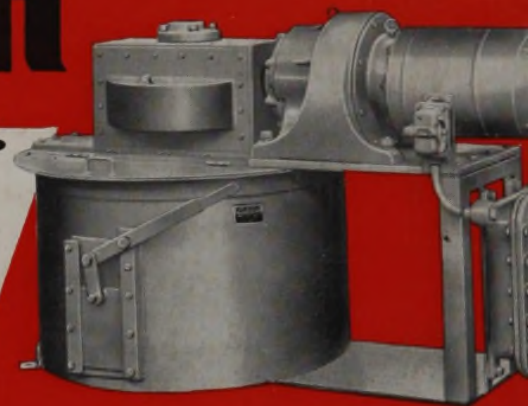


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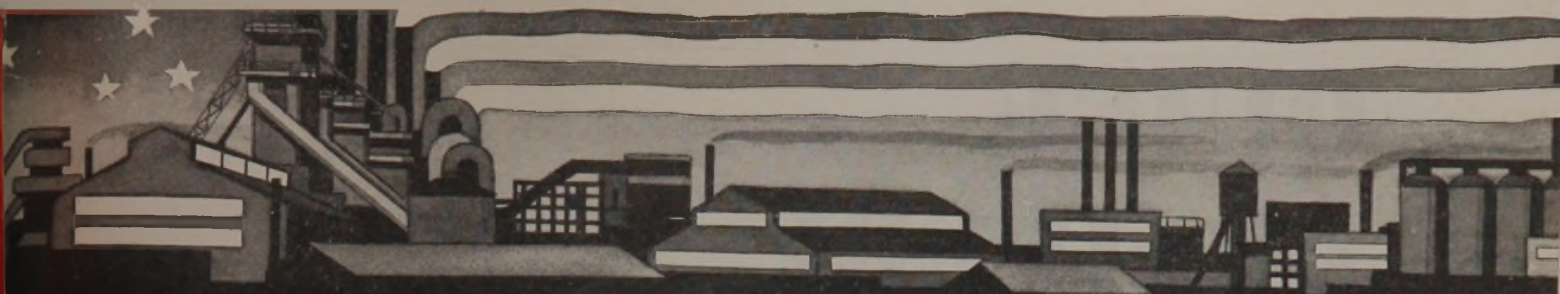
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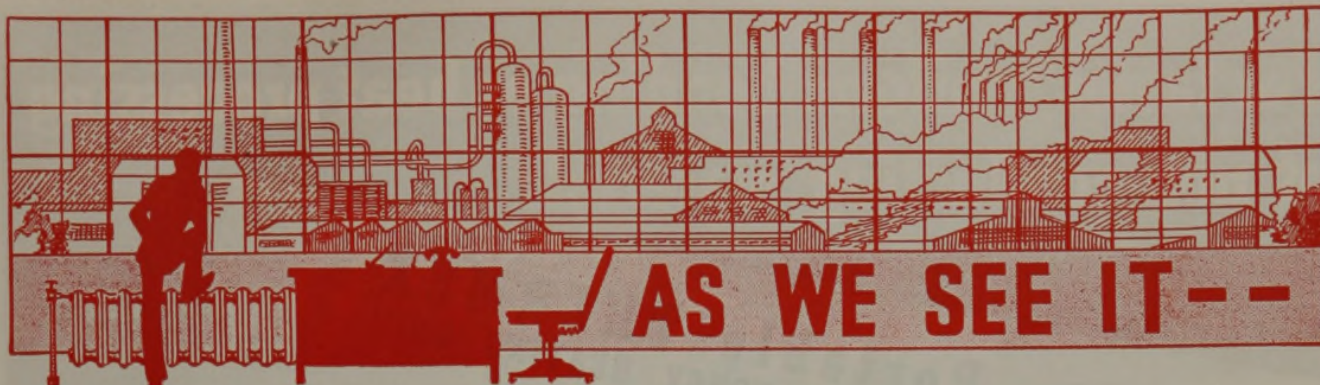
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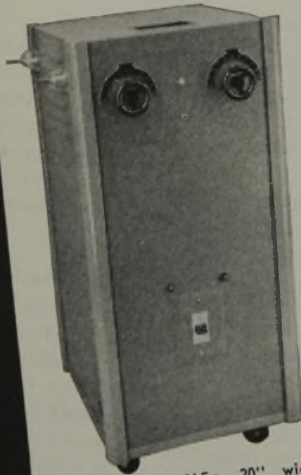
- ▶ **CONCENTRATING SULFURIC ACID** is an essential process particularly in war when large quantities of spent acid must be recovered. Kalous (page 387) describes an improved method for this purpose which uses superheated steam in direct contact with the acid. No acid mist is created to be a nuisance, and efficiency is reported to be high.
- ▶ **HEAT EXCHANGERS** for transferring heat between fluids and solids are widely used. Lovell and Karnofsky (page 391) give a method of solving the problem of design involved in continuous parallel or countercurrent flow of fluid and solid particles. Also treated is the case of stationary solid as in checkerwork or fixed-catalyst beds.
- ▶ **BATCH RECTIFICATION** of binary and complex mixtures is analyzed by Edgeworth-Johnstone (page 407), taking into account fractionation and column holdup and their effect on yields.
- ▶ **THERMODYNAMIC PROPERTIES OF LIQUIDS** are often valuable to know but difficult to determine. Watson (page 398) presents new methods for the general prediction of many properties on the basis of minimum data and the theorem of corresponding states. Applications are in rationalizing fragmentary data to meet requirements in process design problems.
- ▶ **LIQUID-LIQUID EQUILIBRIA** are essential points in solvent extraction processes, now of widening usefulness in industrial operations. Briggs and Comings (page 411) have investigated the effects of temperature on equilibrium in two systems: Benzene-acetone-water and docosane-1,6-diphenylhexane-furfural. The latter is of the type met in solvent refining of lubricating oils.
- ▶ **DESIGN CALCULATIONS** for plate columns are simplified by the methods used by Baker and Lindsay (page 418) in solving the problems met in a number of industrially important situations.
- ▶ **BRITTLE TEMPERATURES** of rubber and other elastomers have been found by Kemp, Malm, and Winspear (page 488) to vary considerably, depending on the method of determination employed. Differences in bending stress cause significant changes in brittle temperature, and the magnitude of these changes depends on the nature of the sample.
- ▶ **POLYBUTENE ADDITIONS** to asphalt paints impart improved properties to the product, according to Evans, Young, and Holmes (page 481). Results presented cover both changes in the paint itself caused by additions of polybutenes of various molecular weights and weathering tests of the products.
- ▶ **VINYLDENE CHLORIDE POLYMERS**, known as Saran, have lately attracted wide attention because of their combination of chemical inertness, strength, and toughness. Reinhardt (page 422) describes these useful products in some detail with due attention to their compositions and methods of fabrication. The appended bibliography of fifty-nine items refers principally to patents.
- ▶ **ELECTRON MICROSCOPY** is a valuable method of solving many chemical properties, according to Zworykin (page 450), who describes latest developments and techniques in the field.
- ▶ **CELLULOSE FIBERS** owe their ability to form strong sheets of paper to the presence of free hydroxyl groups in their molecules, according to Bletzinger (page 474), who has shown that strength and coherence of sheet are reduced as hydroxyl groups are progressively removed by acetylation. Removal of acetyl groups is found to restore felting properties. Beating of acetylated fibers in acetone produces sheets of a strength comparable to those from cellulose beaten in water.
- ▶ **ANTIFOULING PAINTS** for marine use are commonly believed to owe their effectiveness to many factors. Young, Gerhardt, and Schneider (page 432), questioning some of these beliefs, have devised a method of testing designed to reveal the truth and have applied it under practical conditions. Preliminary results reported provide useful starting points for further work. A second paper by Young and Schneider (page 436) continues the investigation with a study of heavy metals. Copper in metallic powder form is shown to be most effective.
- ▶ **PHYSICAL PROPERTIES** of paraffin hydrocarbons are correlated with chemical structure by Francis (page 442) by a method generally applicable to all isomers. Values are given for isomers of nine to eleven carbon atoms.
- ▶ **STRESS-STRAIN PROPERTIES** of fourteen typical plasticized vinyl elastomers have been determined by Reed (page 429) at several temperatures, and the resulting curves are compared with those of rubber.
- ▶ **DENSITIES** of isopropyl alcohol-water mixtures have been determined by Langdon and Keyes (page 459) by an improved pycnometric technique with great accuracy. Results given cover the complete range of compositions at 35° C. Data thus determined are used in a following paper by the same authors (page 464) in an analysis of design factors of plate fractionating columns.
- ▶ **SYNTHETIC CITRUS POWDERS**, especially important as part of military rations, undergo changes on storage at high temperatures encountered in many parts of the world. Isaac (page 470) shows that caramelization of sugars present (browning) is minimized if escape of water vapor is prevented.
- ▶ **DEXTRINS** derived from corn sirups of different degrees of hydrolysis are examined by Evans and Fetzer (page 439) to clear up some of the confusion existing about them.
- ▶ **INTERCONVERSIONS** of weight, volume, and mole fractions in multicomponent systems by graphical methods are described by Leslie (page 495) and by Sun and Silverman (page 497).

*D. Hilleffer*

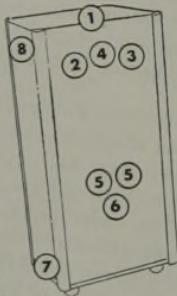
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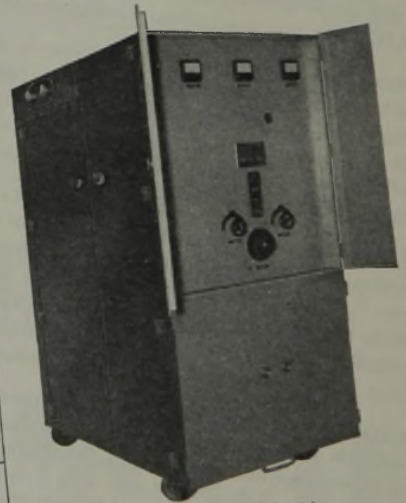
## Portable THERMEX HIGH FREQUENCY HEATING UNIT

### No. 15

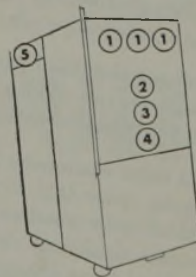
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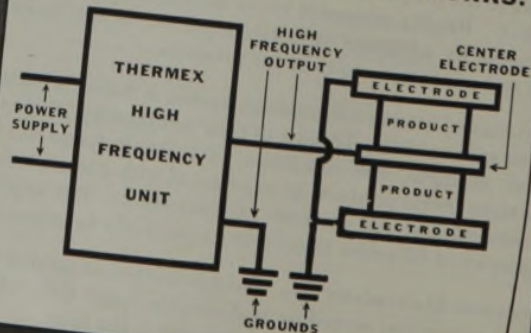


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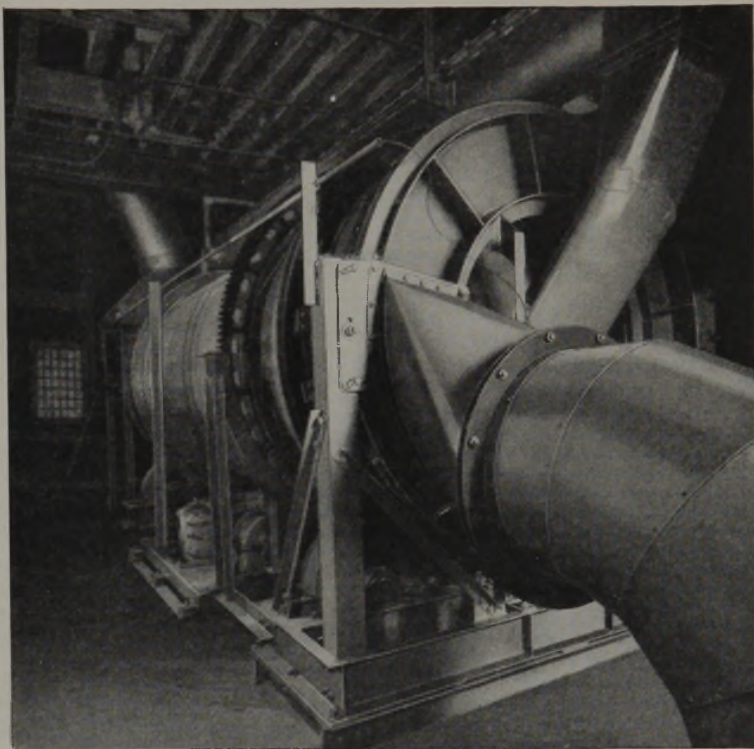
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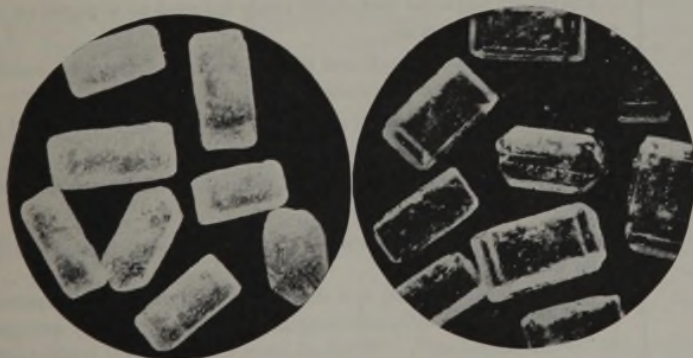
● Cleaner, clearer, more lustrous crystals (a more attractive product for consumer and commercial use)—less fines—less loss. Briefly these are the principal benefits obtained by Franklin Sugar Refining Co. when they adopted the Roto-Louvre method of drying their product. The single unit illustrated replaced two conventional type dryers formerly used, and in addition to occupying considerably less floor space, this Roto-Louvre Dryer has greater capacity.

Engineers who know how to solve drying and dehydrating problems such as yours, have prepared a special book on Roto-Louvre drying. It shows how this method has been successfully applied to a wide variety of drying needs. Ask for Book No. 1911.



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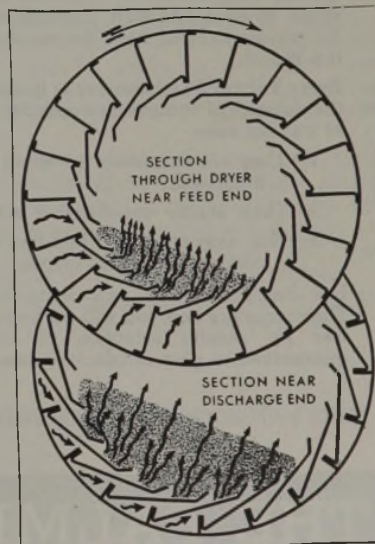


Magnified selected sugar crystals. Dull, dust-coated crystals at left are from conventional dryer; clear crystals at right from Roto-Louvre Dryer.

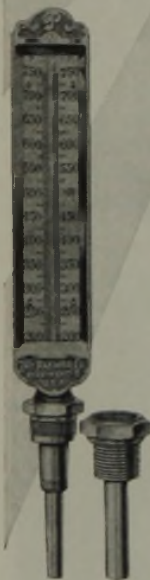
#### A FEW FACTS ON DRYING SUGAR

At Dryer Inlet: Sugar, 1.5% moisture, temperature 120° F. Inlet air, 245° F.  
At Dryer Outlet: Sugar, only 3/100% moisture content, temperature 130° F.  
Outlet Air, 135° F. Discharge Capacity: 36,000 lbs. dried sugar per hour.  
Moisture evaporated by dryer, 545 lbs. Handling capacity increases with decrease of inlet moisture content; and r.p.m. of dryer shell (1 to 6 r.p.m.) is regulated accordingly. On coarse special sugars, the capacity of the unit is greater because of their lower initial moisture content.

This size Roto-Louvre Dryer unit has a shell measuring 6-ft. diameter by 18-ft. long, and is rotated at one to six revolutions per minute from an electric motor. The r.p.m. of the shell can be varied as little or as much as desired, to suit the degree of moisture in the incoming sugar. This dryer combines the advantages of heat exchange by convection, hot inlet air permeating upward through the mass, controlled temperature rise for the material being dried, and the least degradation in the product. Made in eight shell diameters and in various lengths with evaporating capacities from just a few pounds to 12,000 lbs. per hour.



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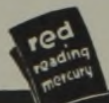
As each ray of light breaks through the dark clouds, after the storm, to fill the earth with sunshine, so each PALMER Thermometer is doing its bit bravely to bring back the sunshine of Peace to the World.

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**R**ATES of reactions, the leading topic planned for May, are necessarily controlling in all chemical production. Now with operating schedules under excessive pressure, the importance of any consideration that might be helpful in increasing output is multiplied many fold. The easy expedient of adding new units to plants can seldom provide the required increment. Hence possibilities of achieving results otherwise must be explored with meticulous care.

That is the purpose and the value of several papers on industrial reaction rates in our May issue. Many types of reactions will be discussed and most useful material presented, particularly on methods of determining and influencing rates. In addition to considerations of basic physical factors involved in rates, particular discussions center about isomerization, gaseous, catalytic, liquid-gas, solid-gas, and gas-solid reactions. While much of the material presented is of general application, such specific problems as ammonia synthesis, base-exchange softening of water, and hydrogenation are covered.

That provides a substantial beginning to an otherwise significant collection of papers.

Propane, said to be the cheapest material next to water in oil refineries, is a substance of considerable interest. Because of its ubiquity in refineries, its thermodynamic properties are essential data in design of equipment. These data will appear in May.

The behavior of lubricating oils is always a fertile field for investigation. Copper, lead, and especially iron in engines have a catalytic effect on oils, and the catalytic susceptibility of different oils is found to vary greatly.

Strontium's special usefulness lends interest to a paper on its recovery from minerals.

Gelatinization of starch and the absorption of water by animal glues will each receive attention.

The cooking process as employed in pulping wood receives further attention, this time with reference to aspen.

Effects of extenders and pigment volume on the life of lusterless enamels will be discussed.

Riboflavin, we shall learn, is adsorbed on lactose crystallized from whey.

Appropriate to spring is a discussion of that group of potent substances significantly affecting plant growth roughly grouped as "plant hormones". We shall learn much of their applications and effects, and some of the myths current about them will be critically examined and exploded.

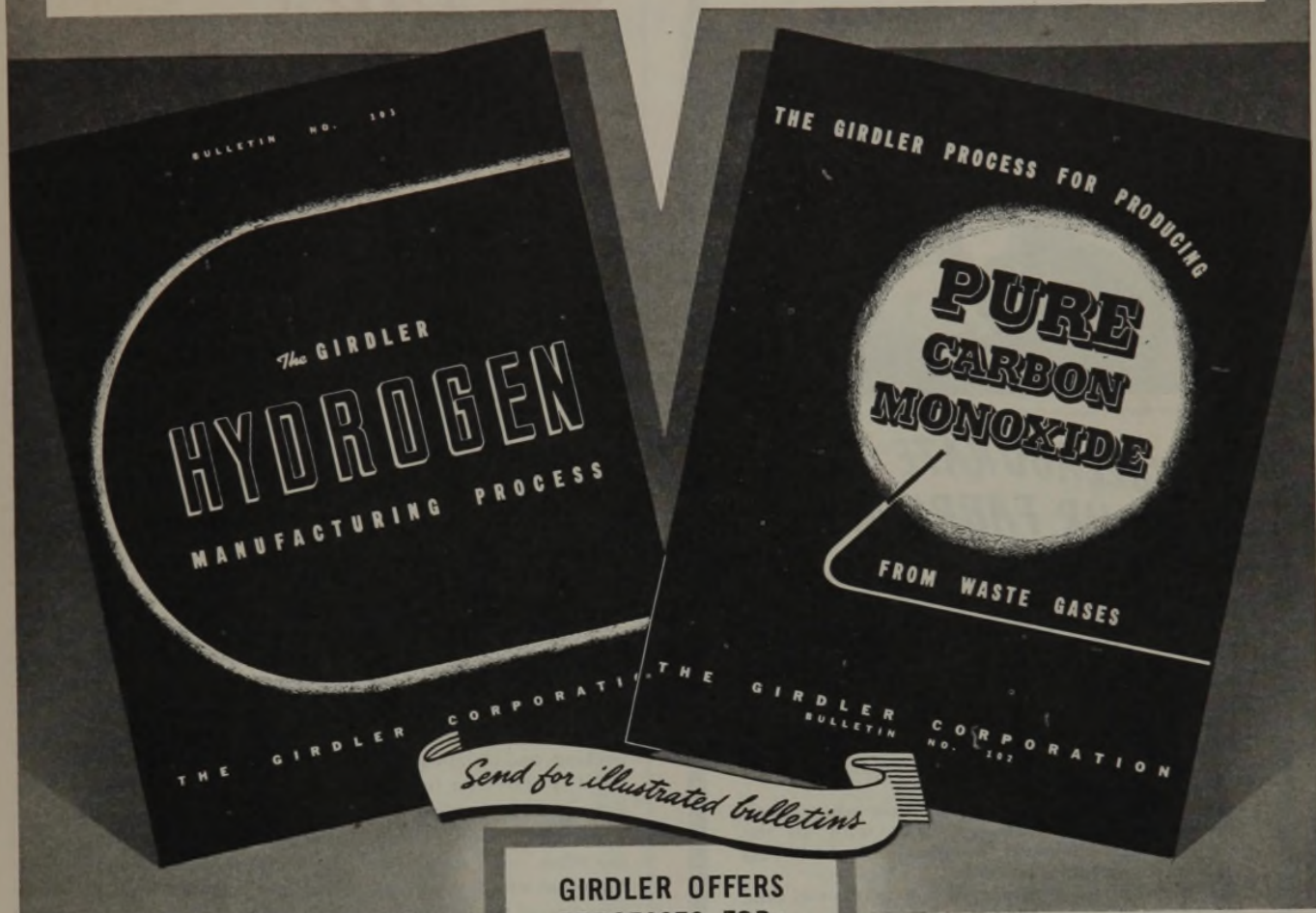
And with the humid season approaching, psychrometric measurements become more interesting.

That, of course, is by no means all, but it suggests reasons why we should not let spring fever prevent our looking carefully into the May issue.

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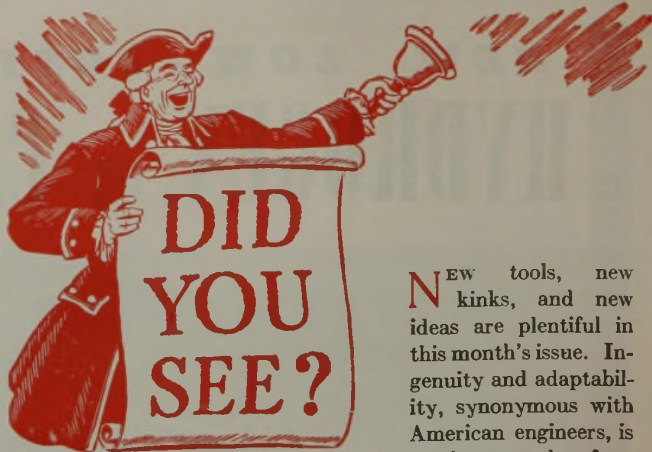


"What to Look for When You Specify Stainless Steel for Your Processing Equipment" — a valuable guide for engineers — sent on request to those who write us on their company stationery.

**S. BLICKMAN, INC.**

1210 GREGORY AVE., WEEHAWKEN, N.J.

TANKS • KETTLES • CONDENSERS • AGITATORS  
 EVAPORATORS • PANS • VATS • CYLINDERS



NEW tools, new kinks, and new ideas are plentiful in this month's issue. Ingenuity and adaptability, synonymous with American engineers, is coming to the fore, much of it stemming

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ISO-FLOW is a trade mark for a new tubular furnace which is designed for heating fluids up to 1600° F. Its place will be in vapor superheating, chemical reactions, concentration, and various other "ops" in our line. However, there is something more than that which causes us to break into print about it. The construction of the unit is such as to require much less of our critical materials. It requires half the steel and alloys, 35 per cent less headers, half the ground space, and just about less of everything. They ought to call it the "sans" job—sans this, sans that.

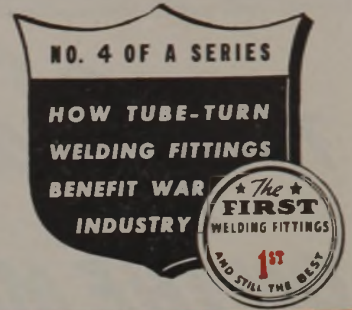
For makers of hydrogen and carbon monoxide, the Girdler Corp. springs out two new processes. Both will do a better job at less cost—for hydrogen, in capacities of 1000 to 1,000,000 cubic feet per hour, and for carbon dioxide, 1000 to 500,000 cubic feet per hour. The carbon dioxide process works on waste gases. For those, like me, who want to know more, Bulletins 102 and 103 from Louisville, Ky., will answer their raised eyebrows.

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CAP. L. LEARY

# Welding piping with Tube-Turn fittings conserves 4 vital materials . . . checks war-time pipe failures, stops leaks!



## 1. NUTS AND BOLTS



Joints welded with Tube-Turn fittings require no nuts or bolts. Maintenance time and trouble spent in tightening bolts is eliminated.

## 2. FLANGES



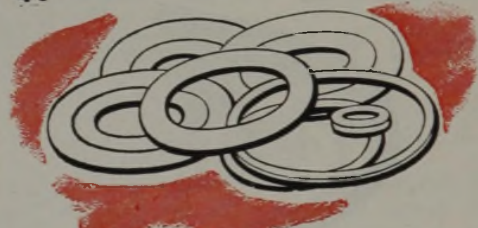
Welding fittings supplant the need for many of the flanged joints necessary in screwed piping—save both weight and critical metal.

## 3. PIPE REPLACEMENT



When welding fittings are used, you never have to replace any pipe because of worn threads or damage due to replacing flanged fittings.

## 4. GASKET MATERIAL



Fewer flanged joints mean fewer gaskets to replace. No materials or time wasted when connections are welded with Tube-Turn fittings.



When you multiply these savings over an entire piping system, the amount of critical materials conserved is tremendous. Tube-Turn welding fittings aid the war effort in *other* ways, too—less danger of plant shut-downs due to piping failures; maintenance is virtually eliminated; less installation time is needed because alignment is easier, only simple butt welds are required, and complete sections may be pre-assembled then welded into position. For *stronger, lighter, permanently leakproof* piping systems—weld with Tube-Turn fittings!

TUBE-TURNS (INC.) LOUISVILLE, KY. Branch offices: New York, Chicago, Philadelphia, Pittsburgh, Cleveland, Dayton, Washington, D. C., Tulsa, Houston, Los Angeles. Distributors in principal cities.

# TUBE - TURN

TRADE MARK

## Welding Fittings and Flanges



## 6 WAYS\*

### TO DO A BIGGER WAR JOB WITH STAINLESS STEEL EQUIPMENT



One of the engineering rooms at S. Blickman, Inc.

## #6 COLLABORATE WITH YOUR FABRICATOR...

To accomplish the miracles of production needed to win the war, the processing industries must take full advantage of the benefits of stainless steel equipment. For a properly fabricated steel processing vessel is a precious instrument of victory. High output, low maintenance and long service life can be built into your equipment if the conditions of operation are accurately known to your fabricator. Often, your fabricator may suggest improvements that will effect a higher yield throughout the life of the equipment.

For that reason, select a fabricator whose engineers have specialized experience with *all* the factors which safeguard the properties of stainless steel during its fabrication.

When you have chosen such a fabricator, take advantage of his engineers' "know-how". Cooperate with them in the planning of your equipment, *right at the drawing board.*

Our experience shows that pooling the knowledge and experience of Blickman engineers with that of our customer's engineers often results in more durable equipment, more quickly fabricated at lower cost. We invite your inquiries.

**All Orders Subject to  
Government Priority Regulations**

*\*Sixth of a series  
of advertisements  
written in the in-  
terest of greater  
war production.*

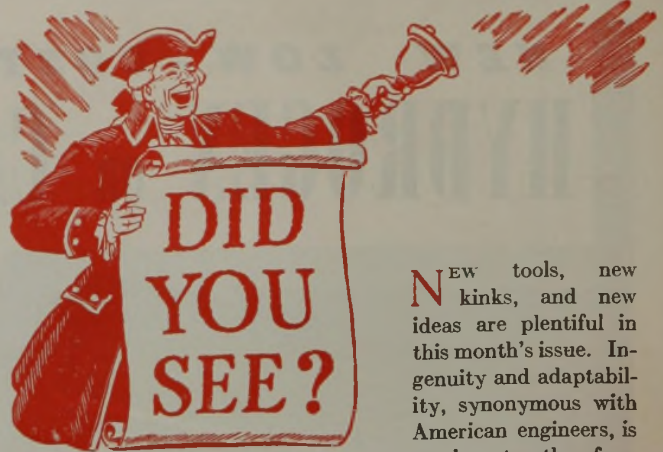


"What to Look for When You Specify Stainless Steel for Your Processing Equipment" — a valuable guide for engineers — sent on request to those who write us on their company stationery.

## S. BLICKMAN, INC.

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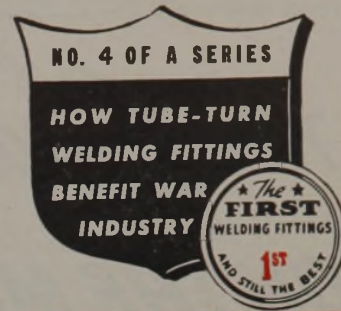
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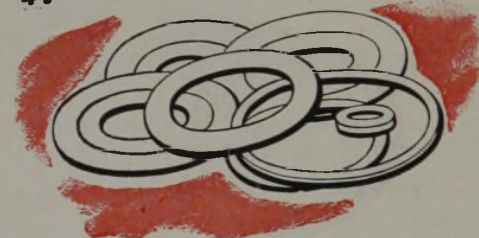
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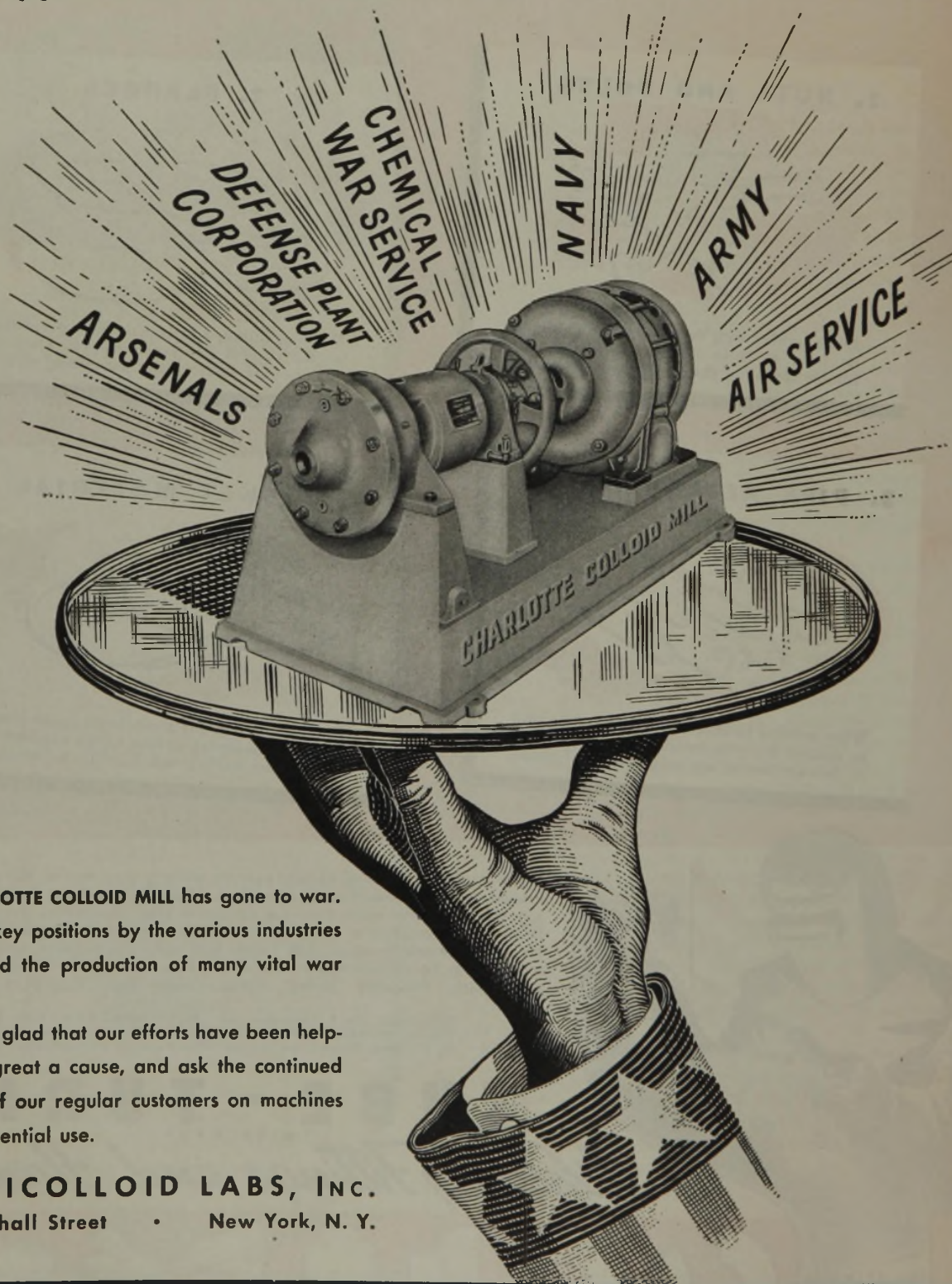
# TUBE-TURN

TRADE MARK

## Welding Fittings and Flanges



# *THE Charlotte IS DOING ITS PART ON THE MANY PRODUCTION FRONTS!*



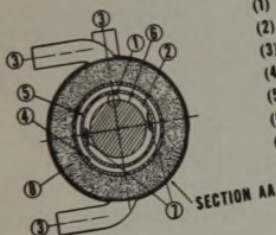
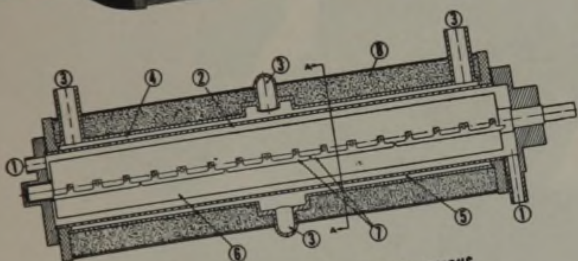
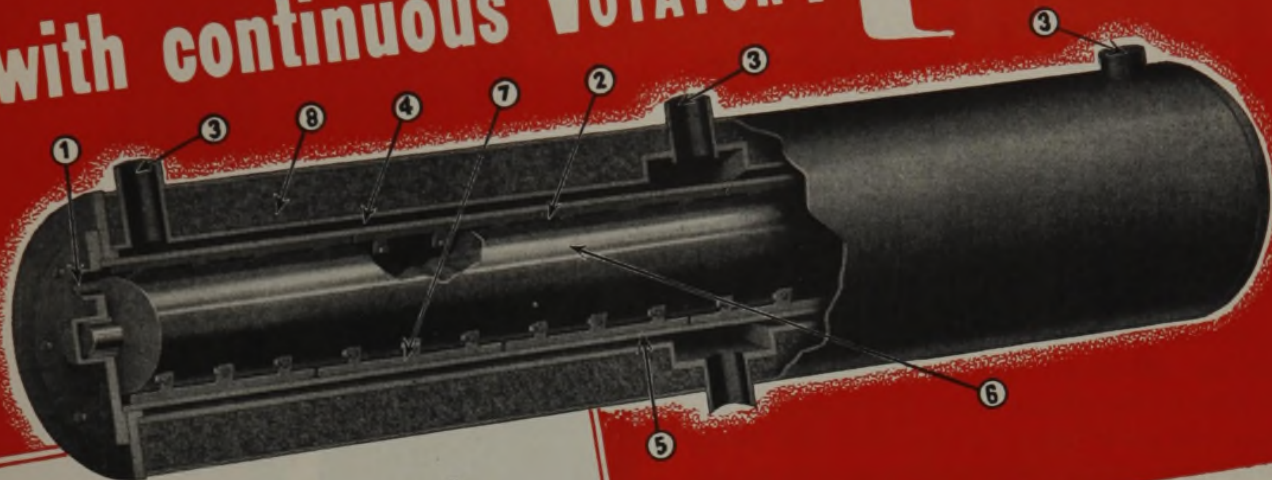
The CHARLOTTE COLLOID MILL has gone to war. Its use in key positions by the various industries has assured the production of many vital war materials.

We are glad that our efforts have been helpful to so great a cause, and ask the continued patience of our regular customers on machines for less essential use.

**CHEMICOLLOID LABS, INC.**  
44 Whitehall Street • New York, N. Y.

# Heat transfer in seconds with continuous VOTATOR!

**OIL PRODUCTS  
AVIATION GASOLINE  
CHEMICALS, RESINS**



- (1) PRODUCT CONNECTIONS
- (2) PRODUCT CHAMBER
- (3) HEAT TRANSFER MEDIUM CONNECTIONS
- (4) HEAT TRANSFER MEDIUM CHAMBER
- (5) HEAT TRANSFER TUBE
- (6) MUTATOR SHAFT
- (7) SCRAPER BLADES
- (8) INSULATION

## Cool or heat liquids or viscous materials faster and better—get simultaneous mixing or emulsifying!

If heating or cooling liquids or viscous materials is an operation in your plant, investigate the many advantages of Votator.

Votator is a fully enclosed heat transfer unit that does the job better and faster than any other known method. Look at the above cut-away view and cross-section diagrams of a Votator and you will readily see the efficiency and simplicity of the Votator.

Since only a thin film of product is passed over a relatively large heat transfer surface, heating or cooling is accomplished practically instantaneously. Accurate and uniform temperature control is maintained at all times. Even though only a small amount of product is treated at any time, tremendous production is achieved because the material passes through the Votator at a high rate of speed.

Votator will also mix, emulsify or aerate a product at the same time it is heated or cooled, if this is desired.

Write for helpful, illustrated booklet describing the many uses for the Votator.

### VOTATOR ADVANTAGES:

Saves critical materials. Reduces heating or refrigeration load. Heat transfer takes place in seconds. Continuous, rapid flow of product. Fully enclosed, sanitary unit. Uniform temperature accurately controlled. Simultaneous mixing, emulsifying or aerating. More economical than batch methods.

# The GIRDLER CORPORATION

*Votator Continuous, Instantaneous Heat Transfer Equipment*

VOTATOR DIVISION

LOUISVILLE, KENTUCKY

# What did he SEE in his crystals?

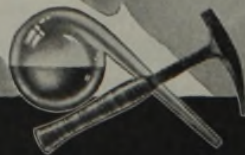
DR. A. E. FOOTE, who conceived this company in 1876, was born too soon to read the future in the crystals and minerals he loved. His idea was simply to supply collections of minerals to universities, museums and scientific groups for furthering the study of mineralogy and geology. He could not foresee . . . then . . . ships nosing into Philadelphia for Foote, bearing tungsten-tin ore from Bolivia, rutile from Brazil, manganese from Cuba, and rare or needed minerals from the four corners of the world. He could not predict Foote engineers circling the globe in search of new mineral deposits, or working side-by-side with scientists in industry to probe the possibilities of strontium, lithium, zirconium and scores of other metals and their compounds. He could not foretell with his "specimens" that Foote would help weld the ships for the African second front, or riddle Jap Zeros with tracer bullets, or help speed Jack Benny or the latest communiqué from Moscow over the nation's networks. Dr. Foote might well have wondered how the beautiful stones of his collections would benefit the refining, chemical, ceramic, metal, electronics and many another industry. But it is for you and for us now to wonder and ponder the next move. We are ready to help you with chemicals, ores, metals and alloys and with a valuable accumulation of experience and research. Write today.



## STRONTIUM, CHEMISTRY'S RIP VAN WINKLE

It seems almost unfathomable that strontium, one of earth's most abundant elements, has been allowed to sleep so long. Except for flares and fireworks strontium salts were little used—until recently. Now, by contrast, strontium is popping up conspicuously in many places. For example, there is the strontium salt bath for the heat treatment of steel, strontium for

reducing the iron and manganese contents of sodium hydroxide in caustic soda purification, and strontium for producing better enamels, glazes, and glasses in ceramics. Where will strontium next be used? We don't know but we'll gladly help you find out. Inquiries concerning strontium salts are invited. Possibly a new and important use may be developed for you.

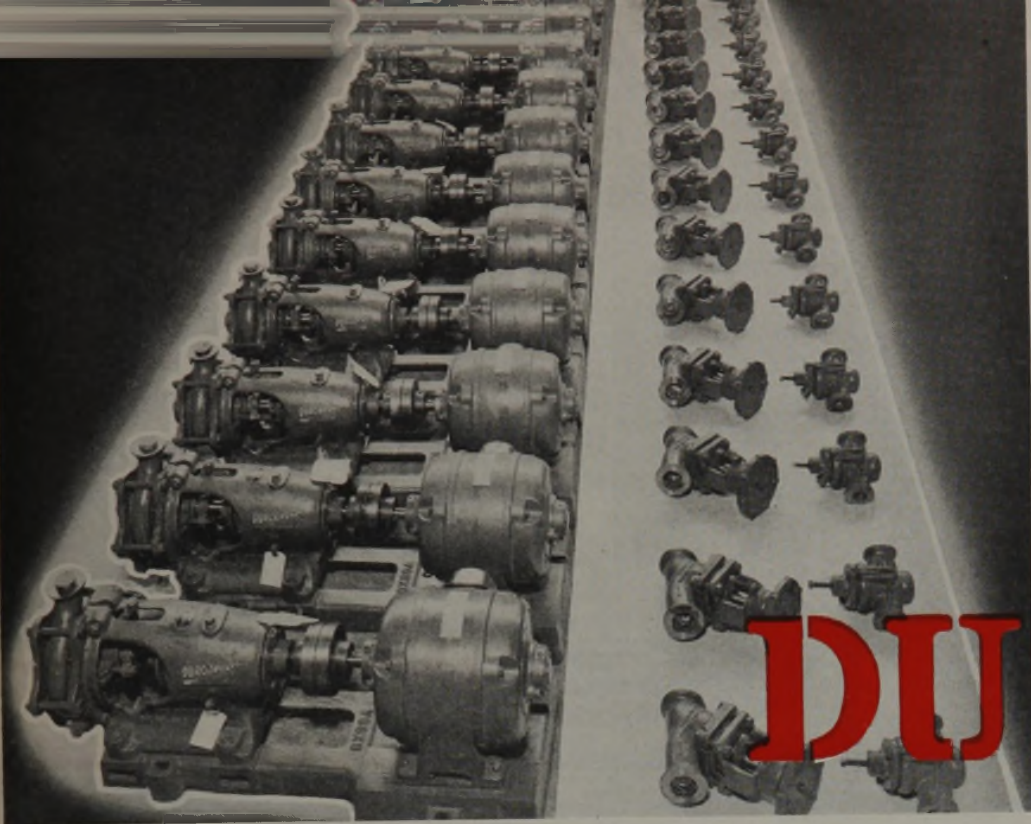


**Foote**  
MINERAL COMPANY

*A Step Ahead  
in Industrial Ores  
and Chemicals*

PHILADELPHIA • ASBESTOS • EXTON, PENNSYLVANIA  
Home Office: 1616 SUMMER STREET, PHILADELPHIA, PA.  
West Coast Representative: GRIFFIN CHEMICAL CO., San Francisco, California





# DURCO

One shipment of Durco pumps and Durco valves for handling corrosive solutions in a new synthetic rubber plant.

**VALVES  
PUMPS  
JETS  
PIPE**

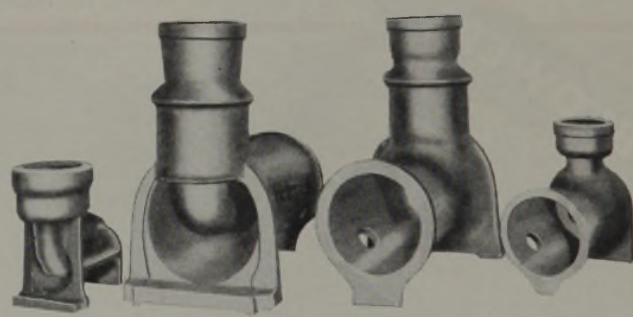
**FOR** *Synthetic Rubber*

In the Copolymer plants for making Buna S rubber from Butadiene and Styrene there will be

- Several Hundred Duriron Pumps
- Several Thousand Duriron Valves
- Several Hundred Duriron Jets
- Miles of Duriron Pipe

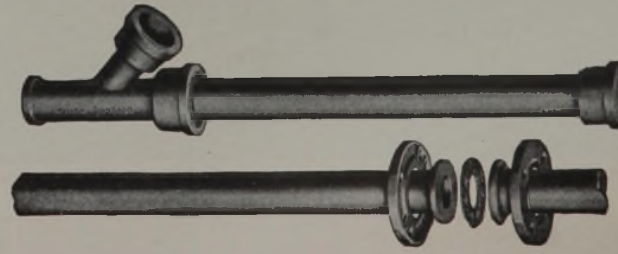
The complete story of just how and where this equipment is used cannot be told at this time. But Durco products are being used in practically every synthetic rubber process for handling corrosive liquors.

The selection of Durco equipment for these important plants is further evidence of its quality reputation. It should give you confidence to bring your corrosion problems to us.



(Above)  
Front and back views of Durco circulating steam jets for use in synthetic rubber plants.

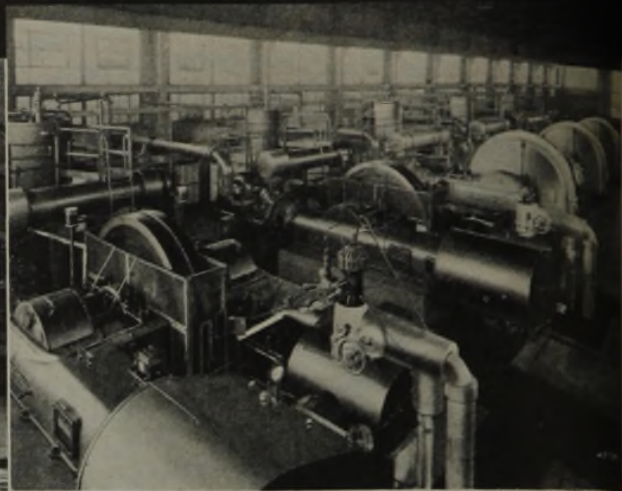
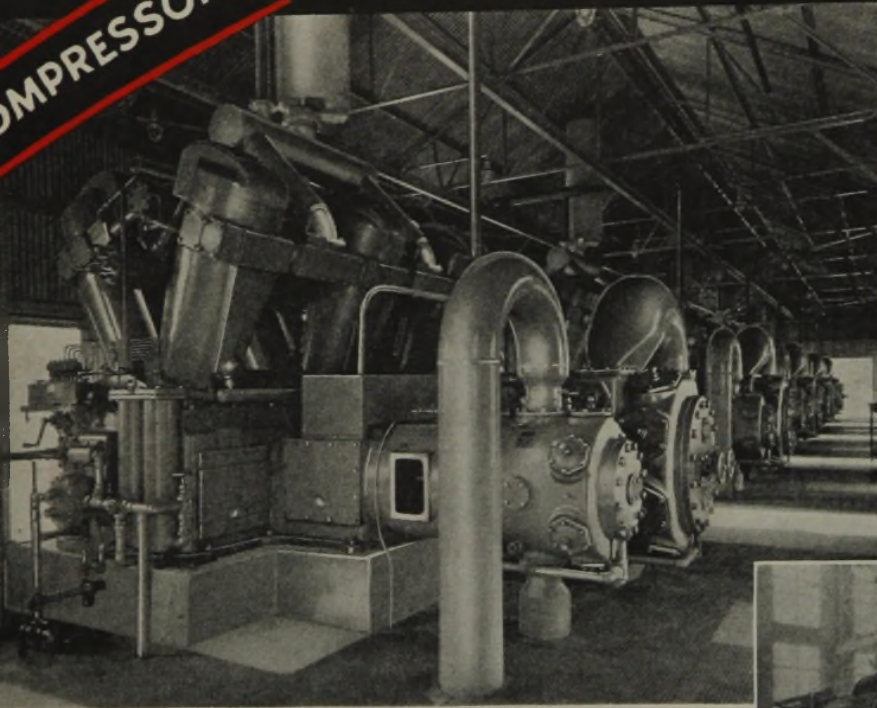
(Below)  
Duriron pipe — bell and spigot and split-flanged — for carrying corrosive liquids and drainage.



**THE**  
*Duriron*  
**COMPANY, INC.**  
DAYTON, OHIO

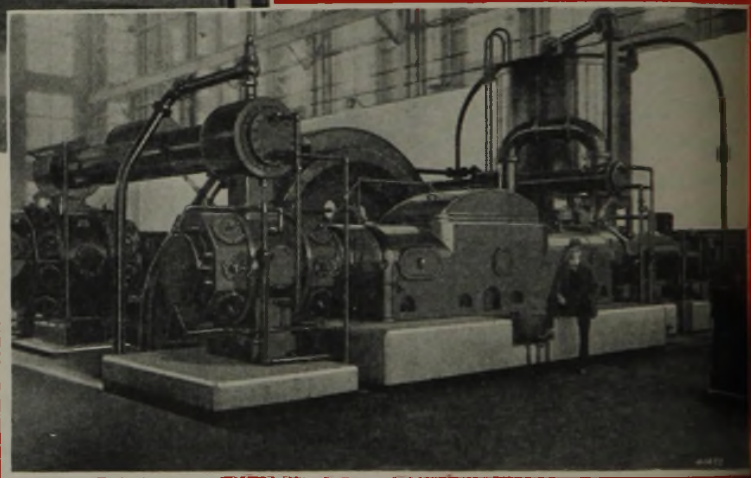
# Ingersoll-Rand Machinery

## COMPRESSORS



Five electric- and five steam-driven high-pressure compressors in a refinery.

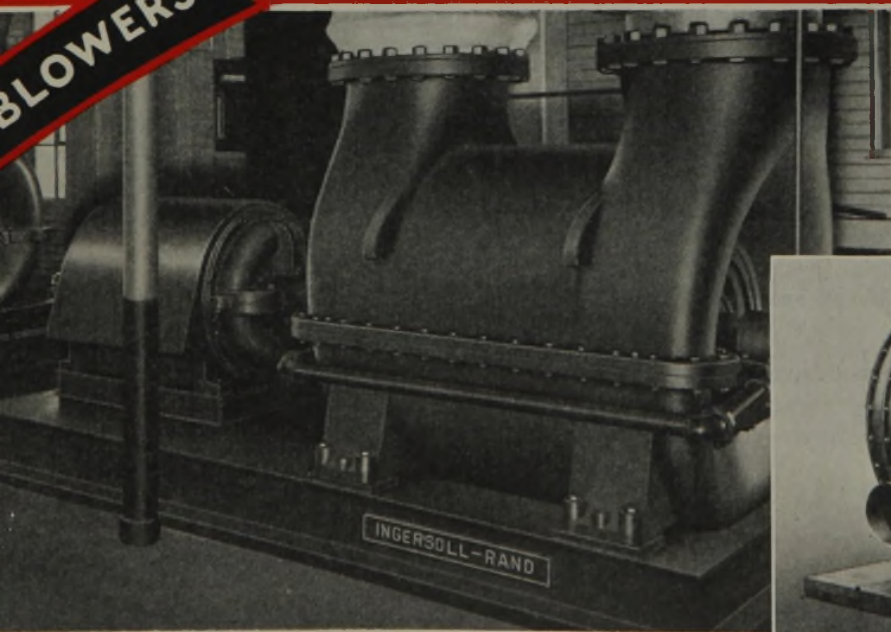
These gas-engine-driven units are compressing natural gas in Arkansas. Ingersoll-Rand compressors range in size from  $\frac{1}{4}$  to 3000 horsepower and are driven by electric motors, steam, oil engines, or gas engines. Pressures range from vacuum to 15,000 lb per sq in. Installations of high-pressure machines total more than 150,000 hp.



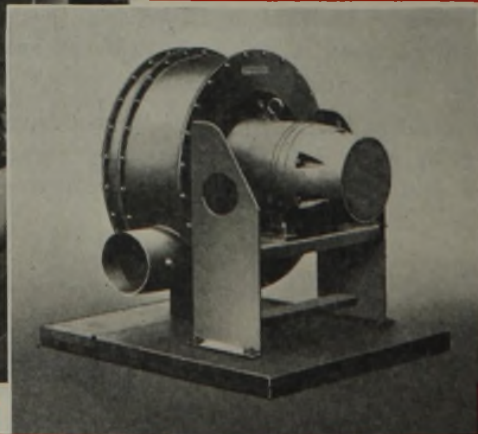
A 2,250-hp, six-stage machine compressing gas to 4,500 lb per sq in. pressure in a synthetic ammonia process.

Blowers for air and many gases are available in sizes from 2 to 14,500 hp. At the left are shown two 400-hp vat agitation units.

## BLOWERS



A Type "G" MOTOR-BLOWER equipped with an explosion-proof motor for use in a munitions plant.



Aftercoolers  
Air & Gas Lift Pumps  
Blowers  
Compressors

Condensers, Surface & Barometric Types  
Core Drills

Diesel & Gas Engines  
Hoists  
Jackbits

Jackhamers

Pumps

# for *Special* Processes

We don't profess to be experts on the many refinery and other chemical processes . . . because each process has its own specialists who know what they need and how to procure the best equipment for the job.

We have, however, earned the reputation of being experts in developing, manufacturing, and applying compressors, blowers, pumps, and vacuum equipment . . . machines that meet the rigid specifications of the process engineers, and that stand up under the operating conditions and continuous service required in recycling, gasoline extraction, and in the manufacture of aviation gasoline, synthetic rubber, synthetic ammonia, explosives, etc.

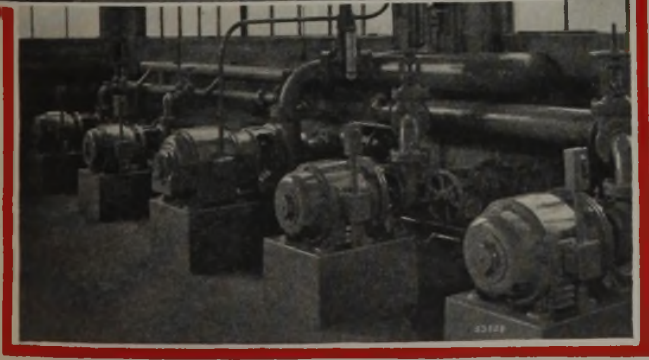
While new cycles or processes are still in the idea stage, our engineers are on the job with more than 50 years' experience in applying Ingersoll-Rand products to the problems of compression, pumping, vacuums, refrigeration, and condensation.

I-R heavy-duty machines are built and rated for continuous full-load operation, 24 hours a day, and they require only a minimum of time and money for inspection and repairs. And whenever new machines or new lines of equipment are developed specially for one industry or another, the keynote of I-R designers is flexibility and standardization of parts. Such a policy provides important advantages to every purchaser of Ingersoll-Rand equipment.

Below is a group of various types of Ingersoll-Rand refinery pumps. I-R pumps range in size from 5 to 100,000 gpm . . . for pressures up to 3,000 lb . . . temperatures up to 800°F . . . and can be built to handle practically any liquid.

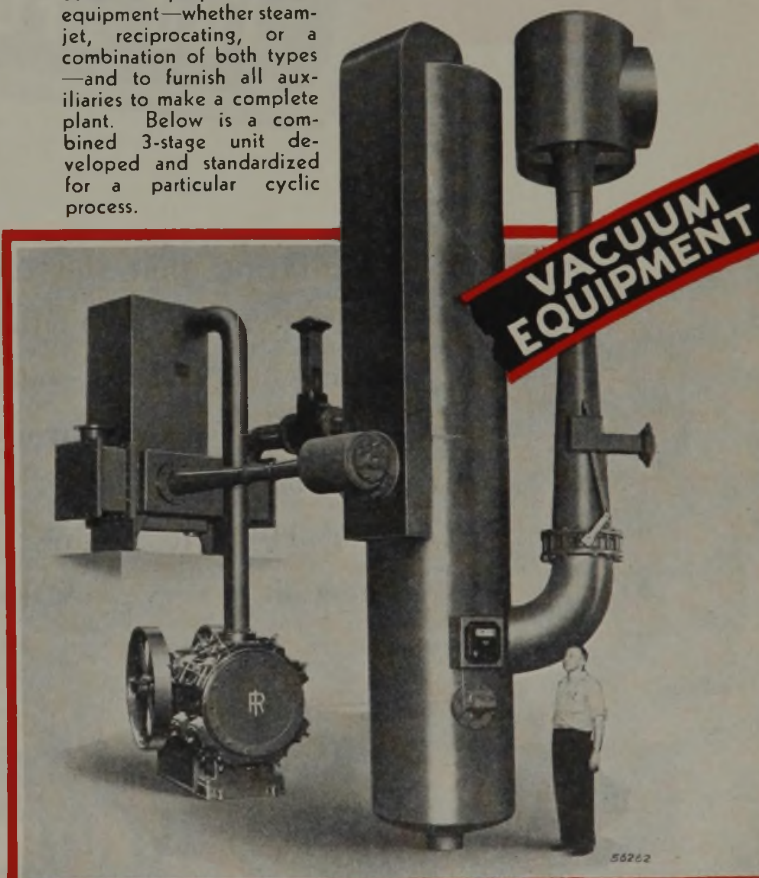
Ingersoll-Rand is in a position to recommend and build the proper vacuum equipment—whether steam-jet, reciprocating, or a combination of both types—and to furnish all auxiliaries to make a complete plant. Below is a combined 3-stage unit developed and standardized for a particular cyclic process.

**PUMPS**



Above are shown several Motorpumps—the versatile little units that have a million uses.

**VACUUM EQUIPMENT**



Atlanta  
Birmingham  
Boston  
Buffalo

Dallas  
Denver  
Detroit  
Duluth

# Ingersoll-Rand

11 BROADWAY, NEW YORK CITY

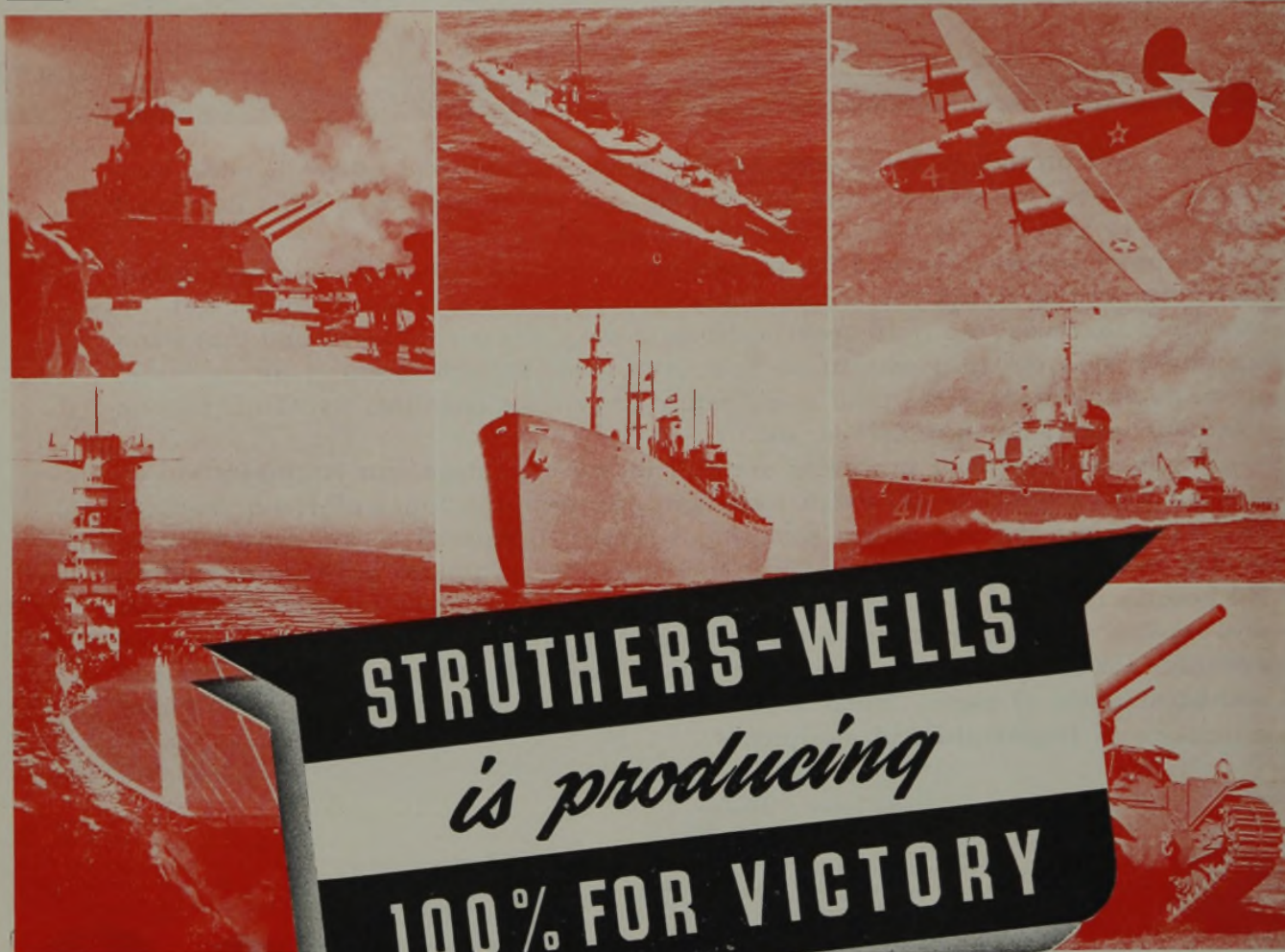
Knoxville

Newark

New York

Picher

Pottsville  
Salt Lake City  
San Francisco  
Scranton  
Seattle  
St. Louis  
Tulsa

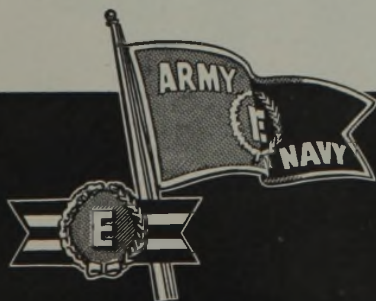


**STRUTHERS-WELLS**  
*is producing*  
**100% FOR VICTORY**

Official Photos U.S. Navy; U.S. Army Signal Corps; U.S. Maritime Commission; U.S. Army Air Force.

It is significant that the facilities of Struthers Wells\* are being devoted to vital Victory production 24 hours a day at a time when difficult specifications and quality demands require such speed, accuracy and ingenuity. These recognized characteristics of the Struthers Wells organization are dedicated 100% to Victory today... tomorrow we will be even more fit to serve you distinctively.

\*In peace times . . . Designers and Fabricators of Processing Equipment such as Heat Exchangers, Evaporators, Condensers, Coolers, Fractionating Columns, Impregnating Apparatus, Kettles, Pressure Vessels, etc. . . . Marine Equipment including Crankshafts, Steering Gears, Capstans, Winches, Windlasses, Boilers, etc.



**STRUTHERS WELLS CORPORATION**  
 Titusville, Penna. and Warren, Penna.

# U.S.I. CHEMICAL NEWS

April



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



1943

## Curbay B-G Helps Meet Egg and Meat War Effort Quotas

### U.S.I.'s B-Complex Supplement Useful in Chick and Hog Feeds

55,000,000,000 eggs, 4,000,000,000 pounds of chicken meat and over 60,000,000 swine fed to 235 pound weight have been set by the Department of Agriculture as the 1943 quotas needed for support of the war effort. With these increased quotas set, Curbay B-G, U.S.I.'s riboflavin feed supplement, is taking on new importance as an aid in supplying the required units of the B-G complex essential in adequate poultry and hog rations.

Curbay B-G has, through the past years, demonstrated its effectiveness in replacing more expensive Vitamin B-Complex supplements—such as dried skim milk powder. The use of U.S.I.'s product has been responsible for releasing millions of pounds of dried skim milk powder for shipment to the United Nations for human food. Thus Curbay B-G represents a double contribution toward meeting increased food requirements.

### Improved Moisture-Proofing Coating Composition Patented

WILMINGTON, Del. — A patent for making a moisture-proof coating composition said to have improved heat-sealing properties and anchorage was assigned recently to a company here.

Plasticizers of the ester type are condensed with resins, either natural, modified or synthetic. Dibutyl phthalate is said to be particularly advantageous as the plasticizer component. Mixing the condensation product with paraffin wax or nitrocellulose, suitable coating compositions are said to be obtained for moisture-proofing regenerated cellulose sheets and films.

The formula for a typical coating of this type is as follows:

	Parts
Nitrocellulose .....	40
Paraffin wax .....	2
Ethyl acetate .....	400
Toluene .....	160
Alkyd resin .....	10
Dibutyl phthalate .....	30

### Color-Dispersing Process Prevents Haze in Films

ROCHESTER, N. Y. — A method for dispersing a coloring material in a water-swallowable photographic colloid (such as gelatin) and maintaining the particle size small enough to prevent haze in the resulting film has been developed by two inventors here.

The coloring material is mixed with a water-insoluble material, such as collodion, in a common solvent, such as butyl acetate. This solution is then added to an aqueous one containing a dispersing agent. The mixture may next be passed through a small homogenizer and the suspension thus formed heated, preferably under vacuum, to remove the butyl acetate. Finally, the suspension of fine particles in the aqueous solution is added to a gelatin emulsion and, after mixing with it, the resulting emulsion is coated.

## Acetoacetarylides Developed By U.S.I. for Research Study

### Aid to Manufacturers in Meeting Post-War Needs Seen in Many New Dye Intermediates Produced on Laboratory Scale

Recognizing the growing importance of yellow pigments and dyestuffs, U.S.I. has developed a number of new acetoacetarylides on a laboratory scale in addition to the five now being produced commercially. Acetoacetarylides have proven particularly valuable in the production of the Hansa and newer yellows where an acetoacetarylide is coupled with a diazotized amino compound, preferably containing nitro groups which help to retain the insolubility in oil and thus prevent bleeding.

### Thymolphthalein as Indicator In Red, Brown Titrations

PROVIDENCE, R. I. — Thymolphthalein is a satisfactory indicator to use in titrating reddish or brownish solutions, where phenolphthalein and methyl orange are not satisfactory, according to findings reported recently in "The Chemist Analyst."

Thymolphthalein is said to change from colorless at pH of 9.3 to blue at 10.5. A convenient solution is described as containing 0.1% of the indicator in an 80% aqueous solution of ethanol.

### Butanol Claimed to Stabilize Ethanol, Hydrocarbon Mixture

Butanol is a practical stabilizer for the preparation of a fuel mixture of hydrocarbons and ethanol of more than 188 proof, according to a recent report.

The addition of 5% butanol to ethanol of 192 proof, for example, is said to give mixtures stable at  $-15^{\circ}$ . It is noted that the water-absorbing power increases with butanol at a greater rate than with ethanol. Practically, the sensitiveness is claimed to correspond to 19.4% per cc. of water added to 100 volumes of mixture.

New impetus to acetoacetarylides as pigment dye intermediates has been brought about by the expanded utility of yellow pigment dyestuffs due to the absorption of chrome yellow production for olive drab pigments. In addition to the Hansa Yellows, toluidine and benzidine yellows have come into favor recently where color tone, brilliance and durability are desired.

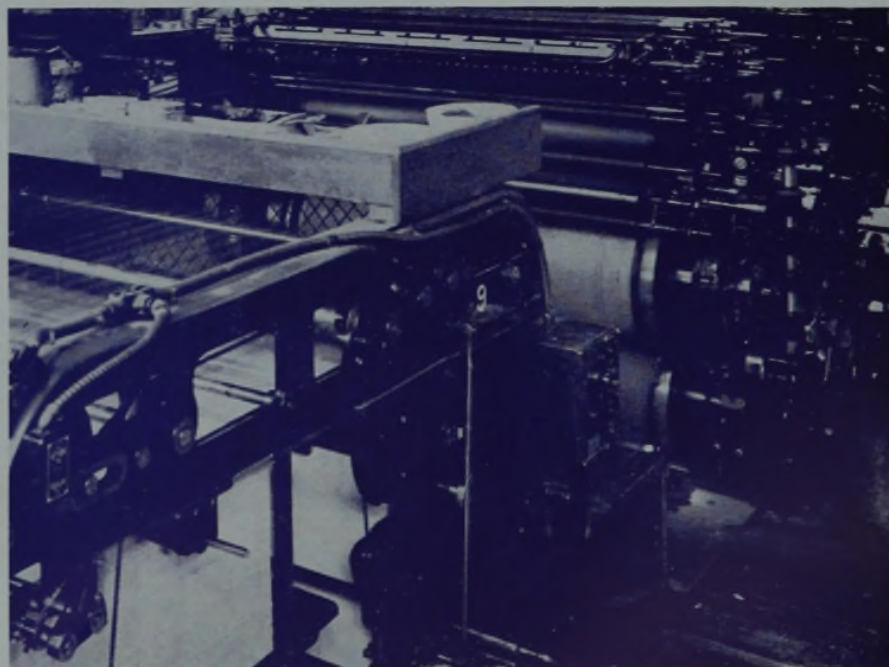
New acetoacetarylides

The heightened interest in acetoacetarylides has both brought about a greater demand for those compounds now commercially available and increased the desire to study new ones with a view to post-war applications. Among the newer acetoacetarylides developed by U.S.I. are the following:

Acetoacet-para-phenetide  
Benzoylacetanilide  
Diacetoacetyl-meta-toluylenediamine  
Diacetoacetyl-para-phenylenediamine  
Acetoacet-para-nitroanilide  
Acetoacet-2, 5-dichloroanilide  
Acetoacetyl-alpha-naphthylamine  
Acetoacetumide (pseudol)  
N,N'-Diacetoacetbenzidine  
Ortho-phenylacetacetanilide

Sample quantities of these new compounds will be gladly sent upon request to manufacturers for laboratory experimentation.

(Continued on next page)



The exacting requirements of modern printing provide one of the outstanding reasons for the use of the Hansa Yellows.

## New Reagent for Sodium Calls for Use of Ethanol

PRINCETON, N. J.—Systematic experiments have shown that a reagent for the determination of sodium can be produced through the use of ethanol. It is at the same time more insensitive toward lithium and more sensitive toward sodium than aqueous reagents now in common use, according to a chemist here.

The composition of this alcoholic reagent is as follows:

Uranyl acetate dihydrate.....	40 grams
Cupric acetate monohydrate.....	25 grams
Glacial acetic acid.....	100 ml.
Ethanol, 95%.....	500 ml.
Water.....	450 ml.

The salts are dissolved in the water and acetic acid at a temperature of 50° to 60° C. and, after cooling down to room temperature, the ethanol added with constant stirring. After standing at least one day, preferably two or three, the mixture is stirred and filtered in the same way as in the preparation of regular aqueous reagents.

## Non-Leafing Aluminum Paste Does Not Require Grinding

LOUISVILLE, Ky.—A new non-leafing aluminum paste has been developed by an inventor here in which the deleafing action is brought about chemically without the need for grinding.

The preferred method of making this paste consists of adding to a regular, full leafing aluminum powder a suitable thinner or carrier in which has been incorporated a deleafing agent consisting of the highly polar active alcohols, esters, ketones, and aldehydes.

A typical formula calls for 60 pounds of aluminum powder (fully polished and leafing), 20 pounds of ethyl acetate and 20 pounds of toluol.

## Ethyl Acetoacetate Used To Extract Lignin From Wood

Ethyl acetoacetate may be used as a solvent in the presence of hydrochloric acid to isolate lignin from white quebracho wood, according to a recent discovery.

Extension of lignin by this solvent is not quantitative, as determined by the König method, but the greater portion is isolated from the other components. A high hydrochloric acid concentration, 10% of the ethyl acetoacetate, and a temperature of 40° for 24 hours are said to give the best extraction.

## New Acetoacetarylides

(Continued from previous page)

One of the most widely known of the acetoacetarylides now produced commercially by U.S.I. is acetoacetanilide. This compound is prepared by reacting ethyl acetoacetate, an important intermediate in dyestuffs and pharmaceuticals itself, with aniline thereby eliminating ethanol. Hansa Yellow G is formed when acetoacetanilide is coupled with diazotized meta-nitro-para-toluidine. The use of other diazotized amino compounds produces slightly different shades.

### Other Compounds

Four other acetoacetarylides which may be used in the same general way to produce the desired shades of yellow are also commercially available from U.S.I. They are acetoacet-ortho-chloroanilide, acetoacet-para-chloroanilide, acetoacet-ortho-toluidide, and acetoacet-ortho-anisidide.

Dyestuff manufacturers are aided in obtaining the desired shade and clarity by the exacting production methods developed by U.S.I. which reduce impurities to extremely small limits. For although such factors as temperature, agitation, and drying time all play important roles in the ultimate clarity of yellow pigments, manufacturers have found through experience that the purity of the intermediates is of utmost importance.

## Ethanol Aids Dispersement Of Vitamin Compositions

NEWARK, N. J.—By the use of ethanol as a solvent, an inventor here claims that fat-soluble vitamin compositions may be easily dispersed in aqueous media.

To produce this water-dispersible composition, the vitamin concentrate is mixed with a solution of ethanol and a substance selected from the group consisting of the alcohol-soluble portions of edible gums.

## Starch Fractionated With Butanol, Isoamyl Alcohols

Butanol and isoamyl alcohols can be used to fractionate starch without retrogradation or hydrolytic degradation, it was reported recently. The precipitated fraction, which has a higher alkali number than the non-precipitated fraction, separates in the form of an addition compound with the butanol. The lower alcohols were ineffective, it is stated, while octyl alcohol and cyclohexanol precipitated all of the starch indiscriminately.

## TECHNICAL DEVELOPMENTS

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

**A slime-preventing chemical** is offered in powdered form for addition to wood pulp in a beater. Five ounces of the chemical to one ton of pulp is said to be adequate. (No. 680)

U S I

**A thermoplastic corrosion-proofing material** has been developed as a substitute for rubber for lining tanks, pipes and pipe fittings. Black in color, it is applied in a similar manner to rubber. This product is claimed to resist attack by non-fuming nitric acid, chromic acid, alcohol, petroleum, gasoline, linseed oil, vegetable oil and soaps. (No. 681)

U S I

**A cellulose paper-base medium** is offered which, it is said, can be impregnated with glue and protein materials, rubber, rubber substitutes, and both natural and synthetic resins either with or without lamination. (No. 682)

U S I

**An emulsifier** has been put on the market which is described as a high dispersion product of oil in water and water in oil that is especially useful in the manufacture of paint products. (No. 683)

U S I

**Skin protectors** which the maker claims can be used on the face as well as the hands and arms have been developed to meet a wide variety of conditions. Among the irritants they are said to counter are cutting and lubricating oils, kerosene, petroleum, solvents, thinners, lacquer, paint, ink, water, fumes, ammonium nitrate, chlorine, acids, and alkalis. (No. 684)

U S I

**A toxic preservative** for cotton rope has been put on the market which is claimed to toughen and stiffen rope, give it wear-resistance and firmness, reduce unwinding of the strands, and generally increase its efficiency. (No. 685)

U S I

**A new method of gas analysis** has been developed in which catalysis is described as superseding slow combustion in standard gas analysis apparatus, thus providing a safer and more accurate method for determination of combustible components. (No. 686)

U S I

**An adjustable automatic pipette** is offered which is said to be equally adaptable to analytical procedures and to operations requiring rapid, accurate measurement of liquids. By a simple adjustment, it is claimed that any desired volume can be delivered within 0.1 ml. (No. 687)

U S I

**An odor neutralizer** for fly spray and disinfectant formulas is being produced which the maker says is an efficacious specific for Lethane 384, Lethane 384 Special, Thanite, Velsicol and Deodorant L-37 MM&R. (No. 688)

U S I

**A viscometer** is announced for testing polymer solutions and other heavy-bodied liquids. Viscosity is determined by inverting glass tubes and comparing the rise of an air bubble in the sample with the rise of a bubble in a tube containing a known standard. (No. 689)

# U.S.I. INDUSTRIAL CHEMICALS, INC.

60 EAST 42ND STREET, NEW YORK



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%<sub>a</sub>  
Absolute  
U.S.I. Denatured Alcohol  
Anti-freeze

\*Super Pyro Anti-freeze  
\*Solox Proprietary Solvent  
\*Solox D-1 De-icing Fluid

### \*ANSOLS

\*Ansol M  
\*Ansol PR

### ACETIC ESTERS

Amyl Acetate  
Butyl Acetate  
Ethyl Acetate

### OXALIC ESTERS

Butyl Oxalate  
Ethyl Oxalate

### PHTHALIC ESTERS

Amyl Phthalate  
Butyl Phthalate  
Ethyl Phthalate

### OTHER ESTERS

\*Dialol  
Ethyl Carbonate  
Ethyl Chloroformate  
Ethyl Formate

### INTERMEDIATES

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

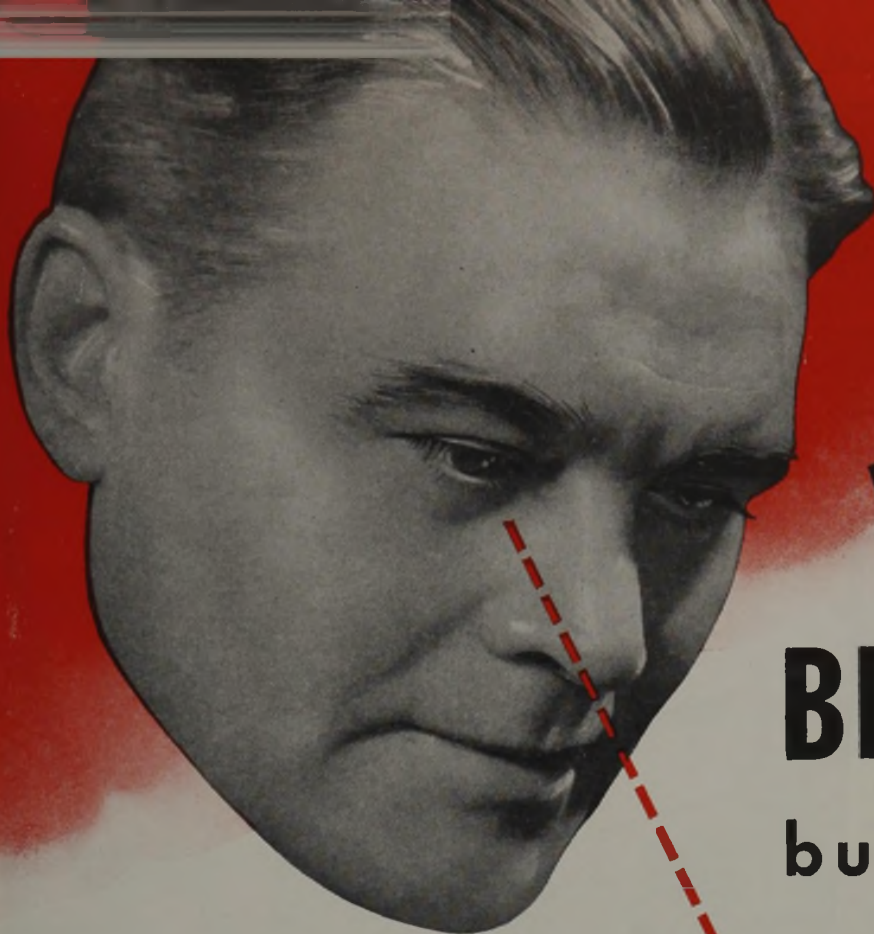
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### ETHERS

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

### OTHER PRODUCTS

Acetone  
Collodions  
\*Curbay B-G  
\*Curbay Binders  
\*Curbay X (Powder)  
Ethylene  
Ethylene Glycol  
\*Indalone  
Nitracellulose Solutions  
Potash, Agricultural  
Urethan  
\*Vacatone



From Idea to Operation

# BLAW-KNOX

builds complete

# PROCESS PLANTS

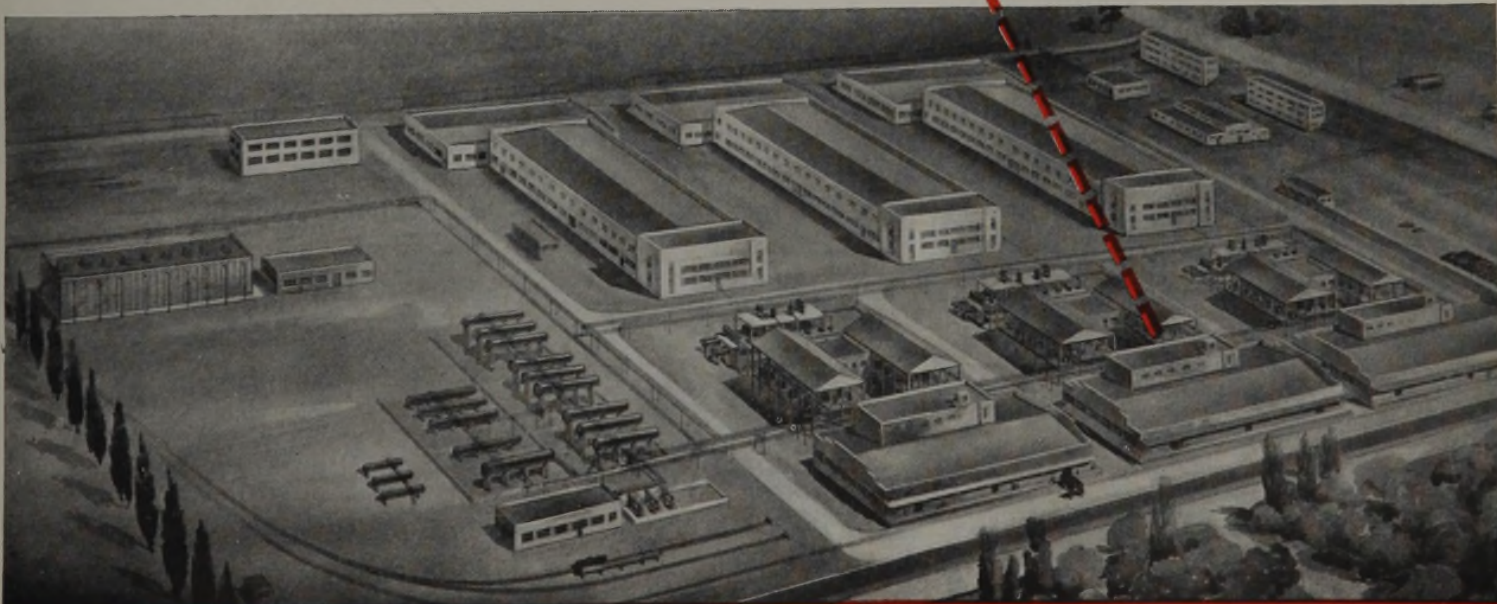
**BLAW-KNOX DIVISION**  
OF BLAW-KNOX COMPANY

2081 Farmers Bank Bldg. Pittsburgh, Pa.  
*Offices and Representatives in Principal Cities*

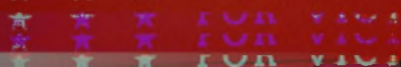
*Complete plants or equipment  
for the following processes...*

Distillation • Gas Absorption • Solvent Extraction  
Solvent Recovery • Heat Transfer • Furnacing  
Cracking • Kilning and Calcining • Polymerizing  
Evaporation • Crystallization • Drying • Mixing  
and Stirring • Organic Synthesis • Emulsification  
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Get maximum efficiency with Blaw-Knox unified control. Research, engineering, fabrication, design and erection of buildings in cooperation with customer's architect and contractor, initial operation—all under a single responsibility.



★ ★ ★ FOR VICTORY BUY U. S. WAR BONDS AND STAMPS ★ ★



# 4800 WORKERS WILL BE HURT TODAY

Today—tomorrow—each day this year—occupational accidents will disable 4,800 essential workers for 20 days or more! 34 million precious man-days of labor lost in a critical year—based on 1942 experience—without including fatal accidents! Think how this man-power waste is delaying Victory.

While disabilities don't often result from piping accidents, they are inexcusable—now or any time. With simple precautions like those following, for example, piping maintenance men can help lessen the hazards to American workers now when they're most needed on the job.

## SAFETY HINTS FOR PIPING MEN

- 1 Don't install valves where getting at them means exposure to danger.
- 2 Support lines firmly to prevent loosening at joints.
- 3 Identify valves so they can be quickly operated in emergencies.
- 4 Install relief valves where there is danger of sudden built-up pressures.
- 5 Inspect sprinkler system control valves regularly. Keep them open always.

The safety hints given here are from "Piping Pointers" Bulletins—a Crane service aiding piping men in hundreds of plants in doing more to help win the war. Giving many "do's and don'ts" and "rights and wrongs" on keeping pipe lines at peak efficiency—conserving critical metals—and speeding piping jobs, these bulletins, based on Crane's 87-year leadership in flow-control engineering, are especially valuable for training new maintenance men. Copies free on request from your Crane Representative or by writing to: Crane Co., 836 South Michigan Avenue, Chicago, Illinois.



**"PIPING POINTERS" BULLETINS—FREE TO ANY PLANT**

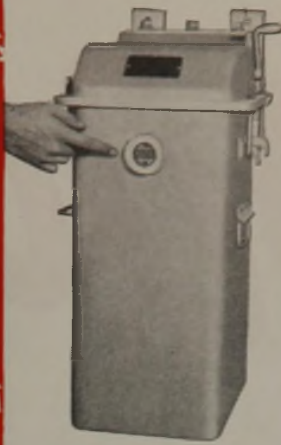


# CRANE VALVES

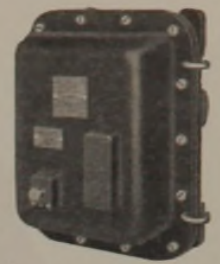


DUST · ACID FUMES ·  
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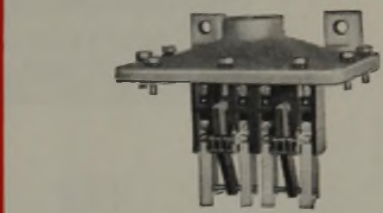
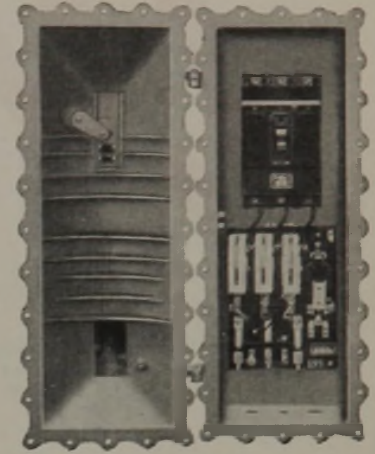
# NAME YOUR HAZARD and we'll meet it!



● Standard magnetic starter enclosed in cast-iron case for Class 1, Group D, application.



● Oil-immersed combination starter for Class 1, Group D, locations. All contacts are at least 6 inches under oil. Easy-to-read indicator provides safety check on oil level.

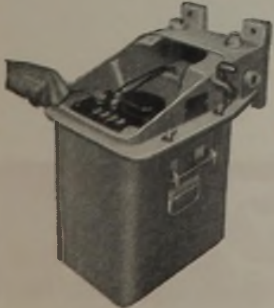


● Air-break combination starter—combining both a circuit breaker and a starter in one unit—for Class 1, Group D, locations. Complete unit is enclosed in a sturdy, cast-iron case.



● Oil-immersed, push-button station for both corrosive and hazardous-gas locations. All contacts are under oil, and entire unit is enclosed in cast-iron case.

● New high-voltage combination starter for 2300- and 4000-volt motors. Contactors are immersed in oil to prevent corrosion.



● Standard oil-immersed combination starter for corrosive locations. New, sealed-off head protects cable and terminals from oil fumes.

## STANDARD MOTOR CONTROLS UP TO 1000 HP FOR CORROSIVE AND HAZARDOUS LOCATIONS

● Readily available standards save hours of engineering time; conserve critical material; can be delivered faster.

No matter what your hazard is—explosive gases, dust, or corrosive vapors—up to 1000 hp, there is a ready-made answer to it in the complete line of standard General Electric controls. And remember these are standard because they have met the test of reliable, on-the-job operation.

Don't worry needlessly about special controls for your processing operations. The chances are that your local G-E sales engineer can offer a standard control that will more than meet your requirements. *General Electric, Schenectady, N. Y.*

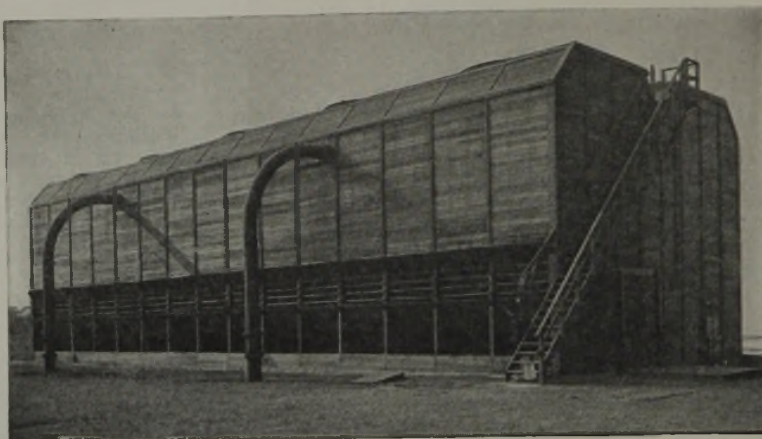
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Induced Draft Cooling Tower of 10 Cells — Two Rows of Five Cells Placed Back to Back.



View of Induced Draft Fans Showing Fan Mounting and Top Deck Construction.



# FOSTER

# *Gallons per minute*

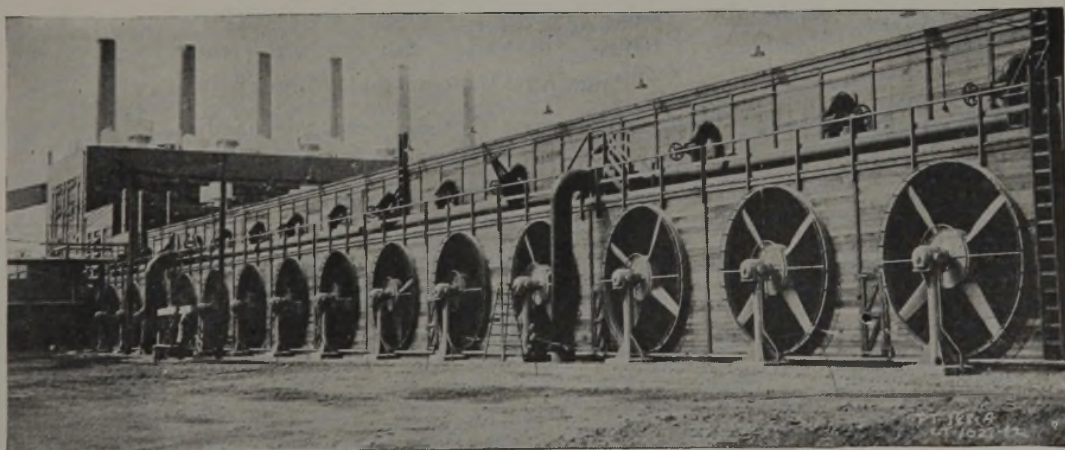
## **67 COOLING TOWERS FOR WAR IN 16 MONTHS**

**AVERAGE CAPACITY MORE  
THAN 15,000 G.P.M.**

**T**HE TOTAL capacity of Foster Wheeler cooling towers furnished during the past year to war industries including petroleum refineries, chemical and synthetic rubber plants, is more than double that of any previous year.

These towers are designed to meet the specific requirements of each plant in order to provide most effective and economic operation. Forced draft, induced draft and natural draft types are designed and constructed — based on many years of operating experience.

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28-Cell Forced Draft Cooling Tower for Munition Work.

# **WHEELER**



*Deep drawing  
made it light and  
strong enough to fly*



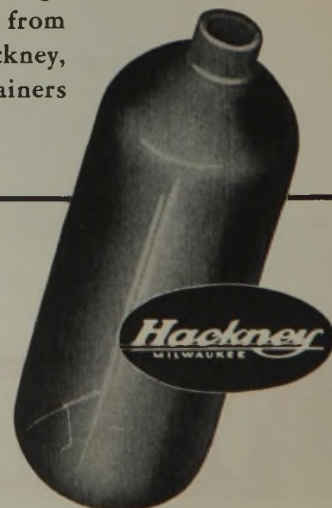
*This cylinder, a reservoir of hydraulic energy for aircraft use, is another example of the way in which the Hackney Deep-Drawing Process helps manufacturers strengthen and reduce the weight of parts simultaneously.*

Hydraulic energy to feather propellers, operate landing gear, flaps, etc., requires accumulators which are light in weight, yet are strong enough to withstand high internal pressures.

**Hackney Cylinders, Drums and Barrels**  
This is but one of the many products developed by Hackney engineers to meet the exacting requirements of wartime service. Hackney production today is 100% for war. Hackney Cylinders, Drums and Barrels are being used by hundreds

of war plants to solve their transportation and storage problems for vital chemicals. Hackney Containers are, therefore, helping to hasten the day when they will again be benefiting all industry.

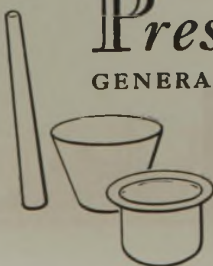
And when that long-hoped-for day arrives, peacetime transportation and storage facilities will benefit by the things learned in this war. For instance, from the research and experience of Hackney, will come better, high quality containers for gases, liquids and solids.




## **P**ressed Steel Tank Company

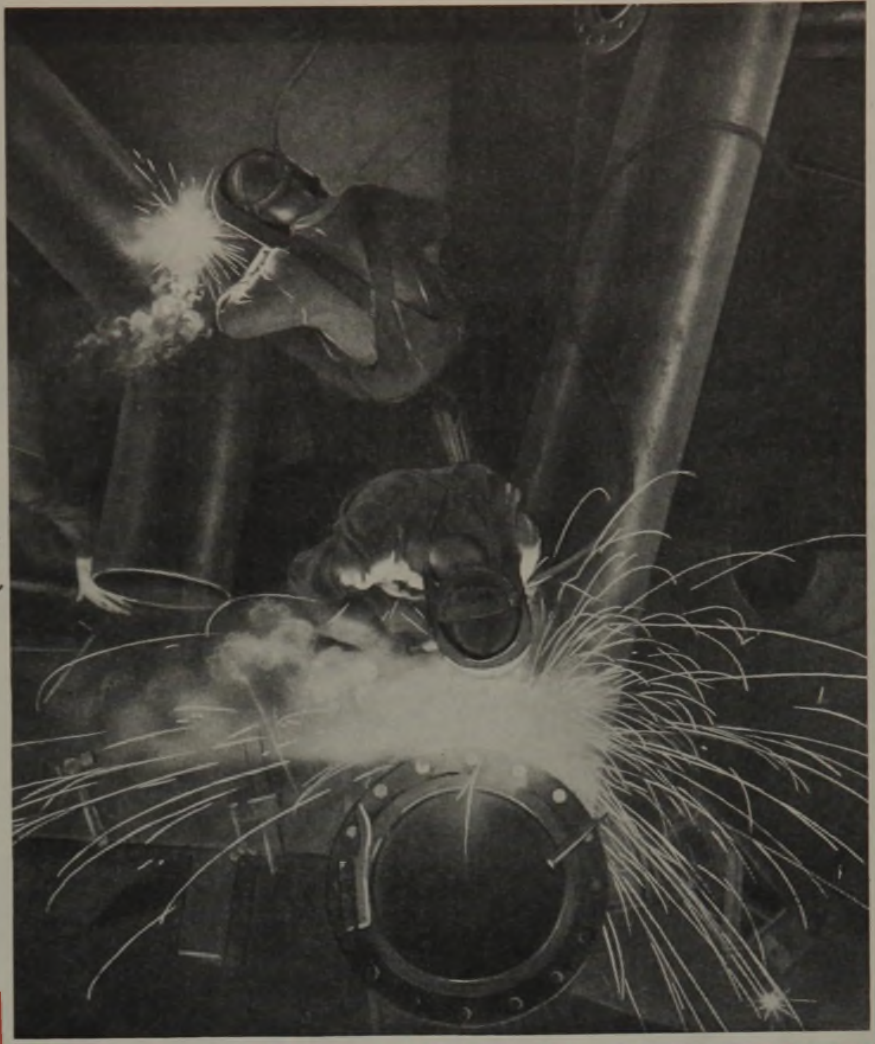
GENERAL OFFICES AND FACTORY • 1451 SOUTH 66th STREET  
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DEEP-DRAWN SHAPES AND SHELLS





**WELDING**  
*Dust-Tight*  
**PIPING in the**  
**JAY-CEE PLANT**



# **JAY-CEE**..JOHNSON CITY, TENN.

**Builds ANYTHING in IRON or STEEL**  
*Not Already Produced as a Specialty*

**JAY-CEE SPECIALTY PRODUCTS PRODUCED IN JOHNSON CITY**

**ALUMINUM PLANTS**

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Pressure Vessels        Special Machinery

**OTHER PLANTS**

Structural Steel        Iron Castings  
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*If it's made of Iron or Steel, draw a picture of it — we'll build it.*

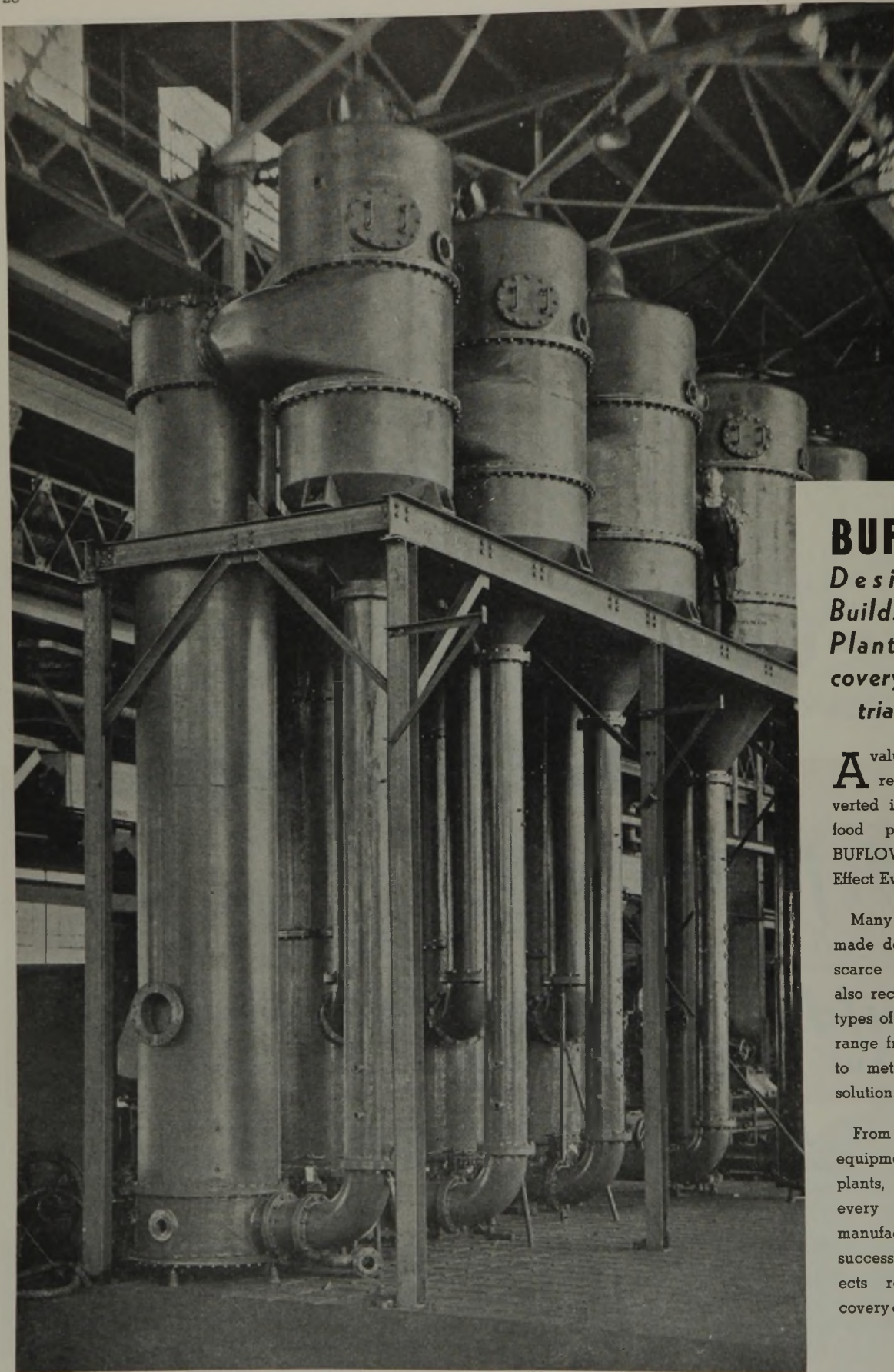
The "Jay-Cee" organization, because of long experience in the fabrication of Iron and Steel, is ideally equipped to serve the chemical and allied industries. So, present your problems to "Jay-Cee" technicians without obligation.

During the past 29 months "Jay-Cee" has contributed greatly to the victory effort by increasing production on war work more than 400%.

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**GRAY IRON and ALLOY IRON CASTINGS — STRUCTURAL STEEL — MISCELLANEOUS and ORNAMENTAL IRON WORK — SPECIAL MACHINE WORK**



## **BUFLOVAK**

*Designs and Builds Complete Plants for Recovery of Industrial Wastes*

A valuable protein is recovered and converted into an important food product by this BUFLOVAK Quadruple Effect Evaporator.

Many other products, made doubly valuable or scarce by the war, are also recovered with other types of equipment. They range from illusive esters to metals in chemical solution.

From single pieces of equipment to complete plants, BUFLOVAK has every engineering and manufacturing facility to successfully handle projects requiring the recovery of industrial wastes.

**BUFFALO FOUNDRY & MACHINE CO., 1549 Fillmore Ave., Buffalo, N.Y.**

NEW YORK — 295 Madison Ave.

ST. LOUIS — 2217 Olive St.

CHICAGO — 1636 Monadnock Bldg.

SAN LEANDRO, CAL. — 763 Bridge Road

CLEVELAND — 822 Keith Bldg.



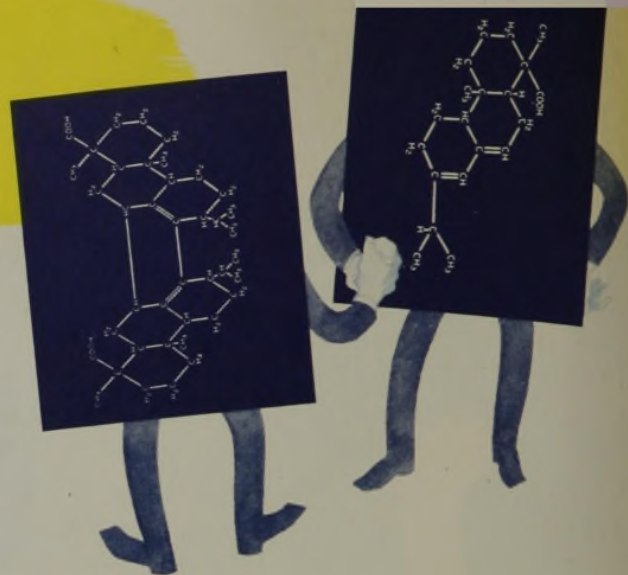
"... and every day we chart some new discovery"

"Each day we gather, some 700 all told, at the Hercules Experiment Station to explore the Unknown Sections of Hercules Land. Instead of maps, we use formulae; instead of ships, test tubes; instead of landing parties, pilot plants. Every day we chart some new discovery, some new idea rich in opportunity to improve a product, to speed up manufacture, to substitute for an exhausted strategic material . . .

*for instance . . ."*

## Rosin now polymerized for added advantages

In the last year and a half, additional important things have been happening in rosin modification, making this material more useful than ever. For example, Hercules Poly-pale\* Resin retains all of rosin's good qualities, but gives a higher melting point, wider solubility, greater viscosity in solution, a lower rate of oxygen absorption, and does not crystallize in solution. Poly-pale Resin extends critical materials—glycerine, phenolaldehyde, maleic anhydride—in production of resins. Write for information.



## Meet the new family of alkyd resins

From Petrex\* comes a new family of alkyd resins—the Petrex Elastomers. They have important properties of elasticity, flexibility, and tackiness, which indicate their utility in many industries.

Uses have already been developed for these elastomers in adhesives, paper impregnation, coated and laminated textiles, waterproof tape backing, "rubber" cements, to mention only a few. Resins may be applied as hot-melts, from solvent solutions, or in emulsion form. You should know more about this interesting new family of elastomeric resins, both for its present use and for its future importance. Write Hercules for further information.

## Low-cost flame-resisting plasticizer



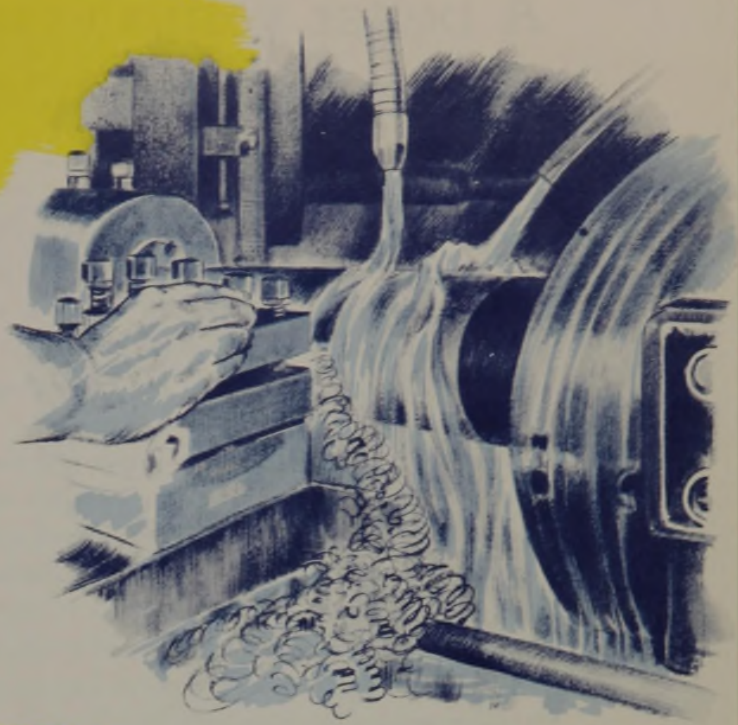
Hundreds of tons of Hercules Chlorinated Paraffin are being used each month as a low-cost, flame-resisting plasticizer. As produced by the Hercules chlorinating process, it is a high-quality product, exceptionally stable for this class of material, and available in bulk quantity. Further information on request.



# Dresinates—a new group of soluble resinates

Dresinate\* is the Hercules name for an interesting new group of water-soluble resinates with excellent wetting, emulsifying, and detergent-assisting properties.

Dresinates are inexpensive, have exceptional qualifications for use in alkaline cleaning compounds, metal-degreasing products, disinfectants, and similar industrial chemical specialties. One interesting recent discovery is the added stability given to petroleum-sulfonate cutting oil emulsions when hard water is encountered. Further information on this interesting new group of resinates may be obtained by writing to Hercules.



# Refresher points on nitrocellulose plastics

In the wide interest in new plastics it is easy to overlook the advantages of the older plastics—nitrocellulose, for example. Just recently, this tried-and-proven product licked a tough job—providing a water-resistant, acid-resistant, transparent, lightweight battery container for portable searchlights. Powered by this 8-volt storage battery, the light throws a 75,000 candle-power beam that must not fail—on sea duty or at vital war plants.

The choice of nitrocellulose plastic was further justified because this time-tested material provided the added advantage of long life under severe service conditions at sea, and the extra strength and toughness required, at low cost.

Hercules does not manufacture finished plastics or lacquers—only the nitrocellulose base. Our experience is therefore available impartially to producers of all plastic materials.



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

# A better varnish-resin with a promising future

The close cooperation of the varnish industry has enabled Hercules to accelerate the development of a new resin—Pentalyn\* M. Used with the oils available today, this resin produces varnishes that develop adequate salt-water resistance, fast dry, toughness, and other properties important in today's finishes.

Continuing research and cooperation with the industry are rapidly demonstrating that the Pentalyn resins are a sound basic development. Under today's conditions, Pentalyn M is outstanding. When varnish makers are again free to choose the oils they prefer in their formulations, the Pentalyns will produce totally new and better finishes. If you would like further information on Pentalyn M or the Pentalyn series of resins, please write Synthetics Department, Hercules Powder Company, Wilmington, Delaware.



## Cleaning dirty fibers quickly



It's the correct balance between terpene alcohols and terpene hydrocarbons that gives Yarmor\* 302-W its ability to penetrate, wet, and emulsify grease and oily or resinous dirt in textiles. Yarmor 302-W contains 70% terpene alcohols. That's why it goes to work quickly, thoroughly, in cotton and wool cleaning operations. The supply situation on Yarmor 302-W is good at the moment, and orders can be filled promptly.

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

**HERCULES POWDER COMPANY**  
INCORPORATED  
922 Delaware Trust Building,  
Wilmington, Delaware

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## CARBON DIOXIDE fills the need for quickly available **STORED ENERGY**

Here's power that can be packed in a handy cylinder, carried anywhere, released at the turn of a valve—in a quick burst or over a long period.

Carbon dioxide is the most compressible of the industrial gases. Stored under 850 pounds pressure at 70° F., there are 30,000 foot-pounds in each pound of carbon dioxide. That's *three times* the energy of the other usual gases!

Walter Kidde & Company has found many interesting uses for this "powerhouse in a package." New applications are being worked out constantly. Perhaps carbon dioxide is the solution to *your* power actuation problem. Our Research and Development Department will be glad to discuss the matter with you.

**Walter Kidde & Company**  
Incorporated

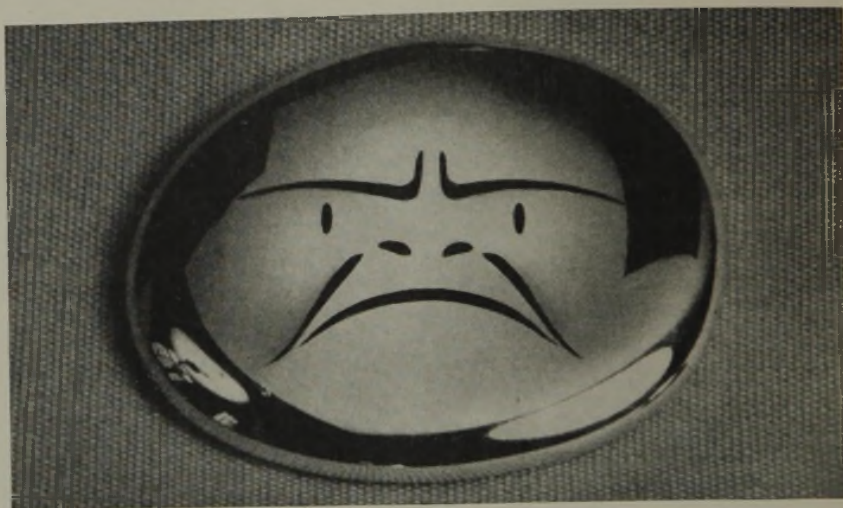
455 West Street, Bloomfield, N. J.



# MISSING

## FROM TAYLOR'S NEW ANEROID MANOMETER

Mr. Hg., alias Hydrargyrum, alias Mercury. Formerly present in flow and liquid level manometers but missing from Taylor's new Aneroid Manometer . . . and good riddance!



**I**T'S true! This new Taylor Manometer for flow and liquid level uses not one drop of precious mercury. What's more, there's no chance of theft or "blowing", no contamination of product, no cleaning.

*No stuffing box! No pivots!* Differential pressure is measured by a metal bellows and transmitted through a torque tube (see cutaway view below). With nothing to wear, nothing to oil, nothing to leak, maintenance is greatly reduced.

This new Taylor Instrument solves the problem of using volatile and other hard-to-handle fluids. Already successfully at work in many plants producing synthetic rubber, high octane gasoline and explosives. It can help improve *your* production of any product requiring measurement or control of flow or liquid level.

**1. Stuffing Box Replaced by Torque Tube.** *No leakage. No friction. No lubrication.*

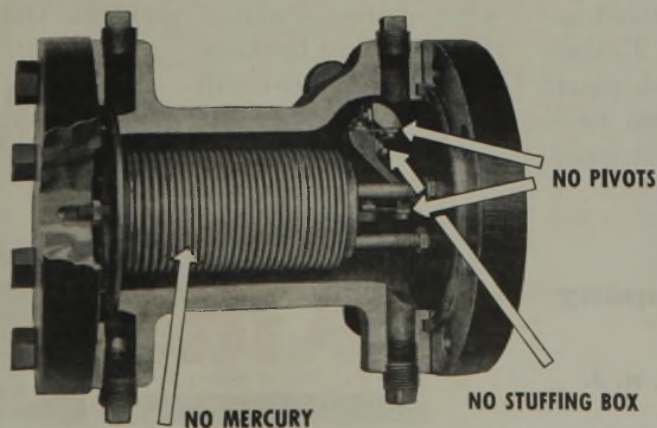
**2. No Internal Pivots—No Springs.** *No friction, lost motion, or wear.*

**3. Faster Response,** *closely follows actual rate of flow, due to greatly reduced displacement.*

**4. Adequate protection** *against over-ranging and reversal of flow.*

**5. Numerous Ranges Available . . .** 0 to 20, 50, 100 or 200 inches of water. 0 to 300, 400, 500 inches on application. *Intermediate ranges also available.*

Ask your Taylor Field Engineer! Call nearest Taylor office or write Taylor Instrument Companies, Rochester, N. Y., or Toronto, Canada. *Instruments for indicating, recording, and controlling temperature, pressure, humidity, flow, and liquid level.*



*Taylor Instruments*

— MEAN —

**ACCURACY FIRST**

**IN HOME AND INDUSTRY**

★ ★ KEEP ON BUYING U. S. WAR BONDS AND STAMPS ★ ★



# Symbol of Freedom

Freedom of initiative, progressive research and speedy commercialization of war processes characterize the Chemical and Petroleum Refining Industries — vital forces in the fight for Victory.



Complete facilities, including a new pilot plant laboratory, for the economic application of their new processes are offered these industries by Foster Wheeler . . . engineers and constructors of complete processing plants for war chemicals.

FOSTER WHEELER CORPORATION  
165 BROADWAY - NEW YORK

**FOSTER WHEELER**



ARMY-NAVY "E"  
 PRODUCTION AWARD  
 ★ ★ PRESENTED ★ ★  
 TO THE D. O. JAMES  
 MANUFACTURING CO.  
 February 27, 1943

#### POWER SAVING PRODUCTS

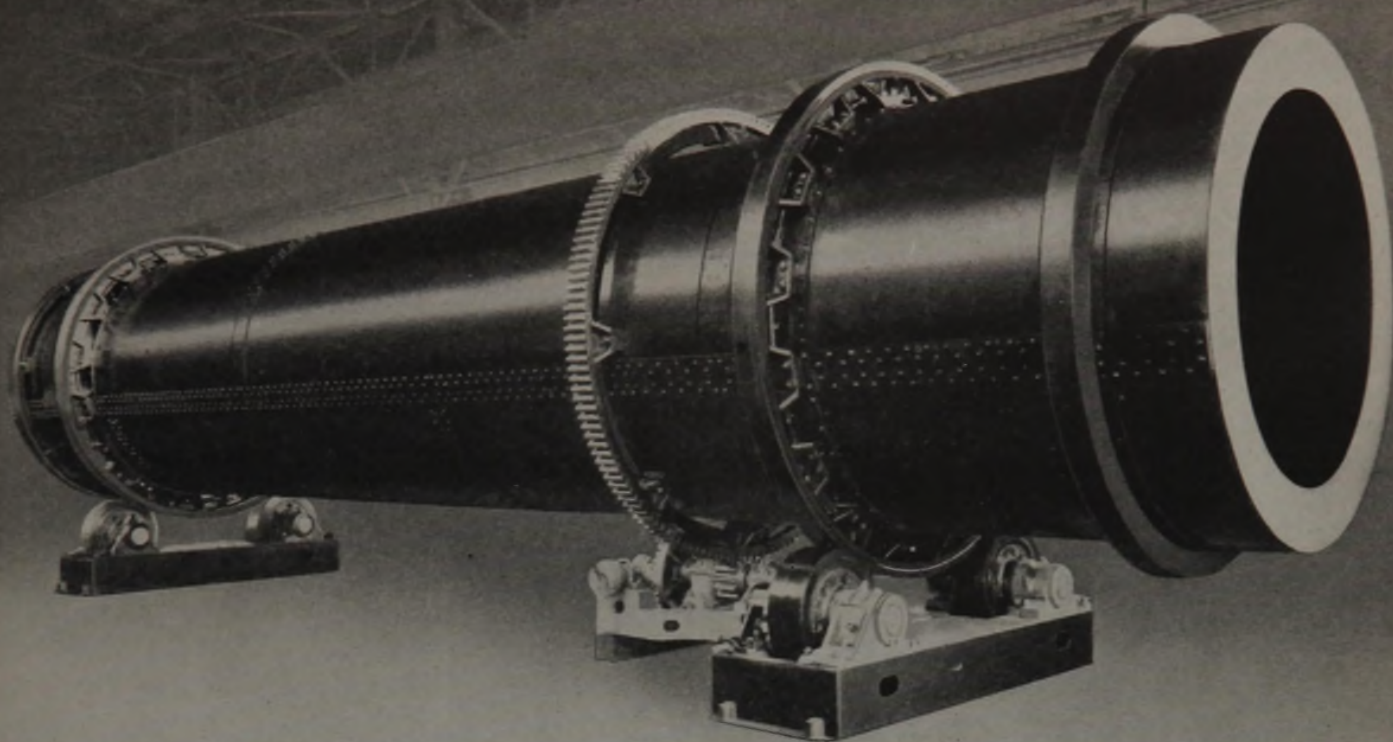
Planetary Spur Gear, Medium and Heavy Duty Worm Gear, Generated Continuous-Tooth Herringbone Gear and Motorized Speed Reducers, in types to drive up, down, horizontally or at an angle, Cut Spur, Straight and Spiral Bevel, Mitre, Spiral, Worm, Internal, Helical and Herringbone Gears in all sizes and of all materials, Sprocket Wheels, Racks, Flexible and Universal Couplings.

**IN APPRECIATION . . .** It is very gratifying to publicly acknowledge our appreciation of receiving the Army-Navy "E" Production Award . . . this ensign and lapel insignia is a testimonial to the mutuality of the cooperation with . . . and the understanding of . . . our employees and management. This cooperative understanding has been productive of successful attainments that have resulted in a schedule maintenance and a quality to our products that make us proud in knowing that after 55 years of making all types of gears and gear reducers that we have again been given the opportunity of serving our country. Lastly . . . may we express extreme appreciation of the combined efforts of our employees, our suppliers, our executive control and management . . . and we solemnly pledge to do all possible to maintain and perpetuate this record of successful achievement during and after this emergency.

**D. O. James** MANUFACTURING CO.

ESTABLISHED  
 1888

1140 W. MONROE STREET CHICAGO  
 Over 55 Years Making All Types of Gears and Gear Reducers



# *Perhaps* YOUR DRYER PROBLEM WILL BE LIKE K-1134

● File No. K-1134 was started when a far-distant company wrote—"What can you do about this problem?" From that point on things happened!

Samples of the material were sent for—received—and subjected to exhaustive tests. All factors, including those of dust, corrosive galvanic action, and sensitivity to heat were carefully studied—checked—rechecked. A Bartlett-Snow special style "D" Dryer, fabricated in part of stainless clad—in part of solid stainless, was recommended—purchased—shipped. Since then, within a period of less than two years, a duplicate of the first dryer was purchased—then 4 more, then 6 more of slightly larger size, making 12 in all.

It's luck, you say, that enables these Bartlett-Snow indirect heat dryers to minimize the dust problem,

to reduce the moisture content of these small carbon particles from 50% to less than 1%—and overcome the galvanic action so that the desired quantity and quality of finished product is secured without damage to the material or the equipment? Not at all. It's technical approach—the use of formulas developed and used only by Bartlett-Snow heat engineers—their ability to study a problem and solve it . . . the plus value—your assurance that the equipment recommended by these experts will be suited exactly to the problem to be met. Let Bartlett-Snow engineers help in solving your heat engineering problems.

**THE C. O. BARTLETT & SNOW COMPANY**  
6207 HARVARD AVENUE, CLEVELAND, OHIO  
30 Church St., New York      First Nat'l. Bank Bldg., Chicago

# BARTLETT-SNOW

DRYERS • CALCINERS • COOLERS • KILNS

Also complete materials handling facilities to meet any requirement  
One contract • One guarantee of satisfactory performance • Unit responsibility

Screw Feeders



Rotary Crushers



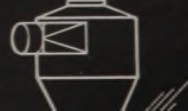
Bucket Elevators



Belt Conveyors



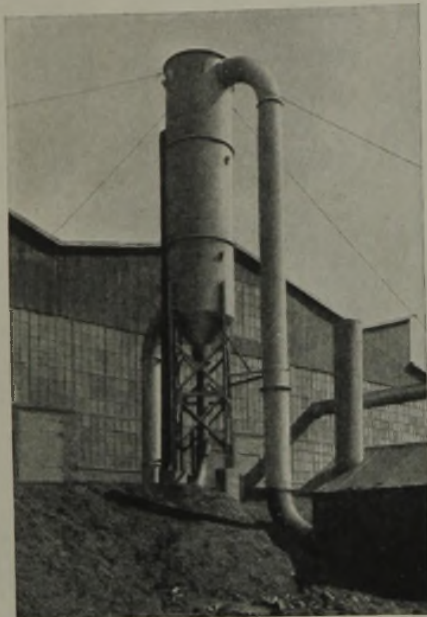
Dust Collectors



Pressure Vessel

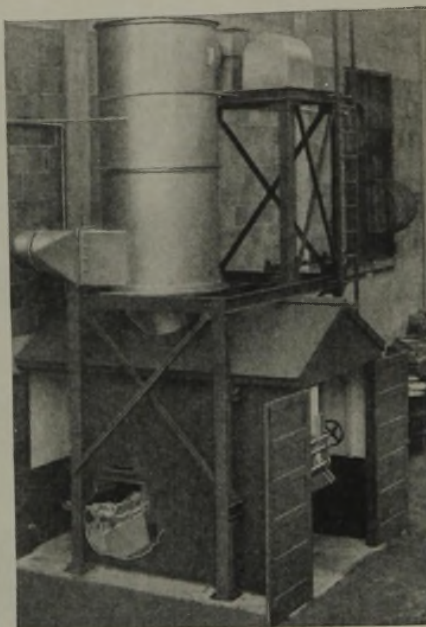


# Multi-Wash Dependability Wins in Three More Plants



## 1. Controlling Odors in a Chemical Plant

This 4,500 c.f.m. Schneible Senior Collector is used for condensing steam to remove an odor arising from a specialized chemical process. The cooling and washing medium is recirculated. The workers in this plant are no longer handicapped by the noxious odor.



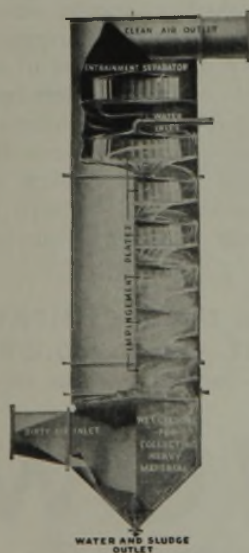
## 2. Controlling Fumes in a Printing Ink Plant

The Schneible Multi-Wash Collector System pictured, installed in a large printing ink plant, eliminates a plant and community nuisance and at the same time recovers valuable oils from the fumes exhausted from varnish kettles.



## 3. Controlling Dust in a Lime Plant

A 10,000 c.f.m. Schneible Multi-Wash Collector removes lime dust from the air exhausted from the hydrator, baggers and other operations in a large lime plant. Working conditions in this establishment were substantially improved and salvaged dust returned to the process system.



Dependable Multi-Wash Collector Systems have scored victories over every dust, odor and fume condition encountered in industry, helping to maintain peak production and salvage valuable by-products in many process plants. They are recovering valuable materials to an extent which often pays for the installation.

Schneible equipment embodies the correct wet-wash principle, which has proved adequate in the toughest cases. There are only two moving parts in the system — the fan and the pump. No attention is required and operation is remarkably maintenance-free. There are no screens, bags or filters — no parts to break, burn, clog or rapidly wear. Water or other cleansing liquid used can be recirculated again and again.

Our engineering staff is prepared to give you real aid in the solution of your dust and fume problems. Write us about them.

### CLAUDE B. SCHNEIBLE COMPANY

3959 Lawrence Avenue

Chicago, Illinois

Engineering Representatives in Principal Cities



# SCHNEIBLE

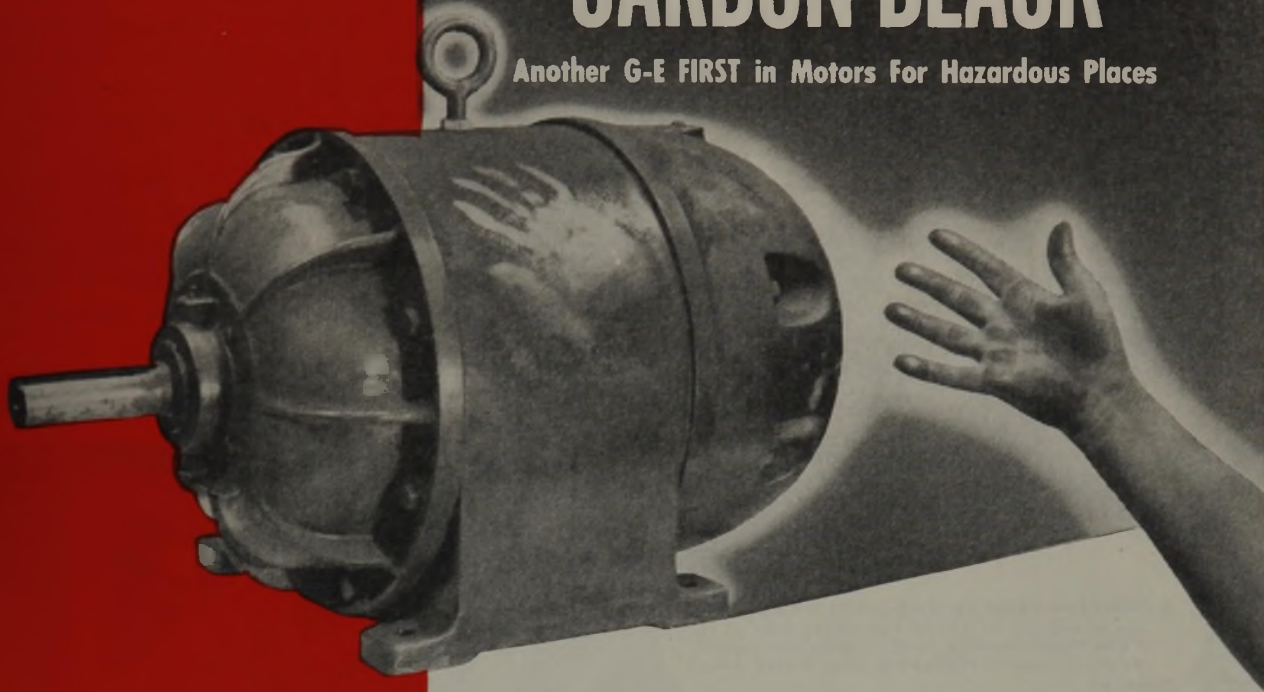
DUST, ODOR AND FUME CONTROL EQUIPMENT



Now... Listed by  
Underwriters' Laboratories, Inc. for

# COAL DUST..COKE DUST CARBON BLACK

Another G-E FIRST in Motors for Hazardous Places



Name your hazard —  
this family  
can meet it

No single enclosed or explosion-proof motor is recommended for all types of hazardous service. General Electric has pioneered in producing a family of motors to meet the dangers of specific gases, vapors, liquids, and dusts. For some hazards, only G-E motors are listed by Underwriters' Laboratories, Inc. Our engineering staff can help you pick the *right* motor, control, and other auxiliary equipment for uninterrupted war production.

