INDUSTRIAL
AND
ENGINEERING CHEMISTRY

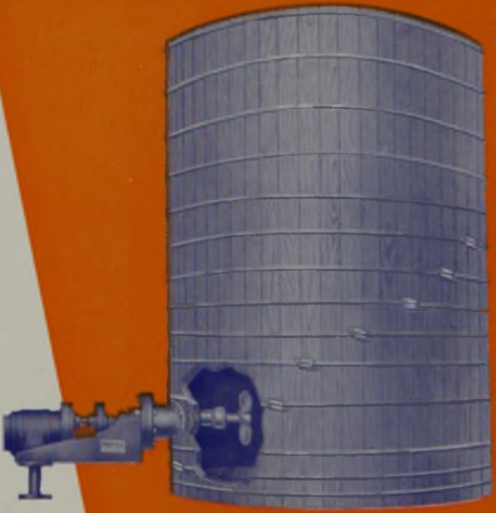
PORTER AGITATED WOOD TANKS

Engineered for Efficiency!

Porter Agitated Wood Tanks are specifically designed and engineered to do a better job more efficiently under a wide range of mill conditions. Although tanks and agitators may be obtained separately, it is advantageous to the buyer to place his order for both together. In addition to getting a job engineered as a unit, proper installation is facilitated by buying both agitators and tanks from one company. Made from the very best grade of lumber, Porter Agitated Wood Tanks are available in a variety of woods and shapes up to 100,000 gallons capacity.


PORTER "WHIRLPOOL" PORTABLE AGITATOR
installed in wood tank


"PORTEREDUCER" AGITATOR
installed in wood tank


PORTER SIDE-ENTERING AGITATOR
built into wood tank

ARMY E NAVY

PORTER
better built
Equipment

Established 1866

Send for illustrated folder.

H. K. PORTER COMPANY, Inc.

PROCESS EQUIPMENT DIVISION • PITTSBURGH, PENNSYLVANIA

INDUSTRIAL AND ENGINEERING CHEMISTRY • INDUSTRIAL EDITION

WALTER J. MURPHY, EDITOR • ISSUED MARCH 3, 1943 • VOL. 35, NO. 3 • CONSECUTIVE NO. 5

UNIT PROCESSES

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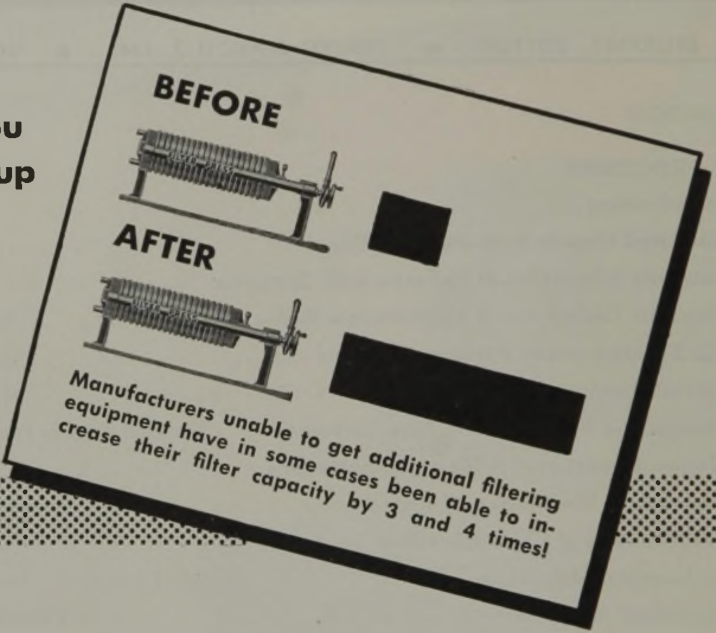
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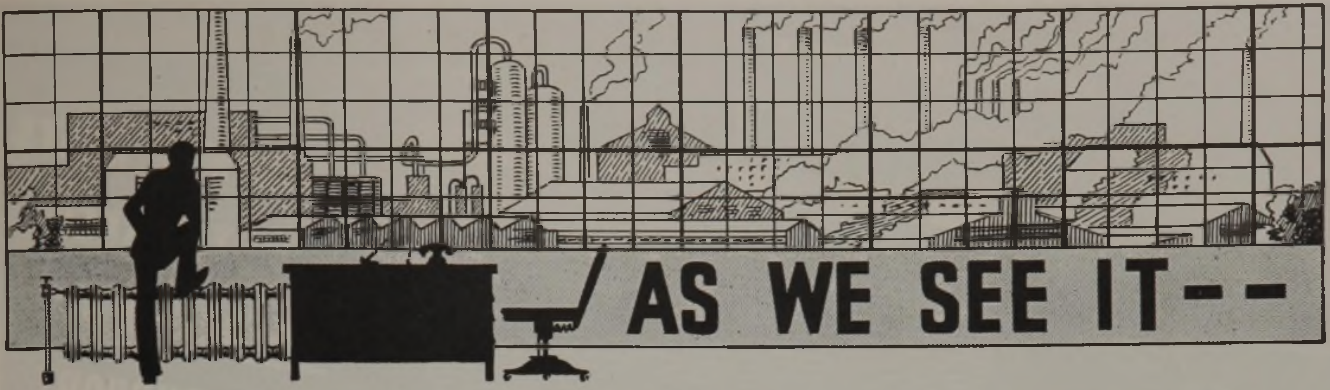


▶ **Unit Processes** are treated in a dozen papers on a wide variety of reactions forming a significant symposium in this issue. Here are discussed the effects of varying conditions on the operation of a number of processes of industrial significance.

▶ **Direct Alkylation of Cresols** by the butane-butene fractions of petroleum refinery gases has been found by Weinrich (page 264) to proceed in the presence of a sulfuric acid catalyst. Di-*tert*-butylphenols thus formed are useful antioxidants for petroleum fractions and softeners for synthetic rubbers. Both laboratory and pilot plant results are given.

▶ **Ethylbenzene**, raw material for producing styrene, is formed by direct alkylation of benzene with ethylene under proper conditions, according to Pardee and Dodge (page 273). Effects of varying pressure, temperature, and catalyst are described for this important alkylation reaction.

▶ **Phthalic Anhydride Production** by the direct catalytic oxidation of naphthalene and naphthalene derivatives has been investigated by Shreve and Welborn (page 279). Two types of oxidizers were used and the effects of varying conditions as well as catalyst are described for naphthalene and four of its derivatives.

▶ **Bagasse**, waste from sugar cane, produces on destructive distillation methanol, acetic acid, and a charcoal which can be satisfactorily briquetted for use, according to Othmer and Fernstrom (page 312). Quantities of bagasse available at sugar *centrals* suggest the possibility of this process for converting it to use.

▶ **Pyrolysis of Wood** in an atmosphere of steam below charring temperatures has been found by Merritt and White (page 297) to produce larger yields of organic acids than commercial pyrolysis and an altered wood of useful properties. Experiments on oak are reported.

▶ **Lignin and Cellulose** in various combinations were subjected to destructive distillation by Katzen, Muller, and Othmer (page 302) to determine the probable genesis of the products. Lignin, they conclude, yields methanol, and cellulose (particularly hemicellulose) yields acetic acid. Products of hydrolysis of wood were raw materials for pyrolysis.

▶ **Tar** and tar-forming constituents in crude pyroligneous acid cause serious trouble in the equipment used to recover its values. Othmer and Katzen (page 288) report that sulfuric acid treatment removes these objectionable constituents as fluid tar oils; they give data on application of the method to pilot and full-scale operations.

▶ **Chlorinolysis** of hydrocarbon derivatives yields hexachloroethane and carbon tetrachloride as ultimate products, according to McBee, Hass, and Bordenca (page 317), who suggest this process as a practicable industrial operation.

▶ **Strontium Carbonate**, the most generally useful compound of this element, can be produced from the sulfate by metathesis with alkali carbonate. Kobe and Deiglmeier (page 323) have studied the process and give data for its optimum operation.

▶ **Sulfonation of 2-Methylnaphthalene** yields monosubstituted compounds interesting as surface-active agents. Shreve and Lux (page 306) have studied sulfonation of this coal-tar product and find that the process is readily carried out in standard equipment.

▶ **Sulfonation of Naphthalene**, using the partial-pressure method of continuously removing water formed in the process, has been shown by Othmer, Jacobs, and Buschmann (page 326) to proceed readily with a minimum excess of acid.

▶ **Neoprene**, originally developed to fill rubber's place in mechanical applications, possesses electrical properties of considerable interest and value, according to Yerzley (page 330), who gives them in detail.

▶ **Pigment Dispersions** such as those in inks, paints, and similar materials may be affected advantageously by the addition of appropriate surface-active agents. Fischer and Jerome (page 336) discuss particularly the influence of such additions to nonaqueous dispersions and the evaluation of various surface-active agents in applications of this kind.

▶ **Polyvinyl Chloride Plastics** require noticeable time to recover from deformation—what may be called "delayed elasticity". This characteristic of a number of plastics is analyzed by Leaderman (page 374) using plasticized polyvinyl chloride as the test substance.

▶ **Ketones** can be produced by the condensation of acid anhydrides with olefins. Byrns and Doumani (page 349) have used polymer gasoline as a source of olefins to be condensed with acetic anhydride. Results on pilot-plant scale are reported.

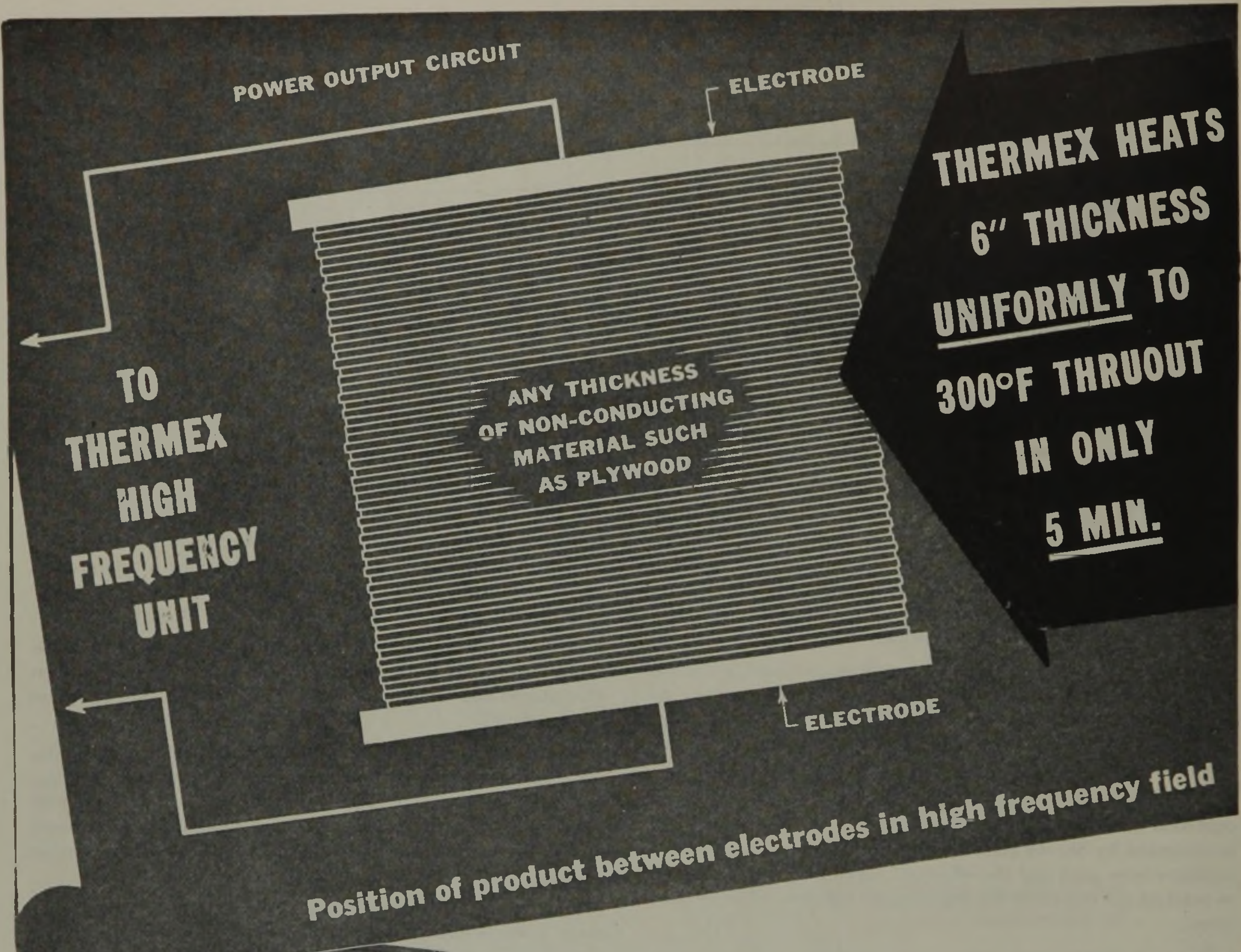
▶ **Coloring of Plastics** is an important element in their value for many purposes. Evaluation of coloring materials for vinyl chloride-acetate plastics on the basis of performance reveals significant differences from their behavior in inks and surface coatings, according to Clark (page 368).

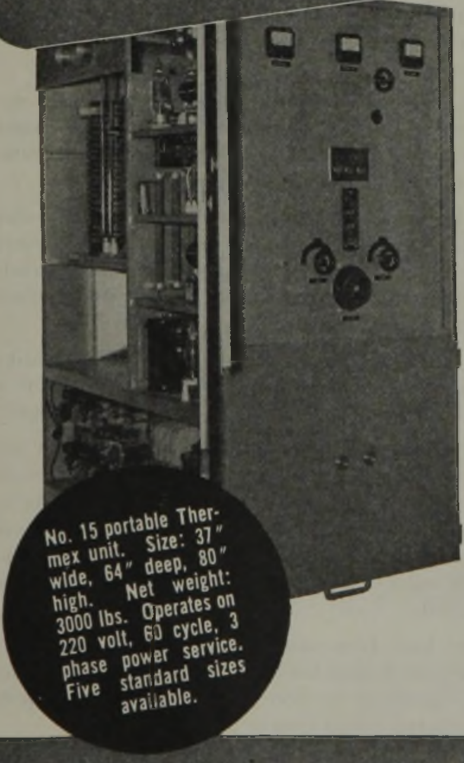
▶ **Azotobacter** (nitrogen-fixing organisms) produced in quantity by the technique described by Lee and Burris (page 354) is a prolific source of several members of the vitamin B complex.

▶ **Corrosion** of the interior of pipe lines carrying refined petroleum products by the water and oxygen unavoidably present is a serious problem. Protection can be secured, according to Wachter and Smith (page 358), by the introduction of sodium nitrite in low concentrations. This method as successfully applied to some 800 miles of pipe line is described as well as the equipment employed.

▶ **Starch Esters** have been examined by Mullen and Pacsu (page 381) with a view to their industrial utilization. They conclude that these substances are more likely to prove valuable in adhesives, sizes, and emulsifiers than as plastics.

DHKilleffer





No. 15 portable Thermex unit. Size: 37″ wide, 64″ deep, 80″ high. Net weight: 3000 lbs. Operates on 220 volt, 60 cycle, 3 phase power service. Five standard sizes available.

Uniform, faster bonding or heat processing of any non-conducting material with Thermex!

Thermex high frequency equipment heats entire mass evenly . . . saves hours over other methods!

The above diagram shows how non-conducting materials may be bonded or heat processed *uniformly* and *quickly*. In this example, a six inch stack of non-conducting plywood panels is heated to 300° F. thruout in only five minutes with Thermex! At least ten hours is required to do the same job by any other method such as with hot plate conductive equipment.

With Thermex, heating is *absolutely* uniform regardless of the thickness of the mass or material. High frequency heating is ideal for practically every non-conducting material. Some of the many advantages of Thermex include: less handling of product, reduced labor cost, no variation in batch production, no surface damage, less danger of overheating, heating can be stopped instantly, no "hot plates" or steam required.

Find out how this remarkable new industrial heating equipment can help in your production. Send for free illustrated booklet today!

The **GIRDLER CORPORATION**

THERMEX HIGH FREQUENCY ELECTROSTATIC HEATING EQUIPMENT

THERMEX DIVISION - - - - - - - - - - - LOUISVILLE, KENTUCKY

GENTLE HANDLING . . . DUST-TIGHT OPERATION WITH THE LINK-BELT Bulk-Flo

CONVEYOR-ELEVATOR-FEEDER

Bulk-Flo is outstanding in its ability to cut handling costs and to conserve critical materials and save space. It minimizes breakage and degradation, prevents leakage and reduces explosion and fire hazards. The necessity for multiple elevating and conveying units is eliminated, because the same unit conveys horizontally, vertically or on an incline.

Bulk-Flo is self-feeding, self-discharging and to a high degree self-cleaning. It handles flowable, granular, crushed, ground or pulverized materials of a non-abrasive, non-corrosive nature under all conditions of loading. Send for catalog No. 2075.

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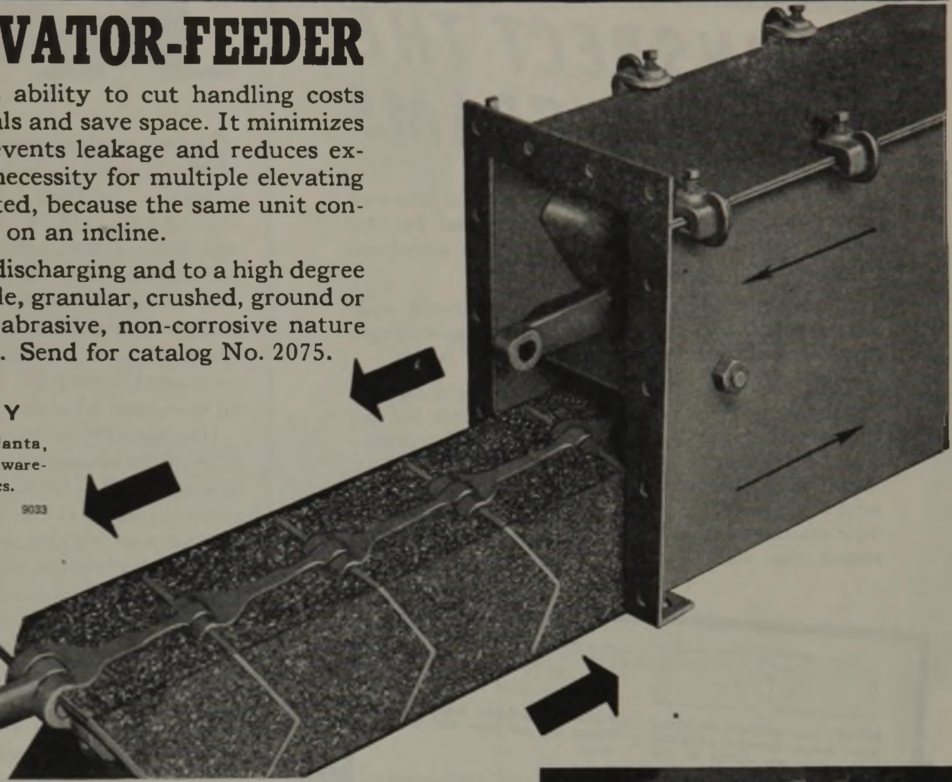


DUST-TIGHT casing prevents leakage. Bulk-Flo conveys and elevates material in a dust-tight casing, making it suitable for handling dusty products. It is successfully used for handling foodstuffs and chemicals where avoidance of contamination or exposure is of prime importance. These illustrations show the construction of casing and flights.

SLOW SPEED

Operating at slow speed Bulk-Flo is recommended for materials that require careful handling . . . minimizes breakage and degradation.

SPLIT DISCHARGE REDUCE DEGRADATION

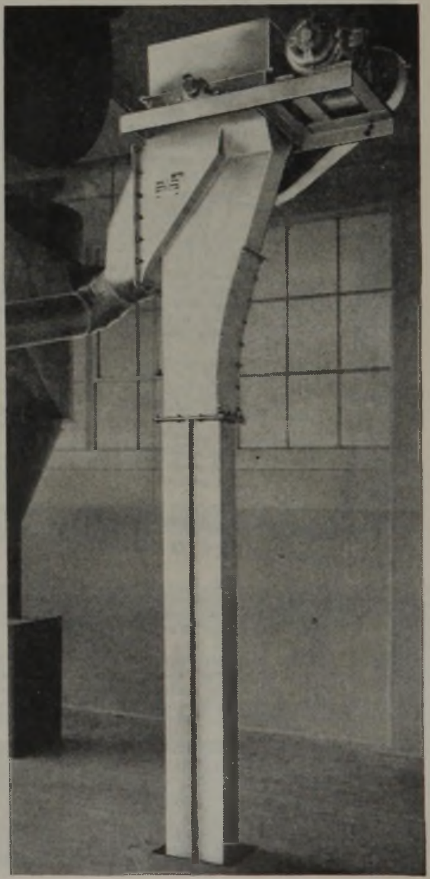
Most of the material falls forward immediately upon reaching gathering chute. The remaining material discharges rearwardly onto chute and flows forward.

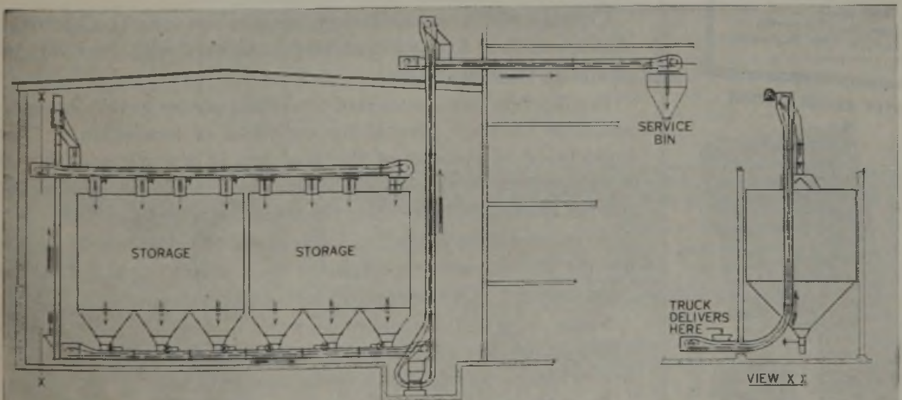
COMPACT DRIVE →

Motorized reducer and chain drive are safe, compact, fully enclosed, easily accessible. Speed changes readily made by changing one sprocket.

SAVES SPACE →

Compact Bulk-Flo casing is so small as to be comparable to a building column. The material moving in a continuous mass occupies almost the entire capacity of the enclosure.





Five Bulk-Flo units with automatic controls handling granulated sugar from trucks to storage bins at 30 tons per hour and transferring from the bins to a service hopper at 7½ tons per hour.

Spying!

With spring now well on its way, important matters must fill our pages to break through the growing lassitude of advancing spring fever. At least, that seems to be the Editor's idea. Leading off the April issue is a piece on that vital and universal material, sulfuric acid. Concentrating used acid is the particular subject this time, and we shall learn of a new method successfully employed in Britain. The basic idea is to use superheated steam as the heat transfer agent for concentrating the acid. The nuisance of acid mist is thus avoided, and significant economies are also effected. At a time when war demands are forcing all acid plant schedules, this article is particularly timely.

Heat transfer we have always with us. The design characteristics of heat transfer between fluids and solids will be developed in some detail. Applications are widely distributed, but for the moment perhaps the most recently prominent is the so-called fluid catalyst now working wonders in aviation fuel. Of course, the familiar checkerwork exchangers also fit the same situation and can be designed on the same basic data.

Distillation and the design of fractionation equipment come up for further discussion. The problem tackled is yields in batch rectification as related to holdup in the column. Both binary and more complex mixtures are studied.

Thermodynamic properties in the liquid state are used in generalizations of wide application. From a minimum of data directly determined, the methods described permit the calculation of values of other properties of liquids and vapors with sufficient accuracy to serve as useful approximations for many purposes of design where available data are fragmentary or unreliable. This ability to expand and to check data in regions where direct determination of values is difficult is proving especially useful in these days when design and construction must go forward ahead of precision measurements.

From such obstruse thermodynamics we next will go to the apparently homely problem of preserving powdered citrus juices. Caramelization of sugar in preparations with citric and tartaric acids proceeds at relatively low temperatures. Apparently storage at the temperatures commonly encountered in this global war may lead to disagreeable changes in such materials. The piece on this subject, which comes from South Africa, suggests ways to prevent or minimize these changes.

Cellulose fibers, we shall learn, seem to owe their sheet-forming abilities to their hydration which is connected with the hydroxyl groups in their molecules.

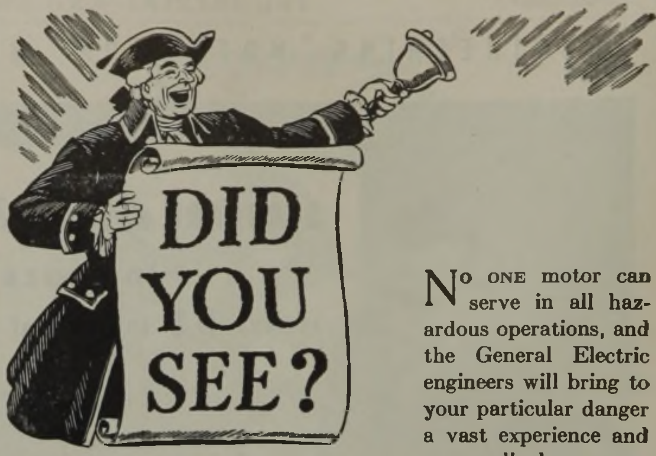
Equilibrium data systems of two liquid phases have been determined as they are affected by variations of temperature. The importance of systems of the kind lies in the widening use of liquid extraction processes in industrial operations such as the solvent refining of lubricating oils and a growing list of others.

Stress-strain characteristics of synthetic elastomers are becoming increasingly important as their uses expand. Data on vinyl polymers variously plasticized will be given.

Vapor compositions obtained from binary solutions (vapor-liquid equilibrium data) will be given for some twenty-five different binary solutions not heretofore reported.

And, of course, there will be more, much more.

YOUR HUMBLE SPY



DID YOU SEE?

No one motor can serve in all hazardous operations, and the General Electric engineers will bring to your particular danger a vast experience and an equally large number of motors, all designed to operate safely in varied atmospheres. Explosion-proof squirrel-cage motors up to 600 horsepower for locations exposed to flammable vapors, a different type for dusty spots where the coal or coke flying around make the whole plant a supercharged bomb, and still another construction for the pyrotechnical twins—aluminum and magnesium—give us some idea about the choice allowed. Naturally the designing engineer as well as the "op's" boys want to know this because, as G. E. points out, a right selection can eliminate the massive fire walls and the intricate arrangements for pushing a drive through the barricade without a bit of atmosphere showing through.

Getting away from unconfined gases to the job of pushing them around pipes in response to $DV\rho/\mu$ (and also responsible to it), the Elliott Company has a smooth message which will take a few bumps out of the task of picking a blower.

Speaking for myself, I like to read the ads of the Aluminum Company. They always have a message, usually teach something, give me facts. An engineer appreciates that. Examples are the two in this month's issue. One points out that an aluminum alloy roof withstood nine years of attack by sour distillate on one side, and dirt, soot, and elements on the other. Then, too, the Alorco Division points home a story on the necessity of not sweating in the mercury-arc rectifier repair room. By using activated aluminas, gases may be dried at either atmospheric pressure or up to 3000 pounds per square inch. Moisture, to a dew point of −110° F., is completely removed. Such ads make a man think, give him the shove to start his mind soaring and "imagineering".

If you want a quick construction job on corrosion-proof vats, such as pickling tanks, consider the message from the Pennsylvania Salt Company. By using their Penchlor acid-proof cement, a tough, lasting bond is made and the cement sets quickly—but good.

The Marley Company specializes in cooling towers; judging by the map they have printed, showing the installations in certain parts of the world for the armed forces in liberty's cause, the preparation to put a couple of "hot-shots" on ice are enormous. Marley's business has increased so much that if 1941 was 1, 1943 is 6. Perhaps that chill Hitler has isn't only from a Russian winter.

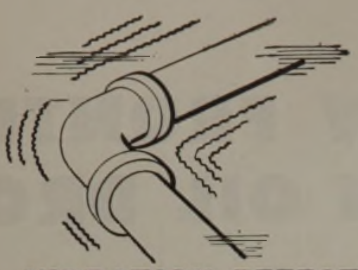
Telegram to the Fairbanks-Morse Company: "Please send me a scale quick. From the list of things you mention in this month's ad, it can do more things than my plant manager."

Calgon, to those of our profession who are running pulp and paper mills, is becoming increasingly important. Look it up in this month's ad. There, you will see that 2–10 p. p. m. of Calgon will inhibit corrosion of iron in the feed water; 30–40 p. p. m. will improve pulp washing in the pit, 0.5–1.0 per cent will do wonders in dispersing pigments in coating operations, and 10–20 p. p. m. helps disperse sizes in the beater. Calgon is the trade name for glossy sodium phosphate products.

Phil T. Press

How to eliminate these piping troubles that hamper war work:

Weld with **TUBE-TURN** WELDING FITTINGS

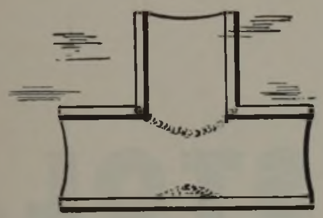


VIBRATION EFFECTS

You need never worry about vibration or strain loosening a *welded* joint.

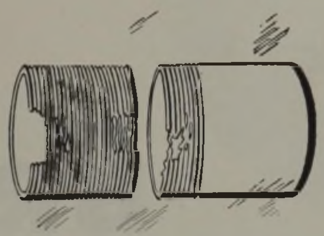
GASKET CHANGES

Fewer flanged joints mean less gaskets—save materials and time.



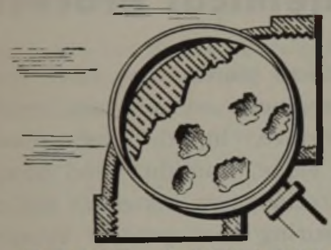
SLAG ACCUMULATION

Butt welds with Tube-Turn fittings virtually eliminate danger of slag.



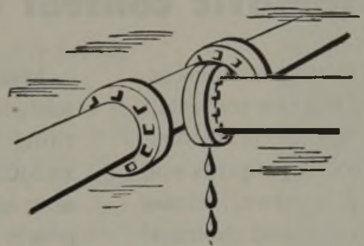
WORN THREADS

Threading thins and weakens metal—causes failures.



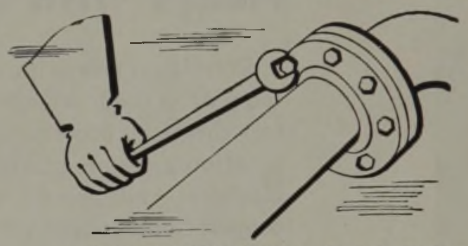
RAPID CORROSION

Tube-Turn fittings resist corrosion because of better metal structure.



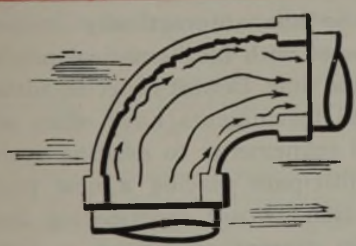
LEAKAGE REPAIRS

No chance of loose connections or leaks with Tube-Turn fittings.



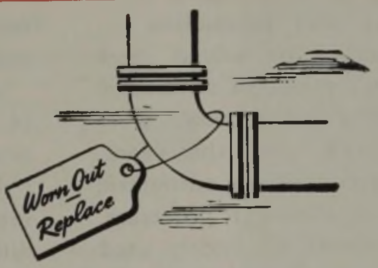
LOOSENED BOLTS

The more welding fittings used, the fewer bolts there are to tighten.



INEFFICIENT FLOW

Easy sweeping radius and no offsets inside mean less pressure loss.



FITTING REPLACEMENT

There's far less time loss or replacement expense with Tube-Turn welding fittings.

SLOW INSTALLATION

Tube-Turn fittings line up perfectly; allow fast, simple, easy butt welding.

NO. 3 OF A SERIES

HOW TUBE-TURN WELDING FITTINGS BENEFIT WAR INDUSTRY

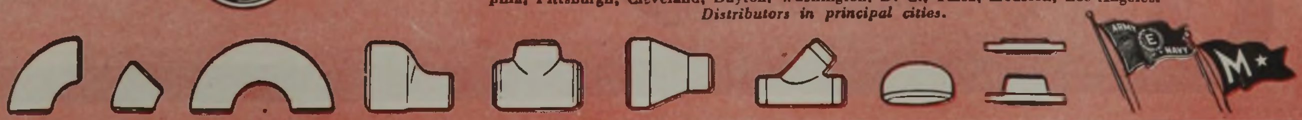
The FIRST WELDING FITTINGS 1ST AND STILL THE BEST

TUBE-TURN

TRADE MARK

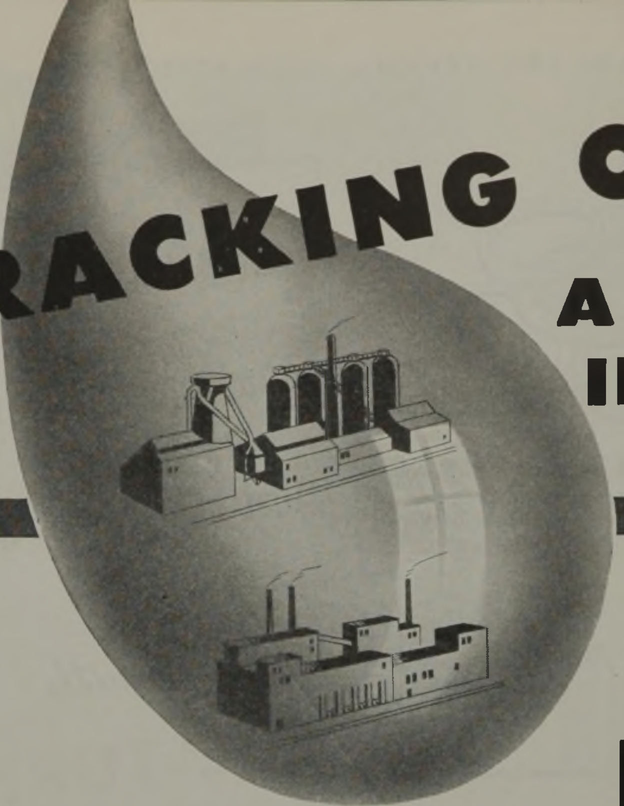
Welding Fittings and Flanges

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.



CRACKING OPEN

A NEW FRONTIER IN AN OIL DROP



BRISTOL..

brings to new refining problems the broadest experience with automatic control of chemical processes

Petroleum refineries are taking an increasing part in the production of the raw materials for chemical processing. Synthetic rubber, aviation gasoline, plastics, cooling liquids and alcohols — all point toward a newer, closer cooperation between oil refinery and chemical process plant.

This may mean, for executives in both fields, additional supervisory worries arising from a new complexity of operating variables affecting cost, quality and production . . . worries which may often be solved most efficiently by new applications of automatic controlling and recording instruments.

Bristol engineers have, over the years, gained wide experience in applying automatic control instruments to chemical processes. Today, Bristol Instruments are widely used in many of the most progressive plants in the country.

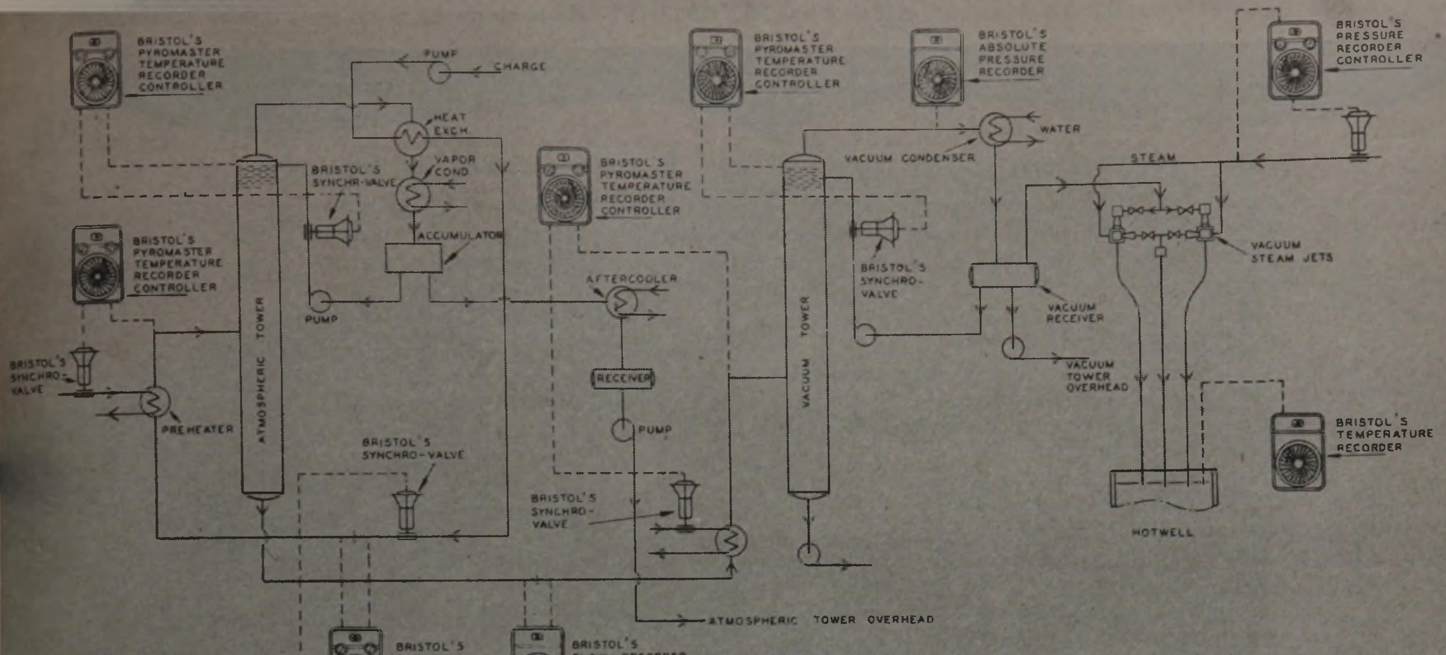
Many chemical plants, that have worked with Bristol engineers on processes involving time, temperature, liquid level, pressure, vacuum, pH value, humidity and flow, are now saving precious raw materials and manpower by insuring that process equipment will operate on the exact production schedule planned for best results. In certain cases, Bristol's Coordinated Process Control has been applied to critical factors never before controlled, or has automatically controlled entire processes with mathematical precision.

At the same time, Bristol's specific advances in individual instruments have often added new control refinements to existing systems.

If you anticipate placing a new product into production, or are experiencing control difficulties in present operations, a note on your letterhead will bring a Bristol engineer to consult with you without cost or obligation.

Engineers Process

AUTOMATIC CONTROLLING AND RECC



OIL REFINING
VACUUM RERUN DISTILLATE UNIT

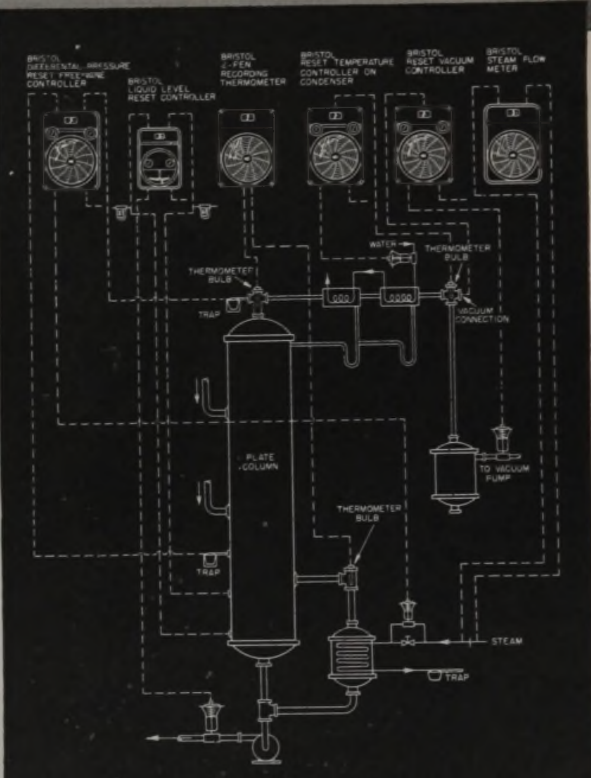
3 Reasons for Top Performance of Bristol's Pyromaster in Vacuum Rerun Distillate Unit

The installations shown on this diagram include Bristol controllers and recorders of temperature, pressure and flow, as well as Bristol's Synchro-Valve designed for accurate response to Bristol's Free-Vane Control. Bristol's Pyromaster features prominently in the success of this application, owing to (1) absence of sparking hazard from open contacts, (2) ease of adjustment, without removing chart or chart dial, or interrupting process, and (3) low maintenance cost, since no oiling or greasing is necessary, and no parts move except when reading changes.

A Bristol Differential Pressure Controller Insures Right Steam Input in 30-Plate Separation Still

Of the many different types of automatic control systems designed by Bristol engineers for still operation, one novel type is shown to the right. This system has proved to be exceedingly satisfactory on a 30-plate column for separating formaldehyde solution and alcohol.

A Free-Vane Differential-Pressure Controller connected to the bottom and top of the column regulates the steam input to the still to maintain a constant outlet temperature. The Differential Pressure Controller "feels" changes in "feed" immediately and increases steam input, making flooding of the column in this case much less likely.



AUTOMATIC CONTROL OF STILL

Control for Better Products and Profits

Bristol's Instrument Co., Ltd.

THE BRISTOL COMPANY
109 Bristol Road, Waterbury, Conn.

The Bristol Co. of Canada, Ltd.
Toronto, Ontario

Red Lead

Special grades of Eagle Red Lead are available for the paint, storage battery, ceramic and varnish industries. $Pb_3 O_4$ content accurately maintained to meet exact requirements of each industry.

Litharge

Eagle Milled Litharges are exceptionally high standard lead oxides. They are finely ground, low in impurities and light brown in color. Available in special grades to suit each industry.

Sublimed Litharge

A fumed, amorphous, light canary yellow monoxide of lead (PbO) of low apparent density. Purest and smallest particle size type of Lead Oxide on the market.

Orange Mineral

Eagle Orange Mineral has a definite orange tone and is noted for its strength, fineness, and uniform color. 95% minimum. Outstanding for paints, colors, inks.

Zinc Oxide

Eagle Zinc Oxide AAA is especially designed for use wherever a lead-free, American process zinc oxide is required. Exceptionally white and bright pigment, having excellent tinting strength and opacity. Produced in a series of varying paint viscosity ranges.

Leaded Zinc Oxides

A complete line of all types and grades, notably Eagle AA 5% Leaded Zinc Oxide; Eagle A 35% Leaded Zinc Oxide; Eagle 50% Leaded Zinc Oxide.

White Lead Carbonate

Three types of Eagle Dry White Lead Carbonate are produced. Unite chemically with linseed oil to form an elastic, deep-anchoring, long-wearing paint film.

Sublimed White Lead

For years, the standard basic sulphate of white lead. For the paint or rubber industries. Exceptionally white and bright. Conforms with ASTM and government specifications.

Lithopone

A precipitated white pigment of normal or regular type. Three general grades — A, AA, AAA, signifying low, medium and high oil absorption respectively. Has a clean, white color.

Titanated Lithopone

Eagle Titanated Lithopone is a precipitated white pigment blended with 15% Titanium Dioxide. Available in grades to suit individual requirements.

Lead Silicate

Eagle Lead Silicate is especially designed for the ceramic industry and is outstanding for uniformity, high purity and advantageous physical properties. Free from uncombined lead oxide and silica. Granular particle size; remarkably dustless.

* * *

Above products are included in the comprehensive line of zinc and lead pigments manufactured by The Eagle-Picher Lead Company for the paint, chemical, varnish, storage battery, rubber, ceramic and other process industries. Eagle-Picher research facilities are available to manufacturers on request. Write for free samples and literature.

EAGLE-PICHER

Industrial Pigments

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THE EAGLE-PICHER LEAD COMPANY

General Offices • Cincinnati, Ohio

VITRIC-10 the quick-setting, acid-proof cement without critical temperature points . . .

SPEEDS CONSTRUCTION ★ LOWERS COSTS

"Vitric-10" quick-setting, acid-proof cement saves days of precious time in putting acid-proof masonry construction into use.

Not only can newly-built acid-proof masonry be ready to use within the amazingly short period of 24 to 36 hours, but actual construction time itself is speeded up immeasurably. With the average air-drying cement only a few courses of brick can be laid per day, lest the slow drying cement be squeezed out of the lower courses of brick. With "Vitric-10", however, the number of courses of brick laid is limited only by the speed and ability of the mason.

"Vitric-10" hardens entirely by internal chemical reaction, taking an initial set within 20 to 25 minutes and a final set within 24 to 36 hours. No artificial heating or drying is required. Unlike the average cement whose surface drying rate is more rapid than the interior rate, "Vitric-10" hardens uniformly throughout the joints and behind the brick, with a minimum of shrinkage.

"Vitric-10" bonds tightly to most construction materials. It is immune to all acids, hot or cold, in any concentration (hydrofluoric acid excepted) as well as to hot or cold salt solutions of all strengths (except those prone to excessive crystal development). "Vitric-10" possesses unusual mechanical strength with minimum porosity; excellent resistance to abrasion; is unaffected by abrupt temperature changes; and is simple to handle and use.

OTHER "U. S. ACID-PROOF" CEMENTS FOR SPECIAL USES

"Pre-Mixt"—requires only the addition of water.

"Portite"—sulphur base heat-and-pour type cement.

"Vitric" Fire-proof Cement—for acid conditions continuously above 500 deg. F.

"Duralon"—a new synthetic resin cement, completely non-porous, with high compressive and tensile strength.

●

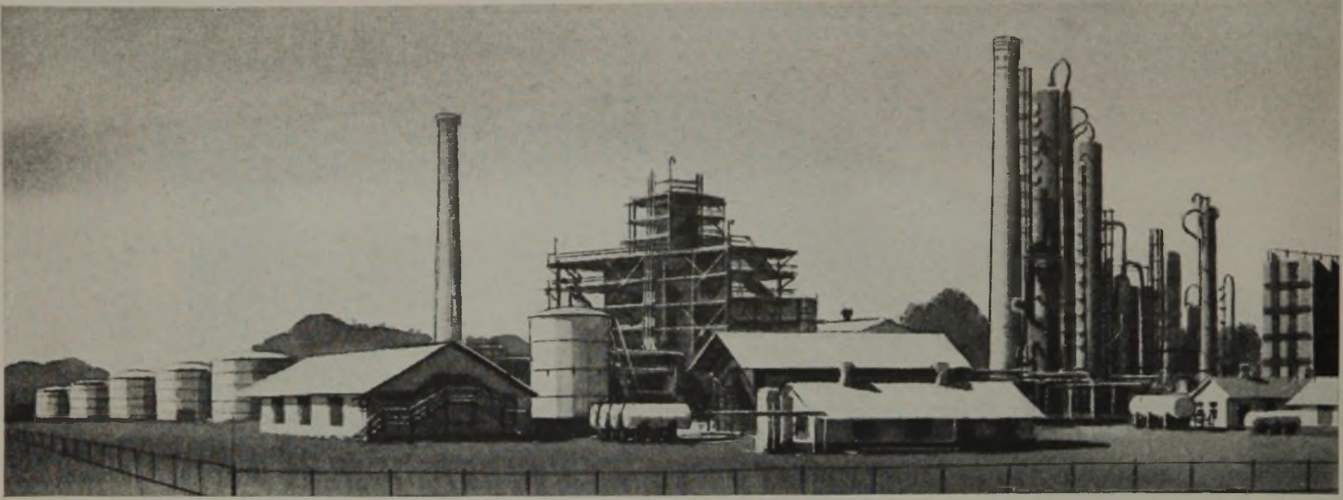
With U.S. Stoneware's "Ussco" Acid-Brick and our wide range of acid-proof cements suitable combinations can be found to work satisfactorily under the most severe operating conditions.

Would you like a sample of "Vitric-10" or other U.S. Stoneware acid-proof cements for your own tests? Or additional literature? Please feel free to write, without obligation, to U.S. Stoneware Company, Akron, Ohio. In Canada: Chamberlain Engineering, Ltd., Montreal.

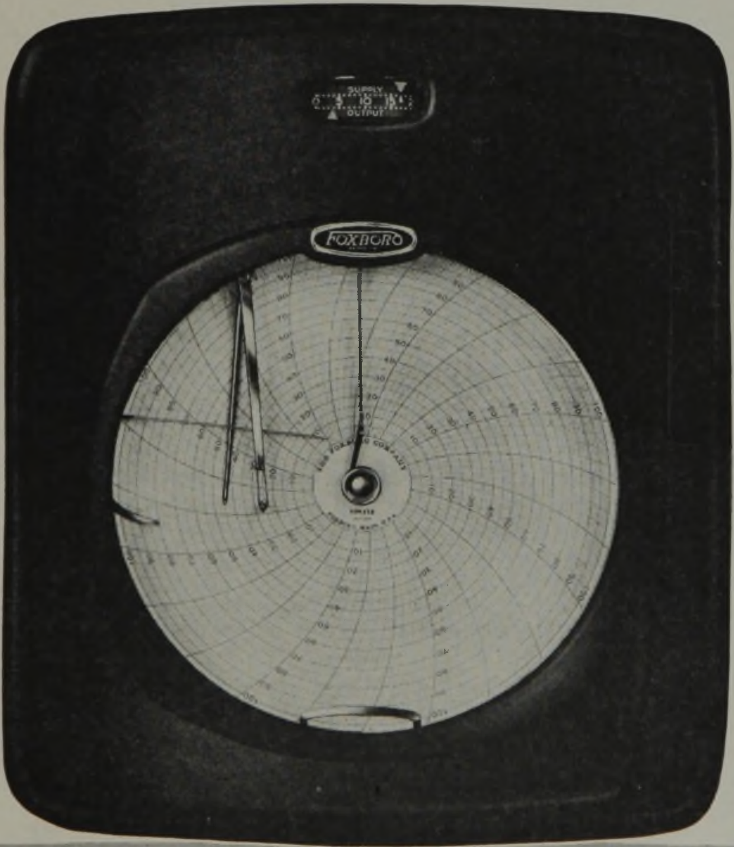
U. S. STONEWARE

AKRON, OHIO

TURERS • ERECTORS OF CORROSION-RESISTANT EQUIPMENT



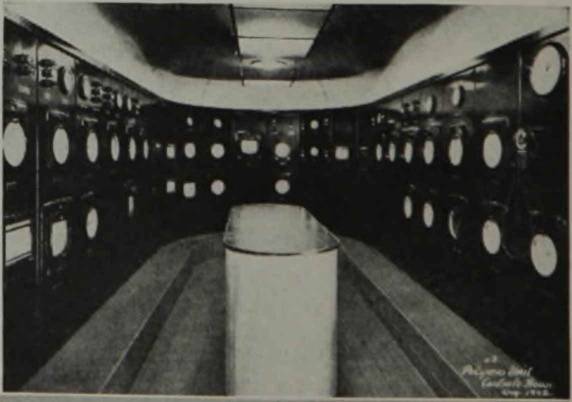
Picture of a 1943-Model



HYPER-RESET in the Stabilog Controller sets new precedents of stability in processing control. By measuring the *rate of change* of every disturbance at the very start and instantly reacting to meet the *maximum*, it brings smoother recovery . . *in as little as ¼ the usual time . . with as much as 50% reduction in the amount of upset!*

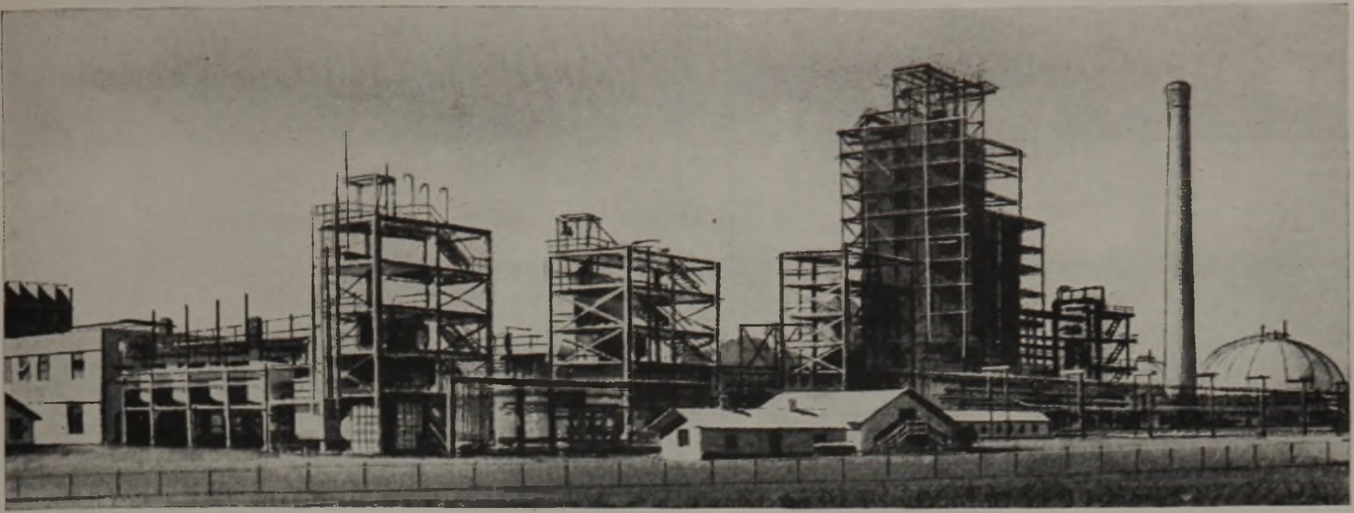
• • •

Polymer Unit Control House of a leading petroleum processer. One of many recent installations of Stabilog Controllers with HYPER-RESET.



Stabilog
REG. U.S. PAT. OFF.

Controllers with HYPER-RESET



RUBBER "PLANTATION"...

... producing bumper wartime crops through aid of modern Super-Controls!

There's a world of difference between the pre-war tropical sources of natural rubber and the wartime synthetic rubber "plantations" now coming into production right within the United States. For, "cultivation" of synthetic rubber is a complex chemical process so exacting that every critical step must be minutely controlled by instruments of super-accuracy and sensitivity.

Since earliest experimental days of synthetic rubber development, Foxboro's famous Stabilog Controller has played a major part in maintaining the delicate balances of temperature, pressure and flow-rate required in this process.

At the very time when America's vast synthetic rubber program started, Foxboro research made available an additional unique refinement .. HYPER-RESET .. in this original stabilizing controller. Today, throughout the country's new synthetic rubber, aviation gasoline, and other war chemical plants, Stabilog Controllers with HYPER-RESET are providing stability *never even approached before* in process operation!

Write for Bulletin A-330 containing detailed information on Stabilog Controllers with HYPER-RESET .. the leading stabilizing controllers in wartime chemical processes. **The Foxboro Company, 74 Neponset Avenue, Foxboro, Massachusetts, U. S. A.** Branches in principal cities of United States and Canada.

• • •

Typical installation of Stabilog Controllers and other Foxboro Instruments for complete, centralized plant control.

.... by FOXBORO

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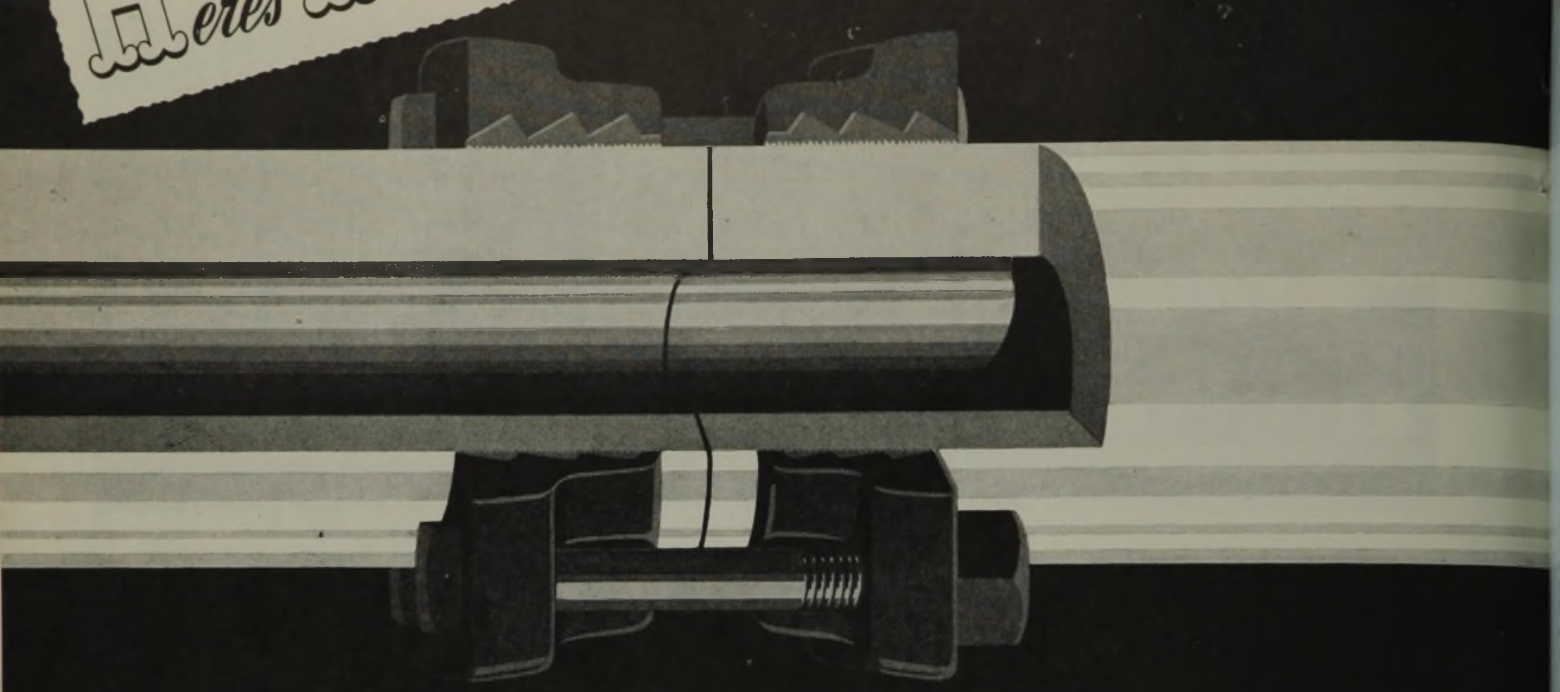
Here's How:



TROUBLE IN PIPING FOR CORROSIVE LIQUIDS FREQUENTLY STARTS WITH GASKETS

Lapp Raschig Rings bring to tower packing all the advantages of Lapp Chemical Porcelain—iron-free purity, high strength, non-crumbling long service. Most sizes are available from stock.

Pipe of *Lapp Chemical Porcelain* is Quickly Installed . . . *Eliminates Gasket Trouble*

We've heard all sorts of tales of woe about corrosion-free piping, joints of which could be made to seal only with thick soft gaskets, drawn tight. A fundamental advantage of Lapp Chemical Porcelain as a material of industrial processing is the ease and accuracy with which it may be machined and ground. In Lapp Chemical Porcelain, pipe ends are fine ground to a smooth flat surface. In installation, we recommend hard thin gaskets; by minimizing the gasket surface exposed to corrosion, much possibility of trouble is eliminated at its source. For special applications, where no gasket material can be tolerated, pipe and valve ends are polished and lapped to a perfect matching fit, making possible installation *without* gaskets.

☞☞☞☞☞ Our ability to grind and polish Lapp Porcelain to fine precision limits also accounts for the remarkable efficiency of the Lapp Valve, in which porcelain only is exposed to the corrosive liquids, and which maintains a tight seal, even under vibration and temperature change.

☞☞☞☞☞ For complete technical data and a surprising story on delivery schedules, write Lapp Insulator Co., Inc., Chemical Division, LeRoy, N. Y.

ARMY E NAVY

Lapp *Chemical Porcelain*

Valves · Pipe · Raschig Rings

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

U.S.I. CHEMICAL NEWS

March ★ A Monthly Series for Chemists and Executives of the Solvents and Chemical Consuming Industries ★ 1943

U.S.I. Establishes New Department for Technical Problems

Will Aid Customers, Explore Potentialities of Products

A Technical Sales Development Department has been established by U.S.I. for the joint purpose of furnishing customers with a technical field service that can aid them in the solution of their problems and of providing the means for a more intensive exploration of both new and old products. The headquarters of the department have been located in a newly constructed laboratory building.

Dr. D. G. Zink will act as director of the new department, A. J. Fisher. Jr., as assistant director, and Norman C. Schultze as chief chemist.

Specifically, the proposed work of the department has been outlined as follows:

1. Investigation of suggestions for new products and their application.
2. Development of new uses of existing products.
3. Furnishing technical field service, including the handling of customers' problems.
4. Study of industrial trends.

The activities of this department will be controlled by a committee comprising Dr. F. J. Metzger, Director of Research; W. O. Griffen, General Production Manager; L. A. Keane, General Sales Manager; Dr. Zink and Glenn Haskell, president of U.S.I., who will act as chairman.

Agar Easily Recovered From Culture Media

A simple procedure for recovering agar from culture media was described recently which was said to provide as satisfactory an agar as the fresh commercial product.

The used media is autoclaved for sterilization purposes and filtered through cheese-cloth to remove coagulated proteins. It is then poured into trays from the freezing compartment of a refrigerator and allowed to cool. The trays are returned to the freezing compartment and left overnight. The following morning, the frozen material is rapidly melted in warm alcohol. The aqueous alcohol, containing the particles of agar, is filtered with cheese-cloth and the agar thus collected washed repeatedly with distilled water. Dehydration of the agar is produced by washing with alcohol.

Acetoacetanilide Used in Making Synthetic Resins

PITTSFIELD, Mass. — Acetoacetanilide, widely used as an intermediate in the production of yellow pigment dyestuffs, has potential utility also in the manufacture of synthetic resins for plastics and coatings.

This fact is revealed in a recent patent granted to an inventor here. In general, the new resins are prepared as condensation products of acetoacetanilide and an aldehyde. Modifying reactants may be included, such as urea, acetamide, or melamine, it is claimed.

Glycerol by Fermentation Made Practicable by U.S.I. Research

Commercial Exploitation of New Procedure Will Provide Additional Supply Sources for This Vitally Needed Material

The wide industrial utility of glycerol, as outlined in the first article on this series in the February issue of U.S.I. CHEMICAL NEWS, coupled with the heavy demand for this material in the manufacture of explosives, serves to indicate the urgent need for a source supplementary to the principal one, which is the saponification of natural oils and fats. Other than the production of glycerol by saponification of fats or by chemical synthesis, the most promising source is fermentation.

Use of "Steering Agents"

With respect to this, it has been known for many years that the normal fermentation of sugar by yeast results in the formation of glycerol to the extent of about 3% of the sugar along with the ethanol which is the main product of the fermentative activity. In recent years it has been found possible to modify the fermentation in various ways so as to increase the relative amount of glycerol. The modifying substances added have been appropriately called "steering agents," and it is a comparatively simple matter to increase the glycerol some five or six fold by adding suitable chemicals to the fermentation. The activities of the yeast may also be steered in the direction of glycerol formation by certain purely physical modifications in the fermentation solution. This knowledge was utilized by the Germans during World War I to manufacture considerable amounts of glycerol by fermentation for use in explosives.

Practical Difficulties

The problem of producing fermentation glycerol has been studied for some years by the Research Staff of U.S. Industrial Chemicals, Inc. This study has been designed to find means of obtaining glycerol from molasses fermentation, since molasses is the principal commercially practical source of the sugar necessary for the process. However, when molasses is used with appropriate steering agents, the recovery of the glycerol produced becomes difficult, because of the fact that after

(Continued on next page)

G. L. Haskell Is Elected To Presidency of U.S.I.

Glenn L. Haskell

NEW YORK, N. Y. — Glenn L. Haskell, first vice-president and director of the company for many years, was named president of U.S. Industrial Alcohol Co. at a recent meeting of the board of directors to succeed Charles S. Munson who was appointed chairman of the executive committee.

Vice-president in charge of sales since 1927, Mr. Haskell joined U.S.I. in 1921, holding successively the posts of Western sales manager at Chicago and general sales manager at New York. He was born in Chicago in 1883 and began his business career in 1900 with the American Distilling Co.

Portable "DRY-ICE" Cabinet Developed for Refrigeration

SILVER SPRINGS, Md. — A constant temperature "DRY-ICE"* cabinet has been developed for use where expensive mechanical refrigeration would not be justified, which is said to provide temperatures from minus 90° F. to 220° F. with a constancy of plus or minus ½° F.

The cabinet is described as portable and ready for operation after packing with "DRY-ICE" and plugging the cord into the current supply. In addition to the type described, a low-temperature model is available with a range from zero to minus 90° F.

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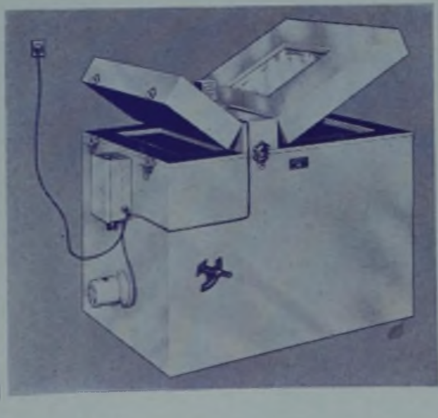
* Pure Carbonic, Incorporated, sells "DRY-ICE" manufactured by U.S.I.



Greater Power, No Corrosion Claimed for New Antiseptic

DANBURY, Conn. — A patent for an antiseptic for the sterilization of surgical instruments at room temperature, which is claimed to be non-corrosive in action and several times stronger in germicidal value than formaldehyde compositions previously utilized, has been assigned to a company here. It can be used either as a liquid or as a vapor.

The composition is a strong solution of formaldehyde in combination with a relatively large amount of ethyl alcohol, a small quantity of methyl alcohol and a very small quantity of a compound containing a reducing anion. A small quantity of an alkalizing agent may also be included.

A typical formula for this antiseptic follows:

U.S.P. formaldehyde (40%)	20%
Ethyl alcohol (96%)	69.5%
Sodium nitrite	0.1%
Sodium hydroxide	0.025%
Ethyl alcohol, specially denatured, (formula No. 30—100 parts ethyl alcohol, 10 parts methyl alcohol)	10%

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March ★ **U.S.I. CHEMICAL NEWS** ★ 1943

New Glycerol Process

(Continued from preceding page)

removal of alcohol by standard distillation procedures, the glycerol has to be separated from stillage containing a relatively large amount of solids other than glycerol. These solids are made up of an assortment of chemical entities of widely differing nature derived from the cane juices and are not easily separated from the glycerol.

U.S.I. Procedure

U.S. Industrial Chemicals, Inc., has developed through the pilot plant stage a process for the manufacture of glycerol from molasses. A modification of the fermentation procedure has been worked out that considerably increases the amount of glycerol formed.

In addition, U.S.I. has a proven process for the recovery of the glycerol from the other sugar solids — and for the final purification to produce dynamite or C.P. glycerol. At the present time, however, the critical materials required for such a project are needed more urgently for other purposes. It is obvious that when they are available, the commercial operation of a process for turning out glycerol from a source other than fats would remove the danger of a shortage by making possible rapid expansion of production of the fermentation glycerol to meet necessary war and civilian demands. Fermentation glycerol is our insurance against shortage of nitroglycerine for explosives.

Describes Preparation Of Multitone Coatings

BROOKLYN, N. Y. — The phenomenon of "blushing" in lacquers — usually a condition to be avoided — can be turned to advantage in the production of multitone coatings, it is claimed by an inventor here.

According to the patent issued on the process, a coating composition that will produce a blushed film is prepared and applied to a surface. If the film is treated with an embossing roller, a partially clear film is produced at some points, while the original blush remains elsewhere, thus resulting in the multitoned effect.

The coating may consist of:

	Parts by weight
Nitrocellulose	13.8
Acetone	5.0
Methanol (C.P.)	74.4
Water	4.2
Glycerol	2.6

New Federal Specification Issued for Lacquer Thinner

WASHINGTON, D. C. — A new federal specification on lacquer thinner (E-TT-T-266) has been issued to allow the use of aliphatic hydrocarbons instead of coal tar and aromatic petroleum hydrocarbons. In order to make this possible, the ester content has been changed from 25-35% to 30-40%, the coal tar and petroleum hydrocarbons, 40-50% to petroleum hydrocarbons 30-40%.

A suggested formulation is butyl acetate 26, ethyl acetate 8, methyl ethyl ketone 15, butanol 12.5, petroleum naphtha 38.5.

Ethanol Said to Improve Dehydrated Castor Oil

CHICAGO, Ill. — The treatment of heat bodied dehydrated castor oil with low boiling alcohols, preferably ethanol, will substantially reduce the acid and acetyl value of such oils and make them suitable for highly water-resisting varnishes, an inventor here claims.

The smallest ratio of ethanol to oil that was found desirable from a practical standpoint was four volumes of ethanol to one of oil. According to the inventor, the only upper limit of ethanol is that dictated by considerations of cost and of the capacity of the handling equipment.

Improved Method Developed To Clean Slides, Coverslips

NEW YORK, N. Y. — A new method for cleaning glass slides and coverslips has been developed here which is claimed to give excellent results, it was reported recently in "The Chemist-Analyst."

The steps to be followed are: soak the used slides and coverslips in xylol for several days; rinse with 95% alcohol for a few minutes; rinse for a few seconds with acidified alcohol (1% HCl in 70% alcohol); and soak in 95% alcohol again; and wipe dry with a clean cloth.

Alkalis in Glass Determined With Denatured Alcohols

HARTFORD, Conn. — Tests conducted here recently show that alcohol denatured with 10% ether (formula SD13A) and alcohol denatured with 10% acetone (formula SD23A) are satisfactory substitutes for 95% alcohol in the determination of sodium and potassium in glass.

TECHNICAL DEVELOPMENTS

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

Protective clothing has been designed to supplement the use of creams and liquids in operations where the exposed skin is subject to abrasive action or where the protection of clothing is of prime importance, it is said. **(No. 670)**

U S I

A new organic alkyl peroxide, t-butyl hydroperoxide, is available commercially which is reported to be suitable for use as a catalytic agent in one or two phase polymerizations, an oxidation agent, a drying accelerator, a combustion accelerator and a bleaching agent. **(No. 671)**

U S I

An acid siphon has been developed for dispensing corrosive liquids from carboys and drums. Made of a semi-flexible plastic impervious to ordinary commercial acids and alkalis, the siphon is said to produce a clean, easily controlled flow. **(No. 672)**

U S I

A substitute for carnauba wax in no-rub polishes is offered which the maker says can be used in amounts as high as 80% while still retaining gloss and other necessary properties in the polish. Available in quantities without priorities, the product is described as a processed type requiring no further processing. **(No. 673)**

U S I

Surface active agents have been developed which are described as non-electrolytes, which are neither sulfates nor sulfonated products and are essentially free from soap, excess fatty acids and inorganic salts. **(No. 674)**

U S I

A synthetic beeswax is now being produced which is claimed to be uniform in quality and to have all the characteristics of the genuine product. Available without priorities, it is said to be an excellent emulsifier and to be free from harmful ingredients. **(No. 675)**

U S I

Five skin-protective creams are said to be useful for protection against dust, sticky compounds, irritants with low water content, strong and dilute acids and alkalis, coolants with more than 10% water, ultra-violet and infra-red rays, and as for general skin conditioning. **(No. 676)**

U S I

A plastic molding material of unusual impact strength is said to have been developed through the use of a fibre filler which provides uniform load distribution. Impact breaking strength is rated at 3.2 to 4 ft. lb.; tensile strength at 6,000 to 7,000 lb. per. sq. in.; and flexural strength at 12,000 to 13,000 pounds. **(No. 677)**

U S I

Lacquers for spray application on wood, metal, plaster, plastic and composition surfaces are offered which are claimed to produce a finish that resembles metal plating. **(No. 678)**

U S I

A static charge meter has been put on the market for testing the resistance of a worker to ground in plants where there is danger of explosion due to static sparks. It consists of a resistance meter with its scale shaded to show safe and unsafe zones, a floor plate on which the worker stands, and connecting leads between the plate and the meter. **(No. 679)**

U.S. INDUSTRIAL CHEMICALS, INC.

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Ethanol (Ethyl Alcohol)
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- U.S.I. Denatured Alcohol Anti-freeze
- *Super Pyro Anti-freeze
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ACETIC ESTERS
- Amyl Acetate
- Butyl Acetate
- Ethyl Acetate

OXALIC ESTERS
- Butyl Oxalate
- Ethyl Oxalate

PHTHALIC ESTERS
- Amyl Phthalate
- Butyl Phthalate
- Ethyl Phthalate

OTHER ESTERS
- *Diatol
- Ethyl Carbonate
- Ethyl Chloroformate
- Ethyl Formate

INTERMEDIATES
- Acetoacetanilide
- Acetoacet-ortho-anisidide
- Acetoacet-ortho-chloranilide
- Acetoacet-ortho-toluidide
- Acetoacet-para-chloranilide
- Ethyl Acetoacetate
- Ethyl Benzoylacetate
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OTHER PRODUCTS
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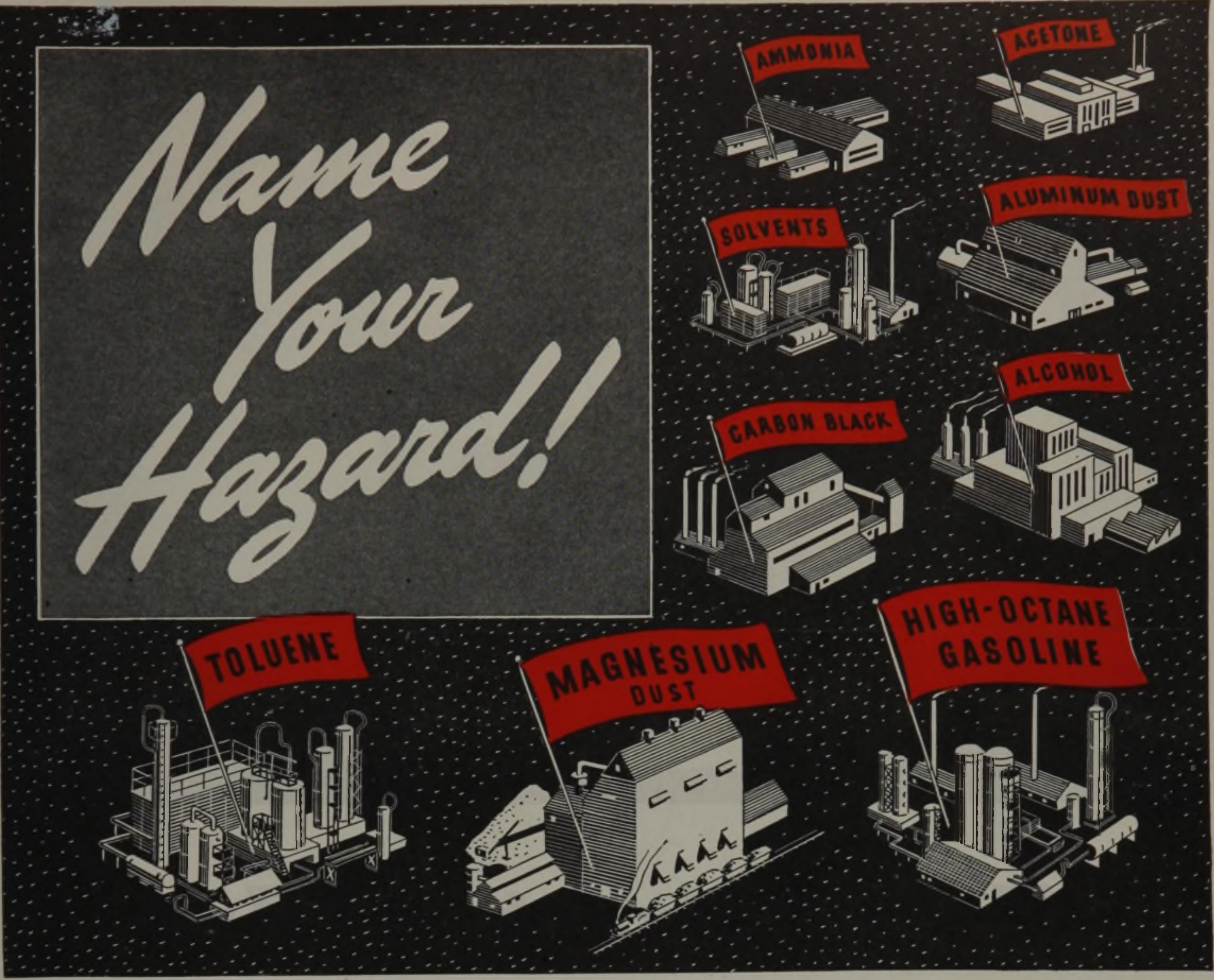
- Collodions
- *Curbay B-G
- *Curbay Binders
- *Curbay X (Powder)
- Ethylene
- Ethylene Glycol
- *Indalone
- Nitrocellulose Solutions
- Potash, Agricultural
- Urethan
- *Vacatone



THERE'S A G-E EXPLOSION-PROOF MOTOR TO MEET IT

No one type of motor is "best" for all kinds of hazardous locations. The *right* selection may eliminate the need for fire-walls to isolate the motor, and for awkward remote-drive arrangements.

Our engineers offer to work with you to select the motor, control, and other auxiliary equipment that best combines simplicity with security on the job.

General Electric builds the most complete line of explosion-proof and dust-tight motors available, tested and listed by Underwriters' Laboratories, Inc., for specific industrial hazards.

Most of these motors are as compact as standard open types, and require even less maintenance because of their totally enclosed construction.

Information on motorizing equipment in hazardous places is given in our publication No. GEA-3647. For this or any other motor assistance that can help speed war production, just call your General Electric Representative. Or write *General Electric, Schenectady, N. Y.*

Three More G-E "FIRSTS" in Motors for Hazardous Places

EXPLOSION-PROOF TO 600 HP

Totally enclosed squirrel-cage motors up to 600 hp are now listed by Underwriters' Laboratories, Inc., for Class I, Group D, locations, where atmospheres may contain gasoline, petroleum vapors, acetone, alcohols, natural gas.

TESTED AND LISTED FOR COMBUSTIBLE DUSTS

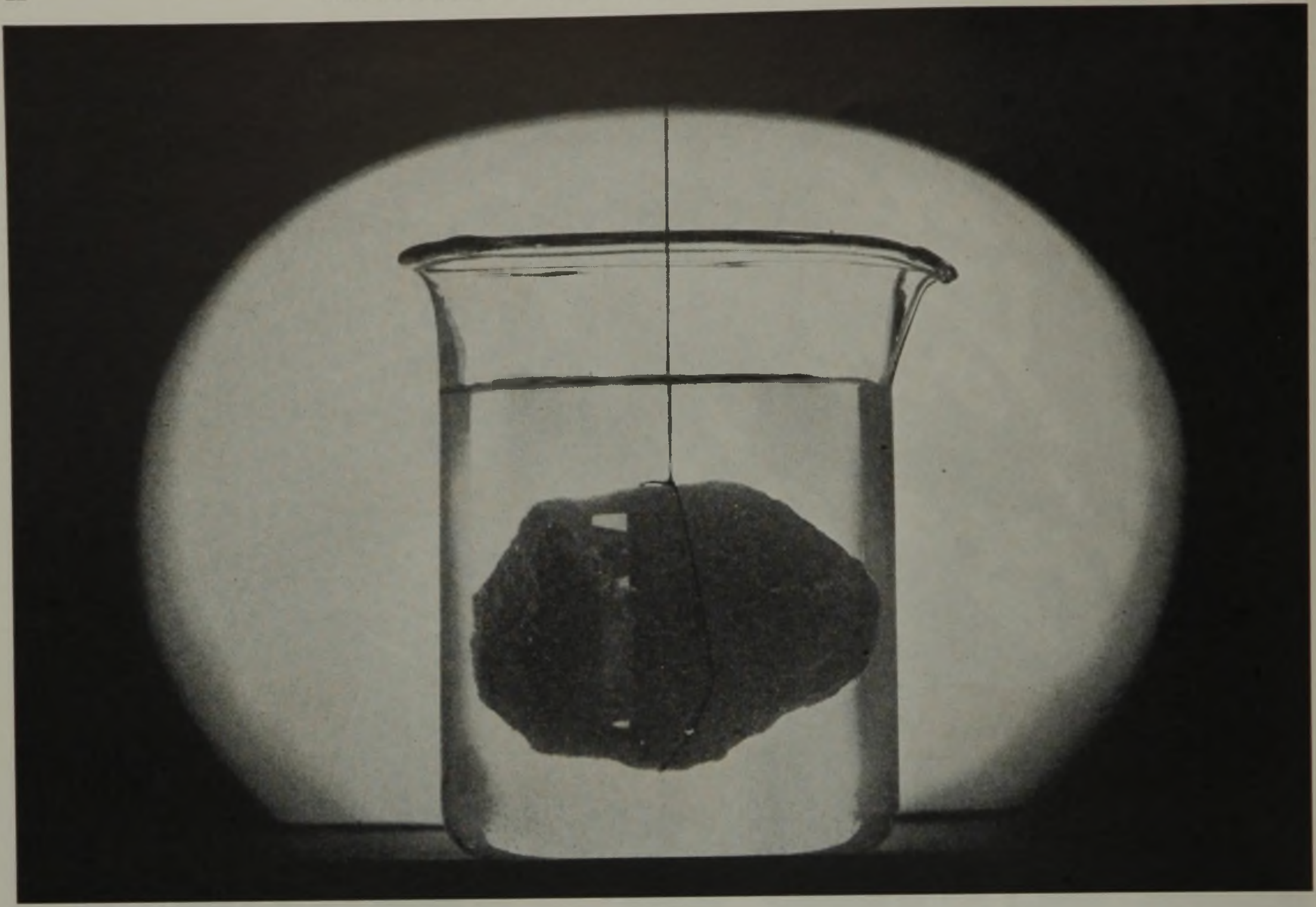
Built in a wide range of types and sizes, this motor is U.L.-listed for Class II, Group F, locations—where coal dust, coke dust, or carbon black may be present.

FOR METAL DUSTS LIKE MAGNESIUM, ALUMINUM

Ordnance plants find wide application for this totally enclosed motor, tested and listed by Underwriters' Laboratories for Class II, Group E, locations.

GENERAL ELECTRIC

750-197-8030



This Refractory Has Almost Zero Absorption!

IF you have a process in which a refractory of *very low porosity* might be valuable, you'll probably be interested in Corhart* Electrocast. Corhart Electrocast Refractories are ultra high-duty products made by melting refractory oxides in electric furnaces, then pouring into molds. After many years of almost exclusive use in the glass industry, Corhart refractories are now being rapidly adopted by several other industries. Here are the reasons:

HIGH FUSION POINT (Cone 37, without any appreciable range of softening below that point.)

LOW POROSITY (Porosity less than 0.5% — absorption practically zero.)

EXTREME HARDNESS (8, Mineralogist's Scale. Harder than glass. Ideally resistant to vibration.)

