor repute; when he finished, their accuracy was such that the platinum resistance thermometer, calibrated at the boiling point of oxygen, the ice point, the steam point, and the boiling point of sulfur, was chosen to define the International Temperature Scale from −190° to +660° C.

A resistance thermometer consists of a suitably mounted resistance coil, usually of platinum, nickel, or copper wire, protected with a sheath and provided with the necessary leads to connect the coil to a resistance measuring network of the desired accuracy. In the simplest form this network is a Wheatstone bridge such as that shown in Figure 1*a*. This arrangement has the disadvantage that leads 2 and 3 to the thermometer resistance, *T*, are in the same arm of the bridge along with the thermometer resistance. Thus, changes in lead resistance caused by variations in ambient temperature are measured as changes in the thermometer resistance. Various means of eliminating this inaccuracy have been devised. Figure 1*b* shows the arrangement most commonly adopted in resistance thermometer installations for industrial process control. By attaching lead 1 to the junction between thermometer resistance *T* and thermometer lead 2, leads 2 and 3 are placed in opposite bridge arms so that changes in their resistances cancel and are not measured as changes in the thermometer resistance.

Modern resistance thermometers have many advantages which make possible more precise temperature measurement and control than are obtainable with other types of equipment. Since the measuring device is a Wheatstone bridge, small variations in the bridge voltage do not affect the accuracy of the readings as they do in the case of potentiometric measurement of thermocouple voltages. This fact makes unnecessary the standard cell and self-standardizing mechanism of the recording potentiometer. Bridge readings are not affected by long leads so that the thermometer bulb may be placed several hundred feet from the recorder when necessary, without sacrificing accuracy. The expense for lead wire is not so great as for thermocouples, since the leads are copper. Resistance thermometers require no cold junction compensation; this eliminates another of the sources of trouble in thermocouple measurements.

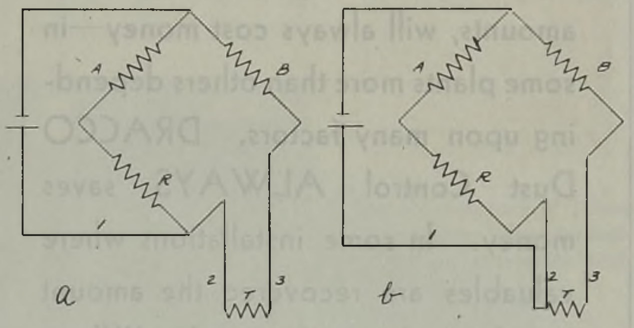


Figure 1 (*Above*). Resistance Measuring Networks

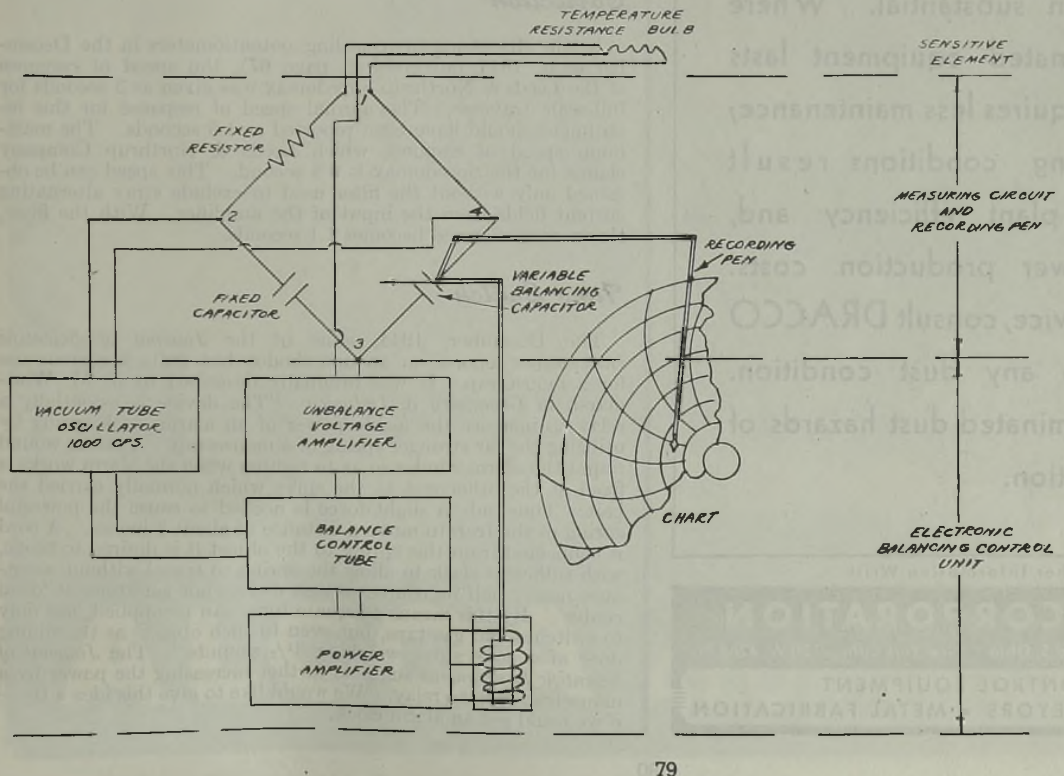


Figure 2 (*Left*). Schematic Diagram of Foxboro Dynalog

Resistance thermometers can be arranged to record temperature differences or the average of several temperatures as a single record. In addition, some makers supply multipoint recorders for as many as sixteen points. Another feature of resistance thermometer temperature measurements is that the bridge can be operated with an alternating current if a suitable balance detector is provided. Thermionic amplifiers are ideal for this purpose. Two recent instruments making use of this fact will be mentioned later.

(*Continued on page 80*)

Instrumentation

In spite of their many good points, resistance thermometers have not been so generally used as thermocouples; probably the major reason is their somewhat higher price. Others are the larger size of the bulbs, compared with a thermocouple junction, and their somewhat slower response. These disadvantages have been reduced in the newer designs to a point where they are not serious for most applications.

Resistance thermometer recorders are available from most manufacturers of recording potentiometers since the two types of instruments are similar in construction. For example, Leeds & Northrup Company has available a line of resistance thermometer instruments and a line of thermocouple instruments. Both lines include the same types, from portable manual indicators through to strip-chart Micromax indicating recorder-controllers.

As mentioned above, the use of an alternating current bridge with a resistance thermometer provides an ideal opportunity for the construction of an electronic recorder. A recent example of this type of instrument is the Pyrotron electronic resistance thermometer discussed in our January column (advertising section page 75). Bailey Meter Company has just published Bulletin 230-A giving complete information on this instrument.

A different example of an electronic resistance thermometer recorder is the Foxboro Dynalog; a schematic diagram is reproduced in Figure 2. There are three unique features. The first is that the bridge contains two capacitance arms. Balance is obtained by adjusting a variable capacitor instead of a slide-wire. This feature gives truly stepless adjustment in contrast to that obtained by adjusting the usual type of slide-wire. A second is that the bridge power supply is a 1000-cycle-per-second vacuum tube oscillator. The third is a solenoid balancing motor in place of the more conventional rotating motor. These three features not only simplify the design and construction of the recorder, but result in superior performance.

The action of the instrument is as follows: When a temperature change occurs, the unbalance voltage from the bridge is amplified and applied through the balance control tube to the power amplifier in such a way as to cause the solenoid motor to rebalance the bridge by means of the balancing capacitor linked to it. The recorder pen is linked to the balancing capacitor and records its motion. The sensitivity of the Dynalog recorder is such that the makers offer it with scale ranges down to 3° in the range −185° to +316° C. Standard balancing speed is 3 seconds for full-scale travel.

Correction

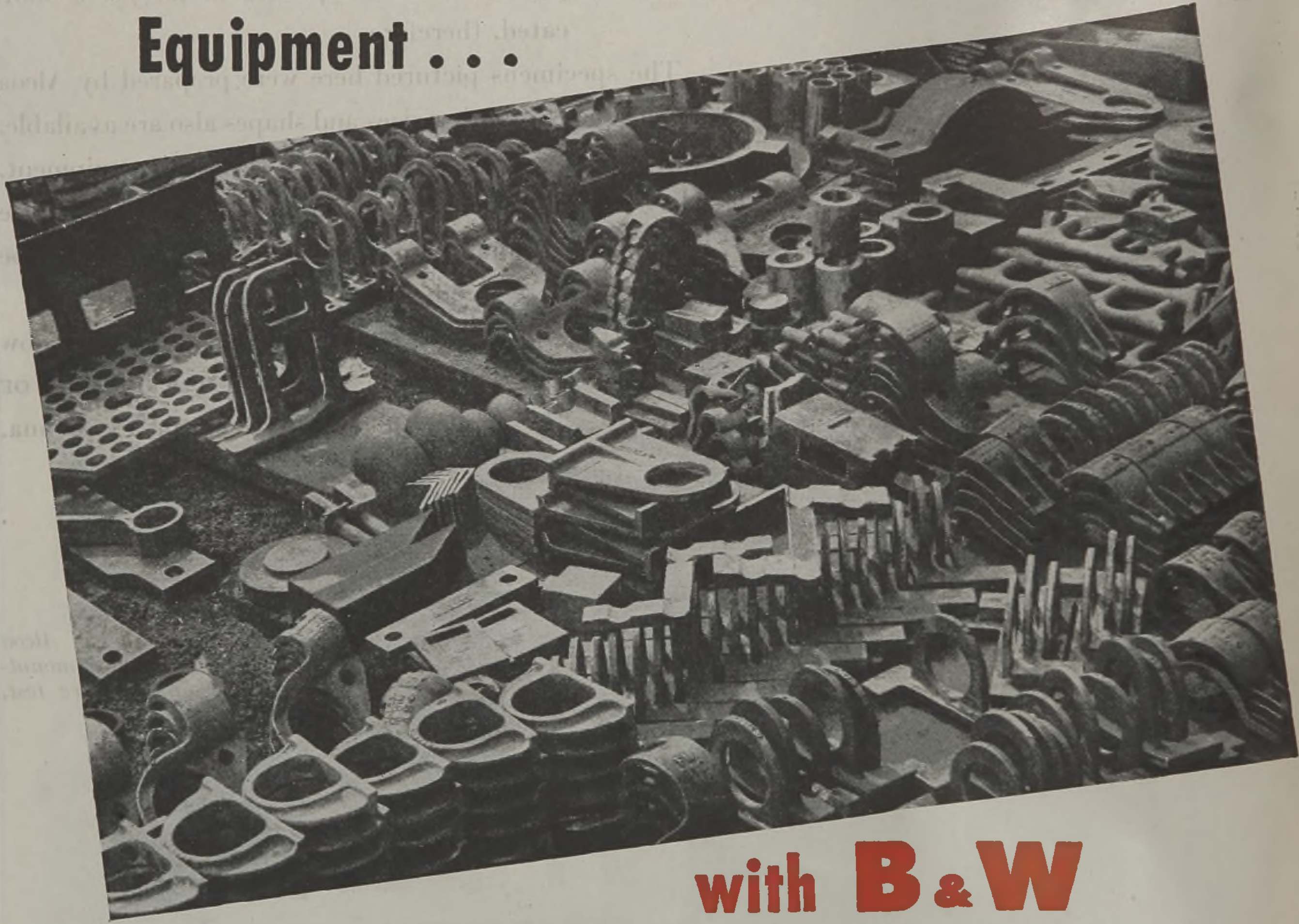
In the discussion of recording potentiometers in the December issue, 1944 (advertising, page 67), the speed of response of the Leeds & Northrup Speedomax was given as 3 seconds for full-scale traverse. The normal speed of response for this instrument should have been reported as 1.5 seconds. The maximum speed of response which Leeds & Northrup Company claims for the Speedomax is 0.8 second. This speed can be obtained only without the filter used to exclude stray alternating current fields from the input of the amplifier. With the filter, the maximum speed becomes 1.1 seconds.

Time Switch

The December, 1944, issue of the *Journal of Scientific Instruments* reports on an unorthodox but quite ingenious use for a mousetrap. It was originally described by J. M. Whitmarsh in *Chemistry & Industry:* "The device is essentially a relay to increase the feeble power of an alarm clock spring by utilizing the far stronger spring of a mousetrap. A string wound round the alarm winder so as to tighten when the alarm works is fixed at the other end to the spike which normally carried the bait. Thus only a slight force is needed to cause the powerful spring of the trap to move a distance of about 3 inches. A cord is connected from this spring to the object it is desired to move, with sufficient slack to allow the spring to travel without assistance nearly half its course so that it does not get stuck at 'dead center'. By this means adequate force can be applied, not only to switches and gas taps, but even to such objects as the sliding door of a coke stove weighing $3^{1}/_{2}$ pounds." The *Journal of Scientific Instruments* suggests further increasing the power by a mousetrap-rattrap relay. We would like to give this idea a try—if we could get an alarm clock.

STRENGTHEN VITAL PARTS

of High Pressure, High Temperature Equipment . . .



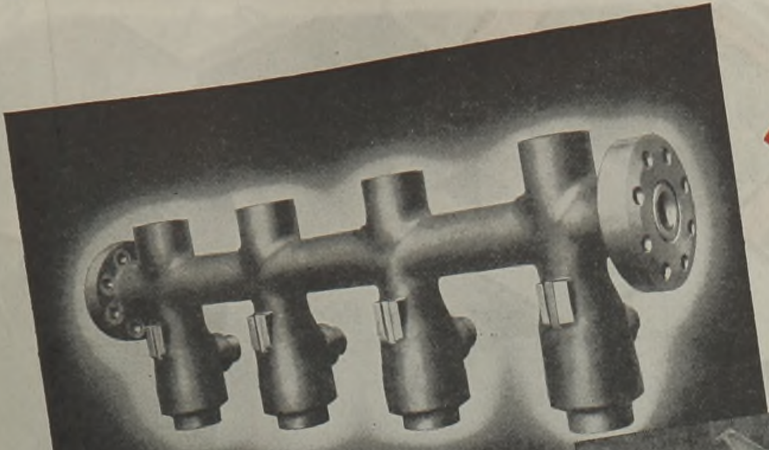
with B&W ALLOY CASTINGS

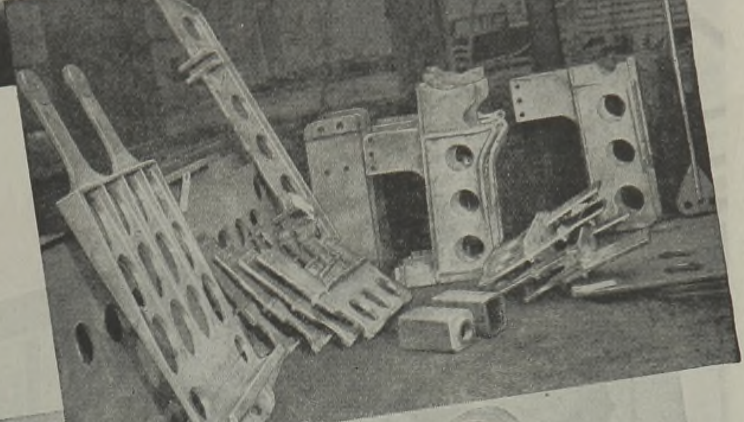
B&W Alloy Castings provide utmost resistance to abrasion, corrosion, oxidation and have high strength even at elevated temperatures. Because of this desirable combination of properties, their use as vital parts in equipment subjected to severe services in high pressure, high temperature conditions keeps costly and time-consuming shut downs for repairs and replacements at a minimum. For example, more than two million tube support castings have been supplied for high temperature furnaces, yet not a single service failure has been reported. Service temperatures range up to 2000 F under conditions requiring high creep strength, consistent with long time stability.

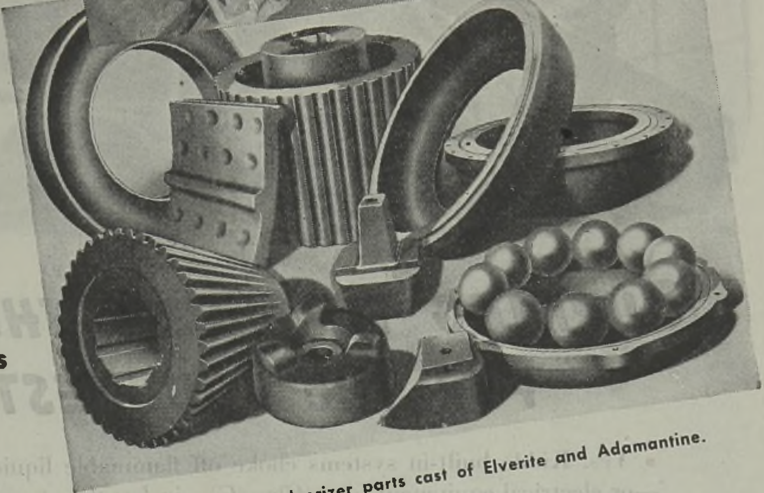
B&W Alloys are available to meet most any requirement of resistance to corrosion, oxidation, abrasion and other adverse conditions encountered in processing equipment.

Castings can be supplied in practically any shape and weight required. They are produced in B&W's own foundry that is modernly equipped with electric induction furnaces, heat-treating facilities, electric welding apparatus and X-ray inspection equipment.

Our experience in helping others to strengthen vital parts with B&W alloy castings is available to you without obligation.







BURNING TIME LESS THAN 20 SECONDS— FOR THE TOUGHEST FIRES

• Yes, Kidde built-in systems choke off flammable liquid fires (Class B) —or electrical equipment fires (Class C)—in *less than twenty seconds.* When *automatic* systems are used, fires are often suffocated before nearby workers realize a blaze has even *started!*

Ordinary water-type extinguishers cannot stop these tough fires. But they can be quickly smothered under clouds of swift carbon dioxide gas—dry, inert, ordorless and non-toxic. And that's the Kidde method! It leaves no after-fire mess, no contamination of mixes or fluids, no damage to electrical equipment. That's why the Kidde system is recognized as one of the speediest, cleanest, safest means of fire extinguishing in use today.

Check the accompanying list of typical industrial fire hazard areas—for safety's sake. If there is one of these danger spots in your plant, call in a Kidde representative—he'll be glad to discuss your fire protection problems.

Kidde Kills Tough Fires

- PROCESS ROOMS
- MIXING TANKS
- AGITATORS
- PUMP ROOMS
- STORAGE AREAS
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Current Developments in PLANT MANAGEMENT

Shall we purchase materials outside or manufacture them in the plant itself?

Discussed by Walter von Pechmann

Decisions on whether to manufacture or to purchase are difficult because many factors have to be calculated on the basis of what will happen in the future. This is especially true today where economic trends are subject to quick and radical changes. I have discussed this problem with many in the chemical industry recently. Although valuable suggestions have been received, the impression persists that decisions are often based on feelings rather than on facts. We believe only too often that comparative cost figures cannot be relied upon, and we then decide for or against manufacturing mainly because of intangible factors. Conducting business on this basis is unsound and dangerous. We should be able to arrive at a decision based on accurately calculated figures if we approach this problem systematically. To do this it is necessary to segregate factors calculated from so-called intangibles to which no value can be attached. We must first determine whether purchase or manufacture is more expensive, and then decide if the difference is worth the trouble of changing established practice. To base decisions solely on the outcome of the lowest calculated cost is

(Continued on page 86)

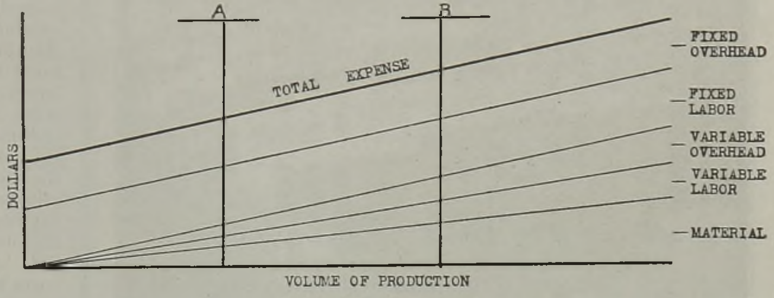


Figure 1 (*Above*). Determination of Manufacturing Expenses at Various Volumes of Production (Cost is Calculated at Points *A* and *B*)

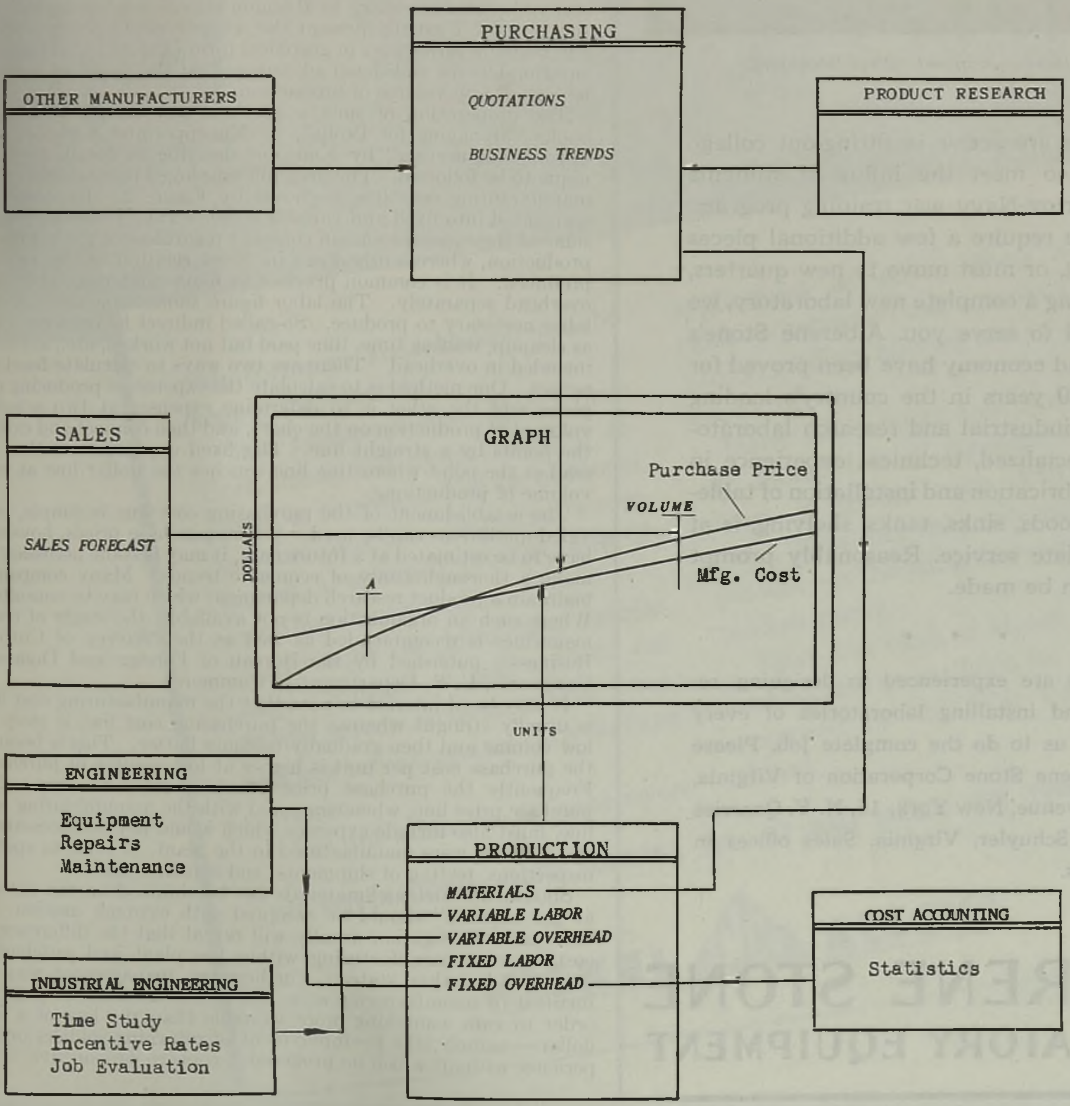
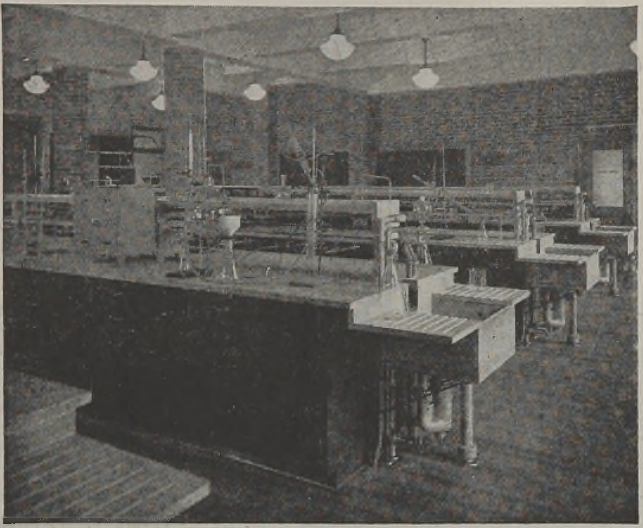


Figure 2 (*Left*). Establishment of Manufacturing Cost Line



often incorrect, since the more expensive method may solve a company problem and by doing so will justify the extra expenditure. It may be advisable to keep in mind that the problem of manufacturing instead of purchasing, or vice versa, is usually instigated by the desire to solve a problem which has little or no bearing on making an immediate additional profit.