## New totally enclosed motors that meet Class II, Group F, combustible-dust hazards

As a part of its full line of motors for hazardous locations, General Electric can now supply motors specifically listed by the Underwriters' Laboratories to meet the dangers of combustible dusts included in Class II, Group F, of the National Electrical Code. Polyphase induction motors of this construction are available from 1 to 75 hp, single-phase types to 10 hp, direct-current types to 30 hp. Vertical motors and gear-motors are also included.

Dust-tight joints, including accurately rabbeted end-shield fits, plus a labyrinth seal and close-clearance bearing lips along the shaft, exclude dust from winding and bearings. External operating temperature at permissible overloads is well below the ignition point of the specified dusts. A one-piece, nonsparking fan (for fan-cooled sizes) assures effective cooling. Easy lubrication and servicing features are part of the well-planned design. For complete details, call or write your local G-E office. *General Electric Co., Schenectady, N. Y.*

BUILDER OF **TRI/CLAD** MOTORS  
REG. U.S. PAT. OFF.

GENERAL  ELECTRIC

# "Pilot Plant Pioneering" IS A HERSEY SPECIALTY

It is also a veritable goldmine from which valuable information and technical data has been compiled over a long period of time.

The Hersey Pilot Dryer assures every Hersey installation of a tested and sure performance... It provides the data from which new methods of drying are developed for well known products... from which original drying systems are designed and performance-tested for completely new products.

This "Pilot Plant Pioneering" is *free*—a service offered to all prospective users of Hersey Dryers. It is a service which "pays for itself", for we find that even if tests show that a certain product is not adaptable to a Hersey Drying System—invariably we have gained much information to add to our already large reserve of factual knowledge.

Send your Drying Problems to Experts. Write for our catalog and materials information sheet—now—today.



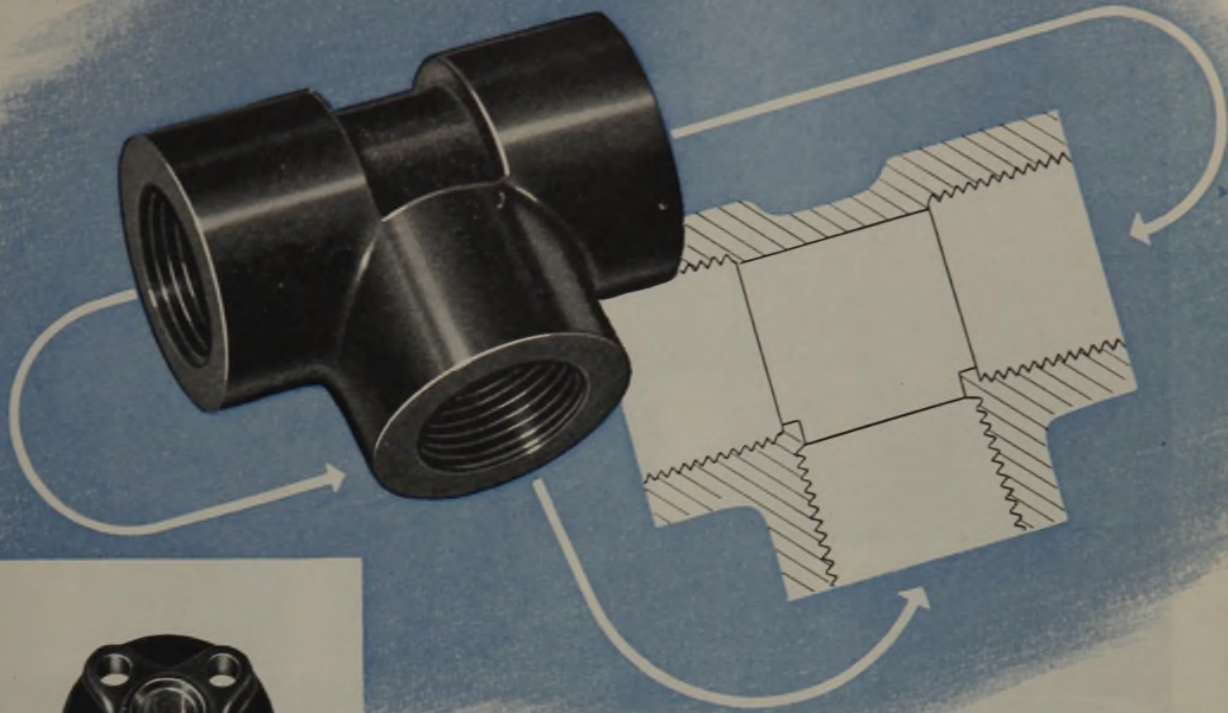
**A PROVING-GROUND FOR DEHYDRATION**

*As a result of tests conducted in this Pilot Dryer during 1942, highly successful dryers were designed and built for:*

**Bagasse  
Sweet Potato Meal  
Starch  
Cranberry Waste  
Silica Gel  
Sliced Potatoes**

*and several other materials which, for the duration, must remain a military secret.*

**HERSEY MANUFACTURING COMPANY DRYING MACHINERY DIVISION**  
E AND SECOND STREETS, SOUTH BOSTON, MASS.



## New Companions for SARAN PIPE

Saran pipe fittings—expertly designed and skillfully molded—provide the latest news in the continuous story of saran developments. Here is another example of the functional use of this exceedingly versatile plastic material—new companion pieces for saran pipe which possess the same outstanding advantages as the pipe itself.

Saran fittings are based on extra heavy iron pipe designs. They possess the same high degree of chemical resistance found in saran pipe and have comparable pressure values. Their successful use in fields requiring extraordinary resistance to corrosive action is attested to by difficult installations in chemical plants.

Saran fittings are thoroughly practical in both design and in application. Together with saran pipe, they form a combination that offers American industry a superior replacement product for many strategic war materials and are an addition to the standard line of building, piping and plumbing equipment.

**THE DOW CHEMICAL COMPANY, MIDLAND, MICHIGAN**

New York • St. Louis • Chicago • Houston • San Francisco • Los Angeles • Seattle

### FUNCTIONAL DESIGN PROVIDES MAXIMUM EFFICIENCY

Saran pipe fittings, ranging from tees to couplings, 90° elbows, flanges and caps, are designed to provide maximum efficiency. Though patterned after standard equipment established in the field, these fittings are made to take full advantage of saran's unusual properties. Flanges, for example, are made with a convex face—which eliminates the need for gaskets. All saran fittings are exceptionally light compared to metal fittings. They employ standard pipe thread—accurately engaging the threads cut on saran pipe with standard tools.

# SARAN

DOW PLASTICS



CHEMICALS INDISPENSABLE  
TO INDUSTRY AND VICTORY



## Take a Basket of Manhours to Your Future Market

There are big savings in centrifugal baskets engineered by AT&M, savings in time and floor space which may revolutionize your costs in the peacetime future.

Many manufacturers, spurred by war production needs, have made substantial savings in manhours and time of process by installing compact centrifugals instead of slower filters or settling tanks, costly ovens or less efficient kiers and autoclaves.

Anything that can be extracted by a filter can be centrifuged, faster, without pauses for cleaning, without double filtrations for superfine substances, without loss of material being filtered.

For example, on a dehydration job, A T & M saved 70% of drying time for one customer — and made available a

\$35,000 machine formerly tied up with drying. *You* may get similar savings in drying, filtering, impregnating or precipitating processes.

Many cases involving lowered costs and increased production have resulted from the purchase of standard A T & M machines. However, A T & M engineers have often adapted centrifugal force to difficult jobs — designing special frameworks, combining operations in special baskets, often eliminating certain troublesome operations entirely.

Now heavily engaged in war production, A T & M recognizes, with you, the importance of planning for peace, in the light of postwar conversion needs. Write us—we keep strict confidence. American

Tool & Machine Co., 1415 Hyde Park Avenue, Boston, or 30A Church Street, New York, N. Y.

### PREPAREDNESS FOR PEACE

... is the second essential for victory. Let us consult with you, as far as national needs permit us, on improvement of processes involving:

DEHYDRATION	IMPREGNATION
FILTRATION	EXTRACTION
PRECIPITATION	COATING

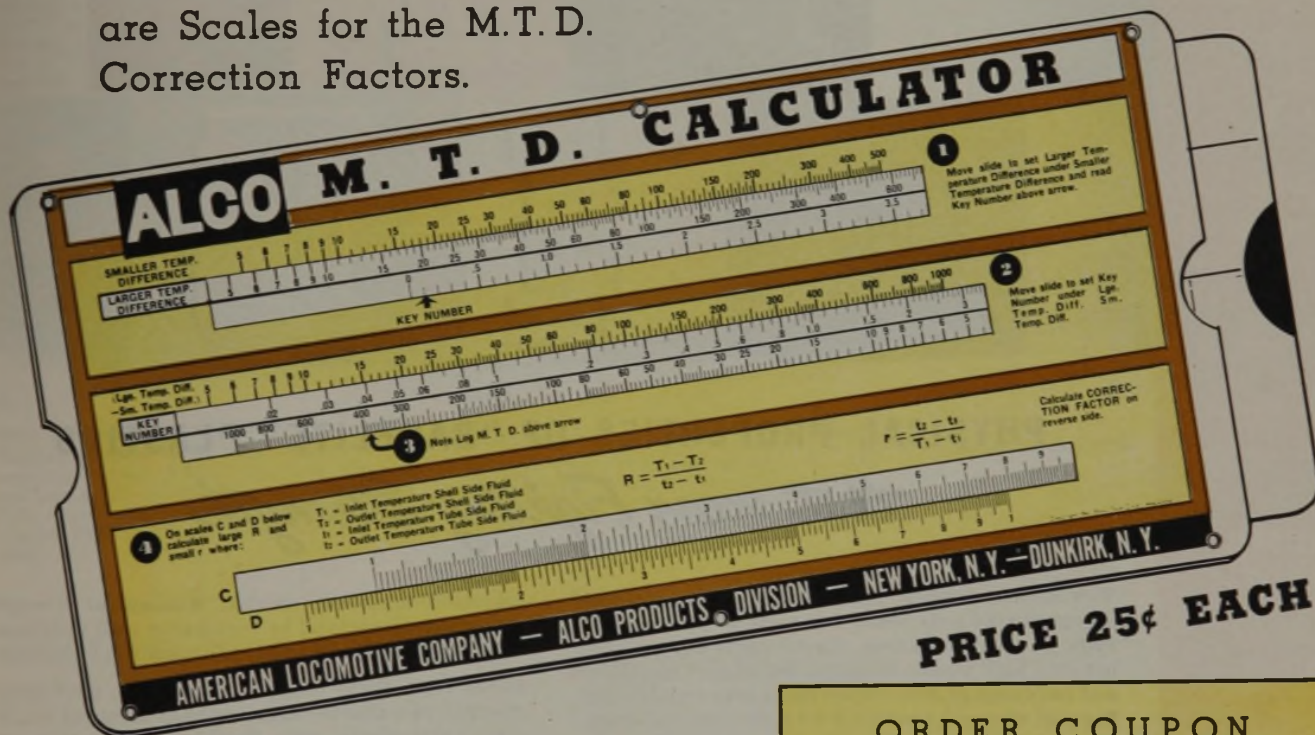
**A T & M CENTRIFUGALS SAVE TIME AND SPACE**

# ALCO

## M. T. D. CALCULATOR

SOMETHING NEW FOR ENGINEERS - AN AID IN THE ESTIMATING OF HEAT EXCHANGER SURFACE

On the Front Side of the Calculator are Scales for the Calculation of the Logarithmic M.T.D. As well as C-D Scales for Multiplication and Division. On the Reverse Side are Scales for the M.T.D. Correction Factors.



**PRICE 25¢ EACH**

Steam Generators  
 Heat Exchangers  
 Feed Water Heaters  
 Diesel Oil & Water Coolers  
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Alco • Fin Heat Exchangers  
 Pre-Fabricated Piping  
 Electric Welded Steel Pipe  
 Pressure Vessels  
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For Complete List Write for Bulletin 1030

**AMERICAN LOCOMOTIVE COMPANY**  
**ALCO PRODUCTS DIVISION**

NEW YORK, N. Y.

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 for the Enclosed ..... Cents.

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IMPACT  
STRENGTH



FLEXURAL  
STRENGTH



TENSILE  
STRENGTH



DIMENSIONAL  
STABILITY



HARDNESS



ABRASION  
RESISTANCE



## PHYSICAL PROPERTIES OF "BAKELITE" PLASTICS

*that mean Fighting Strength*

THE SEVERE SERVICE under which equipment must operate today puts heavy demands on plastic materials. In many instances, plastic parts must possess not only high tensile strength, but impact resistance and hardness as well. Other parts may require high flexural strength combined with dimensional stability and wear and abrasion resistance. Thus the designer and engineer, in selecting plastics, must constantly keep in mind the correct balance of all these physical properties.

The problem may be the selection of a BAKELITE Plastic material possessing high impact resistance, with tensile or flexural strength requirements running a very close second. On the basis of impact resistance alone, it might seem advisable to choose a high-impact BAKELITE Phenolic Molding Material. But such a material might not meet tensile strength requirements! On the other hand, a general-purpose BAKELITE Phenolic that possesses the required tensile strength can have as little as 1/18 the shock resistance of the high-impact material! In such a case, final choice of material may lie between the two extremes.

The design of the part has a lot to do with its ultimate strength characteristics. Frequently, BAKELITE Molding Boards and Blanks are used in conjunction with general-purpose phenolic plastics to provide reinforcement around inserts, and at corners, shoulders, and other points that are

subjected to severe service. Mechanical strength may also be improved by increasing wall thickness, or by making adjustments in fabricating techniques.


Apart from these physical properties, mechanical strength can also be interpreted in terms of *toughness*, particularly with flexible plastics that are not usually tested for impact resistance. *Mechanical fatigue* may also become a major problem where plastics are placed under load, or are subjected to repeated blows, or to continued flexing.

On the facing page are presented the outstanding physical properties of those BAKELITE Plastics of primary importance to war production. Later messages will deal with the chemical, electrical, and thermal properties. For more detailed information write for a copy of Booklet 27—"A Simplified Guide to BAKELITE Plastics."

BAKELITE CORPORATION, 30 E. 42nd St., New York  
Unit of Union Carbide and Carbon Corporation



# BAKELITE

The word "Bakelite" and the  Symbol are registered trade-marks identifying products of Bakelite Corporation

PLASTICS DIVISION

**Thermosetting General-Purpose Phenolics**

These materials provide well-balanced combinations of dimensional stability and other physical properties suitable for everyday requirements. *Impact strength:* 0.26 to 0.40 foot-pounds per inch of notch (Izod). *Tensile strength:* 6,500 to 8,500 pounds per square inch. *Flexural strength:* 8,800 to 13,000 pounds per square inch.

**Thermosetting Shock-Resistant Phenolics**

Four types, offering a wide range of physical properties. All types are dimensionally stable, and resistant to wear and abrasion. Depending upon type, *impact strength:* from 0.46 to 5.4 foot-pounds per inch of notch (Izod); *tensile strength:* from 5,300 to 8,500 pounds per square inch; *flexural strength:* from 6,300 to 11,000 pounds per square inch.

**Thermosetting Phenolic Molding Boards and Blanks**

These are medium-high, impact materials that may be used in molds built for general-purpose phenolics. Can be used alone, or with other

plastics to provide reinforcement at vital points. Supplied as board stock or as blanks approximating shape of finished part. Also sold in diced form suitable for automatic preforming. Depending upon type, *impact strength:* from 1.6 to 2.0 (with grain) and 0.6 to 0.9 (against grain) foot-pounds per inch of notch (Izod); *tensile strength:* from 3,000 to 11,000 pounds per square inch; *flexural strength:* from 8,400 to 25,000 pounds per square inch.

**Special Phenolics**

This group comprises a variety of dimensionally stable, thermosetting materials, for special requirements of heat resistance, low power factor, chemical and water resistance, low friction coefficient, opacity to X-rays, and transparency.

**Thermosetting Ureas**

Most color stable and hardest of all thermosetting plastics. *Impact strength:* from 0.30 to 0.36 foot-pounds per inch of notch (Izod); *tensile strength:* from 9,500 to 12,000 pounds per square inch; *flexural strength:* from 10,000 to 14,000 pounds per square inch.

**Thermoplastic Cellulose Acetates**

Two types—Class I, general purpose, for compression and injection molding, and Class II, heat- and water-resistant, for injection molding only. Both types noted for high impact strength, toughness, and wide color range. *Impact strength:* from 1.4 to 4.0 foot-pounds per inch of notch (Izod); *tensile strength:* from 2,500 to 9,500 pounds per square inch; *flexural strength:* from 5,000 to 15,000 pounds per square inch.

**Thermoplastic Polystyrenes**

Outstanding in dimensional stability, chemical resistance, and dielectric qualities. For compression as well as injection molding. Supplied as crystal-clear material, and in transparent and translucent colors. *Impact strength:* from 0.40 to 0.70 (compression-molded), 0.8 to 1.2 (injection-molded) foot-pounds per inch of notch (Izod); *tensile strength:* 5,500 to 6,500 (compression), 6,500 to 7,000 (injection) pounds per square inch; *flexural strength:* 6,500 to 7,500 (compression), 14,000 to 19,000 (injection) pounds per square inch.

**Physical Properties of Laminated Plastics made with "Bakelite" LAMINATING VARNISHES**

BAKELITE Laminating Varnishes are used in the production of paper-base and fabric-base laminated sheets, tubes, and rods. Laminated plastics made from these varnishes possess excellent dimensional stability, high impact, tensile, and flexural strength, and are extremely resistant to wear and abrasion. In addition, they offer an unusual combination of other properties such as high dielectric strength, resistance to corrosion, and immunity to water, brine, oil, ordinary solvents, most acids, and weak alkalis.

**Physical Values**

Tensile strength of standard paper-base grades ranges from 7,000 to 12,500 pounds per square inch; flexural strength (transverse), from 15,000

to 21,000 pounds per square inch; and compressive strength, from 22,000 to 36,000 pounds per square inch. For standard fabric-base grades, tensile strength ranges from 8,000 to 10,000 pounds per square inch; flexural strength (transverse), from 17,000 to 20,000 pounds per square inch; and compressive strength, from 35,000 to 38,000 pounds per square inch.

**Sheets, Rods, Tubes, Special Shapes**

Laminated sheet stock and gear stock is supplied by laminators and fabricators in various thicknesses and sizes. Tubing can be obtained in lengths from 36 inches, with I.D. from 3/16 of an inch to 72 inches. Larger tubing can be made for special requirements. Rods come in standard

lengths up to 48 inches, and in diameters from 1/8 of an inch to 4 inches. Special shapes are made to order.

**Special Types**

In addition, special laminated plastics have been developed for specific mechanical requirements. Molded-laminated plastics permit the manufacture of such unusually tough and wear-resistant products as heavy-duty bearings. Rubber-laminated plastics combine the rigidity and mechanical strength of laminated plastics with the vibration-absorbing qualities of the rubber interlayer. Tough, densified-laminated woods also are made possible by impregnating wood veneers with a laminating varnish and subsequently applying heat and pressure.

**Physical Properties of "Bakelite" BONDING MATERIALS**

**Phenolic and Urea Resin Wood Glues**

For bonding plywood and other wood products. Glue line is dimensionally stable under extreme conditions of heat, cold, moisture, and impact shocks. Bonded woods are resistant to mould growth.

**Resin Cements for Lamp Basing**

Because of their dimensional stability when subjected to heat, BAKELITE Resin Cements are used widely to set electric light bulbs and radio tubes in their metal or plastic bases. Mechanical shock or vibration does not impair the bond.

**Resin Cements for Bristle Setting**

A tough, tenacious bond for bristles used in brushes of all types is provided with BAKELITE Resin Cements. The bond obtained is unaffected by constant use, or by frequent cleaning in water or solvents.

**Bonding Resins for Glass and Mineral Wool**

To form glass, rock, and mineral wool into easily handled, dimensionally stable insulation batts, the fibers are bonded together with BAKELITE Resins. Heat cold, and moisture do not affect bonding strength.

**Bonding Resins for Abrasive Products**

Abrasive grit, used to form high-speed grinding and cut-off wheels is securely bonded with BAKELITE Resins. This tough, strong bond has made it possible to operate grinding wheels safely, at speeds considerably higher than with other bonds.

**Resins for Brake Linings**

Both woven and molded brake linings are processed with BAKELITE Resin for greater toughness, dimensional stability, and resistance to wear and heat.

**Physical Properties of SURFACE COATINGS made with "Bakelite" Resins**

BAKELITE Synthetic Resins, when formulated into protective coatings, provide such properties as durability, faster drying speed, toughness, hardness or flexibility, resistance to wear and abrasion, and resistance to water and chemicals.

**Phenolic Resins**

For fortifying paints, primers, varnishes, and enamels of all types. Outstanding are the paraphenyl-phenol type of resins BR-17000 and BR-254, which have established new standards of durability for government and industrial specification coatings. Numerous other BAKELITE Phenolic Resins are serving widely diversified coating requirements. Certain types are used to fortify non-phenolic coatings to improve performance.

**Dispersion Resins**

These resins provide coatings with an unusual combination of properties—extremely fast drying time and maximum resistance to moisture. Such coatings dry as fast as *one minute*, entirely by solvent evaporation, without need of baking treatment. Because they are non-oxidizing, they do not become brittle after long years of service. They are especially useful as primers for ferrous and non-ferrous metals, particularly aluminum and magnesium alloys.

**Baking Resins**

For hard, abrasion-resistant coatings for lining cans, drums, and tanks. Baked on immediately after application, they provide high resistance

to heat, chemicals, and moisture. Equipment need not be dismantled nor shipped out of the plant; the coatings can be applied, *right on the job*, by means of special, portable baking apparatus.

**C-9 Resins**

For coatings on cloth, paper, concrete, plaster, brick, plastics, wood, and metal, these versatile resins contribute many unusual physical properties. They are noted for their adhesion and long retention of flexibility. In wet scrub tests, water-emulsion paints made with them far exceed durability required in government specifications. Baking enamels based on them do not blister or flake even when immediately plunged into cold water after long baking.

**Physical Properties of "Bakelite" IMPREGNATING, SEALING, and CALENDERING MATERIALS**

**Calendering Resins for Cloth**

Cloth calendered with BAKELITE Resins gains added toughness with little or no sacrifice in flexibility. The resins impart a high order of resistance to water, chemicals, and heat.

**Resins for Wood Densifying and Stabilizing**

The many important advantages of wood are supplemented by high mechanical strength and excellent resistance properties when impregnated with BAKELITE Resins. In particular,

woods can be compressed into densified wood, known as "compreg," with specific gravity up to 1.37. On parallel-grained specimens, modulus of rupture can reach 38,000 pounds per square inch (with grain), and compressive strength 25,000 pounds per square inch (with grain). "Compreg" is fire retardant, has excellent aging properties, and is resistant to sulphuric and hydrochloric acid solutions.

**Sealing Solutions for Castings**

Castings ordinarily rejected for porosity and small blowholes are reclaimed by forcing

BAKELITE Sealing Solutions into the pores under pressure, and then baking. The sealing solution thus becomes exceedingly hard and tough, unaffected by hot or cold water, steam, oils, chemicals, or heat up to 400 deg. F.

**Impregnating Varnishes for Windings**

As protective coatings and insulating bonds for coils, armatures, and windings, BAKELITE Varnishes remain stable and hard despite elevated operating temperatures and high rotational speeds. Better mechanical strength is also obtained.



## Is Pluto the Last of the Planets?



Nobody knows. It is dangerous to predict a limit in any field of research or science. The very mysteries of space—substance—energy—life—are forever quickening the human impulse to new explorations. . . . And yielding new discoveries!

Take the energy we call *power*. Successively through its journey out of darkness, the world has seen power wrung from the muscles of man and beasts of burden; from winds, waterfalls, steam, electricity and chemistry.

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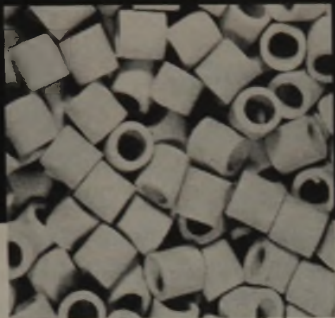
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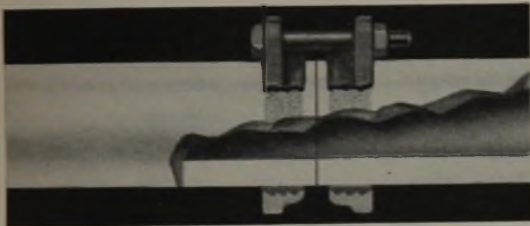
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2-Ethylbutanol	$(C_2H_5)_2CHCH_2OH$	102.17	148.9	1.1
n-Hexanol	$CH_3(CH_2)_4CH_2OH$	102.17	157.2	0.98
Polyethylene Glycol 200	$HO(CH_2CH_2O)_xH$	200 avg.	—	<0.01
Polyethylene Glycol 300	$HO(CH_2CH_2O)_xH$	300 avg.	—	<0.01
Polyethylene Glycol 400	$HO(CH_2CH_2O)_xH$	400 avg.	—	<0.01
“Dehydranone”	$CH_3COCHCOCH: C(CH_3)OCO$	168.06	Melts 108	<0.1



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## EDITORIALS

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### Scientific Regimentation

THE so-called Kilgore Bill (S. 2721 of the 77th Congress, proposing an "Office of Technological Mobilization") is, so to speak, back in Senatorial circulation under a new designation—S. 702. This time, however, it is in reality but a part of a more grandiose Kilgore proposal officially known as S. 607 and described by the author as "A Bill to establish an office of war mobilization, and for other purposes".

Senate Bill 607 proposes, among other things, to set up the following offices within the "Office of War Mobilization": (1) Office of Production and Supply, (2) Office of Manpower Supply, (3) Office of Scientific and Technological Mobilization, and (4) Office of Economic Stabilization.

S. 607 carries an appropriation of 400 million dollars and provides for a Director of the Office of War Mobilization and four Administrators appointed by the Director with the approval of the President, one Administrator, of course, for each of the four so-called offices the bill would create.

Senator Kilgore's S. 702 is in substance now simply an elaboration of a portion of the broader bill S. 607, although actually S. 607 and S. 702 are separate bills. The latter carries an appropriation of 200 million dollars, identical in this respect with S. 2721 which failed to reach the floor in the last Congress.

Possibly the Senator from West Virginia feels that "half a loaf is better than none at all", and therefore has submitted two bills, hoping to salvage something. Senate Bill 607, stripped of a lot of verbiage, would require the President to relinquish his present active role of supreme director of the entire war effort and to appoint a subordinate in his place to assume full command and responsibility. S. 607 would mean in substance that Mr. Roosevelt would turn over to Director X the full direction and authority over WPB, OPA, the Manpower Commission, ODT, OCD, and other war-time agencies. Briefly it would mean that the Nelsons, the Browns, the McNutts, the Byrnes and others in direct command of war agencies would report to an intermediary rather than to the President.

Frankly, there is little evidence to support the contention that the President is ready and anxious to dele-

gate any such extraordinary powers to any appointee even though S. 607 would permit him to designate the "Director" without the advice and consent of Congress. Certainly the President to date has shown no disposition to delegate such broad and all-inclusive authority to any one of his most trusted and intimate advisers, although he does possess sufficient emergency powers to do so. With production curves showing almost unbelievable achievements in the past 12 months and with our military forces registering important victories, it is hardly likely that Mr. Roosevelt for one set of reasons and Congress for a wholly different set will see eye to eye with the Kilgore proposal entirely to revamp at this time the make-up of the existing war agencies.

Senate Bill 702 (Office of Scientific and Technical Mobilization) is essentially the same as its predecessor, S. 2721 of the last Congress. To the chemist, to the chemical engineer, to all scientifically trained men and women, it is a potential threat of regimentation and goose-stepping in war and in peace.

The very wording of the "Declaration of Policy" constitutes a direct insult to the scientific minds of this country and is contrary to the actual facts, as any unbiased study will clearly show.

We do not have "an unassembled and uncoordinated state of information concerning existing scientific and technical resources"; we do know that there is no lack of "an adequate appraisal"; the war effort is not suffering because of "unplanned and improvident training, development, and use of scientific and technical personnel, resources, and facilities in relation to the national need", with the exception of the policy of drafting badly needed technically trained manpower into the armed forces.

In all fairness Mr. Kilgore should indicate specific instances to justify the claim that there have existed delays and "ineffectiveness in meeting the urgent scientific and technical problems of the national defense and essential civilian needs" and, further, should show irrefutable evidence that the bureaucratic setup which he proposes would indeed be a scientific spigot with the answers to all technical problems immediately on tap.

Page 4 of S. 702 states, "This Act may be cited as the 'Science Mobilization Act'". It should be cited as the "Science Regimentation Act".

The Kilgore Bill S. 702 proposes for the United States as complete a program of totalitarianism and state capitalism as exists anywhere in the world today.

### Licenses under Alien Patents

**I**MPEDIMENTS to the working by industry of vested alien-owned patents on the broad scale planned by the Alien Property Custodian are largely removed by a new form of license lately promulgated. Provisions appearing in early forms of license proposed by the Alien Property Custodian have so alarmed prospective licensees as to threaten the value anticipated from the seizures. One provision proved particularly objectionable to industry—namely, a requirement that a licensee open his own patents bearing upon the subject matter of the license to others licensed by the Custodian under the same patent. Although no official announcement has been made of the number of licenses containing such a clause issued to date by the Alien Property Custodian, that number is known to be disappointingly small—one report suggests twenty-five.

The new form of Patent License (Form APC-30, February, 1943) avoids this impediment. In contrast to most legal documents, its language and provisions are extraordinarily simple, as they should be to attract licensees.

On its face, the new license grants the licensee everything (for the initial license fee of \$50 which is not mentioned) and requires of him only that he mark his product and make an annual report of activity. The license is royalty-free, nonexclusive, and nontransferable. Two provisions are especially interesting: One disclaims any rights of the Custodian in the licensee's inventions or patents; the other forbids the use of the license in accomplishing any illegal act.

For purposes of condensation and simplification, the license omits qualifications contained in a separate publication of the Alien Property Custodian, "Patents at Work". This booklet sets forth the policy of the Custodian in considerable detail. In it are contained the details of procuring licenses, the fee charged in lieu of the royalty (\$50 plus \$5 for each additional patent), differences in conditions affecting patents seized from aliens as distinguished from enemy aliens, and much else needed to provide a background for the license itself.

One learns from the booklet that licensees are expected to spend time and money developing licensed patents, but only in the license itself does it appear that the Custodian can terminate it whenever he deems it in the national interest. One also learns that licenses are to be granted to "reputable" persons or firms without stated limitation. In effect this policy places

the vested patents virtually in the public domain until and unless the granted license be terminated by the Custodian.

Obviously, this power reserved to the Custodian to grant licenses and to terminate them will affect use of the patents only so far as it is arbitrarily exercised. Licensees should realize these limitations to the grant and plan accordingly.

### Collective Indexes

**C**OMPARISONS are admittedly "odorous", but when two nations are at war, sometimes interest, reassurance, and even portent are to be found in comparing activities outside the realm of warfare. Germany's *Chemisches Zentralblatt* publishes five-year collective indexes and has recently announced the appearance of Part III of a four-part collective index covering the period 1935-1939, inclusive. The announced price of the first three parts (authors, patents, and formulas) is RM 640 (not a special foreign price), which amounts to \$256 at the exchange rate which prevailed during several years preceding the outbreak of war in 1939, or \$160 at the old rate of several years ago when the mark was considered to be worth about a quarter. Since Part IV, still to appear, is to be devoted to subjects and the subject index is the biggest part of such a collective index, presumably the total price for a set of this five-year index will be between \$400 and \$500.

The publication of a collective index to an abstract journal devoted to the whole field of chemistry is a big and expensive undertaking, but contrast this German price and publication schedule with those for the Third Decennial Index to our own *Chemical Abstracts*. All five volumes of the Third Decennial Index were completed and distributed within two years after the completion of the period covered (1927-1936) and the price was \$100 per set. (Members of the German Chemical Society are permitted to buy the *Chemisches Zentralblatt* at an unannounced special price which may or may not be more generous than the 50 per cent discount allowed members of the AMERICAN CHEMICAL SOCIETY in the purchase of the Third Decennial Index, a discount made possible by the generous support of the project provided by American chemical industry.)

When it is borne in mind that the German index covers 5 years, whereas the American index covers 10 years, the favorable comparison is all the more striking (a ratio of about 10 to 1 on price).

The early appearance of indexes adds to their usefulness. In fairness it should be pointed out that the present German undertaking is proceeding during wartime, when manpower difficulties probably exist. German prices for scientific literature have always been high, largely owing to limited circulation. Publication during wartime is a sign of appreciation of the value of such indexes.

# Improvements in Concentrating Sulfuric Acid

M. J. Kalous

PARKFIELD WORKS, STOCKTON-ON-TEES, ENGLAND

**C**ONCENTRATED sulfuric acid is used in large quantities for the production of such nitro compounds as picric acid, nitrobenzene, pyroxylin, etc.; for the purification of mineral oils such as petroleum; for the manufacture of fatty acids, etc. These industries have the problem of disposing of waste products containing acid, not only for the economical recovery of as much of the acid as possible, but also to comply with regulations that prohibit the discharge of acid into sewers and of acid fumes into the atmosphere. In England the amount of acid fume admissible into the atmosphere is limited by law to the equivalent of 1.5 grains sulfur trioxide per cubic foot of stack exit gas.

In the manufacture of nitro compounds, the spent acid is diluted to about 70-75 per cent, and it has to be denitrated and concentrated before it is suitable for re-use in the processes. Undoubtedly petroleum refining produces the greatest quantity of acid waste (sludge acid), and various methods are employed for separating the acid according to the character of the sludge. In certain cases the treatment is live steam at 3 to 7 atmospheres pressure, and the separated acid ranges from 48 to 60 per cent; for heavy sludge an open-tank separation method may be preferred, and the separated acid contains perhaps 40 per cent. In each case the weak acid is concentrated and used again.

The following figures show the magnitude of the sulfuric acid concentration industry. The total consumption of sulfuric acid in the United States in 1941 amounted to about 6,000,000 metric tons (100 per cent), distributed approximately as follows:

Petroleum industry	800,000 tons
Coal products	500,000
Nitration	700,000
Total	2,000,000

Generally speaking, this consumption covers the make-up for acid which has been lost in the various processes; it is evident that important economies would derive from the reduction of acid losses.

## CONCENTRATION OF ACID FROM NITRATION

Dilute sulfuric acid can be concentrated after denitration by the application of heat indirectly in closed vessels under atmospheric pressure (pot still, flash-film type) or under pressures substantially lower than one atmosphere (Simonson-Mantius process), or by bringing the acid in direct contact with hot gases, such as products of combustion admixed with air (Kessler type, Chemico drum type, Gaillard tower).

Processes based on indirect heating have the advantage that no inert gases come in contact with the boiling strong acid, there is no formation of acid fog or acid mist, and losses

in a correctly designed and well-operated equipment dealing with acid free from organic matter should not exceed 0.5 per cent. The disadvantage of these processes is poor heat transfer from the hot products of combustion to the acid through the thick cast-iron walls of the pots or pipes, resulting in relatively small plant capacities. Another drawback is that the size of the pots which can be satisfactorily cast is limited, the largest having a capacity of about 20 tons sulfuric acid (100 per cent) per day. The life of the pots may be two years or less due to corrosion, effects of heating, and fractures.

In processes working under vacuum, large units can be built of brick-lined mild steel and strong acid can be obtained with fairly low acid losses. The disadvantages are the high cost of the heating medium in the form of live steam supplied from the outside, the cost of a large amount of water required to maintain a vacuum, and the low boiling point of acid under vacuum, which in most cases is not high enough to decolorize the acid.

In processes where acid is brought directly into contact with hot products of combustion and/or air, the heat transfer from the gases to the acid is good; consequently the size of equipment is relatively small for a given capacity compared with the indirectly heated systems. Large units (100 tons sulfuric acid per day or over) can be built of mild steel lined with lead and acid-resisting brick. The life of the equipment may be as long as ten years since the hot acid is in contact with high-quality acid-resisting brick. These processes have one great disadvantage, however—the formation of acid mist which is extremely difficult to deposit and which passes with the stack gases into the atmosphere, causing acid losses and a nuisance in the neighborhood. If the stack gases contain some sulfur dioxide due to decomposition of acid by organic matter, it cannot be recovered economically and must be considered as loss.

It is usual to remove the acid mist in electrostatic precipitators, but the separation is incomplete and the stack gases usually retain some acid mist which causes a severe nuisance if acid is worked to high concentrations. In practice sulfuric acid is not usually concentrated to higher than 92-93 per cent  $H_2SO_4$  by the process of direct contact with hot gases. There is an additional problem of maintaining electrostatic precipitators due to corrosion of electrodes and insulating seal boxes.

**Acid Mist Formation.** When hot inert gases come in contact with boiling strong acid, they become saturated with water vapor and sulfuric acid vapor. They flow in countercurrent to the weaker and cooler acid, and cause acid vapor to condense and the weaker acid to become heated. However, part of the acid vapor condenses so quickly that

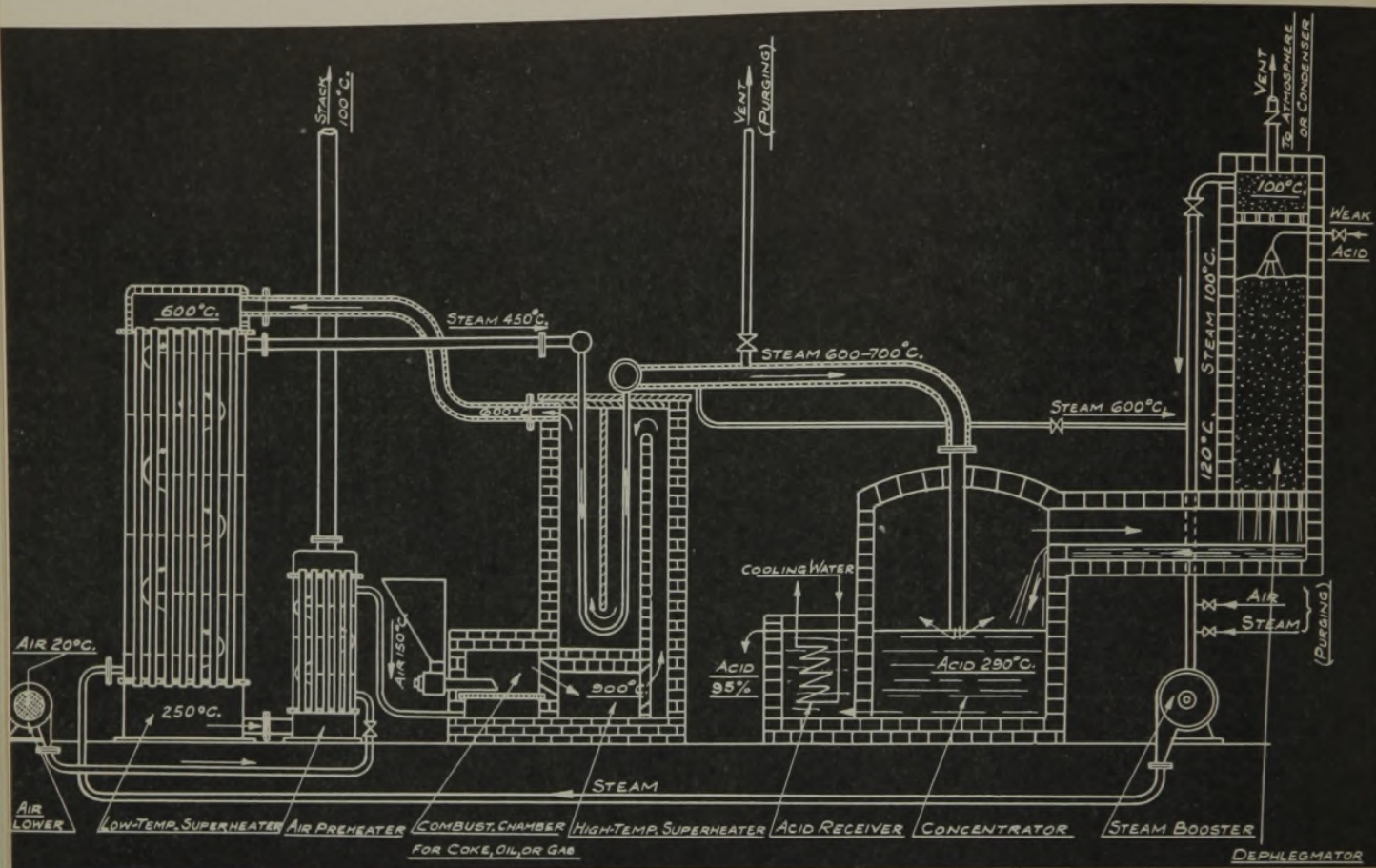


Figure 1. Concentrator with Tube-Type Superheater

acid droplets are formed, minute in one aspect, but of enormous size in comparison with the gas and water molecules among which they are suspended. As their movement is slow, they have little chance to meet water molecules (separated by many more gas molecules), to be absorbed, and to form large drops of weaker acid which could be easily separated.

In the pot still process there is no inert gas in contact with boiling acid; acid molecules can easily meet water molecules, acid vapor can condense in the form of weaker acid, and no acid mist forms in dephlegmators attached to the pot stills.

If heat could be transmitted directly to the acid by a hot gas in which the formation of acid mist is impossible, the advantages of both the pot still and the direct heating by gas processes would be achieved without any of the disadvantages. A suitable gas for this purpose is superheated steam<sup>1</sup>. It can easily be brought to a high temperature and, on parting with its superheat, can transmit heat efficiently to the acid by direct contact, while the formation of acid mist is not possible since no inert gas is present. Figure 1 illustrates one arrangement to apply the new process.

Steam is circulated by a steam booster between the dephlegmator, superheaters, and concentrator. In the superheaters the steam is heated to a temperature between 600° and 700° C. and the superheated steam is brought into direct contact with the acid in the concentrator; it thus gives up a large amount of its superheat and causes the acid to boil.

<sup>1</sup> Kalous, M. J., Brit. Patent 536322 (May 9, 1941); U. S. Patent Application 378,470 (filed Feb. 11, 1941); South African Patent 325, Iran Patent 801, Egyptian Patent 143 (1941); Canadian Patent 479,627, Australian Patent 114,755 (1942).

The steam and acid vapors leaving the concentrator flow countercurrent to the weak acid in narrow channels, the acid vapors condense, and the weak acid is heated and concentrated to a certain extent without the formation of acid mist, as there are no inert gases.

In the dephlegmator the condensing of acid vapors and the heating of weak acid continues, and the vapor leaving the top of the dephlegmator consists entirely of slightly superheated steam free of acid vapors, the partial pressure of sulfuric acid up to 140° C. being practically nil and free of acid mist. Any entrained acid droplets are removed in a droplet separator filled with ring packing. The vapor leaving the separator consists of steam only, and this is passed back to the superheater by the steam booster. An amount of steam corresponding to the dilution water evaporated from the weak acid can be released to atmosphere through a vent fitted with a nonreturn valve, or be condensed in a suitable condenser. The concentrated sulfuric acid flows to a receiver-cooler.

The superheaters may be heated by products of combustion of gas, oil, or solid fuel; air required for combustion can be preheated by waste gases leaving the low-temperature superheater. Steam and air connections are provided for purging the equipment and for starting up. A by-pass line for hot steam facilitates the adjustment of steam temperature in the steam booster in order to prevent steam condensation and corrosion of the booster.

Superheated steam in direct contact with dark colored, boiling, strong sulfuric acid exerts a decolorizing effect on the acid which is an additional advantage of the process.

**Heat Requirement.** It is important to know the degree of steam superheat required for a given acid concentration. The temperature of superheated steam in equilibrium with boiling sulfuric acid of, say, 95 per cent  $H_2SO_4$ , can be calculated as follows:

Let  $t$  = temperature of steam  
 $x$  = evaporated water from acid  
 $290^\circ C.$  = boiling point of 95 per cent acid

The vapors in equilibrium with boiling 95 per cent acid contain about 55 per cent  $H_2SO_4$  and 45 per cent  $H_2O$  by weight, or 18.3 per cent  $H_2SO_4$  and 81.7 per cent  $H_2O$  by volume. For each kg. of superheated steam the total water vapor over the acid =  $1 + x$  kg. and

$$\text{evapd. } H_2SO_4 = (1 + x) \frac{55}{45} = 1.22 (1 + x) \text{ kg.}$$

$$\frac{1.22 (1 + x)}{x} = \frac{95}{5}; x = 0.069 \text{ kg. evapd. } H_2O$$

$$1.22 (1 + x) = 1.3 \text{ kg. evapd. } H_2SO_4$$

heat of evapn. of  $H_2O$  ( $300^\circ C.$ ) = 348 Cal./kg.  
 heat of evapn. of  $H_2SO_4$  ( $300^\circ C.$ ) = 122 Cal./kg.

One kg. of steam (specific heat 0.5) must supply

$$0.069 \times 348 = 24.0 \text{ Cal.}$$

$$1.3 \times 122 = 158.5 \text{ Cal.}$$

$$\text{Total} = 182.5 \text{ Cal.}$$

$$(t - 290) 0.5 = 182.5$$

steam temperature  $t = 655^\circ C.$

The temperatures of steam calculated for equilibrium with boiling acids of various strengths are:

Acid Strength, %	Approx. Steam Temp., ° C.
96	780
95	655
94	555
93	485
92	420

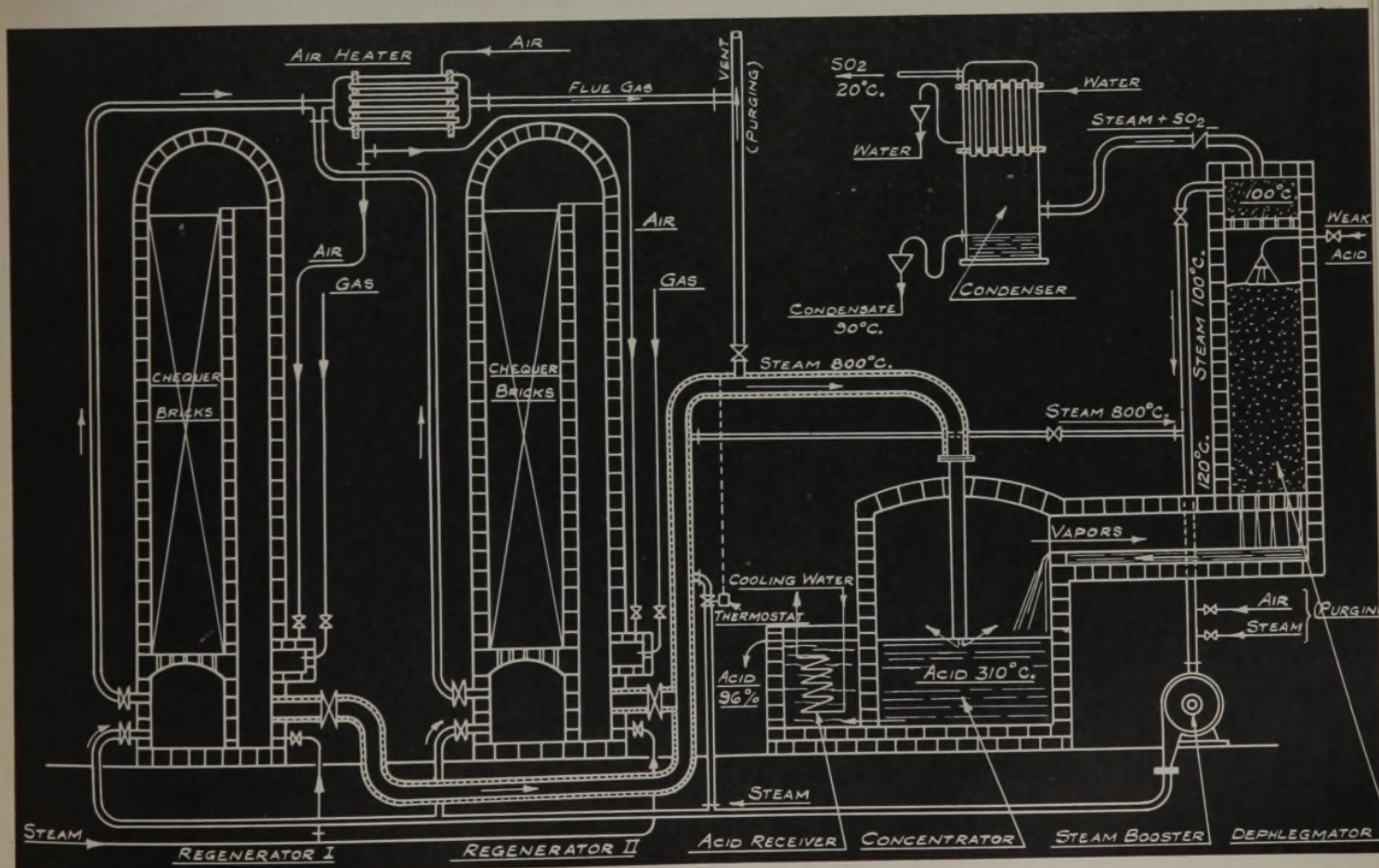
The high steam temperatures for concentrations over 95 per cent  $H_2SO_4$  could be achieved in superheaters working on the regenerative principle of direct heat exchange on refractory materials (Figure 2).

The quantity of heat required for heating weak acid, evaporating water, and dissociating water from the acid is constant; the fuel consumption must, therefore, be similar for all processes, provided the stack gases leave the equipment at equal temperatures. In the new process, however, combustion gases do not come in contact with the acid; they need not, then, be particularly clean but can be obtained by solid fuel firing. Water is used in all processes for cooling the concentrated acid in receivers, and its consumption is identical in all cases. Power consumption will be similar to that of the direct heating by gas processes.

**CONCENTRATION OF ACID FROM OIL PURIFICATION**

The usual oil refining sludge contains a large amount of oil which must be separated. This is achieved by diluting with water and agitating with steam and air; alternatively, the sludge and water, properly proportioned, may be pumped

Figure 2. Concentrator with Regenerator Superheater



into a vessel in which the mixture is treated with steam at 3 to 7 atmospheres pressure, the acid oil and sludge acid being discharged continuously. In some cases the sludge acid, after the separation of acid oil and tar, is subjected to heat treatment under pressure for the purpose of eliminating hydrocarbons. Despite this treatment, the separated acid is often contaminated with carbonaceous matter which, at the high temperature during concentration, tends to decompose some of the sulfuric acid and liberate sulfur dioxide. As the separated acid may contain up to 1.25 per cent hydrocarbons and these can destroy (in the extreme case) up to nineteen times their weight of sulfuric acid, it is possible for acid losses to rise as high as 24 per cent.

In processes operating by direct contact of acid with hot inert gases, when concentrating from 40 to 95 per cent  $H_2SO_4$ , the stack gases contain about 80 moles  $H_2O$  to 276 moles air plus combustion gases per 1000 grams  $H_2SO_4$  (100 per cent). In the superheated steam process 80 moles  $H_2O$  are evaporated from the weak acid and leave the dephlegmator.

Assuming the maximum acid decomposition through action of hydrocarbons to be 24 per cent, the liberated sulfur dioxide would be 2.45 moles and the stack gases, even with this considerable decomposition of acid, would contain only

$$\frac{2.45 \times 100}{276 + 80 + 2.45} = 0.69\% \text{ SO}_2 \text{ by vol.}$$

which at such low concentration could not be used for manufacturing sulfuric acid and would be lost.

Using superheated steam, however, the conditions are different. Steam leaving the concentration equipment and containing

$$\frac{2.45 \times 100}{80 + 2.45} = 2.97\% \text{ SO}_2 \text{ by vol.}$$

can be condensed in a reflux cooler placed on top of a separating column (Figure 2). The temperature at the bottom of the column is maintained near  $100^\circ \text{C}$ ., and that in the reflux cooler close to  $20^\circ \text{C}$ ., so that effective separation of sulfur dioxide from water is achieved. Water at nearly  $100^\circ \text{C}$ . will leave the column practically free of sulfur dioxide and concentrated sulfur dioxide gas will leave the cooler at approximately  $20^\circ \text{C}$ .; it is available at little more than the cost of the cooling water if needed for sulfuric acid manu-

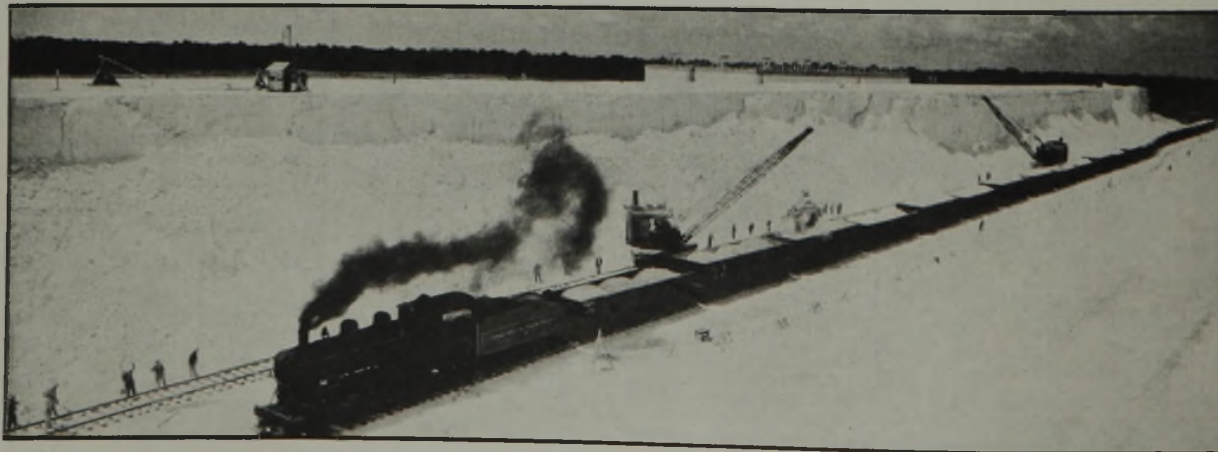
facture. Losses by mist formation and decomposition of acid by action of oil can be reduced to negligible figures in the superheated steam process; only those remain which are connected with the separation of sludge acid from acid oils and tar.

**Design and Construction.** Steam can be superheated on the principle of continuous heat exchange as indicated in Figure 1, perhaps preferably with a superheater in two sections. The low-temperature heat exchanger in which the temperature is raised to  $450^\circ \text{C}$ . can be of mild steel, tube-and-shell construction. No condensation of vapors will take place in this temperature range, and steel is not affected by dry steam. The high-temperature exchanger is made of special steel in U-tube form, steam passing through the tubes with temperature increase from  $450^\circ$  to a maximum of  $700^\circ \text{C}$ . The tubes are heated by combustion products at, say,  $900^\circ \text{C}$ ., so that the temperature of the wall will not exceed  $800^\circ \text{C}$ ., which is not excessive for stainless steel. The loosely hanging tubes can expand individually without causing trouble through unequal expansion.

An alternative means of superheating steam would be to use two heat regenerators (Figure 2), similar in design to those widely employed for blast furnaces (hot blast stoves). While one regenerator is being heated by passing hot products of combustion through it, the other is being cooled by passing the circulated steam through; the steam becomes superheated at the same time. The flow through the regenerators is reversed at regular intervals so as to maintain the heat stored in refractory material inside the regenerators.

The concentrator and dephlegmator can be of mild steel construction, lined with asbestos, lead, and acid-resisting brick. The steam booster can be made of steel for hot runs, or alternatively of acid-proof iron or homogeneously lead-lined steel for runs at about  $100^\circ \text{C}$ . The cooler for steam which contains sulfur dioxide can be made of lead.

**Estimated Cost.** A large unit using the new method costs slightly less, as compared with direct heating by gas methods or with vacuum methods, and considerably less than an equivalent number of pot still units. Estimated operating costs are similar to those of direct heating by gas methods; the new method has the advantage of producing stronger acid with negligible acid losses. As compared with vacuum methods, the operating costs of the new method are lower on account of fuel being much cheaper than the live steam supplied from outside.



Courtesy, Texas Gulf Sulphur Company

*The United States Has the World's Largest Deposits of Sulfur, the Raw Material for Sulfuric Acid*



# Design of Solid-Fluid Heat Exchangers

*A method is presented for solving the problem of continuous, parallel, or countercurrent exchange of heat between solid particles and a fluid. It takes into account the resistance to heat transfer by conduction*

*within the solids. The particles are assumed spherical and therefore a modification of the Schmidt method for graphical solution of problems in conduction can be applied.*

**T**HE exchange of heat between solid particles and a flowing fluid is an important industrial problem. The solids may either be fixed in place, as in the checker-brick regenerator and in fixed-bed catalytic processes; or the solids may move continuously through the exchanger. The latter type is exemplified by the preheating zone of the lime kiln, the heating zone of the charge to a blast furnace, and by catalytic processes which involve heat exchange to catalyst particles of relatively large size. Unsteady-state heat transfer in fixed-bed regenerators has been extensively treated (5); but less is known about continuous exchangers.

The problem to which this discussion is confined is that of the continuous countercurrent or parallel exchange of heat between solid particles and a fluid. Heat is transferred by forced convection between solid and fluid, and by conduction within the solid. There are no heats of reaction or phase changes within the exchanger. Although few actual processes conform with these conditions, the solution may be applied in many cases to give an approximate idea of the design.

The usual assumption made in solving this problem is that the conductivity of the solid is sufficiently high or the particles are small enough so that the temperature of any one particle may be assumed uniform at all times. If the heat transfer coefficient between fluid and solid is constant throughout the exchanger, the familiar derivation (12) for forced-convection continuous exchangers may be applied, leading to the equation:

$$Q = hA \frac{(T - t) - (T_o - t_o)}{\ln \frac{T - t}{T_o - t_o}} \quad (1)$$

Furnas (4) discussed the problem from this point of view, and derived equations for the solid and gas temperatures at any level in the exchanger. Although he did not state his results explicitly in the form of Equation 1, it is readily shown that they can be converted to that form.

There seems to be no experimental verification of this equation in the literature. It is much simpler to experiment with a batch of solids than to set up a continuous exchanger, so that the work has been confined to batch heating and cooling of beds of solid particles.

The most extensive work is that of Furnas (2, 3, 4), who determined the rate of heating and cooling with air of beds of broken iron ore, coke, coal, limestone, iron balls, and blast furnace slag. This work covered a range of particle size from

0.4 to 7.3 cm. and superficial air velocities up to 6.5 feet per second. More recently, Saunders and Ford (7) performed careful

experiments with beds of glass, lead, and steel spheres up to 0.25 inch in diameter, heated by air at superficial velocities up to 2 feet per second.

Both these investigations were performed under conditions which permitted application of the predictions of Schumann (10) concerning a batch of solids heated by gas. He assumed negligible resistance to heat transfer within the particles, and derived equations for the solid and gas temperatures at any level at any time after the beginning of heating. He presented the results in the form of dimensionless plots, which were later extended by Furnas (4) to cover a larger range. In using these curves it was necessary to find by trial and error a value of  $h$  which made the data fit one of the curves. The heat transfer coefficient was uniquely determined in this way, since only one value could be found for a given set of conditions which made the data fit any curve well. On this basis both investigators concluded that Schumann's plots could be used as a basis for design.

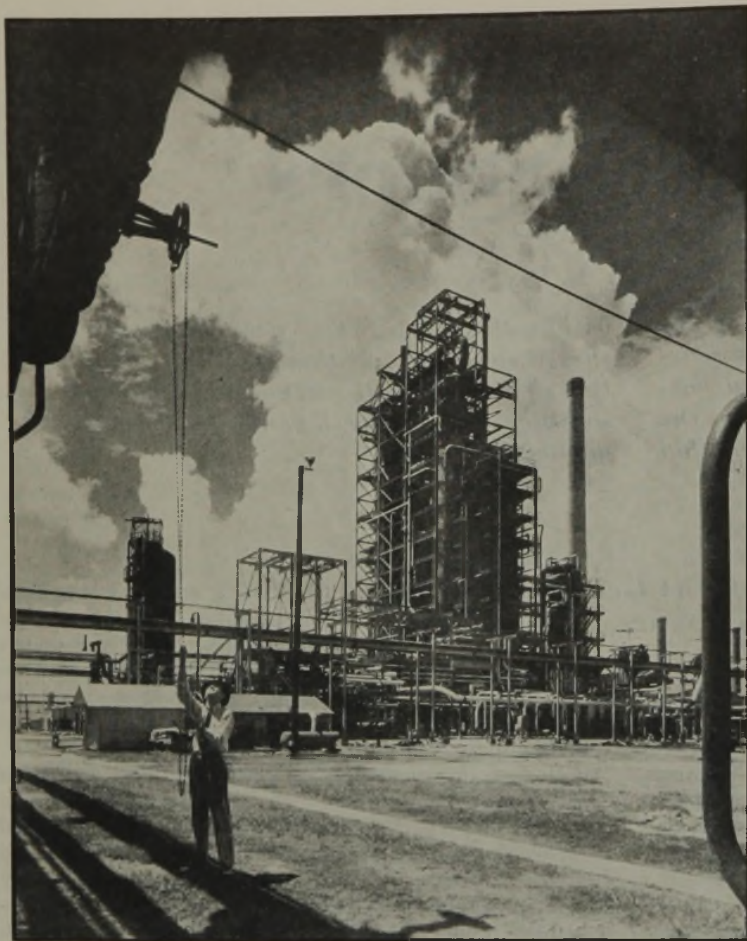
Saunders and Ford (7) eliminated some of the defects of Furnas' apparatus, so that their results are probably more reliable for the prediction of heat transfer coefficients. However, Furnas' data were more extensive; and since his results were self-consistent, they could be used to study the relative variation of heat transfer coefficient with particle size and air velocity. He found that the value of  $h$  which gave the best fit to Schumann's curves was proportional to the 0.7 power of the air velocity, rather than the 0.8 power as is ordinarily expected. He ascribed this to the resistance to heat transfer within the solid particles, neglected in Schumann's analysis.

In the discussion following Saunders and Ford's paper (7) there was some argument about the limit up to which Schumann's assumption was good, and beyond which it was necessary to take into account the resistance to heat transfer within the solid. It is not obvious whether or not the assumption holds in any given case, unless the particles are small, as in Saunders and Ford's work. They concluded that for glass, lead, and iron spheres up to 0.25-inch diameter the assumption of negligible resistance in the solid was valid.

In the following discussion a method is presented for the design of continuous solid-fluid heat exchangers which takes into account the resistance of the solid to heat flow. The particles will be considered as spheres, and the variation of  $h$ ,  $k$ ,  $c$ ,  $c'$ , and  $\rho$  with temperature neglected. Despite these

**C. L. Lovell and George Karnofsky**

PURDUE UNIVERSITY, LAFAYETTE, IND.



Courtesy, Standard Oil Company of America

*A Problem in Catalytic Cracking Is the Design of Solid-Fuel Heat Exchangers*

limitations the method should give more reliable results than Equation 1 when the particles are large and their conductivity is small. It makes possible an estimation of the limiting conditions under which Equation 1 may be safely applied.

**MATHEMATICAL STATEMENT OF PROBLEM**

Spheres of radius  $R$ , initially at uniform temperatures  $t_0$ , fall at the rate of  $N$  spheres per hour through a fluid moving upward in an exchanger whose cross-section area is 1 square foot. The temperature of the fluid is  $T$  at level  $x$ , measured down from the top of the exchanger. The temperature of the fluid at the level  $(x + dx)$  is  $(T + dT)$ .

Taking a heat balance over the differential section:

$$Gc \frac{dT}{d\theta} = ha(T - t_0) \frac{dx}{d\theta} = ha(T - t_0)V \tag{2}$$

Taking a heat balance from the top down to level  $x$ :

$$Gc(T - T_0) = haV \int_0^\theta (T - t_0)d\theta = Nc' \rho \int_0^R 4\pi r^2(t - t_0)dr \tag{3}$$

The temperature of any point in the sphere conforms with the differential equation (Equation 4) for heat conduction.

$$\frac{\partial t}{\partial \theta} = \alpha \left( \frac{\partial^2 t}{\partial r^2} + \frac{2}{r} \frac{\partial t}{\partial r} \right) \tag{4}$$

This equation is subject to the boundary conditions:

$$\text{when } \theta = 0: t = t_0 \tag{5}$$

$$\text{when } r = R: \frac{\partial t}{\partial r} = \frac{h}{k} (T - t_a) \tag{6}$$

The analytical solution of this problem is too complicated to be of any use for computation. The problem can be solved graphically by a modification of the Schmidt method as described below.

The following identities derive from the definitions of the terms:

$$G' = \frac{4\pi}{3} R^3 \rho N = \frac{aR\rho V}{3} = (1 - f) \rho V \tag{7}$$

**SCHMIDT METHOD**

The Schmidt method makes possible the graphical solution of the partial differential equation of heat conduction for any given set of boundary conditions. The application to the heating and cooling of slabs has been described by Schmidt (8), Nessi and Nissolle (6), Sherwood and Reed (11), and others. Only brief references (6, 9) have been found to its application to spheres. Since a different method of application to spheres is developed here from that recommended by Nessi and Nissolle (6), no further discussion of their method is necessary at this point. However, some remarks on their method will be found at the end of the paper.

Consider the differential equation:

$$\frac{\partial t}{\partial \theta} = \alpha \left( \frac{\partial^2 t}{\partial r^2} + \frac{2}{r} \frac{\partial t}{\partial r} \right) \tag{8}$$

$$\text{let } u = \frac{r}{R} \left( \frac{T_0 - t}{T_0 - t_0} \right)$$

$$\text{then } t = -\frac{R}{r} (T_0 - t_0)u + T_0$$

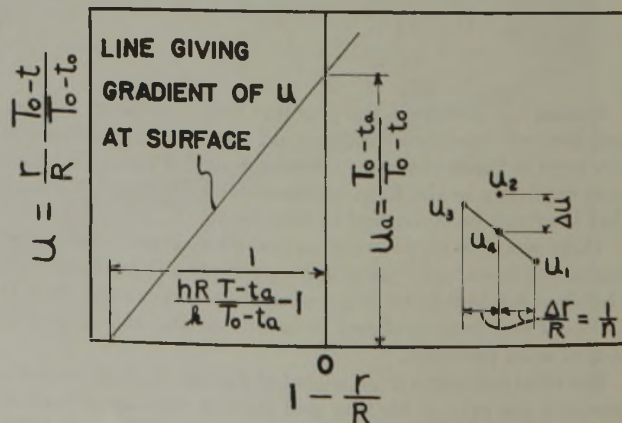


Figure 1. Application of Schmidt Principle to Spheres

$$\frac{\partial t}{\partial r} = -R(T_o - t_o) \left( \frac{1}{r} \frac{\partial u}{\partial r} - \frac{u}{r^2} \right)$$

$$\frac{\partial^2 t}{\partial r^2} = -R(T_o - t_o) \left( \frac{1}{r} \frac{\partial^2 u}{\partial r^2} - \frac{2}{r^2} \frac{\partial u}{\partial r} + \frac{2u}{r^3} \right)$$

$$\frac{\partial^2 t}{\partial r^2} + \frac{2}{r} \frac{\partial t}{\partial r} = -\frac{R}{r} (T_o - t_o) \frac{\partial^2 u}{\partial r^2}$$

Since  $\frac{\partial t}{\partial \theta} = -\frac{R}{r} (T_o - t_o) \frac{\partial u}{\partial \theta}$

$$\therefore \frac{\partial u}{\partial \theta} = \alpha \frac{\partial^2 u}{\partial r^2} \tag{9}$$

Equation 9 is the same as the equation of conduction for unidirectional flow in slabs, so that the Schmidt method may be applied in a manner exactly analogous to its application to slab problems.

Since the Schmidt method is adequately described in easily available references (11), only a brief summary is given here. Equation 9 may be written approximately as the difference equation:

$$\frac{\Delta u}{\Delta \theta} = \alpha \frac{\Delta^2 u}{\Delta r^2} \tag{10}$$

Plot  $u$  against  $1 - (r/R)$  as in Figure 1, and divide the abscissa into  $n$  equal increments, each equal to  $\Delta r/R$ . Let  $u_1, u_2,$  and  $u_3$  represent the values of  $u$  at a given time,  $\theta$ , at the three radii  $r, (r + \Delta r),$  and  $(r + 2\Delta r)$ , respectively. Let  $u_4$  be the value of  $u$  at  $(r + \Delta r)$  at a time  $\Delta\theta$  later.

Substituting in Equation 10:

$$\frac{u_4 - u_2}{\Delta\theta} = \alpha \frac{(u_3 - u_2) - (u_2 - u_1)}{(\Delta r)^2}$$

$$\frac{u_4 - u_2}{u_3 - 2u_2 + u_1} = \frac{\alpha \Delta\theta}{(\Delta r)^2}$$

If  $\alpha \Delta\theta / (\Delta r)^2$  is arbitrarily taken as  $1/2$ :

$$u_4 - u_2 = 1/2(u_3 - 2u_2 + u_1)$$

$$u_4 = 1/2(u_3 + u_1) \tag{11}$$

That is,  $u_4$  lies on a straight line joining  $u_1$  and  $u_3$  as shown in Figure 1. This is the basis of the Schmidt method.

There are several points of interest in connection with the plot of  $u$  against  $1 - (r/R)$ . The numbers  $(r/R)[(T_o - t)/(T_o - t_o)]$  and  $1 - (r/R)$  are dimensionless, so that the results will be of general utility rather than the solutions of specific problems. The well-known Gurney-Lurie plots (5) employ the dimensionless ratios  $(T_o - t)/(T_o - t_o), r/R,$

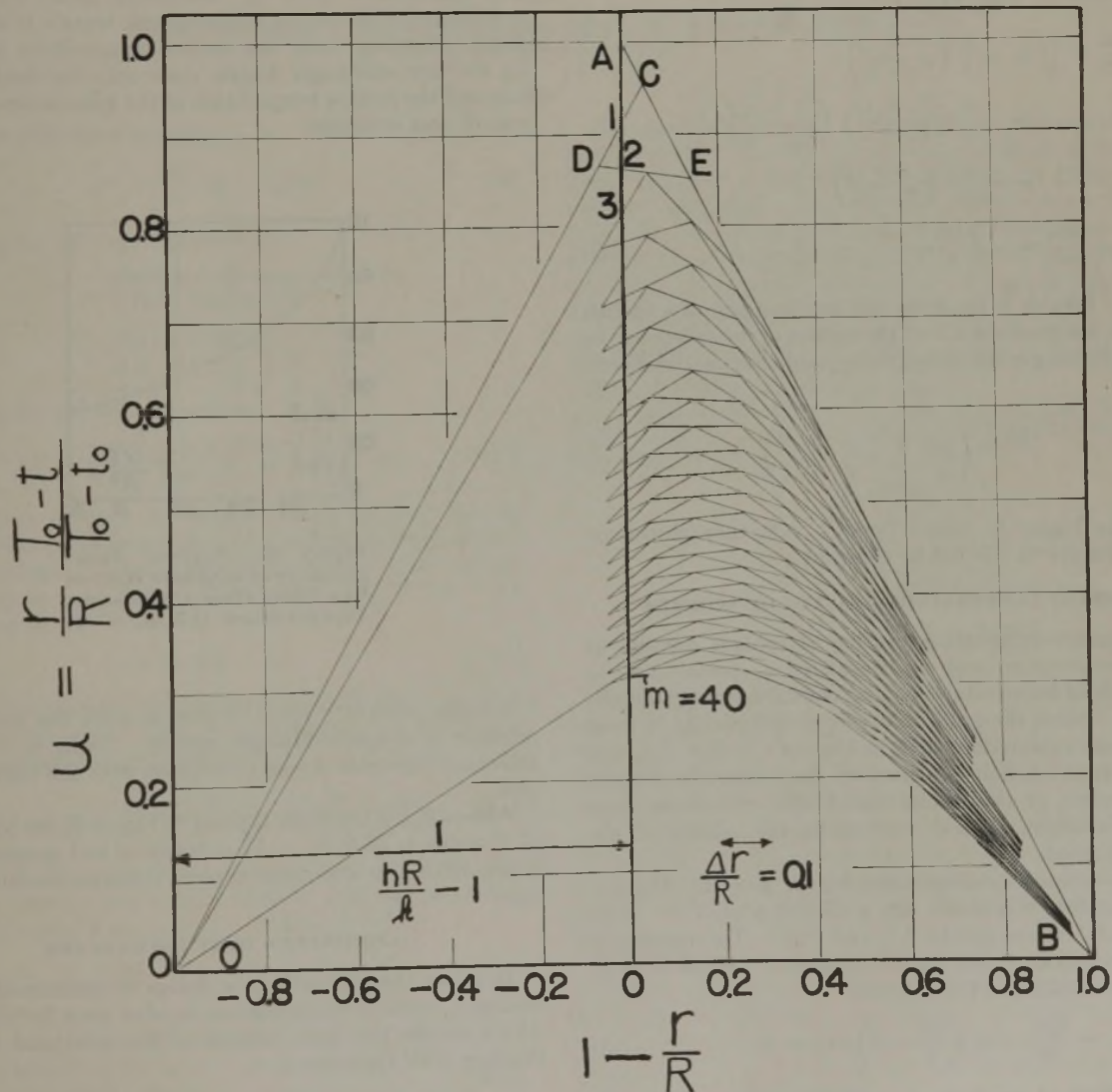


Figure 2. Graphical Construction for Constant-Temperature Heating of Sphere ( $hR/k = 2, n = 10$ )

$\alpha\theta/R^2$ , and  $hR/k$ ; and since all four are inherent in conduction problems involving heat transfer from a fluid by convection, they must all arise in the case under consideration.

Since  $\Delta\theta$  is defined by  $\alpha\Delta\theta/(\Delta r)^2 = 1/2$ , it is a definite increment of time, depending only on the choice of  $\Delta r$ . Then  $\theta$  must be a certain number,  $m$ , of equal increments of time,  $\Delta\theta$ ; i. e.,  $\theta = m(\Delta\theta)$ . Likewise, according to the definition of  $n$  given above,  $R = n(\Delta r)$ , and

$$\frac{\alpha\theta}{R^2} = \frac{\alpha m(\Delta\theta)}{(n\Delta r)^2} = \frac{m}{2n^2} \quad (12)$$

$$\Delta\theta = \frac{(\Delta r)^2}{2\alpha} = \frac{R^2}{2\alpha n^2} \quad (13)$$

Equation 12 gives a convenient method of evaluating  $\alpha\theta/R^2$  when using the Schmidt method.

The Nusselt number,  $hR/k$ , is important in the solution and enters in the following manner: From Equation 6, at  $r = R$ ,

$$\frac{\partial t}{\partial r} = \frac{h}{k} (T - t_a)$$

From Equation 8, at  $r = R$ ,

$$\frac{\partial t}{\partial r} = - (T_o - t_o) \left( \frac{\partial u}{\partial r} - \frac{u_a}{R} \right)$$

$$\text{where } u_a = \frac{T_o - t_a}{T_o - t_o}$$

$$\begin{aligned} \frac{\partial u}{\partial r} - \frac{u_a}{R} &= - \frac{h}{k} \left( \frac{T - t_a}{T_o - t_o} \right) \\ &= - \frac{h}{k} \left( \frac{T_o - t_a}{T_o - t_o} \right) \left( \frac{T - t_a}{T_o - t_a} \right) \\ &= - \frac{hu_a}{k} \left( \frac{T - t_a}{T_o - t_a} \right) \end{aligned}$$

$$- \frac{R\partial u}{\partial r} = u_a \left( \frac{hR}{k} \frac{T - t_a}{T_o - t_a} - 1 \right) \quad (14)$$

Since  $-R\partial u/\partial r$  is the slope of a line on a plot of  $u$  against  $1 - (r/R)$ , the gradient of  $u$  at the surface of the sphere can be found by drawing a line through the points having the coordinates,

$$(0, u_a), \left( \frac{-1}{\frac{hR}{k} \frac{T - t_a}{T_o - t_a} - 1}, 0 \right)$$

as shown in Figure 1. Since  $T$  and  $t_a$  vary through the exchanger, the points will not be constant.

#### CONSTANT-TEMPERATURE HEATING OF SPHERES

The constant-temperature heating of spheres initially at uniform temperature may be considered a special case, in which the fluid temperature remains constant throughout the exchanger. Since the problem is solved analytically in most texts on heat conduction, such as that of Carslaw (1), and since numerical solutions are given by the Gurney-Lurie plots (5), comparison of the results found here with these plots offers a convenient method of checking the validity of the graphical method.

Figure 2 shows the construction for  $hR/k = 2$ . The following procedure was used: On a plot of  $u$  vs.  $1 - (r/R)$  draw line  $AB$  between points (0,1) and (1,0). This represents the initial condition  $t = t_o$  for all values of  $r$ . Since  $T = T_o$  at all times, Equation 14 reduces to

$$- \frac{R\partial u}{\partial r} = u_a \left( \frac{hR}{k} - 1 \right) \text{ at } r = R \quad (15)$$

All the lines of gradient of  $u$  at the surface must pass through a point on the abscissa a distance  $1/[(hR/k) - 1] = 1$

to the left of the  $u$  axis, marked point 0. Let  $n = 10$ ; i. e.,  $1 - (r/R)$  is divided into ten equal increments from  $r = 0$  to  $r = R$ . Find point  $C$  on  $AB$  at the mid-point of the first increment and draw  $OC$ . The intersection of  $OC$  with the  $u$  axis, marked 1, may be taken as the value of  $u_a$  at time  $\theta = \Delta\theta$ ; i. e.,  $m = 1$ , or  $\alpha\theta/R^2 = m/2n^2 = 0.005$ . Although it is known that the exact value of  $m$  is uncertain (11), this arbitrary choice gives good results and is easy to apply.

Join point  $D$ , which is on  $OC$ , half an increment to the left of the  $u$  axis, to point  $E$  on  $AB$  in the middle of the second increment  $\Delta r/R$ . The intersection of  $DE$  with the  $u$  axis, marked 2, represents  $u_a$  at  $m = 2$  or  $\alpha\theta/R^2 = 0.01$ .

The remainder of the construction is best understood by inspection of Figure 2. Since  $u = 0$  at  $r = 0$ , all the construction lines converge at  $B$ . The mid-points which fall in the ninth increment are joined to  $B$ . Although this is not theoretically justifiable, it appears to introduce little error in the construction.

Figure 3 is a plot of  $u_a = (T_o - t_a)/(T_o - t_o)$  against  $\alpha\theta/R^2$  as read from Figure 2. The values of  $u_a$  agree well with those read from the Gurney-Lurie chart for the sphere. Because of the difficulty in reading the Gurney-Lurie chart closely for values of  $\alpha\theta/R^2$  up to 0.2, Figure 3 is much more reliable in this range.

Several points are brought out by the illustrative problem. This construction gives no information about the temperature history of the center of the sphere, since  $u$  is always zero there. However, only the surface temperature is required for the heat exchanger design, since only the fluid temperature and the surface temperature of the spheres determine the rate of heat exchange.

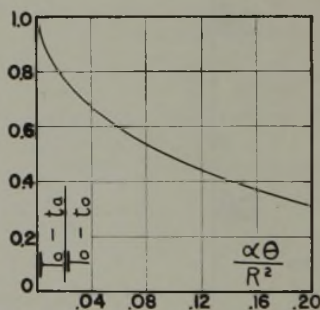


Figure 3. Surface Temperature of a Sphere Heated by a Fluid Held at Constant Temperature ( $hR/k = 2$ )

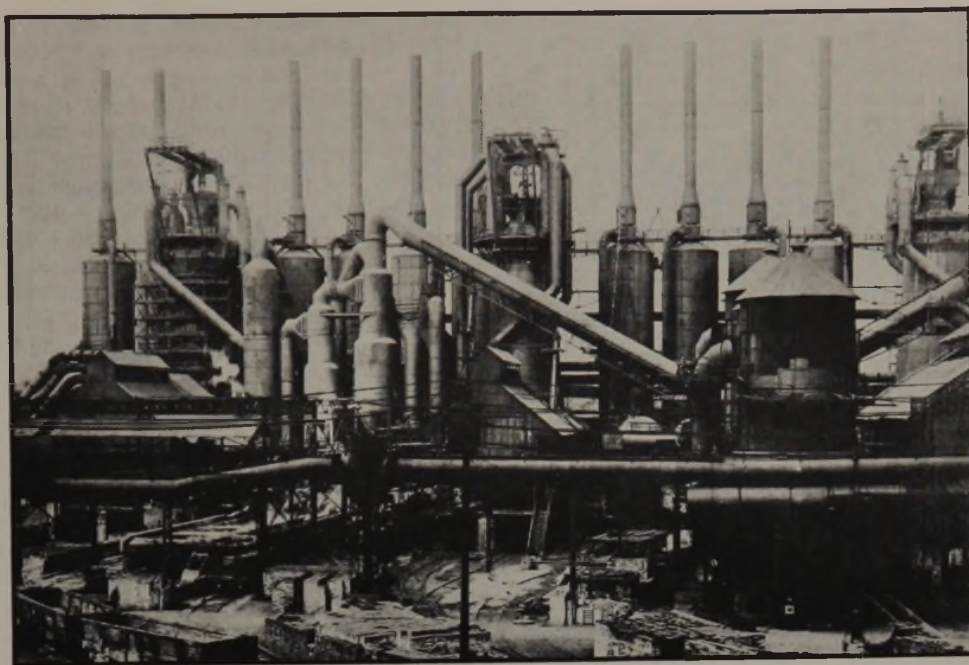
A large value of  $n$  must be chosen, since the surface temperature of a sphere changes rapidly. Using  $n = 5$  in the above problem gave a poor correlation with the Gurney-Lurie plot.

When  $hR/k$  is less than 1, point 0 (Figure 2) lies to the right of  $B$ , since  $1/[(hR/k) - 1]$  is negative and greater than 1. When  $hR/k$  is greater than 1, point 0 lies to the left of the  $u$  axis.

#### CONTINUOUS HEAT EXCHANGERS

To apply the method to the design of continuous heat exchangers, another dimensionless number must be introduced, which relates the heat content of the solid and the fluid. Starting with Equation 2,

$$\frac{dT}{d\theta} = \frac{hA V}{Gc} (T - t_a)$$



Courtesy, U. S. Bureau of Mines

*Heating the Blast Furnace Charge Exemplifies the Industrial Application of Solid-Fuel Heat Exchange*

Written as a difference equation,

$$\Delta T = \frac{haV}{Gc} (T - t_a) \Delta \theta \quad (16)$$

Substituting for  $\Delta \theta$  from Equation 13,

$$\begin{aligned} \Delta T &= \left( \frac{haV}{Gc} \right) \left( \frac{R^2}{2\alpha n^2} \right) (T - t_a) \\ &= \left( \frac{haV}{Gc} \right) \left( \frac{R^2 c' \rho}{2kn^2} \right) (T - t_a) \end{aligned}$$

Substituting for  $aV$  from Equation 7,

$$\Delta T = \left( \frac{hR}{k} \right) \left( \frac{3}{2n^2} \right) \left( \frac{c'G'}{cG} \right) (T - t_a) \quad (17)$$

In any given problem  $\Delta T$  is proportional to  $(T - t_a)$ , and the constant of proportionality is the product of three dimensionless numbers: the Nusselt number  $hR/k$ ;  $3/2n^2$ , which depends only on the arbitrary choice of  $n$ ; and  $c'G'/cG$ . Let this constant be  $B$ . Then

$$\Delta T = B(T - t_a) \quad (18)$$

Using subscript  $m$  to indicate the conditions at the end of  $m$  time increments, and  $(m - 1)$  to indicate  $(m - 1)$  time increments, Equation 18 may be written:

$$T_m - T_{m-1} = B \left( \frac{T_m + T_{m-1}}{2} - \frac{t_{a,m} + t_{a,m-1}}{2} \right) \quad (19)$$

In writing this equation it is assumed that the temperature changes in time  $\Delta \theta$  are small enough so that the use of the arithmetic average is permissible. Solving for  $T_m$ ,

$$T_m = \frac{(B + 2)T_{m-1} - B(t_{a,m} + t_{a,m-1})}{2 - B} \quad (20)$$

Since  $T_m$  and  $t_{a,m}$  are also related by Equation 14, they are uniquely determined for given values of  $T_{m-1}$  and  $t_{a,m-1}$ , which makes possible a stepwise computation process. The former are found by trial and error in a manner best illustrated by a problem.

Limestone is calcined in a continuous, countercurrent, vertical lime kiln. The calcium carbonate is fed in at the top in 2-inch pieces at a superficial mass velocity of 2230 pounds/(square foot)(hour). Flue gas and carbon dioxide from the calcination rise through the bed at a superficial mass velocity of 2500 pounds/(square foot)(hour). If the limestone enters at 100° F. and the gas leaves at 200° F., at what level in the kiln is the gas temperature 400° F.?

Av. specific heat of gas =  $c = 0.25$   
 Av. specific heat of  $\text{CaCO}_3 = c' = 0.28$   
 Density of  $\text{CaCO}_3 = \rho = 162$  lb./cu. ft.  
 Heat transfer coefficient =  $h = 78$  B. t. u./(hr.)(sq. ft.)(° F.)  
 Conductivity of  $\text{CaCO}_3 = k = 1.3$  B. t. u./(hr.)(sq. ft.)(° F./ft.)  
 Fraction void space =  $f = 0.50$

$$\frac{hR}{k} = \frac{(78)(0.0833)}{1.3} = 5.0$$

$$\frac{c'G'}{cG} = \frac{(0.28)(2230)}{(0.25)(2500)} = 1.0$$

$$\alpha = \frac{k}{c'\rho} = \frac{1.3}{(0.28)(162)} = 0.0287$$

In order to apply Equation 18, it is necessary to assign a value to  $B$ . Since the assumption is made that  $\Delta T$  is small compared with  $T - t_a$ ,  $B$  must be small—i. e., less than 0.1. This determines the choice of  $n$ . If  $n$  is set equal to 10, then  $B = 0.075$ , and  $\theta = R^2 m / 2\alpha n^2 = 0.0012m$ .

The problem, then, is to carry out the Schmidt method through the  $m$  time increments required for air temperature  $T_m$  to increase from 200° to 400° F. and, knowing the rate of fall of a particle, to calculate the distance from the top of the kiln.

The graphical construction is shown in Figure 4, which should be interpreted in conjunction with Table I. To simplify the computations,  $t_a$  is arbitrarily set equal to 0, and  $T_a$  to 1. Since the solution is dimensionless, this is permissible. Then  $t_a = 1 - u_a$ , and  $t_a$  can be read directly from Figure 4. Substituting in Equation 20,

$$T_m = 1.078T_{m-1} - 0.039(t_{a,m} + t_{a,m-1}) \quad (21)$$

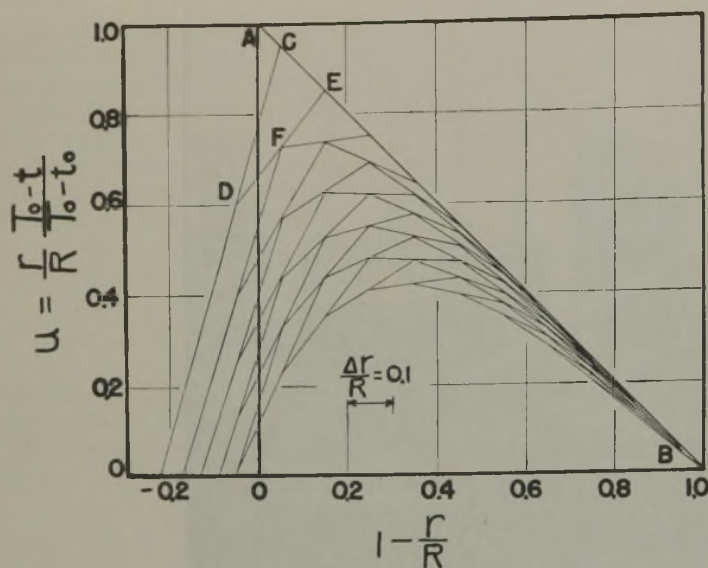


Figure 4. Graphical Construction for Countercurrent Exchanger Design ( $hR/k = 5$ ,  $c'G'/cG = 1$ )

In Figure 4 line  $AB$  is drawn, representing the initial uniform temperature of the sphere. The line representing the gradient of  $u$  at the surface at  $m = 1$  must pass through point  $C$  on  $AB$ , half an increment  $\Delta r/R$  to the right of the  $u$  axis. Also, it must pass through points

$$(0, u_{a,m}) \text{ and } \left[ -1 / \left( 5 \frac{T_m - t_{a,m}}{1 - t_{a,m}} - 1 \right), 0 \right]$$

which satisfy Equations 14 and 21 simultaneously. By trial, a value of  $t_{a,m} = 0.22$  is selected. Since  $t_{a,m-1} = 0$  and  $T_{m-1} = 1$ ,  $T_m = 1.069$  from Equation 21;  $(T_m - t_{a,m}) / (1 - t_{a,m}) = 1.09$ ; and  $1/5(1.09 - 1) = 0.225$ . A line drawn from  $C$  to point  $(-0.225, 0)$  passes through point  $(0, 0.78)$  so that the choice of  $t_{a,m}$  is correct. The computation is systematically carried out in Table I.

The Schmidt stepwise construction is carried out and establishes line  $DE$ . The intersection of  $DE$  with the  $u$  axis gives the value of  $t_{a,m} = 0.335$  at  $m = 2$ . From Equation 21,  $T_m = 1.128$ .

The line representing the gradient of  $u$  at the surface at  $m = 3$  passes through point  $F$  on  $DE$ . Guessing  $t_{a,m} = 0.430$ , then  $T_m = 1.182$ ;  $(T_m - t_{a,m}) / (1 - t_{a,m}) = 1.32$ ;  $1/5(1.32 - 1) = 0.179$ . The line through  $F$  and  $(-0.179, 0)$  passes through point  $(0, 0.57)$ , so that the choice of  $t_{a,m}$  is satisfactory.

Continuing in this fashion, Figure 4 and Table I can be constructed. The correct estimation of  $t_{a,m}$  is not difficult,

Table I. Computation of  $T_m$  by Trial, Using Equations 14 and 21

$m$	$t_{a,m}$	$t_{a,m} + t_{a,m-1}$	$T_m$	$\frac{T_m - t_{a,m}}{1 - t_{a,m}}$	$\frac{1}{5 \frac{T_m - t_{a,m}}{1 - t_{a,m}} - 1}$
1	0.220	0.220	1.069	1.09	0.225
2	0.335	0.555	1.128	1.32	0.179
3	0.430	0.765	1.182	1.32	0.179
4	0.515	0.945	1.235	1.69	0.134
5	0.585	1.100	1.287	2.36	0.093
6	0.650	1.235	1.337	3.70	0.057
7	0.715	1.365	1.386		
8	0.770	1.485	1.434		
9	0.820	1.590	1.485		
10	0.875	1.695	1.534		

since the lines of gradient of  $u$  at the surface become progressively less steep as the construction advances. By laying a straight edge on the paper through point  $F$ , at an angle slightly smaller than that of the gradient line through  $C$ , the value of  $u_{a,m}$  at  $m = 3$  is obviously close to 0.57. The construction is continued until  $T_m = (400 - 100) / (200 - 100) = 3.0$ . Figure 4 and Table I demonstrate the construction up to  $m = 10$ ; when completed  $T_m = 3.0$  when  $m = 40$ . Therefore  $\theta = (0.0012)(40) = 0.048$  hour.

The distance down from the top is:

$$\frac{G'\theta}{(1-f)\rho} = \frac{(2230)(0.048)}{(0.5)(162)} = 1.32 \text{ ft.}$$

When computed from Equation 1 (neglecting resistance to heat transfer through the solid) the distance is 0.88 foot.

Since the computation used dimensionless numbers throughout, the results can be represented by a graph of  $(T - t_0) / (T_0 - t_0)$  against  $\alpha\theta/R^2$ . These can be found directly

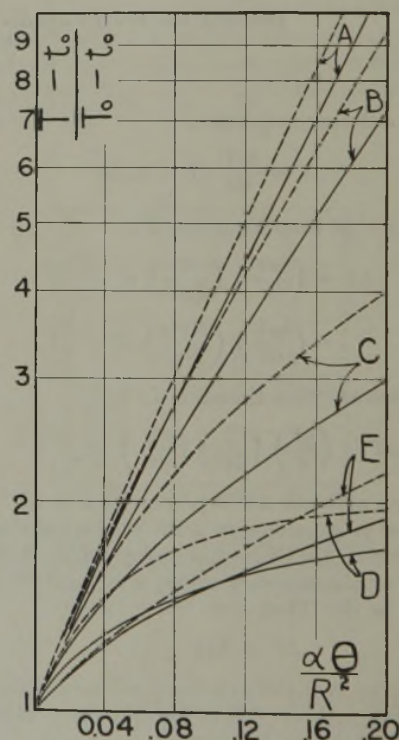


Figure 5. Fluid Temperature as a Function of Time of Fall in Countercurrent Exchanger

Curves A.  $hR/k = 1$ ,  $c'G'/cG = 5$   
 Curves B.  $hR/k = 2$ ,  $c'G'/cG = 2.5$   
 Curves C.  $hR/k = 5$ ,  $c'G'/cG = 1$   
 Curves D.  $hR/k = 10$ ,  $c'G'/cG = 0.5$   
 Curves E.  $hR/k = 2$ ,  $c'G'/cG = 1$   
 Solid lines from graphical construction;  
 dotted lines from Equation 22

from Table I, since  $(T - t_0) / (T_0 - t_0) = T_m$  and  $\alpha\theta/R^2 = m/2n^2 = 0.005m$ . The plot can be used for the design of any exchanger where  $hR/k = 5$  and  $c'G'/cG = 1$ . In Figure 5 such plots are shown for several different values of

$hR/k$  and  $c'G'/cG$ . A complete set of these curves would eliminate the necessity for repeating the graphical construction.

For comparison the values of  $(T - t_o)/(T_o - t_o)$  found by neglecting the resistance to heat transfer in the solid are shown as dotted lines in Figure 5. The equation of these lines can be derived by substituting in Equation 1:

$$Q = c'G'(t - t_o) = cG(T - T_o)$$

$$A = aV\theta = 3G'\theta/R\rho$$

Substituting and rearranging,

$$\ln \left[ \frac{T - t_o}{T_o - t_o} \left( 1 - \frac{cG}{c'G'} \right) + \frac{cG}{c'G'} \right] = 3 \frac{hRc'G'\alpha\theta}{k cG R^2} \left( 1 - \frac{cG}{c'G'} \right) \quad (22)$$

#### METHOD OF NESSI AND NISSOLE

Nessi and Nissole (6) appear to have been the originators of the graphical method for conduction in spheres which is described in the literature. This method uses a plot of  $t$  against  $1/r$ .

Let  $v = 1/r$ ; then substituting in Equation 4,

$$\frac{\partial t}{\partial r} = -\frac{1}{r^2} \frac{\partial t}{\partial v}$$

$$\frac{\partial^2 t}{\partial r^2} = -\frac{1}{r^2} \frac{\partial}{\partial r} \frac{\partial t}{\partial v} + \frac{2}{r^3} \frac{\partial t}{\partial v}$$

$$\therefore \frac{\partial t}{\partial \theta} = \alpha v^4 \frac{\partial^2 t}{\partial v^2} \quad (23)$$

By a proof similar to the one given previously, it may be shown that the Schmidt method can be applied to a plot of  $t$  vs.  $v$ , using equal increments of  $v$ , provided that

$$\frac{\alpha v^4 \Delta \theta}{(\Delta v)^2} = 1/2$$

Since  $v = 1/r$  and  $\Delta v = -(\Delta r/r^2)$ , Equation 23 can be simplified:

$$\frac{\alpha \Delta \theta}{(\Delta r)^2} = 1/2 \quad (24)$$

The increments  $\Delta \theta$  and  $\Delta r$  are variable, since  $\Delta(1/r)$  is constant. The plot extends to  $v = \infty$  when  $r = 0$ . Therefore, this method is more suitable when temperatures near the center of the sphere are desired. However, the variable  $\Delta \theta$  and the large range of  $v$  make it unnecessarily complicated for the heat exchanger design where only surface temperatures are required.

#### NOMENCLATURE

- $a$  = surface area of solids per unit volume of exchanger  
 $A$  = heat transfer area in exchanger  
 $B$  = a dimensionless number,  $3hRc'G'/2n^2kcG$   
 $c$  = heat capacity of fluid, B. t. u./lb. ( $^{\circ}$  F.)  
 $c'$  = heat capacity of solid, B. t. u./lb. ( $^{\circ}$  F.)  
 $f$  = fraction void space in exchanger  
 $G$  = superficial mass velocity of fluid, lb./hr. (sq. ft.)  
 $G'$  = superficial mass velocity of solid, lb./hr. (sq. ft.)  
 $h$  = heat transfer coefficient, B. t. u./hr. (sq. ft.) ( $^{\circ}$  F.)  
 $k$  = conductivity of solid, B. t. u./hr. (sq. ft.) ( $^{\circ}$  F./ft.)  
 $m$  = number of time increments; i. e.,  $\theta = m(\Delta \theta)$   
 $n$  = number of increments of radius; i. e.,  $R = n(\Delta r)$   
 $N$  = number of particles falling per hr. per sq. ft. of cross section  
 $Q$  = heat transferred in exchanger  
 $r$  = distance from center of sphere, ft.  
 $R$  = radius of sphere, ft.  
 $t$  = temperature at any point in a sphere,  $^{\circ}$  F.  
 $T$  = temperature of fluid at any level,  $^{\circ}$  F.  
 $u$  = a dimensionless number,  $\frac{r}{R} \left( \frac{T_o - t}{T_o - t_o} \right)$   
 $V$  =  $dx/d\theta$ , rate of fall of solids, ft./hr.  
 $x$  = distance along exchanger, measured from point of entrance of solids, ft.  
 $\alpha$  =  $k/c'\rho$ , thermal diffusivity of solid  
 $\rho$  = density of solid, lb./cu. ft.  
 $\theta$  = time, measured from time of entrance of a particle into exchanger, hr.

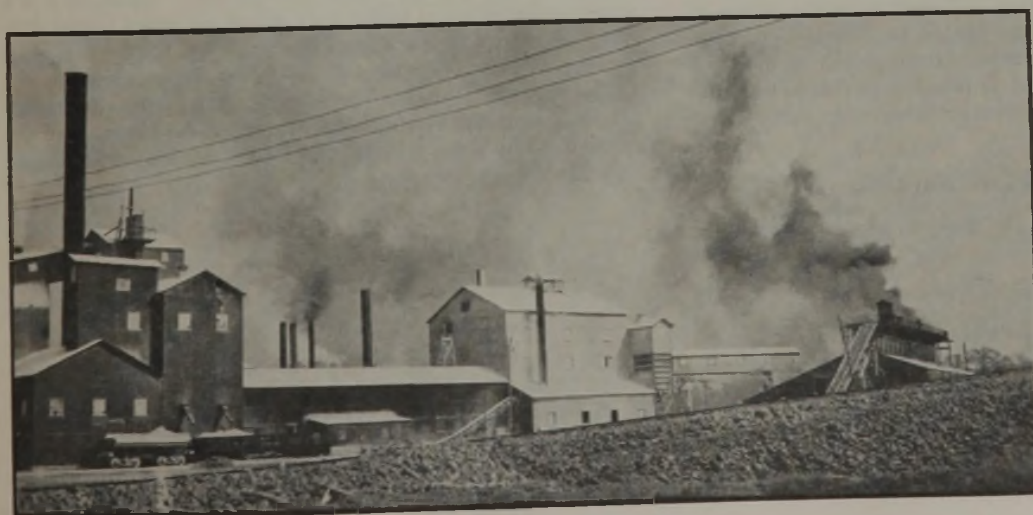
#### Subscripts

- $a$  = surface of a particle  
 $o$  = end of exchanger at which solids enter

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BASED ON A thesis submitted by George Karnofsky to the faculty of Purdue University in partial fulfillment of the requirements for the degree of master of science.



**Burning Lime in a Kiln Is Another Practical Application of the Principles of Solid-Fuel Heat Exchange**

Courtesy, U. S. Bureau of Mines

# Thermodynamics of the Liquid State

## GENERALIZED PREDICTION OF PROPERTIES

K. M. Watson

UNIVERSITY OF WISCONSIN, MADISON, WIS.

*On the basis of a modified application of the theorem of corresponding states, new methods are presented for the general prediction of the following thermodynamic properties of liquids: thermal expansion and compressibility, pressure correction to enthalpy, pressure correction to entropy, pressure correction to heat capacity at constant pressure, heat of vaporization, difference between heat capacity of a saturated liquid and its ideal gas, and difference between heat capacity of saturated liquid and heat capacity at constant pressure.*

*The only data required are the boiling point, the critical temperature, critical pressure, and the liquid density at some one temperature.*

*Like all applications of the theorem of corresponding states, these relations are not rigorously correct. However, deviations from the available experimental data on a variety of compounds, both polar and nonpolar, are sufficiently small to warrant their use for many process problems where reliable data are not available, and for rationalizing fragmentary experimental data.*

**D**URING the past ten years much attention has been directed (2, 4, 7, 8, 10, 23-26) toward the development of generalized relations which permit prediction of the thermodynamic properties of the gaseous state, even at extreme conditions of temperature and pressure, with accuracy sufficient for general engineering purposes. The similar properties of the liquid state have received little attention because of their lesser importance and because of the failure of the theorem of corresponding states to directly correlate liquid properties with accuracy. However, by a modified application of this theorem it is possible to correlate liquid properties with a degree of accuracy similar to the correlations of the gas phase.

### THERMAL EXPANSION AND COMPRESSIBILITY

The equation of state for the gaseous phase is ordinarily written,

$$pv = zRT \quad (1)$$

where  $z$ , the compressibility factor, is a function of reduced temperature and pressure, approximately the same for all substances. If this relation were applied to the liquid state, an expression for liquid density might be written,

$$\rho = \frac{pM}{zRT} = \left( \frac{p_r}{z_r RT_r} \right) \frac{P_c M}{T_c} = \omega \frac{P_c M}{T_c} \quad (2)$$

where  $\omega$ , which might be termed the "expansion" factor, would be a function only of reduced temperature and pressure.

Unfortunately it is found that factor  $\omega$  of Equation 2 is not a generalized function of reduced conditions. Values of  $\omega$  at the same reduced conditions may vary by more than 20 per cent for different compounds. Accordingly, Equation 2 is a rough approximation useful only where no direct liquid density data of any type are available.

Since at least one value of liquid density is available for almost any compound, a more useful relation results by applying Equation 2 to obtain an expression for the ratio of the density at any given condition to that at some reference state designated by subscript 1:

$$\frac{\rho}{\rho_1} = \frac{\omega}{\omega_1}$$

or  $\rho = \frac{\rho_1}{\omega_1} \omega \quad (3)$

It has been found that if  $\omega$  is evaluated as a function of reduced temperature and reduced pressure for one compound on which complete data are available, Equation 3 may be used with satisfactory accuracy for predicting the densities of any other compound for which one liquid density value is available to establish  $\rho_1/\omega_1$ .



Table I. Values of Expansion Factor  $\omega$

$T_r$	Expansion Factor $\omega$							
	$P_r = 0$	$P_r = 0.4$	$P_r = 0.8$	$P_r = 1.0$	$P_r = 1.5$	$P_r = 2$	$P_r = 3$	$P_r = 5$
0.5	(0.1328)	.....	.....	0.1332	.....	0.1338	.....	0.1350
0.6	0.1242	.....	.....	0.1250	.....	0.1258	.....	0.1275
0.7	0.1144	0.1150	.....	0.1158	.....	0.1170	0.1182	0.1202
0.8	0.1028	0.1042	0.1050	0.1056	0.1070	0.1077	0.1098	0.1125
0.9	.....	0.0900	0.0915	0.0926	0.0949	0.0968	0.1002	0.1043
0.95	.....	.....	0.0810	0.0831	0.0872	0.0902	0.0943	0.1000
1.0	.....	.....	.....	0.0440	0.0764	0.0818	0.0875	0.0954

Through Equation 6 the group

$$\frac{J_{\rho_1}}{P_c \omega_1} \left( \frac{\partial H}{\partial p_r} \right)_T$$

may be expressed as a general function of reduced temperature and pressure by the graphical differentiation of Figure 1, remembering that  $\partial(1/\omega) = -(\partial\omega/\omega^2)$ . The results of this operation are summarized in

Figure 1 and Table I give values of  $\omega$  for isopentane, calculated from the measurements of Young (11) and extended to higher pressures by the data of Sage and Lacey (16, 18) on propane and *n*-pentane and Equation 3. Tables II and III compare liquid densities calculated from these curves and Equation 3 with experimental data from the indicated sources for compressed and saturated liquids of various polar and nonpolar types. The agreement is reasonably good with deviations, in general, less than 5 per cent, even for the case of water at 100° C. and above. The anomalous density changes of water at low temperature are not in agreement with the correlation, and selection of 4° C. as the reference conditions instead of 100° C. would increase the maximum deviations in the high-temperature range to approximately 10 per cent. In general, it is desirable to use the highest temperature at which data are available as the reference state, particularly when the high-temperature behavior of polar substances such as water are being calculated.

Figure 2 and Table IV for the range of conditions not close to the critical point.

The effect of pressure on enthalpy may be expressed in a more useful form by graphically integrating Equation 6 to obtain the differences between the enthalpy of a liquid under

PRESSURE CORRECTION TO ENTHALPY

The effect of pressure on the enthalpy of any substance is expressed by the rigorous thermodynamic equation:

$$J \left( \frac{\partial H}{\partial p} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_p \quad (4)$$

Rearranging in terms of reduced conditions,

$$\frac{J}{P_c} \left( \frac{\partial H}{\partial p_r} \right)_T = V - T_r \left( \frac{\partial V}{\partial T_r} \right)_p \quad (5)$$

Combining Equations 3 and 5,

$$\frac{J_{\rho_1}}{P_c \omega_1} \left( \frac{\partial H}{\partial p_r} \right)_T = \frac{1}{\omega} - T_r \left( \frac{\partial \frac{1}{\omega}}{\partial T_r} \right)_p \quad (6)$$

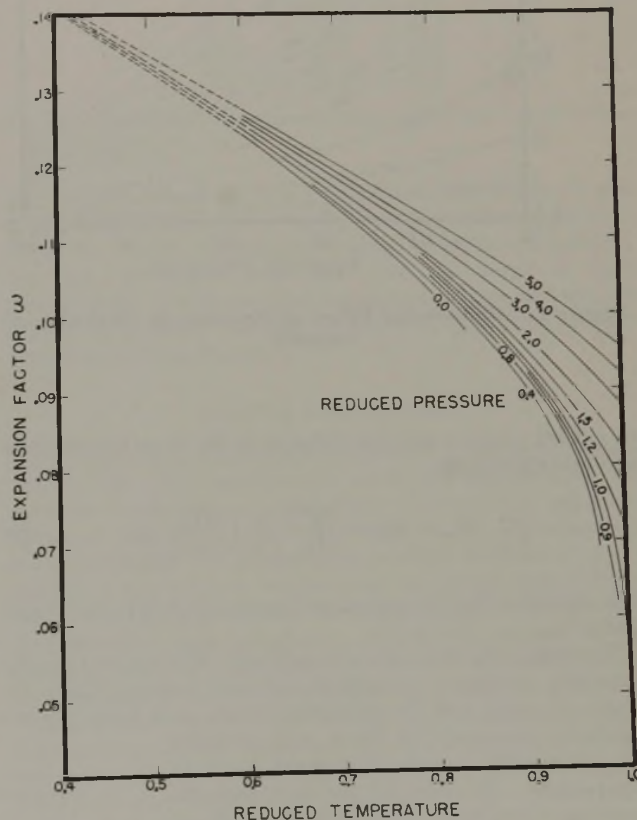


Figure 1. Thermal Expansion and Compressibility of Liquids

Table II. Densities of Compressed Liquids

Pressure, Lb./Sq. In.	Reduced Pressure	Density, Gram/Cc.			
		Calcd.	Exptl.	Calcd.	Exptl.
WATER (12): $\rho_1/\omega_1 = 7.586$ AT 100° C., 1 ATM.					
		204.4° C., $T_r = 0.738$		348.9° C., $T_r = 0.961$	
				374.3° C., $T_r = 1.0$	
1000	0.312	0.842	0.864	0.611	0.616
3206	1.0	0.851	0.874	0.633	0.639
4000	1.248	0.854	0.878	0.633	0.639
5500	1.715	0.858	0.885	0.658	0.660
PROPANE (17): $\rho_1/\omega_1 = 4.807$ AT 21.0° C., 200 LB./SQ. IN.					
		54.5° C., $T_r = 0.878$		71.1° C., $T_r = 0.921$	
				87.9° C., $T_r = 0.966$	
300	0.466	0.453	0.447	0.416	0.422
600	0.934	0.460	0.458	0.460	0.458
1500	2.35	0.485	0.482	0.460	0.458
3000	4.66	0.508	0.506	0.489	0.489
BUTANE (19): $\rho_1/\omega_1 = 5.037$ AT 21.1° C., 250 LB./SQ. IN.					
		71.1° C., $T_r = 0.809$		104.4° C., $T_r = 0.887$	
				121.1° C., $T_r = 0.926$	
250	0.462	0.521	0.522	0.467	0.461
500	0.945	0.526	0.527	0.475	0.472
1500	2.84	0.546	0.545	0.508	0.501
3000	5.67	0.567	0.564	0.536	0.528

Table III. Densities of Saturated Liquids

Temperature, ° C.	Density, G./Cc.		Temperature, ° C.	Density, G./Cc.	
	Calcd.	Exptl.		Calcd.	Exptl.
AMMONIA (21): $\rho_1/\omega_1 = 5.463$ AT -33.3° C., SATD. PRESSURE					
-73.3	0.729	0.730	37.8	0.586	0.584
-45.6	0.698	0.699	93.3	0.488	0.475
-17.8	0.664	0.664	121	0.388	0.380
+10	0.626	0.625	133 (T <sub>c</sub> )	0.240	0.234
ETHYL ALCOHOL (11): $\rho_1/\omega_1 = 6.210$ AT 20° C., SATD. PRESSURE					
0	0.809	0.806	60	0.746	0.755
40	0.768	0.772	80	0.721	0.735
			243.1 (T <sub>c</sub> )	0.273	0.275

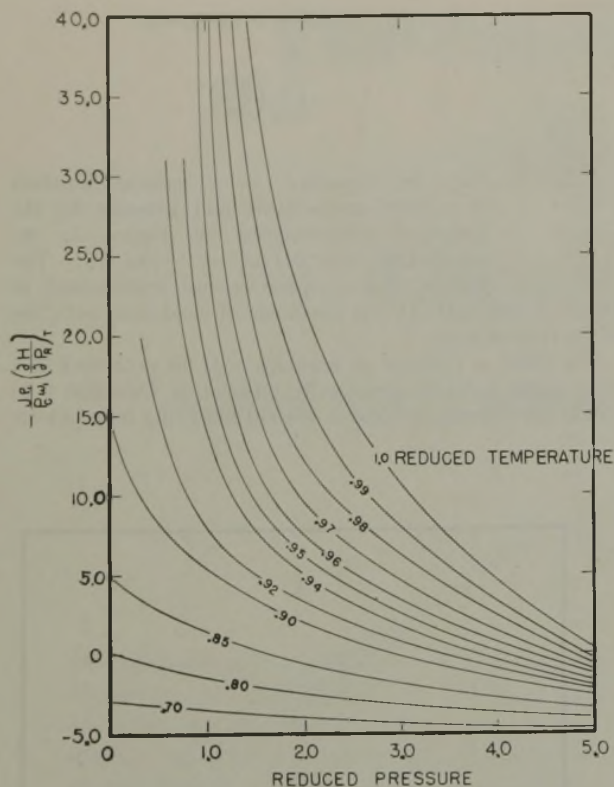


Figure 2. Differential Effect of Pressure on Enthalpy of Liquids

its critical pressure and the enthalpy at the same temperature and other pressures:

$$\frac{J_{\rho_1}}{P_c \omega_1} (H_{cp} - H)_T = \int_{p_r}^{1.0} \frac{J_{\rho_1}}{P_c \omega_1} \left( \frac{\partial H}{\partial p_r} \right)_T dp_r \quad (7)$$

The results of this integration are summarized in Figure 3 and Table V.

Unfortunately few data are available with which to compare the enthalpy corrections calculated from Figure 3. Table VI compares the calculated values and those experimentally evaluated for water and propane. The agreement is reasonably good for both compounds. In view of the fact that the pressure correction is relatively small as compared to the enthalpy changes ordinarily encountered in industrial operations, it is believed that Figure 3 may be safely used for many engineering applications. The fact that a relation based on data for pentane is in even fair agreement with such dissimilar materials as water and propane is reassuring as to its generality.

PRESSURE CORRECTION TO ENTROPY

The effect of pressure on the entropy of any substance is expressed by the rigorous thermodynamic equation:

$$J \left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p \quad (8)$$

Expressing in terms of reduced conditions and combining with Equation 3,

$$\frac{J_{\rho_1} T_c}{\omega_1 P_c} \left( \frac{\partial S}{\partial p_r} \right)_T = - \left( \frac{\partial \frac{1}{\omega}}{\partial T_r} \right)_p \quad (9)$$

Equation 9 may be integrated to obtain a useful correction chart relating the difference between entropy under the critical pressure and entropy at any other pressure under the same temperature:

$$\frac{J_{\rho_1} T_c}{\omega_1 P_c} (S_{cp} - S)_T = \int_{p_r}^{1.0} - \left( \frac{\partial \frac{1}{\omega}}{\partial T_r} \right)_p dp_r \quad (10)$$

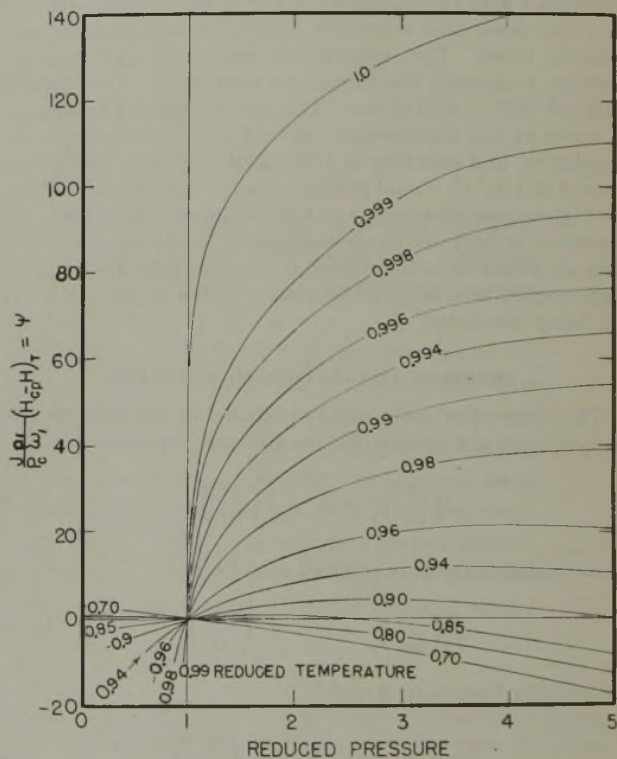


Figure 3. Pressure Correction to Enthalpy of Liquids

Table IV. Values of  $-\frac{J_{\rho_1}}{P_c \omega_1} \left( \frac{\partial H}{\partial p_r} \right)_T$

$T_r$	$P_r = 0$	$P_r = 0.4$	$P_r = 0.8$	$P_r = 1.0$	$P_r = 1.5$	$P_r = 2$	$P_r = 3$	$P_r = 5$
0.7	-3.0	-3.2	-3.4	-3.5	-3.8	-4.0	-4.4	-4.7
0.8	+0.1	-0.6	-1.3	-1.6	-2.2	-2.6	-3.3	-4.1
0.85	+5.0	+3.1	+1.8	+1.3	+0.2	-0.7	-1.9	-3.4
0.90	+15.0	+9.1	+6.3	+5.3	+3.4	+1.9	-0.2	-2.7
0.94	....	....	+19.0	+14.0	+7.7	+4.9	+1.7	-2.0
0.98	....	....	....	....	+20.3	+12.1	+6.2	-0.7
1.0	....	....	....	....	+36.0	+21.8	+10.7	+0.4

Table V. Values of  $\frac{J_{\rho_1}}{P_c \omega_1} (H_{cp} - H)_T = \psi$

$T_r$	$P_r = 0$	$P_r = 0.4$	$P_r = 0.8$	$P_r = 1.2$	$P_r = 1.5$	$P_r = 2$	$P_r = 3$	$P_r = 5$
0.7	+3.1	+2	+0.8	-0.7	-1.8	-3.4	-7.3	-17.2
0.8	+0.8	+0.5	+0.1	-0.2	-0.7	-1.4	-4.0	-12.3
0.85	-3.2	-1.8	-0.5	+0.4	+0.9	+1.0	-0.9	-8.0
0.9	....	-5.0	-1.7	+1.0	+2.2	+3.7	+4.4	+0.2
0.94	....	....	-3.5	+2.1	+5.2	+8.2	+11.8	+10.8
0.98	....	....	....	+10.0	+18	+25.8	+20.2	+39.3
0.99	....	....	....	+15.0	+24.9	+35.0	+47	+54.1
0.999	....	....	....	+46.5	+62.5	+77.8	+97.6	+110.3
1.0	....	....	....	+87.0	+101.5	+115.2	+130.5	....

Values  $[\partial(1/\omega)/\partial T_r]_p$  were obtained from Figure 1 in deriving Figure 2. The resulting integrated pressure correction to entropy is plotted against reduced temperature and pressure in Figure 4 and summarized in Table VII. Table VIII compares values calculated from Figure 4 with experimental values for water and propane. The agreement appears to be somewhat better than that of the enthalpy correction, indicating that generalization is sufficiently sound for useful application.

**PRESSURE CORRECTION TO HEAT CAPACITY AT CONSTANT PRESSURE**

A useful expression for the effect of pressure on heat capacity at constant pressure may be derived by designating the right-hand side of Equation 7 as  $\psi$ , a function of reduced temperature and pressure:

$$\frac{J_{\rho_1}}{P_c \omega_1} (H_{cp} - H)_T = \psi \tag{11}$$

Upon differentiation at constant pressure,

$$\frac{J_{\rho_1}}{P_c \omega_1} \left[ \left( \frac{\partial H_{cp}}{\partial T} \right)_p - \left( \frac{\partial H}{\partial T} \right)_p \right]_T = \frac{1}{T_c} \left( \frac{\partial \psi}{\partial T_r} \right)_p$$

$$\text{or } \frac{J_{\rho_1} T_c}{\omega_1 P_c} (C_{cp} - C_p)_T = \left( \frac{\partial \psi}{\partial T_r} \right)_p \tag{12}$$

The results of graphically differentiating Figure 3 in accordance with Equation 12 are summarized in Figure 5 and Table

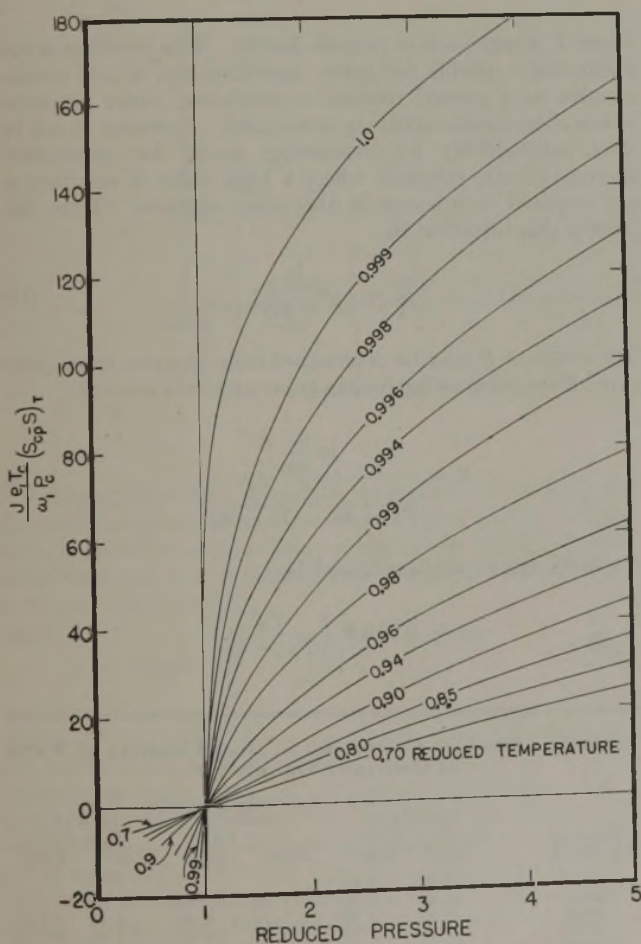


Figure 4. Pressure Correction to Entropy of Liquids

Table VI. Pressure Correction to Enthalpy

Pressure, Lb./Sq. In.	$(H_{cp} - H)_T$ , cal./gram mole					
	204.4° C.		348.9° C.		374.3° C.	
	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
WATER (12)						
1000	23	28	...	...	...	...
2500	8	10	-107	-115	...	...
4000	-8	-9	+75	+79	+1130	+1266
5500	-26	-32	+164	+172	+1370	+1526
PROPANE (17)						
	54.5° C.		71.1° C.		87.9° C.	
300	-29	-25	...	...	...	...
1500	+18	+12	+68	+63	+205	+200
3000	-28	-21	+58	+45	+260	+256

Table VII. Values of  $\frac{J_{\rho_1} T_c}{\omega_1 P_c} (S_{cp} - S)_T$

$T_r$	$P_r = 0.4$	$P_r = 0.8$	$P_r = 1.2$	$P_r = 1.5$	$P_r = 2$	$P_r = 3$	$P_r = 5$
0.7	-4.6	-1.7	+1.1	+3.2	+6.9	+13.8	+25.0
0.9	...	-3.6	+3.8	+8.5	+15.5	+26.9	+44.9
0.94	...	-7.1	+5.6	+12.2	+20.8	+34.7	+53.8
0.98	...	...	+13.2	+24.6	+37.3	+55.1	+79.0
0.99	...	...	+18.3	+31.9	+47.7	+71.0	+99.9
0.996	...	...	+32.1	+50.0	+70.2	+96.9	+130.0
0.999	...	...	+50.7	+76.9	+102.0	+130.9	+165.6
1.0	...	...	+93.2	+113.0	+134.0	+161.5	.....

IX. A comparison of values calculated from Figure 5 with those derived from experimental data for water is shown in Table X. Additional data for testing this relation are scanty, but the agreement with the data on water is sufficiently good to indicate that the generalization did not lose greatly in accuracy through the series of manipulations employed in deriving Figure 5.

**HEAT OF VAPORIZATION**

An empirical graphical generalization was developed by the author (22) which satisfactorily represents the effect of temperature on the heat of vaporization of a variety of polar and nonpolar compounds. A curve, based on the available data for all materials, was presented from which the heat of vaporization at any reduced temperature can be calculated if one value at a known reduced temperature is available. The Kistiakowsky equation offers a satisfactory method of estimating heats of vaporization at the normal boiling points for nonpolar compounds but does not apply to polar materials.

A satisfactory generalized method for estimating the heat of vaporization of any substance at any temperature was developed by Meissner (14). This method shows good agreement with experimental results, particularly at high temperatures. It becomes somewhat unsound at low reduced temperatures, but even in this range the errors are not ordinarily serious. The method here presented is an alternate to Meiss-

Table VIII. Pressure Correction to Entropy

Pressure, Lb./Sq. In.	$(S_{cp} - S) \times 10^4$ cal./gram mole/° K.					
	204.4° C.		348.9° C.		374.3° C.	
	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
WATER (12)						
1000	-115	-100	...	...	...	...
2500	-37	-32	-249	-242	...	...
4000	+38	+33	+194	187	1900	2030
5500	+112	+96	+430	445	2400	2545
PROPANE (17)						
	54.5° C.		71.1° C.		87.9° C.	
300	-235	-238	...	...	...	...
1500	+470	+442	+630	591	+915	+970
3000	+990	+984	+1215	1200	+1670	+1790

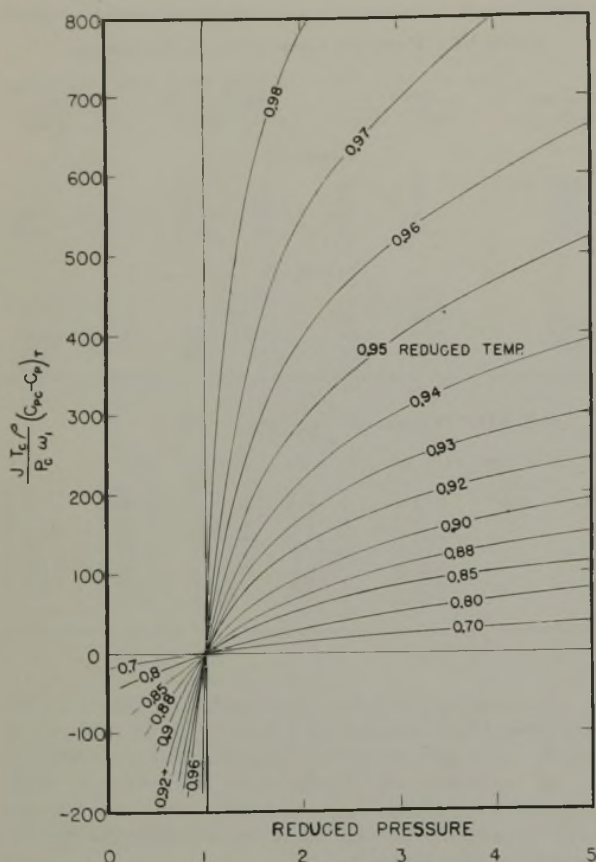


Figure 5. Pressure Correction to Heat Capacity at Constant Pressure of Liquids

ner's method, with the advantage of not involving any graphical relations and consequently being adaptable to mathematical manipulation for the derivation of other thermodynamic functions. It is perhaps somewhat more dependable than Meissner's method at low reduced temperatures.

It has been found that the general curve, referred to above (22) and expressing the relation between heat of vaporization and reduced temperature, is represented by the following empirical equation:

$$\lambda = \lambda_1 \left( \frac{1 - T_r}{1 - T_{r1}} \right)^{0.38} \quad (13)$$

This equation is more convenient to use than the original curve and gives considerably more reproducible results, particularly at temperatures near the critical. It is in good agreement with the available data with the exception of water at low temperatures, below the normal boiling point. As previously mentioned, water is unusual in many of its characteristics in this region.