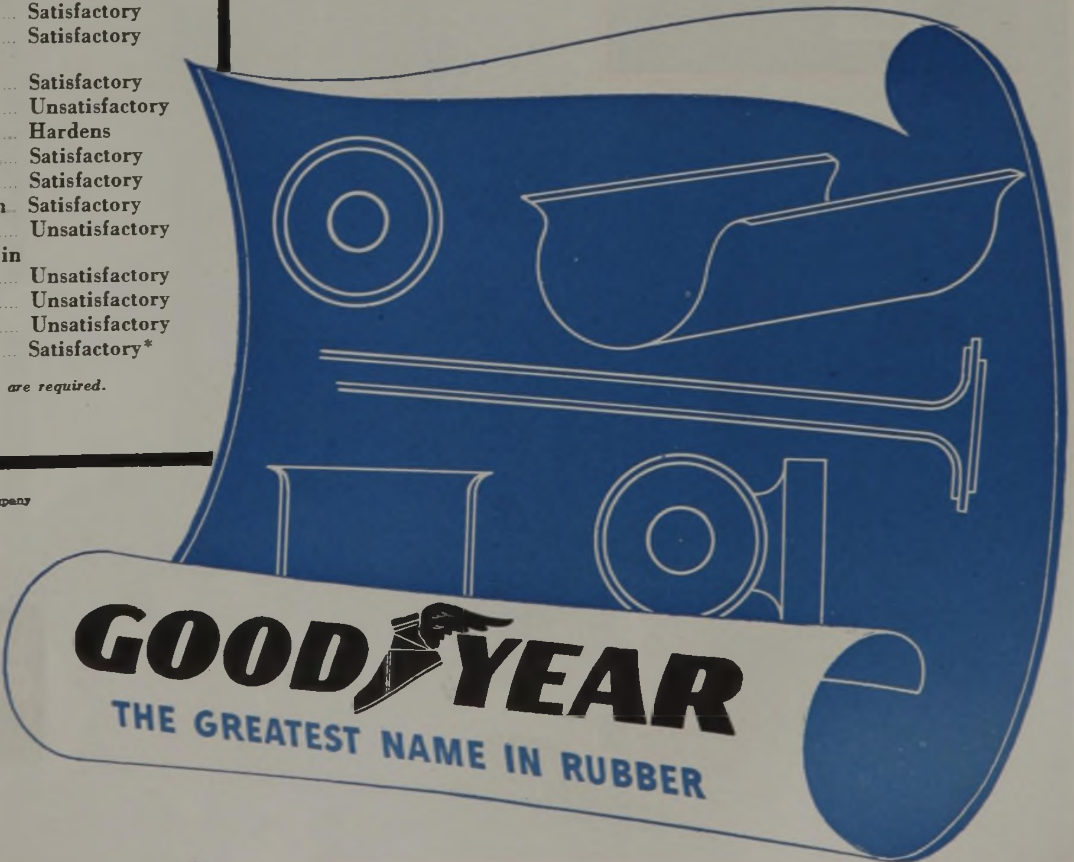
HIGH SPECIFIC GRAVITY (due to composition and structure)

If you are looking for a better refractory we'd like to give you the facts about Electrocast. Perhaps it is the product you have been searching for. Write us. No obligation and no high-pressure follow-up. *Address:* Corhart Refractories Co., *Incorporated*, 16th & Lee Streets, Louisville, Kentucky.

QUALITY ECONOMY
ENDURANCE

CORHART
ELECTROCAST
REFRACTORIES

* Not a product, but a trademark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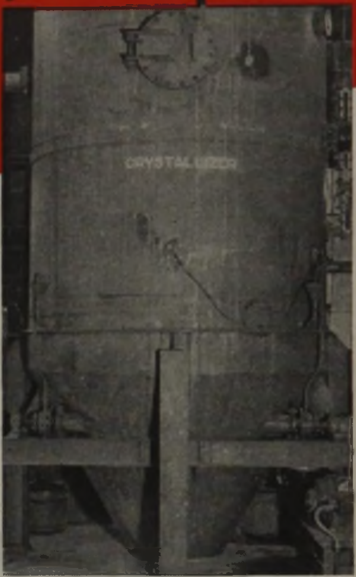
Now you can get
UNIFORM CRYSTALS
at lower cost!
SWENSON CONTINUOUS
VACUUM CRYSTALLIZER
WITH BOOSTER
Manufacturers of
Chemical Equipment
Since 1889

Swenson's wide experience and practical engineering are providing more efficient crystallizers for many processes



Swenson Vacuum Crystallizers may be rubber-lined for use with acid solutions. Swenson makes both mechanical and vacuum crystallizers for continuous or batch operation.

Swenson service to the chemical industry consists of a careful analysis of the conditions peculiar to each operation and the design of special equipment to accomplish the necessary results efficiently and economically. This engineering service has reduced costs and improved product quality in thousands of applications.

To assure optimum results, such specialized service requires a background wider than empirical formulas and calculations . . . it requires a diversified experience with similar applications from which valuable information may be drawn . . . and original research from which new designs may be evolved for the fabrication of equipment.

Swenson engineers have this three-fold background—empirical knowledge, vast experience, and research—and also complete manufacturing facilities under their direct and personal supervision.

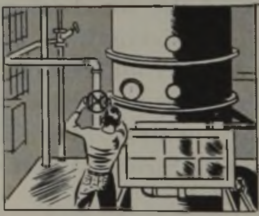
SWENSON EVAPORATOR COMPANY
Division of Whiting Corporation
15671 Lathrop Ave. Harvey, Ill.

ONLY SWENSON PROVIDES THIS FIVE-WAY SERVICE

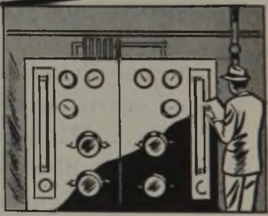
1. Analysis of Requirements

2. Design and Layout

3. Manufacture of Equipment



4. Test Operation



5. Periodic Check-ups

SWENSON

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WARTIME INDUSTRIES

depend on Quick-setting
Self-hardening

PENCHLOR ACID-PROOF CEMENT

REG. U. S. PAT. OFF.

SPEEDY CONSTRUCTION—unusual durability—continued, dependable service...that's what you want in corrosion-resistant equipment. And that's what you *get* when you build with Penchlor Acid-Proof Cement. This tough, long-lasting cement won't tie up your work with the usual delays. It's quick-setting and self-hardening...it's easily handled...no heating required...no drying delays...no acid treatment needed to set.

You can be *sure* Penchlor is dependable. It has been *proved* by years of the toughest service in a wide variety of corrosion-resistant installations. Decide now to use Penchlor Acid-Proof Cement on your next job of corrosion-resistant construction. You'll get: Long Life...Minimum Repairs...Permanent Mortar Set...Less Shrinkage...Strong Adherence to the usual construction materials.

Let us give you the complete story of this exceptionally successful acid-proof cement. Return the coupon for the new, *free*, illustrated booklet.

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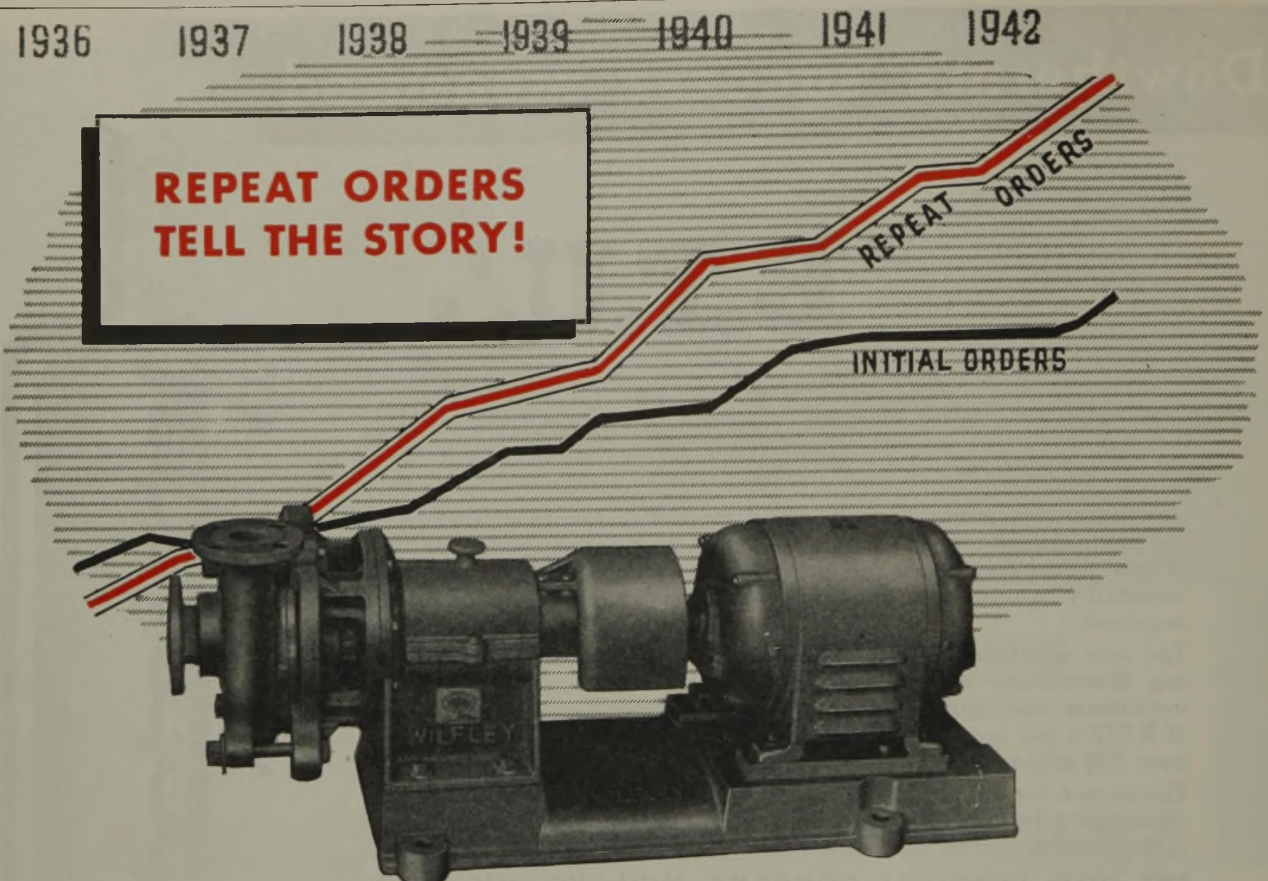
1936
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Which of these HIGH PRESSURE CONTAINERS do *you* need?

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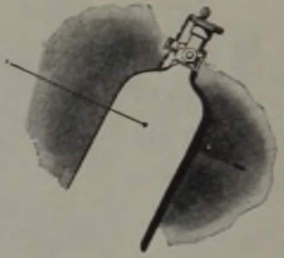

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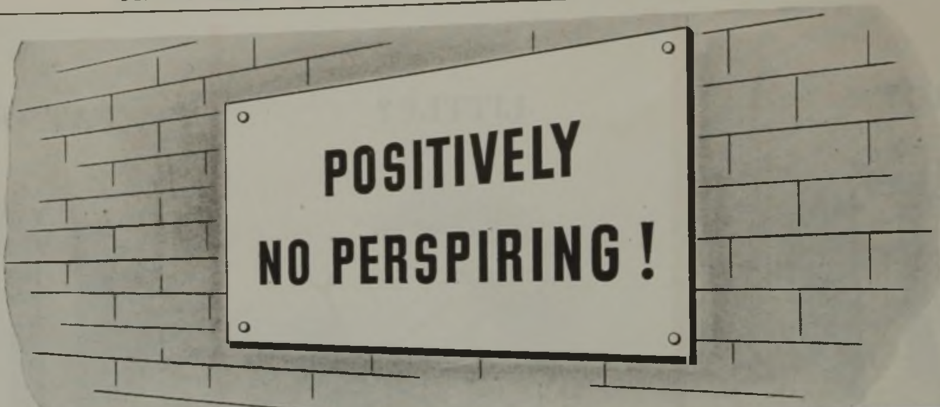

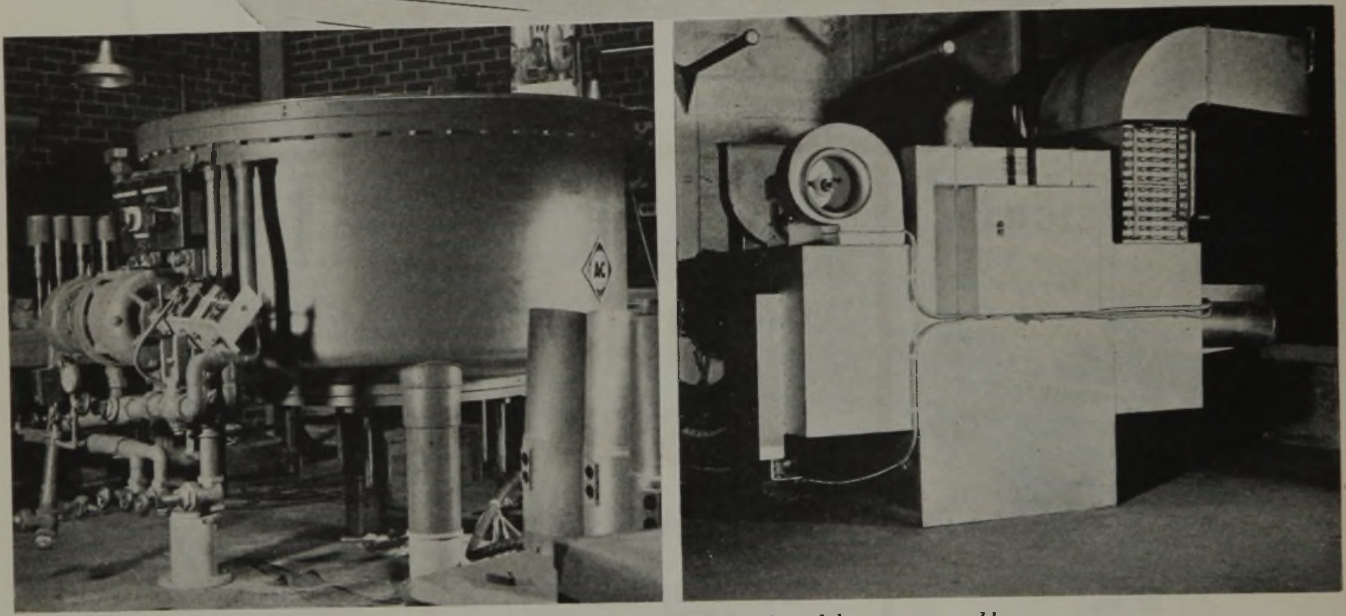

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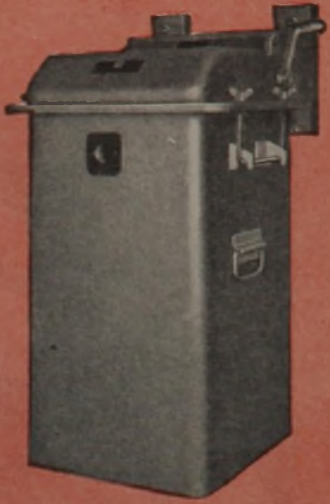
Don't WASTE MAN-HOURS

AND CRITICAL MATERIAL Building Special Enclosures

...there's a STANDARD G-E combination starter to meet every operating condition



CORROSION-RESISTANT

These starters (Type 8) are made in two forms—one for corrosive atmospheres and one for hazardous locations. All their arcing parts and terminals (for use in hazardous locations) are at least six inches under oil.

GENERAL-PURPOSE

The Type 1 enclosure is suitable for general-purpose, indoor applications where atmospheric conditions are normal.

DUST-TIGHT

The Type 5 enclosure is for use in steel mills, cement mills, and other locations where the dust content of the atmosphere is so heavy as to make a dust-tight case desirable. The cases are of heavy sheet metal, equipped with heavy gaskets, clamping bolts, and wing nuts.

FOR HAZARDOUS LOCATIONS

The Type 7 case for Class 1, Group D, locations is made of cast, high-strength alloy. These starters can withstand internal explosions. The flanges, which are securely bolted on all sides, are ground to tolerances that will not permit the escape of hot gases.

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The Type 4 case is suitable for outdoor use, and for installations in damp places indoors, such as in dairies and breweries.

The Navy "E", for Excellence, has been awarded to 92,780 General Electric employees in six plants manufacturing naval equipment.

Order STANDARDS to save time and material

NEVER ENOUGH production time—scarce material urgently needed! Both far too valuable to be spent in building unnecessary control rooms and special enclosures.

But delivered-ready-to-install control isn't all that the General Electric line of standard combination starters offers you.

These starters combine two devices—a fused motor-circuit switch and a magnetic starter—in one compact unit. This saves you one complete mounting job. They come to you completely wired and ready to install—saving all the time and material needed to wire up two individually mounted controls.

If you wish, our local sales engineers will help you select the proper starter for your job from this standard line of G-E combinations—for a-c motors up to 200 hp. *General Electric, Schenectady, N. Y.*

MARLEY COOLING TOWERS serve United Nations fighters and war industries on all fronts.

In addition to the great number of Marley Cooling Towers now speeding American war production, this map indicates recent Marley exports for service in the active war zones.

FACILITIES and "KNOW-HOW" to do the Job Speedily and Right

America's ability to expand its productive capacity so enormously and so quickly has saved the world from disaster . . . . by producing the *right* equipment to do each job that has to be done . . . . and *ahead of schedule.*

As an example, Marley's production at the start of 1943 is *triple* the same figure for 1942, which was *double* that for 1941 . . . . all on war-vital contracts.

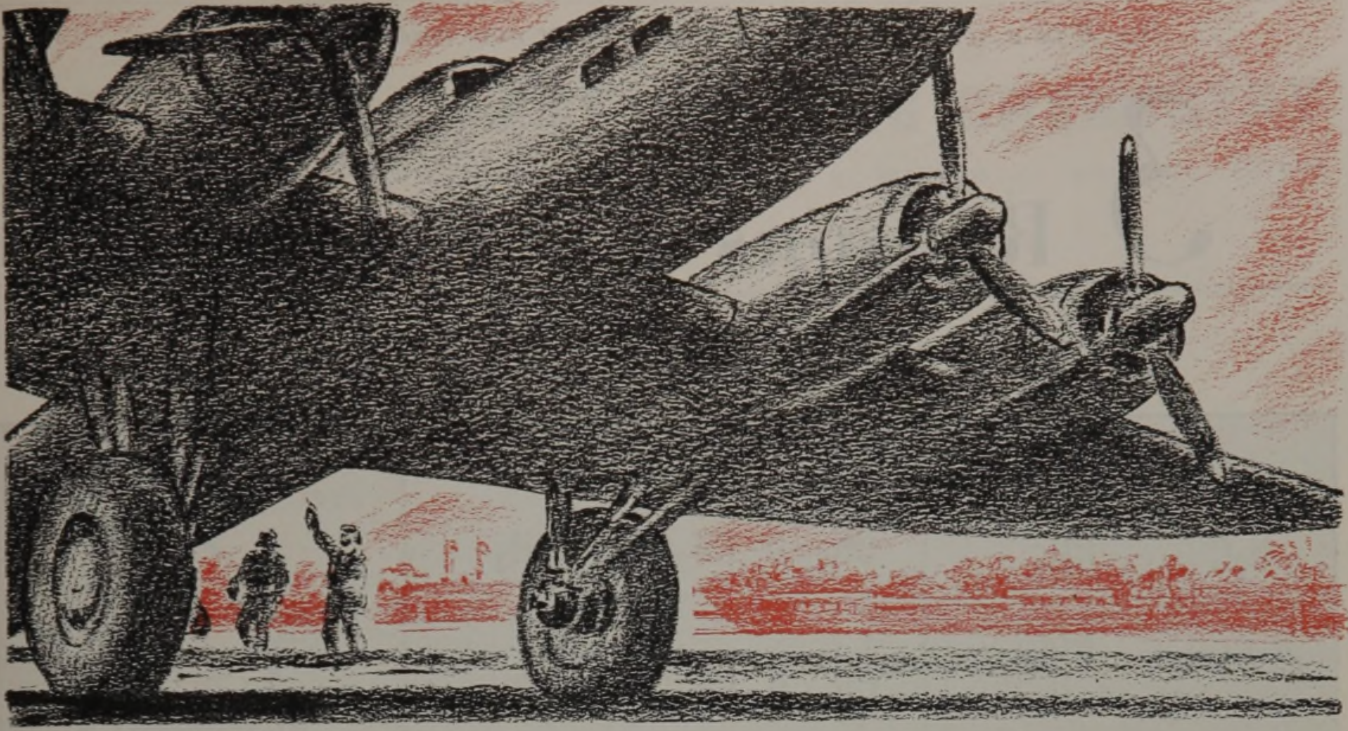
Because Marley had the facilities to swell output swiftly, plants producing essential war supplies have not suffered delay for want of water cooling equipment. And because Marley had the special knowledge and experience to engineer each installation specifically for its job, these plants save much in operating cost and maintenance man-hours.

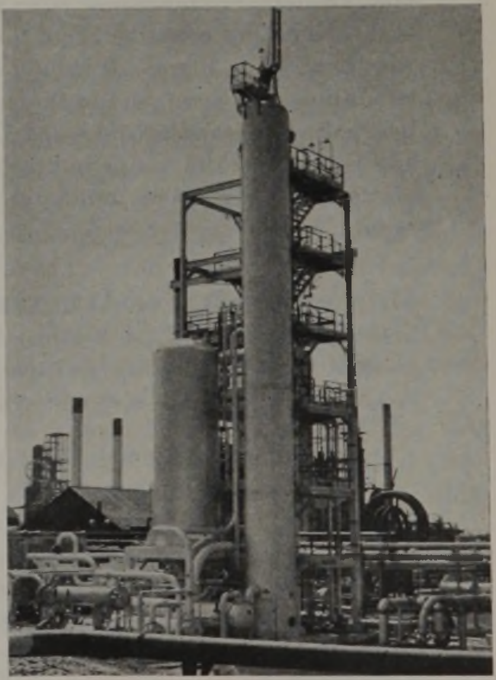
These facilities and this specialized experience have proved to be a definite national asset, and Marley productive capacity is still ahead of demands!

1-43-A

MARLEY COOLING TOWERS

Every MARLEY TOWER *is individually engineered by* THE MARLEY CO., INC. — KANSAS CITY, KANSAS

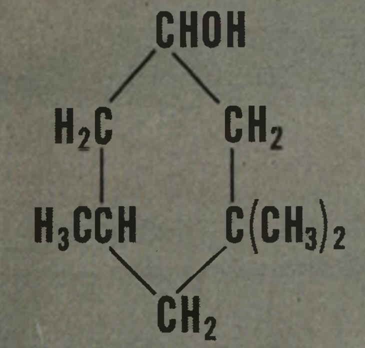




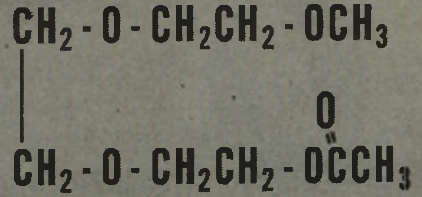
No. 8 in a series of advertisements about new research chemicals.

3 Reasons For Research

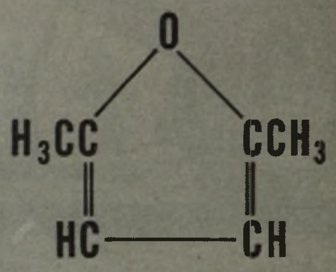
. . . unusual compounds from the laboratories
of Carbide and Carbon Chemicals Corporation.



TRIMETHYLCYCLOHEXANOL



METHOXYTRIGLYCOL ACETATE



DIMETHYLFURAN

TRIMETHYLCYCLOHEXANOL is a high-boiling (198°C. at 760 mm.) cyclic alcohol which is soluble in most organic solvents, hydrocarbons, and oils. Trimethylcyclohexanol is an excellent mutual solvent and coupling agent for many otherwise immiscible liquids. It should have value as an antifoaming agent, and in the manufacture of hydraulic fluids and textile soaps. Other possible applications for the compound include the preparation of plasticizers, xanthates, and wetting agents.

METHOXYTRIGLYCOL ACETATE is a colorless, high boiling (137°C. at 6 mm.) liquid distinguished by low volatility and excellent solvent powers for cellulose esters and synthetic resins. It is probably useful in protective coatings and printing inks having a cellulose ester base. The absence of reactive groups and its non-hygroscopicity suggest its trial as an inert reaction medium and as an "anti-dusting" agent for finely powdered materials.

DIMETHYLFURAN is a water-insoluble liquid which boils at 93°C. It shows promise as a tanning agent, as a diluent for nitrocellulose formulations, and as a solvent for polyvinyl acetate. It has value as a chemical intermediate and readily reacts with maleic anhydride in the Diels-Alder reaction to form an anhydride with possible alkyd resin applications. Its specific gravity is 0.9018.

FOR VICTORY
BUY
UNITED STATES
WAR
BONDS
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STAMPS

Although these new aliphatic chemicals are available now only in research quantities for laboratory investigation, it is probable that commercial quantities could be made for uses that will help win the war.

Reprints of the previous advertisements in this series announcing more than 30 other research chemicals are available on request. Write for them—there is no obligation.

For information concerning the use of these chemicals, address:

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PRODUCERS OF SYNTHETIC ORGANIC CHEMICALS

INDUSTRIAL AND ENGINEERING CHEMISTRY

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY ● WALTER J. MURPHY, EDITOR

EDITORIALS

Education Goes to War

THERE is little solace for those engaged in either production or research in the chemical field, in the present militarized college training programs of the Army and Navy. Of one thing we can be very certain—what higher education our able-bodied young men get will be ordered and directed by officials of the armed services, and most of the emphasis will be placed on military training. The pursuit of scientific knowledge will be subordinated to a plan for training these men to be officers within the next two years.

Unless the war proves to be of much shorter duration than most of us anticipate, the men in militarized courses will be lost to industry and to the universities and other institutions, both private and public, where much of the fundamental research is carried on. Personnelwise all that will be left of the 18-year-old group will be men who are in the draft classification 4F—entirely too few in numbers to take care of the demand for young chemists and chemical engineers that will exist and must be met four years hence. Youths in the 18- to 21-year-old group are at an impressionable age and many will be laboring under a terrific mental handicap when brought into close association with those wearing service uniforms. Then, too, it is highly problematical whether civilians attending colleges and universities where militarized training is in force will receive satisfactory attention. It is inevitable under existing conditions that they will not obtain full and sufficient training.

Necessarily such men must go along in their studies with the greatly accelerated curricula adopted by the armed forces. Neither the students in a civilian status nor the men in the Army Specialized Training Program will qualify at the end of the training period for degrees, either in chemistry or chemical engineering. Actually they will be technicians—nothing else.

What the chemical industry needs to carry out the work assigned to it in this industrialized war, and certainly in the postwar period, is a steady flow of men with sound basic training in chemistry and chemical engineering—not merely technicians poorly trained and ill fitted to assist in the operation of the expanded programs in the chemical, synthetic rubber, petroleum, plastic, and metal industries.

One other factor must be considered. We are justifiably proud of our achievements in the past two years in the field of applied chemistry, but this enviable record has been made possible only because of the work of a great many scientists employed over the past decade in fundamental research. If we cut off the supply of such highly specialized individuals for a long period, we are borrowing heavily on the future and are seriously threatening the success and prosperity of this country. We can be certain that Germany, despite her desperate manpower situation, is not pursuing such a ruinous policy. She did not squander her best technical brains on the fields of Flanders in World War I, and it is a safe bet that she is not losing her potential scientists of the next 20 years in Russia or Tunisia today.

Under public pressure the Army and Navy have given us a training program of sorts, but in truth it is not what they were asked, impartially and in a strictly fact-finding manner, to provide. In its present form it is neither "fish nor fowl". Formulators of the present plan have labored mightily and "have brought forth a mouse". Unless the war is over by the middle of next year, the results will be disastrous. If the responsible officials in the armed forces who dictated the pattern of this program are thoroughly convinced that the war will be won in the next 12 months, then it would indeed have been better to have omitted the technical education angle entirely. If not—then they are seriously jeopardizing the future welfare of this country.

Only time will reveal, of course, the folly of the present plans, unless the programs are completely revised in the light of current constructive criticism so as to hold qualified students in physics, medicine, chemistry, and engineering in our colleges and universities for a sufficient period to provide the same basic training given to such students in the prewar period. Accelerate the program by all means, but make it complete and thus supply industry and scientific research organizations with the trained personnel required to permit them to function properly in the next decade.

Attend Your Technical Meetings

IF BY your presence at technical group sessions you can impart valuable information or "know-how" to others engaged in similar lines of activity, or if by your attendance you can acquire knowledge which will increase your efficiency or that of your associates on the industrial war front, then it is your duty to give of your time and effort, although such action on your part may require considerable personal sacrifice. The soldier at the front does not measure his contribution by any time yardstick. We in the chemical field are shock troops in the army of production.

Certainly under present adverse conditions traveling to and from meetings held in distant cities can no longer be described as "joy-riding", nor can most accommodations be termed "beds of roses"—or can they? The old and, until a year or more ago, popular conception of conventions as a place of refuge for "tired" business executives is not now acceptable to cartoonists. Yet we do have a few individuals with a somewhat "Milquetoast" viewpoint who fear that they will be subjected to severe criticism if they attend a national convention or drive a car to a local section technical meeting, even though no other method of transportation is available. Chemists, chemical engineers, and chemical executives should have no trouble with supersensitive consciences in this matter. If by your presence you can contribute or receive something of a tangible nature related to the war effort, then by all means make your presence felt in gatherings of your technical societies. Many of our necessarily hard-boiled ration boards appreciate the practical value to the war effort provided by such technical sessions and are allowing special allotments of precious gasoline for this purpose.

The April meeting of the American Chemical Society in Detroit will be completely streamlined. All social aspects have been eliminated to provide greater opportunity for informal gatherings and for the exchange of information of mutual advantage to the participants in advancing America's mighty production effort. Much thought and effort have been given to the program and its relationship to the war effort. Only one example need be cited to illustrate this point. The Division of Chemical Education will depart from the usual papers on educational subjects to conduct an all-day Symposium on Chemical Aspects of Civilian Defense. It promises to be one of the highlights of the meeting. Those with sound chemical training are needed in civilian defense work in all parts of the country. Here is a splendid opportunity to obtain the necessary information. It will make sense to the trained chemist who in this particular field must take the initiative in his local community.

The word "morale" is on everybody's lips these days and rightfully so. Technical men are operating under a terrific mental strain in our all-out war program. By the very nature of the work in which many chemists are engaged they do not have an opportunity for close association with their co-workers. Although morale is a rather intangible thing, everyone recognizes its importance. Meetings, such as the one in Detroit in April, are very definitely morale builders for our technical personnel.

* * *

Industry and Selective Service

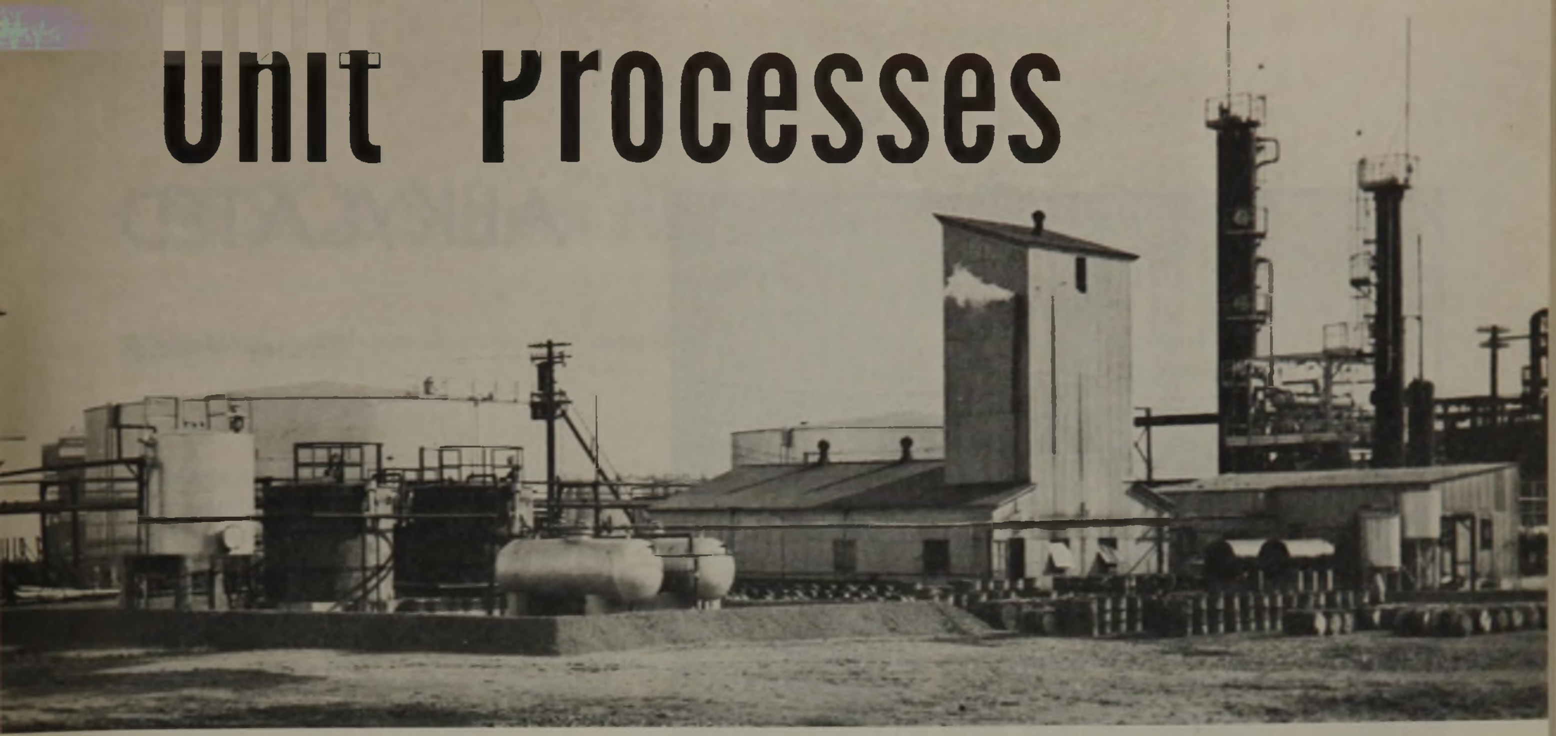
CERTAIN chemical companies are open to criticism for their lack of foresight in not appointing a responsible official to take charge of company matters pertaining to the Selective Service Act. Most concerns of any size are maintaining offices in Washington for the duration, and their representatives have become proficient in the mechanics of handling negotiations with governmental agencies with the possible exception of the Selective Service organization, now part and parcel of the War Manpower Commission.

Unfortunately, some executives in the chemical industry have failed to realize the precarious position of the industry with respect to trained professional personnel. Many company officials, already stung to the quick by partisan and wholly unfair publicity of a purely political nature, have become fearful of personal repercussions and further unfavorable comment on the enterprises they direct, if they should request deferments for necessary men. This is a narrow viewpoint and must be discarded in the interest of the country's war effort.

Many examples could be cited where company officials have shown surprising ignorance of the intent and purpose of the Selective Service Act. Recently an official of one of the larger companies indicated that he did not feel obligated to ask for the occupational deferment of a highly trained skilled professional worker because the man was only 23 years of age and in this executive's opinion Selective Service would hardly consider such an individual indispensable. This reasoning fails to coincide with the program followed in our universities and colleges, where deferments for undergraduate students and teachers in chemistry and chemical engineering have been requested and granted; likewise for graduate students where it can be definitely established that they are engaged in teaching for a certain number of prescribed hours or are doing research work on problems directly related to the war effort.

Industry has much to learn about the workings of the Selective Service Act. Too often little or no attention is given to holding necessary workers in industry until they are about ready to leave for an induction center. This is not fair practice. A definite program or plan of action should be adopted in advance.

Unit Processes



THE seventh Symposium on Unit Processes was held under the auspices of the Division of Industrial and Engineering Chemistry at the Buffalo meeting of the AMERICAN CHEMICAL SOCIETY. The fundamental object of these symposia is to gather sufficient data to place a more quantitative foundation under industrial chemical procedures. It would be desirable to have formulas into which, by substitution of the proper data and evaluation thereof, answers would be forthcoming to give an indication of the proper procedures for the manufacture of chemicals. It is too much to hope for such formulation in the very near future, but it is at least the goal of many working in unit processes.

The unit process conception enables much related knowledge to be classified under its appropriate head of alkylation, oxidation, hydrogenation, and the like. Perhaps when enough data have accumulated, certain formulation can be attempted. At least we can hope for this goal in the kinetics and equilibria of the basic chemistry involved.

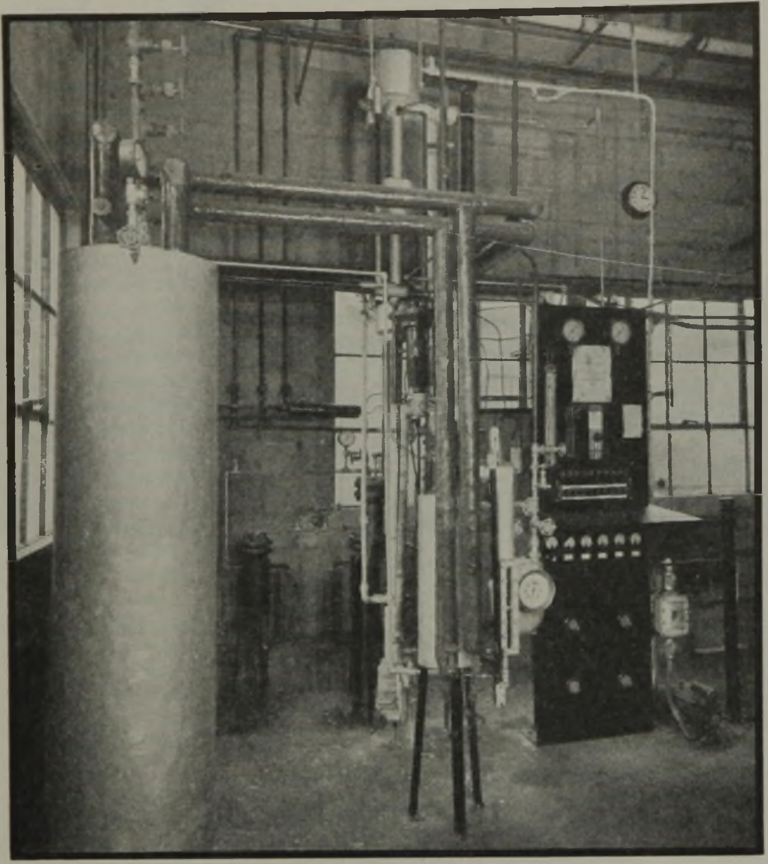
The unit processes directly apply to industry connecting, as they do, basic chemistry with equipment and economics. This chemical engineering aspect has been well supported by researchers in a number of our university laboratories, as exemplified by most of the papers presented at these symposia. The paper by Weinrich (page 264) is particularly welcome because it is a contribution from one of our large industrial organizations. It is to be hoped that more of the chemical companies will study and publish in these fields.

Contributions from industry might well present the general principles underlying the choice of equipment for a given unit process, such as design and applicability of the apparatus for carrying on the unit process. This tie-in of chemical change with equipment needed to commercialize the reaction, brings in the other member of the partnership between unit processes and unit operations, laying emphasis upon heat transfer, agitation, and other physical changes.

R. NORRIS SHREVE

ALKYLATED

Whitney Weinrich



Continuous Pilot Plant Alkylation Reactor with 1-Inch-Diameter Packed Column

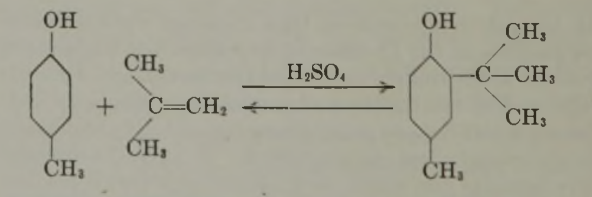
THE search for more efficient antioxidants for petroleum fractions has led many investigators to consider the alkylated phenols. The general reaction between phenols and olefins has been known for a considerable period. Many earlier investigators made and identified monoalkyl and dialkyl phenols which, in contrast to most of the trialkyl derivatives, are soluble in dilute caustic soda solution. Not, however, until about ten years ago was a systematic study started on the reactions and reaction conditions leading to the formation of trialkylated phenols. The literature covering these developments has been adequately reviewed to 1937 (*1*), and the fundamentals upon which the process development studies reported here are based are the subject of a series of papers now being prepared by D. R. Stevens of Mellon Institute and by G. H. Stillson of this laboratory. From this work has emerged a new class of organic chemicals, the trialkylated phenols, which are finding an ever-widening scope of usefulness.

The unique properties of these phenols, of which alkali insolubility is but one example, result primarily from the reduced activity of the phenolic hydroxyl group occasioned by the substituent alkyl groups. Stevens and Gruse (*3*) show the powerful antioxidant effect of certain of the trisubstituted phenols in petroleum fractions. More recently Garvey and Sarback (*2*) reported that dibutyl *m*-cresol is one of the best softeners for compounding certain types of synthetic rubber. Phenols of this class are quite soluble in petroleum fractions and in most organic solvents. The majority of these derivatives are colorless crystalline solids when freshly prepared. Discoloration, which takes place on standing, does not affect their value as oxidation inhibitors. A further distinction of the trisubstituted phenols from the parent compounds is a complete absence of burning action on the skin. Breathing of the vapors, while somewhat disagreeable, has never resulted in ill effects even to men who have operated the semicommercial plant over a period of years.

Trialkylated phenols may be obtained by treating phenols with an excess of *tert*-olefins in the presence of strong acid catalysts. Most investigators have described batch operations using pure olefins for these syntheses. Such processes result in good yields, but the highly concentrated olefins are relatively expensive as compared with the more dilute forms so readily available from petroleum cracking operations. Good yields of the desired products may be obtained from these less concentrated cuts, despite the diluent effect of unreactive paraffins and olefins, if the reaction is carried out in the vapor phase under proper conditions of temperature, pressure, and catalyst concentration. The development of these conditions for alkylations with dilute isobutylene streams constitutes a major portion of the work reported in this paper.

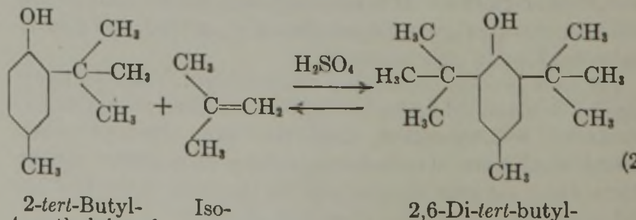
Alkylation Reactions

If a refinery butane-butene fraction is substituted for pure isobutylene, *p*-cresol reacts selectively with the isobutylene of the fraction when the correct reaction conditions are chosen to form the identical alkylated products. The two reversible reactions in this alkylation are cited below as typical examples of the general reactions of tertiary olefins and phenols:



(1)

p-Cresol Isobutylene 2-*tert*-Butyl-4-methylphenol



(2)

2-*tert*-Butyl-4-methylphenol Isobutylene 2,6-Di-*tert*-butyl-4-methylphenol

CRESOLS from REFINERY GASES

GULF RESEARCH AND DEVELOPMENT COMPANY, PITTSBURGH, PENNA.

The corresponding derivatives for *m*-cresol are 4-*tert*-butyl-3-methylphenol and 4,6-dibutyl-3-methylphenol. Only one monobutyl derivative is formed by *m*-cresol and by *p*-cresol, and evidence not yet published indicates clearly the structural formulas given above. *o*-Cresol, on the other hand, forms the two monobutyl isomers indicated in Table II.

In practice, the monobutylation of cresols proceeds almost quantitatively to the right; only traces of cresols are left when correct alkylation conditions are employed. The equilibrium between monobutyl and dibutyl *p*-cresol is approximately in the molal ratio of 1:9, but for *m*-cresol the ratio, 2:8, is somewhat less favorable to dibutylation. When proper conditions for alkylation are chosen, these equilibriums may be reached either with pure isobutylene or with a butane-butene fraction. It is interesting to note that when a *m*-*p*-cresol fraction of 60:40 molal ratio is charged to an alkylation reaction, the resulting monobutyl cut contains the alkylated isomers in the molal ratio of approximately 85:15.

▶ ▶ ▶ Phenols react selectively with the isobutylene contained in refinery butane-butene fractions in the presence of catalytic amounts of concentrated sulfuric acid to form the corresponding *tert*-butyl derivatives. Conditions have been determined for the synthesis of 2,6-di-*tert*-butyl-4-methylphenol and of 4,6-di-*tert*-butyl-3-methylphenol from a commercial *m*-*p*-cresol cut of coal tar acids, and continuous separation of the dibutyl cresols by distillation has been accomplished.

Early pilot plant work on this problem is briefly sketched and is followed by a more complete description of a small commercial plant for the manufacture of the *tert*-butyl derivatives of *m*- and *p*-cresol. The presence of minor proportions of *o*-cresol and of low-boiling xylenols in the cresol cut charged to the process introduces certain purification problems which are discussed in the light of the properties of the alkylated phenols involved.

The paraffins and *n*-butenes present in the refinery gases exert no detectable influence on the alkylation reaction; but a very minor proportion of the *n*-butenes does react with the sulfuric acid catalyst to form esters, at least part of which are suspected of being mono- and di-*sec*-butyl sulfates. Although acid monobutyl esters are quickly removed by washing the alkylate with dilute caustic solution, the neutral alkylate-soluble diesters such as dibutyl sulfate must be hydrolyzed by prolonged heating of the alkylate in the presence of dilute caustic solution at temperatures above 100° C. (212° F.). If these neutral esters are not removed prior to distillation of the alkylate, they will decompose to acidic bodies causing rapid dealkylation of the alkylate.

To utilize a commercial *m*-*p*-cresol fraction, it is necessary for economic reasons that some means be available to separate the monobutyl cresols from the dibutyl cresols and to separate dibutyl *p*-cresol from dibutyl *m*-cresol. Separation by distillation of the cresols from the monobutyl cresols and of the monobutyl from the dibutyl isomers is relatively easy because of boiling point spreads of 24° C. (43.2° F.) and 20° C. (36° F.), respectively. The cresols themselves, however, boil less than 1° C. (1.8° F.) apart, and the monobutyl isomers boil only 3° C. (5.4° F.) apart. The important discovery, which cannot be predicted from previous knowledge, was made by Stevens and Livingstone (*4*) that the dibutyl cresol isomers boil approximately 20° C. (36° F.) apart; thus they can also be separated by distillation. The above investigators appreciated as well that this process could be applied as a means of separating *p*-cresol from *m*-cresol by the dealkylation separately of dibutyl *p*-cresol and dibutyl *m*-cresol.

Pilot Plant Investigations

The present work comprises: (*a*) a description of the equipment used in early batch reactions using pure isobutylene and *p*-cresol and in the continuous packed-tower and bubble-cap reaction systems for contacting a refinery butane-butene fraction with 3° C. (5.4° F.) commercial *m*-*p*-cresol charge stock; (*b*) the establishment of reaction conditions for both the batch and the continuous operations including the washing procedure necessary to free the alkylate from acid-forming by-products that must be removed prior to distillation; and (*c*) the separation of the alkylated cresols by distillation with a discussion of the effect on the purity of the main products by other phenols present in small quantities in the commercial cresylic acids. It was during this period that the design of the bubble-cap alkylation reactors was set and the arrangement and flow of the continuous alkylate washing and distillation systems were determined. The operating semicommercial plant is described later, with a product balance on the complete operation. This development makes available for the first time sizable quantities of alkylated cresols. Among them are monobutyl *m*-cresol and dibutyl *m*-cresol.

Batch Alkylation Experiments

The early pilot plant studies involved the preparation in large laboratory quantities of 2,6-di-*tert*-butyl-4-methylphenol from pure isobutylene and *p*-cresol. The necessary quantities of isobutylene were made by dehydrating *tert*-butanol at about 625° F. over activated alumina under

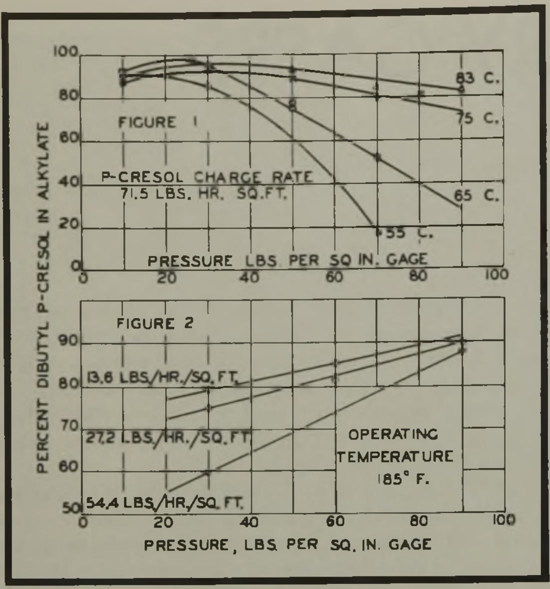


Figure 1. Effect of Pressure on Alkylation of p-Cresol in a 1-Inch Packed Tower at Various Operating Temperatures

Figure 2. Effect of Pressure on Alkylation of p-Cresol in a 4-Inch Bubble-Cap Tower for Varying Rates of p-Cresol Charge

sufficient pressure to condense both the water and the isobutylene formed. Only a trace of alcohol remained in the water layer. Alkylation was carried out at atmospheric pressure or slightly above and at 60–70° C. (140–158° F.) by vaporizing the isobutylene into a rapidly stirred solution of 5 per cent by weight of concentrated sulfuric acid in *p*-cresol. The time of introducing the isobutylene can be varied from several hours to a few minutes and is limited only by the heat transfer surface available to carry away the heat of reaction. Polymerization of isobutylene to diisobutylene and triisobutylene always accompanies alkylation as a side reaction, and the amount of this polymer formed is partly dependent upon the time of reaction. Excessive time may yield 10–20 per cent of polymer by weight of the alkylate, whereas a reaction time of 10 minutes may give as little as 2–3 per cent of polymer with the production of better than 90 per cent of dibutyl *p*-cresol in the alkylate.

Although these observations are qualitative, they show that the rate of addition of isobutylene to phenols is high. When the isobutylene is in the vapor phase, as it should be for minimum polymer formation, the rate of absorption of the gas into the liquid cresol-catalyst phase is the controlling factor. When alkylations were run under sufficient pressure for the isobutylene to be added as a liquid, relatively large proportions of polymer were formed; this was probably because the degree of mixing at the point of contact was not sufficiently violent to prevent high instantaneous concentrations of isobutylene, leading to excessive polymer formation. At some future time the absolute reaction rates of isobutylene with phenols will be measured in a flowing system of proper design so that it will be unnecessary to consider mixing and diffusional effects.

A highly satisfactory type of batch alkylator was used in the early experiments; a 150-gallon V-bottom tank contains cooling coils, and to its bottom is connected the suction of a centrifugal pump discharging through a tubular heat exchanger back to the tank. The full charge of cresol and acid is added to the tank, and the solution is circulated rapidly by the pump while isobutylene vapors are fed to the discharge of the pump ahead of the heat exchanger as rapidly as heat can be removed from the system. When the heat liberated by the reaction starts to drop, the reaction is nearly complete, and it is time to transfer the alkylate to another vessel for washing with hot dilute caustic soda solution agitated with steam. In practice the liquid isobutylene from the *tert*-butanol dehydration unit was fed to a vaporizer just ahead of the point of introduction to the alkylator without intermediate storage. Familiarity with the alkylator enabled the operator to shut down the alcohol dehydrator when the alkylation reaction was completed without wasting isobutylene.

Catalysts

The study of various acid catalysts and modifiers is included in the fundamental work mentioned earlier and is not part of the chemical engineering investigations. However, concentrated sulfuric acid is one of the best and most active of all catalysts; for this reason, together with its cheapness and ready availability in most refineries, the process studies were confined to this one catalyst with excellent results. In most of the pilot plant work, 96–98 per cent acid was dissolved in the cresol charged to the alkylator in amounts equal to 5

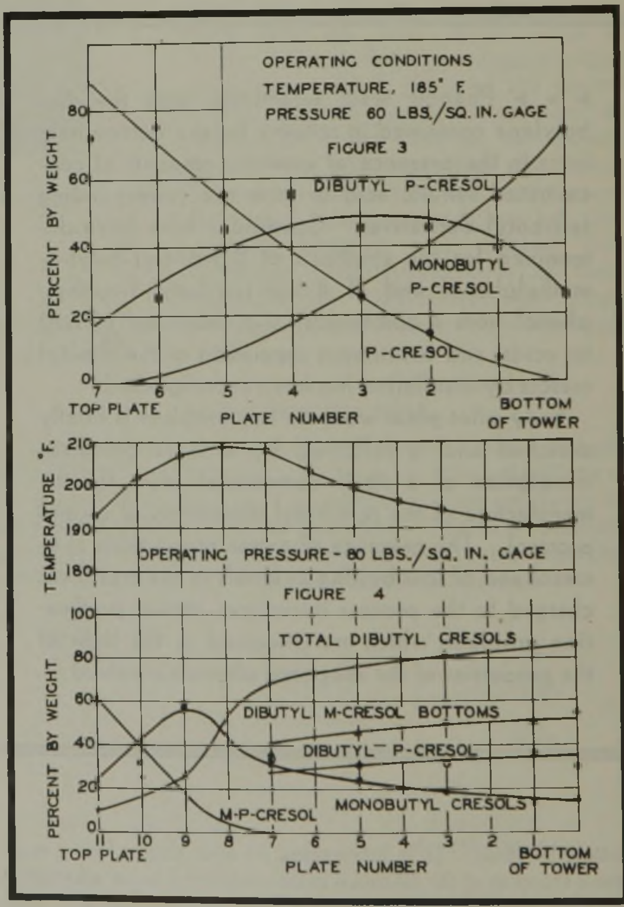


Figure 3. Plate-to-Plate Compositions for the Alkylation of p-Cresol in a 4-Inch Bubble-Cap Tower

Figure 4. Plate-to-Plate Compositions and Temperatures for the Semicommercial 16-Inch Bubble-Cap Reactor

Charge rate in cresol equivalent is 1038 pounds per day or 34.2 pounds per hour per square foot.

weight per cent of the cresol charge. In later commercial operations 104 per cent fuming acid was used, partly because of its availability and partly to compensate for small amounts of water dissolved in the monobutyl cresols returned to the system for realkylation along with the fresh cresol charge. Where recycle materials are present, the amount of acid catalyst to be added is calculated on the cresol equivalent of the mixture and not upon its total weight.

Only a narrow variation in catalyst concentration can be allowed without lessening the efficiency of the operation. Experiment has shown that less than about 3 per cent tends to lower the degree of alkylation, while much more than 5 per cent tends to produce excessive side reaction products such as isobutylene polymers and the formation of high-boiling residues. This is a phase of the work to which considerably more study could be devoted because the loss of cresols due to sulfonation and the formation of the butyl esters must be closely allied with the amount of acid used and its original concentration.

Continuous Studies

Early in this study it became evident that increasing quantities of alkylated cresols would be required. Process development was therefore directed toward the use of a refinery butane-butene fraction, derived from the thermal cracking of petroleum, as a source of isobutylene and a commercial cut of *m-p*-cresols as a source of the cresol isomers. As soon as equipment could be installed in a refinery, a combination of small-scale preparation and process development met the existing demands for the product. As demands increased, new equipment was gradually added to the pilot plant until it grew to semicommercial size. Continuous distillation equipment was installed for separating monobutyl cresols, dibutyl *p*-cresol, and dibutyl *m*-cresol.

The reaction of pure isobutylene and cresols is singularly clean-cut for no substance remains to contaminate the reaction product. However, when a refinery butane-butene fraction containing isobutylene is contacted with cresols, only the isobutylene reacts and the *n*-butenes and butanes remain as an additional phase of the reaction system. It is necessary, therefore, to devise a system whereby the isobutylene-containing gases are contacted with the cresol-acid phase and then are removed as rapidly as the isobutylene is absorbed.

These conditions are readily met by employing a packed tube as a contactor. The cresol-acid phase is fed as a liquid to the top, and the vaporous butane-butene stream enters at the bottom in countercurrent flow. The first reactor used in the laboratory was made of one-inch extra heavy tubing packed with $^1/_6$-inch stainless steel carding teeth and jacketed with water of the desired temperature for control. Series of continuous runs at four temperatures were made over a pressure range but at constant flow rates of gas and cresol-acid mix. Figure 1 shows the results when the butane-butene contained approximately 30 mole per cent isobutylene and about 25 mole per cent pentane-amylene hydrocarbons; the optimum pressure was 20 to 30 pounds per square inch gage. It is important that at the lower temperatures, the degree of alkylation drops off sharply with pressures in the range of 40 to 90 pounds. Raising the temperature from 55° to 75–83° C. largely nullifies the undesirable effects of the higher pressures. Since the capacity of an alkylator is almost a direct function of the operating pressure, it is desirable for the pressure to be as high as is consistent with good alkylation.

Understanding of the phase relations of catalyst, cresols, and butanes is important in interpreting the effects of temperature and pressure. Although concentrated sulfuric acid is miscible in all proportions with *m-p*-cresol, only a few per cent of dissolved butanes will precipitate the acid as a lower phase. Further increases in butanes will eventually cause the separation of a third phase rich in butanes. The concentrated acid that separates them reacts with the olefins present in an alkylation system, and the result is the formation of polymers, sulfuric esters, and resinous materials and a consequent weakening of the catalyst activity. This is the chain of events that occurs in varying degree when the pressure in a mixed vapor- and liquid-phase alkylation system is too high or when the temperature is too low. The presence of hydrocarbons higher in molecular weight than butanes has the same effect as excessive pressure for they will dissolve preferentially in the cresol phase. For the same reasons isobutylene-propane mixtures can be employed at considerably higher pressures because of the reduced tendency for propane to liquefy.

The butane-butene used in the runs summarized in Figure 1 was abnormally high in both isobutylene and higher hydrocarbons. With a feed containing about 18 per cent isobutylene and 6 per cent pentane-amylene, other series of runs were made in which optimum alkylation was obtained at approximately 85 pounds for a temperature of 85° C. (185° F.). The increased pressure compensated for the reduced olefin content; and since a small proportion of higher hydrocarbons was present, the degree of alkylation was equal to that obtained previously at equivalent cresol charge rates. The change in composition of a typical butane-butene fraction is shown in Table I.

Table I. Change in Composition of a Refinery Butane-Butene Fraction on Passage through the Alkylation Tower

	Butane-Butene, Molal %	
	Charged	Spent
Propane-propene	2.8	3.3
Isobutane	6.9	8.1
Isobutylene	18.2	3.8
n-Butenes	30.8	36.3
n-Butane	35.6	41.8
Pentane-amylene	5.7	6.7
	100.0	100.0

A few generalizations can be made on alkylation conditions:

1. The temperature of the reaction should be limited to approximately 100° C., particularly in that portion of an alkylation reactor where high concentrations of dibutyl cresols are present.
2. When sufficient vapor-liquid contact is provided—a condition that can be met in towers of nominal length—the capacity of a tower for any given set of operating conditions and yield is limited primarily by the allowable gas rate through the tower.
3. A large excess of isobutylene is advantageous only under conditions of poor alkylation. When conditions are correct, no advantage is to be gained from having more than 3–4 mole per cent isobutylene in the spent gas from the reactor, and for a charge gas containing 15–20 mole per cent isobutylene, this represents a recovery of 80–90 per cent.

Packed towers 6 and 10 inches in diameter were built and operated for a period, but neither was entirely satisfactory because of the horizontal temperature gradient that developed across the tower created by the heat of butylation of cresol. This value was estimated to be 640 B. t. u. per pound of isobutylene reacted with *m-p*-cresol.

Since it is unavoidable that packed towers develop horizontal temperature gradients, an experimental 4-inch bubble-cap tower was built and placed in continuous operation; it was fitted with seven $2^5/_8$-inch bubble caps, each supported on a separate tray spaced about a foot apart. Each tray embodies an integral circular passageway through which water circulated, allowing individual temperature control. This unit was found to have a capacity almost equal to that of the 6-inch packed tower for *p*-cresol alkylation. A series of tests was made at a constant temperature of 185° F., at pressures varying from 30 to 90 pounds per square inch gage, and for flow rates from 13.6 to 54.4 pounds of *p*-cresol per hour per square foot of tower cross-sectional area. The data from these runs (Figure 2) show that at less than the optimum pressure of approximately 90 pounds per square inch, the flow rate markedly affects the degree of alkylation. For this pressure, however, the degree of alkylation is little affected by flow rates, and the capacity of the tower is determined by the amount of gas that will pass through without serious priming.

For a pressure of 60 pounds per square inch gage and a flow rate of 29.4 pounds of *p*-cresol per hour per square foot, samples of alkylate were withdrawn from each plate and analyzed. These analyses are plotted in Figure 3. *p*-Cresol first reacts with one mole of isobutylene to form monobutyl *p*-cresol. The concentration of the monobutyl derivative passes through a maximum of 50 per cent on about the middle tray of the bubble-cap tower and then drops off sharply at the bottom. The concentration of dibutyl *p*-cresol rises gradually to a concentration of about 75 per cent. Unfortunately for this example the operating pressure was 60 pounds per square inch. If 90 pounds had been used, the degree of dibutylation would have been increased to 90 per cent or better. The peak of the monobutyl curve for the reaction at higher pressure would have occurred nearer the top of the column, and its rise and fall would have been more abrupt. This effect is shown in Figure 4 which represents a series of tests on one of the semicommercial alkylation columns of 16-inch diameter.

Analytical Methods

About 600 cc. of product are drawn into a quart bottle containing an excess of sodium carbonate solution for the neutralization of the acid catalyst. Sodium carbonate is preferable to sodium hydroxide because the carbonate does not dissolve cresols and monobutyl cresols. After shaking well and allowing small amounts of dissolved butanes to escape, approximately 350 cc. of the clear alkylate are weighed into the 500-cc. still pot of a $^5/_8$-inch glass fractionating still, jacketed in the conventional manner for adiabatic operation and packed with $^1/_8$-inch stainless steel carding teeth. A few grams of alcoholic potassium hydroxide solution are added to the still pot to neutralize soluble sulfuric esters as they decompose on heating. The still is operated first at atmospheric pressure to remove the light hydrocarbons, the diisobutylene, and the triisobutylene. When the vapor temperature reaches 185° C., or approximately halfway between the boiling point of triisobutylene and cresol, the still is cooled sufficiently for the distillation to be resumed under a vacuum of 20 mm. mercury absolute. Cuts of isobutylene polymers, monobutyl cresols, and dibutyl cresols are taken in weighed graduated cylinders, and the results of the assay are calculated on a weight basis. Light hydrocarbons such as butanes and pentanes are caught in the solid carbon dioxide–acetone bath.

Semicommercial Designs for Alkylators

Because of the marked success of the 4-inch bubble-cap alkylator over the larger and less efficient packed towers,

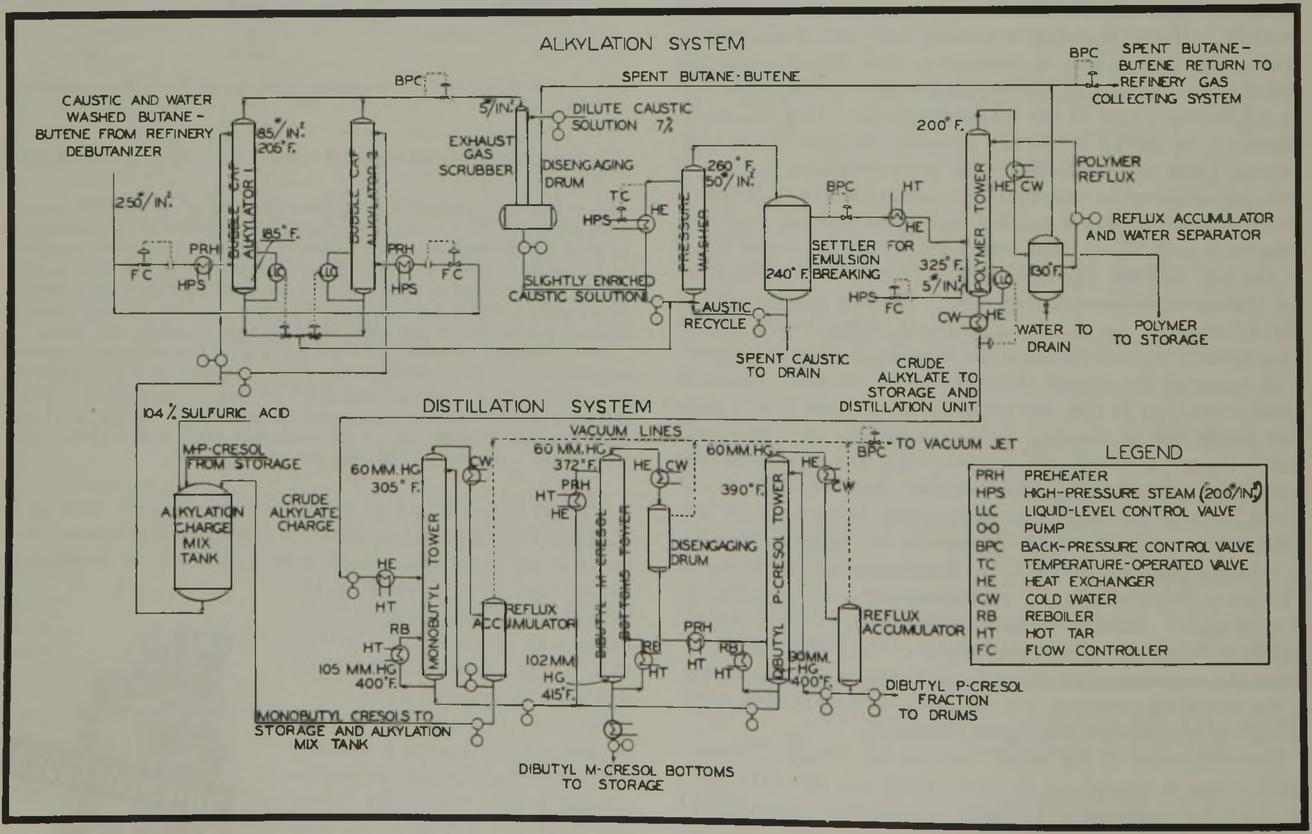


Figure 5. Alkylation and Distillation Systems of the Semicommercial Plant

further emphasis was placed on the bubble-cap type of contactor. One problem, which is uncommon to ordinary fractionating tower design but is present here, is the transfer of the heat of alkylation from each tray. This has been accomplished by spacing the caps to allow cooling coils to be immersed in the liquid on the trays. Since pressure drop is unimportant, and the presence of the cooling coils necessitates a high liquid level to be carried on the trays, the bubble caps are deeply immersed for maximum vapor-liquid contact. For the eleven trays of the 16-inch tower, the spacing is 12 inches; each tray holds twelve pressed-steel bubble caps $2^{3}/_{8}$ inches in diameter. For the 20-inch tower, the tray spacing is reduced to $8^{1}/_{2}$ inches, allowing a tower of the same height to embody fifteen trays with twelve pressed-steel bubble caps of 3-inch diameter. Heat transfer surface for the 16-inch tower consists of helical coils of $^{1}/_{2}$-inch pipe of irregular shape spaced between the risers of the bubble caps. In the 20-inch tower, heat transfer surface consisted of three parallel lengths of straight tubing laid parallel to, but just clearing the trays between, the bubble-cap risers and welded through the walls of the tower. By connecting the tubes by flanged headers, ready access may be had for cleaning out scale or mud accumulating inside the tubes. A 6-inch flanged handhole is welded to the side of the tower between plates in order that the decks may be inspected and repaired. As yet no such adjustments have been found necessary and no detectable corrosion has taken place after several years of operation.

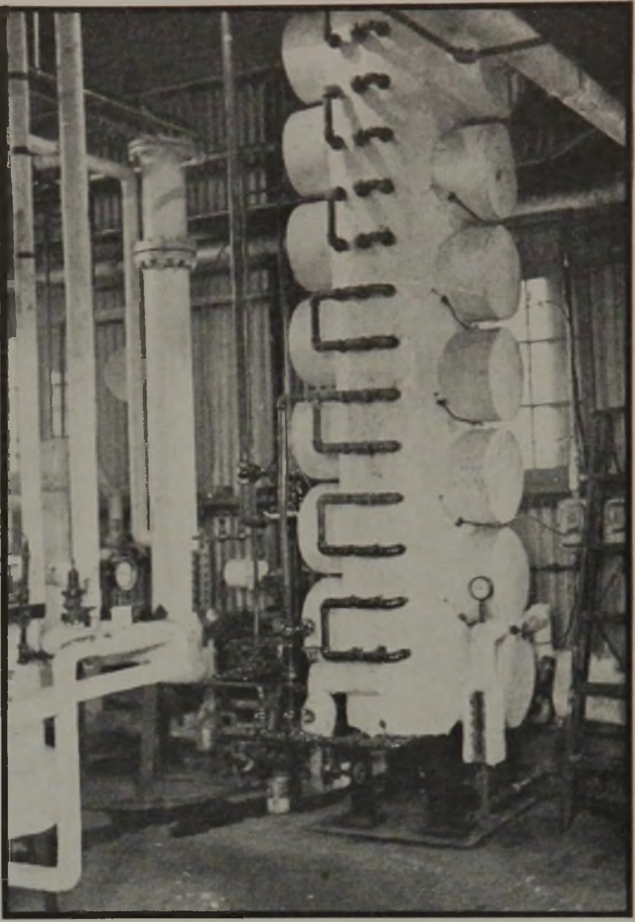
Alkylation

The semicommercial unit to be described comprises an alkylation system followed by a distillation system for the separation of a monobutyl *m-p*-cresol recycle stream for realkylation, a cut of dibutyl *p*-cresol, and a dibutyl *m*-cresol bottoms stream for subsequent handling.

The charge to the alkylators is made up in batches from the monobutyl recycle stream from the distillation towers, fresh *m-p*-cresol from storage, and 5 per cent by weight of 104 per cent fuming sulfuric acid, based on the cresol equivalent content of the mixture and not on the total weight of the charge. It is then picked up and pumped separately to the 16-inch and the 20-inch bubble-cap alkylators operated in parallel (Figure 5). After thorough caustic and water washing of the refinery butane-butene to remove sulfur compounds, the gases proceed through flow controllers to preheaters where vaporization and preheating to about 200° F. take place, to the bottom sections of the alkylators. The alkylated cresols accumulate in the bottom sections of the towers and continuously pass through liquid-level control valves to the pressure washing system.

Temperature control is maintained in the towers by circulating water at a high rate through the heat transfer tubes located on each tray. Circulation is from the top of the tower downward. Since both the heat transfer surface available and the amount of water circulating are large in comparison to the heat to be transferred, only a small temperature difference is required between the water circulating and the reaction product. This is particularly important to avoid overcooling the lower trays in the tower where the heat load is small compared to that in the top of the tower. Temperature control of the circulating water system is maintained by an automatic temperature valve which allows the correct proportion of cold water to enter the system to maintain a constant temperature.

The butane-butene passing through the towers gives up from 80 to 90 per cent of its isobutylene without any detectable change in the other constituents (Table I). Because of the elevated temperature at the top of a tower, the spent butane-butene picks up a small amount of cresol vapors which are scrubbed by precontact with the caustic soda solution required to neutralize the acid alkylate. Any trace of sulfur dioxide produced by the reduction of the sulfuric acid catalyst is thus prevented from entering the refinery gas system.



20-Inch Bubble-Cap Alkylation Tower in Semicommercial Unit

Pressure Washing and Polymer Removal

The acid alkylate from the towers is injected through a stainless steel nozzle into the pressure-washer circulating system where an emulsion of alkylate and dilute caustic is maintained at about 260° F. and 50 pounds per square inch for neutralization of free acid and for the decomposition of potential acid-forming bodies. Circulation is several hundred times the throughput; the average residence time is thus about 40 minutes. A recycle from the bottom of the emulsion settler, into which the effluent from the washer goes, is maintained so that the emulsion shall contain not less than about 25 per cent of the aqueous phase. The fresh caustic solution alone amounts to only about 5 per cent by volume of the alkylate. Since an appreciable amount of butane and other light hydrocarbons is dissolved in the alkylate as it leaves the alkylators, the upper effluent from the settler is partly in vapor phase and includes steam from the washing operation. This mixture then passes through a preheater into the polymer

Table II. Physical Properties of Cresols, Xylenols, and *tert*-Butyl Derivatives

Compound	Melting Point, ° C.	Specific Gravity (*t*/4° C.)				Boiling Point, ° C.			Viscosity, Centistokes		
		Solid	80° C.	120° C.	160° C.	20 mm.	100 mm.	760 mm.	80° C.	120° C.	160° C.
o-Cresol	30.0	......	0.994	0.960	0.924	90	125.5	190.8	1.47	0.784	0.515
6-*tert*-Butyl-2-methylphenol	27	......	0.924	0.894	0.864	118	159	231	1.60	0.906	0.610
4-*tert*-Butyl-2-methylphenol	27	......	0.929	0.899	0.869	132	174	247	4.40	1.58	0.865
4,6-Di-*tert*-butyl-2-methylphenol	51	0.940 (26.7/4)	0.891	0.862	0.833	149.5	194	269	4.75	1.90	1.080
m-Cresol	11.5	......	0.986	0.954	0.921	101	138	202.2	1.76	0.890	0.570
x-*tert*-Butyl-3-methylphenol	21.3	......	0.922	0.892	0.862	129	171	244	2.12	1.03	0.642
4,6-Di-*tert*-butyl-3-methylphenol	62.1	......	0.912	0.882	0.853	167	211	282	9.90	2.87	1.420
p-Cresol	34.7	......	0.986	0.954	0.921	101	138	202.1	2.00	0.992	0.620
2-*tert*-Butyl-4-methylphenol	51.7	......	0.922	0.892	0.862	126.5	167	237	2.55	1.17	0.713
2,6-Di-*tert*-butyl-4-methylphenol	70.0	1.048 (20/4)	0.899	0.870	0.841	147	191	265	3.47	1.54	0.920
2,4-Xylenol	27.0	......	...	...	...	105	143	210	...	...	...
6-*tert*-Butyl-2,4-dimethylphenol	22.3	......	0.917	0.888	0.859	131	174	249	2.10	1.06	0.670
2,5-Xylenol	74.5	1.063 (20/4)	0.965	0.932	0.899	105	143	210	1.61	0.825	0.528
4-*tert*-Butyl-2,5-dimethylphenol	71.2	1.001 (26.7/4)	0.939	0.911	0.883	151	193.5	264	8.30	2.28	1.130
o-Ethylphenol	−18	......	1.037 (20/4)	...	...	101.5	138.5	207	...	...	...
x-*tert*-Butyl-2-ethylphenol	...	......	...	...	...	129	...	...	...	...	...
y-*tert*-Butyl-2-ethylphenol	...	......	...	...	...	141	...	...	...	...	...
4,6-Di-*tert*-butyl-2-ethylphenol	30	......	...	...	...	156.5	...	...	...	...	...
Diisobutylene	...	......	0.7195 (20/4)	...	...	...	43.3	101	...	...	...
Triisobutylene	...	......	0.7590 (20/4)	...	...	70	109	177	...	...	...

towers where almost all the diisobutylene and most of the triisobutylene, together with all butanes, pentanes, and steam are separated from the alkylate. These lighter constituents are usually in large enough proportions to strip out the triisobutylene, but in some cases superheated steam is added to the bottom of the tower as an additional stripping agent. The reflux accumulator serves also as a water separator.

Distillation

The crude alkylate, now essentially free from water and the light hydrocarbons, is pumped from storage to the continuous distillation system which is conventional except for necessary modifications caused by the equipment at hand (Figure 5). The three towers are each 10 inches in diameter and are packed with $^1/_2$-inch Berl saddles which appear to give, under the conditions of vacuum operation employed here, H. E. T. P. values varying from 12 to 30 inches. The first tower serves to separate the monobutyl recycle containing about 10 per cent of dibutyl *p*-cresol. The dibutyl *p*-cresol fraction is separated from the dibutyl *m*-cresol bottoms in two towers instead of one in order to increase the separation without necessitating undue height of tower and pressure drop. Bottoms from the monobutyl tower along with bottoms from the dibutyl *p*-cresol tower are fed to the top of the second tower. Overhead from this tower is condensed, goes to a disengaging

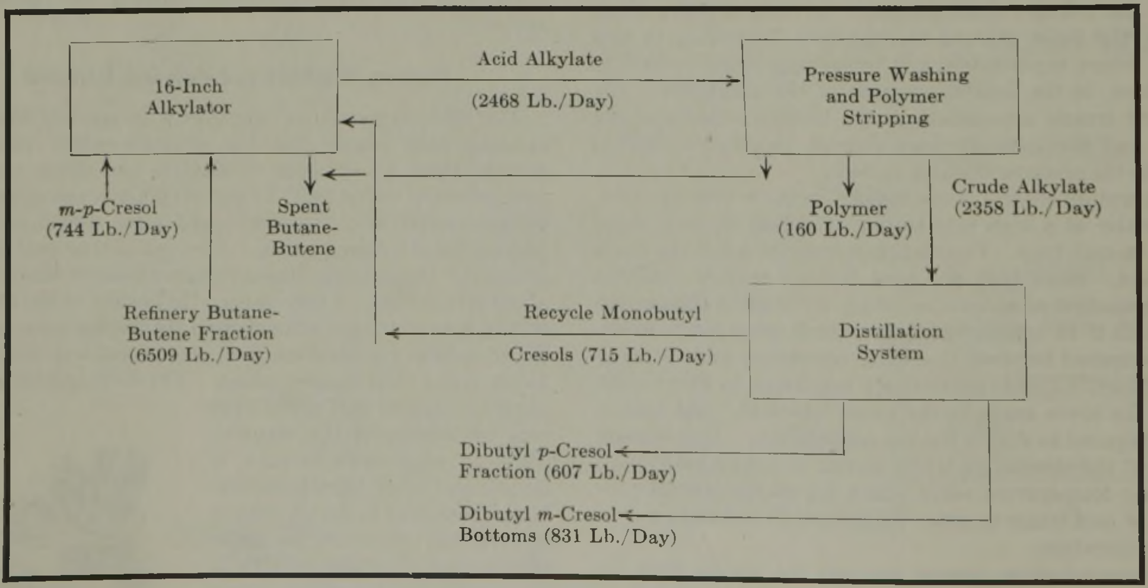
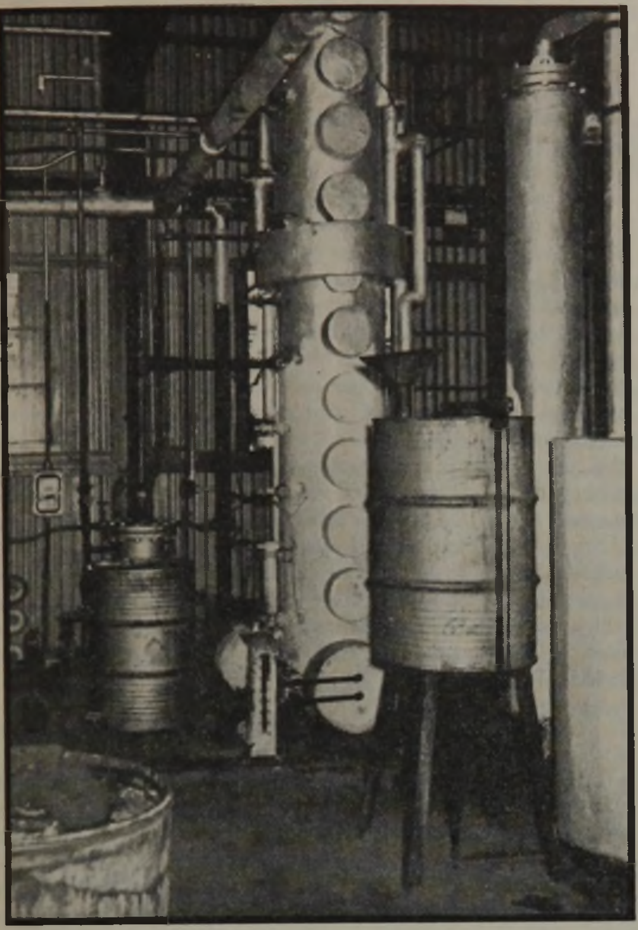


Figure 6. Plant Balance on Alkylation and Distillation Units Using 16-Inch Alkylator Only (All Quantities Expressed as Pounds per Stream Day)



16-Inch Bubble-Cap Alkylation Tower Reactor

drum on which vacuum of 60 mm. mercury absolute is maintained, and proceeds from the bottom of this drum by gravity through a revaporizer to the bottom of the third tower. Dibutyl *p*-cresol product is taken from the top of the third tower, while the dibutyl *m*-cresol bottoms are withdrawn from the second tower. This gives the same results as though the third tower were added to the second tower and operated as a single unit.

Sufficient reboiler capacity has been provided to allow operation at reflux ratios of 3:1 to 5:1. Heat to reboilers and preheaters is given up by hot cracking still tar which flows from an external circulating system maintained at constant temperature and pressure by automatic valves. Circulation is accomplished in this system by a typical refinery hot oil pump, and the temperature is held in the range 500° to 550° F. by allowing just sufficient hot tar from the refinery at about 680° F. to enter the circulating system.

Problems of Semicommercial Operation

Pressure Washing. It is absolutely essential that all potentially acid-forming material be removed from the crude alkylate in order that dealkylation will not occur in the distillation unit. The sulfur content should be reduced to less than 0.1 per cent by weight or to a point below which added contact time in the washer causes no further reduction. A contact time of at least 30 minutes is desirable at 260° F. The spent caustic should not be allowed to drop much below 2 per cent sodium hydroxide by weight for the best results, although it is believed that washing at higher pressures and temperatures or at longer contact times might reduce the allowable minimum caustic concentration. The spent caustic leaves the unit saturated with cresol and monobutyl cresols which may be recovered by benzene extraction of the spent wash water. This loss amounts to about 1 per cent of the cresol equivalent charged. On the scale of operation carried out here, wash water recovery was not justified economically.

Polymer Tower. The primary reason for the installation of the polymer tower is to remove hydrocarbons that are largely vapors at 60 mm. mercury pressure because of their effect in reducing the capacity of the distillation system. Analysis of the polymer reveals that it contains mostly di- and triisobutylene, but it also contains small quantities of the butyl alcohols which appear in an analytical distillation as the diisobutylene azeotrope boiling at about 80° C. Diisobutylene boils at 102–103° C. The water separating in the polymer tower reflux accumulator contains about 5 per cent butanol-water azeotropes; the greater proportion is *tert*-butanol. However, a small but definite proportion of the azeotrope of *sec*-butanol is always found.

Purity of Distillation Products

The commercial *m*-*p*-cresol used (with 3° C. boiling range) contains from 3 to 5 per cent of other phenolic compounds as impurities. These compounds and their alkylated derivatives are listed in Table II. *o*-Cresol, 2,4-xylenol, and 2,5-xylenol were identified either through their alkylated derivatives or by dealkylation of certain fractions and identification of the parent compound. As Table II shows, the monobutyl derivatives of *o*-cresol and of *o*-ethylphenol boil in about the same range as the corresponding *m*-*p*-cresol compounds. This means simply that a certain small concentration of monobutyl impurities will circulate. The monobutyl derivative of 2,4-xylenol boils slightly above the other monobutyls and, therefore, comes out gradually with the dibutyl *p*-cresol fraction. The monobutyl derivative of 2,5-xylenol and the dibutyl derivatives of both *o*-cresol and *o*-ethylphenol boil at essentially the same point as does dibutyl *p*-cresol. Dibutyl *m*-cresol is unique in its boiling point which is 10° C. higher than that of any of the known impurities. These observations are well borne out in practice for a dibutyl *m*-cresol bottoms containing essentially no lower boiling material will dealkylate to 98–99 per cent *m*-cresol; whereas even a close-boiling dibutyl *p*-cresol fraction will yield on dealkylation only about a 92–95 per cent pure *p*-cresol. Thus the impurities are found to concentrate with the dibutyl *p*-cresol fraction; fortunately these impurities act only as diluents and have no adverse effect on the desired uses for the dibutyl *p*-cresol fraction. It is possible, however, to eliminate all these impurities by extremely sharp prefractionation of the *m*-*p*-cresol charge.

Material Balance on Plant Operation

The catalytic addition of tertiary butyl groups to phenols is a markedly efficient process when considered in the light of many organic syntheses. The reactions are singularly clean-cut and are little beset with extraneous products. The loss of isobutylene to the polymers di- and triisobutylene is of small consequence because such polymers may be used directly in motor fuel, they may be depolymerized to produce more isobutylene, they may be used directly to alkylate phenols if there is demand for the tertiary octyl derivatives, or the diisobutylene may be hydrogenated to isooctane. In the following paragraphs a balance has been struck on the operation show-

Table III. Composition of Streams in and from the Semicommercial Unit

	Crude Alkylate, Charge to Distn. Unit	Monobutyl Cresol Recycle	Polymer	Dibutyl Para Cresol Fraction	Dibutyl *m*-Cresol Bottoms
Butanes, pentanes, etc.	...	...	8.5	...	...
Diisobutylene azeotropes with butanols	...	...	10.5	...	...
Diisobutylene	6.2	13.5	46.0	...	...
Triisobutylene			30.5	...	...
m-*p*-Cresol	...	4.5	...	...	...
Monobutyl cresols	23.8	72.0	4.5	7.0	...
Dibutyl *p*-cresol	28.1	10.0	...	92.0	...
Dibutyl *m*-cresol	37.9	...	...	1.0	90.5
Residue[a]	4.0	...	...	...	9.5
	100.0	100.0	100.0	100.0	100.0

[a] Consists of about half alkylated phenol-type compounds boiling above dibutyl *m*-cresol and half nonvolatile compounds of a resinous or tarry nature; this residue also contains essentially all the sulfur in the alkylate.

ing the compositions and amounts of the streams in the plant with the attendant losses.