A few reasons are listed for deciding that purchasing should be replaced by manufacturing: (1) to utilize otherwise idle plant facilities; (2) to retain employees during the reconversion period; (3) to recover material which is hard to obtain; (4) to control the quality of materials to a higher degree; (5) to become independent of suppliers; (6) to gain experience in manufacturing new products. It is obvious that problems of this type can be solved by methods other than starting to manufacture. Many production executives therefore think that top management should not select a certain method and then ask plant management for comparative cost figures; they would prefer to be confronted with the real problem and would like to be asked how to solve it with the least effort.

Before purchase prices can be compared with the manufacturing costs, it is necessary to gain knowledge of the anticipated need for the material under consideration. This information can usually be obtained from the sales department which not only has sale forecast figures available but also is familiar with seasonal fluctuations and anticipated changes in the design of product.

I have found it advantageous to calculate manufacturing costs not only at the anticipated volume of production but also at other levels, because it is important to know at which point it may become necessary to abandon manufacturing again. For this purpose I usually present the comparison of purchase price and manufacturing cost in graphical form (Figure 1). This presentation has the additional advantage that the profit or loss can be seen at any volume of production.

The preparation of such a graph is not complicated. The books "Managing for Profit", by Knoeppel and Seyboldt, and "Profit Engineering" by Knoeppel describe in detail the technique to be followed. The principle employed in establishing the manufacturing cost line is shown by Figure 2. Expenses are segregated into fixed and variable items. This is necessary since some of the expenses remain constant regardless of the volume of production, whereas others are in direct relation to the amount produced. It is common practice to figure material, labor, and overhead separately. The labor figure should contain only the labor necessary to produce. So-called indirect labor items, such as cleanup, waiting time, time paid but not worked, etc., are to be included in overhead. There are two ways to calculate fixed expenses. One method is to calculate the expense of producing one piece, and the other is to determine expenses at two selected volumes of production on the chart, and then connect and extend the points by a straight line. The fixed expenses can then be read at the point where this line touches the dollar line at zero volume of production.

The establishment of the purchasing cost line is simple, provided quotations can be used. Where purchase prices, however, have to be estimated at a future date, it may become necessary to make a thorough study of economic trends. Many companies maintain a product research department which may be consulted. Where such an organization is not available, the study of trade magazines is recommended as well as the "Survey of Current Business", published by the Bureau of Foreign and Domestic Commerce, U. S. Department of Commerce.

It may be of interest to note that the manufacturing cost line is usually straight whereas the purchasing cost line is steep at low volume and then gradually becomes flatter. This is because the purchase cost per unit is higher at low volume of purchase. Frequently the purchase price line is charted too low. The purchase price line, when compared with the manufacturing cost line, must also include expenses which would not be necessary if the material were manufactured in the plant. I refer to special inspections, testing of shipments, and similar items.

Statements such as "materials can be obtained on the outside at less expense" should be accepted with extreme caution. A thorough investigation usually will reveal that the difference of cost between manufacturing within the plant and purchasing outside is less than stated. Furthermore, management may be justified in manufacturing at a cost above the market price in order to gain something more valuable than the loss of a few dollars—namely, the re-employment of returning soldiers or experience without which no progressive concern can survive.

LICK WIRE CLOTH CORROSION

...the way SALT REFINERS DO

Hum-mer Electric Screens built by The W. S. Tyler Company for grading salt. The complete machines and accessories, with the exception of the vibrators, are of Monel. Photo courtesy of Leslie Salt Co., Newark, Calif.

Salt corrosion and abrasion *can* be kept within bounds.

Salt producers find Monel wire cloth strong and tough... highly resistant to corrosion. The use of Monel for the complete Hum-mer screen assures a screened product free of metallic contamination.

Although the Hum-mers handle large tonnages of salt crystals, the Monel screen sections provide long, efficient service against corrosion and abrasion.

Yet this is but one of many severe applications in which Monel wire cloth outperforms other materials for sifting, grading, filtering and conveying corrosives.

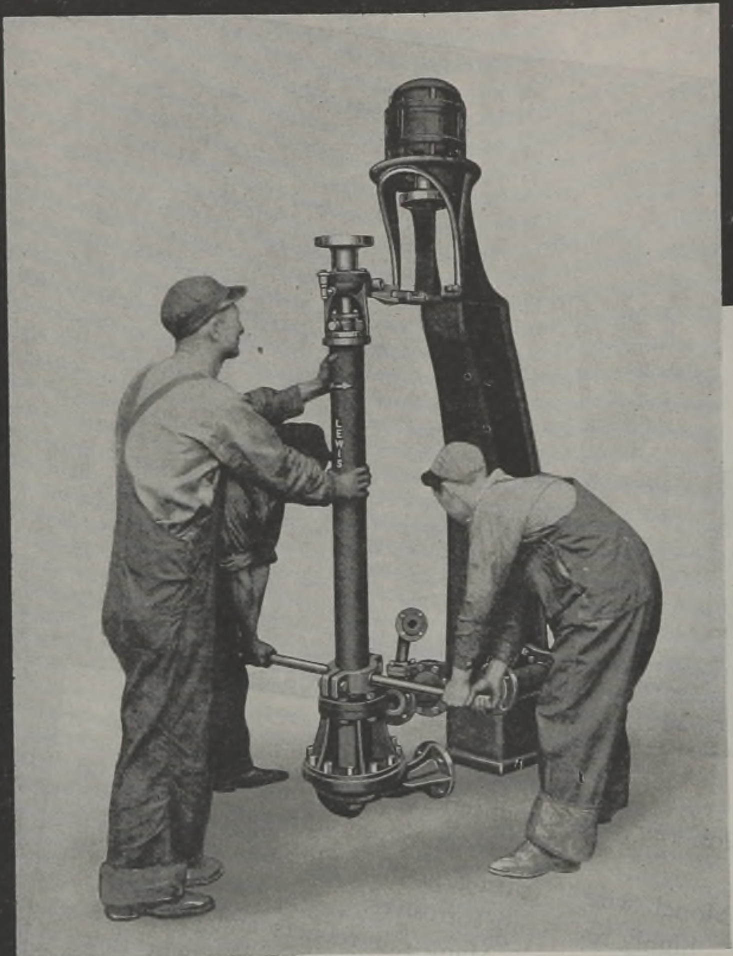
Many salt refiners and producers use Monel for *all* equipment that comes in contact with destructive NaCl. Thus they maintain high output and—at the same time—improve product purity.

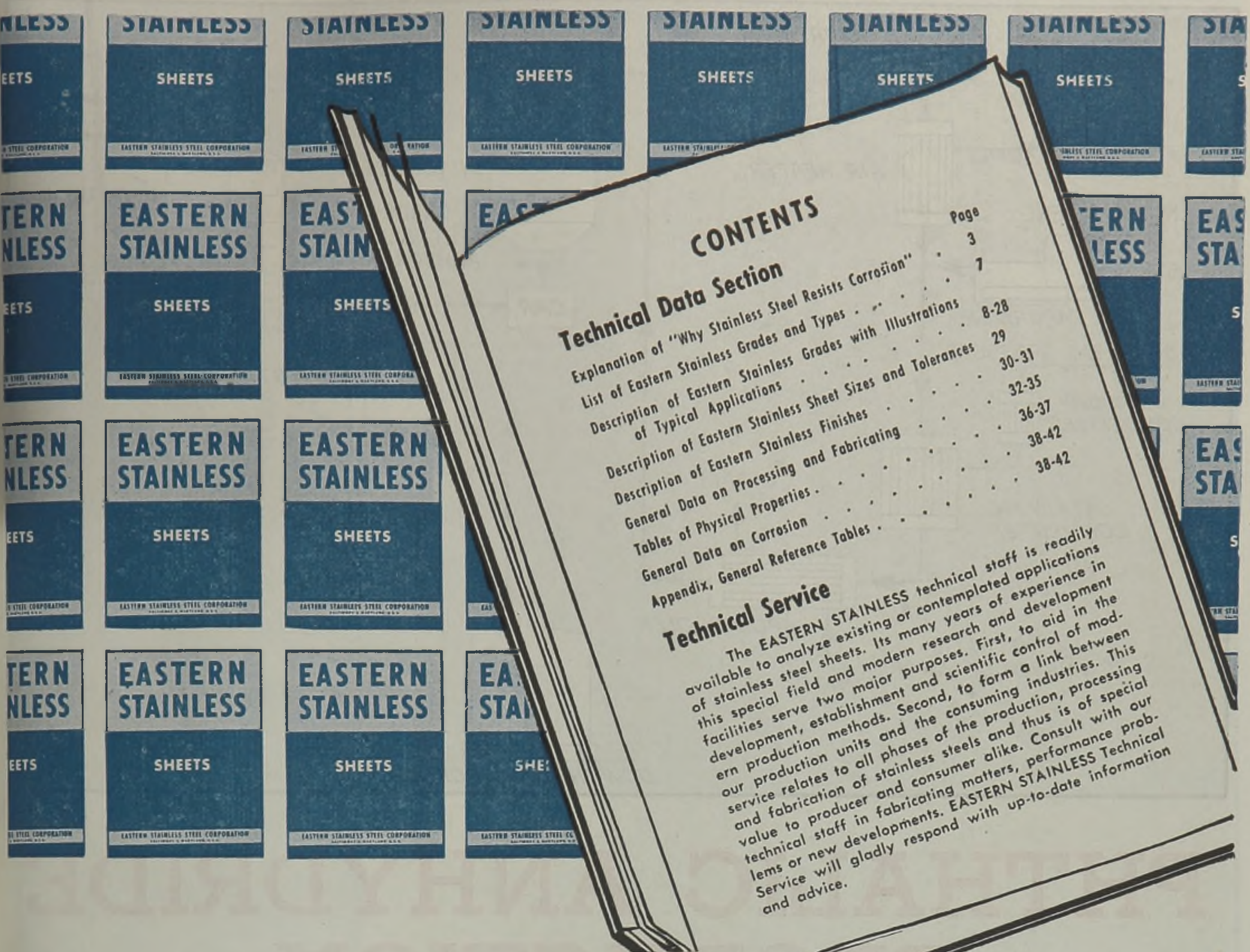
Tyler wire cloth of Monel, Nickel and Inconel is available for all uses approved by the War Production Board.

THE INTERNATIONAL NICKEL COMPANY, INC., 67 WALL STREET, NEW YORK 5, N. Y.

NICKEL INCO ALLOYS

MONEL • "K" MONEL • "S" MONEL • "R" MONEL • "KR" MONEL • INCONEL • "Z" NICKEL • NICKEL • Sheet... Strip... Rod... Tubing... Wire... Castings... Welding Rods (Gas & Electric)





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Technical Service

The EASTERN STAINLESS technical staff is readily available to analyze existing or contemplated applications of stainless steel sheets. Its many years of experience in this special field and modern research and development facilities serve two major purposes. First, to aid in the development, establishment and scientific control of modern production methods. Second, to form a link between our production units and the consuming industries. This service relates to all phases of the production, processing and fabrication of stainless steels and thus is of special value to producer and consumer alike. Consult with our technical staff in fabricating matters, performance problems or new developments. EASTERN STAINLESS Technical Service will gladly respond with up-to-date information and advice.

New 1945 EASTERN STAINLESS *Catalog* will soon be ready!

Your free copy of the comprehensive new 80-page Eastern Stainless catalog will shortly be available. Compiled and edited by Eastern Stainless technical experts, it authoritatively covers modern applications of Stainless Steels in many great industries and institutions including your own.

Complete in every detail, profuse with interesting illustrations, the new 1945 Eastern Stainless catalog will be a valuable addition to your reference files . . . it'll serve you well as an office-handy encyclopedia giving authentic information on how Stainless Steels are best suited to your needs. Today—fill out and mail the coupon at the right. You will be sure to receive your free copy of the 1945 Eastern Stainless catalog as soon as it is ready.

EASTERN STAINLESS STEEL CORPORATION
Baltimore, Maryland Dept. 65

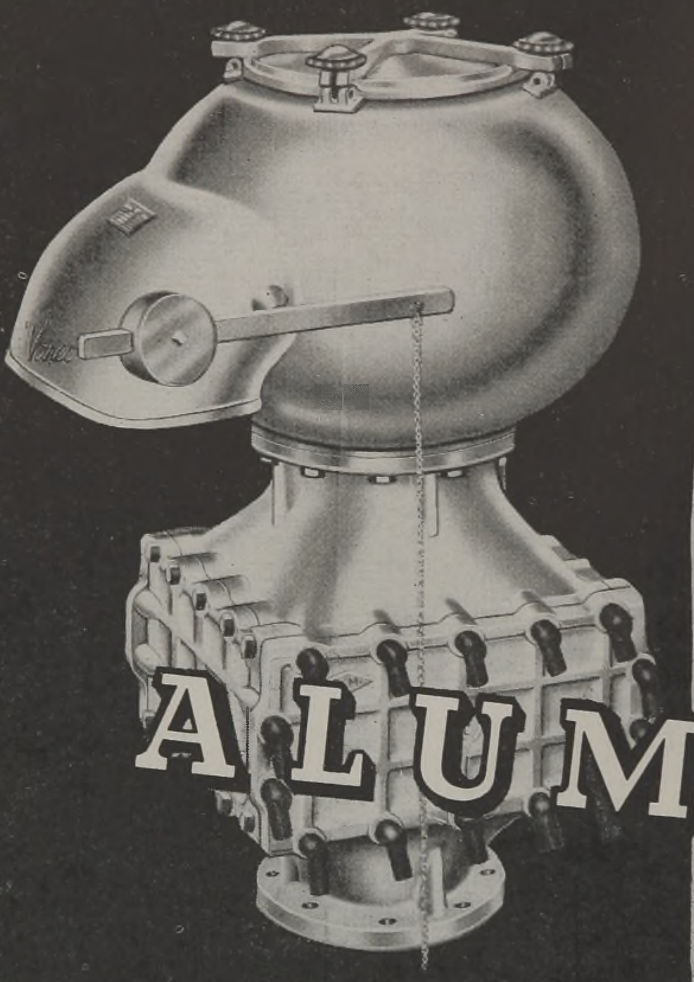
Gentlemen: Please reserve for me a copy of your free 1945 catalog "EASTERN STAINLESS STEEL SHEETS."

Firm name ....
Address ....
City ....State ....
Your name and title..........................

JML Co. B-C8

EASTERN STAINLESS STEEL CORPORATION
BALTIMORE, MARYLAND

SALES REPRESENTATIVES: CHICAGO, 201 N. Wells St. Phone: State 6533 • CLEVELAND, 1010 Euclid Avenue, Prospect 2020 DALLAS, 4533 Livingston Ave., Justin 8-5772 • DETROIT, 6505 Second Blvd., Madison 8570 • DETROIT, 906 Fisher Bldg., Trinity 11465 • LOS ANGELES, 10887 Chalon Road, Arizona 3-8273 • NEWARK, N. J., 972 Broad Street, Market 2-2068 PHILADELPHIA, 7444 Fayette St., Livingston 2002



"Varec"

Approved*

PRESSURE and VACUUM RELIEF VALVES AND FLAME ARRESTERS

again available in

ALUMINUM

*Approved by THE ASSOCIATED FACTORY MUTUALS' LABORATORIES; Approved by U. S. TREASURY DEPARTMENT; Approved by U. S. DEPARTMENT OF COMMERCE, LLOYD'S BUREAU OF SHIPPING, and THE AMERICAN BUREAU OF SHIPPING FOR TANK SHIP SERVICE; and Listed by THE UNDERWRITERS' LABORATORIES.

"VAREC" Research protects users of "VAREC" Pressure and Vacuum Relief Valves and Flame Arresters. Adapting the application of Aluminum to this field, in 1928, "VAREC" Laboratories and Engineering skill are working ceaselessly to develop greater service potentialities from the company's products. Experience gained in unprecedented wartime obligations, added to years of pioneering, is now being reflected in the service of "VAREC" Equipment.

You will want to know more about "VAREC." Our Engineers will be glad to collaborate with you at any time.

TEN *Superior* ADVANTAGES OF ALUMINUM

- **LIGHTER IN WEIGHT** Eliminates the necessity of roof supports in tank.
- **NONCORROSIVE** Will not corrode in most services.
- **NO ELECTROLYTIC ACTION** Has best thermal and electrical potential factors in combination.
- **ALUMINUM STATIC-BALANCED PALLETS** Insure less "Blowdown" loss.
- **GREATER FLOW-CAPACITY** Streamlined and progressively expanding passageways result in greater flow capacity.
- **REPLACEABLE ALUMINUM SEATS** Guarantee maximum performance.
- **LESS MAINTENANCE** Aluminum requires minimum care and inspection.
- **NON-FREEZING** Aluminum construction and design, together with rapid rate of thermal conductivity, prevent accumulation of condensate.
- **WEATHERPROOF** Aluminum is the ideal protection against the elements.

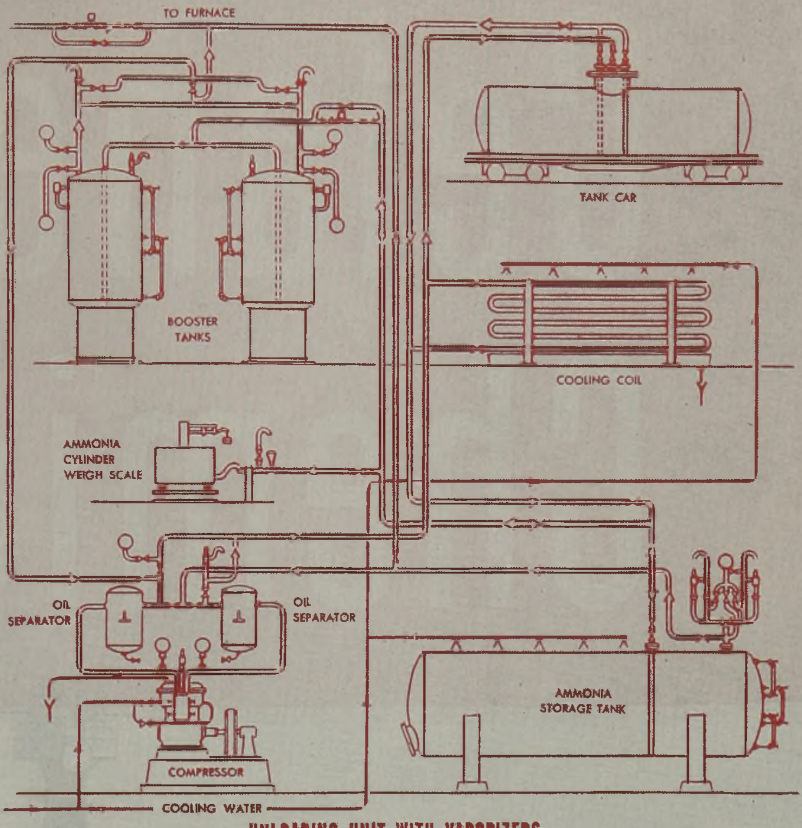
DURABILITY Rugged design insures longer life.