Heats of vaporization may be accurately calculated at any temperature from the rigorously correct Clapeyron equation:

$$\frac{dp_s}{dT} = \frac{\lambda}{T(v_g - v_l)} \quad (14)$$

The molal volume of the vapor,  $v_g$ , may be calculated from the generalized gas compressibility factors while the volume of the liquid,  $v_l$ , is obtained from Equation 3 and Figure 1. Where complete vapor pressure data are not available, excellent approximations can be obtained from only the boiling point and the critical temperature and pressure by use of a reference substance method of plotting such as that introduced

Table IX. Values of  $\frac{JT_c p_1}{P_c \omega_1} (C_{ep} - C_p)_T$

$T_r$	$P_r = 0.4$	$P_r = 0.8$	$P_r = 1.2$	$P_r = 1.5$	$P_r = 2$	$P_r = 3$	$P_r = 5$
0.7	-9	-3	+3	+7	+14	+23	+38
0.8	-28	-9	+6	+16	+30	+52	+80
0.9	..	-42	+30	+62	+98	+142	+192
0.94	..	-75	+70	+143	+216	+303	+392
0.96	..	-190	+146	+272	+400	+518	+662
0.97	..	..	+208	+387	+550	+695	..
0.98	..	..	+385	+608	+778	..	..

by Cox (5) which permits ready determination of  $dp_s/dT$  from the corresponding values for the reference substance. However, this method is rather tedious, and the added labor is frequently not warranted by the improved accuracy obtained.

If the application of Equation 14 is restricted to the normal boiling point, a reasonably good approximation is obtained with the following modified form of the Clausius-Clapeyron equation in which the factor 0.95 represents the average deviation of the vapor from the ideal gas laws at these conditions, together with the effect of the liquid volume:

$$\left( \frac{dp_s}{dT} \right)_B = \frac{p_B \lambda_B}{0.95 RT_B^2} \quad (15)$$

A simple relation between temperature and vapor pressure was developed by Calingaert and Davis (3) as a result of a study of the Cox method of vapor-pressure plotting:

$$\ln p_s = A - \frac{B}{T - 43} \quad (16)$$

where  $T$  is expressed in degrees Kelvin. This equation is not particularly reliable for many materials and is not recommended as a general method of predicting vapor pressures where considerable accuracy is required. However, it can be used satisfactorily for evaluating  $dp/dT$  for generalized thermodynamic relations where a high order of accuracy is not required or inherent in the other relations. Thus, differentiating Equation 16,

$$\frac{dp_s}{dT} = \frac{p_s B}{(T - 43)^2} \quad (17)$$

The constant  $B$  may be determined from any two vapor pressure values, such as the boiling point and critical point:

$$B = \frac{\ln \frac{p_c}{p_B}}{\frac{1}{T_B - 43} - \frac{1}{T_c - 43}} \quad (18)$$

Combining Equations 12 and 14,

$$\lambda_B = 0.95RB \left( \frac{T_B}{T_B - 43} \right)^2 \quad (19)$$

Table X. Pressure Correction to Heat Capacity of Water at Constant Volume (12)

Pressure, Lb./Sq. In.	$(C_{ep} - C_p)_T$ cal./gram mole/° K.					
	260° C., $T_r = 0.824$		315.6° C., $T_r = 0.910$		337.8° C., $T_r = 0.943$	
	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
1000	-0.88	-0.81	..	..	..	..
2000	-0.46	-0.38	-1.98	-1.93	..	..
2500	-0.27	-0.23	-1.15	-0.99	-2.48	-2.61
4000	+0.25	+0.27	+0.87	+0.90	+1.94	+2.02
6000	+0.74	+0.86	+2.18	+2.32	+4.40	+4.41

This equation gives results generally not differing from reliable experimental values by so much as 5 per cent when constant  $B$  is determined from the critical point and boiling point. Somewhat better results are obtained if  $B$  is evaluated from a vapor pressure value less distant from the normal boiling point than the critical temperature, and if the actual compressibility factor of the vapor is used instead of the average value of 0.95.

#### HEAT CAPACITY DIFFERENCE BETWEEN SATURATED LIQUID AND ITS IDEAL GAS

By combining the equations developed above with the generalized expression for the effect of pressure on the enthalpy of gases, it is possible to derive a generalized thermodynamic method for calculating the difference between the heat capacity of a saturated liquid and the same material as an ideal gas at the same temperature and zero pressure. Such a

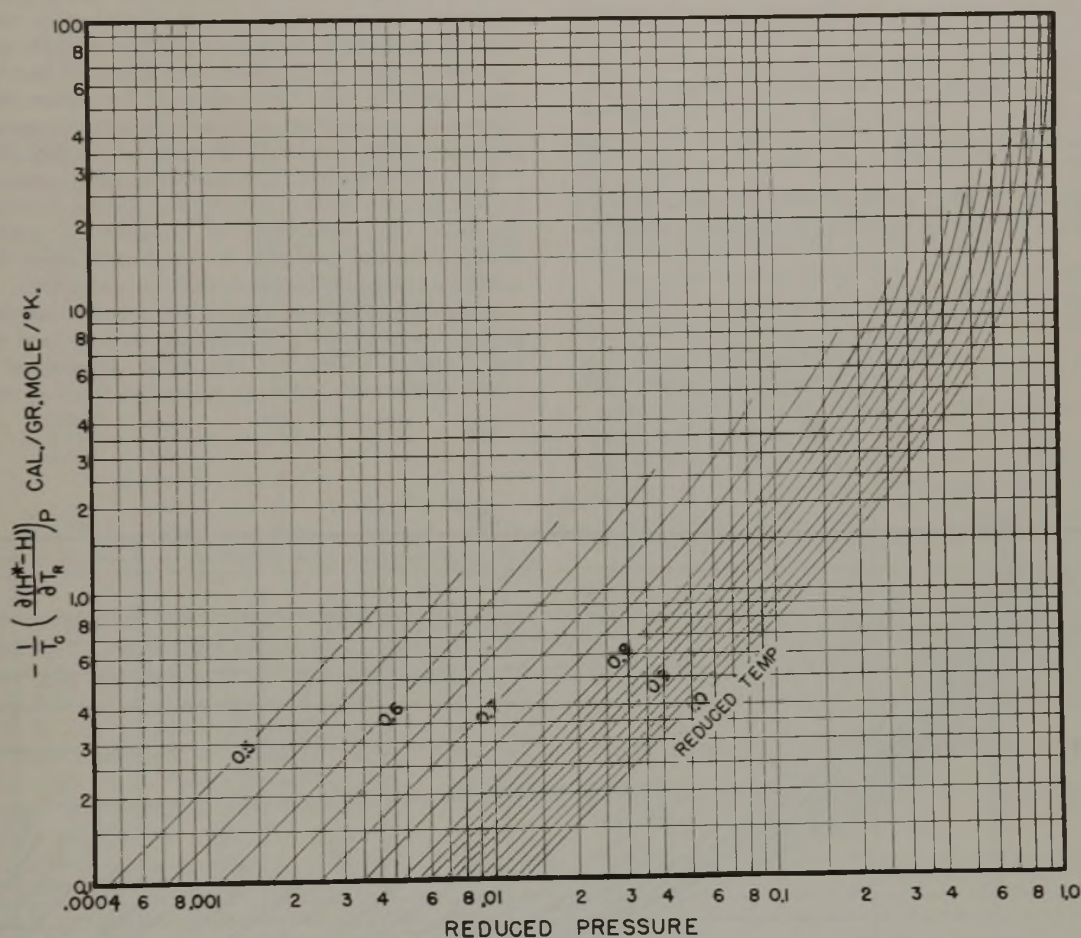


Figure 6. Differential Pressure Correction to Enthalpy of Gases

Combining Equations 13 and 19, an expression is obtained which permits calculation of the heat of vaporization of any substance at all conditions from a knowledge merely of the boiling point and critical temperature and pressure, since  $B$  is also found from  $T_c$  and  $P_c$ :

$$\lambda = 0.95RB \left( \frac{T_B}{T_B - 43} \right)^2 \left( \frac{1 - T_r}{1 - T_{rB}} \right)^{0.38} \quad (20)$$

Table XI compares values calculated from Equation 20 with experimental data for several compounds on which measurements were made at elevated temperatures. The deviations are of the same order as shown by Meissner's method; they are greater in some cases and less in others. Further comparisons indicated that the major source of error is Equation 19 rather than Equation 13, and the over-all accuracy is improved by using the actual compressibility factor at the boiling point instead of the average value of 0.95.

method is of considerable value because of the scarcity and general unreliability of heat capacity data. Recent development of generalized statistical methods (1, 6) derived from spectroscopic observations permits reasonably satisfactory prediction of the heat capacities of the more simple molecules in the ideal gaseous state. These methods, combined with a thermodynamic relation between gaseous and liquid heat capacities and the relations for thermodynamic properties of liquids developed above, will permit complete prediction of heat capacities at all conditions, both liquid and gaseous. Conversely, for complex high-boiling liquids on which liquid heat capacity measurements have been made, such a thermodynamic relation may offer a more reliable method of estimating gaseous heat capacities than the statistical methods. The relation will also be useful in rationalizing experimental observations of gaseous and liquid heat capacities and making them consistent with each other.

There are several methods by which a saturated liquid at temperature  $T_1$  may be converted into a saturated vapor at a

higher temperature  $T_2$ . One is to heat the liquid (maintaining saturation) to  $T_2$  and vaporize it. Another is to vaporize the liquid at  $T_1$ , isothermally expand the vapor to zero pressure, heat the ideal vapor to  $T_2$ , and isothermally compress to saturation conditions. Since the initial and final states are the same in both cases, the enthalpy changes of the two operations must be equal:

$$\lambda_1 + (H_1^* - H_{g1}) + C_{p0}^* (T_2 - T_1) - \frac{(H_2^* - H_{g2})}{\lambda_2 + C_{s1}(T_2 - T_1)} = \quad (21)$$

Rearranging and applying to an infinitesimal temperature change,  $dT$ ,

$$(C_{s1} - C_{p0}^*) dT = -d\lambda - d(H^* - H_{g0})$$

$$C_{s1} - C_{p0}^* = -\frac{d\lambda}{dT} - \frac{d(H^* - H_{g0})}{dT} \quad (22)$$

Since the term  $d(H^* - H_{g0})$  involves both a temperature and a pressure change, it must be expressed in terms of partial differentials:

$$\frac{d(H^* - H_{g0})}{dT} = \left[ \frac{\partial(H^* - H_{g0})}{\partial T} \right]_p + \left[ \frac{\partial(H^* - H_{g0})}{\partial p} \right]_T \frac{dp_s}{dT} \quad (23)$$

All the terms on the right-hand side of Equation 24 may be obtained from generalizations, presumably applicable to all substances. Thus, differentiating Equation 20,

$$\frac{d\lambda}{dT_r} = \frac{-0.361RB}{(1 - T_{rB})^{0.38}} \left( \frac{T_B}{T_B - 43} \right)^2 \frac{1}{(1 - T_r)^{0.62}} \quad (25)$$

A generalized relation between  $(H^* - H_g)$  and reduced temperature and pressure was introduced by Watson and Nelson (23) and improved by several others (8, 10, 24, 26). Graphical differentiation of this relation with respect to reduced temperature at constant pressure permits evaluation of the second term of Equation 24. The first part of the third term similarly may be evaluated by differentiation with respect to reduced pressure at constant temperature. The last part of the third term is evaluated by Equation 17.

For differentiation, a pressure-enthalpy correction chart for the gaseous state was prepared, taking into account the improved data calculated by Edmister (8) and York and Weber (26) and extended to the low reduced temperature range by the Joule-Thomson data on water (11). This chart was graphically differentiated with respect to temperature and pressure, and the data obtained are summarized in Figures 6 and 7 and in Tables XII and XIII. Because of the uncertainty of the basic enthalpy correction chart at conditions in

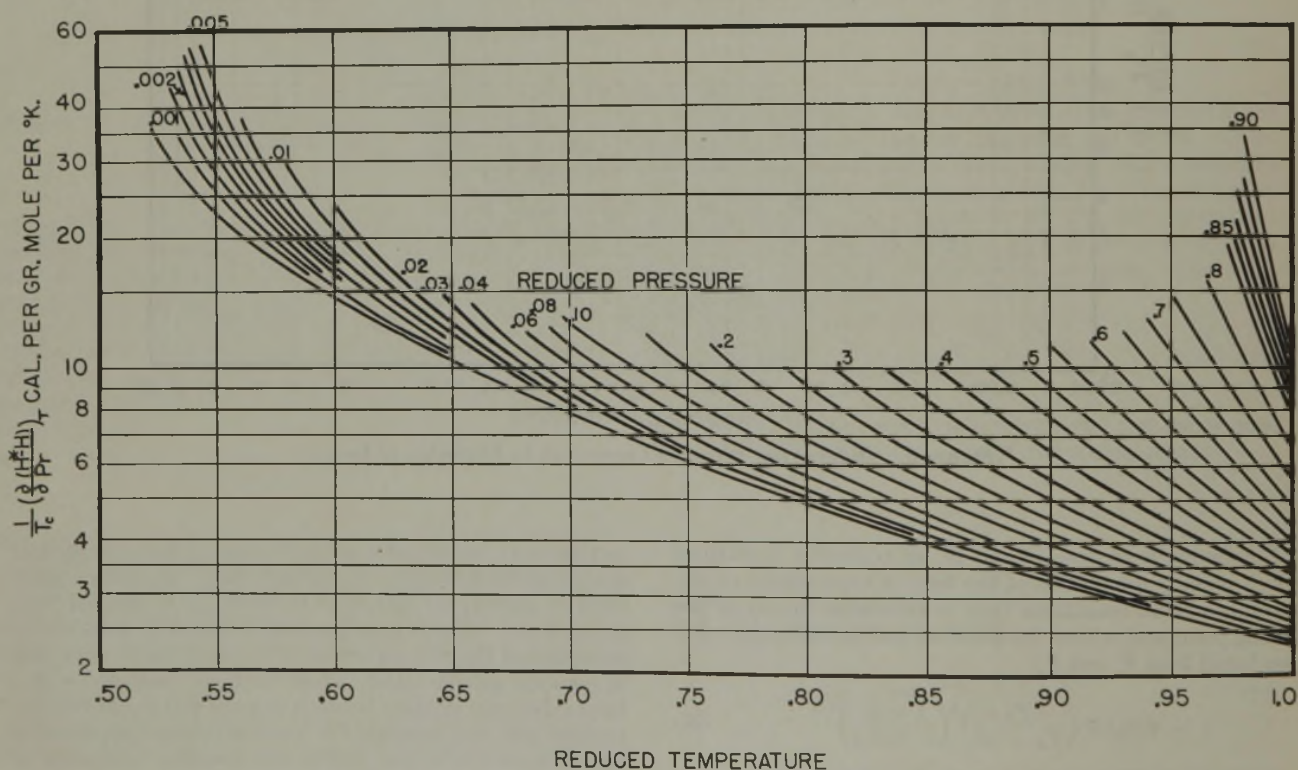


Figure 7. Differential Pressure Correction to Enthalpy of Gases

Substituting Equation 23 in 22 and writing in terms of reduced conditions,

$$C_{s1} - C_{p0}^* = -\left( \frac{d\lambda}{dT_r} \right) \frac{1}{T_c} - \left[ \frac{\partial(H^* - H_g)}{\partial T_r} \right]_p \frac{1}{T_c} - \left[ \frac{\partial(H^* - H_g)}{\partial p_r} \right]_T \frac{1}{P_c} \frac{dp_s}{dT} \quad (24)$$

the saturated region, particularly at low temperatures, the curves of Figures 6 and 7 were adjusted by cross plotting to obtain consistent relations which, when incorporated in Equation 24, gave the best average agreement with the ex-

**Table XI. Heats of Vaporization**

Temperature, ° C.	λ, cal./gram mole		Temperature, ° C.	λ, cal./gram mole	
	Calcd.	Exptl.		Calcd.	Exptl.
WATER (12)					
83	9,680	9,890	277	6,380	6,720
115	9,250	9,530	307	5,460	5,740
147.5	8,800	9,110	322	5,020	5,240
180.5	8,300	8,660	335	4,500	4,670
210.5	7,740	8,140	348.5	3,850	3,980
245	7,100	7,470	364	2,960	3,040
			373.3	1,020	1,060
AMMONIA (21)					
-49.9	5,870	5,770	91.8	3,310	(3,180)
-9.5	5,340	5,260	100	3,045	(3,050)
+31.0	4,690	4,640	108.1	2,730	(2,700)
71.6	3,870	(3,780)	116.2	2,340	(2,250)
			124.3	1,800	(1,640)
BENZENE (11)					
0	8,250	8,350	180	5,700	5,790
60	7,680	7,600	220	4,780	4,850
100	7,000	7,060	260	3,420	3,420
140	6,400	6,440	280	2,160	2,140
ETHYL ALCOHOL (11)					
0	10,450	10,110	160	6,950	7,150
40	9,760	9,900	200	5,650	5,280
80	8,970	9,350	220	4,260	3,960
120	8,090	8,350	240	1,990	1,760
BUTANE (19)					
24.9	5,140	5,050	110.9	3,380	3,170
67.9	4,400	4,310			
PROPANE (17)					
20.8	3,680	3,460	88.1	1,785	1,490
54.8	2,960	2,780	98.1	916	610
73.8	2,410	2,210			
SULFUR DIOXIDE (11)					
-10	5,930	6,090	40	5,180	4,950
+20	5,490	5,400	60	4,810	4,500

perimental values of  $(C_{sl} - C_g^*)$  for water and ammonia. In all of this work Equations 16 and 18 were used for the calculation of vapor pressures, and it is recommended that this procedure be followed in using Figures 6 and 7.

Figure 7 is not in good agreement with  $(\partial H / \partial P)_T$  data calculated by Kennedy, Sage, and Lacey (13) from their Joule-Thomson measurements on *n*-butane and *n*-pentane. Edmister (8) pointed out that the data of these investigators did not conform with his generalized relations. Similarly, Watson and Smith (24) found that a generalized plot of Joule-Thomson coefficients showed large differences from the experimental data. These discrepancies indicate that differentiation of the generalized enthalpy-pressure relation tends to magnify its inherent errors. It is probable that the absolute values of the

functions plotted in Figures 6 and 7 may differ from experimental values for some substances by as much as 50 per cent. However, it is hoped that these errors will tend to compensate one another when the two charts are used together in conjunction with Equation 24 and Equations 16 and 18 for calculating pressures.

Heat capacity data in general are so unreliable that it is difficult to find good comparable values on both the liquid and gaseous state with which to test Equation 24. Table XIV compares values calculated from the equation with experimental data for water, ammonia, pentane, butane, and propane. The experimental values for the hydrocarbons were taken from the general correlation of Holcomb and Brown (9) at temperatures below 70° F. These are actually heat capacities at constant pressure, but at reduced temperatures below 0.8 the difference from the heat capacity of the saturated liquid becomes small. At higher temperatures the data of Sage and co-workers from the indicated sources were selected. These investigators made actual measurements of the heat capacities of the saturated liquid.

The agreement in Table XIV is reasonably good except in the case of butane at the higher temperatures. Although these few comparisons do not confirm the reliability of Equation 24, it is encouraging that agreement is obtained on both nonpolar and highly polar compounds of both low and high boiling points. Figures 6 and 7 are not recommended for reduced temperatures above 0.96 or below 0.55. At reduced temperatures below 0.55 the difference between the heat capacity of the liquid and the ideal gas appears to approach independence of temperature, and it is believed that this assumption is preferable to attempting to extend Figure 7.

In the recommended temperature range it seems probable that the calculated heat capacity differences should not be in error by more than 25 per cent. Although much better accuracy is to be desired, such errors are not too serious, particularly when one is working with materials of high molal heat capacities for which the difference in heat capacities is

**Table XII. Values of  $-\frac{1}{T_c} \left( \frac{\partial(H^* - H)}{\partial T_R} \right)_P$  in Small Calories per Gram Mole per ° K.**

$P_r$	$T_r = 0.55$	$T_r = 0.6$	$T_r = 0.7$	$T_r = 0.8$	$T_r = 0.9$	$T_r = 0.95$	$T_r = 1.0$
0.001	0.140	...	...	...	...	...	...
0.002	0.275	0.181	...	...	...	...	...
0.003	0.415	0.270	0.121	...	...	...	...
0.006	0.88	0.55	0.242	0.126	...	...	...
0.01	...	0.95	0.40	0.210	0.128	...	...
0.02	...	...	0.80	0.42	0.254	0.195	0.158
0.03	...	...	1.23	0.63	0.38	0.29	0.186
0.06	...	...	2.82	1.33	0.77	0.59	0.47
0.1	...	...	...	2.46	1.34	1.0	0.79
0.2	...	...	...	7.0	3.12	2.20	1.63
0.4	...	...	...	...	9.5	5.7	4.0
0.5	...	...	...	...	18.5	8.6	5.7
0.7	...	...	...	...	27	8.6	11.4
0.9	...	...	...	...	...	...	33

**Table XIII. Values of  $\frac{1}{T_c} \left( \frac{\partial(H^* - H)}{\partial P_r} \right)_T$  in Small Calories per Gram Mole per ° K.**

$P_r$	$T_r = 0.55$	$T_r = 0.6$	$T_r = 0.7$	$T_r = 0.8$	$T_r = 0.9$	$T_r = 0.95$	$T_r = 0.98$	$T_r = 1.0$
0.001	25.2	14.6	7.8	4.88	3.29	2.73	2.48	2.32
0.002	32.0	15.8	7.9	4.88	3.29	2.73	2.48	2.32
0.005	46	17.5	8.0	4.88	3.29	2.73	2.48	2.32
0.01	..	20.8	8.1	4.88	3.29	2.73	2.48	2.32
0.02	..	24.0	8.2	4.88	3.29	2.73	2.48	2.32
0.03	..	..	8.5	5.0	3.35	2.73	2.48	2.32
0.06	..	..	10.1	5.25	3.4	2.80	2.50	2.34
0.10	..	..	12.8	6.05	3.65	3.00	2.64	2.44
0.2	..	..	..	7.8	4.20	3.29	2.88	2.63
0.3	..	..	..	11.7	5.0	3.70	3.15	2.84
0.5	..	..	..	..	9.0	5.45	4.15	3.5
0.6	..	..	..	..	..	7.3	5.05	4.0
0.7	..	..	..	..	..	10.9	6.6	4.8
0.8	..	..	..	..	..	..	10.7	6.6
0.85	..	..	..	..	..	..	15.0	8.1
0.90	..	..	..	..	..	..	34.0	11.2

Table XIV. Difference between Heat Capacities of Saturated Liquid and Its Ideal Gas

$T_r$	$T^\circ \text{C.}$	$(C_{sl} - C_{pg}^*), \text{ cal./g. mole/}^\circ \text{K.}$		$T_r$	$T^\circ \text{C.}$	$(C_{sl} - C_{pg}^*), \text{ cal./g. mole/}^\circ \text{K.}$	
		Calcd.	Exptl.			Calcd.	Exptl.
WATER (12)							
0.55	83	11.0	10.0	0.85	277	14.4	13.6
0.60	115	11.5	10.1	0.90	307	17.0	16.4
0.65	147.5	11.5	10.3	0.92	322.5	18.6	18.0
0.70	180.5	11.8	10.7	0.94	335	20.7	20.7
0.75	210.5	11.9	11.2	0.96	348.5	28.0	25.1
0.80	245	12.3	11.6				
AMMONIA (21)							
0.55	-49.9	9.8	9.8	0.85	71.6	12.9	12.6
0.60	-29.8	9.9	1.0	0.90	91.8	15.1	14.7
0.65	-9.5	9.8	10.2	0.92	100.0	17.1	16.2
0.70	+10.7	10.4	10.5	0.94	108.1	16.9	17.8
0.75	31.0	10.7	10.9	0.96	116.2	19.9	20.9
0.80	51.3	11.4	11.5				
n-PENTANE (9)							
0.55	-14.6	9.9	10.0	0.7	55.9	11.4	11.9
0.6	+8.9	10.1	10.4	0.8	103.9	11.6	13.6
n-BUTANE (9, 15, 20)							
0.55	-39.1	8.7	7.6	0.8	67.9	10.3	14.4
0.6	-17.1	8.8	8.7	0.9	110.9	12.9	17.6
0.7	+24.9	9.4	10.9				
PROPANE (9, 15, 20)							
0.55	-67.7	5.2	6.1	0.8	25.6	8.2	9.3
0.6	-49.1	5.8	6.4	0.9	63.0	13.5	13.4
0.7	-11.7	6.3	8.2				

small in comparison to the heat capacity of the vapor. At present no better general method for estimating these properties is available.

#### DIFFERENCE BETWEEN HEAT CAPACITY AT CONSTANT PRESSURE AND HEAT CAPACITY OF SATURATED LIQUID

The heat capacity of a saturated liquid  $C_{sl}$  expresses the change in enthalpy accompanying a simultaneous increase in both temperature and pressure:

$$C_{sl} = \left( \frac{\partial H}{\partial T} \right)_P + \left( \frac{\partial H}{\partial p} \right)_T \frac{dp_s}{dT} \quad (26)$$

In terms of reduced conditions,

$$(C_{sl} - C_{sl})_{TP} = - \left( \frac{\partial H}{\partial p_r} \right)_T \frac{1}{P_c} \left( \frac{dp_s}{dT} \right) \quad (27)$$

Values of  $\frac{1}{P_c} \left( \frac{\partial H}{\partial p_r} \right)_T$  may be obtained from Figure 2, and  $dp_s/dT$  is calculated from Equation 17, permitting complete evaluation of Equation 27.

Table XV. Difference between Heat Capacity at Constant Pressure and Heat Capacity of Saturated Liquid (Water, 12)

$T^\circ \text{C.}$	$T_r$	$(C_p - C_s), \text{ cal./g. mole/}^\circ \text{K.}$	
		Calcd.	Exptl.
204.4	0.738	-0.08	-0.09
287.8	0.867	+0.33	+0.54
315.6	0.910	+0.92	+1.11
326.7	0.927	+1.75	+2.16
337.8	0.943	+3.0	+3.64

Table XV compares results calculated from Equation 27 with the accepted values for water. The agreement is not particularly good, but the quantity sought is not large except at conditions near the critical. Furthermore, it is believed that maximum errors are probably encountered when Figure 2 is applied to water because of the unusually low reduced pressures corresponding to a given reduced temperature at

saturation. As a result, saturation values for water fall on the extrapolated portion of Figure 2 at pressures below the range of the hydrocarbon data from which it was derived. Better accuracy should be obtained from Equation 27 when applied to other materials of lower critical pressures.

#### ACKNOWLEDGMENT

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#### NOMENCLATURE

- $A, B$  = constants in Calingaert-Davis vapor pressure equation  
 $C$  = heat capacity  
 $C^*$  = heat capacity of ideal gas  
 $d$  = liquid density  
 $H$  = enthalpy  
 $H^*$  = enthalpy of ideal gas  
 $J$  = mechanical equivalent of heat  
 $M$  = molecular weight  
 $p$  = pressure  
 $P$  = pressure  
 $R$  = gas law constant  
 $S$  = entropy  
 $T$  = absolute temperature  
 $v$  = molal volume  
 $V$  = volume of  $n$  moles  
 $z$  = compressibility factor (gaseous)  
 $\lambda$  = molal heat of vaporization  
 $\rho$  = liquid density, mass per unit volume  
 $\psi = \frac{J\rho_1}{P_c\omega_1} (H_{sp} - H)_T$   
 $\omega$  = liquid expansion factor
- Subscripts  
 $B$  = normal boiling point  
 $c$  = critical value  
 $cp$  = critical pressure  
 $g$  = gaseous state  
 $l$  = liquid state  
 $r$  = reduced value  
 $s$  = saturated liquid or vapor

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# BATCH RECTIFICATION

## Effect of Fractionation and Column Holdup

*Equations are derived for both binary and complex mixtures showing the yield of distillate of given composition obtainable by batch rectification of a given charge, taking into account both degree of fractionation and column holdup. It is assumed that the reflux ratio is continuously increased throughout the distillation to maintain the product composition constant. The equations for binary mixtures are exact solutions; those for complex mixtures afford a good approximation to results obtained by plate-to-plate calculations.*

*R. Edgeworth-Johnstone*

TRINIDAD LEASEHOLDS, LTD.,  
POINTE-A-PIERRE, TRINIDAD, B. W. I.

**R**OSE, Welshans, and Long (5) and Colburn and Stearns (2) published methods of calculating the distillation curve of a binary mixture subjected to batch rectification, where the effect of column holdup is recognized. In both cases a constant reflux ratio is assumed so that the distillate composition varies continually.

In practice the important question usually is, how much distillate of a given composition can be obtained from a given charge? To conserve heat, common practice is to start with a low reflux ratio and increase it as the cutting point is approached; the composition of the distillate is thus maintained approximately constant at the desired value throughout the distillation. Under these conditions the yield of distillate cannot readily be computed by methods which start by assuming a constant reflux ratio.

Two factors reduce the actual yield of distillate below 100 per cent—incomplete fractionation and column holdup. The relative importance of these factors varies with circumstances and governs the type of column which will be most efficient for a particular duty. For example, packed columns usually have a much lower holdup than plate columns of equal fractionating ability; but the number of theoretical plates which can be economically provided in a packed column is limited by the well-known channeling effect, which increases with the height of the column. In certain circumstances, however, the holdup effect may be preponderant, so that a packed column with relatively few theoretical plates and low holdup will give far better yields than a plate column with many more theoretical plates and a higher holdup. It does not seem possible by existing methods to decide upon the most advantageous arrangement without long and tedious calculations, and then only in the case of binary mixtures.

Equations are developed here which give the yield from batch rectification directly and take into account both the factors mentioned above. The basic assumption is that the reflux ratio is progressively increased throughout the distillation, so as to maintain the distillate composition constant, and reaches infinity at the cutting point. The assumption of

constant distillate composition permits the final distribution of components to be computed from conditions at the cutting point alone, using the comparatively simple equations applicable to total reflux. The method can be extended with good approximation to complex mixtures.

### BINARY MIXTURES

Consider first an ideal column having  $N$  theoretical plates and no holdup. A batch of  $F$  moles of a binary mixture, in which the mole fraction of the more volatile component ( $A$ ) is  $a_f$ , is distilled with progressively increasing reflux ratio to maintain the distillate composition constant at  $a_p$ . This may be done by keeping the overhead vapor at constant temperature by automatic control; a constant rate of heat input to the still is also maintained. If temperature control is not sensitive enough, Bogart's method (1) of calculating how the reflux ratio should vary may be applied. Such conditions will henceforth be referred to as constant distillate composition (C. D. C.) conditions. At the end of the distillation the reflux ratio is infinity.

For total reflux the Fenske equation (4) applies, and the composition of the bottoms is, therefore,

$$a_w = \frac{a_p}{\alpha^{N+1}(1-a_p) + a_p}$$

From material balances at the end of the distillation,

$$\begin{aligned} P + W &= F \\ Pa_p + Wa_w &= Fa_f \end{aligned}$$

Substituting for  $a_w$  and simplifying,

$$P = \left( F \frac{a_f}{a_p} \right) \frac{\alpha^{N+1} - \left( \frac{a_p}{1-a_p} \right) \left( \frac{1-a_f}{a_f} \right)}{\alpha^{N+1} - 1}$$

The total quantity of distillate of composition  $a_p$  contained in the original charge is  $F(a_f/a_p)$ . Dividing by this quantity gives the yield fraction as shown in Equation 1.

$$y = \frac{\alpha^{N+1} - \left(\frac{a_p}{1-a_p}\right) \left(\frac{1-a_f}{a_f}\right)}{\alpha^{N+1} - 1} \quad (1)$$

This equation represents the yield from an ideal column having no holdup. It is less than unity owing to incomplete fractionation—i. e., because  $N$  is finite and a certain quantity of  $A$  must therefore remain in the still.

Now consider an actual column having a holdup of  $Q$  moles per theoretical plate with other conditions the same as for the ideal column. At the beginning of the distillation the column is assumed to be empty. The final bottoms composition,  $a_w$ , is the same as for the ideal column, but there is held up in the column  $NQ$  moles of a mixture, the average composition of which lies between  $a_w$  and  $a_p$ . To calculate the yield fraction it is necessary to find the average composition of this mixture, deduct the total moles of  $A$  and  $B$  held up from those present in the original batch, correct  $F$  and  $a_f$  accordingly, and insert these corrected quantities in Equation 1.

If  $Q\Sigma$  represents the total moles of  $A$  held up in the column, the material balance equations become:

$$\begin{aligned} P + W &= F - NQ \\ Pa_p + Wa_w &= Fa_f - Q\Sigma \end{aligned}$$

The problem is to determine  $\Sigma$ .

Applying the Fenske equation (4), the composition of the liquid on the top plate is:

$$a_1 = \frac{a_p}{\alpha(1-a_p) + a_p}$$

Similarly,

$$a_2 = \frac{a_p}{\alpha^2(1-a_p) + a_p}$$

$$a_3 = \frac{a_p}{\alpha^3(1-a_p) + a_p}$$

$$a_n = \frac{a_p}{\alpha^n(1-a_p) + a_p}$$

The proportion of vapor in the column is assumed to be so small that the average composition of the total material held up is not sensibly different from that of the liquid held up. The total moles of component  $A$  retained in the column are then:

$$Q \left\{ \frac{a_p}{\alpha(1-a_p) + a_p} + \frac{a_p}{\alpha^2(1-a_p) + a_p} + \frac{a_p}{\alpha^3(1-a_p) + a_p} + \dots + \frac{a_p}{\alpha^n(1-a_p) + a_p} \right\} = Q\Sigma$$

The summation of the series represented by  $\Sigma$  was found by Rose, Welshans, and Long (5) to be:

$$\Sigma = \frac{1}{\log \alpha} \log [1 + a_w(\alpha^N - 1)]$$

For present purposes it is more convenient to have  $\Sigma$  in terms of product composition. Substituting according to the Fenske equation:

$$\Sigma = \frac{1}{\log \alpha} \log \left[ 1 + \frac{a_p(\alpha^N - 1)}{\alpha^{N+1}(1-a_p) + a_p} \right] \quad (2)$$

This expression was derived by integrating between 1 and  $N$  theoretical plates, assuming a continuous change of composition. Hence it is strictly valid only for packed columns. For a plate column it gives a value of  $\Sigma$  somewhat too low. This can be seen by putting  $N = 1$ , when for a plate column  $\Sigma$  should be numerically equal to  $a_1 = a_p/[\alpha(1-a_p) + a_p]$ .

The correct value for plate columns is found by integrating between 0.5 and  $(N + 0.5)$  theoretical plates:

$$\Sigma = \frac{1}{\log \alpha} \log \left[ 1 + \frac{a_p(\alpha^N - 1)}{\alpha^{N+0.5}(1-a_p) + a_p} \right] \quad (3)$$

Substituting for  $a_w$  in the material balance equations and simplifying,

$$P = \left( \frac{Fa_f - Q\Sigma}{a_p} \right) \frac{\alpha^{N+1} - \frac{a_p}{1-a_p} \left( \frac{F - NQ}{Fa_f - Q\Sigma} - 1 \right)}{\alpha^{N+1} - 1}$$

Dividing by  $F(a_f/a_p)$  and putting  $Q/F = q$ ,

$$y = \left( \frac{a_f - q\Sigma}{a_f} \right) \frac{\alpha^{N+1} - \frac{a_p}{1-a_p} \left( \frac{1 - Nq}{a_f - q\Sigma} - 1 \right)}{\alpha^{N+1} - 1} \quad (4)$$

Equation 4 gives the yield fraction from an actual batch column operated under C. D. C. conditions; both incomplete fractionation and column holdup are taken into account. It is an exact solution, provided that the appropriate equation is used to evaluate  $\Sigma$  and that the underlying assumptions apply. These assumptions were total reflux at the cutting point, validity of the Fenske equation, and neglect of the effect of vapor on the average composition of the material held up. According to Underwood (6), the Fenske equation may be applied to all binary mixtures in which the components can be assumed to have a constant average relative volatility throughout the distillation, even though they do not conform to Raoult's law.

If the column is not empty at the beginning of the distillation, its contents must be added to the original charge; both  $F$  and  $a_f$  are corrected accordingly.

#### COMPLEX MIXTURES

Consider a mixture consisting of components  $A$ ,  $B$ ,  $C$ , etc., from which a distillate containing a relatively high proportion of  $A$  is required to be separated by batch rectification under C. D. C. conditions.  $A$  and  $B$  are the key components, and the distillate may, without serious error, be assumed to consist of these components only.

Provided the key components obey Raoult's law, the Fenske equation applies in this case at infinite reflux ratio as if the charge were a binary mixture of  $A$  and  $B$  only; that is,

$$\frac{a_w}{b_w} = \frac{1}{\alpha^{N+1}} \left( \frac{a_p}{b_p} \right)$$

For an ideal column with no holdup, the material balance equations are:

$$\begin{aligned} P + W &= F \\ Pa_p + Wa_w &= Fa_f \\ Pb_p + Wb_w &= Fb_f \end{aligned}$$

Evaluating the yield fraction from these equations,

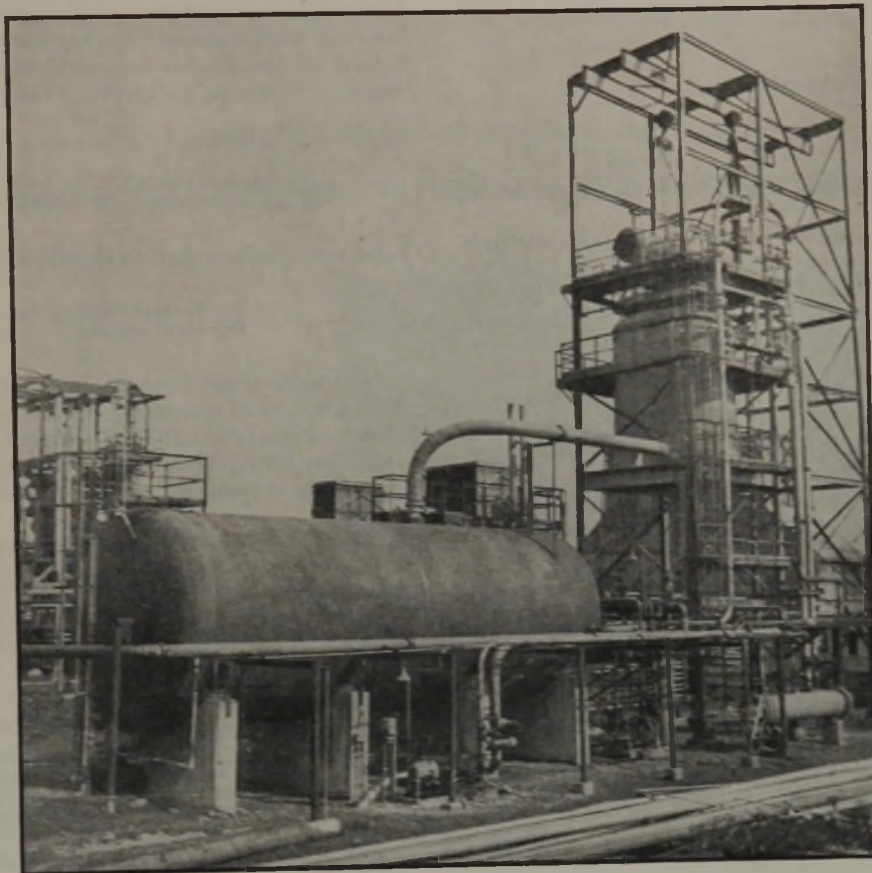
$$y = \frac{\alpha^{N+1} - \frac{a_p}{1-a_p} \left( \frac{q_f}{a_f} \right)}{\alpha^{N+1} - 1} \quad (5)$$

This is the same as Equation 1 except that for binary mixtures  $b_f = 1 - a_f$ . The only effect of the heavier components present is to raise the temperature at the bottom of the column and thus slightly reduce the average value of  $\alpha$  compared with that applying to a binary mixture of  $A$  and  $B$ .

The important difference between binary and complex mixtures lies in the effect of column holdup. Consider a complex

mixture and a corresponding binary mixture in which the relative proportions of *A* and *B* are the same. *F* moles of the complex mixture contain much less of component *A* than *F* moles of the binary mixture owing to the presence of the heavier components. Yet at the end of the distillation the amount of *A* held up in the column from the complex mixture will be nearly as great as that from the binary mixture. Therefore the reduction in yield fraction due to holdup will be much greater in the case of the complex mixture.

consist principally of the key components. The holdup of *A* in this region is thus practically the same as that with the corresponding binary mixture. Lower down the column substantial concentrations of heavier components appear, which reduce the holdup of lighter component per theoretical plate below the value obtaining for the corresponding binary mixture. But since the holdup per plate in that region is already low, the effect on the total quantity of distillate held up is slight.



Courtesy, Foster Wheeler Corporation

*Stedman Batch Distillation Unit at Trinidad*

The fact that nearly as much of component *A* is held up from the complex mixture as from a corresponding binary mixture is easily understood when it is remembered that the lighter component is held up chiefly in the top few plates. Here, even with the complex mixture, both liquid and vapor

An illustration is the plate-to-plate computation of Underwood (6) for a mixture of hexane, heptane, octane, nonane, and decane; the column holdup of hexane may be compared with that which would occur with the corresponding binary mixture of hexane and heptane.

Only the first seven plates need be considered, since below them the hexane concentration is negligible. In this region the only components present in appreciable quantity are hexane, heptane, and octane as shown in Table I. The total column holdup of hexane for the five-component mixture is thus only 6 per cent lower than that for the corresponding binary mixture.

In view of the relatively small proportion the quantity of material held up in the column normally bears to the total quantity of distillate, a reasonable approximation in the case of complex mixtures is to assume that the value of  $\Sigma$  is the same as that calculated for the corresponding binary mixture. This is given by Equations 2 or 3 according as the column is of the packed or plate variety. In other words, the column is assumed to contain *A* and *B* only.

Table I

Plate No.	Mole Fraction (from Underwood Curves)			Mole Fraction Hexane for Corresponding Binary Mixt.
	Hexane	Heptane	Octane	
Distillate	0.54	0.46	Nil	0.54
1	0.345	0.64	0.015	0.350
2	0.18	0.785	0.035	0.186
3	0.095	0.825	0.08	0.103
4	0.04	0.79	0.50	0.048
5	0.02	0.665	0.315	0.029
6	0.01	0.49	0.50	0.020
7	Nil	0.30	0.70	Nil
Total for 7 plates	0.690			0.736

For an actual column with appreciable holdup, the material balance equations applying to a complex mixture are:

$$\begin{aligned} P + W &= F - NQ \\ Pa_p + Wa_w &= Fa_f - Q\Sigma \\ Pb_p + Wb_w &= Fb_f - (NQ - Q\Sigma) \end{aligned}$$

(The column is again assumed to be empty at the start of the distillation.) Combining these with the Fenske equation and solving for  $P$ ,

$$P = \left( \frac{Fa_f - Q}{a_p} \right) \frac{\alpha^{N+1} - \frac{a_p}{1 - a_p} \left[ \frac{F(a_f + b_f) - NQ}{Fa_f - Q\Sigma} - 1 \right]}{\alpha^{N+1} - 1}$$

Dividing by  $F(a_f/a_p)$  and putting  $Q/F = q$ ,

$$y = \left( \frac{a_f - q\Sigma}{a_f} \right) \frac{\alpha^{N+1} - \frac{a_p}{1 - a_p} \left( \frac{a_f + b_f - Nq}{a_f - q\Sigma} - 1 \right)}{\alpha^{N+1} - 1} \quad (6)$$

Equation 6 is an approximate solution for complex mixtures, based upon the assumptions underlying Equation 4 plus the further assumption that the key components follow Raoult's law and that at the cutting point the column contains these key components only.

The last assumption brings the calculated yield fraction slightly below the true value; but since column holdup is usually small compared with the total yield of distillate, the error is likely to lie within the limits of accuracy of the data and simplifying assumptions.

A comparison will be given of the yield fraction as calculated from Equation 4 and that obtained from a plate-to-plate calculation. Consider a mixture of three components  $A$ ,  $B$ , and  $C$  in which  $a_f = b_f = 0.21$ ,  $c_f = 0.58$ ,  $\alpha = \beta = 1.5$ . A thousand moles of this mixture are to be rectified under C. D. C. conditions in a column having ten theoretical plates and a holdup of 2 moles per theoretical plate. The product is required to contain 90 mole per cent of component  $A$ .

A plate-to-plate calculation gave the following figures:  $a_p = 0.897$ ,  $b_p = 0.100$ ,  $c_p = 0.003$ ;  $a_w = 0.025$ ,  $b_w = 0.239$ ,  $c_w = 0.736$ . Moles of each component held up in the column under total reflux are:  $A$ , 8.63;  $B$ , 6.84;  $C$ , 4.53. Material balances based on these figures give:

$$y = 0.867$$

Taking  $a_p = 0.897$  and applying Equation 3,

$$\Sigma = 4.97$$

Substituting in Equation 5 and solving:

$$y = 0.863$$

In the case of complex mixtures such as petroleum, it is usual to treat comparatively narrow fractions as pure components for calculation purposes. Elsewhere it has been shown that the relative volatilities of such fractions at any temperature can be conveniently estimated from their molal average boiling points by the equation (3):

$$\log_{10} \alpha_T = 2.50 \frac{T_b^2 - T_a^2}{T^2}$$

As an example of the use of Equation 6, a certain petroleum distillate contains 4.0 mole per cent of material boiling between 80° and 140° F., and 5.0 mole per cent boiling between 140° and 160° F. This distillate is to be rectified by the batch process, and it is required to separate the 80–140° F. fraction (which is the lightest material present) in a 95 per cent pure

condition. The choice lies between a plate column having ten theoretical plates and a holdup of 15 moles per theoretical plate, and a packed column of five theoretical plates with a holdup of 3 moles per theoretical plate. The charge in each case is 2500 moles, and distillation is to take place under C. D. C. conditions at atmospheric pressure. What will be the respective yield fractions from the two columns?

The molal average boiling points of the key components are found to be 110° and 150° F. From flash vaporization curves or other data the temperatures at the top and bottom of the column are estimated at 120° and 240° F., respectively. Using these temperatures and the equation mentioned above, the relative volatilities of the key components at the top and bottom of the column are calculated to be 2.24 and 1.74, respectively, giving an average relative volatility  $\alpha = 1.99$ :

$$a_f = 0.04 \quad b_f = 0.05 \quad a_p = 0.95$$

$$\begin{aligned} \text{For packed column: } \Sigma &= 3.03 \text{ (Equation 2)} \\ \text{For plate column: } \Sigma &= 3.86 \text{ (Equation 3)} \end{aligned}$$

Substituting these values in Equation 6 and solving,

$$\begin{aligned} \text{For packed column: } y &= 0.550 \\ \text{For plate column: } y &= 0.415 \end{aligned}$$

The utility of the method presented is principally that it offers a means of comparing the suitability of different columns for a separation which is intended to be carried to a high final reflux ratio. Whether this is an economic procedure in any given case must be decided by other methods.

#### ACKNOWLEDGMENT

The author is indebted to Arthur Rose for valuable criticism, and desires to thank the chairman and the board of Trinidad Leaseholds, Ltd., for permission to publish this paper.

#### NOMENCLATURE

- $A, B, C$ , etc. = components in order of decreasing volatility  
 $a_f, a_p, a_w, a_n$  = mole fraction of component  $A$  in charge, distillate, residue, and on  $n$ th plate, counting from top of column, respectively  
 $b_f, b_p, b_w, b_n$  = same for component  $B$   
 $F, P, W$  = total moles of charge, distillate, and residue, respectively  
 $N$  = number of theoretical plates in column  
 $Q$  = moles held up in the column per theoretical plate  
 $q = Q/F$   
 $T_a, T_b$  = molal average boiling points on absolute scale of fractions taken as key components in calculations relating to complex mixtures, ° R. or ° K.  
 $y$  = yield fraction (100 $y$  = per cent yield)  
 $\alpha, \beta$  = average relative volatility of components  $A/B$ ,  $B/C$ —i. e., mean of values at top and bottom temperatures of column  
 $\alpha_T$  = relative volatility of components  $A/B$  at absolute temperature  $T$   
 $\Sigma = \frac{a_p}{\alpha(1 - a_p) + a_p} + \frac{a_p}{\alpha^2(1 - a_p) + a_p} + \frac{a_p}{\alpha^3(1 - a_p) + a_p} + \dots + \frac{a_p}{\alpha^N(1 - a_p) + a_p}$

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# Effect of Temperature on Liquid-Liquid Equilibrium

BENZENE-ACETONE-WATER SYSTEM AND  
DOCOSANE-1,6-DIPHENYLHEXANE-FURFURAL SYSTEM

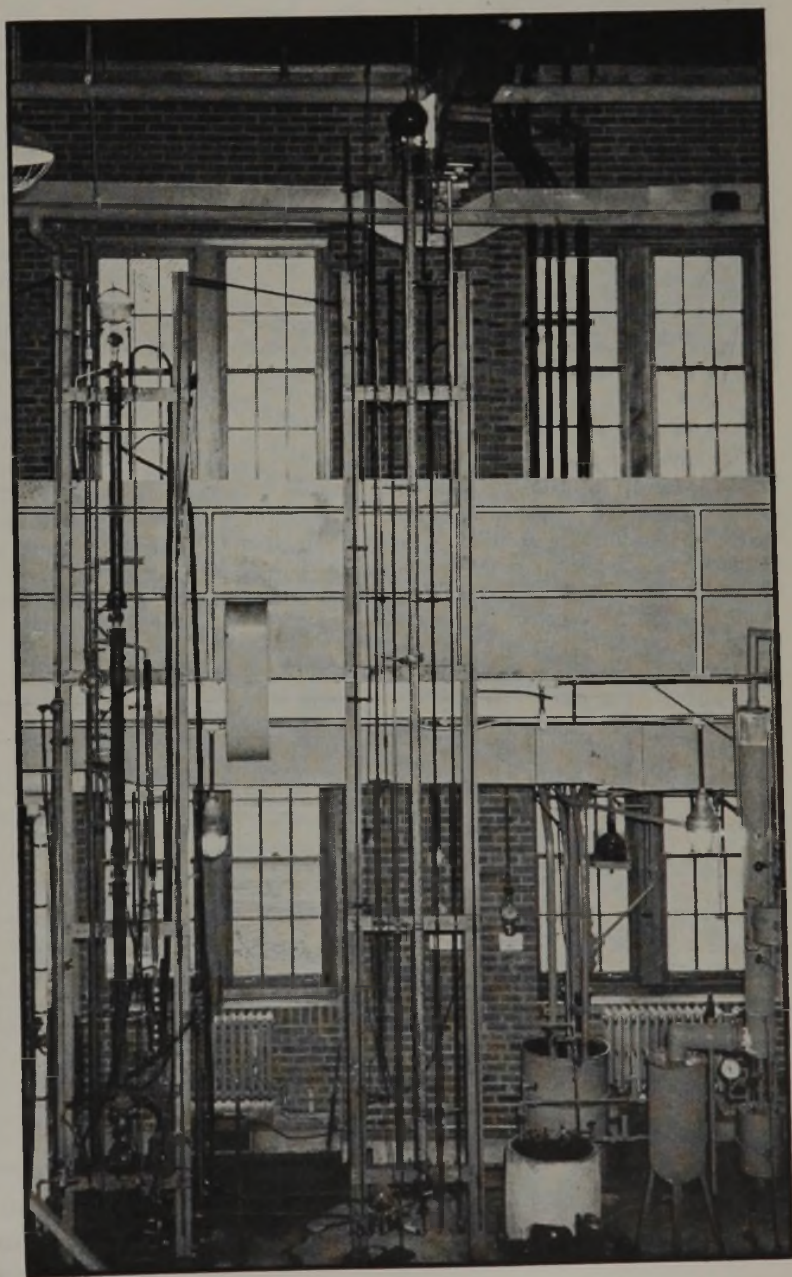
*Stanford W. Briggs<sup>1</sup>*  
*Edward W. Comings*

UNIVERSITY OF ILLINOIS, URBANA, ILL.

**R**ECENT articles (4, 5) have pointed out the expanding application of solvent extraction to industrial separations and have stressed the value of liquid-liquid phase equilibrium studies. A wide variety of ternary systems has been investigated, but the majority of the work has been confined to a single temperature. No relatively complete study of the effect of temperature on equilibrium for a system that is likely to be used in extraction has been published in the readily available literature. Temperature has a marked effect on liquid-liquid phase equilibrium. This effect on two separate systems was determined, and its consequences are discussed.

Phase equilibrium data for the systems benzene-acetone-water and docosane-1,6-diphenylhexane-furfural over a range of temperatures are reported. The former system appears to be representative of many involved in recovering solvents from aqueous solutions by extraction. The latter is related to the complex systems encountered in the solvent refining of lubricating oil. Special experimental methods which are particularly useful in dealing with volatile materials were developed.

<sup>1</sup> Present address, Merck & Company, Inc., Rahway, N. J.



→  
*Experimental Extractor Column  
Used at the Laboratory of  
Merck & Company, Inc.*

## BENZENE-ACETONE-WATER

Reagent-grade acetone, distilled water, and reagent-grade benzene were used without further purification or preparation. Refractive indices of these materials showed no deviations from values given in the literature.

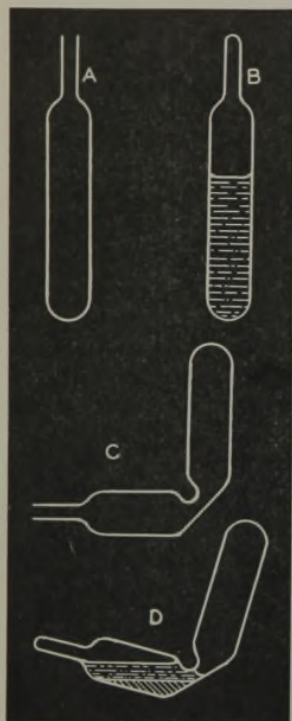


Figure 1. Experimental Glass Tubes

- A. Tube for cloud-point and most of tie-line data.  
 B. Tube A, filled.  
 C. Tube for determining tie lines in system dodecane - diphenylhexane-furfural at 80° and 115° C.  
 D. Tube C filled and in position to remove sample of top layer.

Two different procedures were used, one for determining the temperature at which a solution of known composition was saturated, the other to obtain the compositions of two liquid phases in equilibrium. The determination of the temperature of saturation was obtained by the sealed tube technique (1). This method consisted in observing the tem-

perature at which a cloud formed in a single-phase liquid of known composition. The determination of the compositions of pairs of liquid phases in equilibrium, or the tie lines, was obtained by sampling these phases after equilibrium had been reached at constant temperature. The samples were analyzed by determining the refractive indices with a Zeiss Abbe refractometer.

Glass tubes, about 5-10 cc. in volume (Figure 1A and B), were used for determining the saturation temperature. Acetone, water, and benzene were measured into a tube from carefully calibrated pipets and the tube was sealed. Because of the small effect of temperature on solubility in this system, compositions had to be selected with care in order to obtain a cloud point. The tube was agitated in a stirred liquid bath while the temperature was gradually lowered from a point above that necessary for miscibility to the point at which a cloud formed due to the separation of a second liquid phase. The latter point was recorded as the cloud point temperature (Table I).

Binodal curves representing the boundary between the single-phase and the two-phase regions were constructed at 15°, 30°, and 45° C. by graphical interpolation of the cloud point data. Part of the data was divided into groups, each with a constant ratio of benzene to acetone. The data in each single group resulted in a straight line when plotted as log of per cent water against the reciprocal of the absolute temperature of the cloud point. Similarly, another part of the data was divided into groups in each of which the ratio of acetone to water was constant and the corresponding curves of log of per cent benzene vs. the reciprocal of the absolute cloud point temperature were plotted. The two sets of curves are shown in Figure 2. Compositions at 15°, 30°, and 45° C. from these curves, as well as cloud points which did not fall in these groups and the data of other investigators (2), were used to determine the binodal curves shown in Figure 4 and Table III.

Tie lines were determined by preparing two series of synthetic mixtures of known composition in the two-phase region. One series was rich in benzene; the other, rich in water. Each mixture was sealed into a tube as in measuring cloud points, and the mixture was brought to equilibrium by shaking in a constant-temperature bath. The tip of the tube was then broken open, a sample of the upper phase was transferred to the refractometer by means of a long-nosed

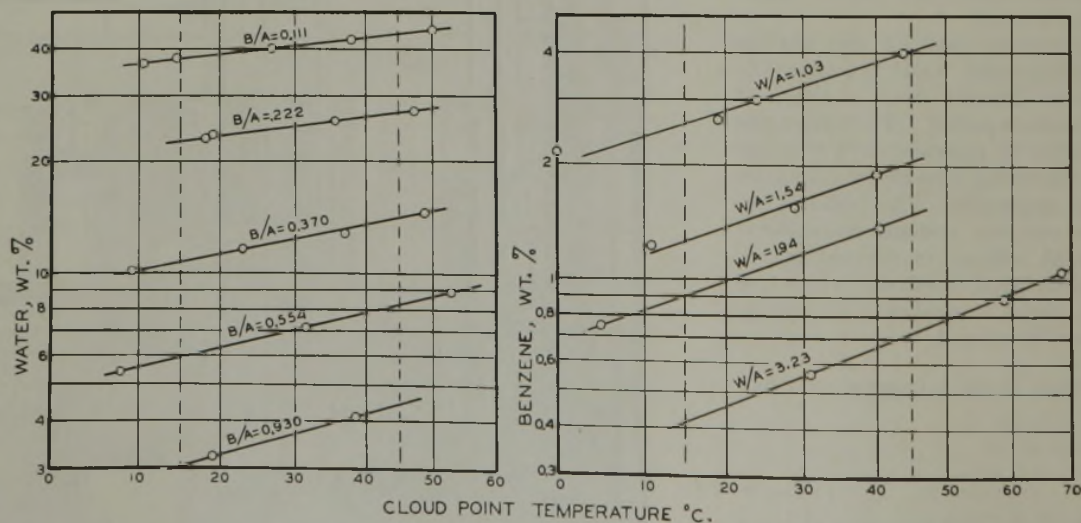


Figure 2. Correlation of Cloud Point Data for System Benzene-Acetone-Water  
 Left, constant ratio of benzene to acetone; right, constant ratio of water to acetone.

Table I. Experimental Solubilities in the System Benzene-Acetone-Water

Weight Per Cent			Cloud Point, ° C.	Weight Per Cent			Cloud Point, ° C.
Benzene	Acetone	Water		Benzene	Acetone	Water	
68.6	30.5	0.9	22.0	1.7	42.90	55.40	13.5
57.3	40.7	2.0	29.0	24.20	65.80	10.00	9.0
46.7	50.1	3.2	19.0	23.60	63.70	12.70	37.0
46.2	49.7	4.1	38.5	14.00	63.30	22.70	18.0
33.1	59.8	7.1	31.5	3.00	42.60	54.40	53.0
32.5	58.6	8.9	52.5	68.50	30.60	0.90	21.0
23.9	64.6	11.5	23.0	1.22	38.80	59.98	11.0
23.1	62.4	14.5	49.0	0.74	33.80	65.46	5.0
13.9	62.9	23.2	19.0	1.37	33.60	65.03	40.5
13.5	61.0	25.5	35.5	2.15	48.20	49.65	0.0
13.2	59.4	27.4	47.0	2.64	48.00	49.36	19.0
6.1	54.8	39.1	22.0	3.00	47.70	49.30	24.0
2.6	44.8	52.6	29.5	4.00	47.20	48.80	44.0
2.3	39.3	58.4	45.5	1.54	38.70	59.76	29.0
6.3	56.2	37.5	14.5	1.90	38.50	59.60	40.0
6.0	54.2	39.8	27.0	1.04	23.40	75.56	67.0
5.8	51.8	42.4	38.0	0.56	23.50	75.94	31.0
5.5	49.5	45.0	50.0	0.89	23.50	75.61	59.0
33.7	60.9	5.4	8.0	0.40	17.00	82.60	22.5
1.3	36.8	61.9	23.5	1.20	26.60	72.20	59.0
6.4	57.2	36.4	10.5	2.80	45.90	51.30	29.0
1.6	43.1	55.3	18.0	67.50	1.50	31.00	40.0
0.5	24.1	75.4	19.5	79.70	0.50	19.80	23.0
82.2	17.0	0.8	56.0	0.60	90.90	8.50	77.0
2.2	42.8	55.0	29.0				

regulated to within 0.2° C. of the standard temperature. The experimental data are listed in Table II. The effect of pressure on the distribution was estimated to be in the order of magnitude of 0.01 per cent per atmosphere. The pressures encountered here were less than one atmosphere gage.

The cloud point data gave the compositions along the binodal curve (Table III), but the corresponding refractive indices were not known. The tie line data gave refractive indices along the binodal curve but not the compositions. These compositions were determined by a trial-and-error method.

This method is illustrated as follows: A benzene-rich mixture was selected from Table II together with two water-rich

dropper, and the refractive index was taken. This whole operation was completed rapidly, the tube remaining partly submerged in the bath. A sample of the lower phase was then transferred in a similar manner and its refractive index was taken. The temperature of the refractometer was

mixtures so that the refractive index of the benzene phase of the former was intermediate between the refractive indices of the benzene phases of the latter. These three mixtures are represented in Figure 3 by points B, W<sub>1</sub>, and W<sub>2</sub>. A trial tie line was drawn through B and through a composition be-

Table II. Experimental Tie Line Data in Benzene-Acetone-Water System

15° C.			30° C.			45° C.		
Over-all Compn., Wt. %			Over-all Compn., Wt. %			Over-all Compn., Wt. %		
Benzene	Acetone	Water	Benzene	Acetone	Water	Benzene	Acetone	Water
15.5	13.8	70.7	15.5	13.8	70.7	15.5	13.8	70.7
24.1	21.3	54.6	24.1	21.3	54.6	24.1	21.3	54.6
66.6	14.8	18.6	66.6	14.8	18.6	66.6	14.8	18.6
49.9	22.2	27.9	49.9	22.2	27.9	49.9	22.2	27.9
19.8	35.3	44.9	19.8	35.3	44.9	19.8	35.3	44.9
19.8	35.3	44.9	19.8	35.3	44.9	19.8	35.3	44.9
40.7	36.5	22.8	40.7	36.5	22.8	40.7	36.5	22.8
16.7	36.5	22.8	16.7	36.5	22.8	16.7	36.5	22.8
16.7	7.5	75.8	16.7	7.5	75.8	16.7	7.5	75.8
16.6	7.4	76.0	16.6	7.4	76.0	16.6	7.4	76.0
71.8	8.1	20.1	71.8	8.1	20.1	71.8	8.1	20.1
71.6	8.0	20.4	71.6	8.0	20.4	71.6	8.0	20.4
16.8	44.9	38.3	16.8	44.9	38.3	16.8	44.9	38.3
29.8	53.5	16.7	29.8	53.5	16.7	29.8	53.5	16.7
12.9	57.7	29.4	12.9	57.7	29.4	12.9	57.7	29.4
12.9	57.7	29.4	12.9	57.7	29.4	12.9	57.7	29.4
23.5	63.3	13.2	23.5	63.3	13.2	23.5	63.3	13.2
23.5	63.3	13.2	23.5	63.3	13.2	23.5	63.3	13.2
26.3	59.0	14.7	26.3	59.0	14.7	26.3	59.0	14.7

Table III. Binodal Curves in Benzene-Acetone-Water System

15° C.				30° C.				45° C.			
Benzene, wt. %	Acetone, wt. %	Water, wt. %	Refractive index	Benzene, wt. %	Acetone, wt. %	Water, wt. %	Refractive index	Benzene, wt. %	Acetone, wt. %	Water, wt. %	Refractive index
0.1	0.0	99.9	1.3316	0.1	0.0	99.9	1.3316	0.1	0.0	99.9	1.3295
0.1	10.0	89.9	1.3394	0.2	10.0	89.8	1.3394	0.2	10.0	89.8	1.3366
0.3	20.0	79.7	1.3463	0.4	20.0	79.6	1.3463	0.5	20.0	79.5	1.3432
0.7	30.0	69.3	1.3524	0.9	30.0	69.1	1.3524	1.1	30.0	68.9	1.3488
1.4	40.0	58.6	1.3577	1.8	40.0	58.2	1.3577	2.3	40.0	57.7	1.3540
3.2	50.0	46.8	1.3630	4.1	50.0	45.9	1.3630	5.3	50.0	44.7	....
9.0	60.0	31.0	....	11.2	60.0	28.8	....	13.6	60.0	26.4	....
24.1	65.3	10.6	1.3872	23.8	64.1	12.1	1.3869	23.3	62.8	13.9	....
99.9	0.0	0.1	1.4940	99.9	0.0	0.1	1.4940	99.9	0.0	0.1	1.4840
89.8	10.0	0.2	1.4777	89.8	10.0	0.2	1.4777	89.7	10.0	0.3	1.4678
79.6	20.0	0.4	1.4622	79.4	20.0	0.6	1.4622	79.3	20.0	0.7	1.4523
69.3	30.0	0.7	1.4470	69.1	30.0	0.9	1.4470	68.7	30.0	1.3	1.4370
58.5	40.0	1.5	1.4321	58.0	40.0	2.0	1.4316	57.5	40.0	2.5	1.4218
47.1	50.0	2.9	1.4170	46.3	50.0	3.7	1.4169	45.5	50.0	4.5	1.4067
34.2	60.0	5.8	1.3996	32.8	60.0	7.2	1.3980	30.9	60.0	8.1	....

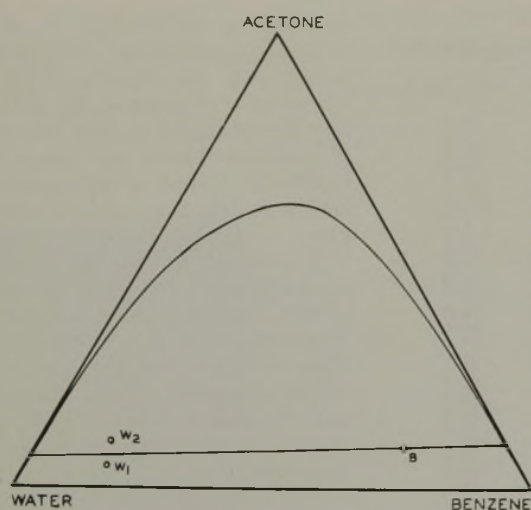


Figure 3. Construction of Tie Lines in Benzene-Acetone-Water System

tween  $W_1$  and  $W_2$  determined by linear interpolation on the basis of the refractive indices of the benzene phases. The intersection of this tie line with the benzene-rich branch of the binodal curve gave a good approximation of the composition of the benzene phase which separated from mixture  $B$ . The composition of the benzene phases from the other benzene-rich mixtures was similarly determined. This gave the relation between refractive index and composition along the benzene-rich branch of the binodal curve. A like procedure was followed for each of the water-rich mixtures, resulting in the relation between composition and refractive index along the water-rich branch of the binodal curve. These preliminary calculations allowed the composition of the benzene-rich layer to be plotted against that of the water-rich layer in equilibrium with it; the conjugate curve at one temperature was thus obtained. This curve was smoothed and used as a basis for repeating the entire calculation which led to the tie lines given in Table IV. The conjugate curves are shown in Figure 4 and the corresponding equilibrium curves in Figure 5.

#### DOCOSANE-DIPHENYLHEXANE-FURFURAL

Docosane was synthesized by the Kolbe electrolytic oxidation of lauric acid. Its refractive index at 45° C. was 1.4358, and its kinematic viscosities at 45° and 85° C. were 6.03 and 2.84 centistokes, respectively. 1,6-Diphenylhexane was made by a Friedel-Crafts condensation of adipyl chloride with benzene, followed by pressure hydrogenation with copper chromite catalyst. Its refractive index at 20° C. was 1.5381, and its kinematic viscosities at 45° and 85° C. were 8.36 and 2.34 centistokes, respectively. Furfural was obtained from Eastman Kodak Company. It was vacuum-distilled within one or two days before use. Its refractive index was 1.5259 at 20° C.

Cloud points were determined in essentially the same manner as in the previous system. The tubes were smaller and the materials were weighed into them. To limit the decomposition of furfural, the temperature was maintained in the vicinity of the cloud

point for only a short time. Cloud point data are given in Table V.

The construction of the binodal curves may be understood by reference to Figures 6 and 7. The cloud points of docosane-furfural mixtures are plotted in Figure 6. For each mixture containing diphenylhexane, the cloud point at the same per cent furfural was taken from this curve. The pairs of points were plotted as log of per cent docosane, on a furfural-free basis, against the reciprocal of the absolute cloud point temperature.  $A$  and  $A'$  (Figure 7) are such a pair.  $A$  is an experimental point, and  $A'$  is the point from Figure 6 which has the same per cent furfural as  $A$ . A straight line through  $A$  and  $A'$  represents fairly accurately the solubility temperatures of mixtures having this same per cent furfural. Another experimental point,  $B$ , having a

Table IV. Tie Lines in Benzene-Acetone-Water System

Benzene Phase Compn., Wt. %			Water Phase Compn., Wt. %			Ratio, Ace- tone in Ben- zene/Ace- tone in Water
Ben- zene	Ace- tone	Water	Ben- zene	Ace- tone	Water	
Temperature, 15° C.						
95.2	4.7	0.1	0.1	5.0	94.9	0.94
89.0	10.8	0.2	0.1	10.0	89.9	1.08
73.4	26.1	0.5	0.3	20.0	79.7	1.30
55.2	43.0	1.8	0.7	30.0	69.3	1.43
39.1	56.5	4.4	1.4	40.0	58.6	1.41
27.6	63.9	8.5	3.2	50.0	46.8	1.28
Temperature, 30° C.						
94.0	5.8	0.2	0.1	5.0	94.9	1.16
86.7	13.1	0.2	0.2	10.0	89.8	1.31
68.7	30.4	0.9	0.4	20.0	79.6	1.52
49.8	47.2	3.0	0.9	30.0	69.1	1.57
34.5	58.9	6.6	1.8	40.0	58.2	1.47
23.9	64.1	12.0	4.1	50.0	45.9	1.28
Temperature, 45° C.						
92.9	6.9	0.2	0.2	5.0	94.8	1.38
84.0	15.6	0.4	0.2	10.0	89.8	1.56
63.6	34.6	1.8	0.5	20.0	79.5	1.73
44.0	51.2	4.8	1.1	30.0	68.9	1.71
29.7	60.6	9.7	2.3	40.0	57.7	1.65

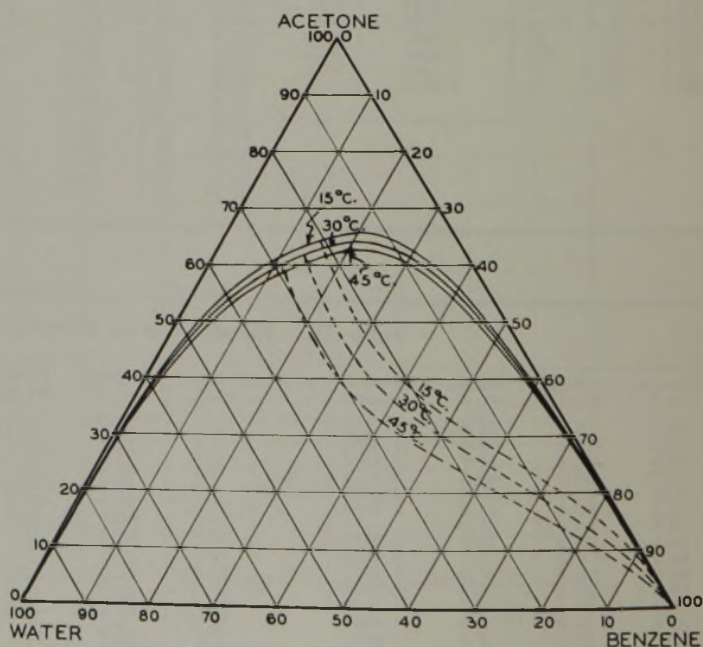


Figure 4. Binodal Curves for Acetone-Water-Benzene System



Table V. Experimental Solubilities in Docosane-Diphenylhexane-Furfural System

Weight Per Cent			Cloud Point, ° C.	Weight Per Cent			Cloud Point, ° C.
Docosane	Diphenylhexane	Furfural		Docosane	Diphenylhexane	Furfural	
86.6	8.5	4.9	44.7	86.8	0.0	13.2	95.0
68.1	16.4	15.5	87.0	7.2	0.0	92.8	115.5
62.5	24.4	13.1	72.7	79.8	0.0	20.2	115.5
65.2	27.9	6.9	43.3	16.3	40.0	43.7	66.5
34.5	44.8	20.7	53.0	7.5	18.4	74.1	89.5
2.1	17.8	80.1	55.0	3.4	8.5	88.1	80.0
0.9	7.5	91.6	43.6	62.1	13.3	24.6	109.5
1.7	0.0	98.3	74.0	17.6	3.7	78.7	132.7
0.6	0.0	99.4	43.2	50.2	28.9	20.9	81.5
28.1	4.0	67.9	136.0	12.3	7.0	80.7	120.5
3.5	29.0	67.5	48.0	18.4	0.0	81.6	139.0
23.2	46.8	30.0	53.0	16.6	8.1	8.1	62.5
18.6	37.7	43.7	75.0	47.4	40.1	12.5	48.0
1.0	0.0	99.0	57.5	94.9	0.0	5.1	54.5
46.1	0.0	53.9	144.3	26.9	0.0	73.1	142.0
93.9	0.0	6.1	61.0	34.3	0.0	65.7	143.0
56.2	0.0	43.8	142.2	29.0	48.5	22.5	42.2
36.7	10.7	52.6	125.3	13.3	15.5	71.2	108.5
58.8	31.3	9.9	51.2	55.4	0.0	44.6	140.5
37.9	20.2	41.9	109.0	38.4	0.0	61.6	143.5
78.9	15.9	5.2	42.5	19.1	23.2	57.7	100.5
47.7	9.6	42.7	127.0	13.4	0.0	86.6	128.6
28.7	5.8	65.5	133.8	65.2	0.0	34.8	134.0
95.4	0.0	4.6	51.5	12.3	0.0	87.7	130.0
59.7	0.0	40.3	140.0				

peratures and the 45° C. tie lines. Glass tubes with a constriction and right-angle bend in the middle (Figure 1C) were employed. Each section of the tube had a volume of about 1 cc. The components of a mixture corresponding to a point in the two-phase region of the binodal curve were weighed and sealed into the section next to the mouth. The tube was gently agitated in an oil bath kept at the desired temperature; care was taken to prevent any of the mixture from flowing into the empty section. After the phases had come to equilibrium and had been allowed to settle out, a sample of the top phase was removed to the empty section in the following way: The tube was tilted until the upper phase was adjacent to the constricted part and the empty section was up, as shown in Figure 1D. The tube was carefully raised so that the empty section

protruded from the oil bath. When the empty section was cooled in this way, the pressure in it decreased and some of the upper phase was sucked into it. The tube was turned over, the liquid in the constriction allowed to drain out, and the constriction sealed closed. The sample of the upper phase was allowed to reach a new equilibrium at 45° C., and the newly formed upper phase was analyzed as in the determination of the 45° C. tie lines. The tie line data are given in Table VII.

The construction necessary in obtaining the tie lines at the higher temperatures is indicated in Figure 8. *S* represents the over-all composition of the original mixture. *U*<sub>2</sub> represents the composition of the upper phase obtained in the 45° C. equilibrium. The 45° C. tie line through *U*<sub>2</sub> will cut the higher temperature binodal curve at *U*<sub>1</sub>, the point representing the composition of the upper phase formed at the higher temperature. A line extending from *U*<sub>1</sub> through *S* to the other part of the binodal curve is a tie line at the higher temperature. Tie lines are shown in Figure 9 and listed in Table VIII.

DISCUSSIONS AND CALCULATIONS

Temperature variation obviously affects the two systems differently. For benzene-acetone-water it alters the slope

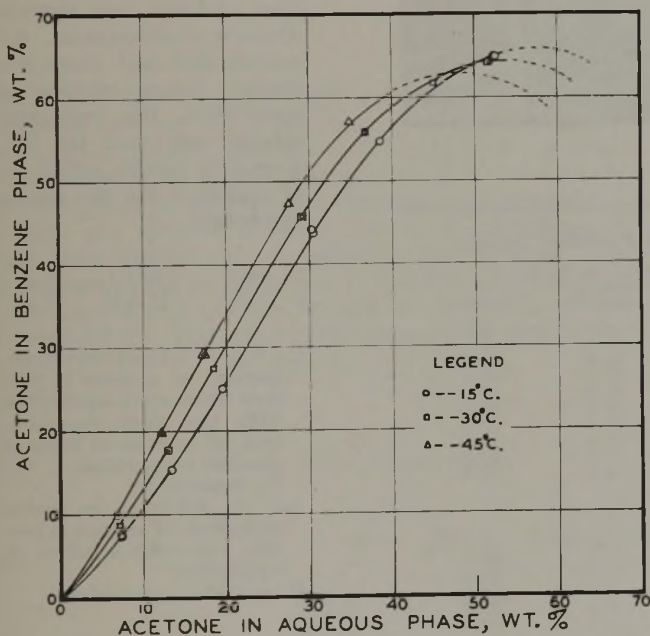


Figure 5. Distribution of Acetone between Benzene and Aqueous Phases

smaller per cent docosane on a furfural-free basis, and the corresponding point *B'* from Figure 6 are also shown. These lines were used to make the small correction in composition required to bring the cloud point to the nearest standard temperature. Solubilities at 45°, 80°, 115°, and 140° C. were obtained in this way. The binodal curves are shown in Figure 9. Compositions from the binodal curves are listed in Table VI.

Tie lines were obtained at 45° C. by the same method employed in studying the system acetone-water-benzene. Refractive indices of the furfural-rich phase were not used since they varied only slightly with composition.

At higher temperatures tie lines were obtained from the binodal curves at higher tem-

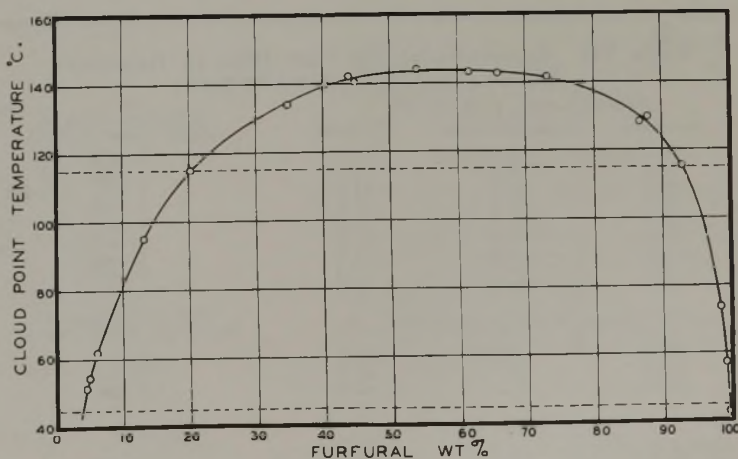
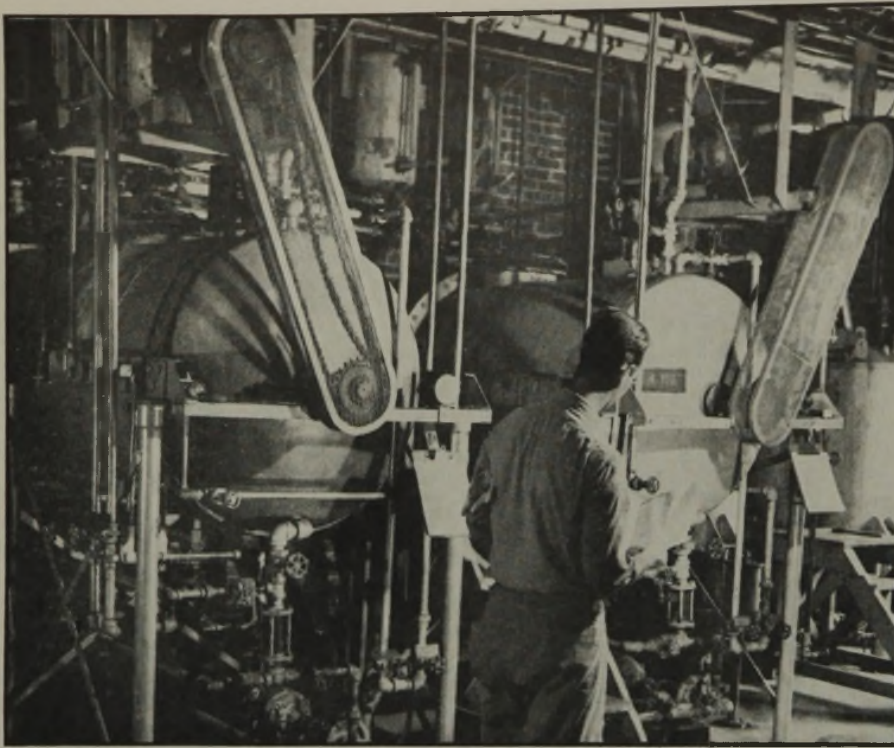


Figure 6. Cloud Point Temperature-Composition Relation for Docosane-Furfural System



Large-Scale Extractor for Vitamin Processes Used by Merck & Company, Inc.

of the tie lines markedly but changes the solubility to a minor degree. In the system docosane-diphenylhexane-furfural it hardly affects the slope of the tie lines but brings about a decided change in solubility. On the other hand, all the effects are quite regular.

The influence of temperature variation on the distribution of acetone in the system benzene-acetone-water may be compared with that predicted from thermodynamic considerations. Assuming that each phase is a perfect binary solution of acetone in the respective solvent and that the difference in partial enthalpies of acetone in the two phases is constant,

$$\ln \frac{C_{B_1}}{C_{B_2}} = \frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$C_{B_1}/C_{B_2}$  = ratio of two concentrations of acetone in benzene which are in equilibrium with the same concentration of acetone in water at absolute temperature  $T_1$  and  $T_2$ , respectively  
 $\Delta H$  = difference in partial enthalpies of acetone in benzene and water solutions at equilibrium  
 $R$  = perfect gas content

Table VI. Binodal Curves in Docosane-Diphenylhexane-Furfural System

Weight % at 45° C.			Refractive Index at 45° C.	Weight % at 80° C.		
Docosane	Diphenylhexane	Furfural		Docosane	Diphenylhexane	Furfural
96.0	0.0	4.0	1.4376	90.3	0.0	9.7
84.0	11.0	5.0	1.4473	50.5	29.5	20.0
67.0	26.0	7.0	1.4612	34.2	35.8	30.0
52.5	37.5	10.0	1.4731	23.8	36.2	40.0
32.6	47.4	20.0		16.2	33.8	50.0
21.3	48.7	30.0		10.7	29.3	60.0
13.2	46.8	40.0		6.9	23.1	70.0
7.7	42.3	50.0		4.6	15.4	80.0
4.4	35.6	60.0		3.0	7.0	90.0
2.6	27.4	70.0		2.2	0.0	97.8
1.5	18.5	80.0				
1.0	9.0	90.0				
0.7	0.0	99.3				

Weight % at 115° C.			Weight % at 140° C.		
Docosane	Diphenylhexane	Furfural	Docosane	Diphenylhexane	Furfural
79.7	0.0	20.3	59.4	0.0	40.6
56.9	13.1	30.0	47.7	2.3	50.0
42.8	17.2	40.0	37.5	2.5	60.0
32.2	17.8	50.0	28.7	1.3	70.0
23.1	16.9	60.0	23.8	0.0	76.2
16.2	13.8	70.0			
11.1	8.9	80.0			
7.2	0.0	92.8			

Table VII. Experimental Tie Line Data in Docosane-Diphenylhexane-Furfural System

Over-all Compn. at 45° C., Wt. %			Refractive Index of Upper Phase at 45° C.
Docosane	Diphenylhexane	Furfural	
18.4	0.0	81.6	1.4376
76.8	9.1	14.1	1.4457
56.4	21.4	22.2	1.4561
53.3	23.1	23.6	1.4584
48.3	32.9	18.8	1.4679
29.0	48.4	22.6	1.4926
14.6	9.8	75.6	1.4462
9.5	41.1	49.4	1.4803
24.4	24.3	51.3	1.4594

Over-all Compn. at 80° C.			Refractive Index of 2nd Upper Phase at 45° C.
Docosane	Diphenylhexane	Furfural	
31.3	3.2	65.5	1.4400
20.8	15.4	63.8	1.4496
21.5	27.9	50.6	1.4644

Over-all Compn. at 115° C.			Refractive Index of 2nd Upper Phase at 45° C.
Docosane	Diphenylhexane	Furfural	
21.8	6.6	71.6	1.4430
21.9	10.5	67.6	1.4466

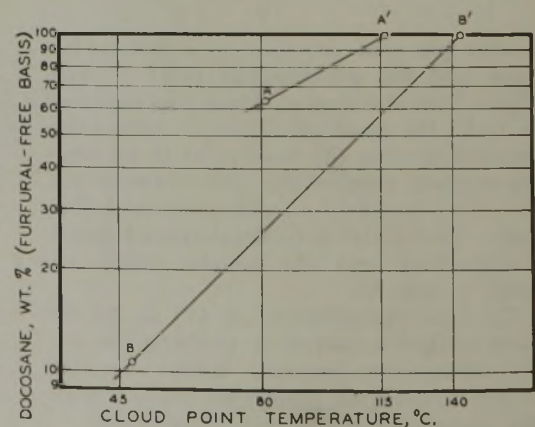


Figure 7. Correlation of Cloud Point Data for System Docosane-Diphenylhexane-Furfural

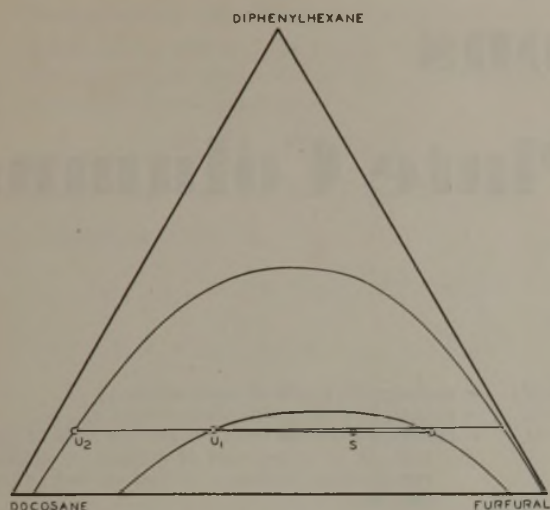


Figure 8. Construction Involved in Obtaining Tie Lines for System Docosane-Diphenylhexane-Furfural at 80° and 115° C.

The best available value for  $\Delta H$  is obtained by taking the difference between the latent heat of solution of acetone in water at infinite dilution as 10.5 kilojoules per gram mole acetone, and the latent heat of solution of acetone in benzene (given in the literature for more than one mole of benzene per mole of acetone), as  $-1.3$  kilojoules per gram mole acetone (3). Substituting this value and the appropriate values of  $R$ ,  $T_1$ , and  $T_2$  into the equation, gives a  $C_{B1}/C_{B2}$  value of 1.28 for 30° and 15° C. and of 1.25 for 45° and 30° C. The ratios of the slopes of the distribution

curves at these temperatures (Figure 5) approach these values at infinite dilution within the accuracy of the measurements.

The average error of cloud point data for the system benzene-acetone-water is estimated to be about 0.2 weight per cent and for the system docosane-diphenylhexane-furfural, 0.5 weight per cent. The average error in tie line data for each system may be somewhat greater.

Table VIII. Tie Lines in Docosane-Diphenylhexane-Furfural System

Docosane Phase Compn., Wt. %			Furfural Phase Compn., Wt. %		
Docosane	Diphenylhexane	Furfural	Docosane	Diphenylhexane	Furfural
Temperature, 45° C.					
85.2	10.0	4.8	1.1	9.8	89.1
69.0	24.5	6.5	2.2	24.2	73.6
43.9	42.6	13.3	6.8	40.9	52.3
Temperature, 80° C.					
86.7	3.0	10.3	2.6	3.3	94.1
73.1	13.9	13.0	4.6	15.8	79.6
50.5	29.5	20.0	9.2	27.4	63.4
Temperature, 115° C.					
70.0	6.3	23.7	9.9	6.7	83.4
62.9	10.4	26.7	12.5	10.5	77.0

Calculations of the number of theoretical stages required for given separations show interesting effects of temperature variation on extraction. In general, fewer stages are required for a high-temperature extraction of acetone from water with benzene than for a low-temperature extraction. Conversely, fewer stages are required for a low-temperature extraction of acetone from benzene with water. The extraction of diphenylhexane from docosane with furfural requires fewest stages at the lowest temperature for a given separation. Operating at an intermediate temperature, or with a temperature gradient through the several stages and returning reflux formed by cooling the extract to the lowest temperature investigated, yields an extract no more pure than that obtained by operating without reflux at the lowest temperature. This does not coincide with the effect of temperature on the extraction of lubricating oils with furfural.

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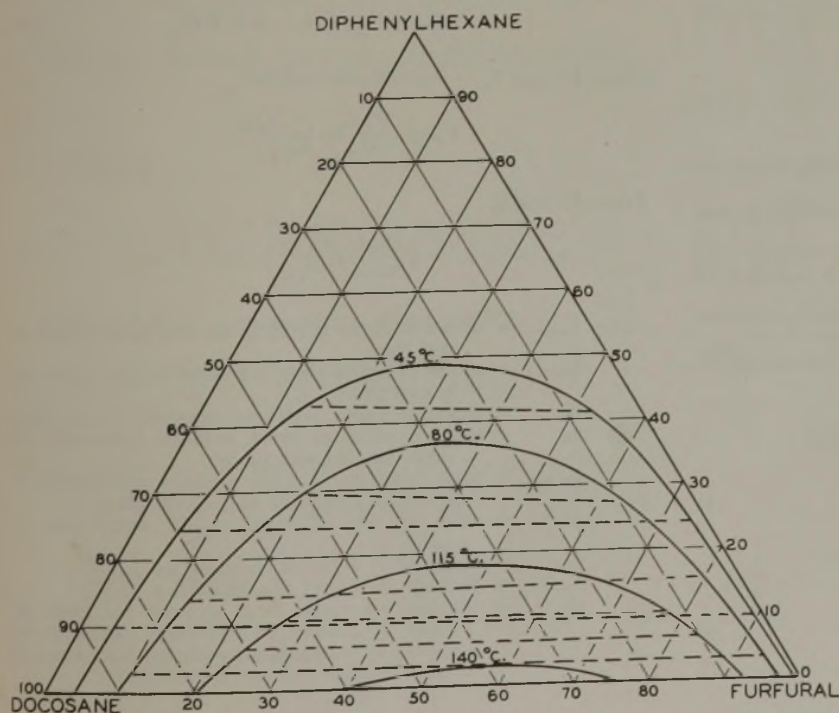


Figure 9. Binodal Curves and Tie Lines for the System Docosane-Diphenylhexane-Furfural at Several Temperatures

# Design Calculations for Plate Columns

E. M. Baker and R. A. Lindsay

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

THE widely used method of McCabe and Thiele (2) for determining the number of plates in a distillation column is based on the assumption of constant molal overflow, a criterion not met in many systems. Ponchon and Savarit (4) presented a method for determining the number of plates required for the separation in such systems. This method lacks the clarity and simplicity desired in teaching distillation calculations. Further, it does not readily lend itself to calculations involving the application of such variables of operation as entrainment and more than one feed or drawoff.

The purpose of this paper is to present a method of calculation which has the simplicity inherent in the McCabe-Thiele method but which is applicable to problems involving the above variables. This method will be presented with regard to four cases: (1) separation of one feed with no entrainment; (2) separation of two feeds, or two drawoffs, with no entrainment; (3) case 1, with entrainment; (4) case 2, with entrainment.

## SEPARATION OF ONE FEED WITH NO ENTRAINMENT

The general material balance equations of McCabe and Thiele may be written:

$$V_n = L_{n+1} + D \quad (1)$$

$$V_n y_n = L_{n+1} x_{n+1} + D x_d \quad (2)$$

From Equations 1 and 2:

$$y_n = x_{n+1} + D/V_n(x_d - x_{n+1}) \quad (3)$$

where  $V_n$  = moles of vapor traveling up rectifying section in unit time

$L_{n+1}$  = moles of liquid traveling down rectifying section in unit time

$D$  = moles of distillate removed in unit time

$y_n$  = mole fraction of more volatile component in vapor leaving  $n$ th plate

$x_{n+1}$  = mole fraction of more volatile component in liquid leaving plate above the  $n$ th plate

$x_d$  = mole fraction of more volatile component in distillate

Similarly, heat balance equations may be written:

$$V_n H_n = L_{n+1} h_{n+1} + D Q_d \quad (4)$$

From Equations 1 and 4,

$$V_n = \frac{D(Q_d - h_{n+1})}{H_n - h_{n+1}} \quad (5)$$

From 5 and 3,

$$y_n = x_{n+1} + \left( \frac{H_n - h_{n+1}}{Q_d - h_{n+1}} \right) (x_d - x_{n+1}) \quad (6)$$

where  $H_n$  = enthalpy of vapor of composition  $y_n$   
 $h_{n+1}$  = enthalpy of liquid of composition  $x_{n+1}$   
 $Q_d$  = enthalpy removed from system per mole of distillate,  $D$ , at upper end of column = enthalpy removed by condenser + that carried away by distillate.

Equation 6 presents the equation of the upper operating line. A value may be chosen for  $y_n$  and a value of  $h_{n+1}$  assumed, the equation solved for  $x_{n+1}$ , and the corresponding value of  $h_{n+1}$  checked against that assumed. A second trial will generally yield a sufficiently accurate value of  $x_{n+1}$  because  $h_{n+1}$  is usually small compared with  $H_n$  and  $Q_d$ , and the variation of  $h_n$  with  $x_n$  is usually small. When the value of  $x_{n+1}$  corresponding to the chosen value of  $y_n$  has been found, a point on the operating line has been determined and a succession of these will fix the line.

The heat and material balances for the lower operating line may be written in a similar manner:

$$V_m = L_{m+1} - W \quad (7)$$

$$V_m y_m = L_{m+1} x_{m+1} - W x_w \quad (8)$$

From Equations 7 and 8,

$$y_m = x_{m+1} + \frac{W(x_{m+1} - x_w)}{V_m} \quad (9)$$

$$V_m H_m = L_{m+1} h_{m+1} - W Q_w \quad (10)$$

From 10 and 7,

$$V_m = \frac{W(h_{m+1} - Q_w)}{H_m - h_{m+1}} \quad (11)$$

From 11 and 9,

$$y_m = x_{m+1} + \left( \frac{H_m - h_{m+1}}{h_{m+1} - Q_w} \right) (x_{m+1} - x_w) \quad (12)$$

where  $V_m$  = moles of vapor traveling up stripping section in unit time

$L_{m+1}$  = moles of liquid traveling down stripping section in unit time

$W$  = moles of waste (bottoms) removed in unit time

$y_m$  = mole fraction of more volatile component in vapor leaving  $m$ th plate

$x_{m+1}$  = mole fraction of more volatile component in liquid leaving plate above  $m$ th plate

$x_w$  = mole fraction of more volatile component in waste

$H_m$  = enthalpy of vapor of composition  $y_m$

$h_{m+1}$  = enthalpy of liquid of composition  $x_{m+1}$

$Q_w$  = enthalpy removed from system per mole of waste at bottom of column = enthalpy removed by waste minus enthalpy added in still ( $Q_w$  is usually a negative quantity)

Equation 12 presents the equation of the lower operating line, and it may be handled in a manner similar to Equation 6.

SEPARATION OF TWO FEEDS WITHOUT ENTRAINMENT

The derivations of the upper and lower operating lines for this case are the same as for case 1. The intermediate operating line may be found as follows:

$$V_i = L_{i+1} + F_2 - W \tag{13}$$

$$V_i y_i = L_{i+1} x_{i+1} + F_2 x_{f_2} - W x_w \tag{14}$$

From Equations 13 and 14,

$$y_i = x_{i+1} + \frac{F_2(x_{f_2} - x_{i+1}) + W(x_{i+1} - x_w)}{V_i} \tag{15}$$

$$V_i H_i = L_{i+1} h_{i+1} + F_2 H_{f_2} - W Q_w \tag{16}$$

$$V_i = \frac{W(h_{i+1} - Q_w) + F_2(H_{f_2} - h_{i+1})}{H_i - h_{i+1}} \tag{17}$$

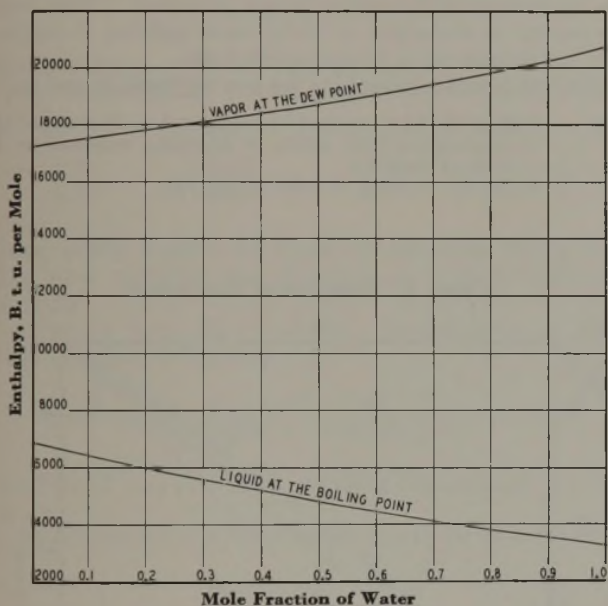


Figure 1. Enthalpy-Concentration Chart for System Acetic Acid-Water

From 15 and 17,

$$y_i = x_{i+1} + \left[ \frac{F_2(x_{f_2} - x_{i+1}) + W(x_{i+1} - x_w)}{W(h_{i+1} - Q_w) + F_2(H_{f_2} - h_{i+1})} \right] (H_i - h_{i+1}) \tag{18}$$

Factoring  $F_2$  from numerator and denominator,

$$y_i = x_{i+1} + \left[ \frac{x_{f_2} - W/F_2 x_w + (W/F_2 - 1)x_{i+1}}{(W/F_2 - 1)h_{i+1} + H_{f_2} - W/F_2 Q_w} \right] (H_i - h_{i+1}) \tag{18A}$$

where subscripts  $i, i + 1 =$  plate  $i$ , located between the two feed plates, and the plate above plate  $i$ , respectively  
 $F_2 =$  moles feed of composition lower in more volatile component per unit time  
 $H_{f_2} =$  enthalpy added to system by  $F_2$  per mole of  $F_2$   
 $x_{f_2} =$  mole fraction of more volatile component in  $F_2$

In Equation 18A the following quantities are usually known and may be replaced with constants:

$$(x_{f_2} - W/F_2 x_w) = A$$

$$(H_{f_2} - W/F_2 Q_w) = B$$

$$(W/F_2 - 1) = C$$

Then Equation 18A becomes:

$$y_i = x_{i+1} + \left( \frac{A + Cx_{i+1}}{Ch_{i+1} + B} \right) (H_i - h_{i+1}) \tag{18B}$$

SEPARATION OF ONE FEED WITH ENTRAINMENT

The method of handling entrainment calculations on a McCabe-Thiele diagram was shown by Baker (1). Concept  $e$  used in this paper is identical with that previously presented; i. e.,  $e =$  moles of entrained liquid per mole of dry vapor. Unfortunately the constructional correction for entrainment is not applicable in this instance owing to the curvature of the "dry" operating line. However, the allowance for  $e$  in the equations presented here merely adds three easily evaluated terms to the equations for no entrainment. It should be noted that symbol  $V$  represents moles of dry vapor;  $L$ , moles of liquid resulting from the condensation of dry vapor; and  $x$  and  $y$ , mole fractions of the more volatile component in  $L$  and  $V$ , respectively.

UPPER OPERATING LINE:

$$V_n y_n + e V_n x_n = (L_{n+1} + e V_n) x_{n+1} + D x_d \tag{19}$$

From Equations 19 and 1,

$$y_n = (1 + e) x_{n+1} - e x_n + \frac{D(x_d - x_{n+1})}{V_n} \tag{20}$$

$$V_n H_n + e V_n h_n = (L_{n+1} + e V_n) h_{n+1} + D Q_d \tag{21}$$

From 21 and 1,

$$V_n = \frac{D(Q_d - h_{n+1})}{H_n + e h_n - (1 + e) h_{n+1}} \tag{22}$$

From 22 and 20,

$$y_n = (1 + e) x_{n+1} - e x_n + \left[ \frac{H_n + e h_n - (1 + e) h_{n+1}}{Q_d - h_{n+1}} \right] (x_d - x_{n+1}) \tag{23}$$

Equation 23 defines the upper operating line.

LOWER OPERATING LINE:

$$V_m y_m + e V_m x_m = (L_{m+1} + e V_m) x_{m+1} - W x_w \tag{24}$$

From Equations 24 and 7,

$$y_m = (1 + e) x_{m+1} - e x_m + \frac{W(x_{m+1} - x_w)}{V_m} \tag{25}$$

$$V_m H_m + e V_m h_m = (L_{m+1} + e V_m) h_{m+1} - W Q_w \tag{26}$$

From 26 and 7,

$$V_m = \frac{W(h_{m+1} - Q_w)}{H_m + e h_m - (1 + e) h_{m+1}} \tag{27}$$

From 27 and 25,

$$y_m = (1 + e) x_{m+1} - e x_m + \left[ \frac{H_m + e h_m - (1 + e) h_{m+1}}{h_{m+1} - Q_w} \right] (x_{m+1} - x_w) \tag{28}$$

SEPARATION OF TWO FEEDS WITH ENTRAINMENT

As in case 2, the question of two feeds only introduces an intermediate operating line between the two feed plates:

$$V_i y_i + e V_i x_i = (L_{i+1} + e V_i) x_{i+1} + F_2 x_{f_2} - W x_w \tag{29}$$

From Equations 29 and 13,

$$y_i = (1 + e) x_{i+1} - e x_i + \frac{F_2(x_{f_2} - x_{i+1}) + W(x_{i+1} - x_w)}{V_i} \tag{30}$$

$$V_i h_i + e V_i h_i = (L_{i+1} + e V_i) h_{i+1} + F_2 H_{f_2} + W Q_w \quad (31)$$

From 31 and 13,

$$V_i = \frac{F_2(H_{f_2} - h_{i+1}) + W(h_{i+1} - Q_w)}{H_i + e h_i - e h_{i+1}} \quad (32)$$

From 32 and 30,

$$y_i = \frac{(1 + e)x_{i+1} - e x_i + (H_i + e h_i - e h_{i+1})[F_2 x_{f_2} - x_{i+1} + W(x_{i+1} - x_w)]}{F_2(H_{f_2} - h_{i+1}) + W(h_{i+1} - Q_w)} \quad (33)$$

Dividing numerator and denominator of the last term by  $F_2$ ,

$$y_i = \frac{(1 + e)x_{i+1} - e x_i + \left[ \frac{x_{f_2} - W/F_2 x_w + (W/F_2 - 1)x_{i+1}}{(W/F_2 - 1)h_{i+1} + H_{f_2} - W/F_2 Q_w} \right] (H_i + e h_i - e h_{i+1})}{(H_i + e h_i - e h_{i+1})} \quad (33A)$$

Using the constants of Equation 18B,

$$y_i = (1 + e)x_{i+1} - e x_i + \left[ \frac{H_i + e h_i - e h_{i+1}}{C h_{i+1} + B} \right] (A + C x_{i+1}) \quad (33B)$$

If entrainment  $e$  is not the same in the two or three sections of the column, then the appropriate value of  $e$  must be used in each section of the column.

### ILLUSTRATIVE EXAMPLE A

It is desired to separate a mixture of acetic acid and water. The feed is available at the boiling point and contains 0.50 mole fraction of water. The distillate is to contain 0.95 mole fraction of water and the bottoms, 0.05. Five moles of reflux will be returned to the column per mole of distillate withdrawn. How many theoretical contacts are required for the separation?

Using equilibrium data available, the common  $x$ - $y$  diagram can be prepared. The enthalpy concentration relationship can be approximated from the available data. Figure 1 is such a plot of the enthalpy of liquid and vapor mixtures. The enthalpy of the liquid was obtained by plotting a smooth curve through the few data available in the literature, and the enthalpy of the vapor was computed by assuming a straight-line relation between the latent heats of acetic acid and water, and then adding the enthalpy of the liquid. Its accuracy is questionable, but it will serve for the purpose of illustrating the application of the methods here presented. More data are needed on enthalpies of liquid-vapor systems, if distillation calculations are to be accurately made.

The first step is to determine the two constants  $Q_d$  and  $Q_w$ :

$$\begin{aligned} Q_d &= 6 \text{ times the heat required to condense 1 mole of vapor of} \\ &\quad \text{composition 0.95 water + enthalpy removed by 1} \\ &\quad \text{mole of distillate} \\ &= 6(20,450 - 3400) + 3400 = 105,700 \end{aligned}$$

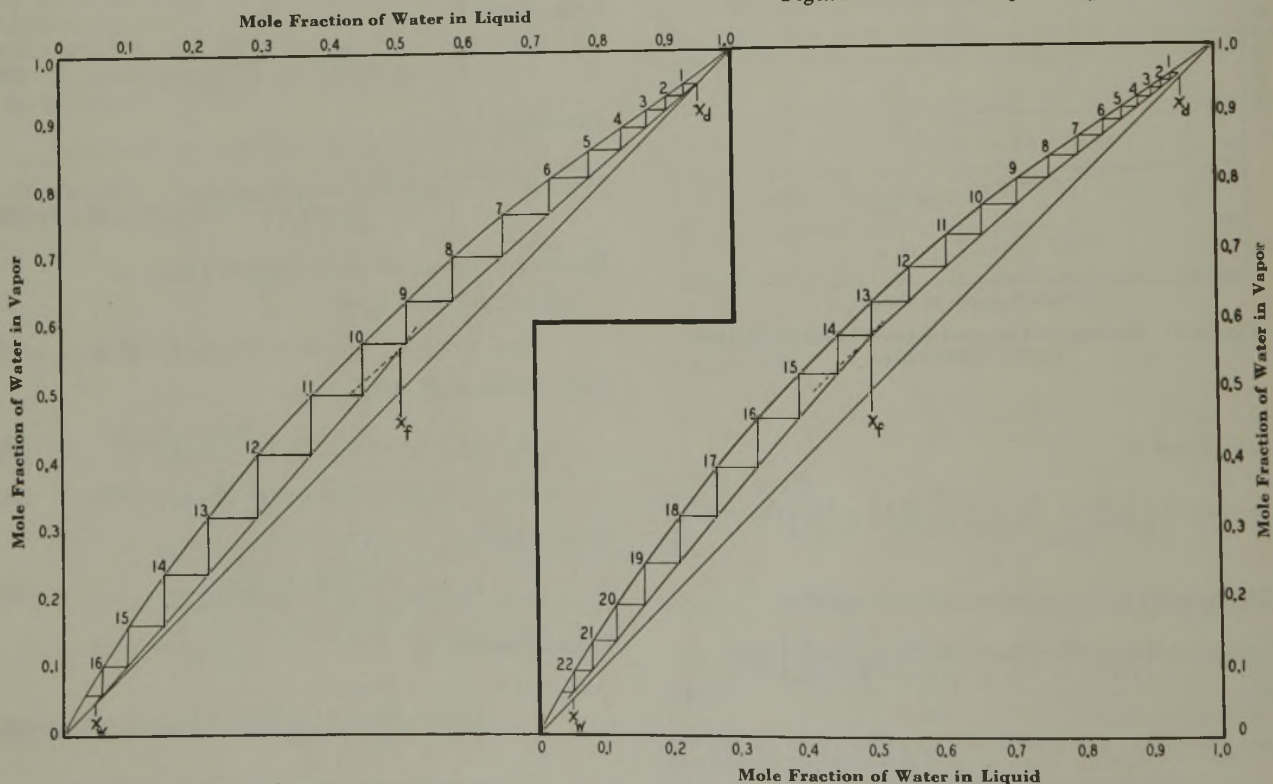


Figure 2. Solution of Example A

Figure 3. Solution of Example B

Equations 6, 12, 18B, 23, 28, and 33B establish the curved operating lines for use in the usual manner as on a McCabe-Thiele diagram. The fact that such equations as 6 and 12 give curved operating lines was pointed out by Randall and Longtin (3). Their use in column design will be illustrated by the solution of two typical problems.

Then these heat and material balance equations may be written:

$$\begin{aligned} F &= W + D = W + 1, \text{ for } D = 1 \\ F x_f &= W x_w + D x_d \\ 0.5F &= 0.05W + 0.95 \end{aligned}$$

Therefore when  $D = 1$ ,  $F = 2$ , and  $W = 1$ :

$$FH_f = WQ_w + DQ_d$$

$$2(4780) = Q_w + 105,700$$

$$Q_w = -96,140$$

The above heat quantities may be read from Figure 1.

The upper operating line (Equation 6) may now be calculated. Take  $y_n = 0.90$ , then  $H_n = 20,220$ . Assuming  $h_{n+1} = 3620$ , Equation 6 becomes:

$$0.90 = x_{n+1} + \left( \frac{20,220 - 3620}{105,700 - 3620} \right) (0.95 - x_{n+1})$$

from which  $x_{n+1} = 0.889$ ; this value does not check  $h_{n+1}$  in Figure 1 so a value of  $h_{n+1} = 3590$  is assumed:

$$0.90 = x_{n+1} + \left( \frac{20,220 - 3590}{105,700 - 3590} \right) (0.95 - x_{n+1})$$

from which  $x_{n+1} = 0.890$ , checking  $h_{n+1}$ .

By this method the following points may be determined:

$y_n$	$x_{n+1}$	$y_n$	$x_{n+1}$
0.90	0.890	0.60	0.542
0.80	0.773	0.50	0.429
0.70	0.657		

These points describe the upper operating line in Figure 2. The lower operating line (Equation 12) may be calculated similarly.

If  $y_m = 0.40$ ,  $H_m = 18,400$ . Assume  $h_{m+1} = 5300$ ; then Equation 12 becomes:

$$0.40 = x_{m+1} + \left[ \frac{18,400 - 5300}{5300 - (-96,140)} \right] (x_{m+1} - 0.05)$$

from which  $x_{m+1} = 0.360$ , checking the assumed value for  $h_{m+1}$ .

By this method the following points may be determined:

$y_m$	$x_{m+1}$	$y_m$	$x_{m+1}$
0.10	0.0954	0.40	0.360
0.20	0.1845	0.50	0.448
0.30	0.2725	0.60	0.531

These points describe the lower operating line in Figure 2.

The upper and lower operating lines may now be drawn through the determined points, intersecting each other directly at  $x = 0.5$  as the feed is liquid at the boiling point. Then the number of equilibrium steps are counted off between these lines and the equilibrium curve, and are found to be 16 and a fraction (Figure 2).

#### ILLUSTRATIVE EXAMPLE B

If in example A it was expected that there would be 0.3 mole of entrained liquor per mole of dry vapor throughout the column, how many contacts would be required? Assume that the operation is carried out so that 5 moles of condensed dry vapor are returned to the column for every mole of distillate withdrawn. This means  $5 + 0.3(6)$  or 6.8 moles actually returned as reflux.

To determine  $Q_d$  and  $Q_w$  it is necessary in this instance to know the composition of the dry vapor and entrained liquor leaving the top plate. It is known that

$$\frac{V_n y_n + e V_n x_n}{V_n + e V_n} = 0.95$$

$$x_n = \frac{0.95(1.3) - y_n}{0.3}$$

Assuming values for  $y_n$  and calculating  $x_n$  until the equilibrium values are reached,

$$y_n = 0.954 \text{ and } x_n = 0.936$$

$$\text{Now } Q_d = 6(20,480) + 1.8(3450) - 6.8(3400) = 105,970$$

$$Q_w = 9560 - 105,970 = -96,410$$

The upper operating line (Equation 23) may now be calculated.

If  $y_n = 0.80$ ,  $H_n = 19,800$ ,  $x_n = 0.706$ , and  $h_n = 4100$ ; assuming  $h_{n+1} = 3910$ , Equation 23 becomes:

$$0.80 = (1 + 0.3)x_{n+1} - 0.3(0.706) + \left[ \frac{19,800 + 0.3(4100) - (1 + 0.3)3910}{105,970 - 3910} \right] (0.95 - x_{n+1})$$

from which  $x_{n+1} = 0.754$ , checking the assumed value for  $h_{n+1}$ .

By this method the following points may be determined:

$y_n$	$x_{n+1}$	$y_n$	$x_{n+1}$
0.90	0.884	0.60	0.528
0.80	0.754	0.50	0.414
0.70	0.636		

These points describe the upper operating line in Figure 3.

The lower operating line (Equation 28) is calculated as follows: If  $y_m = 0.40$ ,  $H_m = 18,400$ ,  $x_m = 0.281$ , and  $h_m = 5680$ ; assuming  $h_{m+1} = 5400$ , Equation 28 becomes:

$$0.40 = (1 + 0.3)x_{m+1} - 0.3(0.281) + \left[ \frac{18,400 + 0.3(5680) - (1 + 0.3)5400}{5680 - (-96,410)} \right] (x_{m+1} - 0.05)$$

from which  $x_{m+1} = 0.344$ , checking the assumed value for  $h_{m+1}$ . By this method the following points may be determined:

$y_m$	$x_{m+1}$	$y_m$	$x_{m+1}$
0.10	0.0872	0.40	0.344
0.20	0.1717	0.50	0.431
0.30	0.257	0.60	0.521

These points describe the lower operating line in Figure 3.

The upper and lower operating lines may now be drawn through the determined points, intersecting each other at  $x = 0.5$  as the feed is liquid at the boiling point. The number of equilibrium steps are counted off between these lines and the equilibrium curve, and are found to be 22 and a fraction (Figure 3).

#### CONCLUSIONS

The authors believe that the broader applicability of the operating lines presented in this paper more than compensate for the slightly greater amount of time required to plot them. The resulting calculation is rigorously correct and therefore has the marked advantage of being free from errors of undetermined extent.

Also, the equations and methods are applicable to quantities in pounds, compositions in weight fractions, and enthalpies in B. t. u. per pound. These units may be more convenient than moles and mole fractions if the original equilibrium data are given in weight fractions.

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# VINYLIDENE CHLORIDE POLYMERS

ROBERT C. REINHARDT

The Dow Chemical Company,  
Midland, Mich.

**A**LTHOUGH vinylidene chloride (1,1-dichloroethylene) has been known for more than a hundred years, extensive work on the polymers of this compound has been limited to the last decade. This work resulted in the introduction to the plastics industry in 1939 of a family of thermoplastics based on vinylidene chloride and known as Saran.

Regnault (34, 35) in 1838 reported the formation of a white noncrystalline precipitate from a liquid boiling between 35° and 40° C.; the liquid was apparently an impure 1,1-dichloroethylene. He considered this precipitate merely an isomeric modification. The liquid was prepared from trichloroethane by reaction with alcoholic potassium hydroxide, a method used by Kraemer (29) and Bauman (2). In 1872 the latter described the formation of a white substance when dichloroethylene was exposed to sunlight. Ostromislenski (33) found that vinylidene chloride polymerized in light to a white amorphous mass insoluble in many solvents.

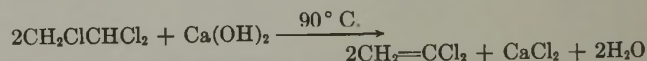
Feisst (17), together with Staudinger (49) and Brunner (48) investigated polydichloroethylene in greater detail. A portion of the polymer used was prepared from an apparently impure dichloroethylene fraction from commercial trichloroethylene. Other studies were made on polydichloroethylene formed as a by-product in the Rheinfelden works of the I. G. Farbenindustrie. This polymer was completely soluble in warm tetrachloroethane, Decalin, and Tetralin, partially soluble in benzene, chloroform, and carbon disulfide, and insoluble in ethers and alcohols; therefore a separation of molecular weights by fractional solubility was possible. The major part of the work involved reactions of the polymer with aniline, resorcinol, quinoline, pyridine, trimethyl amine, and hydrazine, and studies of the products formed. The formation of high-molecular-weight hydrocarbons when the polymer was reduced with hydrogen iodide and phosphorus was reported as evidence that polydichloroethylene was composed of threadlike molecules.

The relation of vinylidene chloride to other polymerizable compounds is noteworthy. The effect of unsymmetrical substitution in ethylene compounds is well illustrated by comparing vinylidene chloride with its two isomers, *cis*- and *trans*-1,2-dichloroethylene, which polymerize only with great difficulty. Ellis (16) and Brooks (10) have commented on

the unsymmetrically substituted ethylenes prepared by early investigators. Sawitsch (45) observed that 1,1-dibromoethylene polymerized to a white solid. Denzel (15) and Biltz (4) made 1-chloro-1-bromoethylene, the polymer of which was found to be insoluble in many solvents. In general, 1,1-disubstituted ethylenes appear to polymerize more easily and form less soluble polymers than the vinyl compounds.

## POLYMERIZATION

Monomeric vinylidene chloride, 1,1-dichloroethylene, is a colorless liquid with a mild characteristic odor. Important properties are given in Table I. The most convenient source of this compound is the reaction of 1,1,2-trichloroethane with aqueous alkali:



Although this general reaction was used by many early investigators, it has been the subject of a number of recent patents (25, 27). 1,1,2-Trichloroethane may be made from petroleum and brine by well known reactions involving ethylene and chlorine. Other methods for the preparation of 1,1-dichloroethylene are based on bromochloroethane (22), trichloroethyl acetate (23), tetrachloroethane (14), and catalytic cracking of trichloroethane (23).

TABLE I. PROPERTIES OF 1,1-DICHLOROETHYLENE

Molecular formula	$\begin{array}{c} \text{Cl} \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{Cl} \quad \text{H} \end{array}$
Molecular weight	96.95
Boiling point	31.7° C. at 760 mm.
Freezing point	-122.1° C.
Density	$d_4^{20} = 1.2129$ ; $d_4^{25} = 1.2085$
Index of refraction	$n_D^{20} = 1.4249$

Carefully purified vinylidene chloride free of oxygen polymerizes very slowly. As ordinarily prepared, however, vinylidene chloride polymerizes readily at temperatures above 0° C. to form a polymer which is insoluble in the



monomer and precipitates as a white powder (37). The presence of dissolved oxygen which reacts to form acid chlorides and peroxides catalyzes the polymerization. Vinylidene chloride is not a vinyl compound, but much of the technique of vinyl chloride polymerizations is applicable to vinylidene chloride. The many chemical catalysts for polymerization which have been used successfully (6, 39, 52) may be classified into five groups: organic and inorganic peroxy compounds, organometallic compounds, organic carbonyl compounds, inorganic salts, and inorganic acids. Benzoyl peroxide in concentrations of 0.05 to 2.0 per cent has been used frequently in laboratory work, and a typical polymerization curve is shown in Figure 1. The straight-line nature of these curves is characteristic and is evidence that the reaction is zero order.

The benzoyl-peroxide-catalyzed polymerizations have little, if any, induction period above 30° C. but usually show a lower polymerization rate for the first few per cent conversion. This behavior is illustrated by the enlarged portion of the curve, inset in Figure 1.

The use of other catalysts or combinations of catalysts causes wide variation in polymerization rates but, in general, does not change the shape of the curves. Thermal polymerization of vinylidene chloride without added catalyst usually does not occur at a rate sufficiently high to be useful, but photopolymerization has been successful both with and without auxiliary chemical catalysis. Light of wave length less than 4500 Å. causes polymerization at temperatures as low as -35° C. Many inhibitors for the polymerization of vinylidene chloride have been described in patents (8, 13).

A solid phase appears during the polymerization of vinylidene chloride, since the polymer is not soluble in the monomer. In mass or bulk polymerizations, where only monomer and catalyst are present, the polymer is a flocculent precipitate below about 10 per cent conversion; between 10 and 20 per

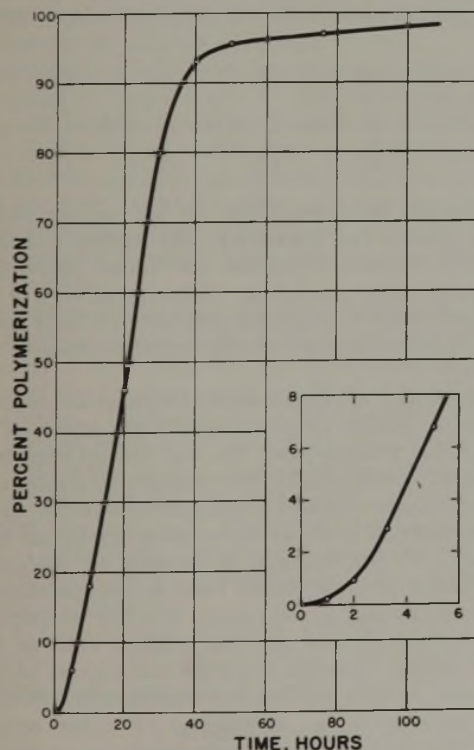


Figure 1. Polymerization of Vinylidene Chloride

Catalyst, 0.50 per cent benzoyl peroxide; temperature, 45° C.; dark.

TABLE II. PROPERTIES OF POLYVINYLIDENE CHLORIDE

Molecular formula	$(-\text{CH}_2-\text{CCl}_2-)_n$
Molecular weight	10,000 to 100,000
Softening temperature	185-200° C.
Decomposition temperature	210-225° C.
Density	1.875 grams/cc. at 30° C.
Index of refraction	$n_D^{20} = 1.63$
Nonflammable; insoluble in all organic solvents at temperatures below 100° C.; unaffected by common reagents at temperatures below 100° C.	

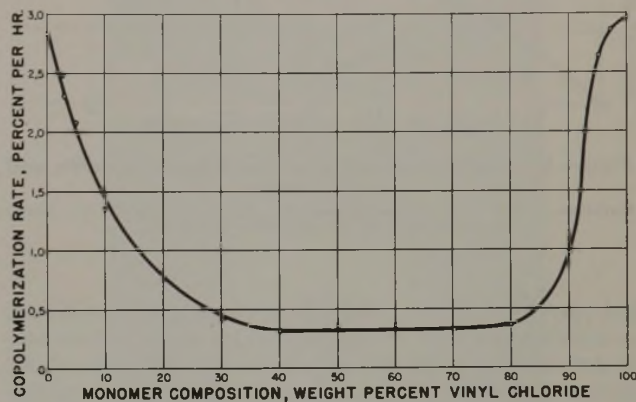


Figure 2. Copolymerization Rate of Vinylidene Chloride and Vinyl Chloride as a Function of Monomer Composition

Catalyst, 0.50 per cent benzoyl peroxide; temperature, 45° C.; dark.

cent conversion the slurry becomes solid; above 20 per cent no liquid is visible, and the porous solid becomes harder with increasing polymerization. With proper choice of conditions the reaction reaches 100 per cent conversion to polymer and results in the evolution of about 20,000 gram-calories per gram mole of monomer. To control the polymerization rate and the physical characteristics of the product, it is often desirable to add to the monomer a solvent or an immiscible liquid and conduct the polymerization in solution, emulsion, or other dispersed system (36). The products of different polymerization methods differ only in minor details.

Polyvinylidene chloride is a white porous powder with a softening range of 185-200° C. and a decomposition temperature of about 225° C. When fused and cooled, the polymer is colorless and nearly transparent. In either form, polyvinylidene chloride possesses two outstanding characteristics—crystallinity, as determined by x-ray diagrams, and insolubility. These will be discussed later in detail.

The distinctive properties of polyvinylidene chloride are given in Table II. The utilization of the polymer as a plastic material in the ordinary sense is difficult because of its high softening range, its tendency to evolve hydrogen chloride at the temperatures required for plastic working, and its incompatibility with usual plasticizers. These obstacles, not necessarily disadvantages, are characteristic of the molecule; but despite them, polyvinylidene chloride can be worked by special methods to produce a unique plastic material. For general use the properties of the polymer are best modified by copolymerization.

#### COPOLYMERIZATION

Vinylidene chloride forms copolymers with many substituted ethylenes (particularly the common vinyl compounds), with dienes and their derivatives, and with a number of other unsaturated compounds. Specific examples are described in many patents; important copolymers of vinylidene chloride are those with vinyl chloride (1, 26, 50, 56), vinyl acetate (50), styrene (51), esters of acrylic and methacrylic acid (12, 53),

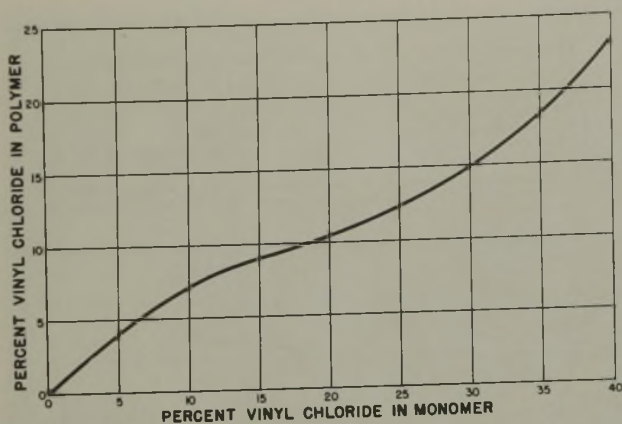


Figure 3. Copolymerization of Vinylidene Chloride and Vinyl Chloride

Catalyst, 0.50 per cent benzoyl peroxide; temperature, 45° C.; dark; approximately 50 per cent polymerization.

and vinyl cyanide (21). Other compounds which are known to copolymerize with vinylidene chloride are butadiene and its derivatives (11, 46, 59), various unsaturated esters (7, 9), unsaturated ethers (5), and halogen-substituted propenes (40).

In general, when vinylidene chloride is copolymerized, each mixture of monomers has a different polymerization rate and produces a polymer of different composition. Usually the product contains a larger proportion of vinylidene chloride than the original monomer composition, and the rate of polymerization is slower than for either monomer alone. Except in rare cases, the products are true copolymers and contain little or none of the individual polymers.

A typical case is illustrated by Figure 2. Although vinylidene chloride and vinyl chloride have nearly identical polymerization rates with 0.5 per cent benzoyl peroxide at 45° C.,

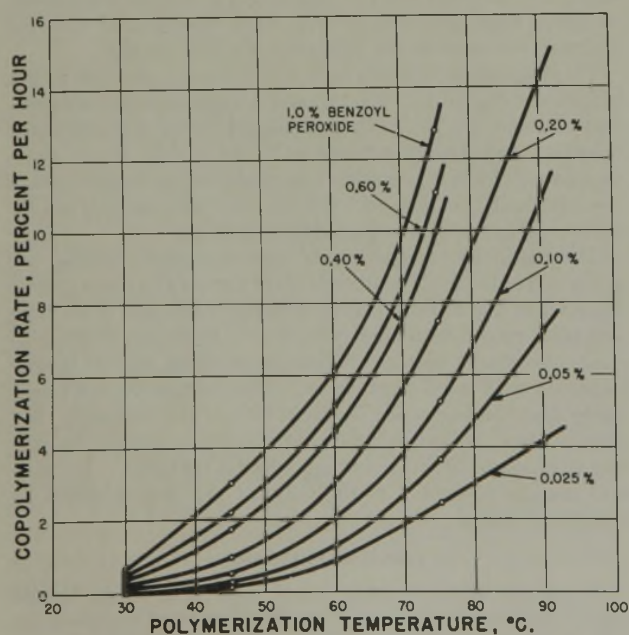


Figure 4. Copolymerization Rate of Vinylidene Chloride and Vinyl Acetate as a Function of Polymerization Temperature and Catalyst Concentration

Monomer composition, 85 per cent vinylidene chloride, 15 per cent vinyl acetate; temperature, 45° C.; dark.

mixtures of the two monomers may have but one tenth the polymerization rate of either component. Figure 3 shows the average polymer compositions produced from a number of monomer mixtures. Since the polymer contains more vinylidene chloride than the monomer, the vinyl chloride concentration in the monomer increases as polymerization progresses; consequently, the product of such a polymerization contains a wide distribution of copolymer compositions in addition to the distribution of chain lengths.