Table III lists the analyses of the various streams in the plant, and Figure 6 shows the relative quantities of each stream. After being stripped, the first of these streams (the crude alkylate) contains 6.2 per cent isobutylene polymers, of which the majority is triisobutylene. Monobutyl cresols average 23.8 per cent, with 28.1 per cent dibutyl *p*-cresol, 37.9 per cent dibutyl *m*-cresol, and 4.0 per cent high-boiling residue. This residue consists of about 50 per cent alkylated cresol-type compounds boiling higher than dibutyl *m*-cresol and about 50 per cent nonvolatile resinous or tarry matter formed as a by-product in the alkylation. Included in this portion are essentially all products containing sulfur. The monobutyl cresol recycle stream contains, in addition to 72.0 per cent monobutyl cresols, 13.5 per cent isobutylene polymers, 4.5 per cent unreacted *m*-*p*-cresol, and approximately 10 per cent dibutyl *p*-cresol. The stream designated as polymer is an overhead stream from the alkylate before it is fed to the fractionating columns and contains a variety of products. The first product to distill in an analysis of this stream is a fraction of light hydrocarbons, consisting mainly of butanes and pentanes, followed by about 10 per cent of the butanol azeotropes with diisobutylene. The remainder is isobutylene polymers and a small proportion of partially alkylated cresols. As mentioned previously, the dibutyl *p*-cresol fraction is the stream in which most of the impurities concentrate; 7.0 per cent of this fraction is listed as monobutyl cresols, but this portion also contained the alkylates from certain of the xylenols. Only about 1.0 per cent of higher boiling compounds are present in this fraction, leaving the remainder of 92.0 per cent as dibutyl *p*-cresol. The dibutyl *m*-cresol bottoms contain essentially no lower boiling compounds but here is concentrated all of the residue formed in the crude alkylate charge.

To visualize the interrelations of the stream to and from the various units, Figure 6 shows the use of the 16-inch alkylator only. Since the completion of the test run from which these data were taken, the capacity of the plant has been more than doubled by the addition of a second alkylator, 20 inches in diameter, whose capacity is about 1.5 times that of the 16-inch alkylator. In summarizing Figure 6, it might be pointed out that the yields of the dibutyl *p*-cresol fraction and of the dibutyl *m*-cresol bottoms are 80 and 110 per cent, respectively, making a total of 190 per cent as compared to a theoretical yield of 204 per cent for dibutylation. If it is assumed that the 9.5 per cent of residue in the dibutyl *m*-cresol bottoms contains no recoverable cresol equivalent and this assumption is borne out in practice, the total remaining dibutyl cresols (Figure 6) account for 91.3 per cent of the *m*-*p*-cresol charged. About a third of the 8.7 per cent loss can be charged to the cresols and partially alkylated cresols lost in solution in the wash water discarded from the pressure washing system. A second third can be attributed to handling loss which is inevitable in relatively small-scale operation of this type, and the remaining third can be charged against the residue.

Acknowledgment

The writer wishes to acknowledge the contributions of many members of these laboratories who participated in this project, and to mention particularly the work of E. J. Loew and J. B. Kirkpatrick who acted as foremen of the semicommercial plant, and of L. H. Huth who conducted the test run from which the majority of the data presented here were taken. This work could never have reached its present state of development without the unfailing cooperation of W. M. Crockett, superintendent of the Philadelphia Refinery of the Gulf Oil Corporation, and of his staff in the erection and operation of the plant.

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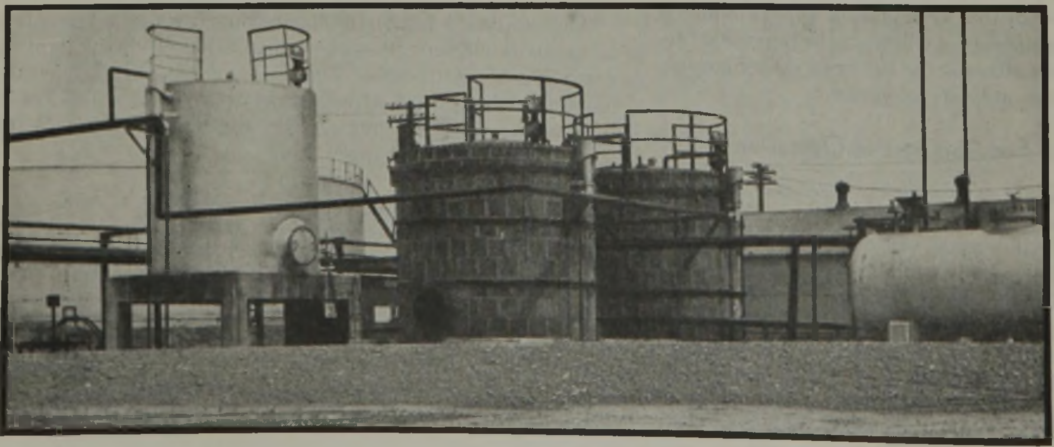

Storage Tanks for Alkylated Cresol Streams in the Semicommercial Unit

CATALYTIC ALKYLATION of BENZENE with ETHYLENE

▶ ▶ ▶ The reaction between ethylene and benzene vapors at pressures up to 200 pounds per square inch gage, temperatures of 230–270° C. and space velocities of about 11–50 cc. (gas, 0° C. and 760 mm.) per hour per cc. of catalyst have been investigated in a flowing system under the influence of eleven different catalysts.

Sodium chloride–aluminum chloride–pumice and phosphoric acid–kieselguhr were the only catalysts giving detectable reactions. Mono- and diethylbenzenes were identified in the liquid products. The former catalysts under some conditions converted as much as 95 per cent of the ethylene to ethylbenzenes.

A series of runs was made to determine the effect of time, pressure, and space velocity on the reaction when the sodium chloride–aluminum chloride–pumice was used. The catalyst was found to have a very short life, the ethylene conversion decreased from 93 to 75 per cent over a period necessary for the conversion of 0 to 1.16 gram mole of ethylene to ethylbenzenes.

Pressure had a surprising influence on the reaction. At atmospheric pressure there was no detectable conversion, while at 200 pounds gage pressure as much as 95 per cent of the ethylene was converted to ethylbenzenes.

The effect of space velocity on the conversion was negligible over the range of about 11 to 50 cc. per hour per cc. of catalyst.

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WITH the development of the uses of styrene over the past few years in the manufacture of resins and synthetic rubber, processes by which it might be synthesized have been of interest. When dehydrogenated, monoethylbenzene produces styrene by the reaction:

$$C_6H_5C_2H_5 \xrightarrow[\text{catalyst}]{\text{heat}} C_6H_5CH{=}CH_2 + H_2 \qquad (1)$$

It is believed that the most important processes in operation at this time for the manufacture of styrene involve monoethylbenzene as the starting material. The large producers of ethylbenzene use an agitated liquid phase for contacting benzene with ethylene in the presence of a metal halide catalyst, such as aluminum chloride. Recently a process for the production of ethylbenzene from ethyl alcohol and benzene has been publicized. Apparently, however, this process is not yet producing commercial quantities of ethylbenzene.

The present investigation is concerned with the reaction of ethylene with benzene in the vapor phase, utilizing an apparatus in which the mixed vapors of ethylene and benzene pass through a catalyst bed where the reaction takes place. Since only one investigator, Komarewsky (*13*), has reported results on this vapor-phase flowing system, the data on the effect of different operating variables, such as pressure, temperature, and catalyst, are meager. The object of this investigation was to find a suitable catalyst to promote the reaction of ethylene with benzene in the vapor phase to form predominantly monoethylbenzene,

$$C_6H_6(g) + C_2H_4(g) \longrightarrow C_6H_5C_2H_5(g) \qquad (2)$$

which might be dehydrogenated to form styrene as indicated in reaction (1). After a suitable catalyst for the reaction was found, the next object was to study the action of this catalyst under various conditions of pressure, temperature, and space velocity.

Previous Work

The alkylation of benzene with olefins has been widely investigated, but most of the work has been confined to liquid-phase batch experiments. The only work of note reported in the literature in which a vapor-phase flow system was employed is that of Komarewsky (*13*). A dehydrogenation catalyst, nickel-alumina, was used in this experiment, and vapors of ethylene and benzene at 350° C. and atmospheric pressure were passed over this catalyst. Analysis of the liquid product led to the conclusion that 5 per cent of the benzene charged was converted to toluene. The remainder was unconverted benzene and some high-boiling residue, representing about 2 per cent of the benzene charge and identified as a mixture of naphthalene and diphenyl. The gas produced by the reaction consisted of hydrogen, methane, and ethane. When benzene alone was passed over the catalyst under the same conditions only a small fraction of it reacted, the products being diphenyl and hydrogen. Under the same conditions ethylene alone was completely decomposed to form carbon, hydrogen, methane, and ethane. According to previous results of Ipatieff and Komarewsky (*10*), ethylbenzene in the presence of the nickel-alumina catalyst at 350° C. decomposed to toluene and methane.

Much work has been done on the benzene-ethylene reaction in which a liquid phase was present. Results of these investigations show that such materials as metal halides, inorganic acids, and acid anhydrides (for example, P_2O_5) catalyze the reaction with the resulting formation of ethylbenzenes, from

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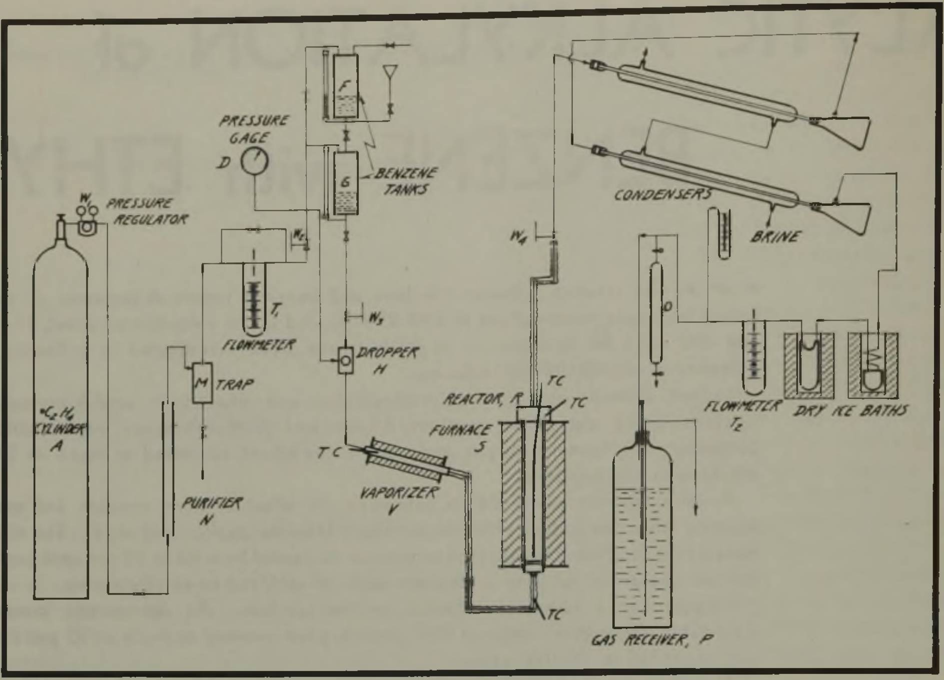

Figure 1. Flow Diagram for Synthesis Apparatus Used in Vapor-Phase Reaction between Ethylene and Benzene

the mono- to the hexaethylbenzene. Low temperatures favor the formation of these ethylbenzenes, but good conversions have been obtained up to 300–400° C. As would be expected, greater conversions occur at high pressures than at low. (Pressures up to 50–60 atmospheres have been reported for the benzene-ethylene reaction.) Since all of the published data resulted from investigations carried out in a batch process where a constant pressure of ethylene was maintained on the reaction mixture for periods of 12 to 60 hours, it is meaningless to give definite conversion figures without complete details of the experiments; these details are beyond the scope of this paper. However, it may be said that benzene conversions to mono-, di-, and higher alkylbenzenes were as high as 100 per cent under certain conditions.

It has been generally concluded that the metal halides are the best catalysts for the aromatic-olefin condensations. Many investigators, dating back to Balsohn in 1879 (*2*), have studied the catalytic effect of these metal halides under various conditions of pressure, temperature, and ratio of reactants. Some of these recent investigators include Ipatieff and Grosse (*6*, *9*), Huber and Reid (*7*), Milligan and Reid (*16*, *17*), and Amos, Dreisbach, and Williams (*1*).

Among the inorganic acids which have been tested as catalysts for the benzene-olefin condensations are sulfuric, *o*-phosphoric, and hydrofluoric. Ipatieff, Corson, and Pines (*8*) and Wunderly, Sowa, and Nieuwland (*24*) reached the conclusion that sulfuric acid does not catalyze the benzene-ethylene reaction but does catalyze the reaction between benzene and olefins of three or more carbon atoms. Ipatieff, Pines, and Komarewsky (*11*) found that *o*-phosphoric acid catalyzed the benzene-ethylene reaction. Hydrofluoric acid was tested by Simons and Archer, (*20*, *21*) and by Calcott, Tinker, and Weinmayr (*5*), and was found to promote the reaction of benzene with olefins of three or more carbons, but these investigators do not mention the use of hydrofluoric acid with benzene and ethylene.

The acid anhydride, phosphorus pentoxide, was used by Malishev (*14*, *15*) and by Truffault (*23*) to effect condensation.

The products resulting from the reaction of benzene with ethylene in the presence of a liquid phase consist essentially of mono- to hexaethylbenzenes. The catalysts mentioned in the above discussion seem to exhibit very little difference in selectivity in the range of conditions where they are appreciably active.

Thermodynamics of the Reaction

The best available thermal data have been used to calculate an equilibrium constant for the reaction between ethylene and benzene in the vapor phase to form monoethylbenzene (vapor),

$$C_6H_6(g) + C_2H_4(g) \rightleftharpoons C_6H_5C_2H_5(g) \qquad (2)$$

The only data which are lacking for this calculation are the specific heat data for ethylbenzene vapor. By subtracting the specific heat equation of methanol vapor (*19*) from the equation of ethanol vapor (*19*), the effect of adding a $—CH_2—$ group to a carbon chain was evaluated. Then by adding the equation for this $—CH_2—$ group to the specific heat equation of toluene (*19*) the following equation was obtained:

$$C_p = 10.3 + 0.072\,T$$

Table I. Thermal Data[a]

Compound	State	Heat of Vaporization	Heat of Formation	Standard Free Energy of Formation	Specific Heat (*19*)
Ethylene	Gas	..	11,975 (*18*)	15,840 (*18*)	$C_p = 6 + 0.015T$
Benzene	Liquid	8100 (*19*)	11,630 (*19*)	....	......
Benzene	Gas	..	....	30,640 (*19*)	$C_p = 6.5 + 0.052T$
Ethylbenzene	Liquid	9900 (*18*)	−5,070 (*19*)	....	......
Ethylbenzene	Gas	..	....	28,460 (*19*)	......
Methyl alcohol	Gas	..	....	....	$C_p = 2 + 0.030T$
Ethyl alcohol	Gas	..	....	....	$C_p = 4.5 + 0.038T$
Toluene	Gas	..	....	....	$C_p = 7.8 + 0.064T$

[a] Units are gram calories, ° K., and gram moles; the reference temperature and pressure are 298.1° K. and 760 mm. Hg, respectively.

This equation should represent the specific heat of ethylbenzene. The units for this equation are gram calories, degrees Kelvin, and gram moles.

Table I lists the data from which the following equation for the calculation of the equilibrium constant, K_p, as a function of temperature may be derived:

$$\log_{10} K_p = \frac{5800}{T} + 5.475 \times 10^{-4}\,T - 1.11 \log_{10} T - 3.691 \quad (3)$$

Table II contains equilibrium constants, K_p, calculated from Equation 3 for Equation 2. Calculations based on a 1:1 molal ratio of ethylene to benzene, atmospheric pressure, and 327° C. indicate that at equilibrium more than 99 per cent of the ethylene should be converted to ethylbenzene.

Table II. Equilibrium Constants for Reaction 2

$[C_6H_6(g) + C_2H_4(g) \rightleftharpoons C_6H_5C_2H_5(g)]$

Temperature			
° K.	° C.	$\log_{10} K_p$	K_p
298.1	25	13.22	1.66×10^{13}
350.1	77	10.28	1.91×10^{10}
400.1	127	8.14	1.38×10^{8}
500.1	227	5.18	1.51×10^{5}
600.1	327	3.22	1.66×10^{3}

Catalysts

Eleven different catalysts were prepared and tested. In these preparations, outlined briefly in the following paragraphs, the following materials were used unless otherwise specified:

Charcoal, activated, animal, 6–20 mesh, J. T. Baker Chemical Company.

Alfrax, 10–16 mesh, Carborundum Company.

Phosphoric acid, 85 per cent (specific gravity 1.71), J. T. Baker Chemical Company.

Boric acid (H_3BO_3), Howe and French, Inc.

Sulfuric acid, 96 per cent reagent.

Zinc sulfate ($ZnSO_4 \cdot 6H_2O$), technical grade, Merck & Company, Inc.

Sodium phosphate ($Na_2HPO_4 \cdot 12H_2O$), Baker & Adamson.

Strontium chloride ($SrCl_2 \cdot 6H_2O$), c. p. granular, J. T. Baker Chemical Company.

Zinc chloride ($ZnCl_2$), c. p. granular, J. T. Baker Chemical Company.

Ferric chloride ($FeCl_3 \cdot 6H_2O$), c. p. granular, Eimer & Amend.

Aluminum chloride ($AlCl_3$), anhydrous, Mallinckrodt Chemical Works.

Silver sulfate (Ag_2SO_4), c. p. powder, J. T. Baker Chemical Company.

Water, distilled.

The percentage catalytic material referred to in each case is based on the difference between the total weight of catalyst and the weight of support (charcoal, Alfrax, etc.) used. Solutions are aqueous unless otherwise specified.

Z-1, PHOSPHORIC ACID–KIESELGUHR. This was the regular Universal Oil Products Company polymerization catalyst. Minute details for its preparation are not available, but from information obtained, it was concluded that a 3:1 weight mixture of phosphoric acid and kieselguhr was extruded from a $^1/_8$-inch orifice into pellets which were baked at 200–260° C. A catalyst prepared in this manner was tested in the synthesis unit and was found to give results almost identical with those obtained when the U. O. P. catalyst was used.

Z-2, PHOSPHORIC ACID–CHARCOAL. Phosphoric acid was poured over charcoal, and the mixture (1.5:1 weight ratio of acid:charcoal) was heated at 250–280° C. for 17 hours and at about 370° C. for 1 hour; after this treatment the material was dry at room temperature and contained about 42 per cent acid.

Z-3, BORON PHOSPHATE–PHOSPHORIC ACID–CHARCOAL. A 14.9 per cent boric acid solution was poured over a phosphoric acid–charcoal mixture and heated with stirring to 240° C. (5.5 hours of heating time). The weight ratio of boric acid solution to 85 per cent phosphoric acid to charcoal was 3:1:1.6. The resulting catalyst contained approximately 18 per cent catalytic material.

Z-4, PHOSPHORIC ACID–SULFURIC ACID–CHARCOAL. A solution of phosphoric acid and concentrated sulfuric acid was poured over charcoal (11.1:1:9.3 weight ratio). This mixture was heated with stirring at 200° C. for about 30 minutes. The excess liquid was separated from the solid by filtration through glass wool; then the solid material was heated at 213° C. for 1.5 hours. The resulting mixture contained about 21 per cent catalyst.

Z-5, ZINC PHOSPHATE PELLETS. Zinc phosphate was precipitated from a hot 56.5 per cent $Zn_2SO_4 \cdot 6H_2O$ solution by addition of a hot 52.5 per cent solution of $Na_2HPO_4 \cdot 12H_2O$. The weight ratio of sulfate to phosphate solution was 1.1:1. The precipitate was filtered from the mixture and washed several times with a total of about 0.5 weight ratio of water (based on phosphate solution) followed by drying at 110° C. for 11 hours. About 3 per cent by weight of graphite was incorporated in the powder to act as a binder; then the mixture was made into pellets $^7/_{32}$ inch in diameter and $^1/_8$ inch long.

Z-6, STRONTIUM CHLORIDE–CHARCOAL. A hot 16.7 per cent solution of $SrCl_2 \cdot 6H_2O$ was poured over charcoal (weight ratio, 2.8:1). This mixture was heated, with frequent mixing, over a hot plate until practically dry and was then dried for 30 minutes at 110° C. Catalytic material contained in the mass was about 30 per cent.

Z-7, ZINC CHLORIDE–ALFRAX. Alfrax was stirred into a 50 per cent $ZnCl_2$ solution (1.75:1 weight ratio). The mixture was stirred, allowed to stand for several minutes, filtered over glass wool, and dried at 110° C. for about 40 hours. The resulting material contained about 14.1 per cent catalyst.

Z-8, FERRIC CHLORIDE–ALFRAX. The method employed in the preparation of this catalyst was similar to that used in Z-7. Hydrogen chloride was evolved during the drying operation, and the result was the formation of iron oxide. For this reason the material was dried for only 1.75 hours at 103° C. The resulting mass contained about 10 per cent catalyst.

Z-9, SODIUM CHLORIDE–ALUMINUM CHLORIDE–PUMICE. The method employed in the preparation of this catalyst was similar to that used by Blunck and Carmody (*4*). The sodium chloride–aluminum chloride salt consisted of approximately a 1:1 molal complex of aluminum chloride and sodium chloride. The complex was made by fusing the salts (with a slight excess of aluminum chloride to take care of sublimation loss in the early stage of the heating process) in a pressure bomb at temperatures up to 265° C. After cooling to room temperature, the bomb was opened and heated again to drive off the excess aluminum chloride. The fused salt was then poured over an equal weight of dry pumice (8–10 mesh) with thorough mixing. The final catalyst contained about 50 per cent catalytic material. This material was very hygroscopic and necessitated storage in a gastight container until it was placed in the catalyst chamber.

The Z-9 catalysts listed in Table III were all prepared according to the above procedure. The different letters (e. g., Z-9a, Z-9c, etc.) signify different batches of catalyst.

Z-10, SULFURIC ACID–ALFRAX. Alfrax was stirred into a 77 per cent solution of sulfuric acid; the mixture was heated for one hour at 100° C. and was then filtered over glass wool. The solid was heated for 4 hours until the temperature

Table III. Summary of Data

Run No.	4	12	19a	19b	19c	19d	20b	20c	20d	23	24	25	26	27	29	30	31a	31b	31c	31d	32
Catalyst, Z—	1	9a	9d	9d	9d	9d	9c	9c	9c	9i	9i	9i	9i	9i	9i	9i	9i	9i	9i	9i	9i
Pressure, lb./sq. in. gage	100	100	100	100	100	100	200	100	50	200	200	100	0	50	200	200	200	200	200	200	200
Temperature, ° C.	239	246	242	239	239	238	266	266	267	268	268	268	268	268	268	268	268	268	268	268	268
Space velocity[a]	27.2	26.6	22.1	21.7	25.3	25.8	19.4	31.5	37.1	19.9	28.8	37.6	53.8	53.1	29.2	39.3	47.2	49.3	57.3	50.2	11.6
C_6H_6:C_2H_4 molal ratio	1.34	1.83	2.07	1.95	1.43	1.73	2.34	2.20	2.28	2.12	2.04	1.91	2.22	2.91	1.77	1.92	2.54	2.00	2.04	1.93	1.61
Duration, minutes	300	195	180	180	180	180	180	120	120	120	150	120	120	120	120	120	120	90	90	90	300
C_6H_6 feed rate, grams/hr.	17.3	19.3	14.1	14.4	18.4	16.3	13.2	14.9	17.9	7.1	15.6	21.0	32.3	31.7	15.1	20.8	26.3	27.4	32.6	28.1	5.2
Liquid product analysis, volume %																					
Benzene	85.4	64.2	62.1	64.2	62.7	68.6	60	76.3	92.9	62.3	57.5	64.4	100	93.3	50.7	52.5	59.0	59.5	63.2	63.3	43.5
Monoethylbenzene	13.5	22.8	32.1	27.9	16.3	21.4	30.8	14.4	7.1	32.5	31.5	21.2	0	6.7	31.3	32.6	30.2	26.7	23.2	22.6	39.6
Diethylbenzene	1.1	7.0	5.8	7.9	11.3	10.0	9.2	9.3	0	5.2	9.2	9.6	0	0	13.2	11.3	7.9	9.4	8.8	9.2	14.5
Higher ethylbenzenes	0	6.0	0	0	9.7	0	0	0	0	0	1.8	4.8	0	0	4.8	3.6	2.9	4.4	4.8	4.9	2.4
Gaseous product analysis, volume %																					
Hydrogen	0	6.8	16.6		7.0		46.7	4.8		0.8	6.6	0.2	0	0.7	1.5	0	16.4		3.3		2.4
Ethane	0	5.3	8.8		7.8		27.3	3.7		22.7	11.0	15.7	0	1.4	18.8	54.5	28.7		15.4		66.0
Ethylene	98.6	86.1	73.4		83.7		24.3	90.3		75.0	81.0	83.5	100	97.0	78.3	42.9	52.7		80.0		29.7
Acid gases (SO_2, CO_2, HCl)	1.4	1.8	1.2		1.5		1.7	1.2		1.5	1.4	0.6	0	0.9	1.4	2.6	2.2		1.3		1.9
C_2H_4 converted, %																					
To monoethylbenzene	12.8	34.7	54.4	44.3	19.7	29.9	59.7	24.8	16.3	56.1	54.1	33.8	0	14.3	48.2	53.7	64.7	44.8	39.3	36.1	54.2
To diethylbenzene	1.6	17.1	15.5	19.6	21.5	22.2	28.4	25.5	0	14.1	25.1	23.9	0	0	31.9	29.5	26.9	25.1	23.4	23.4	32.6
To higher ethylbenzenes (calcd. as tri-)	0	17.6	0	0	23.2	0	0	0	0	0	5.8	14.8	0	0	14.3	12.1	1.6	14.1	16.2	15.6	7.0
Total	14.4	69.4	69.9	63.9	64.4	52.1	88.1	50.3	16.3	70.2	85.0	72.5	0	14.3	94.4	95.3	93.2	84.0	78.9	75.1	93.8

[a] Expressed as cc. vapor (at 0° C., 760 mm.) per hour per cc. catalyst.

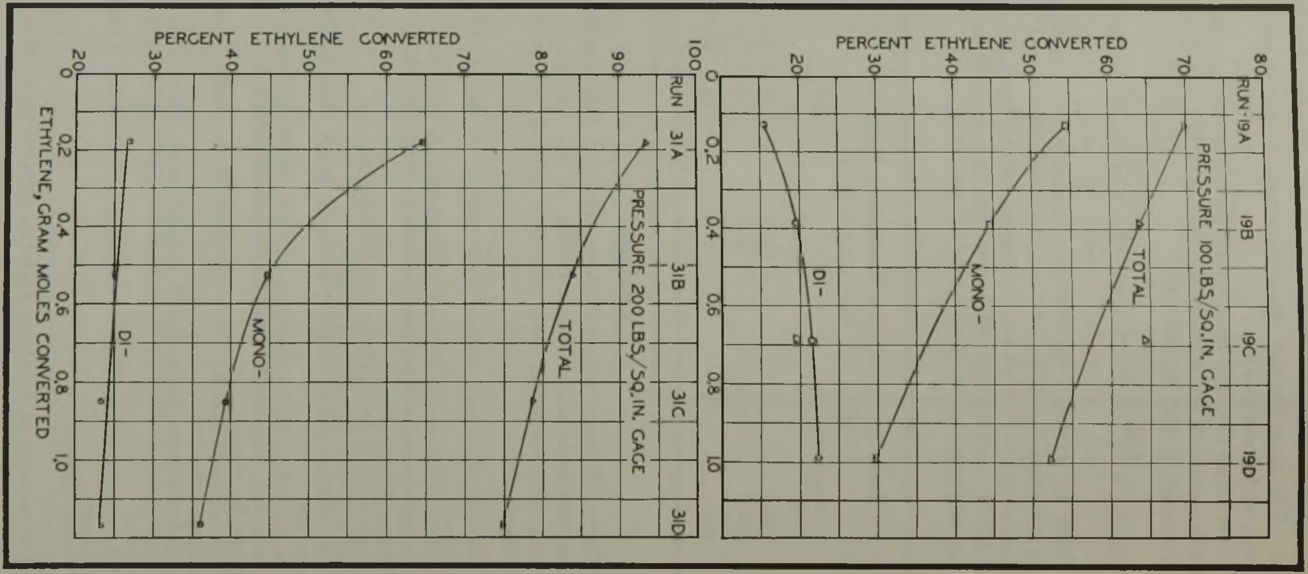

Figure 2. Decrease in Catalyst Activity with Amount of Ethylene Converted

reached 300° C. After this treatment the catalytic content was about 26 per cent.

Z-11, Silver Sulfate–Sulfuric Acid–Alfrax. The method for the preparation of this catalyst was similar to that employed by Stanley, Youell, and Dymock (*22*) and by Bliss and Dodge (*3*). By saturating Alfrax with a solution of silver sulfate and sulfuric acid, filtering, and drying the residue, a material was produced which contained about 4 per cent silver sulfate and about 21 per cent sulfuric acid.

Apparatus and Procedure

The ethylene used in this work came from U. S. Industrial Chemical, Inc., and was at least 99 per cent pure (prepared by dehydration of ethanol over phosphoric acid). The benzene used was Merck's nitration grade which had been further fractionally distilled.

Figure 1 is a flow diagram for the synthesis unit. Ethylene passed from cylinder *A* through pressure regulating valve W_1, purifier *N*, trap *M*, flowmeter T_1, expansion valve W_2, and into benzene dropper *H*. The ethylene-benzene mixture passed from vaporizer *V*, leaving as vapors, and entering reactor *R*, from which the reaction product was expanded through valve W_4, to practically atmospheric pressure. The reaction mixture then passed into a condenser system from which emerged the gaseous product. This flow of gaseous product was noted on flowmeter T_2, sampled continuously by gas sampler *O*, and finally measured by displacement of brine solution from gas receiver *P*. The benzene liquid was fed from tank *G* by gravity into dropper *H*, where it mixed with the ethylene and then passed through the apparatus as noted above.

The flow rates were controlled by $^1/_4$-inch, V-point, needle valves. The ethylene was throttled through valve W_2, from a pressure usually 50–100 pounds per square inch higher than the reactor pressure. The flow rate was noted by reading a pressure differential on manometer T_1, developed by passage of the gas through a short capillary tube. The benzene flow rate was regulated by valve W_3, and noted by counting drops falling through sight glass and dropper *H*. The reactor pressure was maintained by throttling the reaction vapors through valve W_4.

The liquid product was fractionated at atmospheric pressure through a $^1/_2$-inch glass, vacuum, silver-jacketed column packed with 24 inches of $^3/_{16}$-inch stainless steel rings. The various cuts were identified by refractive index measurements as well as by their boiling points.

The effluent gases were analyzed by means of a standard U. S. Steel gas analysis set.

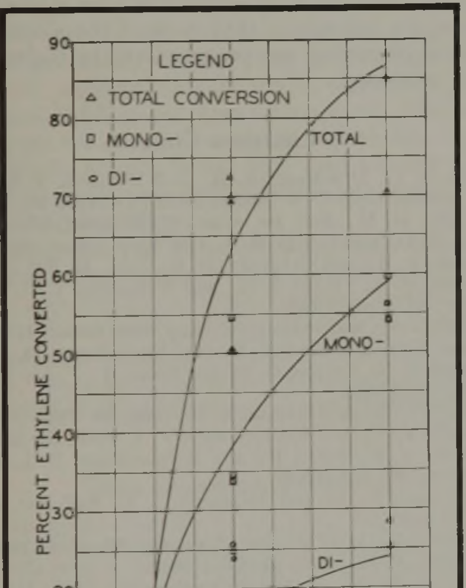

Figure 3. Effect of Pressure on Conversion

Each catalyst was tested by passing through the catalyst bed a mixture of benzene and ethylene vapors in molal ratio of about 2:1, at temperatures of 228° to 245° C., gage pressure of 100 pounds per square inch, and vapor space velocities of 25 to 40 cc. (0° C. and atmospheric pressure) per hour per cc. of catalyst. Sixteen runs were made in this preliminary catalyst study, and

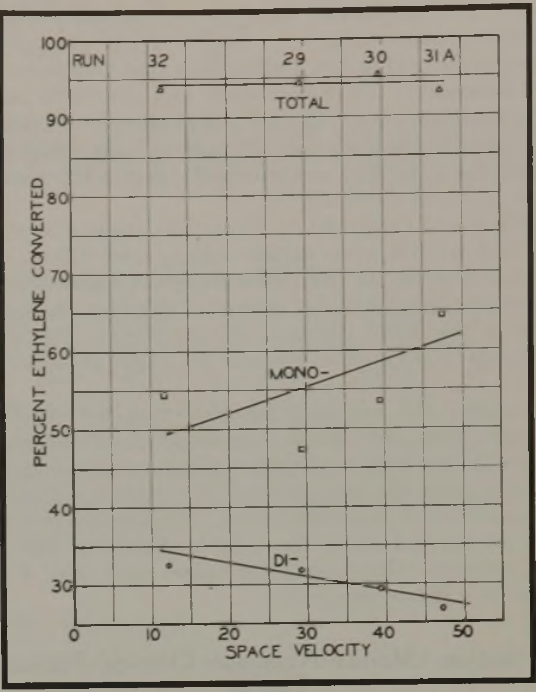

Figure 4. Effect of Space Velocity on Conversion

only two of the catalysts were found to promote a detectable reaction between the ethylene and benzene (the phosphoric acid–kieselguhr and the sodium chloride–aluminum chloride–pumice catalysts).

Following the preliminary catalyst study, the sodium chloride–aluminum chloride–pumice catalyst was investigated in further detail. The activity of this catalyst was studied over a period of time, and the pressure and space velocities were varied in a series of runs. In the investigation of the effect of pressure on the reaction, gage pressures of 0, 50, 100, and 200 pounds per square inch were employed. The effect of space velocity was studied over the range 11.6 to 47.2 cc. per hour per cc. of catalyst (contact times of about 20 to 5 minutes).

A summary of the runs in which reaction was noted is given in Table III. No data are listed for the catalyst test runs where no reaction occurred, but it may be assumed that the operating data and analytical procedures were similar to those listed under runs 4 and 12.

Since the yields of triethylbenzene were only estimated from the distillation residue, they are not plotted as separate curves in Figures 2, 3, and 4. However, they are contained in the "total" conversion curves in these figures. This explains why the sum of the mono- and di- ordinates are not always equal to the total ordinates.

Preliminary Catalyst Study

Phosphoric acid supported on kieselguhr was the first catalyst to be tested. The results indicate that 13–15 per cent of the ethylene was converted to ethylbenzene, predominantly monoethylbenzene with small amounts of diethylbenzene (about 10:1 weight ratio). Since pressure has been found to have such a pronounced effect on the reaction when the sodium chloride–aluminum chloride–pumice catalyst was used, this phosphoric acid–kieselguhr catalyst would probably give satisfactory conversions at pressures of 300–400 pounds per square inch.

Phosphoric acid in forms other than that mentioned above (with kieselguhr) failed to promote any noticeable reaction. Thus, phosphoric acid–charcoal, boron phosphate–phosphoric acid–charcoal, and phosphoric acid–sulfuric acid–charcoal failed to cause ethylene and benzene to react at 100 pounds per square inch and about 240° C.

Sulfuric acid supported on Alfrax was inactive as was also the mixed catalyst, silver sulfate–sulfuric acid–Alfrax. Thus, it stands that sulfuric acid, even though it is a good catalyst for benzene alkylation by olefins of three or more carbon atoms in the liquid phase, does not promote the reaction of ethylene and benzene either in the vapor phase or liquid phase.

Strontium, zinc, and ferric chlorides supported on activated charcoal, Alfrax, and Alfrax, respectively, were found to be inactive in the form employed. Aluminum chloride, in the form of a fused equimolar mixture with sodium chloride supported on pumice, was quite active; ethylene conversion was about 69 per cent under the same conditions of test on the other catalysts (100 pounds per square inch, 246° C., 26.6 cc. per hour per cc. catalyst).

Sodium Chloride–Aluminum Chloride–Pumice Catalyst

Under the conditions of these tests, the sodium chloride–aluminum chloride was in the liquid state; therefore, it was necessary to support the material on a carrier. Pumice (8–10 mesh) was used as the carrier but was not satisfactory because of its varying properties from one lot to another. For example, two different lots of pumice were used; one gave an active and the other an inactive catalyst. It was concluded that the variation in activity was due to the difference in density of the two lots. The more active catalyst was prepared from the less porous lot (density of about 0.46 gram per cc.), and its greater activity may be attributed to a greater and thicker catalytic surface on this pumice than on the more porous material (density of about 0.26 gram per cc.). Some "prepared" carrier would probably be much better than the pumice, but due to lack of time, other carriers were not tested except for one test with activated alumina. In this test the ratios of materials were the same as with pumice, but this catalyst gave only about 20 per cent conversion. It is believed, however, that the only function of these different carriers is to support the catalyst, and that with the same area and thickness of catalytic surface the carrier material would have no effect on the reaction. Tests were made to show that the pumice and the alumina alone had negligible catalytic effect on the benzene-ethylene mixture under the conditions used.

In order to determine the effect of the catalyst on the individual reactants, the benzene and ethylene vapors were passed separately through the catalyst bed. The benzene vapors were unaffected, and the ethylene was decomposed slightly, with about 2 per cent ethane and 0.5 per cent hydrogen in the effluent gas.

Catalyst Activity. Runs 19 and 31 were made to determine the activity of the catalyst over a period of time at 100 and 200 pounds per square inch, respectively. The data used to plot Figure 2 are listed in Table IV, and illustrate the decrease in activity of the catalyst as a function of moles of ethylene converted.

There was a decrease in total conversion from 93 to 75 per cent resulting from the conversion of about 0.19 to 1.16 gram moles of ethylene to ethylbenzene. Indications are that the formation of higher ethylated benzenes is favored with use of the catalyst over a period of time.

Pressure as a Variable. Runs were made at pressures of 0, 50, 100, and 200 pounds per square inch gage. A 300-pound run was attempted, but the capacity of the benzene vaporizer was not sufficient for operation at this pressure.

The great effect of pressure on the reaction is shown in Figure 3. Conversion ranged from 0 at atmospheric pressure to about 90 per cent at 200 pounds per square inch gage. Since the points in this plot are scattered, the reliability of the different analyses has been evaluated, and the points were weighed accordingly in drawing the curve to best represent the true conditions.

Table IV. Catalyst Activity

Run No.	Total Gram Moles Ethylene Converted	Pressure, Lb./Sq. In. Gage	% Ethylene Converted to: Mono-	Di-	Tri-	Total
9a	0.131	100	54.4	15.5	0	69.9
9b	0.383	100	44.3	19.6	0	63.9
9c	0.683	100	19.7	21.5	23.2	64.4
9d	0.991	100	29.9	22.2	0	52.1
31a	0.180	200	64.7	26.9	1.6	93.2
31b	0.521	200	44.6	25.1	14.1	84.0
31c	0.851	200	39.3	23.4	16.2	78.9
31d	1.164	200	36.1	23.4	15.6	75.1

Space Velocity as a Variable. The vapor space velocity was varied from 47.2 to 11.6 cc. (vapor, calculated at 0° C. and atmospheric pressure) per hour per cc. of catalyst. The data for these runs are plotted in Figure 4. It is concluded that the total conversion of ethylene to ethylbenzenes was independent of the space velocity in the range studied. However, there are indications that more of the mono- and less of the diethylbenzenes are produced at the higher than at the lower velocities.

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Based on a dissertation presented by W. A. Pardee to the faculty of the Yale School of Engineering in partial fulfillment of the requirements for the degree of doctor of engineering.

CATALYTIC OXIDATIONS of NAPHTHALENE SERIES

▸ ▸ ▸ Vapor-phase catalytic oxidations were made on commercial naphthalene, practical Tetralin, 95 per cent 2-methylnaphthalene and 70 per cent 1-methylnaphthalene to yield chiefly phthalic anhydride. Quinone by-products were found in small amounts. The most successful catalyst consists of pure pyrolytic vanadium pentoxide fused on glassy silica gel. A tin-bearing vanadium catalyst was tried with but moderate success.

Two complete oxidizers were built and details of construction are given. A small apparatus made entirely of Pyrex was used for systematic investigation of space velocity and yield relations. A stainless steel Downs-type oxidizer was employed for check runs. The maximum yields of phthalic anhydride were 76 per cent from naphthalene, 70 per cent from Tetralin, and 40–50 per cent from methylnaphthalenes.

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THE process variables involved in catalytic vapor-phase oxidation of aromatic compounds are space velocity, or contact time which is its reciprocal function, temperature, the ratio of the reactants, and the nature of the catalyst. Unfortunately in the past, investigators of these reactions have failed to correlate and, in many cases, even to record all their findings on these salient data. The result is that, although the reaction of air on naphthalene vapor to produce phthalic anhydride has been used commercially for at least twenty years, very little detailed and specific information appears in the public print.

This investigation was undertaken to supply some of the missing information, especially that pertaining to problems involved in carrying out such reactions successfully, control of apparatus, behavior of catalysts, nature of the crude products, and possible relations between the process variables. In addition, information has been obtained about the oxidation of substituted naphthalenes which have been studied very little until now.

Glass Oxidation System

Figure 1 shows the small Pyrex apparatus used for systematic investigation of space velocity and yield relations. The vaporizer was made from a 100-cc. Kjeldahl flask and was heated by immersion in a bath of molten paraffin wax, the temperature of which was measured by a mercury thermometer. The preheater, which had a coil height of 6–7 inches and a length of about 60 inches, was made of 8-mm. Pyrex tubing. The catalyst tube, which contained 30–40 cc. of catalyst, was constructed from 25-mm. tubing, with the central downcomer 8 mm. in outside diameter. The annular catalyst bed, the top half inch of which was visible above the bath, was supported by a plug of glass wool; the catalyst temperature was measured by a bare-tipped chromel-alumel thermocouple located in the center of the annular catalyst layer, 1.5 inches from the top of the four-inch long bed. The annular layer was about $^1/_4$ inch thick. The salt bath was a mixture of 40 per cent sodium nitrite, 7 per cent sodium nitrate, and 53 per cent potassium nitrate (*16*) contained in a steel pot, gas-fired and agitated by a propeller. The bath temperature was measured by a chromel-alumel thermocouple. The air-cooled condenser tubes were 1.5-foot lengths of 25-mm. Pyrex tubing; the spare was used in case of plugging of the main system. The hot ends of these tubes were sealed to the catalyst-tube offtake with built-up stoppers of asbestos paper. The cold trap tube, 35 mm. in diameter was immersed in a carbon tetrachloride–chloroform mixture contained in a Dewar bottle and cooled with solid carbon dioxide. The Cottrell precipitator was made from 25-mm. Pyrex and bore a central electrode of $^1/_{16}$-inch steel rod and an outer electrode 1 foot long made from copper window screen.

The air was passed first through a 1-gallon "ballast bottle" to smooth out flow irregularities; it was measured by a differential-water-column flowmeter and mercury-filled manometer. The metered air was introduced directly into the vaporizer. These metering and gas handling devices are not shown in Figure 1.

It is unnecessary to dry or decarbonate the air for these oxidations (*7*). An auxiliary stream of measured air was used for cooling and aerating the catalyst.

All bare unheated parts were insulated with asbestos rope. The vaporizer outlet tube was heated electrically. The reaction tube, preheater, and vaporizer were sealed in series with useful temporary, tight, heat-resistant joints built up from layers of asbestos paper soaked in water glass, alternated with windings of fine copper wire.

Downs Metal Oxidation System

Figures 2 and 3 show the steel Downs-type reactor used for check runs to approximate commercial conditions on a one-tube scale. The air was measured and controlled in a manner similar to the small oxidizer except that two air streams were required in normal operation. The vaporizer and air preheaters were heated by immersion in molten paraffin, the temperature of which was measured. The reaction preheater tube of stainless steel was heated by a small electric tube furnace constructed by winding 8.5 feet of $^1/_8 \times 0.0201$ inch Nichrome ribbon (about 2 ohms) on a cylindrical alundum core, 1 foot long and $1^1/_{16}$ inches i. d. The element was covered with refractory cement, and the unit was insulated by packing with Sil-O-Cel.

The reactor was the type using boiling mercury to remove the heat of reaction; the boiling temperature was regulated by nitrogen pressure on the mercury condenser system. The catalyst tube was a 1-inch stainless-steel pipe welded through the center of a steel jacket, 4.5 inches in diameter and 1 foot long. The tube and jacket were mounted in an electric furnace constructed similarly to the reaction preheater. The alundum core was 1 foot long and $4^9/_{16}$ inches i. d. The heater element was a 40-foot length of $^1/_8 \times 0.0126$ inch Nichrome V

UNIT PROCESSES

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ribbon (approximately 20 ohms) with an extra center-tapped lead. The unit was constructed in a three-legged pot made from 10-inch steel pipe. Figure 4 shows the heater circuit.

The catalyst was supported on a small screen at the level of the jacket bottom, held up by prongs on a thermocouple well extending into the bottom of the tube. The catalyst temperature was measured by chromel-alumel thermocouples buried in the entering and exit layers of the catalyst. The entering thermocouple was bare, the exit sheathed in a thin tubular well. The former was introduced through the packed blank-flange joint at the top of the tube. This flange may be used as an inlet for several thermocouples if desired. The thermocouple circuit is shown in Figure 5.

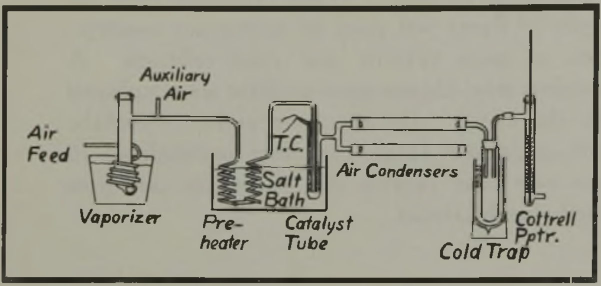

Figure 1. Small Glass Oxidizer

The air-cooled condenser was a 2-foot length of 1-inch Pyrex pipe, followed in the condensing system by an air-cooled trap bottle. The Cottrell precipitator (Figure 2) was made from 50-mm. Pyrex tubing and the screen electrode was 18 inches long. The central electrode consisted of a $^{1}/_{8}$-inch welding rod upon which were mounted discharge rings. Power for the Cottrell precipitator was furnished by a pair of 12,000-volt neon-sign transformers with primaries in parallel and secondaries in series. The primary circuit included a rheostat and voltmeter.

A packed water-scrubbing column (Figure 3) containing a bed, 18 inches long and 35 mm. in diameter, of $^{3}/_{16} \times ^{1}/_{4}$ inch glass rings was substituted for the Cottrell precipitator in several runs. The column was fed from the split discharge of a laboratory centrifugal pump which drew water from a 1-liter beaker into which was dipped the bottom drain tube from the column.

Three flowmeters of differential-liquid-column type having maximum capacities of 80, 150, and 600 liters per hour were used singly or in pairs in this study. These meters were calibrated throughout their entire ranges under the usual small superatmospheric operating pressure of the system with a Sargent wet-test gas meter.

Catalysts

The elements reported as basic catalysts or promoters include most of the cation-forming members of the Periodic Table. More favorable claims for basic materials are narrowed to the Fifth Group elements. Most of the references available are in the patent literature, which is vague at best (*2*, *19*). The oxides of vanadium, molybdenum, tungsten, uranium, and manganese are claimed to give the highest yields of phthalic anhydride from naphthalene (*19*), with vanadium pentoxide seemingly the one preferred. Tin vanadate has the advantage of lower operating temperature (*20*).

Not only the composition but the method of preparation and activation are said to have significant bearing on the effectiveness of the catalyst. The catalysts used commercially are basically vanadium pentoxide with all details of modification closely guarded secrets (*12*). In addition, even with identical preparation and pretreatment, one of two catalysts of vanadium pentoxide made from different lots of commercial ammonium metavanadate may be highly efficient and the other ineffective (*7*). Consequently, some experimentation was necessary to secure a catalyst which was sufficiently active, adhered well to the support, and was stable during repeated use.

The vanadium oxides of interest for catalytic purposes are the red-purple to orange pentoxide, V_2O_5, the blue tetroxide, V_2O_4, and the green trioxide, V_2O_3 (*24*). All three have been identified in catalysts after use (*25*). For catalyst preparation the quinquevalent oxide is available dry by the pyrolysis of ammonium metavanadate or wet as an insoluble, orange, colloidal, or finely crystalline material by acidification of aqueous solutions or suspensions of the metavanadate.

Acid reduction of vanadium pentoxide by sulfurous or oxalic acids results in formation of the more soluble blue vanadyl salts useful for impregnating carriers with higher vanadium concentrations by wet methods. The compounds of this valence stage are blue or reddish brown (*24*).

PRECIPITATED VANADIUM PENTOXIDE. Fifty milliliters of distilled water were saturated near the boiling point with pure commercial ammonium metavanadate (NH_4VO_3). Concentrated sulfuric acid was added dropwise to precipitate the hydrated oxide. Evaporation and grinding gave a fine orange powder. Fusion of the powder in oxygen at bright red heat produced dark purplish-red crystals on the crucible sides and a purplish-black glassy mass in the bottom. Regrinding converted this to a greenish-yellow powder.

VANADIUM-TIN TRIAL CATALYSTS. To obtain a low-temperature tin-vanadium catalyst such as that described by Maxted (*20*), a method based on the Craver patent (*9*), depending on reduction of vanadates to vanadyl salts with oxalic acid, was used with the addition of stannous chloride dihydrate in ratio of the formula $Sn(VO_3)_2$. This catalyst was coated on a very light, porous refractory brick which contained some easily fusible alkali oxides. Such a catalyst was used for runs T-1 MMN, T-1 MN$_1$, T-1 and T-2 MN$_2$, T-1 T, 1 and 2 MN$_2$, 1 to 3 N, and 1 to 3 T, all carried out in the Downs oxidizer. Considerable trouble was experienced with control of the operating temperature of this catalyst,

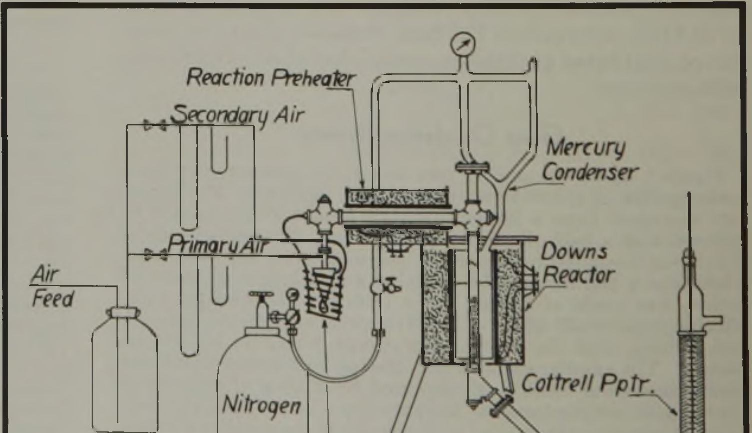

Figure 2. Laboratory Model of Downs Oxidizer

especially after much use. When removed from the tube the catalyst showed evidence of intense fusion.

Vanadium Pentoxide on Silica Gel. The most successful catalyst was prepared by pyrolytically decomposing ammonium metavanadate and fusing the oxide on commercial glassy silica gel (8–10 mesh) until the carrier was completely coated with the pale purplish-red oxide. This catalyst was used for all controllable runs in the glass reactor as well as for runs 1 and 2 TL, 1 to 3 NL, and 1 to 5 MN_2L in the large reactor.

Hydrocarbons[1]

Mixed Methylnaphthalenes. Run T-1 MMN was made with technical mixed methylnaphthalenes containing about 65–70 per cent 2-methylnaphthalene as estimated from rough freezing-point studies related to Figure 6 (*18*).

2-Methylnaphthalene. The runs on 2-methylnaphthalene (MN_2) were made with commercial white, crystalline material melting above 31° C., of purity above 95 per cent (Figure 6).

1-Methylnaphthalene. A technical-grade synthetic product containing about 70 per cent 1-methyl and 30 per cent 2-methylnaphthalenes, based on approximate freezing points, was used in runs of the MN_1 series.

Tetralin. Practical-grade Tetralin was employed in series T. The only impurities to be expected were traces of naphthalene and Decalin.

Naphthalene. The commercial product, melting at 78–9° C., was used in runs of the N series.

Analytical Procedure

By a series of tests based upon previously reported work (*21*), it was decided that both 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone could be determined with sufficient accuracy (within 5 per cent of the quinone content of the crude oxidation products, which, in turn, was less than 5 per cent of the total crude products) by iodometric titration. The data are shown in Tables I, II, and III.

Table I. Titration of Quinone in Presence and Absence of Phthalic Anhydride

(Reagents: 0.2 *N* sodium thiosulfate, unstandardized; 10% KI solution, c. p. conc. HCl; 1,4-naphthoquinone, m. p. 124.5–125° C.)

Sample No.	Quinone, Gram	Phthalic Anhydride, Gram	Thiosulfate, Ml.	Quinone, M. E.	Thiosulfate, M. E.	Discrepancy, %
1	0.1016	0.0000	6.74	1.286	1.349	4.9
2	0.1010	0.6778	6.69	1.278	1.338	4.7

Table II. Iodometric Titration of 1,4-Naphthoquinone and 2-Methyl-1,4-naphthoquinone (M. P. 102–3° C.)

(Reagents: 0.103 *N* sodium thiosulfate, standardized against pure iodine; c. p. conc. HCl; 95% ethanol; pure iodate-free KI)

Sample No.	Quinone, Gram	Thiosulfate, Ml.	Blank, Ml.	Aging Time, Min.	Quinone by Titration, Gram	Error, %
1	0.1776 (Me-)	23.20	−3.30	2	0.1762	0.8
2	0.1578 (Me-)	19.35	−1.85	10	0.1550	1.3
3	0.1519 (1,4-)	20.16	−1.70	10	0.1501	1.2
4	0.2007 (1,4-)	16.58	−0.24	2	0.2006	0.1
5	0.2009 (1,4-)	17.00	−0.24	2	0.2043	3.4

Table III. Effect of Alkali Titration on Quinones

(Reagents: 0.176 *N* HCl, 0.905 *N* NaOH, phenolphthalein)

Sample No.	Quinone, Gram	NaOH, Ml.	HCl, Ml.	NaOH Used, M. E.	Quinone Weighed, M. E.	Error, %
1	0.1589 (1,4-)	5.25	21.05	1.04	1.01	3
2	0.1447 (1,4-)	4.41	17.21	0.96	0.915	4
3	0.1589 (Me-)	4.94	20.45	0.87	0.89	2

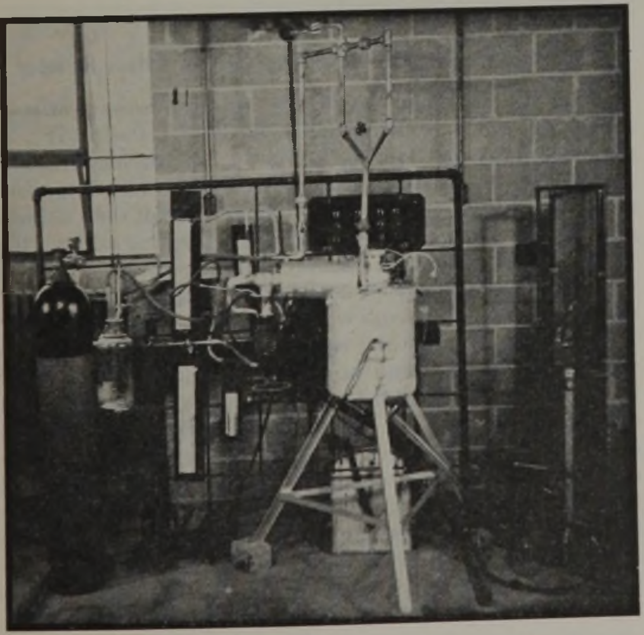

Figure 3. Photograph of Laboratory Downs Oxidizer

In addition, both quinones acted as monobasic acids in the presence of alkali (Table III). This necessitates a correction of any alkaline determination of true acid constituents of the oxidation products. The acidic behavior of the quinones to alkali probably depends upon the oxidation by air of these substances to the hydroxy-substituted derivatives in basic medium (*1*).

The procedure adopted for use on the oxidation product consisted of dissolving a 1.00-gram sample of the test solid in 20 ml. of 95 per cent ethanol, adding 20 ml. of concentrated hydrochloric acid with cooling, and dissolving about 2 grams of iodate-free potassium iodide in the resulting solution. The liquid was titrated immediately with standardized sodium thiosulfate solution and starch indicator solution was added near the end point. If the solution was badly discolored by tarry products, the end point was determined by spot test on starch-iodide paper. Aliquot portions of quinone-bearing aqueous wash liquors were titrated by the same procedure, omitting the alcohol.

The weight of quinone present was calculated by the formula:

$$\text{Wt. quinone} = \text{ml. thiosulfate} \times \text{normality} \times \left(\frac{\text{mol. wt. quinone}}{2000}\right)$$

No blank corrections were used. By adding the potassium iodide last and working rapidly, possible errors from absorbed oxygen (*26*) were minimized; furthermore, liberation of iodine by absorbed oxygen in the reagent mixture on standing frequently did not occur when testing blank samples.

The procedure for determining phthalic anhydride consisted of boiling a weighed 1.00-gram sample of the solid product with 30–40 ml. of distilled water until solution occurred. The solution was cooled rapidly to room temperature and titrated with standardized 1.00 *N* sodium hydroxide against phenolphthalein (for discolored solutions

UNIT PROCESSES

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[1] In tables and text the hydrocarbons are frequently abbreviated according to the initials e. g., T for Tetralin, N for naphthalene, MMN for mixed methylnaphthalenes, and ML_2 for 2-methylnaphthalene, etc.

indicator paper was used). The weight of phthalic anhydride present was calculated by the formula:

$$\text{Wt. P. A.} = \left[(\text{ml. NaOH} \times \text{normality}) - \begin{pmatrix}\text{milliequivalents of}\\ \text{quinone in weighed}\\ \text{sample from qui-}\\ \text{none analysis}\end{pmatrix}\right] \times \left(\frac{148}{2000}\right)$$

When yellow aqueous wash liquors were being examined, 10-ml. aliquot portions were diluted to 30–40 ml. and boiled briefly to remove carbon dioxide. The solutions were cooled and titrated in the usual manner, making the quinone correction.

The results are reported as phthalic anhydride because at no time was an appreciable amount of any other organic acid indicated by the alkaline titrations (neutral equivalents) or by the appearance of other than the characteristic phthalic anhydride needles in the condensate, even when operating on methylnaphthalenes.

A good qualitative test for phthalic anhydride used frequently was the formation of fluorescein by fusion of the unknown samples with resorcinol in the presence of sulfuric acid or other condensing agents (*17*). When the melt was poured into dilute alkali, a characteristic yellowish-green fluorescence was formed if the unknown contained any phthalic anhydride.

Tin-Vanadium Catalyst in Glass Reactor

Three runs on 2-methylnaphthalene were attempted with used tin-bearing vanadium catalyst in the small reactor. Air and ethanol vapor were used to try to raise the catalyst to reacting temperature on hydrocarbon. The air-hydrocarbon mixture was substituted when the heat effect in the catalyst seemed sufficiently vigorous. These two streams of material were alternated whenever necessary. Occasionally the catalyst had to be blown with air alone to cool it. A brief summary of the range of conditions tried follows:

Air flow, liters/hour		200–600
Vaporizer temperature, ° C.		90–125
Bath temperature, ° C.		390–450
Temperature of catalyst, reaction going, ° C.	Minimum	500
	Maximum	920

The reaction was not self-maintaining in the usual catalytic range, 300–500° C., either on alcohol or hydrocarbon. High space velocities with alcohol were necessary to heat the catalyst to a point where it would maintain hydrocarbon oxidation. To keep the tube from burning up, the velocity had to be reduced as soon as hydrocarbon oxidation was underway. This frequently resulted in "losing" the reaction again. The reaction could be run only intermittently.

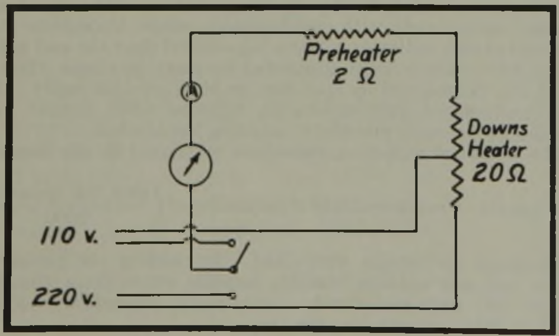

Figure 4. Downs Oxidizer Heater Circuit

The presence of at least one spot in the catalyst glowing at bright red heat and occupying about one third of the catalyst volume appeared to be necessary to maintain the oxidation even intermittently at a partly controlled self-supporting level. In general, this catalyst was uncontrollable after some use and gave only small amounts of tarry and oily oxidation products.

Table IV. Oxidation of Tetralin and Methylnaphthalenes with V_2O_5 on Silica Gel in Small Glass Reactor

Run No.	Space Velocity	Temp., ° C.	Air/Hc. by Wt.	Hc. Wt., Grams	Total Product, Grams	Phthalic Anhydride, Yield %
			Tetralin			
1 TS	4450	470	25.0	10	7.5	67
2 TS	2950	465	14.0	10	7.1	63
3 TS	3420	460	17.5	15	9.5	57
4 TS	4330	466	17.0	20	12.4	54
5 TS	5920	465	14.5	20	14.4	61
6 TS	2010	465	15.5	15	11.6	68
7 TS	2010	465	15.0	10	7.7	66
8 TS	2010	440	15.5	10	6.5	56
9 TS	4300	440	16.0	15	11.7	66
10 TS	6100	440	14.5	20	15.8	60
11 TS	7000	454	12.5	25	13.0	44
12 TS	7100	440	12.0	20	12.0	51
13 TS	3780	440	17.0	10	8.1	70
14 TS	5970	464	16.0	20	15.5	65
15 TS	4800	465	15.0	15	11.5	65
16 TS	3260	465	16.5	10	7.0	60
17 TS	2460	460	15.5	10	7.5	65
18 TS		Bad leak in air condenser plugs				
19 TS	5600	466	17.0	15	12.2	68
20 TS	3950	463	18.0	10	8.6	70
21 TS	8130	442	13.1	20	11.7	50
22 TS	8130	460	14.2	20	13.8	58
23 TS	10000	492	12.2	25	14.0	47
24 TS	12120	472	13.1	30	15.9	44
			1-Methylnaphthalene			
1 MN_1S	4540	468	17.6	15	5.5	33
2 MN_1S	5900	473	13.4	20	Erratic temp.	
3 MN_1S	5300	465	18.7	15	5.5	33
4 MN_1S	5280	467	15.5	15	6.0	36
5 MN_1S	4520	440	16.3	10	4.0	35
			2-Methylnaphthalene			
6 MN_2S	5650	510	18.0	20	4.6	22
7 MN_2S	2300	475	19.0	20	5.5	25
8 MN_2S	2950	465	19.0	15	4.3	27
9 MN_2S	3720	460	22.0	15	4.9	31
10 MN_2S	4370	465	19.7	15	6.3	40
11 MN_2S	5920	464	15.5	20	7.4	29
12 MN_2S	5050	465	16.5	15	5.3	31
13 MN_2S	2000	443	17.0	10	4.0	35
14 MN_2S	4270	440	17.0	20	8.3	35
15 MN_2S	3070	442	20.0	10	4.7	40
16 MN_2S	5030	465	18.0	15	7.6	43
17 MN_2S	4120	465	15.6	20	9.5	43
18 MN_2S	6330	462	16.2	20	6.8	33
19 MN_2S	6300	464	16.2	20	8.9	35
20 MN_2S	3000	460	19.8	10	3.9	34
21 MN_2S	8230	477	17.6	20	8.7	38
22 MN_2S	10000	485	17.5	20	8.5	39

Vanadium Pentoxide on Silica Gel in Glass Reactor

Since the vanadium pentoxide catalyst was relatively stable and easy to control, the runs of the Tetralin (TS), 2-methylnaphthalene (MN_2S), and 1-methylnaphthalene (MN_1S) series were made in an attempt to correlate yield and space velocity and to observe the nature of the products and the behavior of the catalyst when operating with all the variables under control. Thirty milliliters of the catalyst were used, and it was kept hot and well aerated continuously when not in use. The runs were made on hydrocarbon alone.

The air rate, vaporizer temperature, and salt-bath temperature were set ahead of time. A weighed quantity of hydrocarbon was charged to the vaporizer and the air stream diverted into it. The reaction was followed by observing the catalyst thermocouple readings. Minor adjustments of the controls were made as necessary. The reaction was timed from the start of air flow through the vaporizer until the hydrocarbon bubbled no more and the catalyst temperature fell steadily. At this point the air flow and salt-bath temperature were increased to sublime all the products from the top of the catalyst tube and its discharge arm into the air condenser tube. An attempt was made to keep the air rate, time, and temperature of sublimation constant for all runs so that the quantities of product collected would be truly comparative.

The solid product collected in the air condenser, which usually consisted of beautifully formed white or slightly discolored needles, was scraped out and weighed directly. Homogeneously ground samples were analyzed for phthalic anhydride, corrected for quinone content; the presence of any insoluble matter was noted simultaneously. All material adhering to the inside of the air condenser was washed out with hot water, as were the cold trap and Cottrell precipitator. Any oils in these combined washes were separated by adsorption in activated charcoal powder (Nuchar), and the filtered liquor was analyzed for phthalic anhydride, with quinone corrections. The oil was recovered for separate examination. In some special cases where pure yellow needles of quinone separated on cooling the hot wash, they were filtered out and weighed after drying.

Even with this care possible errors crept into several of the runs. Occasionally small leaks were discovered around the plugs for the air condenser. At higher space velocities the Cottrell precipitator failed to remove all the unreacted hydrocarbon from the exhaust gas. At all times small amounts of products escaped the Cottrell precipitator in true vapor form, not subject to electrostatic precipitation. The aftersublimation procedure was not entirely foolproof.

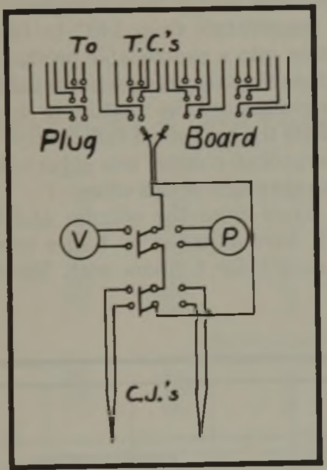

Figure 5. Downs Oxidizer Thermocouple Circuit

Table IV gives an over-all summary of these runs. The space velocity recorded was calculated as liters of entering air per liter of catalyst per hour, corrected to 0° C. and 760 mm., where the air rate is the arithmetic average of meter readings. The catalyst temperature listed is the arithmetic average of the readings of the single thermocouple buried in the catalyst when these readings were steady through the run. Whenever this temperature was variable, the recorded average was obtained by plotting temperature against time and dividing the area under the curve by the total time to give a "graphically integrated" average temperature.

The air-hydrocarbon ratio (air/hc.) was obtained by dividing the total weight of air passed through the vaporizer during actual vaporization of hydrocarbon by the weight of hydrocarbon vaporized.

The weights of products recorded include both the total solid collected directly and the material found by quinone and anhydride analyses of the aqueous washes. No recovered oils are included in these figures. The molecular percentage yield of phthalic anhydride is based on the total found by titration of samples of the solids and washes.

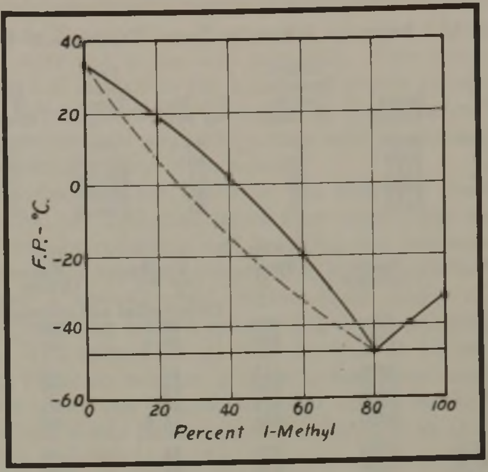

Figure 6. Freezing Points of the System 1- and 2-Methylnaphthalenes

The maximum quinone found in solid air-condenser products was 5 per cent or less for both Tetralin and the methylnaphthalenes. This does not correspond necessarily to maximum formation of that material, for at higher space velocity a larger proportion of it passed through to the trap and Cottrell precipitator. Quinones were present to some extent in all products.

Oily products containing unattacked hydrocarbon, a change in catalyst color from the normal orange to a dark greenish or blue-black, and erratic temperature behavior of the catalyst all were correlated with space velocity ranges above 6000.

During the oxidation of methylnaphthalenes the air-condenser solids usually were quinone yellowish during the early part of the runs, but this was superseded by a pinkish to purple cast with tar formation as the runs proceeded. This type of discoloration was evident in all these runs at some point in the condensing system, often imparting that hue to the wash waters. Upon standing in air, however, the purple washes usually turned yellow.

Finally, the products from 2-methylnaphthalene were much more tarry and impure than those from Tetralin at corresponding space velocities. But the purity of the phthalic anhydride was seldom below 95 per cent.

By cooling of hot saturated wash liquors, 1,4-naphthoquinone was isolated from the products of oxidation of Tetralin and 1-methylnaphthalene, and was identified by simple and mixed melting points.

Tin-Vanadium Catalyst in Downs Reactor

A series of trial runs was made on all the hydrocarbons to be investigated, using new tin-vanadium catalyst. The chief purpose was to test the operability of the apparatus. The mercury jacket was one third full.

Significant data are listed in Table V. These preliminary runs were made with no thermocouples in the catalyst, but a comparison with later runs allowed the average tube exit temperature to be estimated within 25–30° C. from the pressure on the mercury jacket. The condition of the

Table V. Summary of Runs in Downs Reactor with Tin-Vanadium Catalyst

Run No.	Space Velocity	Jacket Pressure, Lb./Sq. In. Gage	Air/Hc. by Wt.	Estd. Exit Temp., ° C.	Hc. Wt., Grams	Product Wt., Grams	Phthalic Anhydride Yield, %
T-1 MMN	3645	20	66	380	50	26	50
T-1 MN_1	3530	20	50	370–80	36	12	29
T-1 MN_2	3455	20	55	370–80	50	13.5	26
T-2 MN_2	3490	20	65	370–80	35	10.2	30
T-1 T	3550	0	35	310–20	40	24	54

Run No.	Space Velocity	Exit Temp., ° C.	Air/Hc., by Wt.	Hc. Wt., Grams	Product, Wt., Grams	Phthalic Anhydride Yield, %
1 N	Uncontrolled and incomplete					
2 N	3170	270	27.7	40	27	3
3 N	3220	390	26.4	30	15	39
1 T	3320	412	37	50	10	17
2 T	3220	420	32	70	22	28
3 T	3200	435	32	50	19	34
4 T	3260	528	35.6	30	19	52
1 MN_2	3300	270	34	40	27	3
2 MN_2	3300	310	33	40	36	2
3 MN_2	Uncontrolled					
3 MN_2	3200	390	42	30	8.4	27
4 MN_2	3140	420	22.5	45	4.0	8.5
5 MN_2	Uncontrolled					
5, 6, 7 MN_2	Diluted catalyst, uncontrolled					
1 MN_2A	Diluted catalyst, alcohol at start, uncontrolled					

catalyst upon removal suggested that there had been some violent departures from this average.

The products were not analyzed; the yields reported are the crude, fairly clean needles from the air condensing system.

In the 2-methylnaphthalene runs a strong, sharp odor of formaldehyde was noticed in the exhaust gas. Tests on brown aqueous condensates and by absorption of some of the exhaust in aqueous-alcoholic sodium bisulfite solution, a test reagent for lower aldehydes (*22*), resulted in copious precipitation of shiny, white plate crystals.

Esterification of a mixture of the solid products from all these runs with anhydrous ethanol in the presence of a little concentrated sulfuric acid gave an oily product which was vacuum-rectified to yield pure diethyl phthalate (checked by density and index of refraction). All losses except column holdup in the rectification were such as to be proportionate for any mixture of esters possibly present. The holdup was less than 10 per cent of the charge and could have contained no esters more volatile than the main product. Since nowhere were other than characteristic phthalic anhydride needles observed in any solid oxidation products from methylnaphthalenes, and since alkaline titration of these products usually checked out as phthalic anhydride, it is extremely unlikely that the esters of either 1- or 2-naphthoic acids were present in the holdup. These are the only possible acid products of the oxidation of methylnaphthalenes having ethyl esters less volatile than diethyl phthalate. Hence, the only acidic product formed in appreciable amount from the oxidation of methylnaphthalenes is phthalic anhydride.

A second series (MN_2) was run in the Downs reactor with fresh tin-vanadium catalyst (Table V). Considerable control trouble was experienced in later runs after the catalyst had been overheated by poorly controlled reactions. Table VI shows the nature of the products from this series.

Vanadium Pentoxide on Silica Gel in Downs Reactor

The exit temperatures (Table VII) are integrated averages for the sheathed thermocouple buried in the exit layer of catalyst. The entering temperatures are integrated averages of the bare thermocouple surrounded by the entering layer of catalyst. Figure 7 is an example of the record of these thermocouples used to obtain integrated averages. Space velocity and air/hydrocarbon ratio are defined as before. The weights of product include crude solids and wash liquor contents. The solid products from runs on methylnaphthalenes contained a deep purple discoloration which was very soluble in water. The mercury jacket was two thirds full in this series.

During runs 1 and 2 MN_2L an attempt was made to hold the space velocity at 4100–4200. The catalyst temperature went wild again, temperatures as high as 1100° C. being observed. The reaction was explosive and produced soot at these high temperatures. The catalyst was ruined (fused to a blue, glassy material). No solid oxidation products were obtained.

Fresh catalyst was used in the subsequent runs. Lowering the vaporizer temperature from 140° to 130° C. seemed to bring the reaction into a controllable productive range. The trouble with those first two runs was probably caused by insufficient air, which placed the mixture in the explosive range and failed to dilute the heat effect sufficiently.

The water-scrubbing column was substituted for the Cottrell precipitator throughout this series.

The yellow liquor from the column and washing liquors from run 2 NL were adjusted to 1 liter in volume and extracted continuously for 6 hours with 100 ml. of benzene.

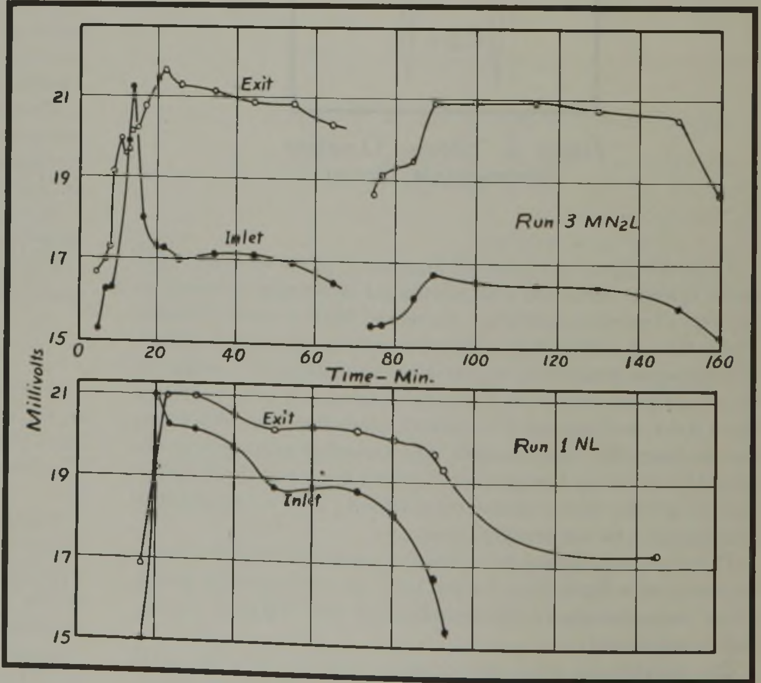

Figure 7. Typical Records of the Catalyst Thermocouples in the Laboratory Downs Oxidizer

Table VI. Account of Materials Based on Analysis of Tin-Vanadium Runs in Downs Reactor

Run No.	Phthalic Anhydride Yield, %	Quinone Yield, %	Hc. Recovered as Such, %	Hc. Lost, %
2 N	3	3	58	36
3 N	39	4	8	49
1 T	17	3	..	80
2 T	28	1	..	71
3 T	34	1	..	65
4 T	52	3	1	44
1 MN_2	3	2	64	31
2 MN_2	2	6	82	10
3 MN_2	27	..	..	73
4 MN_2	8.5	..	..	91.5

The yellow benzene extract was stripped of solvent and dried, and the residue sublimed at 100° C. and 5 mm. pressure to give an orange, semicrystalline condensate. The solid was recrystallized quantitatively from aqueous alcohol to give 0.25 gram of yellow needles which melted at 124–126° C. (corrected). This product was 1,4-naphthoquinone.

The procedure proved capable of isolating quinone from the washes. The process was repeated on the wash liquors from runs 3, 4, and 5 MN_2L. Sublimation of the combined benzene residues gave an oily, orange, semiliquid condensate, similar to that from the naphthalene product except that it was more liquid. Attempts to recrystallize an identifiable solid failed.

Table VII. Summary of Runs in Downs Reactor with V_2O_5 on Silica Gel Catalyst

Run No.	Space Velocity	Inlet Temp., ° C.	Exit Temp., ° C.	Air/Hc. by Wt.	Hc. Wt., Grams	Product Wt., Grams	Phthalic Anhydride Yield, %
1 TL	4160	456	460	16	80	58	65
2 TL	7030	388	475	30	40	32	72
1 NL	4060	462	480	11	60	53	76
2 NL	6860	370	473	28	40	33	72
3 NL	4180	443	480	13	60	43	63
1 MN_2L				Uncontrollable			
2 MN_2L				Uncontrollable			
3 MN_2L	4180	402	490	23	60	31	50
4 MN_2L	4160	420	485	21	50	27	52
5 MN_2L	6960	351	530	40	40	21	51

The crude sublimates from the naphthalene and 2-methylnaphthalene quinone processing were compared. While the naphthalene product was mostly 1,4-naphthoquinone, with perhaps a little phthalic anhydride to lower its melting point, the condensate from the 2-methylnaphthalene product (much more liquid in character) admitted the possibility of a chemically and physically inseparable mixture of 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone as well as traces of phthalic anhydride.

Yields

Curves. Figure 8 shows roughly the relation between molecular percentage yield of phthalic anhydride and space velocity for the temperatures and air/hydrocarbon ratios indicated. These curves are based on runs in the glass reactor with pure vanadium pentoxide catalyst. Since errors in technique could not be entirely avoided, only the runs having the highest yield for a given space-velocity range are plotted. This selection of points probably gives a true picture of the shape and trend of these curves.

Failure of the points to fall exactly on a smooth curve may also be explained partially by the fact that it proved impractical to maintain identical air/hydrocarbon ratios and catalyst temperature thoughout a long series of runs where other variables were not to be held constant. The direction of probable yield correction for individual points to eliminate technical errors and reduce all points to the indicated standard temperature and air/hydrocarbon ratio is shown by arrows originating in some of the points.

These corrections are based on the following reasonable assumptions: (*a*) Technical errors were usually the result of material loss in collecting and handling the products. (*b*) Air/hydrocarbon ratio and temperature higher than the standard caused a lowered yield, within small ranges of these variables, resulting from a greater degree of complete combustion. The reverse of (*b*) may be true at higher space velocities where an increase in these factors may result in an increase in yield, due to more complete attack on the hydrocarbon which would have remained untouched at the standard condition chosen (*4, 5, 12*).

These yield–space velocity curves show the expected form. At low space velocities the losses are caused by complete combustion of the product; at higher space velocities hydrocarbon may come through unattacked. A maximum yield is found between these extremes. This is a general characteristic of catalytic vapor-phase oxidations (*19*).

Maximum Yields. That the maxima exhibited in the yield–space velocity curves should shift along the space velocity axis with changes in temperature is to be expected, because high space velocity (low contact time) should be necessary to produce the same extent of reaction at higher temperature where reaction velocity is higher. The principle of increase in reaction velocity with temperature is quite general, because the effect of increased temperature is the activation of a greater proportion of the participating molecules per unit time to an adequate energy level for reaction.

Figure 8 gives evidence of this shift, although the difference between the temperatures chosen appears insufficient to indicate a marked variation.

Examination of the maxima (Figure 8 and Table VII) shows that naphthalene and Tetralin gave comparable yields which, moreover, were 1.4 to 1.7 times as high as the yields from methylnaphthalenes. Probable pyrolysis of the methylnaphthalenes may be indicated from this fact about the comparative yields and from the apparently greater complexity of the products of the methylnaphthalenes; also purely pyrolytic studies (*3, 14, 15, 23*) show that, in the temperature range of the present study, both naphthalene and Tetralin are relatively stable to heat whereas the methylnaphthalenes are somewhat decomposed.

Comparison with Previous Work. Table VIII summarizes most of the material found in the literature which gave experimental data on yields and conditions.

Behavior of Catalyst

This investigation is the first recorded in which the catalyst has been observed while the reaction was in progress. Visual evidence thus has been added in support of the theory of oxidation-reduction equilibria in the operation of the vanadium pentoxide catalyst. Changes in the surface state of the catalyst also were obvious (*19*).

Weiss, Downs, and Burns (*25*) first established the existence of a

Table VIII. Comparison of Yields with Previous Work

Hydrocarbon	Phthalic Anhydride Yield, %	Temp., ° C.	Space Velocity	Catalyst	Scale of Operation	Reference
$C_{10}H_8$	80	...	...	...	Laboratory	*(8, 11)*
	84	280	...	Sn-V	Laboratory	*(20)*
	66	370	470	V_2O_5	Laboratory	*(12)*
	61	290	...	Sn-V	Laboratory	*(6)*
	69^a	...	...	V_2O_5	Commercial	*(10, 13)*
	76	460–80	4060	V_2O_5	Downs reactor	Table VII
$C_{10}H_{12}$	53	....	...	Sn-V	Laboratory	*(20)* 4 runs
	67	320–60	470	V_2O_5	Laboratory	*(12)* 8 runs
	70	440	3780	V_2O_5	Glass reactor	Table IV
	72	400–75	7030	V_2O_5	Downs reactor	Table VII
$MeC_{10}H_7$	43	465	4120	V_2O_5	Glass reactor	Table IV
	52	420–85	4160	V_2O_5	Downs reactor	Table VII

[a] 80 pounds per 100 pounds.

variable V_2O_4/V_2O_5 ratio in the normal catalyst by quantitative analysis of the catalyst, both before and after oxidations of benzene at varying air/hydrocarbon ratios.

Qualitative observations of the variation of catalyst color in the present investigation indicated that space velocity alone, at constant temperature and air/hydrocarbon ratio, had a pronounced effect on the composition of the catalyst. At space velocities above 6000 in the glass reactor the catalyst was in a reduced state which was undesirable catalytically and led to poor control of the reaction and incomplete attack on the hydrocarbon. The catalyst could be returned readily to an active state by brief aeration at the reaction temperature.

Furthermore, the active catalyst surface was not the original fused macrocrystalline vanadium pentoxide which was charged in new catalyst. Comparison of the orange color of the catalyst after use with the purple-red crystalline nature of fresh catalyst suggested that the active material is in either a microcrystalline or amorphous finely divided state similar to vanadium pentoxide prepared by rapid precipitation of fine, orange vanadic acid in aqueous medium. Accompanying this change in surface state, there would necessarily be an enormous increase in the contact area of the surface. It was likewise noticed that the catalyst was inactive after fusion in the presence of the reaction mixture and that it could not be reactivated readily from this state.

Observations on the tin-bearing catalyst were limited and inconclusive. However, the fact that the initiating temperature range of this catalyst for partial oxidation, once it had been fused in the reactor (500–600° C.), was in the range for the start of noncatalytic oxidation suggested that, by fusion or reduction or both, the catalyst had become an inert material for practical purposes.

Some of the more successful tin-bearing catalysts previously reported were prepared from stannic chloride rather than from stannous chloride dihydrate as tried here. If the latter is the reason for the poor stability of the catalyst discussed, it cannot be rationalized when the treatment accorded these catalysts in the reactor tube is considered; stannous chloride and stannic chloride would both be expected to yield stannic oxide as the result of treatment at high temperature with air containing some water vapor.

Estimation of Heat Transfer Coefficients in Catalyst Tube

The average temperature difference between catalyst and mercury jacket may be used to estimate the magnitude of the effective over-all heat-transfer coefficient in the catalyst tube.