THE PACE SETTER

THE VAPOR RECOVERY SYSTEMS CO.
Consultants, Designers, and Manufacturers of Gas Control and Tank Equipment
COMPTON • CALIFORNIA
NEW YORK CITY • NEW ORLEANS, LA. • HOUSTON, TEXAS
TULSA, OKLA. • AGENCIES EVERYWHERE

HANDLING LIQUEFIED GASES

BLAW-KNOX PLANTS ARE SERVING INDUSTRY



UNLOADING UNIT WITH VAPORIZERS

Ammonia, Carbon Dioxide, Chlorine, Methyl Chloride, Butane, Propane, and Butadiene are handled by Blaw-Knox plants for liquefied gases.

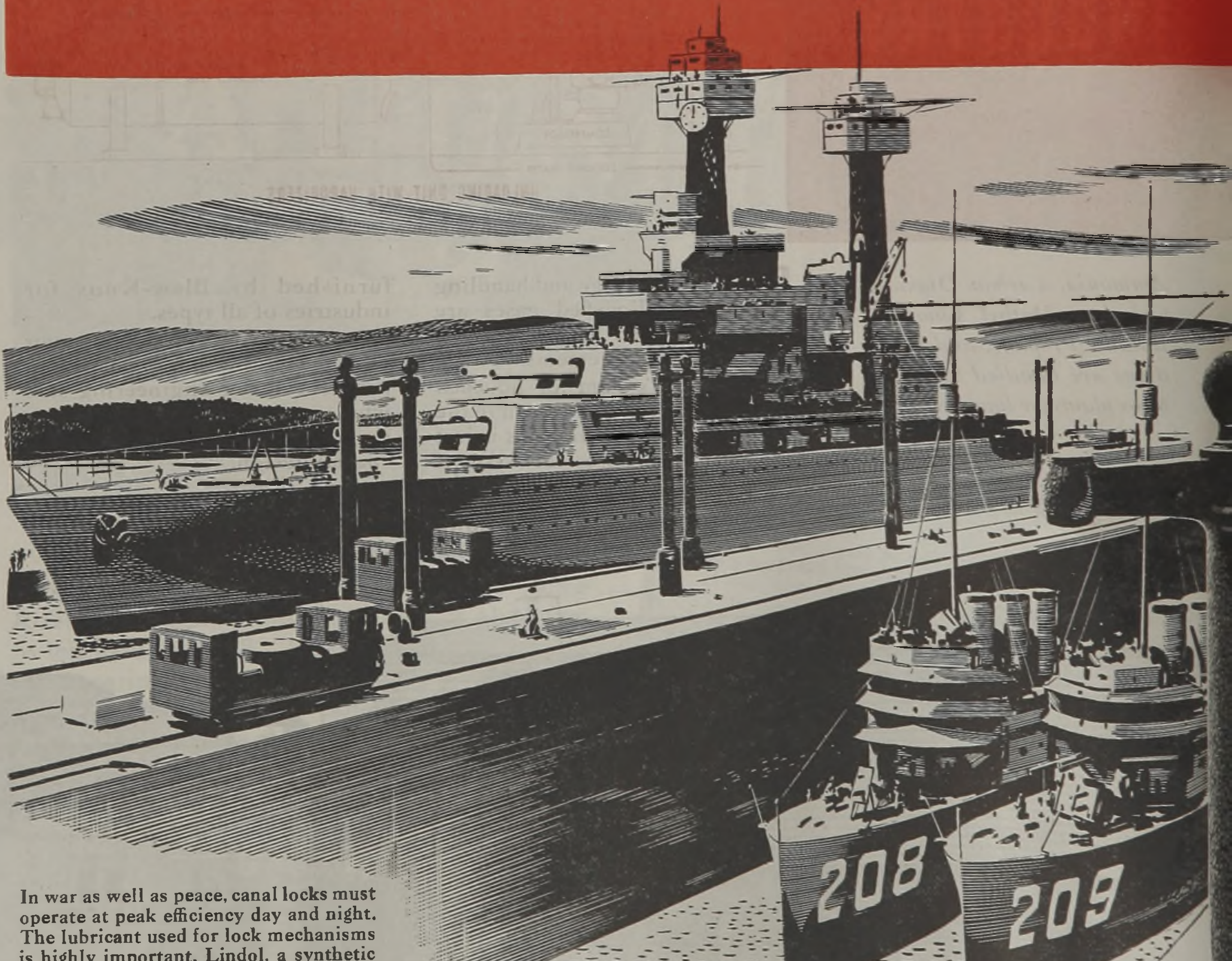
Blaw-Knox storage and handling systems for liquefied gases are serving industry in its wartime production achievements.

The storage system for liquefied anhydrous ammonia shown in the accompanying illustrations is just one of the scores of systems furnished by Blaw-Knox for industries of all types.

We invite you to submit your liquefied gas storage and handling problem to our engineering staff who are prepared to offer an economical system of standard or special design.

BLAW-KNOX DIVISION of BLAW-KNOX CO.
2081 Farmers Bank Bldg., Pittsburgh, Pa.
New York • Chicago • Philadelphia • Birmingham • Washington

BLAW-KNOX PROCESS EQUIPMENT


208
209
O W

Once organic phosphates were "Just a footnote in the text book"

THE RANGE AND SCOPE of Celanese organic phosphates are typical of the results achieved through modern synthetics research. From these hydrocarbons derivatives Celanese has pioneered a group of compounds with many potentialities.

These products of intensive research have been of practical service to engineers seeking materials with specific properties to meet definite needs. Lindol*, Lindol M.P., Lindol E.P., Celluflex* M-142, Cellulube* have shown wide adaptability in meeting various requirements of industry.

As non-flammable *plasticizers* for plastics, vinyl compounds and insulation materials . . . as *water-in-oil* and *oil-in-water* emulsions for waterproof paper and fabric coatings, leathers, water soluble resins, wire drawing and heat transfer liquids . . . as non-flammable *lubricants* and *lubricant additives* for high pressure engines, diecasting machinery, electrical equipment, vacuum pumps and oxygen compressors, these Celanese compounds perform vital functions in a great many operational and manufacturing processes.

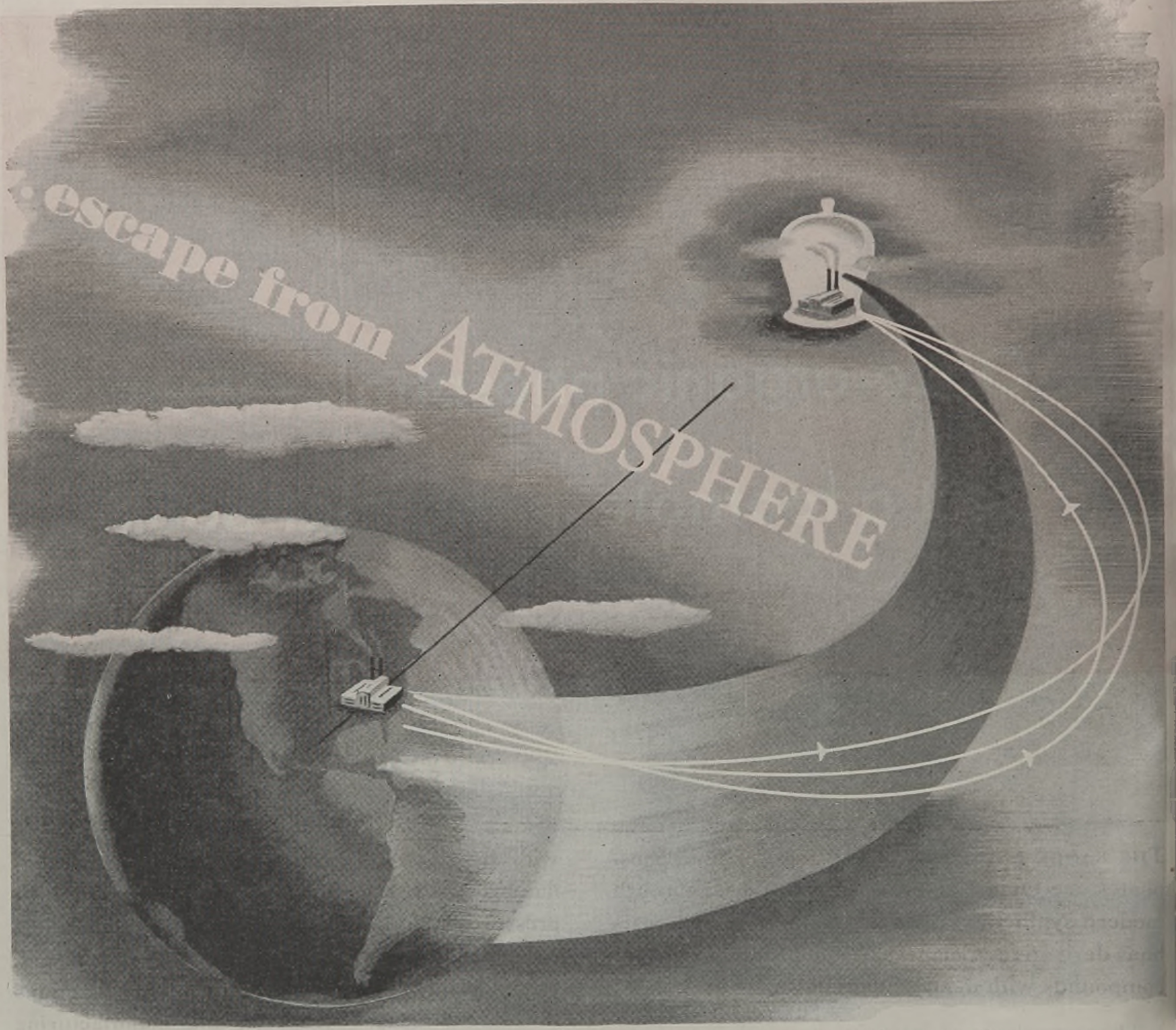
The development of organic phosphates demonstrates the ability of synthetics to accurately control chemical and physical properties. It is an example of the results obtained when materials are created for specific needs and purposes. Celanese Chemical Corporation, *A division of Celanese Corporation of America,* 180 Madison Avenue, New York 16, New York.

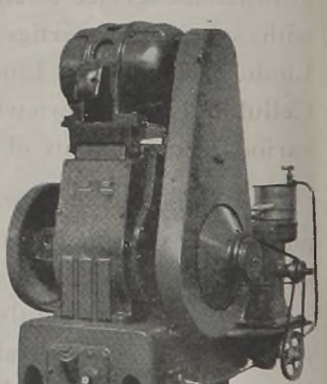
PLASTICIZERS
ORGANIC PHOSPHATES
LUBRICANT ADDITIVES
INTERMEDIATES
DYE-STUFFS

---

*Reg. U. S. Pat. Off.

TEXTILES • PLASTICS • CHEMICALS


escape from ATMOSPHERE



Why 109 Kinds of Optical Glass?

Bending light to the will of man, making it accomplish miracles, this is the job that optical glass does . . . in industry, science, medicine, and in the service of our armed forces.

Creating the required types of glass, and adapting them to the thousands of precision operations they are to perform, is the task of Bausch & Lomb, America's large scale producer of optical glass and the only company currently producing 109 kinds.

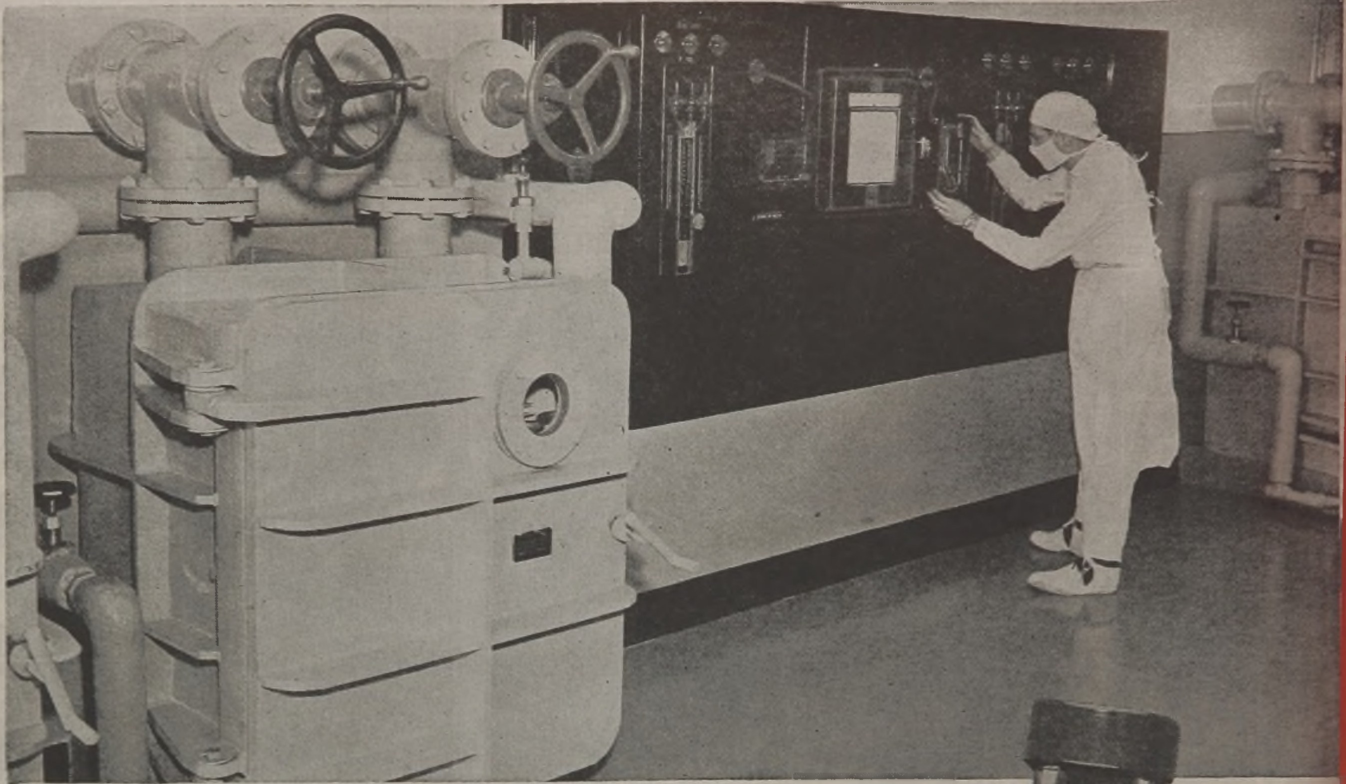
Many of these glasses may look alike, but to the optical expert each is different. That difference is marked by specific qualities of refraction, dispersion, and transmission . . . the properties which determine how light is bent, broken up, and passed through a lens or prism.

Only by having available all of these types of glass . . . and the ability to create new types when needed . . . has Bausch & Lomb been able to meet the optical instrument needs of science and industry in times of peace . . . the needs of our armed forces for highly precise military optical instruments. These combined abilities . . . to create and produce fine optical glass and to utilize its properties to the fullest advantage . . . make Bausch & Lomb America's Optical Headquarters. Bausch & Lomb Optical Co., Rochester 2, New York.

BAUSCH & LOMB

ESTABLISHED 1853

Makers of Optical Glass and a Complete Line of Optical Instruments for Military Use, Education, Research, Industry, and Eyesight Correction and Conservation



Penicillin-drying room at plant of Charles Pfizer & Co., Inc., makers of fine chemicals in Brooklyn. Micromax Recorder, in center of control panel, shows temperature of water in shelves of dryers.

PENICILLIN-Drying Temperatures Detected By Tiny Thermocouples

Because the drying of penicillin solution involves holding temperature within a narrow band, the operation requires speed and accuracy in temperature measurements.

Penicillin solution, in vials, comes to the drying room after freezing. Trays of vials are quickly slid into the 8 Devine dryers and subjected to a high vacuum—one of only a few microns absolute pressure—for dehydration.

Inside the dryers are small Monel-metal pipes which circulate water through the shelves, to sublime the ice present in the penicillin. Miniature thermocouples in the pipes detect the temperature of the water and report it to the Micromax Temperature Recorder, where the process operator can see it on the control panel. A glance at this 8-point Recorder, with a range of from −80 to +160 F, shows a separate, easily-read record for each of the 8 dwarf-size couples—and gives the process operator visible proof of the slightest temperature changes.

These L&N copper-constantan thermocouples were chosen because of their small size and extreme accuracy—the Recorder because of its micro-responsive action and dependability. Other L&N thermocouples and Micromax Recorders, in types suitable for widely differing uses, are described in Catalog N-33A, sent on request.

Close-up of Micromax Recorder on panel shown above. Micromax Recorders are used in the Pfizer plant to report on temperature, pH, and vacuum during the manufacture of penicillin.

Jrl Ad N-33A (22)

LEEDS & NORTHRUP COMPANY, 4920 STENTON AVE., PHILA., PA.

LEEDS & NORTHRUP

MEASURING INSTRUMENTS · TELEMETERS · AUTOMATIC CONTROLS · HEAT-TREATING FURNACES

V depends on me!
A Slogan For Every American

a penny saved is a penny earned

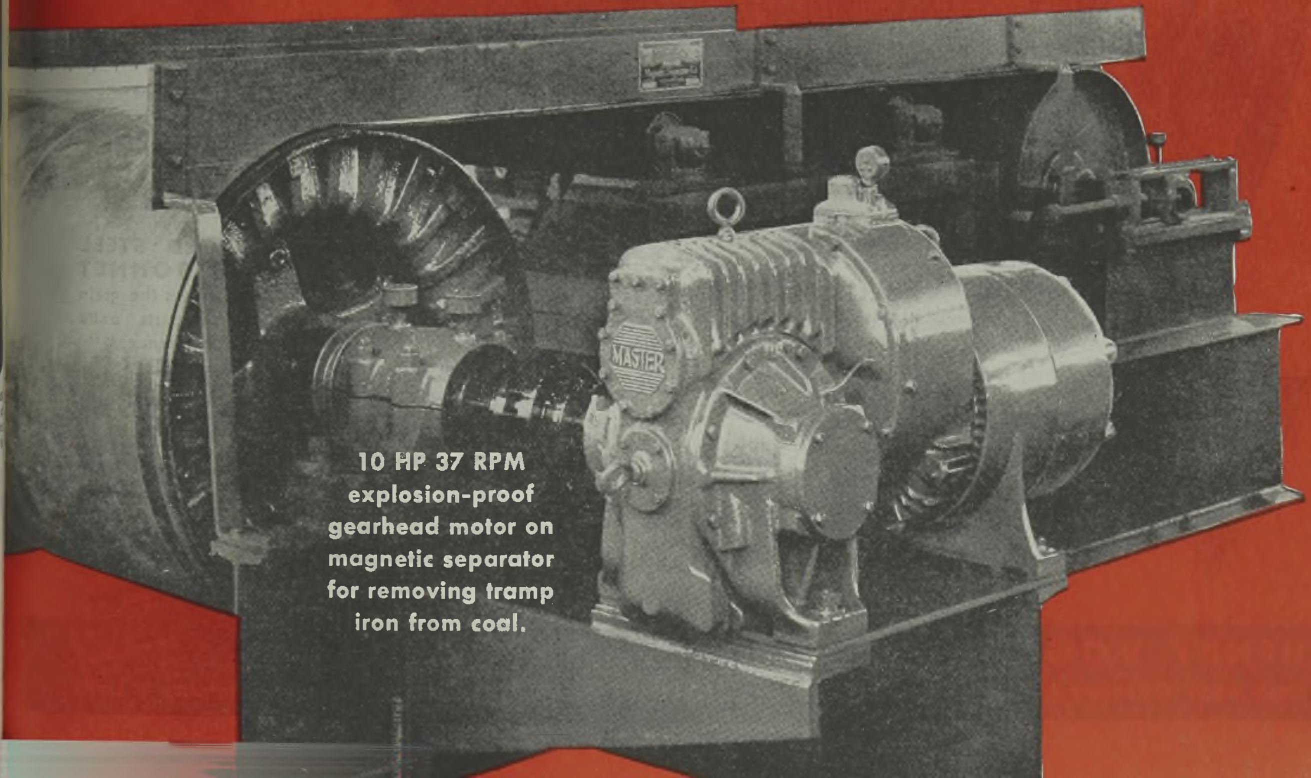
And here's how you make real savings when you use Master Gearhead Motors. Both the motor and gear reduction are built as an integral construction, so you have only one unit to order and handle. You reduce to one third or one quarter your own time for selecting the right equipment, and the time and expense in your purchasing, receiving, and invoicing departments. You save greatly in handling and mounting time. Today time is more than money . . . it's manpower!

But one of the most important savings is usually overlooked. When you buy a gearhead motor, of say 2 horsepower size, both the motor and gear reduction are designed for 2 horsepower load. However, when other types of speed reduction equipment are used, too often you must purchase oversize speed reducing parts that will transmit possibly as high as 5 horsepower, because intermediate sizes are not made.