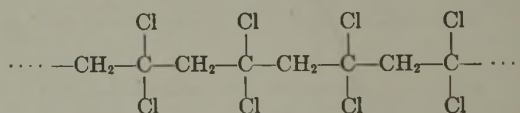
The thermal and peroxide catalysis of copolymerization is illustrated in Figure 4 with 85 per cent vinylidene chloride-15 per cent vinyl acetate monomer composition. Increased temperature is preferable to higher catalyst concentration as a means of increasing the polymerization rate. The relation of viscosity (i. e., chain length) to polymerization temperature for these copolymers is shown in Figure 5.

The methods used for polymerizing vinylidene chloride are applicable with certain changes to the formation of its copolymers. However, the widely varying polymerization rates and the heterogeneous copolymers introduce important complications in the study and development of both process and products.

Vinylidene chloride copolymers may be analyzed by standard methods. Determination of the percentage chlorine is usually sufficient to give the average composition although, as mentioned by Berger (3), the results obtained by this method may be in error by several per cent. Chain lengths are comparatively measured by the determination of solution viscosity; but owing to the extremely limited solubility of certain copolymers, it is often necessary to use only the best solvents at temperatures of 120° C. or above.

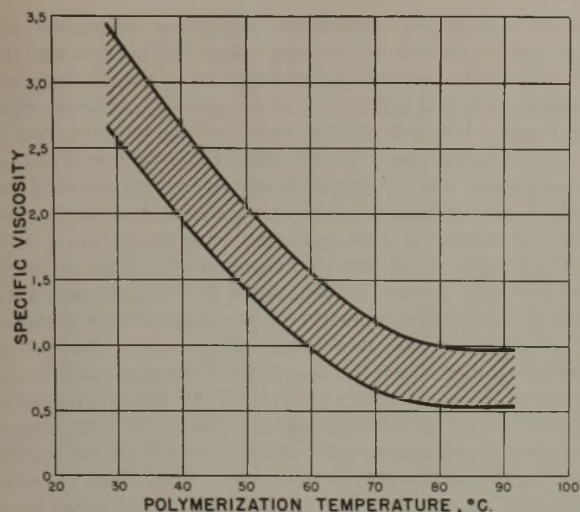
#### STRUCTURE

An important and fundamental property of polyvinylidene chloride—crystallinity—was first noted by Feisst (17), after x-ray diagrams had been made by Hengstenberg and Sauter. Further comments were made by Staudinger (47) who assigned to polyvinylidene chloride the head-to-tail configuration,



and attributed its crystallinity to its regular molecular structure. Natta and Rigamonti (32) studied a number of polymers by electron diffraction and found polyvinylidene chloride to be highly crystalline. Subsequent work of a more accurate and detailed nature has resulted in a fairly complete picture of the fine structure of polyvinylidene chloride and its copolymers.

The examination of representative polymers and copolymers of vinylidene chloride by x-rays results in patterns of which Figures 6A and B are typical; the well defined rings indicate a high degree of crystallinity, the background scattering indicates an appreciable amount of amorphous material, and polyvinylidene chloride is shown to be more crystalline than its copolymers. If, for example, a polymer or copolymer of vinylidene chloride is completely fused at a temperature above its melting point and cooled rapidly to a low temperature, it becomes amorphous and an x-ray pattern such as that of Figure 6C results. Storage of amorphous polymer at suitable temperatures permits gradual recrystallization. Severe mechanical working (e. g., stretching) of either completely amorphous or partly crystalline polymers produces orientation (Figure 6D). Polyvinylidene chloride and copolymers which are largely vinylidene chloride can, therefore, be said to exist in three modifications.



**Figure 5. Specific Viscosity of Vinylidene Chloride-Vinyl Acetate Copolymers as a Function of Polymerization Temperature**

Monomer composition, 85 per cent vinylidene chloride, 15 per cent vinyl acetate; catalyst, 0.50 per cent benzoyl peroxide; dark. Solution, 2 per cent in *o*-dichlorobenzene at 120° C.

1. **CRYSTALLINE.** The normal "as-polymerized" state, giving a sharply defined x-ray pattern but also known to be partly amorphous.
2. **AMORPHOUS.** Soft, easily deformed material obtained by fusing and rapidly cooling crystalline polymer; reverts to the crystalline form under suitable conditions.
3. **ORIENTED CRYSTALLINE.** Tough, strong, showing characteristic x-ray fiber pattern; produced by plastically deforming either partly crystalline or amorphous material.

Accurate measurement and analysis of the x-ray diagrams, together with these considerations, lead to a concept of the structure of polyvinylidene chloride which is adequate to explain observed physical phenomena.

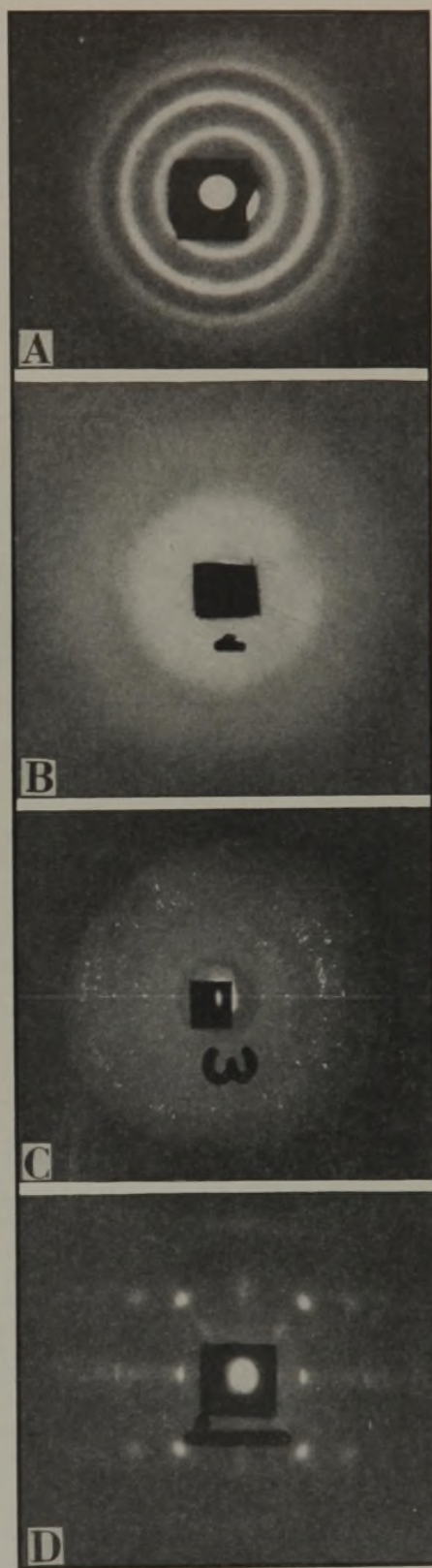
A single chain of polyvinylidene chloride is believed to have the structure of Figures 7 and 8. Monomer units are joined head to tail, with a serpentine configuration of carbon atoms. With a carbon valence bond angle of 120° and a carbon-carbon distance of 1.55 Å., an identity period of 4.67 Å. results.

This structure is in better agreement with the observed reflections than those given by Fuller (18), who suggested a zig-zag arrangement of carbon atoms with the chain shortened by partial rotation.

Solution viscosity and osmotic pressure measurements indicate a range of chain lengths of 100 to 1000 monomer units. As with other high polymers, the chain length is an inverse function of the polymerization temperature and the catalyst concentration. Determination of the branching coefficient,  $n$ , by the method of Houwink (24) gives  $n = 1$ . This unusually low value and the marked tendency to crystallize are strong evidence that the chains are not branched. In the amorphous state they are randomly distributed and probably highly curled. Crystallization involves the movement of portions of such molecules into a macromolecular lattice which has no well defined boundaries.

The unit cell of polyvinylidene chloride is monoclinic and contains four  $-\text{CH}_2-\text{CCl}_2-$  units. Its dimensions have been determined accurately as follows:

$$\begin{aligned}
 a &= 13.69 \pm 0.015 \text{ \AA.} \\
 b &= 4.67 \pm 0.01 \text{ \AA.} \\
 c &= 6.296 \pm 0.010 \text{ \AA.} \\
 \sin \beta &= 0.8212 \pm 0.015 \\
 \text{volume of cell} &= 330.6 \text{ \AA.}^3
 \end{aligned}$$



**Figure 6. X-Ray Patterns Made with Mo K $\alpha$  Radiation (Specimen-to-Plate Distance, 6.5 Cm.)**

- A. Polyvinylidene chloride (powder)
- B. Amorphous vinylidene chloride-ethyl acrylate copolymer
- C. Normally crystalline amorphous vinylidene chloride-vinyl chloride copolymer
- D. Normally crystalline oriented vinylidene chloride-vinyl chloride copolymer (fiber axis vertical)

The dimensions of the "crystallite" are believed to be about 20–30 Å. parallel to the chain axes and about 200–500 Å. at right angles. In the crystalline portions the chains are essentially parallel, although the long-chain molecules undoubtedly traverse both crystalline and amorphous regions. The comparatively low proportion (20–40 per cent) of crystalline regions in fused and recrystallized polymer and the high ratio of length to diameter of the molecules indicate that the amorphous regions are probably the continuous phase. Such a picture is not one of mesomorphic arrangement or of a crystalline modification dispersed in an amorphous one, but rather of a continuous transition between crystalline and amorphous material. Both modifications share in determining the ultimate physical properties.

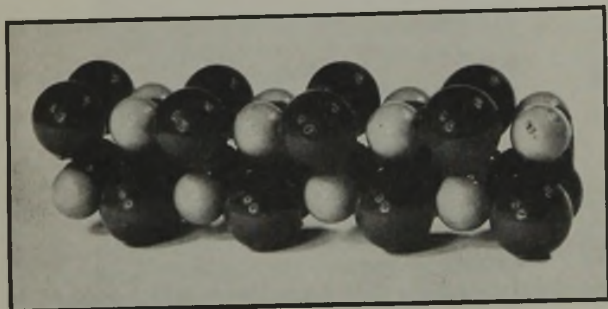


Figure 7. Scale Model of a Portion of the Polyvinylidene Chloride Chain

Copolymerization introduces units in the chain which tend to destroy its regularity and consequently its ability to crystallize, although the introduction of small amounts of other monomers merely results in minor discontinuities in the crystalline regions. The magnitude of the effect varies somewhat with the structure of the copolymerizing molecule; but in general, copolymers which contain less than about 70 per cent vinylidene chloride are essentially noncrystalline. Other effects of copolymerization which are related to the decreased crystallinity are reduced softening temperature and increased solubility in organic solvents.

#### PHENOMENA ASSOCIATED WITH CRYSTALLINITY

Crystalline polyvinylidene chloride (with the exception of the as-polymerized powder) is hard, tough, and resembles ordinary plastic materials in many respects. Amorphous polyvinylidene chloride is soft, rubbery, and capable of being mechanically worked, and tends to crystallize on standing. The oriented modification is strong, tough, and exceedingly flexible. In general these statements are true also for crystalline copolymers, and in fact, the copolymers which fall in this range are those which possess a most advantageous combination of properties for commercial molding and extrusion.

A very narrow softening range is characteristic of the crystalline polymers and copolymers of vinylidene chloride. A few degrees above the softening range these polymers have a sharp, reproducible crystalline melting point, observed by the change in light transmission of a sample heated between crossed Polaroids. This temperature probably corresponds to the melting of the most stable crystalline regions. The process of melting is comparable to the solid-liquid transitions of crystalline compounds of lower molecular weight. At higher temperatures the molten polymer may be quite fluid. The flow data in Figure 9 illustrate the sharp softening point of a crystalline vinylidene chloride-vinyl chloride copolymer as compared with polystyrene.

When a normally crystalline copolymer is heated to a temperature sufficient to melt the crystalline portion and then cooled below the crystalline melting point so that no recrystallization occurs, it is amorphous and is said to have been supercooled (54). When so treated, the tendency to crystallize is a function of many variables, the most important of which are the copolymer composition, the time and temperature of storage, and the presence of addition agents such as plasticizers. Figure 10 shows the wide variation with temperature of the induction time which elapses before recrystallization begins. This induction period, as measured between crossed Polaroids, is a reproducible quantity for any copolymer composition and treatment. The area below either curve denotes the conditions under which the supercooled polymer may be produced and stored. Above about 110° C. the crystallization induction period is increased by the relatively high thermal energy of the polymer chains; below about 60° C. the increase is due to the high internal viscosity. The effect of certain plasticizers in reducing the crystallization induction period (curve B) may be attributed to the increased mobility of the chains. The short induction period at the lowest portion of the curves illustrates why rapid cooling of a fused polymer is usually necessary to produce samples which are amorphous at room temperature.

When crystallization has started, several marked changes occur in the physical and mechanical properties of the polymer. The most important of these are:

1. A gradual development of a typical crystalline x-ray diffraction pattern
2. An increase in hardness
3. An increase in the force required to produce deformation
4. An increase in density
5. Evolution of about 3.4 gram-calories per gram of polymer as heat of crystallization
6. Variations in electrical properties
7. An increase in resistance to the action of solvents

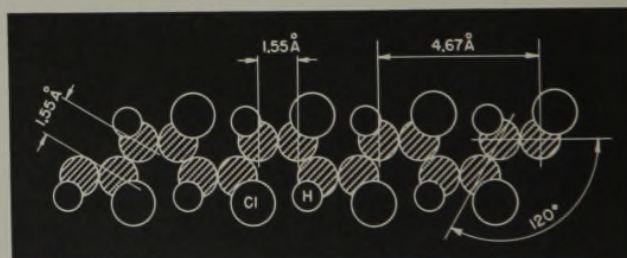


Figure 8. Chain Configuration of Polyvinylidene Chloride (Scale of Interatomic Distances Expanded with Respect to That of Atomic Radii)

Amorphous polyvinylidene chloride and amorphous copolymers of vinylidene chloride prepared from normally crystalline copolymers are similar to natural rubber in two respects other than those already mentioned. For very low elongations, a filament of such amorphous polymers exhibits nearly perfect elasticity until crystallization occurs. Also, if a supercooled filament is stretched to an elongation of 150–250 per cent and allowed to crystallize further, it will elongate slightly without application of load.

#### ORIENTATION

Vinylidene chloride polymers and copolymers exhibit orientation when either the crystalline or amorphous modifications are mechanically worked, but the degree of orientation produced may vary, depending on the polymer composition and treatment. If a filament of polyvinylidene chloride is

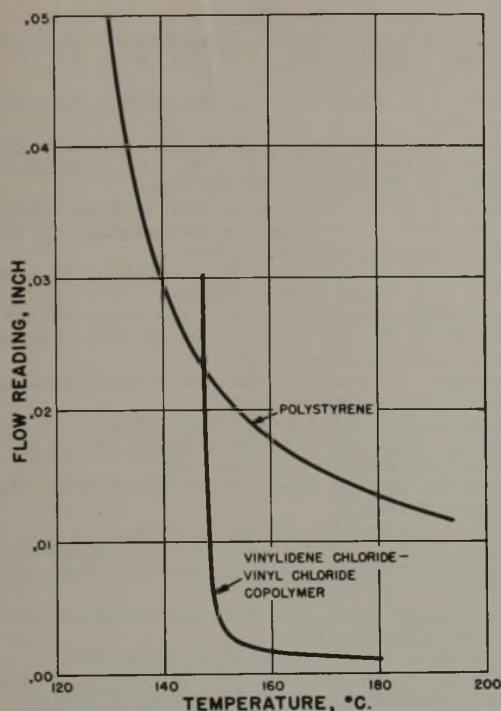


Figure 9. Typical Flow Curves of a Crystalline Vinylidene Chloride-Vinyl Chloride Copolymer and Polystyrene

Flow reading is the equilibrium thickness attained by a film of plastic subjected to a constant load between parallel polished plates heated to the temperatures shown.

stretched at a temperature somewhat above the polymer crystalline melting point and quickly cooled, the strand will show some slight orientation. Crystalline polyvinylidene chloride may also be stretched, with the application of comparatively high loads, and a filament so treated will exhibit orientation together with increased strength and flexibility. However, if a similar filament is supercooled and stretched before crystallization begins, a high degree of orientation results. The x-ray pattern (Figure 6D) is characteristic of this treatment, which may be used to produce fibers of exceptionally high strength and flexibility (55). The load-elongation curve for a supercooled filament (Figure 11) shows that the force required for plastic deformation is nearly constant below 300 per cent elongation, but after orientation has occurred, elastic elongation requires a relatively high load. Supercooled filaments may be stretched to an elongation of 350-400 per cent, depending on previous treatment, and the greatest increase in tensile strength occurs with the last few per cent of stretch. Tensile strengths of 100,000 pounds per square inch have been obtained with optimum stretching conditions but with the sacrifice of other desirable properties.

#### FABRICATION

Certain vinylidene chloride polymers and copolymers may be fabricated by the methods commonly used for thermoplastics; but to take advantage of the unique properties resulting from the crystalline structure, additional methods have been developed. The high softening point and relative thermal instability of polyvinylidene chloride have largely excluded it from the industrial fabrication procedures for which the copolymers of lower softening temperatures are more adaptable. The copolymers now available require special technique in their fabrication. Important considerations are the use of inert metals in hot zones, minimum heating

times, and the incorporation of a satisfactory plasticizer and heat stabilizer.

The remarkable properties of oriented filaments of vinylidene chloride copolymers have stimulated the development of extrusion processes. Modification of the screw-type extrusion machines to permit streamline plastic flow and uniform heating, together with the use of entirely new types of stretching and winding machinery, have resulted in the production of a wide variety of extruded articles. Cordage (0.010-0.100 inch diameter filaments) and tubing have gained industrial prominence, and intensive work on textile fibers is continuing.

Injection moldings of vinylidene chloride copolymers possess unusual toughness and durability, since the molding cycle may be modified to produce finished articles which are partly oriented. The use of cold dies results in supercooled articles suitable for further treatment, while heated dies permit crystallization, desirable for rapid cycles and dimensional accuracy of the finished piece. Economic considerations usually favor injection molding over compression molding, although the latter may be accomplished satisfactorily.

Vinylidene chloride copolymers may be fabricated by a variety of new methods, in that the combination of thermoplasticity with crystallinity permits operations such as cold or hot rolling (30), forging, blowing, stamping, and welding (41).

#### PHYSICAL PROPERTIES

The relative insolubility and unreactivity of polyvinylidene chloride was noted by a number of early workers. This characteristic is not greatly altered by increasing copolymerization until the copolymer contains less than about 85 per cent of vinylidene chloride; consequently, the commercially available copolymers are resistant to the action of all but a few common materials. At temperatures above 100° C. compounds of the type of dioxane (42), *o*-dichlorobenzene (43), and cyclohexanone (44) show some solvent action, but true solutions may not be obtained in many cases. At room temperature high vinylidene chloride copolymers are substantially unaffected by both aliphatic and aromatic hydrocarbons, alcohols, esters, and ketones. Inorganic acids and alkalis have little or no effect, with the exception of concentrated sulfuric acid, sodium hydroxide, and ammonium hydroxide, which cause discoloration. Resistance to water is exceptional; A. S. T. M. tests show 0.00 per cent absorption in

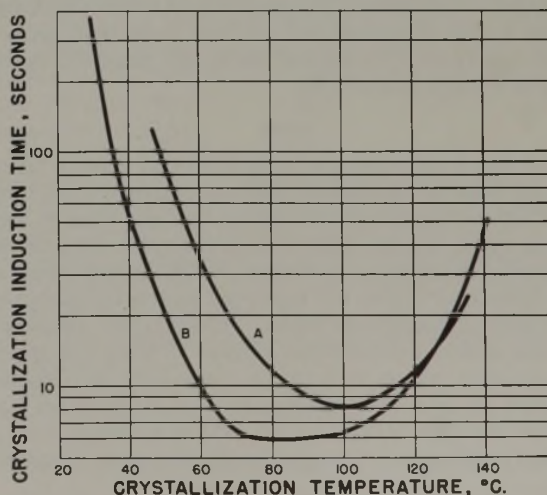


Figure 10. Typical Crystallization Induction Period Curves for a Normally Crystalline Vinylidene Chloride-Vinyl Chloride Copolymer

A, no plasticizer; B, 7 per cent plasticizer. Specimen thickness, 0.050 inch.

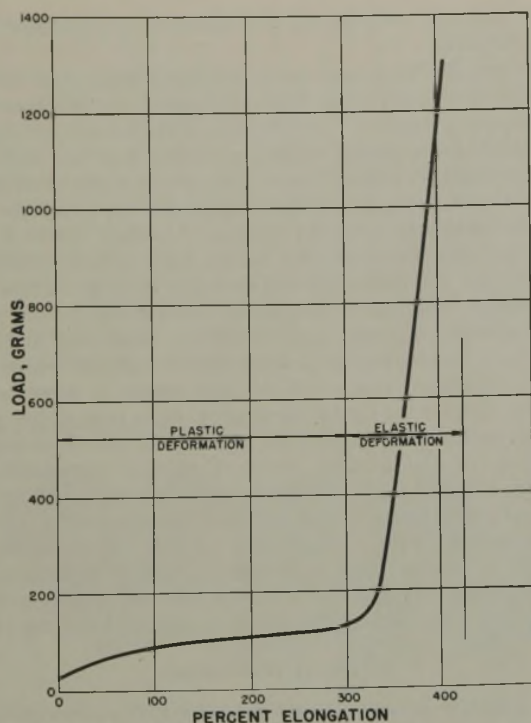


Figure 11. Typical Load-Elongation Curve for a Supercooled Filament of a Normally Crystalline Vinylidene Chloride-Vinyl Acetate Copolymer, Plasticized

Temperature of test, 20° C.; Scott IP2 testing machine; final diameter of filament, 0.011 inch.

24 hours, and less than 3 grams per square meter per 24 hours of water vapor transmission at 45° C. (20).

In view of the low compatibility of crystalline vinylidene chloride polymers and copolymers with other materials, it is not surprising that only a limited number of plasticizers offer advantages (38, 57, 58). Plasticized and stabilized copolymer compositions are available as molding powder or in fabricated shapes under the name of Saran. Heat and light stabilizers, dyes, pigments, fillers, and lubricants have been developed specifically for many applications.

Detailed tabulations of the properties of Saran which are of interest to the fabricator and the user have been given by Goggin and Lowry (19, 20) and the annual plastics properties charts of *Modern Plastics* (31).

#### USES

Saran has found wide use in fields new to plastics because of its combination of chemical inertness, strength, and toughness. Extruded and oriented Saran has been used in heavy textiles, ropes, braids, belts, and in tapes for furniture and transportation seating. Extruded Saran tubing, rods, and other structural shapes are employed as process piping and for a variety of mechanical parts. Injection and compression moldings of Saran have solved difficult molding and application problems where its superior mechanical and chemical properties are essential. A number of basic fabricated forms of Saran (cordage, rattan, tubing, textile filaments, foil, and injection molding) are illustrated in the picture on page 422.

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# Stress-Strain Characteristics of VINYL ELASTOMERS

M. C. REED

Carbide and Carbon Chemicals Corporation, New York, N. Y.

**E**LASTOMER" was suggested by Fisher (3) to designate those synthetic polymeric substances which have rubberlike properties of extension and retraction. Many individual products of this class have been developed in the past few years. Plasticized compounds made from polyvinyl chloride, polyvinyl chloride-acetate copolymer, and polyvinyl butyral constitute an important group of elastomers. They resemble natural rubber to some degree but are characterized by higher hysteresis and greater change in flexibility with temperature changes. The stress-strain characteristics of some typical compounds in this group are the subject of this paper.

The property of deformation under load and of recovery on removal of load is essential to certain applications such as flexible electrical insulation, waterproof clothing, protective sheeting, tubing, and many other articles. Quantitative measurements of the relation of deformation and load under specified conditions are essential to a proper choice of elastomeric materials for technical applications.

In the evaluation of rubber compounds, tensile strength, elongation at break, and the stress-strain diagram are the properties most commonly measured. Other tests, such as those involving compression, shear, or bending, yield useful information, but the stress-strain test was chosen for the investigation of these elastomeric materials primarily for the simplicity of expression of results and its adaptability to operation at various temperatures.

Because of the importance of controlling the temperature of the specimen during test, the ordinary vertical type of stress-strain tester was unsuitable. A machine described by Williams and Sturgis (4) appeared to fulfill the requirements of the test, with certain minor changes (Figure 1).

## STRESS-STRAIN TESTING

**METHOD.** The test specimen is immersed in water in the glass cylinder shown at the left. The specimen is connected through a steel cable over the chart drum to the end of the load beam. As the specimen elongates, the drum rotates and moves the chart vertically. The load, shown near the middle of the beam, is moved laterally through a motor-driven screw toward the left or the outer end of the beam where it

The stress-strain curves of typical plasticized vinyl polymers have been determined at 10°, 25° and 40° C. by an autographic stress-strain machine. The stress-strain diagram of these elastomers in extension is substantially a straight line up to 1000 pounds per square inch during the first elongation cycle, but is markedly concave toward the load axis over the second cycle and shows a reduction in hysteresis on repeated flexure.

Vinyl elastomers exhibit a greater increase in stiffness with decrease in temperature than vulcanized rubber and, for most commercial compounds, a higher modulus of elasticity at room temperature. In the case of vinyl chloride-acetate copolymers, increasing the vinyl chloride content up to 95 per cent reduces the temperature sensitivity. Increase in vinyl chloride content above 95 per cent has no appreciable effect. Polyvinyl butyral elastomers show greater stiffening at reduced temperatures than polyvinyl chloride-acetate copolymers.

strikes a reversing mechanism and returns to the zero or balance position at the right. Another cable, attached to the load, operates over a set of pulleys against a counterweight and moves the pen across the chart laterally. The tank shown in the background contains water which is circulated through the cylinder and back through an overflow pipe. The tank is provided with an electrical heater and with a removable lid so that ice may be added to the water.

The travel of the load is 17.25 inches which produces a stress of 1000 pounds per square inch on a specimen 0.005 square inch in cross section.

For larger specimens additional weights are added to the beam to maintain a uniform scale on the chart. The time required for the complete cycle is 150 seconds, 74 seconds to apply the load and 76 seconds to unload. The temperature was maintained within 0.2° C. of the stated value, and the thickness of the specimen was measured to the nearest 0.0005 inch with a dial gage having a 0.25-inch circular foot and a 3-ounce weight (1).

The specimens were cut 4.75 inches long and 0.5, 0.25, or 0.125 inch wide, depending on the thickness. A special jig was designed for this purpose, and a razor blade in a holder was used as the cutting tool. The specimens were doubled to form a loop and fastened in a clamp, as shown on the table of the machine in Figure 1.

**MATERIALS TESTED.** Included in this study were typical vinyl elastomeric compounds designed for use as wire insulation, shoe-upper stock, aircraft paulins, cloth-coating compound, safety-glass interlayer, and flexible tubing (Table I). All charts reproduced here were rotated 90° counterclockwise from the position in which they were drawn by the machine. Thus, the curves may be viewed in the same aspect as they are usually drawn by hand from data obtained by other types of machines.

## STRESS-STRAIN UNDER VARIOUS CONDITIONS

Figure 2 shows the stress-strain diagram of several familiar materials at 25° C. The unplasticized copolymer resin shows no elongation, as would be predicted from its modulus of elasticity, which is in the neighborhood of 400,000 pounds per square inch. Curve A, therefore, illustrates the accuracy of the machine when applied to a substantially unyielding

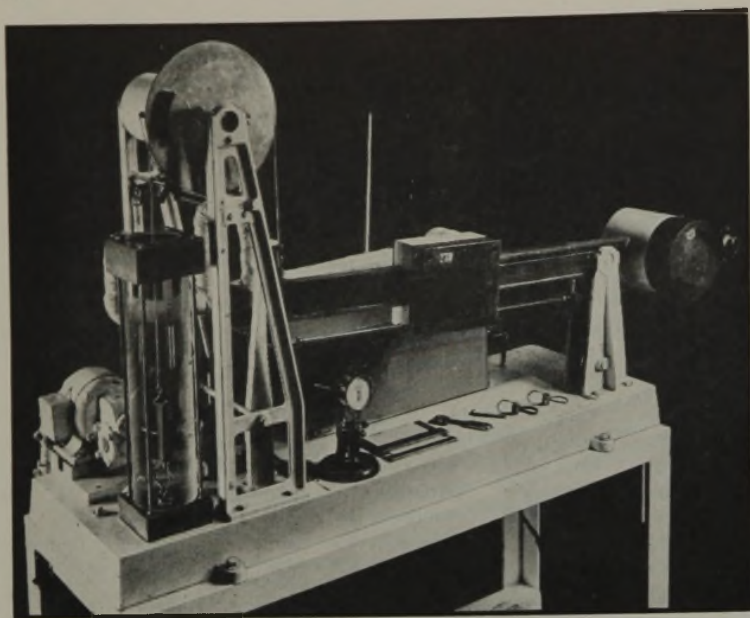


Figure 1. Autographic Stress-Strain Tester

TABLE I. DESCRIPTION OF COMPOUNDS TESTED

1	Unplasticized vinyl chloride-acetate copolymer
2	Rubber tire tread vulcanized 30 min. at 140° C.
3	Unfilled vulcanized rubber
4	Vinyl chloride-acetate copolymer (87% vinyl chloride) plasticized
5	Vinyl chloride-acetate copolymer (90% vinyl chloride) plasticized
6	Vinyl chloride-acetate copolymer (95% vinyl chloride) plasticized with 25 per cent Flexol plasticizer DOP
7	Vinyl chloride-acetate copolymer (95% vinyl chloride) plasticized with 30 per cent Flexol plasticizer DOP
8	Vinyl chloride-acetate copolymer (95% vinyl chloride) plasticized with 35 per cent Flexol plasticizer DOP
9	Vinyl chloride-acetate copolymer (95% vinyl chloride) plasticized with 40 per cent Flexol plasticizer DOP
10	Vinyl chloride polymer, plasticized with 35% Flexol plasticizer DOP
11	Plasticized polyvinyl butyral
12	Plasticized polyvinyl butyral, calendered, more highly plasticized than compound 11
13	Plasticized vinyl chloride-acetate copolymer, electrical insulating type
14	Plasticized vinyl chloride-acetate copolymer, softer electrical insulating type
15	Plasticized vinyl chloride-acetate copolymer, calendered, of type used for thin films
16	Plasticized vinyl chloride-acetate copolymer, soft sheeting type

specimen. Curve *B* shows an extension and recovery cycle on a steel coil spring. The width of the line, as compared with the single lines of the lower curves, represents frictional losses of the machine rather than hysteresis of the spring. The divergence of the two lines is equivalent to approximately 3 per cent of elongation or 20 pounds per square inch as applied to the usual test specimen. The units of load on the ordinate do not apply to curve *B*. Curve *C*<sub>1</sub> represents the stress-strain diagram of a rubber tire tread stock (2) properly vulcanized, and stretched at 25° C. through the first cycle.

As soon as the weight returned to the zero position, a second cycle was shown. The change in shape of the stress-strain curve is started in curve *C*<sub>2</sub>. The hysteresis of the

second cycle was much less than that of the first. The hysteresis was found to decrease still further on repeated flexures, but the changes for each succeeding cycle became progressively smaller. This behavior of rubber is well known, but the writer believes that a study of compounding variables based on the properties of repeatedly flexed rubber, instead of on the first cycles, would yield valuable practical results. This should be particularly true of the new synthetic rubbers, many of which are reputed to have higher hysteresis than natural rubber.

The vertical movement of the load beam was insufficient to show the stress-strain of unfilled rubber up to 1000 pounds per square inch on the same basis as the other curves of these charts. By using a shorter test piece, however, materials having a high degree of extensibility can be stretched with autographic recording.

The effect of temperature on the stress-strain properties of plasticized polyvinyl chloride-acetate copolymer resin is shown in Figure 3. First and second cycles are shown as in curve *C*<sub>1</sub> and *C*<sub>2</sub>, Figure 2.

The effect of temperature on the stress-strain is greater in compound 16 than in compound 14, as evidenced by comparison of the 10° and 40° C. charts. This is a fundamental difference between the two different resins in these compounds. Further data on this point appear in Table II.

Within the range of speed available with this machine, the effect of speed was slight, varying in one instance from 80 per cent elongation at 140 seconds to 100 per cent at 575 seconds. The shapes of the curves were substantially the same.

For best results specimens must not be tested within 40 hours after molding. One compound yielded 110 per cent elongation 30 minutes after molding, 85 per cent after 50 hours of aging, and 80 per cent after 76 hours; the elongation

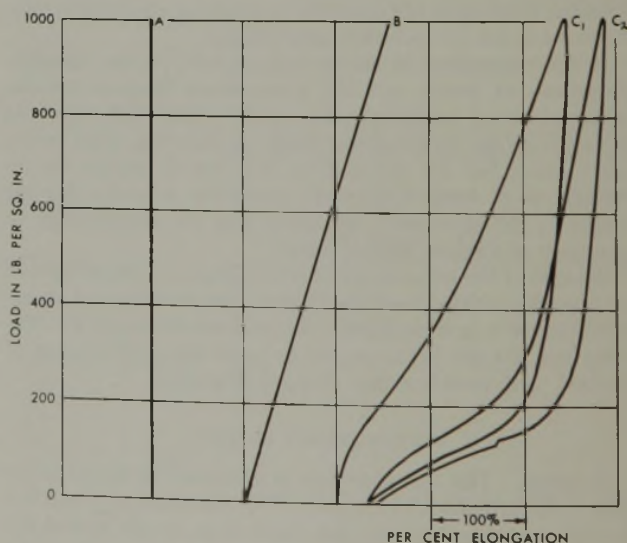


Figure 2. Stress-Strain Diagrams of Familiar Materials at 25° C.

A. Rigid specimen  
B. Steel spring  
C<sub>1</sub>, C<sub>2</sub>. First and second cycle, rubber tire tread



TABLE II. ELONGATION AT 1000 POUNDS PER SQUARE INCH FOR FIRST AND SECOND CYCLES AT THREE TEMPERATURES

Compound No. <sup>a</sup>	% Elongation in First Cycle			% Elongation in Second Cycle		
	10° C.	25° C.	40° C.	10° C.	25° C.	40° C.
1	...	0	...	...	...	...
2	213	240	280	251	283	330
3	600	660	774	690	746	878
4	10	80	...	14	105	...
5	45	122	...	59	147	...
6	12	42	98	15	53	115
7	25	57	124	31	68	142
8	56	113	208	68	133	235
9	96	178	315	115	211	...
10	57	98	186	68	115	216
11	13	57	208	18	73	238
12 <sup>a</sup> (L)	92	225	315	108	271	...
12 (T)	97	230	...	114	290	...
13	27	69	149	34	82	174
14	68	142	263	82	164	304
15 (L)	33	56	83	40	65	95
15 (T)	48	114	208	60	140	234
16	57	139	293	70	160	...

<sup>a</sup> (L) = stretched longitudinally, (T) = stretched transversely.

did not change with further aging. Heating of the aged sample to 100° C. for 15 minutes just prior to testing brought the elongation up to 112 per cent or practically equal to the

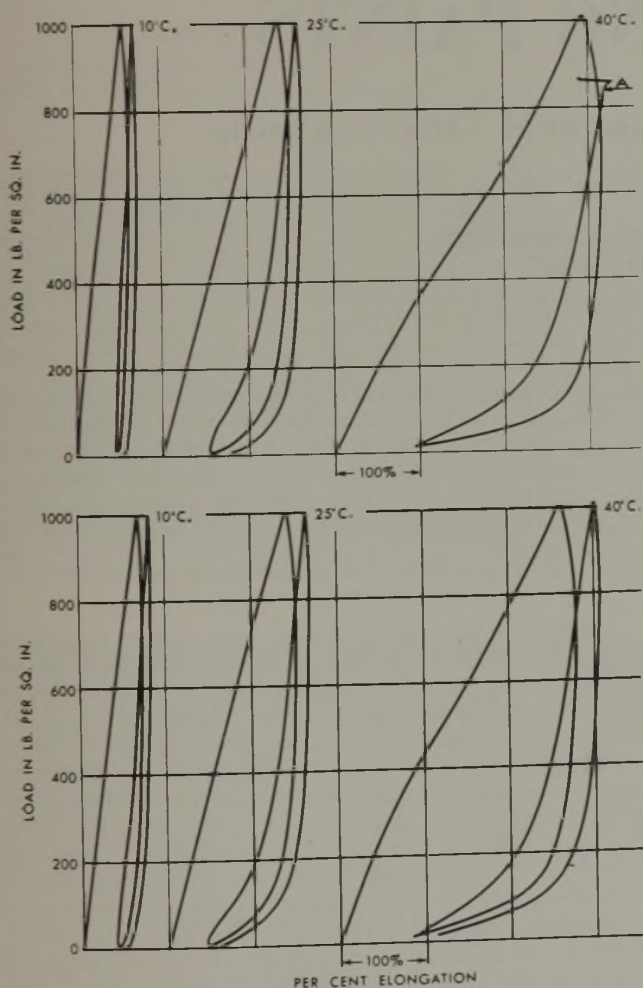


Figure 3. Effect of Temperature on Stress-Strain of Compound 16 (above) and 14 (below), Showing First and Second Cycles

Sample broke at point A.

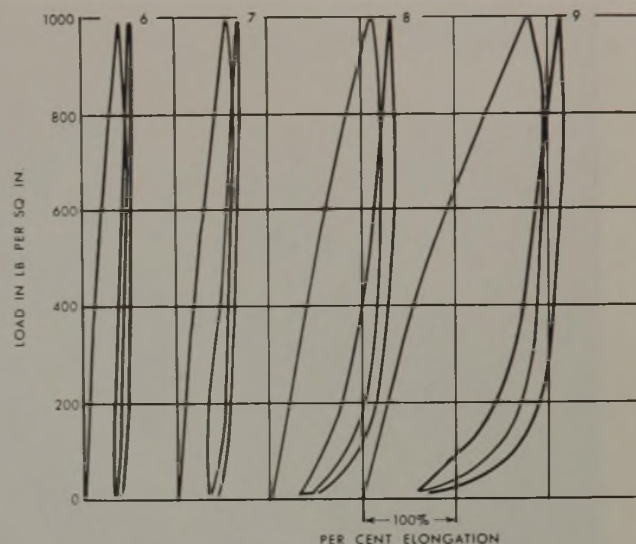


Figure 4. Effect of Plasticizer Concentration on Stress-Strain Compounds 6, 7, 8, and 9 at 25° C.

freshly molded piece. It was also noted that a specimen which had been tested several times came back to its original condition in 3 days of aging in an unstretched condition at room temperature.

The effect of calender grain or other manipulation which fixes strains in a sheet is to decrease the elongation along the strain axis and increase the elongation perpendicular to the strain axis. For this reason all tests were made on sheets molded at a temperature high enough practically to eliminate the strains, except where otherwise noted.

The elongations of several vinyl elastomers at 1000 pounds per square inch are shown in Table II. The method employed in gripping the specimens causes rupture at stresses below the normal tensile strength for these materials; hence elongations at 1000 pounds per square inch could not be obtained in all instances.

No attempt has been made to relate these elongation data to tensile strength, brittleness at very low temperatures, or fatigue life. The detailed effect of kind and amount of plasticizer on elongations of plasticized vinyl copolymer resin is the subject of another study to be published. Variable amounts of any given plasticizer do, however, alter the stress-strain behavior of the compound. This is shown in Figure 4 where 25, 30, 35, and 40 per cent of a common plasticizer were added to an otherwise identical formulation. These charts were made at the same temperature (25° C.), and the effect of the increasing plasticizer content is obvious.

#### ACKNOWLEDGMENT

The author wishes to express his appreciation to L. C. Hosfield of the National Carbon Company for designing and building the machine used in these tests and to J. H. Teeple, formerly of E. I. du Pont de Nemours & Company, Inc., from whom blueprints of the stress-strain testing machine were obtained.

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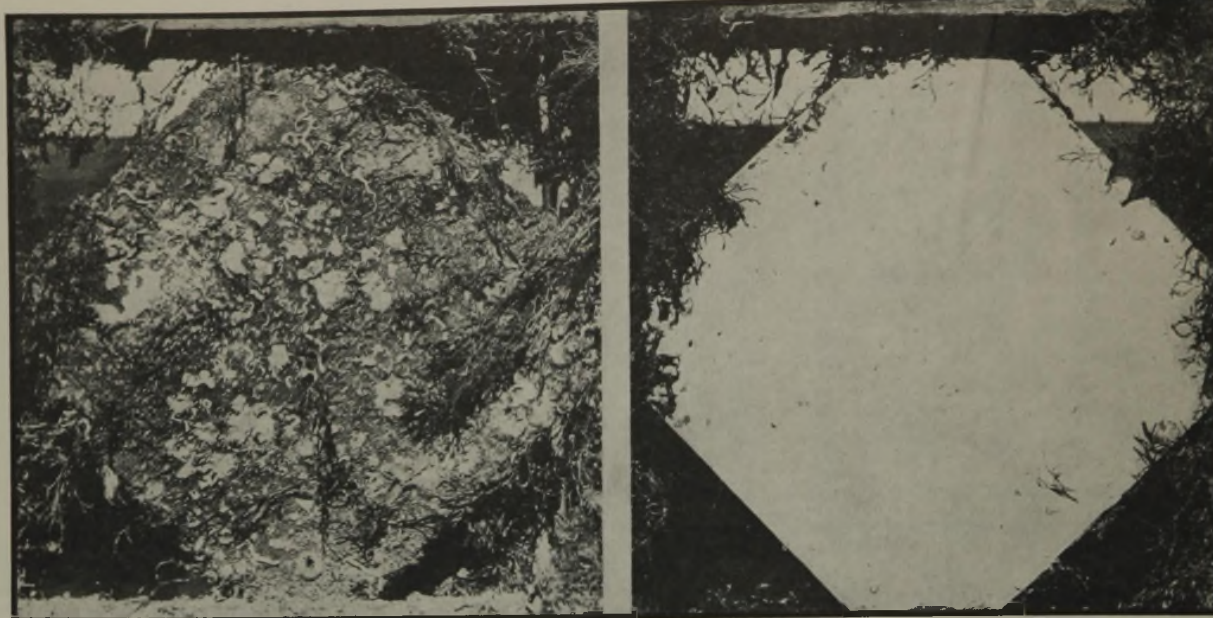


Figure 1. Extent of Fouling at Daytona Beach in 2.5 Months

# ANTIFOULING PAINTS

## Test Procedures and General Observations

G. H. YOUNG, G. W. GERHARDT  
W. K. SCHNEIDER

Mellon Institute, Pittsburgh, Penna.

THE problem of fouling of surfaces subjected to immersion in sea water has long been serious. The major alleviative efforts to date have involved the use of an "antifouling" paint—applied in the too-often vain hope that, by its nature or content of "toxic" agencies, fouling growths would be prevented or at least reasonably inhibited. To this end an almost unlimited number of specific compositions, for which antifouling properties are claimed, appear in the patent and technical literature. In many preparations the beneficial effect is attributed to the composition of the vehicle; in others, to the peculiar fashion in which the several ingredients are compounded together. In by far the greatest number the virtue is ascribed to the presence of one or more "poisons" or toxic agents.

The phototropicity of certain types of fouling organisms has frequently been demonstrated by biological studies. The suggestion has therefore been made that color alone is the most significant factor in antifouling paint performance; the argument of light *vs.* dark paints is still unsettled.

It has more recently been asserted that the only effective approach from the paint standpoint is to strive for extreme exfoliation or "underwater chalking" properties; but the question of chalking coatings or toxic coatings is still unanswered.

In the research reported here additional light is thrown on these controversial phases of the problem of antifouling paint formulation. The experimental paints employed

do not necessarily represent practical or even usable coatings; rather, the several variables have been maintained under as rigid control as possible within the limitations of varnish cooking and formulating techniques. In every case, however, commercially available constituents have been used, of the purity represented by the products procurable on the market.

### THE FOULING PROCESS

The fouling of a ship's bottom, which begins as soon as the ship is water-borne, can be divided into three phases taking place more or less simultaneously: the formation of the slimy microbiological film, the attachment of macroscopic fouling organisms (almost always in larval form), and their growth into the mature forms, visible as barnacles, mollusks, annelids, Bryozoa, algae, and other fouling growths (5). The probable role in the fouling process of the microbiological film has been described by ZoBell, Clapp, and others (2, 8, 9). That such films are universally present on surfaces shortly after submersion in sea water is unquestioned. Nevertheless, evidence that such prior film formation is essential for subsequent attachment of macroorganisms is inconclusive. Our own experiments indicate that slime formation on antifouling paints may eventually vitiate their effect by a simple blanketing action preventing lethal concentrations of the toxic agents from building up at the slime film-water interface. This observation is in agreement with the

findings of the Navy (5). Where sufficiently high toxic concentrations can be realized, in spite of the slime film we have been able to maintain slime-covered surfaces free from macrogrowths for many months.

The principal organisms with which one has to deal on underwater structures may be classified as follows:

- Organisms building hard, calcareous, or chitinous shells
  - Annelids: coiled or twisted tubes
  - Barnacles: cone-shaped shells built up of laminated plates, attached directly or by means of long muscular stalks
  - Bryozoa (encrusting): flat, spreading, multicellular coral-like patches
  - Mollusks: bivalves such as clams, mussels, oysters
- Organisms without hard shells
  - Algae: green, brown, or red filament-like growths, generally near the water line
  - Bryozoa (filamentous): fern-like or tree-like growths, the branches not expanded at the tips
  - Hydroids: stalk-like or branching growths, each branch terminating in an expanded tip
  - Tunicates: soft, spongy masses ("sea squirts")
- Boring organisms
  - Teredo: soft-bodied worms with a cutting shell-like head ("ship worms")
  - Martesia: boring clam-like mollusks
  - Limnoria: shrimp-like drilling arthropods

These types of organisms are described in the Navy's Docking Manual (5). Details concerning morphology and differences among subspecies are contained in most standard biological texts (4).

**PRIMARY TOXICITY**

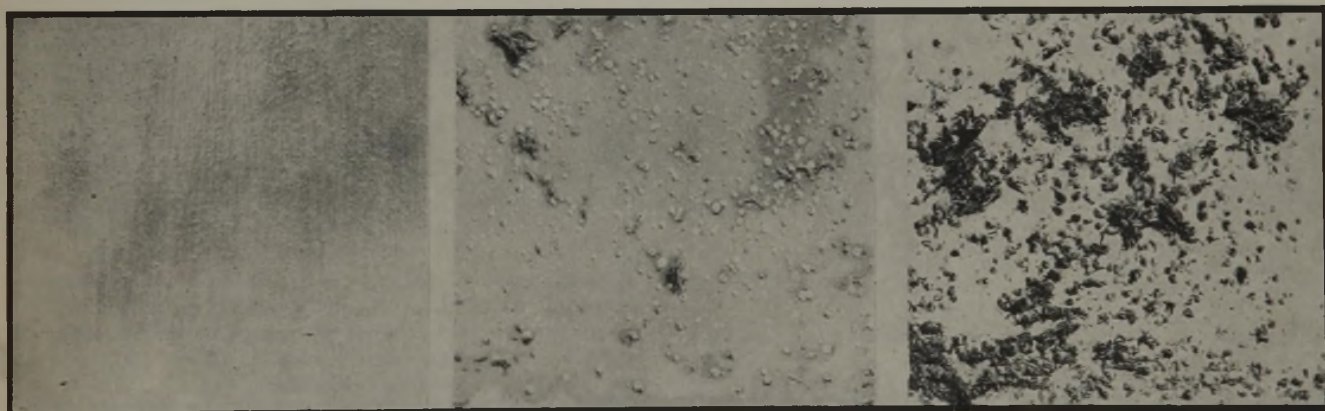
Certain preliminary measurements were made on a wide variety of toxic materials. As test object a fresh-water

arthropod, *Daphnia*, more than superficially similar to the Cypris larva or embryonic *Balanus*, was used because it was not practical to maintain colonies of *Cypris* larvae in an inland laboratory.

Zoological affinities Size, mm.	Cypris Larva	<i>Daphnia</i>
	Crustacea Cirripedia 1-3	Crustacea Cladocera 0.6-1.5
Appearance	Shrimp-like form in a bivalve shell	
Habitat	Surface marine waters	
Light reaction	Strongly positive	
Toxicological reaction	Very sensitive to copper	

**TEST PROCEDURE.** Two or three grams of the substance were placed in 250 ml. of distilled water and shaken at intervals for 24 hours; the resultant solution was arbitrarily assumed to be a saturated solution in water although there is no reason to suppose that complete saturation occurred in every case. Certain of the substances of relatively high solubility were adjusted to a concentration of approximately  $1 \times 10^{-6}$  molar.

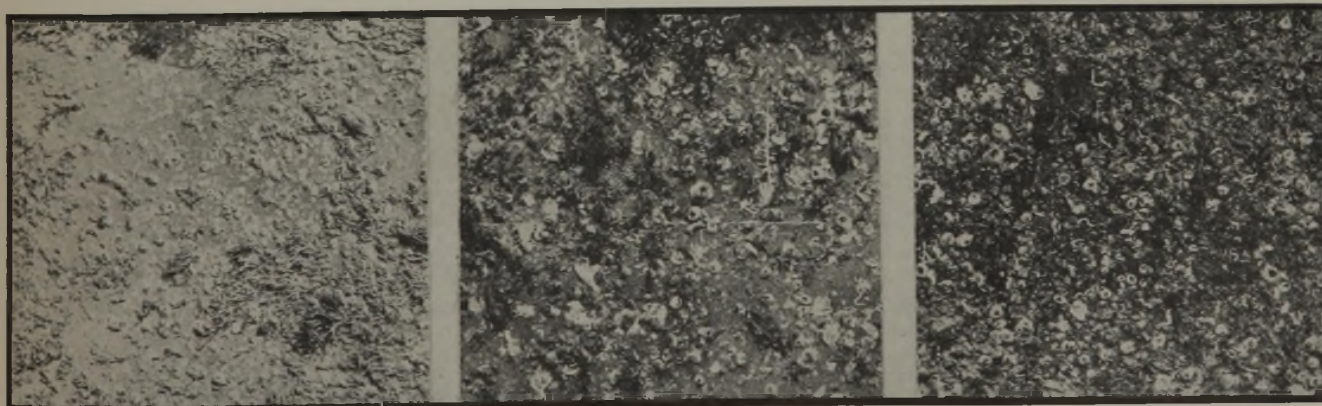
A stock culture of *Daphnia* was started in 70 gallons of tap water to which were added 25 grams of sheep manure and 15 grams of dead fish; the medium was enriched at intervals with a weak suspension of Fleischmann's yeast. Healthy animals from this colony were placed in 20 ml. of their own medium in glass vials 4 inches long and 1 inch in diameter. Three such vials were used in each test. To the first was added distilled water; to the second was added 1 ml. of the "saturated test solution", and the third received 5 ml. of the same solution. The distilled water control was discontinued after the first twenty-five tests demonstrated that it was without effect on *Daphnia*.



Rating 10, perfect

8, very slightly fouling

6, definite fouling



4, medium fouling

2, bad fouling

0, complete fouling

**Figure 2. Arbitrary Rating of Over-all Fouling**

The experimental tubes were observed closely for the first minute for any immediate effect on the behavior of the animal, as determined by an increase in its speed of movement coupled with a certain irregularity of motion. The condition was further recorded after 15 and 30 minutes, 1, 6, 12, and 24 hours; in later experiments observations were discontinued after the sixth hour.

The condition of the animals at the time the observation was made is recorded as dead, dying, some effect, and no effect. "No effect" describes the appearance of the tube when the animals are swimming freely and without apparent discomfort. "Some effect" means that the animals are still swimming freely but are showing jerky irregular motion; recovery from this condition is not infrequent. "Dying" indicates that the animals are lying at the bottom of the tube but are still exhibiting irregular movements of the antennae; some occasionally rise a few millimeters above the bottom of the tube and then sink back. Recovery from this condition was never observed. "Dead" refers to animals lying motionless on the bottom of the tube. (There is some reason to doubt the strict accuracy of this term, as a deep narcosis would have produced the same appearance; this possibility is not of any practical importance in relation to the purpose of these tests.)

#### TESTS ON CHEMICALS

**ORGANIC COMPOUNDS.** A large number of representative organic compounds were evaluated by the test procedure, and certain of them were classified into four groups based on their apparent efficiency as toxic agents:

##### A. USELESS

Tetrachlorobenzene  
Pentachlorobenzene  
Hexachlorobenzene  
Pentachlorophenyl benzoate  
Cinchophene  
Quinoidine  
Carbazole  
Chloral hydrate  
Orris gum  
*p*-Isopropylindene  
Benzyl polysulfide  
Polychloronaphthalene  
Tetramethylphenol sulfide  
Dichlorophenyl benzoate  
Dimethylphenol sulfide

##### B. MODERATELY EFFICIENT

*p*-Dichlorobenzene  
Benzocaine  
Trichloroethyl phosphate  
*p*-Cyclohexylphenol  
*p*-*tert*-Butylphenol  
Naphthalene  
*p*-*tert*-Amylphenol  
Pyridine base residues  
Chlorinated cresols (30% Cl)  
Chlorinated cresols (50% Cl)  
Crude tripyridyl

##### C. EFFICIENT

1,3-Xylenol  
*p*-Cresol  
*o*-Cyclohexylphenol  
2-Chlorophenylphenol  
Quinaldine  
Chlorinated xylenols

##### D. OUTSTANDINGLY EFFICIENT

Thymol  
*o*-*tert*-Amylphenol  
*o*-Cresol  
Cinnamaldehyde  
Tar base (boiling at 260–263° C.)

In view of the fact that sea water abounds in microorganisms, supplementary experiments were carried out to determine whether a high concentration of such forms could blanket the effect of the outstandingly efficient substances. Thus similar tests to those described were carried out in culture medium to which had been added enough yeast to produce an opacity equivalent to that of milk. The results of these laboratory tests did not differ from those made in straight culture medium.

In general, three basic types of organic compounds (1) may be expected to be effective against shell-forming organisms resembling the Cypris larva in their embryonic stages:

1. Certain *o*- and *p*-substituted phenols and their halogenated derivatives

2. Certain cyclic nitrogen bases, of the pyridine and quinoline family, particularly those boiling in the range 258–263° C.; and pitchy residues derived from the prior recovery of the lower boiling pyridines
3. Certain aromatic unsaturated aldehydes, of which cinnamic aldehyde is typical

Mixtures of these three types of toxic compounds are apparently more rapidly effective than are the single reagents. In all cases concentrations of the order of 10<sup>-6</sup> molal were lethal to *Daphnia*.

**INORGANIC COMPOUNDS.** For comparison, a similar evaluation was made of the relative toxicities of the familiar heavy metals used (in the form of oxides, salts, and as metals) in the usual antifouling paints. The death times for 0.001 *M* solutions of a number of the metal chlorides against *Daphnia* follow:

Metal Ion	Death Time, Hr.	Metal Ion	Death Time, Hr.
Mercury (ic)	0.25	Zinc	2.5
Cadmium	1.0	Chromium (ous)	2.5
Copper	1.5	Barium	2.5
Manganese (ous)	1.5	Cobalt (ous)	3.0
Ammonium	1.5	Iron (ic)	3.0
Calcium	1.5	Lithium	3.5
Selenium	1.5	Sodium	No effect
Tellurium	1.5	Potassium	No effect
Iron (ous)	2.0	Lead (ous)	No effect

It is apparent that known experience with heavy metal toxics is rather quantitatively predictable by death time tests on *Daphnia*. That is, the generally employed metallic compounds of mercury, copper, manganese, and zinc are seen to be effectively lethal to *Daphnia*.

#### VEHICLE PERMEABILITY

Early in the investigation it became apparent that one of the major controlling factors in antifouling performance must be the equilibrium permeability to sea water of any vehicle carrying a soluble toxic agent. Accordingly, the water permeability of a wide range of organic film-forming resin films was determined by the familiar method of Wray and Van Horst (6). Relative permeability data for typical organic vehicles, together with data on several formulations containing solid toxic phenols and inert pigmentations, appear in Table I.

These figures show the wide range of permeabilities obtainable with varnish and synthetic resin vehicles. Actual marine exposure, using selected vehicles of permeability rate from 4 to 300 with a constant toxic content, has clearly demonstrated that the optimum permeability range for effective antifouling performance is 75 to 150, with the preferred permeability approximating 100.

TABLE I. WATER PERMEABILITY RATES

Vehicle Type	Added Toxic or Pigment	Water Permeability, Mg. H <sub>2</sub> O/Mil/Sq. In./24 Hr.
25-gal. phenolic varnish 1	None	39.2
	25% 1,3-xylenol	32.8
75% varnish 1 + 25% alkyd R-869	None	120.0
Polycyclopentadiene	None	3.5
	25% 2-chloro-4-phenyl-phenol	4.0
25-gal. ester gum varnish 2	None	49.8
	25% 1,3-xylenol	49.8
	25% 1,3-xylenol pigmented with TiO <sub>2</sub> <sup>a</sup>	204.0
Copolymer of vinyl chloride and acetate	None	17.8
	25% 1,3-xylenol	24.0
	10% celite	14.1
	25% celite	33.4
	50% celite	45.5
Methacrylate	None	127.0
	25% 1,3-xylenol	114.0
Linseed oil	25% 2-chloro-4-phenyl-phenol	362.0
	None	298.0

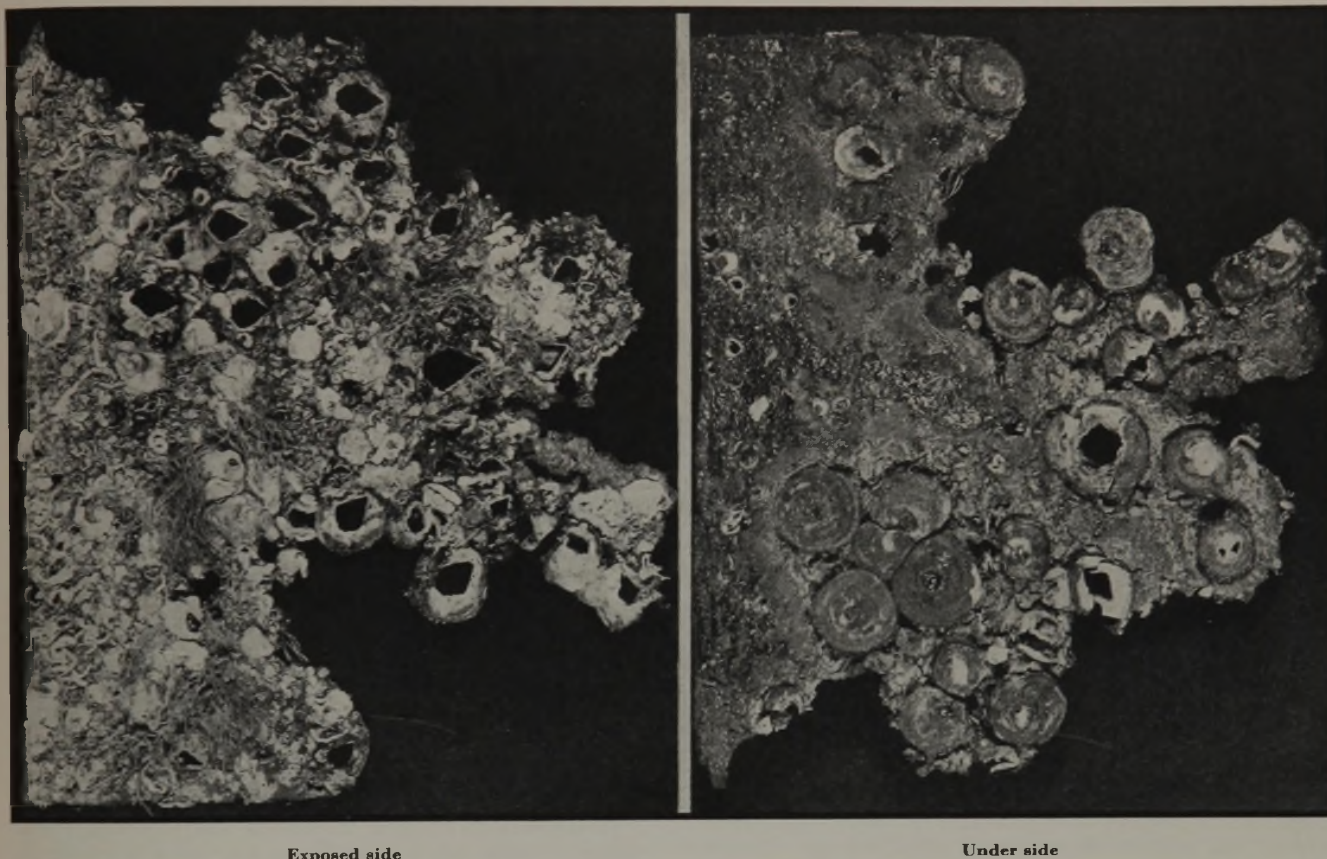
<sup>a</sup> At pigment/varnish ratio of 2/1.

## PANEL EXPOSURE TESTS

While laboratory tests are instructive, they cannot replace actual exposure under fouling conditions. The exposure site chosen is in the Ponce de Leon tidal inlet, one half mile from the Atlantic Ocean on the Florida sea coast, approximately 14 miles south of Daytona Beach. Marine fouling growth at this location is heavy during the entire year. Water temperatures vary between relatively narrow

cases special priming paints or treatments suitable to the specific surface were used.)

The method of rating exposed panels is demonstrated in Figure 2. The occurrence of type of fouling organism is rated on the scale at monthly intervals during the life of the test. For convenience in examination and reporting, the following classification is used: barnacles (all types), mollusks (oysters, clams, and mussels), tube worms (annelids),



Exposed side

Under side

Figure 3. Barnacles Embedded in Soft Paint Film

limits (65–80° F.) from midsummer to midwinter, and the area is free from extraneous contaminating influences such as bilge oil, industrial waste, sewage, etc. The average tide is 3 feet at this site. The test racks are constructed of untreated grade C cypress, slotted to hold 6 × 12 inch metal panels. Wooden panels are usually 7 × 12 × 1 1/8 inches in size; the relatively thick blocks enable teredo attack to be examined with ease. A number of studies were made using rubber. The method of mounting flexible rubber panels is shown in Figure 1. All panels are exposed vertically, at a depth of 24 inches below low-tide level; the racks are reversed biweekly to ensure uniform exposure and to eliminate inshore-offshore effects.

For comparative evaluation of antifouling paints, sand-blasted steel panels are generally used; they are primed with at least two different standardized priming paints (two coats), and finished with a single coat of the antifouling paint. For evaluation on wood, three primer coats of a 40-gallon phenolic spar varnish are applied before the antifouling coat. Unless otherwise noted, all paints are brush-applied. (Certain studies have involved other surfaces; typical are glass, rubber, and the light metals. In these

hydroids (and stalked corals), Bryozoa (encrusting and filamentous), algae and scum (all types).

Examples of these growths are illustrated on the control panel in Figure 1, and the more heavily fouled panels (rating 6 or worse) in Figure 2.

## GENERAL OBSERVATIONS

Subsequent papers in this series will evaluate the various controlling factors in antifouling paint performance. Typical is the effect of vehicle permeability rate; another is that of toxic concentration.

All the data substantially confirm Baerenfaenger's observation (1) that color as such has no effect on the fouling characteristics of a given vehicle-toxic combination. So far the reported sensitivity to pale greens and whites (3) has not been confirmed. Panels 4, 2, 10, and 8 shown in Figure 1 of the following paper (page 436) were selected from a set in which only the toxic content was varied in a series of pigmented vehicles at constant pigment-binder ratio; one group of panels was gray-white and the other was dark brown. The only relation between extent of fouling and a controlled factor in these paints was an inverse

ratio with toxic concentration, an expected but conclusive finding.

On the other hand, a general sensitivity to light has been confirmed. Panels were exposed in bright sunlight, and duplicates in the shade only a few feet away showed heavier fouling. The difference is not marked and certainly cannot influence choice of paint color.

The consistency or hardness of the antifouling paint, independent of its permeability and exfoliating characteristics, may influence the type and extent of fouling. Figure 3 shows a stripped-off paint film which was initially soft and gummy and remained so during immersion. The photograph presents both sides of this stripped film; the embedding tendency of the barnacles, with consequent injury to the underlying surface by contact-corrosion effects, is conclusively demonstrated. In general, we believe that the harder the exposed paint film can be, all other factors being equal, the better protection it will afford against fouling.

#### ACKNOWLEDGMENT

It is a pleasure to record the cooperation and assistance of Peter Gray, associate professor of biology at the University

of Pittsburgh, under whose direction the laboratory evaluations of primary toxicity were carried out.

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## Heavy Metal Compounds as Toxic Agents

G. H. YOUNG AND W. K. SCHNEIDER

THE previous paper described a procedure for the preliminary evaluation of toxic compounds designed for use in antifouling paints. It was demonstrated that the ions of a variety of heavy metals might be expected to have lethal action on Cypris larva and other embryonic fouling organisms. Accordingly, an extensive series of test panels was prepared for marine exposure at Daytona Beach, Fla., involving controlled concentrations of representative heavy metal compounds in a suitable oleoresinous short-oil vehicle. Several commercial antifouling paints were included in the series for comparison purposes.

#### PREPARATION OF PANELS

The wood panels were  $7 \times 12 \times 1\frac{1}{8}$  inch seasoned poplar, primed with three brush coats of a 40-gallon phenolic spar varnish. The steel panels were prepared in duplicate, freshly sandblasted, and primed with two brush coats of two selected anticorrosive primers. A 25-gallon, 60 per cent tung oil-40 per cent linseed oil, phenolic varnish pigmented with zinc tetroxy chromate was one primer; an 8-gallon, 50 per cent tung oil-50 per cent linseed oil, coumarone varnish pigmented with red lead was the other.

The latter varnish was also selected to carry the toxic components because the permeability measurements had demonstrated its optimum moisture transmission characteristics.

The experimental antifouling compositions evaluated are described in Table I; a series of paints comprising two or more toxic agents was prepared from these primary formulations, and the combinations are listed in Table II.

Additional panels were painted with four commercial antifouling paints and with two paints made up according to a Navy formula (1). In one case red cuprous oxide was used; in the other, yellow.

#### EXPOSURE OF METAL COMPOUNDS

The panels were placed on test in December, 1941, and examined at monthly intervals. At the end of one month the following paints still rated 9 or better; at this stage the controls (containing no toxic) rated 7-8: AF-1, 2, 7, 9, 11, 13, 14, 16, 17; proprietary paints 1, 2, and 3; Navy formula 16 with red and with yellow cuprous oxides.

At the end of 2-month immersion, the following paints rated 8 or better, the controls rating 5-6: AF-2, 9, 11, 13, 16; proprietary paints 1 and 3; both Navy formula 16 paints.

At the end of 4.5 months the following paints rated 8 or better, the controls rating 2-3: AF-2 and 11; proprietary paints 1 and 3. The relative appearance of these paints is shown in Figure 1.

TABLE I. EXPERIMENTAL PAINTS CONTAINING SINGLE TOXICS (Vehicle, 50-50 tung-linseed, 8-gallon coumarone varnish (65% solids); pigment-vehicle ratio 2/1)

Code No.	Pigment Composition		Inert	%
	Toxic component	%		
AF-1	Yellow mercuric oxide	60	Barytes	40
AF-2	Copper powder	60	Barytes	40
AF-3	Copper arsenite	60	Barytes	40
AF-4	Red cuprous oxide	60	Barytes	40
AF-5	Zinc oxide	60	Barytes	40
AF-6	Sublimed blue lead	60	Barytes	40

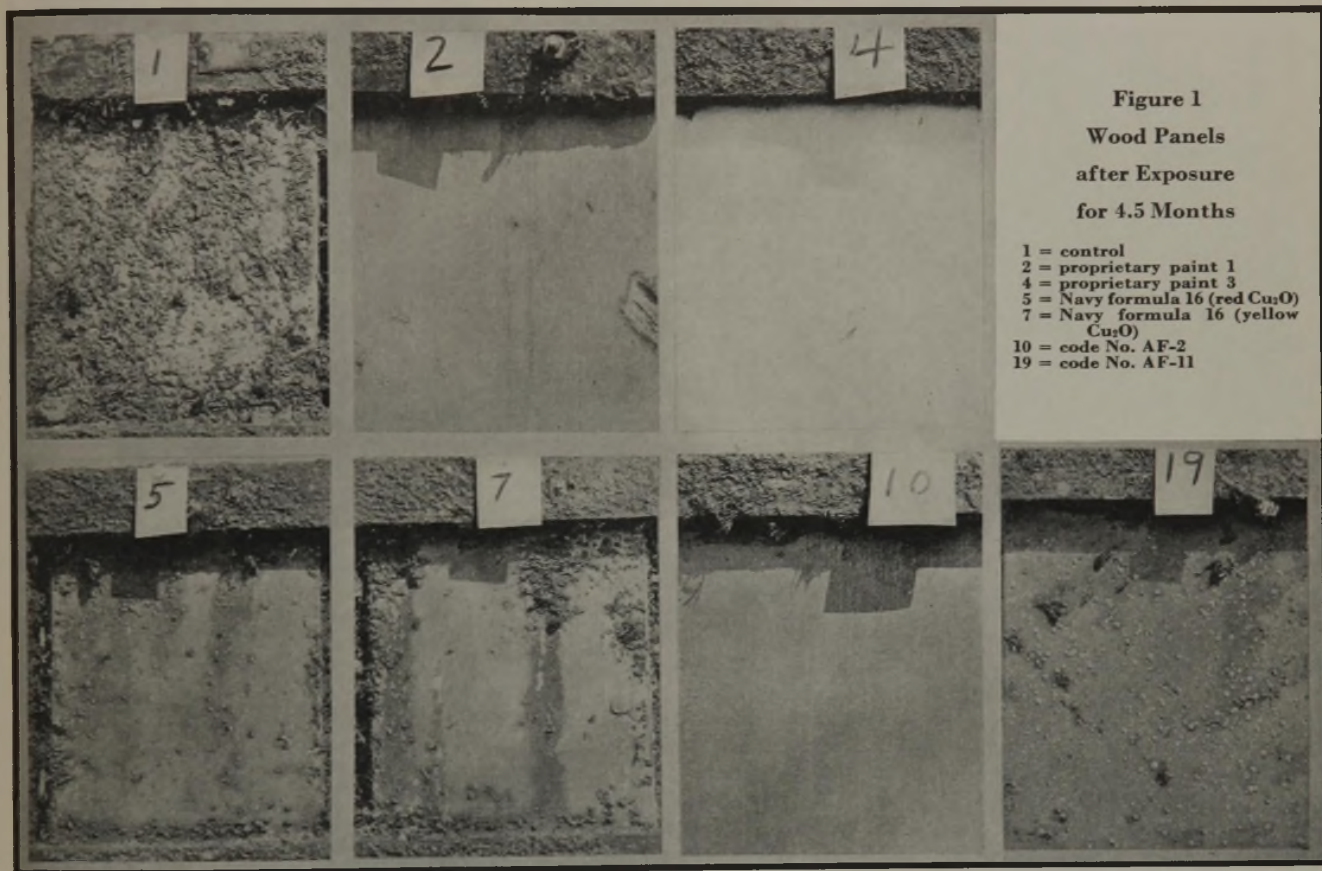
At 6.5-month exposure only AF-2 and proprietary paints 1 and 3 were still actively antifouling, rating 8 or better. Figure 2 illustrates these paints, together with certain of the others, now failing.

After 9 months the two good proprietaries and AF-2 still rated 8 or better; all the remaining panels were rated at 3 or worse and hence were removed.

It is significant that, with the unique exception of proprietary paint 3, only paints carrying a high concentration of metallic copper were really effective after the first several months' exposure. (The toxic agent in proprietary paint 3 is organic in nature.) Cuprous oxide (either red or yellow) is intermediate in antifouling effect, and the remaining compounds were relatively ineffective under the test conditions.

With one exception (AF-7), which failed prematurely, the tabulation almost exactly parallels the order in which the paints ceased to protect against fouling, AF-2 being best and AF-15 poorest.

To verify this relation to active copper content a supplementary panel series was prepared in duplicate in which the vehicle was a 6-gallon tung oil-coumarone type varnish,



A possible exception is mercuric oxide, which appears to have some specificity against algae and other water-line growths, but is definitely inferior even to cuprous oxide against calcareous shell-depositing organisms.

**EFFECT OF COPPER CONTENT**

A study of the pigment compositions of the experimental paints (AF-1 to 16) reveals that, because the pigment-binder ratio was constant, the independent variable can be considered as (a) copper content and (b) copper oxide content. In effect, the remaining "toxic" agents were inert extenders. Rearranging the formulas in the order of decreasing toxic content, the following table results:

Code No.	Percentage of Pigment		
	Copper	Copper oxide	Inert
AF-2	60	0	40
AF-11	30	30	40
AF-7	30	0	70
AF-9	30	0	70
AF-14	20	20	60
AF-13	20	0	80
AF-16	15	15	70
AF-17	10	10	80
AF-4	0	60	40
AF-10	0	30	70
AF-12	0	30	70
AF-15	0	20	80

**TABLE II. EXPERIMENTAL PAINTS CONTAINING SEVERAL TOXICS**

Code No.	Paint Compn. Comprising Equal Parts o
AF-7	AF-1, AF-2
AF-8	AF-1, AF-3
AF-9	AF-2, AF-3
AF-10	AF-1, AF-4
AF-11	AF-2, AF-4
AF-12	AF-3, AF-4
AF-13	AF-1, AF-2, AF-3
AF-14	AF-1, AF-2, AF-4
AF-15	AF-1, AF-3, AF-4
AF-16	AF-1, AF-2, AF-3, AF-4
AF-17	AF-1, AF-2, AF-3, AF-4, AF-5, AF-6

containing only leafed copper powder at loadings of 1, 3, 6, 9, and 12 pounds per gallon. These antifouling paints were applied to freshly sandblasted panels primed with two brush coats of quick-drying red lead (alkyd type vehicle). In one set the copper paint was applied by spraying, in the other by brushing.

Three to four months of exposure at Daytona Beach were sufficient to demonstrate that antifouling efficiency was almost directly a function of copper content, and that a loading of at least 6 pounds per gallon of copper is needed to

produce a highly effective antifouling paint. This result confirms the previous findings and suggests that many copper paints described in the past may have carried insufficient toxic agent for maximum performance (2).

appeared to have some beneficial action against marine algae; their effectiveness against shell-forming organisms, however, was far below that of copper and copper oxide. This effect is undoubtedly attributable to their low ioniza-

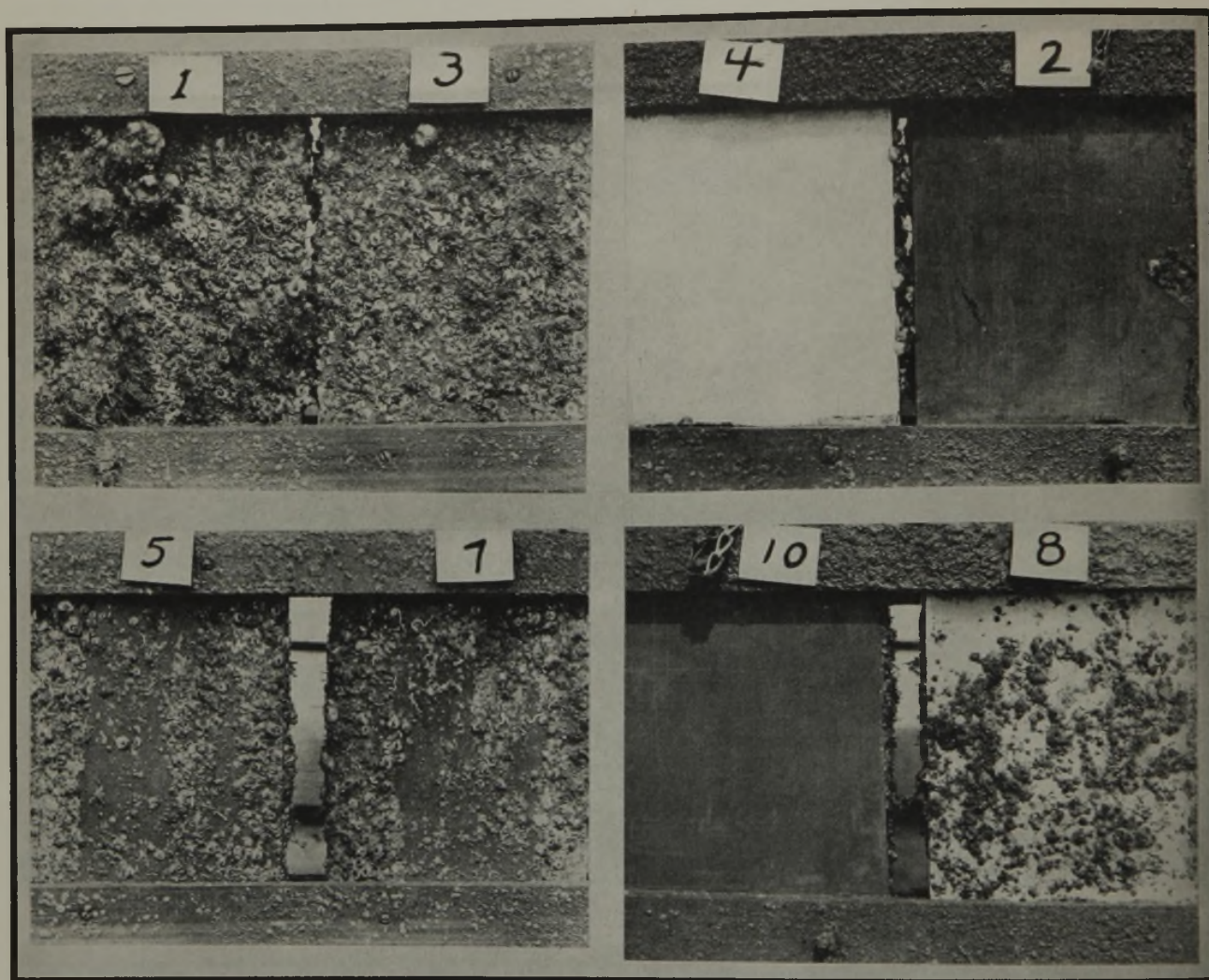


Figure 2. Wood Panels Exposed 6.5 Months

Panel 1 is control (rating 0); panel 3 is proprietary paint 2, which was already fouling at the 2-month inspection. Panels 5 and 7 are Navy formula 16 using red and yellow copper oxide in that order.

Panels 4 and 2 are proprietary paints 3 and 1, respectively. Panel 10 is paint AF-2; panel 8 is another formulation which failed early in the test.

Comparisons of the nature and extent of fouling on the spray-coated panels with those painted by brushing indicated no significant differences. The advantage, if any, favored spray application, as would be expected.

#### OTHER COPPER COMPOUNDS

In a third exposure series the following additional copper compounds were evaluated in test formulations comprising the toxic ingredient in two different vehicles at a constant pigment-vehicle ratio of 1 to 1: copper arsenite, oxychloride, oleate, linoleate, naphthenate, pentachlorophenate, tetrachlorophenate.

Exposure at Daytona Beach demonstrated that none of these compounds is effectively toxic, as employed in antifouling paints. The organic acid salts and the phenates

tion tendency; only compounds capable of releasing copper ion seem to have utility as antifouling agents.

#### ACKNOWLEDGMENT

We are grateful for the cooperative assistance of S. B. Tuwiner, of the Phelps Dodge Corporation, who supplied certain of the materials employed in this investigation.

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# DEXTRINS from CORN SIRUP

## Effect of Dextrose Equivalent of Sirup on Properties

J. W. EVANS AND W. R. FETZER

Union Starch & Refining Company, Granite City, Ill.

**The reducing power, specific rotation, and iodine coloration of dextrins precipitated from commercial corn sirups having dextrose equivalents from 30 to 65 by 80 per cent methanol have been determined. Nine precipitations are necessary to obtain a product of constant reducing power.**

**In this dextrose equivalent range the reducing power of the dextrins passes through a minimum while the specific rotation gradually decreases. The data give some indication of the course of acid hydrolysis of starch.**

dextrins prepared by the action of diastase on starch; only one discusses acid hydrolysis involving different degrees of conversion. The more recent papers have dealt almost entirely with dextrins formed by enzymatic hydrolysis of starch.

### HISTORICAL

Since 1812 it has been known that dextrins are formed when starch is heated with dilute acids; Vogel (18) reported that a gumlike substance as well as sugar was produced when starch was heated with dilute acids. A few years later Biot

and Persoz (4) studied this gumlike material and called it "dextrin" because its solutions rotated the plane of polarized light to the right. These workers heated potato starch with dilute sulfuric acid at 85°, 95°, and 100° C., and added alcohol to the filtered hydrolyzates. White precipitates were obtained from the material heated at 85° and 95° C. These precipitates were soluble in cold water, were reprecipitated by alcohol or lead acetate, gave a red coloration with iodine, and were converted to starch sugars on heating with acids.

Bondonneau (5) examined the dextrins formed in the course of acid saccharification of starch at different stages of the reaction. The dextrins were separated from the other substances in the hydrolyzate by precipitation with alcohol. In the early stages of the reaction, a dextrin (called  $\alpha$ ) was obtained that gave a red coloration with iodine. After the saccharification had been carried on further, another dextrin (called  $\beta$ ) was isolated, which did not color iodine and was stated to be identical with the dextrin formed by the action of diastase on starch paste. On removal of this dextrin a third (called  $\gamma$ ) was isolated from the mother liquor; it gave no coloration with iodine. Bondonneau (6) determined the specific rotation of these dextrins. These data served the purpose for which they were obtained (namely, to show that, on the saccharification of starch, dextrins and dextrose were formed simultaneously), but the work was qualitative in that neither the degree of hydrolysis was reported nor were the concentrations of alcohol used to precipitate the dextrins given.

Lintner and Düll (15) hydrolyzed potato starch suspensions with oxalic acid (0.04 to 0.33 per cent) at pressures of 1.5 to 3 atmospheres for 30 to 60 minutes. The hydrolyzates were neutralized with calcium carbonate and filtered, and the dextrins and sugars were separated by cooling to 0° C. or by precipitating with alcohol. The iodine colorations of all the dextrins were observed, and the reducing powers and specific rotations were determined on all but the amylo-dextrin or the dextrin obtained from the hydrolyzate of the lowest conversion.

The data of this earlier work are interesting because the degree of hydrolysis was expressed as it is today, although

THE term "dextrin" designates the degradation products of starch, regardless of whether they are formed by acid or by enzymatic hydrolysis. These degradation products are soluble in hot and cold water, insoluble in alcohol, dextrorotatory, and copper reducing, and give either a blue, red, or no coloration with iodine. In the industrial sense the term is used to denote the products obtained by roasting starch either alone or with a small quantity of acid or other catalyst. These commercial dextrins are almost completely

soluble in hot water and, in addition to dextrins, contain soluble starch and sugar. This paper covers dextrins in the former sense—i. e., as they occur in acid hydrolysis of starch.

Methods for the identification and particularly the estimation of dextrins in starch hydrolyzates are far from satisfactory. In 1906 Browne (7) proposed a method whereby the sample in question was dissolved in a small amount of water to which was added absolute ethanol to effect a final concentration of approximately 90 per cent. The precipitate so formed was decanted and washed with 95 per cent alcohol. The weighed precipitate was termed "dextrin". Known as Browne's method, it is described by Leach (14) and in the A. O. A. C. methods (2) under "honey". While working reasonably well for the residual dextrins in malt sirup and the small amount in honey, Browne's method encounters difficulty when applied to starch hydrolyzates, particularly in corn sirup where the amount of dextrins in some grades may run as high as 50 per cent. The precipitate obtained is a gummy stringy mass which gives every evidence of occlusion. As a result data on the dextrins in corn sirup are meager, and workers have attempted to apply data on dextrins from other sources to corn sirup. Also it has led to the erroneous impression that the dextrins are the same, regardless of the degree of conversion of the sirup. Considerable confusion has resulted, and the purpose of this paper is to define more clearly dextrins obtained from corn sirups of different degrees of hydrolysis.

Corn sirup is the thick viscous substance obtained, after refining and concentrating, from the incomplete acid hydrolysis of starch or dual conversion (acid hydrolysis followed by enzymic treatment). The sirup is noncrystallizing and contains dextrins, higher sugars, maltose, and dextrose, the proportions depending upon the degree of hydrolysis (9). The degree of hydrolysis is defined by the term "dextrose equivalent" or "D. E.", the percentage of reducing sugars calculated as dextrose on a dry substance basis. The D. E. of commercial corn sirups run from 25 to 70.

Numerous articles (3, 8, 12, 16, 17) have appeared on the iodine color, specific rotation, and reducing power of dextrins. Most of these papers deal with either commercial dextrins or

TABLE I. SUMMARY OF EARLY WORK

Hydrolyzate		Alcohol Used, %	Dextrins Obtained		
D. E.	( $\alpha$ ) <sub>D</sub>		D. E.	( $\alpha$ ) <sub>D</sub>	Iodine coloration
Murky suspension		35 <sup>a</sup>		196	Blue
10-14	183-190	70	2	194	Red-violet
14-18	180-185	75-80	5	192	Red-brown
46.9	142	82-85	7	180	Brown
46.9	142	90	14		Brown

<sup>a</sup> Dextrin separated out on cooling to ° C.

only one sirup falls within present commercial corn sirup ranges. No temperature was given for the specific rotation, and the concentration of alcohol was variable. The data are summarized in Table I.

More recently Hixon (13) studied the physical properties of dextrins isolated from corn sirup, and found that they were not homogeneous but were a mixture of dextrins of different chain lengths.

The alcohol concentration necessary to precipitate dextrins depends on the type of dextrins present, on the concentration of electrolytes, and on the concentration of other carbohydrates. Alcohol concentrations of 35 to 95 per cent have been used; with the lower strength, amylopectin is obtained in a purified condition, and with the higher, the short-chained achedextrin is precipitated. From the quantitative viewpoint, the quantity of dextrin precipitated varies directly with alcohol concentration. Fetzer, Evans, and Longenecker (11) found on precipitating dextrins from a corn sirup (46 D. E.) with alcohol of 70 to 90 per cent strength that the amount of precipitate varied from 1.4 per cent for the lower concentration to 19.8 for the higher. The concentration of the carbohydrate in the above precipitations was 2 per cent.

In the present work the aim was to secure dextrins typical for a sirup of a given D. E. and to have these dextrins as free from other carbohydrates as possible. The dextrins were precipitated from a large quantity of sirup in the lowest alcohol concentration practical and were then reprecipitated until their reducing powers and specific rotations were constant; absence of occluded material was thus indicated.

#### DEXTRINS FROM 42 D. E. CORN SIRUP

The purpose of this work was to ascertain the concentration of alcohol, the number of precipitations, and the temperatures necessary to obtain dextrins with the lowest constant reducing power and the highest constant specific rotation. These constant values apply to dextrins from a sirup of a given dextrose equivalent.

**REDUCING POWER.** The Munsen-Walker method (1) was used to determine the reducing power of the dextrins; it was expressed as dextrose on a dry substance basis. Fehling solutions A and B were mixed immediately before each determination to prevent high results due to auto-precipitation of cuprous oxide. A blank determination was run on each mixture of Fehling solution.

**DRY SUBSTANCE.** Each dextrin sample was dispersed on Filter-Cel and dried to a constant weight in a vacuum oven at 100° C. (10). To disperse on Filter-Cel, 5 to 7 grams of the dextrins were dissolved in 14 ml. of water.

**SPECIFIC ROTATION.** Two to five grams of the material were dissolved in sufficient water to make 100 ml. at 20° C. The angular rotation was read in a 2-decimeter tube at 20° C. using sodium D light. Care was taken that the solutions should be at equilibrium when the final readings were made.

**PRECIPITATION AND PURIFICATION.** The corn sirup was weighed into a wide-mouth bottle, a small

amount of water was poured in to thin the sirup, and sufficient absolute methanol was added to obtain the alcohol concentration desired in the final mixture. The methanol was delivered from a buret at the rate of 100 ml. per minute, and the mixtures were rapidly stirred during the addition. The percentages (by volume) of methanol used were 70, 75, 80, 85, and 90, calculated on the basis of water and methanol contained in the final mixture. Precipitations were carried out at 10, 31, 32, 34, and 60° C., and the mixtures were kept at these temperatures for 10 to 18 hours in all cases except at 60° C. where the mixture was allowed to cool to 32° C. The amounts of corn sirup, water, and methanol used in the first precipitations are given in Table II.

The 70 per cent methanol procedure produced too small an amount of precipitate to be purified.

After standing for 10 to 18 hours, the filtrates were decanted and the precipitates were taken up with water and reprecipitated with methanol. The procedure for the addition of methanol was the same as before. The precipitations were carried out from five to fifteen times, 4 hours being allowed for the dextrins to precipitate and settle after each alcohol addition. After the filtrate was decanted from the final precipitate, the precipitated dextrins were placed on a watch glass and dried in a vacuum oven at 100° C. for 2 hours. At the end of this period the dextrins were scraped from the watch glass, ground in a mortar, and either dried further or stored in a sealed bottle. The data for the purifying procedure are given in Table III with the reducing power (calculated as dextrose) and specific rotation of the purified dextrins.

**RESULTS.** The data show that the reducing power and specific rotation of dextrins precipitated by methanol from corn sirup vary with the number of precipitations, the percentage of methanol, and the temperature of precipitation. With methanol concentrations less than 80 per cent, the amount of dextrins precipitated was too small to work with. Dextrins with a constant minimum reducing power and a constant maximum specific rotation can be obtained from a 42 D. E. corn sirup by precipitating with 80 per cent methanol at 31° C. and purifying with nine reprecipitations. The sirup solids in the precipitation mixture for the first precipitation varied from 10 to 32 per cent, the lowest solids concentration being necessarily in the highest concentration of methanol. A nonreducing dextrin was not obtained from the corn sirup by methanol precipitation, the lowest reducing power being 2.7 per cent (calculated as dextrose).

#### DEXTRINS FROM 29.9 TO 63.4 D. E. CORN SIRUPS

The sirups used were produced by straight acid hydrolysis of cornstarch; the 42 and 54 D. E. sirups were commercial products, and the others were prepared in the laboratory pilot plant. The dextrins were reprecipitated with 80 per cent methanol at 30° C., nine reprecipitations being used for purification purposes. The procedure for this work was the same as described above. The iodine coloration of the dextrins was determined by adding 0.2 ml. of 0.1 N iodine solu-

TABLE II. PRECIPITATION OF DEXTRINS FROM 42 D. E. CORN SIRUP

Sirup, grams	500	500	800	800	800	800	500	500	500
Dry substance, grams	400	400	640	640	640	640	400	400	400
Water, grams	100	100	160	160	160	160	100	100	100
Water added, ml.	300	300	240	240	240	320	300	300	300
Total water, ml.	400	400	400	400	400	480	400	400	400
Methanol added, ml.	935	1200	1600	1600	1600	2720	3600	3600	3600
Final methanol, %	70	75	80	80	80	85	90	90	90
Pptn. temp., ° C.	31	31	10	31	60	32	34	32	32

TABLE III. PURIFICATION OF DEXTRINS FROM 42 D. E. CORN SIRUP

Water added to ppt., ml.	200	240	240	240	240	240	250	300	300	300
Methanol added, ml.	600	960	960	960	960	960	1417	2700	2700	2700
Final % methanol	75	80	80	80	80	80	85	90	90	90
Temperature, ° C.	31	10	31	31	60	60	32	34	32	32
No. times pptd.	10	10	5	10	10	15	5	5	10	15
Reducing power as dextrose (% dry substance)	a	5.1	3.5	2.9	2.7	2.8	4.3	7.8	5.0	4.8
Sp. rotation ( $\alpha$ ) <sub>D</sub> <sup>20</sup>	a	193.5	196.0	198.0	197.5	198.0	194.6	186.5	191.6	191.9

<sup>a</sup> Reduced Fehling solution; sample too small for quantitative determination.

tion to 5 ml. of a 2 per cent dextrin solution. Data for these precipitations and the analysis of the purified dextrans are given in Table IV.

TABLE IV. DEXTRANS FROM CORN SIRUPS PRECIPITATED WITH 80 PER CENT METHANOL AND PURIFIED BY NINE REPRECIPITATIONS

Sirup					
D. E.	29.9	33.9	42.0	54.0	63.4
Sirup, grams	1000	1000	800	1200	1000
Dry substance, grams	761	790	640	960	818
Water in sirup, grams	239	210	160	240	182
Water added, ml.	301	330	240	200	200
Total water, ml.	540	540	400	440	382
Methanol added, ml.	2160	2160	1600	1760	1528
Precipitate					
Water added, ml.	200	200	240	120	120
Methanol added, ml.	800	800	960	480	480
Reducing power as dextrose, %	6.1	6.3	2.8	3.6	5.5
Sp. rotation ( $\alpha$ ) <sub>D</sub> <sup>20</sup>	204.7	201.0	198.0	196.0	192.5
Iodine coloration	Violet	Deep red	Red	Red-brown	Brown

A probable explanation for the phenomenon that occurs with the reducing power of the dextrans lies in the various theoretical ways a starch or dextrin molecule may be split on hydrolysis and also in the rate of hydrolysis of the dextrans and higher sugars so formed. From the above results it appears that, on acid hydrolysis, parts of the starch molecule are split more easily than others, resulting in the simultaneous formation of low- and high-molecular-weight dextrans which are insoluble in 80 per cent methanol. The low-molecular-weight dextrans are hydrolyzed to sugars more rapidly than the larger dextrin molecules are split to low-molecular-weight dextrans. This will result in a decrease in the reducing power of the dextrin fraction during certain stages of hydrolysis. From this it can be reasoned that the low D. E. (29.9 and 33.9) sirups contain a larger amount of low-molecular-weight dextrin or a high-molecular-weight sugar which is insoluble in 80 per cent methanol than does the 42 D. E. sirup. Then if these smaller dextrin molecules are the size to be just insoluble in alcohol, only a slight degree of hydrolysis will make them soluble and thus remove them from the dextrin fraction. There would be a correspondingly small change in the larger dextrin molecules which would not be sufficient to bring the reducing power of the precipitated dextrans back to the initial value. In other words, the smaller dextrin or higher sugar molecules would be removed more rapidly than they are formed in going from a 33.9 to a 42 D. E. sirup. As the hydrolysis proceeded beyond 42 D. E., the dextrin molecules would be shortened which would result in a greater reducing power for the precipitated dextrans. The reducing power of the dextrans would continue to increase with further hydrolysis until the molecules became too small to be precipitated with 80 per cent methanol. This latter statement is borne out by the facts that, as the D. E. increases beyond 42, the reducing power of the dextrans increases and that an 82 D. E. corn sugar does not contain any dextrans which can be precipitated with 80 per cent methanol. Proof must await further research on the composition of starch hydrolyzates.

#### DEXTRANS FROM A DUAL CONVERSION SIRUP

The sample of dual conversion sirup (D. E. 64.8) was taken from a commercial batch which was made by superimposing an enzymatic hydrolysis on an acid hydrolysis. The methods for dextrin separation and analyses are the same as were used for the other corn sirups. The dextrans precipitated with 80 per cent methanol and purified by nine reprecipitations had the following properties:

Reducing power as dextrose, %	5.0
Specific rotation, ( $\alpha$ ) <sub>D</sub> <sup>20</sup>	177.5
Iodine coloration	Brown

The dextrans from the dual conversion sirup had a reducing power slightly lower and a specific rotation much lower than the dextrans from an acid-converted sirup of approximately the same D. E.

#### SUMMARY

Dextrans precipitated with 90 per cent methanol showed a constant reducing power and specific rotation after nine reprecipitations, but these values were not the same as those for the purified dextrans obtained with 80 per cent methanol. In the former case, the reducing power was higher and the specific rotation was lower, indicating that more low-molecular weight fragments were precipitated by the higher alcohol concentration.

Dextrans with a constant minimum reducing power and a constant maximum specific rotation were obtained from a corn sirup by precipitating with 80 per cent methanol at 31° C. and purifying with nine reprecipitations.

A nonreducing dextrin was not obtained from corn sirups with D. E. values between 29.9 and 64.8 by precipitating and purifying with 80 per cent methanol. The lowest reducing power (as dextrose) was 2.7 per cent and was for the dextrans from a 42 D. E. sirup.

Dextrans were precipitated with 80 per cent methanol from acid-converted corn sirups with D. E. values varying from 29.9 to 63.4 and from a dual-conversion sirup (acid enzyme) with a D. E. of 64.8. The dextrans were purified by reprecipitating nine times with 80 per cent methanol, and the reducing power, specific rotation, and iodine-coloration were determined on each sample.

The fact that the reducing power of the dextrans passes through a minimum indicates that, on acid hydrolysis, parts of the starch molecule are split more easily than others; the result is the simultaneous formation of low- and high-molecular weight dextrans which are insoluble in 80 per cent methanol. Apparently these low-molecular-weight dextrans are hydrolyzed to sugars more rapidly than the larger dextrin molecules are split to low-molecular-weight dextrans.

The reducing power, specific rotation, and iodine coloration of dextrans precipitated from corn sirups with 80 per cent methanol are dependent on the D. E. values of the sirups from which the dextrans are obtained.

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# PARAFFIN HYDROCARBONS

## Correlation of Physical Properties

The boiling points, densities, and refractive indices of all possible octanes, nonanes, decanes, and undecanes have been calculated from the same properties of the next lower paraffins (precursors) from which they can be derived by substitution of a methyl group for a hydrogen atom by several defined modes.

The agreement between the separate calculations of the same property, and between these and the observed values when available, is sufficiently good to justify the selections of means as properties of unknown isomers. In some cases these correlations suggest revisions in observed properties.

Paraffin isomers with two branches on nonadjacent carbon atoms have almost identical boiling points. This is probably true also of isomers with two branches on adjacent carbon atoms.

A FORMER paper (6) presented empirical relations between different physical properties of the same paraffin hydrocarbon, and between the same physical properties of various paraffin hydrocarbons. Omitting (in most cases) the first member of each series of "corresponding" homologs, the boiling points, densities, and refractive indices showed good agreement with simple equations formulated for the series. The equations were used to suggest revisions in certain observations which are possibly inaccurate, and to estimate the properties of a few unknown isomers.

The scope of these revisions and estimates was limited to members of corresponding series (mode 1 and parts of modes 2 and 9 in the tables of the present paper); this excludes most of the unknown isomers and many of those whose recorded properties are unreliable. The same limitation in scope applies to relations devised by other authors (1, 2, 5). In fact, none of them attempts to evaluate more than twelve of the thirty-five nonanes or of the seventy-five decanes. Huggins (7) does give a function of molal refraction in terms of structure, but since this property involves density, it is useless in estimating any other property of an unknown isomer, unless the isomer belongs to one of a corresponding series.

The present paper transcends this limitation, so that the properties of all paraffin isomers can be correlated; the recorded ones have been tested for some additional measure of reliability, and the unknown ones estimated. The hypothesis is that the same change in structure in a portion of a paraffin molecule produces substantially the same change (suitably expressed) in physical properties, regardless of the remainder of the molecule. This, of course, cannot be true precisely;

ALFRED W. FRANCIS

Socony-Vacuum Oil Company, Inc., Paulsboro, N. J.

but with a judicious choice of the modes of change it holds fairly well.

THE only change in structure here considered is the increase in molecular size resulting from the substitution of a methyl group for a hydrogen atom (or in one case the intervention of a  $-\text{CH}_2-$  group between two carbon atoms). The paraffin isomer so formed and its precursor are thus still corresponding homologs, though in a more general sense than in the earlier paper. Almost every isomer except the normal one in each group can be derived from two or three or even four precursors, so that a multiple check is possible on estimated values. Moreover, consistency in properties with those of higher paraffins of which an isomer is a precursor furnishes a further check. The several modes of formation selected are defined in Table I, and for clarity skeleton structures are given.

Although somewhat arbitrary in some cases, these modes are logical; they are subdivided so that all changes in one class result in increments in physical properties which are reasonably consistent with one another. Further subdivision would increase this concordance slightly but would diminish the number of cases in each class. As more experimental data became available, the necessity for further subdivision may become apparent. The form of these modes indicates some factors in the effect of structure on physical properties which may apply to other organic compounds. The modes presented are sufficiently comprehensive to cover all but 11 changes (out of 902) in the formation of heptanes, octanes, nonanes, decanes, and undecanes.

The properties computed are boiling point, density, and refractive index, since they are generally reported experimentally and a means of comparison is thus afforded. Molal volumes and refractivities could be derived, but the relations between the directly observed properties are just as simple and theoretically sound. Other properties such as aniline point, octane number, and expansion coefficient can be estimated from the three presented by methods similar to those given previously (6).

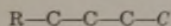
The increments in physical properties between nonanes and decanes, for example, are much less than those between hexanes and heptanes. For comparison of modes of formation in different groups, therefore, it is logical to use the ratio of any such increment to that of the corresponding increment for the normal isomer whose properties are known with adequate accuracy.

Although such a method of adjustment would nearly compensate for decreasing increments among the higher members, it is not precise; and the accuracy can be increased by using as ratios of increments, not constants, but smooth functions of molecular size as recorded in Table II and Figure 1. Identical ratios are suitable for both density and index of refraction; but those for boiling point are quite different. The plots of the former are nearly straight lines sloping away

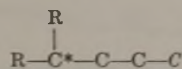
TABLE I. MODES OF FORMATION OF HIGHER HOMOLOGS FROM NEXT LOWER ONES

(Italic *C* is the new carbon atom; R represents alkyl radicals, the same or different, which are constant during the change; carbon atoms marked with an asterisk may have additional branches)

1. Lengthening of *n*-propyl or longer group

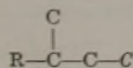


2. Lengthening of ethyl group attached to tertiary or quaternary carbon atom

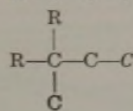


3. Substitution of ethyl for methyl group which is

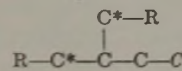
a. One of two methyl groups attached to a tertiary carbon atom



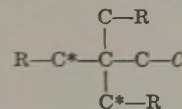
b. One of two or more methyl groups attached to a quaternary carbon atom



c. Attached to tertiary carbon atom, the other two groups being ethyl or longer

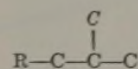


d. Attached to quaternary carbon atom, the other three groups being longer

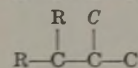


4. Introducing a methyl group into penultimate position of

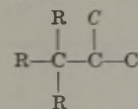
a. *n*-Propyl or longer group



b. Ethyl group attached to tertiary carbon atom

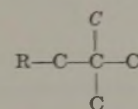


c. Ethyl group attached to quaternary carbon atom

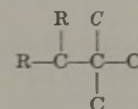


5. Attaching a second methyl group to a carbon atom in 2-position

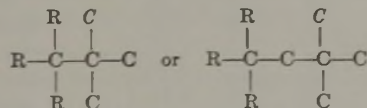
a. The 3-carbon atom is secondary, the 4-carbon atom is not quaternary



b. The 3-carbon atom is tertiary

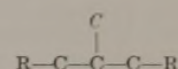


c. The 3- or 4-carbon atom is quaternary

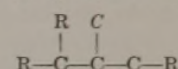


6. Attaching methyl group to secondary carbon atom in 3- or further position

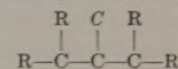
a. Adjacent carbon atoms are also secondary



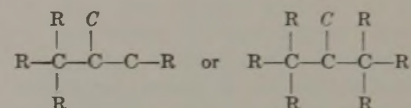
b. One of adjacent carbon atoms is tertiary



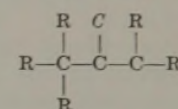
c. Both adjacent carbon atoms are tertiary



d. One or both adjacent carbon atoms are quaternary but neither is tertiary

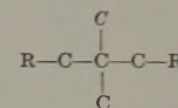


e. One of adjacent carbon atoms is tertiary and the other quaternary

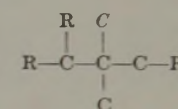


7. Attaching second methyl group to carbon atom in 3- or further position

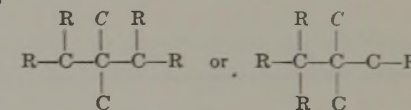
a. With no branch on adjacent carbon atom, and no quaternary carbon within two atoms



b. With one branch on adjacent carbon atom, and no quaternary carbon within two atoms on the other side



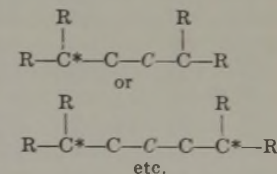
c. With two branches on adjacent carbon atoms



8. Attaching a methyl group to a tertiary carbon atom, the other three groups being longer

Formulas same as 7a, b, c, except R in place of methyl

9. Lengthening a middle chain (between branches) of at least one unsubstituted carbon atom which is not adjacent to two quaternary carbon atoms



from unity with increasing number of carbon atoms. The plots of the boiling point ratios are mostly concave curves, and the values are smaller. The deviations from unity of the ratios for modes 2 and 3a correspond with the "first-member discrepancies" of other papers (1, 2, 5, 6, 7). The method of deriving the ratios is given later.

THE properties of all possible octanes, nonanes, and decanes (neglecting stereoisomers) are computed in Tables III, IV, and V, and compared with the best observed values for the known isomers. Heptanes and lower paraffins are not computed because their ratios in Table II (with four exceptions)

would apply to only a single isomer each, and are of significance only insofar as they give smooth curves when plotted. Such ratios are enclosed in parentheses. Furthermore, the properties of paraffins up to heptanes are known experimentally too well to be improved by such a correlation. This is true also of most of the octanes and some of the nonanes, but of only a few of the decanes. In order to calculate the octanes, the numbers and observed properties of the precursor heptanes are given in Table III.

To illustrate the method of calculation, 3-methylheptane (25, Table III), can be derived from *n*-heptane by mode 6a,

from 2-methylhexane by mode 3a, or from 3-methylhexane by mode 1. The boiling point increment, 27.21° C. for *n*-octane from *n*-heptane, is multiplied by 0.73, 1.06, and 1.00, as listed in Table II; these products, 19.86°, 28.84°, and 27.21° C., are added respectively to the boiling points of the three precursors. Similarly, the density increment, 0.0191, and refractive index increment, 0.0100, for the normal paraffins are each multiplied by 1.10, 1.36, and 1.00, and added to the corresponding properties of the precursors. The slight discrepancy in the boiling point calculated by mode 6a with the observed value is due probably to the fact that 6a was made to include substitution in either the 3- or 4-positions; but further subdivision is undesirable for a reason mentioned previously, in cases where the difference is so small.

The ratios of Table II were derived in essentially the same way reversed. For example, mode 3a applies to four octanes. From their observed boiling points were subtracted those of the heptanes from which they are derived by mode 3a, as follows (numbers in parentheses refer to isomers in Table III):

Octane	Heptane	Difference
119.05 (25)	90.10 (15)	28.95
109.8 (30)	80.70 (20)	29.10
117.85 (33)	89.8 (19)	28.05
109.84 (36)	80.88 (22)	28.96
	Mean 28.77	

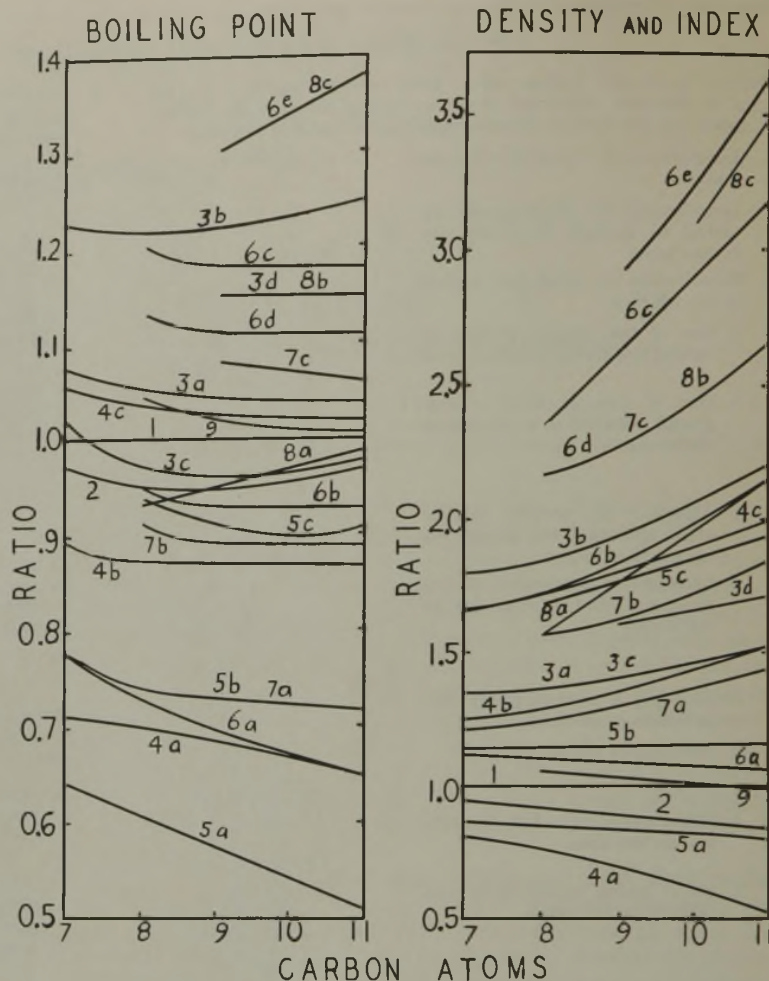


FIGURE 1. RELATIVE RATIOS

TABLE II. RELATIVE RATIOS OF INCREMENTS

Mode No.	No. of Cases	Boiling Point					Density and Refractive Index				
		C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>
1	70	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	
2	87	0.97	0.95	0.95	0.96	0.96	0.94	0.92	0.90	0.87	
3a	70	1.07	1.06	1.04	1.04	1.04	1.35	1.36	1.40	1.46	
3b	58	(1.22) <sup>a</sup>	1.22	1.22	1.23	1.25	(1.78)	1.85	1.93	2.05	
3c	69	(1.02)	0.97	0.96	0.97	0.98	(1.35)	1.36	1.40	1.46	
3d	10	...	...	(1.15)	1.15	1.15	...	...	(1.60)	1.65	
4a	70	0.71	0.70	0.68	0.67	0.65	0.80	0.77	0.69	0.61	
4b	58	(0.89)	0.87	0.87	0.87	0.87	(1.25)	1.28	1.35	1.43	
4c	29	(1.05)	(1.04)	1.02	1.01	1.01	(1.65)	(1.72)	1.80	1.90	
5a	27	(0.64)	0.61	0.58	0.54	0.51	(0.86)	0.86	0.85	0.85	
5b	26	(0.77)	(0.74)	0.73	0.73	0.71	(1.14)	(1.14)	1.14	1.15	
5c	17	...	(0.94)	0.91	0.90	0.91	...	(1.67)	1.79	1.85	
6a	58	(0.78)	0.73	0.70	0.67	0.65	(1.11)	1.10	1.10	1.09	
6b	63	(0.99)	0.95	0.93	0.93	0.93	(1.65)	1.70	1.84	2.00	
6c	15	...	(1.20)	(1.18)	1.18	1.18	...	(2.32)	(2.60)	2.90	
6d	27	...	(1.13)	1.11	1.11	1.11	...	(2.15)	2.25	2.45	
6e	10	...	...	(1.30)	1.34	1.38	...	...	(2.90)	3.25	
7a	23	(0.77)	(0.74)	0.73	0.73	0.73	(1.20)	(1.25)	1.30	1.40	
7b	23	...	(0.91)	0.89	0.89	0.89	...	(1.58)	1.63	1.74	
7c	15	...	...	1.08	1.07	1.06	...	...	2.25	2.45	
7m <sup>b</sup>	8	...	...	...	...	...	...	...	...	2.62	
8a	11	...	(0.93)	(0.95)	0.97	0.99	...	(1.55)	(1.75)	1.95	
8b	10	...	...	(1.15)	1.15	1.15	...	...	(2.25)	2.45	
8c	6	...	...	...	1.34	1.38	...	...	...	3.17	
8m <sup>b</sup>	3	...	...	...	...	...	...	...	...	3.55	
9	39	...	(1.05)	1.02	1.02	1.02	...	(1.06)	1.03	1.02	

<sup>a</sup> Parentheses indicate that the ratio applies to only one isomer.

<sup>b</sup> Mode not included in Table I.

Division of this mean increment by 27.21° C., the difference in boiling points of *n*-octane and *n*-heptane, gives the ratio 1.06.

Similarly, the ratio for density and refractive index was calculated from the observed properties of the same eight isomers as follows:

Density		Difference × 10 <sup>4</sup>
0.7057	0.6787	
0.7002	0.6730	272
0.7194	0.6950	244
0.7162	0.6900	262
Mean 262		
Increment for normal 191		

Refractive Index		Difference × 10 <sup>4</sup>
1.3986	1.3850	
1.3958	1.3820	138
1.4044	1.3920	124
1.4029	1.3895	134
Mean 133		
Increment for normal 100		

100 = 1.33

The ratio 1.36 in Table II, slightly higher than the mean, was selected because of the trend for higher paraffins, and because the third case above seemed less reliable.

Since the number of known cases was sometimes small and some of the observations inaccurate, estimates of properties for the same isomer using different precursors and different modes were sometimes discordant. If one mode gave esti-

hydrocarbons 56, 63, 66, 67, 69, 96, 109, 112, and 113. Improved observations on 65, 95, 115, and 123 also are given there. In the case of 66 the properties given by Levina and Kagan (8) should be considered and are averaged with those selected by Doss. The omission of observations on hydrocarbons 70 and 86 from his third edition (3), though given in the second from a private reference, suggests that the experi-

TABLE III. CALCULATION OF PHYSICAL PROPERTIES OF OCTANES

No.	Hydrocarbon	Pre-cursor Mode	B. P., ° C.	$d_4^{20}$	$n_D^{20}$	No.	Hydrocarbon	Pre-cursor Mode	B. P., ° C.	$d_4^{20}$	$n_D^{20}$
Heptanes (Observed)						Octanes (Continued)					
14	n-Heptane	.. ..	98.42	0.6837	1.3876	31	2,5-Dimethylhexane	15 4a	109.15	0.6934	1.3927
15	2-Methylhexane	.. ..	90.10	0.6787	1.3850	20	9	(109.27)	(0.6932)	(1.3926)	
16	3-Methylhexane	.. ..	91.9	0.6865	1.3882	Observed	109.25	0.6940	1.3929		
17	3-Ethylpentane	.. ..	93.47	0.6982	1.3934	32	3,3-Dimethylhexane	16 7a	(112.04)	(0.7104)	(1.4007)
18	2,2-Dimethylpentane	.. ..	79.21	0.6739	1.3824	18	3b	112.40	0.7092	1.4009	
19	2,3-Dimethylpentane	.. ..	89.8	0.6950	1.3920	21	2	111.85	0.7106	1.4002	
20	2,4-Dimethylpentane	.. ..	80.70	0.6730	1.3820	Observed	112.0	0.7107	1.4008		
21	3,3-Dimethylpentane	.. ..	86.0	0.6930	1.3910	33	3,4-Dimethylhexane	16 6b	117.75	0.7190	1.4052
22	2,2,3-Trimethylbutane (triptane)	.. ..	80.88	0.6900	1.3895	19	3a	118.64	0.7210	1.4056	
						Observed	117.85	0.7194	1.4044		
Octanes						34	2-Methyl-3-ethylpentane	17 4b	117.14	0.7226	1.4062
23	n-Octane (obsvd.)	14 1	125.63	0.7028	1.3976	19	3c	116.19	0.7210	1.4056	
24	2-Methylheptane	14 4a	117.47	0.6984	1.3953	Observed	115.7	0.7191	1.4046		
		15 1	117.31	0.6978	1.3950	35	3-Methyl-3-ethylpentane	17 8a	(118.78)	(0.7278)	(1.4089)
		Observed	117.65	0.6976	1.3954	21	3b	119.19	0.7283	1.4095	
25	3-Methylheptane	14 6a	118.28	0.7047	1.3986	Special est.	118.4	0.7263	1.4073		
		15 3a	118.94	0.7047	1.3986	Observed	118.4	0.7274	1.4079		
		16 1	119.11	0.7056	1.3986	36	2,2,3-Trimethylpentane	18 6d	(109.96)	(0.7150)	(1.4039)
		Observed	119.05	0.7057	1.3982	19	5b	(109.94)	(0.7168)	(1.4034)	
26	4-Methylheptane	14 6a	118.28	0.7047	1.3986	22	3a	109.72	0.7160	1.4031	
		16 2	117.75	0.7041	1.3974	Observed	109.84	0.7162	1.4029		
		Observed	117.7	0.7042	1.3980	37	2,2,4-Trimethylpentane (isooctane)	18 4a	98.26	0.6886	1.3901
27	3-Ethylhexane	16 3c	118.29	0.7125	1.4018	20	5a	97.30	0.6894	1.3906	
		17 2	119.32	0.7158	1.4026	Observed	99.23	0.6919	1.3916		
		Observed	118.7	0.7128	1.4021	38	2,3,3-Trimethylpentane	19 7b	(114.56)	(0.7252)	(1.4078)
28	2,2-Dimethylhexane	15 5a	106.70	0.6951	1.3936	21	4c	(114.30)	(0.7259)	(1.4082)	
		18 1	106.42	0.6930	1.3924	22	3b	114.07	0.7253	1.4080	
		Special est.	106.54	0.6945	1.3930	Observed	(115.1)	0.7253	(1.4072)		
		Observed	106.6	0.6947	1.3930	Selected	114.7	0.7253	1.4076		
29	2,3-Dimethylhexane	15 6b	115.95	0.7112	1.4020	39	2,3,4-Trimethylpentane	19 4b	113.47	0.7194	1.4048
		16 4b	115.57	0.7109	1.4010	20	6c	(113.35)	(0.7173)	(1.4052)	
		19 2	115.65	0.7126	1.4012	Observed	113.5	0.7188	1.4044		
		Observed	115.7	0.7125	1.4017	40	2,2,3,3-Tetramethylbutane	22 5c	(106.46)	(0.7219)	(1.4062)
30	2,4-Dimethylhexane	15 6a	109.96	0.6997	1.3960	Observed	106.5	0.7219	....		
		16 4a	110.95	0.7012	1.3959						
		20 3a	109.54	0.6990	1.3956						
		Observed	109.8	0.7002	1.3958						

mates almost uniformly low as compared with those by other modes, its increment ratio was increased slightly and vice versa. In these adjustments greater weight was always given to experimental values over calculated ones, and to calculations by those modes representing a large number of cases (column 2, Table II) over those with a small number.

A FEW modes apply only to unknown members of some groups of isomers, but the increments can be calculated from the results by other modes. They help in correlation, since it is assumed that the same increment holds for all applications of the same mode even if no cases have been observed experimentally. The properties of the 159 undecanes were computed in this way (Table VI) practically without the aid of experimental observations; only ten undecanes have been observed at all, and few of their properties recorded. The preliminary ratios used in this development were extrapolations of the ratios of Table II for lower paraffins, and required only trifling adjustments to get the "best" values. The use of these properties and further extrapolations permit the convenient calculation for any dodecane.

The observed or experimental values in Tables III, IV, and V are those given in Table I of the earlier paper (6) except as follows: Paraffins described in the literature for the first time since that paper and listed by Doss (3) are included—namely,

mental data were not very reliable; and this applies also to 72 and 143, observed, in small amounts previously by the present author. For these four isomers at least, the calculated properties are preferable. The boiling point and index of 138 are revised slightly upward in view of the observations of Fleming and Buechele (11). The observed boiling points now selected for hydrocarbons 26 and 28 are a trifle higher than those recorded previously (6). The description "unknown" for a paraffin means that its observed properties have not appeared in the published literature, not that it has not been made.

The average discrepancies between the separately calculated values and the selected properties are 0.3° C. in boiling point, 0.0007 in density, and 0.0004 in refractive index. The differences between the selected and the true values should be of the same order in most cases. However, when there is a high concentration of branches, as in hydrocarbons 70 to 75 and in 122 to 150, the modes of Table I become less typical, and the calculations may be somewhat less accurate. The selected values are the observed ones when the latter seem thoroughly reliable from an experimental viewpoint, or when they show good concordance with calculated values. When the observations are moderately discordant with the calculations (e. g., about 1° C. in boiling point), they are enclosed in





TABLE V. CALCULATION OF PHYSICAL PROPERTIES OF DECANES

(Unknown if no observed values are given)

No.	Decane	Precursors	B. P., ° C.	$d_4^{20}$	$n_D^{20}$
76	<i>n</i> -Decane (obsvd.)	41	174.04	0.7299	1.4120
77	2-Methylnonane	41, 42 Obsvd.	166.6 166.8	0.7255 0.7280?	1.4095 1.4099
78	3-Methylnonane	41, 42, 43 Obsvd.	167.3 167.8	0.7322 0.7334	1.4126 1.4125
79	4-Methylnonane	41, 43, 44 Obsvd.	166.2 165.7	0.7316 0.7323	1.4124 1.4123
80	5-Methylnonane	41, 44 Obsvd.	166.0 165.1	0.7315 0.7325	1.4125 1.4117
81	3-Ethyldecane	43, 45	166.5	0.7385	1.4155
82	4-Ethyldecane	44, 45, 46	165.3	0.7375	1.4152
83	2,2-Dimethyldecane	42, 47 Obsvd.	155.3	0.7233 0.7245	1.4084 1.4082
84	2,3-Dimethyldecane	42, 43, 48	164.3	0.7383	1.4157
85	2,4-Dimethyldecane	42, 44, 49 Obsvd.	158.3 153.2?	0.7262 (0.7246)	1.4095 1.4090
86	2,5-Dimethyldecane	42, 44, 49, 50 Obsvd.?	158.4 (159)	0.7264 0.7349?	1.4096 1.4128?
87	2,6-Dimethyldecane	42, 43, 50, 51 Obsvd.	159.2 158.54	0.7274 0.7291	1.4101 1.4107
88	2,7-Dimethyldecane	42, 51 Obsvd.	158.9 (160)	0.7217 0.7226	1.4075 1.4082
89	3,3-Dimethyldecane	43, 47, 52 Obsvd.	160.8 161.2	0.7371 (0.7390)	1.4152 (1.4165)
90	3,4-Dimethyldecane	43, 44, 48, 53	165.0	0.7447	1.4190
91	3,5-Dimethyldecane	43, 44, 49, 54	158.8	0.7328	1.4130
92	3,6-Dimethyldecane	43, 50, 54 Obsvd.	159.8 160	0.7337 (0.7365)	1.4133 (1.4145)
93	4,4-Dimethyldecane	44, 52, 55	159.5	0.7363	1.4147
94	4,5-Dimethyldecane	44, 53 Obsvd.	164.1 161?	0.7438 .....	1.4184 .....
95	4- <i>n</i> -Propylheptane	46 Obsvd.	164.6 161.8?	0.7363 0.7364	1.4148 1.4150
96	4-Isopropylheptane	46, 56 Obsvd.	162.3 158.6	0.7433 (0.7412)	1.4180 1.4171
97	2-Methyl-3-ethylheptane	45, 48, 56	163.2	0.7446	1.4185
98	2-Methyl-4-ethylheptane	46, 49, 57	157.4	0.7325	1.4128
99	2-Methyl-5-ethylheptane	45, 50, 57	158.4	0.7337	1.4131
100	3-Methyl-3-ethylheptane	45, 52, 58 Obsvd.?	165.8 156.3?	0.7508 0.7460?	1.4218 1.4179?
101	3-Methyl-4-ethylheptane	46, 53, 56, 59	164.1	0.7505	1.4218
102	3-Methyl-5-ethylheptane	45, 54, 57	158.9	0.7397	1.4164
103	4-Methyl-3-ethylheptane	45, 53, 59	164.5	0.7507	1.4218
104	4-Methyl-4-ethylheptane	46, 55, 58	164.8	0.7496	1.4215
105	2,2,3-Trimethylheptane	47, 48, 60	157.6	0.7405	1.4170
106	2,2,4-Trimethylheptane	47, 49, 61	147.2	0.7238	1.4088
107	2,2,5-Trimethylheptane	47, 50, 61, 62	148.0	0.7248	1.4091
108	2,2,6-Trimethylheptane	47, 51, 62 Obsvd.?	147.7 (148.93)	0.7194 (0.7229)	1.4062 (1.4077)
109	2,3,3-Trimethylheptane	48, 52, 63 Obsvd.	161.0 160	0.7487 0.7488	1.4207 1.4202
110	2,3,4-Trimethylheptane	48, 49, 53, 64	162.0	0.7502	1.4219
111	2,3,5-Trimethylheptane	48, 50, 54, 65	156.4	0.7395	1.4163
112	2,3,6-Trimethylheptane	48, 50, 51, 65	155.2	0.7345	1.4130
113	2,4,4-Trimethylheptane	49, 55, 66 Obsvd.	151.8 151.5	0.7314 (0.7346)	1.4124 (1.4143)
114	2,4,5-Trimethylheptane	49, 50, 53, 65	156.6	0.7393	1.4162
115	2,4,6-Trimethylheptane	49, 51 Obsvd.	150.5 147.6?	0.7218 0.7223	1.4075 1.4071
116	2,5,5-Trimethylheptane	50, 52, 62, 66	152.8	0.7326	1.4128
117	3,3,4-Trimethylheptane	52, 53, 60, 67	162.7	0.7545	1.4238
118	3,3,5-Trimethylheptane	52, 54, 61, 66 Obsvd.?	153.3 159.1?	0.7384 0.7553?	1.4161 1.4230?
119	3,4,4-Trimethylheptane	53, 55, 63, 67	162.2	0.7545	1.4236
120	3,4,5-Trimethylheptane	53, 54, 64	163.6	0.7571	1.4256
121	2-Methyl-3-isopropylhexane	56, 71	160.0	0.7502	1.4212
122	3,3-Diethylhexane	58, 68	169.6	0.7613	1.4258
123	3,4-Diethylhexane	59 Obsvd.	164.5 160.7	0.7580 0.7514	1.4254 1.4200
124	2,2-Dimethyl-3-ethylhexane	56, 60, 69	156.5	0.7470	1.4195
125	2,2-Dimethyl-4-ethylhexane	57, 61	147.3	0.7315	1.4126
126	2,3-Dimethyl-3-ethylhexane	56, 58, 63, 70	166.4	0.7631	1.4278
127	2,3-Dimethyl-4-ethylhexane	57, 59, 64	162.2	0.7575	1.4255
128	2,4-Dimethyl-3-ethylhexane	56, 59, 64, 71	161.9	0.7574	1.4251
129	2,4-Dimethyl-4-ethylhexane	57, 58, 66	158.0	0.7464	1.4199
130	2,5-Dimethyl-3-ethylhexane	56, 57, 65	155.0	0.7400	1.4163
131	3,3-Dimethyl-4-ethylhexane	59, 67, 69	162.6	0.7616	1.4269
132	3,4-Dimethyl-3-ethylhexane	58, 59, 67, 70	168.7	0.7701	1.4315
133	2,2,3,3-Tetramethylhexane	60, 63, 72	159.0	0.7601	1.4264
134	2,2,3,4-Tetramethylhexane	60, 61, 64, 73 Obsvd.	156.0 156.5	0.7534 0.7548	1.4235 1.4224
135	2,2,3,5-Tetramethylhexane	60, 62, 65	149.5	0.7367	1.4147
136	2,2,4,4-Tetramethylhexane	61, 66, 74	150.8	0.7440	1.4194
137	2,2,4,5-Tetramethylhexane	61, 62, 65	145.0	0.7315	1.4124
138	2,2,5,5-Tetramethylhexane	62 Obsvd.	136.7 136.8	0.7179 0.7685	1.4050 1.4053
139	2,3,3,4-Tetramethylhexane	63, 64, 67, 75	164.1	0.7685	1.4308
140	2,3,3,5-Tetramethylhexane	63, 65, 66	153.0	0.7441	1.4185
141	2,3,4,4-Tetramethylhexane	64, 66, 67, 73	160.5	0.7606	1.4272
142	2,3,4,5-Tetramethylhexane	64, 65	159.5	0.7571	1.4253
143	3,3,4,4-Tetramethylhexane	67, 72	165.5	0.7750	1.4340
144	2,4-Dimethyl-3-isopropylpentane	71	157.8	0.7569	1.4247
145	2-Methyl-3,3-diethylpentane	68, 70	171.2	0.7746	1.4325
146	2,2,3-Trimethyl-3-ethylpentane	69, 70, 72	165.5	0.7757	1.4341
147	2,2,4-Trimethyl-3-ethylpentane	69, 71, 73	154.3	0.7537	1.4230
148	2,3,4-Trimethyl-3-ethylpentane	70, 71, 75	168.7	0.7773	1.4352
149	2,2,3,3,4-Pentamethylpentane	72, 73, 75	161.1	0.7742	1.4336
150	2,2,3,4,4-Pentamethylpentane	73, 74	148.5	0.7496	1.4220

The discrepancies in the properties of 46 (4-ethylheptane) were noted previously (1, 6). It had been observed only once (10) in 1896 by Obereit; he mentioned the possible presence of an oxygen compound, accounting for the high density and refractive index and perhaps the low boiling point.