A simple heat balance can be written about the tube, assuming that the only heat losses of the tube are to the bath and in the heat content of the exit gases above the entering catalyst temperature. Other small effects, such as preheating the gases from 250–300° C. to the entering catalyst temperature by the condensation of mercury vapor on the upper third of the catalyst tube, and such as proportionately small increases in the number of moles of gas leaving over that entering due to the production of carbon dioxide and water vapor, will be ignored. Actually, a material balance shows that the maximum molal increase of the gases possible (by complete combustion of methylnaphthalene at theoretical air ratio) is only about 4.5 per cent. Actual conditions with more than theoretical air and large formation of partial oxidation products minimizes this error.

Table IX. Summary of Hydrocarbon Reactions

Hydrocarbon	Reaction	Theoretical Air/Hc. by Wt.	Gram-cal./Mole at 450° C.
$C_{10}H_8$	Complete combustion	13.0	Q_c = 1,207,000
	To phthalic anhydride	4.84	Q_{pa} = 416,100
$C_{10}H_{12}$	Complete combustion	13.6	Q_c = 1,305,000
	To phthalic anhydride	5.75	Q_{pa} = 501,400
$MeC_{10}H_7$	Complete combustion	13.1	Q_c = 1,357,000
	To phthalic anhydride	5.83	Q_{pa} = 555,100

Such a rough heat balance, based on the law of conservation of energy, for the steady state of both heat and material flow may be expressed as in Equation 1.

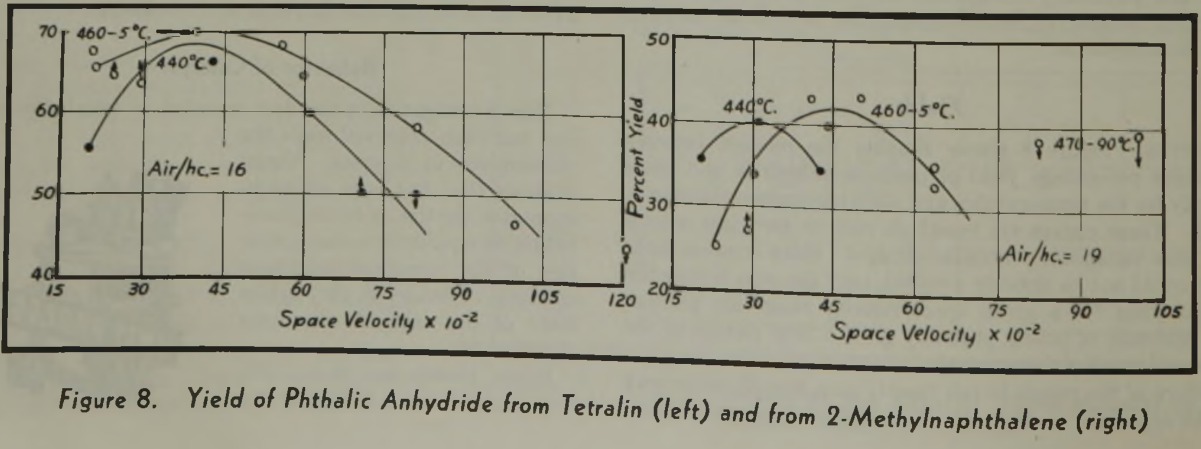

Figure 8. Yield of Phthalic Anhydride from Tetralin (left) and from 2-Methylnaphthalene (right)

Table X. Computation of the Heat Transfer Equation

[Volume of catalyst = 100 cc.; A = 146 sq. cm.; c_p = 0.25 cal./(gram)(°C.)]

Run No.	Space Velocity	Temperature, °C. Exit	Temperature, °C. Inlet	Temperature, °C. Bath	Yield Phthalic Anhydride, %	Ratio Air/Hc.	M	Q_r	$\frac{Q_r}{RM}$	$T_{ex}-T_{in}$	$c_p\Delta T$	$\frac{Q_r}{RM-c_p\Delta T}$	T_c-T_b	$\frac{0.000887\ SV}{T_c-T_b}$	U* Gram-cal. (Sq. Cm.)/(Hr.)(° C.)
1 TL	4160	460	456	398	65	16	132	786,500	373.0	4	1.0	372.0	60	0.0615	22.9
2 TL	7030	475	388	400	72	30	132	726,800	163.5	87	22.0	141.5	31	0.201	28.5
1 NL	4060	480	462	386	76	11	128	604,000	429.0	18	4.5	424.5	85	0.0423	17.9
2 NL	6860	473	370	395	72	28	128	641,000	176.5	103	25.8	150.7	26	0.234	35.2
3 NL	4180	470	442	404	63	13	128	711,500	421.5	27	6.8	414.7	53	0.070	29.0
3 MN:L	4180	490	402	406	50	23	142	956,000	299.0	88	22.0	277.0	40	0.093	25.8
4 MN:L	4160	485	420	406	52	21	142	942,500	310.0	65	16.3	293.7	46	0.0802	23.6
5 MN:L	6960	530	351	406	51	40	142	947,700	166.7	179	45.0	121.7	35	0.177	21.5

* To convert to B.t.u./(sq. ft.)(hr.)(° F.), multiply by 2.05.

$$wc_p(T_{ex} - T_{in}) + UA(T_c - T_b) = \frac{wQ_r}{RM} \qquad (1)$$

$$\begin{bmatrix}\text{heat in gases leaving}\\ \text{above entering cata-}\\ \text{lyst temp.}\end{bmatrix} + \begin{bmatrix}\text{heat lost}\\ \text{through}\\ \text{tube wall}\end{bmatrix} = \begin{bmatrix}\text{total heat liber-}\\ \text{ated by actual}\\ \text{reaction}\end{bmatrix}$$

where w = weight of air, grams/hr.
c_p = gram-specific heat of air at 400–500° C.
U = over-all heat transfer coefficient, gram-cal. (sq. cm.) (hr.) (° C.)
A = inside tube-wall area in contact with catalyst, sq. cm.
R = air/hydrocarbon ratio by weight
M = mol. weight of hydrocarbon
$(T_{ex} - T_{in})$ = av. temp. difference between ends of catalyst mass
$(T_c - T_b)$ = arithmetic av. catalyst temp. minus bath temp. $[(T_{ex} - T_b) + (T_{in} - T_b)]/2$
Q_r = heat liberated per mole hydrocarbon reacted, gram-cal.

Q_r is defined by Equation 2:

$$Q_r = \left(\frac{Y}{100}\right)(Q_{pa}) + \left(\frac{(100 - Y)}{100}\right)(Q_c) \qquad (2)$$

where Y = yield of phthalic anhydride, mol. %
Q_{pa} = heat of reaction to phthalic anhydride
Q_c = heat of complete combustion

The small heat effect in the formation of small amounts of quinones and other products is neglected.

Solving Equation 1 gives Equation 3:

$$U = \left(\frac{w}{A(T_c - T_b)}\right)\left[\left(\frac{Q_r}{RM}\right) - c_p(T_{ex} - T_{in})\right] \qquad (3)$$

It is useful to convert w into terms of space velocity, SV, which was calculated at standard conditions of temperature and pressure:

$$w = \frac{(29\text{ g./mole})\ (SV\text{ l./hr./l. of catalyst})\ (0.1\text{ l. of catalyst})}{22.4\text{ l. /mole}}$$

Inserting this value and the tube-wall area, A = 146 sq. cm., into Equation 3, and solving gives the final form:

$$U = \left(\frac{0.000887\ SV}{(T_c - T_b)}\right)\left[\left(\frac{Q_r}{RM}\right) - c_p(T_{ex} - T_{in})\right] \qquad (4)$$

For estimation of Q_r a survey of the reactions involved with their heat effects at 450° C. is necessary (rough calculations made from known or accurately estimated heats of reaction at 20° C.). Table IX indicates this information. Since the heat effects were not based on complete thermodynamic data, their absolute accuracy may be doubtful; but their comparative values serve adequately for this rough study which is designed primarily to indicate a possible method of attack on the problem of heat transfer in these catalyst tubes.

The data and calculations for solving Equation 4 are summarized in Table X. The limited data and lack of precision in control and measurements here probably make the values of U only approximate. However, with refined calorimetric technique and more extensive data, application of this method of attack will lead to results of both practical and theoretical interest.

Conclusions

1. Naphthalene, Tetralin, and the methylnaphthalenes are oxidized catalytically in the vapor phase to phthalic anhydride as the chief stable partial oxidation product.
2. Methylnaphthalenes produce lower yields of phthalic anhydride than naphthalene and Tetralin under the same conditions.
3. If yield of phthalic anhydride is plotted against space velocity (temperature and air/hydrocarbon ratio constant), the curve for 2-methylnaphthalene shows the same form as that for Tetralin; both curves are of the type usually associated with catalytic vapor-phase oxidations.
4. At space velocities higher than that for maximum yield of phthalic anhydride, darkening or reduction of the catalyst, incomplete attack on the hydrocarbon, and erratic behavior of the catalyst temperature set in gradually and become progressively worse, the higher the space velocity.
5. The simplest preparation of an effective catalyst is afforded by fusion of pure vanadium pentoxide onto a suitable carrier, of which silica gel is a good example.
6. Stannous chloride may not be a satisfactory intermediate for the preparation of the tin vanadate type catalysts.
7. Catalysts may become inactivated by overheating or excessive reduction or both. If the conditions of this destruction of activity are not too severe, the catalyst can be reactivated by aeration at the reaction temperatures.
8. Inactivated catalysts give incomplete attack at excessive temperatures to form difficultly condensable and nonuniform products.
9. A heat balance over the catalyst tube, based on simple temperature and flow measurements, serves to establish the general magnitude of the effective over-all heat transfer coefficient of the catalyst tube; it is, in effect, a packed tube operating at high temperature under the influence of a thermochemical reaction. A method of attack is indicated for problems of this type.

Acknowledgment

We wish to extend thanks to the Lindsay Light and Chemical Company and the Vanadium Corporation of America for donating the ammonium metavanadate for preparing catalysts, to the Reilly Tar and Chemical Company for the gift of the naphthalene and 2-methylnaphthalene, and to the Research Corporation for the design of the Cottrell precipitator used with the Downs reactor. For technical advice we are indebted to C. R. Downs, of Weiss and Downs, and to F. E. Cislak, of the Reilly Tar and Chemical Company.

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Condensed from the Ph.D. thesis of Russell W. Welborn at Purdue University.

TAR ELIMINATION in

Removal of Tar-Forming

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PYROLIGNEOUS acid from hardwood distillation has long been a source of acetic acid of greater or lesser purity; the latter may readily be made as pure as that from any synthetic source, directly and continuously.

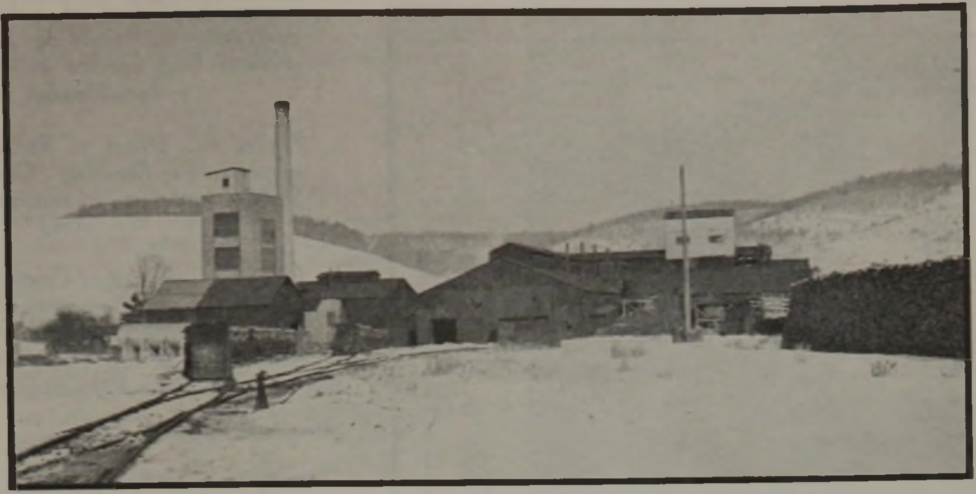
Pyroligneous liquors contain numerous classes of chemical materials—for example, aldehydic and phenolic compounds which condense to form many types of resins or tars. Almost anything that may be done to the liquor, either chemically or physically, causes a combination of some of the molecules. These reactions yield tars which separate in one form or another, ranging from oils to hard, firmly adhering, dense pitches of almost cokelike characteristics. Even the "green" or "settled" or "insoluble" tar which separates from the condensed liquor is not distilled from the wood in that chemical form, but is the product of the combination of various simpler compounds leaving the wood during carbonization.

It is usual to speak of "soluble tars" as those which do not settle out during this step. A more correct expression would be "soluble tar-forming materials", since they are not in tar form then or they would not be soluble. Part of these materials is separated by distilling all of the liquors away from the higher boiling residue which is formed, largely because of the increased speed of combination caused by the higher temperature. The residue is also called "boiled tar", but some of the tar-forming constituents distill over with the "boiled liquors" and are available to form tar at subsequent stages. In fact, hard cokelike scaling occurs on condenser tubes in the vapor spaces of multiple-effect evaporators used for this "primary" distillation as a result of the combination of these materials immediately after having been in the vapor state.

The classical method is the neutralization of the dilute acid with lime to give calcium acetate which is treated, after evaporation to dryness, with sulfuric acid to free the volatile acetic acid. A small amount of tar remained in the commercial calcium acetate. ("Gray acetate of lime" refers to that from pyroligneous liquor which had been first distilled and distinguishes it from the older "brown acetate of lime" made from pyroligneous liquor which had not been distilled away from the bulk of the tar.) Newer methods produce acetic acid directly from the pyroligneous acid. In the Albin-

▶ ▶ ▶ Hundreds of organic compounds have been identified in pyroligneous acid from wood distillation; many of them condense or polymerize to form tars and cokelike pitch at every successive stage of each of the various processes which have been used to recover methanol, acetic acid, and other materials.

It was desired to find a method which would remove easily, with minimum adjustment of equipment and processing, substantially all of the tar-forming materials in a single step early in the processing stages; the continuous plugging of heat transfer and other equipment with tars could then be obviated, and pure materials could be more easily made as finished products. It was found that treatment of the liquors with sulfuric acid for several hours resulted in the



Courtesy, Gray Chemical Company

General Picture of Wood Distillation Plant, Taken from Wood Yards

Loaded buggies at left are ready for retorts. Wood pile shown at right, retort building with five stacks (ten retorts) in center, still house at left.

PYROLIGNEOUS ACID

Constituents by Polymerization and Condensation

Suida process (*1*), a high-boiling solvent extracts the acetic acid from the vapors formed by distilling the liquor, and the solvent and acetic acid are then separated by vacuum distillation. The Brewster process utilizes a low-boiling solvent which removes the acetic acid in a liquid-liquid extraction (*10*). The process of removing the water by an azeotropic distillation with an appropriate organic compound was described previously (*8, 9*). Tar-forming materials cause difficulties in these and every other method of processing pyroligneous liquors.

easy removal of practically all tar-forming constituents as fluid tar oils.

The processing was developed on a laboratory scale to determine the optimum conditions of acid concentration and time of treating liquors from various steps of the refining processes, then on a pilot plant scale, and finally on a plant scale in conjunction with an earlier process for removing methanol and acetic acid by distillation. In a plant handling 60 cords of wood daily, only a few pounds of sulfuric acid per day and no additional equipment were required. A simple plant control method is described; its application to other plant methods of processing was considered, and flow sheets for incorporating this system of detarring are indicated.

Previous Work on Tar Removal

In addition to clogging up machinery and equipment, tars raise havoc with heat transfer (*9*) and discolor the products in the direct methods of making acetic acid as well as in those for acetate of lime (*4, 6*) or sodium acetate (*13*). Many methods have been suggested to remove most or all of the tars, but their failure is evidenced by the fact that only the one mentioned above, the expensive primary distillation method, has been adopted to any great extent. Representative suggested processes follow:

1. Tar separators, in which vapors from the hardwood distillation retorts are scrubbed with liquid tar, are described by Klar, Bergström, and Wesslin (*7*). Both Hawley (*6*) and Bunbury (*4*) point out that tar separators have not been widely adopted because of various operational difficulties.

A related method of tar extraction with wood oils was developed by Barbet (*2*). The vapors from the retorts are partially condensed; the condensate (principally tar oils) is then run countercurrent to the incoming vapors to wash them free of tar.

2. Chlorinated solvents in a cold extraction were used by Othmer (*11*) to remove the tars.

3. Stone (*13*) purifies sodium acetate formed from pyroligneous acid. The tarry impurities accompanying the dry crystals are carbonized at about 200° C.

4. Heat treatment under pressure was used by Othmer (*12*) to remove tars by causing polymerization or condensation of the tarry constituents and precipitating them out of solution.

5. In the Charles-Lambiotte method (*5*) demethanolized pyro-

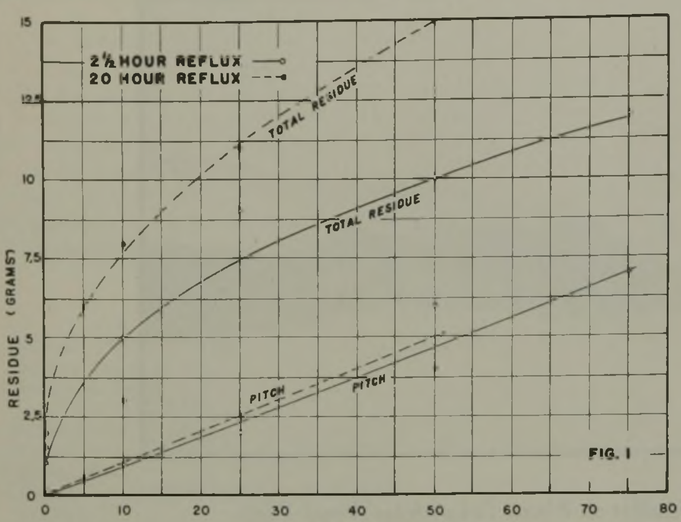


FIG. 1

Figure 1. Effect of Sulfuric Acid Concentration in Removing Tar-Forming Constituents from Settled and Demethanolized Pyroligneous Acid

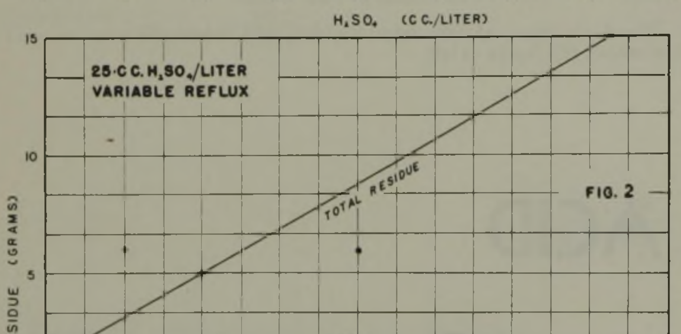


FIG. 2

Figure 2. Effect of Reflux Time in Removing Tar-Forming Constituents from Settled and Demethanolized Pyroligneous Acid

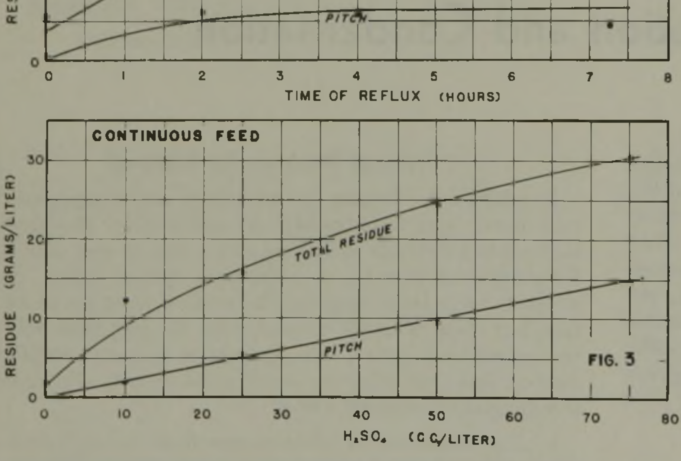


FIG. 3

Figure 3. Effect of Continuous Treatment of Settled and Demethanolized Pyroligneous Acid with Various Sulfuric Acid Concentrations While Vapors Were Removed at the Same Rate as Liquor Was Fed

ligneous vapors are passed through a column in which a solvent for the tars is used as a scrubbing liquid.

6. The most usual method is by evaporation of the raw liquor away from the higher boiling tars as already indicated. Some tar oils are, however, steam-distilled with the liquor; and the additional heat cost is excessive.

Development of the Method

A method was desired which, at a minimum of cost and derangement of processing, would cause the combination of all these tar-forming materials at one time into relatively nonvolatile and readily removable substances. While a method which would fit into the steps of a process using azeotropic distillation was desired, one that was even more general in its application was preferable.

Pyroligneous acid from representative northern and southern plants was used to compare results on liquors from different characteristic wood species. The liquors also came from one of three stages in the processing: (*a*) raw liquor which had merely been settled to remove green or settled tar already formed; (*b*) liquor which had been allowed to settle and then had been distilled to remove methanol; or (*c*) pyroligneous acid which had been settled, demethanolized, and distilled away from the insoluble tars.

From a chemical standpoint, a catalyst might be found which would cause combination and removal of any potential tar-forming body to the subsequent benefit of all processing steps.

PROCEDURE. Pyroligneous acid from one of the points of a process indicated above was heated in the presence of a small amount of the catalytic agent, either under a reflux condenser, during a continuous distillation, or at a constant temperature below the boiling point. Control runs were made without added catalyst. The tarry materials which formed were of three types: a light tar oil floating on top, a heavy semiliquid tar settling to the bottom, and a solid brittle pitch separating from the semiliquid tar on cooling. These constituents were separated by decantation. The tar oil on top of the liquor adhered to the flask and was weighed with the rest of the tarry material and the flask. Treatment with strong caustic soda dissolved the tar oil and semiliquid tar, leaving behind the brittle pitch. The pitch was scraped out and weighed. The flask was then weighed empty and its weight subtracted from the total weight of tars and flask to determine the total residue.

CATALYST. Since the liquors are acidic, an acid catalyst seemed desirable to give a lower pH; a nonvolatile, highly ionized acid was indicated. Sulfuric, phosphoric, and oxalic acids

Table I. Effect of Sulfuric Concentration Acid in 3-Hour Continuous Treatment of Demethanolized Settled Pyroligneous Acid (Pennsylvania)

Distn. No.	H_2SO_4 (66° Bé.), Cc.	Total Dist., Cc.	Total Residue, Grams	Pitch, Grams	G./L. of Dist.		Appearance of Dist.
					Residue	Pitch	
1	0	2855	5	0	1.75	0	Dark brown, colloidal tar
2	10	2680	33	5	12.3	1.9	Clear, colorless
3	25	2850	45	15	15.8	5.3	Cloudy, yellow
4	50	3190	78	30	24.4	9.4	Clear, light yellow
5	75	3140	96	46	30.5	14.7	Same

were compared to determine their relative value in the tar-forming reaction. The following results were obtained on demethanolized settled liquor; 1000 cc. of pyroligneous acid were refluxed for 3 hours in each case with 50 grams of acid catalyst:

Acid	Total Residue, Grams	Pitch, Grams
Sulfuric (66° Bé.)	13	4
Phosphoric (82%)	8	0
Oxalic (solid)	5	0

Since neither methanol nor acetic and homologous acids (the only valuable materials present) would react under these conditions to give water-insoluble materials, the best catalyst appeared to be the one which produced most residue in a given experiment; for less tar-forming material is left by the catalyst which gives the largest mass of insoluble residue.

The above figures show that sulfuric acid is the most efficient material of the three catalysts; it is also the cheapest. Therefore, all further experiments were made with sulfuric acid, since there was no apparent difference either in the residues produced or in the types of tar-forming materials left in the solution.

Sulfuric Acid Concentration

To determine the effect of sulfuric acid concentration on the formation of both total residue and pitch residue, two different times of heating under reflux were used—2.5 and 20 hours; the liquor (from a Pennsylvania source) had been settled and demethanolized; the results of treating 1000 cc. are given in the following table and in Figure 1:

2.5-Hr. Reflux			20-Hr. Reflux		
H_2SO_4 added (66° Bé.), cc.	Total residue, grams	Pitch, grams	H_2SO_4 added (66° Bé.), cc.	Total residue, grams	Pitch, grams
0	1	0	0	2	0.02
10	5	1	5	6	0.5
25	9	2	10	8	3
50	10	6	25	11	2.5
75	12	7	50	15	4

The longer treatment results in considerably greater total residue. A higher concentration did not seem desirable for commercial operation.

Time of Treatment

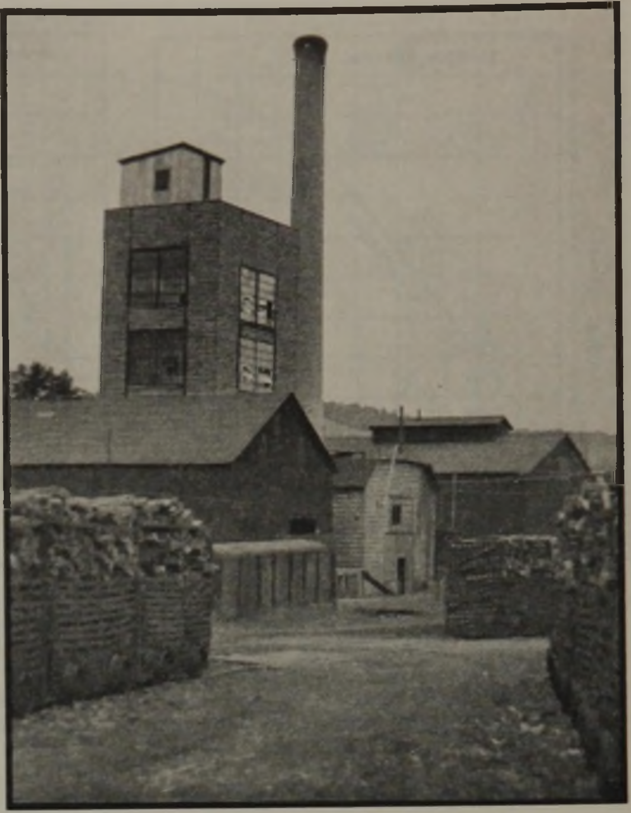
Figure 1 shows that the amount of residue increased with time at a constant concentration of sulfuric acid. To find a suitable time for processing, a control sample of pyroligneous acid was treated with sulfuric acid at room temperature for 24 hours; 2 grams of total residue were produced and no pitch. The results of treating 1000 cc. of demethanolized settled pyroligneous acid (Pennsylvania) with 25 cc. of 66° Bé. sulfuric acid at different times of reflux are shown in the following table and Figure 2:

Reflux Time, Hr.	Total Residue, Grams	Pitch, Grams
1	6	0
2	5	2
4	6	2
7.25	15	1.5

From these and previous runs, it is apparent that time and concentration are interrelated, and that in any industrial processing a longer time would allow a lower concentration of acid (and vice versa) to obtain the same results.

Continuous Treatment

In most industrial processes it would be an advantage to be able to operate continuously; it seemed that the sulfuric acid might be added to a continuously operated still to which the pyroligneous acid was constantly being fed as a liquid and removed as a vapor. The nonvolatile sulfuric acid would always remain with the liquid being treated in the still.



Courtesy, Gray Chemical Company

Close-up of Wood Distillation Plant Showing Loaded Buggies on Way to Retort and Still House in Background

The same liquor was added continuously to a flask which was evaporating the volatile material (water, acetic acid, and methanol). The volume in the flask was one liter, the time of initial reflux before withdrawal of vapors was 3 hours, and the boiling rate balanced the feed so as to maintain an average time in the flask of 3 hours. Several runs were made with different concentrations of sulfuric acid; the results are shown in Table I and Figure 3.

The distillates from the first and third operations of the last run were treated with 25 cc. of 66° Bé. sulfuric acid per liter, and refluxed for 3$^1/_3$ hours to find the amount of tar-forming material which had been volatilized. From the following results it is evident that only about one third as much tar-forming material was present in distillate 3 as in distillate 1 where no sulfuric acid treatment had been given; if distillates 4 or 5 had been used, there would probably have been much less residue:

Dist. No.	Dist. Vol., Cc.	H_2SO_4 (66° Bé.), Cc.	Total Residue, Grams	Pitch, Grams	G./L of Dist.	
					Residue	Pitch
1	2855	71	18	5	6.3	1.75
3	2850	80	7	2	2.2	.63

The conclusion drawn was that if 2.5 per cent by volume of sulfuric acid is added to the primary (or "copper") still of the old calcium acetate process, there would be only one third as much tar-forming material in the distillate, and even less if a greater amount of sulfuric acid was always present in the primary still.

The treated distillates from these runs were tested for sulfur dioxide which would be objectionable in the distillate. This

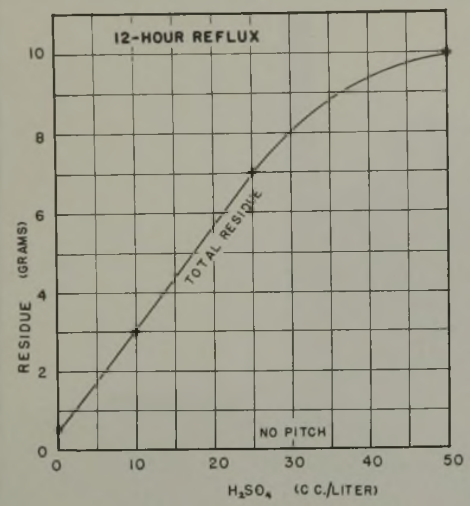


Figure 4. Effect of Sulfuric Acid Concentration in Treatment of Evaporated and Demethanolized Pyroligneous Acid for Removal of Previously Vaporized Tar-Forming Constituents

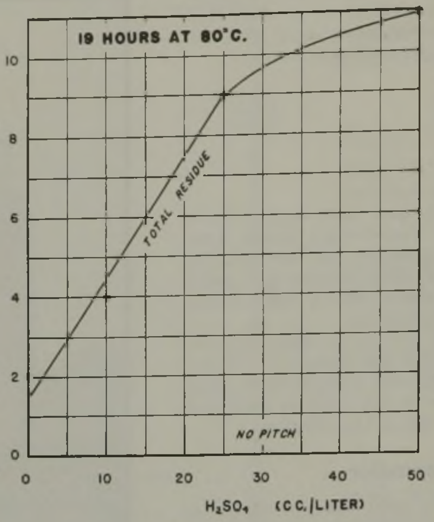


Figure 5. Effect of Treating Evaporated Demethanolized Pyroligneous Acid at Constant Temperature for 19 Hours with Different Concentrations of Sulfuric Acid

was done by distilling over a small sample, adding bromine water and barium chloride, and inspecting for evidence of barium sulfate. In some samples traces of barium sulfate appeared; but the amount was always too small to be measured.

Treatment of Evaporated Demethanolized Pyroligneous Liquor

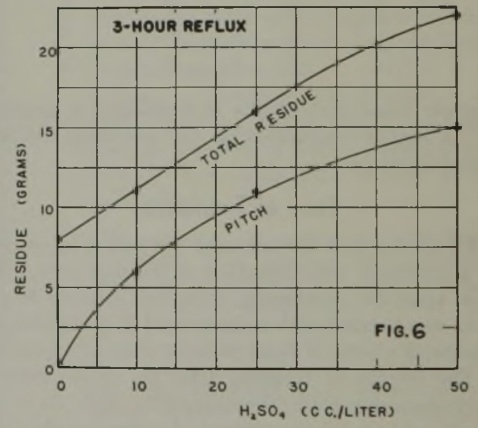
In many plants, after removing insoluble tars and before demethanolizing, the practice is to evaporate the liquor away from the so-called soluble tars. This distillate would be roughly comparable to the distillate of the blank run under "Continuous Treatment". A 12-hour treatment under reflux, with different amounts of sulfuric acid, was made with 1000 cc. of several such samples (from a Tennessee plant); the results follow and are plotted in Figure 4:

H_2SO_4 (66° Bé.), Cc.	Total Residue, Grams	Pitch, Grams
0	0.5	0
10	3	0
25	7	0
50	10	0

Direct comparison cannot be made with Figure 1 because a different time was used and, particularly, because the liquor came from a different plant. But it is interesting to note that considerable tar may be formed even after the liquid has been distilled to remove tar-forming constituents, since only those are removed which have combined to form the boiled or soluble tar. There is, however, no pitch; the heavier bodies which tend to form pitch are evidently removed in the primary distillation.

The last experiment would be directly comparable to plant operations where a distillation unit for acetic acid recovery follows a demethanolizing operation; the treatment with sulfuric acid would be made during this distillation for acid recovery. On the other hand, in some other operations such a distillation might not follow demethanolization, but storage of the hot liquor might be involved. Therefore, the treatment was tried with the liquor held at about 80° C. The results for different concentrations of sulfuric acid at a constant time of 19 hours are shown in the following table and Figure 5; here again, no pitch was obtained:

H_2SO_4 (66° Bé.), Cc.	Total Residue, Grams	Pitch, Gram
0	2	0
10	4	0
25	9	0
50	11	0



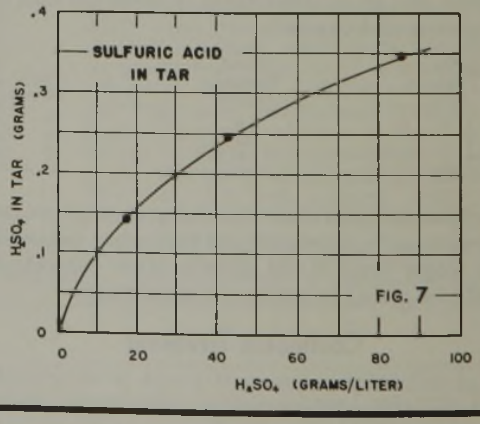


Figure 6. Effect of Treating Raw Settled Pyroligneous Acid under Reflux with Various Sulfuric Acid Concentrations

Figure 7. Distribution of Sulfuric Acid between Aqueous and Tar Layers

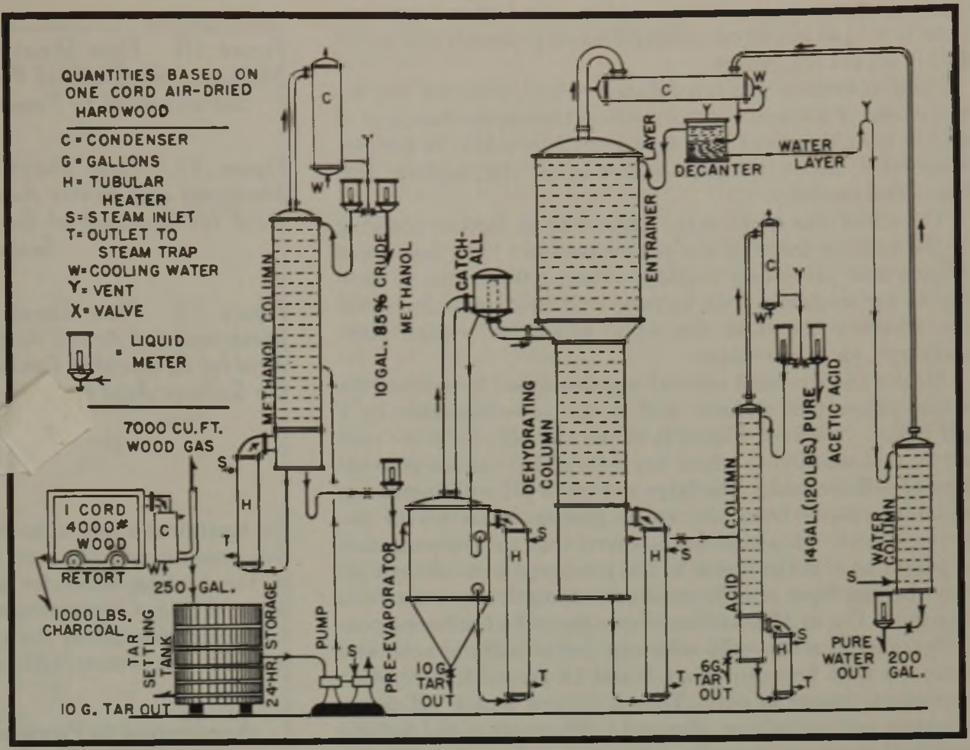


Figure 8. Flow Sheet for Producing Acetic Acid Direct from Pyroligneous Acid by Azeotropic Distillation

Approximate amounts of materials at each stage of the process are shown.

Treatment of Raw Settled Liquor

Some of the volatile materials which are normally removed in the demethanolizing operation might cause tar formation; therefore, a run was made on 1000 cc. of liquor (Tennessee) which had been settled for removal of insoluble tar, but not demethanolized. The following results are indicated in Figure 6 for different concentrations of sulfuric acid after 3-hour reflux:

H_2SO_4 (66° Bé.), Cc.	Total Residue, Grams	Pitch, Grams
0	8	0
10	11	6
25	16	11
50	22	15

Here again direct comparison with Figure 1 is not possible because the materials came from different plants. The total residue in the 3-hour run on this raw liquor was, however, over twice as much as that from a 2-hour run on the demethanolized liquor from the other plant. It appears fair to conclude that the demethanolizing operation removes considerable tar-forming constituents (probably aldehydes) to account for this difference.

Distribution of Sulfuric Acid

In almost every operation it would be desirable to separate the tar layer resulting from the treatment by decantation from the aqueous layer. The presence of sulfuric acid in the tar layer would be bad because of the resulting loss to the treating system of this chemical and because of the disadvantage the strong acid would present to the tar in any subsequent use.

A test was made to determine the amount of sulfuric acid in the tars of run 6. The tar from each sample was boiled with 50 to 250 times as much water; and the water was titrated for acid content on the assumption that practically all of the acid would go into the water. The sample with no sulfuric acid treatment was taken as a blank, and its acid content, assumed to be acetic, was deducted from the values obtained for the other samples. The following distribution of sulfuric acid between the water and the tar layers is plotted in Figure 7:

Run No.	H_2SO_4 in Soln., Grams[a]	Tar, Grams	H_2SO_4 in Tar, Grams
1	0	2	0
2	17.1	4	0.142
3	42.8	9	0.246
4	85.5	11	0.347

[a] 1.71 grams H_2SO_4 per cc. 66° Bé. acid.

Practically all of the sulfuric acid seems to remain in the aqueous layer, and decantation of the tar layer will allow a substantially perfect separation of the tar, free of sulfuric acid.

Application of Tar-Removing Method

The experiments show that the removal of tar-forming constituents may be accomplished either under reflux, during continuous distillation or during heated storage. It was desired to fit this method into a commercial operation such as that of the Gray Chemical Company, using the azeotropic process previously described (*8*, *9*). A flow sheet is given in Figure 8. The technique of tar removal should require no change in equipment by the use of the pre-evaporator as the treating unit, since its size and the amount of liquor handled indicate an average time in the pre-evaporator between 2 and 3 hours.

A small unit was available to test the use of a feed rate of a little over one liter per hour and a sulfuric acid concentration of about 30 cc. of 66° Bé. acid per liter. This run was successful, and distillate condensed from the pre-evaporator was a light straw-colored liquid which was quite different from the usual dark brown liquid obtained at this point. Furthermore, the copper heating unit showed no signs of attack by the sulfuric acid which was in line with known industrial experience where sulfuric acid in even higher concentrations is used as a catalyst in esterification processes with acetic acid in copper equipment.

Plant operation was immediately tried. Pending the development of a simple control method, the required amount of acid to give 3 per cent sulfuric was initially added to the pre-evaporator, and a 12-quart bucket of 66° Bé. sulfuric acid was added each day.

The effect was immediate; there was no further plugging of the heating tubes of the pre-evaporator. The azeotropic column had previously required cleaning from time to time due to tar formation; the sulfuric acid treatment eliminated the necessity for these cleanings, which had meant plant shutdown for several days.

Meanwhile a control method was developed to indicate the actual amount of sulfuric acid in the pre-evaporator by a pH meter. Curve I, Figure 9, shows the pH of a 6 per cent acetic acid solution to which has been added various percentages of sulfuric acid. The large change in pH with increasing amounts results from the much greater ionization of the stronger acid. It is evident, however, that the concentration of acetic acid in the liquor in the pre-evaporator will not always be just 6 per cent (a usual acid strength of pyroligneous liquors). Curve II therefore shows the pH of different concentrations of acetic acid solutions free of sulfuric acid, and indicates that between about 5 and 18 per cent there is no important change in pH. Thus it follows that a pH determination will indicate on Figure 9 the strength of the sulfuric acid in this process, regardless of variations in acetic acid concentration due to operating conditions. A daily determination of pH and the addition of small amounts of sulfuric acid as make-up kept this concentration at 3 per cent, which gave satisfactory results.

Beside eliminating the frequent cleaning of the heating units and periodic disassembly and cleaning of the column, the treatment made unnecessary the use of a forced circulation pump previously used (*8*) to ensure high liquid velocity in the heating tubes for preventing fouling. A 30-horsepower saving of power resulted.

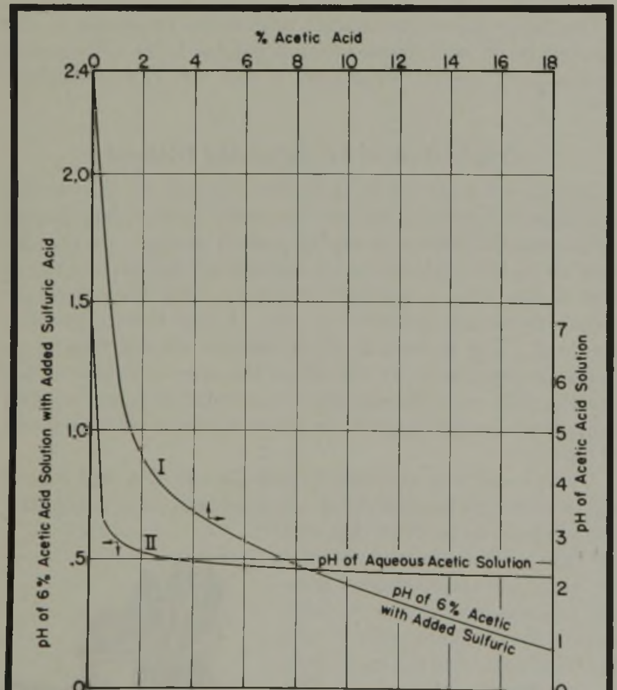


Figure 9. pH of Aqueous Acetic Acid Solutions

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Figure 10. Flow Sheet for Calcium Acetate and Crude Methanol by Classical Process, Modified by Introducing Sulfuric Acid to Remove Tar-Forming Constituents

Figure 11. Flow Sheet for Azeotropic Production of Methanol and Acetic Acid, Modified by Adding Sulfuric Acid for Removal of Tar-Forming Constituents in a Hot Settling Process

Figure 12. Flow Sheet for Azeotropic Production of Methanol and Acetic Acid, Modified by Adding Sulfuric Acid for Removal of Tar-Forming Materials and Recycling the Sulfuric Acid Formed to Prevent Tar Formation in the Demethanolizer

The tars formed in the pre-evaporator were always fluid, settled to the bottom, and were withdrawn every 8 hours.

Application to Processes for Industrial Treatment of Pyroligneous Acid

The simple removal of tar-forming materials may be applied to several industrial processes for separating acetic acid and methanol. Study of the flow sheets of these processes indicates the appropriate places for this step so that no new equipment need be involved; the tar-forming materials may be eliminated so as to produce purer products and prevent the necessity of frequent cleaning of piping and equipment (particularly that for heat transfer). The obnoxious materials are removed as a fluid "sulfuric tar", although this term is not to be construed as meaning that either sulfuric acid or other sulfur compound is present.

Figure 10 is the classical flow sheet for production of calcium acetate and crude wood alcohol. The sulfuric acid is added just prior to the primary still; it may then be operated continuously rather than by the batch operation previously necessary to remove solid tar and pitch formed on both the still and condenser heat transfer surfaces. The sulfuric tar is continuously withdrawn.

Figure 11 indicates the application to the azeotropic process (*8, 9*) but with a preliminary hot storage step using sulfuric acid, which also then enters the pre-evaporator and continues its action there. A longer time of contact (approximately 24 hours in hot settling for sulfuric tar) is thus provided. The tar from the pre-evaporator is returned to the hot storage tank, where it is stripped of acetic and sulfuric acids by the large volume of liquor present. A storage tank having a constant level is used; and the stripped sulfuric tar layer in the bottom is continuously removed by a siphon adjusted to proper level.

A modification (Figure 12) has also been used to take advantage of the solvent power of the sulfuric tar for other materials which may tend to form tar in the demethanolizer. Here the sulfuric tar layer is cycled to the storage tank for feeding the demethanolizer, and passed with this feed to and through this column to keep it from fouling.

Figure 13 indicates the use of the hot storage process prior to extraction with a low-boiling solvent such as ethyl acetate or ether. A heat interchanger cools the demethanolized and detarred liquid before extraction. The acetic acid produced still contains 30 to 40 per cent water which has to be removed subsequently.

Experiments were made which show that the sulfuric tar formed is an excellent solvent for extracting acetic acid; Figure 14 indicates the application of the treating process to the Albin-Suida process using a vaporous extraction with the high-boiling sulfuric tar. The sulfuric tar formed by a storage process and used as make-up for solvent to the system is fed into the middle of the second atmospheric pressure column at a level determined by its original acid concentration. The solvent is then exhausted of acetic acid in the right-hand or vacuum unit and passed to the head of the atmospheric column for the extraction. Since more sulfuric tar is formed than required for make-up solvent, some would be withdrawn from the system. The acetic acid from a process of this type still contains about 10 per cent water which has to be removed subsequently.

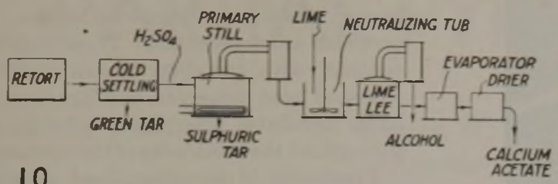
Figure 15 is a flow sheet of a process for using the sulfuric tar formed in the primary tar removal as a solvent for liquid-liquid extraction. Here again excess sulfuric tar over that required for make-up solvent would be withdrawn. Because of the low solubility of the sulfuric tar in water and its low value, it is not necessary to strip the water of the dissolved solvent, as in usual practice, with attendant saving of steam normally used in this distillation.

Finally, Figure 16 indicates a diagram for those cases where the initial evaporation for tar removal takes place in multiple-effect evaporators, prior to subsequent methods for treatment of the liquor. In a forward-feed evaporator of three effects, in which make-up sulfuric acid is added in the initial feed, a small amount of the liquor is continuously withdrawn from the final effect and recycled to the feed end in order to keep the sulfuric acid distributed in all effects. The tar is withdrawn in the standard so-called tar-leg decantation.

The processes referred to here have been covered by patent application and granted patents.

Conclusions

Sulfuric acid treatment of pyroligneous acid at the boiling point, either as raw, demethanolized, or evaporated liquor,



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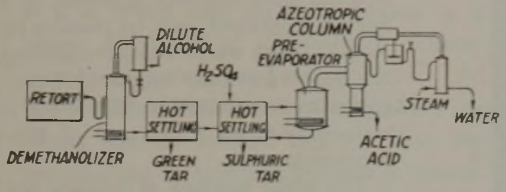

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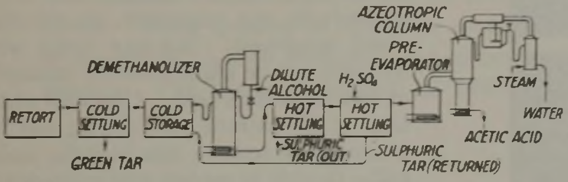

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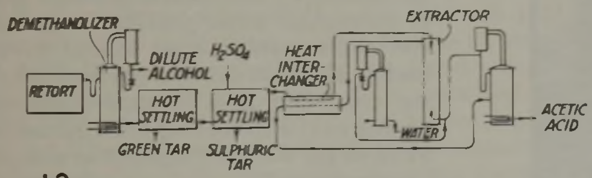

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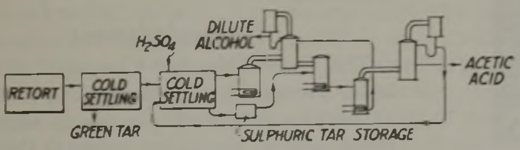

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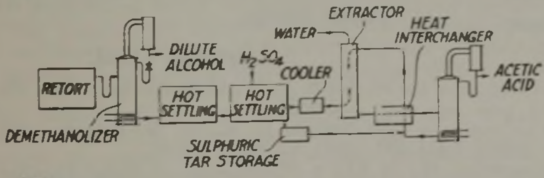

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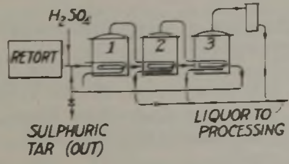

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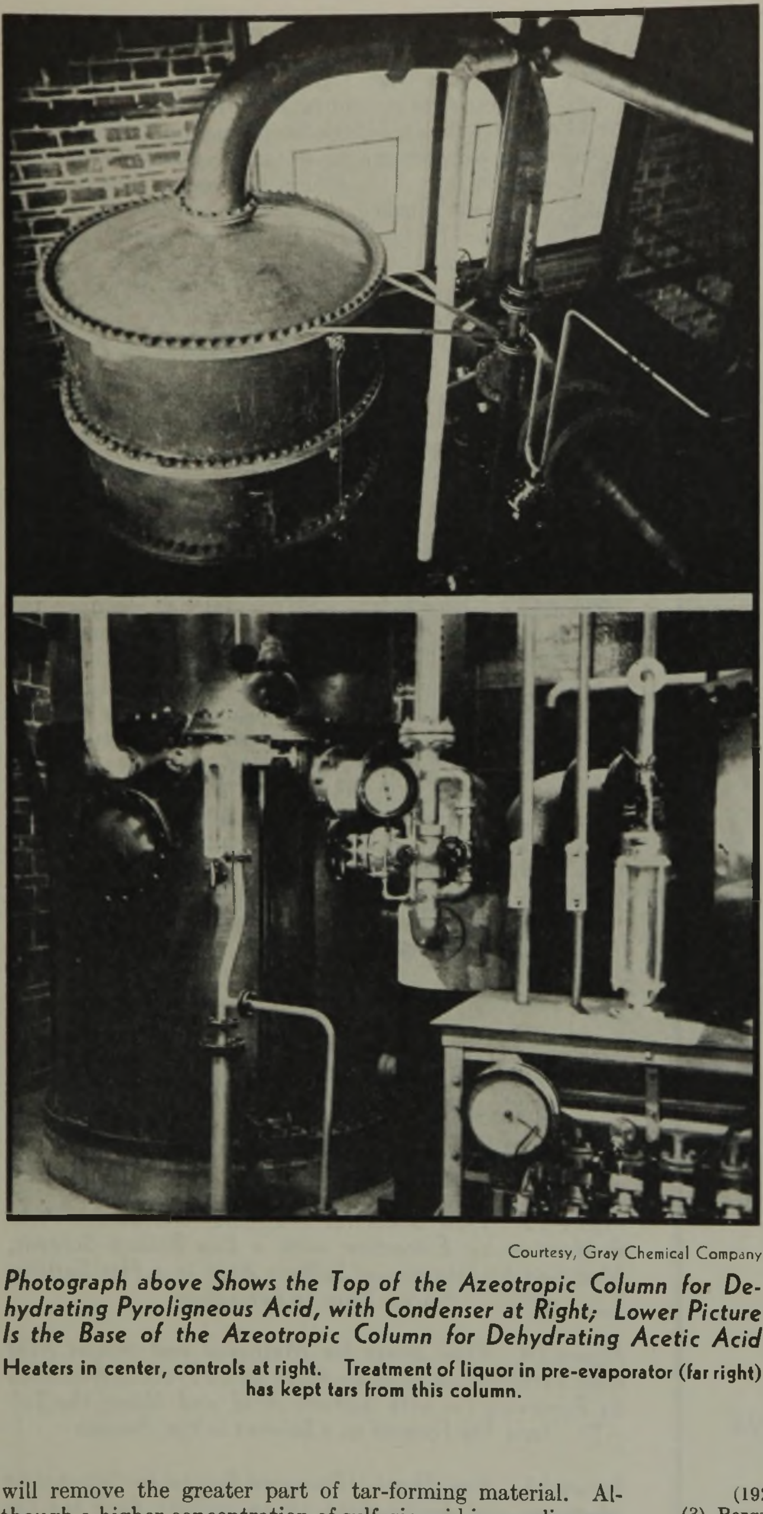
Figure 13. Flow Sheet for Methanol and Acetic Acid Production by Extraction with a Low-Boiling Solvent, Modified by Introducing Sulfuric Acid in a Hot Settling Process Prior to Extraction

Figure 14. Flow Sheet for Methanol and Acetic Acid from Pyroligneous Acid by Albin-Suida Process, Modified by Removing Tar with Sulfuric Acid and Using the Sulfuric Tar Formed as a Solvent in the Process

Figure 15. Flow Sheet of Proposed Process for Separating Methanol and Acetic Acid, Using Sulfuric Acid for Tar Removal and the Sulfuric Tar Formed as a High-Boiling Solvent for Extraction

Figure 16. Flow Sheet of Triple-Effect Evaporator for Removing Tars in Conjunction with Sulfuric Acid, Whereby a Small Amount of the Liquor Is Continuously Recycled from Final to First Effect



Courtesy, Gray Chemical Company

Photograph above Shows the Top of the Azeotropic Column for Dehydrating Pyroligneous Acid, with Condenser at Right; Lower Picture Is the Base of the Azeotropic Column for Dehydrating Acetic Acid

Heaters in center, controls at right. Treatment of liquor in pre-evaporator (far right) has kept tars from this column.

will remove the greater part of tar-forming material. Although a higher concentration of sulfuric acid in pyroligneous is more effective, 3 to 4 per cent gives satisfactory results. Similarly, increased time of treatment gives better results; but the actual time allowable depends on plant operation and may vary from 3 to 6 hours. In a continuous process this time would be controlled by the volume of the treating apparatus.

In a continuous run, the amount of tars precipitated is greater per unit volume of pyroligneous acid than in a batch run, due to the additional effect of evaporation of pyroligneous, an operation going on simultaneously with the polymerization reaction. The distillates of treated pyroligneous acid thus obtained are a clear light yellow liquor which precipitate no further appreciable amounts of tars. These distillates contrast with the dirty brown distillates obtained from untreated pyroligneous; the latter distillates precipitate colloidal tars throughout the remainder of the operations.

Treatment of demethanolized pyroligneous acid with sulfuric acid at 80° C. was also found to be effective in tar removal, but the time required is about 20 hours. Such a treatment may be possible in large storage tanks where the pyroligneous acid is present for that length of time. The optimum concentration of sulfuric in this method is about 8 per cent of the pyroligneous present.

The small amount of sulfuric acid dissolved in the tar may be removed during the usual steaming operation to remove dissolved acetic acid. Sulfuric acid will be washed out, not vaporized, by the steam which condenses; but any losses which do occur will be slight from the standpoint of cost of sulfuric acid. Chemical utilization of the sulfuric acid during the heat treatment to remove tars is slight, and no sulfur dioxide is carried over in the distillate. The concentration of sulfuric acid used in this treatment does not appreciably corrode copper, the material generally used in commercial acetic production. It was also noticed that the tar formed flowed readily when hot and thus obviated one of the usual difficulties in plant operation, where a hard carbonaceous pitch frequently forms on the walls of equipment to a depth of over an inch.

Plant operation in several different processes confirmed the laboratory and pilot plant results.

Acknowledgment

The Gray Chemical Company of Roulette, Penna., furnished samples of liquor at various stages of processing and also cooperated to the fullest extent in the testing and use of the various modifications of the method. Thanks are also due the Tennessee Eastman Corporation of Kingsport, Tenn., for various samples of pyroligneous liquors.

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PARTIAL PYROLYSIS of WOOD

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▸ ▸ ▸ When oak wood is heated in an atmosphere of steam at atmospheric pressure, partial pyrolysis commences below 180° C. At 240° C. the modified wood retains its crushing strength and shows smaller volume changes than the original wood when its moisture content is varied. At that temperature the pentosans have been almost completely decomposed, but two thirds of the cellulose remains and the lignin shows an apparent increase. Three quarters of the total acid and half of the furfural, but no methanol, appear in the condensate. The temperature range of 240–260° C. is critical in spite of control of exothermic reactions. At 260° C. the pyrolyzed wood has a decidedly lower crushing strength and commences to show charring. The cellulose has been almost completely destroyed and the lignin cannot be determined because of the presence of charcoal. Only one third of the methanol has been evolved at 260° C. Most of it is evolved above 280° C. The products at 400° C. show substantially the same methanol as in commercial practice and 25 per cent more acids, the main increase being in formic and propionic acids.

NO ACCURATE studies have been made of the pyrolysis of wood at temperatures below those necessary for the formation of charcoal. This paper presents the results of small-scale experiments in this field. In 1850 Violette (*4*) heated small pieces of alder wood in an atmosphere of steam to various temperatures and found that 280° C. was necessary to obtain a residue which resembled charcoal. This temperature was confirmed by Chorley and Ramsey (*2*) and Klason (*3*), who also showed that a pronounced exothermic reaction took place when wood was heated in absence of air to about 280° C. Klason's results indicated that there was little decomposition of wood by heat at temperatures below 250° C., but in his experiments the temperature was raised rather rapidly. Experiments have also been made on the effect of temperature up to 150° C. in connection with the kiln drying of wood. The wood becomes stiffer and more brittle, but there is no evidence of destructive distillation. There is lack of information on the behavior of wood when heated in the absence of air at temperatures between 200° and 275° C.

Pyrolysis of Oak

The exothermal reaction was recognized to be so great that special precautions would be required to dissipate the heat and keep the temperature uniform. Therefore, heating should be slow, and heat should be applied mainly through a vapor; steam was chosen. It acts partly as an inert gas but also as a reactive agent. The wood was heated in a steel retort set in an electrically heated jacket. Steam at atmospheric pressure was passed through a pipe in the jacket space and so was superheated when it entered the retort. All runs were made at atmospheric pressure. Two thermocouples were used within the retort; one was placed in the vapor space surrounding the blocks and one was inserted in a $^1/_{16}$-inch hole bored in the top of one of the blocks. The temperature of the two thermocouples did not vary over 5° C. from each other except in one test when the temperature difference amounted to 10°. The temperature of the thermocouple within the wood is reported as the temperature of the run in these tests. After the desired temperature was reached, it was not allowed to vary over 5° during the run. The one exception is run 14 when the temperature was purposely raised to 400° C. as the run progressed.

Kiln-dried red oak was the wood tested. In order to measure volume changes during heating, blocks approximately 1 × 1 × 4 inches in size were used. The nine blocks comprising the change were dried at 105° C., cooled, weighed and measured, and placed in the cold retort. The retort was heated by the external heat from the jacket until the temperature had risen to 150° C. Superheated steam at atmospheric pressure was then passed in and the temperature raised in 2 hours to that at which the pyrolysis was to be conducted. This fixed temperature was maintained for 10 hours, superheated steam at atmospheric pressure being introduced throughout the run. The steam and volatile products passed through a condenser and into a receiver where the watery distillate was collected. At the end of the period the retort was allowed to cool to 200° C. before it was opened. The only exception to this method of procedure was run 14 in which the temperature was raised from 270° to 400° C. so as to determine the yields of products when charcoal was formed. Since steam was being employed as a heating agent, the quantity used was large. Its weight was always greater than that of the wood. The duration of the heating period was determined somewhat arbitrarily. Pyrolysis is an irreversible reaction, and therefore it was not feasible to run to equilibrium. The most rapid pyrolysis always occurred at the beginning of a run and was still progressing at a diminished rate at the close of the 10-hour period at the temperature of the test.

Changes in Properties of Oak

The shrinkage of bars sawed tangentially is shown in Figure 1. There is little shrinkage parallel to the grain of the wood, and at the lower temperatures there may be even slight expansion. Figure 2 indicates that the weight and volume decrease rather regularly between 205° and 240° C., quite sharply between 240° and 260°, with a slower decrement to 280° and small decreases from 280° to 400° C.

The compressive strength of the wood was measured on pieces sawed from the test blocks to be approximate cubes which were placed in the testing machine so that the stress was applied parallel to the grain. The effect of partial pyrolysis up to 240° C. was to increase the crushing strength (Figure 2). The strength dropped rapidly after heating only 20° more to 260°. The color of the wood became progressively darker with each increase in temperature, and at 280° it commenced to show a charred appearance.

UNIT PROCESSES

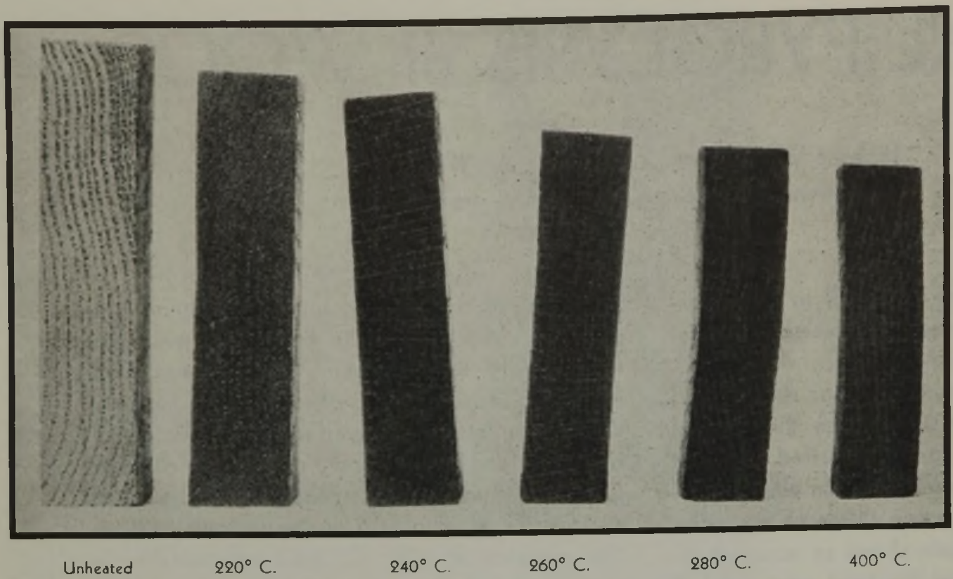

Figure 1. Changes in Size and Appearance of Blocks of Oak Wood Due to Partial Hydrolysis

The volume changes of the partially pyrolyzed wood on exposure to a damp atmosphere are shown in Figure 3. The sample which had been heated to 210° C. gained only half as much weight and expanded only half as much as the sample which had been dried at 105°. The graphs for the samples heated to 240° and 260° parallel that for 210° so closely that the curves for change in length could scarcely be separated.

Volatile Products

The initial temperature of partial pyrolysis cannot be determined readily. A preliminary run at 180° C. showed that about one quarter as much acid was evolved in 10 hours as would be obtained at 400° in the same time. The data for six runs at temperatures varying from 205° to 400° C. are reported in Table I, as well as the analysis of a liquor from a commercial wood distillation plant for comparison. The changes in the more important products are shown in Figure 4. At 205° C. about two thirds of the maximum amount of acetic acid and 40 per cent of the furfural had been evolved. At 240° C. the liquid products contained 80 per cent of the maximum yield of acetic acid with considerable additional amounts of formic and propionic acids, but no methanol. In the interval 240–260° C. the exothermic reaction is reported to begin. The damping influence of the steam prevented any uncontrolled rise in temperature in these tests, but the run at 260° C. marked the first appearance of methanol in the condensate. The amount of furfural also increased sharply and showed a maximum at this temperature. The run at 280° showed rather small increases in all of the products but furfural. In run 14 the temperature was allowed to rise slowly to 400° C. The acids increased to a small extent, and furfural decreased slightly. Two thirds of the methanol was evolved above 280° C. The commercial plant (run C, Table I) apparently obtained only 80 per cent as much acetic acid and only a small fraction as much formic and propionic acids as our partial pyrolysis with steam yielded. The quantity of methanol was about the same in the two methods of treatment. The analysis of the fixed gases showed about three times as much carbon dioxide as monoxide. Hydrogen and hydrocarbons could not be detected in any of the gases analyzed. This would be expected from the large amount of oxygen in the raw material and the low temperature of the operations.

Chemical Changes

Chemical analyses were made on sawdust obtained from blocks during some of the runs (Table II). The methods were those developed by Schorger and his successors at the Forest Products Laboratory as compiled by Bray (*1*). The material soluble in cold water and that soluble in hot water were both decreased to about 40 per cent of the original value at 210° and to about 20 per cent at 240° C. The material soluble in one per cent sodium hydroxide, after deduction of the amount soluble in hot water alone, behaved in the reverse way. The quantity of material soluble in one per cent caustic was one third greater after treatment at 210° than it was in the untreated wood; although it became somewhat less at the higher temperatures, it was still greater after treatment at 240° C. than in the original wood.

The pentosans yielded most readily to heat; over 75 per cent was eliminated by heating to 210° C., and the remainder disappeared at a slower rate in the runs made at successively higher temperatures until at 260° C. the pentosan content was very small. The acetic acid formed by hydrolysis of the treated wood followed much the same course as the pentosans. Only 25 per cent had disappeared in the product obtained at 210° C. and 35 per cent from the product at 240° C. However, when heated only 20° hotter to 260°, almost all of the cellulose was broken down. A further analysis of the cellulose was made on a single sample heated to 210° C. It showed that the pentosans in the cellulose had dropped to about one sixth of the initial figure (12.4 to 2.0) and that the alpha-cellulose had dropped to one third (32.1 to 10.5) while the total cellulose had decreased only from 55.4 to 43.0.

The lignin showed an apparent increase of 20 per cent in the product that had been heated to 210° and stayed about

Table I. Volatile Products of Partial Pyrolysis

Run No.	Temp., ° C.	Yield, as % by Wt. of Unpyrolyzed Wood Dried at 105° C.							
		Total acids	Formic acid	Acetic acid	Propionic acid	Methanol	Furfural	CO	CO_2
8	205	3.82	0.34	3.48	0.00	None	1.54	[a]	[a]
11	220	4.25	0.43	3.39	0.43	None	2.08	0.64	2.25
10	240	5.30	0.55	4.15	0.60	None	2.45	[a]	[a]
13	260	5.86	0.70	4.46	0.70	0.68	4.44	2.4	6.2
12	280	6.32	0.62	4.76	0.94	0.93	4.12	2.4	8.1
14	270–400	6.82	0.73	5.37	0.71	2.25	3.95	[a]	[a]
C[b]	400–450	4.70	0.10	4.36	0.24	2.2	[a]	[a]	[a]

[a] Quantity not measured.

[b] The data in run C are computed from the analysis of the liquor from a commercial wood distillation plant operating on oak. The liquor was analyzed in the same way as the distillates from the experimental work, and the yield was calculated on the assumption that one cord of wood weighed 3200 pounds.

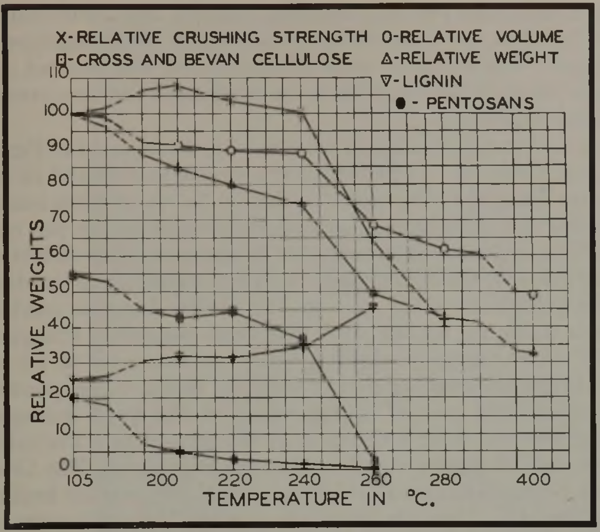

Figure 2. Changes in Oak Wood during Partial Pyrolysis (on Basis of Wood Dried at 105° C.)

at that level in the products heated to 220° and 240° C. Contrary to analyses on the other substances, the lignin apparently increased at the higher temperature of 260°. However, the method for lignin determination consists in treatment with 72 per cent sulfuric acid at room temperature for 16 hours followed by dilution to 3 per cent acid and boiling for 2 hours. The material remaining undissolved is called "lignin". It is probable that some material was becoming insoluble in the acid treatment and so was reported as lignin. This becomes more evident in the product of the 260° run; it obviously contains some charcoal which, being insoluble in acid, is reported as lignin. The decomposition of the wood was so evident in the product heated to 260° C. that no attempt was made to analyze the somewhat charred residue of the 280° run.

An independent check of lignin decomposition is given by the change in percentage of methoxyl groups in the wood after treatment to the several temperatures, together with the amount of methanol found in the distillate. It is usually held that the methanol resulting from pyrolysis of wood comes from the methoxyl groups in the lignin. The data for this discussion are found in Table III. There was a disappearance of 20 per cent of the methoxyl groups of the wood at 220° C., and one third disappeared after heating to 240° C. without the appearance of any methanol in the distillate in either case. Another third of the methoxyl groups disappeared from the sample heated to 260° C., and methanol corresponding to only 10 per cent of the methoxyl groups appeared in the distillate. A further small increase in methanol in the distillate and decrease in methoxyl occurred at 280°, but it is only at temperatures above 280° and below 400° C. that the main portion of the methanol is formed.

Table II. Chemical Analysis of Partially Pyrolyzed Wood

	Yield, % of Unpyrolyzed Wood Dried at 105° C.				
	Dried 105° C.	Run 8, 210° C.	Run 11, 220° C.	Run 10, 240° C.	Run 13, 260° C.
Loss in wt. due to pyrolysis	...	18.6	19.3	25.6	50.7
Solubility in					
Cold water	5.0	1.8	1.4	1.0	[a]
Hot water	8.1	3.2	3.0	1.6	[a]
1% NaOH	24.8	25.5	22.5	19.6	10.3
1% NaOH, cor.[b]	16.7	22.3	19.5	18.0	[a]
Ether	0.5	0.4	0.3	0.2	Trace
Alcohol-benzene	6.3	6.2	5.8	4.0	1.6
Total pentosans	20.0	4.5	2.9	1.1	0.2
Acetic acid by hydrolysis	4.0	0.7	0.6	0.2	[a]
Cross & Bevan cellulose	55.4	42.4	44.5	36.4	1.2
Lignin	25.7	32.4	31.1	34.7	45.3[c]

[a] Quantity not measured.

[b] Corrected for hot water solubility; value obtained by subtracting % hot-water-soluble material from that soluble in 1% alkali.

[c] Includes both lignin and charcoal.

Table III. Change in Methoxyl Groups Compared with Yield of Methanol from Oak Wood

Run No.	Temp., ° C.	Methoxyl Content, %[a]	Methanol Yield, %[a]
Not heated	105	5.87	None
11	220	4.72	None
10	240	4.19	None
13	260	2.33	0.68
12	280	1.94	0.93
14	270–400	...	2.25

[a] Based on unpyrolyzed wood dried at 105° C.

Table IV. Ultimate Analyses of Oak and Its Products

		Composition		
Run No.	Temp., ° C.	C	H	O (by difference)
	Wood and Products of Partial Pyrolysis			
[a]	Not heated	50	6	44
10	240	56.2	5.4	38.4
13	260	69.5	5.1	25.4
12	280	73.6	4.0	22.4
Charcoal (Crossett Chem. Co.)		86.6	3.2	10.2
	Lignin Isolated with 72% H_2SO_4			
	Not heated	65.8	5.0	29.2
10	240	68.2	5.2	26.6

[a] An average composition of hardwood from the literature.

Ultimate Analysis

Ultimate analyses (Table IV) were made of the wood as modified by heating to 240°, 260°, and 280° C. An analysis was also made of a modern commercial charcoal for comparison. The carbon increased and the oxygen decreased progressively as the temperature of pyrolysis rose; the largest change occurred between 240° and 260° C. The greatest change in the hydrogen came, however, between 260° and 280° C.

The lignin (Table IV) from the wood dried at 105° C. contained considerably more carbon and less oxygen than the wood from which it was derived. The lignin from the wood modified by treatment at 240° C. contained still more carbon and less oxygen, but the hydrogen was almost unchanged.

Products of Partial Pyrolysis and of Commercial Carbonization

In commercial carbonization the wood is heated to a final temperature of 400–450° C. and steam is not intentionally introduced into the retorts. It is present in large amounts during the early stages of the run while the wood is being dried but becomes much less during the later stages when pyrolysis is taking place. When the exothermic reaction starts, the temperature rises rapidly to temperatures approaching 400° C. Commercial carbonization differs from the experimental method reported here in at least three evident ways—the final temperature, the rapid rise in temperature due to the exothermic reaction, and the amount of steam present throughout the run.

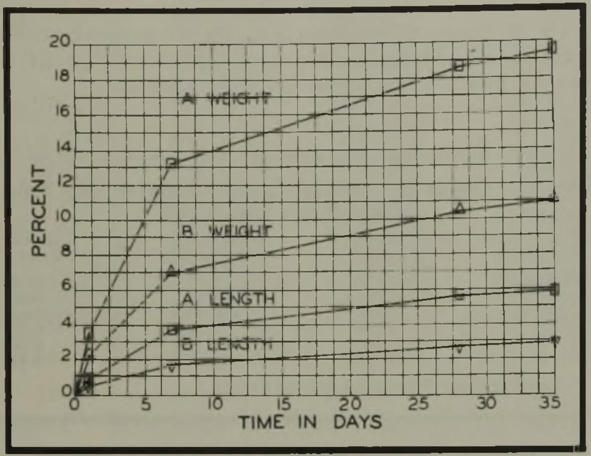

Figure 3. Changes in Length and Weight in Damp Atmosphere

Blocks of wood, 1 × 1 × 4, sawed tangentially and placed in air of 95–100 per cent humidity at 24–26° C. *A* = average of 3 samples dried at 105° C.; *B* = average of 3 samples after partial pyrolysis at 210° C.

The effect of increasing the final temperature was tested in run 14 where the temperature was brought to 270° C. in 2 hours in the usual way. Instead of holding the wood at that temperature, it was raised at a uniform rate in 6 hours to 380° and then to 400° C. in 4 hours more. Data of this run are given in Table I and Figure 2. The solid product was charcoal. The yield of total acid was not much greater, and the furfural was slightly less than at 280° C. The methanol was more than twice as great at 400° as at 280° C.

The results from a commercial carbonization plant operating on oak wood (Table I, run C) indicate that the commercial retort gave substantially the same amount of methanol as our small unit when the temperature in the experimental unit was raised gradually to 400° C. However the experimental unit gave nearly 50 per cent more total acids. The analysis of these acids shows that a considerable part of the increase was in formic and propionic acids. The actual acetic acid was only 20 per cent greater than was found in commercial operation; the amount of propionic acid was three times as great and that of formic acid was seven times as great as in commercial operation. A more detailed analysis of this product at 210° (not given in the table) showed that the pentosans in the Cross and Bevan cellulose decreased from 12.4 in the dried wood to 2.4 in the 210° C. product; the alpha-cellulose decreased from 32.1 to 10.5 per cent. A larger proportion of formic and propionic acid was found in the results with the experimental unit at each temperature. They may be due to the controlled rate of temperature rise or, as seems more probable, to the hydrolytic action of the steam on aldehydes. The larger yield of acetic acid may be explained in the same way.

Progressive Reactions during Partial Pyrolysis

The experimental data reported give a picture of the products formed and the changes in oak wood in the temperature range 180–280° C. In these tests the wood was held for 10 hours at the temperature indicated, in an atmosphere of steam. The reactions were still continuing at a reduced rate after 10 hours, as was to have been expected from an irreversible reaction.

The chemical changes in the wood may be followed in Figure 1 and Table II. The constituents soluble in cold and in hot water dropped to 40 per cent of their initial value when heated to 210° C. The amount of material soluble in one per cent sodium hydroxide increased over 40 per cent, after deduction was made for the amount soluble in hot water. The constituents soluble in ether and in the alcohol-benzene mixture were stable up to 140° C. The most noticeable change at 210° C. was in the pentosans, which had decreased to 4.5 per cent from the 20.0 per cent in the dried wood. The quantity of acetic acid yielded by hydrolysis of the wood decreased in almost the same proportion as the pentosans. The cellulose showed greater stability than the pentosans. The Cross and Bevan cellulose decreased about 20 per cent on heating to 210° C. These experiments confirm the conclusions of previous investigators that the pentosans, both free and associated with the cellulose, are the first of the important wood constituents to break down on pyrolysis.

The lignin was one third greater at 210° than in the unheated wood. This also corresponds to the results of other investigators. We made no studies to determine the chemical nature of this material which is isolated as lignin by the usual method of analysis, except as indicated by the ultimate analysis in Table IV.

There is somewhat more pyrolysis at 220° C. but the trends noted at 210° continue. The modified wood shows little change in lignin content and in Cross and Bevan cellulose in the modified wood. The pentosans in the wood decrease further and the total acid in the distillate increase moderately.

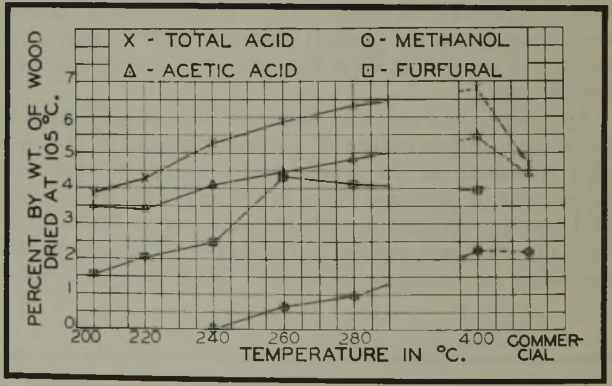

Figure 4. Volatile Products of Partial Pyrolysis of Oak Wood Compared with Results from Commercial Practice

The results at 240° C. show further pyrolysis without any marked change in the character of the products. The quantities of acids and of furfural increase and so does the reducing power of the distillate, as evidenced by its reaction with Fehling solution. No measurable amount of methanol appears in the condensate. One hundred pounds of the original wood contained 8.1 pounds of material soluble in hot water. Only 1.6 pounds survived in the modified wood at 240° C. Similarly, only 36.4 pounds of the 55.4 pounds of Cross and Bevan cellulose survived. The 25.7 pounds of lignin have, however, apparently increased to 34.7 pounds. Thirty per cent of the methoxyl groups of the original wood have disap-

U. S. Dept. Agr. Photograph by Forsythe

An Alabama Sawmill in Full Swing

peared, apparently to form complex groups in the distillate since no measurable amount of methanol was found. The change in the composition of the lignin is shown by the ultimate analysis of Table IV. The apparent lignin at 240° has 2.8 per cent more carbon, 0.2 per cent more hydrogen, and 2.6 per cent less oxygen than the dry lignin isolated from the unheated wood. Calculation indicates that a modified product has been formed whose composition is 75.4 per cent carbon, 5.7 hydrogen, and 19.2 oxygen. There are no indications as to the structure of this compound or complex, but since it is insoluble in 72 per cent sulfuric acid, it is reported as lignin.

The temperature range of 240–260° C. is critical in that the exothermic reaction is supposed to start here. The heating in our work was controlled carefully and the volume of steam was large enough so that no rise in temperature was shown by the thermocouple embedded in the wood. The run at 260° C. showed somewhat more acid in the condensate, but the noteworthy feature was the appearance of methanol to the amount of one third of the maximum yield obtained by carbonization to 400° C. The methoxyl groups in the modified wood from the 260° run were little more than half as great as they were in the residue from the 240° run. The Cross and Bevan cellulose dropped from 36.4 per cent in the 240° product to 1.2 in that from the run at 260° C. The physical properties of the wood modified by heating to 260° C. showed great change. The wood residue at 240° had a somewhat higher compressive strength than the original wood, but the residue at 260° was only 70 per cent as strong. A visual examination of the 260° solid residue showed it to be almost black. An analysis for lignin showed an apparent increase of that constituent from 34.7 to 45.3 based on the weight of the undried wood. However, charcoal, like lignin, is insoluble in 72 per cent sulfuric acid, and it is not easy to separate them. Therefore it is impossible to say how much lignin and how much charcoal were present in the product. The run at 280° C. showed somewhat more acid and methanol. The compressive strength of the wood residue dropped to 41 per cent of that of the original wood.

The only run at a higher temperature was 14, whose temperature was raised slowly from 270° to 400° C. When compared to the 280° run, there was a minor increase in the acid and a slight decrease in the furfural in the condensate. The methanol, however, rose from 0.93 to 2.25 per cent of the weight of the original dry wood.

Commercial Possibilities

The wood distillation industry has traditionally had three major products—charcoal, methanol, and acetic acid. The work reported here indicates the possibilities of an industry with two major products—acids and modified wood residue—obtainable by partial pyrolysis of wood in an atmosphere of superheated steam at temperatures below 260° C. This paper has presented data only on oak wood, but other tests on maple, birch, spruce, and Georgia pine indicate that the same general type of products may be obtained. The yield of acetic acid may be somewhat larger and the amounts of formic and propionic acid several times as large as those now obtained in commercial charcoal plants. Direct condensation of the vapors would give a dilute liquor, but circulation of the vapors through a hot tar oil scrubber, as in the Suida process, would permit the removal of the acids without condensing the steam and allow the steam to be recirculated after being superheated. The time reported here—10 hours at the temperature of the test—was made long in order to carry the reactions reasonably near to completion. Other experiments have shown that with smaller pieces comparable results may be obtained in 1 hour.

A piece of dried wood cut with its long dimension parallel to the grain of the wood will not change in length materially, but it will shrink quite uniformly in cross section. The modified wood from the treatment at 220–240° C. will be stronger and have a higher apparent elastic limit but will be somewhat more brittle than the original wood. It will have smaller volume changes with changes in humidity. The modified wood is brittle enough to be crushed rather readily to yield a wood flour stable at 240° C., which may be incorporated into molding compounds.

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ABSTRACTED from a dissertation for the degree of doctor of philosophy, prepared in the Department of Chemical Engineering at the University of Michigan.

DESTRUCTIVE DISTILLATION of LIGNOCELLULOSE

▶ ▶ ▶ **Compounds with different cellulose and lignin contents, as produced by a wood hydrolysis process, were carbonized to determine the source of the various products. By varying the ratio of lignin and cellulose, a better understanding of the mechanism of distillation may be attained and applied to the treatment of naturally occurring lignocellulose.**

Various lignocellulose compounds, pure cotton cellulose, soluble lignin, and maple wood were destructively distilled in a retort. From the data obtained the following conclusions were drawn: Acetic acid is derived principally from the cellulose while methanol is obtained solely from the lignin. Hemicellulose in wood is the chief source of acetic acid. Soluble lignin forms larger yields of charcoal and noncondensable gases and a lower yield of total aqueous distillate than does cotton cellulose. The various lignocellulose compounds give larger yields of tar than either cotton cellulose or soluble lignin.

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MANY investigators have destructively distilled the natural hard- and softwoods, cellulose, lignin, bagasse, corncobs, and other agricultural waste materials, but none has destructively distilled other than natural lignocellulose compounds. The purpose of this work was to observe and compare the products obtained by carbonizing specially prepared compounds containing "soluble" lignin, "insoluble" lignin, and cellulose in various known and controlled ratios, so as to understand better the mechanism of distillation of naturally occurring lignocellulose.

The reaction of carbonization is exothermic at about 275° C., and the exothermic heat amounts to about 6 per cent of the heat of combustion of wood. Water and carbon dioxide gas (*3*) are first evolved (endothermic stage), followed by the release of illuminants, methane, and aliphatic compounds (exothermic stage); and finally the charcoal and polymerized products (tar) are further broken down to secure larger yields of by-products (third stage). It has been stated (*3*) that cellulose yields very little methanol but considerable acetic acid, whereas lignin in general gives greater percentages of methanol and acetic acid (from the acetyl or methoxyl groups present). The yields of these products are therefore largely dependent upon the relative proportions in which cellulose and lignin are present. Hurd (*2*) states that pentosans give acetic acid and considerable furfural, besides the usual gas and tar by-products. Kurth and Ritter (*5*) also believe that carbohydrates are the source of acetic acid.

Jacobs (*3*) found that resins from the interaction of furfural and phenol are often present. Crude pyroligneous liquors almost invariably contain small percentages of nitrogen compounds, and frequently nitrogen occurs in the noncondensable gases.

The formula of cellulose is $(C_6H_{10}O_5)_x$; the formula proposed for lignin from maple wood (*1*) is $C_{42}H_{30}O_8(OCH_3)_6(OH)_4$ with two ethylenic double bonds and a minimum molecular weight of 910.