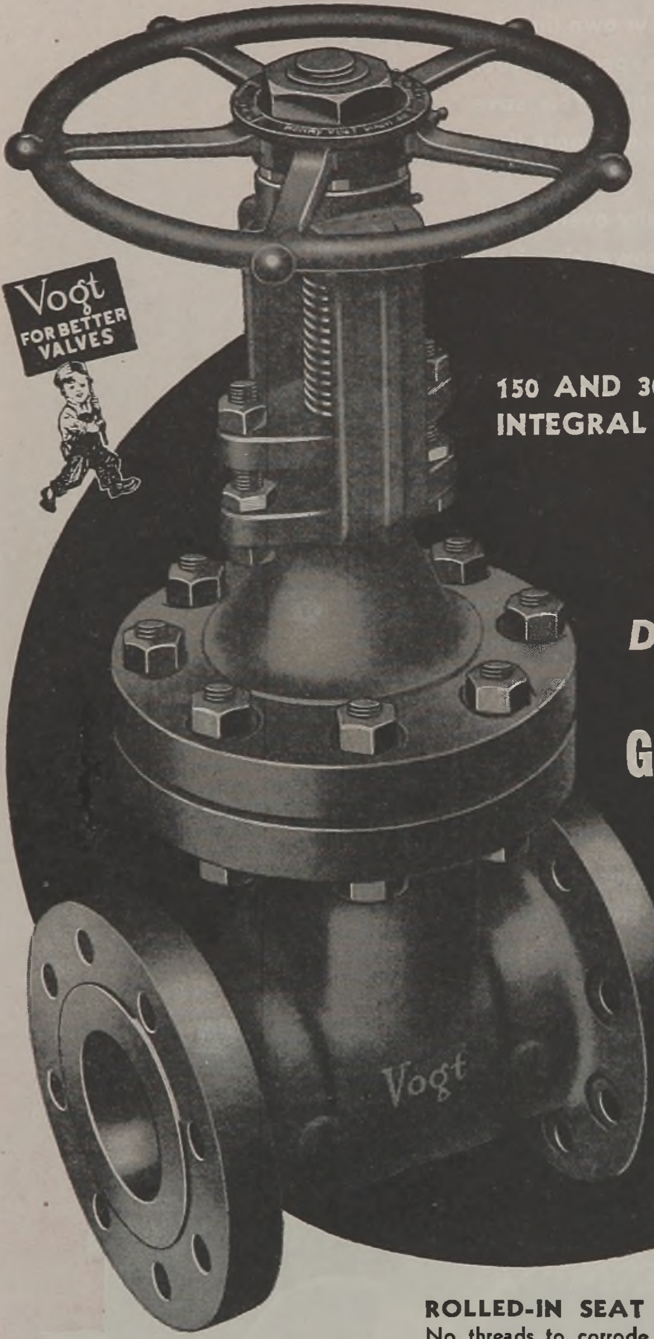
Yes a penny saved is better than a penny earned . . . it's bonus money. And speaking of bonuses, you get a real one in the wide flexibility of gearhead motors made by Master. Motors in any size from 100 down to 1/10 horsepower in all cycles, phases, and frequencies . . . in open, splash-proof, fan-cooled, and explosion proof types . . . with Speedrangers and Unibrakes . . . for every type mounting . . . and over a gear reduction range up to 432 to 1. Any combination of these can be built easily into a compact power package that will add greatly to the economy, appearance, convenience, and safety of your motor driven equipment.

Investigate what a really remarkable job Master gearhead motors can do for you both in your plant and on your products.

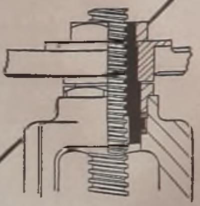
THE MASTER ELECTRIC COMPANY • DAYTON 1, OHIO

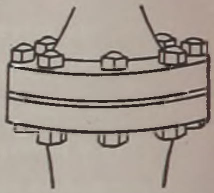


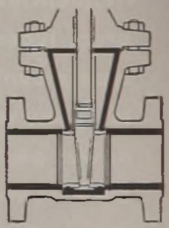
10 HP 37 RPM explosion-proof gearhead motor on magnetic separator for removing tramp iron from coal.

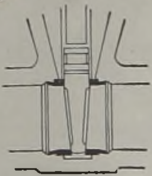


Vogt
FOR BETTER VALVES
Vogt





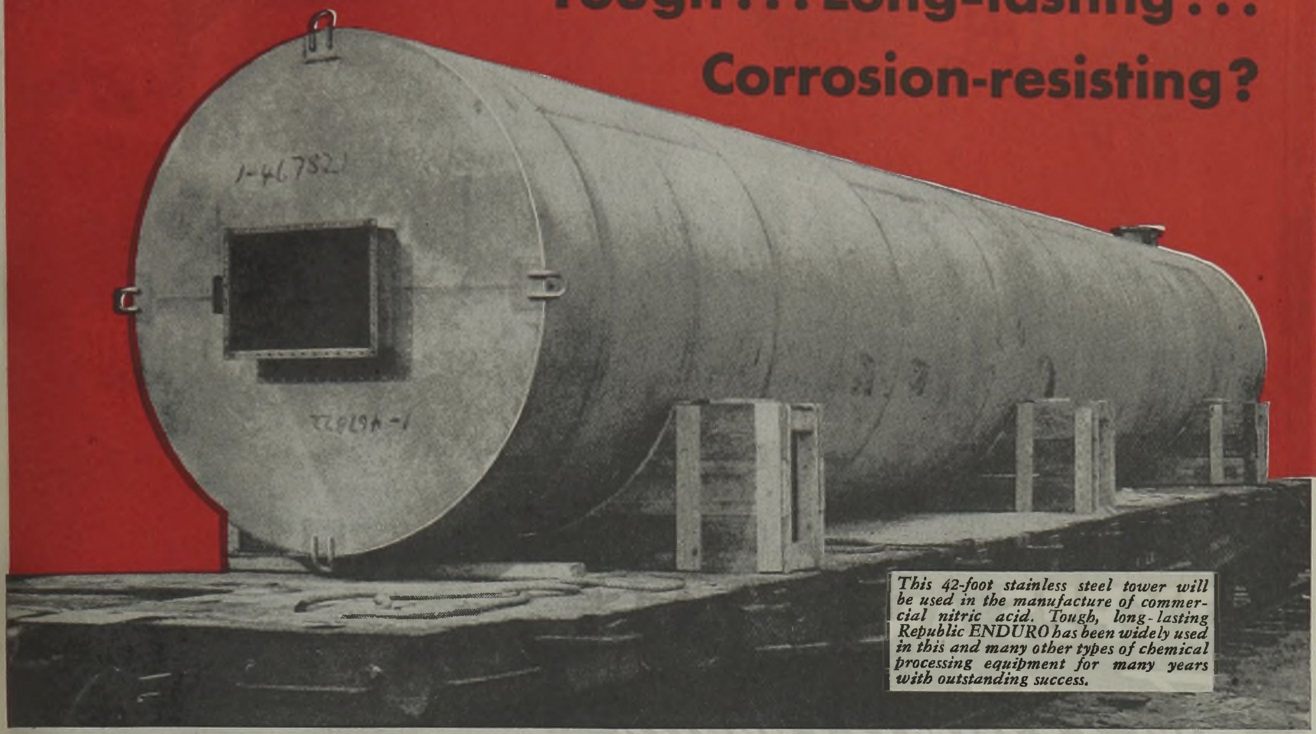




Vogt
DROP FORGED STEEL
GATE VALVES

LOOKING FOR EQUIPMENT THAT'S

Tough . . . Long-lasting . . . Corrosion-resisting?



This 42-foot stainless steel tower will be used in the manufacture of commercial nitric acid. Tough, long-lasting Republic ENDURO has been widely used in this and many other types of chemical processing equipment for many years with outstanding success.

Talk to your friends who use STAINLESS STEEL

● Yes, stainless steel is the *one* all-purpose equipment material for applications involving corrosion and high temperatures—because it lasts longer in severe service.

But don't take our word alone!

Talk to your business acquaintances who already are using stainless steel equipment. Let them tell you about the profitable, money-saving advantages of using stainless steel for trays, tanks, vats, pressure vessels, valves and other chemical processing applications.

Ask them about the various ways in which stainless steel cuts maintenance and replacement costs . . . about the tough, hard surface which provides lifelong protection against rust, corrosion, rough use and abuse.

See if they don't agree that stainless steel resists the action of most acids and alkalies—hot or cold . . . resists scaling at high temperatures . . . and retains its high strength at elevated or sub-zero temperatures.

Above all, remember this: *There is no finer stainless steel than Republic ENDURO*—made by the world's foremost producer of alloy and stainless steels.

Plan now to install ENDURO equipment. For complete details, see your equipment manufacturer or write directly to:

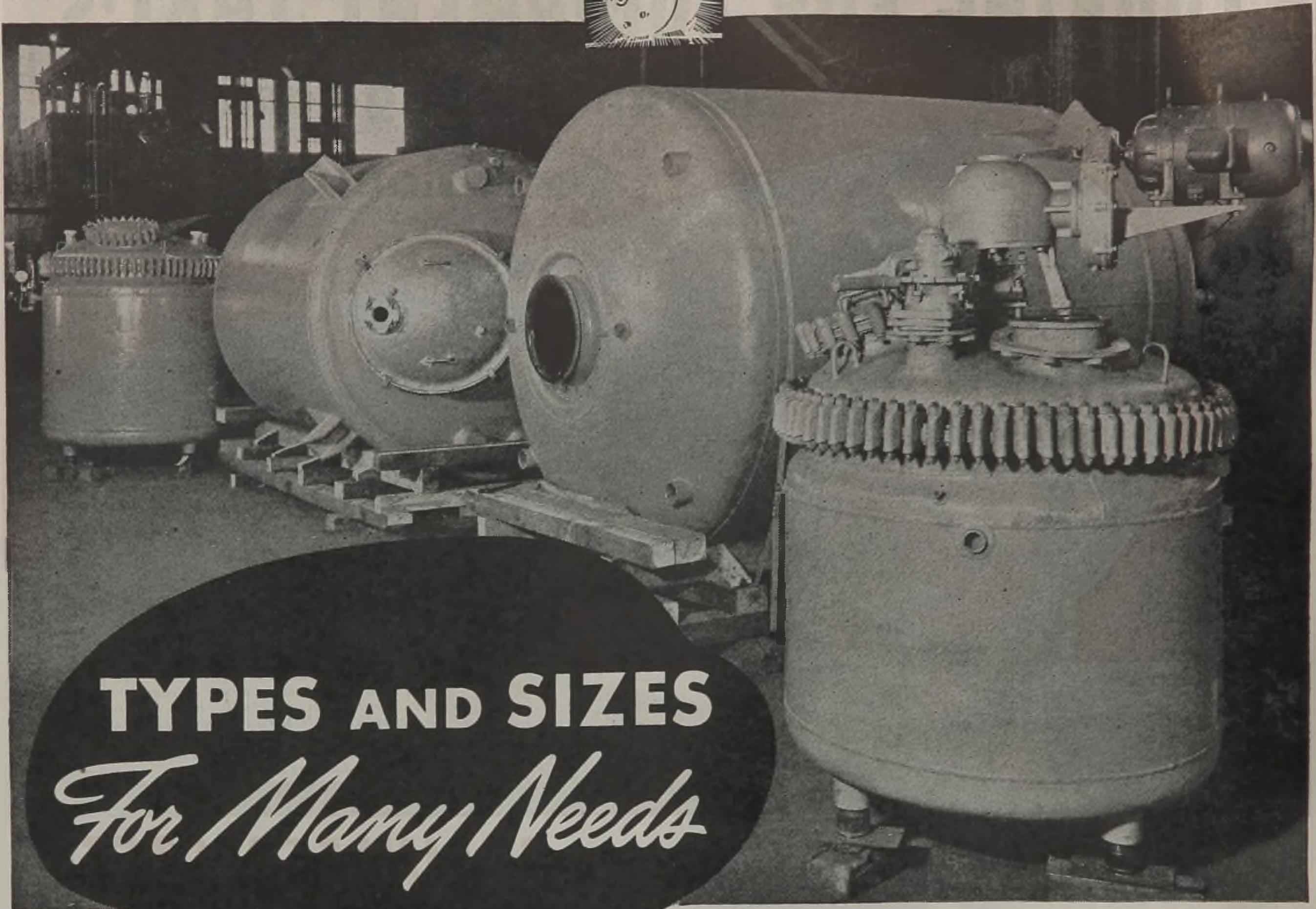
REPUBLIC STEEL CORPORATION
Alloy Steel Division • Massillon, Ohio
GENERAL OFFICES • CLEVELAND 1, OHIO
Export Department: Chrysler Building, New York 17, N. Y.

Republic
REPUBLIC STEEL PRODUCTION FOR VICTORY

ENDURO STAINLESS STEEL
Reg. U. S. Pat. Off.

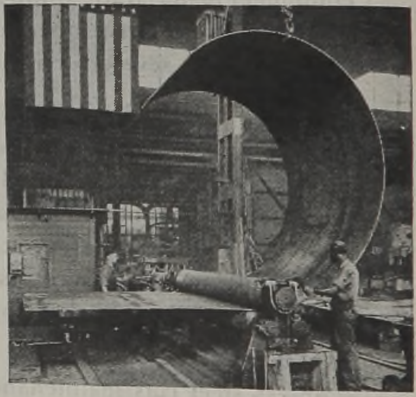
Other Republic Products include Carbon and Alloy Steels—Pipe, Sheets, Strip, Plates, Bars, Wire, Pig Iron, Bolts and Nuts, Tubing

THE INERTNESS OF GLASS **THE STRENGTH OF STEEL**



TYPES AND SIZES *For Many Needs*

● Furnished open or closed, single shell or jacketed, Glascote equipment meets industry's most exacting, acid resistant requirements. The glass, developed by our ceramic engineers specially for this service, is resistant to all acids at any concentration, at low or elevated temperatures, with the exception of hydrofluoric, hot concentrated phosphoric, and certain concentrated alkaline solutions with which there are certain limitations. Sizes for pilot plant, semi-works or full plant operation. Consult Glascote about your reaction, distilling, mixing, storage or crystallizing requirements. Let us help you select a standard, or suggest special equipment that will be exactly suited to your own particular individual needs.



Rolling $\frac{5}{8}$″ x 120″ x 384″ Flat Plate into Cylindrical Shell for 7500 Gallon Blending Tank.

GLASCOTE PRODUCTS, INC.

20901 ST. CLAIR AVENUE • CLEVELAND 17, OHIO
ENGINEERING AND SALES REPRESENTATIVES IN THE PRINCIPAL CITIES
CORROSION RESISTANT EQUIPMENT FOR THE PROCESSING INDUSTRIES

Too many calls take time and money!

LET ONE CALL DO IT ALL

When you need STAINLESS STEELS

NEEDLESS expense is eliminated, much precious time is saved, when you telephone Industrial *first.* For Industrial carries the largest, most diversified stock of Stainless Steels in America.

With its vast inventory—everything in Stainless, from sheets and bars through tubing and wire, to valves, fittings and even bolts and nuts—Industrial is in the unique position of being able to give *same-day attention* to your order. And the odds are in your favor that your order will be filled *completely* . . . as well as *promptly.*

Now, more than ever, it's important you let one call do it all when you need Stainless Steels. Besides saving time and money, you'll be giving the boys and girls in uniform a break . . . for they keep in touch with home by telephone.

Remember . . . if it's Stainless, Industrial has it. And if you have a problem regarding specification or fabrication, Industrial's expert metallurgists are at your service. For speedy handling of your complete order, call Industrial first! INDUSTRIAL STEELS INC., 250 BENT STREET, CAMBRIDGE 41, MASS.

TROwbridge 7000

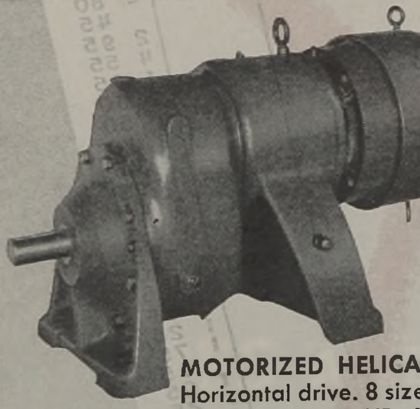
EVERYTHING IN STAINLESS

JML Co CI-DI

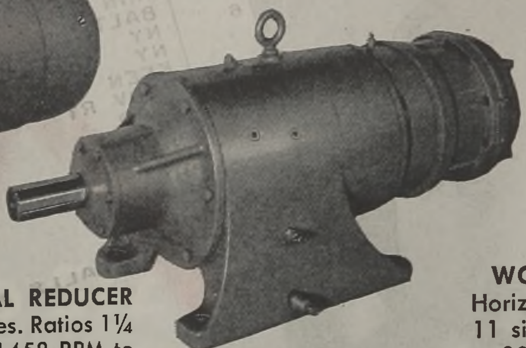
INDUSTRIAL STEELS, INC.

Established 1888

D.O.James MOTORIZED SPEED REDUCERS

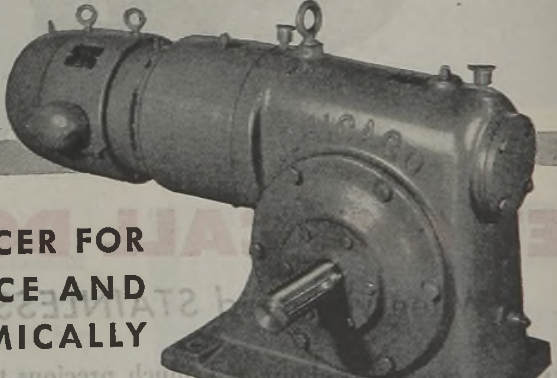


MOTORIZED HELICAL REDUCER
Horizontal drive. 8 sizes. Ratios 1¼ to 9:1. ¾ to 50 HP. 1458 RPM to 128 RPM.



MOTORIZED PLANETARY REDUCER
Horizontal drive. 35 sizes. Ratios 10 to 1200:1. ¾ to 75 HP. 172 RPM to 74 RPM.

MOTORIZED WORM GEAR REDUCER
Horizontal and vertical drive. 11 sizes. Ratios 6 to 65:1. ⅛ to 30 HP. 310 RPM to 25 RPM.



MOTORIZED PLANETARY REDUCER
Vertical drive. 35 sizes. Ratios 10 to 1200:1. ¾ to 75 H.P. ← 172 RPM to 74 RPM.

THE IDEAL GEAR REDUCER FOR LIMITED FLOOR SPACE AND IS OPERATED ECONOMICALLY

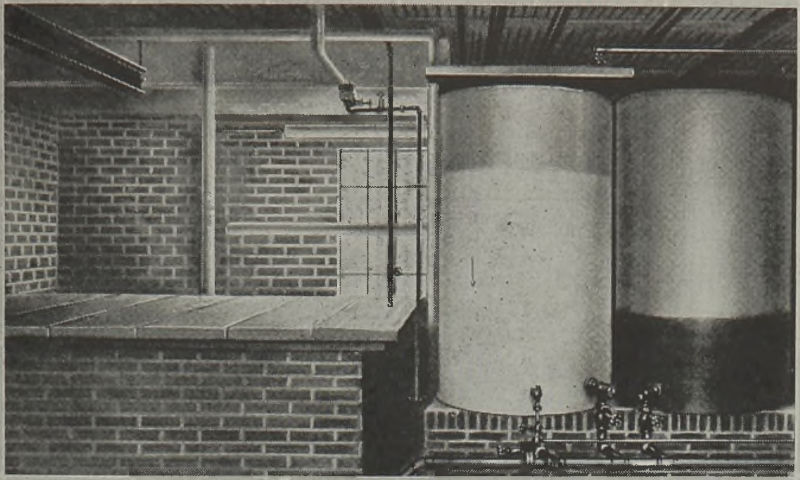
MOTORIZED → HELICAL REDUCER
Vertical drive. 8 sizes. Ratios 1¼ to 9:1. ¾ to 50 HP. 1458 to 128 RPM.

The design and manufacture of D.O.James motorized reducers embodies all the high quality of construction of our standard gear reducers. In addition to this in-built quality you have many advantages—such as compactness, lower cost and elimination of separate supports, thereby saving valuable floor space. D.O.James Motorized Reducers are manufactured to drive up, down, horizontally or at an angle.

D.O.James

Over 57 years makers of every type of gear and gear reducer.

D. O. JAMES MANUFACTURING CO.
1140 W. MONROE STREET, CHICAGO, ILL.




500°
350°

Clear colors,

clean fabrics

with **Calgon***

To get clear, uniform colors in finished woolens, dyers must start with fabrics that are really clean. Not merely free from visible dirt and wool oils, but free as well from the unseen deposits of lime soap, formed in the scouring operations. Presence of such deposits results in colors that are cloudy and streaky, and in goods that may develop rancid odors.

Calgon in raw wool scouring and in piece goods scouring eliminates lime soap. Calgon in the rinse leaves the piece goods cleaner and softer, free of rancid odors, and in the right condition for good dyeing.

All these things mean more piece goods of the highest quality, less that must be degraded or rejected—and consequently mean more profitable operation.

Calgon has a score or more applications in the textile industry—and literally hundreds of applications in other industries from paper making to food processing.

Continuous research in the industrial uses of Calgon is carried on by Calgon, Inc. Its technical facilities are at the service of industrial chemists.

**Calgon is the registered trade-mark of Calgon, Inc., for its glassy sodium phosphate products.*

Calgon used in scouring woolen piece goods removes lime soap, leaving goods softer, cleaner and in better condition for dyeing.

HAGAN
HALL
BUROMIN
CALGON

calgon, inc.

A SUBSIDIARY OF
HAGAN CORPORATION

HAGAN BUILDING
PITTSBURGH 30, PA.

It's easy to make a tight joint with

PYREX PIPE

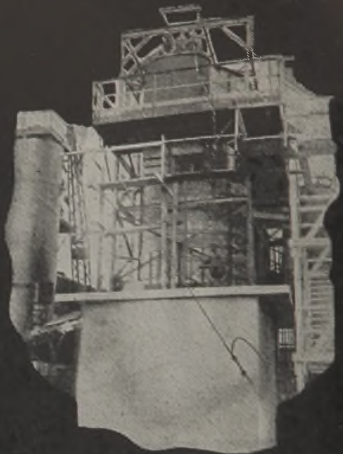
Making a tight joint with Pyrex Pipe is easy. It's an A, B, C operation that any careful workman can perform. No special tools or training are required.