The case of diethylpentane (68, Table IV) is unusual; because of its symmetrical structure it can be derived from only one octane, by a mode not well established since it is applicable to no other nonane and only two decanes. Diethylpentane was observed in only one investigation (9). It was pointed out (6) that the recorded boiling point and density were inconsistent with a reasonable octane number for it, and tentatively the discrepancy was distributed between the two properties. However, a special method of estimating its properties results from the symmetrical series  $CMe_4$ ,  $EtCMe_3$ ,  $Et_2CMe_2$ ,  $Et_3CMe$ ,  $Et_4C$ . The observed densities and refractive indices of this series,  $CR_4$ , agree well with the equations:

$$d_4^{20} = 0.9538 - 1.92/n + 0.00062n + 0.48/n^2$$

$$n_D^{20} = 1.5234 - 0.98/n + 0.00027n + 0.27/n^2$$

This form of equation was used in the former paper (6) for corresponding homologs. Calculated values for the last two members, 35 and 68, appear in Tables III and IV. The agreement indicates that the observations of these two properties on diethylpentane are probably reliable.

Boiling points of corresponding homologs were correlated (6) by equations for the differences between the boiling point of each member and that of the normal paraffin with the same length of longest chain. This arrangement would fail for the above series because each of the last three members has only a five-carbon chain. If, instead, we subtract from the observed boiling point of each member of the series that of the normal paraffin with two less total carbon atoms (because of the two side chains), the following series of increments results (boiling point of neopentane minus boiling point of propane, etc.): 51.62°, 50.23°, 49.92°, 49.66°, 40.78° C. The last increment is evidently far out of line. By any method of extrapolation it should be close to 49.4° C. which, added to the boiling point of *n*-heptane, gives 147.82° for diethylpentane. A mean of this and the other calculated boiling point, 147.28° C., is selected. This would also remove the discrepancy in calculated octane number and likewise be more consistent with the boiling points of the decanes of which it is the precursor.

The observed properties of hydrocarbon 118 (Table V) are discordant with the four calculations, which agree well among themselves. This isomer was made by hydro-



only one investigation. The observed properties of hydrocarbon 70 agree with those calculated for 53; and those of 100 with those for 124, for no apparent reason in either case.

An interesting observation is that isomers with two branches on nonadjacent carbon atoms seem to have nearly identical boiling points. This is exact for nonanes 50 and 51, and is fairly close for the other three nonanes, 49, 54, and 57, as well as for the two octanes, 30 and 31. The nine decanes of this classification (85, 86, 87, 88, 91, 92, 98, 99, 102) all boil at  $158.6 \pm 0.5^\circ \text{C}$ . The increment between this mean and that of the similar nonanes,  $135.22^\circ \text{C}$ ., is almost the same as between the boiling points of *n*-decane and *n*-nonane. The apparent identity in boiling point for isomers of this description is not paralleled by the other two properties, although among some subgroups the values are close for them also.

Omitting octane 33, there may be a similar agreement in boiling point for those isomers with two unbranched side chains on adjacent carbons. These are hydrocarbons 29 and 34 at  $115.7^\circ \text{C}$ ., 48, 53, 56, and 59 at  $141^\circ \text{C}$ ., and 84, 90, 94, 97, 101, 103, and 123 at  $164.25^\circ \text{C}$ . However, this correlation is less satisfactory because the boiling points of all the decanes and two of the nonanes mentioned are calculated.

There are indications of other similar groups, such as isomers with a tertiary butyl radical and another branch not adjacent to it—namely, 61, 62, 106, 107, 108, and 125. Even the single-branched isomers, 24 to 27, 42 to 46, 77 to 82 (and 95?), are close in boiling point, although this is hardly true

for hexanes and heptanes. In close fractional distillation these groups would cause distinct peaks which might be mistaken for individual isomers.

#### ACKNOWLEDGMENT

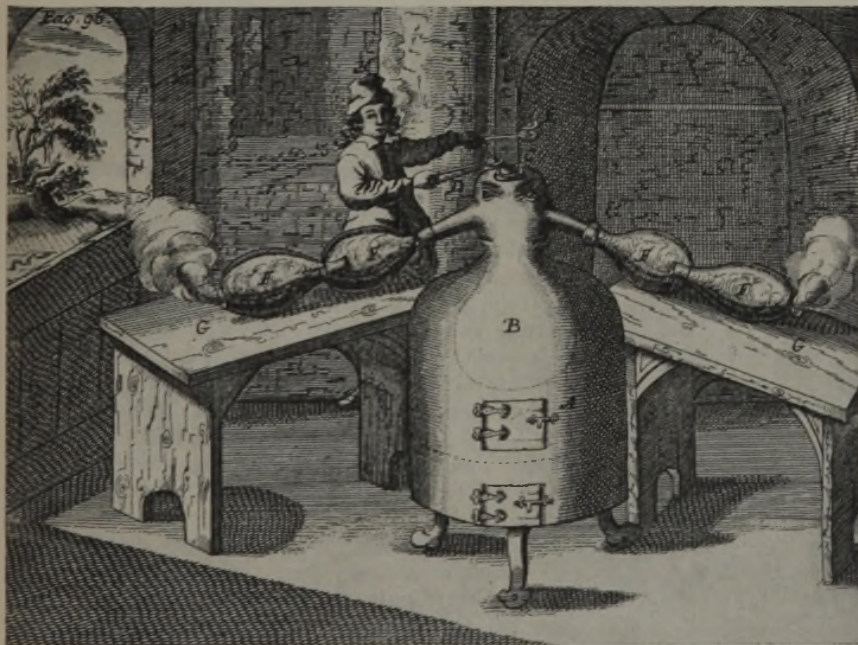
Thanks are due Louis J. Hillenbrand, who checked most of the calculations, and to other colleagues for helpful criticism of Table I and the text.

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## THE IRON MAN WITH TWO NOSES



● Johann Rudolf Glauber (1603–1668), the Dutch industrial chemist of note, whose important accomplishments are well known, wrote a number of books. One of them, "Miraculum Mundi", was published in Frankfurt in 1658. Glauber, borrowing from the earlier alchemists, used many picturesque metaphors; thus he calls his nitric acid still "a two-nosed iron man". This we reproduce as No. 148 in the Berolzheimer series of Alchemical and Historical Reproductions.

The raw material was the "white swan" of Basilius, which was an amalgam of tin and niter, intimately mixed together.

We quote from Christopher Packe's translation of 1689: "First a man is made of iron, having two noses on his head, and on his crown a mouth which may be opened and again close shut. And to each nose of the head glass receivers are to be applied to receive the vapors ascending from the hot stomach. When you use this man you must render him bloody with fire to make him hungry and greedy of food. When he grows extremely hungry he is to be fed with a white swan."

D. D. BEROLZHEIMER

50 East 41st Street  
New York, N. Y.

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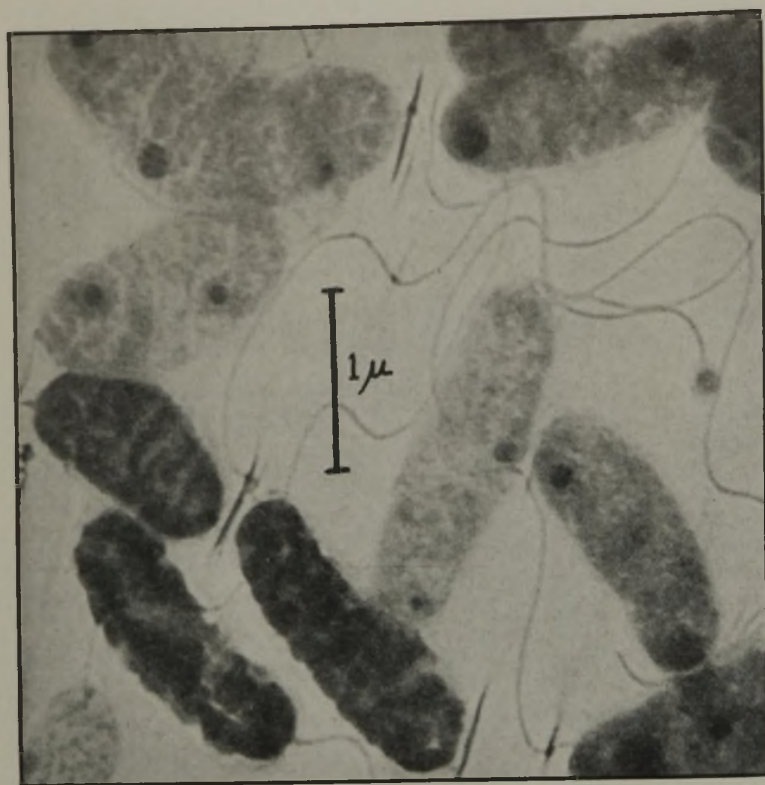


Figure 1. *Bacterium Vibrio-Schuykilliense* ( $\times 24,000$ )

The applications of electron microscopy to chemistry are illustrated by a number of micrographs of chemical materials. Methods of obtaining electron stereomicrographs and electron diffraction patterns with the electron microscope are described. A high-voltage electron microscope is discussed. The replica technique for obtaining electron micrographs of metallurgical specimens is described, and the results of several techniques are shown. The scanning electron microscope and the development of a small electron microscope are discussed briefly.

**P**ROGRESS in science is not uniform and gradual, but takes place in spurts, initiated by radical new departures in theory or in technique. The electron microscope may well be regarded as a development of this type, for it exceeds in power the familiar light microscope of today by a factor of the same order as that by which good modern light microscopes excel those of three centuries ago.

It is natural that this powerful new tool, once perfected, should find immediate application in the study of disease-causing organisms, bacteriology. Figure 1, for example, shows an electron micrograph of a group of flagellated bacteria inhabiting a city water supply. Under a light microscope these would appear as tiny, structureless specks; Figure 1, however, reveals not only the characteristic fine long flagella, but in addition, the copious structure within the organism.

# Electron Microscopy in Chemistry

VLADIMIR K. ZWORYKIN  
RCA Laboratories, Princeton, N. J.

## SIZE AND SHAPE DETERMINATION

The electron microscope has proved just as effective in many branches of chemistry. A few micrographs from the RCA collection will illustrate such applications.

Various kinds of dust and smoke may constitute simply a health hazard; on the other hand, they may find application as preservatives, pigments, insecticides, chemical reagents, and catalysts. In all cases importance attaches to the shape and size distribution of the individual particles, which are usually too small to permit a determination of these factors with the light microscope.

One of the most interesting smokes at present is carbon black; the effectiveness of finely divided carbon as a reinforcing agent of rubber depends largely on its fineness of division. Its most important source is the partial combustion of natural gases. Figure 2 (left) shows the highly inhomogeneous collection of particles from a natural gas flame, which is obtained if no precaution is taken to derive all of the carbon from the same portion of the flame. By contrast, the carbon black derived from a camphor flame (Figure 2, right) has a highly homogeneous distribution; the individual particles are approximately spherical and about 0.000002 inch in diameter.

Most metal smokes have typical particle shapes, characteristic of their crystal structure. A familiar example is magnesium smoke (Figure 3); the individual particles are cubes, oriented in all possible ways with respect to the plane of the micrograph. On the other hand, zinc smoke particles (Figure 4A), prepared by burning zinc in an oxidizing flame, consist primarily of four fine spikes joined together at the center. They deviate greatly in appearance from the constituents of zinc oxide pigment shown (Figure 4B) deposited on a celluloid membrane. For comparison Figure 4C shows the identical material photographed with the light

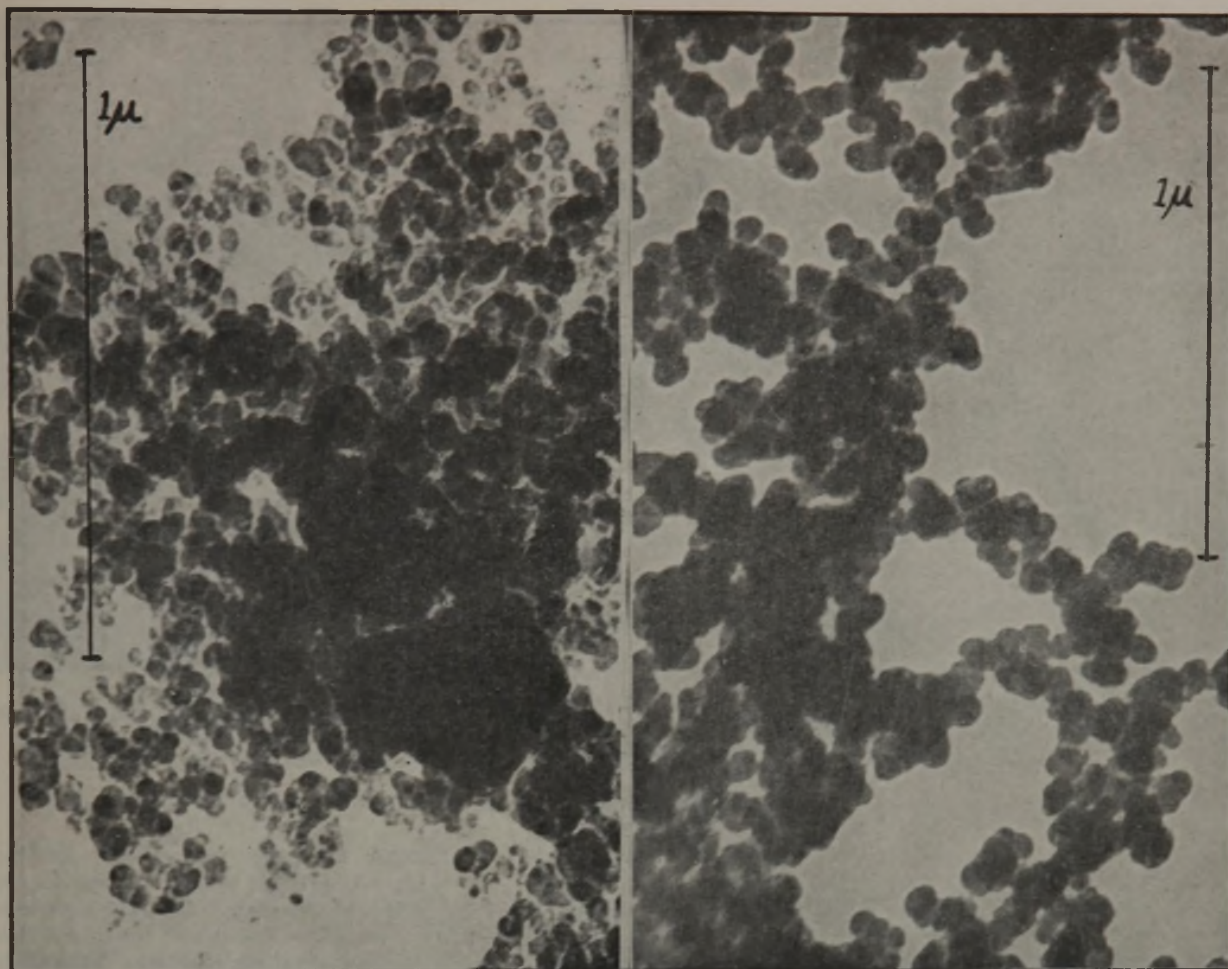


Figure 2. Carbon Blacks from a Natural Gas Flame, left ( $\times 80,000$ ), and a Camphor Flame, right ( $\times 64,000$ )

microscope (the picture and material were furnished by the New Jersey Zinc Company). In this range the light microscope reveals nothing regarding the shape of the particles and very little concerning their size or number.

Frequently an electron micrograph of a sample indicates directly the reason for its peculiar physical or chemical properties. Thus, a certain lot of calcium carbonate showed unusual chemical activity, and the electron microscope revealed the structure shown in Figure 5. The individual particles appeared strongly corrugated and even porous, which indicated an unusually large surface area. Two lots of lead arsenate were examined which differed greatly in their effectiveness. The electron microscope showed that the first of them, which had proved an excellent insecticide of great covering power, was made up of particles in the form of extremely thin small plates; the second, less effective material consisted of relatively thick granular particles (Figure 6).

Fineness of division or surface area are also factors of great importance in many pharmaceutical preparations which are colloidal suspensions. A familiar antiseptic of this type is mercurochrome (Figure 7); the individual particles are far too small to be distinguished by a light microscope.



Figure 3. Magnesium Smoke ( $\times 30,300$ )

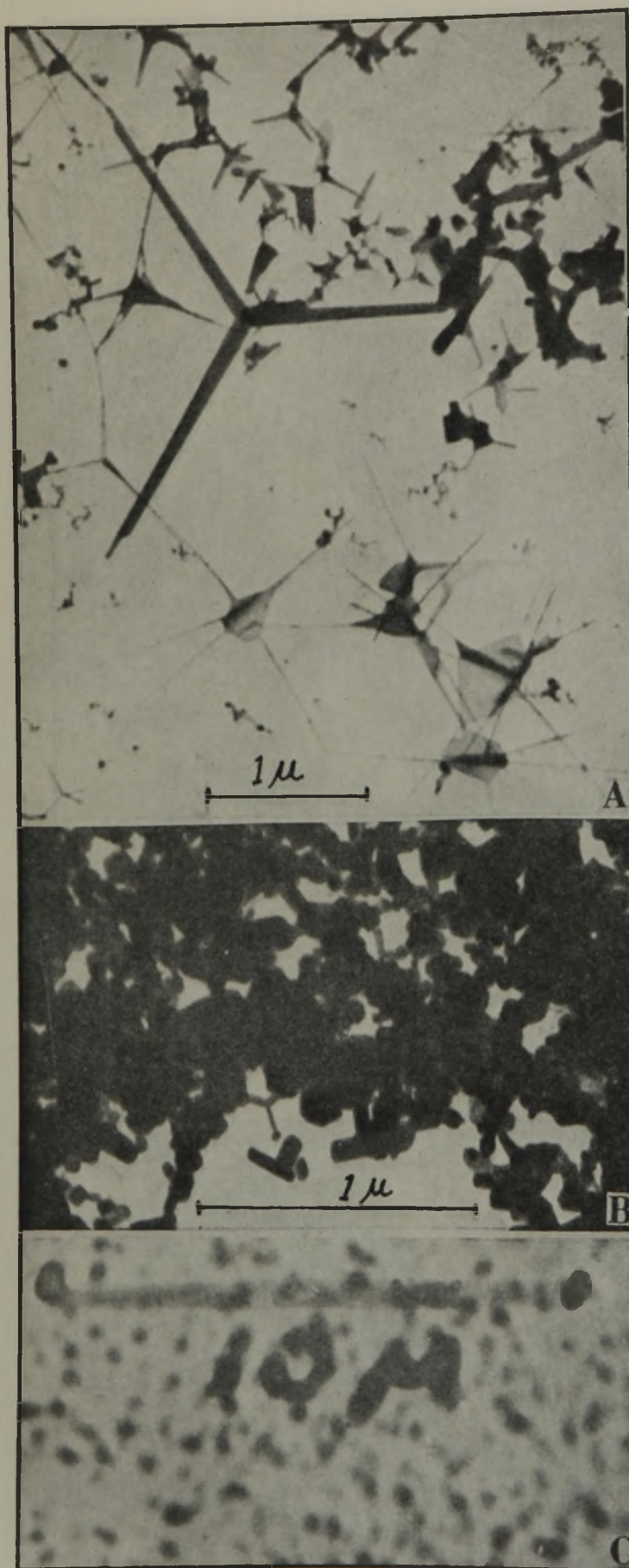


Figure 5. Calcium Carbonate ( $\times 31,500$ )

Another mercurial preparation, merthiolate (Figure 8), exhibits comparably fine dispersion.

A field of constantly increasing importance is the chemistry of organic polymers, such as plastics and synthetic rubbers. While not much can be said about developments in this field at present, it appears certain that the electron microscope will prove a valuable aid in the study of these materials. Figure 9 shows slightly polymerized vinyl chloride, such as is used in the manufacture of hemp rope. Figure 10 represents the same material when fully polymerized to form the artificial rubber Koroseal; the fine dark specks are small enough to constitute a single molecule. Figure 11 shows a thin film of polystyrene separated in characteristic fashion at the center; this is a transparent plastic with certain useful electrical properties.

#### STEREOMICROGRAPHS

The value of the electron microscope as an instrument for determining the shapes and structures of finely divided matter is greatly enhanced by relatively simple accessory equipment. An ordinary micrograph, whether obtained with an electron microscope or with a light microscope, represents the object in two dimensions only; in effect, it shows a projection



Figure 4. A, Zinc Smoke ( $\times 26,000$ ); B, Zinc Oxide Pigment ( $\times 44,000$ ); C, Light Micrograph of Zinc Oxide Pigment ( $\times 8500$ )



Figure 6. Lead Arsenate: Thin Plates at Left ( $\times 29,000$ ); Heavier Granular Structure at Right ( $\times 27,500$ )

of the object on a plane normal to the instrument axis. The characteristics of the object in the third dimension—i. e., in a direction along the axis—can be inferred only indirectly. On the other hand, if the object is viewed from a different angle by each eye, the brain fuses the two images; the result is a perception of the object in its three dimensions. Thus if two micrographs of the same object, inclined by a small angle (e. g.,  $4^\circ$ ) to the axis of the objective in two opposite

directions, are viewed in an ordinary stereoscope, a three-dimensional representation is obtained. In the case of high-power light microscopes this procedure is impractical, since their depth of focus is so small that the required inclination of the object would render the image unsharp except in a very narrow range. The electron microscope, on the other hand, has extraordinarily great depth of focus and is ideally adapted for this purpose. To obtain the two stereoisimages, the object

Figure 7. Mercurochrome ( $\times 71,000$ )

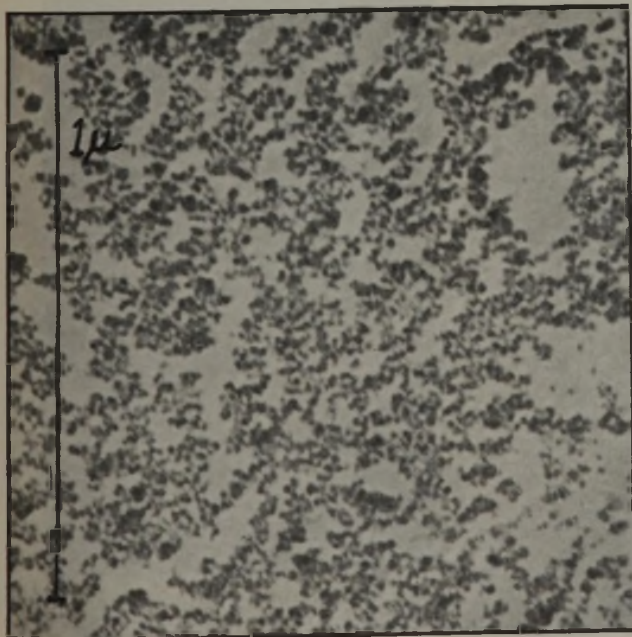
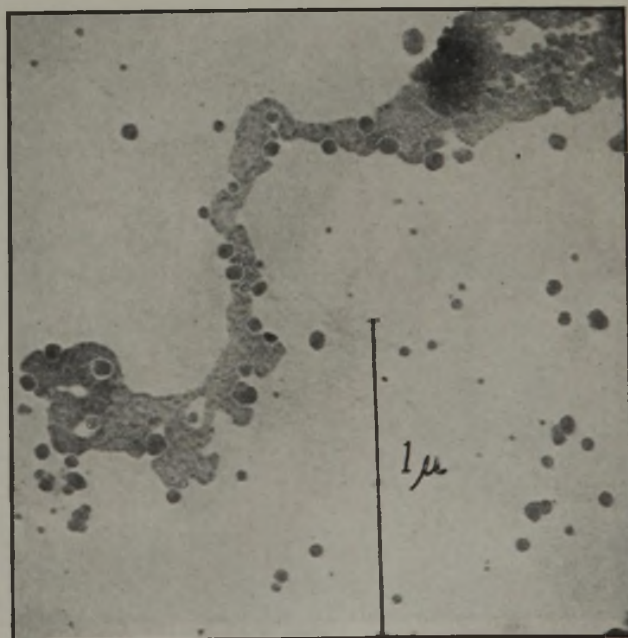


Figure 8. Merthiolate ( $\times 41,000$ )



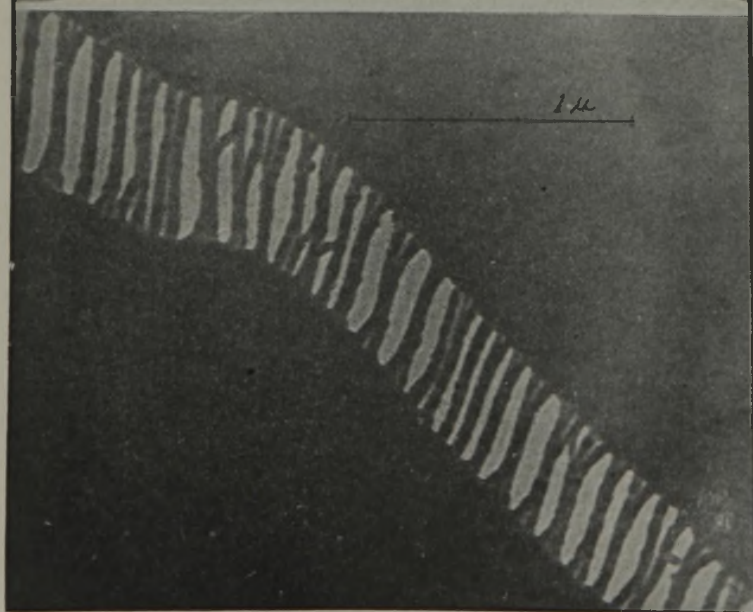
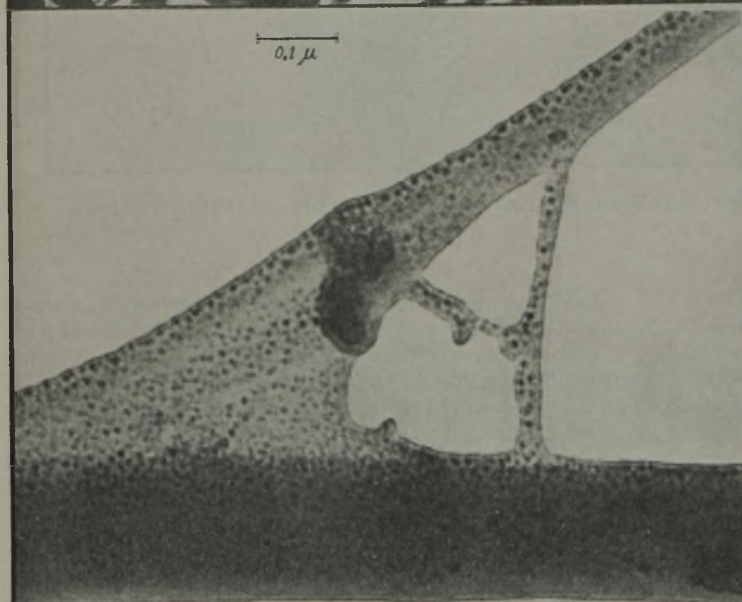
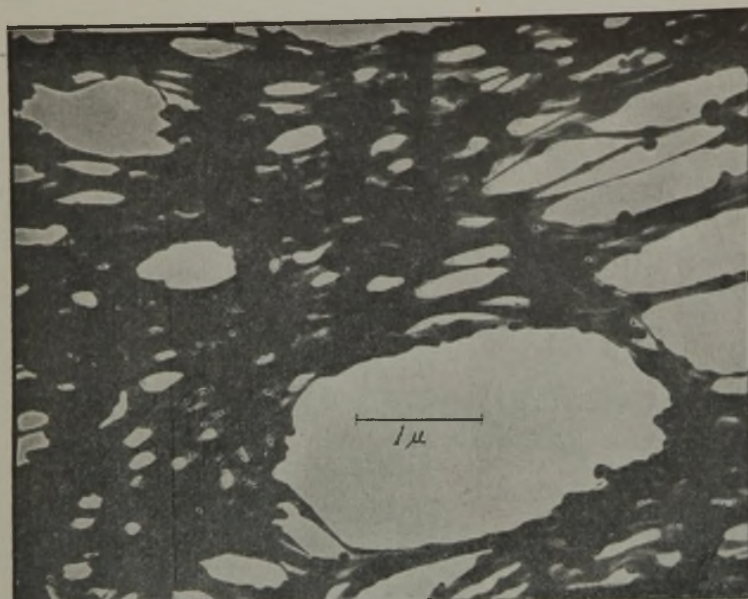


Figure 9 (Top). Slightly Polymerized Vinyl Chloride ( $\times 17,000$ )

Figure 10 (Center). Fully Polymerized Vinyl Chloride, Koroseal ( $\times 105,000$ )

Figure 11 (Bottom). Polystyrene ( $\times 38,500$ )

disk is inserted at the bottom of the special object holder shown in Figure 12, the holder is placed in the object chamber, and a first exposure is made. Then the holder is taken out and the central inclined portion is rotated through  $180^\circ$  about its axis. After the holder has been reinserted backward into the object chamber, the second exposure is made; except for a reversal of its inclination with respect to the optic axis, the object occupies now the same position relative to the objective as in the first exposure. The impression of depth in the resulting stereopictures is striking.

#### DIFFRACTION PATTERNS

Of even greater value, especially for the chemist, is an adapter which converts the electron microscope into a high-precision electron diffraction camera for the determination of the crystalline structures of materials (1). This adapter replaces the usual projector lens by a unit containing, in addition to a magnetic projector lens, a specimen holder and a special focusing lens for the diffraction camera. When the electron microscope is used as a diffraction camera, the specimen is removed from the object chamber and inserted above the special focusing lens. The objective forms an exceedingly fine point image of the source, so that any part of the specimen is

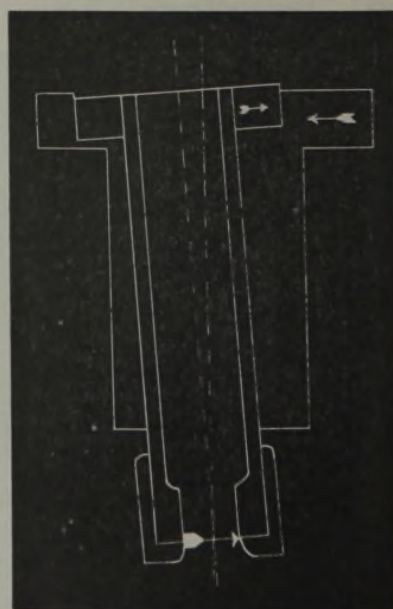
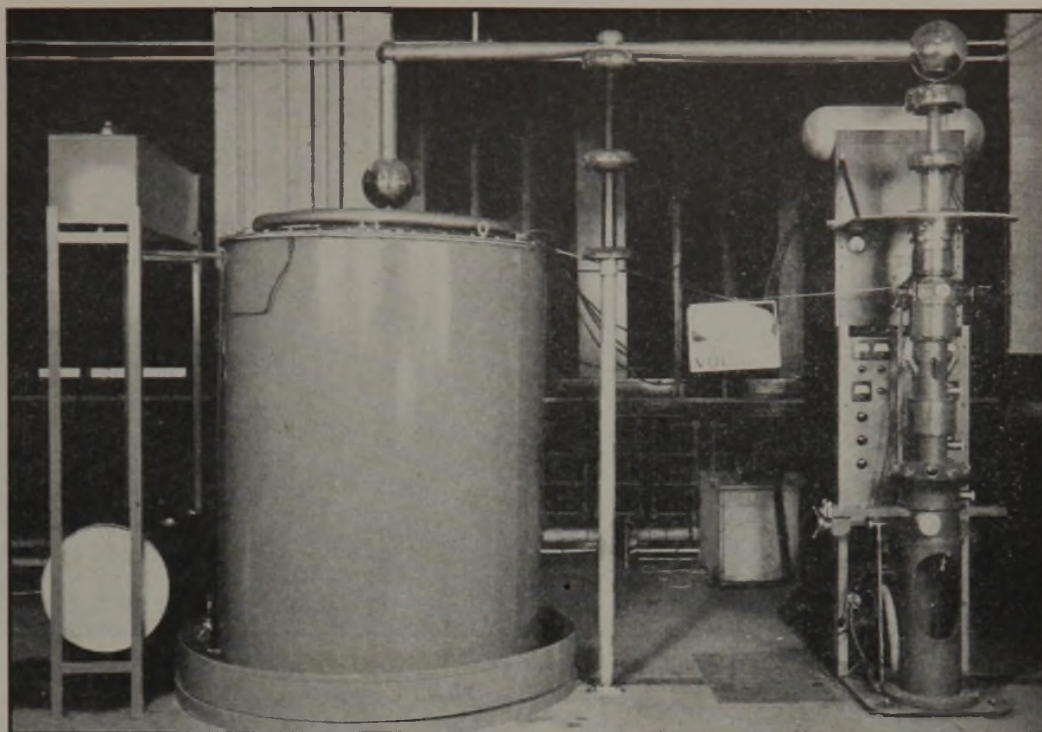


Figure 12. Schematic Diagram of Holder for Preparing Stereomicrographs



**Figure 13. High-Voltage Electron Microscope**



struck by electrons coming from one direction only. The projector lens is rendered inoperative. At the object the incident electrons are deflected or "diffracted" through angles which are characteristic of the relative separations and orientations of the atoms in the crystal lattice of the specimen. The focusing lens serves to concentrate all electrons deflected through a given angle and in a given direction at the same point of the plate.

The specimen holder of the camera is designed for a quick and convenient transfer of a specimen from the object chamber to the camera, so that the diffraction pattern, giving

information regarding the crystalline structure of the material, may be compared directly with the micrograph of the same substance. It is also convenient for the study of any other small specimen, whether transparent or opaque to electrons; in the latter case it must be so oriented that the electron beam just grazes the surface. Provision is made both for moving the specimen back and forth and for rotating it after it has been introduced into the vacuum.

If the substance studied consists of small crystalline particles oriented in random fashion, the deflection of the ray through a given angle may take place with equal proba-

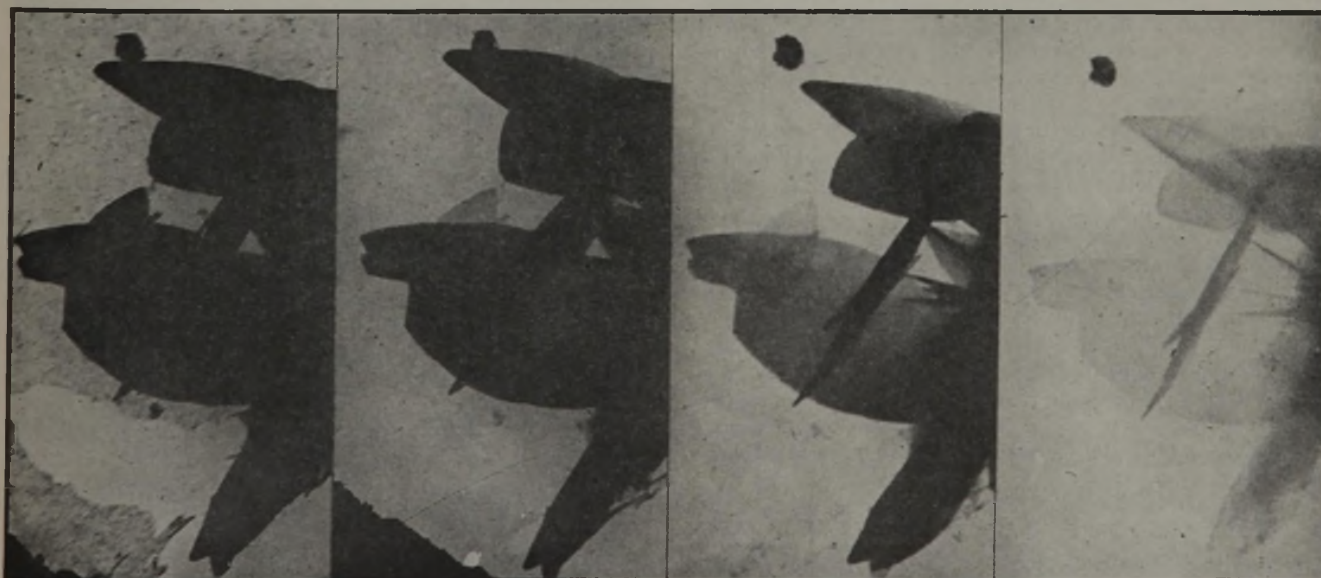
**Figure 14. Aluminum Oxide Monohydrate (Diaspore) Scales Taken at 30 to 200 Kilovolts ( $\times 8800$ )**

30 kv.

60 kv.

100 kv.

200 kv.



Light micrograph (courtesy R. F. Mehl),  $\times 5000$ Replica micrograph,  $\times 25,000$ 

Figure 15. Pearlite Structure in Steel

bility in any azimuth, so that the diffraction points on the plate arrange themselves in circular rings about the axis, giving rise to a so-called Debye-Scherrer diagram. From the diameters of the rings may be determined the spacings and relative orientation of neighboring atoms in the crystal lattice. This can be done to within 3 per cent.

#### HIGH-VOLTAGE MICROSCOPE

It has already been mentioned that the scattering and absorption of electrons by matter is such that only very thin specimens can be examined successfully with the standard electron microscope, which has an accelerating voltage of 60 kilovolts. In many fields of investigation this represents no particular limitation. Particularly in the study of very fine structures and disperse material, where the thicknesses are comparable to the widths of the individual entities, the substances are adequately transparent. Not infrequently the operation at voltages below 60 kilovolts presents a definite advantage; greater image contrasts are possible and, hence, easier recognition of very thin structures. However, in a number of other cases, such as the study of the inner structure of large bacteria and the study of cut sections in histological research, the thickness of the specimen is such that the field appears completely opaque or that interesting structures appear only with inadequate definition. Under such circumstances the use of electrons of greater velocity and, hence, greater penetration becomes profitable.

With this in mind, an electron microscope operating with electrons accelerated through potential differences up to 300 kilovolts was constructed (9). The principal modification of the instrument rests in the high-voltage equipment (Figure 13), which is housed in a large separate oil tank, and in the design of the "electron gun", in which the electrons acquire their high velocity. The latter is divided into two sections, the corona ring separating them being maintained at a potential halfway between that of the cathode and of the ground.

Figure 15 shows the effect of accelerating voltage on the contrast and perception of detail in the image of a group of aluminum oxide monohydrate (diaspore) scales placed

on a thin celluloid film. The latter is clearly visible only in the 30-kilovolt picture. All of the oxide scales, with the exception of a very small one, appear completely opaque so that it is impossible to distinguish one from another. As the voltage is increased, the scales become progressively more transparent and reveal more detail, particularly where they are superposed. At 200 kilovolts all of the scales are largely transparent, even those set practically on edge on the supporting film; the thinnest scale has nearly disappeared. By employing the higher voltages it was found possible for the first time to obtain satisfactory pictures of organic sections prepared with a microtome, though they can scarcely be made thinner than 0.00008 inch.

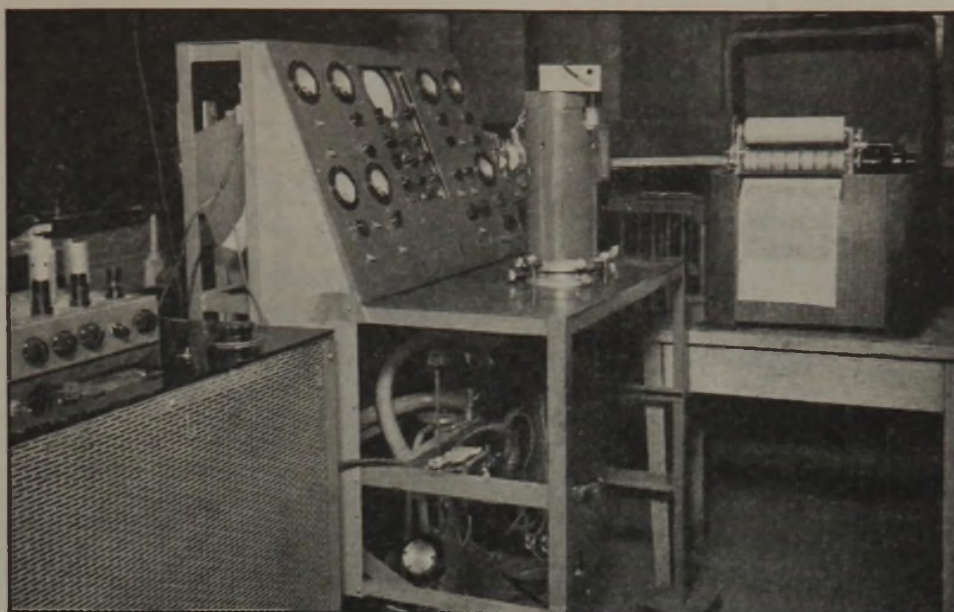
#### REPLICA TECHNIQUE

Although the high-voltage microscope extends the range of thickness which can be examined with the electron microscope, it does not, any more than the standard instrument, make possible the direct observation of the surfaces of opaque specimens. The utilization of electrons reflected at the surface of the specimen for the formation of the image, analogous to the use of reflected light in the metallographic light microscope, does not solve this problem, since reflected electrons are too inhomogeneous in velocity to lead to satisfactory pictures. Two techniques have been worked out, however, which make use of the high resolving power obtainable with electrons in the study of opaque specimens such as polished and etched metallographic sections.

The first of these (10) makes use of the standard electron microscope. It involves the preparation of a plastic replica of the surface, thin enough to transmit electrons readily. A procedure which has given satisfactory results requires an initial evaporation of silver onto the surface in vacuum. The silver coating, bearing the negative imprint of the surface, is then pulled off and a collodion solution flowed over its original surface of contact. When the collodion has dried, the silver may be dissolved off with nitric acid and the positive collodion replica is left.

Figure 15 shows an enlarged oil-immersion light micrograph of fine pearlite structure in steel. The structure is

Figure 16. Scanning Microscope Employing Multiplier and Facsimile Recorder



only partially resolved, since it is to a considerable extent beyond the limit of resolution of any light microscope. Figure 15 also gives an electron micrograph of a replica of the same specimen at four times as great magnification; the detail is sharp and perfectly resolved. It is thus clear that the electron microscope, in conjunction with the replica technique, represents a considerable advance over the metallographic microscope in the resolution of fine surface detail.

#### SCANNING MICROSCOPE

The second method of surface investigation prepares a picture of the surface of the opaque specimen directly. The scanning electron microscope utilized (8) differs basically both from the standard electron microscope and the conven-

tional light microscope. In place of forming the complete image simultaneously, the intensity of a single minute picture element, corresponding to a halftone dot in the printed reproduction of a photograph, is recorded at any one time; as in electric picture transmission and television, the final picture is built up from a great number of such elements of different intensity.

In brief, a succession of electrostatic lenses forms a greatly reduced image of an electron source on the object; the diameter of this "electron spot" is less than 0.000001 inch, corresponding to a single picture element of the final image. The secondary electrons given off by the object where struck by the electron beam measure the relative "brightness" of that particular portion of the object. Returning through

Figure 17. Scanning Micrograph of Carbonyl Iron in Bakelite ( $\times 6000$ )

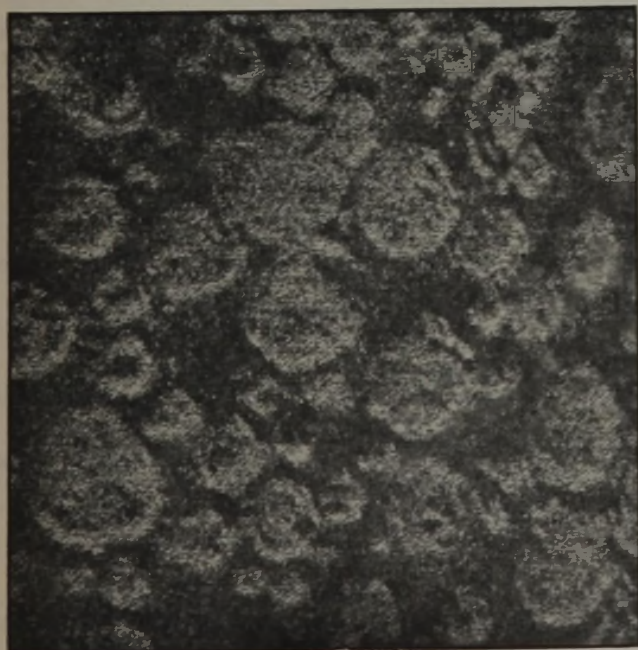
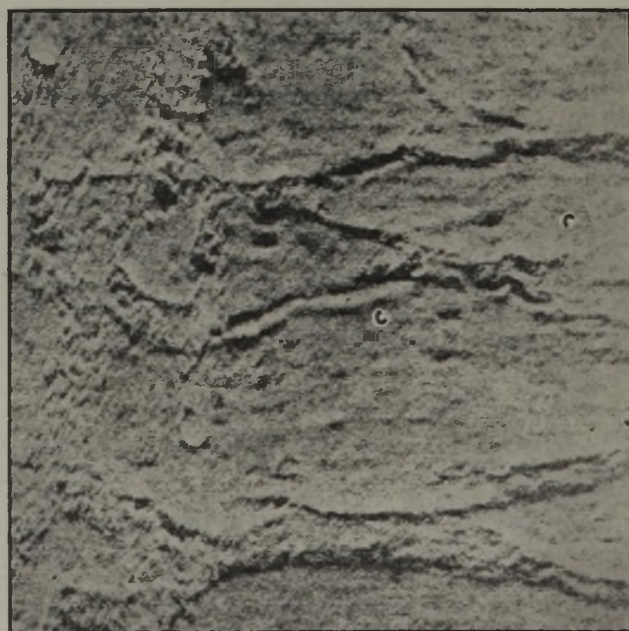


Figure 18. Scanning Micrograph of Slightly Annealed Brass ( $\times 3000$ )



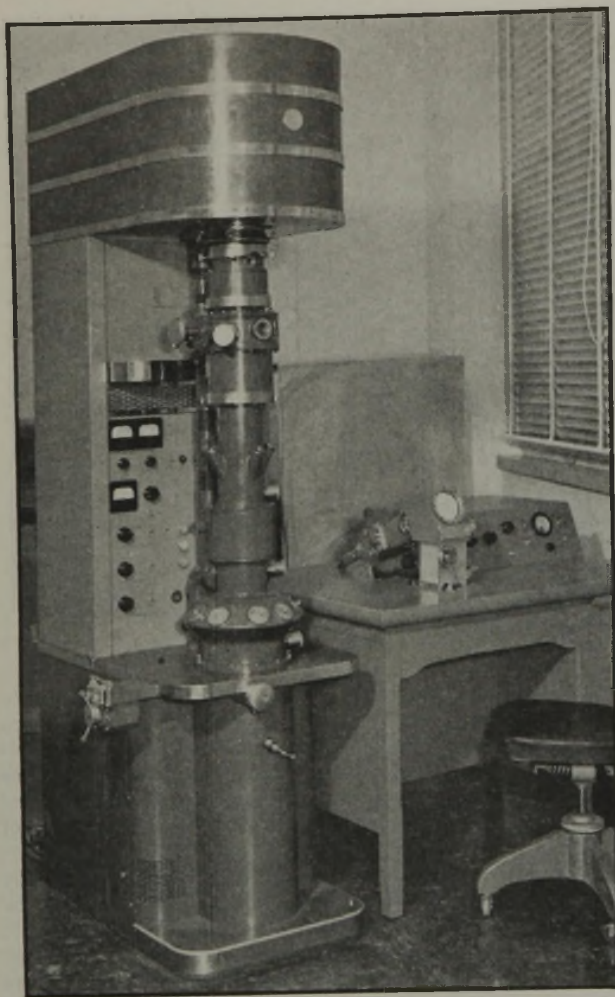


Figure 19. Small Desk-Model Instrument in Comparison with Standard Commercial Electron Microscope



final image on the rear of the fluorescent screen which is deposited on a plate glass disk. The magnification of the microscope, which operates with two magnetic lenses of fixed strength, is approximately 5000. The resolving power of the instrument is such that subsequent enlargements of as high as twenty fold are required to show all the detail present in the negatives.

The small volume of the instrument makes air locks unnecessary, for its complete evacuation takes only about 2 minutes. Focusing is accomplished by varying the stabilized lens current. In view of the small size of the instrument, the relatively few controls required to operate it are all within easy reach.

Figure 19 shows an experimental model of the small type of microscope beside a standard commercial microscope so that the relative sizes of the two instruments may be readily compared.

#### CONCLUSIONS

The electron microscopes described may be expected to play an increasing role in the furtherance of chemical research. The few applications demonstrated will suggest others in related fields. In some cases the interpretation of observations may not be easy. The discovery of the possibility of forming images with electrons has opened up to the scientist vast regions which had heretofore been probed only by the cautious groping of ingenious indirect methods. A barrier to vision, regarded as unsurmountable by the optical designer only a decade ago, has fallen.

Many unsolved problems of basic importance to life and work lie hidden in the unexplored realms of biology, physics, and chemistry, and their subdivisions such as medicine, bacteriology, the study of viruses, metallurgy, ceramics, plastics, and synthetics. Society may look forward with assurance to the time in the relatively near future when the researches made possible by the electron microscope will result in discoveries which will greatly enhance our health, efficiency, and comfort.

With the availability of the small instrument (and it will be available where necessary to the war effort), the broadest attack in the history of science on the so-called submicroscopic mysteries becomes possible.

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the last lens, they fall on an inclined fluorescent screen, whose resulting light emission controls the output current of an electron multiplier. This current, after further amplification, ultimately controls the intensity of the halftone lines in the image printed by a facsimile recorder, the image being recorded in synchronism with the displacement of the fine electron spot relative to the specimen surface.

Figure 16 shows a voltage supply unit, the control panel of the scanning microscope, the vacuum chamber, and the recorder. With this instrument numerous pictures have been obtained with resolutions of the order of 0.000002 inch, considerably better than can be obtained with the light microscope. A typical example is the micrograph of carbonyl iron (Figure 17). The structure of the scanning lines is so fine as to be scarcely visible; the contrast is excellent. Figure 18 shows a specimen of slightly annealed brass. Here also much detail is revealed.

#### SMALL ELECTRON MICROSCOPE

In the study of colloids, viruses, and macromolecules in particular, a fixed magnification and a relatively low operating voltage, giving large contrasts, has proved satisfactory. Hence a new electron microscope has been developed, distinguished by compactness and simplicity of operation. Mounted on an ordinary desk, the microscope column measures only 16 inches from electron source to fluorescent screen or plate. The observer, seated at the desk, views the

# Isopropyl Alcohol-Water System

## Density-Composition Data and Pycnometric Technique

W. M. LANGDON AND D. B. KEYES

University of Illinois, Urbana, Ill.

The density of pure anhydrous isopropyl alcohol, prepared by treatment with calcium oxide and subsequent fractionation until the still liquid and distillate were identical, was found to be  $0.77223 \pm 0.00002$  gram per ml. at  $35^\circ\text{C}$ .

Density-composition data were obtained for the system isopropyl alcohol-water at

$35^\circ\text{C}$ . The average deviation of the experimental values from the smoothed data was within 0.05 mole per cent.

An improved pycnometric technique was developed for determining the composition of alcohol-water mixtures. The densities determined by this method agreed within 2 parts in 50,000.

FOR determining accurately and rapidly the composition of small alcohol-water samples, an improved pycnometric technique has been developed using 6-8 ml. pycnometer bulbs of the Ostwald type, fitted with ground-glass caps (Figure 1). The density-composition data of Lebo (5) for isopropyl alcohol-water mixtures, determined within  $\pm 0.1$  weight per cent, were of insufficient accuracy to be useful as reference values for this study. Also, since density data at  $35^\circ\text{C}$ . were required, new determinations were undertaken. Furthermore, the discordance in the values reported in the literature (1-5, 7) at  $20^\circ$  and  $25^\circ\text{C}$ . necessitated the preparation of pure anhydrous alcohol as a standard.

### PREPARATION OF PURE ANHYDROUS ISOPROPYL ALCOHOL

Isopropyl alcohol (c. p. grade Petrohol, 99 weight per alcohol, Standard Alcohol Company) was purified by drying over powdered calcium oxide followed by fractionation in a laboratory distillation column of seven to eight theoretical plates until the density of the distillate was the same as that of the still liquid.

The alcohol was first subjected to batch fractionation in a large still with four bubble-cap plates. Since the liquid in the still pot was contaminated with rust, the liquid on the first plate was used in the subsequent measurements.

The alcohol from this fractionation was then refluxed over powdered calcium oxide for a period varying from 6 to 36 hours. The top of the reflux condenser was provided with an air drying (sulfuric acid) train to exclude the moisture of the air. Following this operation the alcohol, while still boiling slightly, was filtered under vacuum and then purified by simple distillation under anhydrous conditions. To prevent any gaseous material from remaining in the condensate, the distillate was only partially condensed. The condensed alcohol, while still boiling, was connected to the assembly (Figure 2) and allowed to cool prior to the determination of its density (described in the section of pycnometric technique).

By repeated refluxing with fresh calcium oxide, the density of this alcohol was found to be reduced to  $0.77231$  gram per ml. (in vacuo).

After treatment with calcium oxide, the alcohol was subjected to batch fractionation in a laboratory column giving seven to eight theoretical plates operated at essentially total reflux. To maintain anhydrous conditions, the air inside the column and above the condensate was dried by a sulfuric acid bubbler. Successive samples were removed from the condensate trap to sampling vials connected to the take-off tube by a loose-fitting, one-hole rubber stopper. The moisture absorbed by the top layer of alcohol from the air in the vial did not interfere with the subsequent density determinations since check measurements, in which the vial was filled with anhydrous air, gave the same density value as the above procedure.

When the amount of liquid in the still pot was reduced to approximately 15 per cent of its original volume and the density of the successive condensate samples had approached a minimum value, the still pot was rapidly removed while the alcohol was still boiling; thus none of the holdup in the column could drain back. The still pot was then fitted with the assembly shown in Figure 2 and allowed to cool prior to the density determination.

The density of anhydrous isopropyl alcohol was taken to be  $0.77223 \pm 0.00002$  gram per ml. (in vacuo at  $35^\circ\text{C}$ .), the average minimum value of liquid and condensate samples determined in several runs. The results of a typical run (Table I) show the sensitivity of this procedure to small traces of water. The density of some alcohol dried over calcium oxide differed from the above value for anhydrous alcohol by  $0.00008$  gram per ml. The density of the first fraction, obtained upon distillation of this material in the small laboratory column, differed by  $0.00084$  gram per ml.

### DENSITY-COMPOSITION DATA

80-100 MOLE PER CENT ALCOHOL. Alcohol-rich samples (80-100 mole per cent) were made up by mixing alcohol, which had been dried by refluxing over calcium oxide, with distilled water. The data obtained over the range 98-100 mole per cent alcohol (Table II) were extrapolated back to the density of pure anhydrous alcohol obtained by fractionation in order to compute the density-composition values.

TABLE I. DENSITY OF PURE ANHYDROUS ISOPROPYL ALCOHOL

Sample No. <sup>a</sup>	Density, Gram./Ml. <sup>b</sup>	Sample No. <sup>a</sup>	Density, Gram./Ml. <sup>b</sup>
C	0.77231	8V	0.77232
1V	0.77307	9V	0.77223
2V	0.77260	10V	0.77223
3V	0.77232	L	0.77224
4V	0.77228	L	0.77224
5V	0.77232	L	0.77221
6V	0.77226	L	0.77222
7V	0.77222		

<sup>a</sup> C = liquid charged in still. V = vapor removed as condensate; the numbers preceding indicate successive 10-ml. samples. L = liquid remaining in still pot.

<sup>b</sup> In vacuo at 35° C.

This alcohol was used in making up the samples rather than the pure anhydrous alcohol since it was difficult to prepare adequate quantities of the latter. In addition, the authors felt that this procedure would be as accurate as one using anhydrous alcohol; the extremely hygroscopic nature of the latter, compared to alcohol dried over calcium oxide, would necessitate a more detailed technique.

A 25-ml. Erlenmeyer flask was filled with approximately 15 ml. of alcohol by the assembly (Figure 2) described in the section on "density of alcohol-rich samples". The Erlenmeyer flask was fitted with a one-hole rubber stopper (treated with rich alcohol) which was closed by a tight-fitting glass plug. The alcohol added to the flask was weighed, and appropriate amounts of water were poured in as rapidly as possible and weighed. Throughout these operations care was taken that the rubber stopper was not wet by the alcohol or water at any time. In a similar manner water and then alcohol were weighed out.

The flask was vigorously shaken, and two or three density measurements were made. Up to this time the rubber stopper had not come in contact with the alcohol. To determine whether any material had been extracted from the rubber stopper that might cause the density measurements to be high, five check runs (Table III, runs 24-28) were made using an ordinary 25-ml. glass specific gravity bottle. The capillary opening in the glass stopper was plugged with a thin glass rod. The opening was the same size as that in the rubber stoppers

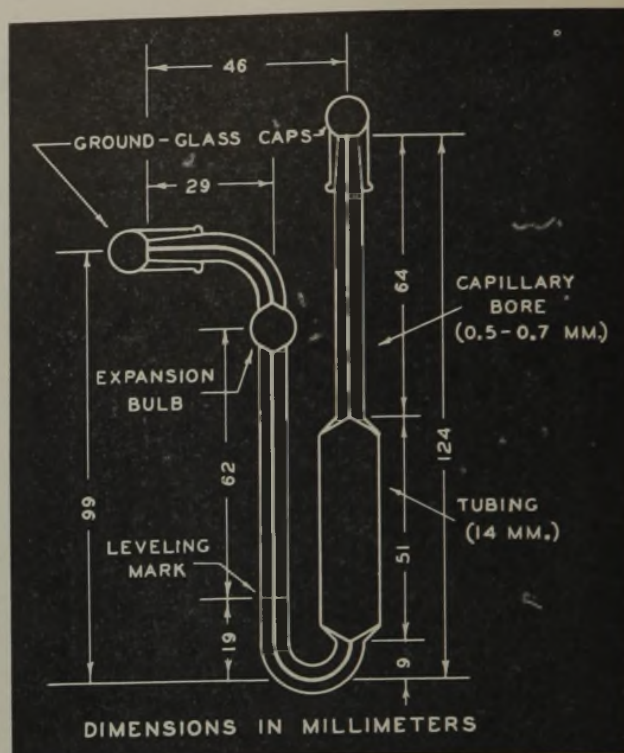


Figure 1. Pycnometer of 4-Ml. Capacity

used with the Erlenmeyer flasks. No appreciable difference was observed between these samples and those made up in the Erlenmeyer flasks.

**0-90 MOLE PER CENT ALCOHOL.** Samples of lower alcohol composition (0-90 mole per cent) were prepared by mixing with water 99 weight per cent alcohol (c. p. grade Petrohol) which had been distilled and collected at the boiling point. No precautions to ensure anhydrous conditions were taken. The density of this alcohol was measured in the manner described above after the preparation of every three or four samples. By reference to the density-composition data of Table II, the amount of water present in the alcohol itself could thus be determined, before dilution. As a check on the continuity of the data obtained with this modification of technique, the range of concentration studied was chosen to include part of the region studied with alcohol dried over calcium oxide. The density-composition data obtained were smoothed algebraically and are presented in Table IV.

#### CALCULATION OF MOLE PER CENT COMPOSITION

In the calculation of the composition of the samples the weights in air were corrected to weights in vacuo by the following equation (8):

$$M = (1 - d/d' + d/d'')m = F(m) \quad (1)$$

$d$  = density of air  
 $d'$  = density of liquid being weighed  
 $d''$  = density of weights  
 $M$  = true weight in vacuo  
 $m$  = apparent weight in air  
 $F$  = factor for converting apparent weight to true weight in vacuo

TABLE II. DETERMINATION OF WATER IN ORIGINAL ALCOHOL<sup>a</sup>

Run No.	Wt. in Air		Wt. Corrected		Mole % Water	Density		Deviation $\times 10^5$
	Water	Orig. alc.	Water	Orig. alc.		Exptl.	Calcd.	
Orig. alc.						0.77233	0.77235	-2
<b>Water Weighed Out First; <math>M_{\text{water}} = 1.0010</math> m; <math>M_{\text{alc.}} = 1.0013</math> m; Anhydrous Conditions</b>								
11	0.0411	19.1266	0.0411	19.0384	0.71	0.77288	0.77287	1
26	0.0439	14.4243	0.0439	14.4431	1.00	0.77318	0.77309	9
10	0.0457	13.6446	0.0457	13.6623	1.10	0.77311	0.77317	-6
3	0.0751	19.3516	0.0752	19.3768	1.28	0.77330	0.77332	-2
1	0.0819	17.8253	0.0820	17.8485	1.51	0.77346	0.77353	-7
27	0.0719	13.4484	0.0720	13.4659	1.75	0.77378	0.77375	3
12	0.1021	17.7160	0.1022	17.7390	1.88	0.77384	0.77388	-4
<b>Alcohol Weighed Out First; <math>M_{\text{water}}</math> and alc. = 1.0013 m; Anhydrous Conditions</b>								
25	0.0204	13.6177	0.0204	13.6354	0.50	0.77275	0.77271	4
13	0.0316	19.1266	0.0316	19.1519	0.55	0.77276	0.77275	1
14	0.0648	17.0506	0.0649	17.0728	1.25	0.77334	0.77330	4
24	0.0662	13.3989	0.0663	13.4163	1.62	0.77367	0.77363	4
16	0.0937	16.8562	0.0938	16.8781	1.82	0.77387	0.77382	5
21	0.0812	14.4525	0.0812	14.4713	1.84	0.77387	0.77384	

<sup>a</sup> Nomenclature:

$M$  = true weight in vacuo, grams

$m$  = apparent weight in air, grams

Orig. alc. = alcohol (containing a slight amount of water) used in samples

Wt. in air = net weight (grams in air) of water and original alcohol used in making up samples

Wt. corrected = grams in vacuo (Equation 1)

Mole % water =  $100(m_{\text{water}}/18.016)/(m_{\text{water}}/18.016 + M_{\text{alc.}}/60.06)$

Density = grams/ml. in vacuo at 35° C. Experimental values determined by pycnometric method; calculated values from equation, density =  $0.77000 + 0.00190 [2.35 + 0.730 (\%) - 0.0226 (\%)^2 + 0.0363 (\%)^3]$ , determined by method of least squares

Since it turned out that the accuracy of the data was within 0.05 mole per cent and the factors for water and alcohol differed by 0.03 per cent, this correction to true weight in vacuo could have been neglected. The values of the apparent weight in air and the true weight in vacuo for all of the runs are listed in Tables II and III, together with the factors used in obtaining them.

Table II lists the data used in determining the composition of the alcohol refluxed over calcium oxide. In calculating these compositions the slight amount of water present in the alcohol itself was first ignored. By extrapolating these data by the method of least squares (9) to the density previously determined for the anhydrous alcohol (0.77223 gram per ml.), the composition of the original alcohol (0.77233 gram per ml.) was found to be 0.16 mole per cent water. This correction was applied to the compositions of Table III.

#### PYCNOMETERS IN DENSITY DETERMINATIONS

The density measurements were made in 6-8 ml. pycnometer bulbs of a modified Ostwald type fitted with ground-glass caps (Figure 1). In using a pycnometer, the bent arm was fitted with a short rubber tube provided with pinch and screw clamps, and another longer tube was attached at this point by a short piece of glass tubing. While the clamps were held open, oral suction was applied to the inverted pycnometer, the straight arm of which was dipped into the sample, and the bulb was filled. The bent arm was immediately closed off by release of the pinch clamp, and the pycnometer was removed from the sample vial and suspended in an upright position in a constant-temperature bath held at  $35 \pm 0.02^\circ \text{C}$ . (A bath above room temperature, usually above  $30^\circ \text{C}$ . in the summer, prevented the freezing of the pycnometer caps and their breakage upon removal.)

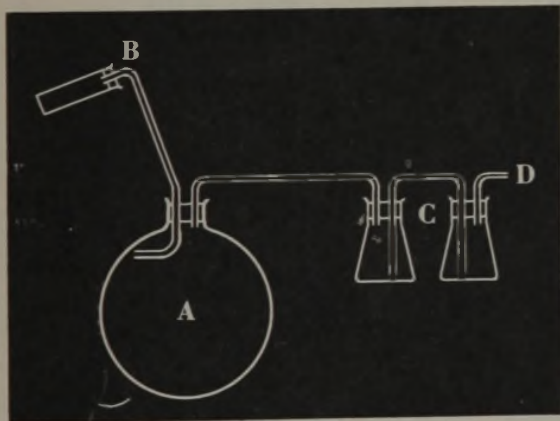


Figure 2. Assembly for Anhydrous Samples

The temperature of the sample was always a few degrees below  $35^\circ \text{C}$ . As the temperature inside the pycnometer approached that of the thermostat, the liquid was forced out of the open (straight) end of the bulb by thermal expansion, while the liquid level in the closed (bent) arm remained essentially constant. When expansion of the pycnometer liquid had ceased at  $35^\circ \text{C}$ ., the level in the closed capillary arm was adjusted to the mark. During this operation precautions were taken to ensure that the open end of the bulb was covered by a thin film of liquid and not by a large bubble. The outside edge of the film of liquid was touched with a blotter, leaving a slight film around the capillary opening. When the remaining film of liquid had evaporated, the rubber tube on the bent arm was straightened, which caused the

liquid to move a short distance into the bulb; the pinch clamp was then removed. This procedure prevented any liquid from being forced out of the open end by the shaking that took place when the pinch clamp was removed. The pycnometer was immediately removed from the bath and dipped into a beaker of distilled water to remove any dirt that might have collected on it from the water in the thermostated bath. Both ends were closed with the ground-glass caps to prevent loss in weight, the bulb wiped with a towel and allowed to come to room temperature. After reaching room temperature, the bulb was wiped lightly with a linen handkerchief to remove any lint from the towel and suspended from the balance.

In all weighings of the pycnometers, a similarly constructed counterpoise was used. The density (grams per ml. in vacuo at  $35^\circ \text{C}$ .) of the sample was calculated from the equation,

$$d_s = (m_s/m_w)(d_w - d_a) + d_a = F(m_s) + d_a \quad (2)$$

where  $d_s$  = density of sample  
 $d_a$  = density of air  
 $m_s$  = apparent net weight of sample in air  
 $F$  = pycnometric factor  $(d_w - d_a)/m_w$ , determined by calibration with conductivity water  
 $d_w$  = density of water  
 $m_w$  = apparent net weight of conductivity water in filled pycnometer

The bulbs were calibrated with conductivity water ( $d_w = 0.99406$  gram per ml. at  $35^\circ \text{C}$ ., 6) and checked against one another with several samples of alcohol-water mixtures. The densities determined by this method agreed to within 2 parts in 50,000 giving a maximum error of approximately 0.02 weight per cent alcohol, or 0.05 mole per cent alcohol.

#### DENSITY OF ALCOHOL-RICH SAMPLES

The preceding technique was modified as follows for alcohol-rich (90-100 mole per cent) samples which absorbed moisture rapidly from the air: The assembly shown in Figure 2 was used in measuring out alcohol which contained more than 99 mole per cent alcohol. It consisted of a sulfuric acid drying train, C, a round-bottom flask, A, containing the anhydrous alcohol, and a bent capillary tube, B, for delivering the alcohol to the sample vial.

The alcohol obtained by refluxing over calcium oxide or by fractional distillation was collected in flask A. The sample vial, or Erlenmeyer flask, was connected to the flask at B by a loosely fitting, one-hole rubber stopper. In the cases where the density of pure anhydrous alcohol was being measured and where alcohol was measured out first, the humid air was forced from the sample vial by supplying air to D with flask A standing straight up. Flask A was then tilted to one side, and alcohol was forced into the vial. In the cases where water was measured out first, the sample vial, containing a weighed amount of water, was filled with alcohol without any excess air passing through the system. When the desired amount of alcohol had been measured out, flask A was partially straightened in order to allow the alcohol in the capillary tube to suck back. The sample vial was then removed and the opening in the stopper closed by means of a tightly fitting glass plug. In a few seconds the air pressure built up enough to force the remaining alcohol in the capillary out and thus leave the assembly ready for another sample.

After the alcohol was weighed (and the desired amount of water measured out if the alcohol had been added first) the sample was mixed. In cases where the density of anhydrous alcohol was being determined, the weighing and mixing were dispensed with. The glass plug was then removed and the end of the pycnometer immediately inserted into the opening. The diameter of the opening was made slightly larger than the pycnometer end to prevent a vacuum in the sample vial while





TABLE III. DENSITY-COMPOSITION DATA (Concluded)

Run No.	Wt. in Air		Wt. Corrected		Wt. from Orig. Alc.		Mole % Water	Density		Deviation × 10 <sup>4</sup>
	Water	Orig. alc.	Water	Orig. alc.	Water	Alcohol		Exptl.	Calcd.	
Alcohol Weighed Out First; $M_{water} = 1.0010 m$ ; $M_{alc.} = 1.0013 m$										
Original alcohol (2.39 weight per cent water)							7.54	0.77859		
78	12.0791	5.6636	12.0912	5.6710	0.1355	5.5355	88.04	0.93799	0.93799	0
79	15.7548	6.0567	15.7706	6.0646	0.1449	5.9197	89.96	0.94682	0.94684	-2
80	16.5732	4.9780	16.5398	4.9845	0.1191	4.8654	91.97	0.95614	0.95614	0
81	13.2565	2.9148	13.2698	2.9186	0.0698	2.8488	93.98	0.96513	0.96515	-2
82	24.9746	3.5880	24.9996	3.5927	0.0859	3.5068	95.98	0.97369	0.97369	0
83	14.3690	1.0106	14.3834	1.0119	0.0242	0.9877	97.98	0.98283	0.98276	7
Alcohol Weighed Out First; $M_{water} = 1.0011$ ; $M_{alc.} = 1.0013 m$										
Original alcohol (1.96 weight per cent water)							6.24	0.77744		
84	6.3071	12.6004	6.3147	12.6168	0.2469	12.3699	63.88	0.85739	0.85734	5
85	12.4941	12.1987	12.5078	12.2146	0.2390	11.9756	78.01		Sample no good	
86	7.0154	10.7005	7.0231	10.7144	0.2097	10.5047	69.65	0.87195	0.87200	-5
87	9.2804	6.9796	9.2906	6.9887	0.1368	6.8519	82.10	0.91274	0.91274	0
88	9.9410	10.8654	9.9519	10.8795	0.2129	10.6666	76.06	0.89109	0.89120	-11
Alcohol Weighed Out First; $M_{water} = 1.0010 m$ ; $M_{alc.} = 1.0013 m$										
Original alcohol (1.96 weight per cent water)							6.24	0.77744		
89	13.3513	6.2896	13.3647	6.2978	0.1232	6.1746	87.83	0.93750	0.93703	47
90	13.0828	8.6410	13.0958	8.6522	0.1693	8.4829	83.91	0.92004	0.92003	1
91	18.0763	7.4540	18.0944	7.4637	0.1461	7.3176	89.26	0.94358	0.94360	-2
92	20.1639	6.0416	20.1841	6.0495	0.1184	5.9311	91.94	0.95600	0.95600	0
93	13.0208	2.8401	13.0338	2.8438	0.0557	2.7881	93.99	0.96519	0.96519	0
94	21.0400	3.8221	21.0610	3.8271	0.0749	3.7522	94.94	0.96925	0.96925	0
95	22.1116	2.3531	22.1337	2.3562	0.0461	2.3101	96.97	0.97806	0.97806	0
96	16.5384	1.1800	16.5549	1.1815	0.0231	1.1584	97.95	0.98253	0.98262	-7
97	25.9444	1.0451	25.9703	1.0465	0.0205	1.0260	98.83	0.98726	0.98726	0

<sup>a</sup> Nomenclature:

- $M$  = true weight in vacuo, grams
- $m$  = apparent weight in air, grams
- Orig. alc. = alcohol (containing a slight amount of water) used in samples
- Wt. in air = net weight (grams in air) of water and orig. alc. used in making up samples
- Wt. corrected = grams in vacuo (Equation 1)
- Wt. from orig. alc. = weight of water (from orig. alc.) equals  $M(\text{orig. alc.})$  times weight % water in orig. alc.; weight of alc. (from orig. alc.) equals  $M(\text{orig. alc.})$  times weight % alc. in orig. alc.
- Mole % water =  $100(M_{water}/18.016)/(M_{water}/18.016 + M_{alc.}/60.06)$
- Density = grams/ml. in vacuo at 35° C. Experimental values determined by pycnometric method; calculated values from Table IV

<sup>b</sup> Sample made up in 25-ml. specific gravity bottle.

TABLE IV. PHYSICAL DATA OF ISOPROPYL ALCOHOL-WATER SYSTEM<sup>a</sup>

$x$	$d$	$d'$	$x$	$d$	$d'$	$x$	$d$	$d'$	$x$	$d$	$d'$
0	0.99406	0.00590	26	0.88468	0.00305	51	0.82788	0.00166	76	0.79443	0.00107
1	0.98816	0.00531	27	0.88163	0.00296	52	0.82622	0.00163	77	0.79336	0.00105
2	0.98285	0.00466	28	0.87867	0.00290	53	0.82459	0.00160	78	0.79231	0.00103
3	0.97819	0.00441	29	0.87577	0.00281	54	0.82299	0.00157	79	0.79128	0.00102
4	0.97378	0.00427	30	0.87296	0.00275	55	0.82142	0.00154	80	0.79026	0.00101
5	0.96951	0.00427	31	0.87021	0.00267	56	0.81988	0.00151	81	0.78925	0.00100
6	0.96524	0.00443	32	0.86754	0.00261	57	0.82837	0.00148	82	0.78825	0.00099
7	0.96081	0.00453	33	0.86493	0.00252	58	0.81689	0.00145	83	0.78726	0.00097
8	0.95628	0.00463	34	0.86241	0.00243	59	0.81544	0.00142	84	0.78630	0.00096
9	0.95165	0.00463	35	0.85998	0.00236	60	0.81402	0.00139	85	0.78534	0.00094
10	0.94702	0.00462	36	0.85762	0.00231	61	0.81263	0.00137	86	0.78440	0.00092
11	0.94240	0.00459	37	0.85531	0.00227	62	0.81126	0.00135	87	0.78348	0.00091
12	0.93781	0.00456	38	0.85304	0.00223	63	0.80991	0.00133	88	0.78257	0.00090
13	0.93325	0.00444	39	0.85081	0.00219	64	0.80858	0.00130	89	0.78167	0.00089
14	0.92881	0.00427	40	0.84862	0.00216	65	0.80728	0.00128	90	0.78078	0.00089
15	0.92454	0.00414	41	0.84646	0.00208	66	0.80600	0.00126	91	0.77989	0.00089
16	0.92040	0.00408	42	0.84438	0.00201	67	0.80474	0.00124	92	0.77900	0.00089
17	0.91632	0.00398	43	0.84237	0.00195	68	0.80350	0.00121	93	0.77811	0.00088
18	0.91234	0.00383	44	0.84042	0.00190	69	0.80229	0.00118	94	0.77723	0.00087
19	0.90851	0.00373	45	0.83852	0.00186	70	0.80111	0.00115	95	0.77637	0.00087
20	0.90479	0.00363	46	0.83666	0.00182	71	0.79996	0.00114	96	0.77550	0.00087
21	0.90116	0.00352	47	0.83484	0.00179	72	0.79882	0.00112	97	0.77463	0.00084
22	0.89764	0.00337	48	0.83305	0.00176	73	0.79770	0.00110	98	0.77379	0.00081
23	0.89427	0.00327	49	0.83129	0.00172	74	0.79660	0.00109	99	0.77298	0.00075
24	0.89100	0.00317	50	0.82957	0.00169	75	0.79551	0.00108	100	0.77223	.....
25	0.88779	0.00311									

<sup>a</sup> Nomenclature:

- $x$  = mole per cent alcohol
- $d$  = density in vacuo of isopropyl alcohol-water mixtures at 35° C., g./ml.
- $d'$  = density difference for interpolation, g./ml.

the bulb was being filled. The pycnometer was filled as rapidly as possible in the manner described. During the filling operation the top layer of alcohol was only momentarily in contact with the air that displaced the alcohol. Preliminary tests (with pure anhydrous alcohol) showed that the top layer of alcohol took up very little water during this operation and that the mixing of the top layer with the main body of alcohol was so slight that the density determination was not noticeably affected.

After the pycnometer was placed in the water bath, the procedure was modified slightly. After the bulb had been in the bath 3 minutes, the level was adjusted to 1/8 inch above the leveling mark and the liquid wiped off the end. The level was then adjusted to 1/4 inch above the mark, and the open end of the pycnometer covered with one of the ground-glass caps. This cap was removed at the time of the final adjustment when the liquid had reached 35° C. The remaining steps were the same as previously described.

## DISCUSSION OF DENSITY-COMPOSITION DATA

The density-composition data obtained for the system, isopropyl alcohol-water, were smoothed algebraically and listed in Table IV. In the range 0-10 mole per cent alcohol the data did not vary in a regular manner. Since check samples gave the same results, no attempt was made to smooth these data. The average deviation, except runs 48-55 and 89 which were neglected, was approximately 0.00004 gram per ml. (0.05 and 0.01 mole per cent error at 100 and 0 per cent alcohol, respectively).

In determining the amount of water in the alcohol which was dried by refluxing over calcium oxide, negative deviations from the smooth data were observed for those samples in which the water was weighed first, while positive deviations were noted when the alcohol was weighed first. This was to be expected, since the first method would tend to give lower density measurements due to the evaporation of a slight amount of water during the measuring out of the alcohol. In the second set of samples the deviation in the positive direction was caused by the evaporation of the alcohol during

the period when the water was measured out. The error involved in using these two methods was probably not compensative because the effect of evaporation on the weights of each component, as measured, would be less in the case where the water was measured out first. However, it was felt that by using these two methods a more correct result could be obtained.

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## Plate Factors in Fractional Distillation of Isopropyl Alcohol-Water System

The fractional distillation of isopropyl alcohol-water mixtures was studied in a four-plate bubble-cap column at superficial vapor velocities,  $U = 0.5$  to 1.2 feet per second, and at reflux ratios,  $L/V = 1, 2/3,$  and  $1/2$ .

Both over-all Murphree and local plate efficiencies showed nearly constant values over the range 18 to 55 mole per cent alcohol but decreased rapidly above 55 per cent. The local efficiency decreases at low concentrations of alcohol. Changes in reflux ratio and superficial vapor velocity affected these efficiencies very little.

The observed effect of viscosity on the formation of vapor bubbles, coupled with the parallel trends of plate efficiency- and viscosity-liquid composition curves, is suggested as further indication of the significance of physical properties of the liquid in plate-column fractionations.

The effect of barometric pressure on the results is discussed.

THE rapid growth of industries which employ distillation processes has emphasized the need of a more fundamental and analytical treatment of the problem of fractionating column design (5). The present investigation is a continuation of the work initiated by Keyes and Byman (6) and is confined to a study of the continuous rectification of mixtures of isopropyl alcohol and water in a bubble-cap column of four plates. This system was chosen because the

great variation of its physical properties with change in composition should have a marked effect on column operation. Moreover, the close similarity of this system to that of ethyl alcohol and water, studied by Keyes and Byman (6), allowed a critical comparison of the results.

## BUBBLE-CAP COLUMN

The apparatus comprised the following pieces of equipment: 65-gallon steam-heated kettle, four-plate rectifying column, total condenser, reflux and product rotameters, reflux heater, and sample coolers. The column was constructed of sheet copper and had a free vapor space of  $5 \times 5$  inches. Each plate was provided with a single bubble cap. The product stream from the condenser was recycled to the kettle to provide continuous operation. With the exception of an external heating element around the vapor take-off line and the sample coolers described below, the column is the same as that described in detail by Keyes and Byman (6).

Each of the vapor and liquid samples were drawn from the column through a 6-inch length of  $3/16$ -inch copper tubing surrounded by a water-cooled jacket; the ends of the sampling tubes projected 2 inches inside the sampling wells so that the liquid could be drawn directly from the main body of the stream.

PROCEDURE. Runs were made at reflux ratios (reflux to total vapor) of 1:1, 2:3, and 1:2, covering almost the entire composition range of the binary system isopropyl alcohol-water. In general, the runs were made at a superficial vapor velocity, based on the maximum cross section of the vapor path through the column (25 square inches), of 1 foot per second. To determine whether entrainment was taking place, runs were also made at velocities varying from 0.5 to 1.2 feet per second. In the region of the azeotrope where the difference between vapor and liquid compositions was small, most of the runs were made at a reflux ratio of 1:1.

Details of operation are described by Keyes and Byman (6). The apparatus was run for one or more hours until steady-state conditions were obtained. The rectification was continued at steady state for a minimum period of 4 hours in all cases except when the still liquid was less than 5 mole per cent alcohol; in that case the distillation was continued for 10 hours. At this point temperatures were recorded, and the operations continued throughout the sampling period of 3.5 to 4 hours.

Five samples of the liquid entering the top plate and leaving each of the four plates were taken simultaneously with five samples of vapor entering the bubble caps of the four plates and leaving the column above the top plate. All of the samples were

drawn from the column at a rate of 8 ml. per hour. The first 8 ml. of each sample served to purge the lines and were set aside; later they were returned to the kettle together with the analyzed portions. Three sets of 8-ml. samples were taken consecutively, except in the case of the initial runs (Table I, runs 1-26) where only one or two sets were taken. This procedure indicated whether or not the column was at equilibrium and showed the reliability of the samples. It was particularly important at very low alcohol concentration where the samples tended to become side streams and depleted the alcohol in the still.

The compositions of the several samples were determined pyrometrically from the density-composition data given in the second paper of this series (11). The equilibrium values used in calculating the plate efficiencies were taken from the first paper (10).

#### DISTILLATION RESULTS

The principal results of this investigation are summarized in Table I and in Figures 1 to 4. A detailed discussion of the derivation and calculation of the plate efficiencies,  $E_o$  and  $E$ , was given by Keyes and Byman (6).

The over-all Murphree efficiency,

$$E_o = 100(Y_n - Y_{n-1}) / (y_n^* - Y_{n-1})$$

where  $Y$  = composition of vapor leaving plate

$y^*$  = composition of vapor in equilibrium with liquid leaving plate

$n$  = plate under consideration

was computed directly from the vapor and liquid compositions for each case. In the case of total reflux, the values for the efficiencies for the fourth plate at concentrations between 65 and 69 mole per cent alcohol were found to be unreliable, probably because of small changes in the distillation rate; they were therefore neglected in plotting the curves.

The local Murphree efficiency,  $E$ , was calculated by the expression,

$$E = [100R/m] [\ln(1 - E_o m / 100R)]$$

where  $R$  = reflux ratio,  $L/V$

$m$  = slope of vapor-liquid equilibrium line, taken at arithmetic mean composition of liquid entering and leaving plate

According to Figure 4, both the over-all Murphree efficiency in terms of vapor compositions,  $E_o$ , and the local efficiency,  $E$ , show a marked variation with the composition of the liquid phase in the rectification of mixtures of isopropyl alcohol and water. Changes in reflux ratio and in the rate of distillation (superficial vapor velocity) have little influence on these efficiencies. These primary conclusions are derived mainly from the experimental values plotted in Figures 1, 2, and 3.

The characteristics of the vapor-liquid equilibrium relation prevented experimental study over the entire composition range for any given reflux ratio. At total reflux it was possible to investigate the range from 20 to 95 mole per cent alcohol; for the reflux ratio  $L/V = 2/3$ , the range from 10 to 65 mole per cent alcohol; and for  $L/V = 1/2$ , from 3 to 40 mole per cent alcohol.

In the case of total reflux, the range from 20 to 95 mole per cent was investigated at velocities varying from 0.8 to 1.2 feet per second. For the reflux ratio  $L/V = 2/3$ , separate curves are plotted for velocities of 1.1, 0.9, and 0.5-0.7 foot per second. The runs at different velocities for the reflux ratio  $L/V = 1/2$  are plotted on one graph (Figure 3). At high alcohol concentrations the accuracy of the data was such that no significant conclusions could be drawn, and the curve in that region is represented by a dotted line.

#### OVER-ALL MURPHREE AND LOCAL PLATE EFFICIENCIES

The influence of liquid composition on both over-all and local efficiencies is clearly shown by the curves in Figures 1, 2,

and 3. At  $L/V = 1$ , the value of  $E_o$  is practically constant at 91 per cent over the range of liquid composition, 20 to 55 mole per cent alcohol. In the range 55 to 68 mole per cent alcohol, the over-all efficiency dips sharply from 90 to 70 per cent. For the same reflux ratio the local efficiency shows a more gradual decrease with increasing liquid composition over the range 35 to 68 mole per cent alcohol; the local efficiency varies linearly from 85 at 35 mole per cent alcohol to 77 at 55 mole per cent. The curve then breaks sharply to 63 at 68 mole per cent alcohol. In the region of high alcohol concentration (above the azeotrope, 68.35 mole per cent alcohol) the curve shows the reverse tendency; the efficiencies are practically constant in the range of liquid concentrations from 95 to 80 mole per cent alcohol, and then break sharply close to the azeotrope composition.

For the reflux ratio  $L/V = 2/3$ , the same variation was observed as in the case of total reflux. However, over the median concentration range the effect of liquid composition on the over-all efficiency was more pronounced; there was a linear decrease from 98 to 91 over the range 15 to 55 mole per cent alcohol. In the range from 55 to 65 mole per cent the curve was practically coincidental with that for total reflux—that is, a sharp decrease from 91 to 80 per cent. The curve for local efficiency was identical with that for total reflux, being displaced lower by 3 per cent.

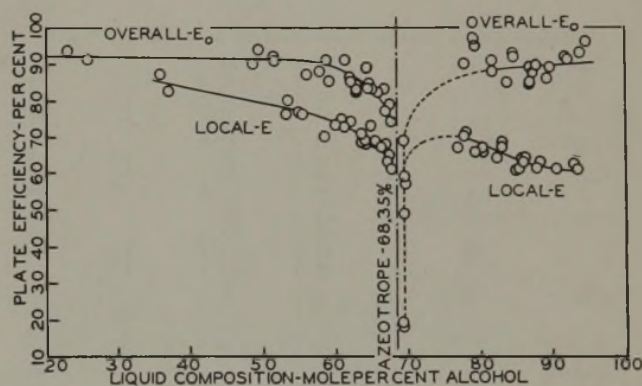


Figure 1. Plate Efficiencies at Total Reflux  $L/V = 1$  and Superficial Vapor Velocity  $U = 0.8-1.2$  Feet per Second

The curve for the reflux ratio  $L/V = 1/2$ , extending over the region of 3 to 40 mole per cent alcohol, shows a more pronounced change than those for the other reflux ratios; its efficiency is 220 at the low composition and 95 at the high. The curve for the local efficiency, however, shows the marked effect of the concentration gradients existing upon the plate. Where the over-all efficiency goes down sharply, the local efficiency increases at approximately the same rate to a maximum at 20 mole per cent alcohol.

In the regions where the operating line approaches the equilibrium curve closely, large deviations from the mean curve are noted. Since the calculation of the individual efficiency in these regions involves the subtraction of two numbers which are of the same order of magnitude, followed by subsequent division of the remainder by another value similarly derived, the values are extremely sensitive to errors. For the reflux ratio  $L/V = 1/2$ , the operating line was closer to the equilibrium curve than in the other two cases. Since the changes in alcohol concentration from plate to plate were extremely small, the calculated efficiencies show deviations of several hundred per cent. The same effect is to be noted in

TABLE I. SUMMARY OF EXPERIMENTAL RESULTS

NOMENCLATURE

$U_4$  = superficial vapor velocity above fourth plate, ft./sec.  
 $n$  = number of plate from bottom of column  
 $X_n$  = composition of liquid leaving plate, mole % alcohol

$X_{am}$  = arithmetic mean of composition of liquid entering and leaving plate  
 $E_o$  = over-all Murphree efficiency in terms of liquid composition  
 $E$  = local plate efficiency in terms of vapor composition

Run	$U_4$	$n$	$X_n$	$X_{am}$	$E_o$	$E$	Run	$U_4$	$n$	$X_n$	$X_{am}$	$E_o$	$E$
HIGH CONC. RANGE (69-94 MOLE % ALCOHOL); $L/V = 1$							MEDIUM CONC. RANGE (45-68 MOLE % ALCOHOL); $L/V = 2/3$ (Cont'd)						
61	0.8	4	86.8	85.2	85	61	34	1.1	4	63.2	64.2	88	67
		3	89.5	88.2	86	61			3	60.4	61.8	88	67
		2	92.0	90.8	92	61			2	56.6	58.5	93	70
		1	94.0	93.0	93	61			1	50.6	53.7	94	74
62	1.0	4	87.0	85.5	84	61	41	0.6	4	62.7	63.8	89	67
		3	89.7	88.3	89	63			3	59.5	61.1	91	69
		2	92.1	90.9	91	61			2	54.8	57.1	96	74
		1	94.2	93.1	96	62			1	46.3	50.5	94	77
1	0.8	4	78.1	76.9	90	67	42	0.7	4	62.3	63.5	87	65
		3	80.9	79.4	88	66			3	59.0	60.7	88	68
		2	83.9	82.4	85	64			2	54.2	56.6	97	73
		1	86.9	85.4	89	64			1	45.0	49.6	96	78
6	0.9	4	79.2	77.9	95	70	43	0.9	4	62.1	63.3	85	65
		3	81.7	80.5	88	66			3	58.6	60.4	89	68
		2	84.6	83.1	93	68			2	53.5	56.0	100	74
		1	87.8	86.2	90	64			1	44.6	49.0	95	77
7	1.2	4	79.1	77.7	97	71	44	1.1	4	62.5	63.4	76	59
		3	81.6	80.4	91	67			3	58.4	60.4	85	65
		2	84.6	83.1	92	67			2	53.2	55.8	97	63
		1	87.4	86.0	87	63			1	44.3	48.7	93	76
24	1.0	4	69.1	69.0			LOW CONC. RANGE (8-60 MOLE % ALCOHOL); $L/V = 2/3$						
		3	69.3	69.1	19	18	55	0.6	4	59.4	61.2	88	68
		2	69.4	69.3	69	59			3	53.7	56.5	101	79
		1	69.8	69.6	69	57			2	42.0	47.8	99	80
									1	14.6	28.3	99	87
MEDIUM CONC. RANGE (50-68 MOLE % ALCOHOL); $L/V = 1$							MEDIUM CONC. RANGE (40-60 MOLE % ALCOHOL); $L/V = 1/2$						
25	1.0	4	67.9	68.0			37	0.6	4	60.5	62.1	87	65
		3	67.7	67.8	74	61			3	56.7	58.5	95	69
		2	67.4	67.6	79	65			2	51.0	53.8	105	76
		1	67.0	67.2	77	63			1	42.0	46.5	99	78
27	1.0	4	67.4	67.6			38	0.7	4	59.6	61.5	88	65
		3	66.8	67.1	83	68			3	55.4	57.5	95	68
		2	65.9	66.4	82	67			2	49.7	52.6	99	73
		1	64.5	65.2	83	69			1	40.5	45.1	97	75
29	1.0	4	67.0	67.3			39	0.7	4	58.9	61.0	90	64
		3	66.0	66.5					3	54.5	56.7	97	66
		2	64.7	65.4	85	69			2	48.2	51.4	102	75
		1	62.0	63.4	85	68			1	39.1	43.6	97	74
31	1.2	4	65.9	66.4			40	1.0	4	59.8	61.6	91	62
		3	64.2	65.0	89	73			3	55.5	57.6	100	71
		2	61.3	62.8	91	74			2	49.8	52.6	103	76
		1	55.9	58.6	87	70			1	40.4	45.1	98	76
47	0.9	4	65.0	65.6	83	68	LOW CONC. RANGE (2-55 MOLE % ALCOHOL); $L/V = 1/2$						
		3	62.8	63.9	82	68	51	0.5	4	55.9	58.8	91	67
		2	59.1	61.0	85	73			3	47.8	51.8	93	73
		1	51.5	55.3	91	76			2	28.4	38.0	101	85
48	1.2	4	64.8	65.4					1	5.0	16.7	130	99
		3	62.8	63.8	83	69	53	0.7	4	51.7	55.6	92	65
		2	58.9	60.8	91	75			3	40.3	46.0	91	71
		1	51.2	55.0	92	77			2	18.3	29.3	104	86
49	0.9	4	62.4	63.5	84	69			1	4.1	11.2	127	84
		3	57.8	60.0			52	0.7	4	49.6	54.5	91	64
		2	49.5	53.5	94	80			3	34.4	42.0	83	67
		1	25.6	37.0	91	84			2	8.2	21.3	139	109
50	1.2	4	62.1	63.3	86	71			1	2.8	5.5	220	57
		3	57.7	59.9	88	73	54	1.1	4	49.6	54.1	93	67
		2	48.7	53.2	90	76			3	36.0	42.7	84	66
		1	22.6	35.6	94	87			2	12.0	24.0	121	97
28	0.9	4	66.6	66.9					1	3.4	7.7	151	78
		3	65.8	66.2	77	60							
		2	64.8	65.3	79	61							
		1	63.5	64.1	82	62							
30	1.0	4	65.7	66.2									
		3	64.4	65.0	88	67							
		2	62.6	63.5	91	69							
		1	60.3	61.4	86	67							
36	0.5	4	64.1	65.0	83	64							
		3	62.0	63.1	86	68							
		2	58.4	60.2	92	73							
		1	52.7	55.6	95	75							
35	0.8	4	63.2	64.2	82	64							
		3	60.7	62.0	85	65							
		2	57.1	58.9	89	68							
		1	51.1	54.1	92	72							

the case of the reflux ratio  $L/V = 1$  in the range above the azeotrope composition, where the trend of the efficiency curve is not well defined.

Neither the over-all Murphree nor the local plate efficiency represents the "actual" efficiency which, in general, lies in a median range between  $E_o$  and  $E$ . The assumption of rectilinear liquid flow with uniform concentration gradients used

decreasing liquid head with decreasing reflux ratios. Carey *et al.* (2) showed that the efficiency of rectification increases with the depth of submergence of the bubble-cap slots. Measurements made by Byman (1) indicate that the plate holdup is slightly and consistently less for the lower reflux ratios. If the effective bubble-slot submergence at moderate vapor rates can be considered proportional to the volume of

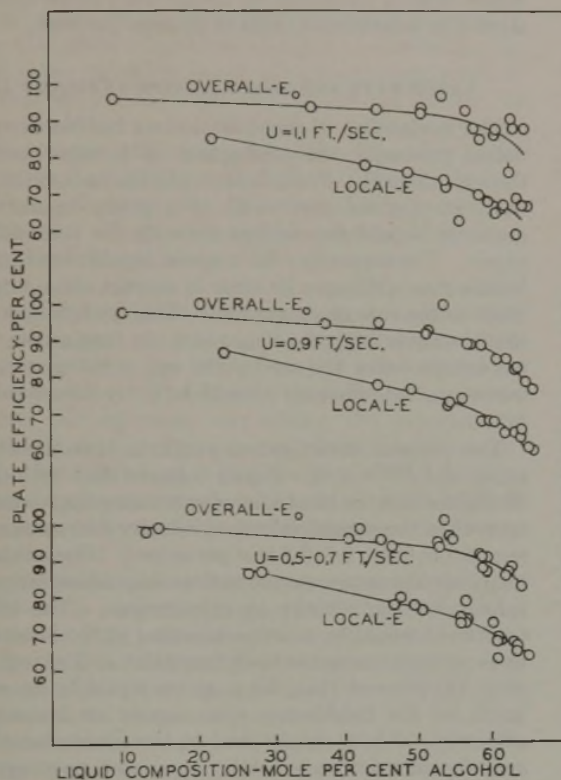


Figure 2. Plate Efficiencies at Reflux Ratio  $L/V = 2/3$

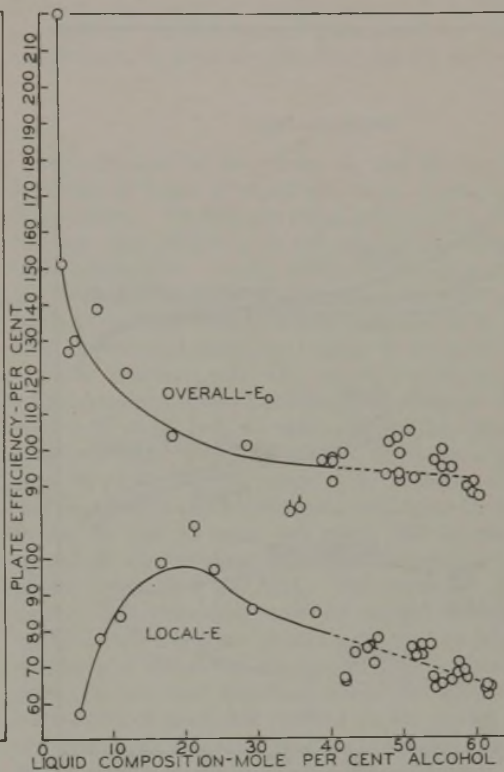


Figure 3. Plate Efficiencies at Reflux Ratio  $L/V = 1/2$  and Superficial Vapor Velocity  $U = 0.5-1.1$  Feet per Second

in the derivation of  $E$  (6) is less valid for the present case than for large-scale operations with plates of greater dimensions, since the liquid on each plate (of the laboratory column) is well agitated even at low rates of distillation. However, the trend of the "true" efficiency is probably best represented by the curves for local efficiency. This is shown by the parallel nature of the curves for local efficiency at reflux ratios of  $L/V = 1$  and  $2/3$ .

#### INFLUENCE OF REFLUX RATIO

It is reasonable to expect that, when a rectifying column is operated at moderate vapor velocities so that entrainment is absent, the actual performance of the plate should not be greatly influenced by variations in the reflux ratio. Therefore the increase in the over-all Murphree efficiency and the decrease in the local efficiency with decreasing reflux ratios are of interest. It is possible that greater mixing occurs on a plate when the liquid velocity (reflux ratio) and vapor velocity are increased. This behavior, in turn, would have a tendency to decrease the over-all efficiency. As Figure 4 shows, this is actually the case; the curve for the over-all Murphree efficiency at  $L/V = 1$  lies below that for  $L/V = 2/3$ , and the latter lies below that for  $L/V = 1/2$ .

Byman (1) advanced an explanation for the opposite effect observed for the local efficiency; he attributes the variation to

liquid retained on each plate, we would expect the efficiency to decrease slightly with decreasing reflux ratios.

#### EFFECT OF SLOPE OF EQUILIBRIUM CURVE

The curves for the over-all Murphree efficiency given in Figure 2 for  $L/V = 2/3$  show several points consistently above the mean. As Table I shows, these points were obtained for runs covering the same concentration range—namely, 44 to 62 mole per cent alcohol. A large deviation below the mean is also to be observed in the case of  $L/V = 1/2$  (Figure 3) for runs covering the range 3 to 50 mole per cent alcohol. In the regions where this phenomenon occurs, the operating line approaches closely to the equilibrium curve; the result is a different degree of concentration gradient on the several plates. The deviation of the corresponding points for the local efficiency is much less as the calculations tend to minimize these variations.

This influence of kettle composition offers an explanation for the difference in results obtained by Kirschbaum (8) and by Keyes and Byman (6) working on ethyl alcohol-water mixtures. Kirschbaum, using a seven-plate column with a low alcohol concentration in the kettle, found a sharp decrease in over-all efficiency at both high and low alcohol concentrations. However, while the over-all efficiency curve showed a practically constant maximum value over the median con-

centration range, a second maximum was observed between 60 and 70 weight per cent ethyl alcohol. Since this second maximum corresponds to the deviations discussed above, it can probably be attributed to the same cause. This explanation is confirmed by the results of Keyes and Byman (6) who used essentially the same column described here. They obtained the same results as Kirschbaum, except that the

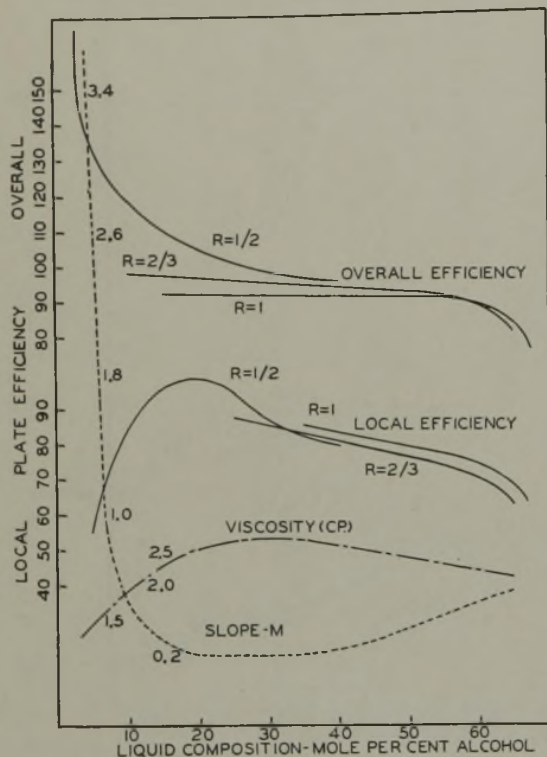


Figure 4. Plate Efficiencies and Physical Properties of Isopropyl Alcohol-Water Mixtures

second maximum between 60 and 70 weight per cent ethyl alcohol was missing. Since their investigation involved a large number of runs covering practically the entire alcohol composition range and since their curve took into account all compositions, the second maximum observed by Kirschbaum would not be expected to occur.

The relatively greater slope of the equilibrium line for the isopropyl alcohol-water system, as compared to that for ethyl alcohol-water, prevented the present investigation from covering as low a concentration range as did that of Keyes and Byman (6). The over-all efficiency, however, shows the opposite behavior to their results in the low concentration range, since it increased rapidly with decreasing alcohol concentration. That this apparent contradiction is due to the greater slope of the vapor-liquid equilibrium curve is shown by the behavior of the local efficiency; the latter decreased at approximately the same rate at which the over-all efficiency increased. If the nature of the equilibrium relation had permitted investigation at still lower alcohol concentrations, the over-all efficiency curve would be expected to decrease. At very low concentrations the concentration gradients on the first plate would decrease in the same manner found for the top plates at high alcohol concentrations, though to a much smaller extent.

The variation in efficiency with liquid composition cannot be attributed entirely to concentration gradient effects. While this gradient influences the nature of the curves for different reflux ratios, the over-all trend shows a definite effect of liquid composition. In the case of high alcohol concentration the gradients are very small, and the efficiency of reflux ratios  $L/V = 1$  and  $2/3$  are practically coincidental in that they decrease at the same rate. The effect of the liquid compositions is also shown by the behavior of the local efficiencies which increase from a minimum of 63 per cent at 65 mole per cent alcohol to a maximum of 99 at 20 mole per cent.

#### VAPOR RATE AND PHYSICAL PROPERTIES OF LIQUID

The mechanism of rectification in a bubble-cap column involves primarily the interaction of a vapor bubble rising through a liquid. Preliminary analysis leads to the conclusion that, for a given slot width in a given liquid, the bubble diameter should depend but little on the rate of flow of the vapor. Consequently, for a given liquid depth, the rate of bubble rise and hence its time of contact should depend very little on the rate of vapor flow. This leads to the conclusion that, however high the vapor rate, so long as the vapor does not escape below the skirt of the cap or entrainment becomes excessive, the efficiency should be little influenced by vapor rate.

The present investigation confirms this theory at reflux ratios of  $L/V = 2/3$ . Figure 2 shows that both the over-all Murphree and the local efficiency increase approximately 2 per cent when the superficial vapor velocity decreases successively from 1.1 to 0.9 to 0.5-0.7 foot per second. Since this increase is relatively the same over the entire composition range, the effect cannot be due entirely to entrainment. The effect of entrainment would be more pronounced at the lower concentrations owing to excessive froth formation in that region. Carey *et al.* (2) showed that, for a given liquid, a decrease in the width of the bubble-cap slots causes an increase in plate efficiency. These results lead to the conclusion that bubble size depends to some extent upon slot openings. Various investigators (15) have shown that the depression of the liquid inside the bubble cap below the top of the slots is proportional to the  $2/3$  power of the vapor rate through the slots. It is probable that the minor effect of the vapor rate on the efficiency is due to this increased slot area with increased vapor velocity and the resultant increase in bubble size. As previously mentioned, increased vapor velocity causes increased mixing and a decrease in over-all efficiency.

Schnurmann (13, 14) showed that the size of bubbles produced by forcing a gas through porous plates was substantially independent of the pore size and the manner in which they were introduced. In general, the bubble size varied inversely with the viscosity of the liquid. His study of the ethyl alcohol-water system showed that the maximum in the viscosity-composition curve corresponded to a minimum in the bubble size. This investigation also showed that the final size of the bubbles was a result of the degree of coalescence of the smaller bubble leaving the porous plates. The curve for the viscosity of isopropyl alcohol-water mixtures as a function of liquid composition is given in Figure 4 together with the curves for over-all and local plate efficiencies. A comparison of the trend of the viscosity-composition relation with the efficiency curves partially confirms the tentative conclusion that the plate efficiency may be expected to reach a maximum at about the same liquid composition at which the bubble size is smallest or the viscosity is greatest. A comparison of these viscosity data (obtained at 25° C.) with those for ethyl alcohol-water at 25° C. and at the boiling point (3) shows that the maximum occurs at nearly the same alcohol concentration in both cases.

The only effect of using the boiling temperature is to lower the absolute magnitude of the viscosity curve and, as a result of rapidly increasing temperature with decreasing alcohol concentration below the maximum, to cause a sharper decrease in that region.

#### PRESSURE EFFECTS

Since the column used in this investigation was operated at atmospheric pressure and the plate efficiencies were calculated on the basis of the vapor-liquid equilibrium relation at 1 atmosphere, the effect of pressure should be considered. In the range of vapor velocities involved in the present work, it was found that the pressure drop throughout the column, as indicated by the kettle manometer, and accordingly through each plate, was essentially constant and approximately equal to the static head above the top of the bubble-cap slots (2 mm. mercury). Consequently, the top plate was usually operating at the average barometric reading, 740 mm. mercury, and the bottom plate at 748 mm.

To determine the effect of pressure on the vapor-liquid equilibria of isopropyl alcohol-water mixtures, several runs were made at atmospheric pressure during the course of the equilibrium study (10); the alcohol content was varied from 40 to 55 mole per cent. The effect of this lower pressure was so small that the difference was within the experimental accuracy of the data (0.1 mole per cent alcohol in this range) and could not be determined. The design of the equilibrium still prevented measurements being made at pressures considerably higher or lower than 1 atmosphere where the change would be measurable.

Since the isopropyl alcohol-water system resembles that of ethyl alcohol-water very closely, an examination of the variation of the latter with pressure would be pertinent. Extrapolation of the data (4, 12) given for the change of the azeotrope composition of ethyl alcohol-water with pressure shows that the alcohol content increases approximately 0.07 mole per cent for a decrease in pressure from 760 to 740 mm. mercury. If the change is of the same order of magnitude for the isopropyl alcohol-water system, the calculated plate efficiencies would not be noticeably affected until the alcohol concentration was within a few mole per cent of the azeotropic composition (68.35 mole per cent alcohol). However, the sharp decrease in the plate efficiencies found at an alcohol concentration between 55 and 68 mole per cent cannot be explained by pressure effects. In this region the behavior of the equilibrium relation with pressure results in an actual equilibrium vapor greater than that used in the calculation. This would cause the calculated efficiency to be higher than actually existed on the plate.

Kirschbaum's measurements (7, 9) on the ethyl alcohol-water system show that, for alcohol concentrations below 10 mole per cent, the equilibrium curve for 50 mm. mercury lies below that for 760 mm. At 10 mole per cent the curves cross over, so that the one for 760 mm. becomes the lower. This behavior might explain the sharp increase found by Keyes and Byman (6) for very low alcohol concentrations in the ethyl alcohol-water system. Since the runs in that region were made with reflux ratios of 2/3 and 1/2, the driving force was relatively small. Owing to the steepness of the equilibrium curve in that region, it is possible for the calculated driving force to be several times larger than the actual driving force; the result would be very low calculated plate efficiencies. In the case of isopropyl alcohol-water mixtures, the curve is considerably steeper than that for ethyl alcohol-water, and runs could not be made at such low alcohol concentrations. It is possible that, if the investigation could be carried to lower concentrations, the same effect would be noted. As it was, the steepness of the curve resulted in such

concentration gradients across the plates that the curve for the over-all plate efficiency went down almost vertically in this region. The effect of the concentration gradients is shown by the local efficiency curve which increases at approximately the same rate as the over-all efficiency curve decreases.

The very small efficiencies found for alcohol concentrations immediately above the azeotrope for the runs at total reflux might be caused by pressure effects. In this region a lower pressure influences the equilibrium curve in the same manner as described for low alcohol concentration; the result is an equilibrium vapor lower than that used in the calculations.

#### CONCLUSIONS

Both the over-all Murphree,  $E_o$ , and the local efficiency,  $E$ , in terms of vapor composition, vary markedly with liquid composition. Changes in reflux ratio and in the rate of distillation (superficial vapor velocities) have little influence on these efficiencies. At the reflux ratio  $L/V = 1$ , the value of the over-all Murphree efficiency is practically constant at 91 per cent over the range of liquid composition 20 to 55 mole per cent alcohol and decreases rapidly to 70 at 68 mole per cent alcohol; the local efficiency shows a more gradual decrease with increasing alcohol composition, from 85 at 35 mole per cent to 77 at 55 mole per cent with a sharp break to 63 at 68 mole per cent. For  $L/V = 2/3$ ,  $E_o$  shows a linear decrease from 98 to 91 over the range 15 to 55 mole per cent alcohol, and was practically coincidental with that for total reflux between 55 and 65 mole per cent; the curve for the local efficiency was identical with that for total reflux, being displaced lower by 3 per cent. The curve for the reflux ratio  $L/V = 1/2$ , extending over the range 3 to 40 mole per cent alcohol, shows a more pronounced change from an over-all efficiency of 220 at the low composition to 95 at the high; the curve for the local efficiency shows the marked effect of the concentration gradients existing on the plate; it increases at approximately the same rate at which the over-all efficiency decreases to a maximum at 20 mole per cent.

The influence of the kettle composition on the degree to which the operating line approaches the equilibrium curve is responsible for large deviations from the mean for reflux ratios of  $L/V = 2/3$  and  $1/2$ .

The pronounced effect of viscosity on the formation of vapor bubbles (13, 14), together with the parallel trends of plate efficiency- and viscosity-liquid composition curves, seem to emphasize the significance of physical properties of the liquid in plate-column fractionations.

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# STORAGE OF Synthetic Citrus Powders

## Caramelization by Citric or Tartaric Acid and Various Sugars at High Temperatures

WILLIAM EDWYN ISAAC

Government Low Temperature Research Laboratory,  
Cape Town, Union of South Africa

Lemonade and orangeade powders containing a high proportion of citric acid undergo caramelization when stored at 98° and 110° F. if they are packed in containers (bottles and cans) which prevent the escape of water vapor. Under these conditions citric acid loses water of crystallization which brings about the hydrolysis of sucrose. The liberated fructose is then caramelized.

Caramelization occurs with sorbose, fructose, or any sugar liberating fructose on

hydrolysis. Aldohexoses and sugars liberating aldohexoses on hydrolysis do not caramelize in the presence of citric acid.

Caramelization in orangeade and lemonade powders containing citric acid held at high temperatures can be prevented by using anhydrous citric acid or by substituting glucose for sucrose. Caramelization does not occur (in the absence of added water) if *d*-tartaric acid is substituted for citric acid.

THE maintenance of troops in hot climates has brought to the fore many problems of food storage in the tropics. This problem arose in the consideration of artificial lemonade as a potential source of ascorbic acid in cases of vitamin C deficiency. The very small amounts of ascorbic acid lost on storing certain lemonade powders at 90° F. (32° C.) for 6 weeks indicated that much longer storage periods at this temperature were possible for lemonade powders containing a large amount of sugar, or containing tartaric acid and a smaller proportion of sugar. (In the latter type, more sugar is added when the lemonade is prepared for drinking.) Such lemonade powders not only retained nearly all the added ascorbic acid but were in good physical condition after 7 weeks at 90° F. It was deemed advisable, however, to carry out tests at higher temperatures on powders with a high ratio of acid to sugar, which would mean adding more sugar to the lemonade or orangeade for drinking.

### STORAGE CONDITIONS

Preliminary tests were made on orangeade and lemonade powders stored in tins for a month at 110° F. (43° C.). Some of these powders contained citric acid and others tartaric acid. Unless otherwise stated, citric acid containing water of crystallization was used. When removed from storage, the powders showed varying degrees of discoloration, caking, and hardening; some were dark brown, amorphous, and consolidated. The light brown discolorations apparently represent stages in the changes resulting finally in the dark brown, hard, amorphous mass. The term "caramelization" will refer here only to the latter condition. The powders containing tartaric acid did not caramelize although some were discolored. There is no evidence to indicate whether or not the

pale yellowish discolorations in mixtures containing tartaric acid represent slight caramelization. The results obtained from these preliminary tests indicated that a comparison of the storage behavior of powders containing citric acid with those containing tartaric acid was important.

In the final series of tests, samples of the various powders were stored for 8 weeks at 98° and 110° F. (37° and 43° C.) in cardboard boxes, glass bottles, and sealed cans. The boxes and cans were lined with Waxtex waxed paper. The storage rooms were dark, and had a rapid air circulation and low relative humidity. The relative humidity of the room at 98° F. was about 25 per cent and that at 110° F., about 15 per cent.

Tests were conducted in duplicate; the agreement was usually close, and the divergence was never important. The recipes for the various powders are given in Table I. No coloring matter was added.

### CARAMELIZATION BY CITRIC ACID

The most outstanding result was the effectiveness of citric acid in producing caramelization. It was again found that if tartaric acid was used, caramelization did not take place although some of the powders were discolored.

Lemonades L-8, L-2, L-3 and L-4 (Table II) are arranged in order of increasing proportion of citric acid to sugar; the degree of caramelization increases with an increasing proportion of citric acid. This result, which was general throughout the tests, indicates the effectiveness of citric acid in producing caramelization.

EFFECT OF STORAGE TEMPERATURE. Caramelization was affected also by storage temperature. There was much more caramelization at 110° than at 98° F. (Table II).



TABLE I. RECIPES OF ARTIFICIAL ORANGEADE AND LEMONADE POWDERS<sup>a</sup>

ORANGEADE POWDERS WITH SUGAR IN FORM OF SUCROSE		
O-1	Citric acid Sucrose Oil of bitter orange	45.5 grams 136.6 grams 1.4 cc.
O-2	Same as O-1, plus oil of sweet orange	1.4 cc.
O-3	Same as O-6, plus oil of sweet orange	0.7 cc.
O-4	Same as O-1, plus oil of sweet orange	0.7 cc.
O-5	Same as O-6, plus oil of sweet orange	1.4 cc.
O-6 (basic recipe)	Citric acid Sucrose Oil of bitter orange	90.8 grams 136.6 grams 1.4 cc.
O-7	Citric acid Sucrose Oil of bitter orange	23 grams 136 grams 1.4 cc.
O-8	Tartaric acid Sucrose Oil of bitter orange	23 grams 136 grams 0.7 cc.
LEMONADE POWDERS		
L-1 (basic recipe)	Tartaric acid Sugar (sucrose) Oil of lemon	136 grams 272 grams 5.7 cc.
L-2 to L-8 have the basic recipe of L-1 with the acid content varied, as follows:		
L-2	Citric acid	136 grams
L-3	Citric acid	204 grams
L-4	Citric acid	272 grams
L-5	Tartaric acid	272 grams
L-6	Tartaric acid	204 grams
L-7	Tartaric acid	68 grams
L-8	Citric acid	68 grams
ORANGEADE POWDERS WITH SUGAR IN FORM OF GLUCOSE		
GO-1	Tartaric acid Glucose Oil of bitter orange	45 grams 136 grams 1.4 cc.
GO-2	Citric acid Glucose Oil of bitter orange	45 grams 272 grams 1.4 cc.
GO-3	Citric acid Glucose Oil of bitter orange	90 grams 136 grams 1.4 cc.
GO-4	Citric acid Glucose Oil of bitter orange	90 grams 272 grams 1.4 cc.
GO-5	Citric acid Glucose Oil of bitter orange	68 grams 136 grams 1.4 cc.
GO-6	Citric acid Glucose Oil of bitter orange	68 grams 272 grams 1.4 cc.

<sup>a</sup> Two ounces of basic recipes O-6 or L-1 together with 1 $\frac{1}{4}$  or 1 $\frac{1}{2}$  pounds of sugar were made up to 6 pints with water. The essential oils were dissolved in a small amount of alcohol and thoroughly mixed with the sugar-acid mixture. The powders were spread out to dry before packing. The substitution of citric acid for tartaric gives a better drink, but about one and a half times (lemonade) to twice (orangeade) as much citric acid must be used, according to tasting tests made in this laboratory.

EFFECT OF ESSENTIAL OILS. The proportion of acid and sugar in the basic recipes of the orangeade and lemonade powders were different and thus only a limited number of samples with different essential oils, but with approximately the same ratio of acid to sugar, are available for comparison. Table III indicates that the nature and amount of essential oil make little difference.

The result of the following experiment was in agreement with this conclusion: Five per cent water was added to two lots of powder L-4 (equal amounts of sucrose and citric acid, together with oil of lemon) and to two similar lots of powder without oil of lemon. These mixtures were put into glass bottles with screw-on aluminum lids and kept for a week at 130° F. (54° C.). At the end of that time the mixtures with and without oil of lemon were all completely caramelized.

EFFECT OF TYPE OF PACKAGE. The degree of caramelization was also affected by the type of container. Thick cardboard boxes lined with waxed paper were superior to bottles and cans; in only two cases did caramelization occur in cardboard containers although there were discoloration and varying degrees of caking and hardening, especially when the powders contained citric acid. The two exceptions were powders O-6 and O-7 at 110° F. which showed only slight caramelization. Powders packed in bottles and especially those in cans became caramelized even if other conditions were favorable.

The somewhat greater degree of caramelization in lemonade and orangeade powders packed in sealed cans may be related to a catalyzing of the reaction by the can itself. However, the difference is more likely to be due to the complete prevention of water vapor loss from a sealed tin; also the powder was wrapped in waxed paper and was thus not in direct contact with the can. Caramelization was only slightly more apparent in cans than in bottles.

#### MECHANISM OF CARAMELIZATION

Further experiments were carried out to determine the role of moisture, whether the action of citric acid was due to its acidic nature, and whether caramelization in sugar-acid mixtures was peculiar to sucrose or a derivative of sucrose. These experiments were carried out in duplicate with the exception of the xylose-citric acid, the sorbose-citric acid, and the raffinose-citric acid mixtures.

IMPORTANCE OF MOISTURE. Five per cent distilled water was added to powder L-3, and samples were stored at 110° F. in the three types of container. At the end of a week all three powders were caramelized. Although caramelization was not so severe as that in the powders with lower moisture content stored for a longer period, it showed that carameliza-

TABLE II. COMPARISON OF CITRIC AND TARTARIC ACIDS IN PRODUCING CARAMELIZATION IN LEMONADE POWDERS (STORED IN GLASS CONTAINERS FOR 8 WEEKS)

Acid Content of Powder	Powders with Citric Acid				Powders with Tartaric Acid				
	Powder No.	Condition of powder		Powder No.	Condition of powder		Powder No.	Condition of powder	
		98° F.	110° F.		98° F.	110° F.		98° F.	110° F.
1/5	L-8	Light brown; caked; no caramelization	Medium brown; caked; slight caramelization	L-7	Very slight yellow; caked	Very pale yellow; slightly caked	L-1	Same as L-7	Pale yellow; some caking
1/3	L-2	Light medium brown, hard compact lump; some diffuse caramelization	50-66% caramelized; remainder, light brown	L-6	No discoloration; slightly caked	Same as L-7	L-5	Same as L-6	Same as L-1
2/5	L-3	Same as L-2, but about 20% caramelized	Complete or nearly complete caramelization	L-4	Light medium brown; about 50% caramelized	Completely caramelized; very hard			

TABLE III. EFFECT OF ESSENTIAL OILS ON CARAMELIZATION OF SUGAR CITRIC ACID MIXTURE

Type of Container	Temperature, ° F.	Lemonade Powder L-3 (5.7 cc. lemon oil in 476 grams)	Orangeade Powders <sup>a</sup> , 227 Grams		
			O-3 (1.4 cc. bitter + 0.7 cc. sweet oil)	O-5 (1.4 cc. of bitter + 1.4 cc. sweet oil)	O-6 (1.4 cc. bitter oil)
Glass	98	Light medium brown; 20% caramelization	Light medium brown; about 20% caramelization	Medium brown; about 25% caramelization	25-60% caramelization
Tin	98	About 30% caramelization	Yellowish brown; diffuse caramelization	Medium brown; about 50% caramelization	Medium brown; about 66% caramelized
Glass	110	Approx. complete caramelization	80-100% caramelized	100% caramelized	50-100% caramelized

<sup>a</sup> Products containing orange oil as likely to discolor even when there is no caramelization.

TABLE IV. PER CENT WATER LOSS FROM MOISTENED SUGAR STORED A WEEK IN DIFFERENT CONTAINERS

Type of Container	Sugar		Sugar + 0.5% Added Water		Sugar + 1% Added Water	
	98° F.	110° F.	98° F.	110° F.	98° F.	110° F.
Cardboard box	1.9	1.9(5)	2.1	2.4	2.4	2.9
Glass bottle	0.6	0.74	0.76	0.85	1.2	0.8

tion will take place in each type of container if enough water is present.

It was also shown that moistened sugar lost more water from the cardboard than from the glass containers under the conditions of rapid air circulation and low relative humidity in the storage rooms (Table IV).

These two experiments indicate that insufficient moisture accumulated in the cardboard containers to permit the initiation of caramelization.

This result was conclusively shown later by the fact that lemonade and orangeade powders packed in cardboard boxes completely caramelized when kept for about 6 months under ordinary room conditions in a damp suburb of Cape Town. The same powders had not caramelized in storage at 98° F.

**TYPE OF ACID.** Mixtures were made of equal parts of citric acid and sucrose and of tartaric acid and sucrose. To each of the mixtures was added 5 per cent water. They were then put into glass bottles with screw-on metal lids and kept at 130° F. for a week.

At the end of this period both sets had undergone caramelization. The citric acid-sucrose mixture had almost completely liquefied and was dark brown (almost black) in color. The liquefied part resembled a thick, dark colored molasses. Caramelization was less complete in the tartaric acid-sucrose mixture; it had become a hard, glassy, solid mass of medium dark brown color, interspersed with small whitish granules.

That citric acid brings about caramelization under conditions where tartaric acid does not is related to the fact that citric acid contains water of crystallization while ordinary *d*-tartaric acid is anhydrous. The water of crystallization of citric acid supplied at least part of the moisture necessary for caramelization at 98° and 110° F., as indicated by the efflorescence of citric acid crystals during the discoloration of the powders which occurred before obvious caramelization had taken place. It was also shown that samples of the citric acid used gave off water within a day when enclosed in dry stoppered test tubes incubated at 104° F. (40° C).

To test the theory that caramelization in citric acid-sucrose mixtures stored at high temperatures depended upon the liberation of water of crystallization, a mixture of sucrose and anhydrous citric acid containing 40 per cent citric acid (proportions of powder L-3) was stored in bottles at 110° F. for a month. For comparison, a similar bottled mixture containing ordinary crystallized citric acid (control) was stored. After 2 weeks the control showed extensive caramelization while the mixture containing anhydrous citric acid showed none. At the end of a month the control was almost completely caramelized, but the anhydrous citric acid-sucrose mixture still showed no trace of caramelization.

**TESTS WITH GLUCOSE.** A set of orangeade powders was prepared in which glucose monohydrate was substituted for sucrose. The proportion of citric acid present was sufficient to bring about caramelization if sucrose had been used. The powders were stored at 110° F. in sealed cans for 8 weeks; at the end of that time there was no caramelization although in two (of six) lots there was slight discoloration (Table V). These powders were kept for a further period of about 6 months at room temperature in a damp suburb of Cape Town. No caramelization took place although the cans had been opened so that the powders were only partly covered by the lids.

Anhydrous glucose was also tested. The following mixtures were

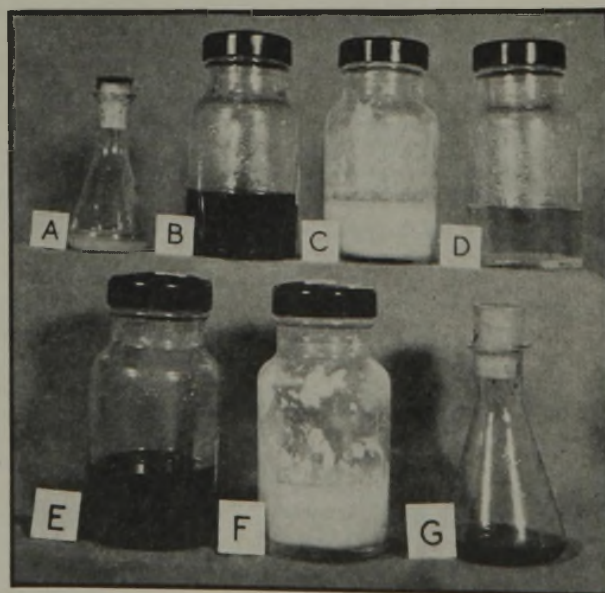


Figure 1. Mixtures of Equal Parts of Citric Acid and Different Sugars with 5 Per Cent Water after 4-7 Day Storage at 130° F.