Material Used

SOURCE. The lignocellulose compounds were supplied by the Northwood Chemical Company which uses a continuous dilute sulfuric acid hydrolysis to produce lignocellulose residues for plastics. In a typical continuous hydrolysis run (*4*) one pound of maple wood flour (24 mesh) is suspended in 10 pounds of water containing 0.3 pound of sulfuric acid. This suspension is then pumped at a rate of 0.5 gallon per minute (2-minute hydrolysis at 300 pounds per square inch) through a steam-heated double-pipe heat exchanger; the temperature of the suspension leaving the tube by an automatic valve ranges from 170° to 180° C. A yield of approximately 56 per cent lignocellulose residue results. The residue is filtered, washed, dried, and ground.

ANALYSIS. For the isolation of soluble lignin, the dry hydrolyzed substance obtained from the hydrolysis process is extracted in a Soxhlet apparatus with methanol. The methanol extract is poured into several times its own volume of water. The soluble lignin which precipitates is filtered, washed, and dried. The lignin which is not extracted with methanol is called "insoluble" lignin.

The insoluble lignin is determined by treating the dry extracted material with 72 per cent sulfuric acid at 20° C. for 2 hours. This mixture is diluted to a 3 per cent solution and refluxed for 4 hours to convert the cellulose to sugars. The residue is the insoluble lignin. Subtracting the percentage of soluble and of insoluble lignin from 100 gives the percentage of cellulose remaining unhydrolyzed after the original process. Small amounts of hemicellulose thus are included, although most of this fraction is hydrolyzed in the early stages of the process.

The percentage compositions of the lignocellulose compounds used follow:

Compound No.	15/29	316	345	333
Soluble lignin	15%	15	9	33
Insoluble lignin	29%	36	43	29
Total lignin	44%	51	52	62
Cellulose	56%	49	48	38

Carbonization Procedure

RETORT. The retort (Figures 1 and 2) was built of a 4-inch standard steel pipe with a flange screwed on each end. Two end plates were made of $^1/_4$-inch steel and drilled with mating bolt holes for $^5/_8$-inch bolts. Gaskets of $^1/_4$-inch sheet asbestos were made for each end and were impregnated with a graphite-water paste before use. A $1^1/_2$-inch steel pipe vapor neck, $6^1/_2$ inches long and threaded at its upper end, was welded on at the midpoint.

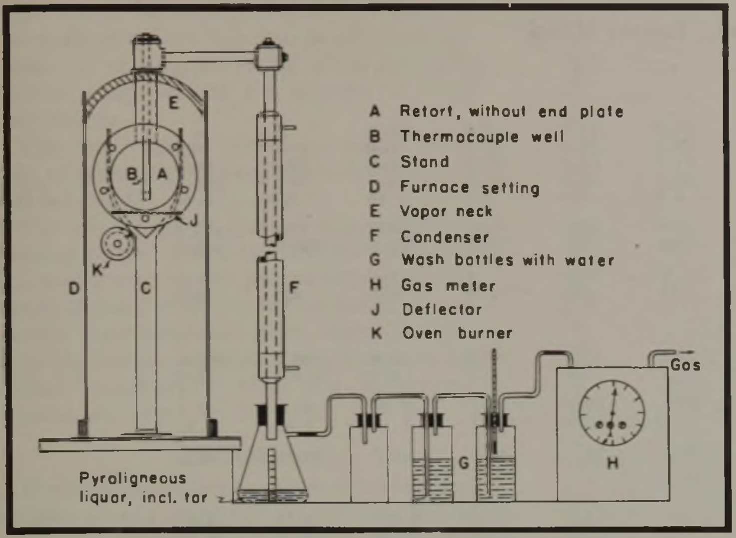

Figure 1. Diagram of Apparatus, Showing End Cross Section of Furnace Housing

A $1\frac{1}{2} \times 1\frac{1}{2} \times \frac{3}{4}$ inch tee was joined to the vapor neck; its $\frac{3}{4}$-inch branch was connected to a $\frac{3}{4}$-inch cross by a $\frac{3}{4}$-inch horizontal iron pipe, $9\frac{1}{2}$ inches long. This cross connected the condenser with the pipe and had two plugs for cleaning. The upper $1\frac{1}{2}$-inch opening of the first tee was bushed to a $\frac{1}{2}$-inch iron pipe with the lower end capped and extending to about $\frac{3}{4}$ inch from the bottom of the retort. This $\frac{1}{2}$-inch well held the thermocouple. Pipe fittings were joined with graphite-water paste. This retort was mounted on two $1\frac{1}{4}$-inch pipe stands, 22 inches high.

Condenser. This consisted of a $\frac{3}{4}$-inch copper tube, 47 inches long, surrounded by a $1\frac{1}{4}$-inch copper-tube cooling jacket $34\frac{1}{2}$ inches long. The condenser was connected to the horizontal line leading from the retort.

Furnace Setting. The retort was enclosed within a setting built out of $\frac{1}{4}$-inch transite. The top was covered with two semicylindrical sections of 1-inch, 85 per cent magnesia, standard 6-inch pipe covering. Even with these precautions considerable heat was wasted, but this was not regarded as objectionable.

The combusted gases escaped around the vapor neck and kept it sufficiently hot to prevent clogging with condensing tars; the horizontal pipe connecting the vapor neck with the condenser was covered with $\frac{1}{2}$-inch magnesia pipe lagging to prevent it from clogging.

The gas-fired cast-iron oven burner, $1\frac{3}{4}$ inches in diameter, had a double set of $\frac{1}{16}$-inch burner holes, $\frac{1}{4}$ inch apart along its length. This was supported $1\frac{1}{2}$ inches below a protecting sheet metal plate on the bottom of the retort with bricks and metal straps around the retort. The protecting sheet metal plate, 4 inches wide and $\frac{1}{16}$ inch thick, was $\frac{1}{4}$ inch below the bottom of the retort and supported from it by iron wire.

Collection of Condensable Products. The pyroligneous liquor was collected in a 2000-ml., side-arm Erlenmeyer flask connected at the bottom of the condenser. The noncondensable gas then passed through three 16-ounce baffle bottles to scrub out any entrained liquids still remaining in the gas. The first bottle was empty; in the second and third bottles the gas bubbled through water. The third bottle had a thermometer for obtaining the temperature of the gas going to the gas meter.

Temperature Measurement. The temperature of this retort was measured by a calibrated chromel-alumel thermocouple inserted in the thermocouple well described under "retort". The pyrometer used was calibrated every 5° C.

Procedure. Material to be carbonized was charged from one end of the retort in such a way that a free vapor space remained amounting to 20 per cent of the retort volume. The retort was then closed. The retort was heated, and the temperature was controlled by adjusting the gas supply. The data were taken every half hour. When the exothermic point of the carbonization was reached, as indicated by the large amounts of products given off, the gas supply was throttled so that the distillation would not be too rapid. The run was completed when the flow of noncondensable gases stopped.

When cooled, the retort was opened at both ends, and the charcoal was pushed from one end into a large paper bag at the other end. The pyroligneous acid was poured into a large graduate and allowed to settle. After several days the amount of aqueous distillate, light tar, and heavy tar were measured and recorded.

Cleaning the Apparatus. The vapor neck, connecting lines, and condenser were cleaned by running a $\frac{1}{4}$-inch capped pipe through them after removing the plugs from the cross and tee. Sometimes a swab soaked with dilute sodium hydroxide and then with water was used. The retort never required cleaning, and the charcoal produced was readily removed.

Analyses

Aqueous Distillate. The aqueous distillate was titrated using a pH meter for total acidity, reported as acetic acid. Crude methanol was determined by distilling 50 cc. of the aqueous distillate with 50 cc. of water in a fractionating column with ten bubble plates; 10 cc. were distilled over under 100° C., and the specific gravity of this sample was determined. The percentage methanol corresponding to this specific gravity was determined from tables.

Gas. The noncondensable gases were analyzed in the Bureau of Mines Orsat apparatus. Carbon dioxide, illuminants, oxygen, carbon monoxide, methane, hydrogen, and nitrogen (by difference) were determined.

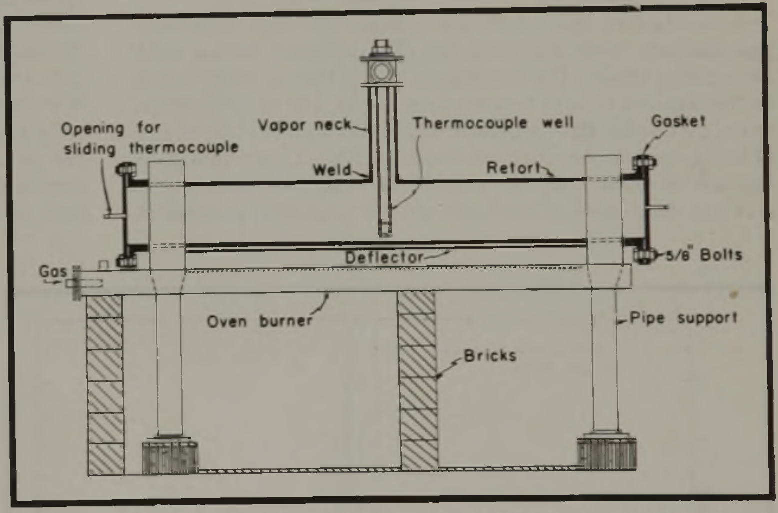

Figure 2. Longitudinal Cross Section of Retort and Housing

Tar. After the tar obtained was weighed, the phenolic and acidic tars were determined. Ten grams of tar were dissolved in ether, and a 10 per cent sodium hydroxide solution was added to extract the phenolic and acidic tars. The aqueous alkaline layer was decanted and acidified with dilute hydrochloric acid, and more ether was added to dissolve the phenolic and acidic bodies again formed by the acidification. The ether layer was separated and evaporated on a hot plate to give the phenolic and acidic tars, which were weighed.

Table I. Summary of Data

Run Number	7	8	9	10	11	12[a]	13[b]
Material used							
Compn. (dry basis), %							
Soluble lignin	15.0	33.0	15.0	9.0	100.0	0.0	0.0
Insoluble lignin	29.0	29.0	36.0	43.0	0.0	23.9[c]	0.0
Total lignin	44.0	62.0	51.0	52.0	100.0	23.9[c]	0.0
Cellulose	56.0	38.0	49.0	48.0	0.0	76.1[d]	100.0
Moisture, %	6.5	4.5	4.5	4.5	5.75	6.34	5.49
Weight charged, grams							
Wet basis	2268	2000	2000	1269	1000	1100	453.6
Dry basis	2121	1910	1910	1212	942.5	1030.3	428.7
Total time, hours	10	5	5 1/2	4	5 1/2	4	4 1/2
Maximum temperature, ° F.	714	753	804	730	823	855	840
Yields (dry basis), %							
Fully carbonized material (charcoal)	38.5	45.8	40.0	37.8	55.8	30.3	27.55
Partially carbonized material	7.23	2.4	0.0	0.0	0.0	0.0	0.0
Total aqueous dist. (excluding tars)	27.1	21.0	29.4	30.0	12.35	40.9	47.1
Total tars	8.07	12.3	10.5	11.7	7.15	8.05	6.95
Noncondensable gases (by difference)	19.1	18.5	20.1	20.5	24.7	20.75	18.4
Analysis of aqueous dist., %							
Acetic acid							
Original dry material basis	1.485	0.956	1.413	2.14	0.477	6.31	3.17
Total aqueous dist. basis	4.37	3.71	4.15	6.17	2.59	13.2	5.99
Methanol							
Original dry material basis	0.976	1.074	1.038	0.693	1.92	0.612	0.0
Total aqueous dist. basis	2.87	4.18	2.91	2.00	10.42	1.28	0.0
Phenolic and acidic tars in total tar, %							
Original dry material basis	3.79	5.17	4.21	5.44	3.88	3.30	1.88
Total tar basis	47.0	42.0	40.0	46.3	55.0	41.0	27.0

[a] Maple chips.
[b] Cotton cellulose.
[c] Extractive-free basis (wood contains 5.65% extractives).
[d] Includes approximately 25% hemicellulose.

Summary of Experimental Data

In addition to half-hourly temperature readings, liquor and gas analyses were made on samples collected during each 30-minute period. During each run it was thus possible to plot curves against time of temperature run as well as both differential and cumulative amounts of gas and liquid obtained and of the amounts of each of the constituents. This voluminous amount of data and the graphs showing the moment-by-moment conditions of each run are not presented because of space limitation. In general, the conclusions reached were based on the over-all results in Table I. However the periodic numerical data and graphs illustrated the exothermic reaction and its effect in producing volatile products, and aided in understanding the runs.

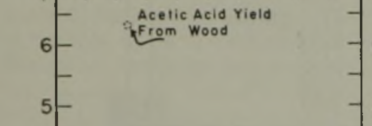

Figure 3. Yields (Per Cent of Dry Material Charged) of Acetic Acid and Methanol as a Function of Composition of Material Charged (Cellulose and Lignin)

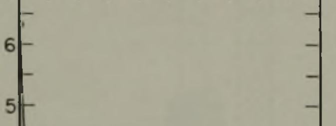

Figure 4. Yields (Per Cent of Dry Material Charged) of Acetic Acid and Methanol as a Function of Soluble Lignin Present

In run 7 there was the usual exothermic reaction during the period from 4 to 6 hours for hydrolyzed lignocellulose sample 15/29. The noncondensable gas analyses during this time showed a rapid decrease in carbon dioxide and a rapid increase in methane and hydrogen, particularly after the exothermic reaction was ended.

In run 8 (hydrolyzed lignocellulose 333) the exothermic reaction was somewhat better controlled and resulted in a more regular evolution of products. The gas analyses indicated little change in carbon dioxide and a slight increase in methane, paralleled by a decrease in hydrogen content toward the end of the exothermic reaction.

Hydrolyzed lignocellulose 316 (run 9) was also carbonized with a well-controlled exothermic period. In this case, however, both the carbon dioxide and monoxide in the gases decreased rapidly, while methane and hydrogen increased rapidly.

Carbonization in run 10 (hydrolyzed lignocellulose 345) with a low soluble lignin content resulted in an early exothermic reaction, but this was probably due to a more rapid input of heat to the retort during the first hour. Yields and gas concentrations indicated the same general trend as in run 9.

Run 11 on pure soluble lignin showed a delayed exothermic reaction for this material. The unusual gas analyses showed large yields of methane and hydrogen in the gas throughout the run, but a rapid increase in carbon monoxide after the exothermic stage was at the expense of these components.

The very regular curves for maple wood (run 12) generally followed the data of Othmer and Schurig (*6*).

For cotton cellulose (run 13) the exothermic reaction started within the first hour and was practically over by the second hour. During the exothermic stage the carbon monoxide and dioxide concentrations were high, particularly the latter; methane and hydrogen increased considerably after the exothermic reaction was over.

Conclusions

Previous experimenters have reported that cellulose gives a large yield of acetic acid and no methanol, whereas lignin gives a large yield of both acetic acid and methanol. The results obtained here by destructively distilling soluble lignin, various lignocellulose compounds, maple wood, and cotton cellulose contradict many of the previous reports with respect to the source of acetic acid and methanol.

Plots of the various lignocellulose compounds against yield of acetic acid and methanol (Figure 3) show that methanol is derived solely from the lignin. None of the hydrolyzed lignocellulose compounds contained any appreciable amounts of hemicellulose, while the maple chips had a hemicellulose content of about 25 per cent. Since the yield of acetic acid was much higher for the maple wood than for any of the hydrolyzed lignocellulose compounds, it may be said that hemicellulose in the wood is the chief source of acetic acid. This also helps to answer a question raised by Othmer and Schurig (*6*) because the summation of acetic acid, yields from lignin, hemicellulose, and cellulose did not equal the yield from the wood itself. This is probably due to losses of hemicelluloses during isolation of the various wood components. The low yield of acetic acid obtained from the soluble lignin contradicts other reports that large yields of acetic acid are obtained from lignin. This is probably due to the fact that other experimenters did not use pure lignin but material that contained hemicellulose. The soluble lignin used in this research was tested and found to contain no hemicellulose.

From the plot of percentage soluble lignin against yield of acetic acid and methanol (Figure 4) it is evident that the proportion of soluble lignin present has some effect upon the percentages of acetic acid and methanol obtained from the various lignocellulose compounds. Since the wood itself has no soluble lignin, the run for maple is plotted at 0 per cent.

It was observed from run 11 on soluble lignin and run 13 on cotton cellulose that about twice as much methane and hydrogen are obtained from soluble lignin as from cotton cellulose; more carbon dioxide, carbon monoxide, and illuminants are obtained from cotton cellulose than from soluble lignin. These results are reasonable when the formulas of cellulose and lignin are compared.

From the plot of the summary of yields (Figure 5), it is obvious that soluble lignin gives larger yields of charcoal and noncondensable gases and a lower yield of total aqueous distillate than does cotton cellulose. The various lignocellulose compounds give larger yields of tar than either cotton cellulose or soluble lignin.

Higher yields of acetic acid and methanol from wood as compared with commercial yields check Othmer and Schurig's data (*6*). It is evident that accurately controlled carbonization is a prime factor in this respect.

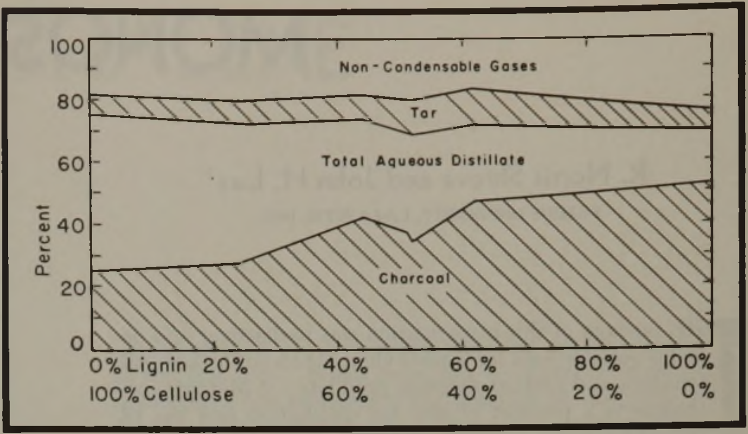

Figure 5. Summary of Yields (Per Cent of Dry Material Charged) as a Function of Cellulose and Lignin in Material Charged

The fully carbonized cotton cellulose obtained in run 13 retained its original fluffy cotton structure. This material might make a suitable filtering material where mechanical strength was not important.

From the low yields of acetic acid and methanol, the destructive distillation of lignocellulose compounds obtained by the hydrolysis of part of the cellulose, hemicellulose, etc., would probably not be profitable.

Soluble lignin produces the largest amounts of phenolic and acidic tars in its total tar, while cotton cellulose gives the smallest. The lignocellulose compounds and maple wood have 40 to 50 per cent phenolic and acidic tars in their total tars. The isolation of phenolic and acidic tars from the total tars would yield an increase in profit. The tar analysis of run 10 showed a larger total yield of phenolic and acidic tars than any other substance destructively distilled in this research. This lignocellulose compound contains a small percentage of soluble lignin; a similar compound is produced as a waste material when soluble lignin is extracted from hydrolyzed lignocellulose compounds. Therefore, the destructive distillation of such a hydrolyzed lignocellulose compound has a possibility of being profitable when its phenolic and acidic tars are considered.

Acknowledgment

The materials were furnished by the Northwood Chemical Company, of Phelps, Wis.; the work was undertaken and supported as part of the general program of wood research of this company. Special thanks are due to A. O. Reynolds of the company for his interest.

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MONOSULFONATION of

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▶ ▶ ▶ **The sulfonation of 2-methylnaphthalene with a small excess of sulfuric acid has been studied, and the positions of the entering sulfonic acid groups were found to be mainly the 8 position at 40° C., the 6 position at 90–95° C., and the 7 position at 160° C. Many derivatives of the sulfonic acids were made and their possible uses**

THE purpose of this investigation was to discover and develop possible uses for 2-methylnaphthalene through sulfonation and further reaction products. 2-Methylnaphthalene is a product of coal tar distillation and has recently became more available at higher purity as a result of improvements in the tar separation processes. 2-Methylnaphthalene occurs in coal tar to the extent of 1.5 per cent (*10*) and in petroleum fractions of about the kerosene range to the extent of 1.5–2.0 per cent (*5*).

Wendt (*12*) first sulfonated 2-methylnaphthalene in 1892 and reported that sulfonation occurred even at room temperatures; however, he was unable to identify any products. Years later in 1925 Dziewoński, Schoewóna, and Waldmann (*1*) sulfonated 2-methylnaphthalene at 90° to 100° C.; they obtained 2-methylnaphthalene-6-sulfonic acid in good yields and identified it by conversion to 2-methyl-6-naphthol. Dziewoński and Wulffsohn (*2*) in 1929 sulfonated 2-methylnaphthalene with chlorosulfonic acid in nitrobenzene at 30° to 40° C. and obtained 2-methylnaphthalene-8-sulfonic acid, but reported no other isomer. Later Vesely and Pac (*8*) sulfonated with chlorosulfonic acid in carbon tetrachloride at −5° C. and reported a 25 per cent yield of 2-methylnaphthalene-8-sulfonic acid and a 7 per cent yield of 2-methylnaphthalene-1-sulfonic acid. Vesely and Strusa (*9*) also prepared another derivative of 2-methylnaphthalene by treating Tetralin with bromine, magnesium, and dimethyl sulfate which gave a mixture of 5- and 6-methyl-Tetralin. Sulfonation of the latter gave 6-methyl-Tetralin-7-sulfonic acid which was converted to the corresponding tetrahydronaphthalene derivatives.

Plan of the Investigation

The raw material for the sulfonation was white, solid 2-methylnaphthalene (melting point 32.5° C.) of about 98.5 per cent purity which is now available commercially. This compound was sulfonated in four different ways. Sulfonation at 40° C. gave mainly 2-methylnaphthalene-8-sulfonic acid; at 90–95° C., 2-methylnaphthalene-6-sulfonic acid; and at 160° C., 2-methylnaphthalene-7-sulfonic acid. As it was desired to make derivatives containing functional groups on the same ring as the methyl group, the opposite ring was hydrogenated. The ring without the methyl group was no longer aromatic, and any sulfonation that took place was on the ring containing the methyl group to give 6-methyl-Tetralin-7-sulfonic acid.

The sulfonation products were isolated by precipitation of the barium salts. The use of calcium salts was tried, but they could not be obtained in so good a crystal form as the barium salts. Also, the advantage of the greater solubility of the calcium salts was outweighed by the difficulties of handling their slimy condition.

Three methods for the production of sodium salts from barium salts were tried. The first, by means of the reaction

$$Ba(SO_3CH_3C_{10}H_6)_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaSO_3CH_3C_{10}H_6$$

was chosen because nearly quantitative yields of the sodium salts were obtained. Later it was found that yields from the reaction

$$Ba(SO_3CH_3C_{10}H_6)_2 + Na_2CO_3 \longrightarrow BaCO_3 + 2NaSO_3CH_3C_{10}H_6$$

were also almost quantitative, and since sodium carbonate is less expensive its use was more desirable. The use of the barium salts necessitates the handling of large volumes of solutions. Much time and heat are also required for the concentration and crystallization of these solutions. With these in mind and to achieve economy, the reaction

$$CH_3C_{10}H_6SO_3H + NaCl \longrightarrow HCl + CH_3C_{10}H_6SO_3Na$$

was investigated for each of the four sulfonic acids reported. The reaction proved valuable for the preparation of the ordinary sodium salts but did not seem applicable to the making of sodium 6-methyl-1,2,3,4-tetrahydronaphthalene-7-sulfonate because of its much greater solubility. Another case where it was not advisable to prepare the sodium salts direct was that of the sulfonic acid made at low temperatures—namely, sodium 2-methylnaphthalene-8-sulfonate. Here it was found that the other isomer formed in the reaction could not be separated by recrystallization of the sodium salts. If the presence of another isomer is not a great disadvantage—i. e., for wetting agents—the direct method may be used even for the sodium salt of the 8-sulfonic acid.

The apparatus for the sulfonations consisted of a 500-ml. three-neck flask equipped with a mercury-seal motor-driven stirrer, 360° C. thermometer, and dropping funnel.

Barium 2-Methylnaphthalene-8-sulfonate

To 0.5 mole (71 grams) of 2-methylnaphthalene were added dropwise 71 grams of concentrated (93 per cent) sulfuric acid with stirring. The reaction was allowed to proceed for 8 hours, the temperature being maintained at 40° C. by a water bath. At the end of that time the reaction mixture was

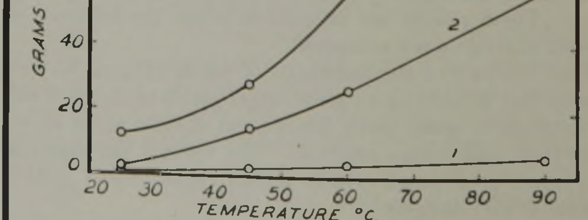

Figure 1. Variation in Solubility of Barium Salts with Temperature

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2-METHYLNAPHTHALENE

studied, since 2-methylnaphthalene is now available commercially.

The most promising of these derivatives appear to be the sodium salts which have good wetting properties and are easily made. It was found that the derivatives could be made in existing industrial equipment with little difficulty.

diluted to a volume of about 0.5 liter by pouring it into cold water. On standing, the unsulfonated 2-methylnaphthalene collected in a cake on top of the solution and was easily removed. There remained in suspension in the solution a small amount of sulfone which was formed during the reaction. When filtered the sulfone was obtained as a small white cake. (A more accurate analysis of the hydrocarbon and sulfone was obtained by treating the mixture with excess concentrated sulfuric acid, diluting, and filtering.) The solution was then heated to boiling and neutralized while hot with barium oxide. The barium sulfate formed in the reaction was removed by filtration and washed with 500-ml. portions of boiling water until no separation of the barium 2-methylnaphthalene-8-sulfonate took place on cooling. The washings were then added to the filtrate, and the resulting solution was made slightly acidic with acetic acid. The resultant solution of barium sulfonate was clarified by absorbent charcoal if it was dark and then concentrated to 2000 ml. On cooling, barium salts of the sulfonic acids crystallized out and were filtered from the solution. Concentration of the solution yielded a second crop of crystals which were recrystallized before being added to the first crop. Since there was a difference in solubility between the two fractions of barium salts, it was obvious that more than one isomer was present, and the presence of a small amount of the 6 isomer was detected.

In a saturated solution of the 2,8 barium salt the 2,6 barium salt was completely salted out. This means that, in order to separate the two isomers, one need only dissolve the salt mixture in water, evaporate the solution to the point at which it is saturated with respect to the more soluble 2,8 barium salt, allow crystals of the 2,6 isomer to form, and filter this 2,6 isomer from the mixture. Since the amount of the 2,6 isomer at 40° C. is about 13 grams per 100 grams of mixture, the point to which the solution must be concentrated is easily estimated.

The solubility of the barium salt of the pure 2,8-sulfonic acid is shown in Figure 1 and Table I. This barium salt, formed at low temperatures, is the most soluble of the isomers, which is an aid in its purification by recrystallization. Also the low-temperature sulfonic acid is hydrolyzed by live steam, as would be expected for an alpha acid.

The results given for the amounts of salts formed are figured on the dry basis although the barium salts crystallize with water attached. An example is the barium salt of 2,8-sulfonic acid which analyzed $Ba(SO_3CH_3C_{10}H_6)_2.3H_2O$. Results in several low-temperature sulfonations are given in Table II.

Barium 2-Methylnaphthalene-6-sulfonate

In the sulfonation apparatus 71 grams of 93 per cent sulfuric acid were added dropwise to 71 grams of 2-methylnaphthalene maintained at 95° C. by a steam cone. At the end of 8 hours the reaction mixture was poured over 100 grams of ice and allowed to stand until the unsulfonated 2-methylnaphthalene collected on the surface. The cake of unsulfonated hydrocarbon was lifted from the surface of the solution, and the solution was filtered to remove the sulfone formed. The solution was heated to boiling and neutralized hot with barium oxide; the separation was then continued as in the previous case. On recrystallization all of the fractions had the same solubility in water. The results of several runs are given in Table III.

Table I. Effect of Temperature on Solubility of Salts of Sulfonic Acids in Water

Isomer	Solubility, Grams/Liter 25° C.	45° C.	60° C.	90° C.
		Barium Salts		
2,8	12.1	28.0	56.9	117.2
2,6	2.01	15.1	27.3	58
2,7	0.57	2.9	4.8	6.6
		Sodium Salts		
2,8	43.2	84.1	100.4	168.0
2,6	31.0	65.3	92.1	144.0
2,7	19.0	52.9	80.0	134.6

Table II. Sulfonation Runs at 40° C. Producing Barium 2-Methylnaphthalene-8-sulfonate[a]

Run No.	Time, Hours	Crude Ba Salt		Unreacted Hydrocarbon Recovered		Sulfone		Pure 8 Barium Salt			Miscellaneous Isomers[b]	
		Grams	% Converted	Grams	%	Grams	%	Grams	% Converted	% yield	Grams	%
1	4	47	32.5	46.1	65.1	...	...	...	...	..	..	...
2	4	45.1	31.1	46	64.8	...	...	...	...	..	..	...
3	6	91	62.8	...	...	...	...	...	...	..	..	...
4	6	89	61.5	24	33.8	...	...	...	...	..	..	...
5	6	89.5	61.9	24	33.8	0.8	0.9	73	50	76	12	8.3
6	6	91	62.8	24	33.8	0.7	0.8	72	50	75	16	11.1
7	8	96	66.2	...	...	...	...	...	...	..	..	...
8	8	102	70.3	...	...	...	...	...	...	..	..	...
9	8	102	70.3	20.2	28.4	1.1	1.3	76	54	75	18	12.4
10	8	100	69.0	19.8	28.0	1.2	1.4	78	54	74	17	11.7
11	8	100.5	69.2	20.3	28.6	1.1	1.3	77	53	77	18	12.4
12	24	90	62.0	0.0	0.0	26.1	36.7	...	...	..	..	...

[a] Theoretical barium content, 23.66%; analysis showed all actual values between 23.6 and 23.8%.

[b] Mixtures of 2,6 and 2,8 isomers obtained by crystallization in recovering the given amount of pure 2,8 barium salt.

UNIT PROCESSES

Barium 2-Methylnaphthalene-7-sulfonate

This salt was prepared in the same manner as those previously described, except that the reaction was carried out at 160° C., and the mixture was poured into 250 grams of ice. The barium salt formed was recrystallized until it was white in color. It was not very soluble in hot water, so that large volumes of solutions had to be handled. Here again only one principal product was formed, as shown by the fact that a salt of only one solubility was found.

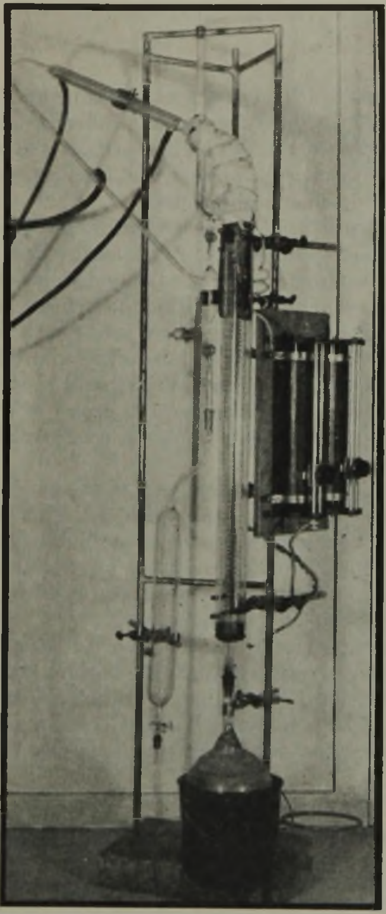


Figure 2. Lecky Distillation Column

To obtain an accurate analysis of the amount of unsulfonated 2-methylnaphthalene it had to be removed from the solution by steam distillation. Also, it was advantageous to extract the sulfone later with ether; even then a white compound was not obtained. If the latter procedure is followed, there is no point in using the 250 grams of ice mentioned above. The reaction mixture may merely be poured into cold water, allowed to stand until cool, and then filtered. This removes the sulfone, unsulfonated 2-methylnaphthalene, and other tarry by-products which are formed. If the recovery of the unsulfonated hydrocarbon is not desired, the latter method is the more desirable. The results of several runs at high temperatures are given in Table IV.

Barium 6-Methyl-1,2,3,4-tetrahydronaphthalene-7-sulfonate

Hydrogenation of 2-Methylnaphthalene. Recrystallized 2-methylnaphthalene (170 ml.) and Raney nickel catalyst (20 grams) suspended in 50 ml. of 95 per cent alcohol were placed in a hydrogenation unit; hydrogen was admitted until a pressure of 1200 pounds per square inch was reached at 20° C. The shaker was started and heat was applied. When 150° C. was reached, the pressure was 1740 pounds. After 5 hours the temperature was raised to 185° C., and the reaction was allowed to proceed for another 10 hours. Then agitation was stopped, the pressure released, and the product removed. The reaction mixture was separated from the Raney nickel by filtration.

Purification and separation of the hydrocarbon mixture was carried out in the Lecky column shown in Figure 2. Fractions obtained and their boiling points at 12 mm. pressure were: 2-methyl-Decalin, 89° C.; 2-methyl-Tetralin, 101° C.; 2-methylnaphthalene, 114° C. Results are shown in Table V.

Sulfonation of 6-Methyl-1,2,3,4-tetrahydronaphthalene. One-fourth mole (36.5 grams) of the tetrahydro compound was placed in the sulfonation apparatus with 40 grams of 93 per cent sulfuric acid. The temperature was maintained at 80° C. for 4 hours, and then increased to 100° C. for 4 more hours. After sulfonation was complete, the reaction mixture was treated as the other sulfonic acids; the only variation was that the mixture was treated with benzene to extract sulfones and unsulfonated hydrocarbon rather than to allow them to settle out. No sulfone or hydrocarbon was found in the extract. Results are shown in Table V.

Sodium Salts of Methylnaphthalene Sulfonic Acids

Use of Sodium Sulfate or Carbonate. One tenth mole (57.9 grams) of the barium salt of the sulfonic acid was placed in 2 liters of water and then heated to boiling. To this was added one tenth mole of sodium sulfate (14.2 grams) or sodium carbonate (10.6 grams), and the mixture was kept in suspension by stirring. When the reaction was completed, the barium sulfate or carbonate formed was filtered from the solution. On concentration of the solution, the sodium salt of the sulfonic acid separates out. Here the reaction must be carried out with small quantities of the barium salt because of its relatively low solubility in water. The yield with sodium sulfate is practically quantitative (48.8 grams), and with sodium carbonate is slightly less (47.9 grams, 98.5 per cent).

Direct Production of Sodium Salt. The sulfonation mixture resulting from the reaction of 71 grams of 2-methylnaphthalene with 71 grams of 93 per cent sulfuric acid for 8 hours was poured into 250 ml. of water while stirring. Any sulfone or unreacted methylnaphthalene was removed at this

Table III. Sulfonation Runs at 90–95° C. Producing Barium 2-Methylnaphthalene-6-sulfonate[a]

Run No.	Time, Hours	Crude Ba Salt		Unreacted Hydrocarbon Recovered		Sulfone		Pure 6 Barium Salt		
		Grams	% converted	Grams	%	Grams	%	Grams	% converted	% yield
13	4	94	65.0	23	32	0.8	0.9	94	65.0	95.6
14	5	90	62.2	24	34	0.85	1.0	90	62.2	95.7
15	6	116	80.0	8.6	12	2.0	2.3	116	80.0	89.7
16	6	115	79.4	8.9	13	2.0	2.3	115	79.4	89.9
17	6	115	79.4	8.5	12	2.0	2.3	115	79.4	89.4
18	8	123	84.8	6.3	8.8	3.6	4.1	123	84.8	83.1
19	8	124	85.5	5.9	8.3	3.7	4.2	124	85.5	92.5
20	8	121	83.5	6.3	8.8	3.7	4.2	121	83.5	91.5
21	8	121	83.5	6.0	8.4	3.6	4.1	121	83.5	91.5

[a] Theoretical barium content, 23.66%; analysis showed all actual values between 23.7 and 23.9%; no other isomers found in this temperature range.

Table IV. Sulfonation Runs at 160° C. Producing Barium 2-Methylnaphthalene-7-sulfonate[a]

Run No.	Time, Hours	Crude Ba Salt Grams	Crude Ba Salt % converted	Unreacted Hydrocarbon Recovered Grams	Unreacted Hydrocarbon Recovered %	Sulfone Grams	Sulfone %	Pure 7 Barium Salt Grams	Pure 7 Barium Salt % converted	Pure 7 Barium Salt % yield	Barium Content, %[b]
22	4	116	79.9	8.0	11.2	4.4	5.0	116	79.9	79.9	24.5
23	4	112	77.2	8.5	11.9	4.8	5.3	112	77.9	87.2	24.5
24	4	113	78.0	8.0	11.2	4.5	5.1	113	78.0	88.0	24.5
25	6	125	86.4	2.0	2.8	5.5	6.4	125	86.4	88.7	25.0
26	6	126	86.9	1.5	2.1	6.0	6.7	126	86.9	89.0	24.9
27	6	126	86.9	2.0	2.8	6.8	6.7	126	86.9	89.6	25.0
28	8	129	89.0	None		7.8	9.0	129	89.0	89.0	25.1
29	8	130	89.5	None		7.9	9.1	130	89.5	89.5	25.2
30	8	128	88.4	None		7.5	8.5	128	88.4	88.4	24.2

[a] No other isomers found at this temperature.
[b] Theoretical barium content, 23.66%.

Table V. Results of Preparation of Barium 6-Methyl-1,2,3,4-tetrahydronaphthalene-7-sulfonate

	Run A	Run B
Hydrogenation with Raney Nickel Catalyst Using 170 Grams 2-Methylnaphthalene		
2-Methylnaphthalene recovered, grams	65	47
2-Methyl-Tetralin obtained, grams	63	86.8
2-Methyl-Decalin obtained, grams	10	7
Loss in intermediate fractions, %	30	29
Conversion to 6-methyl-Tetralin, %	36	49
Yield of 6-methyl-Tetralin, %	58	69
Sulfonation Using 36.5 Grams 6-methyl-Tetralin and 40 Grams 93% H_2SO_4 for 8 Hours		
Barium salt obtained, grams	64.0	65.5
Conversion in sulfonation, %	87.1	89.0

point either by extracting with benzene or by filtering if the temperature was kept low enough to solidify the hydrocarbon. Then the solution was poured into a salt solution of the following composition: 2,8-sulfonic acid, 200 grams sodium chloride, and 300 ml. water; 2,6- and 2,7-sulfonic acids, 150 grams sodium chloride and 300 ml. water. The resulting solutions were agitated for several hours and filtered. A second crop of crystals was obtained on the addition of more sodium chloride. The two fractions were then put together and recrystallized from water. The yields (based on hydrocarbon recovery) were 88 grams of the 2,8 sodium salt (74 per cent), 99 grams of 2,6 sodium salt (84 per cent), and 95 grams of 2,7 sodium salt (78 per cent). Figure 3 and Table I show the solubility of the sodium salts, and Figure 4 and Table VI the influence of sodium chloride on the solubility of the sodium salts.

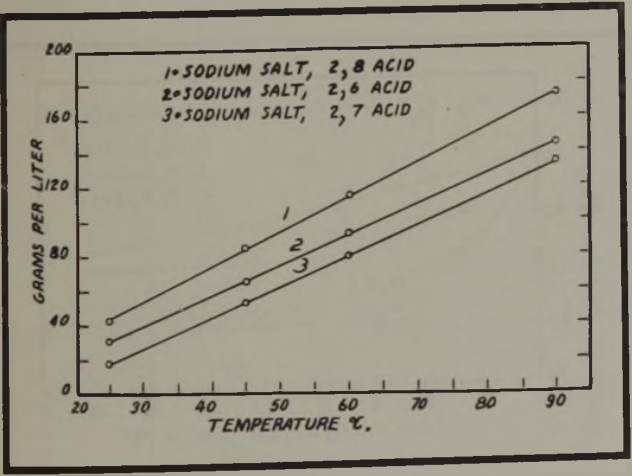


Figure 3. Variation in Solubility of Sodium Salts with Temperature

Comparison of Sulfonation Results

Tables II, III, and IV compare the effects of different variables during sulfonation. Figure 5 is a plot of data from these tables showing the variation with both time and temperature of unsulfonated 2-methylnaphthalene. The figures for naphthalene (*3*) are included so that inferences may be drawn as to the effect of the methyl group on the ease of substitution in the aromatic nucleus. Here, as with toluene and benzene, the aromatic compound with the methyl group is much more reactive.

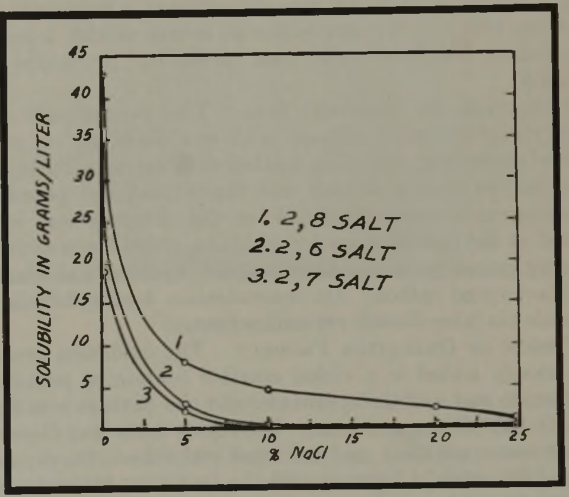


Figure 4. Effect of Sodium Chloride on Solubility of Sodium Salts of Sulfonic Acids

The sulfone formation should be noted, as these compounds may cause the loss of a large amount of hydrocarbon. Run 12, Table II, shows that 36.7 per cent of the hydrocarbon was converted to sulfone.

Derivatives of Sulfonic Acid Salts

Using methods described by Shriner and Fuson (*6*) and Groggins (*4*), sulfonyl chlorides, sulfonamides, naphthols, methyl ethers, and amino compounds were made. Table VII shows the derivatives and their melting points. All compounds except 2,7 derivatives are listed in the literature (*1*, *2*, *7*, *8*, *9*). [An exception is the 2-methyl-7-naphthylamine made from the corresponding nitro compound by Vesely and Pac (*8*). They gave the melting point as 105° C.]

Identification of Sulfonic Acids

Since the melting points are listed in the literature (*1*, *2*, *7*, *8*, *9*), no further proof is needed for any compounds except the

Table VI. Effect of Sodium Chloride on Solubility of Sodium Sulfonates in Water

NaCl, %	Solubility, Grams/Liter		
	2,8 Salt	2,6 Salt	2,7 Salt
0	43.2	31.0	19.0
5	8.1	3.0	2.0
10	4.8	0.9	0.8
20	2.3	0.7	0.5
25	0.5	0.2	0.1

Table VII. Melting Points of Derivatives of 2-Methylnaphthalene and 6-Methyl-Tetralin

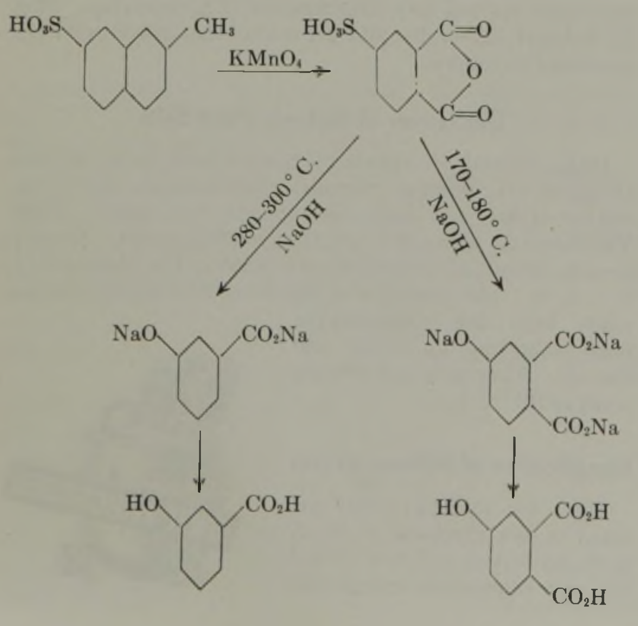
	M. P. of Derivative, ° C.				
	—SO_2Cl	—SO_2NH_2	—OH	—OMe	—NH_2
2-Methylnaphthalene					
2-Me-6-	97–8	204–5	128	79	128
2-Me-7-	63–4	163–4	101–2	78	103–4
2-Me-8-	95–6	195–6	109	41	56–7
6-Methyl-Tetralin	...	155	89	..	....

2,7 derivatives. Also, there is no record in the literature of any sulfonation of 2-methylnaphthalene at a temperature as high as 160° C. To prove the structure of the 2-methylnapthalene-7-sulfonic acid, an oxidation procedure was followed.

Oxidation of Sulfonic Acid. The barium salt of 2-methylnaphthalene-7-sulfonic acid was dissolved in water, heated to boiling, and then treated with excess sulfuric acid. The barium sulfate formed was filtered out and potassium permanganate was added. After the solution was maintained at the boiling point for 24 hours, alcohol was added to destroy excess permanganate and the solution was clarified with activated carbon. On concentration 4-sulfophthalic anhydride (as later shown) crystallizes out.

Fusion of Oxidation Product. The oxidation product was slowly added to a nickel crucible containing potassium hydroxide and sodium hydroxide, and the mixture was fused at 170–180° C. for one hour. The fusion mass was dissolved in hot water, acidified, and extracted with ether. On evaporation of the ether, 4-hydroxyphthalic acid was obtained, melting at 203–204° C. (*11*).

Fusion in the same manner at about 300° C. gives *m*-hydroxybenzoic acid (melting point 201° C.) on acidification. This is an expected reaction since many phthalic acid derivatives substituted in the 4 position decarboxylate easily. The reactions were:



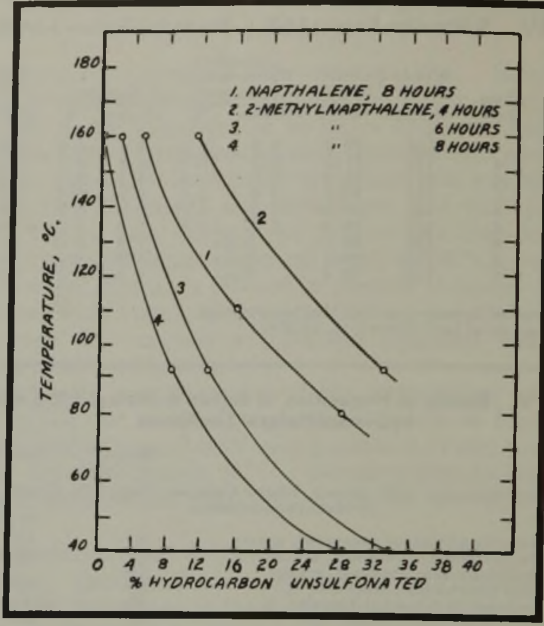


Figure 5. Effect of Temperature on Amount of Hydrocarbon Sulfonated

The 2-methylnaphthalene-6-sulfonic acid was known to be absent by comparison of solubilities (2,6 barium salt, 2 grams per liter; 2,7 barium salt, 0.57 gram per liter); therefore the 2-methylnaphthalene-7-sulfonic acid was the only compound which would give the above reactions on oxidation and fusion. This establishes the structure of the starting material as 2-methylnaphthalene-7-sulfonic acid.

Industrial Possibilities

Wetting Agent Tests. The sodium salts of the sulfonic acid were found to have wetting properties, and an attempt was made to evalulate their possibilities. Surface tension, stability, and viscosity measurements were determined, and attempts were made to apply the Draves wetting test to the compounds.

These compounds were found to be stable to both acids and bases, even in boiling solutions with concentrations as high as

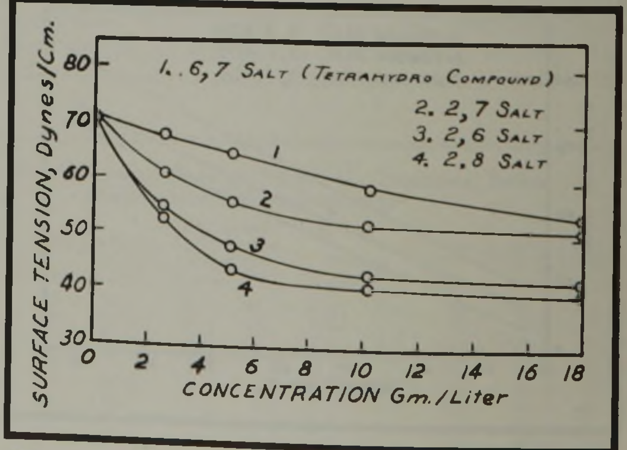


Figure 6. Surface Tensions of Solutions of Sodium Salts of the Sulfonic Acids

Table VIII. Viscosities and Densities of Aqueous Solutions of Sodium Salts of Sulfonic Acids at 25° C.

Concn., Grams/Liter	2-Me, 6-SO_3Na		2-Me, 7-SO_3Na		2-Me, 8-SO_3Na		6-Me, 7-SO_3Na[c]	
	Density[a]	Viscosity[b]	Density	Viscosity	Density	Viscosity	Density	Viscosity
0.50	0.9971	0.886	0.9981	0.876	0.9978	0.875	0.9982	0.897
1.25	0.9973	0.905	0.9983	0.903	0.9983	0.866	0.9984	0.906
2.50	0.9978	0.913	0.9984	0.926	0.9985	0.911	0.9985	0.907
3.75	0.9980	0.923	0.9986	0.936	0.9990	0.928	0.9980	0.908
5.00	0.9983	0.944	0.9990	0.942	0.9995	0.944	0.9996	0.909

[a] Gram per cc. [b] Centipoise. [c] Tetrahydro compound.

Table IX. Surface Tensions of Aqueous Solutions of Sodium Salts of Sulfonic Acids

Concn., Grams/Liter	Surface Tension, Dynes/Cm.			
	6-Me,7-SO_3Na (tetrahydro compd.)	2-Me,7-SO_3Na	2-Me,6-SO_3Na	2-Me,8-SO_3Na
2.5	67.8	61.8	55.1	53.5
5.0	64.9	56.2	47.9	43.8
10.0	68.6	53.0	43.5	41.0
18.0	53.5	51.1	41.7	39.6

15 per cent, and the wetting-out power in these concentrated solutions was increased. In addition, these compounds resisted precipitation in hard water. Viscosity and density data for dilute solutions are given in Table VIII. Surface tension measurements, made in the du Noüy tensiometer, are shown in Figure 6 and Table IX. The maximum surface tension lowering is nearly approached by one per cent solutions. The Draves test was of little use in estimating the value of these compounds.

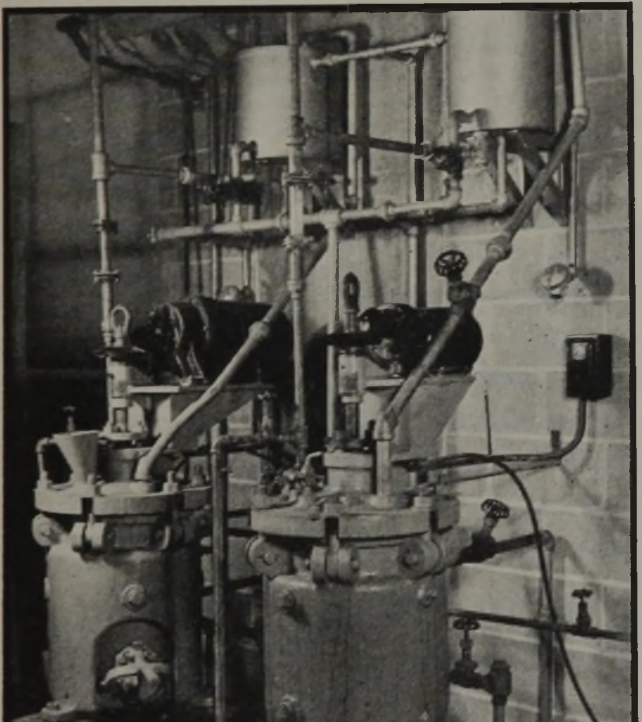


Figure 7. Sulfonator

Production. To determine the possibility of adapting the compounds made in this investigation to commercial production, runs were carried out in large sulfonation and fusion pots (Figures 7 and 8) which are similar to those used in semiworks industrial practice. A series of reactions was run on naphthalene and then on 2-methylnaphthalene, making sodium salts of sulfonic acids and naphthols, so that processes could more easily be compared. It was found that 2-methylnaphthalene sulfonic acids and derivatives could be easily produced in ordinary equipment by varying the time and temperature of the reactions.

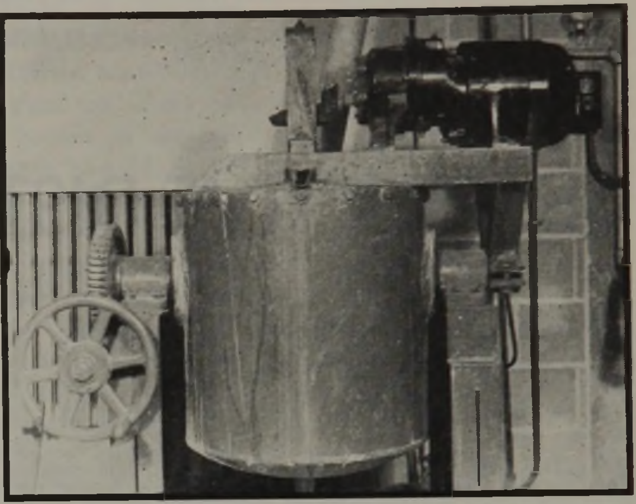


Figure 8. Fusion Pot

Conclusions

1. 2-Methylnaphthalene can be sulfonated with 93 per cent sulfuric acid; sulfonation takes place in the 8 position at 40° C. (75 per cent yield), in the 6 position at 90–100° C. (90 per cent yield), and in the 7 position at temperatures above 160° C. (88 per cent yield).

2. 2-Methylnaphthalene can be hydrogenated to 6-methyl-Tetralin with hydrogen and a Raney nickel catalyst. Sulfonation of this compound gives 6-methyl-Tetralin-7-sulfonic acid.

3. Derivatives of the sulfonic acids, such as salts, sulfonyl chlorides, sulfonamides, naphthols, ethers, and amino compounds, can be made in the usual manner.

4. The sulfonic acids and their derivatives listed above can be made on a large scale by methods and apparatus now in commercial use.

5. The sodium salts of the sulfonic acids show definite wetting-out properties. They have the following advantages which may make them of use commercially: low cost, stability in dry form, resistance to precipitation in hard water,

stability in solutions of concentrated acids and bases, near maximum wetting in one per cent solutions, and ease of manufacture.

Acknowledgment

The authors wish to thank the Reilly Tar and Chemical Corporation for the generous supply of material for this investigation.

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Based upon a thesis submitted by John H. Lux to the faculty of Purdue University in partial fulfillment of the requirements for the degree of doctor of philosophy.

DESTRUCTIVE DISTILLATION of BAGASSE

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IN THE manufacture of sugar from cane, one residual product is the fiber bagasse, sometimes known in the British colonies as "megasse". The origin of the name "bagasse" was traced back to Provence, France, where it was applied to refuse from olive oil mills—hence, anything worthless.

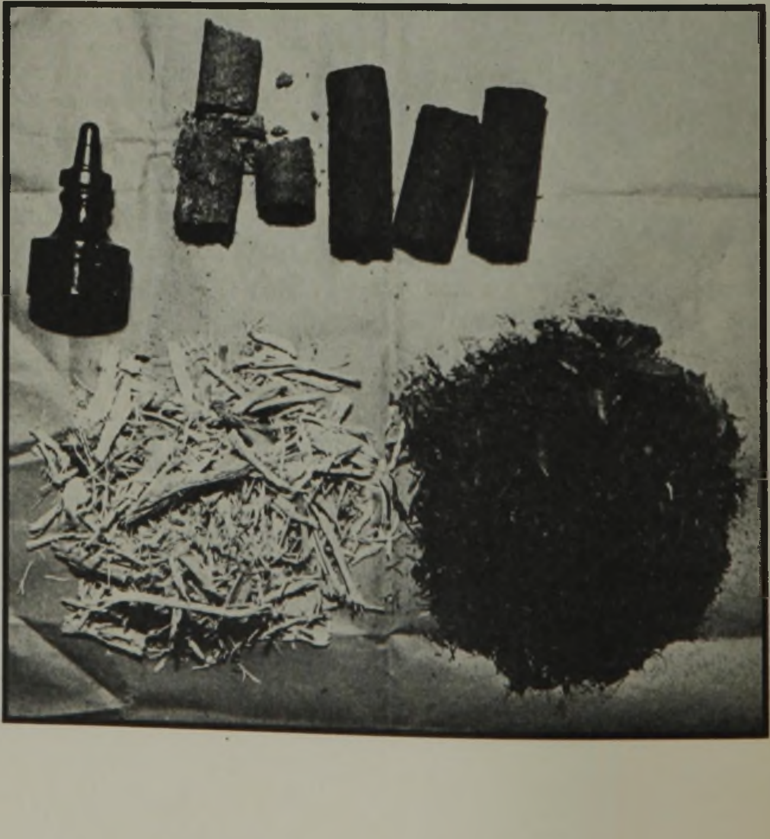
One investigator (*2*) reports that the Louisiana varieties of sugar cane yield 400 to 580 pounds of wet bagasse per ton of cane, or an average of 20 to 30 per cent of the total amount of cane ground. In the case of a sugar *central* producing 1000 tons of sugar per day, about 480,000 pounds of wet bagasse would be produced.

Bagasse is a straw-colored, bulky fibrous substance. It consists of 25 to 40 per cent fiber cellulose, 0.1 to 0.15 per cent unknowns (albuminoids, gums, etc.), 6 to 10 per cent sugar, and 40 to 55 per cent water. Its ultimate analysis (*3*) on the dry basis is: carbon, 43 to 47 per cent; hydrogen, 5.4 to 6.6; oxygen, 45 to 49; ash, 1.5 to 3 per cent.

The heating value of dry bagasse is 8300 B. t. u. per pound (*2*). For bagasse containing 42.8 per cent moisture, the heat value was found to be 4800 B. t. u. per pound and for that containing 56.7 per cent moisture, it was 3620 B. t. u. per pound. The net heating values are 2200 to 3350 B. t. u. per pound. Thus, 1 pound of wet bagasse will evaporate 2 to 3.5 pounds of water from and at 212° F. Assuming coal to have 14,000 B. t. u. per pound, 4 to 6 pounds of bagasse are equivalent to a pound of coal.

The bagasse from a sugar *central* producing 1000 tons of sugar in 24 hours will generate from 1160 to 1440 boiler horsepower during that time. About 60 tons of coal per day would be needed to do the same work.

Bagasse is also processed by cooking and then fashioned into sheets of building or insulating board, approximately $^7/_{16}$ inch thick and 4 feet wide, which are cut into lengths of 8 × 12 feet. This material bears the trade name "Celo-



Bagasse and Products (India Ink Bottle for Size Comparison)
***Lower left,* raw bagasse; *lower right,* charcoal; *above left,* fractured briquet using starch binder; *above right,* briquet using molasses binder.**

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[1] Present address, E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

tex". However, this process consumes only a small fraction of the total bagasse available.

Paper pulp has also been made with low alpha-cellulose content.

In some regions—for example, Puerto Rico—bagasse is returned to the soil as a very poor fertilizer. Experiments to develop bagasse as ensilage, as a food itself, or as a carrier for molasses have been unsuccessful.

The tremendous amounts of bagasse available at single points and the fact that charcoal is an important domestic fuel in most tropical countries made desirable the investigation of the carbonization of this waste plant fiber.

▶ ▶ ▶ Bagasse is the wood stem of the sugar cane after expressing the juice. Unlike the stalks of most other types of plants which are also waste cellulosic material, it is readily available in large quantities at single points, the sugar *centrals.* Furthermore, most of the countries in the tropics where bagasse is produced use charcoal in large quantities as a domestic fuel.

Experiments were undertaken to determine yields of several products when bagasse is carbonized in a retort under different conditions of temperature and time. Per short ton of dry bagasse, approximately 1050 pounds of charcoal, $1^1/_5$ gallons of crude methanol, and 53 pounds of acetic acid were obtained. The amount of charcoal was considerably greater than would be produced from an equivalent weight of dry wood; while the volatile constituents were in each case considerably lower.

The charcoal was formed into experimental briquets by the addition of a small amount of starch or molasses before compression and drying. It appears that the carbonization of bagasse could be profitable in those locations where it is available in quantity.

Carbonization Apparatus

RETORT. The heating chamber or retort (Figure 1) consisted of a heavy iron can with an airtight cover. One-gallon white-lead paint cans were used, since they are made of comparatively heavy sheet and have no soldered seams. The covers of these cans have rolled lips, which were made airtight by packing the overlapping cover with a plumber's packing compound. A layer of asbestos cement was laid outside of this.

Two holes were drilled through the cover. One, with $^3/_4$-inch iron pipe bushing, served as an outlet for the distillation products; the other, with a $^1/_2$-inch iron pipe bushing, held a thermocouple well.

The junction between the bushings and the can cover was made airtight by placing large metal washers on each side of the cover. A layer of $^1/_8$-inch asbestos paper was placed between the metal washers and the cover. A metal nut was used to press the washers and two asbestos strips against the cover. All joints were then given a coating of plumber's filler and finally a layer of asbestos.

A $^3/_4$-inch iron pipe was inserted inside the larger bushing. This pipe line was attached to the condenser by a union, two elbows, and three short pieces of pipe.

The thermocouple well was made by placing a $^1/_2$-inch capped pipe inside of the smaller bushing and projecting into the retort.

The retort rested on several sheets of metal, to protect it from the direct flame. The assembly was supported by a large laboratory tripod.

CONDENSER. The Liebig type condenser (Figure 1) consisted of 27.5 inches of copper tubing of $^3/_4$-inch iron pipe size, jacketed by a $1^1/_2$-inch-diameter copper tube and having an inlet and an outlet for cooling water.

FURNACE SETTING. An outer shell was made from a 5-gallon iron can container by removing the bottom. Two holes were drilled in the top of this container to correspond to the condenser and thermocouple outlets from the retort. A larger hole provided for the escape of the products of combustion. The outside and top were covered with a $^1/_2$-inch mesh screening; it served as a foundation for an asbestos paste which was forced in and around the screening to a thickness of 1.5–1.75 inches. A cotton net was placed on the outside of this asbestos layer.

Three metal legs were fastened by bolts to the shell to support it in position over and around the retort.

Temperatures up to 1000° F. were attained in the retort by a large Méker burner. Greater heat economy would have been attained if the bottom had been closed so that only enough air for combustion could enter the furnace.

TEMPERATURE MEASUREMENT. The retort temperature was measured by a Bristol thermocouple in the well in the top of the can and an indicating pyrometer. They were calibrated, and temperatures could be read to 5° F.

RECEIVERS. Three bottles were placed in series as receivers. The first bottle was a side-arm flask calibrated for rough measurement of volume by a scale pasted on the side and attached to the bottom of the condenser by a rubber stopper. The noncondensable gas passed through the flask and left by means of the side arms.

To remove all tar before allowing the gas to pass to the meter, a second small collecting bottle was used with a short inlet tube and an outlet tube which extended into the center of the bottle. During several of the tests it became coated with tar, indicating the need for such a trap.

Finally, the gas bubbled through about 100 cc. of water in an 8-ounce bottle and then passed to the gas meter. The solution in the third receiver became slightly acid during the run.

IMPORTANCE OF CLEANING. The tar driven off had a tendency to clog the pipe lines. The condenser and connections were cleaned by forcing a metal bar through the pipe to break up any solid pitch clinging to it. Pieces of cotton waste, either dry or soaked in methanol, were pushed through the pipe to clean off fluid tar, which is done more readily immediately after a run, since the tars harden to pitch after several days.

Plan of Distillation

PROCEDURE. A weighted amount of bagasse was added, the retort was sealed, and the outer shell was placed around the retort. The condenser, collecting bottles, thermocouple, and Méker burner were arranged. The burner was lit; and the retort temperature, volume of distillate, and dischange temperatures were recorded at definite time intervals. In later experiments the volume and composition of the gas were also determined periodically.

Three products are obtained: charcoal, condensable liquids, and noncondensable gases. The charcoal remained in the retort and was removed and weighed after cooling; the condensable distillate was collected mainly in the first receiver; and the noncondensable gas was measured, analyzed, and vented to an exhaust duct.

The liquid product was later distilled away from the accompanying tar, and the volatile product was weighed. The distillation was usually continued until the tar showed signs of decomposition. The tar residue solidified upon cooling. The distillate was titrated for total acidity with

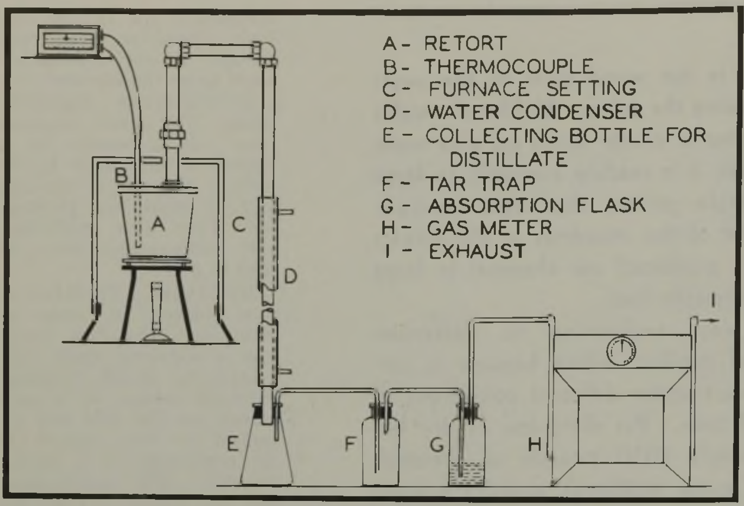

Figure 1. General Arrangement of Apparatus

sodium hydroxide, using phenolphthalein as both inside and outside indicator. In later experiments a Beckman pH meter was used to determine the end point. These titrations were not absolute since all acids present were assumed to be acetic acid. Slight errors would also be introduced by the presence of phenols and aldehyde.

After the solution was made strongly alkaline, it was again distilled until all of the methanol present was evaporated, as indicated by a boiling temperature equal to that of water. This distillate was then weighed; and the specific gravities were determined to obtain the percentage of alcohol by volume from the tables.

Gas Analyses were made at 15-minute intervals during the carbonization to study the composition of the gas during the different stages of carbonization. An Orsat apparatus was used to determine carbon dioxide, oxygen, and carbon monoxide.

Moisture and Ash. The stock of bagasse to be used was thoroughly air-dried, and the moisture remaining was determined to be 6.5 per cent.

The ash content of the finished charcoal was determined for run 6 to be 9.3 per cent. The standard method of difference was used after all combustible matter has been burned off. The ash content of the original bagasse was 3.9 on a dry basis.

Experimental Carbonizations

The rate of heating, time of heating, and maximum temperature were investigated. Table I and Figure 2 show the data obtained.

Run 1. After the bagasse had been heated rapidly for 25 minutes, the rate of heating was reduced slightly. The run continued for a total of 225 minutes and to a final maximum temperature of 840° F. These conditions were not satisfactory; the yields of acetic acid and tar were well below those obtained under other conditions. The yield of charcoal was also low.

Run 2. Rapid heating for a short time resulted in a distillate which was high in tar and contained an average yield of acetic acid. Although this test was comparatively short, the rate of heating was great enough to make possible a maximum temperature of 755° F. in the retort. The conditions—rapid heating, short time, and, mainly, high maximum temperature—gave a minimum yield of charcoal, approximately 25 per cent below the best condition (run 8).

Run 3 was not completed and was disregarded.

Run 4. Heat was applied at the same rate as run 2. This was the shortest test made (80 minutes) with the result that the maximum temperature attained was much lower than in run 2. The charcoal yield for this test was approximately 16 per cent greater than for run 2. The yield of total distillate was virtually the same for the two tests, but there was a slight decrease (about 9 per cent) in the acetic acid content of the distillate.

Run 5. The charge was slowly heated to 350° F. Approximately 35 minutes were required to raise the temperature 100°, while in run 2, whose temperature-time curve had the greatest slope, only 7 minutes were needed to effect a similar temperature rise. Above 350° F. the temperature rise was

Table I. Experimental Data

Run number	1	2	4	5	6	7	8	9
Bagasse charged, grams	243.0	326.7	271.1	269.5	281.9	275.7	276.4	270.9
Dry bagasse, grams	227.2	305.5	253.5	252.0	263.6	257.8	258.4	253.3
"Charcoal" residue								
Weight, grams	92.4	117.8	113.5	100.4	111.7	120.88	135.11	...
%, dry bagasse basis	40.66	38.56	44.77	39.84	42.37	46.89	52.29	...
Total distillate								
Volume, cc.	26.8	63.7	54.8	41.0	76.5	55.4	67.2	...
Wt. including tar, grams	29.3	71.10	58.1	45.8	81.3	64.55	72.51	...
%, dry bagasse basis	12.90	23.27	22.92	18.17	30.84	25.04	28.06	...
Noncondensable gaseous product								
Wt. (by difference), grams	121.3	137.8	99.5	123.3	88.9	90.27	68.78	...
%, dry bagasse basis	53.39	45.11	39.25	48.93	33.73	35.02	26.62	...
Distillate after tar removal								
Weight, grams	20.0	47.4	45.9	33.8	61.87	50.40	60.25	...
%, dry bagasse basis	8.80	15.52	18.11	13.41	23.46	19.55	23.32	...
Tar								
Weight, grams	9.3	23.7	12.2	12.0	19.43	14.15	12.26	...
%, dry bagasse basis	4.09	7.76	4.81	4.76	7.37	5.49	4.74	...
Acetic acid, %								
Dry bagasse basis	0.344	2.29	2.095	1.49	2.44	1.735	2.64	...
Total dist. basis	2.665	9.72	9.13	8.25	7.90	6.92	9.43	...
Total dist. minus tar basis	3.91	14.59	11.55	11.10	10.39	8.87	11.35	...
Methanol, % by weight								
Dry bagasse basis	...	...	...	0.3663	...	0.616	0.422	...
Total dist. basis	...	...	...	2.01	...	2.455	1.503	...
Dist. minus tar basis	...	...	...	2.73	...	3.15	1.81	...
Total vol. gas produced, cu. ft.	...	...	...	...	...	0.52	0.205	0.34
Max. temp. attained, ° F.	840	755	630	800	785	750	618	678
Total heating time, min.	225	115	80	230	260	110	120	130

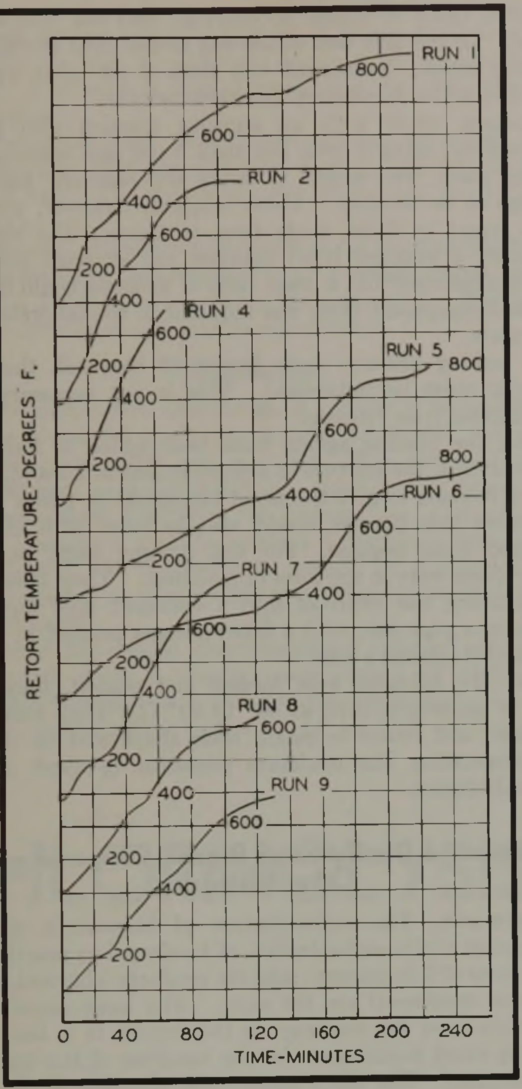

Figure 2. Temperature of Retort at Progressive Times during the Destructive Distillation of Bagasse

much more rapid—15 minutes for a 100° rise. In this test the distillate separated into two distinct layers—an oily tar and a clear red water layer. The distillates obtained for runs 1, 2, and 4 were pale yellow and did not separate by gravity.

Run 6. The rate of heating was changed; a high initial rate was continued for 80 minutes, followed by 30 minutes at approximately constant temperature, 340° F., and then about 140 minutes of moderate heating. The yields of acetic acid and tar were high, but only an average amount of charcoal was produced. The tar was very oily and light brown in color; the tars obtained from the other tests were black.

Run 7. The time and final temperature were approximately the same as those for run 2, but the rate of heating was not so high initially. The charcoal yield was high, being inferior only to that of run 8, while only average amounts of acetic acid and tar were produced. The yield of methanol was somewhat higher than that obtained for runs 5 and 8.

Run 8. This test was made to determine the effect of applying heat at a moderate rate for a short time. Since the final temperature was only 618° F., a high yield of charcoal was obtained. This yield was approximately 10 per cent greater than in run 7 and about 35 per cent greater than run 2, which had the poorest yield. The highest yields of acetic acid and tar were also obtained. The yield of methanol was, however, below that of run 7.

In Figure 3 the total volume of noncondensable exhaust gases and the volume of carbon dioxide and carbon monoxide are plotted against time during runs 7, 8, and 9. The maximum percentages of carbon monoxide obtained were 8.1, 4.5, and 5.3, respectively. The gas in each case burns with a blue flame, but the heat content is evidently low.

Trends Shown by Tests

It is difficult to specify conditions for which the highest yields of acetic acid, tar, charcoal, and combustible gas may be obtained because of the many variables. However, possible trends may be deduced.

Charcoal yields are shown, as would be expected, to be lower with a higher rate of heating and with a higher maximum temperature attained in the retort. A higher rate of heating probably causes the driving off of more of the carbon in the form of heavier molecules with a higher ratio of carbon to hydrogen and oxygen while a slower rate probably allows the cracking or decomposition of these molecules to give a correspondingly higher carbon residue. A lower final temperature simply allows more volatile material to remain in the charcoal.

The effect of maximum temperature is best illustrated by comparing runs 2 and 4, where the rate of heating was virtually the same, the only variation being the total time and maximum temperature. In run 4 the total time was 80 minutes with a maximum temperature of only 630° F.; the maximum temperature in run 2 was 755° F. As a result, the quantity of charcoal obtained at the lower temperature was 14 per cent greater than that at the higher temperature.

The trend toward higher charcoal yields for low rates of heating is demonstrated by runs 7 and 2; the total time and final temperatures were virtually the same, but the rate of heating for run 7 was lower than for run 2. The charcoal yield for run 7 was approximately 18 per cent greater than that obtained for run 2. The trend toward increased charcoal yields for low rates of heating is further substantiated by comparison of run 1 with run 5, where the rate of heating was considerably lower. The charcoal produced for the two tests are practically the same despite the fact that the charge for run 1 was heated 40° higher. Thus the statement that the charcoal yield is improved by slow heating is indirectly substantiated.

The maximum retort temperature seems to have a more important effect on the amount of charcoal produced than the rate of heating. The importance of maximum temperature is illustrated by run 8 where the highest charcoal yield was obtained. In this test the rate of heating was moderate, but owing to the shortness of this run the final temperature attained was only 618° F.

If the above results are classified according to the rate of applying heat—for example, high rate and low rate—and these general headings are subdivided according to the time required to complete the test, analysis of the problem of determining the best operating conditions is simplified.

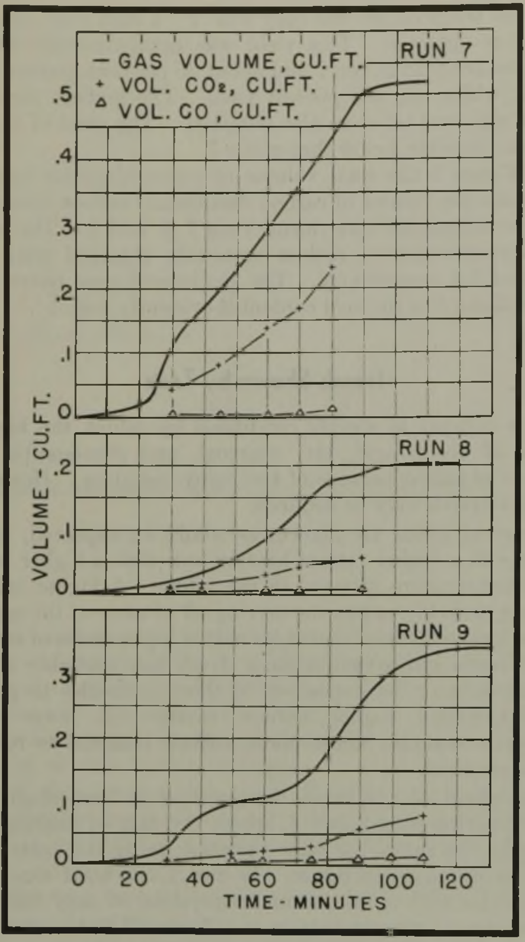

Figure 3. Evolution of Gases

Classifying the results in such a manner, a slight trend toward increased acetic acid yields were observed for high rates of heating; an exception is run 6. Perhaps this can be explained, since the initial rate of heating for this test was high—that is, for the heating period between room temperature and 250° F.

These results are not to be regarded as final or as describing the complete story on the destructive distillation of bagasse. Such factors as size of retort, design of furnace and method of applying heat, method of charging the retort, etc., affect the time, rate of heating, and yield relationship. However, these results indicate a trend and show that the destructive distillation of bagasse gives valuable products, the exact amounts of which will vary somewhat with the design and operation of plant units. The results merely prove that this process is worthy of further consideration.

Fuel Briquets from Charcoal

The charcoal produced was fluffy and bulky and given to dusting. It had no mechanical strength. To reduce the apparent density, fuel briquets were made which utilized even the fine material present in large amounts which were otherwise almost valueless.

Both starch and molasses were tried as binding material for the briquets in preference to other materials such as tars or pitch or sulfite liquors from pulp manufacture. Molasses has the special advantage that it is produced in large quantities at the sugar *central*. The briquets were made of several different ratios of binder to charcoal, and the results compared. In the first test water was added until the charcoal became moist. Somewhat less than 5 per cent molasses was then added to produce a suitable briquet.

Briquets made with an aqueous solution also proved satisfactory, using a little less than 5 per cent starch. Sufficient water was added to make the charcoal just fluid enough to be handled. These briquets, however, were not quite equal to these made from molasses. The molasses produced a stronger bond between the charcoal particles; and it is believed that a lower ratio of molasses could be used in plant equipment than was required in the laboratory experiments.

In making briquets from hardwood charcoal, the lump material must be pulverized. This is not necessary with the charcoal from bagasse.

After the binding agents have been added to hardwood charcoal dust, the mixture in a plant is sent to a set of rollers having recesses to give the usual biscuitlike or pillow shape. Doubtless this process would also be used with charcoal obtained from bagasse. For the present tests, however, the briquets were in the form of cylinders. They were made by ramming the charcoal into a standard pipe nipple of 1-inch iron pipe size, with a fitted plunger pressed in with a standard machinist's vise.

After the briquets were formed and shaped, they were dried in an electric oven at 88° to 90° C. They were then examined and found to retain their shape and be capable of withstanding the moderate pressures required of any charcoal briquet.

Destructive Distillation of Bagasse Compared with Other Materials

Hardwood. The carbonization of bagasse is directly comparable to the carbonization of hardwood as practiced in many parts of this country; and the products (charcoal, acetic acid, and methanol) are the same. The same sequence of operations used for working up the liquors in a hardwood distilling plant would serve for the handling of the distillate from bagasse. The usual commercial amounts of products from dry hardwood (*4, 6*) are listed in Table I, although much higher amounts have been obtainable (*5*). Using run 8 as an example, the amounts of products from the same amount of dry bagasse are shown in Table II. Almost twice as much charcoal, while less acetic acid and much less methanol, are produced.

Table II. Comparison of Products from Carbonization of Hardwood, Wheat Straw, Corncobs, and Bagasse (Run 8)

	Wood	Wheat Straw (*1*)	Corncobs (*7*)	Bagasse
Weight of material, lb.				
Raw	4000	3000	3360	3210
Dry	3000	[a]	3000	3000
Charcoal produced, lb.	1000	1000	900	1570
Gas, cu. ft.	7000	1050 lb.	600 lb.	1080
Total dist., gal.	250	104	144	93.5
Tar discharged, gal.	26	11	14.7	9.74
85% crude methanol, gal.	10	..	4.0	1.82
Acid as 100% acetic, lb.	120	26	78	77

[a] Moisture content not given.

Wheat Straw. Because of the physical similarity of bagasse to wheat straw, it is interesting to compare the products obtained on the basis of 3000 pounds of dry material. The results on wheat straw are those of Faith (*1*) who states: "The chief objection to the utilization of straw is the cost of collection. With the present trend to the widespread use of combines (for harvesting) instead of binders, the straw is spread around the field instead of being stacked. Consequently the cost of collection is out of proportion to the value." The same is true of most other agricultural cellulosic wastes.

The charcoal from wheat straw (*1*) was extremely light and analyzed: 57.8 per cent fixed carbon, 10.5 volatile matter, 31.7 ash. The potash content of the ash was 2.25 per cent K_2O.

CORNCOBS. Experimental values on destructive distillation of corncobs have been reported (*7*). Average values are included in Table II, converted to the same basis. The collection of corncobs might also be uneconomic.

Conclusion

In the destructive distillation of bagasse it is possible to produce five useful products—namely, acetic acid, methanol, charcoal, combustible gas, and tar. The yields of acetic acid, charcoal, and methanol were great enough to envision the destructive distillation of bagasse on a commercial scale. Bagasse is a waste product already collected at the sugar *central*. If the products formed by distillation can be used nearby, as seems possible, transportation costs would be a minimum.

Although the regions where bagasse is obtained are mainly agricultural, there is usually some market for acetic acid and methanol as well. The gas produced might be used for the carbonization operation or for fuel at the sugar *central*. Fortunately, the chief product is charcoal which fits well into the economy of many tropical sugar countries where it is used as a domestic fuel. Much better yields of charcoal and lesser yields of acetic acid and of methanol are indicated from bagasse than from hardwoods.

The charcoal is bulky and comes as a fine, pulverent material. It is easily made into briquets with a small amount of starch or of molasses, which is another by-product of the same industry. The texture of the charcoal indicates that it might be suitable for activated carbon.

It thus seems that bagasse might be profitably carbonized in some locations because of the products, particularly charcoal, and the fact that the valueless bagasse is available at a single point, the sugar *central*, in large quantities. The physical nature of bagasse indicates that the advantages of continuous carbonization by the modification of a continuous retort used for wood waste should be realized.

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CHLORINOLYSIS of CHLOROPARAFFINS

▸ ▸ ▸ **The chlorinolysis reaction has been applied to chlorinated derivatives of ethane, propane, isobutane, butane, hexane, heptane, octane, and tetradecane. Carbon tetrachloride and hexachloroethane are products of the reaction in each case. It seems possible that any polycarbon chloroparaffin can be converted to carbon tetrachloride and hexachloroethane in good yields by chlorinolysis with an excess of elemental chlorine. Hexachloroethane may be subsequently converted to tetrachloroethylene, a valuable solvent.**

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BY ANALOGY to such terms as hydrogenolysis, hyrolysis, ammonolysis, and alcoholysis, indicating a chemical reaction in which hydrogen, water, ammonia, or alcohol, respectively, effects a rupture of the molecule undergoing these reactions, the term "chlorinolysis" has been suggested (*9*) to describe the process of chlorinating an organic compound under conditions which rupture the carbon-carbon bonds to yield chloro compounds with fewer carbon atoms than the starting material.

A survey of the literature reveals only a few examples of chlorinolysis in which elemental chlorine was the chlorinating agent. The most significant reference to chlorinolysis with elemental chlorine is that of Grebe, Reilly, and Wiley (*4*); their's is a patented process for the preparation of chlorocarbons, principally carbon tetrachloride and tetrachloroethylene, by passing preheated chlorine and paraffin hydrocarbons through a bath of molten metal chlorides such as a eutectic mixture of aluminum chloride, ferric chloride, and sodium chloride. According to a patent issued to I. G. Farbenindustrie A.-G. (*7*), carbon tetrachloride may be prepared by passing aliphatic hydrocarbons of more than one carbon atom or their chlorinated products with chlorine over activated carbon or other substances of large surface area at 400° to 650° C. The chlorine was 20–40 per cent in excess of the quantity theoretically necessary for the formation of carbon tetrachloride. The high-pressure, high-temperature chlorinolysis of chloropentanes for the production of carbon tetrachloride and hexachloroethane was described by McBee, Hass, and Pierson (*9*).