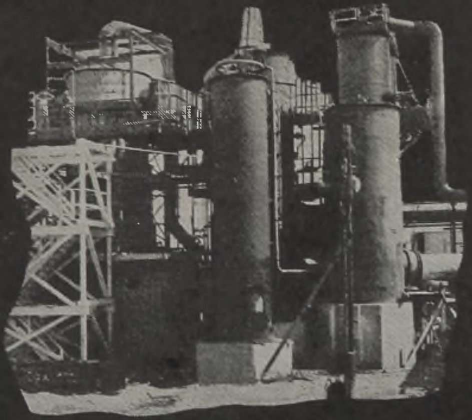
HERE'S HOW IT'S DONE

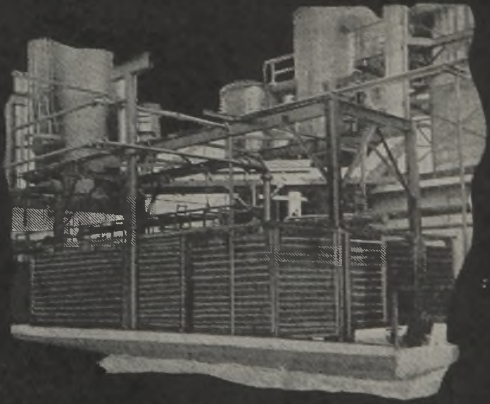
1. Mount metal flanges on pipes before they are placed in hangers. Inserts can be handled easier if they are curled over sharp radius before insertion in flange.
2. Flanges should be pulled up on the inserts so that the metal flange face is nearly flush with the end surface of the insert.
3. Gaskets should be lined up with the inner surface of the pipe so that no part protrudes into the pipe to cause obstruction to flow. To avoid slippage, gaskets should be kept thoroughly dry during installation.
4. As the pipe lengths are put into place, tighten the flange bolts enough to bring the glass pipe ends snug against the gasket, but not enough to compress it.
5. When all pipes and fittings are connected and the line is complete, begin at fixed end and work to the opposite end tightening the flange bolts. Do this evenly and pull them up quite tightly. Use a 6″ or 8″ end-wrench if possible.

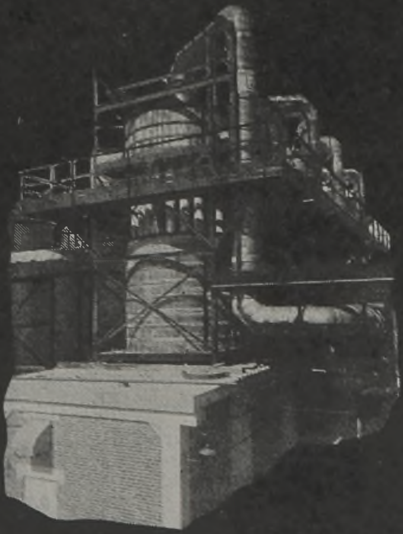
Once installed, Pyrex Pipe brings to your processing operations many important advantages. Its transparency permits you to inspect product flow and condition at every stage of processing. Its resistance to thermal shock allows flushing of lines with steam or hot water for visible cleanliness. Its chemical stability virtually eliminates corrosion, contamination, scaling and pitting. It is rugged enough to meet plant operating conditions. For further information, write Industrial Sales Dept., IE-5.

CORNING GLASS WORKS
CORNING, NEW YORK










. . . operate at 115 volts.
. . . of faulty operation look for low line voltage.
. . . damage due to high line voltage.
Isn't that asking a lot of several million people who wouldn't know how to look for low voltage, or what to do about it if they found it?
This equipment is designed to operate at
115 V-AC
60 cycles
As a protection against voltage fluctuations a CONSTANT VOLTAGE TRANSFORMER has been built-in as a component part of this equipment. Rated performance will therefore be maintained at all times, regardless of input voltage fluctuations as great as ±15%.
30

EAGLE-PICHER

Industrial Pigments

Red Lead • Special grades of Eagle Red Lead are available for the paint, storage battery, ceramic and varnish industries. Pb_3O_4 content accurately maintained to meet exact requirements of each industry.

Litharge • Eagle Milled Litharges are exceptionally high standard lead oxides. They are finely ground, low in impurities and light brown in color. Available in special grades to suit each industry.

Sublimed Litharge • A fumed, amorphous, light canary yellow monoxide of lead (PbO) of low apparent density. Purest and smallest particle size type of Lead Oxide on the market.

Orange Mineral • Eagle Orange Mineral has a definite orange tone and is noted for its strength, fineness, and uniform color. 95% minimum. Outstanding for paints, colors, inks.

White Lead Carbonate • Three types of Eagle Dry White Lead Carbonate are produced. Unite chemically with linseed oil to form an elastic, deep-anchoring, long-wearing paint film.

Sublimed White Lead • For years, the standard basic sulphate of white lead. For the paint or rubber industries. Exceptionally white and bright. Conforms to ASTM and government specifications.

Zinc Oxide • Eagle Zinc Oxide AAA is especially designed for use wherever a lead-free American process zinc oxide is required. Exceptionally white and bright, having excellent tinting strength and opacity. Produced in a series of varying paint viscosity ranges.

Leaded Zinc Oxides • A complete line of all types and grades, notably Eagle AA 5% Leaded Zinc Oxide; Eagle A 35% Leaded Zinc Oxide; Eagle 50% Leaded Zinc Oxide.

Lithopone • A precipitated white pigment of normal or regular type. Three general grades — A, AA, AAA, signifying low, medium and high oil absorption respectively. Has a clean, white color.

Titanated Lithopone • Eagle Titanated Lithopone is a precipitated white pigment blended with 15% Titanium Dioxide. Available in grades to suit individual requirements.

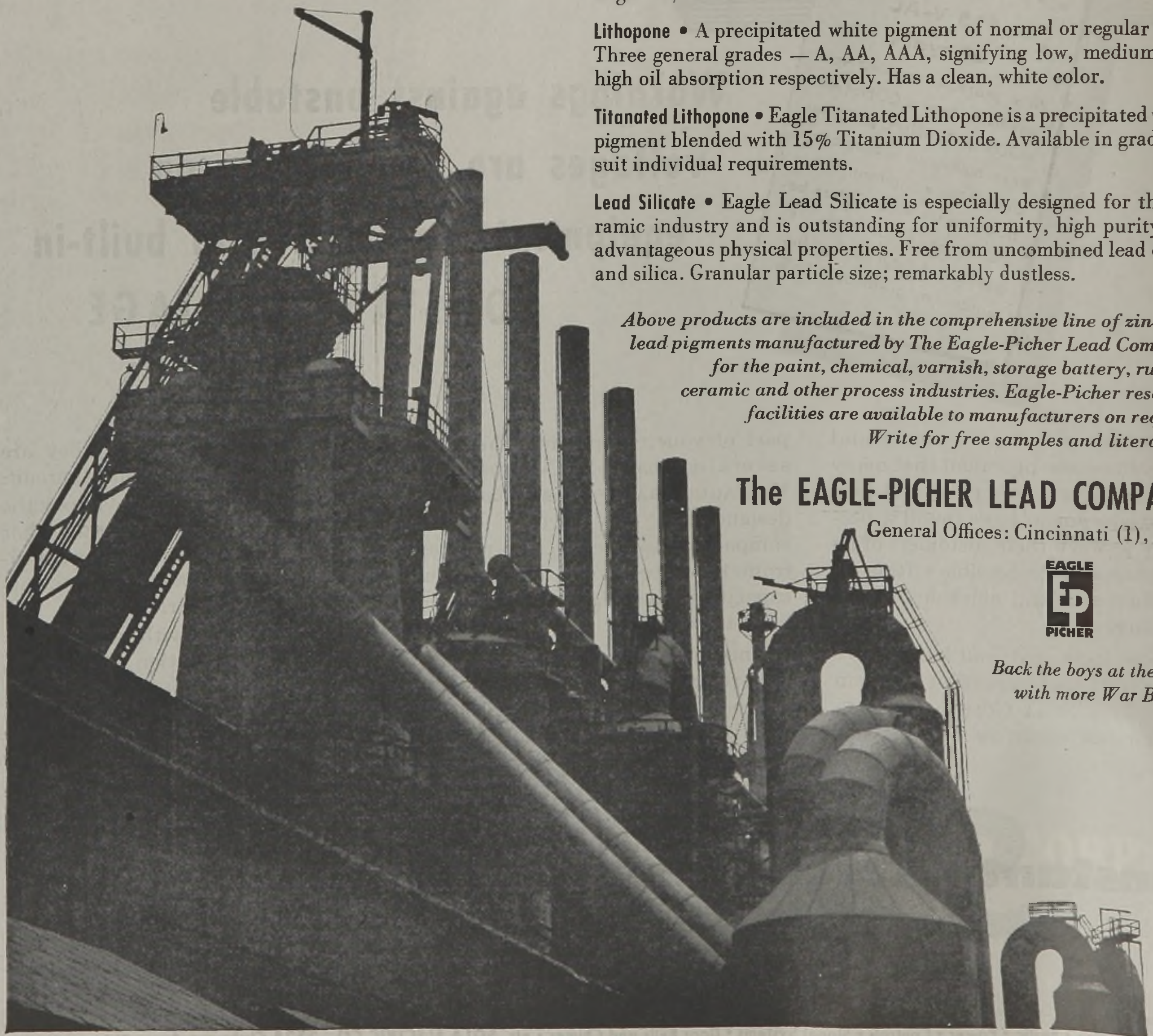
Lead Silicate • Eagle Lead Silicate is especially designed for the ceramic industry and is outstanding for uniformity, high purity and advantageous physical properties. Free from uncombined lead oxide and silica. Granular particle size; remarkably dustless.

Above products are included in the comprehensive line of zinc and lead pigments manufactured by The Eagle-Picher Lead Company for the paint, chemical, varnish, storage battery, rubber, ceramic and other process industries. Eagle-Picher research facilities are available to manufacturers on request. Write for free samples and literature.

The EAGLE-PICHER LEAD COMPANY
General Offices: Cincinnati (1), Ohio

EAGLE EP PICHER

Back the boys at the front with more War Bonds!



A FEW FACTS ABOUT CORHART PRODUCTS

Corhart Electrocast Refractories are high-duty products manufactured by melting selected and controlled refractory batches in electric furnaces, and casting the molten material into molds. After careful annealing, the finished shapes are ready for shipment. Dense, high-melting refractories, they are especially designed for resistance to corrosive action.

PRODUCTS

CORHART STANDARD ELECTROCAST is a high-aluminous refractory.

CORHART ZED ELECTROCAST is Zirconia-bearing.

CORHART ELECTROPLAST is a high-temperature plastic refractory made from Standard Electrocast which has been ground and crushed. Especially designed for ramming. Furnished dry.

CORHART MORTAR is a high-quality cement for laying up Electrocast, clay brick, or any aluminous refractory.

CHARACTERISTICS OF STANDARD ELECTROCAST

POROSITY: Less than 0.5%—therefore virtually no absorption.

FUSION POINT: Cone 38 without any appreciable softening below that point.

HARDNESS: 8, Mineralogist's scale.

SPECIFIC GRAVITY: Blocks weigh approximately 183 lbs. per cu. ft.

COEFFICIENT OF EXPANSION: 0.000006 between room temperature and 900° C.

SPECIFIC HEAT: 0.25 cal. per gm. per °C. at 980° C.

THERMAL CONDUCTIVITY: 25 BTU per sq. ft. per hour for gradient of 1°F. per inch.

COMPOSITION: Standard Electrocast is of an aluminous crystalline nature.

CORROSION: Because of low porosity and inherent chemical make-up, Corhart products are highly resistant to corrosive action.

APPLICATIONS

Most heat processes present spots where a better refractory material is needed in order to provide a balanced unit and reduce the expense of repeated repairs. It is for such places of severe service that we invite inquiries regarding Corhart Products as the fortifying agents to provide the refractory "balance" desired.

The following is a partial list of applications for which Corhart Products are suggested:

ELECTROLYTIC CELLS — for production of Magnesium and other light metals.

SILICATE OF SODA FURNACES — sidewalls, bottoms, and breastwalls.

HEARTHS AND SMELTERS — for non-ferrous metals.

ALKALI AND BORAX MELTING FURNACES — fast-eroding portions.

GLASS FURNACES — the entire installation of flux walls and bottoms, breastwalls, ports, tuckstones, forehearths, recuperators, etc.

RECUPERATORS—tile, headers, separators, etc.

ENAMEL FRIT FURNACES — flux walls and bottom.

BRASS FURNACES — metal contact lining.

ELECTRIC FURNACES — linings for rocking type, and rammed linings of Electroplast for this and other types.

BOILERS — clinker line.

STOCK SHAPES AND SPECIALS

Standard and Zed Electrocast are made in stock shapes and in many special shapes. The weight of individual pieces may run to 3500 pounds.

IF YOU NEED A BETTER REFRACTORY—

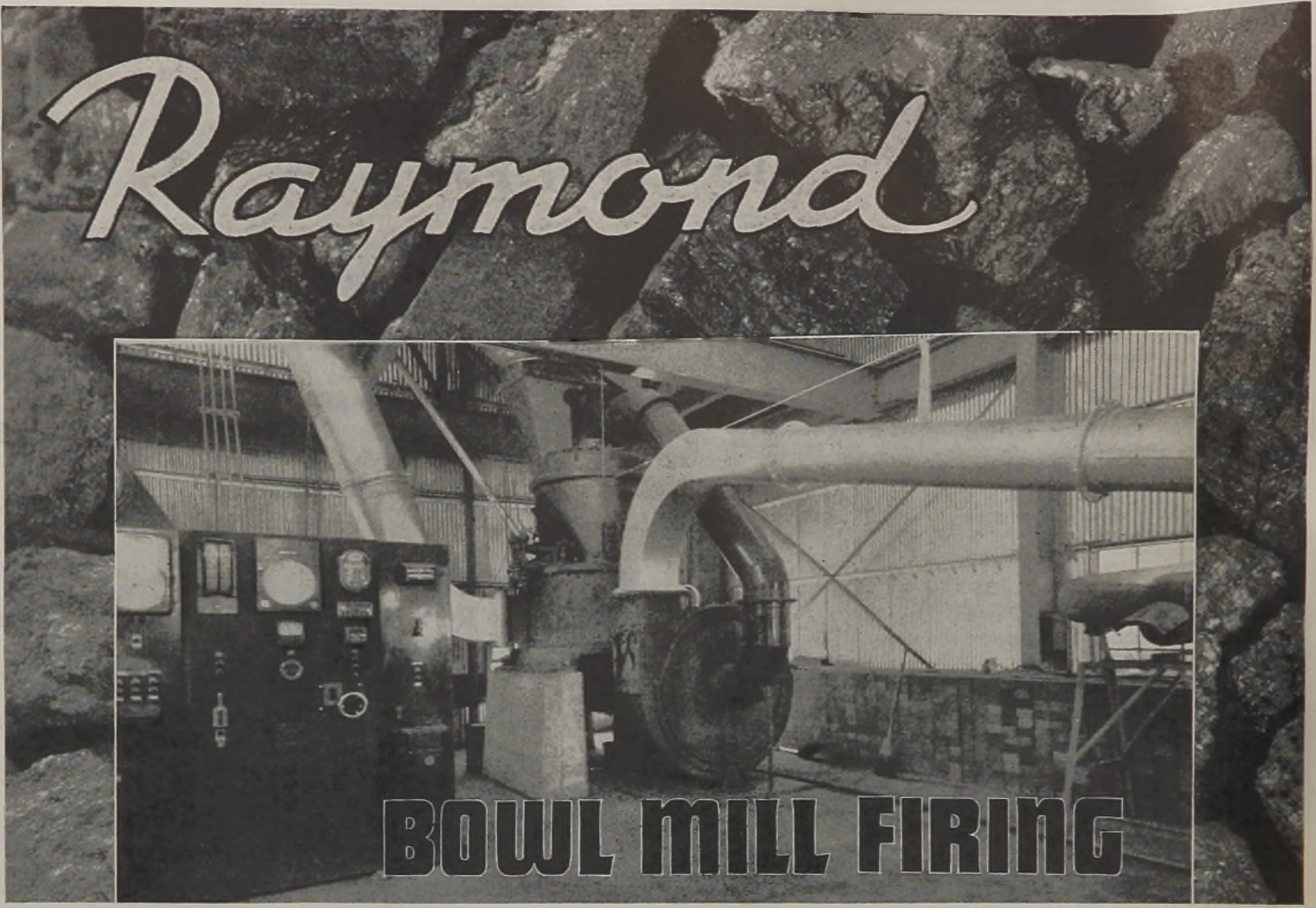
● Corhart Electrocast Refractories are high-duty products which have proved considerably more effective than conventional refractories in certain severe services. If your processes contain spots where a better refractory is needed to provide a balanced unit and to reduce frequent repairs, Corhart Electrocast Refractories may possibly be the answer. The brief outline at the left gives some of the basic facts about our products. Further information will be gladly sent you on request.

Corhart Refractories Company, *Incorporated,* Sixteenth and Lee Streets, Louisville 10, Kentucky.

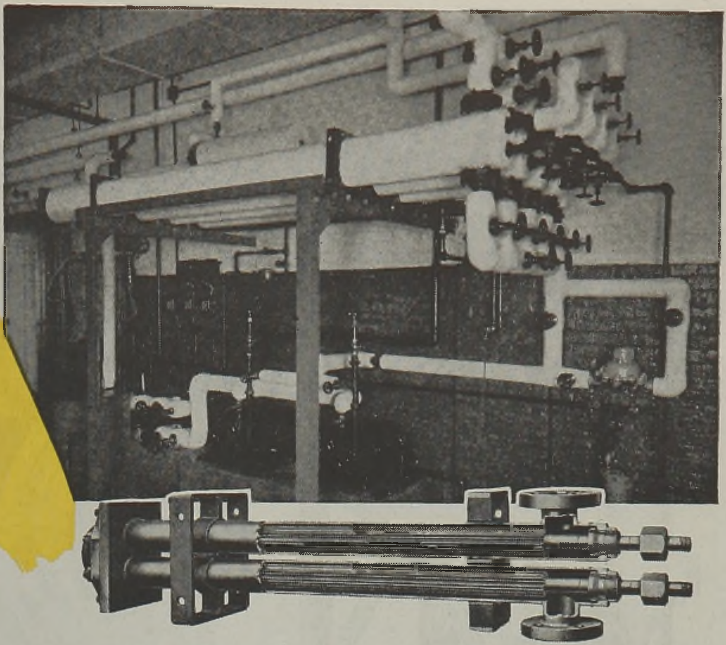
"Corhart" is a trade-mark, registered U. S. Patent Office.

QUALITY ECONOMY ENDURANCE

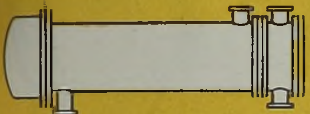
CORHART ELECTROCAST REFRACTORIES


Raymond
BOWL MILL FIRING

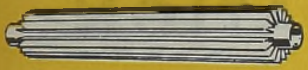
TWIN G-FIN SECTION FUEL OIL HEATER



ONLY G-R BUILDS THIS WIDE VARIETY OF HEAT TRANSFER APPARATUS



SHELL and BARE TUBE
Heaters, Coolers, Condensers, Heat Exchangers



G-FIN
Longitudinal-finned elements for greater heat conductivity

K-FIN
Helical-finned elements for vapors and gases

BENTUBE SECTIONS
with scale-shedding elements for hard or salt water

TUBEFLO SECTIONS
Non-clogging design for residuum and other dirty fluids

Simple

Just a pipe within a pipe—that's the principle of the Twin G-Fin Section. The G-Fin inner pipe, through which the steam passes, has longitudinal fins to provide greater surface for transfer of heat to the oil flowing through the outer pipe.

Readily Installed

The Twin G-Fin Section is easily handled, and can be placed close against a wall, ceiling or floor . . . wherever most convenient. Movable supports further assist convenient installation.

Easy To Clean

The G-Fin heating elements or pipes may be completely removed from the shells for cleaning, without disturbing the oil connections. No special tools are required.

Flexible Capacity

These units are standard and interchangeable. They may be arranged in series or parallel; and at partial loads, sections may be cut in and out to maintain constant oil temperature.

Compact

The longitudinal G-Fins provide at least six times as much heat transfer surface as bare tubes . . . the result: the Twin G-Fin unit has fewer tubes than any other type of heater.

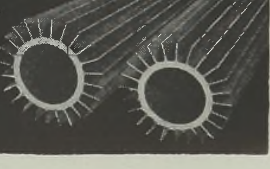
Leak-proof

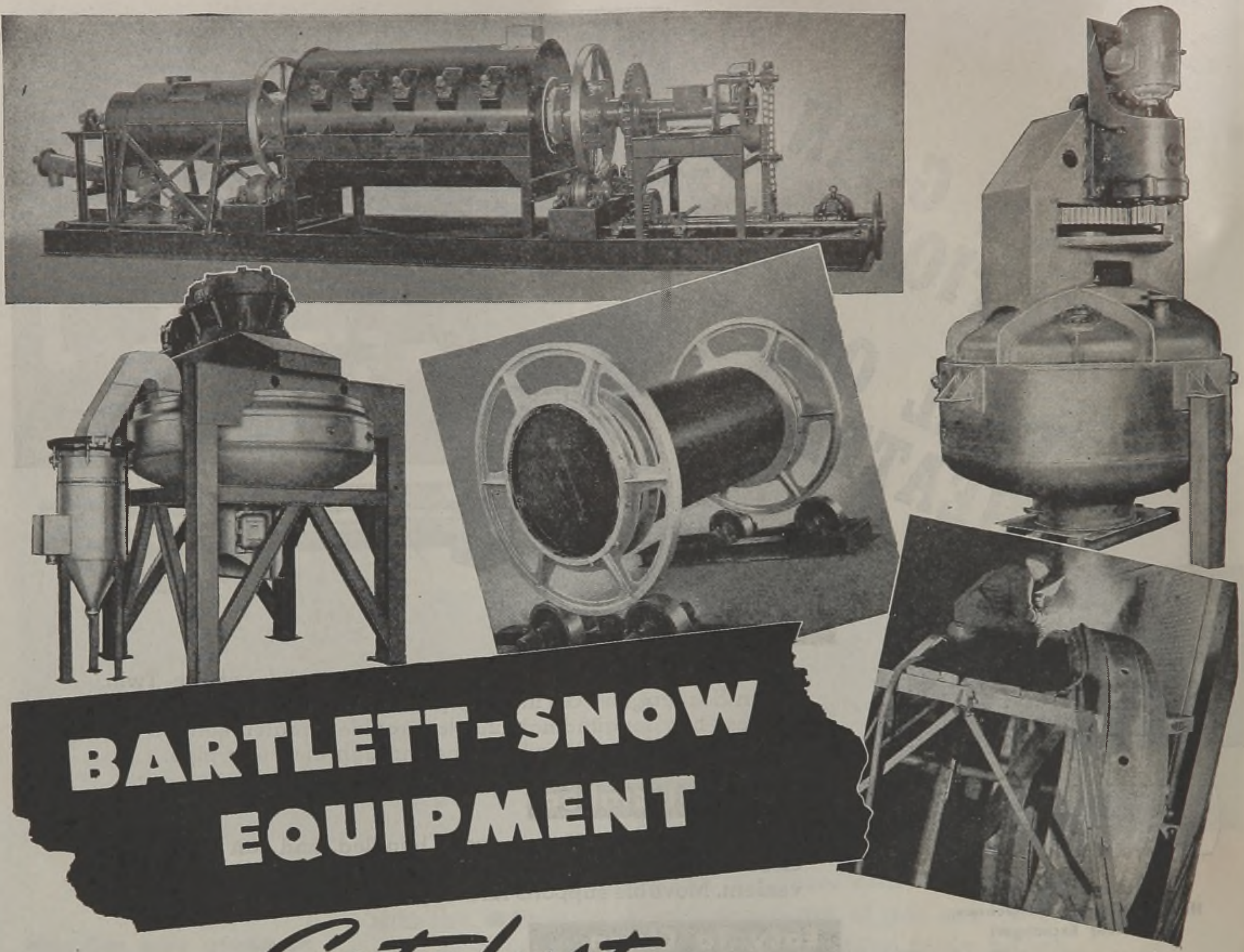
Leakage between steam and oil cannot occur because there are no internal joints.