- |             |              |              |
|-------------|--------------|--------------|
| A. Xylose   | C. Galactose | F. Lactose   |
| B. Fructose | D. Glucose   | G. Raffinose |
|             | E. Sucrose   |              |

TABLE V. EFFECT OF GLUCOSE ON KEEPING QUALITY OF ORANGEADE POWDERS CONTAINING CITRIC ACID (PACKED IN CANS AT 98° F. FOR 8 WEEKS)

Acid Content of Powder	Orangeades with Glucose		Orangeades with Sucrose	
	Powder No.	Condition of powder	Powder No.	Condition of powder
1/7	GO-2	Unaffected	O-7	Light medium brown; caked and hard
1/5	GO-6	Similar to GO-2	.....	.....
1/4	GO-4	White; somewhat more cohesive than GO-2	O-1	Light brown; caked; slight diffuse caramelization
			O-2	Similar to O-1
			O-4	Light brown; caked; about 33% caramelized
1/3	GO-5	Pale yellowish brown; decidedly cohesive	....	.....
2/5	GO-3	Similar to GO-5	O-6	Medium brown; about 66% caramelized
			O-5	Medium brown; about 50% caramelized
			O-3	Light yellowish brown; caked; diffuse caramelization

put into bottles with aluminum lids and stored for a month at 110° F.:

1. Equal amounts of citric acid and sucrose (control)
2. Equal amounts of citric acid and anhydrous glucose
3. Equal amounts of anhydrous citric acid and anhydrous glucose

Before the month was out, the control was completely caramelized; the other two mixtures were unaffected at the end of the month. Mixture 3, containing only anhydrous constituents, was still a fine powder; mixture 2, containing ordinary citric acid, was compacted but not caramelized. From this behavior and the obvious moisture on the sides of the bottles, it was clear that the citric acid had given off water of crystallization.

This test also showed that compacting in itself is not necessarily an indication of the beginning of caramelization.

TESTS WITH OTHER SUGARS. Mixtures were made of equal portions of citric acid and the sugar to be tested. Five per cent water was added to each mixture, and they were kept at 130° F. for 4-7 days. The results are given in Table VI and Figure 1.

TABLE VI. EFFECT OF CITRIC ACID IN PRODUCING CARAMELIZATION OF SUGARS

SUGAR	RESULT
Pentose	
Xylose	Pale yellowish color
Monosaccharides	
Ketohehexoses	
Fructose } Completely caramelized; dark	reddish brown sirup
Sorbse }	
Aldohehexoses	
Glucose	Pale yellow
Galactose	No discoloration
Disaccharides	
Sucrose	Almost completely liquefied. A dark brown (almost black) color
Maltose } No caramelization	
Lactose }	
Trisaccharide	
Raffinose	Medium dark brown sirup

Sucrose hydrolyzes to glucose and fructose. The sample of sucrose used did not reduce Fehling solution and, unless subjected to prolonged boiling, did not give an osazone with phenylhydrazine and acetic acid. The stored citric acid-sucrose mixture gave a copious precipitate of cuprous oxide with Fehling solution and an abundant osazone precipitate with phenylhydrazine and acetic acid. Glucosazone could be distinguished under the microscope.

Maltose gives glucose on hydrolysis. The sample of maltose used did not reduce a fresh solution of Barfoed reagent. After one week at 130° F. an additional 4 per cent of water was added to the maltose-citric acid mixture. At the end of the second week the mixture was tested for glucose. There was some tardy reduction of a fresh Barfoed solution which indicated that a certain amount of hydrolysis had taken place.

Lactose hydrolyzes to glucose and galactose. Barfoed reagent is not reduced by lactose but is reduced by glucose and galactose. Neither the original sample of lactose nor the stored lactose-citric acid mixture reduced Barfoed reagent which was, however, shown to be reduced by a glucose-citric acid mixture.

With weak acid, raffinose hydrolyzes to fructose and melibiose. In the presence of strong acid, melibiose breaks down further to give glucose and galactose. Raffinose does not reduce Fehling solution and does not form an osazone with phenylhydrazine. Hydrolyzed raffinose will give positive results for both of these reactions; the sample of raffinose used here did not give these reactions. The stored raffinose-citric acid mixture reduced Fehling solution and yielded an osazone precipitate. Microscopic examination showed the presence of more than one type of osazone, but crystals of the glucosazone type were distinguished.

STORAGE OF SUGARS AT HIGH TEMPERATURES. Samples of glucose, fructose, sucrose, and lactose were stored for 22 weeks at 98° and 110° F. in glass bottles with screw-on metal lids. With the exception of fructose, they were in excellent condition at the end of the period, and were neither discolored nor caked. At 98° F. fructose had darkened from pale yellowish white to straw color but showed little caking; at 110° F. fructose was decidedly darker in color than at 98° F.; it was light yellowish brown and caked, and small isolated drops of a brown sirupy liquid had appeared on the sides of the bottle.

#### SUMMARY AND CONCLUSIONS

A mixture of sucrose and citric acid containing sufficient moisture caramelizes rapidly at high storage temperatures. Under these conditions the water of crystallization of citric acid is a source of moisture. The higher the proportion of citric acid present, the greater the amount of caramelization in a given time due to the water of crystallization of the citric acid.

If the water of crystallization given off by citric acid is allowed to escape or if anhydrous citric acid is used, no caramelization takes place.

The first stage in the caramelization of a sucrose-citric acid mixture is the hydrolysis of sucrose. Caramelization results from the liberation of fructose, since a fructose-citric acid mixture undergoes complete caramelization whereas a glucose-citric acid mixture does not caramelize.

Ordinary *d*-tartaric acid is anhydrous, but in the presence of added moisture this acid also brings about inversion of sucrose followed by caramelization.

Caramelization results only from the interaction of citric acid with the ketohehexoses fructose and sorbose and with those

sugars which yield fructose on hydrolysis (sucrose and raffinose). This result suggests that caramelization is a property of the ketohexoses and of sugars which yield ketohexoses on hydrolysis. Neither of the two aldohexoses tested (glucose and galactose) nor the aldopentose xylose caramelized in the presence of citric acid. This was also true of the disaccharides (maltose and lactose) which yield aldohexoses on hydrolysis.

Fructose is susceptible to discoloration on heating, especially in acid solution. Dehydration takes place and results in the formation of compounds (hydroxymethylfurfural, hymatomelanin acid) which readily undergo polymerization to form dark colored substances (1). Even in the absence of citric acid, fructose darkens when stored at high temperatures in the dark; the higher the temperature, the greater the amount of darkening.

It thus seems that in artificial lemonade and orangeade powders containing a high proportion of citric acid and stored at high temperatures, the citric acid gives off water of crystallization which, if not allowed to escape, brings about hydrolysis of sucrose to glucose and fructose. Then the fructose undergoes caramelization which, once started, liberates water for further inversion and caramelization. The higher

the storage temperature and the greater the proportion of citric acid, the greater the amount of available water of crystallization and, consequently, the greater the amount of caramelization during a given storage period, provided the moisture does not escape from the container.

An artificial lemonade or orangeade powder intended to be kept under tropical conditions should contain a greater proportion or all of the sugar to be ultimately added. If a powder of smaller bulk is required, either glucose (preferably anhydrous) can be substituted for sucrose or tartaric acid can be used in place of citric, or both of these substitutions can be made. Powders should be dry before packing.

If glucose is substituted for sucrose, allowance should be made for its being less sweet. Its relative sweetness has been variously evaluated from 50 to 73.4 per cent of that of sucrose (2). Citric acid gives a pleasanter drink than tartaric acid, but about one and a half times to twice as much citric acid is needed.

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# Effect of Acetylation on Water-Binding Properties of Cellulose

## RAG STOCK

JOHN C. BLETZINGER

Sterling Pulp and Paper Company, Eau Claire, Wis.

THE pronounced affinity of cellulose for water—i. e., its hygroscopicity and ability to swell—is chiefly attributed to its abundance of free hydroxyl groups. If part or all of these groups are replaced by ester groups, hygroscopicity and swelling ability decrease. For example, Sheppard (15) found that the water-binding capacity of cellulose acetate decreased with increasing acetyl content and that a fibrous triacetate took up only 9 per cent water compared with 16 per cent for the unacetylated cotton fiber.

The forces by which the water molecules are held to the hydroxyl groups of the cellulose have been ascribed to secondary valences in the older literature (10, 21), whereas today they are believed to be hydrogen bonds (7).

No doubt the same forces are operative when cellulose fibers are beaten in the presence of water, as a step preparatory to the formation of a sheet of paper. As beating progresses, the water-binding capacity of the cut, bruised, and fibrillated fibers increases, evidently due to a considerable increase of their external surface. As a result, an increasing number of free hydroxyl groups are made accessible to water—i. e., to "hydration", as this phenomenon is known to the paper manufacturer. Hydration, combined with the mechanical disintegration exerted by the beating device, develops

the physical strength properties inherent in the cellulosic material so treated. After a certain time of beating, depending upon the nature of the material and the efficiency of the beater, the fibers acquire their maximum strength properties.

When the sheet is formed on the paper machine or a hand-sheet-making device by the mechanical removal of the water and subsequent drying, strong forces of surface tension are developed between the interfaces of hydrated adjacent cellulose fibers and fibrils, by which their surfaces are drawn more closely together. As this process continues, the hydroxyl groups release more and more of their water molecules and eventually approach one another so closely that the secondary valences (or hydrogen bonds) satisfy one another directly, and bonding between fiber and fibrillae surfaces is accomplished (2, 21).

In the light of Sheppard's results, it is conceivable that both hydration and bonding of the fibers would be seriously impeded if part or all of the free hydroxyl groups in cellulose were replaced by hydrophobic ester groups. A direct proof could thus be furnished for the assumption that the water binding of cellulose fibers during beating and the bonding of fiber surfaces during sheet formation are a function of their

free hydroxyl groups. It was hoped that such results would be obtained by subjecting cellulose fibers of increasing acetyl content to the processes of beating and sheet formation, by investigating the behavior of the acetylated fibers during these processes, and by ascertaining the physical properties of the sheets.

Several months after the present investigation had been finished, a publication by Brown and Harrison (1) appeared which deals with the properties of sheets prepared from partially acetylated kraft pulp fibers, with the object of commercial preparation of a material of reduced affinity for

through the courtesy of the Gilbert Paper Company. To facilitate the preparation of handsheets from this material, it was cut to somewhat shorter fiber length in a laboratory beater, under conditions which had practically no other effect upon the material.

#### METHOD OF ACETYLATION

To avoid any uncontrollable influence upon the beating effect, the method of Hess and Ljubitsch was modified in as much as the pretreatment of the cellulosic material with

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The ability of cellulose fibers to become hydrated, develop a sufficient number of bonding forces, and produce a coherent sheet of paper of sufficient physical strength properties is the function of their hydroxyl groups. Rag stock fibers which were partially acetylated without degradation and loss in tensile strength, were insoluble in the usual organic solvents, and contained more than 8-9 per cent acetyl gradually lost their papermaking properties as the acetyl content increased; fibers having 20-25 per cent acetyl were incompatible with water. However, with fibers having acetyl contents below 8-9 per cent, hydration and physical strength properties increased and attained a maximum at about 6 per cent acetyl. This phenomenon is explained on the assumption that the beating of cellulose fibers, in which the distances

between chain molecules have been increased by the introduction of acetyl groups, renders a greater number of free hydroxyl groups accessible to hydration until, with further introduction of acetyl groups, this increased availability of free hydroxyl groups is counteracted and eventually overshadowed by the hydrophobic character of the more highly acetylated fibers. Sheets of excellent physical strength properties and uniformity were obtained from the more highly acetylated fibers when water was replaced by acetone as a beating medium. This result is explained by the solvation of the acetyl groups by the acetone (in analogy with the hydration of hydroxyl groups by water in unacetylated fibers) and the development of bonding forces between the acetyl groups of adjacent fibers when the sheet is formed.

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atmospheric moisture and enhanced electric resistance. Kraft pulp, having a moisture content of about 5 per cent, was acetylated with acetic anhydride and anhydrous zinc chloride at elevated temperature for several hours. Samples of varying acetyl content were beaten (in water) and converted into handsheets, which were tested for physical strength properties. In confirmation of some of the results reported below, it was found that, with increasing acetyl content: (a) the resistance of the pulp to hydration increased to such an extent that beating could be completely inhibited, if a sufficient number of hydroxyl groups were blocked (approximately at the monoacetyl stage) and (b) the physical strength properties decreased. On the basis of these results, the direct functioning of the hydroxyl groups of cellulose in the development of physical strength properties was recognized; the assumption was made that the hydroxyl groups which are affected on acetylation are, for the most part, those located on the surface of, rather than within, the micellar structure of the fiber.

It is fortunate that the acetylation method of Hess and Ljubitsch (5) has made available a technique which permits the conversion of cellulose into a fibrous acetate without degradation (16, 17). The method consists of allowing the cellulosic material to stand in the presence of acetic anhydride and pyridine—i. e., without using an acid catalyst. It was thus possible to study the effect merely of the introduction of acetyl groups and to compare the results obtained with the acetylated fibers with those derived from the original material.

The original material tested consisted of a No. 1 rag stock as used for the manufacture of fine paper, and supplied

aqueous alkali—originally used to facilitate the reaction—was omitted. Under these conditions the time to reach a certain acetyl content was considerably longer than by the original method.

For example, an acetyl content of 26.5 per cent (corresponding to 35.5 per cent combined acetic acid) required about three months.

The moist rag stock was allowed to stand in pyridine overnight and was then freed from the aqueous pyridine by filtering. The procedure was repeated until practically all the water had been displaced by pyridine. The pyridine-containing material was acetylated by adding to it acetic anhydride which had been diluted with pyridine. The mixture (containing 10 cc. of anhydride and 16 cc. of pyridine per gram of cellulose) was placed in a constant-temperature bath at 25° C. and stirred for the length of time required to reach the desired acetyl content. For higher degrees of substitution, the stirring period at 25° was extended to 24 hours and was followed by a longer period at 39° C. without stirring (except for occasional shaking). At the end of the acetylation procedure, the acetylated fibers were separated from the liquid on the Büchner funnel and washed several times with pyridine. The pyridine was then displaced by ethanol and the latter by ether, and the material was dried in a current of dry air.

The acetyl content of preparations which had been dried in a vacuum desiccator over calcium chloride was determined according to the method of Murray, Staud, and Gray (12)—i. e., with alcoholic sodium hydroxide as the saponifying agent. The results follow:

Total Time of Acetylation	Acetyl Content, %	Total Time of Acetylation	Acetyl Content, %
10 min.	4.25	24 days	23.35
60 min.	6.18	31 days	25.00
5 hr.	9.22	90 days	26.46
11 days	20.05		
21 days	22.52	72 hr. <sup>a</sup>	14.20

<sup>a</sup> The rag stock was beaten in a standard laboratory beater and the water in the beaten stock was replaced by pyridine before the acetylation.

The fact that the reaction slowed down considerably after 11 days and did not reach more than about 27 per cent acetyl after 3 months may possibly be interpreted to mean that, under the conditions here employed, the hydroxyl groups available on the surface of the chain bundles are the ones chiefly acetylated. This interpretation would seem to be in agreement with the observation of Hess (4) that the x-ray pattern of cellulose did not change until an acetyl content of about 28 per cent had been reached. This acetyl content corresponds to about 48 per cent of the total number of free hydroxyl groups. Mark and Meyer (11) calculated that 30–50 per cent of the available hydroxyl groups are located on the micelle surfaces.

The rag stock which had been beaten before acetylation required a considerably shorter time for reaching a certain acetyl content than the unbeaten material, which is in agreement with the assumption that, on beating, the external fiber surface is increased.

In appearance, the acetylated material could not be distinguished from the unacetylated rag stock. All samples were insoluble in water, acetone, chloroform, and mixtures of chloroform and alcohol. This insolubility, which was observed also by Staudinger and Daumiller (16), indicates that no appreciable degradation of the cellulose had occurred. Indeed, the degree of polymerization of the acetylated samples was less than 10 per cent below that of the original cellulose, and the tensile strength of single fibers had increased rather than decreased.

The degree of polymerization of some of the acetylated samples and of the original rag stock was derived from viscosity measurements in cuprammonium hydroxide, using Staudinger's equation and a  $K_m$  constant of  $5 \times 10^{-4}$  for the conversion of the specific viscosity data into molecular weights (17, 20). The degree of polymerization of the unacetylated cellulose was obtained by dividing the molecular weight by  $162(C_6H_{10}O_5)$  and that of the acetates by extrapolation to the cellulose weight. This was justified because the acetates were completely saponified in the cuprammonium hydroxide solution (16). The cuprammonium hydroxide solution was prepared, and the viscosity measurements were

TABLE I. EFFECT OF ACETYLATION ON DEGREE OF POLYMERIZATION OF RAG STOCK CELLULOSE<sup>a</sup>

Material	Hr. Contact with Cuam	$c_D$	$\eta_{sp}$	$\frac{\eta_{sp}}{c}$	Molecular Weight	D. P.
Rag stock	22	0.00128	0.1280	100.0	200,000	1235
	42	0.00128	0.1496	117.0	234,000	1444
	66	0.00128	0.1500	117.0	234,000	1444
Rag stock	78	0.00104	0.1148	110.4	221,000	1364
	100	0.00137	0.1590	116.0	233,000	1437
	150	0.00137	0.1592	116.3	233,000	1438
Acetylated (9.22% acetyl)	90	0.00141	0.1492	105.9	212,000	1309
	97	0.00141	0.1484	105.3	211,000	1302
Acetylated (25.0% acetyl)	115	0.00137	0.1401	102.3	205,000	1261
	114	0.00150	0.1591	106.1	212,000	1309
	108	0.00171	0.1850	108.5	217,000	1340

<sup>a</sup> Cuam is cuprammonium hydroxide. The concentration term ( $c_D$ ) is given as grams per liter, divided by 162, the molecular unit of cellulose.  $\eta_{sp}$  is specific viscosity and  $\eta_{sp}/c$  is specific viscosity divided by concentration. D. P. is degree of polymerization. All weights are on an oven-dry basis.

made in the apparatus described by Heuser and Green (6). The maximum viscosity values, found by following the change of viscosity with time of contact, were used for the conversions. The results are shown in Table I.

The degree of polymerization of the acetate with 9.52 per cent acetyl had dropped by only 9 per cent, and that of the acetate with 25 per cent acetyl by only 7 per cent. Staudinger and Jurisch (19) showed that a drop in the degree of polymerization of cellulose fibers is accompanied by very little loss in physical strength properties as long as the degree of polymerization remains above 1000. Hence, scarcely any loss was to be expected from the limited degradation encountered in the experiments described above.

#### TENSILE STRENGTH OF ACETYLATED AND UNACETYLATED FIBERS

Tensile strength was determined with a Saxl tensile tester, which permits the testing of single fibers (14). Since it was difficult to handle the relatively short fibers of the rag stock in the apparatus, the effect of acetylation upon tensile strength was ascertained with long-staple cotton fibers.

The material was an upland cotton (Mexican variety) from North Carolina, taken from the same lot which had been used by Heuser and Green (6) as a material in which degradation was at a minimum. After removal of hull and other residues, the crude fibers were extracted for about 24 hours with ethanol in a Soxhlet apparatus and then bleached with an aqueous alkaline one per cent hypochlorite solution at a pH of 8.4 for 20 minutes at room temperature with mechanical stirring. The bleached fibers were washed with water, followed by washing with dilute aqueous acetic acid and again with water. The water was displaced by ethanol and the latter by acetone, after which the acetone was removed by dry air. The treated fibers were as fluffy as absorbent cotton and showed a high degree of whiteness.

The bleached fibers were soaked in pyridine overnight, the excess pyridine was removed, and the material acetylated at 25° C. as described above. The material was removed from the acetylation mixture after 47 hours, when it had an acetyl content of 9.43 per cent. A second sample acetylated for 37 days at 39° C. had an acetyl content of 18.38 per cent.

TABLE II. TENSILE STRENGTH OF INDIVIDUAL COTTON FIBERS BEFORE AND AFTER ACETYLATION

Material	No. of Tests	Initial Length, Cm.	Tensile Strength (Breaking Load), Grams
Bleached cotton	53	0.69	4.2
Acetylated, 9.43% acetyl	35	0.57	4.7
Acetylated, 18.3% acetyl	36	0.55	5.5

The strength tests were made with a number of fibers taken from different portions of the moisture-conditioned sample. The average results shown in Table II—i. e., that careful acetylation does not impair the tensile strength of cellulose fibers but rather increases it—confirm those of Sakurada (13); he acetylated ramie with a mixture of acetic anhydride, acetic acid, and calcium acetate at the boiling point of the mixture for 49 hours. It may be assumed that higher acetyl contents would have increased the tensile strength of individual fibers still further.

The preparation of paper stock from unacetylated and acetylated rag stock was carried out in a special beating device built essentially according to that described by Laroque (9). It represented a simplified rod mill in that it was equipped with a single heavy rod instead of a number of thinner rods (Figure 1).

The rod was enclosed in a cylindrical beating vessel (a 6-inch extra-strong pipe, 12 inches long and 6 inches wide) into which the cellulosic material was placed, the vessel being rotated by two shafts on which the flanges of the vessel rested. The openings of the beating vessel were closed watertight with blind flanges, employing rubber gaskets. The rod consisted of a 4-inch standard pipe with a machined plug welded into each end. Its weight could be varied by changing the number of lead shots which could be placed inside through the plug at one end. The weight of the rod was usually adjusted to 30–35 pounds. The beating vessel and the rod were made of stainless steel. An amount of 10–25 grams of cellulosic material could be processed

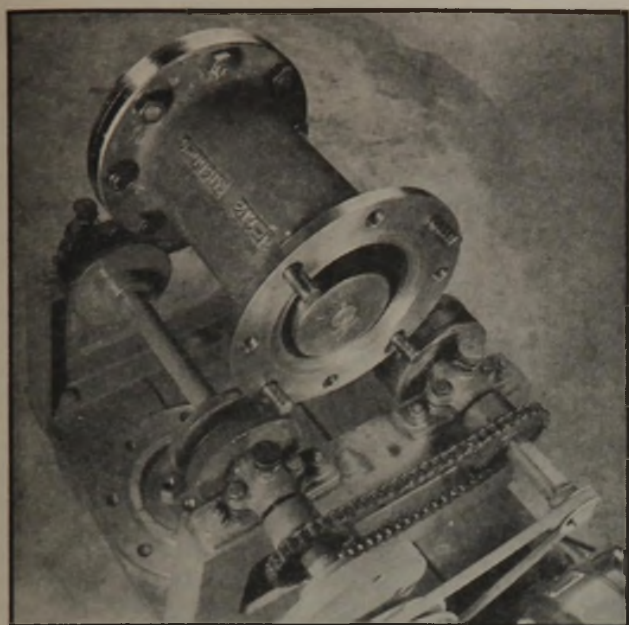


Figure 1. Beating Device

in one charge (compared with 1-2 grams in Laroque's device). The best consistency being 20 grams of cellulosic material in 2000 cc. of water.

To facilitate and homogenize the beating action, the cellulosic materials were first defibred by mere mechanical agitation in the presence of water in a British disintegrator as used in standard pulp testing; 4 minutes (12,500 revolutions) usually were sufficient. The beating was carried out by allowing the beating vessel (with its flanges bolted on tightly) to rotate for 300 minutes—i. e., for the same length of time required by unacetylated rag stock to develop its maximum strength properties. This seemed to be justified because a longer beating time raised the physical strength properties of the acetylated stock only slightly. (In the course of further studies on beating, it was found that the combined action of the British disintegrator and the beater was about equal to the use of the beater alone, if the beater roll was replaced by hard-rubber-covered lead balls, 1.5 and 1.7 inches in diameter, supplied by Rubber Surfacers, Inc.)

The acetyl content of the fibers remained practically unchanged on beating:

Acetyl before beating	4.25%	After beating	4.50%
Acetyl after beating	8.12	After beating	7.72

At the end of the beating period, the material was removed from the vessel, diluted with water, homogenized in the British disintegrator, and brought to a consistency of 0.20 per cent. Handsheets were prepared from the diluted suspension according to Standard T 205 m-40 of Technical Association of the Pulp and Paper Industry.

The handsheets were tested for tensile, bursting, and tearing strength and for apparent density according to standard procedures which were essentially the same as those suggested by TAPPI. The data in the following tables and figures refer to a pressure applied to the wet sheets of 50 pounds per square inch, unless otherwise stated.

EFFECT OF PROGRESSIVE ACETYLATION

The effect of progressive acetylation upon behavior of the rag stock during mechanical treatment, its ability to form a coherent and homogeneous sheet of paper, and the physical strength properties of the sheets were studied both with samples which had been merely defibred in the British disintegrator and with those which had been beaten in the beating device.

The effect of increasing acetyl content upon the physical properties of the sheets made from the unbeaten stock is shown in Table III and in Figure 2, in which the percentage

of hydroxyl groups replaced by acetyl groups (calculated from the acetyl content of the samples) is plotted against the physical strength properties and the apparent density of the sheets. In contrast to the effect of defibration upon unacetylated fibers, the replacement of hydroxyls by acetyl groups reduced the tensile, bursting, and tearing strengths, as well as the apparent density of the sheets, and this effect increased considerably with increasing acetyl content of the fibers.

TABLE III. EFFECT OF ACETYLATION ON PHYSICAL STRENGTH PROPERTIES AND APPARENT DENSITY OF DEFIBERED (UNBEATEN) RAG STOCK

Acetyl Content, %	Hydroxyl Replaced by Acetyl, %	Apparent Density, Basis Wt./Caliper	Bursting Strength, Lb./Sq. In./100 Lb. of Basis Wt.	Tensile Strength, Lb./100 Lb. of Basis Wt.	Tear Factor
Original (unacetylated)	0.00	{ 8.20 7.83	{ 26.6 27.9	7.0	{ 3.56 3.15
4.25	5.57	7.00	25.3	6.4	2.73
6.18	8.17	7.45	21.3	5.2	2.19
9.22	12.68	6.10	13.5	3.2	1.84
20.00	31.43	3.77	12.3	2.1	..
25.00	41.60	4.47	..	0.8	..

Moreover, in attempting to process the acetylated pulps, it was found that even the introduction of as small an amount of acetyl as 4 to 6 per cent considerably reduced the ability of the fiber surfaces to become wetted with water and of the fibers to settle on standing. With higher acetyl contents, the repulsion of water was still more noticeable and defibering was greatly impeded. There was a persistent tendency of the acetylated fibers to flocculate and clump together. Increasing the acetyl content of the pulp magnified this tendency, so

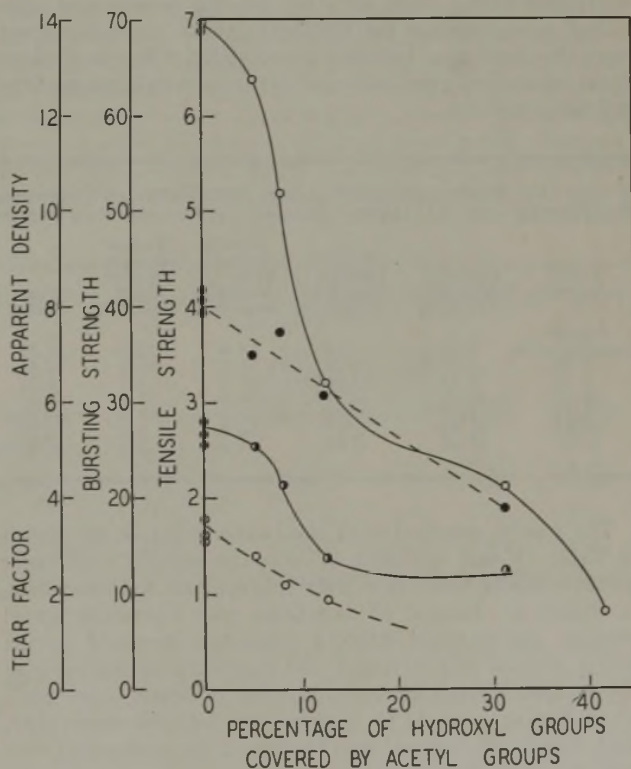


Figure 2. Effect of Acetylation upon Physical Strength Properties and Apparent Density of Defibred Unbeaten Rag Stock

- Tensile strength
- Bursting strength
- - -●- - - Apparent density
- - -○- - - Tear factor

that it was difficult, if not impossible, to prepare a sheet of even moderate uniformity under these conditions.

The freeness of the disintegrated stock, determined with the Schopper-Riegler apparatus, increased with increasing acetyl content, although not to such an extent as would have been expected.

The decrease in apparent density with increasing acetyl content seems to indicate that the acetylated fibers were less pliable and more rigid and hence not so compressible as were the unacetylated fibers. Indeed, to reduce the sheet formed of acetylated fibers to the same apparent density as shown by the sheet from the unacetylated fibers, a much higher pressure than 50 pounds per square inch had to be employed. As an example, the sheet prepared from the fibers with 4.25 per cent acetyl content required a pressure of 1800 pounds per square inch to produce the apparent density of 7.83 possessed by the sheet prepared from the original rag stock pressed at 50 pounds. Under these conditions, the physical properties of the highly pressed sheet more closely approached those of the original rag stock.

A comparison of the strength values of sheets from acetylated fibers with varying acetyl content at the same apparent density gives an idea of the bonding capacity of the fiber surfaces. When the strength properties of the 4.25 per cent acetyl cellulose sheet are interpolated to the apparent density of the 6.18 per cent acetyl cellulose sheet (7.45), a bursting strength of 26 pounds and a tensile strength of 6.7 pounds are obtained as compared with 5.2 and 21.3 pounds, respectively, for the 6.18 per cent acetyl cellulose sheet. This comparison seems to indicate that, even if the number of contacts between adjacent fibers were the same, the strength of the sheet with the higher acetyl content would be lower, which may be interpreted to mean that the bonding between surfaces in mutual contact is less for the higher than for the lower acetylated fiber. Thus, since the bonding decreases as more acetyl groups replace the hydroxyl groups, it would appear that the attraction between unacetylated fibers in a sheet must depend to a great extent upon the hydroxyl groups of the cellulosic material.

TABLE IV. EFFECT OF ACETYLATION UPON PHYSICAL STRENGTH PROPERTIES AND APPARENT DENSITY OF BEATEN RAG STOCK

Acetyl Content, %	Hydroxyl Replaced by Acetyl, %	Apparent Density, Basis Wt./Caliper	Bursting Strength, Lb./Sq. In./100 Lb. of Basis Wt.	Tensile Strength, Lb./100 Lb. of Basis Wt.	Tear Factor
Original (unacetylated)	0.00	10.78	54.6	18.3	3.22
4.25	5.57	10.38	57.7	18.8	3.41
6.11	8.17	10.25	61.3	19.3	3.21
8.12	11.07	9.99	49.8	17.1	3.35
9.22	12.68	10.28	52.5	17.6	3.05
20.05	31.43	7.07	13.8	5.0	1.36
23.35	37.80	6.89	10.2	3.4	0.85

The results obtained with the beaten samples are shown in Table IV and in Figure 3. For the samples with lower acetyl contents, they are in a striking contrast to those shown in Figure 2. Instead of decreasing with increasing acetyl content, the physical strength properties increased as the acetyl content was increased and reached a maximum with the samples having an acetyl content of about 6 per cent. These findings seem to be in agreement with the observation that, within the range of zero to about 6 per cent acetyl content, no difficulties in wetting and no agglomeration of the fibers were encountered; on the contrary, coherent and homogeneous sheets were easily formed. However, samples with more than about 9 per cent acetyl behaved like those of the first series and showed a rapid drop in physical strength properties.

The freeness of the beaten stock (550) first decreased, reached a minimum value of 365 at an acetyl content of 6.11 per cent and increased with further increasing acetyl content—i. e., to 780 at an acetyl content of 23.35 per cent. These observations are in good agreement with the initial increase and subsequent decrease of the physical strength properties and with the initial compatibility and the subsequent incompatibility of the acetylated materials with water.

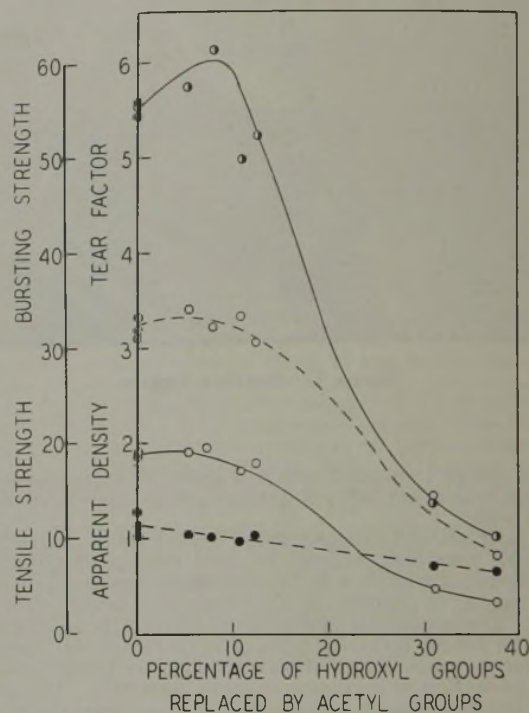


Figure 3. Effect of Acetylation on Physical Strength Properties and Apparent Density of Beaten Rag Stock

—○— Tensile strength  
 -○- Bursting strength  
 -●- Apparent density  
 -○- Tear factor

To explain the difference in the behavior of the unbeaten and the beaten fibers with a relatively low acetyl content, the assumption may be made that the acetylated surface of the fibers prevents the hydroxyl groups from becoming hydrated as long as the fibers are not beaten. As stated earlier, beating develops the external surface of the fibers and thus exposes more hydroxyl groups to hydration; the result is increased bonding of fiber surfaces and strength properties of the sheets. However, this does not explain the fact that the bonding and the physical properties increased above those which may be obtained by beating unacetylated fibers. It seems safe to assume that the introduction of acetyl groups widens the distance between the micelles (chain bundles) of the fibers. It is also possible that, as a result of the incompatibility of the acetyl groups with water, repelling forces are developed between the water molecules mechanically held in the capillaries of the fibers and the acetyl groups on the surfaces which would aid in the loosening of the structure. Such condition may be expected to further the development of the external surface on beating and, consequently, result in the exposure of a greater number of hydroxyl groups to hydration than could be made available by beating the un-



acetylated fibers under the same conditions. As a result, the acetylated fibers (with acetyl contents up to about 6 per cent) would be in a state in which the bonding between fibers is increased with subsequent improvement of the physical properties of the sheets. However, with samples having acetyl contents above this range, the increased availability of free hydroxyl groups would have less and less effect, because the hydrophobic character of the fibers would become more and more pronounced and eventually predominate the hydration effect.

If this hypothesis is correct, the hygroscopicity of sheets made from beaten fibers should increase with increasing acetyl content until the optimum of the physical strength properties is obtained and should fall only after more acetyl has been introduced.

In the light of the modern concept of the molecular and micellar structure of cellulose, it may be assumed that the hydroxyl groups which are exposed on the micellar surfaces are located in both the primary and the secondary positions of the glucose residues. Since the resistance of the acetylated fibers to hydration and subsequent bonding was observed even with materials in which only a limited number of the surface-exposed hydroxyl groups were substituted, the question arises as to whether the acetyl groups are present in the primary or the secondary positions or are distributed uniformly or nonuniformly over the two types of positions. The answer to this question would be of interest because it would show which of the two types of hydroxyl groups are involved in the phenomena of hydration and bonding of cellulose fibers when a sheet of paper is prepared.

It would appear that some information on this question could be obtained by subjecting the partially acetylated fibers to the reactions (tosylation and subsequent iodination) which Cramer and Purves (3) used to determine the positions in which the acetyl groups are located in commercial secondary cellulose acetates.

#### FIBERS REGENERATED FROM ACETYLATED RAG STOCK

If it were possible to restore the papermaking properties of the acetylated rag stock by restoring its hydroxyl groups, convincing evidence would be furnished in favor of the hypothesis that the partial substitution above a certain level of the hydroxyls in cellulose by ester groups is responsible for the diminished hydration and the loss in physical strength properties.

Staudinger and co-workers (18) have shown that the cellulose constituent of an acetate may be regenerated without degradation if the acetyl groups are saponified in a nitrogen atmosphere. This precaution was employed when a portion of the solution which served for the determination of the acetyl content of the acetylated samples (according to Murray, Staud, and Gray) was used for the saponification of an acetylated rag stock sample with 14.20 per cent acetyl content. (This sample was obtained by the acetylation of beaten rag stock, Table I.)

The sample was allowed to stand in the mixture of alkali and ethanol at room temperature in an apparatus which allowed all manipulations to be carried out in a nitrogen atmosphere. After 65 hours the sample was freed of the solution and washed several times with alcohol and subsequently with distilled water. Traces of alkali were removed with a small amount of dilute acetic acid, and the salt thus formed was washed out with distilled water. The material was free of combined acetic acid.

A sample of the regenerated fibers was processed in the British disintegrator according to the procedure previously described. For comparison, a sample of the acetylated rag stock (from which the cellulose had been regenerated) and a

sample of the original (unacetylated) beaten rag stock were subjected to the same treatment. The original sample was treated with pyridine and washed as it would have been for acetylation. These treatments, however, had no undesirable effects. The stocks were converted into handsheets, which were tested as described above. The results are shown in Table V.

TABLE V. PHYSICAL PROPERTIES OF SHEETS PREPARED FROM RAG STOCK REGENERATED FROM ACETYLATED RAG STOCK

Material	Bursting Strength, Lb./Sq. In./100 Lb. of Basis Wt.	Tensile Strength, Lb./100 Lb. of Basis Wt.	Tear Factor	Apparent Density
Original (beaten) rag stock <sup>a</sup>	68.7	20.79	3.73	10.45
Acetylated (beaten) rag stock	24.5	7.10	2.12	8.70
Regenerated material	55.7	18.42	3.42	10.43

<sup>a</sup> This sample resulted from beating a portion of the original rag stock in a standard laboratory beater (Valley Iron Works) to a freeness of 260.

The data indicate that the physical strength properties and the apparent density of the regenerated material were very nearly the same as, or approached those of, the original rag stock. Indeed, this comparison clearly shows the importance of the role which the free hydroxyl groups in cellulose play in the preparation of paper.

#### SHEETS FROM ACETYLATED FIBERS SUSPENDED IN ACETONE

Kress and Bialkowsky (8) have shown that swelling is a prerequisite for realizing the effect of defibration and beating and for producing a coherent and homogeneous sheet of paper. Therefore, it was thought that acetylated fibers also could be defibered, beaten successfully, and converted into a coherent strong sheet of paper if, instead of water, a medium were chosen in which the acetylated fibers would swell. Because the acetylated fibers were capable of swelling in acetone without dissolving, this liquid was selected as the medium.

TABLE VI. DEFIBRATION AND BEATING OF ACETYLATED FIBERS IN ACETONE

Material	Treatment	Bursting Strength, Lb./Sq. In./100 Lb. of Basis Wt.	Tensile Strength, Lb./100 Lb. of Basis Wt.	Tear Factor	Apparent Density
8.12% acetyl	British disintegrator	20.7	2.3	1.55	4.73
Same	Beater	32.8	7.5	3.30	5.07
25% acetyl	British disintegrator	139.0	31.4	3.82	7.50
Unacetylated rag stock	Beater	54.6	18.3	3.22	10.78

Although the original (unacetylated) rag stock was readily wetted by acetone and sank to the bottom of the liquid, it strongly resisted defibration when the mixture was subjected to the action of the British disintegrator. Even with mixtures of acetone and water, it was difficult to accomplish any appreciable degree of defibration, and coherent and homogeneous sheets could not be formed. If, however, an acetylated sample (8.12 per cent acetyl) was treated in acetone in the same manner, the difficulties were less pronounced and disappeared almost entirely on beating. Indeed, beating under the conditions described earlier produced a coherent and rather

uniform handsheet with physical strength properties distinctly better than those developed by the action of the British disintegrator (Table VI).

The compatibility of acetyl groups with acetone, which became noticeable even with the material containing only a relatively small amount of acetyl, was very pronounced with a sample containing 25 per cent acetyl. Under the action of the British disintegrator, this material broke up readily and produced a uniform sheet with surprisingly good physical strength properties. Indeed, bursting and tensile strength were considerably above the values which could be developed from the unacetylated rag stock on beating under optimum conditions (Table VI).

This result may be interpreted to mean that the bonding forces between acetyl groups of adjacent fiber surfaces in acetone are considerably stronger than those between hydroxyl groups in water. This interpretation is supported by the fact that the apparent density of the acetylated sheets was even lower than that of the sheets prepared from the unacetylated rag stock on beating (7.50 against 10.78).

The sheets were remarkably resistant to water; they floated on the water surface for a considerable time before sinking. Brought into contact with ink, they behaved like strongly sized paper.

The fact that, on beating and in sheet preparation, acetylated fibers in acetone behave in much the same way as unacetylated fibers in water seems to suggest that similar phenomena are involved—i. e., the solvation of acetyl groups by acetone (as compared with the hydration of hydroxyl groups by water in unacetylated fibers), and the subsequent bonding between acetyl groups of adjacent fibers as the acetone is evaporated from the sheet.

The results obtained so far seem to permit the prediction that it is possible to obtain the same effect—i. e., a strong sheet of paper—from other cellulose derivatives including ethers, provided the medium used is compatible with the specific type of derivative groups. In other words, the effect is expected to be governed by the degree of swelling and solvation which, in turn, depends upon the nature of the group as well as upon that of the medium. Likewise, it may be expected that the longer the groups introduced into the cellulose fiber, the more pronounced will be the water-repellent properties of the sheet, or the smaller will be the number of such groups that have to be introduced to obtain the same effect as with a greater number of shorter groups. Finally, it appears that the process of preparing paper from cellulose derivative fibers as described here and studied for scientific reasons may have commercial possibilities.

#### SUMMARY

1. Rag stock fibers were acetylated with acetic anhydride and pyridine according to the method of Hess and Ljubitsch, omitting the alkaline pretreatment.

2. Some of the fibrous preparations of varying acetyl content (4.25 to 26.7 per cent) were subjected to viscosity measurements in cuprammonium hydroxide. The viscosities were converted into molecular weights according to Staudinger's equation. The results showed that the degree of polymerization of the rag stock cellulose changed very little on acetylation. The greatest decrease amounted to less than 10 per cent.

3. Likewise, it was shown that the tensile strength of cotton lint prepared from raw cotton by extraction with ethanol, followed by careful bleaching, did not decrease but rather increased on acetylation.

4. Samples of rag stock of increasing acetyl content were subjected to mere disintegration (defibration) in the British disintegrator and to beating in a specially constructed beating

device. Sheets were formed by hand and tested for physical properties according to standard procedures.

5. It was found that the acetylated material which was merely defibered became increasingly incompatible with water and increasingly resistant to the attempt to form a uniform and coherent sheet as the acetyl content increased. Likewise, the physical strength properties and the apparent density of the sheets decreased with increasing acetyl content and became practically zero with fibers containing 24 per cent acetyl.

6. This result shows that the ability of cellulose fibers to become hydrated on mechanical treatment in the presence of water and subsequently bonded together on the removal of water to form a coherent and strong sheet of paper is essentially a function of their hydroxyl groups.

7. In contrast, the physical strength properties of sheets which had been prepared from beaten samples increased with increasing acetyl content, reached a maximum at an acetyl content of about 6 per cent, and dropped only after the acetyl content was further increased.

8. A hypothesis is presented to explain the difference between the behavior of the merely defibered and the beaten acetylated materials.

9. The physical properties of sheets prepared from rag stock which had been regenerated from the acetylated material by saponification were nearly the same as those obtained with the unacetylated original material.

10. When acetylated rag stock was defibered or beaten in acetone instead of in water, sheets of excellent uniformity and even greater strength properties were obtained than from the unacetylated rag stock beaten in water. In addition, the sheets were remarkably resistant to the penetration of water and ink. These results are explained by the assumption that, in analogy with the behavior of unacetylated fibers in the presence of water and when the water is removed, the acetylated acetone-swollen fibers are solvated by the acetone as beating progresses, and are bonded together through secondary valences of their acetyl groups as the acetone is allowed to evaporate.

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# ASPHALT-POLYBUTENE PAINTS

H. C. EVANS<sup>1</sup>, D. W. YOUNG,  
AND R. L. HOLMES<sup>2</sup>

Standard Oil Company of New Jersey,  
Elizabeth, N. J.

Accelerated weathering and normal weathering tests have been conducted on seventy experimental asphalt-polybutene cutbacks, with and without fillers, and the results are critically discussed. Results indicate that polybutene reduced or completely eliminated the tendency of the several asphalts to alligator, slightly reduced the tendency to check, reduced surface hardness, and increased the length of time before dusting began.

RECENT work on the general subject of petroleum asphalt-polybutene blends has followed two general lines, the first being a study of the effect of polybutene on the physical properties of asphalt as determined by standard laboratory instruments. It has been found that, in general, the softening point, penetration, ductility, and similar standard asphalt tests are influenced not only by the molecular weight of the polybutene but also by the type of asphalt in which it is blended.

These observations prompted the second portion of the program. This work is more practical and is a study of the effect of low concentrations of polybutene on the weathering and surface consistency characteristics of several asphalt films.

## EFFECT OF POLYBUTENE ON COLLOIDAL STRUCTURE

The effect of the addition of polybutene on the colloidal structure of asphalt raises several problems. A number of them were previously discussed by Thomas *et al.* (2). Limited quantities of polybutene will dissolve in the oily medium without destroying the colloidal structure of the asphalt. It is thought that viscosity can be raised in this manner enough to decrease markedly the loss of oily constituents by evaporation and the leaching action of water. Since the medium's resistance to oxidation will be improved by the polybutene addition, oxidation as an accelerating force in the loss of the oil phase will be lessened, and the retention of the medium will be more dependent upon resistance to volatilization and moisture permeability. Both the latter should be improved by the addition of polybutene. This has been borne out by an actual weathering comparison of a straight asphalt and an asphalt-polybutene coated on a roof and exposed for 210 days. While the straight asphalt coat became brittle and showed cracking, the polybutene blend remained soft and pliable; this behavior indicated successful retention of the oil components by the latter.

The stability of the colloidal system itself will be profoundly influenced by the addition of polybutene. Surface tension and absorption effects will play decisive roles in this consideration. Research with rubber indicates that small amounts of rubber powder blended into asphalt produce changes in the properties of the asphalt due to the selective absorption of the lighter hydrocarbons from the bitumen; a disperse system of swollen grains of rubber is thus formed in an asphaltic bitumen of the same type as the original but harder. High-molecular-weight polybutenes might be comparable to rubber in this respect; but those of lower molecu-

lar weight (less than about 30,000 as determined by the Staudinger method, 1) will be so much more soluble in the oil phase that the system will remain a two-phase system of asphaltene micelles, now dispersed in an oil-polybutene medium.

It seems likely that the addition of polybutene will result in lowering the interfacial tension of the medium micelle. This will tend to produce positive absorption or a concentration of the polybutene at the interface as the concentration of polybutene in the solution increases. Flocculation of the disperse phase would be the ultimate result if the concentration of polybutene in the oil phase was increased to the proper point. It can also be postulated that selective absorption of the resinous protective bodies of the micelles by the polybutene may also result in destruction of the micelles and precipitation of the asphaltenes.

From theoretical considerations, therefore, it would seem that the concentration of polybutene of a given molecular weight in solution will be limited by the extent of solubility as well as by absorption and surface tension effects. If optimum improvement in weathering properties made desirable the incorporation of polybutene above the limit of compatibility, it would be still essential to protect the stability of the colloidal system. This might be effected artificially by the addition of a fluxing agent, possibly one of the cheaper resins of the desirable softening point and toughness. In high concentrations the polybutene would bloom to the surface in the form of a thin film, and would protect the asphalt by its own qualities from the action of oxygen and water. The surface, however, would be far too tacky for practical application; at any rate, such high proportions of polybutene, even if dried by the use of fillers, is getting out of the paint range into that of tapes and mastics. Certain finely divided mineral fillers might profitably be added, nevertheless, to the asphalt-polybutene solution, both to stabilize the solution and to increase hardness and lessen tackiness.

## EFFECT OF POLYBUTENE ON PHYSICAL PROPERTIES

Since such physical properties of asphalt as softening point, penetration, and ductility are closely related to viscosity, it is apparent that such a substance as polybutene, known to have a profound effect on the viscosity-temperature of oils, should considerably affect the properties of asphalt. Work has been done on the solubility of polybutene in asphalts, and the extent of compatibility has been found to be a function both of the molecular weight of polybutene and the origin of the asphalt. Table I lists the results obtained from seventy-four experiments on asphalt-polybutene blends.

Ninety-four steel panels were coated with asphalt-polybutene paints. Coating from solution instead of applying as a

<sup>1</sup> Present address, Stanco Distributors, Inc., New York, N. Y.

<sup>2</sup> Present address, Raybestos-Manhattan, Inc., Stratford, Conn.

## WEATHERING TESTS

TABLE I. PHYSICAL PROPERTIES OF ASPHALT-POLYBUTENE BLENDS

Polybutene %	Mol. wt.	Type of Asphalt	Softening Point <sup>a</sup> , °F.	Penetrations <sup>b</sup>			Ductility at 77° F. <sup>c</sup>	Susceptibility Factor <sup>d</sup>
				32° F.	77° F.	115° F.		
0	..	Oxidized Columbian,	176	16	27	52	3 1/2	1.69
0.5	1,500	S. P. 160-180° F.	165	5	16	49	..	3.20
1.0	1,500		164	4	17	50	..	4.25
2.0	1,500		165	6	17	52	..	2.83
5.0	1,500		159	7	20	66	..	2.86
10.0	1,500		150	15	31	99	..	2.07
16.0	1,500		142	25	49	161	..	1.96
20.0	1,500		137	35	67	234	..	1.91
0	..	Oxidized Columbian,	190	15	23	38	2 1/2	1.53
0.5	1,500	S. P. 180-200° F.	190	16	23	38	2 1/2	1.44
1.0	1,500	(36% oil, 29.5 resin,	190	16	23	39	2	1.44
2.0	1,500	34.7 asphaltene)	191	16	23	39	2 1/4	1.33
5.0	1,500		191	21	28	44	2 1/4	1.39
10.0	1,500		193	23	32	48	2 1/2	1.07
20.0	1,500		209	41	44	60	1 1/2	..
0	..	S. P. 110° F.	108	15	99	300+	100+	6.60
0.5	1,500	Same	108	11	104	300+	100+	9.46
1.0	1,500	Same	106	15	112	300+	100+	7.47
2.0	1,500	Cracking-coil tar	104	19	130	300+	100+	6.85
5.0	1,500	Wax tailings substitute	99	23	207	300+	100+	9.00
10.0	1,500	Same	94	51	300+	300+	100+	5.9+
20.0	1,500	Same	125	107	119	300+	31, 60, 71	1.11
0	..	Steam-reduced, S. P.	171	4	12	37	2 1/2	3.00
0.5	1,500	160-170° F.	176	5	15	41	..	3.00
1.0	1,500		176	5	15	43	..	3.00
2.0	1,500		179	6	14	39	..	2.33
5.0	1,500		166	8	19	55	..	2.38
10.0	1,500		164	11	20	61	1	1.82
0	..	Oxidized Columbian,	176	16	27	52	3 1/2	1.69
0.5	15,000	S. P. 160-180° F.	180	15	27	51	3	1.80
1.0	15,000		197	16	27	51	3	1.69
2.0	15,000		183	16	29	48	2 1/2	1.81
5.0	15,000		194	22	33	50	2 1/2	1.50
10.0	15,000		232	26	31	42	0	1.19
20.0	15,000		217	..	..	..	..	..
0	..	Oxidized Columbian,	190	15	23	38	2 1/2	1.53
0.5	15,000	S. P. 180-200° F.	211	15	21	35	..	1.40
1.0	15,000		209	16	22	36	..	1.37
2.0	15,000		207	16	24	38	..	1.50
5.0	15,000		219	22	30	47	..	1.36
10.0	15,000		251	23	29	39	..	1.26
0	..	S. P. 110° F.	108	15	99	300+	100+	6.60
0.5	15,000	Same	109	14	89	300+	100+	6.36
1.0	15,000	Cracking-coil tar	110	9	85	300+	100+	9.45
2.0	15,000	Wax tailings substitute	110	12	88	300+	100+	7.33
5.0	15,000	Same	108	21	112	300+	100+	5.34
10.0	15,000	Same	112	35	138	300+	67	3.94
20.0	15,000	Same	86	83	300+	300+	..	3.6+
0	..	Steam-reduced, S. P.	171	4	12	37	2 1/2	3.00
0.5	15,000	160-170° F.	174	4	12	34	5	3.00
1.0	15,000		186	5	12	36	4 1/2	2.40
2.0	15,000		176	6	14	38	5 1/2	2.33
5.0	15,000		183	5	15	40	5 1/2	3.00
10.0	15,000		189	6	17	41	4 1/2	2.83
20.0	15,000		199	6	19	42	1	3.17
0	..	Oxidized Columbian,	190	15	23	38	2 1/4	1.53
0.5	40,000	S. P. 180-200° F.	204	16	24	40	2 1/4	1.50
1.0	40,000		215	15	23	38	2 1/2	1.53
2.0	40,000		214	22	26	44	3 1/2	1.18
5.0	40,000		234	16	25	41	1	1.56
10.0	40,000		265	27	20	30	0	0.74
20.0	40,000		285	32	34	46	1	1.06
0	..	S. P. 110° F.	108	15	99	300+	100+	6.60
0.5	40,000	Same	112	10	92	330+	100+	9.20
1.0	40,000	Cracking-coil tar	109	30	89	300+	100+	2.75
2.0	40,000	Wax tailings substitute	112	37	79	300+	97	2.14
5.0	40,000	Same	119	44	86	300+	82	1.95
10.0	40,000		156	37	65	208	54	1.75
0	..	Steam-reduced, S. P.	171	4	12	37	2 1/2	3.00
0.5	40,000	160-170° F.	177	5	12	30	1	2.40
1.0	40,000		171	6	13	37	6	2.16
2.0	40,000		175	4	14	36	5 1/2	3.50
5.0	40,000		195	19	33	47	1	1.73
10.0	40,000		209	5	7	35	1	1.40

<sup>a</sup> By ring and ball method (A. S. T. M. D5-25).<sup>b</sup> A. S. T. M. method D36-26. <sup>c</sup> A. S. T. M. method D113-39.<sup>d</sup> Ratio of penetration at 77° to penetration at 32° F.

hot melt or enamel has been the practice; slight improvement could be more easily noted and any definite improvement of coat would more easily justify polybutene addition, since, in general, poor weathering results are obtained with asphalt in thin films. Seventy-six of the panels were tested for accelerated weathering in a Weather-ometer. Sixty-eight of the samples were also tested on steel in the 45° southern exposure weathering racks on the roof of the General Engineering Building at Bayway, N. J.

Mixtures of 5, 10, 15, and 20 per cent polybutene of 6000 and 15,000 molecular weight in asphalts of 110° F. softening point (S. P.), 160-180° F. S. P. oxidized, 180-200° F. S. P. oxidized, and 220-235° F. S. P. oxidized were made up at about 100° C. in the laboratory Baker-Perkins kneader-mixer. Visual observations of brightness and homogeneity of the resulting panels, as a rough criterion of solubility, bore out the previously determined limits (Table II). However, above the limit of actual solubility of polybutene in asphalt, there may be intermediate stages of incompatibility above which compatibility again occurs, but where the asphalt simply acts as a filler in the polybutene and no actual solution of polybutene in asphalt occurs. Yet when enamels were made up in 2-20 per cent concentrations of polybutene from the blends, the solubility seemed to follow a straight-line decrease with increasing polybutene concentration. This would indicate, therefore, that during the period in which the solvent is evaporating, there is a breakdown of the colloidal structure of the film which is partially inhibited at high concentrations of polymer where the viscosity prevents this aggregation.

Though not the best solvent for asphalt, Varsol No. 2 was first used for cutting back the highly viscous kneader-formulated mixtures. After several methods were tried for mixing the polymer-asphalt blend with light hydrocarbon solvents, mechanical shaking for 8 hours at room temperature in the laboratory shaker was found the simplest means for obtaining a homogeneous paint.

In Varsol there was some trouble with thixotropic gel formation, but stirring was ample to break the viscosity. This was especially noticeable in the higher polybutene concentration.

No attempt was made to control the viscosity of the cut-backs; in each case sufficient solvent was added to give satisfactory paint consistency. Actually, in painting the panels, two-coat applications were found to be 0.003-0.005 inch thick for a wide range of consistencies.

Steel panels (12 × 6 inches) were coated with the paints

TABLE II. EFFECT OF POLYBUTENE ON PHYSICAL PROPERTIES OF ASPHALT-POLYBUTENE PAINTS<sup>a</sup>

Physical Property	Mol. Wt. of Polybutene	Cracking-Coil Tar, 110° F. S. P.	Steam-Reduced Asphalt, 160-170° F. S. P.	Oxidized Columbian Asphalt, 160-180° F. S. P.	Oxidized Columbian Asphalt, 180-200° F. S. P.
Softening point	1,500	Lowers	Lowers	Lowers	No effect
	15,000	No effect	Raises	Raises	Raises
	40,000	Raises	Raises	Raises	Raises
Penetration	1,500	Raises	Raises	Raises	Raises
	15,000	Raises slightly	Raises slightly	Raises at 32°, lowers at 115° F.	Raises at 32°, remains same at 115° F.
	40,000	Raises at 32°, lowers at 115° F.	Approx. unchanged at 32° and 115° F.	.....	Raises at 32°, raises slightly at 115° F.
Ductility	1,500	Lowers	Lowers	.....	Lowers
	15,000	Lowers	Raises (?)	Lowers	.....
	40,000	Lowers	Raises (?)	.....	Lowers
Susceptibility factor, penetration at 77° F./penetration at 32° F.	1,500	Lowers	Lowers	.....	Lowers
	15,000	Lowers	Unchanged	Lowers	Lowers
	40,000	Lowers	Lowers	.....	Lowers
Solubility <sup>b</sup>	1,500	20%	16%	.....	.....
	15,000	5%	5%	.....	5%
	40,000	0.5%	0.5%	.....	0.5%

<sup>a</sup> Physical properties determined on blends of 0.5, 2, 5, 10, and 20% polybutene.

<sup>b</sup> As determined by visual observation of homogeneity.

and submitted to a slippage test. Lines are drawn parallel to the 12-inch side, 1 inch apart. The panels are placed vertically on their 12-inch sides in an oven at 160° F. for 5 hours, and the increase in distance between lines is measured. By this method all paints containing 110° F. S. P. asphalt were discarded as too soft; the 160-170° F. S. P. steam-reduced asphalt was substituted for it in later work.

Examination of the panels made for the above test showed that, upon standing, the tendency of the polybutene to bloom to the surface of the 10, 15, and 20 per cent blends left the films with a blotched appearance; this indicated a breakup of the asphalt-polybutene colloidal structure during solvent evaporation. As these films were characterized by extreme tack, it was decided to withhold weathering tests on the mixtures until a more general study could be made of solvation and evaporation.

Twenty-eight sets of panels were then painted with 0, 1, 3, and 5 per cent polybutenes of 6000 and 15,000 molecular weight in four asphalts: 220-235° F. S. P. oxidized, 180-200° F. S. P. oxidized, 160-180° F. S. P. oxidized, and 160-170° F. S. P. steam-reduced. Test panels were placed on the southern exposure racks of the General Engineering Building, and in accelerated conditions in a vertical position in the Atlas Weather-ometer. Results on the accelerated tests are listed in Table III. Each cycle of the Weather-ometer consists of 16-hour exposure to a carbon arc light and finally 2 hours of

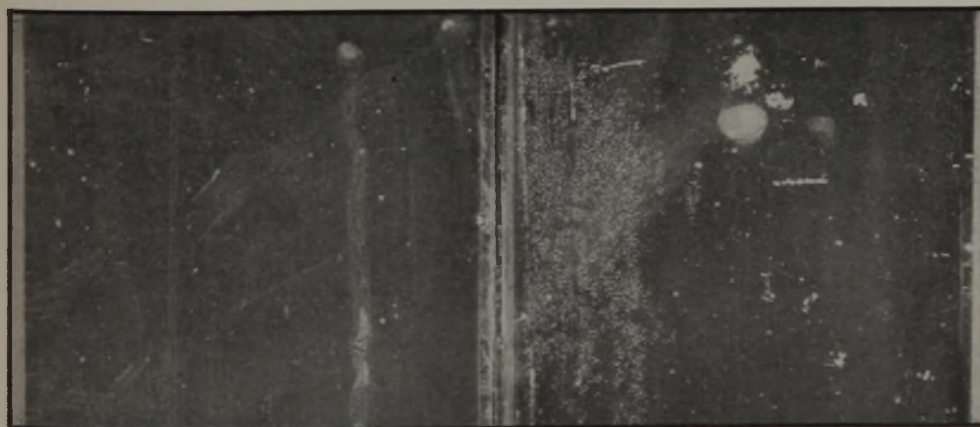
tap water spray at room temperature. Although this test does not give satisfactory quantitative results for asphalt coatings, it shows qualitative results for comparison.

#### COATINGS IN ACCELERATED TESTS

After two cycles, all of the coats had lost their original luster and all showed checking except the 1, 3, and 5 per cent 6000-molecular-weight polybutenes in 220-235° F. S. P. oxidized asphalt, and the 5 per cent 15,000-molecular-weight polybutene in 220-235° F. S. P. oxidized and in 160-180° F. S. P. oxidized asphalts. Checking was particularly bad in the 160-170° F. S. P. steam-reduced asphalt paints, some of which had started to alligator. All blanks had suffered more than their corresponding polybutene blends with the exception of the 160-180° F. S. P. oxidized asphalt. The 220-235° F. S. P. oxidized asphalt paints were, in general, noticeably superior to those of the other asphalts.

After four cycles all samples were marked by considerable dusting, except for the 5 per cent 15,000-molecular-weight polymer blends where the condition was, at most, merely incipient. Many coats had begun to alligator, and at the end of six cycles, this alligating had reached a maximum. The three 5 per cent 15,000-molecular-weight blends in the oxidized asphalts were, in general, the best. The steam-reduced asphalt blends showed bad flow failures. At ten cycles all samples were dusting badly, with the exception of the 5 per cent 15,000-molecular-weight blends, but checking and alligating had begun to disappear.

By thirty-eight cycles there had been a general leveling off in the appearance and character of the paints that continued throughout the rest of the test. At this point the 160-180° F. S. P. oxidized asphalt blends showed a slight advantage over the others. All the 160-170° F. S. P. steam-reduced asphalt panels had failed except for the 3 and 5 per cent 15,000-



Sample 91-6E, asphalt-polybutene paint

Sample 91-6G, asphalt paint (note checking)

Figure 1. Comparison of Weather-ometer Test on Asphalt Paints, with and without Polybutene (Table III)

TABLE III. RESULTS OF WEATHER-OMETER TEST ON ASPHALT-POLYBUTENE PAINTS

Sample Number	Type of Asphalt	Polybutene		Solvent		Thickness of Coat, In.	No. of Cycles	Appearance at End of Test				
		%	Mol. wt.	Name	%			Checking	Rusting	Condition	Chalking	
91-6A	Oxidized, S. P. 220-235° F.	1	6,000	Varsol 2	56.5	..	63	Yes	None	Fair	Yes	
6B		3	6,000		58.3	..	63	Slight	Slight	Good	Yes	
6C		5	6,000		60.0	..	63	Slight	Slight	Good	Yes	
6D		1	15,000		56.5	..	63	Yes	None	Good	Yes	
6E <sup>a</sup>		3	15,000		60.0	..	63	None	Slight	Good	Yes	
6F <sup>a</sup>		5	15,000		60.0	..	63	Large checks	Slight	Fair	Yes	
6G <sup>a</sup>	..	..	..	..	..	..	..	..	..	..		
91-7A	Oxidized, S. P. 180-200° F.	1	6,000	Varsol 2	52.0	0.0038	63	Yes	On corners	Good	Yes	
7B		3	6,000		52.0	0.0038	63	Yes	Slight	Good	Yes	
7C		5	6,000		52.0	0.0038	63	Yes	Slight	Good	Yes	
7D		1	15,000		52.0	0.0038	63	Very slight	None	Good	Yes	
7E		3	15,000		52.0	0.0038	63	Very slight	Slight	Good	Very slight	
7F		5	15,000		52.0	0.0038	63	Yes	Yes	Good	Yes	
7G		..	..		..	..	..	..	..	..	..	..
91-8A	Oxidized, S. P. 160-180° F.	1	6,000	Varsol 2	52.0	0.0038	63	Large checks	Yes	Fair	Yes	
8B		3	6,000		52.0	0.0038	63	Fine checks	Slight	Good	Very little	
8C		5	6,000		52.0	0.0038	63	Yes	Yes	Poor	Yes	
8D		1	15,000		52.0	0.0038	63	Large checks	Yes	Good	Yes	
8E		3	15,000		52.0	0.0038	63	None	None	Good	Very slight	
8F		5	15,000		52.0	0.0038	63	Large checks	Yes	Poor	Yes	
8G		..	..		..	..	..	..	..	..	..	..
8G		..	..		..	..	..	..	..	..	..	..
91-9A	Steam-reduced, S. P. 160-170° F.	1	6,000	Varsol 2	54.5	..	63	Slight	Yes	Fair	Yes	
9B		3	6,000		54.5	..	63	Yes	Yes	Poor	Yes	
9C		5	6,000		54.5	..	63	Wide checks	Slight	Poor	Yes	
9D		1	15,000		52.0	..	63	Slight	Yes	Fair	Yes	
9E		3	15,000		52.0	..	63	Large checks	Slight	Poor	Yes	
9F		5	15,000		52.0	..	63	Deep	Yes	Poor	Yes	
9G		..	..		..	..	..	..	..	..	..	..
91-16A <sup>b</sup>	Oxidized, 230° F.	10	6,000	Solvesso 3	50.0	..	50	None	None	Good	Yes	
16B <sup>b</sup>	Oxidized, 230° F.	5	15,000		50.0	..	50	Yes	None	Good	Yes	
16C <sup>b</sup>	Oxidized, 190° F.	5	15,000		50.0	..	50	Yes	None	Good	Yes	
16D <sup>b</sup>	Oxidized, 170° F.	5	15,000		50.0	..	50	Yes	None	Good	Yes	
16E <sup>b</sup>	Steam-reduced, 165° F.	5	15,000		40.0	..	50	Slight	None	Good	Yes	
..	..	..	..		..	..	..	..	..	..	..	
91-16F <sup>b</sup>	Oxidized, 230° F.	10	6,000	Varsol 2	62.5	..	50	None	Very slight	Good	Yes	
16G <sup>b</sup>	Oxidized, 230° F.	5	15,000		60.0	..	50	Yes	Yes	Fair	Yes	
16H <sup>b</sup>	Oxidized, 190° F.	5	15,000		60.0	..	50	Slight	Slight	Fair	Yes	
16I <sup>b</sup>	Oxidized, 170° F.	5	15,000		53.5	..	50	Yes	Yes	Poor	Yes	
16J <sup>b</sup>	Oxidized, 170° F.	5	15,000		50.0	..	50	Yes	Yes	Poor	Yes	
..	..	..	..		..	..	..	..	..	..	..	
91-17A	Oxidized, 230° F.	10	6,000	Solvesso 3	53.5	..	50	None	None	Good	Yes	
17B	Oxidized, 230° F.	5	15,000		50.0	..	50	Slight	None	Fair	Yes	
17C	Oxidized, 170° F.	5	15,000		50.0	..	50	Faint	None	Good	Yes	
17D	Steam-reduced, 165° F.	6	15,000		40.0	..	50	Very little	Slight	Good	Yes	
91-18A	Oxidized, S. P. 220-235° F.	1	87,590	Solvesso 3	50.0	..	50	Yes	Slight	Fair	Yes	
18B		1	87,590		50.0	..	50	Yes	Slight	Fair	Yes	
18C		3	87,590		50.0	..	50	None	Slight	Good	Yes	
18D		5	87,590		60.0	..	50	None	Slight	Good	Yes	
18E		10	87,590		68.67	..	50	None	None	Good	Slight	
18F		20	87,590		73.0	..	50	Large & small checks	None	Good	None	
..		..	..		..	..	..	..	..	..	..	..

<sup>a</sup> Figure 1.<sup>b</sup> Plus 5% sodium sulfonate or "M" soap.

TABLE IV. ASPHALT-POLYBUTENE PAINTS GIVING PROTECTION IN ACCELERATED WEATHERING TEST

Code No.	91-6B	91-6F	91-7C	91-7F	91-8B	91-8F
Polybutene Per cent	3	5	5	5	3	5
Mol. wt.	8000	15,000	6000	15,000	6000	15,000
Oxidized asphalt S. P., °F.	200-235	200-235	180-200	180-200	160-180	160-180
Varsol 2, %	58.3	60	52	52	52	52

TABLE V. ASPHALT-POLYBUTENE PAINTS GIVING PROTECTION IN NORMAL WEATHERING TEST (IN VARSOL 2)

Sample Number	Order of General Appearance	S. P. of Oxidized Asphalt, °F.	Polybutene	
			%	Mol. wt.
91-7F <sup>a</sup>	1	180-200	5	15,000
91-6B <sup>a</sup>	2	220-235	3	6000
91-8C	3	160-180	5	6000
91-7C <sup>a</sup>	4	180-200	5	6000
91-6A	5	220-235	1	6000

<sup>a</sup> Sample gave good results in accelerated test.

molecular-weight blends. All coatings were dusting considerably, and the 220-235° F. S. P. oxidized asphalt paints had assumed a brownish tinge while the steam-reduced asphalt paints were definitely brown.

At the end of the accelerated test, the six panels of series 91-6 to 9, inclusive, were found to give good protection and have the best appearance (Table IV).

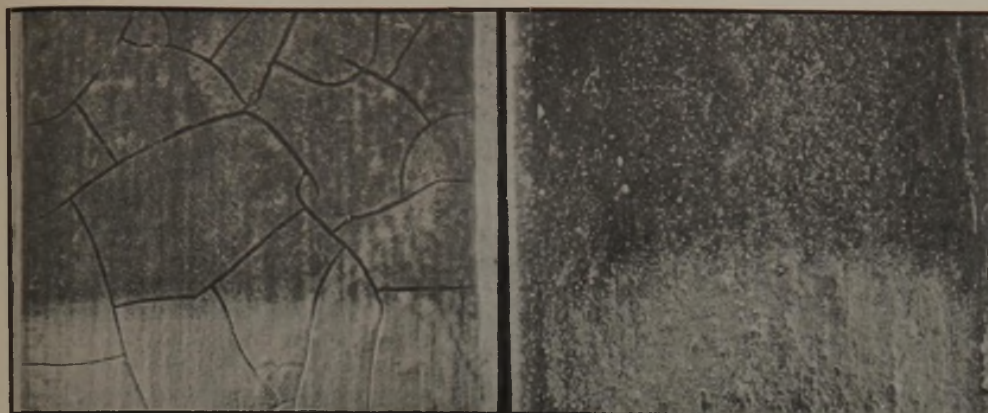
## COATINGS IN EXPOSURE TESTS

Steel panels painted with paints 91-6A to 6G and 91-7A to 7G, inclusive, were placed on the General Engineering Building on April 17, 1940. Panels painted with paints 91-8A to 8G and 91-9A to 9G, inclusive, were also exposed to the weather on the same roof on April 22, 1940. On September 3, 1940, most of the paints had failed to give adequate protection. The paints formulated without polybutene had failed completely in every case. The samples all showed a great deal of weathering, but the paints that gave the best protection are listed in Table V.

Shortly after the above panels had been placed under test, work was instigated to standardize the mixing procedure and to develop the best solvent for use in polybutene-asphalt paints. Blends of the following were made up in Solvesso 3 (aromatic solvent):

Paint Number	Polybutene %	Mol. wt.	S. P., °F.	Asphalt Type
1	10	6000	220-235	Oxidized
2	5	15,000	220-235	Oxidized
3	5	15,000	160-170	Steam-reduced
4	5	15,000	160-180	Oxidized

These blends were submitted to the best mixing procedure and panels were coated. The coatings showed higher luster and homogeneity than the corresponding Varsol paints. Also, in the course of twenty-three cycles of accelerated weathering there was far less checking than with the Varsol equiva-



Alligatoring

Checking

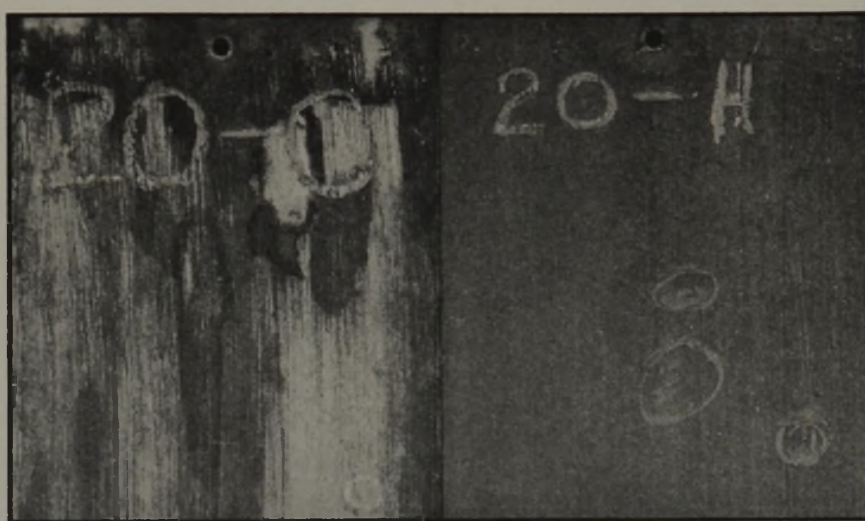
Figure 2 (Left). Difference between Alligatoring and Checking in Asphalt Films after 63 Cycles in the Weatherometer

lents and no alligatoring. Moreover, the 160–170° F. S. P. steam-reduced asphalt sample showed no flow tendencies in contrast to the similar Varsol paint.

To further improve mixing, samples of the above paints were given a thorough treatment in a colloid mill and painted out for comparison. Paints 1, 2, and 3 gave no evidence of improved mixing; paint 4 suffered a large drop in viscosity. The film of this paint was soft and tacky. However, during the time before a viscosity determination could be made (24 hours), the viscosity had returned to the original, and a later painted film showed no signs of breaking down. This may have been due

Figure 3 (Below). Effect of Polybutene on Weathered Asphalt Paints with Red Lead Primer (Table VII)

Circles indicate inspection points.



Sample 91-20-C, without polybutene

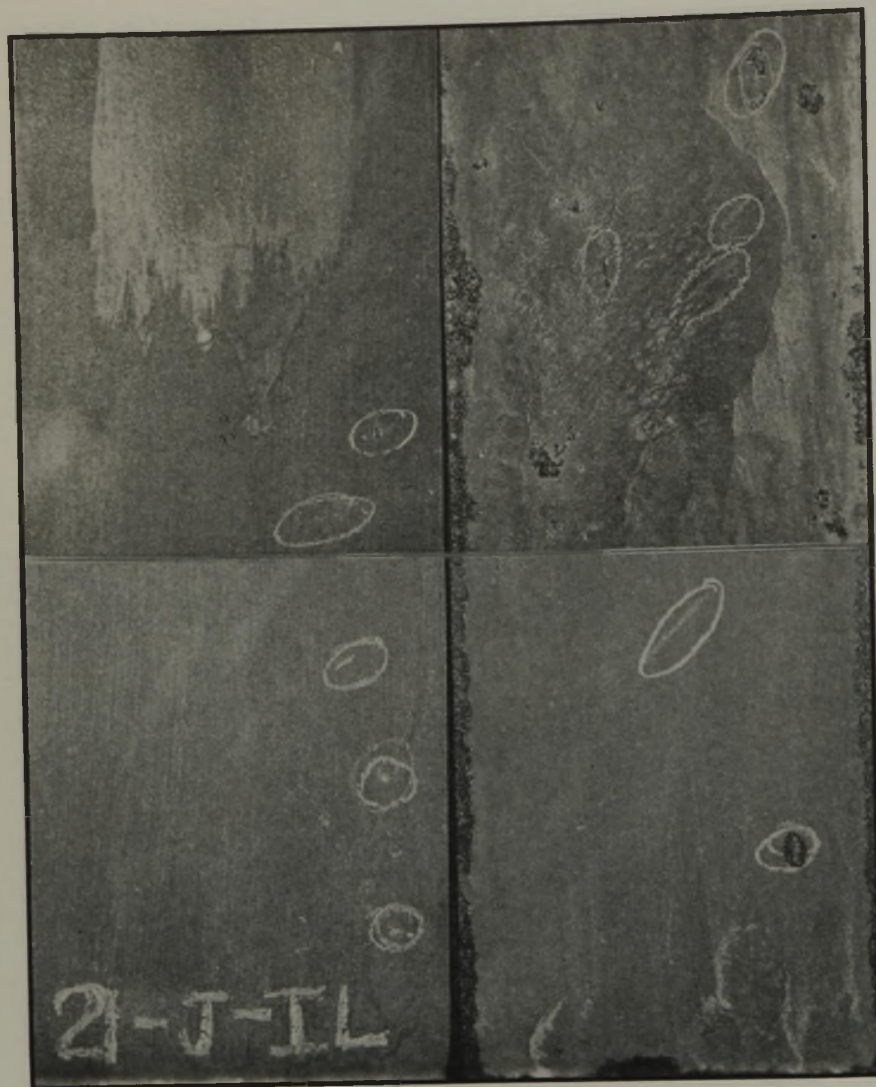
Sample 91-20-H, with polybutene

TABLE VI. WEATHER-OMETER TEST ON FILLED ASPHALT-POLYBUTENE PAINTS

Sample Number	Polybutene		Solvecso 2, % by Wt.	Filler		No. of Cycles	Appearance at End of Test			
	% <sup>a</sup>	Mol. wt.		Name	%		Checking	Rusting	Condition	Chalking
Oxidized Asphalt, Softening Point 160–180° F.										
91-20A	0	..	60	Mica	15	50	Yes	Yes	Poor	Yes
20B	0	..	60	Slate flour	35	50	Slight	In spots	Fair	Yes
20C	0	..	60	Silica powder	15	50	Yes	Slight	Fair	Yes
20D	0	..	60	Talcum powder	25	50	Yes	Slight	Fair	Yes
20E	0	..	60	Marble flour	15	50	Yes	Slight	Fair	Yes
91-20G	5	15,000	60	Mica	15	50	Slight	No	Good	Slight
20H	5	15,000	60	Slate flour	35	50	Slight	No	Good	Slight
20I	5	15,000	60	Silica powder	15	50	Slight	No	Good	Slight
20J	5	15,000	60	Talcum powder	25	50	Slight	No	Good	Slight
20K	5	15,000	60	Marble flour	15	50	Slight	No	Good	Slight
Steam-Reduced Asphalt, Softening Point 160–170° F.										
91-21A	0	..	50	Mica	15	50	Yes	In spots	Poor	Yes
21B	0	..	50	Slate flour	35	50	Slight	No	Fair	Yes
21C	0	..	50	Silica powder	15	50	Yes	No	Good	Yes
21D	0	..	50	Talcum powder	25	50	Slight	Slight	Good	Yes
21E	0	..	50	Marble flour	15	50	Yes	Slight	Fair	Yes
21F	0	..	50	Asbestos	10	50	Yes	Yes	Poor	Yes
91-21G <sup>b</sup>	5	15,000	50	Mica	15	50	No	No	Good	Slight
21H	5	15,000	50	Slate flour	35	50	Slight	No	Good	Slight
21I <sup>b</sup>	5	15,000	50	Silica powder	15	50	No	No	Good	Slight
21J	5	15,000	50	Talcum powder	25	50	Slight	Slight	Fair	Slight
21K <sup>b</sup>	5	15,000	50	Marble flour	15	50	No	No	Good	Slight
21J + 1L <sup>b</sup>	5	15,000	50	{ Talcum powder Ilmenite	{ 25 10	50	No	No	Good	Slight

<sup>a</sup> Calculated on asphalt.

<sup>b</sup> Paints that gave best protection.



Red lead primer

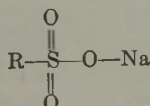
No primer

Figure 4. Effect of Primer on Weathered Asphalt Paint 21-A (above) and on Asphalt-Polybutene Paint 21-J-IL (below)

Circles indicate inspection points; note rusting around edges of panels without primer.

to the thixotropic characteristics of plastic oxidized asphalt and the polybutene.

In an attempt to improve the bond of the paints to steel and to improve the compatibility of polybutene in asphalt, sodium sulfonate or sodium alkyl sulfonate (molecular weight about 450),



was added to asphalt-polybutene paints

91-16A to 16J, inclusive (Table III). During the first twenty cycles these paints showed definite promise; there was far less checking and alligatoring on the painted panels. However after fifty cycles there was no great improvement, but slightly less rusting was noted when the sodium sulfonate was used.

Higher molecular weight polybutene mixtures have also been studied. Five paints containing 1, 3, 5, 10, and 20 per cent polybutene of 87,590 molecular weight were tested in the Weather-ometer (Table III, samples 91-18A to 18F, inclusive). Paints containing polybutene of this molecular weight contain lower solids content for comparable consistencies. This may be shown by the fact that for 1 per cent polybutene of 87,590 molecular weight, 50 per cent Solvesso 3 is required to give a consistency similar to 20 per cent polybutene of 87,590 molecular weight in 73 per cent Solvesso 3. Polybutene of this molecular weight is also considerably less compatible with asphalts. The resulting composition should be classed as a mastic and for that reason a discussion of compatibilities may be irrelevant.

The blends of 87,590-molecular-weight polybutene after fifty cycles have shown the best results of any tested to date. Slight dusting was noticed in the 5 and 10 per cent blends, but no dusting at all with the 20 per cent blend. Samples formulated with more than 1 per cent high-molecular-weight polymer were almost free from

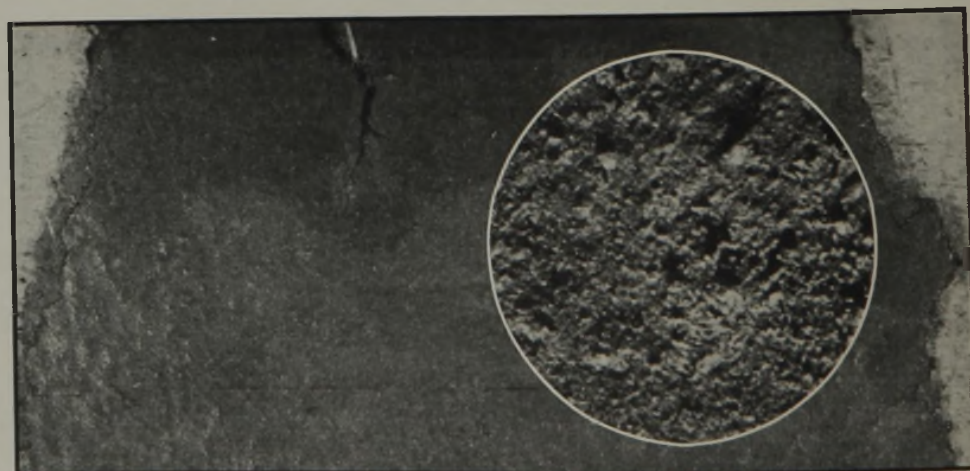


Figure 5. Weathered Asphalt-Polybutene Mica-Filled Paint

The tear occurred in removing the sample from the roof; the circle shows a section magnified 25 times.



TABLE VII. TWO-YEAR WEATHERING TEST ON FILLED ASPHALT-POLYBUTENE PAINTS

Sample Number	Polybutene		Solvesso 2, % by Wt.	Filler		Red Lead Primer	General Appearance			Condition
	% <sup>a</sup>	Mol. wt.		Name	% <sup>a</sup>		Checking	Peeling	Chalking	
Oxidized Asphalt, Softening Point 160-180° F.										
91-20A	0	..	60	Mica	15	No	Yes	Yes	Heavy	Very poor
20B	0	..	60	Slate flour	35	No	Yes	Yes	Heavy	Poor
20C	0	..	60	Silica powder	15	No	Yes	Moderate	Yes	Poor
20D	0	..	60	Talcum powder	25	No	Yes	Extreme	Yes	Poor
20E	0	..	60	Marble flour	15	No	Yes	Extreme	....	Failure
91-20A	0	..	60	Mica	15	Yes	Yes	Yes	Yes	Fair
20B	0	..	60	Slate flour	35	Yes	Yes	Slight	Slight	Fair
20C <sup>b</sup>	0	..	60	Silica powder	15	Yes	Yes	Slight	Heavy	Poor
20D	0	..	60	Talcum powder	25	Yes	Yes	None	Slight	Fair
20E	0	..	60	Marble flour	15	Yes	Yes	None	Heavy	Fair
Oxidized Asphalt, Softening Point 160-180° F.										
91-20G	5	15,000	60	Mica	15	No	None	Slight	Slight	Poor
20H	5	15,000	60	Slate flour	35	No	Yes	Slight	Slight	Fair
20I	5	15,000	60	Silica powder	15	No	Slight	Yes	Slight	Poor
20J	5	15,000	60	Talcum powder	25	No	Slight	Slight	Heavy	Fair
20K	5	15,000	60	Marble flour	15	No	...	Extreme	Heavy	Failure
91-20G	5	15,000	60	Mica	15	Yes	Slight	None	Slight	Fair
20H <sup>b</sup>	5	15,000	60	Slate flour	35	Yes	None	None	Slight	Good
20I	5	15,000	60	Silica powder	15	Yes	None	None	Slight	Good
20J	5	15,000	60	Talcum powder	25	Yes	None	None	Heavy	Good
20K	5	15,000	60	Marble flour	15	Yes	None	None	Heavy	Good
Steam-Reduced Asphalt, Softening Point 160-170° F.										
91-21A <sup>c,d</sup>	0	..	50	Mica	15	No	Yes	Yes	Heavy	Poor
21B	0	..	50	Slate flour	35	No	Yes	Yes	Yes	Good
21C	0	..	50	Silica powder	15	No	Yes	Slight	Yes	Poor
21D	0	..	50	Talcum powder	25	No	Yes	Yes	Very heavy	Poor
21E	0	..	50	Marble flour	15	No	Slight	Yes	Heavy	Poor
91-21A <sup>c,d</sup>	0	..	50	Mica	15	Yes	Slight	None	Slight	Fair
21B	0	..	50	Slate flour	35	Yes	None	None	Slight	Good
21C	0	..	50	Silica powder	15	Yes	None	None	Slight	Good
21D	0	..	50	Talcum powder	25	Yes	None	Slight	Slight	Fair
21E	0	..	50	Marble flour	15	Yes	Slight	Slight	Slight	Fair
Steam-Reduced Asphalt, Softening Point 160-170° F.										
91-21G <sup>e</sup>	5	15,000	50	Mica	15	No	None	Yes	Slight	Fair
21H	5	15,000	50	Slate flour	35	No	None	Yes	Slight	Good
21I	5	15,000	50	Silica powder	15	No	Slight	Slight	Slight	Fair
21J	5	15,000	50	Talcum powder	25	No	Yes	Slight	No	Good
21K	5	15,000	50	Marble flour	15	No	Slight	Slight	Slight	Good
21J + 1L <sup>d</sup>	5	15,000	50	{ Talcum powder Ilmenite	{ 25 10	No	None	Slight	Slight	Fair
91-21G <sup>e</sup>	5	15,000	50	Mica	15	Yes	None	None	Slight	Good
21H <sup>e</sup>	5	15,000	50	Slate flour	35	Yes	None	None	None	Excellent
21I <sup>e</sup>	5	15,000	50	Silica powder	15	Yes	None	None	None	Excellent
21J <sup>e</sup>	5	15,000	50	Talcum powder	25	Yes	None	None	None	Excellent
21K <sup>e</sup>	5	15,000	50	Marble flour	15	Yes	None	None	None	Excellent
21J + 1L <sup>d</sup>	5	15,000	50	{ Talcum powder Ilmenite	{ 25 10	Yes	None	None	Slight	Good

<sup>a</sup> Calculated on asphalt. <sup>b</sup> See Figure 3.

<sup>c</sup> Average thickness of paint film of series 91-21A to 21J, approximately 0.0076 inch.

<sup>d</sup> See Figure 4. <sup>e</sup> Paints that gave best protection.

checking or any other types of failure. These paints were not tested under normal weathering conditions.

Several filled asphalt-polybutene paints were prepared in the laboratory kneader and tested for weathering characteristics. Two coats of each paint were placed on steel, and the plates were tested in the Weather-ometer and on the roof of the General Engineering Building. Some tests were also conducted with the paints over steel that had been given a primer coat of red lead. The experimental paints did not brush so easily over red lead as over the clean polished steel. Table VI lists the composition of each paint and results observed in the Weather-ometer. They indicate that polybutene reduces the chalking and improves the surface consistency of filled asphalt paints.

It appeared desirable to compare a filled asphalt-polybutene blend with other commercial asphalt and coal-tar roof coating. Therefore, an asphalt-polybutene mica-filled blend was formulated and placed on roofing paper covering a portion of the Pipe Trench Building at Bayway. At the same time eight other well-known commercial products, some with a guarantee of ten years, were also placed on a part of the same building.

After thirteen months the asphalt-polybutene mica-filled product was rated first, based on durability, application, and cost to the company by a disinterested neutral observer (Figure 5). All of the products tested showed some evidence of chalking.

Of considerable interest is the two-year actual weathering test for filled paints 91-20A to 21J + 1L, inclusive. The results are listed in Table VII. It is evident that the presence of a red lead primer coat gives improved protection to metal when asphalt-polybutene paints are used. Also 5 per cent of 15,000 molecular weight polybutene increased the weathering resistance of a number of the experimental filled asphalt paints. The improved weathering property of asphalts conditioned with polybutene may be due in parts to the ability of this stable polymer to plasticize the product film and, therefore, to eliminate so-called structural hardness (3).

#### CONCLUSIONS

1. Less than 10 per cent polybutene of 6000-15,000 molecular weight in oxidized and steam-reduced asphalts reduced or completely eliminated the tendency of the asphalts to alligator, slightly reduced the tendency to check, reduced surface hardness, and increased the length of time before dusting began.

2. Films having better appearance and resistance to weathering were formed from cutbacks containing highly aromatic solvents than from cutbacks containing highly paraffinic solvents.

3. Polybutene of 6000-15,000 molecular weight also improved the weathering resistance of inert filler-asphalt films.

With fillers steam-reduced asphalts were more favorable than oxidized asphalts; without fillers the reverse was true.

4. All coatings on red lead primer were superior to those on polished steel.

5. In general, the improvement was proportional to the polybutene content, the polybutene film of higher molecular weight having better physical properties; but films containing over 10 per cent polybutene were either too tacky, for the low-molecular-weight polybutene, or too viscous for easy application in the case of the polybutene of higher molecular weight.

#### ACKNOWLEDGMENT

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# Brittle Temperature of Rubber under Variable Stress

A. R. KEMP, F. S. MALM,  
AND G. G. WINSPEAR

Bell Telephone Laboratories, Murray Hill, N. J.

THE projected use of synthetic elastomers on a large scale for outdoor service presents a pressing need for information dealing with their properties at subzero temperatures. Under extreme cold weather conditions insulation, cable jackets, tires and tubes, and many other items must be capable of being (repeatedly) flexed without failure at temperatures of  $-50^{\circ}\text{C}$ . or lower.

In a previous paper (25) a method was presented for determining the critical temperature of fracture where the sample is bent rapidly through an angle of approximately  $90^{\circ}$ . Although this test provides an excellent technique for the comparison of various rubber compositions, it was realized that the procedure should be revised to include the effect of varying the magnitude of stress as well as the rate of bending in order to simulate more closely certain types of service. The present paper does this and also reviews some of the work already carried out in the field of low-temperature rubber testing.

Early investigation (21) showed that crude rubber increased in tensile strength at low temperatures. Le Blanc

and Kröger (17) described this phenomenon as cold vulcanization. The observation that rubber which had been elongated and cooled in liquid air could be disrupted into fibrous fragments was reported by Hock (11). Mark and Valko (19) associated this phenomenon with brittleness and conducted experiments which showed that, under given test conditions, the "critical point" of raw rubber was  $-67^{\circ}\text{C}$ .

Ruhemann and Simon (22) observed that a sharp rise in the specific heat of smoked sheet rubber occurred in the range  $-65^{\circ}$  to  $-75^{\circ}\text{C}$ .

Bekkedahl (1) found that at  $-70^{\circ}\text{C}$ . a sharp change of slope occurs in the temperature-volume curve with both supercooled amorphous and crystalline raw rubbers. This observation is important because it demonstrates that the state of brittleness develops at the same point independently of the existence of either physical state. Differences in the brittle points of crystalline and amorphous smoked sheet rubber, as determined by the fracture method described in the previous work (25), were found to be slight.

Aside from the fracture method (13, 16, 25) other procedures used in investigations of rubber at low temperatures may be grouped according to the method of test into three general types involving deflection (15, 18), penetration (20), and elastic

This paper supplies the need for a method to determine the temperature at which rubber and similar materials fracture under variable bending stress. Although the brittle temperature is sharply defined under high-speed bending through a sharp angle, it is lower as the speed of application or the magnitude of the stress is reduced. In some instances decreases of more than  $28^{\circ}\text{C}$ . in brittle temperature resulted from

reductions in bending stress such as might be encountered in service.

Vulcanized pure gum natural rubber and plasticized polyvinyl chloride-acetate copolymer showed the largest changes, whereas the compounded and vulcanized natural and synthetic rubbers involved in this study exhibited a reduction in brittle temperature from  $5^{\circ}$  to  $10^{\circ}\text{C}$ . in going from the highest to the lowest stress employed.

deformation (7, 8, 9, 14, 24, 26). The method of Koch (15) may be considered a representative test for measuring the resistance to deflection of an elastic material at low temperatures. Penetration measurements by a dead-weight indentation method as reported by Nagai (20) represent this type of low temperature test. The work of Sagajillo *et al.* (24) demonstrated the combined effects of elastic deformation and temperature lowering on rubber. This testing procedure is similar to the T-50 method (9) commonly used for determining the state of vulcanization in certain flat-curing carbon-black-reinforced rubber compounds; the interpretation of the data is the important difference.

Although the deflection, penetration, and elastic deformation tests detect appreciable changes in certain properties of rubber at low temperatures, it would be difficult to predict the performance of a given material tested by these methods with reference to its being subjected to a sudden bending stress. The deflection method used by Koch (15) defines the point of maximum stiffness in rubber and gives indications of increased resistance to deformation at temperatures above the brittle point, but would not permit the prediction of how a given material would respond to severe or rapid mechanical deformation in service. The data published by Nagai (20) on decreasing penetration values observed with lowering of the temperature are of little value aside from furnishing a rough indication of increased hardness under these conditions. It will be shown later that hardness tests do not correlate with brittleness tests on bending.

#### APPARATUS AND METHOD

In the improved apparatus shown in Figure 1 the quadrant, A, upon which the fixtures, B, for varying the bending stress are mounted, is rotated by a worm drive, C, which utilizes interchangeable gears to vary the rate of deformation. This mechanism is driven by a  $1\frac{1}{2}$ -horsepower squirrel-cage motor, operating at 1140 r. p. m. and using a four-thread twelve-pitch worm wheel of thirty teeth with 2.5-inch (6.35-cm.) pitch diameter and a sixty-tooth 5-inch (12.7-cm.) pitch diameter wheel with a corresponding worm gear; this arrangement gives quadrant speeds of 150 and 75 r. p. m. The fast speed was selected on the basis of duplication of results obtained for a large variety of rubber and synthetic elastomer compositions in tests using the manually operated apparatus previously described (25). The right-angle bend is obtained by setting the rigid breaking arm, D, 0.25 inch (6.3 mm.) beyond the arc described by a block 0.25 inch square; the block is mounted on the periphery of the quadrant and flush with the back of the slot, E, in which the test specimen, F, is inserted. When testing by the application of a bending stress controlled in intensity by a selected arbor, a strip of 0.01-inch (0.254-mm.) spring steel, G, is inserted in the slot before the test specimen; the clearance of the breaking arm is adjusted so that in the test cycle the sample is bent rapidly to conform with the profile of the arbor. The immersion tank is insulated, H, by a double wrapping of aluminum foil, a 0.5-inch (1.27-cm.) layer of fiber glass, and an asbestos board enclosure. At the brittle fracture point, determined by rotation at the fast speed with an arbor of 1-inch (2.54-cm.) radius, three or four breaks usually occur in a specimen 1.5 inches (3.81 cm.) in length, and a temperature is found where a given material will be intact after a bending cycle but will fail when this temperature is lowered 1° C. When this point is determined, five specimens are tested successively at a temperature 1° C. above the point of failure; if all are intact after being put through the test cycle, the brittle fracture point is stated as the temperature between the observed points of survival and failure. A calibrated Weston dial thermometer was used for temperature measurements in this work.

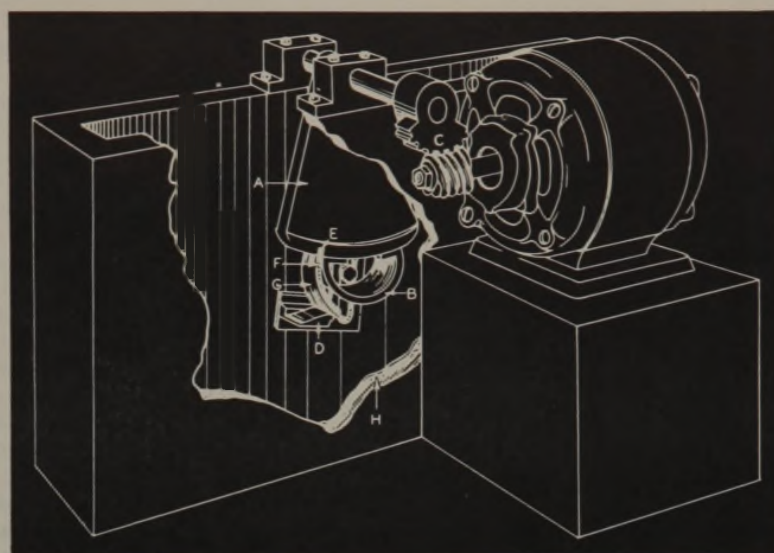


Figure 1. Apparatus for Determining Critical Temperature of Fracture on Bending

Experience in manipulating the acetone-solid carbon dioxide conditioning bath has shown that certain precautions are necessary to assure accurate temperature control. The procedure consists of placing 3.5 pounds (1.59 kg.) of crushed solid carbon dioxide in the insulated tank which is 14 × 2 × 8 inches (35.56 × 5.08 × 20.32 cm.) and adding acetone in small quantities until a saturated solution is obtained as indicated by a temperature of -78° C. Circulation is then induced by a motor stirrer, and the total acetone added is increased to 2 liters. Approximately 30 minutes are required to reach a condition of equilibrium where an immediate lowering of the temperature is noted upon the addition of a small quantity of the pulverized refrigerant. The quantities of a refrigerant and liquid mentioned produce an equilibrium temperature of approximately -70° C. In determining the brittle fracture point, it is standard practice to establish the approximate temperature of failure by preliminary tests at 10° C. intervals and then continue testing at 1° C. ascending intervals until the temperature of survival is noted. The heat transfer in the system resulting from inserting a test specimen and reimmersing the quadrant produces a rise of less than 1° C., and the temperature rise between -60° and -50° C. averages about 0.25° C. per minute. Exactly 5 minutes are allowed for the conditioning of each test specimen except in the case of highly plasticized materials, such as Koroseal and Vinylite, which are tested after a 2-minute immersion to minimize the possible effects of solvent action on their structure. The use of both acetone and ethyl alcohol as cooling media have been found to produce results which check closely with those from similar tests conducted in an air atmosphere after longer conditioning periods.

#### BRITTLE TEMPERATURE OF RUBBER COMPOSITIONS

Table I contains brittle fracture point data for pure gum and high-quality mechanical rubber compositions tested under controlled conditions of variable bending stress and rate of deformation. The results as stated were found by numerous check tests on the same materials to be reproducible within ±0.5° C. It was shown, however, in our previous work that raw rubber from different sources varies in brittle point over a range of about 4° C. which results in a wider limit of reproducibility from batch to batch.

With the decreased magnitude of the bending stress and rate of deformation, the pure gum vulcanizate does not fail at -78° C., but the brittle fracture point of the carbon-black-reinforced rubber is lowered only 6.5° C. by the less severe conditions of test, and a further decrease in rate of deformation by using a quadrant speed of 37.5 r. p. m. failed to lower further the temperature of fracture for the latter material.

TABLE I. EFFECTS OF VARIABLE BENDING STRESS AND RATE OF DEFORMATION ON BRITTLE FRACTURE POINTS OF RUBBER VULCANIZATES

Compound No.	1	2
Smoked sheet	100.00	100.00
Mercaptobenzothiazole	0.50	0.75
Zinc dimethyl dithiocarbamate	...	0.10
Sulfur	3.50	3.00
Stearic acid	0.50	2.00
Zinc oxide	6.00	10.00
Channel black	...	30.00
Semireinforcing black	...	30.00
Phenyl- $\alpha$ -naphthylamine	...	2.00
Sunlight aging inhibitor	...	2.00
Cure, min. ( $^{\circ}$ C.)	80(126)	20(141.5)

Rate of Deformation (Quadrant Speed), R. P. M.	Radius of Bending Stress, Cm.	Brittle Fracture Point, $^{\circ}$ C.	
		Pure gum	Carbon black stock
150	Right angle	-56.5	-58.5
	2.54	-61.5	-60.5
	3.81	<sup>a</sup>	-63.5
75	Right angle	-58.5	-60.5
	2.54	-61.5	-62.5
	3.81	<sup>a</sup>	-65.0

<sup>a</sup> No failures observed at  $-78^{\circ}$  C. ( $-108.4^{\circ}$  F.).

Brittle fracture point data under variable stress for a series of reclaimed rubber compositions (Table II) showing the effects of adding semireinforcing black, clay and whiting, mineral oil, blown asphalt, and smoked sheet. The brittle point of the uncompounded reclaimed rubber was  $-49^{\circ}$  C. These data show that the temperature of fracture varies with both the speed and magnitude of the bending stress.

As previously found (25), the nature of the rubber used is more important than minor changes in the composition. Undoubtedly lower speeds or less severe bending stresses than those employed in these tests would result in still lower temperatures at which these compositions would fracture.

#### BRITTLE TEMPERATURE OF SYNTHETIC ELASTOMERS

In view of the increasing amounts of synthetic elastomers now becoming available to the rubber industry and the immediate possibility of their extensive use, the need for information pertaining to their low-temperature properties becomes urgent. In contrast to rubber, considerable improvement may be effected in some of these materials by the use of certain compounding ingredients. Wide variations in brittle points were observed during the previous work (25) in different types of the same general class of material, as well as in the same material from different sources.

**SYNTHETIC THERMOPLASTIC ELASTOMERS.** Considerable information is available on the low-temperature properties of polyvinyl chloride which, although a hard plastic at room temperature, can be converted into a flexible and elastic material by the incorporation of chemical plasticizers in sufficiently large quantities. Russell (23) reported that the  $\mu$  form of polyvinyl chloride is brittle at  $81^{\circ}$  C., but that a mixture consisting of 60 parts of this material and 40 parts of dibutyl phthalate by weight (Koroseal) exhibited a brittle point of  $-46^{\circ}$  C. His method for brittle point determination consisted of conditioning bars of the materials for 5 minutes in an alcohol bath at the temperatures stated, removing them, and immediately bending them double.

Fuoss (5) observed that plasticized polyvinyl chloride behaves similarly to rubber in that, at a certain definite temperature, a sudden change in mechanical and electrical properties is noted. He refers to this point at which brittleness occurs as an internal melting point. Since the unplasticized material is in a general class of hard plastics, including cellulose acetate and polystyrene which are also extensively used in their unplasticized form and as such are evaluated by their resistance to plastic flow, this terminology is correct. However, in the case of the plasticized materials which are useful in their flexible and elastic condition, the term "brittle point" is a more significant designation. Davies, Miller, and Busse (3), also studying the electrical properties of this material, stated that three variables—temperature, frequency of current, and ratio of plasticizer to polyvinyl chloride—can be made to produce roughly equivalent results. The chemical significance of plasticizer action on these materials is beyond the scope of this work; however, reference may be made to the work of Houwink (12) who suggests that the brittleness of a substance will depend upon the distance over which the interacting molecular forces work. Considerable insight on the mechanics of plasticizer action with particular reference to cellulose acetate is given in a recent article by Gloor and Gilbert (10).

Table III lists brittle fracture data for plasticized polyvinyl chloride and polyvinyl chloride-acetate copolymers which may be considered average materials of their types. The samples tested were strips  $1.75 \times 0.5 \times 0.075$  inch ( $4.45 \times 1.27 \times 0.19$  cm.) cut with scissors from sheets molded from the calendered materials under a pressure of 500 pounds per square inch (89.25 kg. per sq. cm.) for 5 minutes at  $141.5^{\circ}$  C. and cooled for 5 minutes under pressure. The immersion time in the acetone-solid carbon dioxide bath was exactly 2 minutes for each test, and the brittle fracture points stated were verified by the observation of five consecutive cases of survival at temperatures  $0.5^{\circ}$  C. above the stated points. Some difficulty was encountered in testing these materials. In the various test cycles occasional cases of nonfailure were observed as much as  $10^{\circ}$  C. lower than the brittle fracture points stated: thus there is the possibility of a heterogeneous condition in plasticized mixtures of the types investigated.

**VULCANIZABLE SYNTHETIC ELASTOMERS.** Synthetic elastic polymers which more closely resemble rubber include butadiene polymers, acrylonitrile and styrene copolymers of butadiene, polychloroprene and its diolefin copolymers, polyiso-

TABLE II. BRITTLE FRACTURE POINTS OF ALL-RECLAIM AND LOW-RUBBER-CONTENT COMPOSITIONS<sup>a</sup>

Compound No.	3	4	5	6	7	8
Whole tire reclaim	67.50	67.50	67.50	67.50	62.50	57.50
Semireinforcing black	21.65	...	...	21.65	21.65	21.65
Hard clay	...	31.00	...	...	...	...
Ground limestone	...	...	32.40	...	...	...
Light-process oil	7.00	7.00	7.00	...	7.00	7.00
Mineral rubber (m. p. $310^{\circ}$ F. or $154^{\circ}$ C.)	...	...	...	7.00	...	...
Sulfur	1.00	1.00	1.00	1.00	1.00	1.00
Tetramethylthiuram monosulfide	0.15	0.15	0.15	0.15	0.15	0.15
Di- <i>o</i> -tolylguanidine	0.10	0.10	0.10	0.10	0.10	0.10
Sunlight aging inhibitor	2.00	2.00	2.00	2.00	2.00	2.00
Antioxidant	0.30	0.30	0.30	0.30	0.30	0.30
Smoked sheet	...	...	...	...	5.00	10.00

Rate of Deformation (Quadrant Speed), R. P. M.	Radius of Bending Stress, Cm.	Brittle Fracture Point, $^{\circ}$ C.					
		3	4	5	6	7	8
150	Right angle	-47.5	-46.5	-47.0	-43.5	-47.5	-50.0
	2.54	-50.5	-51.5	-51.5	-46.0	-51.5	-51.5
	3.81	-52.5	-53.5	-53.5	-49.5	-53.5	-55.5
75	Right angle	-50	-49.5	-49.5	-44.5	-51.0	-51.5
	2.54	-51.5	-55.5	-53.5	-46.0	-52.5	-53.5
	3.81	-54.5	-57.5	-56.5	-50.0	-54.5	-56.5

<sup>a</sup> Cured 20 minutes at  $141.5^{\circ}$  C.

TABLE III. BRITTLE FRACTURE POINTS OF PLASTICIZED POLY-VINYL CHLORIDE AND POLYVINYL CHLORIDE-ACETATE COPOLYMER

Rate of Deformation (Quadrant Speed), R. P. M.	Radius of Bending Stress, Cm.	Brittle Fracture Point, ° C.	
		Polyvinyl chloride polymer 9	Polyvinyl chloride-acetate copolymer 10
150	Right angle	-25.5	-50.0
	2.54	-32.5	-70.5
	3.81	-46.5	a
75	Right angle	-30.0	-56.0
	2.54	-38.5	-72.0
	3.81	-51.5	a

a No failures observed at -78° C. (-108.4° F.).

TABLE IV. BRITTLE FRACTURE POINTS OF BUNA S COMPOSITIONS<sup>a</sup>

Compound No.	11	12	13
Buna S	100.00	50.00	50.00
Smoked sheet	...	50.00	25.00
Whole tire reclaim	...	...	50.00
Carbon black (special)	50.00	50.00	50.00
Blown asphalt	25.00	25.00	25.00
Sulfur	2.00	2.00	2.00
Stearic acid	2.00	2.00	2.00
Zinc oxide	15.00	15.00	15.00
Accelerator A	1.00	1.00	1.00
Accelerator B	1.50	1.50	1.50

Rate of Deformation (Quadrant Speed), R. P. M.	Radius of Bending Stress, Cm.	Brittle Fracture Point, ° C.		
150	Right angle	-51.5	-51.5	-49.5
	2.54	-54.5	-52.5	-51.5
	3.81	-59.5	-58.5	-53.5
75	Right angle	-54.5	-55.5	-51.5
	2.54	-58.5	-56.5	-53.5
	3.81	-63.5	-60.5	-57.0

a Cured 20 minutes at 141.5° C.

butylene and its diolefin copolymers, and various types of organic polysulfides. These materials, mixed in various proportions with vulcanizing agents and typical rubber compounding ingredients and vulcanized by heating, exhibit widely varying low-temperature properties (25) owing to their different chemical structures. Koch (15) applied his deflection test to an undisclosed butadiene-styrene copolymer composition and observed a freezing point of -66° C., which is in agreement with the brittle point range of -66° to -70° C. for this material observed in the previous work (25). Bekkedahl and Scott (2) recently reported a second-order transition point of -23° C. for Hycar OR (modified butadiene-nitrile copolymer), using the technique previously described in their work on rubber. These authors also stated that no first-order transition was observed in the material studied. The brittle point of this material was found in our earlier work to be about -25° C. Garvey, Juve, and Sauser (6) reported low-temperature observations for a number of Hycar OR compositions.

Table IV shows the brittle fracture points under variable stress of three butadiene-styrene copolymer compositions. These results are similar to those in Table I in respect to the effect of varying the nature of the stress. It was previously shown (25) that a good Buna S tire tread stock (without the blown asphalt) had a brittle fracture point of -66° to -70° C. under a right-angle bend at high speed. These results show that the brittle temperature of synthetic rubber is more sensitive to compounding than natural rubber. For this reason greater care must be taken in compounding Buna S for low-temperature service.

Yerzley and Fraser (27) recently investigated the effects of low temperatures on the Shore A hardness, elastic deflection,

and mechanical deflection (torsion) of neoprene compositions; they proposed the term "freeze factor" to express the ratio of the observed change in hardness produced by low temperatures to the maximum possible increase in hardness for a given material. A new interpretation of this effect, designated as "F-50" (4), was recently proposed to define the temperature where half the maximum possible increase in Shore A hardness is observed.

A comparison of data obtained by Shore A hardness measurements and brittle fracture point tests for the same series of Neoprene FR compositions is shown in Table V along with the Shore A hardness values for the various compositions at their respective brittle fracture points. The fracture test indicates that compound 17, containing 30 parts of dibutyl sebacate, would be serviceable at a temperature 5° C. lower than the best of the series as indicated by the hardness observations. Composition 17, subjected to bending tests at a quadrant speed of 37.5 r. p. m. over a 3.8-cm. radius arbor, showed no failure at -76° C.; compound 14 exhibited a brittle fracture point under these conditions at -67° C.

The addition of dibutyl sebacate and diisobutyl adipate resulted in an appreciable lowering of the brittle fracture points of a typical neoprene GN composition (Table VI); the order of improvement was the same as in the series of tests with Neoprene FR compounds. Cooling curves made for the two plasticizers showed that both are in a solid state at temperatures above the fracture points of the compounds in which they were used, and that freezing occurs well within the conditioning time allowed according to the testing procedure. Swelling tests on vulcanized base compound 19 in diisobutyl

TABLE V. COMPARISON OF LOW-TEMPERATURE PROPERTIES OF NEOPRENE FR COMPOSITIONS<sup>a</sup> AS DETERMINED BY SHORE A HARDNESS AND BRITTLE FRACTURE TESTS

Compound No.	Softener (30 Parts by Wt.)	F-50 Temp., ° C.	Brittle Fracture Point <sup>b</sup> , ° C.	Hardness at Brittle Fracture Point
14	Diisobutyl adipate	-54	-58.5	80
15	Dibutyl phthalate	-46	-61.5	92
16	Coal-tar softener	-43	-50.5	93
17	Dibutyl sebacate	-40	-66.5	92
18	Light-process oil	-38	-53.0	95

a Base formula: Neoprene FR 100.0, stearic acid 1.0, Neozone A 2.0, soft black 100.0, sulfur 1.0, litharge 10.0.

b Rate of deformation, 150 r. p. m.; right-angle bend.

TABLE VI. BRITTLE FRACTURE POINTS OF NEOPRENE GN COMPOSITIONS

Compound No.	19	20	21
Neoprene GN	100.0	100.0	100.0
Magnesium oxide	7.0	7.0	7.0
Zinc oxide	2.0	2.0	2.0
Antioxidant	1.0	1.0	1.0
Semireinforcing black	35.0	35.0	35.0
Petroleum softeners	2.0	2.0	2.0
Stearic acid	0.25	0.25	0.25
Accelerator	0.25	0.25	0.25
Diisobutyl adipate	...	15.0	...
Dibutyl sebacate	...	...	15.0

Rate of Deformation (Quadrant Speed), R. P. M.	Radius of Bending Stress, Cm.	Brittle Fracture Point, ° C.		
150	Right angle	-41.5	-51.5	-55.5
	2.54	-45.5	-56	-58.5
	3.81	-46.5	-57	-60
75	Right angle	-43	-54	-57
	2.54	-46.5	-56	-59
	3.81	-50.5	-58	-62

adipate and dibutyl sebacate showed appreciable increases in weight after 12-hour immersion at 60° C. The neoprene immersed in dibutyl sebacate increased 80 per cent by weight as compared to a 70 per cent increase for the sample immersed in diisobutyl adipate. On the basis of these observations and the brittle fracture test results, it appears that increased solvent action may offer a better guide to the selection of materials for lowering the brittle fracture point than the freezing point observations on the plasticizers.

#### CONCLUSIONS

1. The temperature at which natural and synthetic elastomers fracture on bending depends on the rate of application and the magnitude of the stress applied. The slower the rate of bending and the less the angle of bend, the lower will be the temperature of fracture.

2. A study of the stresses under varying types of service at subzero temperatures must be made in order to select intelligently the laboratory test conditions which will best simulate performance in the field.

3. In the case of synthetic elastomers having high fracture temperatures, the addition of certain types of plasticizers serve to correct this difficulty.

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# Ternary Liquid

## A Method of Tie Line Interpolation

CHARLES E. DRYDEN<sup>1</sup>

GRAPHICAL methods for the design of rectification equipment have been presented by Ponchon (10) and Savarit (11) and extended to liquid-liquid extraction by Maloney and Schubert (5); for practical use by these methods, equilibrium data for the distribution of the components between the phases must be on a solvent-free basis. All tie line interpolation methods so far reported (1, 2, 4, 6) necessitate the use of the triangular diagram to calculate the distribution relation of the solute between the solvent and diluent layers on a solvent-free basis (also termed "concentration data", 7) for each successive theoretical stage in an extraction system.

A straight-line plot on rectangular coordinates of the solute distribution relations on a solvent-free basis may be obtained from three points on the ternary diagram of the system considered. Tie line data, on a solvent-free basis in the case of extraction, may be obtained from this plot and applied directly to the stepwise calculation of theoretical stages by the Maloney-Schubert method without further use of the ternary diagram.

In those cases where it is found applicable, the method thus has the advantage of limiting the use of the triangular diagram to the procurement of the above mentioned straight-line plot. This plot is readily applied to the computation of theoretical stages in solvent extraction by the Maloney-Schubert method; the triangular diagram is used together with any one of the tie line methods previously cited to accomplish the same purpose—i. e., to obtain solvent-free distribution relations for each successive stage in the design of a solvent extraction unit.

#### THEORETICAL ASPECT

Varteressian and Fenske (14) found that for the system methylcyclohexane-aniline-*n*-heptane the distribution of one component (i. e., the solute) between two liquid phases, the solvent layer and the diluent layer, may be expressed by a hyperbolic equation of the type,

$$y = \frac{\beta x}{1 + (\beta - 1)x} \quad (1)$$

where  $x$  = weight fraction of solute in diluent layer on solvent-free basis

$y$  = weight fraction of solute in solvent layer on solvent-free basis

$\beta$  = a constant dependent on the system involved; it is a function of the osmotic pressure ratios of solvent and diluent

Equation 1 may be rearranged in the form,

$$\frac{x}{y} = \left( \frac{\beta - 1}{\beta} \right) x + \frac{1}{\beta} \quad (2)$$

<sup>1</sup> Present address, National Oil Products Company, Harrison, N. J.

# and Binary Vapor-Liquid Systems

## for Phase Equilibrium Relations

Princeton University, Princeton, N. J.

A method of correlating equilibrium distribution relations of the solute between conjugate phases on a solvent-free basis in liquid-liquid systems and its application to the graphical solution of the Maloney-Schubert diagram for theoretical extraction stages is presented, together with the analogous vapor-liquid equilibrium method.

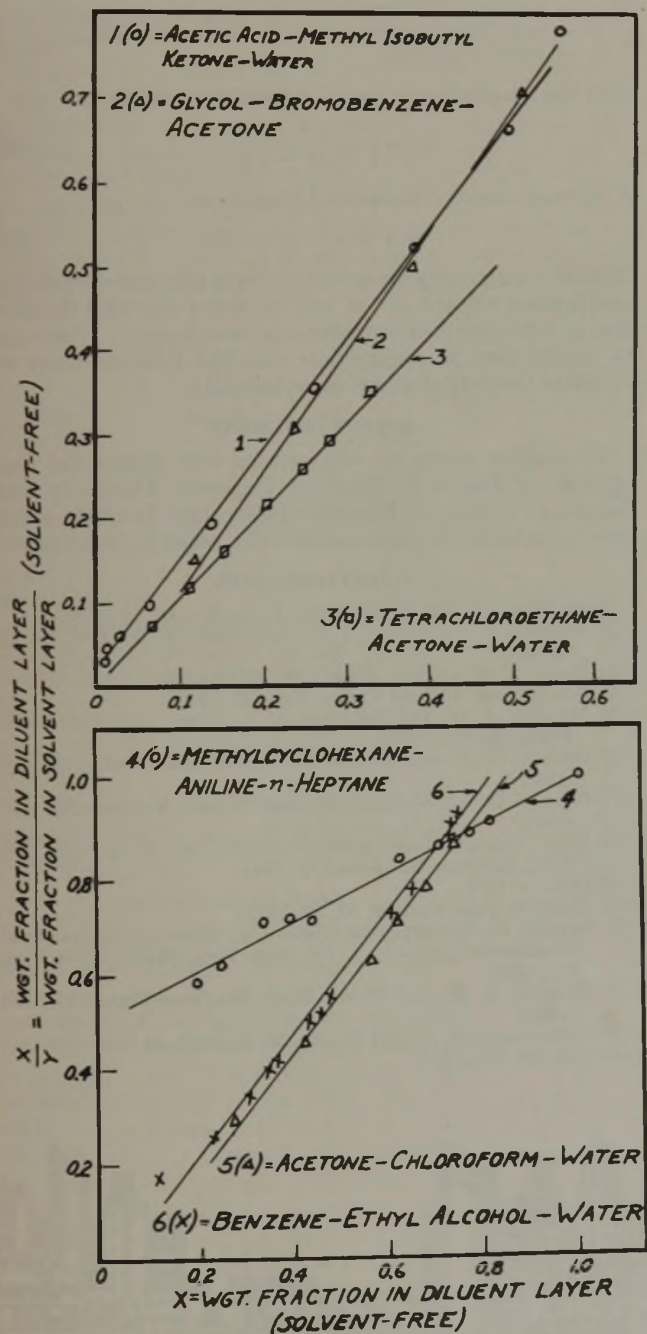


Figure 1

A straight line results when  $x/y$  is plotted against  $x$ , if the equation is obeyed and  $\beta$  is a constant. Thus, if the ratio of the solute in the diluent layer,  $x$ , to the solute in the solvent layer,  $y$  (i. e.,  $x/y$ ), is plotted against the solute in the diluent layer,  $x$ , all on a solvent-free basis, a straight line should result when the system approximates Equation 1 as set down above.

### APPLICATION OF THE METHOD

Some of the data reported in the literature for liquid-liquid systems have been tested by the above method. Some systems found to conform to the hyperbolic Equation 1 are listed in Table I, and plots of the data for some of them are shown in Figure 1. The resulting curves are straight lines well within the accuracy of experimental measurement. Systems which do not follow the law include methylcyclohexane-acetic acid-water, isophorone-acetic acid-water, furfural-acetone-water, and isoamyl alcohol-acetone-water.

TABLE I. SYSTEMS CONFORMING TO HYPERBOLIC EQUATION 1

No.	System	Reference
1	Acetic acid-methyl isobutyl ketone-water	(6)
2	Glycol-bromobenzene-acetone	(12)
3	Tetrachloroethane-acetone-water	(6)
4	Methylcyclohexane-aniline-n-heptane	(14)
5	Acetone-chloroform-water	(3)
6	Benzene-ethyl alcohol-water	(13)
7	Di-n-butyl ether-ethyl alcohol-water	(6)
8	Diisopropylcarbinol-acetic acid-water	(6)
9	Methyl isobutyl ketone-acetone-water	(6)
10	Fenchone-acetic acid-water	(6)

That the method does not apply to all systems is to be expected since it is an idealized relation. It appears to be limited to systems in which the ternary solubility line approaches the sides of the triangle, in which case the solvent and the diluent are substantially immiscible, or to systems in which only one pair of components is completely miscible. In the first type of system a rule for determining the validity of the method can be derived as follows:

$$\text{If } m = (\beta - 1)/\beta \text{ and } k = 1/\beta,$$

$$\begin{aligned} a_1, b_1, c_1 &= \text{components in solvent layer} \\ a_2, b_2, c_2 &= \text{components in diluent layer} \end{aligned}$$

where  $a$  = solvent  
 $b$  = diluent  
 $c$  = solute

$$x = \frac{c_2}{(b_2 + c_2)} \quad (3)$$

$$y = \frac{c_1}{(b_1 + c_1)} \quad (4)$$

Substituting for  $(\beta - 1)/\beta$ ,  $1/\beta$ ,  $x$ , and  $y$  the above equivalents in Equation 1,

$$\frac{\frac{c_2}{c_2 + b_2}}{\frac{c_1}{c_1 + b_1}} = m \left( \frac{c_2}{c_2 + b_2} \right) + k \quad (5)$$

Since  $a_1 + b_1 + c_1 = 1$ ,

$$b_1 + c_1 = 1 - a_1 \quad (6)$$

Substituting Equation 6 in Equation 5,

$$\frac{\frac{c_2}{c_2 + b_2}}{\frac{c_1}{1 - a_1}} = m \left( \frac{c_2}{c_2 + b_2} \right) + k \quad (7)$$

Rearrangement of Equation 7 gives:

$$\left( \frac{c_2}{c_1} \right) \left( \frac{1 - a_1}{c_2 + b_2} \right) = m \left( \frac{c_2}{c_2 + b_2} \right) + k \quad (8)$$

In every case  $(c_2/c_1) > 1$ , since subscript 2 refers to the diluent layer. For most of the systems plotted by this method,  $k$  has a very small value—i. e., high osmotic pressure ratio between the solvent and diluent. This would indicate that, as  $c_2$  approaches zero,  $(1 - a_1)/(c_2 + b_2)$  approaches zero more rapidly than  $c_2/c_1$  approaches infinity so that in the limit  $k$  would be zero. Equation 5 then reduces to

$$m = (b_1 + c_1)/c_1 \quad (9)$$

$$\text{or } b_1/c_1 = m - 1 \quad (10)$$

Substituting  $m = (\beta - 1)/\beta$

$$\beta = -(c_1/b_1) \quad (11)$$

Thus, since Equation 2 can represent a straight line only when  $\beta$  is constant, we may make the generalization that the method holds where the diluent increases proportionally to the solute in the solvent layer.

In systems where only one pair of components is completely miscible, it is possible for the left-hand side of Equation 8 to be greater than zero in the limit, as in the case of methylcyclohexane-aniline-*n*-heptane.  $\beta$ , the osmotic pressure coefficient, will then have positive values which can be computed from the type of extrapolation plot presented in this paper. This suggests the correlation method for testing experimental data to determine whether the value of  $\beta$  is constant over wide concentration ranges at one temperature and whether  $\beta$  can be expressed as a function of temperature so that systems can be represented at any temperature. Work along this line is being conducted in this laboratory.

Another important use of this method of tie line correlation is in solving the Maloney-Schubert diagram for theoretical stages in an extraction system. Using three or four points on the ternary diagram of the system, a plot of the solvent distribution relations on a solvent-free basis is made by the

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#### BINARY VAPOR-LIQUID SYSTEMS

In an analogous manner vapor-liquid equilibrium in binary mixtures may be interpolated if equilibrium compositions are known for two points and if Raoult's law applies; i. e., the relative volatility is approximately constant over the entire range employed.

If  $y$  = mole fraction of more volatile component in vapor  
 $x$  = mole fraction of more volatile component in liquid  
 $\alpha$  = relative volatility

then the  $x$ - $y$  relation in terms of relative volatility is:

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \quad (12)$$

A rearrangement of Equation 12 results in:

$$y/x = \alpha - (\alpha - 1)y \quad (13)$$

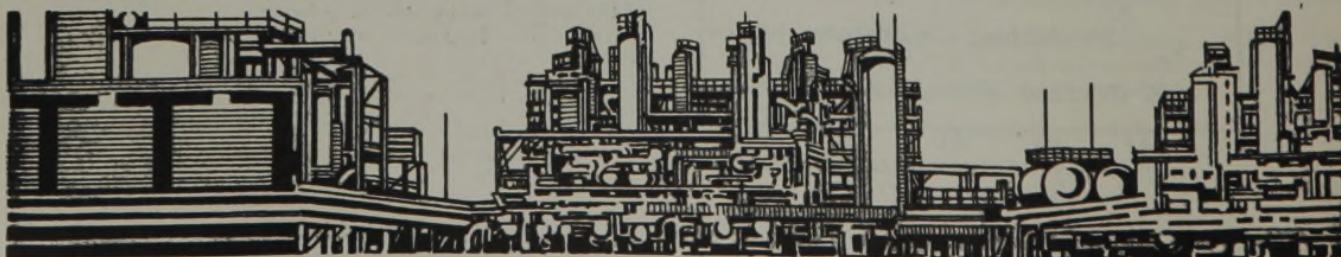
Plots of  $y/x$  against  $y$  for systems such as nitrogen-oxygen (8), and benzene-toluene (9), as well as others following Raoult's law, give straight lines on rectangular coordinates. These can be readily used in conjunction with the Ponchon chart to calculate theoretical plates in rectification.