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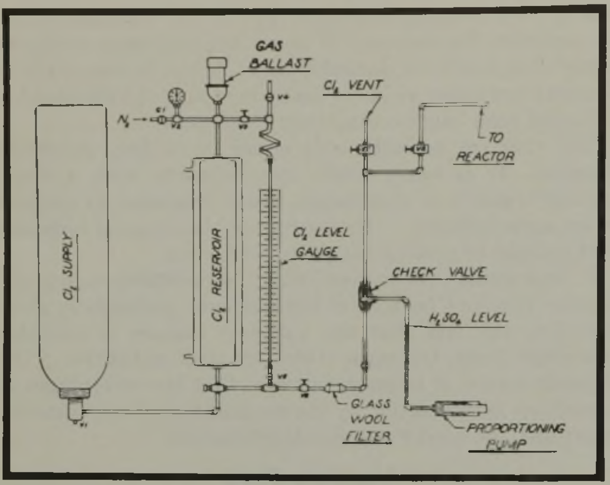

Figure 1. Chlorine Pumping Mechanism

There are several references to the chlorinolysis of hydrocarbons and their chlorinated derivatives by chlorinating agents other than elemental chlorine. Eckert and Steiner (*1*), Merz and Weith (*10*) and Gnehm and Banziger (*3*) obtained carbon tetrachloride, hexachloroethane, and hexachlorobenzene by chlorinating a variety of aromatic compounds with antimony pentachloride. Hoffmann (*6*) reported that hexachlorobutadiene was obtained from the chlorination of trichlorodioxypicoline, $C_6H_4O_2NCl_3$, with phosphorus pentachloride. Hartmann (*5*) chlorinated certain aliphatic compounds with antimony pentachloride, using iodine as a catalyst, and obtained carbon tetrachloride, hexachloroethane, hexachlorobenzene, and hexachlorobutadiene. Ruoff (*11*) and Krafft and Merz (*8*) chlorinolyzed a number of aromatic compounds with chlorine in the presence of iodine. The compound Cl_3I was believed to be one of the reactants. Shvenberger and Gordon (*12*) obtained carbon tetrachloride and tetrachloroindene by chlorinating naphthalene in the presence of chlorides of the metals of groups III and VIII.

The chlorinolysis reaction has now been applied to chlorinated derivatives of ethane, propane, isobutane, butane, hexane, heptane, octane, and tetradecane. The chlorinolysis of chloroheptanes ($C_7H_{12}Cl_4$) has been studied extensively, and the effect of varying the conditions of temperature, pressure, and rate of feed of reactants has been determined.

Chlorinolysis in Sealed Tubes

In extending the chlorinolysis reaction to various paraffin hydrocarbons, it seemed desirable to carry out initial experiments on a small scale, for it is well known that chlorine forms explosive mixtures with hydrocarbons and certain of the partially chlorinated derivatives. Therefore a series of sealed tube experiments was conducted as a preliminary study of the general applicability of the chlorinolysis reaction. The compounds under investigation were sealed in $^1/_2$-inch iron-pipe-size nickel tubes, 4 feet in length, with elemental chlorine in excess of that theoretically necessary for the replacement of all hydrogen atoms. These nickel tubes were then placed in heavy iron pipe for safety and heated to a desired reaction temperature. Chloroheptanes and chlorooctanes were found to give carbon tetrachloride and hexachloroethane when heated at 250° C. As the temperature is increased, the reaction time for chlorinolysis is decreased. The use of iron equipment instead of nickel was unsatisfactory because of the catalytic reaction of iron and iron chlorides on the decomposition and polymerization of organic chlorides. In an attempt to shorten the period of chlorinolysis, the use of catalysts was studied briefly. Aluminum chloride, sulfur dioxide, and benzoyl peroxide were found to be ineffective.

A series of experiments was made to determine the applicability of the chlorinolysis reaction to compounds other than chlorinated hydrocarbons. 1-Butoxybutane and pyridine gave hexachloroethane when subjected to chlorinolysis with elemental chlorine. Cyclohexanol yielded hexachlorobenzene when chlorinated at 265° C.

Apparatus for Continuous Chlorinolysis

The apparatus (Figures 1 and 2) was essentially that described in an earlier publication (*9*). It was fabricated from ferrous metals with the exception of the reactor and the product condenser which were made of nickel. A dual proportioning pump was used to introduce chlorine and the chloroparaffins continuously into a $^1/_2$-inch iron-pipe-size nickel tube having a capacity of 210 ml. The nickel tube, which was the reactor, was surrounded by a salt bath heated by immersion heaters. The product of the reaction passed from the nickel tube reactor through a water-cooled condenser into a receiver maintained at the same pressure as the reactor. The desired pressure in the system was obtained by filling the reactor and receiver with nitrogen at the beginning of an experiment. As the product collected in the receiver, the nitrogen was allowed to escape slowly to maintain a uniform pressure. Safety disks were mounted at each end of the reactor tube. These disks were made to rupture at 2000 pounds per square inch pressure.

Little difficulty was experienced in pumping liquid chlorine at pressures as high as 1000 pounds per square inch according to the procedure described in the previous publication. This consists essentially of using a cone-type check valve in the chlorine line between the chlorine supply tank and the reactor and maintaining concentrated sulfuric acid in the line connecting the check valve and the pump. By this procedure the chlorine did not come into direct contact with the pump, and hence the problem was essentially one of pumping sulfuric acid at high pressure.

Application of Chlorinolysis Reaction

In order to determine the general applicability of the chlorinolysis reaction it was studied with a variety of chloroparaffins.

Table I. Chlorinolysis of Miscellaneous Chloroparaffins

Experiment No.	71	42	65	26	66	32	38	39	67
Temperature, ° C.	400	400	400	400	400	435	350	400	310
Pressure, lb./sq. in.	1000	750	750	1000	1000	500	500	750	500
Chloroparaffin	$C_2H_4Cl_2$	$C_3H_4Cl_4$	$C_3H_4Cl_4$	Iso-$C_4H_8Cl_2$	Iso-$C_4H_8Cl_2$	$C_4H_7Cl_3$	$C_4H_6Cl_4$	$C_4H_6Cl_4$	$C_4H_6Cl_4$
Moles	0.75	1.7	0.9	1.6	1.0	0.9	0.8	1.5	1.75
Chlorine, moles	8	14	21	21	18	10	7	18	19
Ratio Cl_2:chloroparaffin	11:1	8:1	23:1	13:1	18:1	11:1	9:1	12:1	11:1
Rate of feed, min./mole	20	30	60	75	80	72	28	27	20
Product, % by weight									
CCl_4	72	16	22	46	42	13	5	8	0.5
C_2Cl_6	28	84	78	54	58	60	80	66	99.0
Residue	...	...	...	...	...	27	15	26	0.5

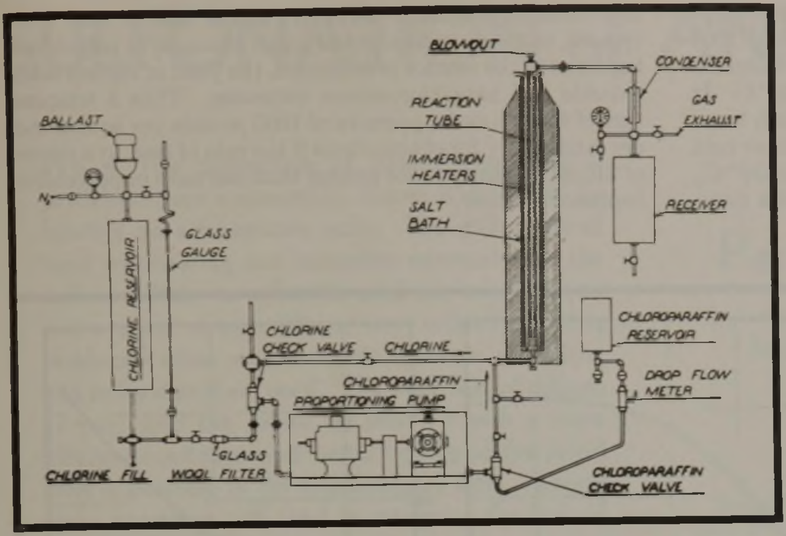

Figure 2. Chlorinolysis Apparatus

In the chlorinolysis of 1,2-dichloroethane, carbon tetrachloride and hexachloroethane were obtained as the only products. Presumably it should be possible to maintain conditions which would cause perchlorination without chlorinolysis; but at the conditions given in experiment 71, Table I, 72 per cent of the product was carbon tetrachloride, which was probably formed from the chlorinolysis of hexachloroethane. Therefore, it may be concluded that in the chlorinolysis of compounds with three or more carbon atoms, some of the hexachloroethane which is formed may be further chlorinolyzed.

Table II. Chlorinolysis of Chloroheptanes

Experiment No.	47	48	49	50	51	52	53	54	59	60	61	62	63
Temperature, ° C.	400	400	280	350	350	425	450	400	300	400	400	400	400
Pressure, lb./sq. in.	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	750	500
$C_7H_{12}Cl_4$, moles	1.0	1.0	0.6	0.8	0.8	0.8	1.0	0.7	1.0	0.7	1.0	1.0	0.8
Chlorine, moles	20	18	20	21	21	18	24	23	32	35	30	28	27
Ratio, Cl_2:$C_7H_{12}Cl_4$	20:1	18:1	33:1	26:1	23:1	24:1	24:1	33:1	32:1	50:1	30:1	28:1	34:1
Rate of feed, min./mole	40	25	65	50	44	50	50	60	50	100	40	40	44
Product, % by weight													
CCl_4	29	25	26	37	36	39	40	39	31	37	34	31	18
C_2Cl_6	30	29	23	26	25	37	26	29	26	35	28	13	18
C_6Cl_6	26	25	34	37	20	6	16	11	32	19	21	44	41
Residue	15	21	17	...	18	18	17	21	11	8	17	12	22
Product, grams	527	427	209	231	331	341	258	295	370	310	340	450	386

Several experiments were conducted with tetrachloropropanes. The products of chlorinolysis are carbon tetrachloride and hexachloroethane. A change in pressure from 750 to 1000 pounds per square inch had no appreciable effect on the relative proportions of carbon tetrachloride and hexachloroethane in the product. However, the ratio of these two chlorocarbons was affected by varying the exposure time. As would be expected, the yield of carbon tetrachloride increased as the rate of feed of tetrachloropropanes to the reactor was decreased. The average mole ratio of hexachloroethane to carbon tetrachloride for the series of experiments with tetrachloropropanes was about 3:1. Since a satisfactory carbon balance was obtained, it must be concluded that the reaction is more complicated than that of simple cleavage of the carbon-carbon bonds. Presumably there are combinations of free radicals. Otherwise the ratio should not have been greater than one mole of hexachloroethane per mole of carbon tetrachloride.

For studying the chlorinolysis of an isobutane derivative, 1,2-dichloro-2-methylpropane was used as the starting material. Carbon tetrachloride and hexachloroethane were the only products of the reaction. No attempt was made to study the effect of varying conditions on the relative proportions of the products. Experiments 26 and 66, Table I, show that an average of 44 per cent of the product was carbon tetrachloride. This relatively high percentage of carbon tetrachloride should be expected from a consideration of the branched-chain structure of the isobutane molecule. Two carbon-carbon cleavages are necessary for the direct formation of hexachloroethane from the chlorinolysis of the isobutane molecule.

The series of experiments with tetrachlorobutanes is of particular interest. From experiments 67, Table I, it appears possible to obtain hexachloroethane with the almost complete exclusion of other reaction products. However, if the temperature and pressure are increased beyond approximately 300° C. and 500 pounds per square inch, respectively, the yield of carbon tetrachloride increases.

Chlorinolysis of Chloroheptanes

Polychloroheptanes were selected for a more intensive investigation of the chlorinolysis reaction because they are available from typical paraffin hydrocarbons. A mixture of isomeric heptanes boiling at 94–98° C. at 750 mm. obtained by fractionation of commercial heptane was used as the starting material. The fraction was chlorinated in the liquid phase, in the presence of light at about room temperature, to polychloroheptanes with an average composition of $C_7Cl_4H_{12}$. These polychloroheptanes were then subjected to chlorinolysis (Table II).

EFFECT OF TEMPERATURE. The extent and rate of chlorinolysis are determined by the variables: temperature, rate of feed, pressure, and ratio of reactants. Since it was determined by preliminary experiments that the mole ratio of chlorine to polychloroheptanes had no pronounced effect on the yield of carbon tetrachloride and hexachloroethane, so long as the ratio was maintained above 18:1, respectively, no special attempt was made to regulate accurately the excess of chlorine in the reaction mixture. The use of a large excess of chlorine merely decreases the capacity of the reactor and aids in the discharge of the product from the receiver.

Using a rate of feed of 50 minutes per mole of polychloroheptanes (i. e., 50 minutes for one mole of polychloroheptanes to be pumped to the reactor) at a pressure of 1000 pounds per square inch, a series of experiments was conducted in which the temperature was varied from 280° to 450° C. It was found that at 280° C. a chlorocarbon other than hexachloroethane and carbon tetrachloride constituted 34 per cent of the product; as the temperature was increased to 425° C., the yield of this material decreased to 6 per cent and a maximum yield, 76 per cent, of carbon tetrachloride and hexachloroethane was obtained (Figure 3). This additional chlorocarbon which melts at 39° C. and boils at 140° at 10 mm. was reported (*9*) to be hexachlorobutadiene, but Fruhwirth (*2*) proved rather conclusively that it is octachlorocyclopentene. No attempt has been made to identify this material.

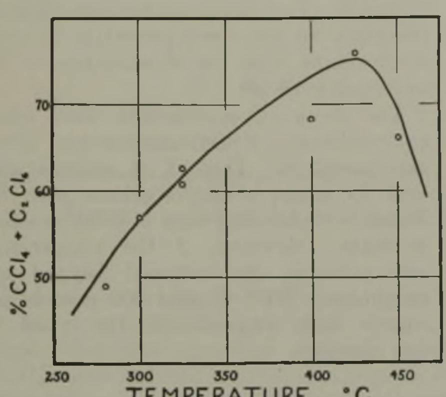

Figure 3. Effect of Temperature on Chlorinolysis of Chloroheptanes

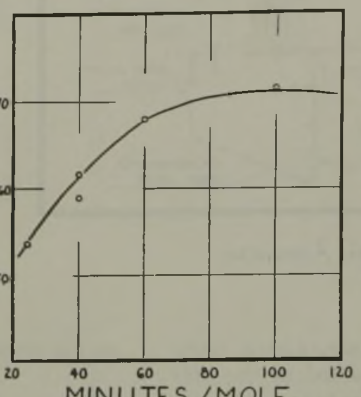

Figure 4. Effect of Rate of Feed of Reactants on Chlorinolysis of Chloroheptanes

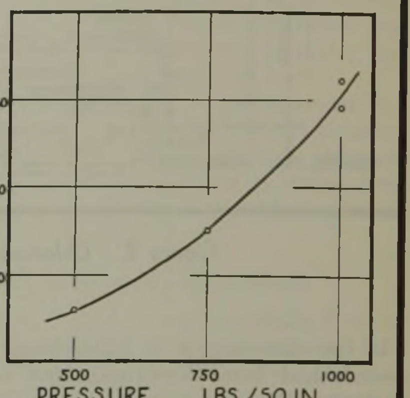

Figure 5. Effect of Pressure on Chlorinolysis of Chloroheptanes

As the temperature was increased beyond 425° C. at 1000 pounds per square inch pressure, the yield of carbon tetrachloride and hexachloroethane decreased. Since chlorinolysis presumably takes place most readily when chlorine is in the liquid phase, owing to an effective high concentration of the reactants and an increased contact time, it is possible that at such high temperatures the amount of chlorine in the liquid phase has been decreased to the extent of limiting the reaction. As the temperature is increased, it becomes necessary to increase the pressure substantially in the reactor in order to increase the solubility of chlorine in the material being chlorinated and maintain a uniform concentration of chlorine in the liquid phase.

EFFECT OF CONTACT TIME. Because of the complexity of the reaction, it is impossible to calculate accurately the exposure time of the reactants in the reactor. However, to obtain data on the effect of exposure time of the reactants on the yields of carbon tetrachloride and hexachloroethane, a series of experiments was performed varying the rate of feed of polychloroheptanes at 1000 pounds per square inch pressure at 400° C., with a ratio of chlorine to polychloroheptanes ($C_7Cl_4H_{12}$) of at least 18:1. Figure 4 shows that if the polychloroheptanes are pumped to the reactor at a rate less than one mole of polychloroheptanes per hour (i. e., when more than 60 minutes were required to pump a mole of polychloroheptanes to the reactor having a capacity of 210 ml.), there is no substantial increase in the yield of carbon tetrachloride and hexachloroethane. However, as the rate of feed is increased, or the time required to pump one mole of polychloroheptanes to the reactor is decreased, the yield of carbon tetrachloride and hexachloroethane decreases. Thus a temperature of 400° C. and a pressure of 1000 pounds per square inch are satisfactory for chlorinolysis if the rate of feed to a reactor of 210 ml. capacity is not greater than one mole of polychloroheptanes per hour.

EFFECT OF PRESSURE. Since the chlorinolysis reaction usually proceeds most satisfactorily in the liquid phase, high pressures are employed. The effect of pressure was studied in a series of experiments conducted at approximately 400° C. and a rate of feed of about one mole of polychloroheptanes per 40 minutes. Figure 5 shows that, as the pressure is increased from 500 to 1000 pounds per square inch, the total yield of carbon tetrachloride and hexachloroethane is increased from 36 to 62 per cent. Not only is the yield of carbon tetrachloride and hexachloroethane increased by high pressures, but there is also less black, tarry material in the product.

The optimum conditions, therefore, for obtaining highest yields of carbon tetrachloride and hexachloroethane from polychloroheptanes are as follows: a pressure of 1000 pounds per square inch, a mole ratio of chlorine to chloroheptanes greater than 18:1, a temperature of 425° C., and a rate of feed not greater than one mole of polychloroheptanes per hour to a reactor of 210 ml. capacity.

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ABSTRACTED from a thesis submitted to the faculty of Purdue University by Carl Bordenca in partial fulfillment of the requirements for the degree of doctor of philosophy.

SULFONATION of ANILINE

Application of Partial-Pressure Distillation

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▶ ▶ ▶ The production of sulfanilic acid by a partial-pressure evaporation system is shown to be feasible on a laboratory scale. The difficulties of local overheating and complete conversion of the aniline sulfate to sulfanilic acid are overcome so that a yield of over 95 per cent sulfanilic acid is produced when stoichoimetric amounts of aniline and sulfuric acid are used. The small loss of diluent (7 per cent) can easily be lowered with a more efficient condenser and better sealing of the joints than is possible in the experimental work. Larger scale operation will tend to minimize the loss of diluent.

These results suggest the possibility of producing sulfanilic acid by the partial-pressure evaporation system continuously on a larger scale. However, the problem of the sulfanilic acid caking in larger scale operation must be met. By the use of proper agitating equipment, it may be possible to prevent this caking and thereby make possible a continuous process for the sulfanilic acid production.

ONE of the important intermediates in the production of azo dyes is the organic acid *p*-aminosulfonic, generally termed "sulfanilic", acid. These dyes are prepared by coupling diazotized amines with other amines and with sulfonic acids. The United States produces about 1.5 million pounds of sulfanilic acid annually.

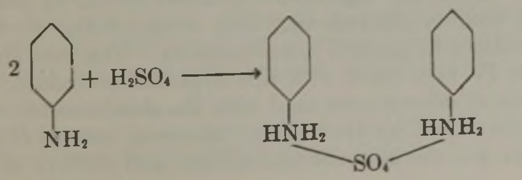
In making sulfanilic acid, water formed by the reaction between aniline and sulfuric acid must be removed. One commercial process does this by baking the aniline sulfate (the initial reaction product) in vacuum oven; another process uses 50 per cent excess concentrated sulfuric acid to withdraw the water.

The over-all yield of pure sulfanilic acid on the basis of aniline charged from the "bake" process is over 80 per cent. The yields by the sulfonation process (*1*) are equivalent to 92 and 93 per cent on the basis of aniline charged.

Although the commercial methods do result in high yields of sulfanilic acid, both of them have drawbacks. Both processes are batch operations; the bake process requires considerable handling before the final product is obtained; and the sulfonation process uses a large excess of sulfuric acid which cannot be recovered.

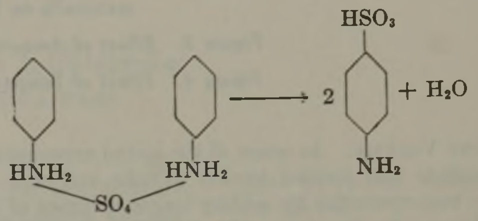
The formation of sulfanilic acid by the reaction of sulfuric acid and aniline may be considered to take place in two steps (*1*):

The sulfuric acid and aniline first react to produce the salt of the dibasic acid:



(1)

In the dehydration stage the sulfonic acid group shifts to the para position, and water is removed to form sulfanilic acid:



(2)

It was felt that the partial-pressure method might facilitate removal of the water of reaction as it has in previously reported cases (*2*, *3*). Accordingly, the feasibility of carrying out the reaction was investigated, using an acid-treated hydrocarbon fraction in the kerosene range as an entrainer.

Sulfanilic Acid Production

Kerosene fractions of different boiling ranges were used. They were always pretreated by boiling under reflux while agitating with concentrated sulfuric acid for several hours. A heavy scum of carbonaceous matter was removed, the two layers were separated, and the kerosene layer was washed with sodium carbonate solution and water, and finally distilled.

The apparatus consisted of a one-liter three-neck flask fitted with a moisture determination tube, a condenser, and a thermometer. (See Figure 1 of the paper by Othmer, Jacobs, and Buschmann, page 326). In the flask were placed the sulfuric acid (commercial 93 per cent) and the diluent. The aniline was poured in slowly over a period of 2 minutes. In all runs 40 grams (39 cc.) were used. Immediately the aniline and the sulfuric acid reacted to form a pinkish-white precipitate, aniline sulfate, with the evolution of heat. The mass was agitated violently and heated gently. Vapors of diluent and water bubbled through the molten mass of aniline sulfate and passed up to the condenser where both the diluent and the water condensed. The water collected at the bottom of the moisture determination tube, and the diluent refluxed back into the flask.

Effect of Variables on Acid Yield

Several variables affect the production of sulfanilic acid by the partial pressure method; they were investigated individually in so far as it was possible to maintain the other variables constant.

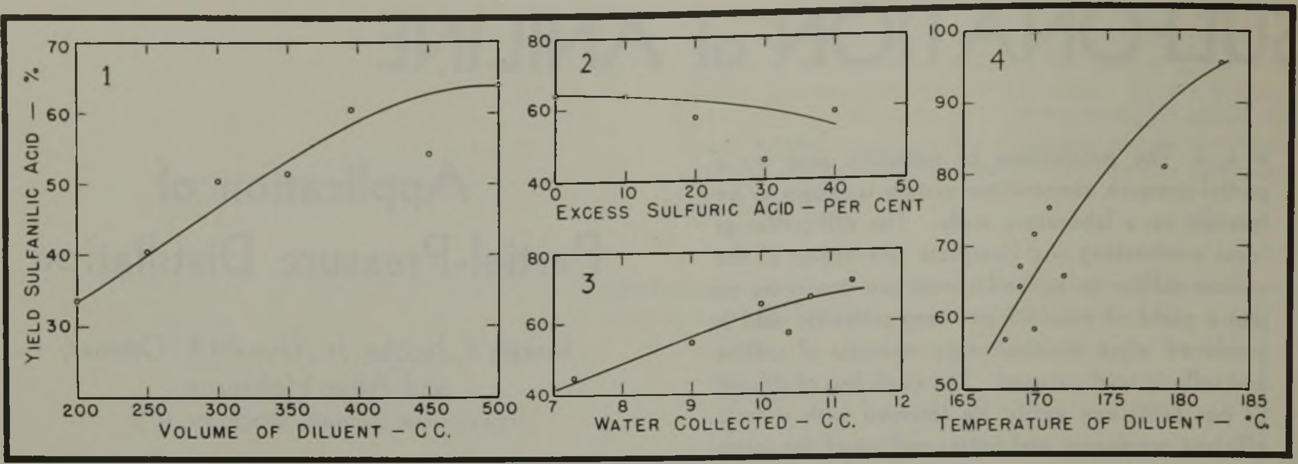


Figure 1. Effect of Amount of Diluent on Yield of Sulfanilic Acid

Figure 2. Effect of Amount of Sulfuric Acid over That Required Stoichiometrically on Yield of Sulfanilic Acid

Figure 3. Effect of Amount of Water Removed on Yield of Sulfanilic Acid

Figure 4. Effect of Temperature of Reaction on Yield of Sulfanilic Acid

DILUENT VOLUME. In some of the initial experiments the aniline sulfate first formed tended to cake and char. This difficulty was overcome by adding larger volumes of hydrocarbon diluent (boiling range 155–190° C.). In order to test quantitatively the effect of larger amounts of diluent, a series of runs was made in which the volume of diluent was varied. It might ordinarily be expected that the amount of hydrocarbon present would have little effect upon yield. But in this case the caking of the aniline sulfate and the consequent reduction in yield seems to be influenced by the quantity of diluent.

The effect of increasing the volume of diluent is shown in Table I and Figure 1.

EXCESS SULFURIC ACID. The use of the partial pressure method is predicated upon the ability of the diluent to remove the water of reaction as it is formed and hence maintain a high concentration of sulfuric acid. If this concentration is maintained, the necessity for using excess sulfuric acid is eliminated since its only function in ordinary sulfonations is to keep the desired high acid concentration.

A series of runs was made in which the quantity of excess sulfuric acid was varied while the temperature and amount of water removed were kept substantially constant. The results are shown in Table II and plotted in Figure 2; they indicate that the sole function of excess acid in a sulfonation is to remove chemically the water formed by the reaction and prevent the sulfonation acid from falling below a limiting concentration.

Table I. Effect of Volume of Diluent

(Temperature, 169° C.; excess H_2SO_4, 1%; water removed, 9.0 cc.)

Volume of Diluent, Cc.	Yield of Sulfanilic Acid, %	Volume of Diluent, Cc.	Yield of Sulfanilic Acid, %
200	34.4	400	61.3
250	40.3	450	54.3
300	50.5	500	64.3
350	51.9		

Table II. Effect of Excess Sulfuric Acid

% Excess H_2SO_4	Temperature, ° C.	Cc. Water Removed	% Yield
0	169	10.0	64.0
10	169	9.8	64.3
20	170	10.4	58.4
30	170	9.4	45.7
40	170	9.7	60.3

Table III. Effect of Amount of Water Removed

Cc. Water Removed	Temperature, ° C.	% Yield	% Diluent Recovered
7.3[a]	168	45.6	80.0
9.0[a]	163	51.9	77.3
10.0	170	65.8	86.0
10.4	168	57.0	85.0
10.7	169	67.2	84.0
11.1	170	71.7	86.0

[a] These runs were made with less kerosene and therefore show a somewhat lower recovery.

Table IV. Effect of Reaction Temperature (Boiling Point of Diluent) on Yield

Temperature, ° C.	Cc. Water Removed	% Yield	% Diluent Recovered
168	10.4	57.0	85.0
169	10.7	67.2	84.0
169	9.8	64.3	63.2
170	10.4	58.4	86.0
170	11.1	71.7	86.0
171	11.3	75.3	77.3
172	10.0	65.8	86.0
179	11.0	81.0	85.0
183	11.0	95.7	93.0

WATER REMOVAL. Different amounts of water were withdrawn from the reactants in order to observe the effect on sulfanilic acid yield. The conditions were kept constant for these runs, including the optimum amount of kerosene (500 cc.) and the theoretical amounts of sulfuric acid for the fixed amount of aniline. The results are shown in Table III and Figure 3; they indicate that the reaction yields are practically proportional to the amount of water removed within the range studied in this series.

REACTION TEMPERATURE. Higher boiling fractions of kerosene were tried in order to find the effect of reaction temperature on the yield of sulfanilic acid. In previous runs a simple single-blade agitator operating at low speeds was used. However, high-speed agitation served to produce a more uniform reaction mass and, consequently, allowed the sulfonation to proceed more smoothly. The runs shown in Table IV were made with this improved procedure. Again 500 cc. of diluent were used with the stoichiometric amount of sulfuric acid for the aniline. However, instead of feeding aniline into the kerosene and sulfuric acid mixture as in previous runs, the sulfuric acid was poured into the kerosene and aniline over a period of 2 minutes. The results are shown in Table IV and Figure 4.

It is evident that a combination of the optimum values of all the variables causes the production of high yields of sulfanilic acids. These yields are somewhat better than those obtained in industry. The most favorable yields of sulfanilic acid were obtained when operating at 183° C., using no excess sulfuric acid, and removing the theoretical amount of water (in this case 11 cc.). These conditions are those of the last run in Table IV.

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STRONTIUM CARBONATE

Conversion from Strontium Sulfate by Metathesis with Alkali Carbonate Solution[1]

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▸ ▸ ▸ **The optimum conditions for the conversion of strontium sulfate to the carbonate by the action of solutions of alkali carbonates have been determined. The operation of a pilot plant for the chemical beneficiation of a mixed strontium sulfate-carbonate ore is described.**

STRONTIUM carbonate is the material from which most soluble strontium salts are made. The chief military use of the latter is in tracer bullets and other pyrotechnics. Practically all of the strontium minerals and compounds have been imported in the past, but during a national emergency domestic sources must be scrutinized and methods developed to utilize the materials directly available.

Several of the western states have important deposits of celestite ($SrSO_4$) which sometimes has been weathered to strontianite ($SrCO_3$). Arizona has reserves estimated at 200,000 tons. California has the largest known reserve of 600,000 tons. A large area of Texas is underlaid with celestite. Washington has a small deposit highly weathered, estimated as 10,000 tons (*7*).

Thus, strontium sulfate is available domestically in large quantities. The same is true of available imports, the bulk of which has been celestite imported from England. The conversion of this material to the acid-soluble strontium carbonate is an important problem.

Conversion to Carbonate

The standard method of producing a soluble strontium salt has been to reduce the celestite with coal breeze in a reverberatory type furnace to produce the soluble sulfide, which is then leached from the black ash. The reduction is approximately 60 to 80 per cent complete, and some carbonate and oxide are produced. The sulfide solution is filtered to remove ash particles and then treated with acid to produce the desired salt. Dilute nitric acid can be used, but considerable free sulfur is formed by the oxidation of the hydrogen sulfide evolved. The more usual process is to precipitate the carbonate, either by adding soda ash or directly carbonating the solution with kiln gases rich in carbon dioxide and removing the hydrogen sulfide thus formed. One of the objections to this process is the hydrogen sulfide evolved.

The metathetical conversion of strontium sulfate to the carbonate with solutions of alkali carbonates has been studied by a number of workers. Piva (*12*) reacted a slight excess (5 to 10 per cent) of ammonium carbonate solution with celestite and precipitated strontium sulfate, transposing 82.85 per cent of the former and 98.75 per cent of the latter in 3 hours. Gallo (*6*) investigated similar materials and found 90.5 and 98.5 per cent transposed, using the optimum conditions. Thomas (*13*) used about 5 per cent excess of sodium carbonate in solutions and ground in a ball mill at 60° C. for one hour, filtered, washed, and then repulped and reground for another hour to remove soluble sulfates. Elledge and Hirsch (*4*) similarly agitated ground celestite with sodium carbonate solution, but they added sodium hydroxide in an amount from 27 to 100 per cent by weight of the strontium sulfate; increased conversion is claimed. An interesting medium for the reactions is fused sodium chloride used by Booth (*1*) who claims 99.9 per cent conversion with 17 per cent excess sodium carbonate.

At equilibrium, the constant for the metathesis,

$$SrSO_4 + Na_2CO_3 \rightleftharpoons SrCO_3 + Na_2SO_4$$

can be calculated from the solubility products. The solubilities of strontium carbonate at 25° and 40° C. as determined by Townley, Whitney, and Felsing (*14*) are 0.5525×10^{-4} and 0.7026×10^{-4} gram mole per 1000 grams of water. The corresponding values for strontium sulfate as determined by Gallo (*5*) are 0.735×10^{-3} and 0.772×10^{-3} gram mole.

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[1] This is the third paper in a series on Metathesis between Solids and Solutions; for previous papers, see literature citations (*8*) and (*9*).

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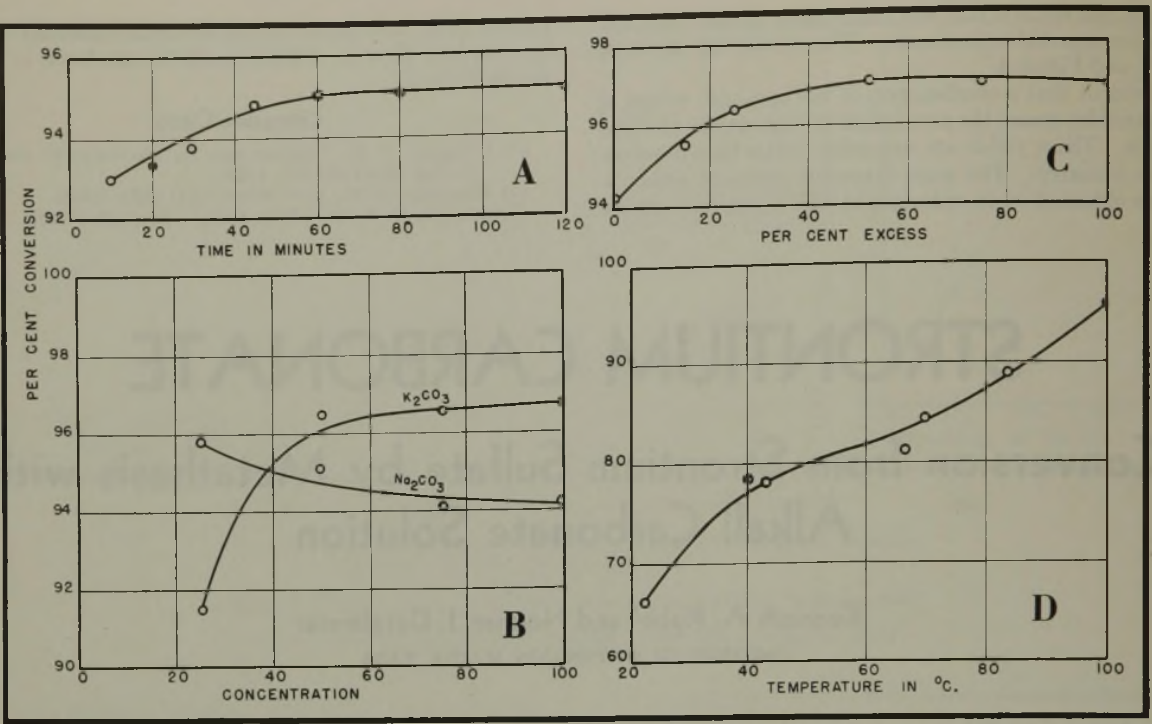

Figure 1. Effect of Time, Concentration, Excess Sodium Carbonate at Constant Volume of Solution, and Temperature on Conversion

$$\frac{K_1 = (Sr^{++})\,(SO_4^{--})}{K_2 = (Sr^{++})\,(CO_3^{--})} = \frac{(SO_4^{--})}{(CO_3^{--})} = K$$

From the solubility products, K_1 and K_2, calculated from the solubility data, the ratio of sulfate to carbonate ions in a solution saturated with respect to both solid phases can be obtained:

$$\frac{K_1}{K_2} = \frac{(SO_4^{--})}{(CO_3^{--})} = \frac{(0.735 \times 10^{-3})^2}{(0.5525 \times 10^{-4})^2} = 175 \text{ at } 25^\circ \text{ C.}$$

At 40° C. a similar calculation shows that the sulfate ion concentration is 121 times greater than the carbonate concentration. These formulas show qualitatively that the reaction can be expected to proceed almost completely to the conversion to strontium carbonate. However, the changing ionic strength of the solution causes the value of the solubility product to increase so that no quantitative value is expected.

Effect of Variables on Conversion

The major part of this investigation was made on natural celestite, ground to pass 200 mesh. It analyzed 97.9 per cent strontium sulfate. Baker's C. P. grade, precipitated strontium sulfate was used in other runs. The sodium and potassium carbonates were Baker's C. P. grade, and the ammonium carbonate was a commercial product.

In the majority of runs agitation was provided by mounting the heater and flask on a mechanical shaker, as shown by Doumani and Kobe (*3*). Some runs were made in a Charlotte laboratory-type colloid mill, in which the temperature was controlled by the water jacket surrounding the grinding head.

After each run the slurry was filtered and a sulfate determination made using the volumetric barium chromate paste method described by Kolthoff (*11*). Attempts to use internal indicators, such as THQ, were unsuccessful because traces of strontium ion interfered with the end point.

EFFECT OF TIME. In the shaker 1.0 mole of strontium sulfate as celestite was shaken with 1.15 moles of sodium carbonate in 1 liter of solution at the boiling point for various times. The results are shown in Figure 1*A*; the reaction is quite rapid under these conditions, and equilibrium is attained in one hour, which time was used in subsequent runs.

EFFECT OF CONCENTRATION. Equivalent amounts of strontium sulfate as celestite were shaken with one liter of boiling sodium carbonate solution; the concentration of the latter was increased each run (Figure 1*B*). This decrease in conversion is relatively small and undoubtedly due to the decreased concentration of strontium sulfate in solution. Gallo (*6*) recommended at least five parts of water per part of celestite, which is a reacting solution about 1 molar in carbonate. Thomas (*13*) used a concentrated solution almost 2.5 molar in carbonate, which increases the capacity of a given piece of apparatus.

EFFECT OF EXCESS REACTANT. The effect of an excess of sodium carbonate in a constant volume of boiling solution was studied by treating 1.0 mole of strontium sulfate as celestite with 1 liter of sodium carbonate solution containing from 1.0 to 2.0 moles. Figure 1*C* shows that the conversion is a maximum at 50 per cent excess sodium carbonate. The helpful effect of excess reactant is retarded by the deleterious effect of increased concentration shown in Figure 1*B*.

EFFECT OF TEMPERATURE. The effect of temperature of reaction was studied by shaking 0.25 mole each of strontium sulfate as celestite and of sodium carbonate in 1 liter of solution for 2 hours at various temperatures. It is apparent in Figure 1*D* that the reaction must be carried out at as high a temperature as practicable. Although strontium sulfate has an inverted solubility curve (*5*) above 40° C., the decrease in solubility due to increased temperature apparently is a minor factor in comparison with other factors. No data are available for the solubility of strontium carbonate above 40° C.

EFFECT OF TYPE OF STRONTIUM SULFATE. The conversion was studied with four types of strontium sulfate: natural celestite; precipitated and calcined strontium sulfate; precipitated, dried, and powdered strontium sulfate; and freshly precipitated strontium sulfate that was not allowed

Figure 2. Pilot Plant for Chemical Beneficiation of Celestite-Strontianite Ore

to dry or cake. Equimolar amounts (0.25 mole) of the strontium sulfate and sodium carbonate in 1 liter of solution were allowed to react for one hour at the boiling temperature. The conversions[3] differed markedly, as had previously been found with barium sulfate (*10*):

Type	% Conversion
Freshly precipitated	96.2
Celestite	95.8
Precipitated, dried, powdered	91.7
Precipitated and calcined	90.3

The natural celestite was soft and easily crushed, whereas the dried precipitate was hard and gritty. A similar result had been observed with calcium phosphate by Kobe and Doumani (*8*).

Equilibrium in the System

The equilibrium point in this metathetical reaction should be obtained by starting from either side of the equation,

$$SrSO_4 + Na_2CO_3 \rightleftharpoons SrCO_3 + Na_2SO_4$$

The forward reaction was studied with 0.25 mole each of strontium sulfate and sodium carbonate in 1 liter of solution at boiling temperature. The reverse reaction used 0.25 mole of precipitated strontium carbonate and sodium sulfate under the same conditions. The percentage of total carbonate that appeared as sodium carbonate in the final reaction solution was 4.2 in the forward reaction and 6.1 in the reverse reaction. This small difference in concentration of sodium carbonate at equilibrium may be due to a difference in physical structure between the strontium salts used and those formed in the reaction.

Table I. Conversions with Ammonium Carbonate

Mole/Liter of Soln.		Temp., ° C.	Conversion, %	Time, Hr.	Method
$SrSO_4$	$(NH_4)_2CO_3$				
0.25	0.25	22	26.9	2	Shaker
0.25	0.50	22	34.2	2	Shaker
0.25	0.25	44	62.7	2	Shaker
0.25	0.25	27	57.0	1	Colloid mill
0.25	0.25	45	73.4	1	Colloid mill

Other Carbonates

Although the conversion should be a function of the carbonate ion activity only, previous work showed that other factors frequently enter to prevent this equality. As shown on Figure 1*A*, somewhat higher conversions are obtained with potassium carbonate under similar conditions.

Conversions of 90 to 98 per cent were reported by Gallo (*6*) and Piva (*12*), using ammonium carbonate. In this work the best conversion obtained with ammonium carbonate under the optimum conditions of Gallo was only 73.4 per cent (Table I). It was thought that the low conversion might be due to the decomposition and volatilization of ammonium carbonate; however, an ammonia balance after each run accounted for at least 0.24 mole from 0.25 mole.

Pilot-Plant Operation

In the state of Washington a deposit of celestite is available which is highly weathered with formation of considerable strontianite. Analysis of a sample from a 5-ton lot shows:

Fe_2O_3	0.54	SiO_2	0.52
CaO	5.03	SO_3	12.30
SrO	60.08	CO_2	20.08
BaO	0.49	Not analyzed	0.96

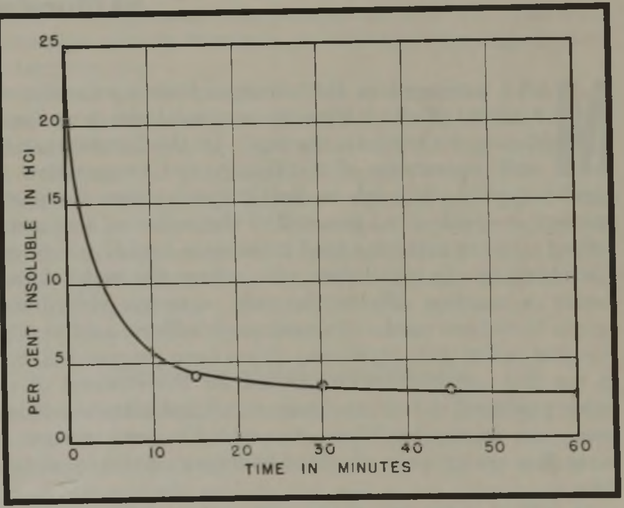

Figure 3. Rate of Conversion in Rotating Mixer

This corresponds to approximately 54 per cent strontium carbonate and 28 per cent strontium sulfate, after allowances are made for barium sulfate and calcium carbonate. This ground ore has a number of uses, such as the removal of iron from caustic solution (*2*). However, if the sulfate is converted to carbonate, the ore will have the value of strontianite, whereas without chemical beneficiation it has only the value of celestite, despite the large amount of strontium carbonate present.

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[3] The percentage conversion may well have been the function of the rate of solubility which would be influenced by the physical condition of the strontium sulfate.

The equipment for this conversion consisted of a concrete mixer, two large wooden tanks, and necessary pump, steam, and water lines. It was assembled as shown in Figure 2. A charge of 200 pounds of ore (ground to 200 mesh), 40 pounds of sodium carbonate (a 25 per cent excess), and 15 gallons of hot water were placed in the concrete mixer. A temperature of about 90° C. was maintained by blowing live steam into the slurry in the mixer during operation. The mixer was allowed to rotate for one hour, and the course of the reaction followed by determining the residue insoluble in dilute hydrochloric acid (Figure 3).

Further operations were limited to a 30-minute period of agitation, after which the charge was dumped into a 350-gallon tank. One day's operation of 1400 to 1600 pounds of ore about filled the tank. After standing overnight to settle, the clear liquor on top was pumped off, more water added, and the slurry pumped to a 400-gallon tank. This was worked twice by decantation in 24 hours, and the thick slurry taken to a plate dryer. Less than one per cent of water-soluble material remained in the dried product.

Acknowledgment

The pilot-plant experiments were carried out by Edward Ammer of the Manufacturers Mineral Company of Seattle.

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SULFONATION of NAPHTHALENE

Application of Partial-Pressure Distillation

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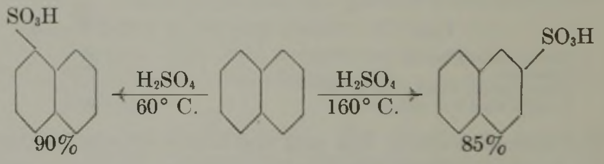
MANY processes in the chemical industry involve the removal of water from aqueous solutions or as formed during a chemical reaction. In the former case the unit operations of distillation and evaporation are usually applied, although in certain special cases the partial pressure method—i. e., removal of the water as a constant-boiling mixture with an added immiscible liquid—has proved desirable (*5*). In the latter case, where the water formed during a reaction affects the rate, chemical dehydrating agents have been used. An example is sulfuric acid in nitration and sulfonation reactions; it has been proposed (*4*, *6*, *7*) to use the partial-pressure method for the removal of this water produced in both the sulfonation and nitration of benzene. An immiscible liquid was added in each case to remove the water as a constant-boiling mixture by distillation.

A logical extension of the sulfonation of benzene is the sulfonation of other aromatics. β-Naphthalene sulfonic acid is necessary for the manufacture of β-naphthol, an important dye intermediate; and it was felt that the partial-pressure method might be applicable to the sulfonation of naphthalene.

Chemistry of Naphthalene Sulfonic Acids

The number of sulfonic acids of naphthalene, naphthol, and naphthylamine is extremely large, and their importance is growing. More and more technical applications for the acids are being found. The sulfonic acids of naphthalene can be converted to α- or β-naphthol, the most important dye intermediates in the production of azo dyes.

When naphthalene is sulfonated, two isomeric monosulfonic acids are formed. The temperature of the sulfonation determines the relative amount of each obtained. It has not been possible to produce one form of the sulfonic acid alone. A mixture of the two is always formed. When the reaction is performed at 40° C., the α-monosulfonate is the predominate form:



When the sulfonation is carried out at 40° C., the ratio of alpha/beta form is close to 96/4. When the sulfonation temperature is raised to 160° C., the beta compound represents 85 per cent of the total sulfonic acids formed. A number of isomers may be formed on further sulfonation, and their separation is usually difficult. The isolation of the individual sulfonic acids have always presented a problem in industry.

At present the monosulfonation of naphthalene is usually carried out with a 25 to 40 per cent excess of sulfuric acid, of 93 to 98 per cent strength.

In the preparation of the alpha compound, the sulfuric acid is placed in a reaction container and the naphthalene is added, keeping the temperature below 60° C. When the beta form is desired, the naphthalene is melted and the acid is added to the hydrocarbon, maintained at a temperature of 160–165° C. To determine the completion of a reaction, samples are taken at intervals and steam-distilled. When no naphthalene is steam-distilled, the reaction is complete.

When naphthalene-2-sulfonic acid is the desired product, the alpha form of the acid is decomposed by dry steam and is removed with the naphthalene by steam distillation.

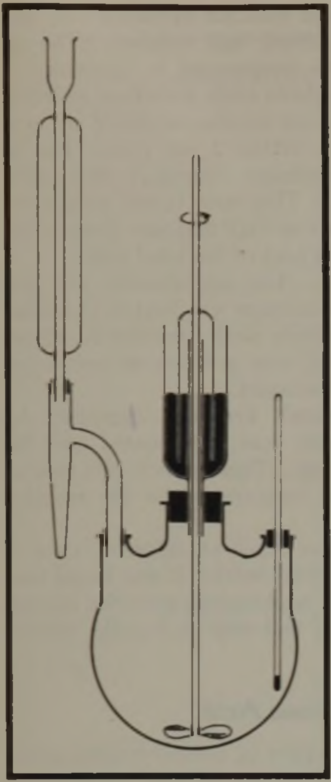


Figure 1. Sulfonation Apparatus

Flask with liquid-sealed agitator and thermometer; condenser for reflux, with calibrated moisture determination tube for decanting water in condensate (heavy layer) and returning oil layer to flask.

▶ ▶ ▶ In extending the technique of partial-pressure evaporation to the sulfonation of naphthalene, several of the process variables have been investigated. Naphthalene was sulfonated with as little as one per cent excess sulfuric acid; high yields were obtained by removing the water formed during the reaction in its constant-boiling mixture with kerosene.

The maximum yield was found when exactly the stoichiometric quantity of water was distilled from the reaction flask. When a lesser quantity of water was removed, the reaction did not go to completion; when more than the theoretical amount of water was removed (as was sometimes the case), this was evidently possible only because of decomposition or charring of product, with resulting lower yield. The effect of varying the amounts of excess sulfuric acid was also investigated. Sulfone formation was found to be a function of the amount of water removed in the partial-pressure distillation.

Since naphthalene is soluble in kerosene, the recovery of any unreacted naphthalene is very simple in this method.

Because of the reduction in the amount of excess acid required, the excellent heat control which is possible, as well as the general simplification in procedure, the use of kerosene in a partial-pressure distillation in the sulfonation of naphthalene appears to offer some advantages over conventional methods; a continuous process can probably be utilized.

A study of rates of sulfonations has shown that, as the water of reaction is formed, the rate of sulfonation will decelerate. Unless this water is removed so as to prevent excess dilution, the reaction will stop at a definite sulfuric acid concentration, different for each organic substance. Therefore, it is of great economic importance to remove this water of reaction, either mechanically or by chemical combination. Various methods have been devised to accomplish this purpose:

1. Use of Oleum. This method for keeping up the sulfur trioxide concentration has been used for some time; the excess sulfur trioxide combines with the water of reaction to form sulfuric acid. This method has been proved practical in the disulfonation of benzene and naphthalene. The oleum and organic compound should be added gradually and concurrently to a large volume of the cyclic acid, thus taking up the water of reaction as quickly as it is formed.
2. Use of Vacuum. Reduced pressure (*1*, *2*), as a means of removing the water of reaction, has some technical advantage in the sulfonation of phenol and benzene.

Evaluation of Losses. In the sulfonation processes used, the following losses are incurred (*3*), which are those commonly encountered in the case of naphthalene sulfonation to form β-naphthalene sulfonic acid:

Tar formation	Less than 1%
Sulfone formation	0.5 to 1.0%
Unreacted crude naphthalene	Less than 1.0%
Isomeric sulfonic acids	15 to 20%
Solubility losses in mother liquors	15 to 20%
Mechanical losses	Less than 0.5%

Proposed Method

The removal of water in this process is essentially a partial-pressure evaporation, involving, however, several complications. The water must be formed by the reaction before it can be removed. When the water is formed, it dissolves the sulfuric acid in the reaction mass. Since sulfuric acid has a great affinity for water, the vapor pressure of water is considerably lowered. In all cases various hydrocarbon fractions were added to the reaction, so that the combined vapor pressure of the diluent and the water was greater than atmospheric pressure and thus sufficient to boil the water out of the sulfuric acid. This was, in effect, the same as the use of a vacuum equal to the difference of the atmospheric and the partial pressure of the diluent.

To perform the reaction at optimum conditions and to produce the maximum amount of naphthalene-2-sulfonic acid, the reaction must take place at 160–165° C. The diluent must be chosen, therefore, to boil within a range close to this temperature.

Sulfonation Apparatus. The sulfonations were performed in a three-neck one-liter flask, fitted with a 15-cc. moisture determination tube, a water-cooled reflux condenser, and a thermometer (Figure 1). The agitator was fitted into the middle neck of the flask and consisted of a glass rod with the end bent into a paddle. This simple blade was enough to keep the acid layer dispersed throughout the kerosene layer. Lubricating oil was used in the seal, which consisted of two concentric copper pipes, fitted with corks and a glass tube. The heat was supplied by a Bunsen burner.

Separation of Reaction Products

One of the most difficult problems to be faced in a sulfonation process is the separation of the reaction products. If only one sulfonic acid is formed, the simplest method is to convert the sulfonic acid to the salt of an alkaline earth. When several isomers are formed, as with naphthalene, the method is more complex. In all subsequent discussions, it was assumed that a constant amount of 15 per cent α-sulfonic acid was always formed. The analytical scheme was concerned only with the total amount of naphthalene sulfonic acid formed. Several possible methods of separation were tried. Recovery of the pure naphthalene sulfonic acids by crystallization did not give quantitative results despite the use of hydrochloric acid for salting out the pure acids. Fractional precipitation of the sodium salts was attempted but found to be inadequate. The method of analysis finally adopted follows.

ANALYSIS. The sulfonation mass was dissolved in 200 cc. of water. The resulting solution was so darkened by tar and carbon that clarification was necessary. Because carbon and tar pass through ordinary filter paper, the commercial filtration method was adopted (*1*). Decolorizing charcoal was added to the solution, it was brought to a boil and then filtered, and the process was repeated until the solution was a straw color.

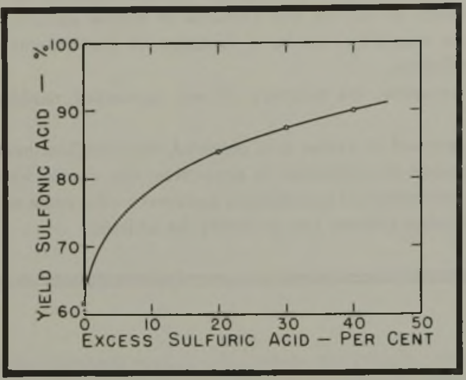


Figure 2. Effect of Excess Sulfuric Acid on Yield of Sulfonic Acid in Preliminary Experiments

The total volume of solution was measured, and an aliquot portion used for analysis. The solution was exactly neutralized with calcium hydroxide, the end point being determined by adding phenolphthalein. The solution was then evaporated to about half its volume or about seven times the weight of the reactants dissolved in the sample, and then filtered hot. The gypsum was separated from the calcium salts in solution. The solution was cooled in an ice bath, and the precipitated salts were filtered. The remaining solution was evaporated to dryness to obtain all of the sulfonates. Before the sulfonation mass was analyzed, the solution of acids and tar was left to stand at least overnight. Some of the tar and sulfones settled out of solution and this facilitated filtration.

To make sure there was no serious error in the method of analysis, two blank runs were made. To make these runs, some of the free sulfonic acids were needed. The first step, therefore, was to prepare some free acid; some of the filtered solution from a run made previously was evaporated to about half its volume. This point was approximated by a boiling point of 115° C. The solution was cooled, and half its volume of strong hydrochloric acid was added. The vessel containing the acid was placed in an ice bath. After a few minutes white crystals appeared in the liquid until the mass seemed almost solid. These crystals were filtered and dried; special precautions had to be taken, because the beta form is deliquescent. Air which had been dried by bubbling through concentrated sulfuric acid and passing through a drying tube was passed over the acids in a sealed container. The acids were then in the dry condition.

DETERMINATIONS. Two equal samples of the acid were removed from the drying vessel and quickly weighed. To duplicate the conditions in this experiment, weighed amounts of 93 per cent sulfuric acid were placed in the beakers with the sulfonic acids. Each sample was diluted with ten times its weight of water. The solutions were heated to boiling and passed separately through activated charcoal to see if any was absorbed. The charcoal was washed with water, and the washings were added to the filtrate.

The solutions were neutralized with hot hydrated lime, and the gypsum was filtered off, dried, and weighed. The remainder of the solutions were evaporated in casseroles at about 95° C. The calcium sulfonic acids were then weighed. These determinations checked one another within 2 per cent and checked the true figures within 2 per cent. The α-sulfonic acid forms a monohydrate; therefore, the determination will be slightly low. This error is not serious because the molecular weights are so high and also because the alpha form is only about 15 per cent of the total yield.

EXPERIMENTAL PROCEDURE. The naphthalene was dissolved in the diluent, and the mixture was heated to boiling in the reaction flask. The sulfuric acid (commercial 93 per cent acid) was fed in gradually from a dropping funnel discharging below the surface of the liquid.

Varsol, a sulfuric-acid-treated kerosene (supplied by Colonial Beacon Oil Company) was fractionated and the cut of 165–175° C. was collected. This fraction was used as the diluent in all runs. The temperature in the reaction mass was always 160° C.

Several preliminary runs were made at different ratios of kerosene to naphthalene in a given batch; it was found that 4 parts of kerosene to 1 part of naphthalene provided enough liquid to make the batch fluid and easy to handle without substantial charring.

Effect of Excess Acid

Excess sulfuric acid is necessary in ordinary sulfonations to take up the water formed during the reaction. The use of excess acid in a partial-pressure sulfonation also tends to increase the dehydrating effect and thus influence the yields. Several runs were made with varying amounts of excess acid but a constant amount of removed water (Table I, Figure 2).

Table I. Effect of Excess Acid on Yields

(9.5 cc. water removed; 50 grams naphthalene and 150 grams diluent used)

% Excess Acid Used	Total Yield Sulfonic Acids, %	% H_2SO_4 Used	% Acid Unreacted	% Kerosene, Carbonized	Analysis of Reaction Mass, %		
					Sulfonic acid	H_2SO_4	Tar, sulfones, etc.
0	61.7	62.3	11.3	9.35	54.0	5.0	41.0
20	84.0	70.0	11.6	8.00	69.5	5.5	25.0
30	87.5	..	..	..	..	..	..
40	90.0	65.0	28.2	7.85	71.5	14.5	14.0

While excess sulfuric acid did increase the yield, it is shown later that better dehydrating conditions (optimum rates of agitation and heating and optimum values for other variables) will produce high yields with no excess acid.

Effect of Amount of Water Removed

In the preliminary runs the yields varied considerably with the amount of water removed from the reaction mass. The theoretical quantity of water produced by the reaction between naphthalene and the stoichiometric quantity of sulfuric acid is 7.04 grams. If the water in the sulfuric acid is also taken into account, the total amount of water to be removed (using 1 per cent excess sulfuric acid) is 9.94 grams. However, even more than this amount could be removed simply by continuing the dehydration process.

A series of reactions was carried out in which all conditions were kept constant except the amount of water removed. Fifty grams of naphthalene, 42.1 grams of sulfuric acid, and 150 grams of diluent were used in each run. The results in Table II and Figure 3*A* show that the optimum yield of the naphthalene sulfonic acids is obtained by removing

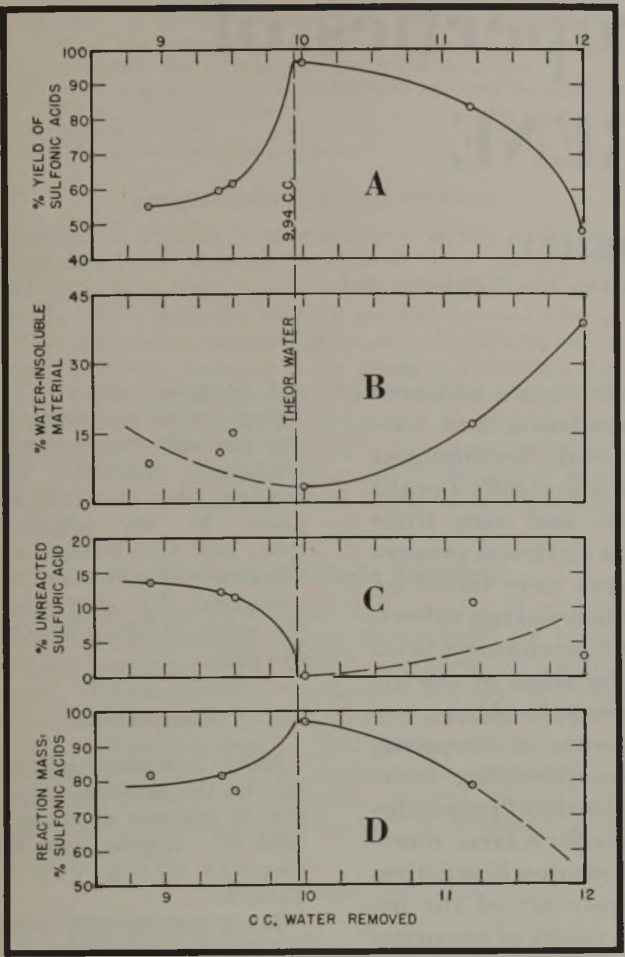


Figure 3. Effect of Amount of Water Removed on Yields of Sulfonic Acid and on Formation of Insoluble Materials

the theoretical amount of water. Evidently, the removal of more water causes side reactions and excessive charring of the kerosene entrainer.

Since the reaction producing sulfones involves the loss of an additional molecule of water, the amount of water taken off should have an effect on sulfone formation. Accordingly, the data for water-insoluble materials (tar and sulfones) in Table II were plotted in Figure 3*B*. These insoluble materials are the sum of the degradation products from both the naphthalene and the kerosene since there is no simple analytical method available for differentiating between them. These data are not, therefore, directly comparable to those on yields in the second column.

A sulfuric acid balance was made for these various runs and the percentage of original sulfuric acid which did not react was plotted against the amount of water given off in Figure 3*C*; *D* indicates the percentage of sulfonic acid in the reaction mass. In both cases the best results are those obtained by the removal of nearly the theoretical amount of water.

Table II. Effect of Water Removed on Yields and on Formation of Insoluble Materials

(Stoichiometric amount of acid used in each case)

Cc. Water Removed	Total Yield Sulfonic Acids, %	% Acid Unreacted	% Kerosene Carbonized	Analysis of Reaction Mass, %		
				Sulfonic acid	H_2SO_4	Tar, sulfones, etc.
8.9	55.0	13.6	2.40	82.0	9.5	8.5
9.4	59.5	12.2	9.35	81.3	7.8	10.9
9.5	61.7	11.3	9.35	77.0	7.0	15.0
10.0	96.0	0	<1.00	96.2	0	3.7
11.2	83.7	10.5	2.00	78.0	5.0	17.0
12.0	48.0	3.0	Very large	<60.0	...	38.6

Optimum Conditions

The sulfonation of naphthalene involves several dehydrating reactions of which only one is desirable. Therefore, to determine optimum conditions, a dehydrating condition must be attained which has the least effect on the undesirable reactions and the maximum effect on the desirable ones. In normal sulfonations and nitrations, this is accomplished by varying the quantity of sulfuric acid; in the partial-pressure method, it can be done only by varying either the temperature or the rate or amount of water removal.

Thus, a run was carried out with the stoichiometric amount of acid under the optimum conditions of correct amount of water withdrawal, slightly improved agitation, and somewhat higher rate of heating. Fifty grams of naphthalene were dissolved in 200 grams of kerosene, and 42.1 grams of 93 per cent sulfuric acid were charged into the reaction flask; the mass was then heated with violent agitation. A total of 10 cc. of water was removed, and the mass was analyzed for total sulfonic acid and sulfone. The yield of sulfonic acid, based upon naphthalene, was 96 per cent and the sulfone formation was 3.2 per cent. No unreacted sulfuric acid was found in the mass.

The use of a diluent in this type of operation seemed to offer an opportunity for the development of continuous methods. A small packed glass column was set up in the laboratory, and sulfuric acid and a hydrocarbon solution of naphthalene were fed simultaneously to the top of the column. Kerosene vapors were passed countercurrently, and the water of reaction was continuously distilled out with the hydrocarbon. The sulfonation proceeded smoothly; yields comparable with batch operation were obtained by withdrawal and analysis of the bottoms product.

Conclusions

While the use of the partial-pressure method in the sulfonation of naphthalene has not been investigated exhaustively, enough of the optimum conditions have been determined to project the sulfonation of naphthalene in the presence of kerosene as having several advantages:

1. The use of excess acid can be eliminated without substantial loss of yield.
2. Temperature control can be maintained accurately by proper selection of the kerosene entrainer. Sudden surges of heat will be merely absorbed as latent heat of the diluent.
3. Unreacted naphthalene can be recycled in the kerosene and thus recovery problems are simplified.
4. It appears that a continuous process might be developed for production use.

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Electrical Properties of NEOPRENE

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Electrical data on neoprene are reviewed with respect to both insulating and conducting properties. The early development of neoprene was directed principally toward mechanical applications, and very little attention was given to its electrical properties. However, early types were tested by electrical laboratories using, among others, formulas designed for the mechanical field. Most of the results fell far short of the insulating properties of natural rubber.

More recent developments of neoprene, both in types and in compounding technique, have resulted in electrical properties that are entirely adequate for a large number of uses, some of which are now in practice. It is hoped that this summary of the insulating and conducting values of neoprene may be useful in suggesting solutions to a miscellany of industrial problems.

THIS review is based upon data selected from tests conducted over a period of years. Under the circumstances it does not happen that identical neoprene was used throughout. Several types are referred to in the compounds. Each group of tests is consistent within itself, but direct comparison from group to group is not justified. Neither do exact values within a group have individual merit, but the trends of electrical quantities with controlled changes of the variable under study are of primary importance. In general, numerical values reported are the average of results obtained on two samples, but all conclusions have been confirmed by numerous parallel and related tests.

Unless otherwise specified, tests were made at 82° F. after the samples had been dried in a desiccator for at least 16 hours. Conventional methods (*1*, *2*) were used. For all tests except those on dielectric strength, tin foil electrodes 0.001 inch thick, adhered to the test slab by a thin film of petrolatum, were utilized. The test specimens were usually 6 × 6 × 0.075 inch except for occasional samples which were approximately 0.020 inch thick. In the case of the direct-current resistivity test, the upper electrode was a 3-inch-diameter disk of tin foil surrounded by a guard ring. The lower electrode was a 6-inch square of tin foil. The Leeds & Northrup test set employed consisted of a sensitive galvanometer and an Ayrton shunt. An alternating-current bridge was used for measurements of conducting stocks. For the tests of power factor and dielectric constant, the upper electrode was a 3-inch-diameter disk of tin foil without a guard ring. The lower electrode was a 6-inch square of tin foil. General radio equipment was utilized, consisting of a type 716A capacitance bridge complete with the necessary auxiliaries. A telephone headset was used for detection of null points. All tests reported here were conducted at frequencies of 1000 cycles per second.

For the determination of dielectric strength, an American Transformer Public Utility test set, type TS, having a secondary voltage range from 100 to 50,000 volts was used. The electrodes were of the standard A. S. T. M. type (*2*). Ordinarily the test specimens were about 0.020 inch thick and 6 inches square. The voltage across the electrodes was gradually increased until breakdown occurred. The gage was then measured adjacent to the punctured spot, and the voltage and dielectric strength were calculated by dividing the value of the voltage by this gage.

Early Data

Early published information on the electrical properties of neoprene appeared in 1936 (*7*). Results from this report are given in Table I.

It is immediately apparent that the resistivities of all three compounds were distinctly low in comparison with that of rubber insulation, which ordinarily has a value approximating 10^{15} ohm-cm. Also, the dielectric constant for all three compounds was high in comparison with that for most rubber insulation. Both of these trends were distinctly unfavorable from the standpoint of insulation. On the other hand, the values for dielectric strength, except for uncompounded vulcanizate 750D–1, were roughly comparable with rubber. The results make it desirable to survey the possible methods of improving the electrical properties of neoprene which follow:

1. Compounding with litharge.
2. Purifying the crude neoprene.
3. Including carbon black in the formula as an absorber for electrolytes.

TABLE I. EARLY DATA ON THREE NEOPRENE COMPOUNDS

Compound No.	750D–1	750D–3	750D–5
Neoprene Type E	100	100	100
Extra light calcined magnesia	...	10	2
FF wood rosin	...	5	10
Phenyl-β-naphthylamine	...	2	2
Sulfur	...	1	1
Zinc oxide	...	10	...
Litharge	...	...	20
Cure at 307° F., min.	60	20	20
Electrical properties			
D. C. resistivity, ohm-cm.	2.2×10^9	3.1×10^{11}	9.0×10^{11}
Dielectric constant	8.2	7.3	7.2
Dielectric strength, volts/mil	380	860	720

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4. Including large amounts of superior insulating substances.
5. Mixing with rubber insulation to provide a compromise between the electrical properties of rubber and the superior mechanical and chemical properties of neoprene.
6. Conditioning treatments of vulcanized neoprene to improve its electrical properties.
7. Adjusting the cure.
8. Modifying the neoprene polymer.

Compounding with Litharge

Litharge is superior to magnesia and to zinc oxide as a curing agent for neoprene insulation. For example, the data of Table I show a pronounced difference in favor of litharge. It is probable that the reaction between litharge and the degradation products of neoprene forms salts having lower dissociation constants in the presence of moisture than have the corresponding salts of zinc and magnesium. The higher resistivity of litharge compounds is attributed primarily to this factor. In addition to the advantage of litharge electrically, neoprene compositions containing it are definitely less combustible than compositions containing zinc oxide.

Purification of Crude Neoprene

As various tests have shown, the amounts of chlorine-bearing electrolytes that might be suspected in normal neoprene compounds are difficult to detect by chemical means. Yet the possibility remains that they may be present in sufficient amount to cause the inferior electrical characteristics of untreated neoprene. With this possibility in mind, a sample of Neoprene Type E was acetone-extracted and then water-washed. This specially purified neoprene was compounded and tested for electrical characteristics in the following formula:

COMPOUND 1333N–112

Purified Neoprene Type E	100
Extra light calcined magnesia	3
FF wood rosin	5
Sulfur	1
Phenyl-α-naphthylamine	2
Litharge	20
D. C. resistivity, ohm-cm.	2.8×10^{12}
Dielectric constant	7.8
Power factor, %	1.25

The improvement in resistivity as the result of purification was substantial; it was also suggested by Kemp (*5*). Although the dielectric constant was not greatly changed, the power factor was relatively low in comparison with contemporary tests of unpurified neoprene specimens. Acetone washing, however, is not practical from a production standpoint, and at the time of these tests it could only be hoped that advances in the technique of neoprene production would result in improved electrical properties.

Inclusion of Carbon Black

The practice with certain types of rubber insulation is to include moderate amounts of carbon black in the formula as an absorber for impurities and electrolytes (*9*). The possibility of following a similar procedure for neoprene was investigated in the stocks shown in Table II.

Although the improvement in power factor and resistivity is slight for the compound containing 3 parts of carbon black, the trend appears to be favorable. On the other hand, the dielectric constant increased and as a consequence the loss factor increased by the inclusion of even this small amount of carbon black. For ordinary applications of insulation the loss factor is not of prime importance. It may be preferable in many cases to make a sacrifice with respect to loss factor in order to increase the value of the resistivity. However, as the quantity of black is increased, the loss factor increases out of all proportion to the gain in resistivity. As a consequence it appears advisable to limit the carbon black content of insulating compounds to about 5 parts of carbon black.

TABLE II. EFFECT OF CARBON BLACK ON FORMULA 1333N (CURED 40 MINUTES AT 307° F.)

Formula 1333N-	87	88	89	90	91
Neoprene Type E	100	100	100	100	100
Extra light calcined magnesia	3	3	3	3	3
FF wood rosin	5	5	5	5	5
Semireinforcing black	...	3	10	20	30
Phenyl-β-naphthylamine	2	2	2	2	2
Sulfur	1	1	1	1	1
Litharge	20	20	20	20	20
Electrical properties of dry slabs					
D. C. resistivity, ohm-cm.	4.9×10^{11}	5.2×10^{11}	6.3×10^{11}	6.4×10^{11}	6.5×10^{11}
Dielectric constant	7.74	8.43	9.72	13.28	17.33
Power factor, %	2.1	2.0	2.1	2.8	4.1
Loss factor	0.16	0.17	0.20	0.39	0.71

Inclusion of Insulating Material

The effect of various materials is shown in Table III, based upon Neoprene Type E compounded with magnesia and zinc oxide. Although higher values for the resistivity would have resulted from compounding with litharge, it was thought that the effects of the fillers would be demonstrated at least as well in the zinc oxide formulation. The inorganic fillers were compared on an equal basis of 40 volumes per 100 volumes of neoprene. The organic fillers were used in amounts approaching the maximum permissible in a practical formulation.

Control formula 1333N–200 is inferior in all insulating properties with the exception of one value for resistivity, three for dielectric constant, and one for power factor. In a general way it is interesting to note that the d. c. resistivity is increased by compounding with inert, inorganic fillers but that these increase the dielectric constant. All other materials except cottonseed oil increase the d. c. resistivity, decrease the dielectric constant and power factor. It is possible that the cottonseed oil used in this test was of an inferior grade electrically and that the results are not necessarily typical of this processing material. It is also obvious that, with the exception of the stock containing cottonseed oil, the loss factor for all compounds is lower than that of the control stock.

Inclusion of Natural Rubber

Rubber itself is a possible compounding ingredient for neoprene, and the following two compositions were blended by weight in the amounts indicated in Table IV to determine its possibilities. Slabs were press-cured 40 minutes at 287° F.:

COMPOUND 1333N–210

Neoprene Type GW	100
Catalpo clay	100
Blanc fixe	100
Medium-process oil	5
Cottonseed oil	5
Semireinforcing black	5
Paraffin	5
Phenyl-β-naphthylamine	2
Litharge	20

COMPOUND 1333–50

Smoked sheets	100
Zinc oxide	78
Gilder's whiting	115
Phenyl-α-naphthylamine	2
Paraffin	5
Litharge	10
Accelerator[a]	0.4
Sulfur	3

[a] 90% zinc salt of mercaptobenzothiazole and 10% di-*o*-tolylguanidine.

The results indicate a progressive improvement in insulating properties as the percentage of rubber is increased.

Table III. Effect of Insulating Materials on Formula 1333N (Press-Cured 40 Minutes at 307° F.)

Formula 1333N–	200	201	202	203	204	205	206	207	208
Neoprene Type E	100	100	100	100	100	100	100	100	100
Extra light calcined magnesia	10	10	10	10	10	10	10	10	10
FF wood rosin	5	5	5	5	5	5	5	5	5
Whiting	...	...	...	118	...	...	...	...	...
Barytes	...	...	...	...	194	...	...	...	...
Crown clay	...	...	113	...	...	...	...	...	...
Cottonseed oil	...	...	...	...	...	20	...	...	...
Mineral rubber	...	...	...	...	...	...	50	...	...
Mineral oil	...	...	...	...	...	...	...	20	...
Paraffin	...	...	...	...	...	...	...	...	10
Phenyl-β-naphthylamine	2	2	2	2	2	2	2	2	2
Neophax B[a]	...	100	...	...	...	...	...	...	...
Zinc oxide	10	10	10	10	10	10	10	10	10
Electrical properties after 13 days in desiccator at 25° C.									
D. C. resistivity, ohm-cm.	1.7 × 10^{11}	8.2 × 10^{11}	3.1 × 10^{12}	6.3 × 10^{11}	4.7 × 10^{11}	9.3 × 10^{10}	1.1 × 10^{12}	2.8 × 10^{11}	7.5 × 10^{11}
Dielectric constant[b]	7.88	6.62	8.40	8.67	8.56	7.10	5.88	6.62	7.20
Power factor[b], %	3.8	2.6	3.4	3.0	2.4	4.4	2.4	3.0	3.5
Loss factor[b]	0.30	0.17	0.28	0.26	0.20	0.31	0.14	0.19	0.25

[a] A special grade of factice (vulcanized oil).

[b] At 1000 centipoises.

On the other hand, the improvement is most rapid for rubber contents of more than 50 per cent. There may be many possibilities in the future for insulating mixtures of neoprene and rubber, where greater resistance is required to heat, sunlight, oil, and flame than is possible with rubber alone. The advantages of neoprene are gradually lost, however, as the percentage of rubber is increased, and the present mixtures with rubber appear to be an impractical way of improving the electrical properties of neoprene.

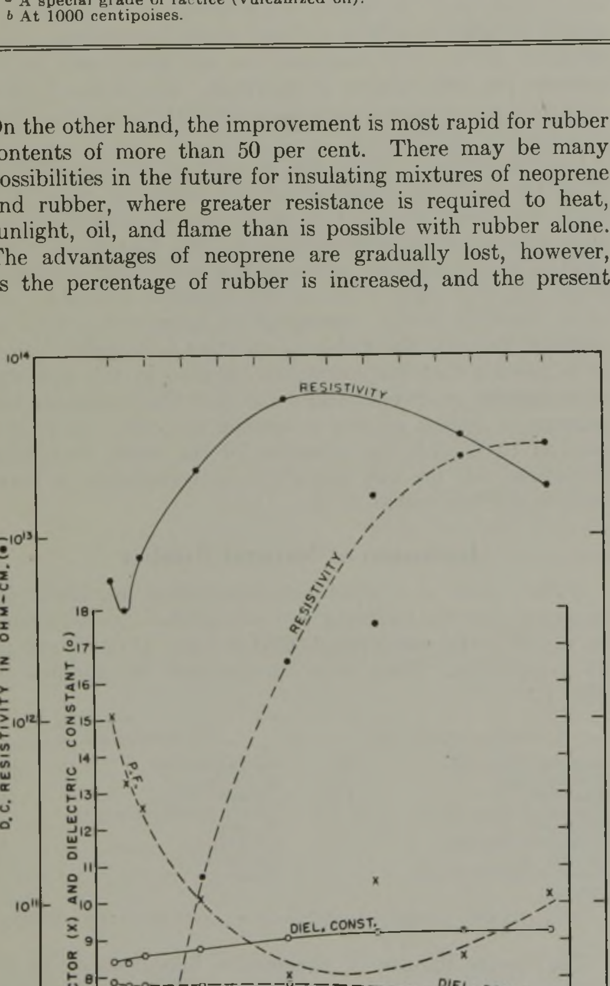

Figure 1. Comparison of Stocks, Compounded (Solid Curves) and Uncompounded (Dotted Curves)

Conditioning Treatments

Three practical compounding approaches to the insulation problem are offered by the foregoing. They are inclusion of carbon black, activation with litharge, and inclusion of proper insulating materials. The combination of these principles in a practical formula for wire insulation is exemplified by the following composition:

Compound 1333N–209

Neoprene Type GW	100
Blanc fixe	100
Catalpo clay	100
Paraffin	3
Medium-process oil	5
Semireinforcing black	5
Phenyl-β-naphthylamine	2
Litharge	20

Compound 1333N–209 was extruded as 3/64-inch wall insulation No. 14, solid AWG tinned copper wire; the following history of resistance per 1000 feet of wire indicates possibilities in conditioning treatments for neoprene-insulated wire:

Step No.	Treatment	Temp., ° C.	Megohms/ 1000 Ft.
1	Original immersed in water	29	13.5
2	After 24-hr. immersion	29	2.8
3	Plus 30 min. at 1500 volts	29	9.2
4	Total immersion 44 hrs.	29	3.8
5	44-hr. immersion + 3.5 hr. at 1500 volts	29	10.4
6	17-hr. drying in 70° C. oven	24	44.0
7	Plus 4.5 hr. at 1500 volts after oven drying	24	32.9

It is recognized that rubber insulation, which is slightly low in resistivity, can be improved by subjecting it to high voltage for a time without detracting from the other desirable insulating properties. The preceding data on neoprene insulation show that extensive exposure to high voltage likewise increases its resistance. It is also significant that the initial period of immersion caused a severe drop in the resistance per thousand feet of wire while the trend after continued immersion and extensive exposure to high voltage was to restore the d. c. resistivity almost to its initial value. The highest value attained after 17 hours of drying in the 70° C. oven was probably the combined result of reduction in moisture content and of tighter cure. Although these results would not be considered typical of any normal test procedure, they indicate gradual improvement

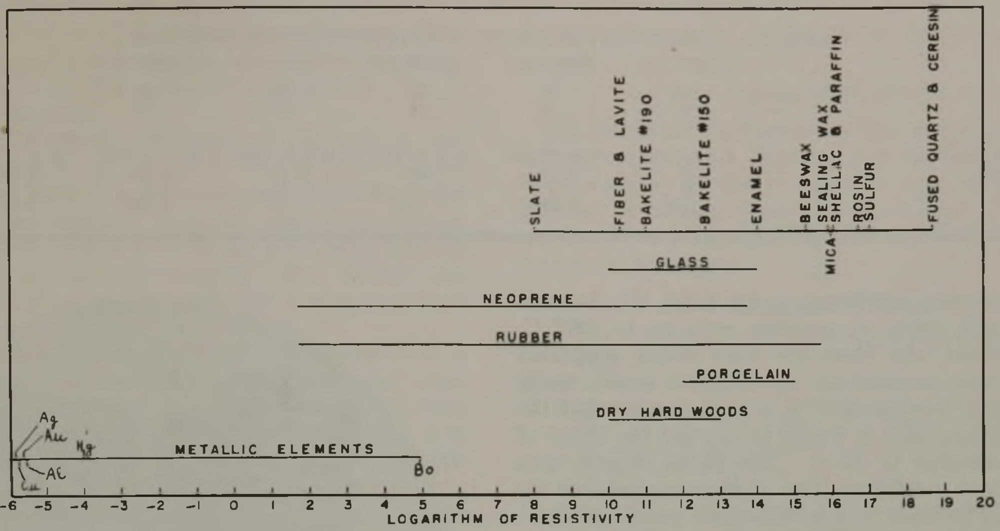

Figure 2. Resistivity Spectrum for Insulating Materials

of electrical properties under severe conditions and are reassuring from a service standpoint.

Adjustment of Cure

A further possibility with respect to electrical properties is the adjustment of cure. The following data illustrate the idea that more extensive knowledge of compounding principles for neoprene may result in superior electrical properties even with the present types of neoprene. The data also indicate the stability of the electrical properties of neoprene under severe aging conditions. The compounds compared (cured 30 minutes at 40 pounds) are as follows:

Compound No.	1333N-216	1333N-217
Neoprene Type GN	100	100
Hexamethylene ammonium hexamethylene dithiocarbamate	...	0.25
Paraffin	5	....
Phenyl-β-naphthylamine	2	....
Semireinforcing black	5	....
Catalpo clay	100	....
Blanc fixe	100	....
Medium-process oil	10	....
Litharge	20	....

Measurements were made of d. c. resistivity, dielectric constant, and power factor after aging for various intervals in a 141° C. oven. The trends of these various quantities for the two compounds are shown in Figure 1. Comparison of the resistivity curves for the compounded and uncompounded stocks indicates conclusively that neither was cured to its maximum effectiveness electrically as originally prepared. The maximum attained by the compounded sample after 48 hours was 5.7×10^{13} ohm-cm., while that attained by the uncompounded specimen after 120 hours was 3.2×10^{13} ohm-cm. The discrepancy between the two may be the result either of the difference in state of cure or of the presence of insulating extenders in the compounded stock. Also, the dielectric constant for the uncompounded material is lower at all points than that of the compounded material. In per cent power factor, the compounded stock is definitely superior at all aging intervals to that of the uncompounded stock although it appears possible that a longer exposure at 141° C. might bring these two values together. On the other hand, the uncompounded material had become hard and brittle by the end of 121 hours, and more extensive exposure would not have been practical.

Modification of the Polymer

The history of neoprene is a series of eventful improvements in physical properties. Thus, as a further possibility it can be expected that future modifications of neoprene will have electrical properties vastly superior to those displayed by current types. Neoprene Type FR, the latest addition, shows interesting possibilities:

Compound No.	1333N-218	1333N-219
Neoprene Type FR	100	...
Neoprene Type GN	...	100
Piperidine pentamethylene dithiocarbamate	...	0.1
Phenyl-α-naphthylamine	2	2
Blanc fixe	100	100
Clay	100	100
Semireinforcing black	5	5
Process oil	10	10
Paraffin	5	5
Litharge	20	20
Cure at 287° F., min.	40	30
Stress at 300%, lb./sq. in.	275	550
Stress at 500%, lb./sq. in.	425	650
Tensile strength, lb./sq. in.	700	1125
Elongation at break, %	950	810
Hardness	44	67
Electrical properties		
D. C. resistivity, ohm-cm.	1.2×10^{13}	4.2×10^{12}
Power factor, %	0.9	1.6
Dielectric constant	7.3	8.3
Loss factor	0.066	0.12

Effect of Temperature on Resistivity

The effect of temperature upon the resistivity of neoprene is indicated by the following compound and data:

Compound 1333N-220

Neoprene Type GN	100
Piperidine pentamethylene dithiocarbamate	0.25
Phenyl-β-naphthylamine	2
Gastex (carbon black)	5
Ground mica	150
Paraffin	5
Shellac	15
Medium-process oil	10
Litharge	20
Cure at 287° F., min.	30

Temperature, ° C.	Resistivity, Ohm-Cm.
25	5.46×10^{12}
40	1.13×10^{12}
60	1.62×10^{11}
80	6.01×10^{10}
100	1.89×10^{10}

Table IV. Electrical Properties of Neoprene-Rubber Mixtures

Formula 1333N–	1333N–210	1333N–211	1333N–212	1333N–213	1333N–214	1333N–215	1333–50
Neoprene (1333N–210)	100	95	75	50	25	5	...
Rubber (1333–50)	...	5	25	50	75	95	100
Electrical properties							
D. C. resistivity, ohm-cm.	6.6×10^{12}	8.0×10^{12}	9.0×10^{12}	2.9×10^{13}	2.4×10^{14}	9.4×10^{14}	9.4×10^{14}
Dielectric constant	8.2	8.14	7.36	6.41	5.94	5.05	5.03
Power factor, %	1.3	1.2	1.3	1.2	0.9	0.5	0.5
Loss factor	0.106	0.098	0.095	0.077	0.053	0.025	0.025

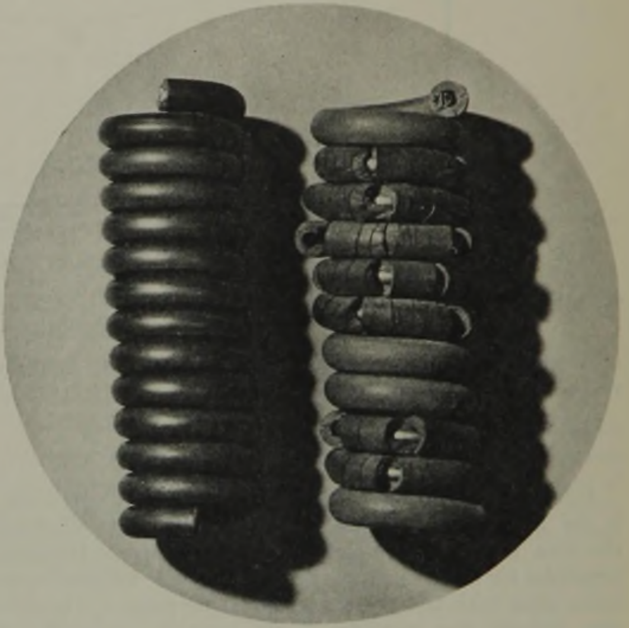

Figure 3. Superior Resistance to Heat Shown by Neoprene over Rubber

There are electrical conditions under which the decrease of resistivity with rising temperature even up to 100° C. could be permitted, and there are more severe conditions under which high-temperature applications would invite failure. It is not easy to state in a general way what the allowable limits are, and it would be beyond the scope of this paper to attempt to do so. The limits depend upon many factors, and careful analysis of high-temperature applications should be made to determine their practicability.