For complete description of this superior fuel oil heater, write for our Form 714.

THE GRISCOM-RUSSELL CO.
285 Madison Ave., New York 17, N. Y.

GRISCOM-RUSSELL
TWIN G-FIN SECTION
The Universal Heat Exchanger





BARTLETT-SNOW EQUIPMENT

FOR *Catalyst* PREPARATION

● Long experience, and a searching, technical, mathematically exact approach to problems of surface evaporation or diffusion, corrosion, abrasion, dust condition and possible galvanic action,—has enabled Bartlett-Snow Heat Engineers to make noteworthy contributions to the art of catalyst preparation.

Typical of many, are a stainless steel equipment—jacketed—that separates distilled water from an impregnated catalytic support, discharges the dried material through an enclosed plug gate without any dust loss whatever . . . Cylinders of special design and construction that withstand the high temperatures of producing oxides . . . Equipment for processing in a reducing atmosphere, at 2000°F., that exhausts the hot gases safely, and discharges the processed material, first cooled to normal temperatures, continuously, at the desired rate per hour.

Whether yours is a problem of crystallization, oxidation, or reduction . . . or merely a simple drying, calcination, or heat treatment, call the Bartlett-Snow Heat Engineers,—It's your assurance that the equipment recommended will prove thoroughly suited to all phases of your requirement. Our Bulletin No. 89—more than 50 pages—and profusely illustrated—contains much technical data on heat processing of interest to development and operating men. Send for a copy.

THE C. O. BARTLETT & SNOW CO.

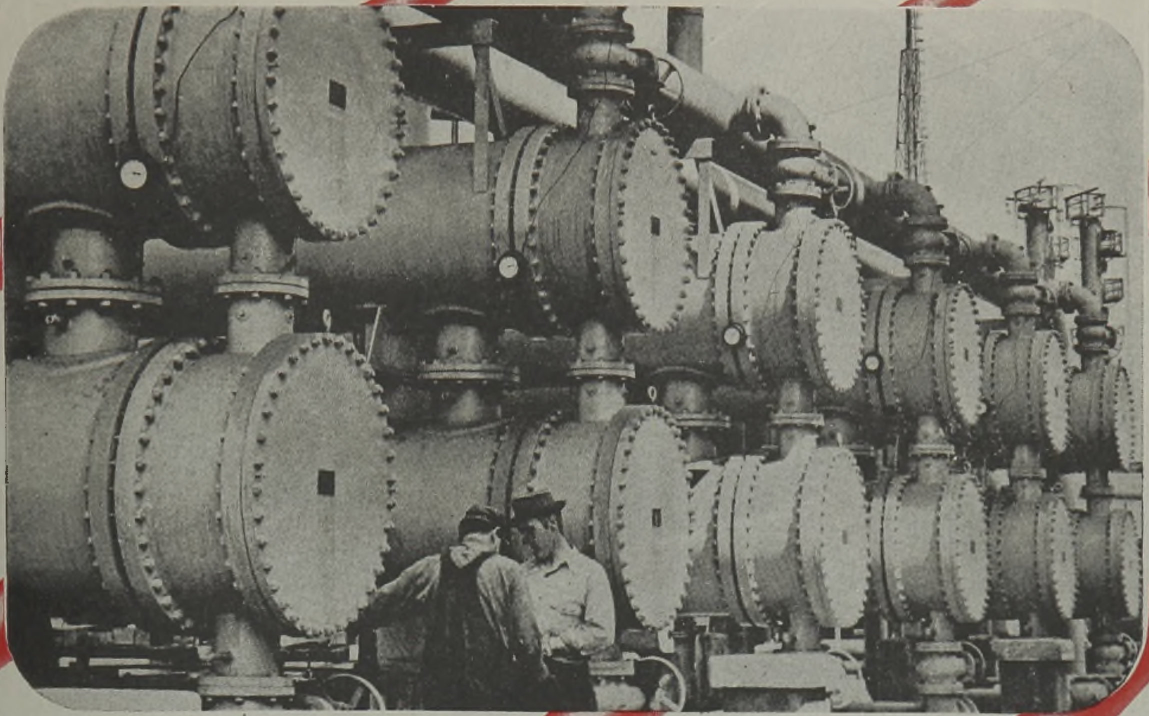
6207 HARVARD AVENUE • CLEVELAND, OHIO

Engineering and Sales Representatives in Principal Cities

DRYERS • CALCINERS • KILNS • PRESSURE VESSELS

• • COMPLETE MATERIAL HANDLING FACILITIES TO MEET ANY REQUIREMENT • •
ONE CONTRACT • ONE GUARANTEE OF SATISFACTORY PERFORMANCE • UNIT RESPONSIBILITY

GET BACK "ON STREAM" QUICKLY
WITH TUBING THAT GOES IN FAST



● When heat exchangers, condensers and evaporators are down for retubing, the easiest way to get them back "on stream" in a hurry is to install Republic ELECTRUNITE Tubing.

ELECTRUNITE Tubes go in *FAST* because they are *uniform* in diameter, *uniform* in wall thickness and *uniform* in concentricity. They are made by the electric resistance welding method—*the only method* consistently providing these qualities of uniformity throughout every length.

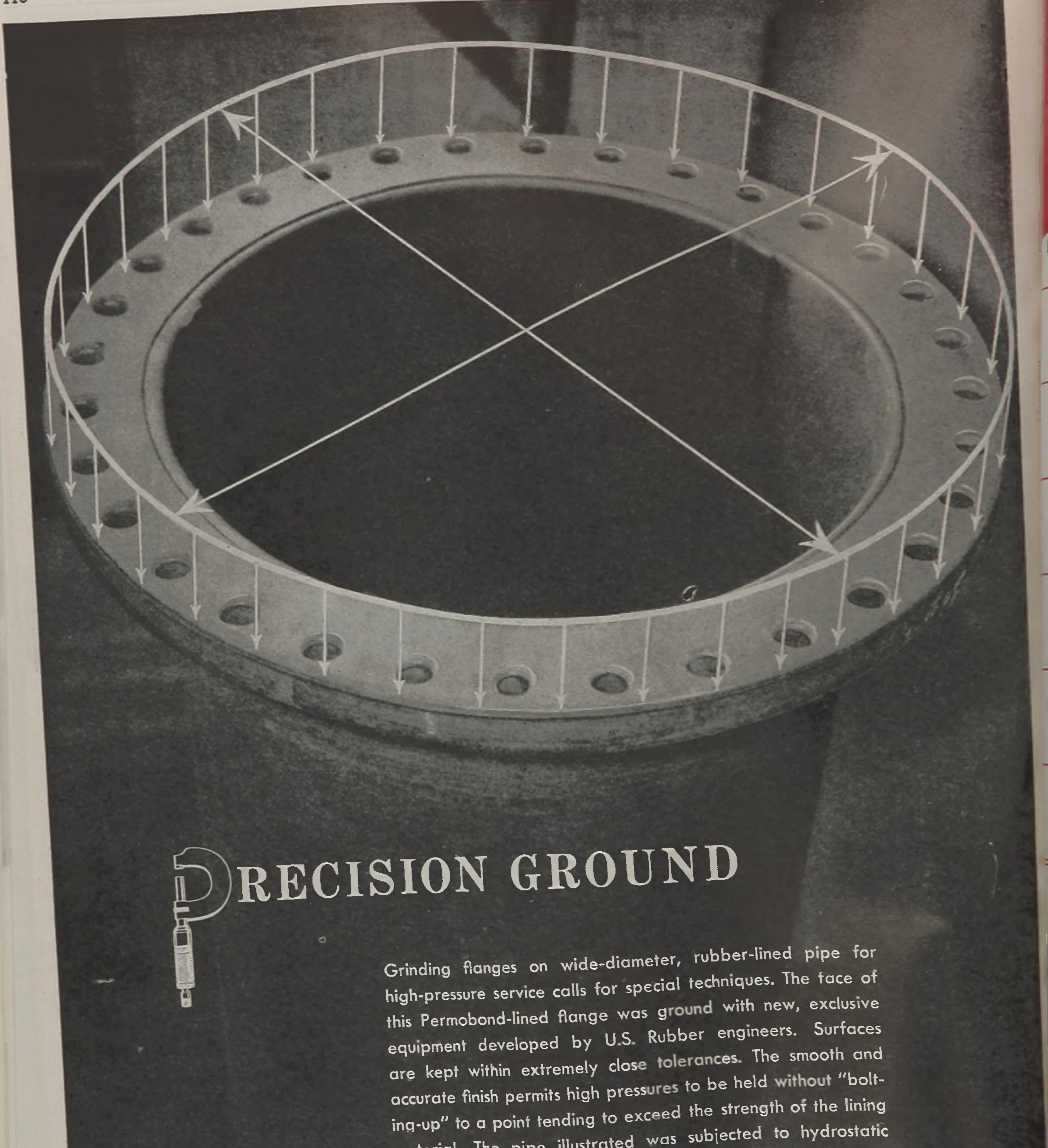
Rolling-in and beading over to tight, non-leaking joints are equally easy when working with ELECTRUNITE Tubing, because Republic's full normalizing process provides uniformly high ductility and freedom from trouble-causing hard spots in the metal.

And you can depend upon ELECTRUNITE Tubes for satisfactory long-life performance, too. Every ELECTRUNITE Tube is hydrostatically tested at pressures much higher than code requirements . . . your assurance that each is strong and sound throughout.

Available in carbon steel in sizes from ½ to 5 inches O.D. and in Enduro Stainless Steel in sizes from ⅜ to 3 inches O.D. If you would like to have more information, write us.

REPUBLIC STEEL CORPORATION
STEEL AND TUBES DIVISION • CLEVELAND 8, OHIO
Export Department: Chrysler Building, New York 17, New York

Republic
ELECTRUNITE
Reg. U. S. Pat. Off.
BOILER, CONDENSER AND
HEAT EXCHANGER TUBES



PLASTICIZERS AND MODIFIERS

TO HELP THE RUBBER MANUFACTURER

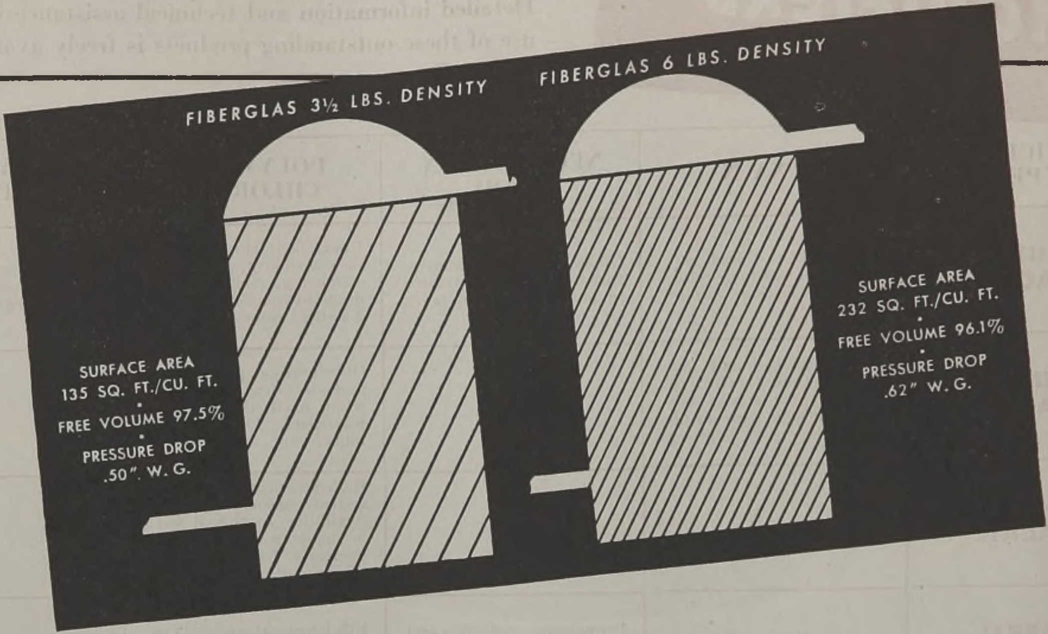
In the extensive line of plasticizers and modifiers developed by The Resinous Products & Chemical Company, the rubber compounder will find aid in solving many of the problems confronting him today. Detailed information and technical assistance in the use of these outstanding products is freely available.

	PLASTICIZER TYPE	BUNA N	NEOPRENE GN (GRM)	POLYVINYL CHLORIDE	POLYVINYL BUTYRAL
ESTER OR MONOMERIC TYPES	**DIBUTYL SEBACATE**	High resilience and outstanding low-temperature flexibility. Excellent drape.	Outstanding low-temperature flexibility. Widely used in both rubber and latex.	Unexcelled for low-temperature flexibility, plasticizing efficiency, resilience and drape in PVC and copolymers. Excellent color stability.	High efficiency, excellent low-temperature flexibility, color and light stability.
	DIBENZYL SEBACATE	Good resilience and low-temperature flexibility. Excellent for stocks subjected to high temperature service.		Outstanding permanence and electrical properties, when used as secondary plasticizer. Low flammability.	
	DIOCTYL SEBACATE			High plasticizing efficiency and extreme low-temperature flexibility combined with permanence at higher temperatures. Excellent dielectric properties.	
	DICAPRYL PHTHALATE	Good plasticizing efficiency. For use in soft stocks.	Permanence, resilience and lasting low-temperature flexibility. Particularly useful for molded goods.	Efficiency, satisfactory low-temperature flexibility and excellent permanence at very low cost.	
	PLASTICIZER 35			Highly efficient, low-cost secondary plasticizer.	Extreme efficiency, excellent permanence and good low-temperature flexibility. Good low-cost, general purpose plasticizer in coated goods.
	PLASTICIZER 36			High efficiency, extreme low-temperature flexibility, low cost, excellent drape.	High efficiency, permanence and good low-temperature flexibility.
MERIC TYPES	**PARAPLEX G-25**	Outstanding for permanence and resistance to extraction by hot oils. Good low-temperature flexibility.		Unexcelled for permanence and resistance to extraction and migration. Superior resistance to weathering, especially ultra violet.	
	PARAPLEX AL-111	Permanence, excellent heat and oil resistance. A low-cost, non-migrating plasticizer.	Permanence, reasonable low-temperature flexibility. Low-cost processing aid, particularly for milling, molding and extruding.		
	PARAPLEX RG-8				Permanence and high efficiency. Low-cost resinous type, well suited to formulation of adhesives for combining, etc. — because of desirable tack.
	SPECIAL TYPES	Resin R6-3 is outstanding for permanence and resistance to hot oils.			AMBEROL ST-137, UFORMITE MM-55 and AMBERLITE PR-14 all well suited for thermosetting of PVB compositions, both calender and solvent types.

PARAPLEX, AMBEROL, UFORMITE and AMBERLITE *are trade-marks, Reg. U. S. Pat. Off.*
Represented by Cia. Rohm y Haas, S.R.L., Carlos Pellegrini 331, Buenos Aires, Argentina, and agents in principal South American cities.

THE RESINOUS PRODUCTS & CHEMICAL COMPANY
WASHINGTON SQUARE, PHILADELPHIA 5, PA.

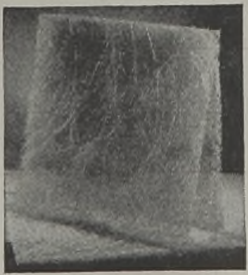
NEW FIBERGLAS* TOWER PACKING TECHNIQUE INDICATES HIGHER PRODUCTION CAPACITY



For some time, it has been standard practice to install Fiberglas Tower Packing at a density of 3½ pounds per cubic foot. At this density a surface area of 135 sq. ft./cu. ft. was provided, with a free volume of 97.5%.

Recently, however, chemical engineers have successfully obtained even higher production capacities and efficiencies than were possible when the standard practice was followed. By installing Fiberglas Tower Packing at 6-pound density a surface area of 232 sq. ft./cu. ft. is provided—with only a drop of 1.4% to 96.1% in free volume.

In atmospheric-pressure packed columns containing Fiberglas Tower Packing, vapor velocities of 7 ft. per second have been obtained. As the decrease in free volume is relatively small, when the Tower Packing is used at 6-pound density, the vapor velocity remains approximately the same.



Fiberglas is glass in fiber form. Consequently, the individual fibers are incombustible . . . do not absorb moisture . . . will not rot or decay and are resistant to most chemicals. The glass fibers in Fiberglas Tower Packing average approximately .0080" in diameter. They are arranged in jackstraw manner and are bonded together with a fugitive binder to give sufficient rigidity of form for easy handling during application.

Perhaps you, too, can increase production capacity, obtain greater efficiency or effect other improvements by using Fiberglas Tower Packing. Samples for experimental work, together with all use and application data available, will be furnished without charge. Write: *Owens-Corning Fiberglas Corporation, 1951 Nicholas Building, Toledo 1, Ohio.*

In Canada, Fiberglas Canada Ltd., Oshawa, Ontario.

Free Samples

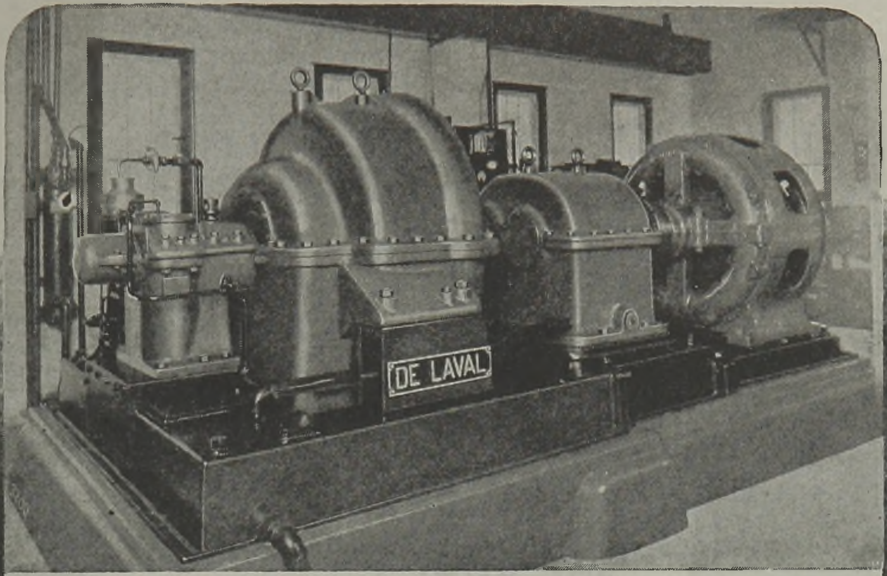
Write for folder containing samples of seven *Fiberglas Basic Fibers* ranging in diameter from .00022" to .0080".

FIBERGLAS TOWER PACKING

*T. M. Reg. U. S. Pat. Off.

ARMY E NAVY

SEVENTEEN YEARS OF UNINTERRUPTED SERVICE



De Laval two-stage centrifugal compressor with speed-increasing gear, installed in the Houston Sewage Treatment Plant, where it delivers 12,000 c. f. m. against 6 lb. pressure at 3600 r. p. m. compressor speed and 1200 r. p. m. motor speed.

...*not one minute for Repairs!*

Since September, 1927 when this De Laval motor-driven geared compressor was placed in service in the City of Houston Sewage Treatment Plant, it has operated better than 99 per cent of the time, without ever requiring repairs or overhauling.

Such operation is typical of De Laval dependability. De Laval water works pumps installed more than thirty years ago still give excellent service. De Laval geared turbine ship propulsion units have traveled upwards of 2,000,000 miles without requiring major repairs; and De Laval worm reduction gears have operated for years hidden in the abrasive dust of cement plants.