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# Graphical Interconversions for Multicomponent Systems

JOHN D. LESLIE

University of British Columbia, Vancouver, Canada

**I**N A RECENT article Sun and Silverman<sup>1</sup> developed two simple graphical methods for converting weight, volume, and mole fractions into one another, and also parts by weight into weight, volume, and mole fractions, in binary systems.

By a simple extension, the present paper makes the first of these methods applicable to multicomponent systems. Although binary systems are perhaps more common, multicomponent systems have increased greatly in importance in recent years. This should justify the slight added complications in the following method.

These graphical methods are very general in nature by virtue of the fact that all the above mentioned conversions can be expressed in two simple equations:

$$P_A = \frac{\frac{Q_A}{S_A}}{\frac{Q_A}{S_A} + \frac{Q_B}{S_B} + \dots + \frac{Q_N}{S_N}} \quad (1)$$

$$P_A' = \frac{\frac{Q_A}{S_A'}}{\frac{Q_A}{S_A'} + \frac{Q_B}{S_B'} + \dots + \frac{Q_N}{S_N'}} \quad (2)$$

$Q_A + Q_B + Q_C + \dots + Q_N = 1$  usually, but this is not a necessary condition. Our problem is to find  $P_A$  or  $P_A'$  knowing the other quantities in the equation. Equation 2 is usually given in the form:

$$P_A' = \frac{Q_A S_A}{Q_A S_A + Q_B S_B + \dots + Q_N S_N}$$

The alteration above is made so that both equations may be covered by one graphical method.

## GRAPHICAL METHOD

We consider a system of four components; the extension to a system of  $N$  components will be obvious. Lay out in one corner of the graph paper, following Sun and Silverman, the rectangle  $ABCD$  as in Figure 1. Let  $CD$  represent unity. Using suitable scales, plot points  $E(Q_A, S_A)$  and  $F(Q_B, S_B)$  as shown, with  $A$  and  $B$  as respective origins. Connect  $AE$  and  $BF$ ; and through the point of intersection,  $G$ , draw line  $GH$  parallel to the base  $AB$ . With  $B$  as new origin, plot point  $J(Q_C, S_C)$  to the right of  $BD$ . Let the line joining  $B$  and  $J$  cut  $GH$  at  $P$ . At this stage the method must be altered slightly since we have no origin for the next point,  $K(Q_D, S_D)$ .

The method of Sun and Silverman for the interconversions of weight, volume, and molar compositions in binary systems has been extended to multiple systems. This should increase considerably the usefulness of the method.

Lay off  $BM = Q_D$  and  $BN = S_D$  as shown and join  $MN$ . Then draw through  $P$  a line parallel to  $MN$ , and let it intersect  $AB$  produced at  $R$ .  $R$  is the required origin, and point  $K(Q_D, S_D)$  is located as shown. Now join  $RD$  and extend to cut  $AC$  produced at  $S$ . Join  $S$  to  $G'$  and let  $SG'$  cut  $CD$  at  $T$ . Then  $CT = P_A$ .  $P_A'$  can be obtained similarly using the coordinates  $(Q_A, S_A')$ ,  $(Q_B, S_B')$ , . . . in place of  $(Q_A, S_A)$ ,  $(Q_B, S_B)$ , . . . It will be noted that one new origin must be found by the procedure above for every pair of components beyond two. Another point worth noting is that, in order to have point  $S$  at a convenient height above  $AB$ , line  $CD$  can be raised or lowered after point  $R$  has been found. In fact,  $CD$  need not be placed at all until after the rest of the graph has been drawn. Merely choose  $S$  at a suitable point on  $AC$  produced and get  $D$  by letting  $RS$  cut the perpendicular on  $B$ .

Picking out pairs of similar triangles we have:

$$\frac{AG'}{GG'} = \frac{AE'}{EE'} = \frac{Q_A}{S_A} \quad (3)$$

$$\frac{BG'}{GG'} = \frac{BF'}{FF'} = \frac{Q_B}{S_B} \quad (4)$$

$$\frac{BP'}{PP'} = \frac{BJ'}{JJ'} = \frac{BP'}{GG'} = \frac{Q_C}{S_C} \quad (5)$$

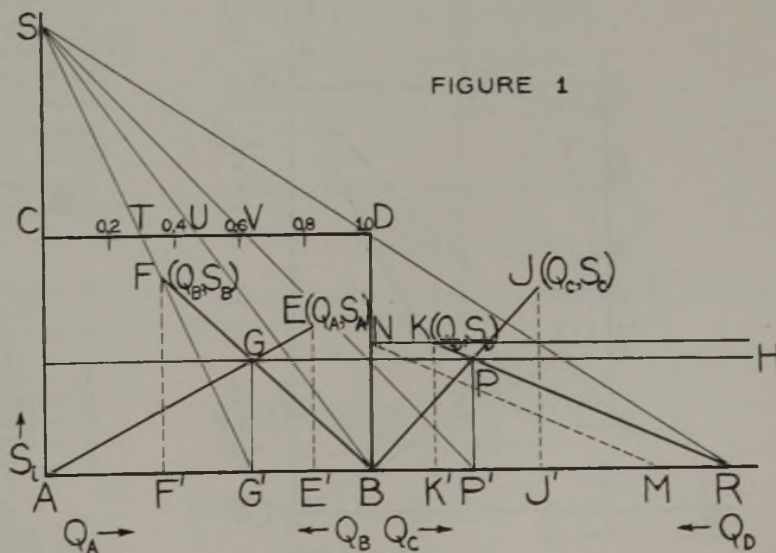


FIGURE 1

<sup>1</sup> IND. ENG. CHEM., 34, 682 (1942).

Substituting for  $(\beta - 1)/\beta$ ,  $1/\beta$ ,  $x$ , and  $y$  the above equivalents in Equation 1,

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Lay off  $BM = Q_D$  and  $BN = S_D$  as shown and join  $MN$ . Then draw through  $P$  a line parallel to  $MN$ , and let it intersect  $AB$  produced at  $R$ .  $R$  is the required origin, and point  $K(Q_D, S_D)$  is located as shown. Now join  $RD$  and extend to cut  $AC$  produced at  $S$ . Join  $S$  to  $G'$  and let  $SG'$  cut  $CD$  at  $T$ . Then  $CT = P_A$ .  $P_A'$  can be obtained similarly using the coordinates  $(Q_A, S_A)$ ,  $(Q_B, S_B)$ , . . . in place of  $(Q_A, S_A)$ ,  $(Q_B, S_B)$ , . . . It will be noted that one new origin must be found by the procedure above for every pair of components beyond two. Another point worth noting is that, in order to have point  $S$  at a convenient height above  $AB$ , line  $CD$  can be raised or lowered after point  $R$  has been found. In fact,  $CD$  need not be placed at all until after the rest of the graph has been drawn. Merely choose  $S$  at a suitable point on  $AC$  produced and get  $D$  by letting  $RS$  cut the perpendicular on  $B$ .

Picking out pairs of similar triangles we have:

$$\frac{AG'}{GG'} = \frac{AE'}{EE'} = \frac{Q_A}{S_A} \quad (3)$$

$$\frac{BG'}{GG'} = \frac{BF'}{FF'} = \frac{Q_B}{S_B} \quad (4)$$

$$\frac{BP'}{PP'} = \frac{BJ'}{JJ'} = \frac{BP'}{GG'} = \frac{Q_C}{S_C} \quad (5)$$

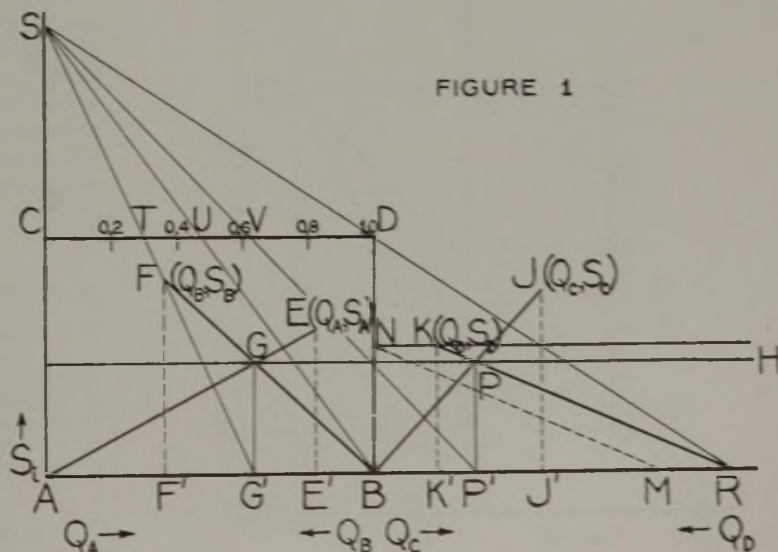


FIGURE 1

<sup>1</sup> IND. ENG. CHEM., 34, 682 (1942).

Substituting for  $(\beta - 1)/\beta$ ,  $1/\beta$ ,  $x$ , and  $y$  the above equivalents in Equation 1,

$$\frac{\frac{c_2}{c_2 + b_2}}{\frac{c_1}{c_1 + b_1}} = m \left( \frac{c_2}{c_2 + b_2} \right) + k \quad (5)$$

Since  $a_1 + b_1 + c_1 = 1$ ,

$$b_1 + c_1 = 1 - a_1 \quad (6)$$

Substituting Equation 6 in Equation 5,

$$\frac{\frac{c_2}{c_2 + b_2}}{\frac{c_1}{1 - a_1}} = m \left( \frac{c_2}{c_2 + b_2} \right) + k \quad (7)$$

Rearrangement of Equation 7 gives:

$$\left( \frac{c_2}{c_1} \right) \left( \frac{1 - a_1}{c_2 + b_2} \right) = m \left( \frac{c_2}{c_2 + b_2} \right) + k \quad (8)$$

In every case  $(c_2/c_1) > 1$ , since subscript 2 refers to the diluent layer. For most of the systems plotted by this method,  $k$  has a very small value—i. e., high osmotic pressure ratio between the solvent and diluent. This would indicate that, as  $c_2$  approaches zero,  $(1 - a_1)/(c_2 + b_2)$  approaches zero more rapidly than  $c_2/c_1$  approaches infinity so that in the limit  $k$  would be zero. Equation 5 then reduces to

$$m = (b_1 + c_1)/c_1 \quad (9)$$

$$\text{or } b_1/c_1 = m - 1 \quad (10)$$

Substituting  $m = (\beta - 1)/\beta$

$$\beta = -(c_1/b_1) \quad (11)$$

Thus, since Equation 2 can represent a straight line only when  $\beta$  is constant, we may make the generalization that the method holds where the diluent increases proportionally to the solute in the solvent layer.

In systems where only one pair of components is completely miscible, it is possible for the left-hand side of Equation 8 to be greater than zero in the limit, as in the case of methylcyclohexane-aniline-*n*-heptane.  $\beta$ , the osmotic pressure coefficient, will then have positive values which can be computed from the type of extrapolation plot presented in this paper. This suggests the correlation method for testing experimental data to determine whether the value of  $\beta$  is constant over wide concentration ranges at one temperature and whether  $\beta$  can be expressed as a function of temperature so that systems can be represented at any temperature. Work along this line is being conducted in this laboratory.

Another important use of this method of tie line correlation is in solving the Maloney-Schubert diagram for theoretical stages in an extraction system. Using three or four points on the ternary diagram of the system, a plot of the solvent distribution relations on a solvent-free basis is made by the

above method. The required equilibrium relation (on a solvent-free basis) in each stage can be computed directly from this straight-line plot without further use of a complete ternary diagram for the system and without involving tie line interpolation methods previously cited. The Maloney-Schubert method, in conjunction with the tie line correlation presented in this paper, gives a much more rapid and accurate determination of theoretical stages required for a given separation in a system where the binodal curve is pinched close to the solvent end of the triangular diagram.

#### BINARY VAPOR-LIQUID SYSTEMS

In an analogous manner vapor-liquid equilibrium in binary mixtures may be interpolated if equilibrium compositions are known for two points and if Raoult's law applies; i. e., the relative volatility is approximately constant over the entire range employed.

If  $y$  = mole fraction of more volatile component in vapor  
 $x$  = mole fraction of more volatile component in liquid  
 $\alpha$  = relative volatility

then the  $x$ - $y$  relation in terms of relative volatility is:

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \quad (12)$$

A rearrangement of Equation 12 results in:

$$y/x = \alpha - (\alpha - 1)y \quad (13)$$

Plots of  $y/x$  against  $y$  for systems such as nitrogen-oxygen (8), and benzene-toluene (9), as well as others following Raoult's law, give straight lines on rectangular coordinates. These can be readily used in conjunction with the Ponchon chart to calculate theoretical plates in rectification.

#### ACKNOWLEDGMENT

The author wishes to acknowledge with thanks the suggestions of Joseph C. Elgin of Princeton University and Donald F. Othmer of Brooklyn Polytechnic Institute which were valuable in the preparation of this paper for publication.

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# Graphical Interconversions for Multicomponent Systems

JOHN D. LESLIE

University of British Columbia, Vancouver, Canada

IN A RECENT article Sun and Silverman<sup>1</sup> developed two simple graphical methods for converting weight, volume, and mole fractions into one another, and also parts by weight into weight, volume, and mole fractions, in binary systems.

By a simple extension, the present paper makes the first of these methods applicable to multicomponent systems. Although binary systems are perhaps more common, multicomponent systems have increased greatly in importance in recent years. This should justify the slight added complications in the following method.

These graphical methods are very general in nature by virtue of the fact that all the above mentioned conversions can be expressed in two simple equations:

$$P_A = \frac{\frac{Q_A}{S_A}}{\frac{Q_A}{S_A} + \frac{Q_B}{S_B} + \dots + \frac{Q_N}{S_N}} \quad (1)$$

$$P_A' = \frac{\frac{Q_A}{S_A'}}{\frac{Q_A}{S_A'} + \frac{Q_B}{S_B'} + \dots + \frac{Q_N}{S_N'}} \quad (2)$$

$Q_A + Q_B + Q_C + \dots + Q_N = 1$  usually, but this is not a necessary condition. Our problem is to find  $P_A$  or  $P_A'$  knowing the other quantities in the equation. Equation 2 is usually given in the form:

$$P_A' = \frac{Q_A S_A}{Q_A S_A + Q_B S_B + \dots + Q_N S_N}$$

The alteration above is made so that both equations may be covered by one graphical method.

## GRAPHICAL METHOD

We consider a system of four components; the extension to a system of  $N$  components will be obvious. Lay out in one corner of the graph paper, following Sun and Silverman, the rectangle  $ABCD$  as in Figure 1. Let  $CD$  represent unity. Using suitable scales, plot points  $E(Q_A, S_A)$  and  $F(Q_B, S_B)$  as shown, with  $A$  and  $B$  as respective origins. Connect  $AE$  and  $BF$ ; and through the point of intersection,  $G$ , draw line  $GH$  parallel to the base  $AB$ . With  $B$  as new origin, plot point  $J(Q_C, S_C)$  to the right of  $BD$ . Let the line joining  $B$  and  $J$  cut  $GH$  at  $P$ . At this stage the method must be altered slightly since we have no origin for the next point,  $K(Q_D, S_D)$ .

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The method of Sun and Silverman for the interconversions of weight, volume, and molar compositions in binary systems has been extended to multiple systems. This should increase considerably the usefulness of the method.

Lay off  $BM = Q_D$  and  $BN = S_D$  as shown and join  $MN$ . Then draw through  $P$  a line parallel to  $MN$ , and let it intersect  $AB$  produced at  $R$ .  $R$  is the required origin, and point  $K(Q_D, S_D)$  is located as shown. Now join  $RD$  and extend to cut  $AC$  produced at  $S$ . Join  $S$  to  $G'$  and let  $SG'$  cut  $CD$  at  $T$ . Then  $CT = P_A$ .  $P_A'$  can be obtained similarly using the coordinates  $(Q_A, S_A')$ ,  $(Q_B, S_B')$ , . . . in place of  $(Q_A, S_A)$ ,  $(Q_B, S_B)$ , . . . It will be noted that one new origin must be found by the procedure above for every pair of components beyond two. Another point worth noting is that, in order to have point  $S$  at a convenient height above  $AB$ , line  $CD$  can be raised or lowered after point  $R$  has been found. In fact,  $CD$  need not be placed at all until after the rest of the graph has been drawn. Merely choose  $S$  at a suitable point on  $AC$  produced and get  $D$  by letting  $RS$  cut the perpendicular on  $B$ .

Picking out pairs of similar triangles we have:

$$\frac{AG'}{GG'} = \frac{AE'}{EE'} = \frac{Q_A}{S_A} \quad (3)$$

$$\frac{BG'}{GG'} = \frac{BF'}{FF'} = \frac{Q_B}{S_B} \quad (4)$$

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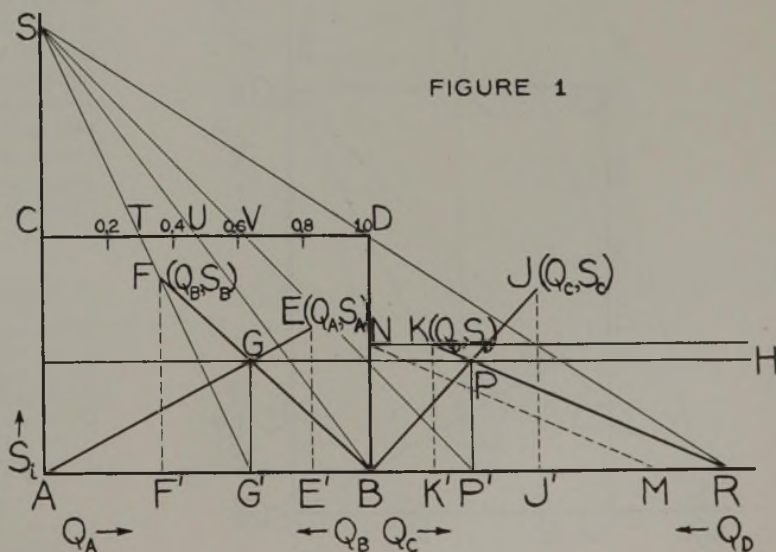
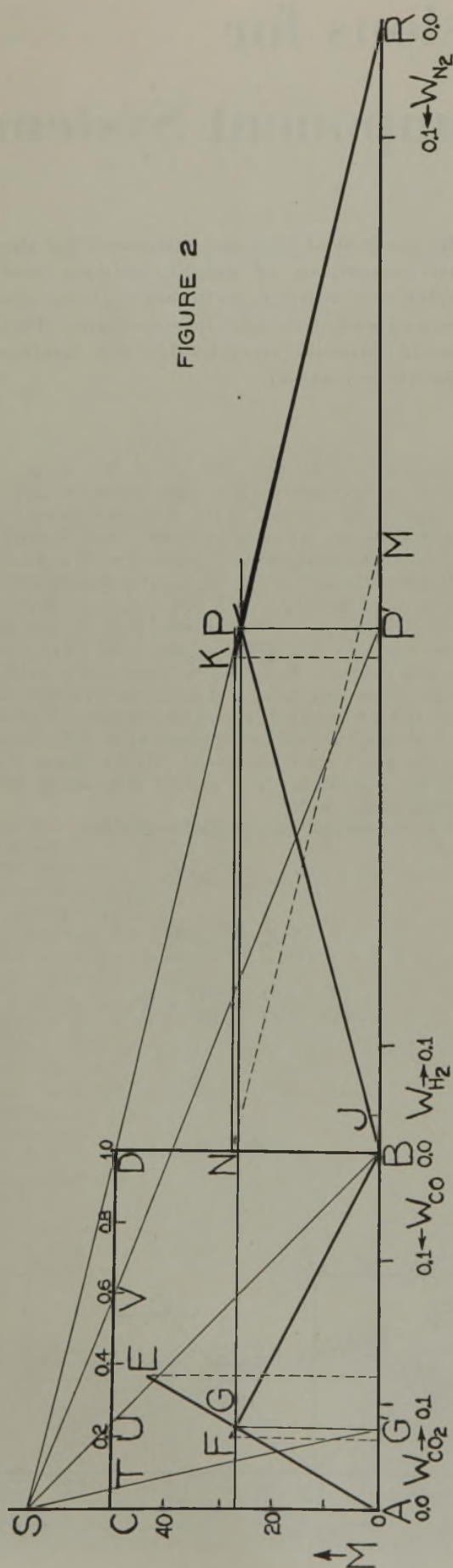


FIGURE 1

FIGURE 2



$$\frac{RP'}{PP'} = \frac{RK'}{KK'} = \frac{RP'}{GG'} = \frac{Q_D}{S_D} \tag{6}$$

Substituting Equations 3 to 6 in Equation 1,

$$P_A = \frac{\frac{AG'}{GG'}}{\frac{AG'}{GG'} + \frac{BG'}{GG'} + \frac{BP'}{GG'} + \frac{RP'}{GG'}} = \frac{AG'}{AR} \tag{7}$$

Again,  $\frac{AG'}{CT} = \frac{SA}{SC} = \frac{AR}{CD}$  (8)

Hence  $AG'/AR = CT/CD$ , and from Equation 7,  $P_A = CT/CD = CT$  (if  $CD = 1$ )

Joining  $S$  to  $B$  and  $P'$ , and letting  $SB$  and  $SP'$  cut  $CD$  at  $U$  and  $V$ , respectively, we can show similarly that  $P_B = TU$ ,  $P_C = UV$ , and then obviously  $P_D = VD$ .

EXAMPLE

As an example we shall consider a sample of blast furnace gas having the composition

CO <sub>2</sub>	12.5%	H <sub>2</sub>	3.6%
CO	26.8	N <sub>2</sub>	57.1

In this example  $S_i = M_i$ ,  $Q_i = W_i$ , and we wish to find  $P_i = X_i$ :

$M_{CO_2} = 44.01$	$W_{CO_2} = 0.125$	$X_{CO_2} = ?$
$M_{CO} = 28.01$	$W_{CO} = 0.268$	$X_{CO} = ?$
$M_{H_2} = 2.016$	$W_{H_2} = 0.036$	$X_{H_2} = ?$
$M_{N_2} = 28.02$	$W_{N_2} = 0.571$	$X_{N_2} = ?$

Figure 2 gives the graphical solution of the problem and follows the scheme of Figure 1.  $E$ ,  $F$ ,  $J$ , and  $K$  are the points with coordinates  $(W_{CO_2}, M_{CO_2})$ ,  $(W_{CO}, M_{CO})$ ,  $(W_{H_2}, M_{H_2})$  and  $(W_{N_2}, M_{N_2})$ , respectively, and they are plotted from the origins as shown.  $NM$  is the construction line parallel to  $KR$ . It is purely coincidence that  $RK$  and  $RDS$  are nearly colinear in this diagram. The results as read from  $CD$  are:

Mole fraction of CO <sub>2</sub>	= $X_{CO_2} = CT$	= 0.056
Mole fraction of CO	= $X_{CO} = TU$	= 0.189
Mole fraction of H <sub>2</sub>	= $X_{H_2} = UV$	= 0.353
Mole fraction of N <sub>2</sub>	= $X_{N_2} = VD$	= 0.402

Although the method is more cumbersome here than when dealing with binary systems, it should be capable of rapid manipulation if carried out frequently, and should give sufficiently accurate results if done on large size ( $2 \times 3$  meter) graph paper. It should be noted that for ternary systems the extra origin  $R$  is unnecessary, and in this case the method will be almost as rapid as that for binary systems. It will be necessary only to plot the point  $J(Q_C, S_C)$ , drop the perpendicular  $PP'$ , and produce  $P'D$  to get  $S$ . The rest will follow as above. For all systems having odd numbers of components, the last part of the construction will proceed likewise.

NOMENCLATURE

- $M$  = molecular weight
- $\rho$  = density
- $W$  = weight fraction
- $V$  = volume fraction
- $X$  = mole fraction
- $U$  = part by weight
- $Q$  = a quantity which may be  $W$ ,  $V$ ,  $X$ , or  $U$
- $S$  = a quantity which may be  $M$ ,  $\rho$ ,  $(M/\rho)$ ,  $(\rho/M)$ , or unity
- $S'$  = a quantity which is similar to  $S$ , but is the product formed from the remaining  $(N - 1)$  of the  $N$  components—e. g.,  $S_C' = M_A M_B M_D \dots M_N$
- $P$  = a fraction which may be  $W$ ,  $V$ , or  $X$
- Subscripts  $A, B, C, \dots, N$  = components of multicomponent system

# Interconversions of Polycomponent Compositions by Graphical Methods

KUAN-HAN SUN<sup>1</sup> AND ALEXANDER SILVERMAN

University of Pittsburgh, Pittsburgh, Penna.

Simple graphical methods are proposed for the interconversion of weight, volume, and mole fractions, and for conversion into

these fractions from compositions expressed in parts by weight or volume or as number of moles, in a polycomponent system.

IN TWO recent papers<sup>2</sup> the authors presented graphical methods for the interconversions of binary and ternary compositions. The present paper deals with the interconversions of compositions of a polycomponent system by graphical methods.

Similar to those for the binary system, polycomponent conversion equations may be written as follows:

## MOLE FRACTION $\rightleftharpoons$ WEIGHT FRACTION

For mole fraction from weight fraction:

$$X_1 = \frac{W_1}{\sum \frac{W}{M}}, X_2 = \frac{W_2}{\sum \frac{W}{M}}, \dots \quad (1)$$

For weight fraction from mole fraction:

$$W_1 = \frac{M_1 X_1}{\sum M X}, W_2 = \frac{M_2 X_2}{\sum M X}, \dots \quad (2)$$

## VOLUME FRACTION $\rightleftharpoons$ WEIGHT FRACTION

For volume fraction from weight fraction:

$$V_1 = \frac{W_1}{\sum \frac{W}{\rho}}, V_2 = \frac{W_2}{\sum \frac{W}{\rho}}, \dots \quad (3)$$

For weight fraction from volume fraction:

$$W_1 = \frac{\rho_1 V_1}{\sum \rho V}, W_2 = \frac{\rho_2 V_2}{\sum \rho V}, \dots \quad (4)$$

## MOLE FRACTION $\rightleftharpoons$ VOLUME FRACTION

For mole fraction from volume fraction:

$$X_1 = \frac{V_1}{\sum \frac{V}{(M/\rho)}}, X_2 = \frac{V_2}{\sum \frac{V}{(M/\rho)}}, \dots \quad (5)$$

For volume fraction from mole fraction

$$V_1 = \frac{X_1 (M_1/\rho_1)}{\sum X (M/\rho)}, V_2 = \frac{X_2 (M_2/\rho_2)}{\sum X (M/\rho)}, \dots \quad (6)$$

## PART BY WEIGHT $\rightarrow$ WEIGHT, MOLE, OR VOLUME FRACTION

For weight fraction from part by weight:

$$W_1 = \frac{U_1}{\sum U}, W_2 = \frac{U_2}{\sum U}, \dots \quad (7)$$

For mole fraction from part by weight:

$$X_1 = \frac{U_1}{\sum \frac{U}{M}}, X_2 = \frac{U_2}{\sum \frac{U}{M}}, \dots \quad (8)$$

For volume fraction from part by weight:

$$V_1 = \frac{U_1}{\sum \frac{U}{\rho}}, V_2 = \frac{U_2}{\sum \frac{U}{\rho}}, \dots \quad (9)$$

## NUMBER OF MOLES $\rightarrow$ WEIGHT, MOLE, OR VOLUME FRACTION

For weight fraction from number of moles:

$$W_1 = \frac{M_1 U'_1}{\sum M U'}, W_2 = \frac{M_2 U'_2}{\sum M U'}, \dots \quad (10)$$

For mole fraction from number of moles:

$$X_1 = \frac{U'_1}{\sum U'}, X_2 = \frac{U'_2}{\sum U'}, \dots \quad (11)$$

For volume fraction from number of moles:

$$V_1 = \frac{U'_1 (M_1/\rho_1)}{\sum U' (M/\rho)}, V_2 = \frac{U'_2 (M_2/\rho_2)}{\sum U' (M/\rho)}, \dots \quad (12)$$

## PART BY VOLUME $\rightarrow$ WEIGHT, MOLE, OR VOLUME FRACTION

For weight fraction from part by volume:

$$W_1 = \frac{\rho_1 U''_1}{\sum \rho U''}, W_2 = \frac{\rho_2 U''_2}{\sum \rho U''}, \dots \quad (13)$$

For mole fraction from part by volume:

$$X_1 = \frac{U''_1 / (M_1/\rho_1)}{\sum \frac{U''}{(M/\rho)}}, X_2 = \frac{U''_2 / (M_2/\rho_2)}{\sum \frac{U''}{(M/\rho)}}, \dots \quad (14)$$

For volume fraction from part by volume:

$$V_1 = \frac{U''_1}{\sum U''}, V_2 = \frac{U''_2}{\sum U''}, \dots \quad (15)$$

The above equations can be summarized by the following two types of general equations:

$$\text{Type 1: } P_1 = \frac{Q_1}{\sum \frac{Q}{S}}, P_2 = \frac{Q_2}{\sum \frac{Q}{S}}, \dots \quad (16)$$

$$\text{Type 2: } P_1 = \frac{Q_1 S_1}{\sum Q S}, P_2 = \frac{Q_2 S_2}{\sum Q S}, \dots \quad (17)$$

$$\sum Q = 1 \text{ (in most cases)}$$

<sup>1</sup> Present address, Eastman Kodak Company, Rochester, N. Y.

<sup>2</sup> IND. ENG. CHEM., 34, 682, 872 (1942).

## GRAPHICAL METHODS

The problem is to know  $Q_1, Q_2, Q_3$ , etc., and  $S_1, S_2, S_3$ , etc., in Equations 16 and 17 (types 1 and 2, respectively) and how to obtain  $P_1, P_2, P_3$ , etc., by graphical means. The following methods have been devised for the two types of equations:

FOR EQUATIONS OF TYPE 1. On any graph paper, assign the whole length or suitable length of abscissa to  $AB$  as unity, as indicated in Figure 1. Ignoring the above assignment, plot points  $S_1, S_2, S_3$ , etc., arranged in ascending order, on the abscissa by choosing a suitable scale. It is obvious that if  $S_1, S_2, S_3$ , etc., are arranged in ascending order,  $Q_1, Q_2, Q_3$ , etc., will be in random order. Plot point  $a$  so that its horizontal ordinate equals  $S_1$  and its vertical distance from  $AB$  equals  $Q_1$ . Connect points  $Aa$  and prolong to intercept line  $BB'$  at  $D$ . Draw line  $CD$  parallel to  $AB$ . Plot point  $b$  so that its horizontal distance equals  $S_2$  and its vertical distance from line  $CD$  equals  $Q_2$ . Connect  $Cb$  which cuts line  $BB'$  at  $F$ . The process is repeated until the last point ( $d$  in Figure 1) is plotted and the final intercept on line  $BB'$ ,  $I$ , is obtained. Connect  $AI$  which intercepts horizontal lines  $CD, EF$ , and  $GH$  at  $C', E'$ , and  $G'$ , respectively. Points  $A', D',$  and  $F'$  are their corresponding vertical projections on lines  $AB, CD$ , and  $EF$ . Then  $AA', C'D', E'F'$ , and  $G'H$  will equal  $P_1, P_2, P_3$ , and  $P_4$  required, if they are read off from the graph, according to the assignment that  $AB = 1$ .

The proof is simple. Since  $AB$  is assigned unity (or any constant), it is obvious from simple geometry that  $BD, DF, FH$ , and  $HI$  equal  $Q_1/S_1, Q_2/S_2, Q_3/S_3$ , and  $Q_4/S_4$ , respectively, and  $BI$  equals  $\Sigma(Q/S)$ . Again, by simple geometry, it is apparent that  $AA', C'D', E'F'$ , and  $G'H$  equal  $(Q_1/S_1)/\Sigma(Q/S), (Q_2/S_2)/\Sigma(Q/S), (Q_3/S_3)/\Sigma(Q/S)$ , and  $(Q_4/S_4)/\Sigma(Q/S)$  or  $P_1, P_2, P_3$ , and  $P_4$ , respectively.

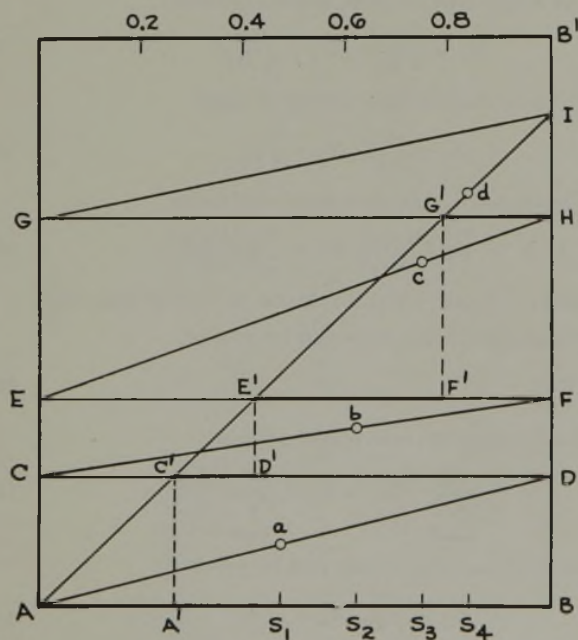


Figure 1

FOR EQUATIONS OF TYPE 2. As in type 1, consider  $AB$  unity. Ignore the assignment temporarily and plot  $S_1, S_2, S_3$ , and  $S_4$  in ascending order on abscissa  $AB$  (Figure 2). Plot point  $a$  on line  $BB'$  so that  $Ba = Q_1$ . Join  $Aa$  and locate point  $a'$  on it so that its horizontal ordinate equals  $S_1$ . Draw line  $CD$  passing through  $a'$  parallel to  $AB$ . Similarly, locate  $b$  on  $BB'$  so that  $Db = Q_2$  and locate point  $b'$  on line  $Cb$  with a

horizontal ordinate equal to  $S_2$ . Draw line  $EF$  passing  $b'$  and repeat the process until the last point  $I$  is obtained. Join  $AI$ , then  $AA', C'D', E'F'$ , and  $G'H$ , read from the graph considering  $AB = 1$ , will give the fractions  $P_1, P_2, P_3$ , and  $P_4$  sought. The proof is simple and similar to that for type 1.

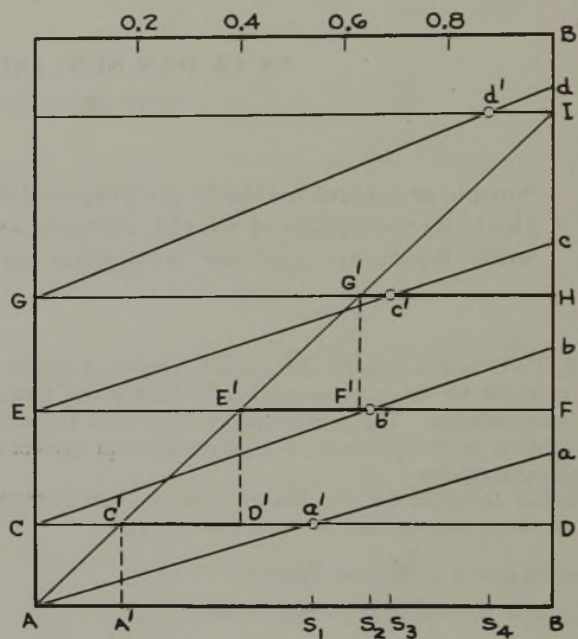


Figure 2

Although only a quaternary example has been chosen for Figures 1 and 2, it is obvious that they will serve any poly-component system equally well. The methods may seem complicated. They are simple to operate after the fundamentals involved are mastered. The methods should prove useful for such cases as a quaternary system in which compositions of two components are fixed while the other two vary.

## NOMENCLATURE

$M$  = molecular weight  
 $\rho$  = density  
 $W$  = weight fraction  
 $V$  = volume fraction  
 $X$  = mole fraction  
 $U$  = part by weight  
 $U'$  = number of moles  
 $U''$  = part by volume  
 $Q$  = a quantity which represents  $W, V, X, U, U'$ , or  $U''$   
 $S$  = a quantity which represents  $M, \rho, (M/\rho)$  or unity  
 $P$  = a quantity which represents  $W, V$ , or  $X$

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CONTRIBUTION 476 from the Department of Chemistry, University of Pittsburgh.

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JOHN GRISWOLD



## Cooperating with Uncle Sam

Four independent refiners joined together in 1931 to build the world's first cooperative Dubbs-cracking unit. Its purpose was to crack the oils from their respective refineries to the best advantage of all. Universal designed it. It was enlarged in 1939.

Now those refiners have taken a fifth party into their cooperative set-up—Uncle Sam. He wants 100-octane gasoline—and lots of it.

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### Says Oil and Gas Journal:

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That's the kind of cooperation going on throughout the refining industry today.

OIL IS AMMUNITION—USE IT WISELY

CARE FOR YOUR CAR FOR YOUR COUNTRY

Universal Oil Products Co  
Chicago, Illinois



Dubbs Cracking Process  
Owner and Licensor

THE REFINERS INSTITUTE OF PETROLEUM TECHNOLOGY

## GRAPHICAL METHODS

The problem is to know  $Q_1, Q_2, Q_3, \text{etc.}$ , and  $S_1, S_2, S_3, \text{etc.}$ , in Equations 16 and 17 (types 1 and 2, respectively) and how to obtain  $P_1, P_2, P_3, \text{etc.}$ , by graphical means. The following methods have been devised for the two types of equations:

**FOR EQUATIONS OF TYPE 1.** On any graph paper, assign the whole length or suitable length of abscissa to  $AB$  as unity, as indicated in Figure 1. Ignoring the above assignment, plot points  $S_1, S_2, S_3, \text{etc.}$ , arranged in ascending order, on the abscissa by choosing a suitable scale. It is obvious that if  $S_1, S_2, S_3, \text{etc.}$ , are arranged in ascending order,  $Q_1, Q_2, Q_3, \text{etc.}$ , will be in random order. Plot point  $a$  so that its horizontal ordinate equals  $S_1$  and its vertical distance from  $AB$  equals  $Q_1$ . Connect points  $Aa$  and prolong to intercept line  $BB'$  at  $D$ . Draw line  $CD$  parallel to  $AB$ . Plot point  $b$  so that its horizontal distance equals  $S_2$  and its vertical distance from line  $CD$  equals  $Q_2$ . Connect  $Cb$  which cuts line  $BB'$  at  $F$ . The process is repeated until the last point ( $d$  in Figure 1) is plotted and the final intercept on line  $BB'$ ,  $I$ , is obtained. Connect  $AI$  which intercepts horizontal lines  $CD, EF,$  and  $GH$  at  $C', E',$  and  $G'$ , respectively. Points  $A', D',$  and  $F'$  are their corresponding vertical projections on lines  $AB, CD,$  and  $EF$ . Then  $AA', C'D', E'F',$  and  $G'H$  will equal  $P_1, P_2, P_3,$  and  $P_4$  required, if they are read off from the graph, according to the assignment that  $AB = 1$ .

The proof is simple. Since  $AB$  is assigned unity (or any constant), it is obvious from simple geometry that  $BD, DF, FH,$  and  $HI$  equal  $Q_1/S_1, Q_2/S_2, Q_3/S_3,$  and  $Q_4/S_4$ , respectively, and  $BI$  equals  $\Sigma(Q/S)$ . Again, by simple geometry, it is apparent that  $AA', C'D', E'F',$  and  $G'H$  equal  $(Q_1/S_1)/\Sigma(Q/S), (Q_2/S_2)/\Sigma(Q/S), (Q_3/S_3)/\Sigma(Q/S),$  and  $(Q_4/S_4)/\Sigma(Q/S)$  or  $P_1, P_2, P_3,$  and  $P_4$ , respectively.

horizontal ordinate equal to  $S_2$ . Draw line  $EF$  passing  $b'$  and repeat the process until the last point  $I$  is obtained. Join  $AI$ , then  $AA', C'D', E'F',$  and  $G'H$ , read from the graph considering  $AB = 1$ , will give the fractions  $P_1, P_2, P_3,$  and  $P_4$  sought. The proof is simple and similar to that for type 1.

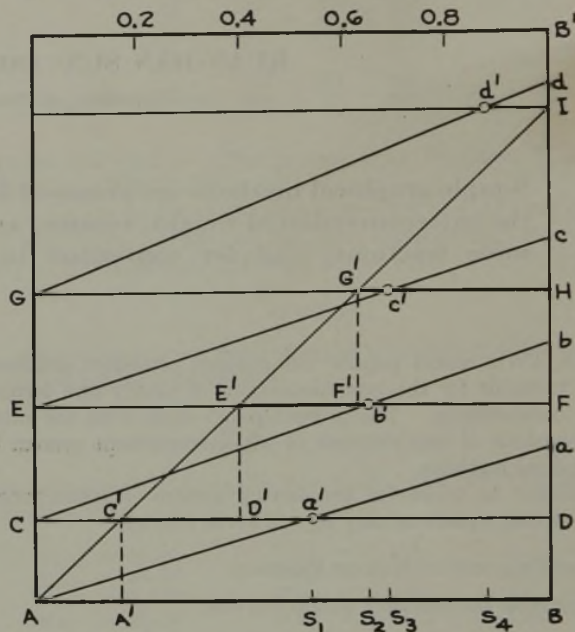


Figure 2

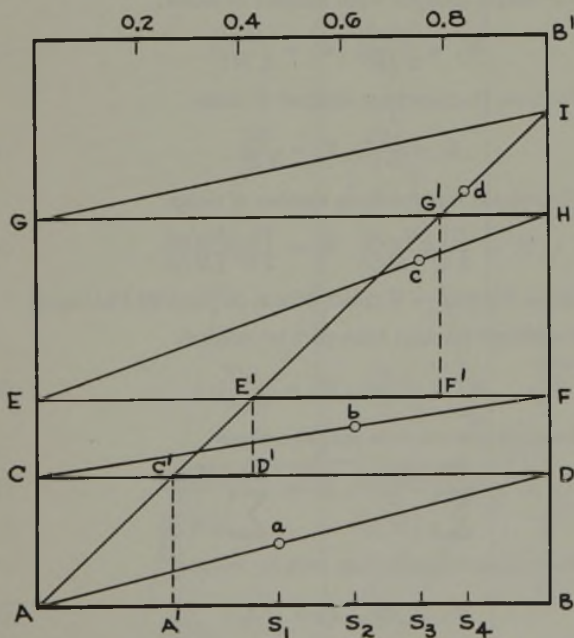


Figure 1

**FOR EQUATIONS OF TYPE 2.** As in type 1, consider  $AB$  unity. Ignore the assignment temporarily and plot  $S_1, S_2, S_3,$  and  $S_4$  in ascending order on abscissa  $AB$  (Figure 2). Plot point  $a$  on line  $BB'$  so that  $Ba = Q_1$ . Join  $Aa$  and locate point  $a'$  on it so that its horizontal ordinate equals  $S_1$ . Draw line  $CD$  passing through  $a'$  parallel to  $AB$ . Similarly, locate  $b$  on  $BB'$  so that  $Db = Q_2$  and locate point  $b'$  on line  $Cb$  with a

Although only a quaternary example has been chosen for Figures 1 and 2, it is obvious that they will serve any polycomponent system equally well. The methods may seem complicated. They are simple to operate after the fundamentals involved are mastered. The methods should prove useful for such cases as a quaternary system in which compositions of two components are fixed while the other two vary.

## NOMENCLATURE

- $M$  = molecular weight
- $\rho$  = density
- $W$  = weight fraction
- $V$  = volume fraction
- $X$  = mole fraction
- $U$  = part by weight
- $U'$  = number of moles
- $U''$  = part by volume
- $Q$  = a quantity which represents  $W, V, X, U, U',$  or  $U''$
- $S$  = a quantity which represents  $M, \rho, (M/\rho)$  or unity
- $P$  = a quantity which represents  $W, V,$  or  $X$

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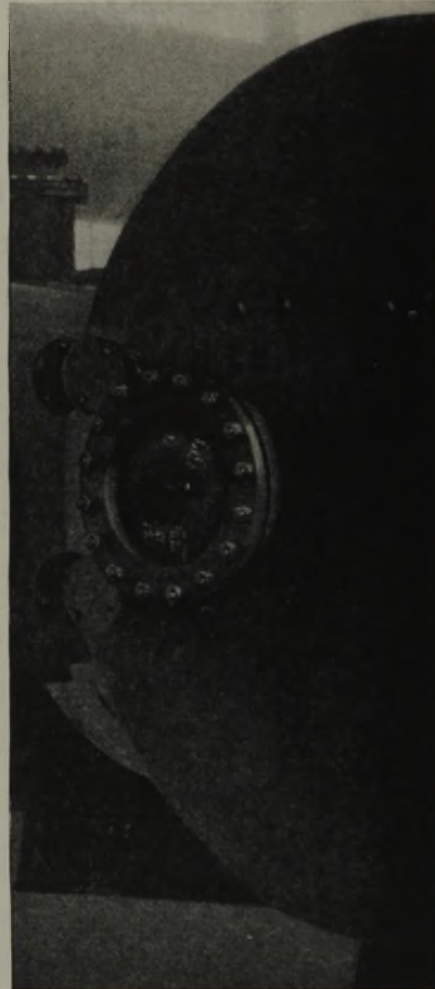
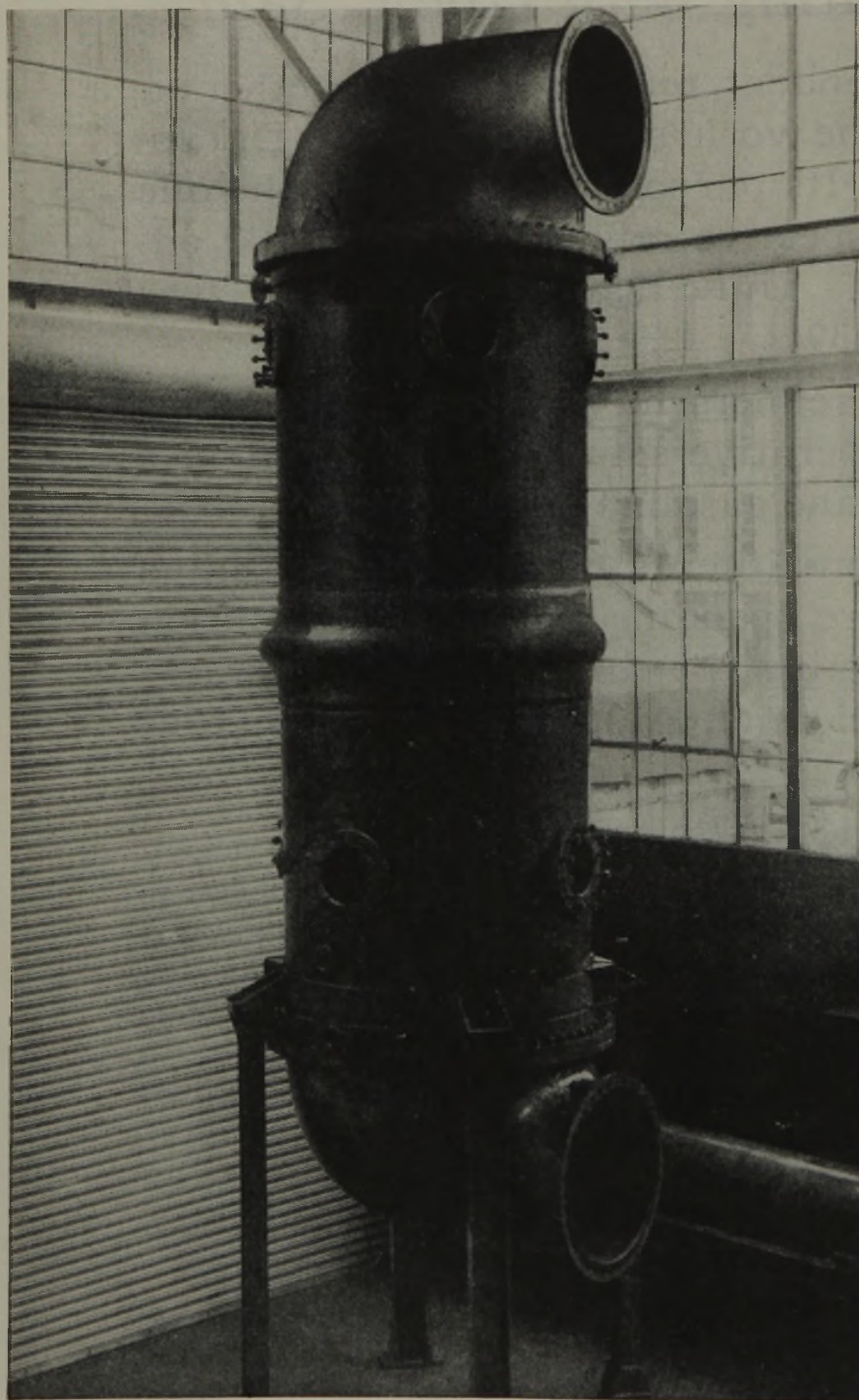
Universal Oil Products Co  
Chicago, Illinois



Dubbs Cracking Process  
Owner and Licensor

THE REFINERS INSTITUTE OF PETROLEUM TECHNOLOGY

# Metal at work



## EVERDUR\* STILL KETTLE

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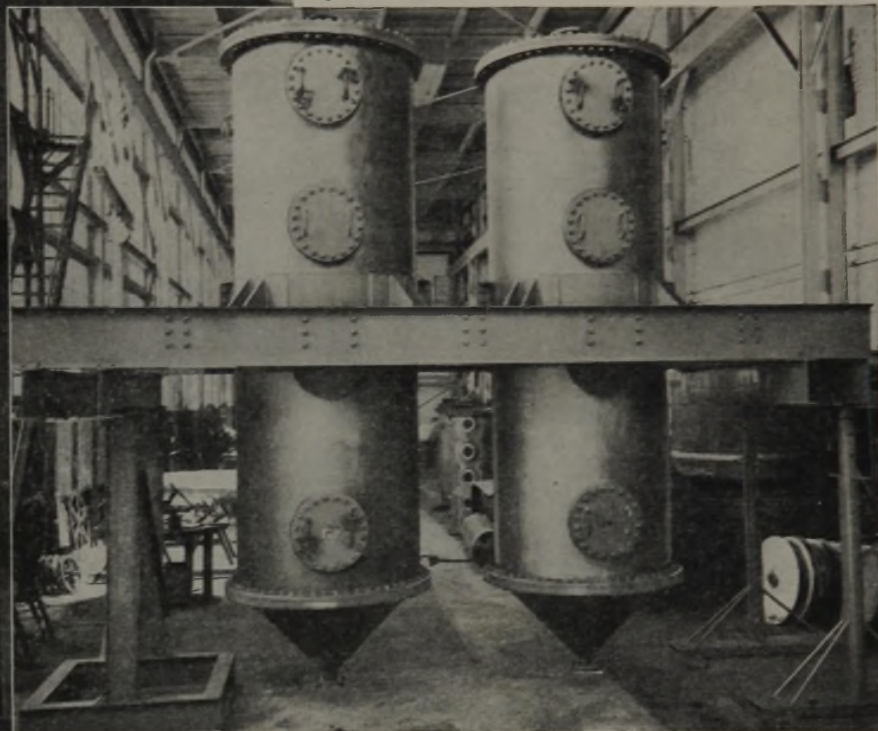
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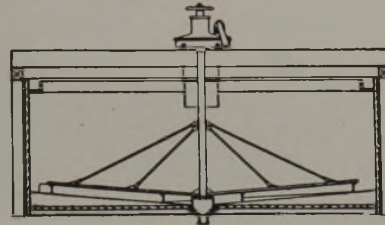
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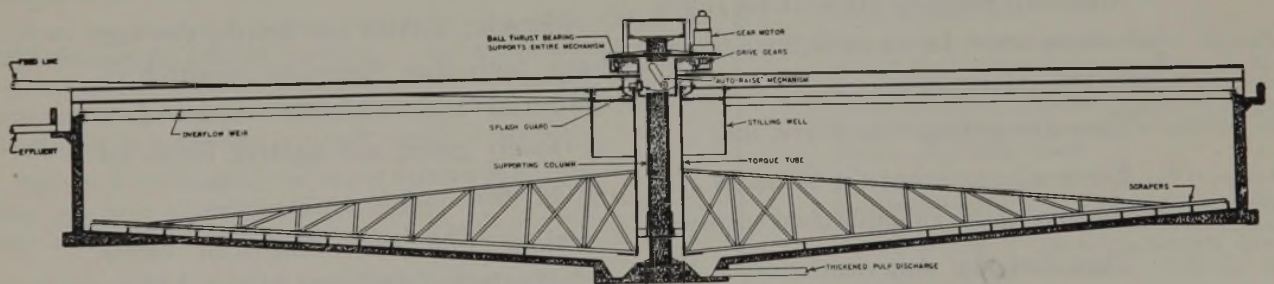
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### Bulletin 31-C



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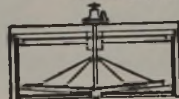
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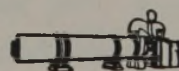
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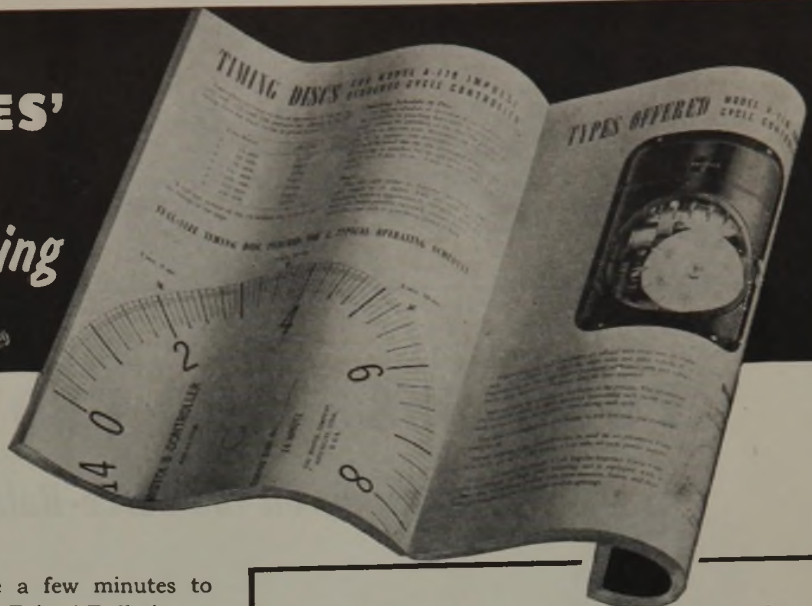
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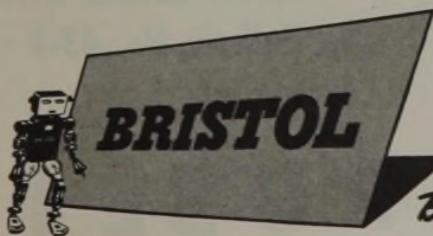
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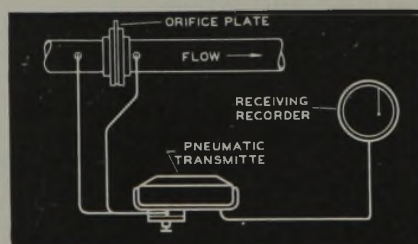
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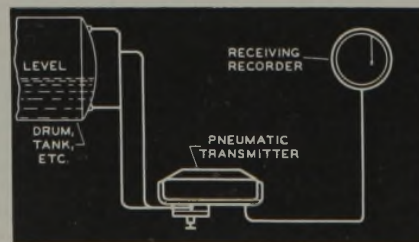
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*Typical installation for measuring flow.*



*Typical installation for measuring liquid level.*

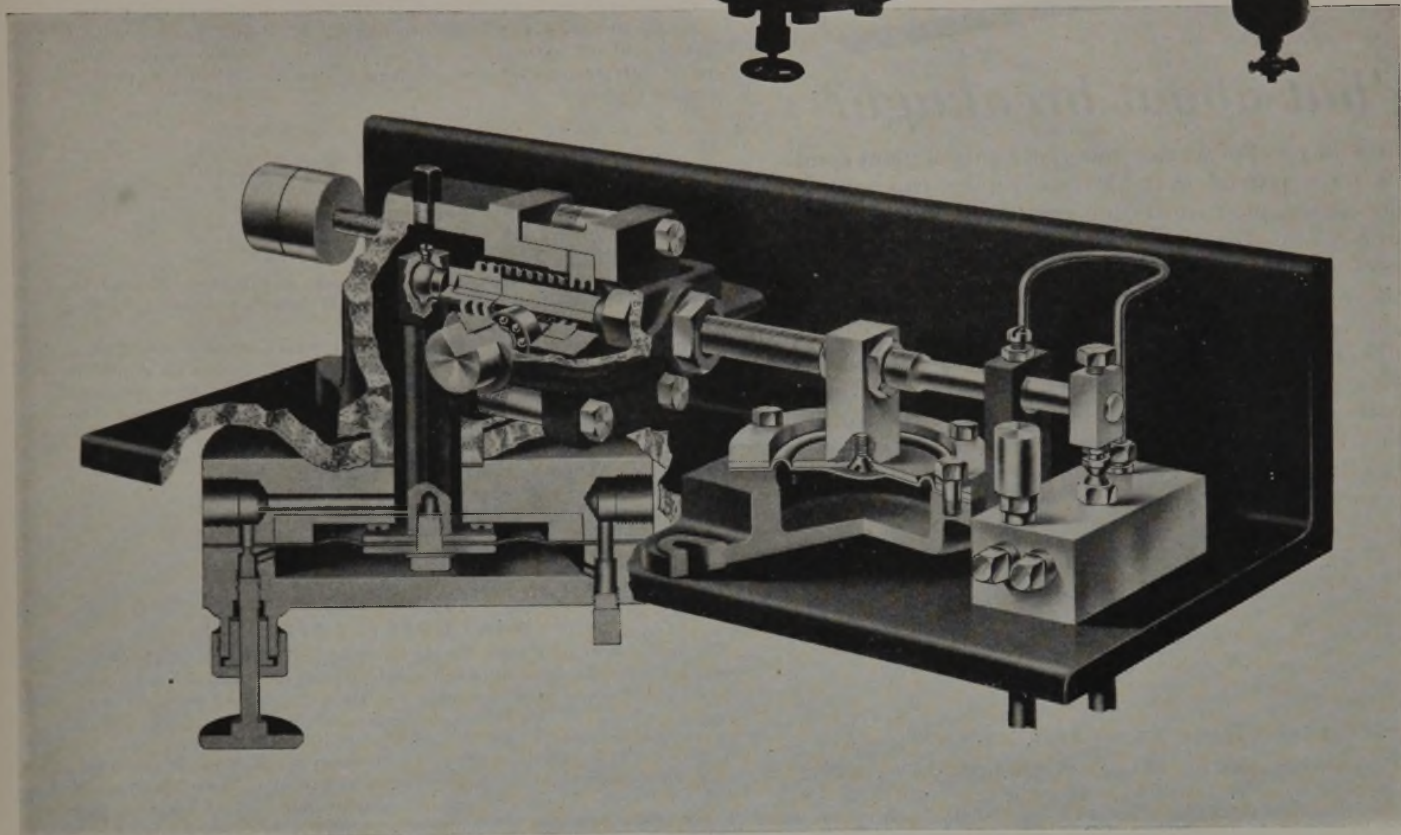
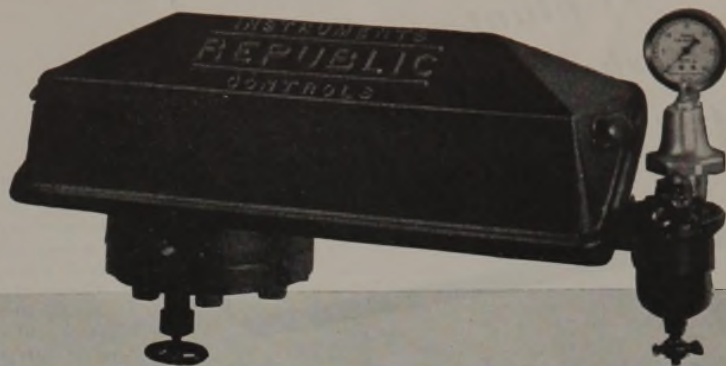
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# Transmitter



*Exterior and cut-away view of the Republic Pneumatic Transmitter.*

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**SENSITIVITY** — due to the negligible motions required for complete operation of all parts for full scale change, no appreciable hysteresis results from reversal of direction of measurement change. The hysteresis loop is so small that it is undetectable by ordinary means, being less than  $\frac{1}{20}$  of 1%.

**RESPONSIVENESS** — due to the fact that there is virtually no volume displacement, the Republic Pneumatic Transmitter is able to follow flow changes almost instantaneously. The time required to produce full output pressure at the transmitter is in the nature of fractions of a second, after the differential is imposed. Therefore a receiving instrument installed adjacent to the transmitter

will show flow changes almost instantly. With 500 feet of  $\frac{1}{4}$  in. O. D. tubing, the full value of the change will have registered on a Republic receiver in 15 seconds. This is the overall lag in the system not merely the transmission lag.

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**NO VIBRATION EFFECT** — the Republic transmitter is unaffected by any normal frequency of vibration ordinarily encountered in industrial or process plants.

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**GLASS PIPING!**



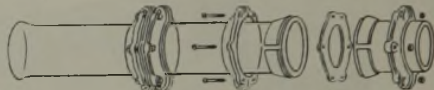
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**IS IT EASY TO INSTALL?**

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**WHAT DOES IT COST?**

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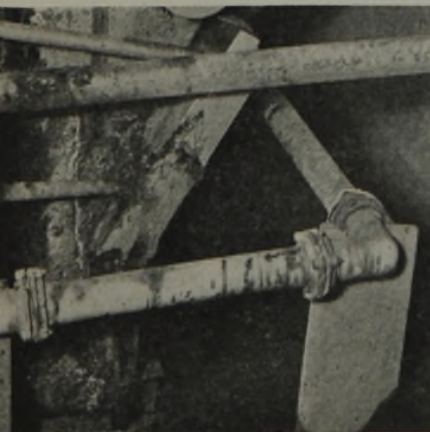
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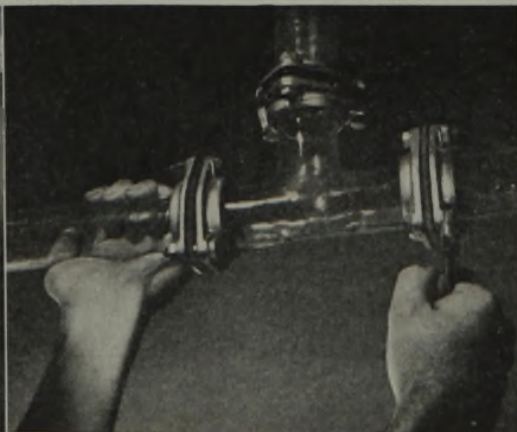
Accessories: Joints are compression type—with conical pipe ends compressed to a self-centering gasket by metal flanges and clamping bolts. We supply gaskets of materials suited to the liquid or gas you want to convey.

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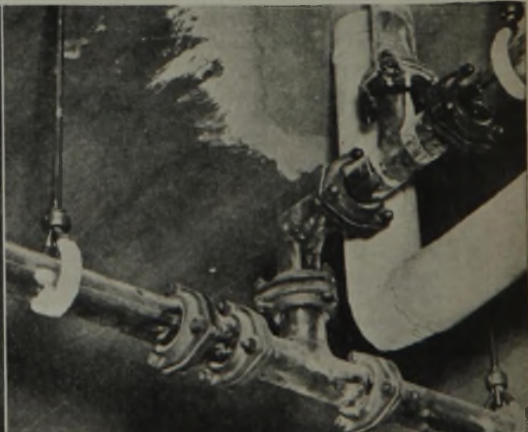
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THAN YOU  
EXPECT



OF course, Fairbanks Scales are big, husky, and accurate. You have a right to expect these things in *any* good scale — and particularly of Fairbanks Scales with the world's broadest scale manufacturing experience behind them.

The feature about Fairbanks Scales that may surprise you the most, is their ability to do things you *don't* expect of scales.

Here are a few of many jobs done by Fairbanks Scales:

- They count small parts — more accurately than manual counting
- They weigh carloads of coal in motion and make a printed record of each weight
- They automatically control paint ingredients
- They automatically control aggregates
- They "keep the books" in steel plants, making printed records of incoming and outgoing shipments
- They keep accurate records on chlorination in water treatment
- They record the *flow* of liquid chemicals
- They guard secret formulas in compounding
- They control batching in bakeries
- They prevent disputes by eliminating the human element in weighing.

AND all of these things, only the beginning of the story, they do automatically and mechanically thereby eliminating human errors.

How Fairbanks Scales can be fitted into your production flow to speed up operations and eliminate errors may prove to be the most interesting discovery you ever made. Investigate now. Write Fairbanks, Morse & Co., 600 S. Michigan Ave., Chicago, Illinois.



DIESEL ENGINES  
PUMPS  
MOTORS  
GENERATORS  
SCALES

WATER SYSTEMS  
FARM EQUIPMENT  
STOKERS  
AIR CONDITIONERS  
RAILROAD EQUIPMENT



# FAIRBANKS-MORSE

# Scales

What every plant operator should know about  
**GLASS PIPING!**

**What about breakage?**

Nearly 20 years of service under all kinds of plant conditions have proved that "PYREX Piping can take it" under actual plant operating conditions. Glass in this form is *not* as strong as metal, but workmen instinctively respect glass and quickly learn to handle it without breakage. With reasonable care in avoiding installation strains or sharp impact, PYREX Piping will give years of trouble-free service. The glass itself is very hard—about twice as resistant to abrasion as ordinary glass. Thus, it is particularly suitable for abrasive, corrosive slurries. PYREX Piping is recommended for working pressures up to 100 lbs. per sq. in. You can install and use this piping with confidence.



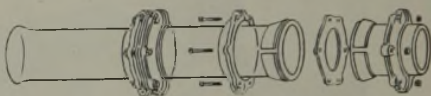
**IS GLASS PIPING AVAILABLE NOW?**

Yes. Glass-making materials are still fairly plentiful. We do need priority ratings that enable us to get accessories (flanges, gaskets), to assign necessary labor, and to establish the position of your order in our production line. With such priorities we have been making 6 to 8-week deliveries.  
*Available sizes and lengths:* 1", 1½", 2", 3", and 4" diameters—and any length from 6 inches to 10 feet (longer lengths on special request). There are corresponding ells, tees, return bends, and reducers.  
*Accessories:* Joints are compression type—with conical pipe ends compressed to a self-centering gasket by metal flanges and clamping bolts. We supply gaskets of materials suited to the liquid or gas you want to convey.



**WHERE DOES IT GIVE BEST SERVICE?**

Wherever hot or corrosive liquids or gases must be conveyed . . . wherever products must be protected from contamination . . . wherever it is important to know what is happening *inside* a line . . . there PYREX Piping gives you its most profitable service.  
 Chemical plants use it to eliminate their corrosion problems, because it resists all hot or cold acids (except HF). Food and beverage manufacturers like it because it's easy to keep clean, either by simple flushing or with steam or strong hot cleaning solutions. It helps to produce a purer product.



**IS IT EASY TO INSTALL?**

Plant workmen have found it easy to make installations themselves. In fact, green plant mechanics have recently done first-rate installations with PYREX Piping.  
 You may install from one piece to a whole system—for PYREX Piping may be joined to existing metal lines and equipment. And it is hung and supported much like other types of piping. (See photo at bottom of page). We do recommend that hangers and supports be padded, to minimize scratching.

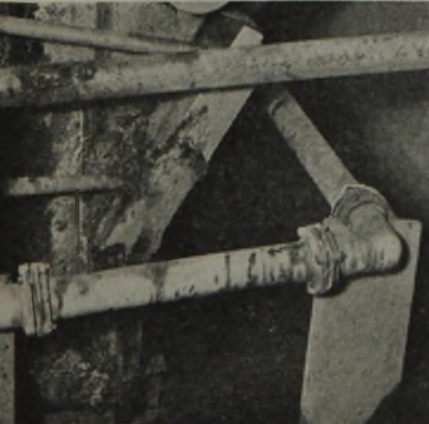


**WHAT DOES IT COST?**

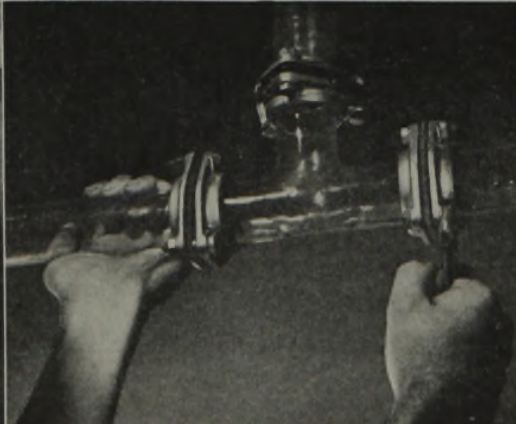
The initial cost of PYREX Piping (accessories included) is about the same or less than the cost of full-weight copper or brass piping, in comparable sizes, and is considerably less than the cost of stainless steel. And because PYREX Piping does not wear out under acid attack, it gives long trouble-free service, with resultant low long-time cost.  
 The left-hand photograph at the bottom of the page is an example. That PYREX Piping has carried a slurry of crushed quartz and sulphuric acid for over eight years—without one cent of maintenance.

**WATCH FOR CORNING ADVERTISEMENTS!**

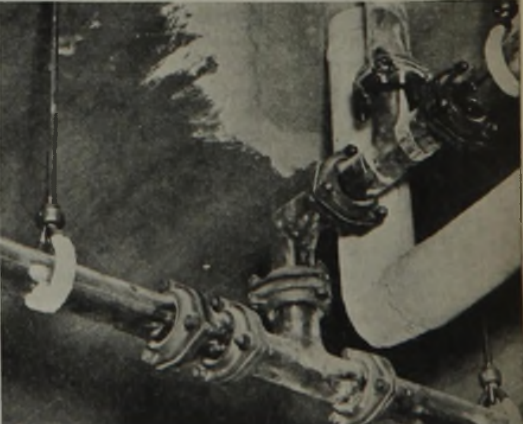
Watch this magazine for more information in Corning's advertisements headed "What every plant operator should know about Glass Piping." And Write for PYREX Piping Bulletin No. 814. Industrial Division, Corning Glass Works, Corning, N. Y. Branch Offices: New York, 718 Fifth Ave.; Chicago, Merchandise Mart.



Sulphuric acid and crushed quartz line.



PYREX Piping is easy to install.



Chemical laboratory drain line.

"PYREX" is a registered trade-mark and indicates manufacture by Corning Glass Works, Corning, N. Y.

**CORNING**  
 Glass Works  
 Corning, New York

**Pyrex Industrial Glass**

# SCALES

THAT DO MORE  
THAN YOU  
EXPECT



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## FAIRBANKS - MORSE

# Scales



DIESEL ENGINES  
PUMPS  
MOTORS  
GENERATORS  
SCALES

WATER SYSTEMS  
FARM EQUIPMENT  
STOKERS  
AIR CONDITIONERS  
RAILROAD EQUIPMENT



# CONCRETE SAVERS — PQ SILICATES



**CONCRETE** tanks, warehouse floors, runways and concrete structures are "expendable".

Increase their span of life with a surface coat of PQ Silicate of Soda. In addition, the silicate treatment is a time-saver because it is easy to apply either by brush or spray.

Applied in proper consistency to the surface, PQ Silicate reacts chemically to form insoluble films in the concrete. Thus, the structure is protected and made to last longer. Let us know the area to be treated and for what service. We'll suggest the correct quantity of PQ Silicate needed.

*Acidproofing:* Silicate renders concrete resistant to attack not only by acids, but by other deteriorating solutions, such as sugar and salt.

*Waterproofing:* Treatment of concrete walls, tanks, building blocks, reservoirs, stops up the pores, making the concrete less permeable.

*Oilproofing:* Protects against disintegration by oil penetration of storage tanks, floors, runways.

*Wearproofing:* Stop wear of the surface and dusting by the PQ Silicate Treatment.

*Concrete anchorage of bridge treated with PQ Silicate.*

## PHILADELPHIA QUARTZ CO.

Established 1831 . . . General Offices and Laboratory: 125 S. Third Street, Philadelphia, Pa.  
Chicago Sales Office: Engineering Bldg. Sold in Canada by National Silicates Ltd., Toronto, Ont.





The pressure vessel shown below is one of three such vessels fabricated for the U. S. Navy. It is 106 in. in diam. by 68 ft. 3 in. long and is designed to store oxygen at 300 lbs. per sq. in. pressure. The vessels were stress-relieved.

## Tailor Made FOR STORING OXYGEN

FABRICATED true to its specifications, this pressure vessel has been "recruited" by the Navy for a specific job. It's one of three such vessels to be used for storing oxygen at 300 lbs. per sq. in. pressure. Similar welded steel pressure vessels are familiar sights at refineries, chemical plants, synthetic rubber plants and other types of industries.

The designing and fabricating of these vessels is an old story at our plants. Manufac-

turing skill and complete facilities for x-raying and stress-relieving are available at our Birmingham plant. Vessels up to 13 ft. 2 in. in diameter and as long as can be shipped can be handled in the stress-relieving furnace. At our other plants we are equipped to fabricate pressure vessels to API-ASME specifications.

We may be able to help you if welded steel pressure vessels or other types of storage tanks are needed to meet your specific production schedule. Write, outlining your needs, to

# CHICAGO BRIDGE & IRON COMPANY

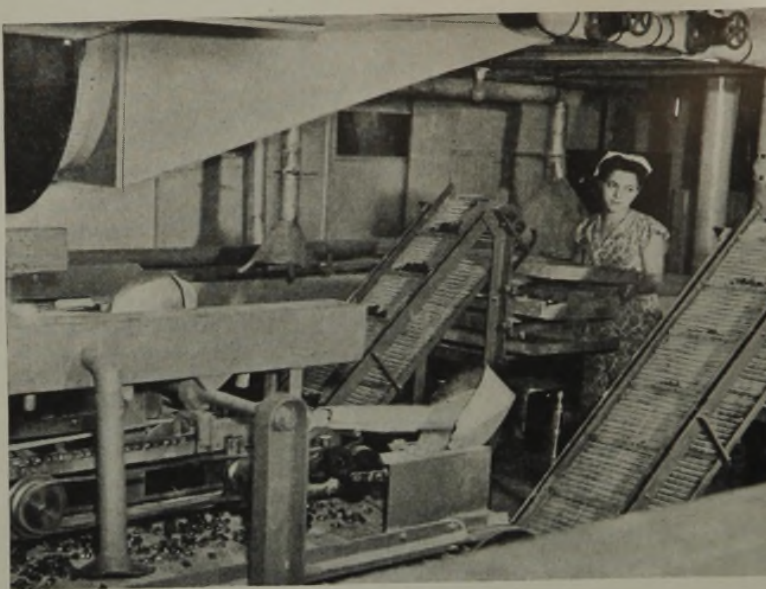
Chicago ..... 2428 McCormick Bldg.  
 New York ..... 3374-165 Broadway Bldg.  
 Havana ..... 402 Edificio Abreu  
 Philadelphia ..... 1636-1700 Walnut St. Bldg.

Cleveland ..... 2253 Guildhall Bldg.  
 Birmingham ..... 1574 North Fiftieth St.  
 Washington ..... 330 Bowen Bldg.

Houston ..... 5639 Clinton Drive  
 Tulsa ..... 1636 Hunt Bldg.  
 Greenville ..... York Street  
 San Francisco ..... 1066 Rialto Bldg.

Plants in BIRMINGHAM, CHICAGO and GREENVILLE, PA. In Canada: HORTON STEEL WORKS, LIMITED, FORT ERIE, ONTARIO

## ARE YOU Working Under A Cloud?



Difficult drying days, erratic behavior of processes, off-quality products, all can be caused by excessive moisture in the air. The Drug Industry discovered years ago that they can avoid many of these faults by controlling atmospheric moisture with Lectrodryers.

The packaging room pictured here is held at a definite dryness. No chance of those products picking up unwanted moisture; they leave the plant as the manufacturer intended. A Lectrodryer handles that drying job.

Perhaps you can profit by some of the lessons learned in the pharmaceutical industries. Lectro-

dryers can help you standardize drying operations in your present driers, regardless of outside weather conditions. You can obtain a greater degree of dryness than is now possible with your present equipment. Conditioned air will safeguard the quality of products being processed and packaged.

If you have a drying problem—air, gases or organic liquids—let us advise you on it. Lectrodryer's engineers base their recommendations on experience gained in solving hundreds of such problems, in many industries. Write PITTSBURGH LECTRODRYER CORPORATION, 305 32nd Street, Pittsburgh, Pennsylvania.



LECTRODRYERS DRY WITH ACTIVATED ALUMINAS

P I T T S B U R G H

# LECTRODRYER

C O R P O R A T I O N

Reg. U.S. Pat. Off.

Acetoacetanilide, bbls., fib. . . . .	lb. . . . .	
smaller lots . . . . .	lb. . . . .	
Acetone, CP, <sup>1</sup> dms., c.l., dlvd. E.*	lb. .08½-	
tanks, dlvd. . . . .	lb. .09 -	
l.c.l., dlvd. . . . .	lb. .07 -	
* OPA ceiling for Eastern territory (the State of New Mexico, Colorado, Wyoming, Montana and all States east thereof); ceilings ½c. per lb. higher for Western territory (all other States of the United States).		
Acetonitrile, dms., works . . . . .	lb. 1.00 - 2.00	
Methyl (see M). . . . .	lb. 1.00 -	
Acetophenone, bbls., keg . . . . .	lb. 1.00 -	
dms., 50 lbs. . . . .	lb. 1.08 -	

# ... but it costs only 1/2 cent a pound to recover Acetone with Columbia Activated Carbon

**B**ECAUSE of their low-operating expense and their high over-all efficiency—usually greater than 95 per cent—solvent recovery plants using Columbia Activated Carbon recover acetone and other volatile solvents for a half cent a pound . . . or less . . . a fraction of the cost of new solvent.

The table shows typical operating costs for a large plant recovering acetone with Columbia Activated Carbon. This plant, like all of the solvent recovery plants that we design and supply, is equipped to separate and purify the recovered solvents so that they can be re-used immediately.

Solvent recovery plants using Columbia Activated Carbon can recover all kinds of volatile solvents . . . esters, ketones, alcohols, hydrocarbons, chlorinated compounds, ether, and carbon bisulfide . . . with high efficiency and low cost comparable to the record of this acetone recovery unit.



In almost every type of manufacturing operation where solvents are vaporized under conditions which permit collection of the vapor-laden air, these solvent recovery plants can help in-

sure the supply of solvents and lower manufacturing costs. More than \$65,000,000 worth of solvents will be recovered annually by plants now in operation or under construction.

We design and supply complete solvent recovery plants to fit specific requirements—plants with guaranteed operating characteristics that quickly pay for themselves.

If you vaporize solvents in your operations, and would like more information about solvent recovery with Columbia Activated Carbon, write for our 28-page booklet.

### Typical Operating Expense of a Large Plant (Per Pound of Solvent Recovered Ready for Re-Use)

Steam at 40¢/1000 lb. . . . .	\$0.0020
Electric power at 1¢/KWH . . . . .	0.0008
Water at 10¢/1000 gal. . . . .	0.0010
Supervision . . . . .	0.0005
Maintenance . . . . .	0.0004
<b>Total, Per Pound . . . . .</b>	<b>\$0.0047</b>

This plant has the capacity to handle 3,000 pounds per hour of acetone and 30,000 cubic feet per minute of vapor-laden air measured at 100°F.

The word "Columbia" is a registered trade-mark of Carbide and Carbon Chemicals Corporation.

Representative Industries For Which We Have Designed and Supplied Complete Solvent Recovery Plants Include: Rayon, Artificial Leather, Lacquer Coatings, Rubber, Rotogravure Printing, Smokeless Powder, Plastics, and Transparent Wrappings.

For information concerning the uses of "Columbia" Activated Carbon, address:

**CARBIDE AND CARBON CHEMICALS CORPORATION**

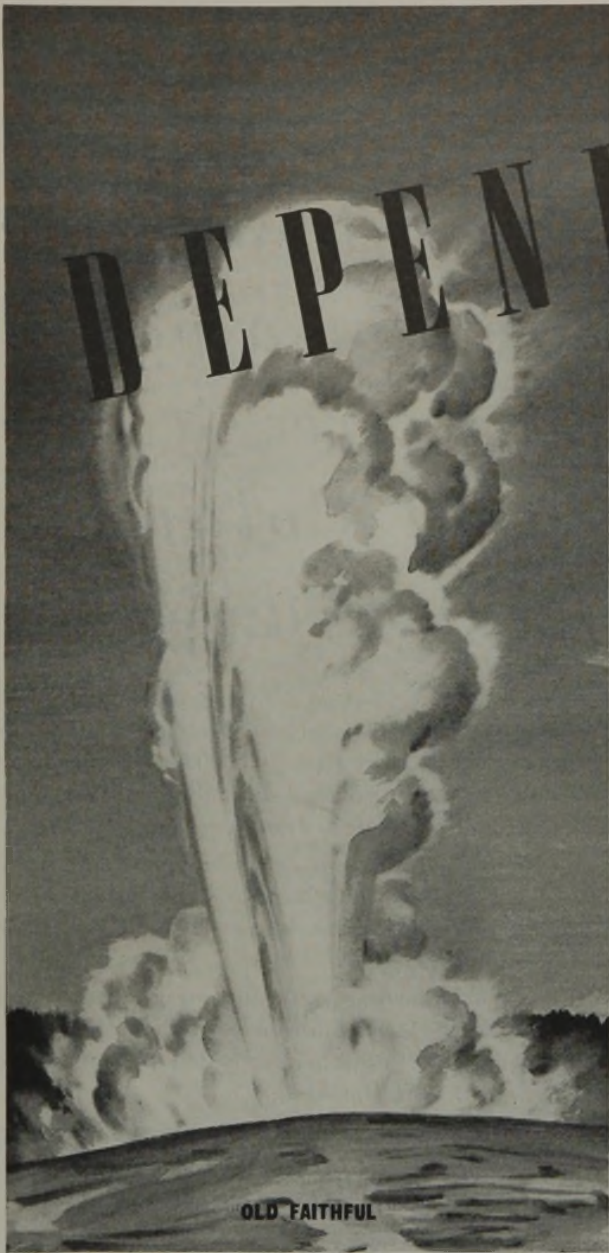
Unit of Union Carbide and Carbon Corporation



30 East 42nd Street, New York, N. Y.

PRODUCERS OF SYNTHETIC ORGANIC CHEMICALS

# DEPENDABILITY



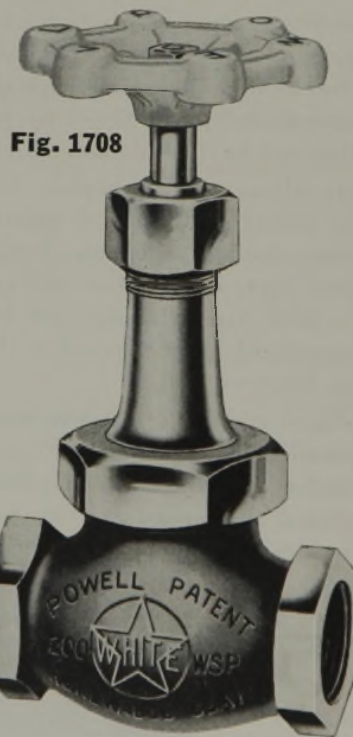
For many years "Old Faithful" has been a byword for dependable performance. Once every hour, day in and day out, as far back as man can remember, this famous geyser in Yellowstone Park has spouted for four minutes. In this brief time ten to twelve thousand gallons of water rush forth, the column rising to an average height of 140 feet. Then the flow ceases abruptly, to reoccur an hour later.

For dependable performance in every process of the Chemical Industry, Powell Valves, too, are famous—the result of nearly a century of concentration on making valves—nothing but valves—the best valves it is possible to make. Powell Quality costs no more at the start and saves in the long run.

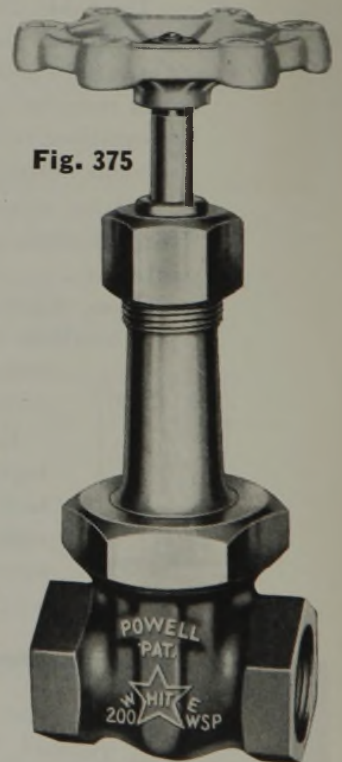
## The Wm. Powell Company

*Dependable Valves Since 1846*

**Cincinnati, Ohio**



**Fig. 1708**



**Fig. 375**

**Fig. 375**—200-pound Bronze Gate Valve with screwed ends, union bonnet, inside screw rising stem and special hard bronze disc. Sizes  $\frac{1}{4}$ " to 3", inclusive.

**Fig. 1708**—200-pound Bronze Globe Valve with screwed ends, union bonnet, renewable seat, and regrindable, renewable hard bronze semi-cone, plug-type disc. Sizes  $\frac{1}{4}$ " to 3", inclusive.

The **POWELL** Line includes Globe, Angle, Gate, Check, Relief, Y, Non-Return and other types of valves in bronze, iron, steel, pure metals and special alloys to meet Industry's demands for **DEPENDABLE FLOW CONTROL EQUIPMENT**.

# POWELL VALVES



Nine hundred of these 43-pound aluminum housings were salvaged in a year's time by building up their worn, iron inserts by metallizing. The large amount of precision machining that would be required for finishing new castings was avoided. The old bearings were re-used, and the reworked assemblies gave more service than originally.

Thus the war effort is being aided by conservation of materials and labor, and the continuation in service of hard-to-get equipment.

The iron insert in this housing is subjected to severe thrust from the gears, so it must be anchored solidly. This is taken care of by cast-

ing it integrally with the aluminum housing. Building up a worn insert by metallizing does not disturb this security, nor does the work reduce the high strength of the aluminum. The added metal is bored out and the original bearing put back in place, ready for additional months of service.

Perhaps there's a cue here on means of maintaining *your* hard-working aluminum alloy equipment. Alcoa engineers will gladly advise you on methods of safeguarding it by cathodic protection, protective coatings, inhibitors, or metallizing. ALUMINUM COMPANY OF AMERICA, 2154 Gulf Building, Pittsburgh, Pennsylvania.

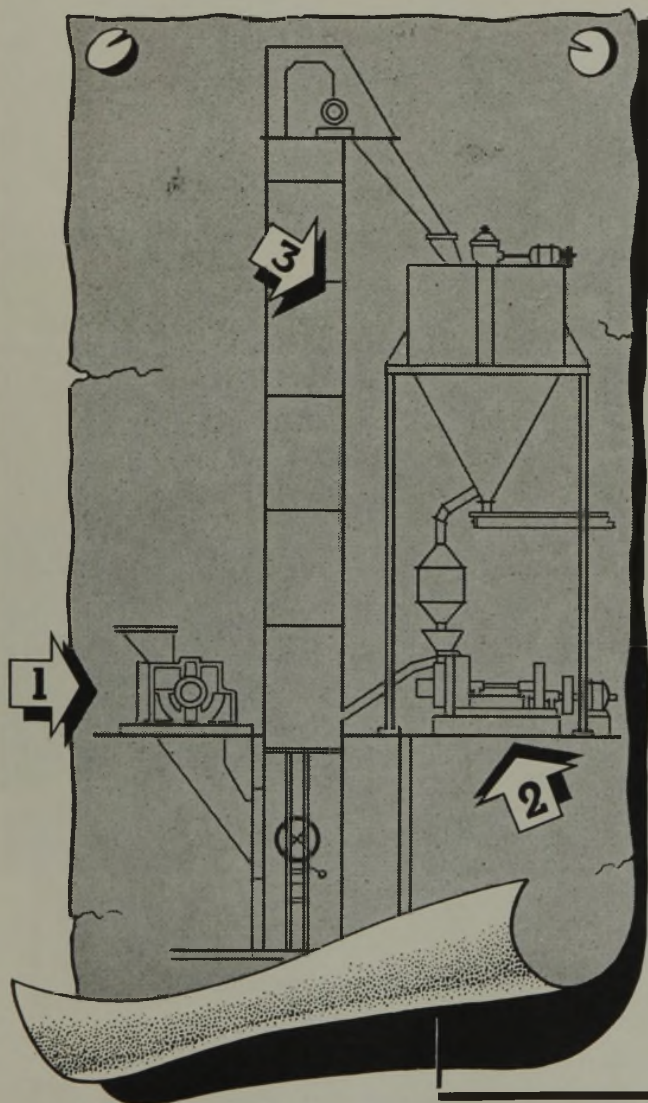
# ALCOA



# ALUMINUM

# STREAMLINE YOUR PROCESS WITH STURTEVANT CUSTOM-MADE UNITS!

Groups of machines coordinated for maximum production and *Continuity of Operation*



Streamlined Units are composed of Sturtevant machines, each serving a particular and predetermined service, each of a quality and capacity equaling the mechanism preceding or following, with every Elevator, Conveyor, Spout, Chute, Hopper or Bin *made for that particular Unit* and assembled in the shop to avoid errors and save erection costs in the field . . . Thus you purchase a *balanced Unit*, standardized by experience — we alone responsible for its production. Erected quickly at low cost, it is ready to operate in short order.

If you have had experience with purchasing equipment from different sources and assembling the various items at your plant, you can appreciate the time and money savings effected by these Sturtevant CUSTOM-MADE UNITS.

The flow sheet illustrates a *Closed Circuit Pulverizing and Air Separating Unit*. The fines are removed, by Air Selection, from the output of the preliminary grinder before it is fed to the pulverizer. After the material is processed in the Pulverizer, the Air Selector again separates and removes the fines, while the over-size is returned to the pulverizer for refinishing.

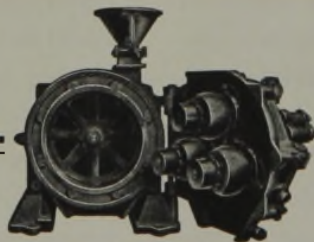
1.



### The GRINDER

A Sturtevant Swing Sledge Mill for coarse and medium reduction — (1" to 20 mesh). Open door accessibility. Grinds soft, moderately hard, tough or fibrous substances. Built in several types and sizes.

2.



### The PULVERIZER

A Sturtevant Ring Roll Mill built for grinding soft and moderately hard materials to a fineness of 10 to 200 mesh.

3.

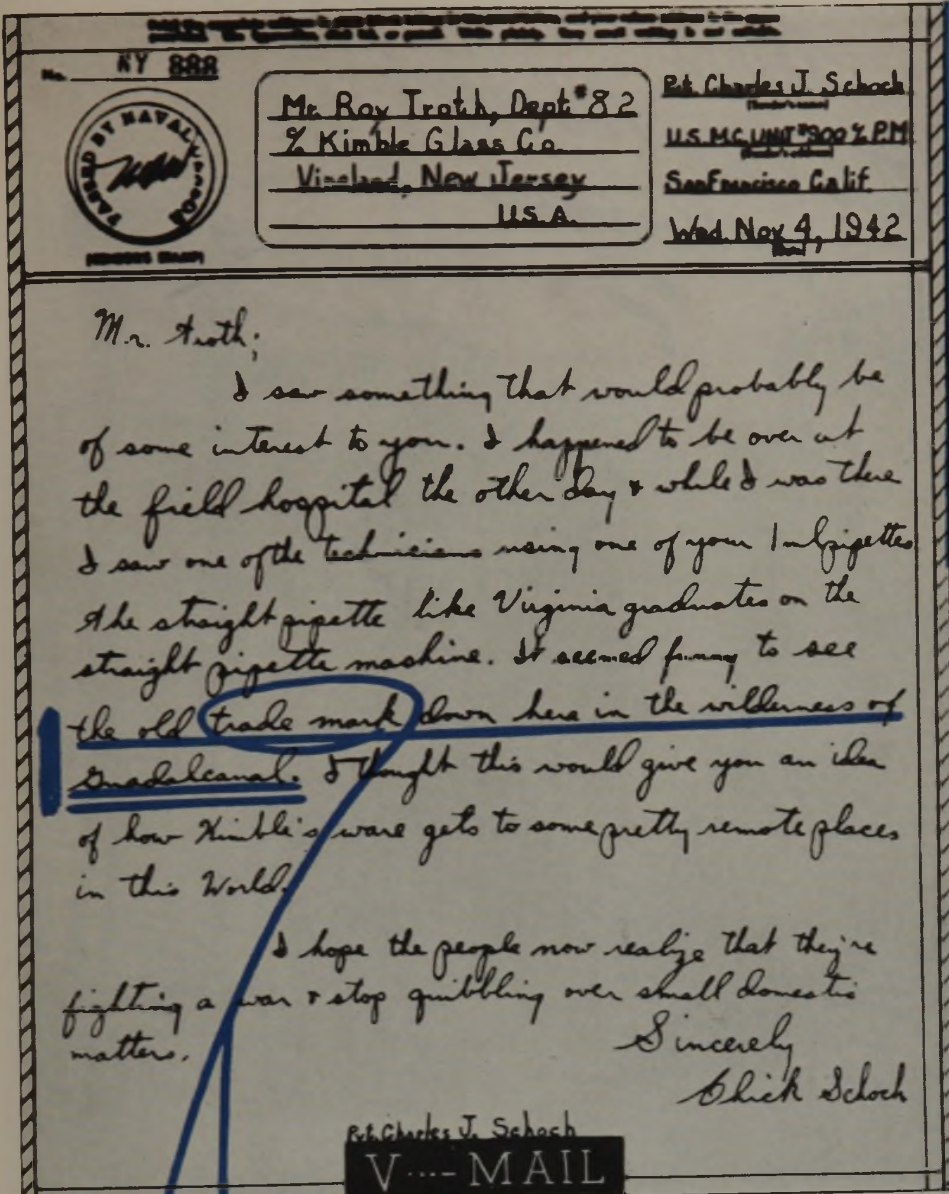


### The SELECTOR

A Sturtevant Air Separator for finest separation of dry materials. Range of work 40-400 mesh. Capacities 1/4 ton to 50 tons per hour. Large feed opening, steep cones, rigid construction, Ball and Roller bearings. Sizes: 3' to 18' diameter.

Consult our competent engineering staff for full details

**STURTEVANT MILL CO. 2 HARRISON SQUARE BOSTON, MASS.**



**Thanks,  
Chick,  
for  
Letting  
Us Know**

**Virginia is Proud of Her Part,  
and We All Share Her Pride**

Kimble laboratory glassware and containers for plasma and vital drugs are serving our armed forces, even in the most remote places. Like this pipette, they carry the trade mark which symbolizes the Kimble slogan . . .

**"KEEP 'EM LIVING"**

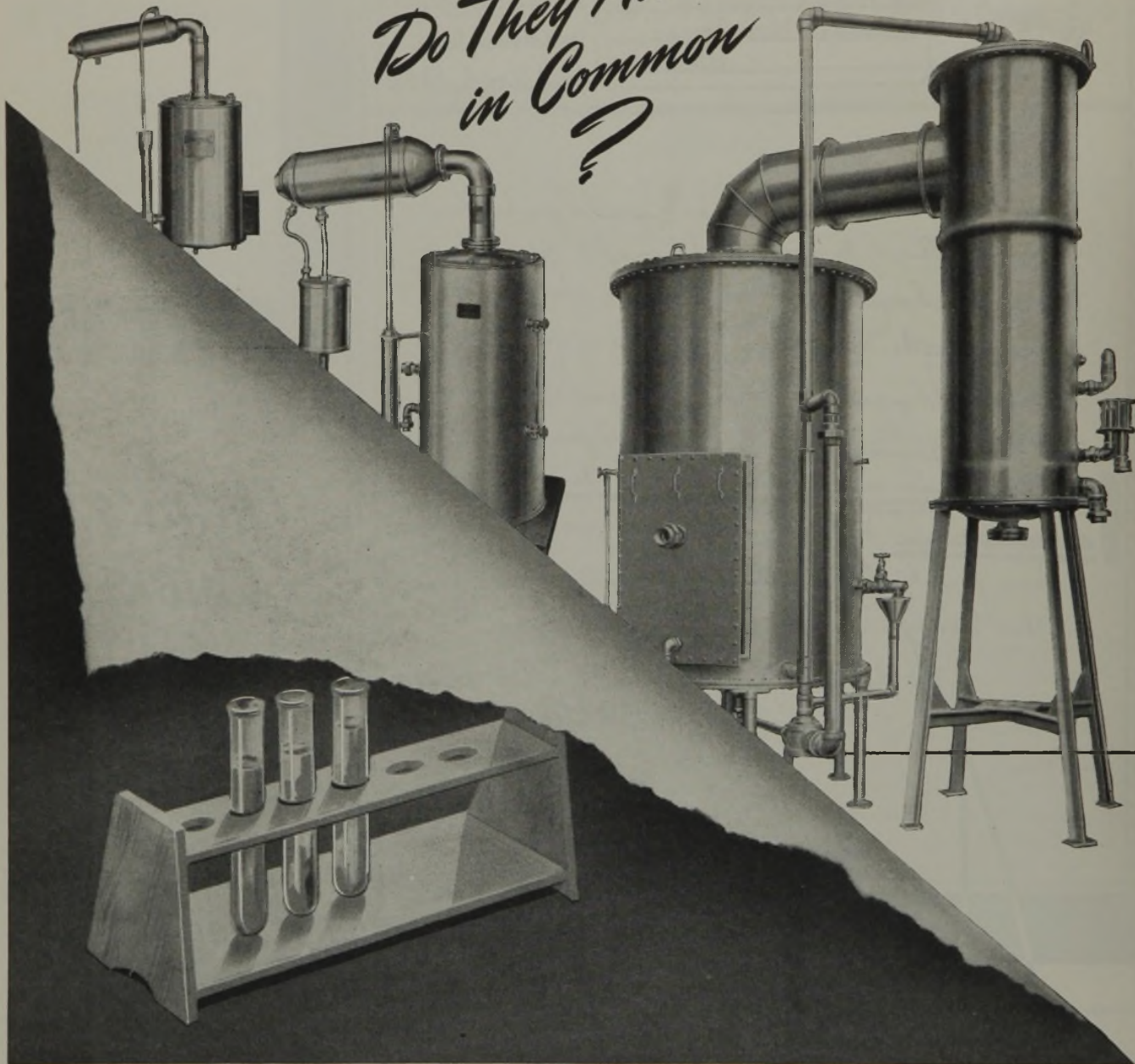


*The Visible Guarantee of Invisible Quality*

**KIMBLE GLASS COMPANY . . . VINELAND, N. J.**

NEW YORK • CHICAGO • PHILADELPHIA • DETROIT • BOSTON • INDIANAPOLIS • SAN FRANCISCO

*What  
Do They All Have  
in Common  
?*



Here are three test tubes containing distillates of three different Barnstead Water Stills—a three, a thirty, and a three hundred gallon per hour size still.

Now analyze these distillates and you'll find that they all have the same standards of purity.

This is important—not only to those who want a consistent pure water supply in both their lab and plant, but also to those whose demand for pure distilled water

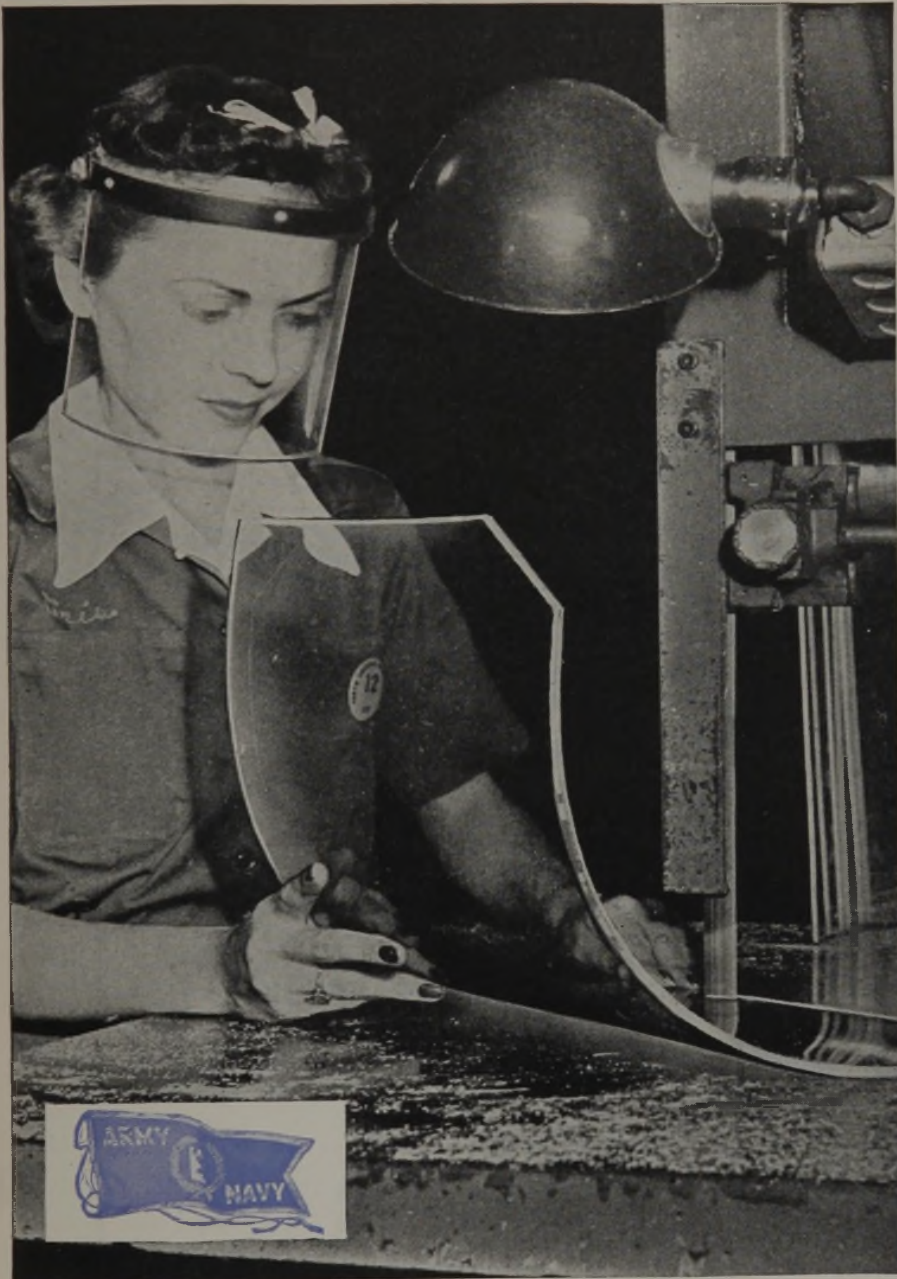
has been stepped up. If you now have a Barnstead 10 gallon still, for example, and you really need 20 gallons of distilled water per hour, you don't have to replace your old still with a new 20 gallon still. You simply add a new Barnstead 10-gallon still. And you don't have to worry about performance comparisons—the new versus the old. All Barnstead Stills are designed to produce the same consistent grade of distillate year after year.

**Barnstead**  
STILL & STERILIZER CO. Inc.

5 LANESVILLE TERRACE, FOREST HILLS, BOSTON, MASSACHUSETTS



# PLEXIGLAS . . . protector of America's production soldiers



*This worker in North American Aviation's Texas plant wears a transparent, light-weight PLEXIGLAS face shield. Through the use of such devices, eye injuries in the plant were reduced by one-half in five months.*

**L**IGHT-WEIGHT, permanently transparent, shatterproof PLEXIGLAS safety shields are comfortable to wear and handy to use. Women as well as men wear largest size PLEXIGLAS protectors without tiring.

At all times these crystal-clear acrylic plastic shields provide users with an unhampered view of their hands and work.

Due to many direct military applications, the amount of PLEXIGLAS which can be supplied for safety shields today is limited. After the war, however, these ideal safety devices will be available to American industry.

. . . .

*Rohm & Haas Company, Washington Square, Philadelphia, Pa.; 8990 Atlantic Blvd., South Gate, Los Angeles, Calif.; 619 Fisher Bldg., Detroit, Mich.; 930 No. Halsted St., Chicago, Ill. Canadian Distributor — Hobbs-Glass Ltd., Montreal, Canada.*

THE CRYSTAL-CLEAR  
ACRYLIC PLASTICS

**PLEXIGLAS**

SHEETS AND RODS



**CRYSTALITE**

MOLDING POWDER

PLEXIGLAS and CRYSTALITE are the trade-marks, Reg. U. S. Pat. Off., for the acrylic resin thermoplastics manufactured by the Rohm & Haas Company.

# ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA, PA.

Manufacturers of Chemicals including Plastics . . . Synthetic Insecticides . . . Fungicides . . . Enzymes . . . Chemicals for the Leather, Textile and other Industries



# WANTED!

## IDEAS • INVENTIONS • PATENTS

On Machinery, Equipment and any Article  
that can be sold to the CHEMICAL and  
PROCESS INDUSTRIES, or to Manu-  
facturers of FOODS, DRUGS and  
PHARMACEUTICALS.

*A large equipment manufacturer  
now serving these industries wishes to contact  
men with new ideas, or improvements  
upon present methods.*

*Address by Mail Only*

**K. CLARK WITHEROW**  
**ROOM 1908 — R. K. O. BUILDING**  
**NEW YORK, N. Y.**

# ALL THESE FEATURES . . .

## SIZED IN COMPRESSION

Originally made slightly oversize, the Midwest Elbow is then reheated and reduced to accurate size and shape in dies which compress the metal at a forging heat—it is not extruded or stretched.

## DIMENSIONAL ACCURACY

Compression-sizing assures exceptional dimensional accuracy and uniformity. Special tools machine the ends to exact included angle.

## STRESS RELIEVED

Reheating to a forging temperature normalizes both the plate and the weld, relieving the stresses set up during the forming and welding operations.

## UNIFORM WALL THICKNESS

and true circular cross section are inherent advantages resulting from the unique manufacturing process.

## TANGENTS

All Midwest Elbows have tangents that facilitate the lining up and welding.

## "LONG TANGENTS" AT SAME PRICE

Optional is Midwest "Long Tangent" elbow which adds 25% of the nominal pipe size to the center-to-end dimension of the American Standard Elbow at no increase in price.

# ONLY IN MIDWEST BUTT-WELDING ELBOWS

**MIDWEST PIPING & SUPPLY CO., Inc.**

Main Office: 1450 South Second St., St. Louis, Mo.

Plants: St. Louis, Passaic (N.J.) and Los Angeles

Sales Offices: Chicago—645 Marquette Bldg. • Houston—229 Shell Bldg. • Los Angeles—520 Anderson St. • New York—(Eastern Division) 30 Church St. • San Francisco—535 Call Bldg. • Tulsa—533 Mayo Bldg.



**MIDWEST WELDING FITTINGS SAVE TIME, IMPROVE THE DESIGN, AND REDUCE THE COST OF PIPING SYSTEMS**



## AMERICA'S WAR PRODUCTION DEPENDS ON TANKS LIKE THESE

Take a good look at these huge spherical tanks. Chances are your hose, your belts, your packings may come from them or from others just like them.

These are used for storing butadiene in the first of the synthetic plants operated by U. S. Rubber Company . . . a second will soon be in production.

Having worked in the field of synthetic rubber since 1921 we know what uses each of the five basic types of

synthetic rubber is best suited for . . . Neoprene, Buna-S, Buna-N, Butyl and Thiokol . . . U. S. Rubber uses all five types . . . knows which one to select for the performance required . . . and how to compound the specific synthetic rubber for the specific task. This experience is important to you.

Our booklet on synthetic rubber will give you much valuable information. Send for your copy.

*Mechanical Goods Division*

# UNITED STATES RUBBER COMPANY

ROCKEFELLER CENTER • NEW YORK



# ALOYCO

## PERMANENTLY CLEAN

# IS THE NAME FOR FLUID CONTROL!

**ALOYCO** Stainless Steel Valves and Fittings are better than an insurance policy against shutdowns in fluid lines. They help to keep production at peak in the vital chemical, process and food industries by preventing corrosion, stain and contamination.

The recognized superiority of Aloyco Stainless Steel Valves and Fittings is due to concentration on this one type of product. Stainless Steel Valves and Fittings are not part of the Aloyco line — they are the entire line. They do not receive part of the attention of our engineering and production department — they receive all of it. We make a wide range of styles and sizes in all standard stainless steel analyses.

Although our facilities are allocated 100% to essential war production these days, we are always glad to discuss post war applications with those who are mapping the industrial pattern of the future.

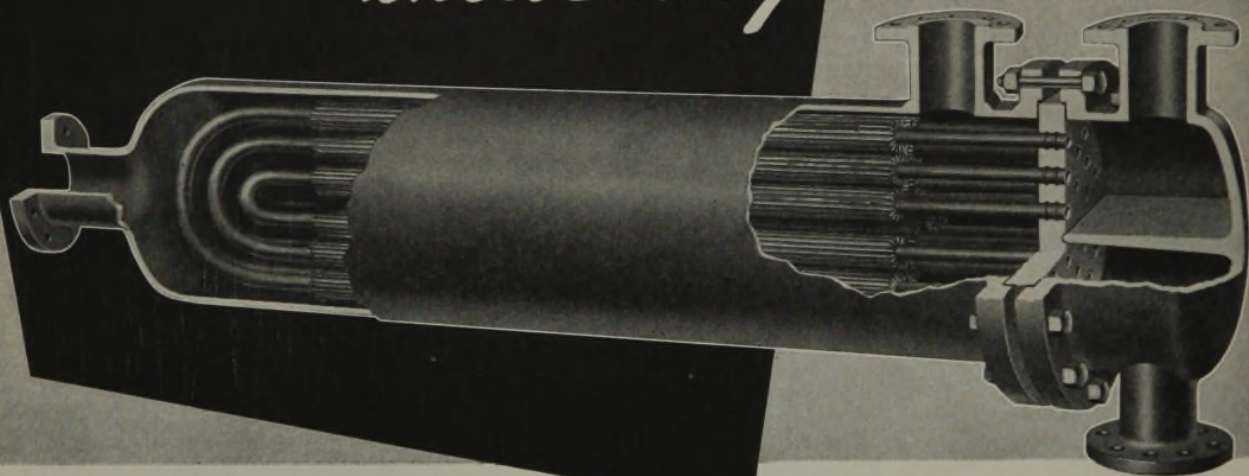


*Stainless Steel*  
**VALVES and FITTINGS**

GATE 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.**  
1300 WEST ELIZABETH AVENUE — LINDEN, NEW JERSEY

*This cut-away view  
shows why*



## BROWN FINTUBE HEAT EXCHANGERS

*Give extra capacity for any exchange between liquids  
and gases...or other materials having unequal  
heat transfer co-efficients*

● Because Brown integrally bonded Fintubes, having the desired number and depth of fins, are used in effecting the heat transfer,—the primary and secondary tube surfaces of Brown Fintube Heat Exchangers can be proportioned to the transfer co-efficients of the materials being heated or cooled, thereby compensating for any deficiency in the heat transfer rate of one or another of the commodities.

This avoids the necessity of using hundreds, sometimes thousands of feet of bare tubing to satisfy the requirement of the commodity having lower heat transfer co-efficient. It permits a fewer number, or shorter, Brown Fintubes to be used for a given heat transfer service than if plain bare tubes were

used . . . and results in smaller shells, less back pressure, less pressure drop, and many other important savings in manufacturing, shipping, installation and maintenance costs.

Six standard and many special types of Brown Fintube Heat Exchangers meet every requirement for effecting transfers between liquids and gases, or other commodities having unequal transfer co-efficients,—and provide the high thermal efficiency and trouble-free operation that only Brown resistance-welded integrally bonded Fintubes can give you.

More complete details, engineering assistance, estimates, and descriptive literature furnished gladly on request. Let us quote on your heat exchanger requirements.



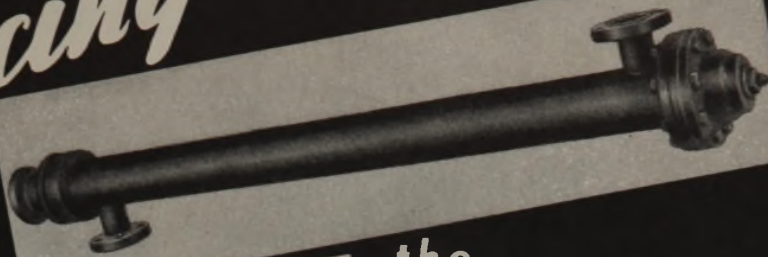
Brown Integrally Bonded Fintubes are used in all Brown Fintube Heat Exchangers—in exchangers made by most other manufacturers—and are available in a wide variety of sizes, and in mild carbon or special steels, for practically any heating or cooling requirement.

# THE BROWN FINTUBE CO.

120 FILBERT STREET • ELYRIA, OHIO

MANUFACTURERS OF INTEGRALLY BONDED FINTUBES AND FINTUBE HEAT EXCHANGERS

*Introducing*



the

**SHELLFIN**

..... the **STANDARDIZED**  
**shell & finned tube HEAT EXCHANGER**

\* Patent Applied For

**What is the SHELLFIN?**

It is a *standard design* shell and finned tube heat exchanger conceived and developed by Downingtown engineers to be built on a cost-saving, time-saving production basis. With only minor changes in its construction, such as baffle spacing and length combinations of units, it meets the conditions found in a wide variety of uses for heat exchangers.

**How does the SHELLFIN work?**

One fluid passes through the tubes, cooling or heating the second fluid which passes outside and across the tubes in the shell, its path being directed by the "segment cut" baffles in the tube bundle, exactly like most other units. EXCEPT that the finned tubing compensates for difference in heat transfer rate between shell fluid and tube fluid.

**Where can the SHELLFIN be used?**

Use it for almost any form of heat exchange between two fluids in medium temperature ranges, where the heat transfer rate of one fluid is materially greater than that of the other. Use it for *cooling* oils, benzene, toluene and similar organic compounds, alcohols, chemical compounds generally . . . for cooling jacket water for diesel or gas engines, drain and condensate cooling . . . for air cooling in compression systems . . . for *heating* any of the above or similar fluids . . . for *condensing* organic vapors, hydrocarbon oil vapors, refrigerants . . . for *evaporating* organic liquids, light hydrocarbons and refrigerants.



**COMPLETE ENGINEERING SERVICE** is available by Downingtown heat transfer engineers, who developed and tested this unit. Recommendations can be made for application of the Shellfin to most duties, whether liquid to liquid for cooling or heating, for vapor cooling or heating, for condensing or other duty. Recommendations are conservative, allowing ample fouling factors.

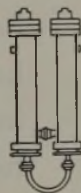


**FINEST "CUSTOM-BUILT" FEATURES** are incorporated in the SHELLFIN.

The bundle is entirely removable for easy inspection, cleaning, or repair. Tubes are straight and can be cleaned easily just by removing the head and running a tube cleaner through. "Outside packed" closure gives maximum tightness combined with utmost accessibility from outside. External joints throughout eliminate possibility of unsuspected leakage from one fluid to another as may happen with buried joints. Compact design, low weight, makes installation and handling easier.



**VERY HIGH EFFICIENCY.** The special design of the SHELLFIN tube bundle, across which the fluid flows, gives a high heat transfer rate with minimum pressure loss (especially observable with liquids of medium viscosity.) This has been thoroughly tested and proved.



**FLEXIBLE IN APPLICATION.** For large jobs the "SHELLFIN" is applied in multiple units. Initial cost is about the same as for one large exchanger and you get a number of advantages: First, if the operation is critical and a standby unit is required, only one or two additional SHELLFIN units can be used where doubled capacity would be required on a larger unit. Second, SHELLFIN units can be added where fractional increase in capacity is necessary over that of an original installation. Third, if a process becomes obsolete, SHELLFIN units may be recombined and changed.

A NEW FOLDER DESCRIBES ALL SHELLFIN FEATURES in detail . . . answers all your questions about this versatile unit. Get your copy now—if only for your reference file; just fill in and mail the coupon.

**DOWNINGTOWN IRON WORKS** • Downingtown, Pennsylvania.

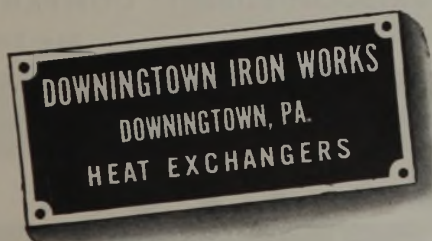
• Please send a copy of your new SHELLFIN data folder to

NAME ..... TITLE .....

COMPANY .....

ADDRESS .....

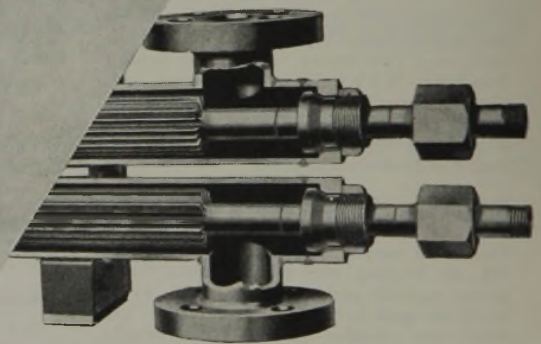
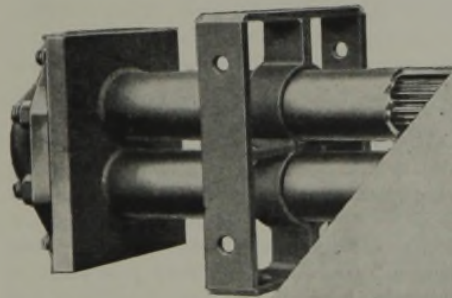
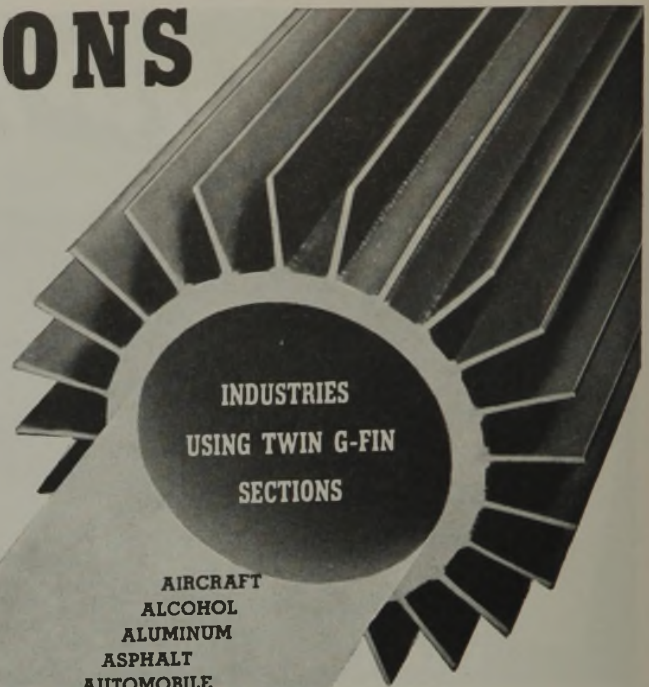
IBC-443



Fabricators of Quality Products—Since 1913

# 30,000 SECTIONS

## IN SERVICE THROUGHOUT INDUSTRY



- AIRCRAFT
- ALCOHOL
- ALUMINUM
- ASPHALT
- AUTOMOBILE
- BAKING
- BREWING
- CASTOR OIL
- CEMENT
- CHEMICAL
- CHOCOLATE
- COKE
- COPPER
- CORK
- DISTILLING
- DRUG
- DYEING
- FLOUR
- FOOD
- FOUNDRY
- GAS PRODUCING
- GELATIN
- GLASS
- LEAD
- LUMBER
- MACHINERY
- MARINE
- METALLURGICAL
- MUNITIONS
- ORDNANCE
- OXYGEN
- PAINT
- PETROLEUM
- PHOTOGRAPHIC FILM
- POWER GENERATING
- PULP AND PAPER
- RAILROAD
- RAYON
- RUBBER
- SOAP
- STEEL
- TOBACCO
- TOLUENE
- WORSTED

The roster of almost 800 concerns which have purchased Twin G-Fin Sections shows that these units are being used in practically every industry and on a wider range of heat transfer services than any other heat exchanger design on the market.



Catalog on Request

THE GRISCOM-RUSSELL COMPANY  
285 Madison Avenue . . . . . New York

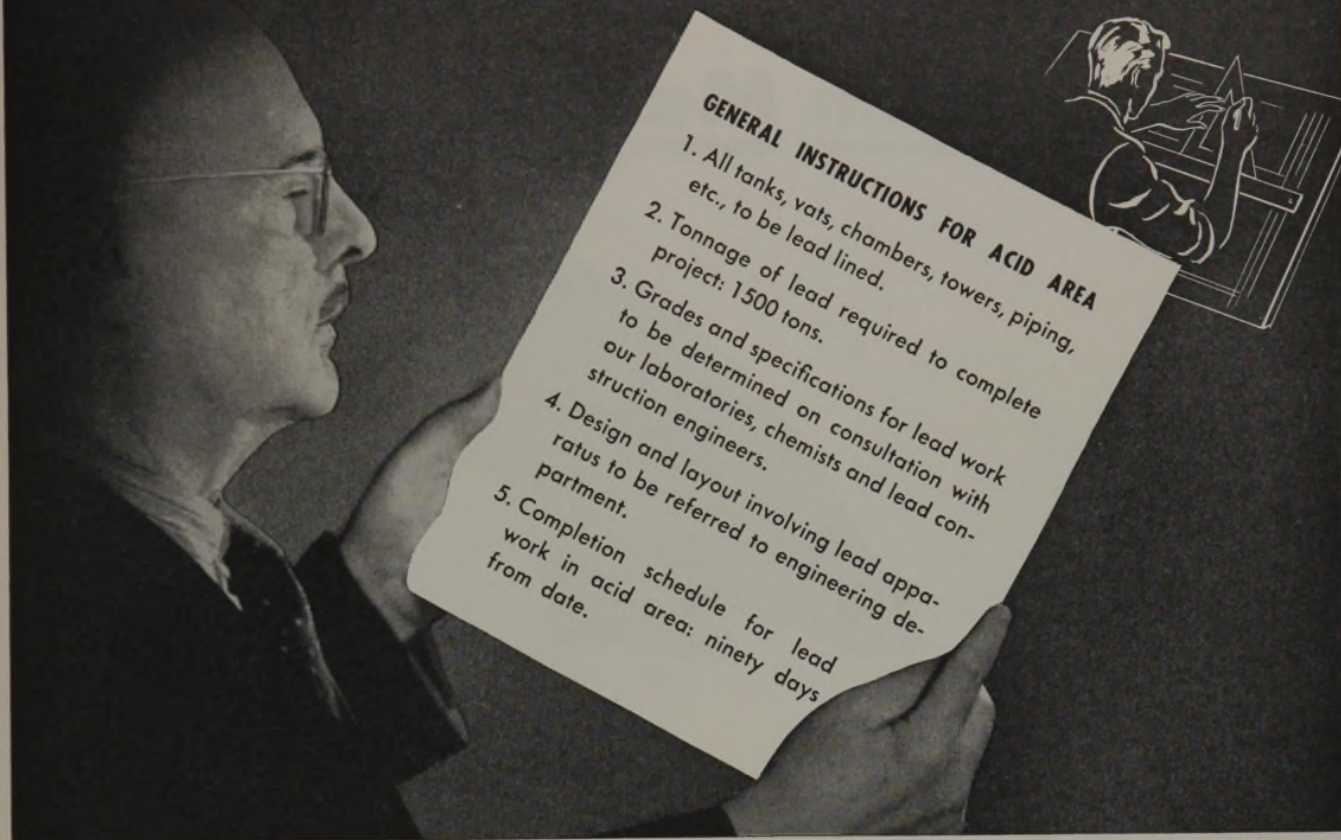
# GRISCOM - RUSSELL

## TWIN G-FIN SECTION

*The Universal Heat Exchanger*



## A TOUGH LEAD CONSTRUCTION JOB SIMPLIFIED!



### GENERAL INSTRUCTIONS FOR ACID AREA

1. All tanks, vats, chambers, towers, piping, etc., to be lead lined.
2. Tonnage of lead required to complete project: 1500 tons.
3. Grades and specifications for lead work to be determined on consultation with our laboratories, chemists and lead construction engineers.
4. Design and layout involving lead apparatus to be referred to engineering department.
5. Completion schedule for lead work in acid area: ninety days from date.

## ASARCO AND ANDREWS COMBINED, MINE, SMELT, FABRICATE AND INSTALL LEAD THROUGHOUT AMERICA

**T**HE Andrews Lead Construction Corporation is a wholly owned subsidiary of the American Smelting and Refining Company. Asarco has created this lead burning and construction organization to expand and simplify the use of lead by the chemical and allied industries.

Asarco's interest in the successful performance of lead is, we believe, greater than that of any individual lead company in America. We possess extensive mining properties, smelting and refining units, fabrication mills and presses, and must insure favorable attention for lead through accomplishment of the excellent performance for which this metal has long been noted.

This ultimate achievement is assured by the engineers, technicians and lead burning crews of our Andrews Lead Construction Corporation. They can be entrusted with every problem attendant upon the use of lead, including those of design, selection of lead and performance of lead apparatus.