Conducting Neoprene

The insulating qualities of neoprene do not cover the entire range of electrical properties that are of technical interest today. Electrical conductivity in neoprene is also important, and is attainable by the same means and to the same extent as for rubber. The following data are based upon established commercial products and do not indicate the possibilities of new blacks which have recently been offered and may soon be developed. The data illustrate the range of values attainable with several types of carbon black. Litharge was not used in these formulas since its effect on insulating qualities was not required.

Base Compound

Neoprene Type GN	100
Hexamethylene ammonium hexamethylene dithiocarbamate	0.25
Stearic acid	0.5
Phenyl-α-naphthylamine	2
Extra light calcined magnesia	4
Light-process oil	8
Zinc oxide	5
Carbon black	As indicated
Cure at 287° F., min.	30

Type of Black	A. C. Resistivity, Ohm-Cm. 50 parts	A. C. Resistivity, Ohm-Cm. 100 parts
Acetylene	2.7×10^2	1.2×10^2
Soft carbon	1.6×10^8	2.0×10^7
Semireinforcing	1.0×10^8	6.7×10^4
Channel	8.5×10^7	1.7×10^6

As a further illustration of the conductivity obtainable, the following data show the trend in A. C. resistivity values with increasing amounts of acetylene black:

Base Compound

Neoprene Type GN	100
Hexamethylene ammonium hexamethylene dithiocarbamate	0.3
Phenyl-α-naphthylamine	1
Extra light calcined magnesia	4
Acetylene black	As indicated
Light-process oil	1
Zinc oxide	5
Cure at 287° F., min.	30

Parts of Acetylene Black	A. C. Resistivity, Ohm-Cm.
0	1×10^{12}
10	2×10^8
20	9×10^7
30	3×10^4
40	6.4×10^2
50	1.4×10^2
75	1.4×10^2

It is not intended to go extensively into the phenomena of conducting neoprene compositions, but the effects appear similar to those for rubber which are covered extensively elsewhere (for example, by Juve, *4*).

The fact should be kept in mind that whether a material is a resistor or a conductor is relative. Rubber is an insulator in comparison with most metals, but it is a conductor in comparison with fused quartz and purified ceresin wax. Neoprene likewise is an insulator in comparison with most metallic elements, but whether it is an insulator or conductor with respect to rubber depends upon the particular compounds compared. Figure 2 illustrates what might be called the "resistivity spectrum" for electrical materials. The horizontal axis shows the range of resistivity which has been measured, plotted logarithmically to provide a practical spread of values on the chart. At the various vertical levels the horizontal lines show the range of resistivity values which have been published in various reference works (*3*) in comparison with neoprene and rubber for which values have been assumed in this paper. The range for rubber is taken to be 50–5 $\times 10^{15}$ ohm-cm. although higher values have been reported for purified rubber (*6*). The range for neoprene is taken to be 50–5 $\times 10^{13}$. The range for metallic elements begins with silver at 1.47×10^{-6} and may be extended to the value for the metalloid boron at 8×10^4. Both neoprene and rubber overlap this range. At the other end of the range, neoprene overlaps published values for such insulating materials as slate, phenolic resins, fiber, Lavite, glass, porcelain, and dry wood. It does not quite attain the published value for enamel, and is distinctly inferior to the high values attained by various waxes, mica, rosin, and sulfur. This would seem to indicate rather conclusively that, since slate, fiber, Lavite, phenolic resins, glass, and porcelain are useful as insulation for low-voltage service, neoprene may have parallel utility in combination with its other desirable properties.

An aspect of the superior resistance of neoprene to heat is shown by Figure 3. A length of No. 14 AWG copper wire was covered with $^3/_{62}$-inch neoprene insulation, and another length was similarly insulated with heat-resistant rubber. After 15 months in a 70° C. air oven, both samples were wound on a half-inch mandrel. The rubber was brittle enough to crack badly, while the neoprene showed no signs of failure.

Code specifications based upon the characteristics of a given material are not necessarily proper criteria for other materials. For example, a code wire specification of 1500 megohms per thousand feet (*8*) for rubber-insulated wire is not based upon the electrical demands made upon this insulation but upon a characteristic value of rubber as a quality control. Specifications for neoprene-insulated wire based upon its electrical properties would be adequate to ensure satisfactory performance of the wire under many conditions of low-voltage service. The dielectric strength test specified for code wire, on the contrary, is not indicative of the electrical properties of rubber, but is set up as a means of detecting pinholes and other flaws in the extruding coating. The test applied to $^3/_{64}$-inch wall insulation at 1500 volts works out to 32 volts per mil. This is obviously a trivial exposure for a solid film of either rubber or neoprene, which can be made to have a dielectric strength of at least 800 volts per mil.

Acknowledgment

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Presented before the Division of Rubber Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.

LAZARUS ERCKER, THE ASSAYER

By R. White

In 1683 Sir John Pettus published in London his "Fleta Minor: The Laws of Art and Nature in Knowing, Judging, Assaying, Fining, Refining, and Inlarging the Bodies of Confined Metals". This is a free translation of the earlier German "Assays" (*Beschreibung allerfürnemisten mineralischen Ertzt und Bergwercksarten*, Prague, 1574) of Lazarus Ercker (Erskerus), whose portrait is reproduced here as "The Assayer", a copy from White's engraving.

This is No. 147 in the Berolzheimer series of Alchemical and Historical Reproductions. The numbered articles are: (2) Scales; (3) Cases for the Weights; (4) Bottles for Aqua Regis, Aqua Fortis, Aqua Vitrioli, Aqua Argentea or Quicksilver.

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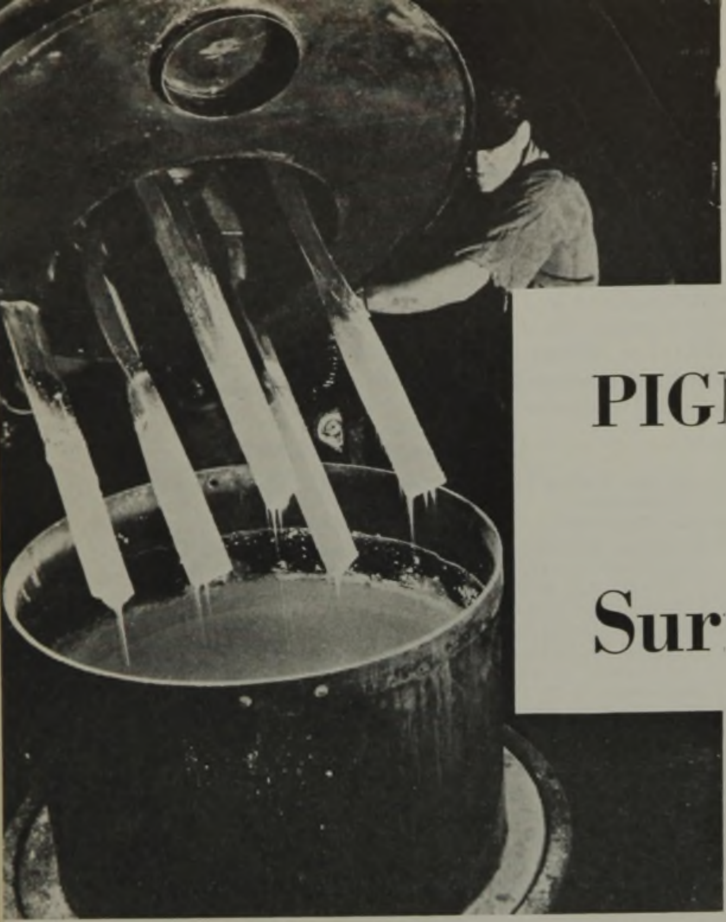

PIGMENT DISPERSION with Surface-Active Agents

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OF THE large number of reagents now marketed as surface-active agents, many are of distinct utility in the dispersion of pigments in the nonaqueous media used as vehicles in the paint and printing ink industries. Industrial uses for these compounds in aqueous systems are extraordinarily varied (*1*, *7*, *10*, *16*, *23*, *27*). That extensive application is possible for surface-active agents in nonaqueous systems is becoming apparent from a growing number of patents relating to specific products and processes as well as papers describing experiments (*2*, *3*).

The addition of small quantities of reagents to provide desirable working properties for paints and printing inks is not an innovation, for the practice extends back to the origins of the industry. Commonly used materials include soaps, tallow, stearin pitches, waxes, gilsonite, etc. (*28*). While the function of these substances is neither entirely clear nor simple, one important result of their addition is the change in flow properties of the composition, rendering it either more fluid or contributing to an increase in consistency or body. The synthetic compounds now commercially available greatly extend the number of reagents available for incorporation in pigment dispersions. The object of this work was to make a systematic survey of the surface-active agents on the market with reference to the manner in which they affected the dispersion of pigments and to obtain data from which fairly general deductions could be drawn.

Representative surface-active agents were selected from each of the several classes of commercial species available. The effect of these compounds on typical pigment vehicle combinations was studied in relation to the pigment and vehicle types, concentration, and method of addition. The rate of dispersion and final tinting strength of the mixtures were measured since these factors are important. However, it was the change in rheological properties of the dispersion that was taken as the primary physical criterion of the effect of a given surface-active agent. The results obtained have been an aid in selecting surface-active agents for specific formulations of analogous systems.

The theoretical basis for the use of surface-active agents has been extensively discussed in the literature. The assumption usually made is that a monomolecular film, adsorbed and oriented at the interface of the solid and the liquid, produces a marked transition in the properties at the interface (*4*, *9*, *15*, *18*, *20*, *29*).

Definitions

The term "surface-active agent" has come into use as a general designation for compounds which in small quantities modify the properties of a system by adsorption at an interface. The terms "wetting agent" and "dispersing agent" are frequently used synonomously, and although some writers attempt a distinction there is no general agreement on special meanings. The terms used in this paper follow the general usage in paint and printing ink technology as noted below (*8*, *11*, *13*, *21*, *22*).

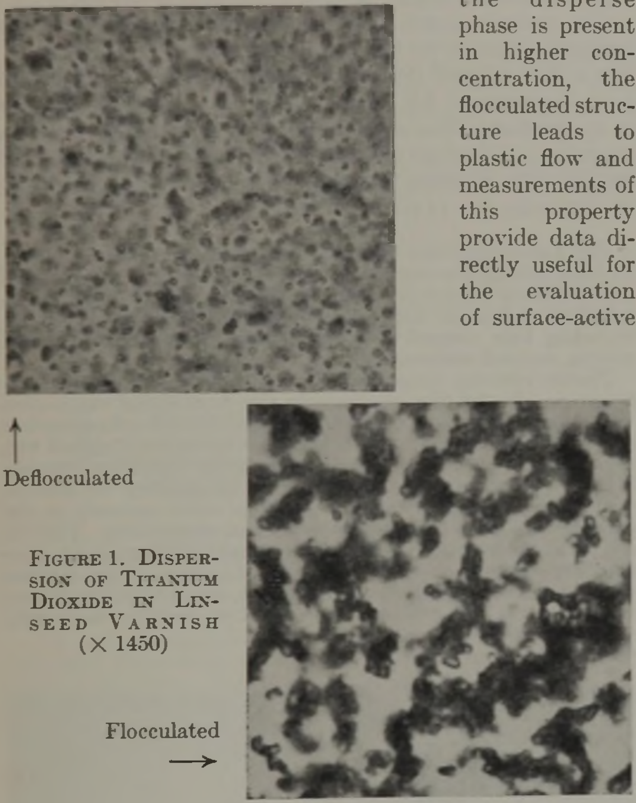
Pigment powders are considered as aggregates or masses of homogeneous particles which require an appreciable amount of mechanical work to separate the component particles. "Aggregates" are to be distinguished from "floccules" and the state of "flocculation" where the combination of pigment particles is disrupted by weak mechanical forces or by a change in the interfacial chemical forces. "Deflocculation" represents the state in which the pigment particles are independent or unclustered. The "ultimate working unit" may be an individual pigment particle or group of particles so firmly held together that they remain intact during a commercial application. "Grinding" is the process by which pigment aggregates are reduced to the size of ultimate pigment particles, with an implied reference to some device for the application of mechanical work. "Dispersion", a generic term, refers to any process, procedure, or state relating to heterogeneous systems of solids and immiscible liquids.

In the paint and printing ink industries a pigment-vehicle system in which the pigment is finely divided and deflocculated is considered without exception a good dispersion.

Where aggregates are present in the disperse phase, even though the particles are deflocculated, the material is usually considered a poor dispersion. There is less agreement in nomenclature, however, where the disperse phase is finely divided but highly flocculated. It is in this last case that surface-active agents are of greatest possible utility.

Flocculation and Yield Value

The flocculation and wettability of pigments in low-viscosity suspensions were studied in detail by Ryan, Harkins, and Gans (*18*). Solids which are deflocculated settle slowly to small final volumes; flocculation is shown by rapid settling to high final volumes. Where the disperse phase is present in higher concentration, the flocculated structure leads to plastic flow and measurements of this property provide data directly useful for the evaluation of surface-active agents. The connection between flocculation and plastic flow, as measured by plastic viscosity and yield value, has been shown by Green and others (*6, 13, 19, 25*). The photomicrographs of Figure 1 illustrate a deflocculated and flocculated dispersion of titanium dioxide in linseed varnish. The yield value of the deflocculated dispersion is low, 300 dynes per sq. cm.; that of the flocculated dispersion, identical in formula except for the addition of a trace of flocculating agent, is of the order of 35,000 dynes per sq. cm. The former is fluid, the latter is a semisolid.


↑ Deflocculated

Flocculated →

FIGURE 1. DISPERSION OF TITANIUM DIOXIDE IN LINSEED VARNISH (× 1450)

In the evaluation of surface-active agents for pigment dispersion, the change in flow properties of the dispersed system thus may be taken as the primary criterion for the effectiveness of the reagent, measurable as the magnitude of the change of plastic viscosity and yield value. The control of flow properties or consistency is essential both in the manufacturing and use of many products. For many purposes it is desirable to decrease the yield value of a dispersion, resulting in a fluid composition from a combination initially highly plastic. Deflocculation also permits an increase in the quantity of the disperse phase with retention of useful flow properties. On the other hand, it is sometimes desirable to increase the yield value of a pigment dispersion, and this result may sometimes be obtained by the proper selection of surface-active agents.

Plan of Experiment

Because of the countless combinations of pigments, vehicles, and surface-active agents, a complete survey was neither feasible nor necessary. Instead, experiments were limited to representative types of dispersions, selected on the basis of wetting characteristics.

For this purpose pigments considered as hydrophobic, neutral, and hydrophilic were chosen. Vehicles included glycerol, a Litho varnish, mineral oil, and a varnish composed of a phenolic resin in mineral oil solvent. Surface-active agents were selected to include at least one of each of the major classes; preference was shown for compounds of fairly well characterized chemical identity and uniformity rather than for proprietary compounds of unknown or undisclosed composition.

Data in this paper are taken from a large compilation of experimental results obtained during the last six years. In addition, information from experiments on other aspects of the subject of pigment dispersion—for example, the

The effect of surface-active agents on pigment dispersions has been studied to aid in formulating general principles for commercially important products such as printing inks and paints.

Because of the number of combinations possible, the experiments were limited to major types of pigment-vehicle systems as determined by basic wetting characteristics. Well characterized surface-active agents were selected, each representative of a class of compounds. Additional variables included dispersion procedures, concentrations, pigment-vehicle ratios, and methods of addition. Data are given on the rate of strength development as a measure of dispersion rate and the rheological properties of the compositions.

While a degree of specific action is associated with each reagent, several criteria have been established to aid in the selection of surface-active agents for special purposes. The degree of flocculation, indicated by measurements of plastic viscosity and yield value, can be materially affected by surface-active agents. The rate of pigment strength development appears to be a secondary effect related to the change in plastic viscosity. The utility of surface-active agents in this field is indicated.

Table I. Surface-Active Agents Used

Trade Name	Type	Supplier[a]
Aerosol OT	Dioctyl ester of sodium sulfosuccinic acid	American Cyanamid & Chemical Corp.
Aresket 300	Monobutyl diphenyl sodium monosulfonate	Monsanto Chemical Co.
Benzidine	Organic amine	National Aniline & Chemical Co., Inc.
Copper oleate	Soap	Shepherd Chemical Co.
Daxad 23	Polymerized sodium salt of alkyl aryl sulfonic acid	Dewey and Almy Chemical Co.
Duponol ME	Sodium salt of lauryl sulfate	E. I. du Pont de Nemours & Co., Inc.
Gilsonite (Selects)	Bitumen	Allied Asphalt & Mineral Corp.
Ink Lengthener EE	Petroleum residue	Sun Oil Co.
Lecithin	Plant phosphatide	W. A. Cleary Corp.
Nacconol NR	Sodium alkyl aryl sulfonate	National Aniline & Chemical Co., Inc.
Santomerse D	Alkyl aryl sulfonate	Monsanto Chemical Co.
Sapamine KW	Diethyl aminoethyl stearylamide hydroacetate	Ciba Co., Inc.
Tergitol 7	Sodium salt of *sec*-alcohol sulfate	Carbide & Carbon Chemicals Corp.
Zinc naphthenate	Soap	Nuodex Products Co., Inc.

[a] Compounds similar to those listed are available from other suppliers under different trade names. The substances used were considered as examples and are but a small part of the total number tested. Inclusion of a given substance in the list should not be construed as a specific recommendation for that product.

direct transfer of aqueous pigment pulps to oil dispersion (flushed colors)—have contributed to an understanding of the role of surface-active agents, but space limitations prevent the inclusion of all relevant data.

The surface-active agents tested are identified as completely as possible in Table I. Some of the compounds are suitable only for dark-colored products; for carbon black a number have become well known—e. g., benzidine and copper oleate (*24*, *26*).

The pigments were typical commercial products. Toluidine red is an azo dyestuff prepared by coupling diazotized *m*-nitro-*p*-toluidine with β-naphthol. Barium lithol toner is the barium salt of the compound formed by coupling diazotized β-naphthylamine-α-sulfonic acid (Tobias acid) with β-naphthol. Representative of the larger class of organic colors, toluidine toner and barium lithol toner may be considered hydrophobic pigments. Iron blue, of the type known commonly as Milori blue, is prepared by the oxidation of ferrous ferrocyanide, and for simplicity may be considered as ferric ferrocyanide. Iron blue is considered neutral in wetting properties (*5*), but some commercial species are definitely hydrophilic. Ultramarine, considered hydrophilic, is the synthetic pigment obtained by the reaction of sulfur, carbon, sodium carbonate, and clay. The titanium dioxide used was a typical commercial material of anatase crystalline type. Carbon black or channel black, manufactured by the combustion of natural gas, is considered hydrophobic or organophilic (*5*), but this pigment exhibits variable wetting characteristics depending on previous treatment and adsorbed moisture.

Because the moisture content of pigments is variable and depends on storage conditions, all pigments were heated for 24 hours in an oven at the following temperatures immediately before use:

Toluidine toner, barium lithol toner	65° C.
Iron blue	80
Ultramarine blue, titanium dioxide, carbon black	105

The purpose of this drying schedule was to reduce variations in pigment properties without modifying the pigment character from its normal condition; pigments, especially carbon black, are often stored in a hot room before use.

The vehicles used were as follows: Linseed or Litho varnish, obtained by the heat polymerization of linseed oil, was a dark-colored type with an acid number of 13, bodied to a viscosity of 5.9 poises, at 30° C. Glycerol was the C. P. product. The mineral oil was a refined ink oil with a viscosity of 5.8 poises at 30° C. The resin varnish contained 40 per cent modified phenolic resin in a mineral solvent; the viscosity was 14 poises at 30° C.

The dispersions were prepared, except where otherwise noted, by hand mixing the ingredients, and grinding (five tight passes) on a three-roll laboratory mill. A sequence of operations was established so that all dispersions were prepared in the same way, including time elapsed between milling and examination, mill setting, and mill temperatures.

Plastic viscosity measurements were made on rotational viscometers. In the first experiments two commercial viscometers were used. One was a Stormer equipped with a cylindrical bob and cup; the other was a MacMichael viscometer equipped with a continuously variable speed transmission and lever counter. While both of these instruments were satisfactory for low-viscosity oils and pigment dispersions, they failed seriously on dispersions exhibiting highly thixotropic and plastic flow. The values obtained for printing inks were completely discordant, since plastic-viscosity and yield value are a function of the shearing stress and the attainment of constant thixotropic breakdown levels (*12*, *14*). The Stormer, operated by weights, necessarily

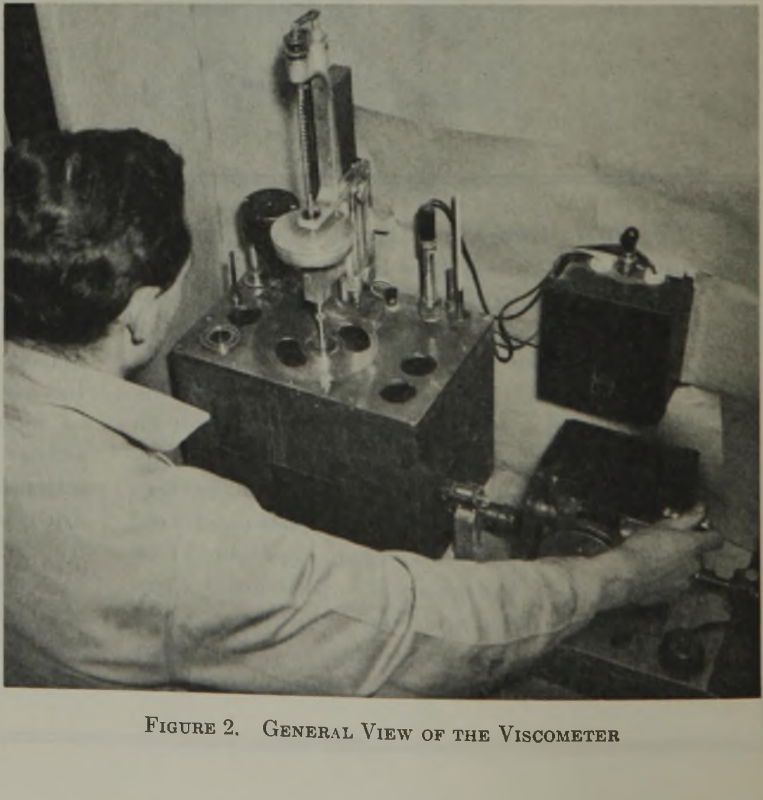


Figure 2. General View of the Viscometer

imposes a variable maximum shearing stress, since the greatest weight, rather than the highest rotational speed of the bob, is constant. The MacMichael viscometer was capable of higher shearing stresses at speeds to 240 r. p. m., but the maximum speed of the cup in this instrument was not even approximately reproducible for highly plastic dispersions. Variable shear, together with inadequate temperature control, made the values so obtained of relative significance only.

The data of this paper were obtained on the viscometer described by Green (*12*) as constructed in these laboratories, which overcame the operational difficulties enumerated above. This instrument (Figure 2) embodies the essentials of precise machining and alignment, rugged construction, temperature control of ±0.1° C., and accurately reproducible speed control.

With this viscometer a measurement includes the following steps: The pigment dispersion is placed in a cup, and after temperature equilibrium is reached, the cup is started rotating at a low speed. Readings are taken at increasing speeds to a maximum of 200 r. p. m. The cup is operated at this speed until equilibrium in thixotropic breakdown is attained (2 to 10 minutes) as indicated by an unchanging deflection on the torsion dial. Readings are then taken at decreasing speeds for eight to fifteen speed settings. A curve is obtained from the data by plotting revolutions per minute as the ordinate and degrees of deflection as the abscissa. The slope of the straight line part of the curve is a function of the plastic viscosity, and the intercept is a function of the yield value (Figure 3).

The instrumental data were converted to poises and dynes per sq. cm. by the following equations (*12, 17*):

$$U = 9.55\,(T - T_2)S/\text{r. p. m.}$$
$$f = T_2C$$

where U = plastic viscosity, poises
f = yield value, dynes per sq. cm.
S = $(1/R_b^2 - 1/R_c^2)/4\pi h$
C = $S/\ln(R_c/R_b)$
T = torque
T_2 = intercept on torque axis
R_b = radius of bob, cm.
R_c = radius of cup, cm.
h = height of cup, cm.

All measurements were made at 30° ± 0.1° C. The instrumental constants were determined both by direct calibration with torque measurements and calibration with viscosity reference standard oils obtained from the National Bureau of Standards.

For the determination of tinting strengths, white bleaching inks were prepared by grinding zinc oxide in each of the vehicles used in the tests. The pigment dispersions were reduced with the appropriate white ink, and the deviation from standard strength, taken as 100 per cent, was observed visually and calculated from the relative proportions of white and tinting material.

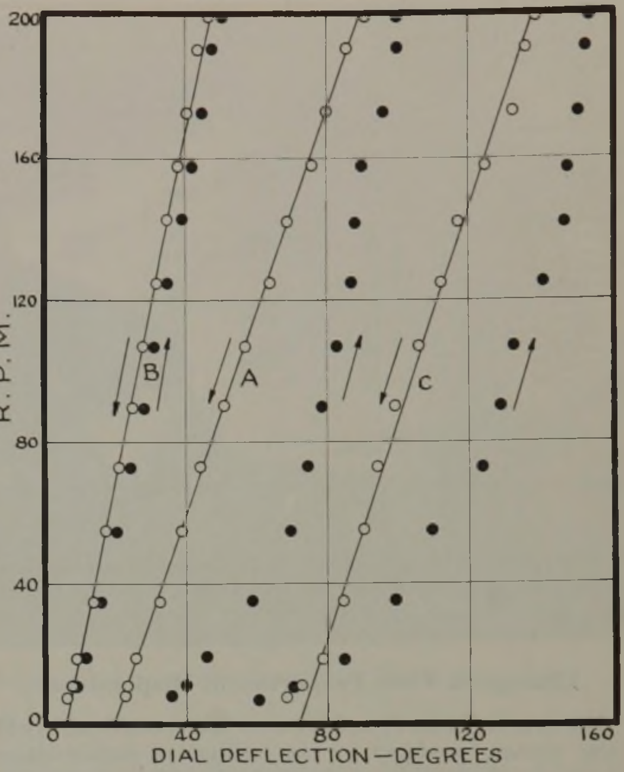


FIGURE 3. VISCOMETER CURVES FOR ULTRAMARINE BLUE IN MINERAL OIL

A, control, no reagent; *B*, plus Aerosol OT; *C*, plus Aresket 300. Solid circles represent readings at increasing shearing stresses (up curve); open circles, at decreasing shearing stresses (down curve). Torque conversion: 1° = 96.2 dyne-cm.)

Concentration of Surface-Active Agents

A quantity of reagent estimated to form a monomolecular film on the pigment particle may be considered the minimum to register a change in properties of a dispersion. Calculations of this quantity for commercial pigments on the basis of a number of arbitrary assumptions were reported (*2*); while these figures are only estimates, they serve as a rough guide. For many pigments 1 per cent by weight is sufficient; for pigments of small particle size, such as organic toners and carbon black, 2–3 per cent is required.

In one series of experiments the effect of concentration of different surface-active agents was determined. An observable change in yield value was obtained in most cases at 0.5 to 1.0 per cent, with the maximum result at approximately 3 per cent. For commercial applications the minimum useful quantity should be known; for the purposes of these tests, however, 3 per cent was used for all pigment-vehicle systems except carbon black where 5 per cent was employed. Large excesses of surface-active agents are of

TABLE II. EFFECT OF SURFACE-ACTIVE AGENTS ON FLOW PROPERTIES OF ULTRAMARINE BLUE AND IRON BLUE

	Ultramarine Blue						Iron Blue					
	39.7% by vol. in glycerol		32.0% by vol. in mineral oil		43% by vol. in linseed varnish		29.8% by vol. in glyercol		20% by vol. in mineral oil		28% by vol. in linseed varnsh	
Reagent	U^a	f^b	U	f	U	f	U	f	U	f	U	f
None (control)	41	0	46	1900	100	580	8.3	37	106	6900	90	2600
Aerosol OT	20	0	28	530	160	890	8.3	260	32	5500	78	2200
Aresket 300	41	0	46	6700	130	890	8.6	830	81	6350	98	2200
Daxad 23	32	0	..	..	131	880	14^c	0	61	9000	92	2400
Duponol ME	51	0	50	7200	130	2300	8.8	130	38	2700	83	2300
Lecithin	65	7700	23	74	110	3500	57	1400	23	410	85	2400
Nacconol NR	37	0	..	..	161	1370	8.8	130	74	6600	84	1800
Santomerse D	..	..	..	..	..	..	9.9	350	69	5200	81	1700
Sapamine KW	42	4500	41	1250	110	1200	70	8000	77	4400	81	2300
Tergitol 7	30	0	90	1400	110	960	7.3	300	89	9300	114	1700
Zinc naphthenate	60	1970	35	180	145	590	d	d	47	4400	78	2200
Water	..	..	d	d	d	d	..	..	d	d	d	d

[a] Plastic viscosity in poises.
[b] Yield value in dynes per sq. cm.
[c] Calculated at r. p. m. <100; dilatant at higher speeds.
[d] Too high to measure.

TABLE III. EFFECT OF SURFACE-ACTIVE AGENTS ON FLOW PROPERTIES OF BARIUM LITHOL TONER AND CARBON BLACK

	Barium Lithol Toner						Carbon Black					
	19.8% by vol. in glycerol		34.2% by vol. in linseed varnish		20.8% by vol. in mineral oil		9.7% by vol. in glycerol		11.6% by vol .in mineral oil		15.3% by vol. in linseed varnish	
Reagent	U[a]	f[b]	U	f	U	f	U	f	U	f	U	f
None (control)	31	1120	90	3080	40	2100	3.0	3800	45	7300	57	10,400
Aerosol OT	38	6050	110	6800	39	1680	3.1	2000	48	6000	55	8,650
Aresket 300	13	4380	120	5310	37	2640	8.4	1550	44	7100	69	8,260
Benzidine	..	...	..	..	..	..	17.0	5870	47	7700	53	770
Copper oleate	..	...	..	..	..	..	4.8	2600	41	4230	64	2,500
Daxad 23	27	865	105	7080	42	2880	6.2	1780	37	6300	56	10,900
Duponol ME	7.3	220	110	7520	43	2600	5.6	1200	44	8650	75	9,880
Gilsonite	..	..	..	..	..	..	..	..	46	3760	63	7,300
Ink Lengthener EE	..	..	..	..	..	..	14.0	3080	43	6060	55	7,930
Lecithin	44	8260	79	2690	35	1100	12.0	6640	34	6250	68	6,000
Nacconol NR	22	4380	116	5020	42	2840	6.1	1390	40	7500	66	7,200
Santomerse D	6.1	0	127	2060	41	2450	6.9	1250	42	7020	53	9,620
Sapamine KW	69	12,700	63	4370	45	2550	7.8	2600	38	6250	57	8,650
Tergitol 7	43	7120	..	..	41	1780	4.4	820	40	7100	65	10,700
Zinc naphthenate	95	19,100	66.8	8400	48	2260	21.0	4100	38	5960	69	8,060
Water	..	....	168	7360	56	6540	..	..	..	..	70	8,850

[a] Plastic viscosity in poises.
[b] Yield value in dynes per sq. cm.

little advantage since insoluble reagents act as an addition to the disperse phase while fluid and soluble materials merely extend the vehicle.

Change in Flow Properties of Dispersions

The data in Tables II and III show the viscosity and yield value changes produced by the addition of surface-active agents on dispersions of pigments in different vehicles. Where the yield value of a dispersion is high initially, as in the case of toluidine toner in glycerol, a number of reagents decrease this value. The magnitude of the change is large. In the glycerol system, compounds with some solubility are most effective. Somewhat similar results can be noted for carbon black. Iron blue and ultramarine, however, show high initial fluidity without surface-active agents, and the addition of these reagents merely serves to increase the yield value in the majority of cases.

In linseed varnish, considered a good wetting vehicle in the trade, all pigments appear to show comparatively high fluidity, and added reagents act rather to increase yield value and thus reduce fluidity. When mineral oil is used as vehicle, however, the dispersions are of lower fluidity than similar dispersions in linseed varnish, and surface-active agents show reduction in yield value. In some cases the reduction is marked—for example, lecithin and iron blue. Ultramarine in mineral oil shows a striking reduction in yield value with the addition of lecithin and zinc naphthenate.

The change in flow characteristics as measured is apparent even on casual examination. A reduction in yield value, such as that shown by the addition of lecithin to iron blue in mineral oil, represents the difference between a heavy nonfluid paste and a product which will pour readily from the container.

Several advantages can accrue from the use of surface-active agents; some have already been noted. Not only is it possible in some cases to increase the pigment content of a dispersion while retaining necessary flow properties, but also to decrease the flocculation to a point where a composition changes to a fluid from a condition initially highly plastic. Such an application is found in printing inks which must show maximum obscuring power at low film thickness and yet be sufficiently fluid to follow the fountain rollers on the press at high speeds. The opposite result may also be obtained, for should an increase in yield value be desired, a suitable surface-active agent may be added. Thus zinc naphthenate added to iron blue dispersed in glycerol increases the yield value from 37 dynes per sq. cm. to a value exceeding the practical limit of measurement on the viscometer.

Some pigments when dispersed in vehicles are water sensitive and form stiff, pasty masses on chance contamination with water. Surface-active agents serve to prevent this large increase in yield value, and a spectacular example is that of dispersions of titanium dioxide (Table IV). In mineral oil a trace of moisture added to the dispersion increases the yield value to such an extent that a stiff, semisolid results which cannot be measured. If, however, zinc naphthenate, lecithin, or Aerosol OT (as examples of possible reagents) are added during grinding, the subsequent addition of water, while increasing the yield value in most cases, does not convert the dispersion into a semisolid.

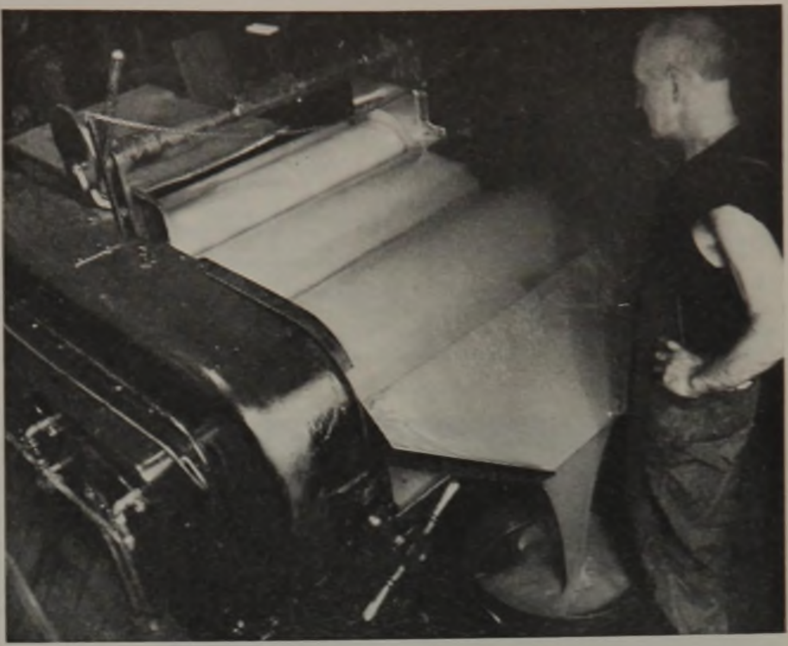
TABLE IV. CHANGE IN FLOW PROPERTIES OF TITANIUM DIOXIDE DISPERSIONS ON ADDITION OF WATER

	Before Water Addition		After Water Addition	
Reagent[a]	U[b]	f[c]	U	f
25.8% TiO_2 by Volume in Mineral Oil				
None (control)	[d]	[d]	[d]	[d]
Zinc naphthenate	35	2900	53	4400
Lecithin	22	1300	18	1500
Aerosol OT	40	3600	31	3200
31.3% TiO_2 by Volume in Linseed Varnish				
None (control)	58	740	[d]	[d]
Zinc naphthenate	44	780	60	1440
Lecithin	68	8200	50	10000
Aerosol OT	61	3400	55	6400

[a] 3% by weight on pigment.
[b] Plastic viscosity in poises.
[c] Yield value in dynes per sq. cm.
[d] Stiff paste; could not be measured.

In pigment dispersions of comparatively low pigment volume, the rheological effect of surface-active agents is much less marked. This result is readily understood, for where the particles are widely spaced, flocculation (when present) shows microscopically as a loose reticulum of clustered particles which can be disturbed at low shearing stresses. If, on the other hand, the particles are crowded, the force of flocculation produces a structure which on shearing in the viscometer is reflected in a yield value of appreciable magnitude.

Settling of the dispersed phase on dilution, however, is a more sensitive test. Where a surface-active agent has effectively deflocculated the pigment particles, the settling volume is small and the cake of settled pigment difficult to redisperse. This hard settling in paints is a recurrent difficulty and can be largely prevented by addition of surface-active agents which promote flocculation.



White Pigment Dispersion on Production Three-Roll Mill

In formulation problems the selection of surface-active agents can be facilitated by the use of compounds indicated for analogous systems. This procedure is not infallible, but it has the advantage of reducing the empirical testing necessary. For example, reagents effective for ultramarine blue can be tested with lithopone, titanium dioxide, and most types of chrome yellow.

Rate of Dispersion and Pigment Tinting Strength

The rate at which aggregates of a dry pigment disperse in a vehicle to the maximum fineness is of primary importance in manufacturing operations. That surface-active agents increase the rate of dispersion is a frequent claim, but the complexity of the process excludes any simple generalization; the evaluation must be based, in addition to specific pigment and vehicle factors, on (*a*) type of milling operation, (*b*) rate of mill output as compared with a control dispersion, and (*c*) rheological properties of the dispersion.

For roll mill dispersion, as typified by the three-roll mill, disintegration of aggregates is accomplished first by an actual crushing of particles, 10 microns and larger in size, at the start of a batch grinding operation, and finally by shearing within the plastic mixture; the latter reduces the aggregate size to the dimensions of ultimate pigment particles less than 1 micron in diameter. Internal friction resulting from flocculation of the pigment particles is of small comparative magnitude and may be considered negligible.

The output of a roll mill is directly proportional to the viscosity of the mix when roll clearance and operating speeds remain constant. Surface-active agents which increase the plastic viscosity, act to increase mill output rates, and the addition of these reagents is a useful production device. Essentially the same result may be obtained, however, by formulation with higher viscosity oils, by increase in the pigment content, or both, using preferably a deflocculating combination of vehicles and reagents. When the dispersion is satisfactory, the product can be extended with additional vehicle to give the desired pigment-vehicle ratio.

Somewhat different considerations apply to colloid mill and to ball and pebble mill operation. The mixture fed into a colloid mill should be fluid, since any appreciable yield value will markedly reduce the rate at which the dispersion will flow into the mill. In ball and pebble mills the mixture should allow cascading of the grinding medium, and if the yield value is excessively high the balls or pebbles will pack, especially in small mills, with consequent reduction in attrition (*8*).

It is evident that an improved dispersion rate resulting from an increase in mill efficiency by the addition of surface-active agents is a secondary effect of such reagents. Final pigment tinting strength appears to be directly related to the change in plastic viscosity of the mixture produced by the addition of surface-active agents. This is shown by the statistical data in Table V. The strength differences were in the range of 2 to 10 per cent, sufficiently large to be outside the errors of the measurement. Although no direct experimental evidence has been obtained to show that surface-active agents facilitate the breakdown of pigment aggregates, such a result is not unlikely. The data for carbon black suggest that with this pigment at least a favorable effect is found.

Table V. Relation of Pigment Strength to Plastic Viscosity (Three-Roll Mill Dispersions)

	No. of Experiments	
	Colors[a]	Carbon black[b]
Increase in plastic viscosity	76	64
Increase in strength	74	104
Decreased or unchanged plastic viscosity	87	152
Decrease or no change in strength	89	112

[a] Includes toluidine toner, iron blue, ultramarine blue.
[b] Includes "long" and "short" carbon blacks.

Methods of Addition

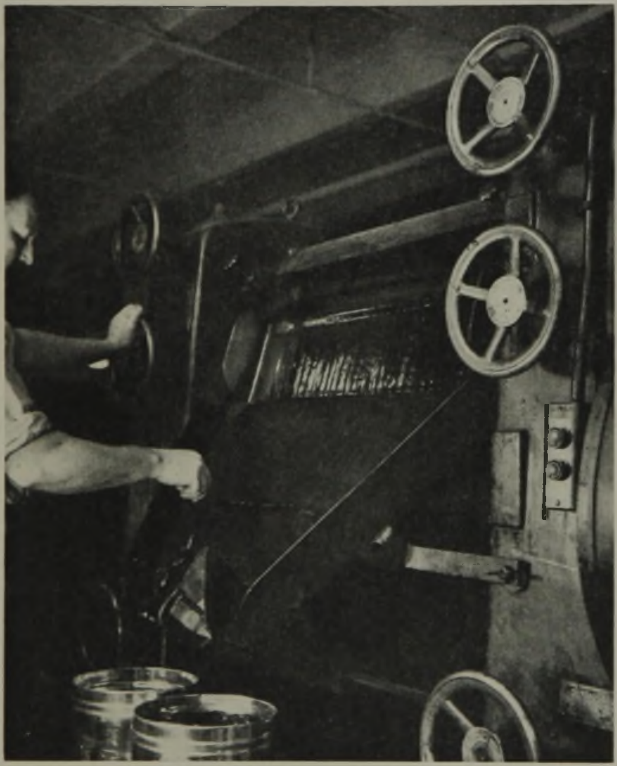
Of considerable practical interest are the several ways in which surface-active agents may be incorporated in a dispersion. Except where noted, the experiments were performed by mixing all ingredients of the formulation and then grinding. This procedure, designated *A*, follows manufacturing operations where a premix of all ingredients is made in a Pony mixer or dough mixer. Alternate methods included: *B*, solution or dispersion of reagent in vehicle; *C*, addition of reagent to pigment dispersion already prepared; *D*, treatment of dry pigment by mixing with a solution of surface-active agent in a volatile solvent to form a paste, followed by evaporation of solvent at low temperatures. Each of these methods has an analog in commercial practice.

Experimental results are shown in Table VI. Of the four methods of adding surface-active agents, the chief differences noted were in the degree rather than the direction of change in flow properties. Coating the pigment prior to incorporation in a dispersion is effective and practical from the stand-

Table VI. Method of Incorporating Surface-Active Agents

Pigment	Pigment Concn., % by Vol.	Vehicle	Reagent	Yield Value in Dynes/Sq. Cm.[a] Control	Method *A*	Method *B*	Method *C*	Method *D*
Ultramarine	20.8	Mineral oil	Zinc naphthenate[b]	3000	120	90	100	0
Ultramarine	37.0	Phenolic resin varnish	Santomerse[b]	3800	120	0	240	710
Toluidine toner	22.0	Glycerol	Santomerse[b]	620	0	0	0	0
Toluidine toner	27.3	Mineral oil	Lecithin[b]	1150	550	660	560	220
Iron blue	24.3	Mineral oil	Lecithin[b]	10,000	2580	1770	2600	770
Carbon black								
Short	13.7	Linseed varnish	Benzidine[c]	1100	330	260	400	430
Long or flow	9.0	Phenolic resin varnish	Lecithin[c]	620	160	160	140	500
Short	9.8	Mineral oil	Gilsonite[c]	970	660	430	770	970
Long or flow	13.7	Linseed varnish	Zinc naphthenate[c]	350	290	290	260	660

[a] *A*, all ingredients mixed and ground; *B*, reagent in vehicle; *C*, reagent added to dispersion after grinding; *D*, coating pigment.
[b] 3% on pigment by weight.
[c] 5% on pigment by weight.



Take-off Apron of Five-Roll Production Mill

point of the color manufacturer, but essentially equivalent results are obtained if the reagent is added at the time the preliminary mixture of pigments, vehicles, and other components is made. The latter method is preferred in many manufacturing operations.

Conclusions

1. Surface-active agents may be evaluated by observing their effect on the flow properties of pigments dispersed in nonaqueous media. The change in plastic viscosity and yield value, as correlated with the extent of flocculation of the dispersed phase, can be measured most conveniently on a rotational viscometer.
2. The greatest reduction in yield value has been observed in dispersions in which the pigment and vehicle are of differing wetting characteristics. Where the dispersed phase is deflocculated, the addition of surface-active agents sometimes causes an increase of yield value.
3. The rate of pigment dispersion and the final strength of a pigment are indirectly related to the action of surface-active agents. Inasmuch as dispersion on a roller mill is accomplished primarily by internal shearing of the mixture of pigment and vehicle, an increase in viscosity results in greater shearing stresses and more rapid disintegration of pigment aggregates. When the viscosity is decreased, less shear results, and both the rate of dispersion and final strength are lower. For soft grinding pigments, surface-active agents have no appreciable effect on the rate of dispersion. In the ball mill and colloid mill the influence of surface-active agents on over-all mill efficiency is of consequence, since the operation of these mills requires materials sufficiently fluid to permit ball mobility in the case of the ball mill and proper feeding of the mix in the case of the colloid mill.
4. While the breakdown of pigment aggregates may be facilitated by the addition of surface-active agents, no conclusive evidence has been obtained to demonstrate this effect, partly because it is intimately connected with the efficiency of the grinding operation.
5. In many formulations a decrease in yield value, resulting in greater mobility, is desirable; it is then possible to obtain fluid compositions from dispersions initially highly plastic. Alternately, it is possible to increase the pigment content, maintaining the yield value within practical limits.
6. Any useful effect shown by surface-active agents will, excluding exceptional cases, be obtained with relatively small quantities as calculated on the dispersed phase. While the amount necessary depends on the result desired, a quantity of the order of 3 per cent or less is ample. Larger quantities, if soluble or fluid, act as vehicle components; if insoluble, as additions to the dispersed phase.
7. Of the four methods of addition, the chief differences noted were in the magnitude rather than the direction of change of flow properties.
8. Because there is a measure of specific action associated with the use of surface-active agents, the procedure suggested for routine testing is to select different types of compounds for a quick experimental survey, and then to test more thoroughly related species of the compounds giving the most effective results.

Acknowledgment

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COAL OXIDATION

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By oxidation in three stages, bituminous coal is transformed into furfural-soluble substance with a yield of 90 per cent or better of the coal proper. The furfural solutions may be considered as systems of two completely miscible substances. Methods for the separation of furfural and ash-free carbonaceous material are pointed out, and possible uses are listed.

As DESCRIBED in a patent (*1*), bituminous coal in a properly oxidized condition is readily soluble in furfural. The solution of the carbonaceous material in the organic solvent is easily prepared and separated from mineral matter and fusain, and the recovery of both solvent and solute offers no serious problem. The ash-free carbonaceous material thus obtainable appears to lend itself readily to numerous uses in the production of heat, power, and chemical commodities.

In the original work preceding the patent (*2*, *4*), excess nitric acid was used to accomplish the required oxidation within the short period of one hour. For economic reasons it appeared desirable to accomplish a considerable part and perhaps all of the oxidation work by the use of air.

Air oxidation of coal in a "gas-solid" system, resulting in transformation of the coal proper into humic acids, has been reported in the literature as a tedious and time-consuming process. Wheeler and his associates (*7*) treated pyridine-extracted bituminous coal at 150° C. for several weeks with a current of moist air, and obtained transformation into so-called ulmic acids. Morgan and Jones (*5*) and Yohe and Harman (*8*) accomplished essentially the same conversion of coal proper into hydroxycarboxylic acids by exposing, for several weeks, finely ground coal to air in a drying oven kept at 150° C.

We have established that acid groupings may be introduced into the coal proper in reasonably short time by the use of air at elevated temperatures in the presence of small amounts of promoting substances such as vanadates or nitrates. The percentage of acid groupings is further increased by a second step of air oxidation at a lower temperature. Finally, a treatment with a greatly diminished amount of nitric acid is used to give a product which is easily soluble in cold furfural. Furfural-soluble substance is obtained after the air-oxidized preparation has been treated with 1–2 parts of nitric acid. In former work 8–10 parts of nitric acid were necessary to oxidize raw coal to a stage where the product was furfural soluble.

Apparatus and Methods

Oxidations were carried out either in an ordinary electric drying oven or in an electrically heated rotary furnace. The rotary furnace was equipped with an automatic feeding device and a temperature control unit. Auxiliary apparatus to regulate the composition, the moisture content, and the rate of flow of the oxidizing gas were also provided. The setup is shown in Figure 1.

To ascertain the effect of oxidation, three analytical methods were used:

1. Alkali Digestion. A 0.5-gram sample was placed into a 250-cc. Erlenmeyer flask equipped with reflux condenser, and 1 cc. alcohol and 25 cc. 0.1 *N* sodium hydroxide solution were added. The mixture was boiled for 30 minutes and filtered and the filtrate was titrated with 0.1 *N* hydrochloric acid solution, phenolphthalein being used as indicator.

2. Modified Alkali Digestion. In cases of extensive oxidation, the alkaline filtrates became too dark for convenient titration. In these cases 25 cc. of a 0.1 *N* calcium chloride solution were added just before filtration. This reagent causes precipitation of insoluble Ca humate according to the equation:

$$\text{Hum. Na}_{2n} + n\text{CaCl}_2 = \text{Hum. Ca}_n + 2n\text{NaCl}$$

The other conditions of procedure 1 remain unchanged.

3. Calcium Acetate Decomposition. A 0.5-gram sample and 25 cc. of a 0.1 *N* calcium acetate solution were placed into a 250-cc. Erlenmeyer flask equipped with reflux condenser; the mixture was refluxed for 30 minutes, cooled, and filtered. The residue was carefully washed with water, and the filtrate containing acetic acid was titrated with 0.1 *N* sodium hydroxide solution, phenolphthalein being the indicator. The reaction as indicated in the equation,

$$\text{Hum. H}_{2n} + n\text{Ca(CH}_3\text{COO)}_2 = \text{Hum. Ca}_n + 2n\text{CH}_3\text{COOH}$$

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proceeds to an equilibrium which depends upon the acid strength of the particular hydroxycarboxylic acid used in the test. Thus, while procedures 1 and 2 provide estimates of the percentage acid groupings that have been introduced by oxidation, method 3 is indicative of acid strength. Under the conditions of these determinations, furfural-soluble preparations were found to combine with 40 cc. or more of 0.1 *N* sodium hydroxide solution per gram and to decompose 30 cc. or more of the acetate solution.

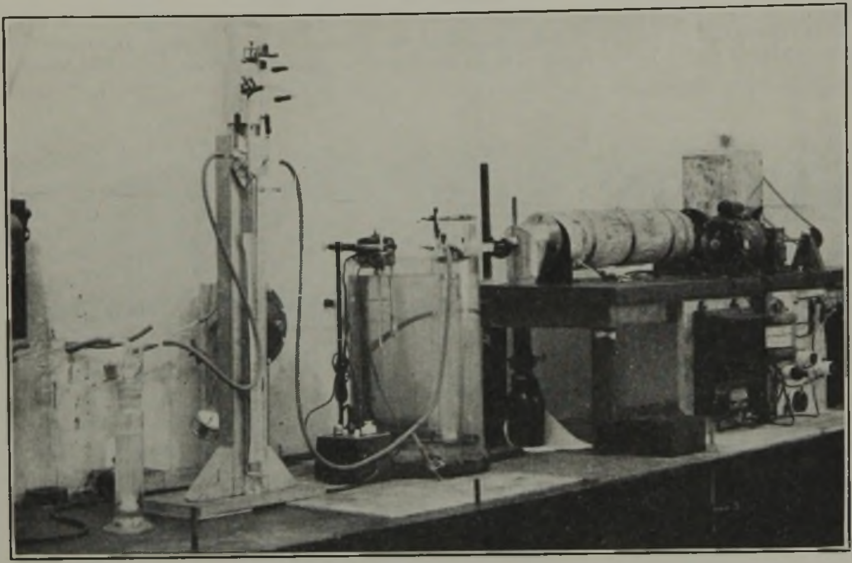

FIGURE 1. ROTARY FURNACE WITH AUXILIARY EQUIPMENT

◆

Oxidation Procedures

PROCEDURE 1. Twenty-gram samples of powdered coal were placed in shallow pans and kept in the drying oven at 150° C. for a number of weeks. The progress of oxidation is illustrated in Table I. The coal used in these experiments was a Central Pennsylvania coal, Upper Freeport seam, 0.9 per cent moisture, 30.1 per cent volatile matter, 6.1 per cent ash, 62.9 per cent fixed carbon. The coal was ground to pass a 50-mesh sieve.

TABLE I. OXIDATION OF COAL IN A DRYING OVEN AT 150° C.

Oxidation period, weeks	0	1	2	3	4	5	6
0.1 *N* NaOH, cc./g.	1.0	8.7	11.4	19.0	22.3	44.0	44.6
0.1 *N* $Ca(Ac)_2$, cc./g.	...	...	3.7	5.8	8.0	11.2	14.4

By ascribing definite equivalent weights to the various intermediate products of the oxidation, the figures of Table I assume a clearer meaning. Computation shows that the equivalent weights of the various hypothetical coal acids dropped from 10,000 to 225 during 6 weeks. Weathered coals and coal samples that had received a brief oxidizing treatment in the rotary furnace attained an equivalent weight of 250 or less in 3 to 4 weeks. In experiments extended to 10 weeks, no further essential decrease of equivalent weight was noted, but the acetate figures improved to 20 cc. per gram or better. In these cases furfural-soluble substance was shown to be present by the following procedure: The oxidized preparations were extracted with alkali, the alkaline solutions were precipitated with acid, and the precipitate was treated with furfural.

PROCEDURE 2. In a considerable number of experiments powdered coal was passed through the rotary furnace at a rate of 160 grams per hour, corresponding to a contact time of approximately 5–7 minutes; simultaneously a countercurrent of air (or of an air-oxygen mixture) was sent through the oven. In these experiments temperatures between 150° and 350° C., air and air-oxygen mixtures of varying moisture content and at various rates of flow, and a number of potential catalysts or promoters (various vanadates, sulfates, and nitrates) were tested. On the basis of these tests ammonium nitrate was found to be the most effective and convenient. It was established in the early phases of this work that air at 350° C. was just as effective an oxidizing agent as an air-oxygen mixture at lower temperatures. In most experiments the coal was passed through the oven repeatedly because the length of the oven permitted only a short period of contact. After each pass the progress of oxidation was ascertained. Results are presented in Table II; the rate of air flow was 1500 cc. per minute, and the yield 160 grams per hour.

The smaller the particle size, the more quickly the effect of air oxidation is noted. In large scale operations the use of a Raymond bowl mill or similar equipment would make it possible to introduce coal sprayed with suitable substances at temperatures up to 350° C. and to obtain a −200 mesh oxidized product at some suitable lower temperature—e. g., 100° C.

TABLE II. AIR OXIDATION OF COAL IN A ROTARY FURNACE AT 350° C.

Pass No.	1	2	3	4	5
0.1 *N* NaOH, cc./gram					
Test 1	3.3	4.8	5.9	10.8[a]	12.0[a]
Test 2	6.4[a]	10.2[a]	11.8	...	...

[a] 5 grams ammonium nitrate per 1000 grams of coal added.

By increasing the number of passes, preparations of an equivalent weight of 500 or less were obtained. At this stage they were easily further oxidized at a lower temperature, giving rise to products of the desired percentage of acid groupings though not of the desired acid strength.

PROCEDURE 3. This second stage of air oxidation was carried out as follows: 500 grams of coal preoxidized at 350° C. were placed in a porcelain dish, 100 cc. of a 25 per cent ammonium nitrate solution were added, and with constant stirring the mixture was brought to dryness by heating gradually on an electric hot plate to about 150° C. Agitation at this temperature was continued until white fumes were no longer visible. The time to complete the operation varied from 30 to 75 minutes. The results of a number of runs are compiled in Table III.

Table III. Oxidation of Coal Preparations at 150° C. in Presence of 5 Per Cent Ammonium Nitrate

Experiment No.	1	2	3	4	5
0.1 N NaOH, cc.					
Before treatment	1.8	10.2	20.5	20.5	20.5
After treatment	11.6	25.0	38.6	37.4	39.2

Experiment 1 refers to original coal. The results were essentially the same when 10 per cent of ammonium nitrate had been added. During the operation, ammonia combined with the hydroxycarboxylic acids, while a considerable quantity of nitrogen oxides, together with excess ammonium salt, escaped.

Procedure 4. Preparations that had been passed five to ten times through the rotary furnace at 350° C. and subsequently were treated with 5 per cent ammonium nitrate, as indicated in section 3, showed an alkali consumption of 30–40 cc. 0.1 N sodium hydroxide and an acetate number of 3–7. In order to increase the acid strength to the point where acetate numbers of 25 or better are obtained, a treatment with nitric acid still offers the most convenient and quickest procedure.

In order to ascertain the minimum amount of nitric acid necessary to give, in each case, the maximum yield of furfural-soluble substance, 50-gram samples of the air-oxidized preparations were treated for 1–2 hours with increasing amounts of nitric acid, and the yield of furfural-soluble substance was determined. The alkali number of the samples was 24.0 cc. 0.1 N sodium hydroxide per gram; the acetate number was 2.7 cc. 0.1 N calcium acetate per gram. The following table is illustrative of the results:

Cc. conc. HNO_3	50	75	100	125	150
Furfural-sol. substance, %	<40	60	80	>90	>90

Other wet oxidation experiments with this same sample of preoxidized coal, but conducted with dilute nitric acid, indicated that the same results may be achieved if the time is materially increased. Experiments of this type established the fact that the higher the alkali and acetate numbers, the less nitric acid is needed to accomplish the desired results. Two examples of procedure are added: One hundred grams of a preparation with an alkali value of 39 and an acetate value of 7 were placed in an Erlenmeyer flask immersed in cold water, and 100 cc. of concentrated nitric acid were added in four portions. After the first violent reaction subsided, the mixture was heated in a boiling water bath for 1–2 hours, diluted with water, filtered through a Büchner funnel, washed free from nitric acid, and air-dried. In another case 100 grams of a preparation with an alkali value of 29 and acetate number of 3 were placed in a 2-liter round-bottom flask and cooled with ice, and 250 cc. of concentrated nitric acid were added. The remaining procedure was essentially the same as described above. In either case, 100 grams of oxidized coal gave approximately 120 grams of washed air-dried product. In addition, a certain amount of soluble substance appeared in the dark colored filtrates and wash water. In both cases the isolated product was soluble in furfural to 90 per cent or better. Fusain and mineral matter are insoluble.

Preparation and Properties of Furfural Solutions

One thousand cubic centimeters of furfural were placed in a 2-liter beaker equipped with a stirrer, and 250 grams of product were gradually introduced. Stirring was continued for 30 minutes, the whole operation taking approximately one hour. The mixture was then centrifuged, and the resulting solution of approximately 22 per cent strength was poured through a paper filter.

The filtered solutions were concentrated under vacuum to approximately 40 per cent strength. To separate furfural and coal substance, several methods were found to be efficient; precipitation with isopropyl ether, precipitation by pouring into excess water, or steam distillation and, undoubtedly, spray evaporation or the use of drum dryers would serve the same purpose on a plant scale. It was noted that a small fraction of the product is soluble in water and isopropyl ether.

As previously shown (*4*), the solutions of oxidized coal in furfural do not exhibit the Tyndall phenomenon and cannot be classified as colloidal systems. In the present investigation we have established that the solubility of the oxidized coal substance (hydroxycarboxylic acids) has no limiting value. By mixing the components at room temperature and atmospheric pressure, solutions up to 30 per cent strength have been prepared. These solutions were easily filterable in the absence of suspended particles; their specific gravities were measured and found to be represented by the expression

$$(1.154x + 1.600y)/100$$

where x = percentage furfural
y = percentage oxidized coal

By concentration in vacuo, solutions of much greater strength were prepared. Finally it was observed that the addition of a small amount of furfural to an excess of the oxidized coal gave a system that assumed the consistency of an asphalt on standing. In view of these facts any system composed of coal, oxidized to the proper stage, and furfural may be classified as a binary system comprising two completely miscible liquids. It has been recognized that amorphous, nonuniform substances may be considered as liquids (*9*).

Past experiences and tentative experimental work have disclosed the following possible uses of this new material. The ash-free carbonaceous substance recovered from the furfural solution may be used as an ash-free powdered fuel, either as such or in the possible preparation of a colloidal fuel; as a starting material for the production of active carbon, carbon black, various plastics, paints and varnishes, tanning agents, and insecticides (*6*). It may be used in the staining of wood and in the purification of water (*3*). It may be of value in soil beneficiation, it is amenable to hydrogenation, and finally, in mixture with strongly swelling coals, it will give blends of greatly diminished coking pressure and coke of improved quality and smaller ash content.

Acknowledgment

The aid and assistance of Frieda Fuchs is gratefully acknowledged.

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Effect of Oxidation on Reactivity and Swelling of Illinois Coals

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The effect of oxidation of laboratory samples on reactivity and British swelling index numbers has been studied. Samples were exposed up to 8–9 months and tests were made at various intervals. Agglutinating values were determined occasionally to demonstrate that oxidation did take place. Three sets of whole coal and banded ingredients representing high-volatile bituminous ranks A and C were studied.

IN ADDITION to the usual proximate and ultimate analyses, several special laboratory tests have been developed for determining the characteristics and behavior of coals under different conditions. In general, these special tests measure over-all characteristics under specified conditions rather than specific properties or constituents such as those measured in the proximate and ultimate analyses. Some of these special tests are the C. R. L. reactivity test (*6*, *7*), British Standards swelling test (*3*, *4*), agglutinating value test (*1*), and various means for determining plastic properties and swelling characteristics of coal when heated.

The fact that Illinois coals are distinctly banded makes it possible to study the characteristics not only of the whole coal but also of the constituent bands vitrain, clarain, durain, and fusain. This report deals with the effect of oxidation of whole coal and constituent bands on ignition temperatures as measured by the C. R. L. reactivity test and swelling as measured by the British swelling index test. The agglutinating value test was used to indicate oxidation of samples during exposure.

Samples and Procedure

Three sets of samples, including whole coal and banded constituents, from Henry, Macoupin, and Gallatin Counties were used for this work. These samples represented coals with approximate moisture levels of 19, 13, and 5 per cent and high-volatile bituminous ranks C, C, and A, respectively. The whole coals were about 2-inch channel samples cut down, crushed to pass a 4 mesh sieve, and sealed in friction-top cans in the mines. The banded ingredient samples were hand-picked, crushed to −4 mesh size, and sealed in friction-top cans in the mines. All samples were further crushed to desired sizes in the laboratory.

The samples were air-dried and crushed in a Braun type 6 CP pulverizer to −20 mesh and to finer sizes in a ball mill. The −40 +60 mesh samples were used for reactivity determinations, −60 mesh samples for British swelling index (B. S. I.) tests and −200 mesh samples for the agglutinating value tests. Proximate constituents, total sulfur, and calorific values were determined on −60 mesh samples according to standard A. S. T. M. procedures (*2*). The various special tests were made on the samples soon after receipt from the mines and again after various intervals of exposure. All samples were kept in stoppered bottles for 2 to 4 weeks following the first determination, and were then exposed to the laboratory atmosphere in shallow dishes with frequent stirring for the duration of the studies. The mesh size of exposed samples was that used in each particular test—that is, −40 +60 mesh for ignition temperature samples, −60 mesh for B. S. I. test samples, and −200 mesh for agglutinating test samples. U. S. Standard sieves were used for sizing all samples.

The C. R. L. reactivity test was that described by Sebastian and Mayers (*6*) and by Sherman, Pilcher, and Ostborg (*7*). The equipment used was almost a duplicate of that described by Sherman and coauthors with the exception that split, hinged type refractories were provided to permit more rapid

TABLE I. ANALYSES OF COAL SAMPLES

Lab. No.	Description	Basis[a]	Moisture, %	Ash, %	Volatile, %	Fixed C, %	Total S, %	B. T. U.
			Henry County					
C-2425	Whole coal	A. R.	19.3	8.9	31.6	40.2	3.85	10,332
		Dry	..	11.0	39.2	49.8	4.77	12,802
C-2427	Clarain	A. R.	18.2	9.0	32.7	40.1	3.53	10,453
		Dry	..	11.0	40.0	49.0	4.32	12,772
C-2428	Durain	A. R.	16.2	6.3	33.8	43.7	3.23	11,252
		Dry	..	7.5	40.3	52.2	3.85	13,426
C-2429	Fusain	A. R.	25.2	10.5	17.3	47.0	7.82	9,161
		Dry	..	14.1	23.1	62.8	10.46	12,255
			Macoupin County					
C-2405	Whole coal	A. R.	14.0	10.2	34.1	41.7	4.50	10,624
		Dry	..	11.9	39.7	48.4	5.23	12,354
C-2406	Vitrain	A. R.	15.3	2.9	35.4	46.4	2.81	11,503
		Dry	..	3.4	41.8	54.8	3.32	13,579
C-2407	Clarain	A. R.	13.4	3.7	39.0	43.9	3.60	11,696
		Dry	..	4.3	45.0	50.7	4.16	13,502
C-2408	Durain[b]	A. R.	13.3	11.9	34.5	40.3	2.88	10,514
		Dry	..	13.7	39.8	46.5	3.33	12,130
C-2409	Fusain	A. R.	20.3	8.0	14.0	57.7	4.95	10,379
		Dry	..	10.0	17.6	72.4	6.20	13,017
			Gallatin County					
C-2416	Whole coal	A. R.	5.1	9.4	36.8	48.7	3.03	12,584
		Dry	..	10.0	38.8	51.2	3.19	13,267
C-2417	Vitrain	A. R.	4.4	7.7	37.6	50.3	2.31	13,109
		Dry	..	8.1	39.3	52.6	2.42	13,706
C-2418	Clarain	A. R.	3.6	9.9	35.6	50.9	2.65	12,749
		Dry	..	10.3	36.9	52.8	2.74	13,221
C-2419	Fusain	A. R.	17.8	15.6	19.0	47.6	3.50	9,693
		Dry	..	18.9	23.2	57.9	4.26	11,789

[a] A. R. = as received. [b] Probably dull clarain.

TABLE II. RESULTS OF SPECIAL TESTS AND OF OXIDATION

Lab. No.	Description	Ignition Temperature			British Swelling Index		Agglutinating Value	
		T_{15}, °C.	T_{75}, °C.	Days stored	Index No.	Days stored	Kg.	Days stored
		Henry County Samples						
C-2425	Whole coal	164	186	0	4.5	4	...	...
		163	188	8	3.5	11	...	...
		167	187	14	3.0	21	4.6	14
		165	192	42	2.5	45	3.3	47
		168	192	95	1.0	95	3.4	99
		172	194	222	1.0	210	2.8	221
C-2427	Clarain	163	185	1	3.5	4	...	...
		167	188	10	4.0	11	4.8	15
		162	187	19	4.0	21	...	...
		163	188	45	4.0	45	3.1	55
		168	188	96	3.5	95	2.6	94
		172	189	223	2.5	210	2.6	221
C-2428	Durain	175	193	4	3.5	4	...	...
		170	191	7	...	...	...	...
		167	192	12	3.0	11	4.9	13
		167	190	21	2.5	21	...	...
		172	192	46	1.5	45	2.5	49
		175	194	109	1.0	95	3.3	102
		176	195	224	1.0	210	...	...
C-2429	Fusain	170	208	6	1+	4	...	...
		172	204	13	1+	11	...	...
		180	203	24	1+	21	...	...
		178	205	47	1+	45	...	...
		179	207	110	1.0	95	...	...
		181	204	224	1.0	210	...	...
		Macoupin County Samples						
C-2405	Whole coal	160	188	2	4.5	1	...	...
		165	191	5	4.5	5	...	...
		167	192	12	...	...	4.7	14
		164	192	18	...	...	...	...
		161	192	21	4.5	20	...	...
		166	196	47	3.5	61	3.5	48
		170	194	112	2.0	113	2.5	114
		169	196	271	1.5	266	1.7	270
C-2406	Vitrain	160	189	2	3.5	1	...	...
		156	184	5	4.0	5	...	...
		159	190	19	3.5	20	...	...
		162	192	22	...	...	...	...
		164	190	48	4.5	61	...	...
		162	192	113	4.5	113	...	...
		158	193	268	3.5	266	...	...
C-2407	Clarain	159	190	3	3.5	1	...	...
		160	191	6	4.0	5	...	...
		163	194	20	4.0	20	...	...
		165	195	23	...	...	5.5	27
		166	194	49	4.5	61	4.1	51
		163	196	114	4.5	113	3.7	116
		165	196	271	3.5	266	3.3	271
		Macoupin County Samples (*Cont'd.*)						
C-2408	Durain[a]	161	189	3	3.5	1	...	...
		165	191	9	3.5	5	...	...
		169	192	11	...	...	...	...
		165	190	20	3.5	20	4.1	23
		166	189	25	...	...	...	...
		...	...	...	...	...	3.2	55
		...	...	...	3.0	61	...	...
		173	195	116	1.5	113	2.6	116
		168	198	272	1.0	266	2.3	271
C-2409	Fusain	179	222	4	2.0	1	...	...
		...	...	...	1.5	5	...	...
		183	230	11	...	...	...	...
		186	220	21	1.5	20	...	...
		177	224	26	...	...	...	...
		191	224	50	...	...	...	...
		190	222	118	...	...	...	...
		185	234	272	...	...	...	...
		Gallatin County Samples						
C-2416	Whole coal	267	254	0	7.0	2	8.3	2
		207	252	3	7.0	4	...	...
		202	253	10	7.0	11	...	...
		209	254	56	7.0	59	...	...
		206	256	63	...	...	5.5	64
		207	254	102	6.5	106	...	...
		212	260	241	6.0	235	5.5	239
C-2417	Vitrain	210	258	1	6.5	2	...	...
		215	272	4	6.5	4	8.7	3
		211	267	7	...	...	...	...
		208	265	9	...	...	...	...
		209	270	10	6.5	11	...	...
		208	261	59	6.0	59	...	...
		206	270	65	...	...	5.7	65
		213	257	106	5.0	106	...	...
		210	265	109	...	...	5.7	114
		213	262	245	5.0	235	5.0	240
C-2418	Clarain	211	254	2	6.5	2	...	...
		204	260	5	6.5	4	...	...
		208	255	8	...	...	...	...
		207	259	11	6.5	11	8.3	16
		209	255	59	6.5	59	5.6	65
		211	254	107	6.5	106	5.4	114
		209	255	246	6.0	235	...	...
C-2419	Fusain	211	258	3	1+	2	...	...
		212	254	7	1+	4	...	...
		214	256	11	1+	11	...	...
		210	255	60	...	...	...	...
		209	252	112	...	...	...	...
		214	257	247	...	...	...	...

[a] Probably dull clarain.

cooling of the furnaces between runs. Determinations were made in both oxygen and air and these results are indicated as T_{15} and T_{75}, respectively.

The B. S. I. test was essentially that of the British Standards Institution (*3*), the principal modification being the substitution of a Fisher high-temperature burner for the Teclu burner specified in the British standard method.

Agglutinating value determinations were made according to the "Proposed Method of Test for Agglutinating Value of Coal" as published by the American Society for Testing Materials (*1*). Silicon carbide was the inert material used in these tests, the ratio being 15 silicon carbide to 1 coal. The apparatus for crushing test buttons was designed and built in this laboratory.

Discussion of Results

Analyses of the coals are given in Table I. The results of special tests and the effects of oxidation on the characteristics measured by these tests for samples from Henry, Macoupin, and Gallatin Counties are listed in Table II. Table III presents data on a Franklin County whole coal in which exposure was made on −40 +60 mesh coal for both reactivity and agglutinating tests. The main purpose of this study was to determine the effect of oxidation of laboratory samples during storage on the characteristic ignition temperatures and B. S. I. values. Although the agglutinating value data are not complete, they serve their purpose of demonstrating that oxidation did take place. This test was used because it has been found quite sensitive to oxidation of samples.

The sample from Macoupin County designated as durain (Table II) appeared to be durain when picked in the mine, but later examination in the laboratory indicated that it was mainly a dull clarain. The other hand-picked banded ingredients were probably not pure ingredients but, it is believed, were concentrates of sufficient purity to show the predominating characteristics.

Table III. Data for Franklin County Whole-Coal Sample C-2445

Ignition Temperature			Agglutinating Value	
T_{15}, ° C.	T_{75}, ° C.	Days stored	Kg.	Days stored
182	229	1	5.1	0
184	232	14	3.9	15
182	228	37	3.1	39
184	230	127	...	...
182	228	135	2.0[a]	132

[a] Based on average of eleven buttons.

A considerable amount of data is presented for comparison of the characteristics of different rank coals and banded ingredients. However, only the effect of oxidation on these characteristics is considered here. Comparisons based on these data and other information not included in this paper will be considered in another report.

In order to judge whether the rather small differences in characteristic ignition temperatures as related to various times of laboratory exposure were significant, it was necessary to have some basis of interpretation. For this purpose standard deviations for duplicate and triplicate values of T_{15} and T_{75} were calculated. Values three times these standard deviations were used as limits. They were found to be 12° and 11.5° C., respectively. It was considered that, if variations exceeding these limits were found, they would indicate a significant trend. Table II shows that the differences in characteristic ignition temperatures, determined after various times of exposure compared to the original values are, in general, considerably smaller than these limiting values. In some cases higher values are reported for samples exposed for longer times. This is more noticeable for the lower rank coals from Henry and Macoupin Counties than for the higher rank coal from Gallatin County. However, it is not possible to estimate the significance of these small increases on the basis of the limited data included in this report. It is concluded that laboratory exposure up to 8 or 9 months does not affect significantly the characteristic ignition temperatures of the samples studied. At the same time the agglutinating value data indicate that oxidation of samples did take place. This is evidenced by the decreasing values as exposure time increases.

It was mentioned earlier that exposure of samples was made in the size used for the various tests. Exposure of reactivity samples was in −40 +60 mesh size and of agglutinating value samples in −200 mesh size. The question arose as to whether oxidation of −40 +60 mesh coal might be negligible even though quite appreciable for −200 mesh samples. To answer this question a whole coal from Franklin County, Ill., was exposed in −40 +60 mesh size for both ignition temperature and agglutinating value tests. For the agglutinating value tests the −40 +60 mesh material was ground to −200 mesh at the time of the tests. The results obtained (Table III) indicate that oxidation did take place in the −40 +60 mesh size as evidenced by the decreasing agglutinating values with increased time of exposure. At the same time characteristic ignition temperatures remained practically the same.

In the interpretation of the effect of oxidation on the British swelling index, a value three times the standard deviation was taken as a limit. This limit was found to be 0.9. A difference of one unit, therefore, was considered significant. The data in Table II, in general agreement with previous experience (*5*), indicate that the B. S. I. numbers decrease with increased exposure time of samples. The values for the higher rank Gallatin County samples show a smaller decrease than those for the lower rank coals from Henry and Macoupin Counties. Values for clarain from Henry and Gallatin Counties show the smallest decrease of the banded ingredients from these two sources. Fusain does not swell, and the values greater than 1 in Table II indicate the presence of other swelling coal material in these samples.

Attention is called to the fact that original B. S. I. numbers for whole coals are higher than those for individual petrographic constituents. Although no definite reason can be given for this at present, the authors have recently noted that the addition of small amounts of fusain to clarain and vitrain results in small increases in B. S. I. numbers for these two constituents. Additional studies are being made.

Conclusions

1. Exposure of −40 +60 mesh samples of whole coal and banded ingredients up to 8 or 9 months to the laboratory atmosphere does not appear to influence significantly the characteristic ignition temperatures of these samples.
2. B. S. I. numbers decrease with increased time of exposure of samples.
3. B. S. I. numbers of the higher rank Gallatin County coal show less decrease with increased time of exposure than do the lower rank coals.

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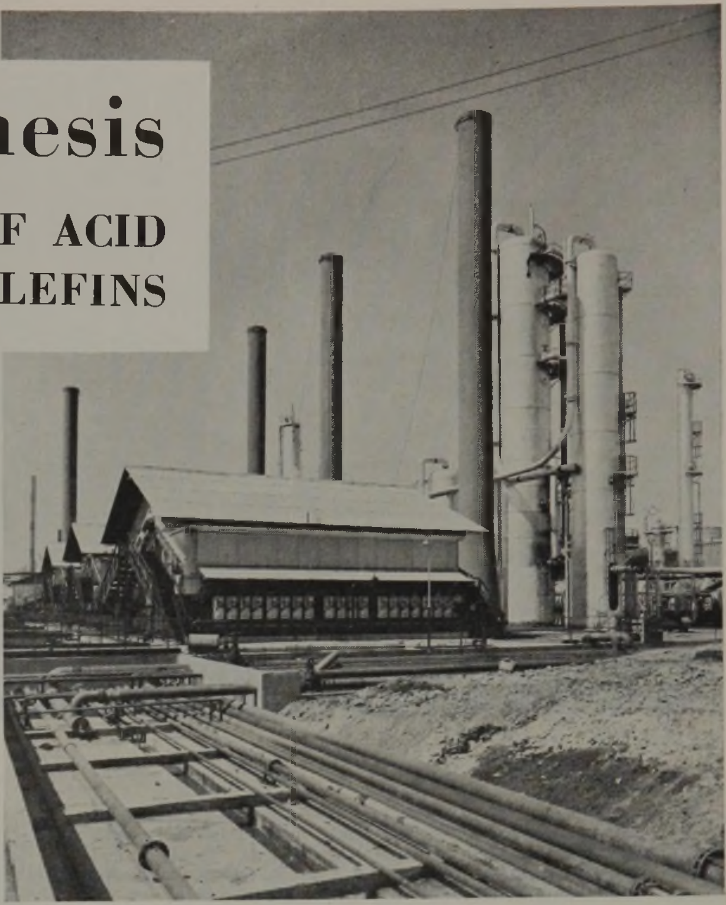
Possible New Uses for Coal—Correction

An unfortunate error has been found in the article by H. C. Howard (February issue of Industrial and Engineering Chemistry). At the bottom of the second column, page 156, the structural formulas of brazan and fluorenone, as well as their respective carbon-hydrogen ratios, were interchanged.

Ketone Synthesis

THE CONDENSATION OF ACID ANHYDRIDES WITH OLEFINS



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THE past two decades have witnessed rapid strides in the production of chemical derivatives from petroleum, particularly those derived from cracking-plant gases. Outstanding have been methods for the production of ketones; as production has increased and cost decreased, whole new processes have been developed, based on the unique properties of various ketones. In general, the methods employed for synthesis of the lower members involve dehydrogenation or oxidation of secondary alcohols (*2*), but these have not been commercially applied to higher molecular weight ketones because of the difficulty in procuring the necessary alcohols. It is known, however, that olefins will combine directly with acyl halides, as acetyl chloride, in the presence of such catalysts as zinc chloride, aluminum bromide, or aluminum chloride to form chloro ketones. These compounds lose hydrogen chloride rather readily under some conditions to give unsaturated ketones. Normally the products obtained in moderate yields are mixtures of saturated ketones, unsaturated ketones, and chlorinated hydrocarbons (*4, 5*). Saturated hydrocarbons, such as hexane, have also been reacted with acetyl chloride and aluminum chloride to give a saturated ketone (*6*). There has been only one report on the reaction of an olefin with an acid anhydride. This is the reaction of isobutene with acetic anhydride and zinc chloride to give mesityl oxide (*4*).

A synthesis of unsaturated methyl ketones by reaction of branched-chain olefins with acetic anhydride is given. Zinc chloride and sulfuric acid have been found to be effective condensing agents; optimum yields of ketones are obtained with less than one mole of condensing agent per mole of reactants. The methyl octenyl ketone obtained as the principal product from diisobutylene has been shown by ozonolysis to be 4,6,6-trimethyl-3-heptene-2-one.

Polymer gasoline, obtained from cracking-plant gases by polymerization with solid phosphoric acid, has been shown to be a suitable source of olefins. Pilot plant experiments are reported.

The general equation involved in the reaction of acid anhydrides with olefins may be represented as:

$$C_nH_{2n} + (RCO)_2O \longrightarrow C_nH_{2n-1}COR + RCOOH$$

Although various types of olefins and acid anhydrides may be employed in this reaction, the present paper deals exclusively with the reaction of branched-chain olefins of seven or more carbon atoms with acetic anhydride in the presence of various condensing agents.

Apparatus and Materials

The preparation of the ketones on a laboratory scale was carried out with standard chemical apparatus. The equipment employed on a pilot plant scale is illustrated in Figure 1:

The reactions were performed in a 265-liter (70-gallon) stainless-steel drum, *A*, with tapered bottom and outlet valve. The heat of mixing and heat of reaction were removed by tap water which was passed through 30.5 meters (100 feet) of copper coil, *B*, 1.59 cm. ($^5/_8$ inch) o. d., placed securely about the inner circumference of the drum. A Lightnin mixer, *C*, was used, turning a shaft 30.5 cm. (3 feet) long and 1.91 cm. ($^3/_4$ inch) in diameter. The blades were 7.63 cm. (3 inches) long and about 5.1 cm. (2 inches) wide.

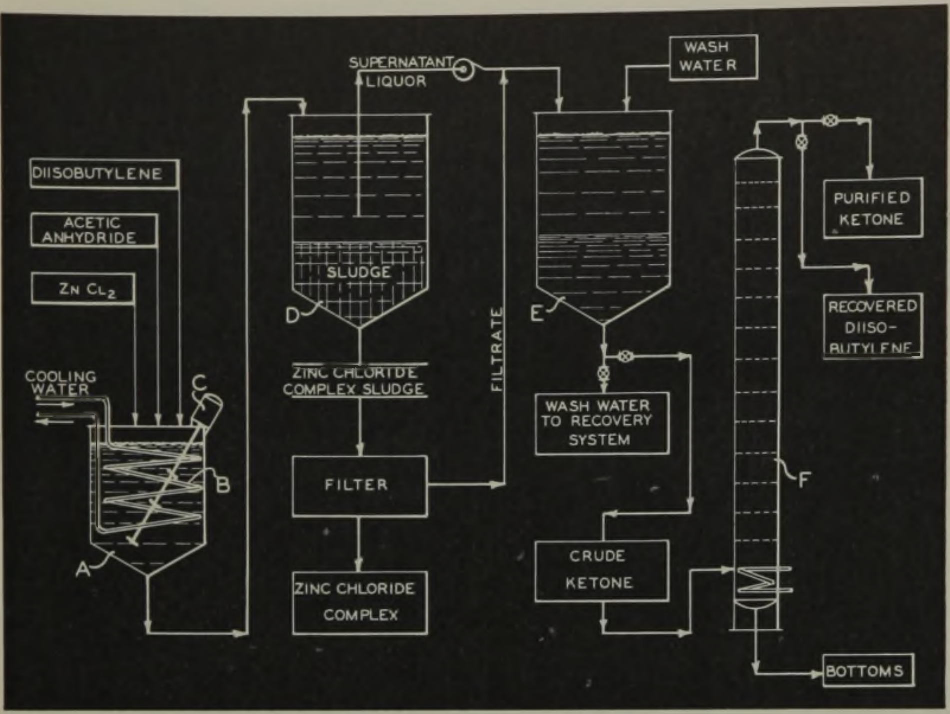

Figure 1. Pilot Plant for Synthesis of Ketones from Olefins and Acetic Anhydride

All chemicals employed in the manufacture of the ketones on a pilot plant scale were of technical grade; in the laboratory both technical and reagent quality chemicals were used. The technical acetic anhydride was from Carbide & Carbon Chemicals Corporation; the technical zinc chloride (granular, 94 per cent) from E. I. du Pont de Nemours & Company, Inc., and the boron trifluoride and technical antimony trichloride from Harshaw Chemical Company. Olefins were obtained from the following sources: Polymer gasoline manufactured by Union Oil Company of California; diisobutylene from *tert*-butyl alcohol by polymerization with sulfuric acid (*7*) and also from Shell Chemical Company and Standard Oil Company of New Jersey; diamylenes from Sharples Solvents Corp., cyclohexene from Eastman Kodak Company; and mixed octylenes from Shell Chemical Company.