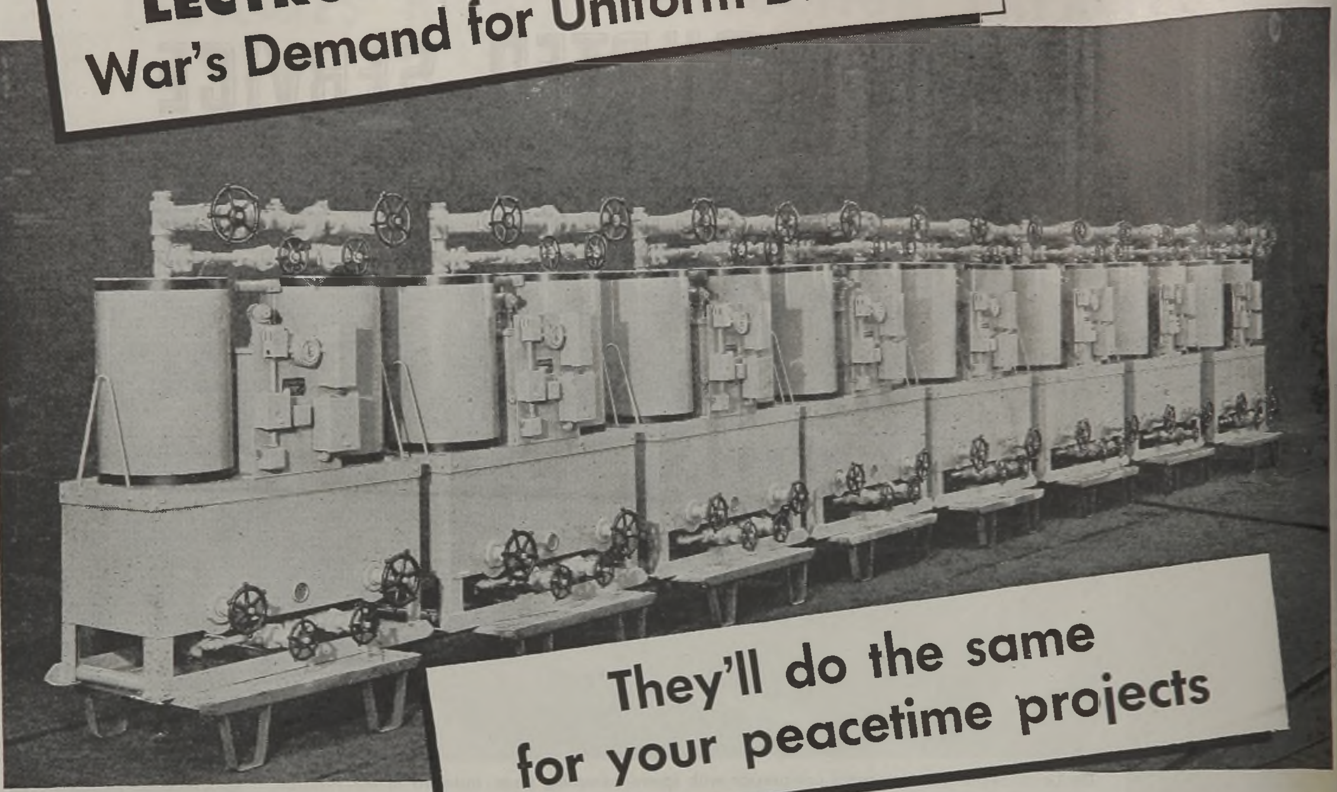
M-50

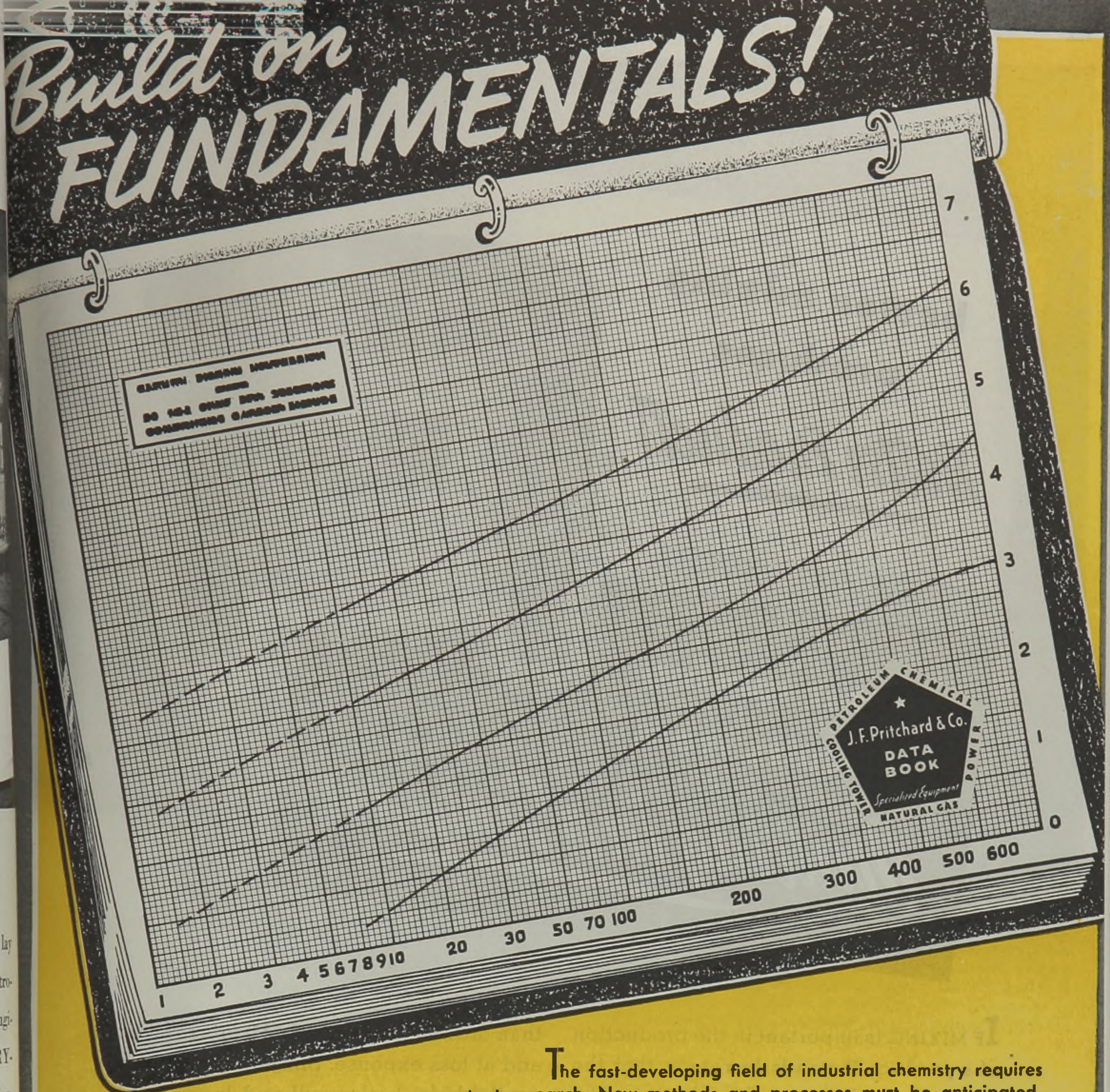
TURBINES • HELICAL GEARS • WORM GEAR SPEED REDUCERS CENTRIFUGAL PUMPS • CENTRIFUGAL BLOWERS and COMPRESSORS • IMO OIL PUMPS

DE LAVAL

STEAM TURBINE COMPANY • TRENTON 2, NEW JERSEY

SALES OFFICES: ATLANTA • BOSTON • CHARLOTTE • CHICAGO • CLEVELAND • DENVER DETROIT • DULUTH • EDMONTON • GREAT FALLS • HAVANA • HELENA • HOUSTO KANSAS CITY • LOS ANGELES • MONTRE NEW ORLEANS • NEW YORK • PHILADELP PITTSBURGH • ROCHESTER • ST. PAUL • LAKE CITY • SAN FRANCISCO • SE TORONTO • TULSA • VANCOUVER • INGTON, D. C. • WINNIPEG




Build on FUNDAMENTALS!
7
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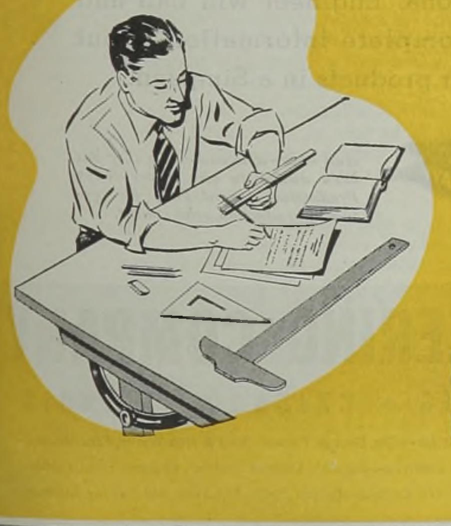
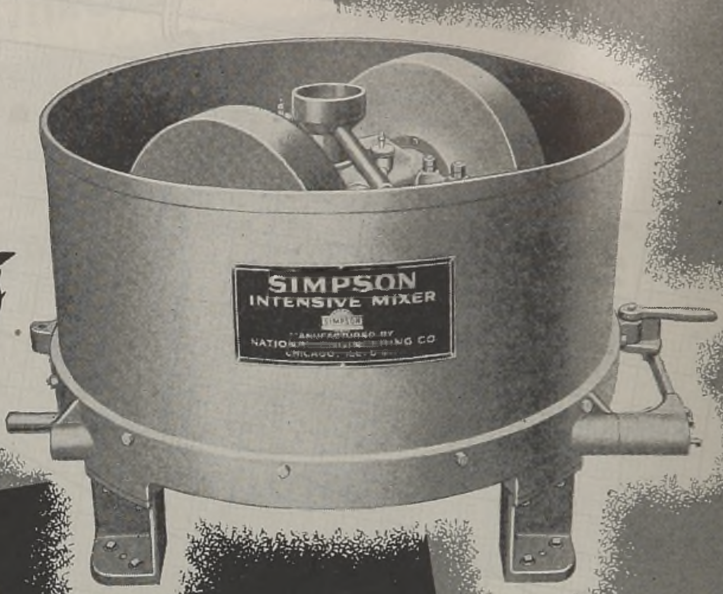
PETROLEUM CHEMICAL POWER NATURAL GAS COOLING TOWER
J. F. Pritchard & Co.
DATA BOOK
Specialized Equipment



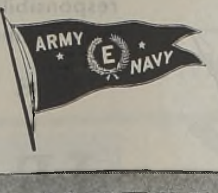
better mixing produces Better Products



better mixing results from Mulling in a Simpson

IF MIXING is important in the production of a product, it stands to reason that the more thorough the mixing, the finer the product. That's why pharmaceuticals, plastics, powders, graphite, ceramics and many other dry, semi-dry and plastic materials are mixed in Simpson Mixers.

The Simpson method of mixing by "mulling" not only mixes more thoroughly than ordinary methods, but it mixes faster, and at less expense. Simpson Mixers are available for both small and large batch mixing. Write for full information. If you'd like, a National Engineer will call and give you complete information about mulling your products in a Simpson.



And now—a second white star has been added to our Army-Navy Production Award Flag—for continued production achievement.

SIMPSON INTENSIVE MIXERS

NATIONAL ENGINEERING COMPANY

MACHINERY HALL BUILDING • CHICAGO, ILLINOIS

Manufacturers and Selling Agents for Continental European Countries:—The George Fischer Steel & Iron Works, Schaffhausen, Switzerland. For the British Possessions, Excluding Canada and Australia—August's Limited, Halifax, England. For Canada—Dominion Engineering Co., Ltd., Montreal, Canada. For Australia and New Zealand—Gibson, Battle & Co., Pty., Ltd. Sydney, Australia

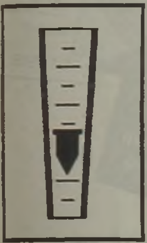
ROTAMETERS

A quiet advertisement for a noise-weary World —the Rotameter and its advantages to you for flow rate measurement and control

With all the noise in the World today, perhaps you will appreciate advertisements of a more quiet sort. So we are taking this simple way of telling you about our product.

We make rotameters for flow rate measurement and control, and we believe it is important that you know about them because they offer advantages which you cannot obtain in any other flow rate measuring device. First, let us describe the principle of the rotameter.

The Principle of the Rotameter



The rotameter is an "area-type" meter in which the variation in area is obtained by means of a vertical *tapered* tube with the smallest diameter at the bottom. A weight of fixed diameter (called the "float") moves freely within this tapered tube and hence the area between the float and tube *increases* as the float rises. This area then becomes a measure of the flow and for every flow rate there is a fixed position of the float in the tube. Therefore, the rotameter can be accurately calibrated to read directly in flow rate. This method of flow measurement gives advantages of great importance.

The Advantages of the Rotameter

Succinctly stated, the main advantages of our rotameter are as follows:

(1) Since the metering tube is usually transparent, the main metering elements (float and tube) and the fluid being metered are *clearly visible.* High accuracy may be maintained because dirt accumulations are immediately perceived and because a secondary remote reading instrument, when used, may be quickly checked against the primary metering element, the rotameter.

(2) A wide flow range may be obtained in one rotameter. A ratio of 20 to 1 from maximum to minimum flow is easily reached if necessary.

(3) Since area variation is measured (rather than head), the calibration curve of the rotameter is practically a straight line so that a direct reading scale with evenly spaced divisions is obtained. There is no compression of the divisions at low flows, so the same high metering accuracy is gained *throughout the flow range.*

(4) Because the area between the float and tube increases when the flow rises, the pressure drop across the float is low and *constant.* Pumping costs are reduced and low initial head may be tolerated by using an oversize meter with a light float.

(5) Our patented Stabl-Vis rotameter compensates for normal variations in viscosity and density so that viscous oils and chemicals, such as concentrated sulphuric acid, may be measured accurately in spite of wide temperature changes.

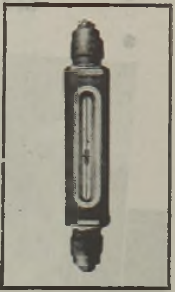
(6) The metering float travels a distance of at least 5 inches, and meters are obtainable with float travel as long as 24 inches. Hence, by shortening the flow range and lengthening the float travel, higher accuracies may be obtained with the rotameter than with any other flow rate measuring device.

(7) The float moves freely in the metering tube so there is no friction or hysteresis. Therefore, the rotameter reaches the Instrument Engineer's ideal goal of high accuracy, *consistently maintained* during years of service.

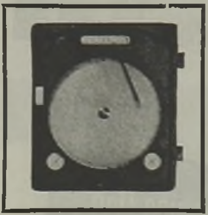
(8) Due to its simplicity, the rotameter is readily made corrosion proof and, therefore, may be used to measure flows of gases, liquids and slurries that no other meter will handle with continuous success.

(9) Also, due to its simplicity, the rotameter is easy to install and reasonable to maintain.

The Scope of Fischer & Porter Rotameters



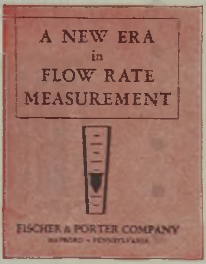
We originated the precision-bore tapered rotameter tube of boro-silicate glass, and have designed and built a full line of rotameters to solve the varied flow rate problems of Industry. We can measure liquid flows from 0.15 cubic centimeters per minute up to 14,000 gallons per minute, and gaseous flows from 3 cubic centimeters per minute up to 16,000 cubic feet per minute. Temperatures to 750° F. and pressures to 10,000 p.s.i. can be provided for in our equipment. Flow indication, flow recording, flow totalization and automatic flow control are all available to you in designs which have been proved by many field installations to be practical, accurate and dividend-paying meters.



A steady stream of basic improvements in the rotameter have come from our research laboratories. A most recent worthwhile development has been a marked betterment in the electrical inductance-bridge method of telemetering the position of the rotameter float to a remote recording or controlling instrument. This method in the past has been somewhat discredited by Instrument Engineers because it was subject to errors from temperature and voltage variations, and because it lacked power. Because of the great simplicity of the inductance-bridge principle, we decided not to accept this dictum, so we went to work to overcome its weaknesses. Today we can guarantee that our new circuit is not affected by wide variations in either temperature or voltage, and furthermore it has *three times* the power of any previous comparable instrument, so that the pen now positions with speed, positiveness and accuracy.

One of our most important new product announcements has been a Ratio Controller for controlling one or more flows at a fixed proportion of a main, varying flow. This controller is rapidly becoming a real factor in enabling many industries to carry on continuous reactions or percentage blendings with speed and accuracy.

How to obtain "A New Era in Flow Rate Measurement"



A NEW ERA in FLOW RATE MEASUREMENT

FISCHER & PORTER COMPANY

HATBORO • PENNSYLVANIA

We have prepared an interesting bulletin entitled, "A New Era in Flow Rate Measurement," which expands the above material into a profusely illustrated, semi-humorous and instructive manual for those who have flow rate control problems and who would, therefore, like to know more about our rotameters. If you will write to us, we will gladly send you a free copy without any obligation. If, in the same letter, you can outline one of your most important flow rate problems, we'll tackle it gladly and try to come up with a good answer for you.

FISCHER & PORTER COMPANY

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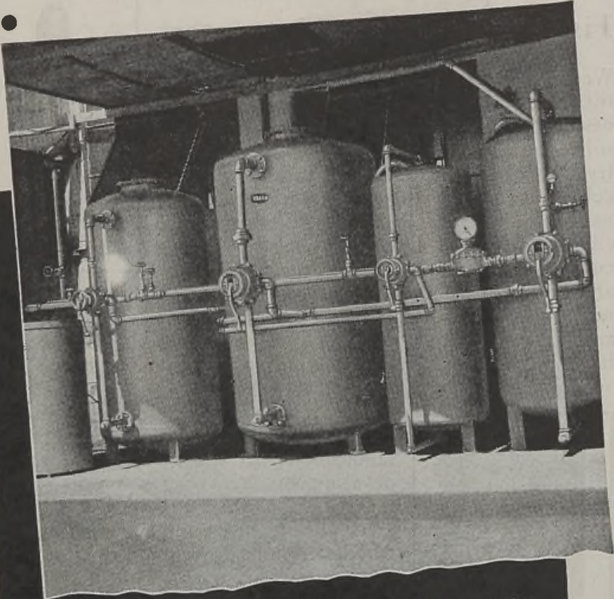
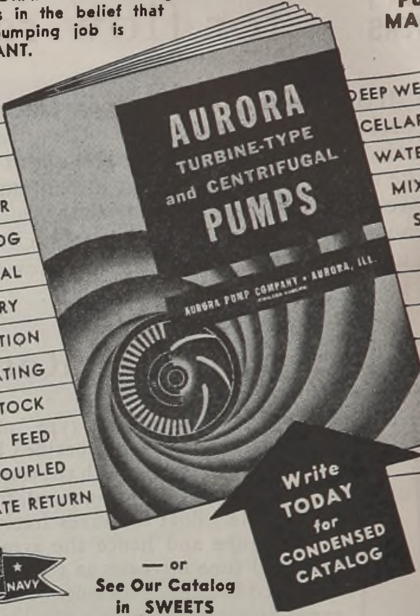
Fischer & Porter Company has pioneered EVERY basic rotameter improvement!

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EXPERIENCES AND EXPERIMENTS WITH STRONTIUM SALTS

Except for the chromate, which is subject to priority, strontium salts are now available in quantity. Many are the uses, practical and experimental, to which they have been put as our scoreboard quickly shows:

	Carbonate	Chloride	Chromate	Fluoride	Hydroxide	Oxalate	Stearate	Sulphate	Tartrate
Air Conditioning		X							
Ceramics	X			X	X			X	
Depilatory	X				X				
Driers					E		E		
Heat Treating	X	X			X				
Inhibitor (Corrosion)			X						
Inorganic Salts	X	E			X				
Lubricants					X		X		
Luminescent Pigments	X				X				
Oil Additives					X		X		
Organic Salts	X	E			X				
Pyrotechnics	X					X			X
Soaps					X		X		
Wax					E		E		
Welding		X		X					

"E"—Experimental

Foote Strontium Salts now obtainable are these:

Strontium Carbonate, tech. grade—min. 92.5% $SrCO_3$

Strontium Carbonate, pure grade—min. 98.0% $SrCO_3$

Strontium Chloride, anhydrous—min. 98.0% $SrCl_2$

Strontium Chloride, Hexahydrate—technical grade

Strontium Chromate*—typical SrO 49.7%

Strontium Fluoride, C.P.

Strontium Hydroxide, Octahydrate; technical grade

Strontium Oxalate, C.P.

Strontium (Di) Stearate

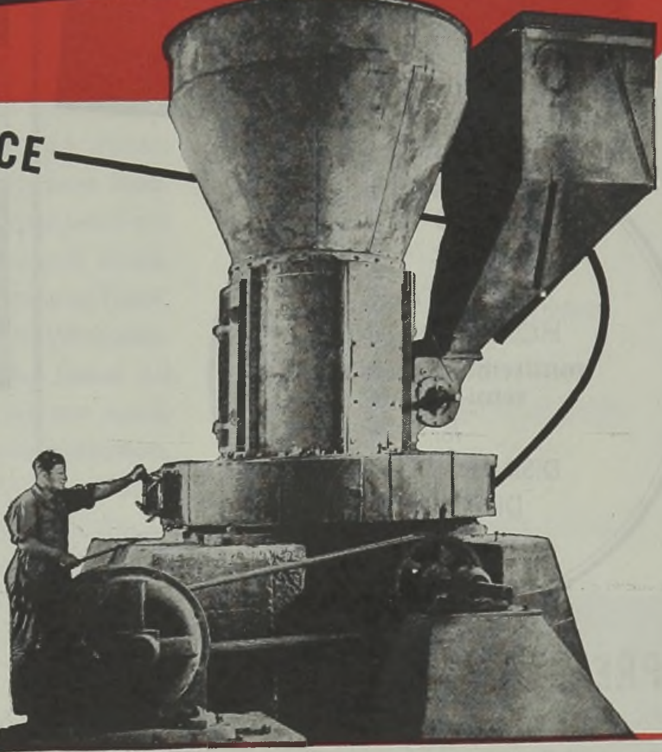
Strontium Sulphate (Natural Celestite) min. 92% $SrSO_4$

Strontium Tartrate, trihydrate, assay min. 81%

*Subject to priority restrictions.

For information and prices write, wire or telephone.

WHERE SIZE IS A SCIENCE



This is one of many types of mills used by Foote for producing from ores and minerals the grindings and granulations consumed by industry. The all-important control of particle size through grinding, and the processes related to grinding such as tabling, calcining, drying and magnetic separation are reduced to a science at Foote's three plants.