## THE ANDREWS LEAD CONSTRUCTION CORP.

LEAD BURNING CONTRACTORS



120 BROADWAY, NEW YORK, N. Y.

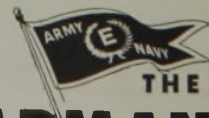
# Man from Mars



... or a

## Hollywood Cab-starter?

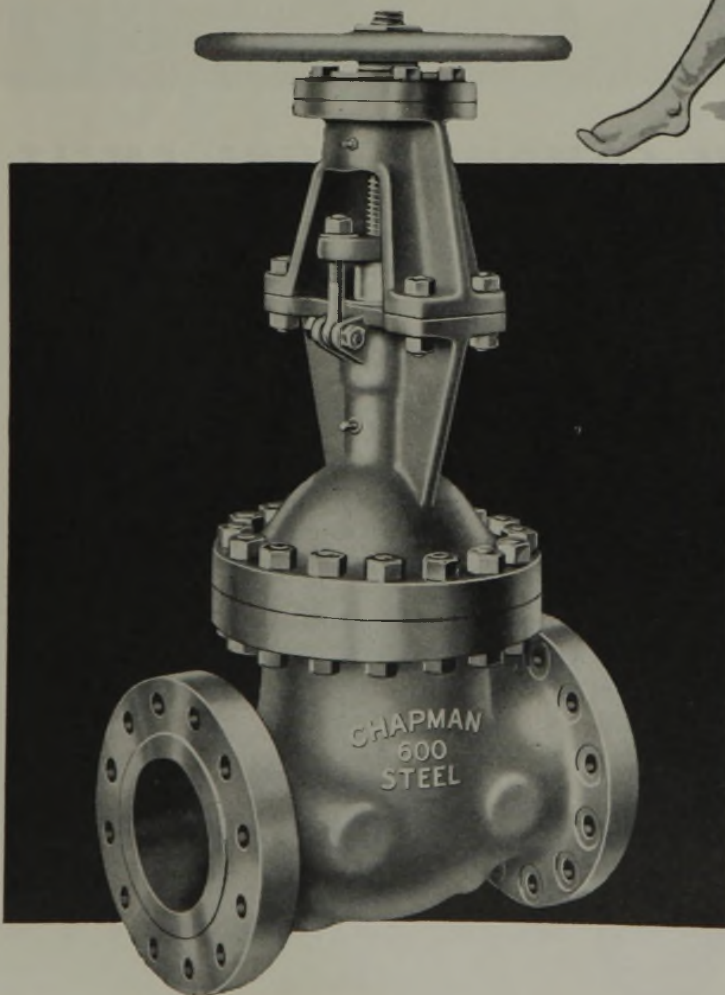
Strangers are often more fictional than truth. So don't let the first disturbing contact with a new process or an unfamiliar valve-problem hold you up for a special order for valves and equipment which you may well be able to get... without delay or premium prices... from Chapman. For Chapman is an "old hand" at working out equipment for new processes (such as synthetic rubbers) and for special problems. And much of this equipment is added, as it is developed and service-proved, to Chapman's Standard Line... which includes all types of iron, bronze and steel valves... plus valves of chrome and molybdenum alloys. So always "check with Chapman" first of all, to see what you can save yourself in time, trouble and expense.



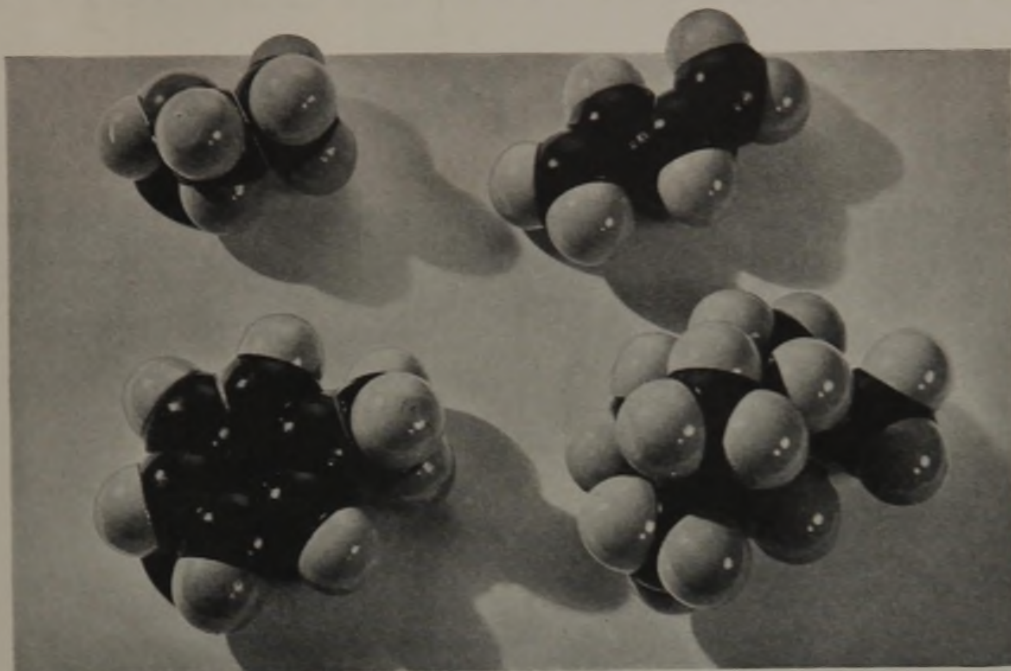
# THE CHAPMAN VALVE

Manufacturing Company

INDIAN ORCHARD, MASSACHUSETTS



# THEY CRACK BETTER WHEN THEY'RE DRY



Taking the moisture out of liquids and gases before they enter catalytic reaction chambers is a sound way to increase yields and improve control of the end products. In the making of materials for high-octane gasoline or for synthetic rubber, the process frequently goes faster and better when a dryer filled with Alorco Activated Alumina is on-stream ahead of the catalytic chamber.

Alorco Activated Alumina removes moisture from liquids and gases down to dew-points below  $-150^{\circ}$  F. Many drying installations have been on the job for years.

In addition to its work as a moisture-remover, several grades of Alorco Activated Alumina are used in reactors as catalysts and catalyst carriers. The petroleum, explosives, and synthetic rubber industries use one or more of the Alorco Activated Aluminas as catalysts or carriers in several of

their processes devoted to the production of war materials.

Other Aluminas suitable for catalytic purposes are:

**TABULAR ALUMINA**, a porous form of granular corundum, having high strength and permanence at elevated temperatures.

**HYDRATED ALUMINA C-730**, an extremely fine, powder alumina, which is active after an initial heating to  $500^{\circ}$  F.

**MONOHYDRATED ALUMINA C-50**, a substantially inactive powder alumina, with particle size of about one micron.

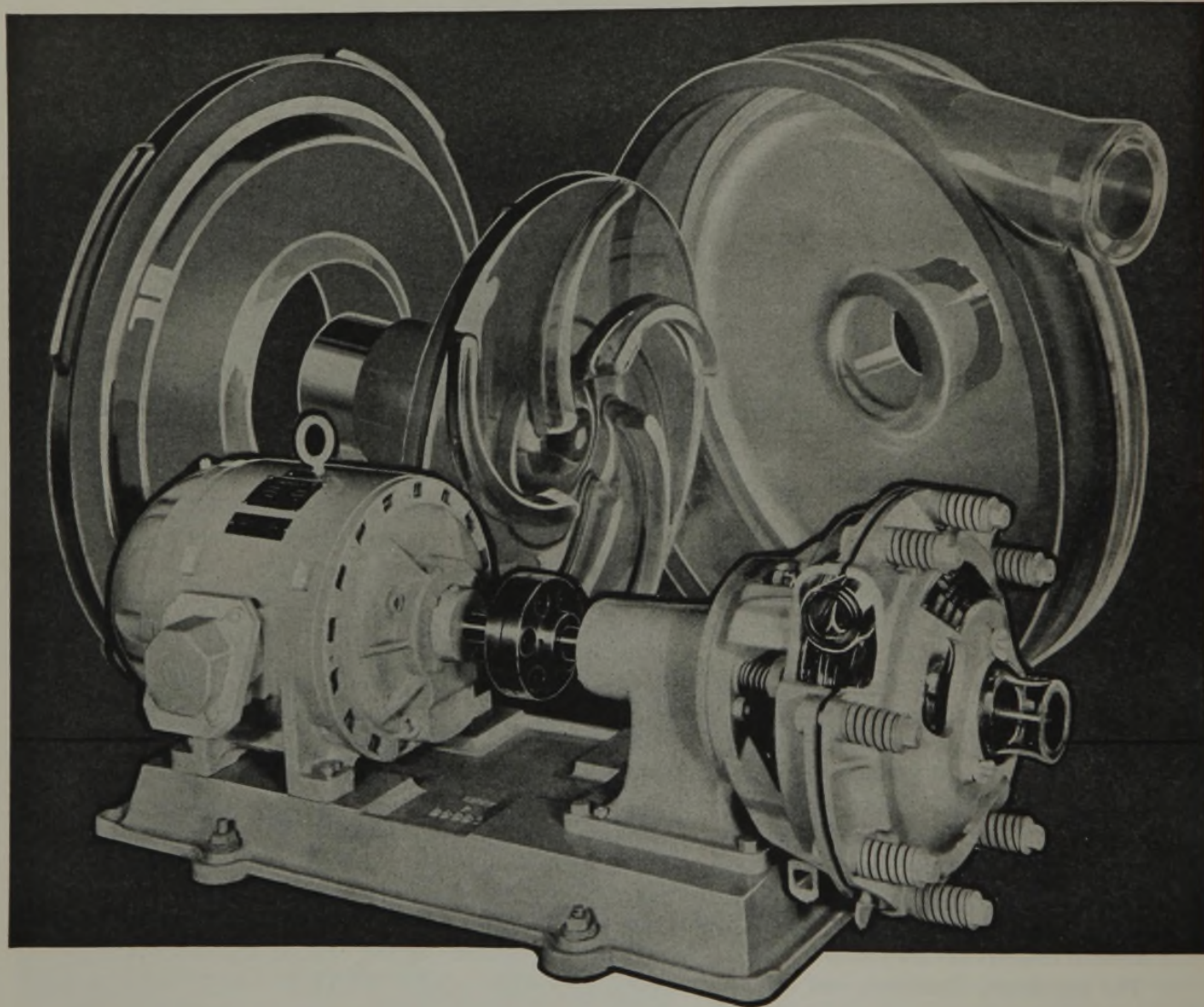
If you are making war materials requiring the use of catalysts and catalyst supports, write for samples. **ALUMINUM COMPANY OF AMERICA** (Sales agent for **ALUMINUM ORE COMPANY**) 1911 Gulf Building, Pittsburgh, Pa.



## ALUMINUM ORE COMPANY

ALUMINUM AND FLUORINE COMPOUNDS

# *Handle hot corrosive acids, or brine chilled liquids, with the Nash Pump of Glass*



Casing and moving element of this remarkable centrifugal pump are of "PYREX" brand heat and shock resisting glass. Hot acids, or brine cooled liquids may be pumped with equal facility. • The balanced glass impeller, rotating at 1760 R. P. M., delivers 6000 gallons of acid or other liquid per hour against a 65 foot head. • Perfect transpar-

ency permits constant observation of the interior of this pump and the material being handled. If cleaning is necessary, pump can be taken apart in a few moments. Reassembly is as quick, and adjustment is almost automatic. • There are many more exciting facts about this successful non-metallic pump. Write for your copy of Bulletin D-313 now.

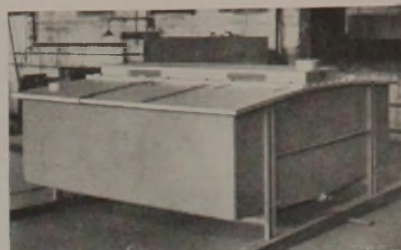
**NASH ENGINEERING COMPANY**  
207 WILSON POINT ROAD, NORWALK, CONN.



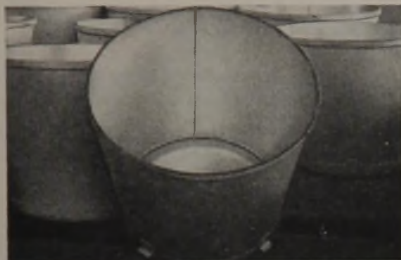
Cereal Cookers fabricated from IngAclad



Golden corn syrup is protected in color and flavor by having tanks lined with IngAclad SHEETS.



Milk Storage Tank, 1,600 gallon capacity, installed for the Libby, McNeill & Libby plant, at Patterson, Calif.



Direct-fired Paint and Varnish Kettles fabricated from IngAclad assure good heat conductivity and freedom from discoloration.

*Unretouched photo showing machine turning from IngAclad Stainless-Clad Plate.*



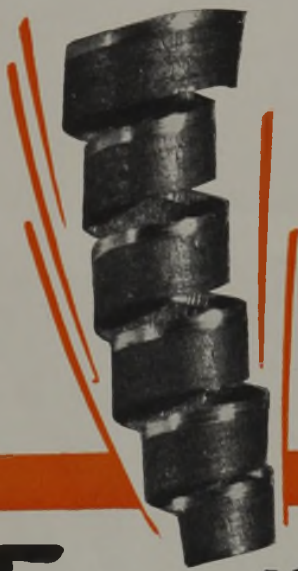
Stainless Vacuum Steaming Tank nearly 24 ft. long by 8 ft. in diameter. IngAclad made possible large savings in material cost.



Table Tops of 11 gauge polished IngAclad, used by Testing Laboratory, U. S. Department of Agriculture.



Thirteen tons of 3/16" IngAclad Plate used for top section and covers of these Soap Kettles installed in a Canadian plant.



# To SERVE and to SAVE!

To those holding high-rated war orders, IngAclad is available in Sheets 18 to 8 gauge, and in Plate form. Regularly supplied clad with 18-8 Stainless, but also available in other analyses.

*We also produce Ingersoll Solid Stainless and Heat-Resisting Alloys. Send us your inquiries.*

Designed as a peacetime product for *servicing* the Process Industries and for the *saving* of precious alloys, IngAclad has become even more vital in time of War. New applications have been found by our Engineers cooperating with the Armed Services. When Peace is won, the knowledge of these achievements will speed the conversion of many plants to corrosion-resisting equipment through the lower material cost IngAclad makes possible.

*Plan now for plant and product improvement tomorrow. Investigate IngAclad today. Write for special IngAclad Folder.*

## INGERSOLL STEEL & DISC DIVISION BORG-WARNER CORPORATION

310 South Michigan Avenue, Chicago, Illinois  
Plants: Chicago, Illinois; New Castle, Indiana; Kalamazoo, Michigan

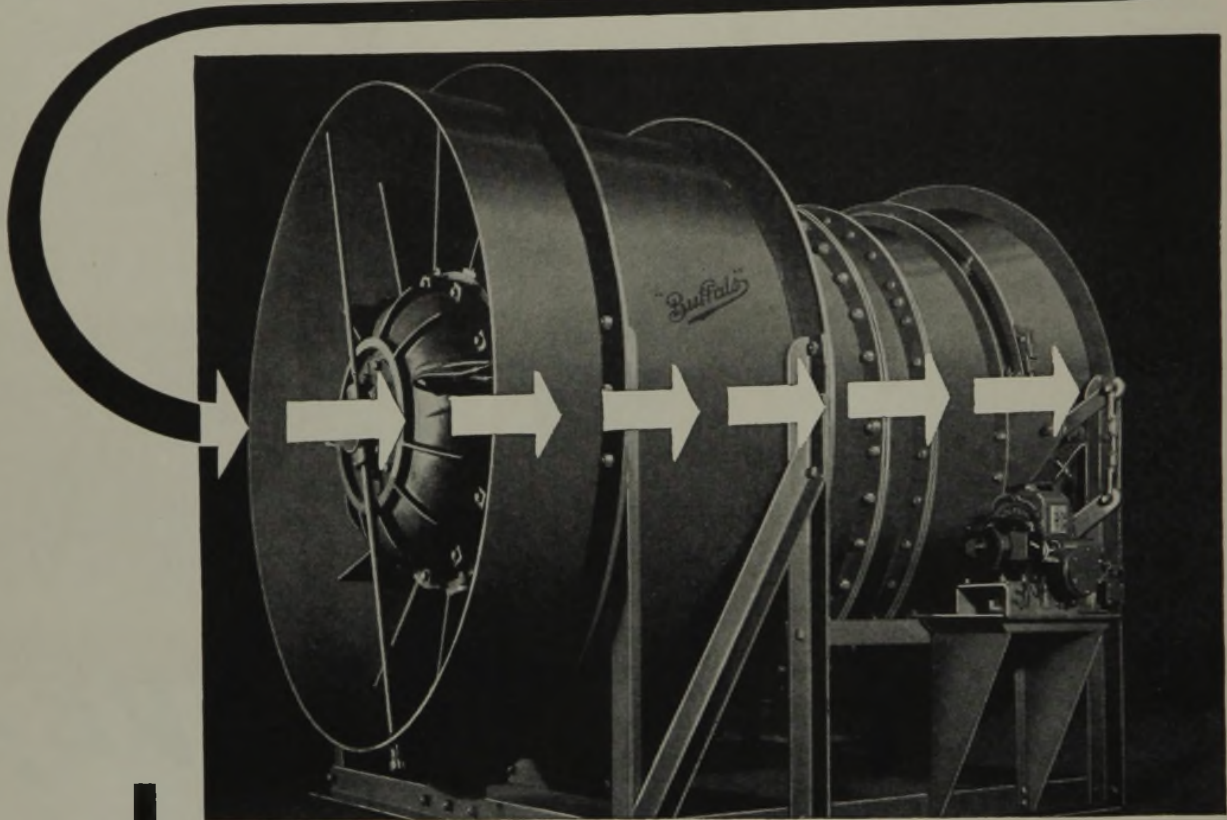
*"A Borg-Warner Product"*

# INGACLAD

STAINLESS-CLAD STEEL

# AIR TAKES THE

# Straightaway



In power-saving... *“Buf-flow”* **AXIAL FLOW FANS**

The “straightaway” flow of air through a “Buf-flow” Axial Flow Fan — plus the non-rotating movement of the air current as it leaves the outlet — explains both the efficiency and the power-saving features of this Buffalo-developed design. The wasted motion of air turbulence is reduced to a minimum by means of special directional guide vanes,

thus preventing losses common in ordinary propeller fan. The result is an exceptionally high capacity operating against pressure losses, quieter operation, marked power savings. These advantages — plus the sturdy, durable construction and the non-overloading characteristic — makes Buf-flow Axial Flow Fans unexcelled for air handling problems.

## BUFFALO FORGE COMPANY

153 Mortimer St.

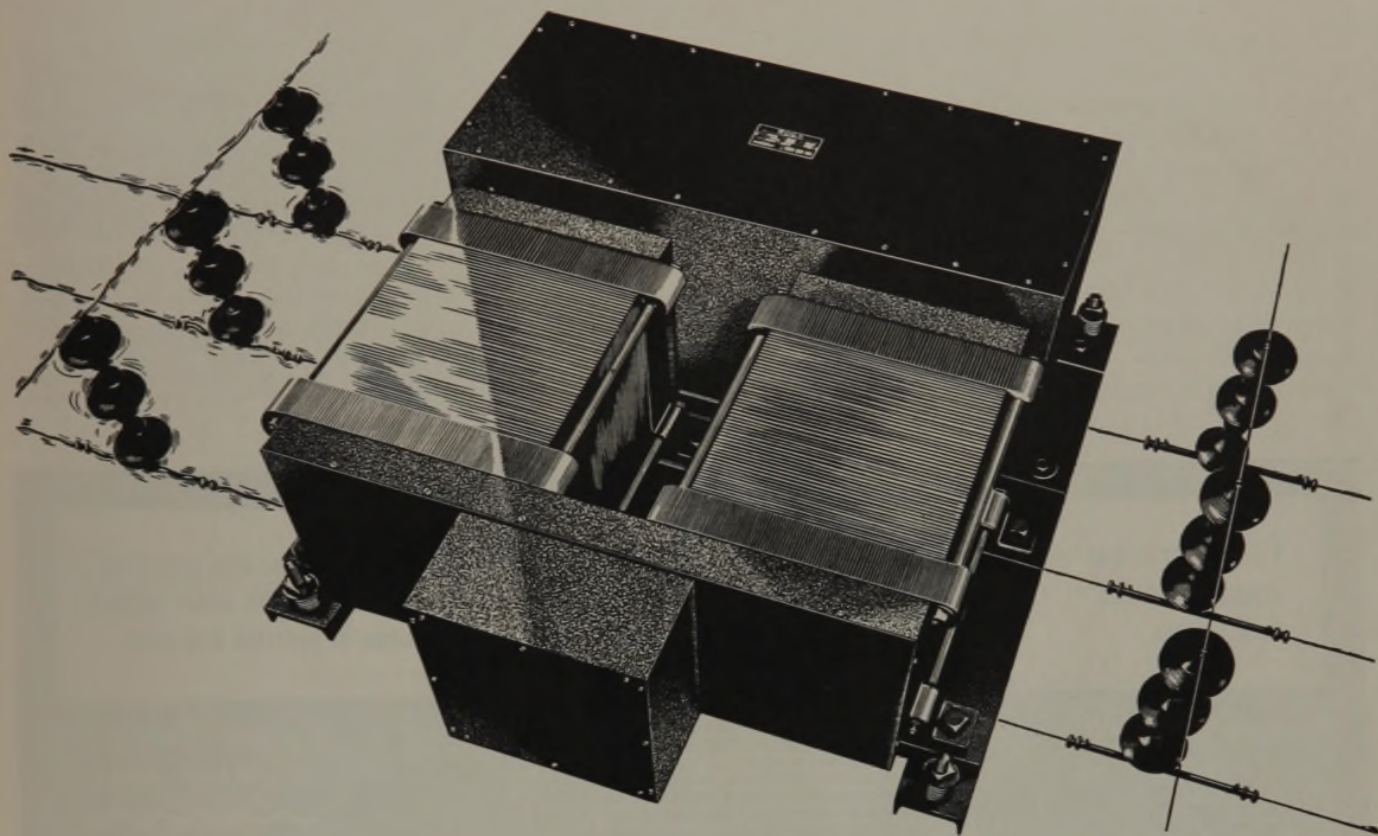
Buffalo, N. Y.

Branch Engineering Offices in Principal Cities  
Canadian Blower and Forge Co., Ltd., Kitchener, Ont.

*“Buf-flow”*

# AXIAL FLOW FANS

# Industry steadies its "nerves"



**F**ACED with production schedules that have no precedent in history, American industry finds the fluctuating voltages of its over-loaded power lines wholly inadequate to meet the "deadly" precision demanded for total war.

Vital "nerve centers" of production lines are geared for precise performance when operated at specific line voltages. Any variation from these rated values, and there are many these days, may well mean lagging production schedules and a noticeable lack of uniformity in products.

Fluctuating line voltages are no problem in plants where Sola "CV's" have taken over. Even though the peaks and valleys of power consumption may cause a voltage variation of as much as 30%—the vital "nerve centers" of their pro-

duction lines continue to operate smoothly and with unerring precision.

Day and night, without care or supervision, Sola Constant Voltage transformers maintain positive control over electrically operated instruments and machines that are indispensable to the nation's war effort. These transformers are available in standard units with capacities ranging from 15 KVA, which might be used for an entire communications system for instance, to the small 10 VA units for vacuum tubes. Special units can be built to specifications.

---

**Note to Industrial Executives:** *The problems solved by Sola "CV" transformers in other plants may have an exact counterpart in yours. Find out. Ask for bulletin SCV-74*

## SOLA Constant Voltage Transformers

**Transformers for:** Constant Voltage • Cold Cathode Lighting • Mercury Lamps • Series Lighting • Fluorescent Lighting • X-ray Equipment • Luminous Tube Signs • Oil Burner Ignition • Radio • Power • Controls • Signal Systems • Door Bells and Chimes • etc. **SOLA ELECTRIC CO., 2525 Clybourn Ave., Chicago, Ill.**

# How Calgon helps speed America's war effort:

## 7. IN THE OIL REFINERIES

**O**UT of the cracking, polymerization, alkylation, fractionating equipment of the oil refineries flow hot streams of products which must be condensed and cooled. The rivers of water pumped to accomplish this cannot do so effectively if calcium carbonate or hydrated iron oxide build up insulating barriers on the heat-transfer surfaces. Nor can irreplaceable equipment survive unless the corrosive action of the cooling-water supply is checked.

Calgon plays its modest but helpful part to keep the refineries "on stream." Because it prevents calcium carbonate scale, stabilizes iron-bearing water, and forms an adsorbed protective film on metal surfaces, it has found a place in cooling water throughout industry.

Condensers in one refinery scaled up so badly that every 30 days they had to be taken off the line and cleaned mechanically — a tedious, costly job. Calgon treatment stopped

scale formation—kept the condensers on the line continuously.

Calgon treatment is being widely used in all process industries so, no matter what kind of plant you operate, the chances are that scale and corrosion troubles can be corrected with Calgon.\* The treatment can be started immediately. Only a simple feeding apparatus is necessary. Write for complete details.

\*Calgon is the registered trade-mark of Calgon, Inc. for its glassy sodium phosphate products.

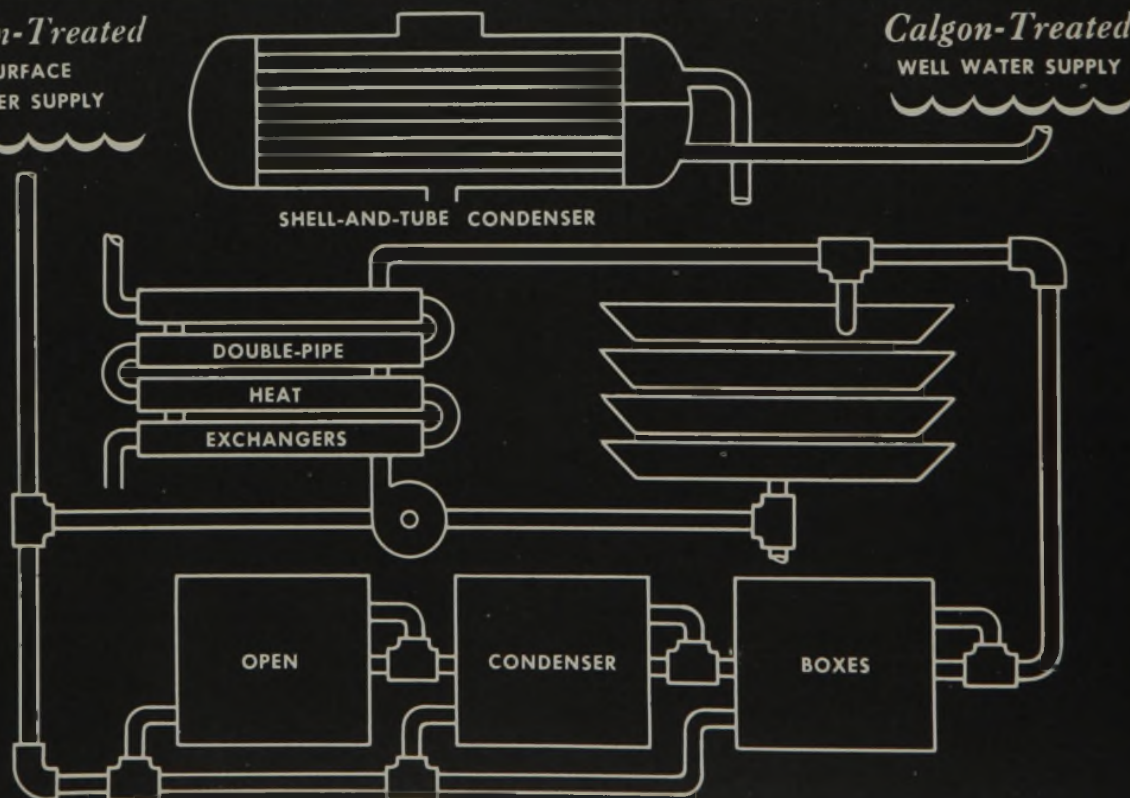
1-5 ppm. of Calgon stabilizes water against deposition of calcium carbonate scale.

2-10 ppm. of Calgon minimizes corrosion of iron and steel equipment.

2 ppm. of Calgon for each ppm. of dissolved iron stabilizes water against deposition of hydrated iron oxide.

*Calgon-Treated*  
SURFACE  
WATER SUPPLY

*Calgon-Treated*  
WELL WATER SUPPLY



HAGAN  
HALL  
BUROMIN  
CALGON

**calgon, inc.**

A SUBSIDIARY OF  
HAGAN CORPORATION

HAGAN BUILDING  
PITTSBURGH, PA.





# Working Surfaces in *New* Pfizer Laboratories

Chas. Pfizer & Co., Inc. has recently completed a Laboratory and Office Building which provides the latest and most modern facilities for its research and analytical staffs.



*New building, Chas. Pfizer & Co. Inc., Brooklyn, N. Y. View in General Analytical Laboratories is shown at top of page.*

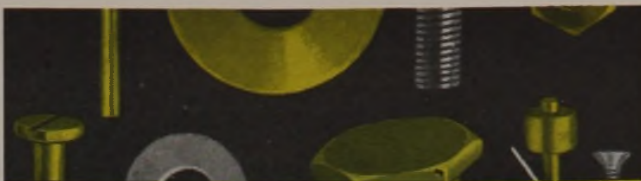
Inselecting Alberene Stone for table tops and sinks, this fine, new laboratory chose the material whose durability and lasting economy have been demonstrated in the country's leading laboratories for more than fifty years.

Despite heavy demands due to industry's Victory program, prompt deliveries can be made of Alberene Stone sinks, fume hoods, table tops, etc.

Alberene Stone Corporation of Virginia, 419 Fourth Avenue, New York. Sales offices in principal cities. Quarries and mills at Schuyler, Virginia.

Inquiries will receive immediate, executive attention.

## ALBERENE STONE LABORATORY EQUIPMENT



### HARPER stocks or makes **EVERLASTING FASTENINGS**

IN  
THESE  
FORMS

OF  
THESE  
ALLOYS

ITEM	Brass	Bronze	Copper	Everdur	Monel	Stainless
<b>Cap &amp; Mach. Screws:</b>						
Hexagon head	STOCK	To Order	To Order	To Order	To Order	To Order
Flat head	STOCK	To Order	To Order	STOCK	STOCK	STOCK
Round head	STOCK	To Order	To Order	STOCK	STOCK	STOCK
Filister head	STOCK	To Order	To Order	STOCK	STOCK	STOCK
Special	To Order	To Order	To Order	To Order	To Order	To Order
<b>Bolts:</b>						
Machine	To Order	STOCK	To Order	STOCK	STOCK	STOCK
Carriage	STOCK	STOCK	To Order	STOCK	STOCK	STOCK
Flat head	To Order	STOCK		To Order	To Order	To Order
Round head	To Order	To Order		To Order	To Order	To Order
Oval head	To Order	To Order		STOCK	To Order	To Order
Hangar	To Order	STOCK		To Order	To Order	To Order
Stove	STOCK	To Order	To Order	To Order	To Order	To Order
Special	To Order	To Order	To Order	To Order	To Order	To Order
<b>Screws:</b>						
Thumb	STOCK					
Lag	STOCK	STOCK	To Order	STOCK	STOCK	STOCK
Wood	STOCK	To Order		STOCK	STOCK	STOCK
Set	STOCK			STOCK	STOCK	STOCK
Knurled	STOCK					
Special	To Order	To Order	To Order	To Order	To Order	To Order
<b>Studs</b>	STOCK	To Order	To Order	To Order	To Order	To Order
<b>Threaded Rod</b>	STOCK	To Order	To Order	To Order	To Order	To Order
<b>Nuts:</b>						
Knurled	STOCK					
Heavy American Standard	STOCK	STOCK	To Order	STOCK	STOCK	STOCK
Light American Standard	STOCK	To Order		STOCK	STOCK	STOCK
Regular American Standard	STOCK	STOCK		STOCK	STOCK	STOCK
Machine screw	STOCK			STOCK	STOCK	STOCK
Castellated	STOCK	To Order	To Order	To Order	STOCK	STOCK
Wing	STOCK			STOCK	STOCK	STOCK
Special	To Order	To Order	To Order	To Order	To Order	To Order
Cap	STOCK	To Order	To Order	To Order	STOCK	STOCK
<b>Washers:</b>						
Regular	STOCK	To Order	STOCK	STOCK	STOCK	STOCK
Lock				STOCK	STOCK	STOCK
Special	To Order	To Order	To Order	To Order	To Order	To Order
<b>Cotter Pins</b>	STOCK			To Order	STOCK	STOCK
<b>Rivets</b>	STOCK	To Order	STOCK	STOCK	STOCK	STOCK

In the above table, "STOCK" means carried in stock; "To Order" means made to order. Harper stocks a total of 4320 items . . . large quantities of each. Many are "Unusual and hard to get." Besides, the Harper special order department is fully equipped with dies, tools, taps and special machinery to make a variety

of "super-unusual and out of the ordinary" fastenings.

**You Need Our Catalog**  
... and reference book. 80 pages—4 colors—193 illustrations—numerous tables and other data. Free when requested on company letter-heads.

**THE H. M. HARPER COMPANY**  
2632 Fletcher St. • Chicago

Offices in  
Principal Cities

Eastern Branch  
45 W. Broadway,  
New York City

I. N. Van  
Nuys Bldg.,  
210 W. 7th St.,  
Los Angeles



# SUPER REFRACTORIES BY CARBORUNDUM

## INCREASE PRODUCTION . . . CUT MAINTENANCE COSTS

## . . . REDUCE OPERATING COSTS . . . INCREASE EFFICIENCY

*In applications like these . . .*

Aluminum Melting Furnaces  
Annealing Furnaces  
Boiler Settings  
Brass Melting Furnaces  
By-Product Coke Ovens  
Carburizing Furnaces  
Ceramic Kilns  
Chemical Process Furnaces

Electric Furnaces  
Heat Treating Furnaces  
Hydrocarbon Cracking  
Regenerators  
Lime Kilns  
Magnesium Melting Furnaces  
Muffle Furnaces  
Muffle Roasters

Muriatic Acid Furnaces  
Oil Refining Still  
Reheating Furnaces  
Rotary Kilns  
Tunnel Kilns  
Water Gas Sets  
Zinc Refining  
Zinc Retorts

**T**HE chart below gives you a quick summary of the characteristics of five super refractories by Carborundum which are doing a big job on the war production front. Each of these super refractories is made in many modified compositions providing a wide range of physical properties.

*Please remember that our entire current production is going to war industries.*

CARBOFRAX		MULLFRAX	
1. Heat Conductivity, 109 Btu.	2. Refractoriness, PCE Cone 37-40	1. Heat Conductivity, 15 Btu.	2. Refractoriness, PCE Cone 38-39
3. High Spalling Resistance	4. High Abrasion Resistance	3. High Spalling Resistance	4. Medium Abrasion Resistance
5. Low Thermal Expansion	6. Specific Heat, 0.285	5. Medium Thermal Expansion	6. Weight, 9-in. Straight, 9.5 lb.
7. Weight, 9-in. Straight, 9.25 lb.			

ALFRAX BI		ALFRAX K		MULLFRAX S	
1. Heat Conductivity, 7 Btu.	2. Refractoriness, PCE Cone 38	1. Heat Conductivity, 21 Btu.	2. Refractoriness, PCE Cone 37-39	1. Heat Conductivity, 7 Btu.	2. Refractoriness, PCE Cone 37-38
3. Good Spalling Resistance	4. Low Abrasion Resistance	3. Medium Spalling Resistance	4. High Abrasion Resistance	3. High Spalling Resistance	4. Medium Abrasion Resistance
5. Medium Thermal Expansion	6. Specific Heat, 0.320	5. Medium Thermal Expansion	6. Specific Heat, 0.330	5. Medium Thermal Expansion	6. Weight, 9-in. Straight, 7.8 lb.
7. Weight, 9-in. Straight, 4.5 lb.		7. Weight, 9-in. Straight, 10.1 lb.			

**REFRACTORY CARBORUNDUM PRODUCTS**

Refractory Division, **THE CARBORUNDUM COMPANY**, Perth Amboy, N. J.

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(Carborundum, Carbofrax, Alfrax and Mullfrax are registered trade-marks of and indicate manufacture by The Carborundum Company)

# A LESSON IN WATER COOLING

LESSON 1 OF A SERIES

## PUMPING COSTS

TOTAL PUMPING HEAD is the amount of pressure required to circulate a liquid through a given system. The PUMPING HEAD required for a cooling tower is part of this total head and is that pressure necessary to lift water from the tower's base to its inlet and overcome friction within the distribution system.

The table indicates how very important PUMPING HEAD actually is when measured in terms of operating cost. These costs as tabulated will vary for any given installation in direct proportion to the actual GPM circulated and the power rate in effect.

Unlike other tower operating costs resulting from the use of power, pumping head is generally figured on a full-time maximum GPM basis since this

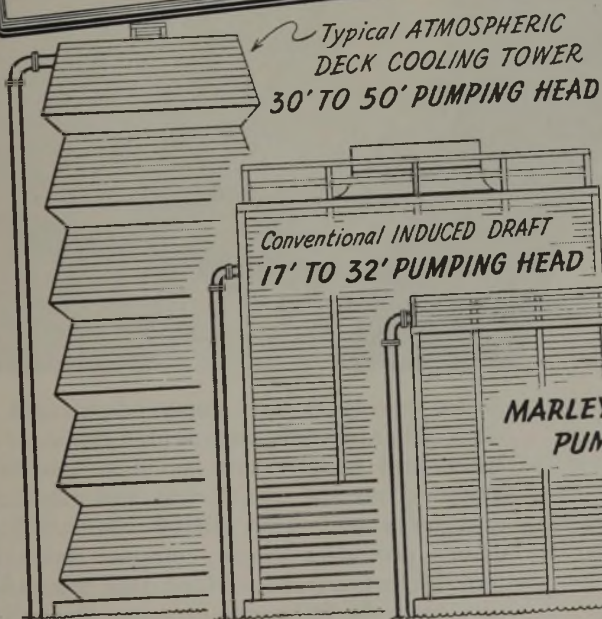
### Cost Per 1000 GPM

at 1¢ per KWH and 70% Pump-and-Motor Efficiency

Pump Head	24 Hr. Day	30 Day Month	365 Day Year	Five Years	Ten Years
15'	\$ .97	\$29.10	\$354.05	\$1770.25	\$3540.50
20'	1.29	38.70	470.85	2354.25	4708.50
25'	1.62	48.60	591.30	2956.50	5913.00
30'	1.94	58.20	708.10	3540.50	7081.00
35'	2.26	67.80	824.90	4124.50	8249.00
40'	2.58	77.40	941.70	4708.50	9417.00
45'	2.91	87.30	1062.15	5310.75	10621.50
50'	3.23	96.90	1178.95	5894.75	11789.50

constitutes normal operating practice. Therefore any additional or unnecessary pumping head becomes a large factor in the complete comparative cost analysis so necessary for the intelligent selection of a cooling tower.

Relative pumping heads required by cooling towers of different types, designs and "makes" deserve the most careful study and comparison.



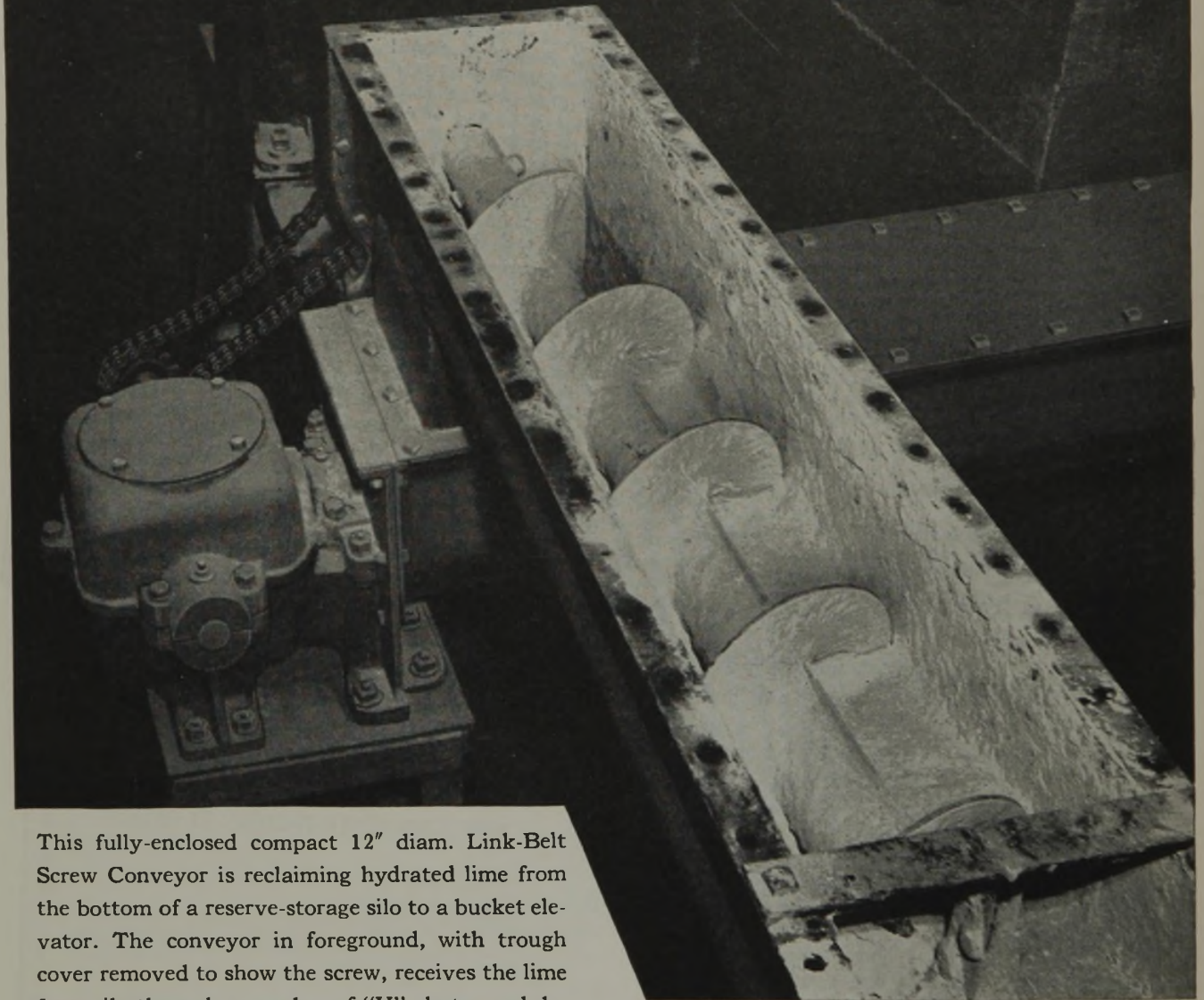
MARLEY ENGINEERS HAVE ALWAYS KEPT PUMPING HEADS EXCEPTIONALLY LOW WITHOUT ADVERSELY AFFECTING OTHER FACTORS OF DESIGN



## COOLING TOWERS

THE MARLEY COMPANY, INC.  
FAIRFAX AND MARLEY ROADS — KANSAS CITY, KANSAS

# Another Engineered Application!



This fully-enclosed compact 12" diam. Link-Belt Screw Conveyor is reclaiming hydrated lime from the bottom of a reserve-storage silo to a bucket elevator. The conveyor in foreground, with trough cover removed to show the screw, receives the lime from silo through a number of "V" chutes and delivers to the screw conveyor below, extending at 90° to the bucket elevator. A motorized reducer with the addition of a right angle enclosed lubricated counter-shaft trough-end operates both conveyors.

#### LINK-BELT COMPANY

9068

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Screw conveyors offer many advantages in handling bulk materials, such as high efficiency; power, space and maintenance savings—low first-cost. They permit the use of dust and moisture-proof enclosures and with direct connected reducer drives, provide a simple, compact conveying system. There is a standard Link-Belt design for every service in the full range of sizes. Book No. 1289.

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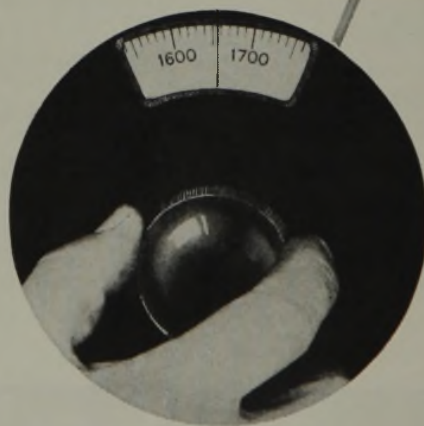
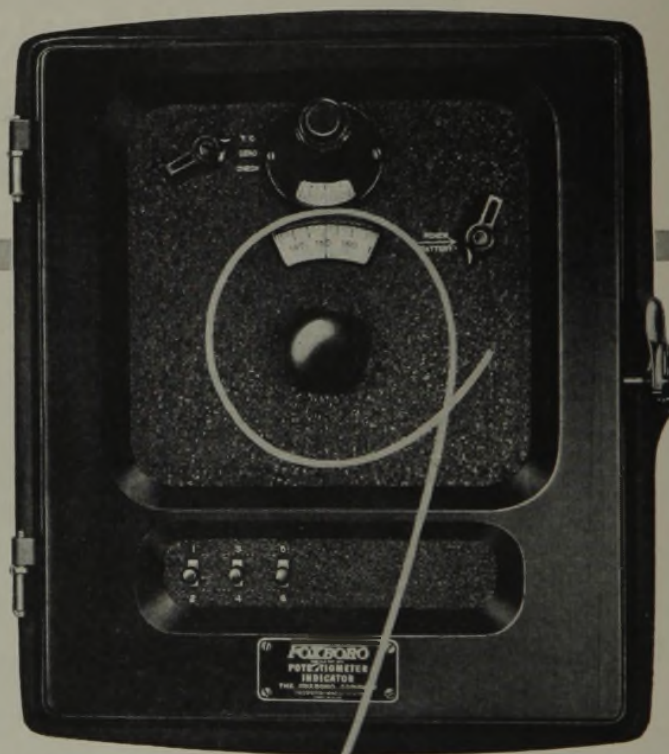
**AN INDICATING PYROMETER  
THAT GIVES UNUSUAL ACCURACY  
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Here's a practical solution to wartime production problems of getting high-accuracy temperature information under today's speeded-up shop conditions!

Foxboro Potentiometer Indicators combine thermal precision approaching laboratory standards, with simplicity of operation that practically eliminates chances of inaccurate setting or reading by operators. Every detail is specially designed for ease and accuracy!

For example, the patented Foxboro Auto-Vernier Rheostat incorporates coarse and fine adjustment slide-wires in a single unit for standardizing the measuring circuit with precision. The extra-large dial provides an open, 17 inch temperature scale which can be easily read to very small units. Further, the vernier setting knob permits precision setting of the measuring slide wire.

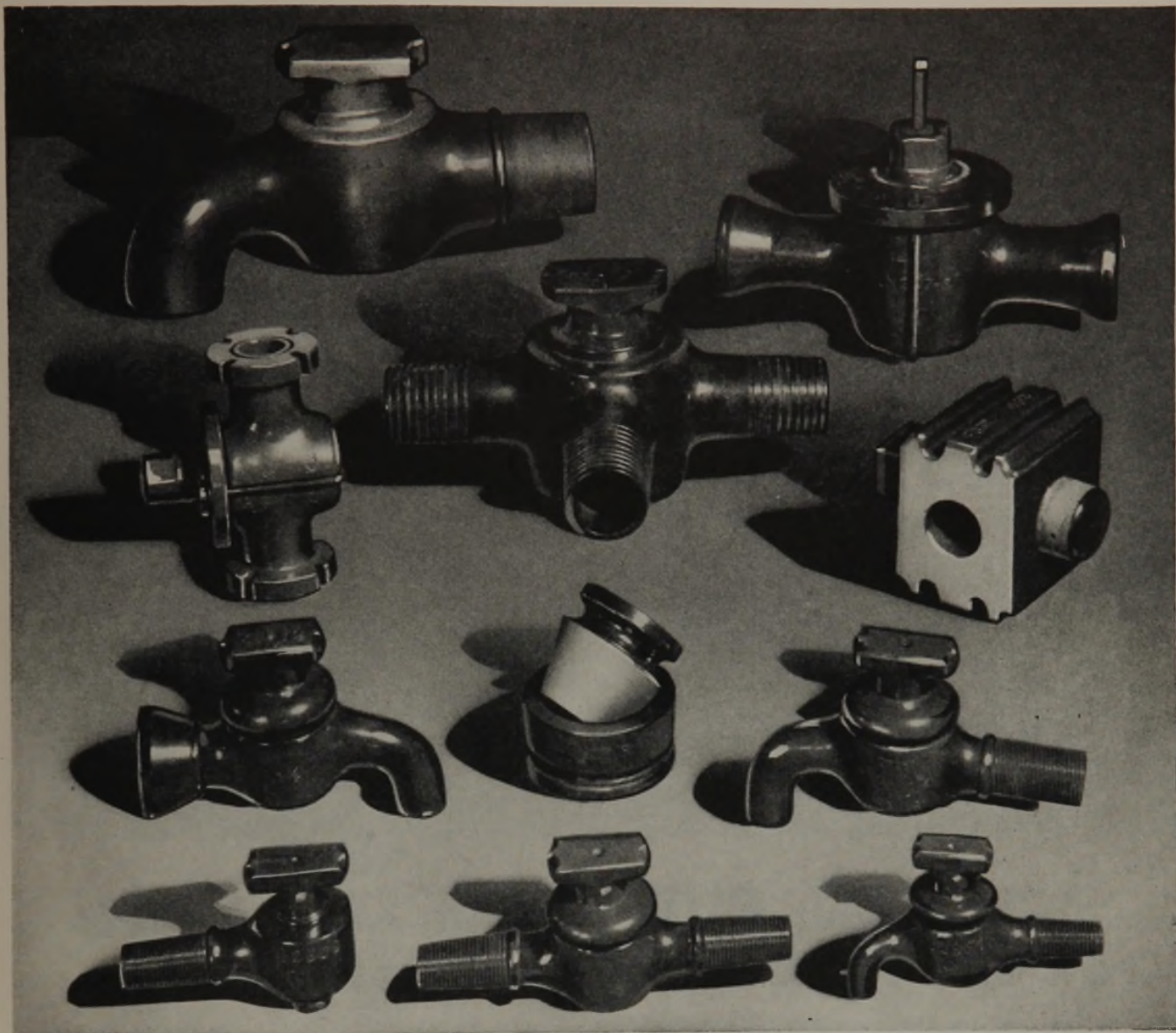
These are merely two of the better-engineered features of Foxboro Potentiometer Indicators that give guaranteed accuracy of 1/4 of 1% of scale value . . . and permit easy reading to 1/6, or even 1/10, of 1% of scale. Write for complete details in Bulletin A-305. The Foxboro Company, 54 Neponset Avenue, Foxboro, Mass., U. S. A. Branch offices in principal cities of United States.



Extra-large, extra-open dial of Foxboro Potentiometer Indicator enables quick, accurate setting. Built-in key-switches for 1 to 18 thermocouple connections also add to ease of reading.

Potentiometer Instruments by **FOXBORO**

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Maurice A. Knight supplies stoneware piping and valves for pipe lines, tanks and other installations where acids or corrosives are handled. The entire body of Knightware valves is acid-proof.

Shown in the picture are straightway types, bibs, a block cock, drop valve, spigot and two Knight Nordstrom lubricated plug cocks. Each valve is hydraulically leak-tested. There are no metal parts for acids to corrode. Flanges may be either conical

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When writing for estimates on Knightware acid-proof valves, piping or stoneware, please give us engineering data and the purpose for which they are to be used.

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\* Consult GLOBE engineers regarding new applications and selection of the right characteristics of stainless tubes for your specific needs.

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★ BOILER TUBES  
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*Tubes*

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For temperatures up to 3500° F and 4500° F



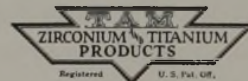
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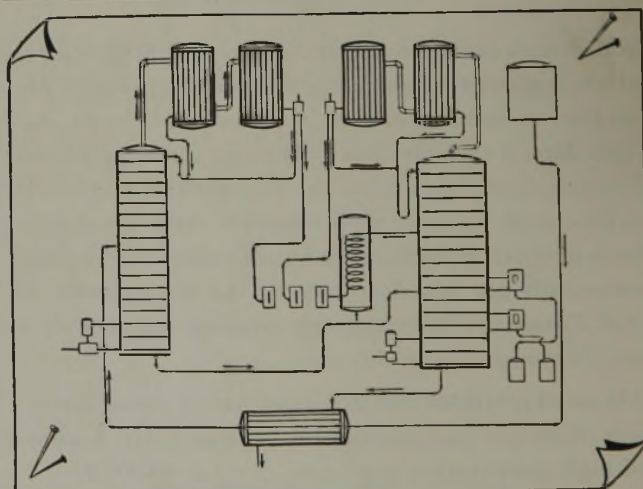
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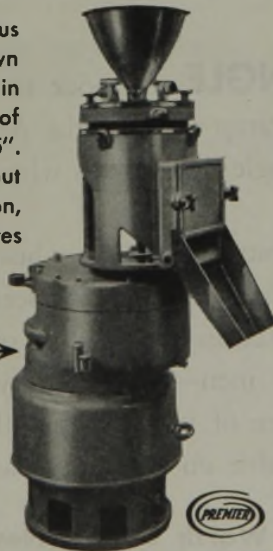
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*"THEY'RE ALWAYS DEPENDABLE"*

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**Y**ES, every WeldELL\* can pass this test for true circularity—or any other test for dimensional accuracy. A number of steps in their production contribute to this uniform accuracy, and as a final precaution every fitting is given a special truing operation to bring it to exact size before machining bevels and lands.

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★ No other fittings for pipe welding combine the features found in WeldELLS. In addition to extreme dimensional accuracy these features include:

- **Seamless**—greater strength and uniformity.
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- **Precision quarter-marked ends**—simplify layout and help insure accuracy.
- **Selective reinforcement**—provides uniform strength.
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- **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.
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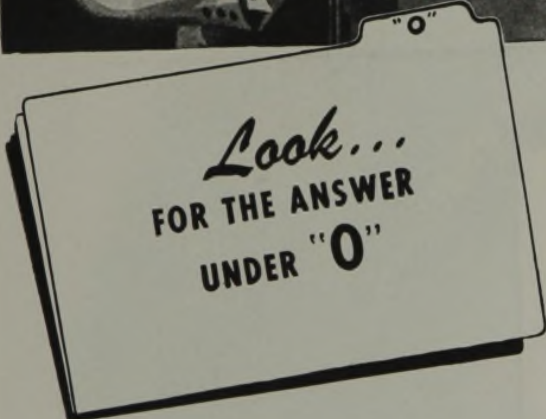


\* WeldELLS and many other Taylor Forge Products are produced in Byers Genuine Wrought Iron.

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Note  
TO THE  
EXECUTIVE  
OF TOMORROW



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FOR THE ANSWER  
UNDER "0"

● Tomorrow's business leader will have at his command an array of new materials and methods which are a guarantee of a better world to come. The lighter metals, the science of electronics, advanced plastics have already been much discussed. Another important place to look for the answers is in the science of *Optics*.

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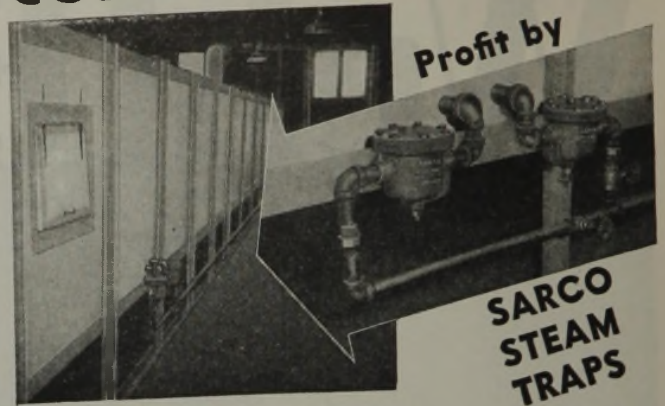
Today the armed forces need our best and undivided effort and we can offer our services to Industry only on an "After Victory" basis. Let us leave nothing undone to hasten that day.

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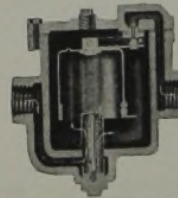
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SARCO  
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TRAPS

This continuous dryer, more than 60 feet long, is putting the finishing touch on miles of waterproofed fabric.

The load on the steam coils is heavy and continuous. That is why Sarco Inverted Bucket traps were chosen to drain the coils.

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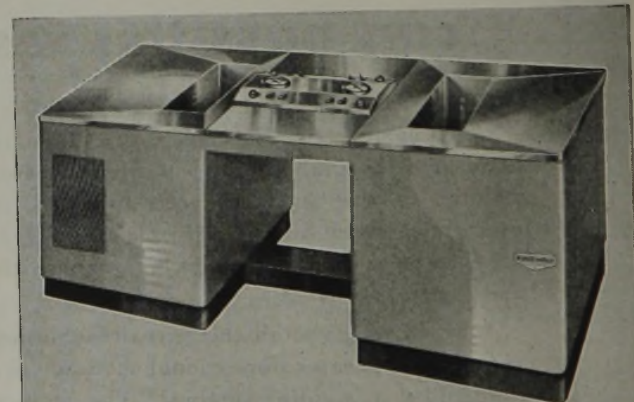


A built-in strainer keeps dirt and scale from the valve. A separate strainer is not necessary. Can be equipped with air by-pass for rapid elimination of air and gas. Standard sizes to 900 lbs. Catalog No. 350.

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SAVES STEAM

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Originally, people thought of air conditioning only in terms of *temperature*. It cooled the air on a warm day. Temperature was air conditioning's *first dimension*.

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Then, air conditioning took on a fourth dimension . . . *dust exclusion*.

And now, air conditioning is cooperating in an important new field . . . controlled air *pressure*. This is needed for the testing of men and equipment under the conditions of stratosphere flying.

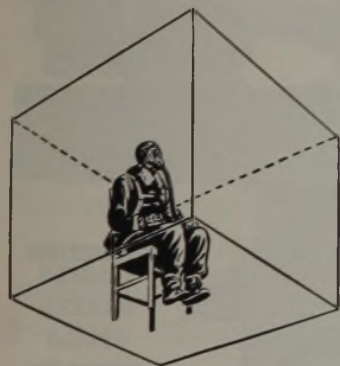
Today, air conditioning faithfully repro-


duces *exact climates* . . . from the parched heat of the Sahara to the frigid cold of Northern Russia. The equipment that does this must be more flexible, more compact than ever before . . . with precise control of temperature and humidity.

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Then, as now, look to General Electric as the outstanding supplier of up-to-date air conditioning and industrial refrigeration equipment of all kinds.

*Air Conditioning and Commercial Refrigeration Department, Division 434, General Electric Company, Bloomfield, New Jersey.*

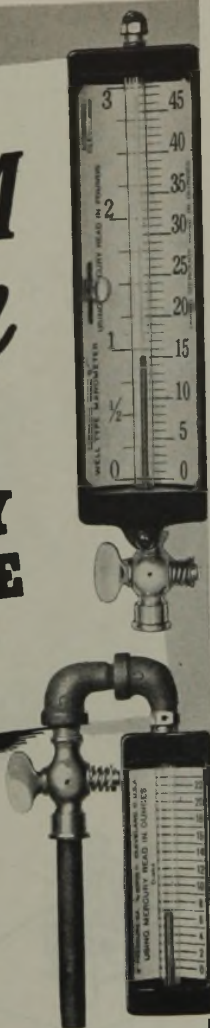


*Air Conditioning by*  
**GENERAL  ELECTRIC**

**MERIAM**

*non-spill*

**MERCURY  
PRESSURE  
GAUGES**



★ These accurate, compact, direct reading gauges—either as portable or permanent installations—have a wide application for measuring low range air and gas pressures.

They are designed so that the mercury cannot be lost from the gauge either through spilling or over-pressuring. They are available in the 3" and 6" sizes to measure 22 oz. and 48 oz. respectively. Unit scale graduations are in ounces. Each gauge is furnished complete with pet cock and necessary mercury. Housings of the gauges are of cast semi-steel, accurately machined to insure leak-proof fitting of all the component parts. The housing, finished in dull black baked enamel, protects on three sides the heavy walled Pyrex, centrally located tube. Write for Bulletin 3 containing full details.

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Pressures Up To 100,000 lb. p.s.i.  
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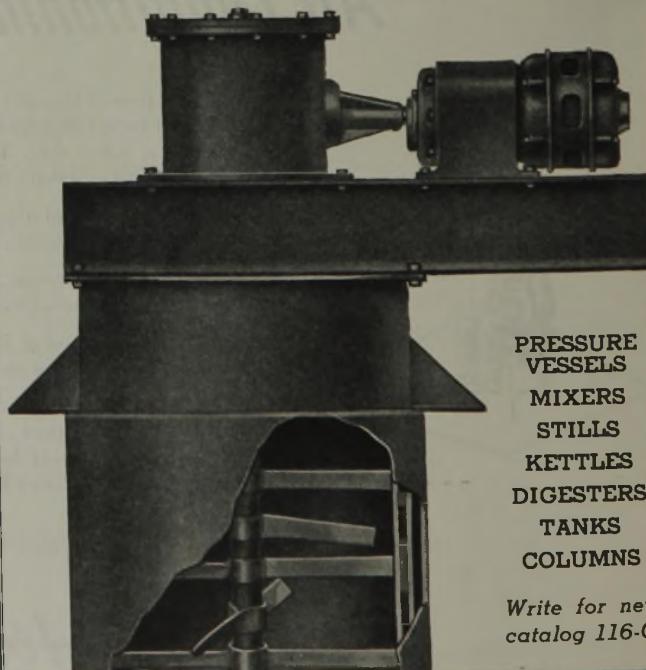
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FROM PILOT PLANT TO PRODUCTION LINES



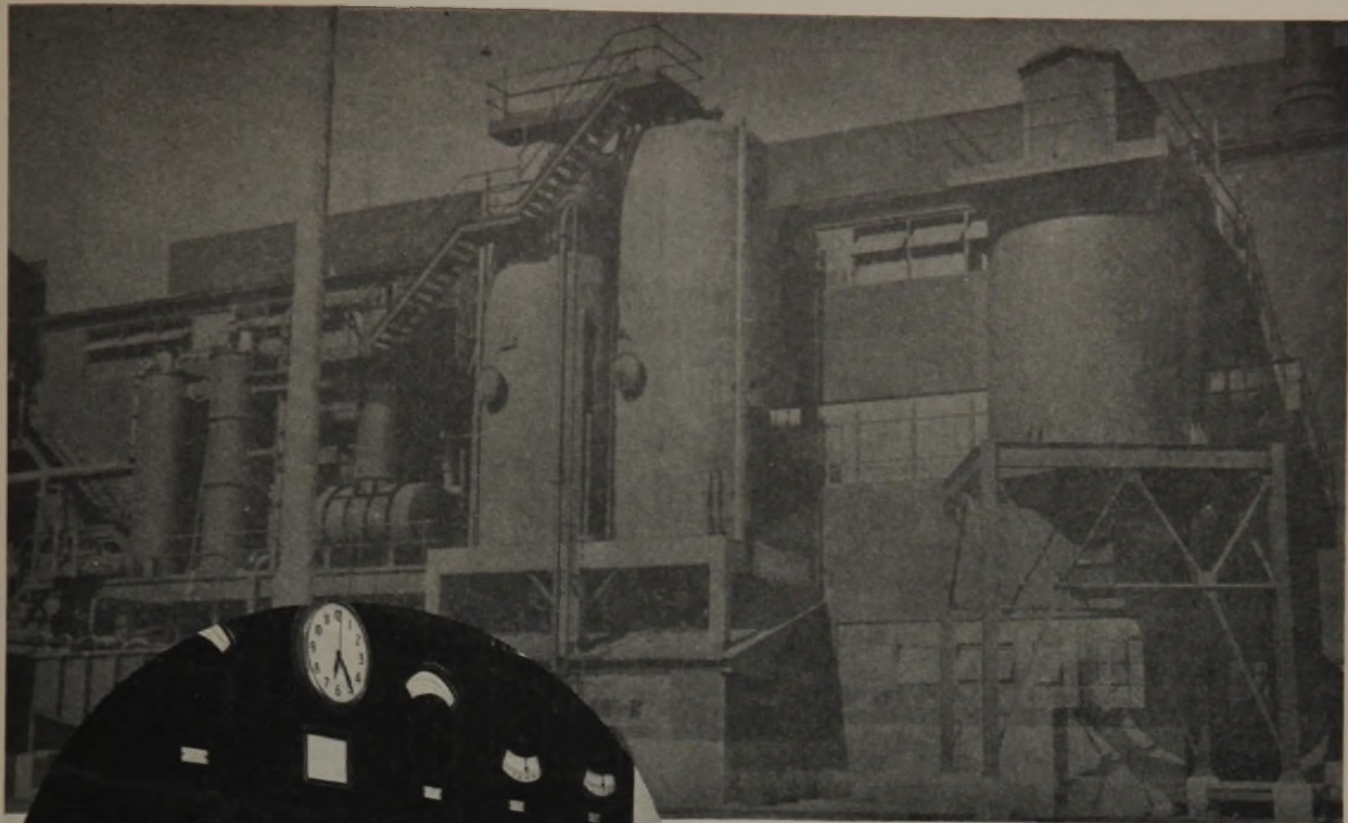
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GOVERNS A COMPLETE CHEMICO ACID PLANT

CENTRALIZED CONTROL makes the operation of a CHEMICO Acid Production or Recovery Plant simple . . . effective . . . efficient. A single instrument board immediately shows changes in temperature and pressure at all parts of the plant...automatically records important data on temperature and

acid strength. The most remote parts of the plant are conveniently controlled . . . labor expense is minimized . . . process operations

are readily standardized . . . and uniform results can be assured. These are some of the reasons why "CHEMICO PLANTS are PROFITABLE INVESTMENTS".



**CHEMICAL CONSTRUCTION CORPORATION**

30 ROCKEFELLER PLAZA • NEW YORK

Cables, Chemiconst, New York

• European Representatives, Cyanamid Products, Berkhamsted, Herts., England

**CHEMICO PLANTS are PROFITABLE INVESTMENTS**

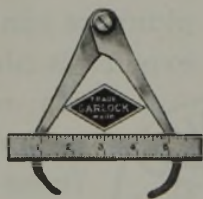


"...if you produce 'em!"

"The production lines will determine whether we hold the battle lines," said Donald M. Nelson.

Our fighting men will "deliver the goods" if we'll produce them and transport them to the vital points where they are needed.

So it's up to us back home to exert every effort to supply torpedoes, guns, ships . . . everything our fighters need. Let's go, America!



THE GARLOCK PACKING COMPANY, PALMYRA, NEW YORK  
Manufacturers of GARLOCK Packings,  
Gaskets and KLOZURE Oil Seals

In Canada: The Garlock Packing Company of Canada Limited,  
Montreal, Que.

**GARLOCK**

AMERICA'S PIONEER  
PRODUCER OF  
**WIRE CLOTH**

We help you get longest life, and lowest annual cost—result of 85 years' experience in manufacturing wire cloth for every use. All weaves, for screening, filtering, separating, grading, cleaning, or processing. Any metal, in types of cloth to give longest service under chemical action, corrosion, abrasion, moisture, or high temperature.

**FREE BOOK** contains charts, diagrams, tables of wire sizes, meshes, and weights . . . 151 illustrations. Wickwire Spencer Steel Co., 500 Fifth Avenue, New York. Or Buffalo, Worcester, Chicago, San Francisco.

**WICKWIRE SPENCER**  
WIRE CLOTH

THERE'S A  
*"Success Story"*  
BEHIND EACH  
SEALING MATERIAL  
IN THE  
**FEL-PRO**  
MATERIAL SAMPLE FOLDER

**36 Samples** of Fel-Pro Sealing Materials in this FREE book—and each one has a history of "making good." Take the case of the manufacturer who wanted a gasket material resistant to petroleum products — strong chemicals — high compression. Everything had failed until he came to Fel-Pro. Our engineers developed Lignoflex for him. It met every requirement — and is now used by other plants having similar problems. Besides Lignoflex, you will find in this book Felpak and Blutex, and 33 other sealing materials. Also full specifications, technical data, suggested applications. Send for your copy of this FREE book today.

**Special Sealing Materials Developed to Fit Your Needs**  
Write us in detail about your difficult sealing material problems. Our Special Development Staff may be able to develop a new product that exactly fits your requirements.

Put it up to  
**FEL-PRO**  
for solutions to problems involving Gaskets, Moulding, Stripping, Mechanical Packing and other types of Sealing Materials

FEL PRODUCTS MFG. CO., 1519 CARROLL AVE., CHICAGO, ILLINOIS

# Busy Chemicals for the War and After



## Making FLARES Now— Stopping FLARE-UPS Later



When modern war demands night flights, the call goes out for Hexachlorbenzene—because Hexachlorbenzene is an important ingredient of flares and helps guide planes to safe landings.

In striking contrast to this use, Hexachlorbenzene can lessen other important hazards which are met in peace as well as war. It can serve as an ingredient of fire-proofing compositions to impregnate textiles, wood, cellulose films, rubber, etc.—and to water-proof them too. Hexachlorbenzene is one of more than ninety

**HOOKER CHEMICALS**  
which are available to do

their share in a busy world. In war and peace, members of the HOOKER technical staff constantly seek to expand the applications of these products. Their research often discovers unusual versatility in a chemical which leads to wholly unsuspected uses.

Like many another future-probing industrial organization, HOOKER is learning much from its wartime studies. Its findings—pooled with the thinking of others—perhaps your own—can be invaluable to you in the days to come.

HOOKER welcomes consultation on plans for post-victory product development and on present priority needs for busy chemicals. It's never too early to tackle tomorrow.

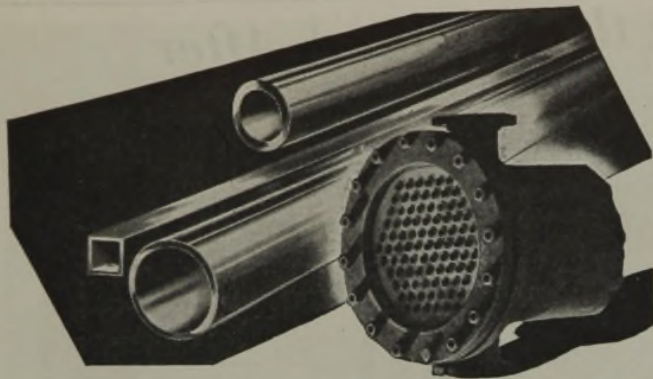
<b>HOOKER HEXACHLORBENZENE <math>C_6Cl_6</math></b>	
<i>Hooker Specifications:</i>	
DESCRIPTION: White or Cream Colored Crystalline Solid, with practically no odor; it is quite inert chemically and highly stable under all conditions.	
MELTING POINT: 225° C. Minimum	
SOLUBILITY Gms/100 gms AT 50° C.:	
Water .....	Insoluble
Benzene .....	10
Carbon Tetrachloride .....	8
Ether .....	8
SIZE: Percentage Through U. S. Standard Sieves	
No. 50 .....	Minimum 99.0%
No. 100 .....	Minimum 95.0%

HOOKER ELECTROCHEMICAL CO., NIAGARA FALLS, N. Y.  
New York City

Tacoma, Wash.

# HOOKER CHEMICALS





There is no time for production hold-ups where heat exchangers are made,—so Carpenter Welded Stainless Tubing helps to "get 'em out faster"—and better.

HOW THESE

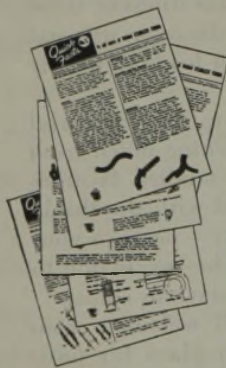
## UNIFORM TUBE WALLS

help to boost **OUTPUT**  
and conserve metals

The *uniform wall thickness* of this Welded Stainless Tubing permits the use of lighter gauges without sacrificing strength. And *lighter gauges* mean easier forming, cutting and welding . . . an important plus wherever skilled workers are at a premium! Then too, the use of Welded Stainless Tubing, pioneered by Carpenter, helps to conserve metal.

*Longer service life* is one feature of equipment and parts made from Carpenter Welded Stainless Tubing. There are no thin spots to "give out" as a result of constant heat, corrosion, pressure or wear.

If you would like help in applying this tubing to your design or production problems, let us know. Carpenter's service representatives can help you get the most from Welded Stainless Tubing.



*If you use Welded Stainless Tubing, or are planning its use, ask for Carpenter's QUICK FACTS bulletins. A note on your company letter-head will start them on the way—to help you use this Welded Stainless Tubing to best advantage.*

Carpenter Welded Stainless Tubing resists corrosion, heat and wear; meets Government specifications; is 100% hydrostatically tested; has a high strength/weight ratio.

**THE CARPENTER STEEL COMPANY**  
Welded Alloy Tube Division      Kenilworth, N. J.

**Carpenter**  
**WELDED**  
**STAINLESS TUBING**

Reduce boiler scale  
TO GET MAXIMUM  
**POWER!**



WITH an accurate two minute check on the pH and phosphates in your boiler water, you may prevent scale in your boiler . . . increase heat transfer . . . and get more heat with less fuel. The Taylor Boiler Water Comparator is equipped with a High (5-100 ppm) or Low (0-25 ppm) Phosphate Comparator, together with Cresol Red (pH 7.2-8.8), Phthalein Red (8.6-10.2) and Acyl Red (10.0-11.6) color slides. All color standards carry

AN UNCONDITIONAL GUARANTEE  
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## LaMOTTE CHEMICAL CONTROL SERVICE

Embraces a Wide Field

pH . . . Boiler Feed Water . . . Chlorine  
Soils . . . Water Treatment, Electroplating,  
Papermaking, Sugar Processing, Leather, etc.

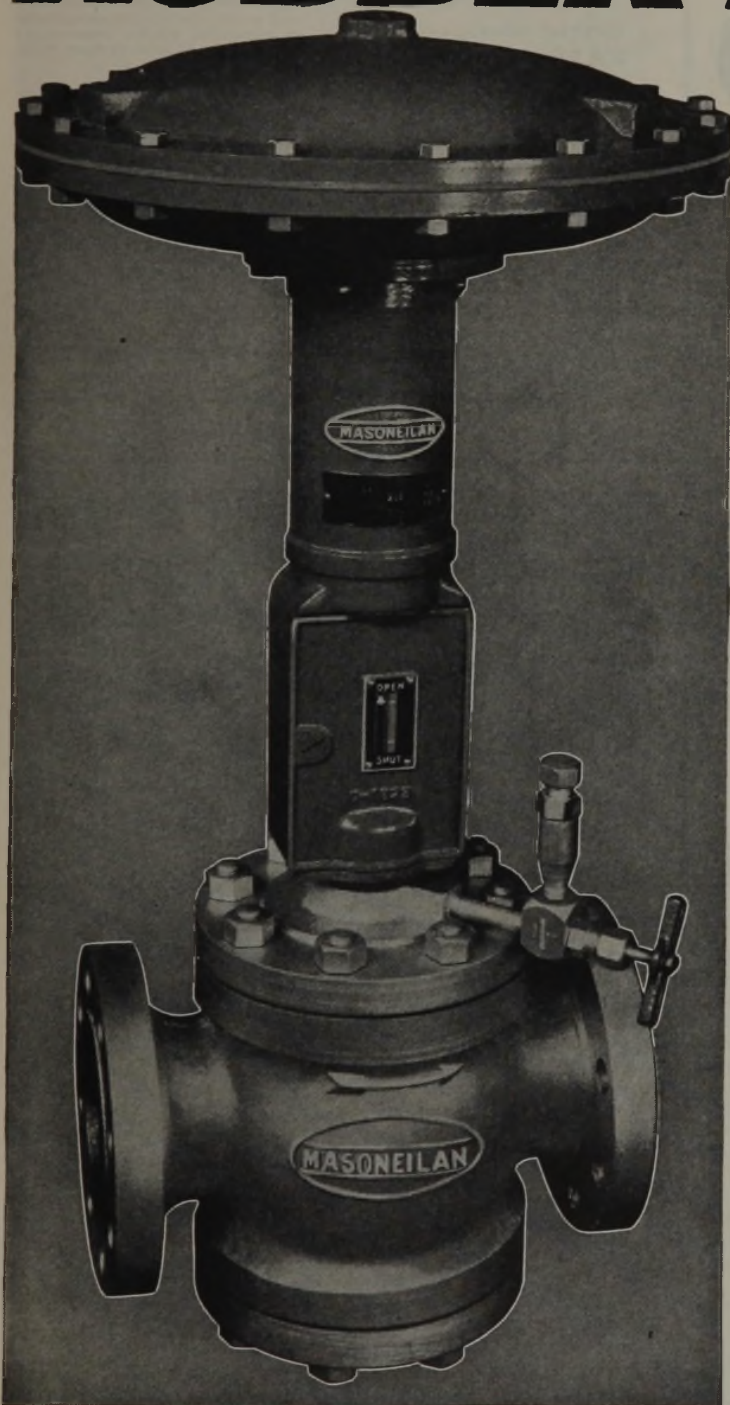
If you have an operation requiring routine chemical control tests, we will gladly tell you how they can be simplified with standardized outfits that are accurate, inexpensive, and easy to operate. There is no charge or obligation for this service.

The LaMotte Research Department, in cooperation with authorities, has developed standard tests for every industry. Hundreds of operators have come to us with their problems, and we have supplied definite data concerning the application of tests to their specific operations. Simply write us, outlining the nature of the operation involved.

**LaMOTTE**  
**CHEMICAL PRODUCTS CO.**

Originators of Practical Application of pH Control  
Dept. F., Towson, Baltimore, Md.

# ... UNDER THE SPREADING RUBBER PLANTS



When some day the wheels of the nation roll on tires made by the synthetic rubber plants now spreading across the country, it will be because automatic controls made the processes possible. And many of these controls will include Masoneilan Control Valves. Rubber plants already operating and others to come will depend on the accuracy, in-built quality and sturdiness of these valves which have earned them a top spot in the esteem of the petroleum and chemical industries.

If some of our friends are unable to obtain Masoneilan Control Valves when they want them, remember that the most vital war-winning industries come first. That valve you wanted may be helping to make the tires on which the jeeps will roll into Berlin.



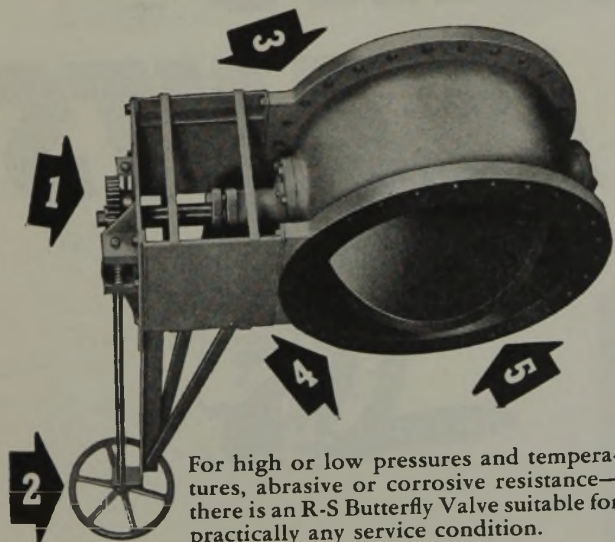
**MASON-NEILAN REGULATOR CO.**  
**BOSTON, MASSACHUSETTS**

# Simplify



## Control and Shut-Off for Inaccessible Locations

15 to 900 P. S. I.



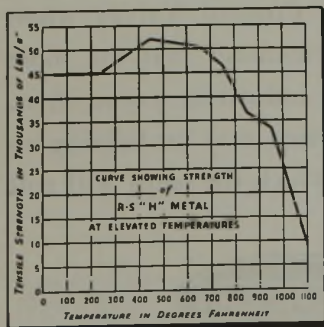
For high or low pressures and temperatures, abrasive or corrosive resistance—there is an R-S Butterfly Valve suitable for practically any service condition.

Typical of the skill and versatility of R-S Engineers is this standard 125 pound valve with extension shaft and hand wheel for inaccessible locations. Consider these outstanding features.

1. Oversize gear and worm.
2. Six hand wheel revolutions complete full vane movement.
3. Husky vane shaft mounted in grease-sealed stuffing box.
4. Body and vane can be cast of special R-S "A" or "Abrasive" metal for extra-long wear.
5. Beveled vane is precision machined—seats wedge-tight against valve body. Constructed to any A.S.M.E. dimensional standard. Sizes to 72-inches.

VALVE DIVISION  
**R-S PRODUCTS CORPORATION**  
Germantown Ave. & Berkley St., Philadelphia, Pa.

**A SUBSTITUTE  
FOR STEEL!**

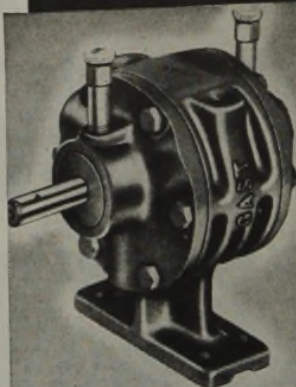


R-S Engineers have developed special metals for resistance against heat, abrasion and corrosion. For example, R-S "H" Metal is an alloy semi-steel that machines like cast iron. Tensile up to 50,000 p.s.i. Withstands high pressures and penetration of steam and gases up to 1000°F. Stress relieved up to 1400°F.

Request detailed information and Catalog No. 10-B.

**R-S Streamlined BUTTERFLY VALVES**

## Solve EXPLOSION-PROOF problems with GAST AIR MOTORS



### SPECIAL ADVANTAGES OF GAST AIR MOTOR

- No reciprocating parts or springs.
- Automatic take-up for wear.
- Low maintenance—cannot be burned out.
- Positive starting in any position.
- Exceptional compactness for power developed.

**GAST**  
ROTARY AIR  
MOTORS & PUMPS

★ **COST MUCH LESS**  
*Than explosion-proof electric motors*

★ **VARIABLE SPEED**  
*over a wide range  
Up to 3,000 R.P.M.*

★ **PROMPT DELIVERY**

On explosion-proof applications where compressed air is available, the Gast Air Motor provides power at much lower first cost and practically no service cost (based on 7 year record).

The Gast Air Motor is particularly applicable to war-production jobs such as driving mixing equipment in munitions plants, process industries, etc. It delivers from 1/20 to 1 H.P.

Because it employs the same Rotary principle as the famous Gast Air Pumps, the Gast Air Motor offers the same economy and long life advantages.

Write for **FREE Catalog on GAST AIR MOTORS — PUMPS — COMPRESSORS**

*Contains full descriptions, engineering data, and many application photographs on the complete Gast line which includes 12 sizes, Gast Rotary Air Pumps, 1/2 to 23 C.F.M. Pressures up to 30 lbs.*

**GAST MFG. CORP.**  
133 Hinkley Street  
Benton Harbor, Michigan

**DISH WASHER**

**Where could I use a THERMOSWITCH?**

**SPACE HEATERS**

**GOLD EMBOSsing**

**PACKAGE MACHINERY**

**LABELING MACHINES**

**BLOWER TYPE HEATERS**

**AIR CRAFT METAL SPRAYER**

**HOT WATER STORAGE TANK**

**BABY INCUBATOR**

**WELDING EQUIPMENT**

**STERILIZER**

**OIL TEMPERATURE**

**MOBILE KITCHEN**

**MOLDING PRESS**

**HOT PLATES**

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**OVENS**

**POTS**

**LINOTYPE METAL**

**VULCANIZER**

SENSITIVITY ± .1°F. MANY TYPES AVAILABLE  
WRITE FOR CATALOG

**Fenwal**  
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MASSACHUSETTS

# Unique

*in Properties and Performance*

## NATIONAL AND KARBATE TRADE-MARK TRADE-MARK CARBON AND GRAPHITE PRODUCTS

are being used successfully in a wide range of important applications in the mechanical, electrical and process industries because of the many advantages offered by their unique combination of physical and chemical properties.

- Resistance to severe thermal shock.
- No deformation at high temperatures.
- Not wet by molten metals — no sticking.
- Mechanical strength maintained at high temperatures.
- No reaction with most acids, alkalies and solvents.
- Low thermal expansion.
- High rate of heat transfer (Graphite and Graphite Base "Karbate" products).
- Low rate of heat transfer (Carbon and Carbon Base "Karbate" products).
- Good electrical conductivity.
- Self-lubricating.
- Available in impervious grades.
- Available in highly permeable (Porous Carbon and Graphite) grades.
- Easily and accurately machined and fabricated.
- Molded and extruded in special shapes when quantity justifies.

Thirty-five foot high "Karbate" absorption tower equipped with graphite trays and bubble caps. One of many examples of the application of these materials.

Carbon and graphite materials are available in the form of:  
Brick, Blocks, Beams, Plates, Flat or Hollow Tile,  
Slabs, Pipe, Tubes, Rods, Cylinders, Cement, Paste.

A variety of sizes permits fabrication of all types of equipment from small intricate parts to huge all-carbon structures.

Conventional design has been improved and simplified new design made possible by the use of "National" and "Karbate" carbon and graphite products. Following are some of the more important applications:

Heat Exchangers . . . Towers and Tower Equipment . . . Raschig Rings and other Tower Packings . . . Pipe, Valves and Fittings . . . Tanks, Tank Linings and Miscellaneous Containers . . . Filter and Diffuser Elements . . . Packing, Piston and Seal Rings . . . Bearings . . . Molds, Mold Plugs, Inserts and Stools . . . Ground Anodes . . . Welding Electrodes, Rods, Plates and Paste . . . Brushes and Contacts . . . Miscellaneous Electrical and Chemical Specialties.

### NATIONAL CARBON COMPANY, INC.

Unit of Union Carbide and Carbon Corporation



CARBON SALES DIVISION, CLEVELAND, OHIO

General Offices: 30 East 42nd St., New York, N. Y.

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The most important thing when buying a Heat Exchanger is the "know-how" of the manufacturer!

Whitlock has the "know-how" — the result of years of the closest kind of cooperation with some of the nation's largest users of this equipment. This experience, plus these manufacturing facilities are at your service:

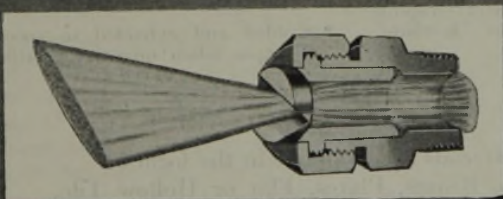
1. Whitlock operates its own plate fabricating and machine shops.
2. Whitlock welders are qualified to make pressure vessels to A.S.M.E. Code requirements, U-68 or U-69.

3. Whitlock X-ray testing equipment available for use when specified.
4. Whitlock can test up to 10,000 lbs. hydrostatic pressure or 4500 lbs. by "air under water" method.

Discuss your next job with —

**THE WHITLOCK MANUFACTURING CO.**

84 South St., Elmwood Hartford, Conn.  
 District Offices In New York, Boston, Chicago, Philadelphia, Detroit, Richmond



No cores or vanes in this flat spray atomizing nozzle. Wearing parts are easily renewable and cost little.

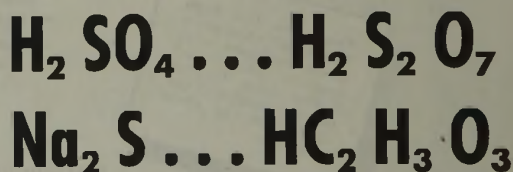
*How to Get*  
**BETTER RESULTS**  
*In Spray Operations*

Spray nozzles do better, faster work, more economically, when engineered for the jobs they do. Since the many types and sizes of Spraying Systems nozzles are engineered, they save time, power and material. For example, if your process requires a flat spray using 3.5 GPM at 20 lb. water pressure with an effective spray angle of 25°, the right Spraying Systems nozzle will do the job in just that way.

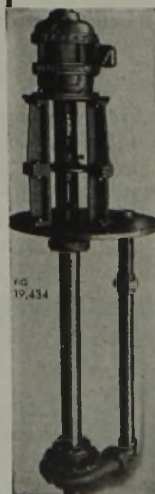
Our engineers make cost-free recommendations — offer valuable suggestions concerning your spraying problems. Write and describe your spray operations — you'll receive prompt attention.

**SPRAYING SYSTEMS COMPANY**  
 4027 West Lake Street Chicago, Illinois

**SPECIALISTS IN THE DESIGN AND MANUFACTURE OF SPRAY NOZZLES**



*need sturdy* **TABER**  
**Vertical Chemical Pumps**



Ordinary sump pump construction is not satisfactory for pumping chemical solutions. This fact has been proved by Taber over many years' experience with some of the largest chemical plants. From this priceless experience Taber has designed a series of vertical chemical pumps suitable for most any processing system. Write for helpful new Bulletin V-837.

**TABER PUMP CO.**  
 Est. 1859  
 293 Elm St. Buffalo, N. Y.

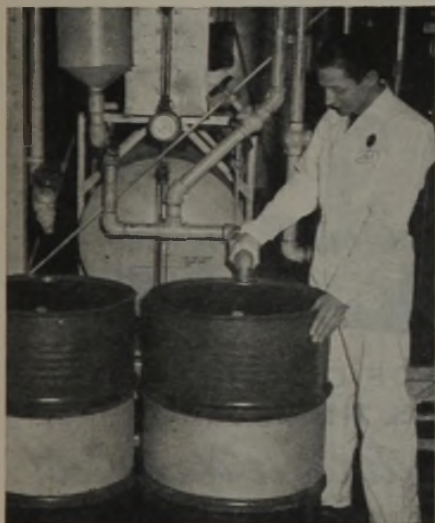




A 42½-ton Pan American Clipper being serviced with gas and oil in Tri-Sure-equipped drums, before flying with vital war equipment to Africa.

# AFRICA BOUND!

This vital air service  
demands big, fast  
powerful planes —  
and gas and oil that  
are protected by  
Tri-Sure Closures



Photographs courtesy Pan American Airways

No chances can be taken with a Clipper's oil supply. Drums are sealed with leak-proof, tamper-proof Tri-Sure Closures.

Africa bound! These giant Pan American Clippers are a symbol of America's pre-eminence in the air, as they speed war-vital men and materials across the ocean, and help to maintain one of America's most important aerial lifelines.

*On this gigantic ferry service the precious fuel, on which depends so much the safe carriage of human lives and war materials, is safeguarded by Tri-Sure's perfected seal, plug and flange.*

**Tri-Sure**  
Reg. U. S. Pat. Off.  
**CLOSURES**

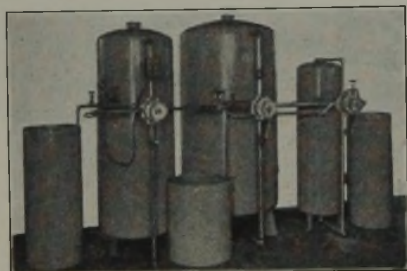
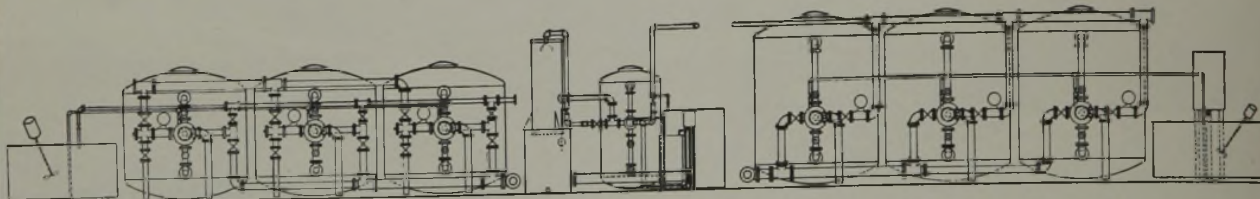
AMERICAN FLANGE & MANUFACTURING CO. INC., 30 ROCKEFELLER PLAZA, NEW YORK, N. Y.  
TRI-SURE PRODUCTS LIMITED, ST. CATHARINES, ONTARIO, CANADA

# DE-IONIZED WATER *replaces* DISTILLED WATER

## AT A FRACTION OF THE COST!

Without *heat*, without fuel, ILLCO-WAY De-ionizing units are daily producing the equivalent of single-distilled water . . . meeting exacting standards in aircraft factories, synthetic rubber plants, chemical industries, etc. . . . This modern economical method is based on ion exchange, and uses Amberlite resins.

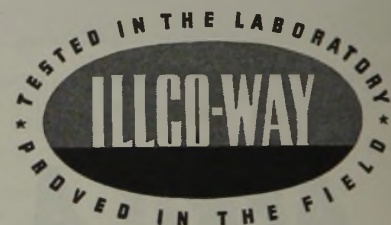
**10,000 GALLONS FOR LESS THAN A DOLLAR!** — on average raw water supply. When water supply is low in dissolved solids, cost may be considerably less!



Unit (above) designed and installed by ILLCO Engineers in an aviation gasoline plant to produce a continuous flow of 36,000 gallons per hour of De-ionized water, at a cost of 7 cents per 1,000 gallons.

**PHARMACEUTICAL PLANT** installation at left has capacity 1,700 gallons per hour. Other units have permissible flow of 100 gallons, increasing up to 50,000 gallons per hour . . . Send for literature.

**ILLINOIS WATER TREATMENT CO.**  
852 CEDAR STREET, ROCKFORD, ILLINOIS



### This is the *Step-Valve*



**. . . that Pumps Liquid Latex, Salt Slurries, Acid Sludge, Other "Difficult" Materials**

Try Milton Roy Pumps for those "impossible" jobs . . . you'll be amazed at the way the patented Step-Valve handles them, without clogging or air-binding. Use Milton Roy Pumps for accurate volume control, from one quart to 2600 gals. per hour; for pumping against high pressures, up to 20,000 lbs. per sq. in.; for pumping light solvents as well as heavy, viscous materials; for practically all chemical services.

These pumps are simple, rugged, with few moving parts, built-in integral-gear motors and adjustable stroke from zero to maximum capacity (while operating if desired) for precise volume control. For description of Simplex, Duplex and Special Types, specifications of entire line and complete information, write for Catalog 941.

*We are still making prompt deliveries of most standard units. If we can help in your war effort 'phone or wire.*

**MILTON Roy PUMPS**  
1365 E. MERMAID AVE., CHESTNUT HILL, PHILA. PA.

### "You Can Rely on Roper"

**16**  
Standard Sizes

**3**  
Standard Series

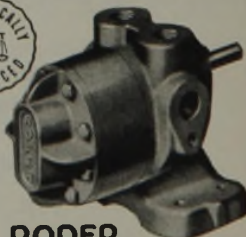
**21**  
Standard Drives and Mountings

**THOUSANDS OF COMBINATIONS... SELECT A MODEL THAT'S PRACTICALLY**

*Custom Built to fit Your Job!*

"PUMP as you never pumped before" is the order for every Roper Pump installed in America's war plants. And Ropers are pumping like sons of guns . . . driving an unflinching flow of oil into the lubricating and hydraulic systems that help convert metals into munitions and engines of war.

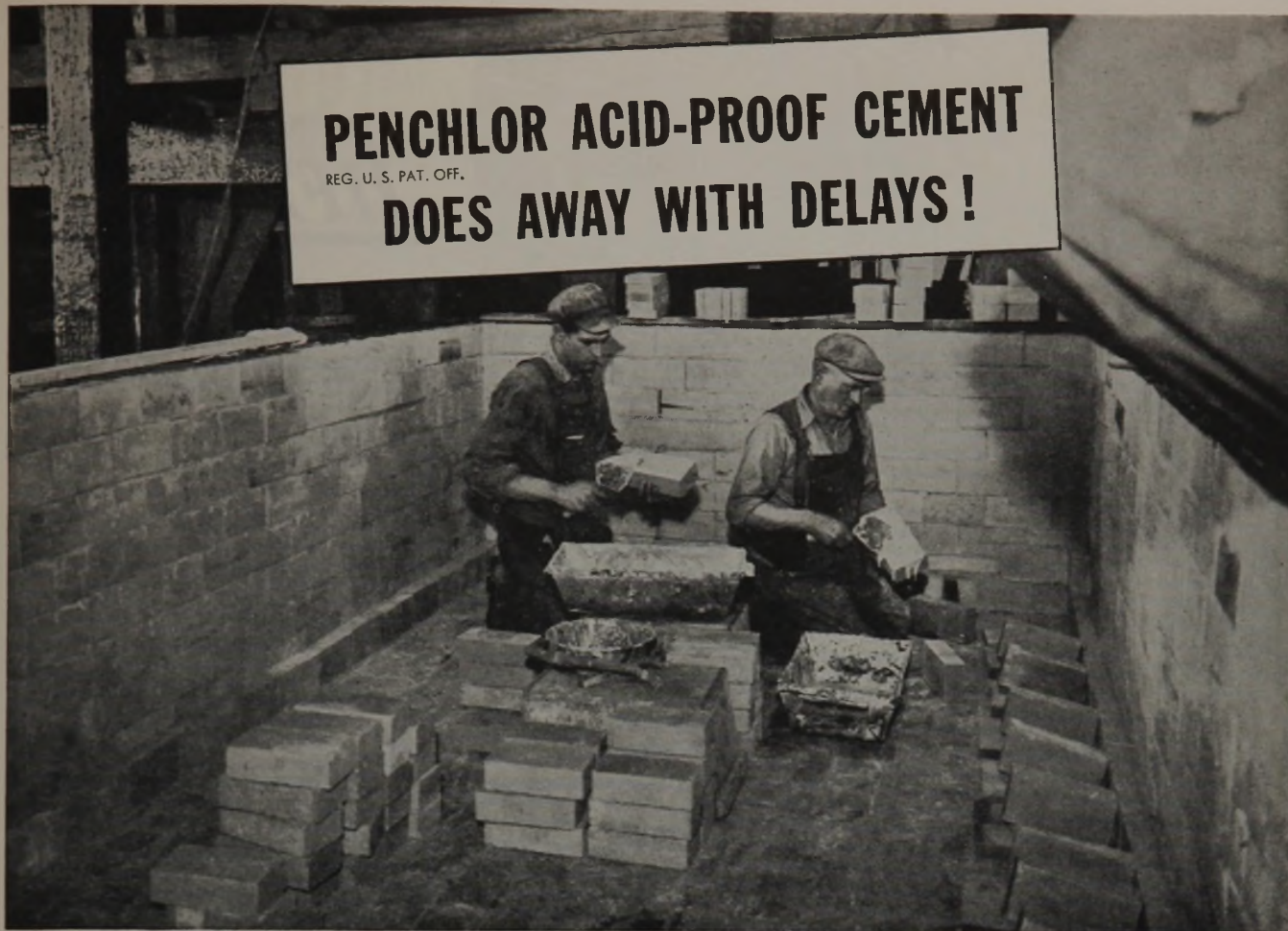
And there are good reasons why Ropers are selected to do the tough war time jobs . . . only two moving parts . . . hydraulically balanced . . . easier to install . . . easier to service . . . longer lasting because of minimum wear . . . quick adaptability to any job because of models with nearly every capacity, pressure, speed, drive, mounting and piping arrangement.



Write For Catalog No. 934

**GEO. D. ROPER CORP., ROCKFORD, ILL.**

**PENCHLOR ACID-PROOF CEMENT**  
 REG. U. S. PAT. OFF.  
**DOES AWAY WITH DELAYS!**



Penchlor Acid-Proof Cement is the fast-setting, self-hardening sodium silicate cement that gets corrosion-resistant equipment into service *quickly!* No long waiting periods... No acid treatment necessary to harden.

And Penchlor Acid-Proof Cement keeps production rolling, too, because it is *long-lasting*—it's good for years of continuous runs without a shut-down! You *know* you can rely on Penchlor. Behind it is a proven record of highly satisfactory performance in the roughest, toughest acid-proof service.

Let us tell you more about adaptable, easy-to-handle, time-saving Penchlor Acid-Proof Cement. Return the coupon *now* for the big, new, *free*, illustrated booklet.

**USED BY THESE INDUSTRIES**

*and many others*

- |                                  |                            |
|----------------------------------|----------------------------|
| CHEMICAL<br>Acids, Alum, etc.    | PETROLEUM<br>METAL WORKING |
| PLATING<br>Including galvanizing | PULP AND PAPER             |
| MUNITIONS                        | TEXTILE<br>Including rayon |

*Also used in the manufacture of:*

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 SPARK PLUGS • GLASS, ETC.

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 MANUFACTURING COMPANY**  
*Chemicals*

1000 WIDENER BUILDING, PHILADELPHIA, PA.

NEW YORK • CHICAGO • ST. LOUIS • PITTSBURGH • WYANDOTTE • TACOMA



PENNSYLVANIA SALT MANUFACTURING COMPANY  
 Dept. IEC, 1000 Widener Bldg., Philadelphia, Pa.

I would like to have a free copy of your new booklet No. 6 on Penchlor Acid-Proof Cement.

NAME \_\_\_\_\_

TITLE \_\_\_\_\_

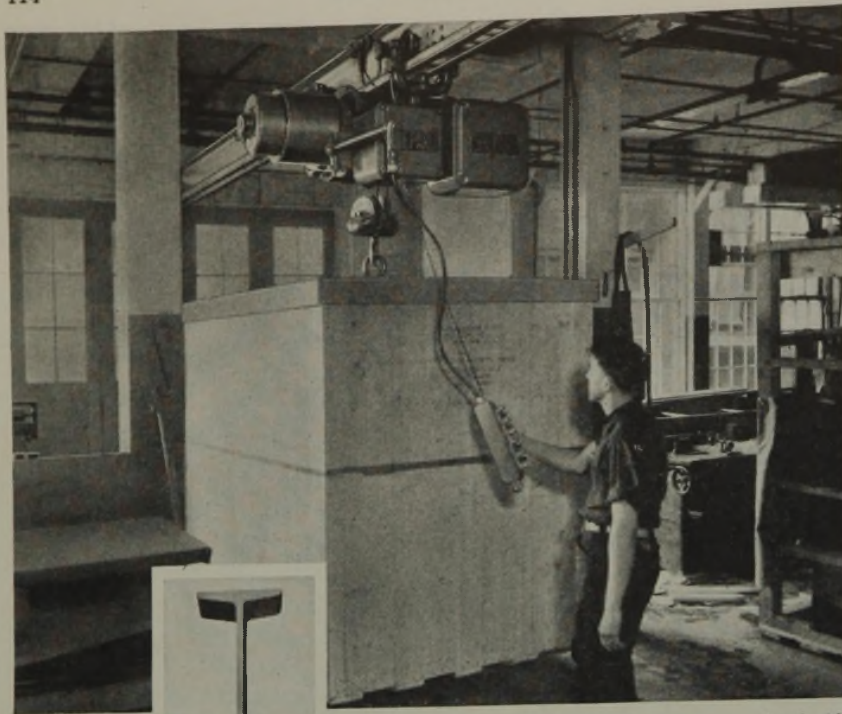
COMPANY \_\_\_\_\_

ADDRESS \_\_\_\_\_

Where conditions require a cement of unusual strength and high resistance to abrasion, consider these Penn Salt resin cements: *Asplit*, for conditions always acid... *Causplit*, for alternate acid and alkaline conditions. These are easy to handle and will withstand a wide range of corrosive conditions up to 350 degrees F.

\* \* \*

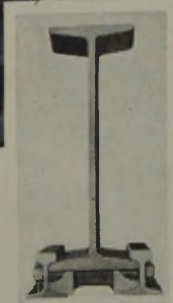
At your service, without obligation, is the long experience of our engineers in handling acids and alkalis in our own plants. Write fully. Or if you prefer, use the coupon.



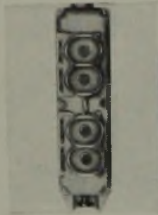
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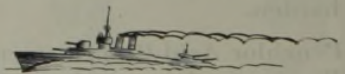
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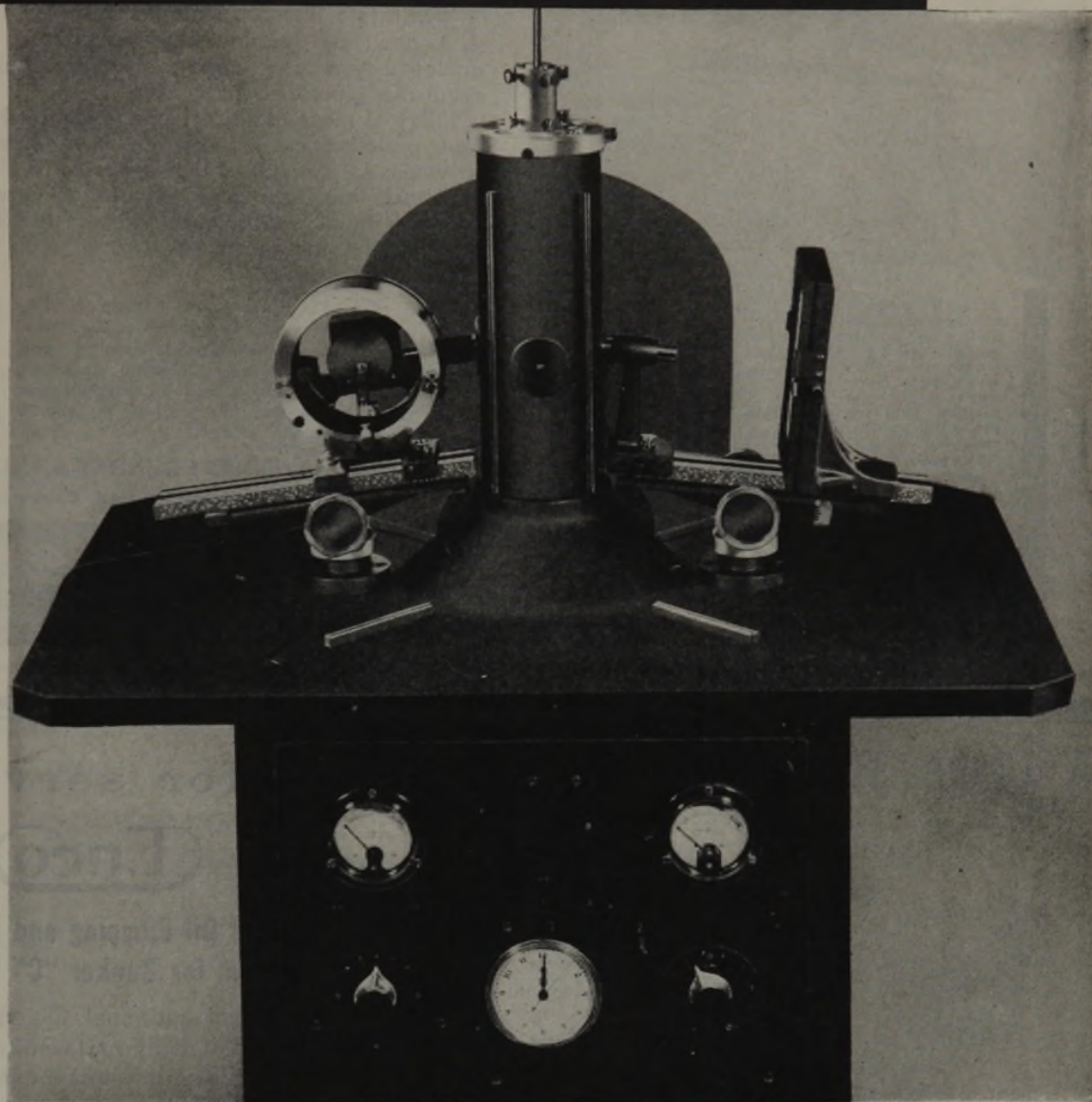
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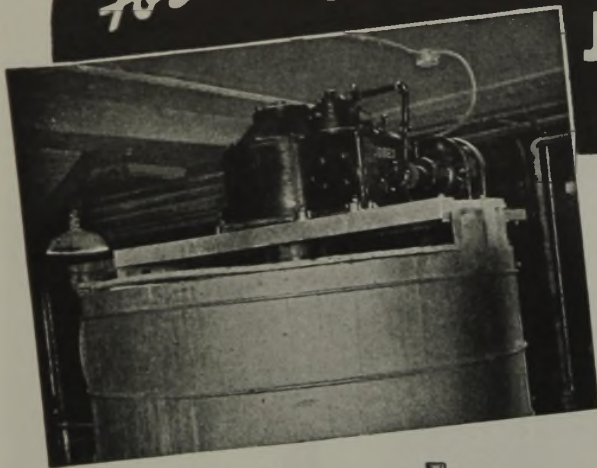
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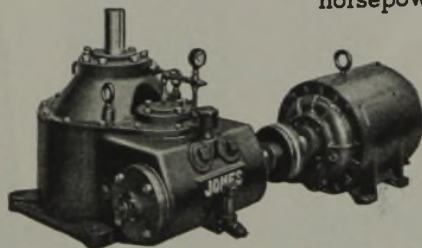
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{ Bulletin 18 contains not only complete information about Kinney Liquid and Vacuum Pumps, but also valuable data regarding the selection and care of pumps in general. }

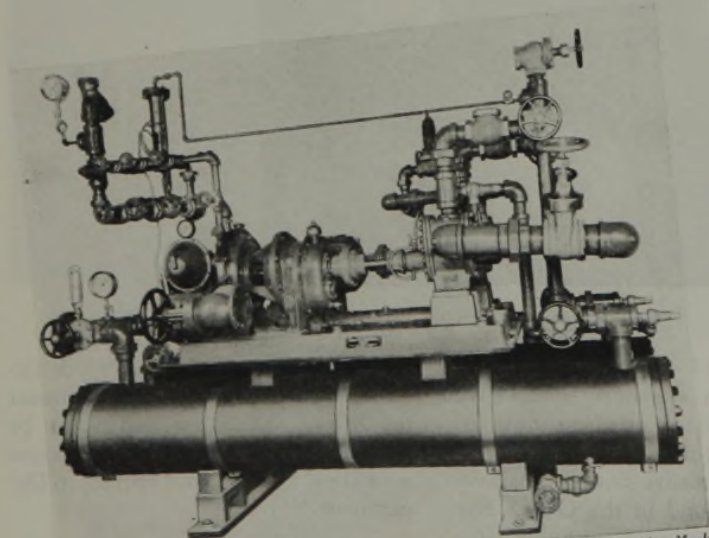


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KINNEY PUMPS give reliable service in war plants.

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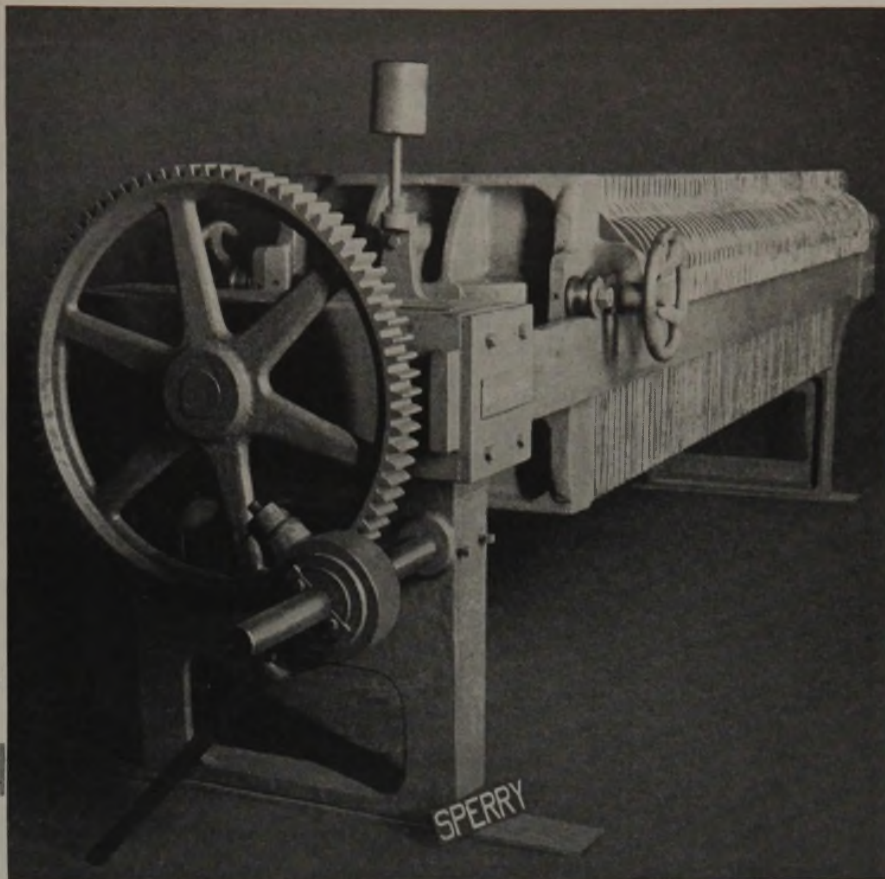
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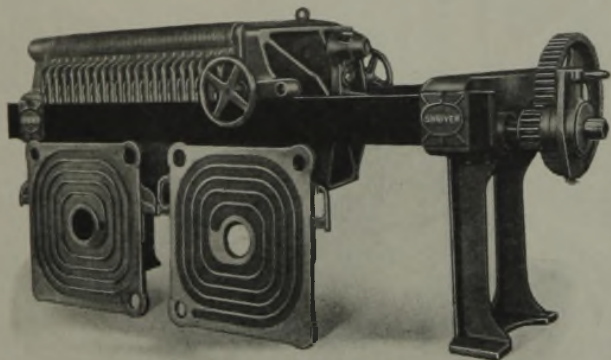


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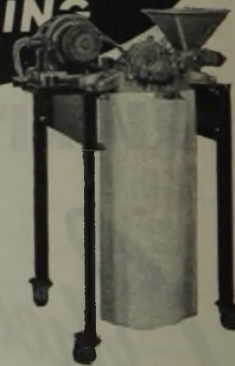
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A.C.S. Monograph No. 88

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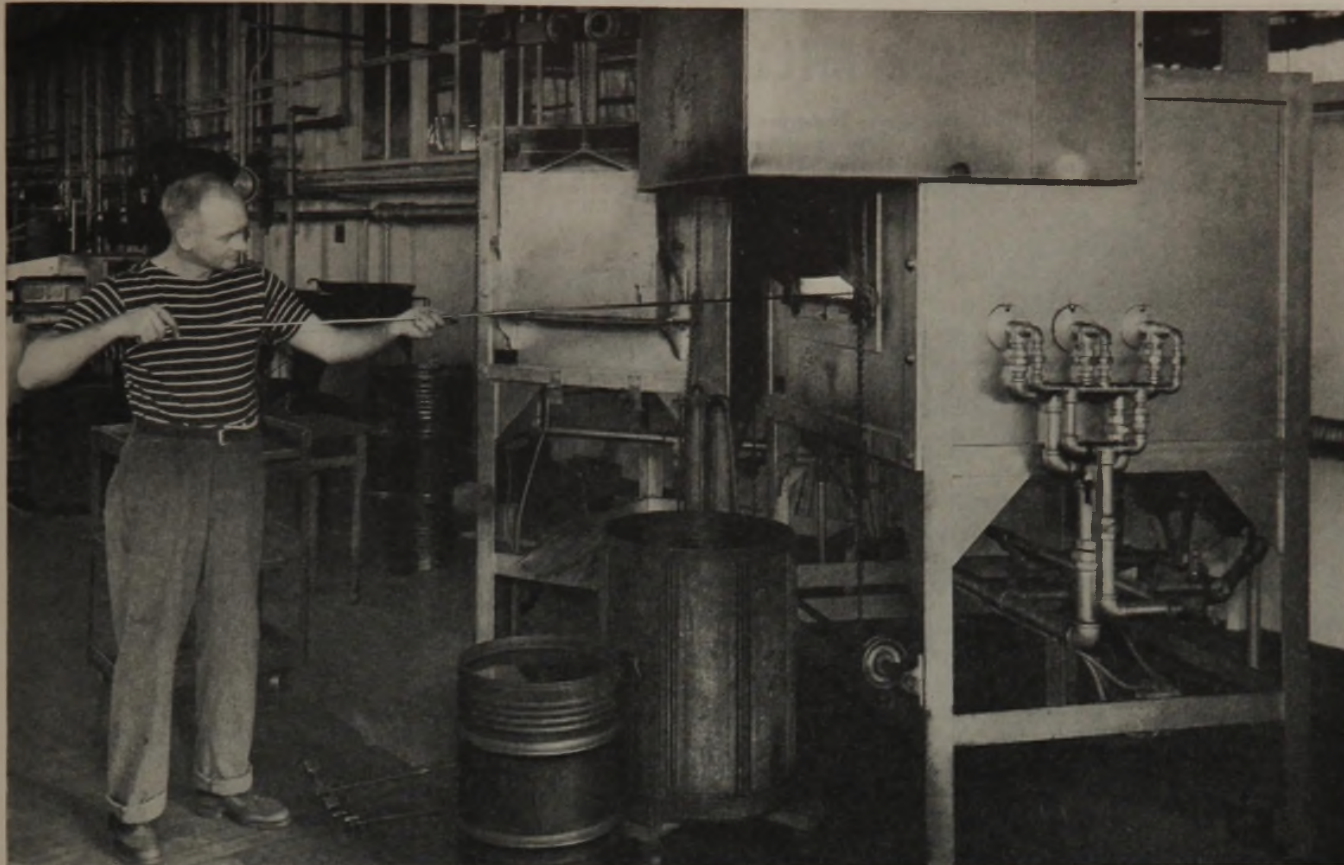
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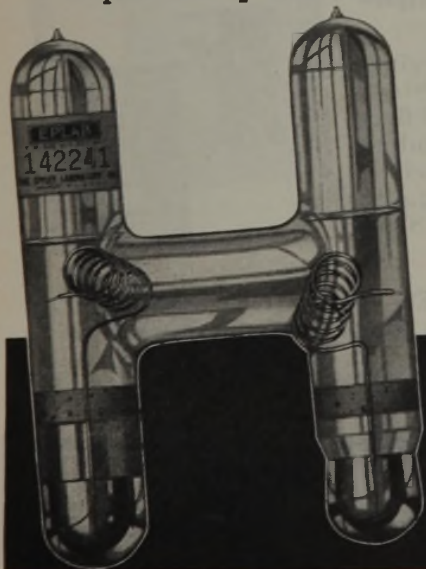
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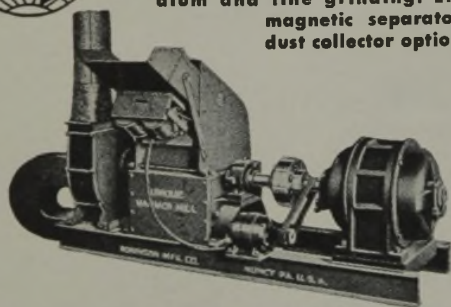
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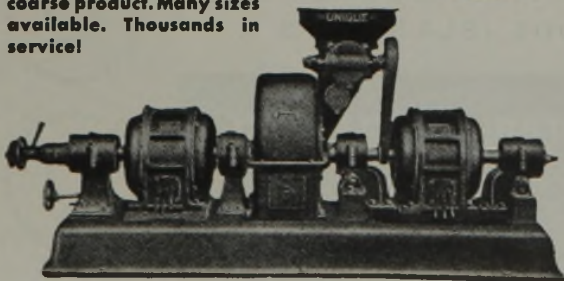
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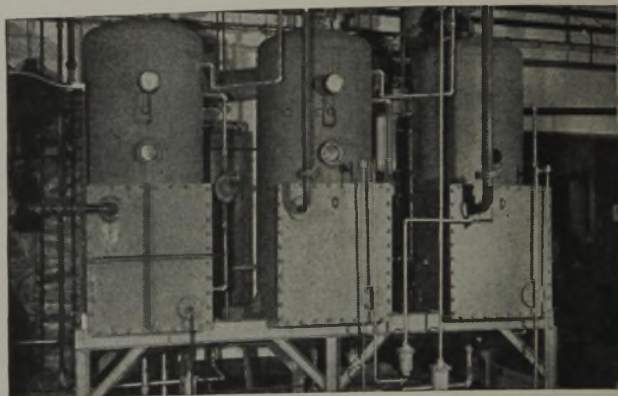
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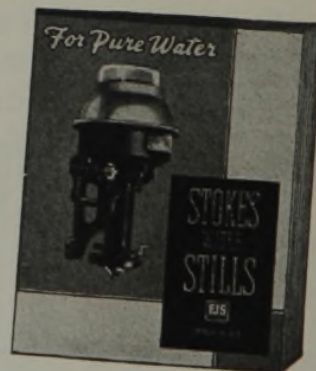
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The development of engineering under the Roman Empire greatly increased the industrial use of ceramics. During the age of Augustus, Rome's foremost architect, Marcus Vitruvius Pollio, advocated the use of vitrified stoneware pipe over lead to guard the purity of drinking water.



## Masterpieces OF POTTERY

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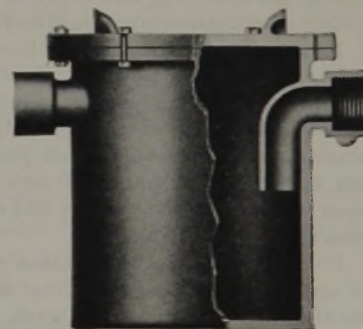
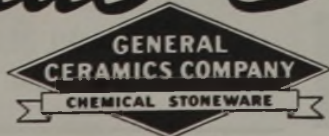


FIG. 770—SUMP

*Other products include Steatite Insulators made by General Ceramics & Steatite Corp., Keasbey, N. J.*

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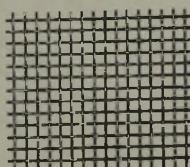
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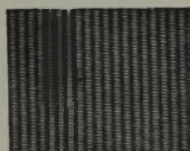
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by J. W. Turrentine  
President, American Potash Institute  
A. C. S. Monograph No. 91

186 Pages. Illustrated. \$3.50

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by Fritz Mayer

Formerly Professor of Chemistry  
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Translated and Revised by A. H. Cook

Department of Chemistry, Imperial College of Science  
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A. C. S. Monograph No. 89

354 Pages. \$10.00

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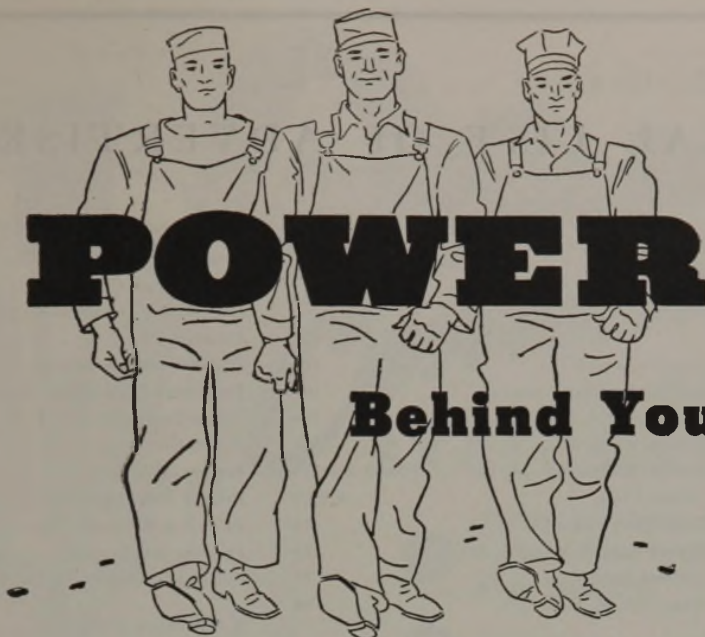
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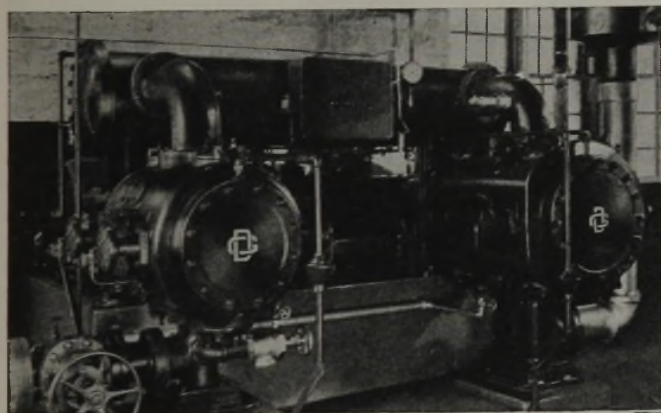
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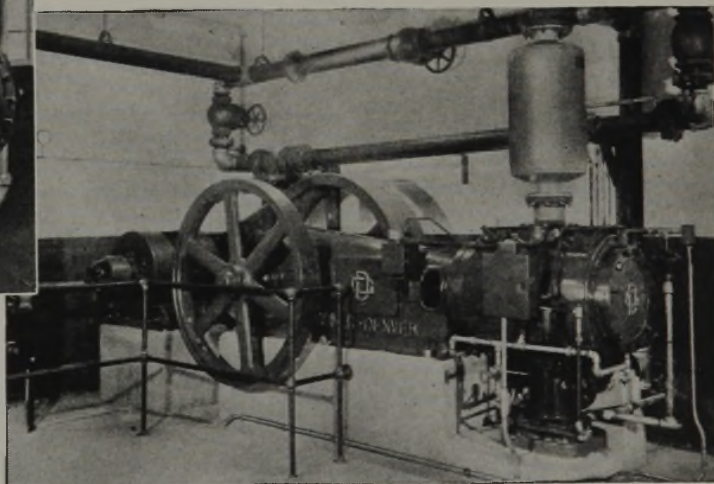
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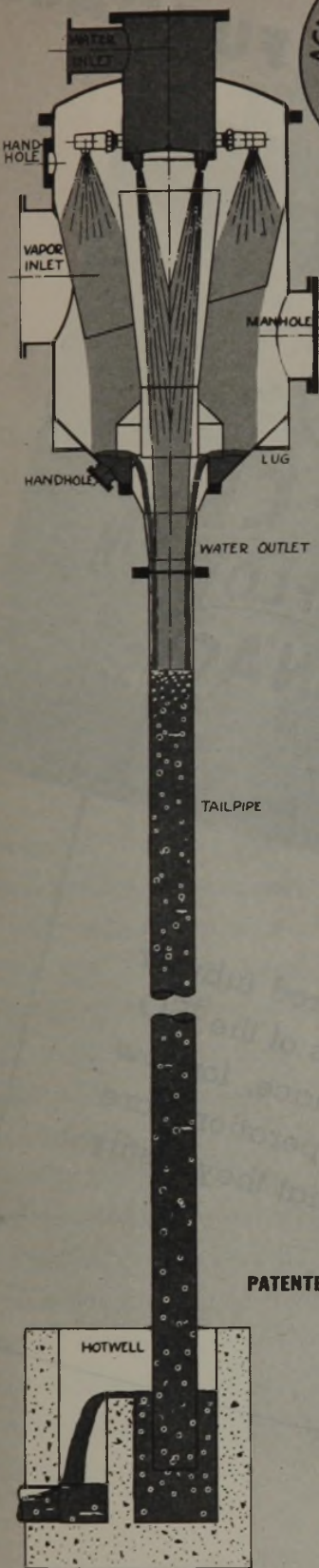
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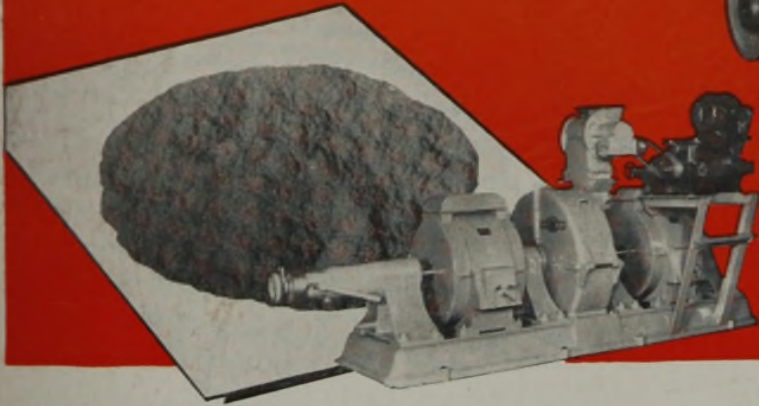


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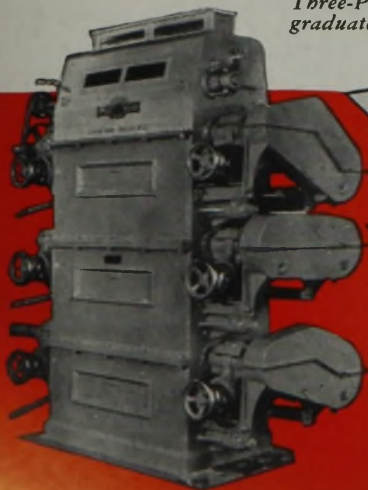
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