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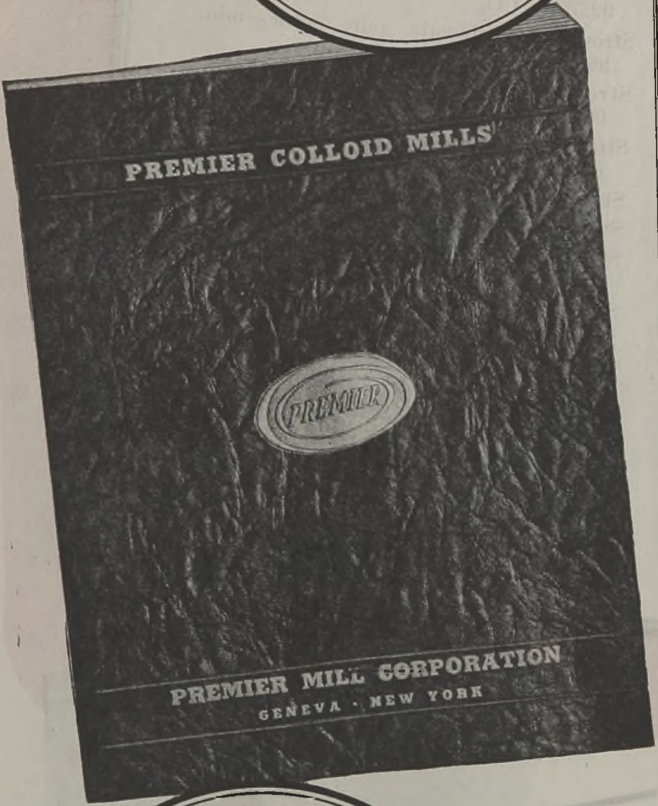
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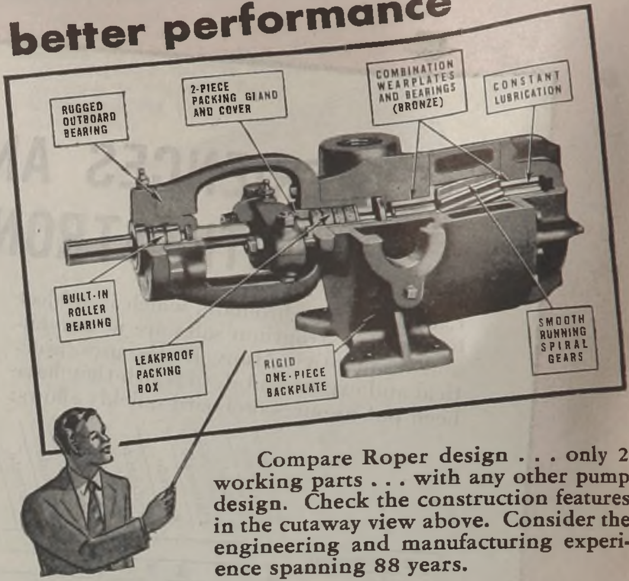
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RIGID ONE-PIECE BACKPLATE
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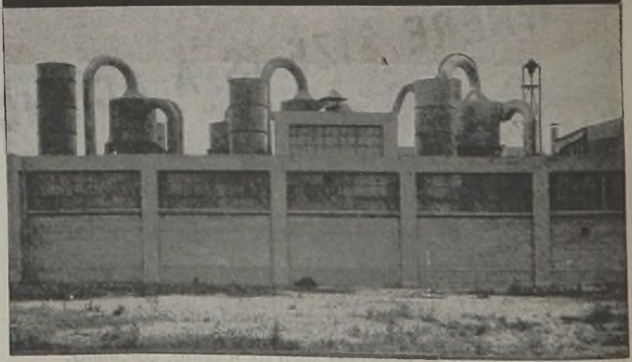

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Nash Compressors produce 75 lbs. pressure in a single stage, capacities to 6 million cubic feet a day in a single structure. No valves, gears, pistons, sliding vanes, or other enemies of long life complicate a Nash. Original capacity is maintained throughout a long life. Investigate the Nash Compressor now.

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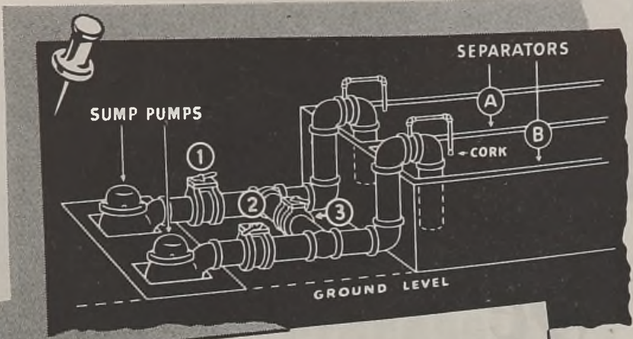

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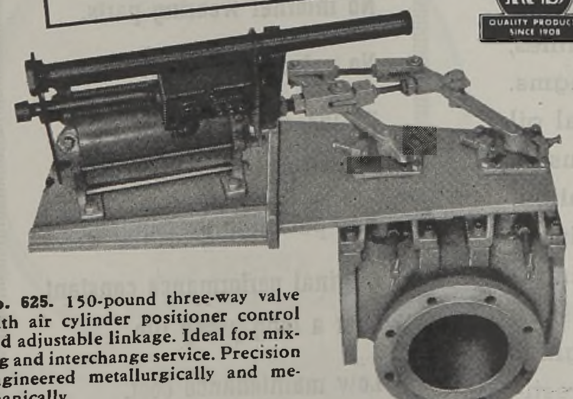

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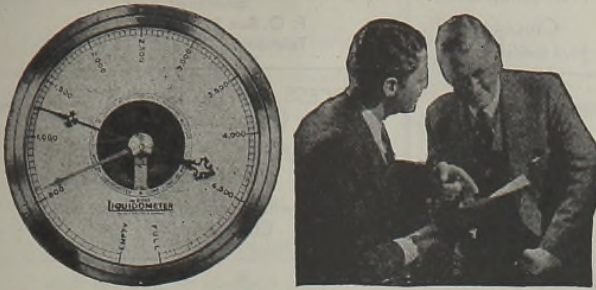
LIQUIDOMETER
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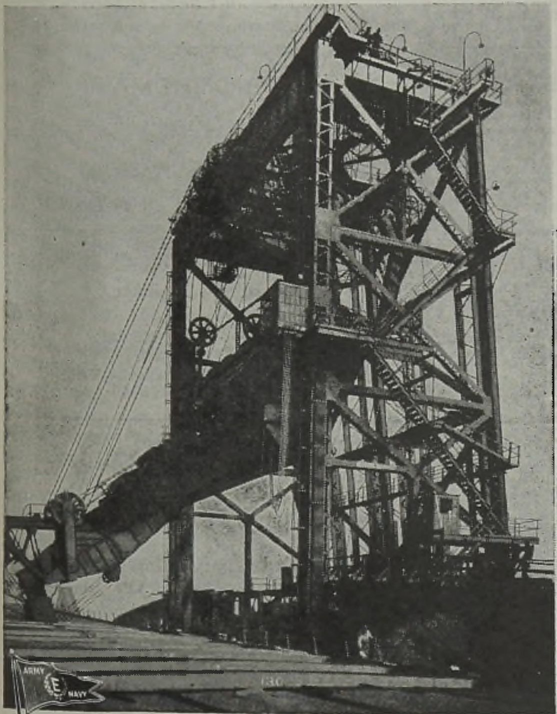
500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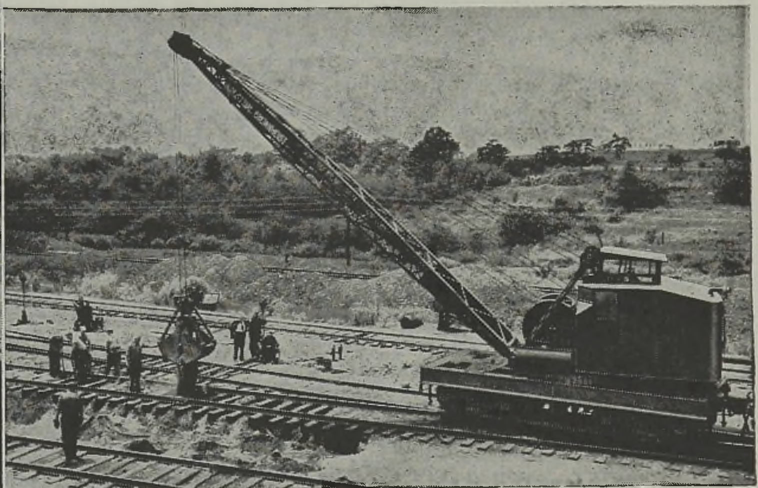

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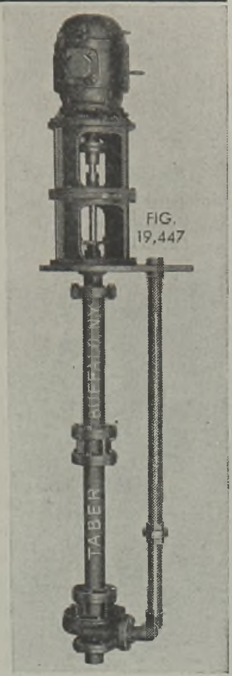
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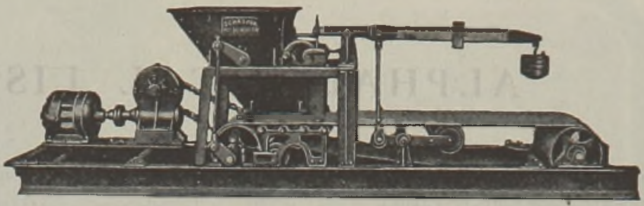
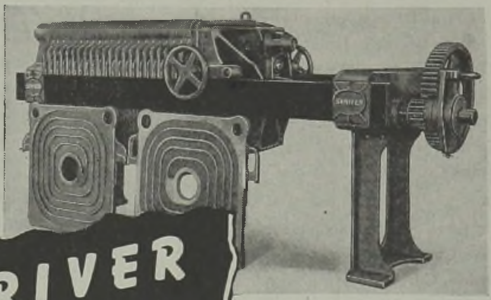
TABER

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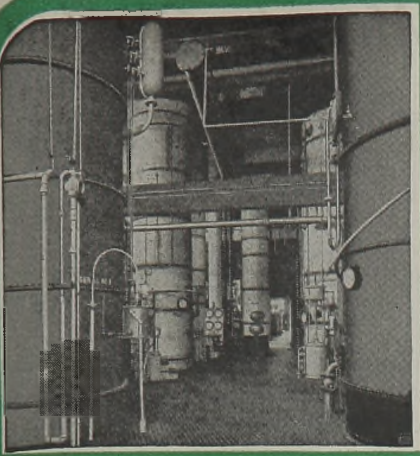

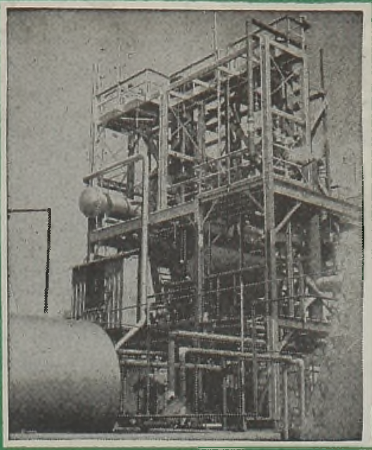

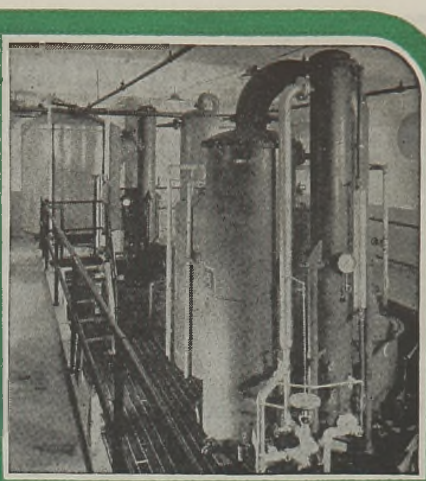

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Last-Minute Flashes

FROM THE EDITOR'S DESK

According to the Department of Commerce, the U.S.S.R. is now the second largest producer of petroleum products in the world, being superseded only by the United States. This is expected to have an important effect on postwar trade.

★ Estimates, based on the sound selling of airplanes to the public, expect that as many as 400,000 planes will be in the hands of civilians some ten years after the war.

★ Westinghouse Electric and Manufacturing Company will hereafter be known as Westinghouse Electric Corporation.

★ According to Washington rumors at the time of this writing, the supply situation in penicillin has improved to the point where it will be taken off allocation.

★ An oil refinery in Curaçao will be built by Royal Dutch Shell. It will cost about seven million dollars, and approximately two million dollars worth of the equipment will be purchased in the United States. None of it will be Lend-Lease, according to Petroleum Administration for War.

★ Paper is getting tighter and tighter, and allocations for the second quarter are down some 103,000 tons for paper manufacture. The cuts are necessary because of the smaller supply of wood, nitration pulp increases, and shortages of sulfite and sulfate pulp.

★ The Mexican buttonwood tree may be a source of tannin if plans for its utilization work out. A mixture of the bark and wood is said to contain about 12% by volume of tannin. However there are many difficulties to its utilization, and the whole plan seems to wait on suitable Yankee cash and ingenuity.

★ More lead is going to be made available to ceramic-ware makers for coating purposes.

★ Distillers may use a better grade of corn for making alcohol during the second quarter of this year.

★ Although the output of copper for the month of March reached a new high, producers are cutting closer than ever to required tonnage.

★ A new plant is being built at Lake Charles, La., by Cities Service Company. It will produce toluene, butadiene, and aviation gasoline, and completion is expected by 1946. Capacity for toluene is about 570,000 barrels a year, butadiene around 55,000 tons, and gasoline approximately 6,000,000 barrels.

★ Although the official estimates on conversion to civilian materials at war's end in Europe were once stated as 12% at the end of three months, 20% after six months, and possibly 35% in a year, new data on the subject indicate that these figures were unduly pessimistic. It is now rumored that for the same periods, the conversion will be 24, 35, and 50%, respectively. The apparent rapid decline of German resistance is said to be responsible for the changed estimate.

★ Antimony has become critical again, having been out of that status for some time. Reason is a new fireproofing process developed by the Army.

★ WPB states that production for the year after V-E day will amount to forty-eight billion dollars.

FOR PURITY OF PRODUCT AND LONG PLANT LIFE...

Lapp Chemical Porcelain

To the engineer who, discouraged with contamination of product (even what he may think "unavoidable") and with even occasional operation stoppages for maintenance, repair, cleaning, or replacement, Lapp Chemical Porcelain offers advantages that can't be overlooked. Pipe, valves and vessels of this material offer laboratory purity in industrial-scale installations, rugged mechanical strength and freedom even from gasket trouble (it uses only thin hard ones). Write for the information pertinent to your processes. *Lapp Insulator Co., Inc., Chemical Porcelain Division, LeRoy, N. Y.*

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Lapp porcelain has a hard, smooth surface. This is a glaze fired at high temperature (2300°F) to a body which is itself inherently dense, homogeneous and *non-porous.* Flow is unobstructed by unevennesses (or swollen gaskets). Cleaning is necessary less often, faster and easier when it is necessary.

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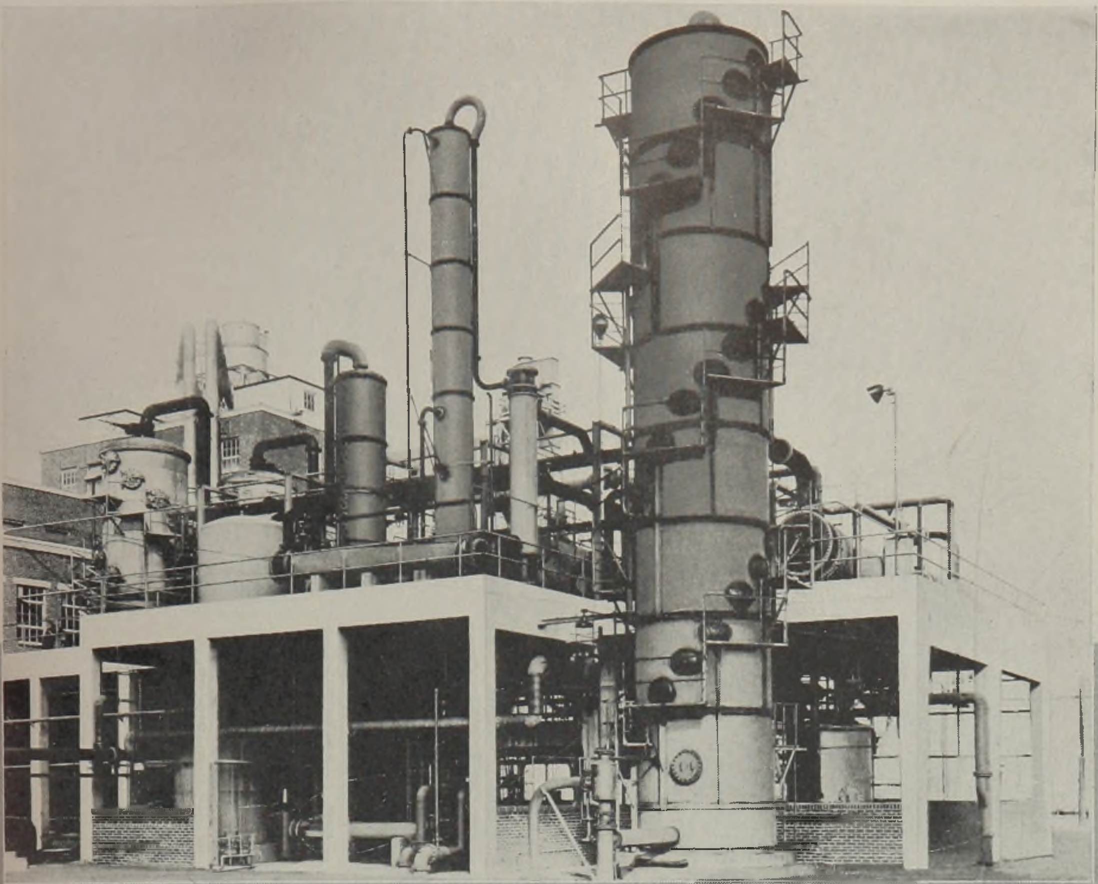

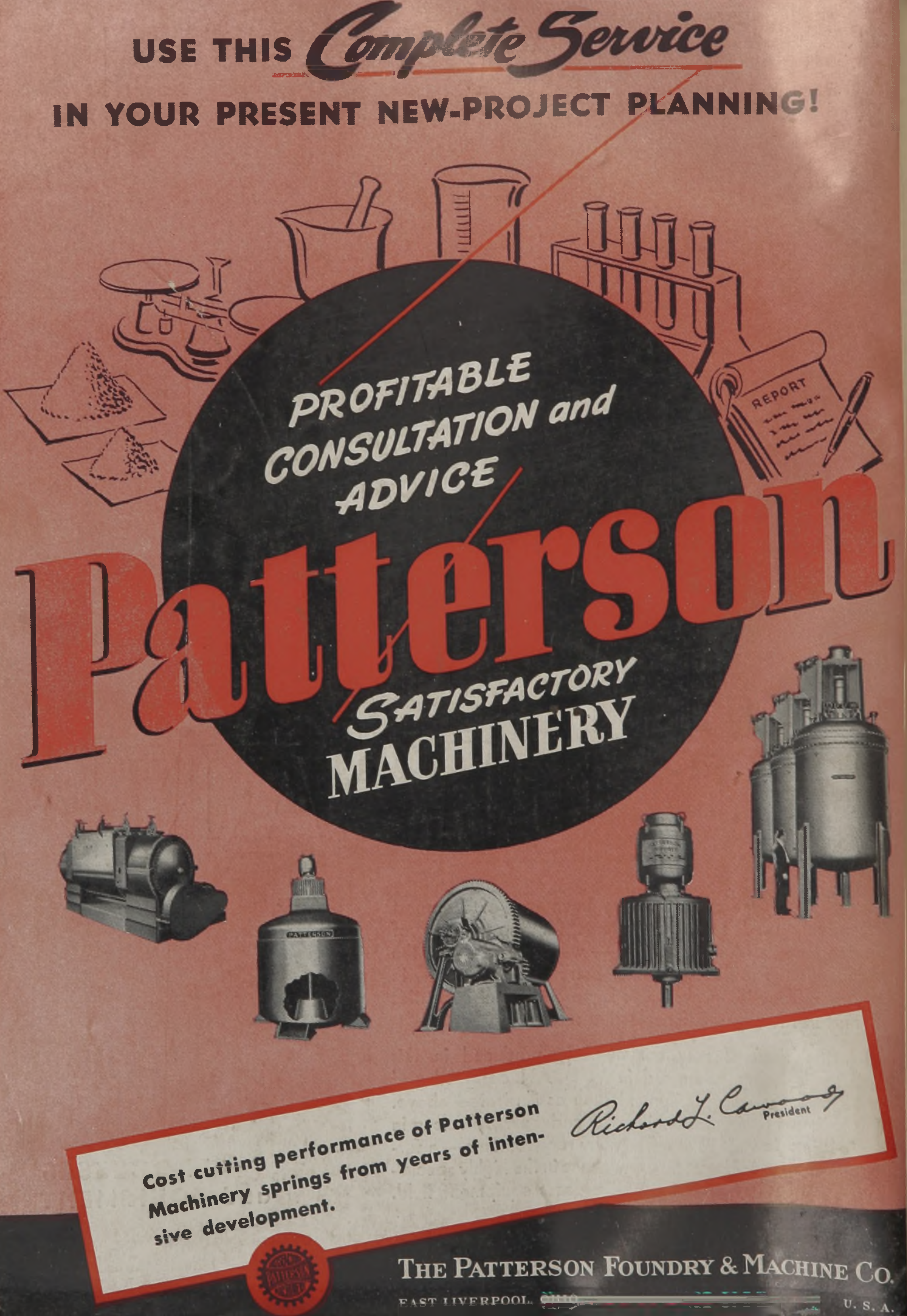

REPORT
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