Methyl Octenyl Ketones from Diisobutylene

Typical of the reaction of branched-chain olefins with acetic anhydride is the reaction of diisobutylene in the presence of suitable condensing agents to give methyl octenyl ketones:

$$C_8H_{16} + (CH_3CO)_2O \longrightarrow C_8H_{15}COCH_3 + CH_3COOH$$

The following conditions are typical of those employed for the preparation of these compounds from diisobutylene on a pilot plant scale, using the equipment represented in Figure 1.

Into the 265-liter stainless-steel drum are charged 74.0 kg. (163 pounds or 1.52 pound moles) of 95 per cent acetic anhydride and 77.2 kg. (170 pounds or 1.52 pound moles) of diisobutylene. While stirring there is added to the mixture a total of 52.6 kg. (116 pounds or 0.80 pound moles) of 94 per cent anhydrous zinc chloride at such a rate that the temperature is maintained below 45° C. by the cooling water. Initially the reactants form two phases, but the addition of approximately one pound of zinc chloride is sufficient to cause them to become miscible. Data for a typical pilot plant experiment in Table I show that three hours time was required for the addition of the zinc chloride. Granular zinc chloride was employed throughout this work since it dissolves more rapidly than the fused product. However, it must be added carefully so as to prevent accumulation of appreciable amounts at localized points and consequent formation of a sticky mass. When this occurs, the mechanical stirrer is inadequate to remove the mass from the walls of the reaction vessel. After the addition of all the zinc chloride, stirring is continued for about 3 hours to permit the last traces of zinc chloride to dissolve and to allow the reaction mixture to cool to nearly atmospheric temperature before it is transferred to the settling tank, *D;* if transferred when the final reaction period has been only 2.5 hours, there will be sufficient heat evolved in the settling tank to raise the temperature above 50° C. During the reaction period a complex forms between zinc chloride and a diketone, and crystallizes from solution to give small, well-defined crystals.

The reaction mass is allowed to remain in the crystallizing and settling tank for about 24 hours, after which time the supernatant liquid may be decanted from the crystalline sludge which has settled to the bottom of the tank. The sludge is then withdrawn and filtered to recover about 24.1 kg. (53 pounds or 0.16 pound mole) of zinc chloride complex and a further quantity of liquid product. The supernatant liquor and the filtrate are pumped into the washing tank, *E*, and washed with 178 liters (47 gallons) of water in three equal portions. The last traces of acetic acid are neutralized with a dilute solution of caustic. The crude washed ketone is first topped to remove unreacted diisobutylene (9.55 kg. or 21 pounds) and then fractionated to obtain a narrow-boiling ketone fraction (53.1 kg. or 117 pounds). The fractionation of the methyl octenyl ketone may be carried out at atmospheric pressure, *F;* however, it is more desirable to employ steam or reduced pressure as given in Table II. The steam or vacuum distilled product has the following typical properties:

Specific gravity, $d^{15.5}_{15.5}$	0.850
Refractive index, n^{25}_{D}	1.4537
Engler distillation (50 ml.), ° C.	
Initial	186.5
10% over	189.0
20%	189.5
50%	190.0
90%	191.0
Dry	193.5

Table I. Pilot Plant Data for Preparation of Methyl Octenyl Ketone

(Reactants: 170 lb. diisobutylene, 163 lb. 95% acetic anhydride, 116 lb. 94% zinc chloride; cooling water rate, 13.3 lb./min.; air temperature, 31° C.)

Time, Min.	Temperature, ° C. Reaction	Inlet water	Outlet water	Time, Min.	Temperature, ° C. Reaction	Inlet water	Outlet water
0[a]	21.0	...	...	115	41.6	32.8	39.6
5	24.4	...	...	120	41.0	32.8	39.2
10	28.0	...	...	125	41.2	32.8	39.0
15	33.8	...	...	130	41.4	32.8	39.4
20	38.0	...	...	135	41.8	32.8	39.6
25[b]	41.0	...	...	140	42.8	32.8	40.0
30	42.2	36.0	42.3	145	42.8	32.8	40.2
35	42.8	34.0	41.2	150	43.6	32.8	40.6
40	43.0	32.8	41.2	155	43.6	32.8	40.6
45	42.8	32.8	41.0	160	43.6	32.8	40.4
50	42.6	32.8	40.6	165	42.6	32.8	39.8
55	42.8	32.8	40.8	170	42.0	32.8	39.2
60	42.0	32.8	40.4	175	41.0	32.8	38.4
65	42.4	32.8	41.0	180[c]	40.4	32.8	38.2
70	42.6	32.8	40.8	195	38.6	32.8	36.8
75	42.8	32.8	41.2	210	37.2	32.8	35.8
80	42.8	32.8	41.0	225	36.2	32.8	35.0
85	43.0	32.8	40.4	240	35.8	32.8	34.6
90	43.0	32.8	40.2	255	35.0	32.0	33.8
95	42.8	32.8	40.4	270	34.6	31.8	33.4
100	42.0	32.8	40.0	285	34.0	31.4	33.2
105	41.6	32.8	39.6	300	33.8	31.2	33.2
110	42.0	32.8	40.0	480[d]			

[a] Anhydrous zinc chloride slowly added during entire reaction period.
[b] Cooling water passed through copper cooling coils.
[c] All zinc chloride added.
[d] Reaction product transferred to crystallizing and settling tank.

Ketones from Polymer Gasoline

Polymer gasoline, prepared commercially by copolymerizing propene-butene mixtures using solid phosphoric acid as catalyst, was found to be an excellent source of branched-chain olefins. A 113.6-liter (30-gallon) portion of commercial polymer gasoline was fractionated in a sixty-plate column (thirty theoretical plates) using a reflux ratio of 10 to 1. The four cuts corresponding to the most well-defined plateaus of the distillation curve (Figure 2) are indicated as *A*, *B*, *C*, and *D*, respectively. The properties of these fractions and the yields of ketone obtained by reaction with acetic anhydride in the presence of sulfuric acid and zinc chloride are given in Table III. When zinc chloride was used as the condensing agent, the reactions were carried out by first dissolving the zinc chloride (0.5 mole) in the acetic anhydride (1.0 mole), cooling, adding the hydrocarbon (1.0 mole) at 40–50° C. with vigorous shaking in a glass-stoppered bottle at frequent intervals, and then keeping at room temperature for 18 hours. When sulfuric acid was used as the condensing agent, the reactions were carried out by first mixing the 98 per cent sulfuric acid (10 ml.) with the acetic anhydride (1 mole), cooling, adding the hydrocarbon (1.0 mole) at 30–35° C. and allowing to stand at room temperature for 18 hours. By inspection of the yields of ketones in Table III, it is apparent that the lower boiling olefins gave the highest yields of ketones. Fractionation data and physical properties of the ketone from cut *B* are given in Table IV.

Polymer gasoline prepared commercially by the copolymerization of a feed gas containing butenes and propene in the ratio of 0.402 mole of butenes per mole of propene, using solid phosphoric acid as catalyst, was fractionated to obtain two broad cuts which represented 68 per cent of the stabilized gasoline. The lower boiling fraction, 90–100° C., gave a 53 per cent yield of ketone; and the higher boiling fraction, 100–110° C., gave a 51 per cent yield of ketone using zinc chloride as the condensing agent. This represents the conversion of over 50 per cent of the olefins contained in the polymer gasoline to ketones.

Constitution of Unsaturated Methyl Ketones

In all cases where the constitution of the ketones obtained by reaction of olefins with acetic anhydride was determined, they were found to be unsaturated aliphatic methyl ketones. Only certain olefins are reactive—in general, those olefins which have a branched chain not far removed from the double bond. The point of attachment of the acetyl group to the olefin is not always closest to the double bond, as might be expected.

The general method for determining the constitution of the unsaturated methyl ketones consisted of the following: The ketones were purified by fractionation and then converted to a solid derivative, usually the semicarbazone whose ultimate analysis was determined. Since most of the branched-chain olefins used were mixtures of isomers, each of which is capable

Table II. Fractionation of Methyl Octenyl Ketones from Diisobutylene

(10 theoretical plates; reflux ratio 8:1)

Cut No.	Still Temp.[a], ° C.	Vapor Temp.[a], ° C.	Pressure[a], Mm. Hg	Volume, Ml.	n_D^{25}	$d_{15.5}^{15.5}$
1	123.3	108.9	50	88	1.4472	0.841
2	121.1	111.1	50	107	1.4525	0.850
3	121.7	111.7	50	101	1.4534	0.850
4	122.8	111.7	50	103	1.4541	0.850
5	123.9	111.7	50	103	1.4542	0.850
6	125.0	111.7	50	104	1.4542	0.850
7	126.7	111.7	50	102	1.4541	0.850
8	131.7	112.2	50	97	1.4542	0.850
9	132.8	112.2	45	100	1.4543	0.848
10	134.4	110.0	37	99	1.4541	0.846
11	141.1	107.8	30	94	1.4541	0.844
12	141.1	127.8	20	104	1.4522	0.816
13	138.9	127.8	20	96	1.4505	0.804
14	138.9	128.9	20	107	1.4501	0.802
15	138.9	128.9	20	103	1.4500	0.801
16	143.3	128.9	20	96	1.4495	0.800
17	148.9	129.5	20	100	1.4495	0.800
18	175.6	128.9	20	93	1.4497	0.802
Bottoms	...	...	..	135	...	...
Loss	...	...	..	68	...	...
Charge	...	...	..	2000	...	...

[a] Uncorrected.

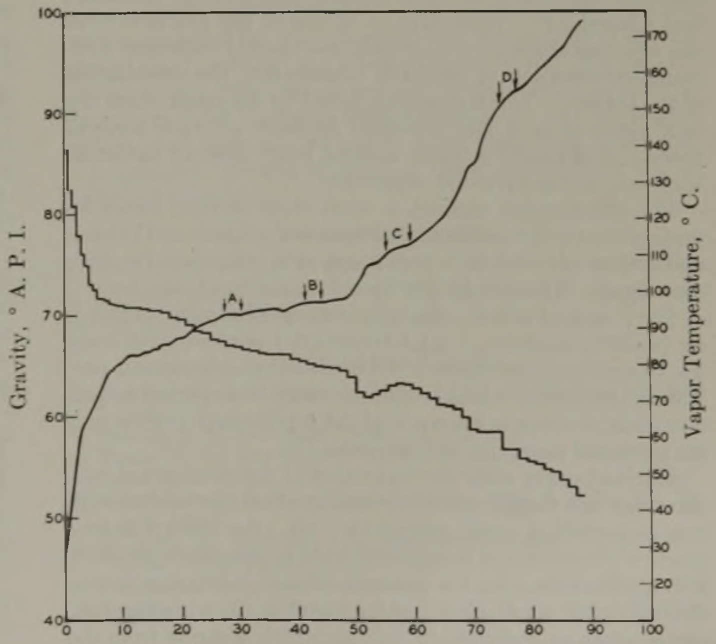

Figure 2. Fractionation of Commercial Polymer Gasoline

Table III. Ketones from Polymer Gasoline Using Zinc Chloride and Sulfuric Acid as Condensing Agents

Cut No.	Assumed Formula	B. P.[a], ° C.	Sp. Gr., $d^{15.5}_{15.5}$	Ketone Yield[b], Mole %	
				H_2SO_4	$ZnCl_2$[c]
A	C_7H_{14}	93.3	0.702	36	45
B	C_7H_{14}	97.2	0.698	41	62
C	C_8H_{16}	111–113	0.681	35	39
D	C_9H_{18}	151–155	0.634	26	25

[a] Uncorrected.
[b] Based on assumed formula.
[c] Condensing agent used.

Table IV. Fractionation of Ketone from Cut *B* of Polymer Gasoline

(20 theoretical plates, reflux ratio 10:1, pressure 40 mm. Hg)

Cut No.	Still Temp., ° C.	Vapor Temp., ° C.	Vol., Ml.	n^{27}_{D}	$d^{15.5}_{15.5}$
1	94	70.0–81.0	35	1.4347	0.855
2	94	81.0–82.0	30	1.4362	0.854
3	94	82.0–82.5	37	1.4367	0.854
4	94	82.5–83.0	57	1.4368	0.854
5	96	83.0–83.5	51	1.4368	0.853
6	97	83.5–84.0	55	1.4368	0.853
7	98	84.0–84.0	67	1.4370	0.853
8	102	84.0–84.5	78	1.4372	0.853
9	108	84.5–85.0	22	...	...
Bottoms		Above 85.0	37	...	...

of existing in *cis* and *trans* forms, it was generally not possible to obtain solid derivatives of constant melting point. The existence of the acetyl group in the methyl ketones was ascertained by the haloform reaction. The method of Fuson and Tullock (*3*), which employs dioxane as a solvent with the sodium hypoiodite in water, was found to be effective; in the absence of dioxane, negative results were obtained due to the insolubility of the ketones in water. The presence of a double bond in the ketones was indicated by bromine absorption in carbon tetrachloride or glacial acetic acid solution and by bromide-bromate titration; some of the unsaturated ketones exhibit appreciable substitution of halogen as well as addition. The position of the double bond in the unsaturated ketones was determined by ozonolysis in pentane solution at about −40° C. The ozonides were usually decomposed by water alone or with water and zinc dust as described by Whitmore and Church (*8*). Identification of one of the products from the decomposition of the ozonide was usually sufficient additional information to establish conclusively the constitution of the ketone. This was accomplished by the preparation of a solid derivative of the ozonolysis product, ultimate analysis thereof, and finally a mixed melting point with an authentic specimen of the expected compound.

The considerable amount of work done in the present investigation on the problem of structure of unsaturated ketones and olefins resulted in a rapid and safe procedure for their ozonolysis. This will be described in some detail elsewhere.

The principal ketone obtained from diisobutylene, which is an isomeric mixture of 2,4,4-trimethyl-1-pentene with some 2,4,4-trimethyl-2-pentene, is 4,6,6-trimethyl-3-heptene-2-one. This is the ketone which would normally be expected to predominate, since it is known that 2,4,4-trimethyl-1-pentene is the principal isomer in diisobutylene (*7*).

Simultaneously with the formation of the methyl ketones, diketones are formed by the reaction of certain olefins with two molecules of acetic anhydride—viz., the methyl ketone reacts with additional acetic anhydride to give what probably is a 1,3-diketone. In the presence of zinc chloride as a condensing agent, these diketones are found as zinc chloride complexes, often as well-defined crystals which separate from the reaction mass. Work is being carried on to determine the structure of these zinc chloride complexes, a problem which is complicated by their stability and the difficulty involved in removing zinc chloride.

Effect of Some Condensing Agents

Various condensing agents were tried in the reaction of acetic anhydride with branched-chain olefins. Many were without effect; others, although effective for condensation, caused undesirable reactions such as polymerization of the olefin and ester formation. Zinc chloride was found to be most effective with practically all the olefins tried. Some data on the effect of the amount of zinc chloride used in the reaction of acetic anhydride with diisobutylene are given in Table V. Aluminum chloride caused considerable polymerization of olefins and, consequently, low yields of ketone. When used with diisobutylene, the yield of ketone was especially low, producing a liquid product of very wide boiling range. Boron trifluoride was found to be effective, provided it was used in low concentrations. Acetic anhydride absorbs one mole of boron trifluoride, forming a crystalline compound (*1*). This crystalline addition compound was treated with equal moles of diisobutylene at room temperature to yield only polymers of diisobutylene and no ketone. By first mixing the acetic anhydride and the diisobutylene and then passing in the boron trifluoride at 0–10° C. until no more was absorbed, a 65 per cent yield of methyl octenyl ketones was obtained; the unreacted diisobutylene was polymerized. Sulfuric acid was found quite effective as a condensing agent; however, there was usually considerable evidence for reaction

Table V. Reaction of Diisobutylene with Acetic Anhydride in the Presence of Zinc Chloride

(Reaction temp. 40° C. during addition of diisobutylene, then room temp.; reaction time 18 hours; reactants 1.0 mole diisobutylene, 1.0 mole acetic anhydride, variable amounts of $ZnCl_2$)

Run No.	$ZnCl_2$, Moles	Recovered, ml.		Bottoms[b], Ml.	Ketone Yield, Mole %
		Diisobutylene	Diketone[a]		
G810-A	0.13	80	5	3	39
G810-B	0.25	60	10	4	44
G813-A	0.40	51	18	3	55
G809	0.50	35	19	7	57
G813-B	0.60	29	20	6	60

[a] As reaction product with NH_4OH.
[b] Residue after distillation of ketone at atmospheric pressure.

Table VI. Reaction of Diisobutylene with Acetic Anhydride in the Presence of Sulfuric Acid

(Reactants, 2 moles diisobutylene, 2 moles acetic anhydride; reaction time 18 hours)

Run No.	98% H_2SO_4, Ml.	Temp., ° C.	Diisobutylene Recovered, Ml.	Bottoms[a], Ml.	Ketone Yield, Mole %
F6897-A	15	25	135	11	35
-B	20	25	102	22	41
-C	25	25	83	25	39
-D	30	25	82	56	34
-E	35	25	89	51	31
F6898-A	14	25	159	8	25[b]
-B	16	25	145	8	30[b]
-C	18	25	125	8	34[b]
-D	20	25	112	10	38[b]
-E	15	113[c]	105	29	41
-F	20	95[c]	104	30	38
F6900-A	15	90[c]	143	5	31
-B	20	95[c]	110	10	39
-C	25	95[c]	91	18	41
F6883-C	50	104[c]	54	30	25[d]
F6886-A	3	B. p.	240	6	8[e]
-B	10	B. p.	159	9	36[e]
-C	15	B. p.	81	28	47[e]
F6888-A	16	104[c]	73	34	39[e]
-B	50	104[c]	50	25	28[d]
-C	20	104[c]	135	10	30[d]

[a] Residue after distillation of ketone at atmospheric pressure.
[b] Diisobutylene added more rapidly than in previous runs.
[c] During addition of diisobutylene.
[d] Reaction time 3 hours.
[e] Reaction time 1 hour.

between the olefins and sulfuric acid, and the resulting ketones were more difficult to purify. Some data dealing with the reaction of acetic anhydride with diisobutylene using sulfuric acid as a condensing agent are given in Table VI.

Mild catalysts such as antimony trichloride are effective condensing agents with some branched-chain olefins.

Heat of Reaction and Coefficient of Heat Transfer from Pilot Plant Data

The heat of reaction when one mole of diisobutylene is reacted with one mole of acetic anhydride in the presence of 0.5 mole of zinc chloride at 36–37° C. was determined in a calorimeter to be 8800 calories. These mole ratios are the same as that used in the pilot plant, the data of which are in Table I. From the latter data the coefficient of heat transfer between the copper coil and the reaction mixture was calculated during the 1-hour period following the initial 40-minute period (i. e., from 40 to 100, inclusive). The following well-known equation was used:

$$Q/\Theta = HA\Delta T$$

From the amount of cooling water and the increase in temperature, Q/Θ = 11,350 B. t. u. The $^5/_8$-inch copper coil of 100-foot length has an area of 16.3 square feet. The temperature difference at the entrance from cooling coil to reaction mixture is 17.8° F.; at the exit it is 3.6° F. This gives a log mean temperature difference of 8.9° F. The value of H, the coefficient of heat transfer hence is 78.3 B. t. u. per (hour) (square foot) (° F.). These data are important in the design of plant equipment.

Discussion

The reaction of olefins with acetic anhydride, as previously described, appears to be a special case of the Friedel-Crafts type of condensation. In two important respects, however, it differs from the usual synthesis of ketones from aromatic hydrocarbons and acetic anhydride or acetyl chloride. From the data in Tables V and VI, it will be noted that no advantage is gained when more than about 0.5 mole of condensing agent is used per mole of reactants; by contrast, 1 mole or more has always been used when aluminum chloride is employed in Friedel-Crafts condensations. In various laboratory-scale experiments with diisobutylene it has been found that as much as 10 moles of ketone have been produced per mole of zinc chloride. Similarly, sulfuric acid has an efficiency approximately equal to that of zinc chloride. This appears to be the first instance in which sulfuric acid has been shown to bring about condensations of acid anhydrides to give ketones. Although acetic acid is formed as a reaction product, no appreciable amount of esters was formed, provided the amount of sulfuric acid used was small.

The reaction is simple to execute; the major precaution which must be taken is to remove the heat of reaction in order to prevent the mixture from reaching temperatures which give high-boiling polymers from the olefins and, consequently, a lower yield of ketone. The method of catalyst addition employed in the pilot plant was different from that used in most of the laboratory experiments, without substantial variation in yield, and was primarily a matter of convenience. Preliminary addition of zinc chloride to the acetic anhydride as carried out in the laboratory produces a rather viscous fluid with liberation of considerable heat. When the olefin is added, further heat is liberated, and the rate of reaction can be partially controlled by the vigor of shaking or stirring. In attempting to use the same procedure on a pilot plant scale, it was found that the viscosity of the zinc chloride–acetic anhydride solution was so great that the mechanical stirrer was inadequate to dissolve all the zinc chloride. Control of temperature during addition of olefin was also more difficult.

The data in Table II are included partly to illustrate an undesirable type of side reaction, polymerization of the olefins. In this experiment the zinc chloride was suspended in the diisobutylene with vigorous stirring while acetic anhydride was added slowly. Inspection of Table II shows that there is a sharp rise in the temperature distillation data, following removal of the ketone, and a large proportion of a higher boiling fraction is obtained. This product appears to be tetraisobutylene from polymerization of diisobutylene under these conditions. Similarly, it will be noted that under some conditions boron trifluoride gave only polymers, whereas a good yield of ketone was obtained when the boron fluoride was introduced gradually.

An additional side reaction occurs with zinc chloride as a condensing agent to give a diketone–zinc chloride addition product as a crystalline compound which separates readily from the reaction mixture. Attempts to free this diketone complex of zinc chloride with liberation of the zinc chloride residue have been unsuccessful. Reaction of the complex in water solution with ammonium hydroxide yields a nitrogen base which was used to determine the amount of diketone formed, as given in Table V.

Polymer gasoline has been emphasized in the present investigation because it represents a cheap source of branched-chain olefins in large volume. The data obtained indicate that the number of isomers present in any given boiling point range is not great and that ketone fractions suitable for many industrial uses may readily be obtained by simple fractionation. It is possible that the method may be extended to a determination of the structures of the original olefins through a study of their ketone derivatives. Other olefins which have been studied less extensively include mixed amylenes, mixed octylenes from copolymerization of 1-butene and 2-butene with isobutylene, diamylenes, and cyclohexene.

The utilization of new derivatives of this type cannot readily be estimated. However, a number of interesting possibilities have been developed. Because of their pleasant odor they may be of utility in the production of the cheaper grades of perfumes, particularly those used in industrial products. They are also of interest as high-boiling solvents. A number of derivatives have been prepared by standard procedures, such as the corresponding methyl octyl ketone, methyl octyl carbinol, and esters of the carbinol. These have characteristic odors which are also of interest in perfumes. Reduction of the methyl octenyl ketone to the methyl octenyl carbinol has been carried out in good yield with aluminum isopropoxide. Details of many of these preparations will be published elsewhere.

Acknowledgment

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Large-Scale Production of Azotobacter

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The production of azotobacter by a large-scale technique is described. The final fermentation is carried out in a 200-gallon pilot-plant yeast fermenter. Yields were obtained of 10–11 pounds of cell paste (85 per cent moisture) in 300 liters of medium in 32 hours. The efficiency of the conversion of sugar to cells was 15 per cent. The total nitrogen fixed was 32 mg. per 100 ml., equal to about 96 grams in the fermenter.

Assays of the cells for several members of the vitamin B complex show that azotobacter cells grown in a nitrogen-free sucrose–mineral salts medium have a vitamin content equal or superior to that found in yeast. When grown in a molasses medium, the cells are higher in biotin, thiamine, and pantothenic acid than when grown in a sucrose medium, and are slightly lower in nicotinic acid and riboflavin.

A number of cell-free enzymes have been prepared from cells grown by this method. The results are discussed as to possibilities of improving the yields when growing the organisms on a large scale. Several uses are suggested.

THE availability of an abundant supply of azotobacter would greatly facilitate many researches. Recent contributions in the field of biological nitrogen fixation have supplied evidence for the similarity of the nitrogen-fixing reaction in the symbiotic system (nitrogen fixation through association of root nodule bacteria and leguminous plants) and the free-living nonsymbiotic system of the organisms of the family Azotobacteriaceae. The nonsymbiotic system of azotobacter offers certain advantages for studies on the mechanism of the nitrogen-fixing reaction, especially those which deal with the enzyme systems concerned directly or indirectly in the fixation reaction. A study of the cell-free enzymes of azotobacter may give valuable leads to the mechanism of the reaction. Large quantities of cells are a prerequisite for such studies.

Various microorganisms have proved to be excellent sources of vitamins and a variety of other biological products. Since azotobacter possesses the highest respiration rate of any known organism, it might be expected to contain a high level of respiratory enzymes and vitamins; this point was investigated in connection with the development of a technique for growing azotobacter on a large scale.

Fermentation Methods

Azotobacter vinelandii is grown in Burk's (*1*) mineral salts solution plus 2.0 per cent sucrose, sodium molybdate (0.1 p. p. m. molybdenum), and ferrous sulfate (3 p. p. m. iron). In certain experiments high-test Cuban molasses replace sucrose as the carbohydrate source. The temperature for growth is 30° C., the pH 7.2.

First-generation cultures are grown in twelve 6-ounce bottles containing 15 ml. of medium per bottle. After 24 hours 12 Roux bottles, each containing 100 ml. of medium, are inoculated with these cultures. After a second incubation period of 24 hours, each of six 10-liter bottles containing 6 liters of medium are inoculated with two Roux bottle cultures. As shown in Figure 1, the bottles are closed with sterile units consisting of rubber stoppers fitted with necessary glass and rubber tubing connections. A porous stone diffuser connected to the inlet glass tubing is suspended in the medium. The medium is aerated rapidly through the porous stone diffusers with air sterilized by passage through a large cotton filter. Smaller cotton filters are attached to each bottle. After 24 hours the final culture is inoculated with the bottle (third-generation) cultures. The apparatus for growing the final culture (Figure 2) is a 200-gallon copper fermenter used for the pilot-scale production of yeast. Its fittings are steam and cold water lines, a line furnishing air filtered through cotton, and a supplementary air line from a motor-driven blower. This air, which is not filtered, is used only when large volumes of air are

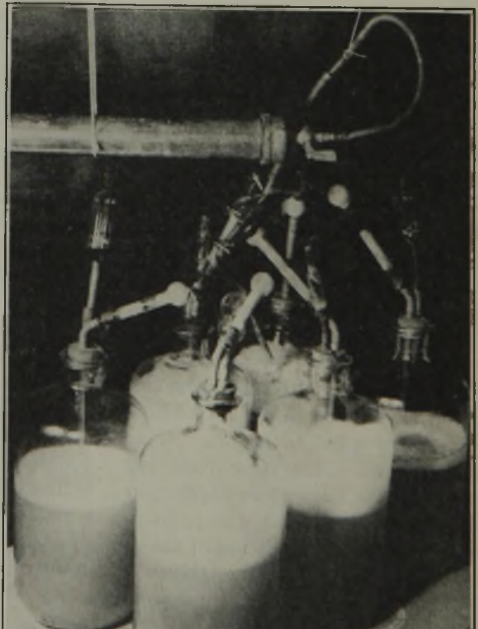

FIGURE 1. TEN-LITER BOTTLES FOR SECOND-GENERATION CULTURES

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needed and danger from contamination is at a minimum. The steam for heating or water for cooling is supplied through an interior coil; the air line is fitted inside the fermentation tank with large porous stone diffusers.

The medium (250–300 liters) is placed in the fermenter and sterilized for 2 hours at 10 pounds steam pressure. The medium is cooled by passing cold water through the inner copper coil and is then inoculated with 36 liters of the 24-hour third-generation culture. The medium in the fermenter is aerated rapidly for 30–34 hours, during which time periodic samples are removed from a jet at the bottom of the fermenter for microscopic examination and for determinations of total sugar, total nitrogen, soluble nitrogen, pH, dry weight of cells, and Q_{O_2} (cu. mm. oxygen uptake per mg. dry weight of cells per hour). Q_{O_2} (N) values (cu. mm. oxygen uptake per mg. cell nitrogen per hour) are calculated from the Q_{O_2} values and the percentage nitrogen in the cell.

TABLE I. SUMMARY OF ANALYTICAL RESULTS

Time, Hours	Experiment 2								Experiment 3			
	Mg. Nitrogen/100 Ml.		Dry wt., mg./100 ml.	Sugar, mg./100 ml.	Oxygen Uptake			pH	Total N, mg./100 ml.	Dry wt., mg./100 ml.	Sugar, mg./100 ml.	pH
	Total N	Sol. N			Cu. mm./hr./ml.	Q_{O_2}	Q_{C_2} (N)					
0	1.19	..	10.8	1306	..	..	....	7.2	2.19	50.9	1950	7.2
8	3.78	0.36	33.5	1132	550	1640	16,200	7.3	4.35	67.3	1750	7.22
14	9.99	0.79	77.7	834 1330[a]	1700	2185	18,500	7.0	12.00	124.2	1388	7.05
20	14.60	1.08	118.4	1036 1570[a]	2205	1865	16,300	7.0	24.28	223.1	698	7.04
26	17.15	1.17	147.5	1404	1970	1330	12,300	6.8	29.32	273.1	396	7.07
32	19.13	1.23	156.0	1271	1675	1070	9,400	6.6	33.40	314.8	144	7.72

[a] Sucrose added to fermentation.

Nitrogen determinations are made by the semimicro-Kjeldahl method of Umbreit and Bond (*9*). Soluble nitrogen is determined in the same manner on an aliquot of the supernatant obtained in making the dry weight determination. Total dry weights are obtained by centrifuging 100-ml. aliquots in celluloid cups at 4500 r. p. m. for 15 minutes; the cells are resuspended in distilled water and centrifuged for 10 minutes at 3500 r. p. m. in tared glass centrifuge cups. The cells are then dried at 95° C. and weighed.

Total sugars are run by the method of Stiles, Peterson, and Fred (*7*). Q_{O_2} values are measured by making the proper dilution of the cells, placing them in the Warburg microrespirometer, and observing the rate of oxygen uptake for 30 minutes at 32° C. pH determinations are made with the Beckman pH meter.

At the end of the fermentation the cells are concentrated in a power-driven separator of the type used in the manufacture of yeast. Two passages of the final ferment through the separator reduce the final volume from 300 to approximately 50 liters, or a sixfold concentration of the bacterial cells. The cell cream is then concentrated to a paste in a Sharples supercentrifuge at a speed of 35,000 r. p. m. A yeast press was not available, but it would perhaps be equally suitable for recovering the cells.

Fermentation Efficiency

EXPERIMENT 1. This preliminary experiment was made to test the methods and become familiar with the operation of the equipment. Cotton-filtered air from a 30-pound pressure line was used throughout. No extensive analyses were made during this run which was stopped after 33.5 hours. After 19.5 hours, 6.25 mg. of nitrogen had been fixed per 100 ml. of medium; the final fixation was 12.2 mg. per 100 ml. Subsequent experiments indicate that the fixation in this experiment may have been limited by diminished carbohydrate supply (2 per cent sucrose furnished). The total yield of cell paste was 1675 grams with a moisture content of 85.2 per cent. This is equivalent to 248 grams of dry cells. Microscopic examinations showed no contamination during the period of growth.

TABLE II. EFFICIENCY OF CELL PRODUCTION AND NITROGEN FIXATION

Time, Hours	Mg. per 100 Ml.			N Fixed, Mg./g. Sugar	Sugar Converted to Dry Cells, %
	N fixed	Dry wt.	Sugar used		
		Experiment 2			
0–8	2.56	22.7	174	14.7	13.1
8–14	6.24	34.3	298	20.9	11.5
14–20	4.63	40.7	298	15.5	13.7
20–26	2.53	29.0	166	15.3	17.5
26–32	1.98	8.8	133	14.9	6.6
		Experiment 3			
0–8	2.16	16.14	200	10.8	8.2
8–14	7.65	56.9	362	21.2	15.7
14–20	12.28	98.9	690	17.8	14.33
20–26	5.04	50.0	302	16.7	16.55
26–32	4.08	41.7	252	16.2	16.19

EXPERIMENT 2. Sucrose was again used as the carbohydrate source, and aeration was by cotton-filtered air from the 30-pound pressure line. Periodic analyses were made for total nitrogen, soluble nitrogen in the supernatant after cells were removed, dry weight of cells, total sugar, Q_{O_2}, and pH. Microscopic examinations were also made at each harvest.

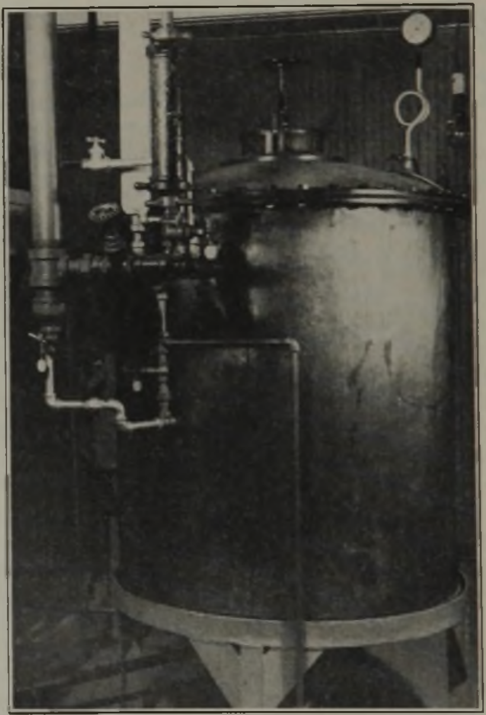

FIGURE 2. 200-GALLON COPPER FERMENTER FOR FINAL CULTURES

The analytical results of experiment 2 are given in Table I and a graph of the data in Figure 3. The efficiency of production during various periods is summarized in Table II. The total yield of cell paste (Figure 4) was 2350 grams. The cell paste contained 79.6 per cent moisture, corresponding to a yield of 480 grams of dry cells. The dried cells contained

11.98 per cent nitrogen; thus 57.5 grams of nitrogen were fixed.

Figure 3 shows that the logarithmic growth phase was attained quickly (as would be expected with the large inoculum) and continued through the first 14 hours. Table II indicates that the greatest efficiency of production was attained in the log phase during the 8–14 hour period. During this time 20.9 mg. nitrogen were fixed per gram of sucrose utilized, as compared to 14.7 mg. fixed in the previous 8-hour period (the first 8 hours of the run) and 15.5 mg. during the subsequent 6-hour period. However, the dry weight of cells obtained per unit of sucrose utilized was somewhat lower during this period. In other experiments the efficiency in converting sugar to cells was also higher during the log phase.

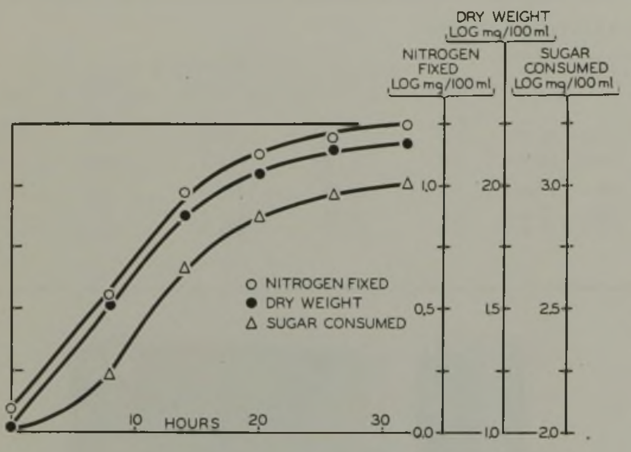

Figure 3. Graph of Data for Experiment 2

The over-all efficiency (0–32 hours) was 16.8 mg. nitrogen fixed per gram of sucrose utilized, an excellent result for this reaction. Cellular material represented 13.5 per cent of the sugar utilized. The rate of respiration was highest during the log phase when the Q_{O_2} was 2185 and the Q_{O_2} (N) was 18,500.

Experiment 3. Since molasses furnishes carbon more economically than commercial sucrose, high-test Cuban molasses was tried as the source of carbohydrate. The culture was aerated with cotton-filtered air from the 30-pound laboratory air pressure line during the first 14 hours, and then aerated more rapidly with unfiltered air from the motor-driven blower during the remainder of the fermentation.

Samples were removed periodically for analysis. The results are given in Tables I and II and Figure 5. The growth curve is typical. The lag phase continued about 6–8 hours, followed by the log phase which lasted through the 20-hour period; at that time the phase of negative acceleration was reached. In experiment 2 the log phase lasted only until the 14–16 hour period and had reached the phase of negative acceleration at 20 hours. The difference can be explained largely by the fact that in experiment 3 a greater rate of aeration (use of motor-driven blower) was started at the 14-hour point and continued throughout. The analytical data (Table II) show clearly the effect of additional aeration during the 14–20 hour period. The comparable results of experiments 2 and 3 during this period are as follows:

	Total Increase during 14–20 Hr. Period over Preceding 14 Hr., %	
	Expt. 2	Expt. 3
Total nitrogen fixed	46.0	102.0
Total cell yield	52.8	79.5[a]
Total sugar utilized	60.2	119.5

[a] Smaller percentage increases in cell yield in Expt. 3 can be explained by the high 0-hour dry weight due to the higher solids content of the molasses medium.

The effect of additional aeration is further emphasized by comparing the two experiments during the 8–14 hour period when the rates of aeration were identical:

	Total Increase during 8–14 Hr. Period over Preceding 8 Hr., %	
	Expt. 2	Expt. 3
Total nitrogen fixed	162.0	176.0
Total cell yield	132.0	85.0
Total sugar utilized	171.0	181.2

The latter table shows that, during a period in which the rate of aeration was identical in both experiments, the rate of nitrogen fixation, increase in cell yields, and sugar utilization were nearly the same. It is impossible to say definitely what the effect of still greater rates of aeration would be; owing to the highly aerobic nature of azotobacter, one would expect further increasing rates of fixation with increasing rates of aeration although the degree of increase per unit increase in aeration would become less. This has proved to be true in the production of commercial yeast in grain and molasses media.

In experiment 3, 31.2 mg. nitrogen were fixed per 100 ml. of medium in 32 hours which is excellent for large-scale procedures. This represents a total for the 300 liters of 93.6 grams nitrogen fixed. The net cell yield was 263.9 mg. per 100 ml. or a total of 792 grams of dried cells, corresponding

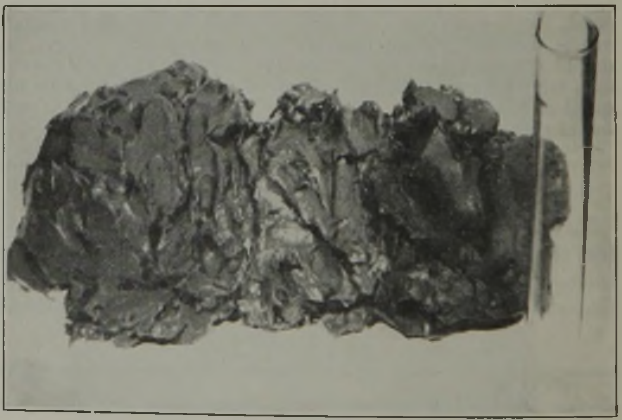

Figure 4. Total Yield, 2350 Grams, of Cell Paste (100-Ml. Graduate Shown for Comparison)

Table III. Vitamins of B Complex in Cells of *Azotobacter vinelandii*

	Riboflavin		Nicotinic acid		Biotin			Thiamine		Pantothenic Acid		
					Cells					Cells		
	Cells[a]	Medium[b] (cells removed)	Cells	Medium (cells removed)	Hydrolyzed	Unhydrolyzed	Medium (cells removed)	Cells	Medium (cells removed)	Hydrolyzed	Unhydrolyzed	Medium (cells removed)
Sucrose as carbohydrate source	350	1.0	590	3.0	2.56	0.039	0.0098	33.0	0.0	152	59	0.77
Molasses as carbohydrate source	304	...	480	...	4.23	0.44	....	96.0	...	184	70	..
Brewer's yeast, av.	50	...	550	...	2.0	0.8	....	40	...	150	50	..

[a] Values for cells expressed in micrograms per gram dry cells.
[b] Values for medium (cells removed) expressed in micrograms per ml.

to 5270 grams (11.6 pounds) of cell paste with a moisture content of 85 per cent.

Table II shows that the greatest efficiency in nitrogen fixation was again evident during the log growth phase (8–14 hour period) when 21.2 mg. nitrogen were fixed per gram sucrose used. As regards cell yield from sugar utilized, the greatest efficiency was unexpectedly attained during the latter part of the fermentation. This may be explained in part by the more rapid rate of aeration during this part of the fermentation. The differences in efficiency are small, however, and may not be significant. The over-all efficiency (0–32 hours) was 17.3 mg. nitrogen fixed per gram of sugar used; 14.6 per cent of the sugar utilized was converted to cells.

Bacteria in Preparation of Cell-Free Enzymes

Many of the cells obtained in the foregoing experiments have been used in the preparation of cell-free enzymes. The techniques for obtaining the cell-free preparations and the results were reported by Lee, Burris, and Wilson (*3*). Oxalacetic acid and α-ketoglutaric acid decarboxylases, hydrogenase, cytochrome oxidase, and dehydrogenases for succinic, malic, and lactic acids have been demonstrated in cell-free preparations of azotobacter.

Vitamins in Azotobacter

Current interest in microorganisms as sources of vitamins led to an examination of azotobacter for various members of the B complex. The results are given in Table III. Assays have been run on the cells grown on a medium containing pure sucrose (experiment 2) and molasses (experiment 3) as the carbon sources. Average values for the amount of these vitamins in brewer's yeast are included for comparative purposes. Microbiological assay methods were used for biotin (*4*), pantothenic acid (*8*), riboflavin (*5*), and nicotinic acid (*6*). The thiochrome method was used in the thiamine determinations (*2*). Results of experiment 2 show that *Azotobacter vinelandii*, growing in a nitrogen-free mineral salts medium, synthesizes various members of the B complex to such an extent that its cells are at least equal to brewer's yeast in all vitamins for which assays were made and are superior in their contents of biotin and riboflavin. When grown in molasses medium (experiment 3) azotobacter cells again exceed brewer's yeast in contents of riboflavin and biotin and, in addition, are higher in thiamine. The organism when grown in molasses contains more biotin, thiamine, and pantothenic acid than when grown in sucrose medium. On the other hand, molasses-grown cells appeared to be slightly lower in riboflavin and nicotinic acid.

Advantages of the Method

Although azotobacter is a rapidly growing, highly aerobic organism, about 15 per cent of the total sugar consumed in these experiments was recovered in dry weight of cells. This is a good yield when one considers that this organism has a very high rate of respiration and would be expected to convert most of an available carbon source to carbon dioxide and water. One must also consider that, as the organism was grown in a nitrogen-free medium, its nitrogen supply was obtained through the fixation of atmospheric nitrogen. Energy for this fixation process is furnished by the carbon source in the medium which would further reduce the efficiency of the organism in converting a carbon source to cellular material.

Yeast grown under optimum conditions in grain wort medium with rapid aeration commonly give yields of 30 per cent dry yeast from the sugar utilized. This is superior to that obtained with azotobacter. However, the excellent results with azotobacter thus far indicate that studies to determine the optimum conditions of aeration, sugar concentration, salt mixture, age of inoculum, conditions for growing inoculum, and other factors may aid not only in increasing the efficiency of the process but also in cutting down the time of fermentation and increasing the yield of cells per unit volume of medium.

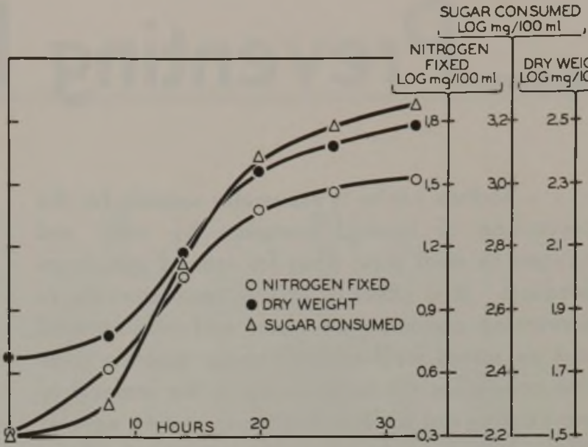

Figure 5. Graph of Data from Experiment 3

The organism grows rapidly in an inexpensive mineral salt–sugar medium. Molasses is perhaps the cheapest source of sugar for the medium during peacetime, and it is an excellent carbohydrate source for the growth and fixation of nitrogen by azotobacter in this process. Further studies may show that the mineral salts contributed to the medium by the molasses may allow reduction in the quantities of salts which must be added.

Several points favor the growth of azotobacter on a large scale: (1) The organism grows rapidly in an inexpensive nitrogen-free medium with acceptable yields. The use of such a medium would greatly reduce troubles from contamination. (2) Azotobacter can synthesize vitamins to such an extent that the cells are equal or superior to yeast in vitamin content. Thus it has potential use as a food supplement comparable to the present day use of yeast. (3) The interesting biochemical nature of the organism—namely, high rate of respiration—makes it a potential source for study, isolation, and manufacture of new biochemical compounds.

Acknowledgment

The copper fermenter was kindly loaned to the University of Wisconsin by the Red Star Yeast Company of Milwaukee. The authors are indebted to various members of the Departments of Agricultural Bacteriology and of Biochemistry of the university for the vitamin assays.

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Preventing Internal Corrosion

SODIUM NITRITE TREATMENT FOR GASOLINE LINES

» » » Sodium nitrite is especially suitable for the prevention of internal corrosion by water and oxygen in steel pipe lines for refined petroleum products. It is effective in low concentrations in preventing corrosion on clean mill-scale-covered and on rusted steel surfaces under gasoline pipe line conditions; it tends to aid in the removal of pre-existing rust scale and blisters; and no adverse effects have been found on the quality of refined products moved through a pipe line.

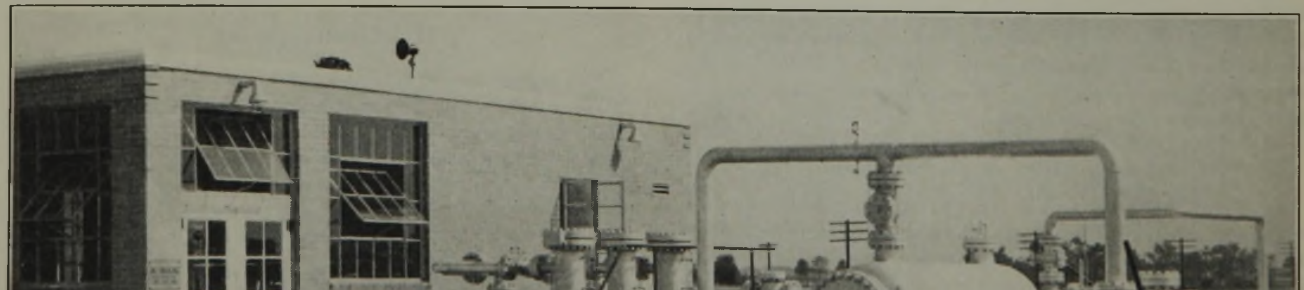
Sodium nitrite has been successfully used for the inhibition of internal corrosion in more than 800 miles of pipe lines for refined oil products. The use of mechanical scraping measures for the removal of old rust scale while injecting sodium nitrite continuously into a pipe line has been shown to achieve a clean nonrusting pipe line with a flow factor significantly higher than the design value usually taken for new pipe.

PRACTICALLY every long pipe line has had to contend with internal corrosion which produces scale and blisters of corrosion products, extending in some degree of severity through the entire length of the steel line. The important practical results have been decrease of throughput capacity and increase of operating costs for a line (*11*). Other, usually less important, results are deterioration or contamination of the refined products and loss in thickness of pipe wall. The steps taken to counteract these adverse effects have been chiefly palliative, although some attempts have been made to apply preventive measures (*16*). None of the preventive measures thus far proposed appear to have had success.

A study of this problem was undertaken at the Emeryville Laboratories of Shell Development Company in cooperation with the Products Pipe Line Department of Shell Oil Company, Inc. The most attractive possibilities were offered by sodium nitrite as a corrosion inhibitor. It was tested in part of a Shell products line with encouraging results. Extension of the treatment was gradually made until it was being applied to all of the products lines operated by Shell Oil Company. After over two years of use, the inhibitor and its method of application have provided a complete and economical solution of the problem of internal corrosion of products pipe lines (*21*).

The Corrosion Problem

Steel will rust when exposed to water and oxygen; both are usually present in a gasoline line. Gasoline from the refinery enters a line saturated with water from the refinery chemical treaters at temperatures higher than atmospheric.



Pumping Station on a Products Pipe Line

# of Pipe Lines

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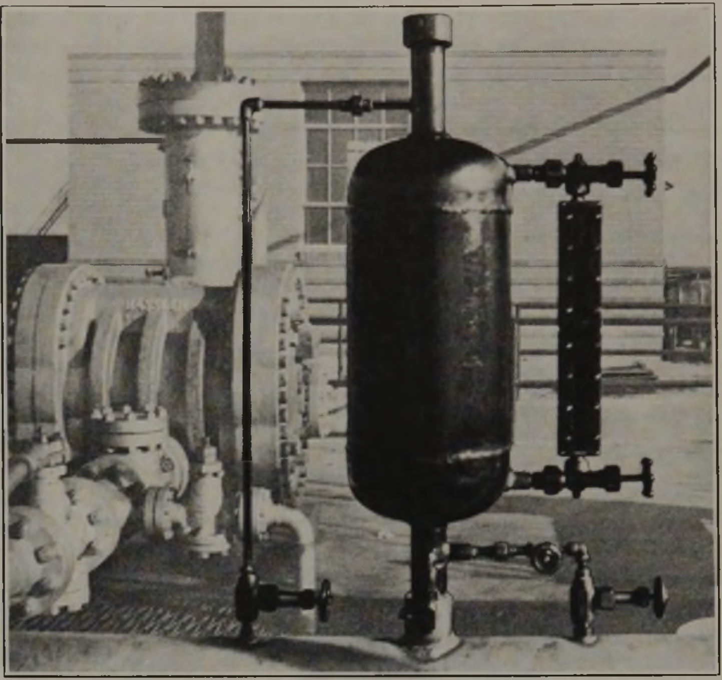

Inhibitor Injector at a Pumping Station

Reduction of its temperature to the lower underground temperature precipitates part of its water content as a separate water phase. If the gasoline has not been in prolonged storage in tanks, entrainment of the final wash water and sometimes of the chemical treating solution may carry these liquids into the line. The quantity of water carried into a line may be small in comparison with the volume of gasoline handled; but it is adequate in most cases to cause rusting over the entire inner surface of a line.

The solubility of water in gasoline varies with the chemical composition of the gasoline. A fairly representative solubility table for a regular-grade gasoline may be taken as follows:

Temp., °F.	Gal. Water/ 1000 Bbl. Gasoline	Temp., °F.	Gal. Water/ 1000 Bbl. Gasoline
40	1.8	80	3.0
50	2.1	90	3.3
60	2.4	100	3.6
70	2.7	110	4.0

Therefore, carrying 20,000 barrels per day from storage tanks at 100° F. through underground pipe at 60° F. would give about 24 gallons of water per day as a separate water phase. The volume of entrained water may be taken in a first approximation as likely to be about as large. This estimate agrees roughly with observations on operating lines. Since the largest temperature drop occurs in the first few miles of line, the greatest water dropout is also found in the first section of line.

Moreover, a new-laid line is often tested for soundness and absence of leaks at welded joints by pumping water in and permitting it to remain there under pressure for as long as several days. In one known instance, sea water was used for this purpose. Further, it is occasionally necessary to introduce slugs of water into a line during certain maintenance operations or when making construction changes.

One gallon of water amply supplied with oxygen is capable of reacting with 26 pounds of iron according to the equation for rust corrosion:

$$2\mathrm{Fe} + 2\mathrm{H_2O} + \mathrm{O_2} = 2\mathrm{Fe(OH)_2}$$

It may be calculated, then, that 24 gallons of water daily would be capable of corroding 100 miles of 8-inch pipe at an average rate of about 5 mils per year (1 mil = 0.001 inch). If, as appears reasonable, we assume that a given volume of iron will give twenty to thirty times its volume of rust (*6*, *10*), this corrosion rate will result in the formation of about $^1/_8$ inch of rust scale uniformly distributed over the inner pipe wall each year.

Neutral water is relatively noncorrosive in the absence of oxygen. The corrosion rate of steel is approximately proportional to the concentration of oxygen in water up to about saturation by air at one atmosphere (*4*). Usually an ample quantity of oxygen is transferred by the gasoline to the water in a pipe line, because oxygen is about six times as soluble in gasoline as in water, and the volume of gasoline may be many thousand times greater than the volume of water in a line. The gasoline acquires its oxygen from contact with air in refinery fractionating column accumulators, treating systems, and storage tanks, and its air content tends to be replenished at intermediate tankage on long pipe lines and perhaps through packing gland leakage at pumps.

An example of the rapid development of rust scale and blisters in gasoline pipe lines was shown by a short length of pipe cut from a new 8-inch line which had been operating for about 4 months. The pipe sample was taken about 300 feet from the first pumping station. Inspection showed that the interior surface of the sample was badly rusted. It was almost entirely covered with small rust blisters about $^1/_{64}$ to $^1/_{32}$ inch high, roughly $^1/_8$ inch apart; shallow pits were found under the blisters, and the surface between the blisters was covered with mill scale.

Analysis of the rust scale (which was exposed to the air for many days after sampling and before analysis) gave the following results:

Fe as Fe_2O_3	76.4%	S (total)	1.1%
Si as SiO_2	1.5	C	2.0
Pb as PbO	5.7	Ignition loss	11.0

This scale apparently consists chiefly of hydrated iron oxide. The lead and sulfur probably came from entrained plumbite solution from the refinery treating plant. The silicon may have come from soil clay inadvertently introduced in laying the line or in removing the sample. Subsequent analysis of sediment samples from a long line, which were protected from contact with air in transit, showed 3.9 per cent ferrous oxide in a sample taken 115 miles from the origin, 9.7 per cent in one taken 223 miles, and about 6 per cent in one taken 410 miles from the origin of the line.

Table I. Composition of Water Samples from a Pipe Line

Miles from origin of line	115	115	223	352
pH	9.9	10.0	9.3	8.9
Concentration, mg./liter				
Total solids				
Dried at 130° C.	7410	26,400	4570	5250
Ignited at 500° C.	2560	17,900	500	650
Organic carbon	1275	...	2620	1600
Fe_2O_3	105	6800	9	12
Al_2O_3	235	238	1	8
SiO_2	67	312	10	23
Alkalies as Na_2O	990	2000	173	270
CaO	25	0	15	20
MgO	19	47	4	11
PbO	0	5000	0	0
Cl^-	43	228	11	43
S^{--}	0	...	...	0
SO_4^{--}	105	666	38	120
HCO_3^- (includes weak acids)	860	...	268	350
CO_3^-	130	1300	144	0

An additional example is given by the reported loss (*19*) of about 11 per cent of a gasoline line's original throughput capacity after one year of operation without mechanical cleaning. Occasional scraping was only slightly effective in preventing further decline, the total loss in capacity in the first 2.5 years amounting to about 23 per cent of the original capacity.

Corrosion Factors in Gasoline Lines

Some discussion has already been given on two important corrosion factors in gasoline lines—namely, the presence of a separate water phase and the presence of oxygen. The following consideration of these and additional factors shows that complexities exist which may considerably modify the observable corrosion effects.

The presence of water is required to obtain any rusting at all. Moreover, on clean steel the water must be present as a separate liquid phase in contact with the steel to cause appreciable rusting. This has been demonstrated in simple experiments; gasoline containing water in solution caused no visible corrosion on polished steel specimens after several weeks when the temperature was maintained sufficiently high so that there could be no condensation of moisture on the steel surface. It is reported (*20*) that a rusted steel surface is hygroscopic and will take up moisture from a humid atmosphere (about 65 per cent relative humidity), causing further rusting of the steel. Although this may be due to the presence of traces of inorganic salts (*23*) on the air-rusted surface, it can be taken that this effect may occur in a rusted gasoline pipe line. The corrosion rates, however, are likely to be much lower than when liquid water is present, perhaps less than one tenth as great according to inconclusive experiments made in the course of this investigation.

The form in which the liquid water is present may exert a large influence on the corrosion effects. A layer of water in the bottom of the pipe, resulting from flow velocities too low to maintain all the water in suspension, will tend to localize the formation of scale mainly to the bottom segment of the pipe, filling it ultimately with a solid cake of rust. The rust blisters formed initially under these conditions tend to be rather broad and later appear more like a thick scale than like well-defined individual blisters.

Droplets of water on the steel surrounded by gasoline are especially conducive to rapid corrosion and to the formation of blisters (*5*). The rust blister once formed acts as a porous retainer, preventing the water drop from being swept away by the flow of gasoline, and the greater accessibility of the edge of the water drop to oxygen carried by the gasoline is favorable to differential aeration conditions which cause corrosion.

The quantity of water in a pipe line affects chiefly the distribution and total quantity of rust and has only minor influence on the rate of corrosion. As already indicated, more water is found in the first section of line than in succeeding lengths. Correspondingly, a greater total quantity of rust is found near the origin of a line (*14*).

The composition of the water may exert a large influence on the intensity of corrosive attack. This is shown by the corrosion rate values (Table VI) obtained under identical laboratory test conditions with different water samples from a Shell pipe line. An example of the range of compositions encountered in pipe line water is given in Table I; because of the adventitious nature of the water in a pipe line, no correlation between corrosion rate and composition was attempted.

However, tests in which distilled water was used as the aqueous phase (Table II) gave corrosion rates of roughly the same magnitude as those obtained in identical tests with pipe line water.

In general, everything else being equal, the higher the gasoline flow velocity in a pipe line, the greater the corrosion rate. This follows because, if rust is present, part of the steel surface is screened by the rust from oxygen carried by the gasoline, and the supply of oxygen to the unscreened part of the surface promotes attack in accordance with the principles of differential aeration (*15*).

It would be expected that refined hydrocarbon products would make no important direct chemical contribution to increase the rate of rusting by water. This is confirmed by the results of corrosion experiments in Tables II and X. The corrosion rate with ordinary regular-grade gasoline present was not significantly different from the rate with the same gasoline which had been previously water-washed; with fuel oil present, somewhat lower corrosion rates were obtained. It is more likely that the minor effects with different refined petroleum products are ascribable to the influence of physical and interfacial property differences.

Table II. Influence of Water and Gasoline Composition on Corrosion

(Rotating bottle tests with polished steel rod; 20 ml. of water and 70 ml. of gasoline in each bottle; duration, 14 days)

Corrosive Medium		Corrosion Rate, Mils/Year	Appearance of Steel
Gasoline	Water		
Blend of 5 pipe line samples	Blend of 4 pipe line samples	4.6, 4.3	Rusted all over
Same	Distd. water	6.5	
Blend washed with excess distd. water	Distd. water	4.2	
Regular-grade gasoline	Tap water	2.0	Rusted all over
Regular-grade gasoline	0.05% NaCl (distd. water)	3.6	Rusted all over
Same	0.10% NaCl (distd. water)	4.3	

Temperature is known to be an important factor in corrosion, the rate of rusting increasing about in proportion to increase of temperature (*17*) in the operating range of pipe lines. The practical result would be to enhance the corrosion rate near the origin of the line where the temperature of the gasoline is generally somewhat higher than in more distant parts of a line. The increase in corrosion rate from this cause is probably never greater than about 50 per cent.

The mill scale which normally covers the surfaces of new pipe probably acts as a corrosion accelerating factor (*9*). The intensity of attack tends to be increased at breaks in the scale because the mill scale is cathodic with respect to steel, and during the early life of a line the cathodic scale-covered area is large compared to the anodic scale-free areas.

The importance of oxygen as a factor in the rusting of steel pipe lines is illustrated by the results of simple experiments given in Table III.

Table III. Oxygen as a Corrosion Factor

(Rotating bottle tests with polished steel rod; 20 ml. of water and 70 ml. of gasoline in each bottle; duration, 14 days)

Conditions	Corrosion Rate, Mils/Year	Appearance of Steel
Gasoline and water as received from pipe line, air in gas space replenished 6 times	4.5	Rusted all over
Same gasoline and water after being de-oxygenated by bubbling N_2 through them, N_2 in gas space, bottle sealed	0.5	About 50% slightly tarnished

Mechanical Scraping of Pipe Lines

To overcome the steady decline in throughput capacity, most long pipe lines are scraped regularly to clean off excessive rust (*13*). This is a palliative measure to prevent eventual complete blocking of a line with rust scale. Use of scrapers involves additional operating costs and difficulties and, generally, is only partly effective in removing rust.

It seems reasonable to expect that mechanical cleaning of rusting steel will tend to increase the rate at which the corrosive action proceeds. Removal of scale would permit easier access of oxygen to the steel. Also it is known (*1*) that the corrosion rate of clean, bright steel in water is rapid at first, then declines as the surface becomes covered with a heavy layer of rust. Thus even partial cleaning of the rusted steel would be expected to give corrosion rates which tend to approach the initial rates in magnitude; it probably augments pitting rates in already well-developed pits.

Some experimental evidence has been obtained which indicates that, under rusting conditions, a more thoroughly cleaned, rusted steel produces rust more rapidly than one less vigorously cleaned. Four strips, $^3/_4 \times 6$ inches in size, were cut from a length of 8-inch pipe which had been rusted in gasoline line service. Two were cleaned on the rusted surface by brushing gently with a small bristle brush, and two were cleaned with a steel brush. They were then exposed to a flowing mixture of gasoline and tap water. After 10 days the strips were removed, washed in acetone, and dried, and the rust was removed and weighed from that surface which had been exposed inside the pipe. Rust was again removed by the same method used on each strip before the test. The strips were replaced in the apparatus, and the test was continued for another 10 days. After five such cycles the following results were obtained:

Surface Treatment	Total Rust Removed, Grams/Ft. of 8-In. Pipe/Year
Bristle-brushed	20, 23
Steel-brushed	59, 145

The rate of rust formation on the steel-brushed strips was several times greater than that on the bristle-brushed pieces. Also, larger and more numerous rust blisters formed between cleanings on the steel-brushed pieces.

Observations (*14*) on a gasoline pipe line have led to the qualitative conclusion that scraping increases the average rate of corrosion. Conclusions have also been reached (*22*) that water mains which have been mechanically cleaned develop throughput-reducing rust at a much faster rate than those which have not been cleaned, and that rust blisters can re-form after mechanical cleaning with incredible rapidity. Verification of the great speed with which rust is formed on clean steel under flow and moisture conditions, as in gasoline lines, is found in the experiments with uninhibited water summarized in Table XII.

Methods of Corrosion Prevention

Removal of Water. Since water is the controlling factor in gasoline pipe line corrosion, it seems logical to consider means of preventing water from entering a line in the first place. Water might be removed from the refined products entering the line by such procedures as distillation, refrigeration, and adsorption or absorption by chemicals. Each method would involve additional costly plant equipment and operating costs, with the possible exception of the adsorption method. The gasoline entering one short pipe line has been dehydrated (*16*) for several years, apparently to the satisfaction of the operators. Fluorite, a commercial bauxite, is used as adsorbent, and the entering gasoline, freed as far as possible from entrained water, is reported to lose 40 to 50 per cent of its moisture content. Although it is claimed that the original flow factor has been maintained consistently, this method is subject to one fundamental disadvantage. It makes no provision for water which may inadvertently get into the line. The effects of water are cumulative; therefore, although not so evident during the first few years of operation, they are likely to grow to serious proportions in time. In addition to the possibility of temporary failure of the dehydrators permitting entry of water, occasionally it becomes necessary to introduce slugs of water into a line during certain maintenance operations or when making construction changes. These tend to increase in frequency with the age of the line. Also, on a long line the gasoline may absorb moisture in intermediate line tankage.

Removal of Oxygen. Corrosion in gasoline lines also could be prevented if no free oxygen were permitted to enter the lines. So-called mechanical means of deaeration (distillation, evacuation, or blowing with inert gas) are not feasible for a number of practical reasons. Chemical agents which react with oxygen might be employed in either of two ways: They might be used in additional plant installation for pretreating the gasoline entering a line or they might be injected in aqueous solution with the gasoline into the line. The former procedure would be subject to the disadvantage that it makes no provision for inadvertent admissions of oxygen. Only one chemical, sodium sulfite, has been proposed for the latter procedure. It has been tested on two pipe lines (*16*) with no evidence of material benefit. Further discussion of this treating agent is given later.

Corrosion Inhibitors. For gasoline pipe lines this method of preventing internal corrosion is attractive because the volume of corrosive medium (water) is small, costly plant equipment would not be required and inhibiting procedures can usually be varied easily to meet different operating requirements.

Before any inhibitor could be accepted as a general solution to the problem of internal corrosion of gasoline pipe lines, it must meet several important requirements:

1. It must be effective in preventing rust corrosion on clean, on mill-scale-covered, and on already-rusted steel surfaces under gasoline pipe line conditions.
2. It should not tend to harden and perpetuate rust scale and blisters once they are formed on the pipe wall.
3. Its use must result in no adverse effects upon the quality of the refined products which may be transported through the line.
4. The cost of applying the inhibitor must be low.

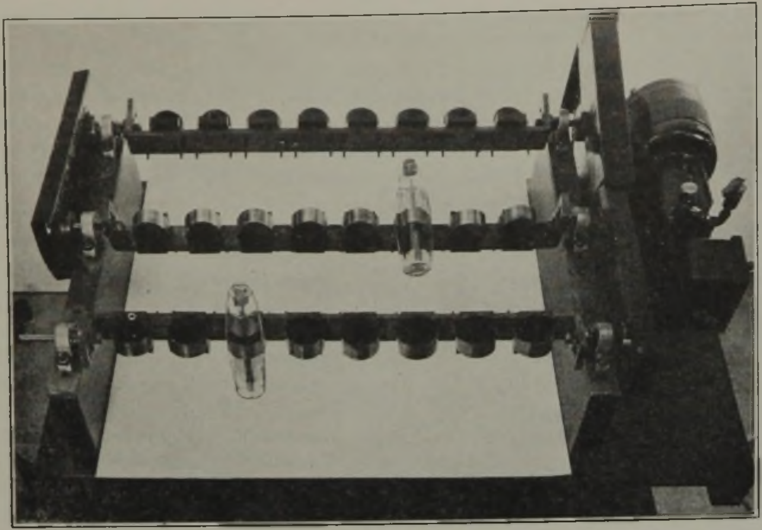

Figure 1. Bottle Rotating Machine for Laboratory Corrosion Tests

As will be shown, sodium nitrite is the only one of a number of inhibitors which was found to meet all these requirements.

Applicability of Certain Inhibitors

There are several useful rust inhibitors which are soluble in water and low in cost. They were tested for applicability to gasoline pipe lines.

Sodium chromate is a powerful inhibitor of rusting which has been successfully used in many aqueous systems, notably in refrigerating brines and air-conditioning waters. Corrosion tests (Table IV) showed that it was almost as effective as sodium nitrite in preventing rusting of cleaned steel surfaces by samples of pipe line water; however, several of its properties are serious obstacles to its use in gasoline lines.

Sodium chromate acts as an oxidizing agent even in alkaline solution. It reacts with many organic compounds, such as alcohols, aldehydes, and unsaturated hydrocarbons, and is reduced to chromic ion which has no corrosion inhibiting properties. Thus also it would tend to deplete a finished gasoline of its gum inhibitors and to affect the color of the dyed or undyed gasoline. In the presence of corrosion products which usually exist before use of inhibitors is begun in a pipe line, the effect of the chromate is greatly reduced (*2*). This effect is shown by the experimental results summarized in Table XI. A further point against the use of sodium chromate is the fact that it reacts with entrained sodium plumbite solution to precipitate lead chromate.

Disodium phosphate and sodium silicate ($Na_2O.3SiO_2$) tested in 0.1 per cent concentration gave partial inhibition in the simple bottle rotating tests (Table IV), in that parts of the steel surface were not rusted. However, those areas which were attacked were covered with hard, projecting rust blisters. It is possible that concentrations of these substances higher than 0.1 per cent might give complete protection on polished steel surfaces, but the danger of occasional formation of hard scale which could not be removed by normal scraping operations is an important objection. On steel surfaces already well rusted, these substances would be much less effective in preventing further rusting; they would tend to accelerate pitting rates (*8*) in already formed pits, and would harden the rust scale already present through formation of insoluble iron phosphates or silicates.

Tests of sodium hydroxide in 0.1 per cent solution in pipe line water showed that it was fairly effective in preventing corrosion of polished steel specimens, but several high rust blisters formed rapidly on mill-scale-covered steel. It produced stable emulsions of water in gasoline which did not break completely even after standing for one hour. Further, it is known (*7*) that pH control inhibitors (which include also sodium carbonate, phosphates, and silicates) are ineffective and even have an adverse effect when pre-existing corrosion products are present.

Inhibitors of the sodium sulfite type depend for their effect upon reaction with and removal of oxygen present. About 9 pounds of sodium sulfite are required to react with 1 pound of oxygen (*18*). In normal pipe line operation this means that a minimum of about 0.2 pound of sodium sulfite would be required for each barrel of gasoline, since gasoline contains about 0.02 pound of oxygen per 42-gallon barrel when saturated with air. The use of such quantities of inhibitor is impracticable from a cost and operating standpoint. When used in practically permissible quantities—e. g., about 1 per cent of the water present—no inhibitive action was apparent in laboratory tests (Table IV).

Several proprietary compounds were tested at length to determine if they might be practical as gasoline pipe line inhibitors. Sodium Chrom Glucosate was no more effective in preventing corrosion in laboratory tests than equal quantities of sodium chromate, and possessed all of the disadvantages of the latter as well as a marked tendency to give stable emulsions of water in gasoline. A gasoline-soluble inhibitor, mercaptobenzothiazole, was proposed (*12*) and tested in a few gasoline pipe lines (*16*). It has not found general acceptance because its advantages are still somewhat problematical.

Typical results of corrosion experiments with the inhibitors discussed are summarized in Table IV.

Table IV. Corrosion Tests with Inhibitors

(Rotating bottle tests with polished steel rod in 20 ml. water and 70 ml. regular-grade gasoline in each bottle, for 14 days)

Origin of Water Sample	Inhibitor, Weight % of Water	Corrosion Rate, Mils/Year	Appearance of Steel
Blend from pipe line	None	4.6	Rusted all over
	$NaOH$, 0.1	2.3	Several rust spots
	Na_2SO_3, 1.0	4.6	Rust blisters all over
	Na_2SO_3, 0.1	5.0	Same
	Na_2CrO_4, 0.1	0.0	Bright all over
	Na_2HPO_4, 0.1	2.5	Many hard rust blisters
	$Na_2O.3SiO_2$, 0.1	3.0	Same
	Mercaptobenzothiazole, 0.01[a]	4.2	Many rust blisters
	$NaNO_2$, 0.1	0.0	Bright all over
Tap water	None	2.0	Rusted all over
	Mercaptobenzothiazole, 0.01[a]	4.0	Same
	Chrom Glucosate, 0.04	0.2	Several rust spots
	$NaNO_2$, 0.1	0.0	Bright all over
From pipe line	None	5.0	Rust blisters all over
	Sodium Chrom Glucosate, 0.035	1.2	Several large rust blisters
	Same, 0.05	0.4	Same
	Same, 0.1	0.0	Bright all over
	Quachrom Glucosate, 0.05	3.0	Rusted all over
	Mercaptobenzothiazole, 0.01[a]	4.5	Rust blisters all over

[a] Concentration in weight % of the gasoline.

Laboratory Corrosion Test Method

A large number of corrosion tests were made with pipe line water samples and with many different inhibitors. A simple apparatus and procedure was used in these exploratory and comparative tests. Although the test method does not reproduce conditions precisely as they occur, it probably includes all essential factors which operate to cause corrosion in gasoline lines.

A 4-ounce oil sample bottle was filled with 20 ml. of a water sample and 70 ml. of a gasoline sample. A 6-inch rod of low-carbon steel (SAE 1015), polished bright with No. 0 emery cloth, was firmly suspended in the bottle by inserting it into a hole drilled part way through the cork stopper used to seal the bottle. The bottle was then placed in a rotating machine which turned it end over end at the rate of 60 r. p. m. An air space of about 30 ml. was left in the bottle, and the air was replenished once every 2 days. The usual duration of these tests was 14 days at room temperature (75–85° F.). Mixtures of gasoline and water formed a coarse emulsion when rotated in the machine, the gasoline-water interfaces constantly moving over the surface of the steel rod. The corrosion results were determined by visual inspection and by the weight loss obtained after cleaning the rusted rod electrolytically, followed by rubbing with a soft eraser.

The test bottle assembly and bottle rotating machine are illustrated in Figure 1. Typical rods after corrosion tests, with and without inhibitor, are shown in Figure 2.

That the amount of rusting in these experiments is not very sensitive to the relative proportions of gasoline and water in the bottles is shown by tests on mixtures of 20 ml. of a pipe line water sample and 70 ml. of gasoline, and with 1 ml. of the same water and 90 ml. of gasoline (Table V).

Table V. Influence of Gasoline-Water Volume Ratio in Corrosion Test

(Rotating bottle tests with water and gasoline samples from pipe line same in both experiments; duration, 14 days)

Gasoline, Ml.	Water, Ml.	Corrosion Rate, Mils/Year	Appearance of Steel
70	20	4.5	Rusted all over
90	1	5.9	Large area rusted

Corrosion Experiments with Sodium Nitrite

Corrosion tests by the rotating-bottle method were made with water sampled from various points along a 450-mile gasoline line at different times over a period of almost a year. The results are summarized in Table VI. Each of these water samples was also tested under identical conditions with 0.1 per cent by weight of sodium nitrite added to the water; in every case no sign of rust or rust blisters could be found on the steel specimen at the end of the test; each steel rod remained bright all over and unchanged in appearance.

Table VI. Corrosion Tests with Pipe Line Water Samples in Absence of Inhibitor

(Rotating bottle tests with polished steel rod in 20 ml. pipe line water and 70 ml. regular-grade gasoline in each bottle, at 75–85° F. for 14 days)

No. Water Samples	Corrosion Rate, Mils/Year	Appearance of Steel
0	0	
6	0.1–0.4	Many rust blisters, the rest bright
6	0.5–1.4	
0	1.5–2.4	
1	2.5–3.4	
5	3.5–4.4	Rust and rust blisters all over
6	4.5–5.4	
5	5.5–6.4	
1	6.5–7.4	
0	Over 7.4	....

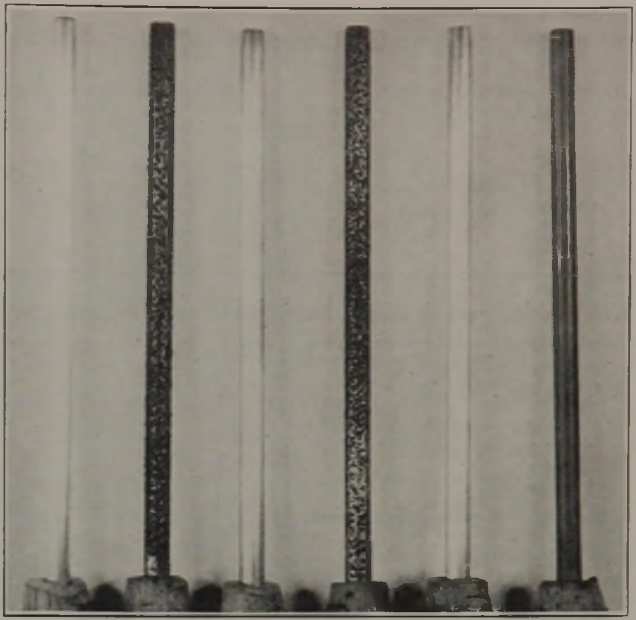

Figure 2. Steel Rods after Corrosion Tests with Pipe Line Water Samples

No correlation was found between the distance from the pipe line origin at which the water sample was taken and the corrosiveness of the sample to steel. Samples taken at the origin, or 55 or 115 miles away from it, were no more corrosive in general than samples taken at the terminal station 450 miles from the origin.

The corrosion rate values fall into two groups, around 0.5 and 5 mils per year. Although this effect is probably related to the composition of the waters, the precise nature of the relation was not investigated. It probably involves the variable presence of certain concentrations of refinery treating solutions in the line water. The magnitudes of corrosion rate values obtained in these tests are in substantial agreement with the values estimated by Pearson (*14*) for the average penetration rate of several operating pipe lines. His calculations indicate rates of 0.3 to 6 mils per year.

The effects of concentrations of sodium nitrite below 0.1 per cent in a composite pipe line water sample are shown by the results in Table VII.

Table VII. Influence of Sodium Nitrite Concentration on Rusting of Steel by Pipe Line Water

(Rotating bottle tests on blend of 4 water samples, pH 9.0, from pipe line and regular-grade gasoline, for 14 days)

$NaNO_2$ Concn., Wt. % of Water	Corrosion Rate, Mils/Year	Appearance of Steel
0	4.3	Rusted all over
0.01	3.7	Many rust blisters
0.02	3.0	Same
0.04	0.6	Partly rusted
0.06	0.0	Bright all over
0.08	0.0	Same
0.10	0.0	Same

The influence of hydrogen-ion concentration on the effectiveness of sodium nitrite as an inhibitor is shown by the results of corrosion tests given in Table VIII. Under these conditions it was necessary for the water to be at a pH greater than 6 initially in order to prevent corrosion completely. The efficacy of sodium nitrite in preventing corrosion of steel covered with mill-scale is shown by the results of experiments summarized in Table IX.

Table VIII. Influence of pH on Behavior of Sodium Nitrite as Rust Inhibitor

(Rotating bottle tests on blend of 4 water samples from pipe line and regular-grade gasoline; 0.06% $NaNO_2$ added to water in each test; pH adjusted by H_2SO_4 or NaOH; duration, 14 days)

Initial pH	Final pH	Corrosion Rate, Mils/Year	Appearance of Steel
11.3	10.6	0.0	Bright all over
9.0	...	0.0	Same
6.0	8.1	0.8	Tarnished
4.7	8.4	7.6	Rusted all over

Table IX. Efficacy of Sodium Nitrite on Mill-Scale-Covered Steel

(Rotating bottle tests on blend of 4 water samples, pH 9.0, from pipe line and regular-grade gasoline, for 18 days)

Surface Condition of Steel Rod	$NaNO_2$ Concn., Wt. % of Water	Corrosion Rate, Mils/Year	Appearance of Steel
Polished bright	None	4.6, 4.3	Rusted all over
	0.1	0.1	Bright all over
Mill-scale covered	None	3.9, 3.3	Many rust blisters
	0.1	0.1	No rust, no change

Although gasoline (of various grades) is the principal material transported through products pipe lines, kerosene, various grades of fuel oil, and Diesel fuel may also be handled during part of a line's operating time. That sodium nitrite is effective in preventing rusting in the presence of these heavier products, usually with a high sulfur content, is demonstrated by the results of corrosion tests in Table X. The areas of steel which were rusted in the absence of inhibitor are smaller than those obtained under comparable conditions with gasoline. This effect is probably related to the fact that the heavier oils hinder the wetting of steel by water to a greater degree than the lighter oils.

Prevention of Further Rusting of Rusted Steel

It is essential that a corrosion inhibitor intended for use in pipe lines be capable of preventing the further rusting of already rusted steel surfaces. That sodium nitrate does this is shown by the results of laboratory experiments summarized in Table XI. A gain in weight in these tests indicates further rusting. The rusted rods which had been exposed to sodium nitrite actually lost a little weight.

Table X. Action of Sodium Nitrite as Inhibitor in Presence of Fuel Oils

(Rotating bottle tests using 70 ml. of oil sample and 20 ml. of 0.05% NaCl in distilled water, for 7 days)

Oil Sample	$NaNO_2$ Concn. in 0.05% NaCl Soln., Wt. %	Corrosion Rate, Mils/Year	Appearance of Steel
No. 3 fuel oil[a]	No water present	0.1	Slight discoloration
	0	2.7	50% rusted
	0.1	0.1	No rust, bright all over
Cracked furnace oil[b]	No water present	0.1	Slight discoloration
	0	2.0	Rust blisters on 10% of area
	0.1	0.1	No rust, bright all over

[a] Total sulfur, 0.71 weight %; sulfur as mercaptans, 0.02.
[b] Total sulfur, 0.96 weight %; sulfur as mercaptans, 0.04.

Table XI. Efficacy of Inhibitors with Rusted Steel

(Same conditions as for rotating bottle corrosion tests; regular-grade gasoline and tap water; steel rods heavily rusted all over in water before tests; duration, 28 days)

Inhibitor Concn., Wt. % of Water	Wt. Change of Rusted Rods, Mg.
0.1 $NaNO_2$	−10 − 1
0.1 Na_2CrO_4	+13 +13
None	+42 +57

Effectiveness of Sodium Nitrite at High Volume Ratios of Gasoline to Water

In a gasoline pipe line operating at a throughput of 20,000 barrels (840,000 gallons) per day, injection of, say, 5 gallons of sodium nitrite solution daily corresponds to a ratio of 168,000 volumes of gasoline to 1 volume of inhibitor solution (assuming no free water is present in the line). The simple rotating bottle corrosion test involved agitation of a mixture of 70 ml. of gasoline with 20 ml. of an aqueous phase in contact with a steel rod in a bottle. The efficacy under flowing conditions of sodium nitrite solutions at ratios to gasoline comparable to those in a pipe line was tested under conditions more closely approaching those in a pipe line. A diagram of the apparatus is given in Figure 3.

Fifteen liters of regular-grade gasoline were circulated by a centrifugal pump through a half-inch diameter glass tube in the axis of which was supported a 14-inch length of quarter-inch steel tubing with one end closed by welding. The steel tube, which was the corrosion test specimen, was arranged to permit internal water cooling (approximately 60° F.) throughout each experiment. The gasoline (at about 70–80° F.) flowed over the steel specimen at linear velocities of 4.3 to 4.9 feet per second. Water or inhibited solutions were fed into the suction side of the pump and emerged into the glass tube as finely dispersed droplets in the gasoline. After passing through the glass tube, the water was removed from suspension in the gasoline by a separator, one part of which was filled with fine glass wool. The separator functioned efficiently and gave a crystal-clear gasoline for recirculation. The aqueous phase was introduced through fine capillary tubing, the rate at which it entered the pump being kept constant by adjusting the height of the feed container to maintain a constant hydrostatic head.

Results obtained with this apparatus are summarized in Table XII. These results indicate that a solution of 0.1 per cent sodium nitrite prevents rusting at a gasoline: water ratio of at least 200,000: 1 under conditions simulating some of those in pipe lines, and that the protection given the steel will persist for a time after injection of nitrite has been stopped. It appears also that the higher the nitrite concentration in the water, the smaller the quantity of solution which need be injected.

These results suggest that sodium nitrite forms a protective film on steel which is capable of withstanding small amounts of uninhibited mildly corrosive water for a limited time. Several qualitative observations have been made of the persistence of protection on steel which had been immersed for short times in sodium nitrite solution and then subjected to limited amounts of moisture in the absence of the inhibitor.

Mechanism of Sodium Nitrite Action

Insufficient evidence has been obtained thus far to enable a complete and reliable description of the mechanism by which sodium nitrite prevents rusting. However, as mentioned earlier, it appears likely that sodium nitrite prevents rusting by forming a thin but highly protective film over the surface of the steel. This film is invisible to the unaided eye, the steel remaining bright and apparently unchanged even after prolonged immersion in a nitrite solution. The nitrite probably acts predominantly as an anodic type inhibitor with little or no effect on the cathodic reaction of the rusting

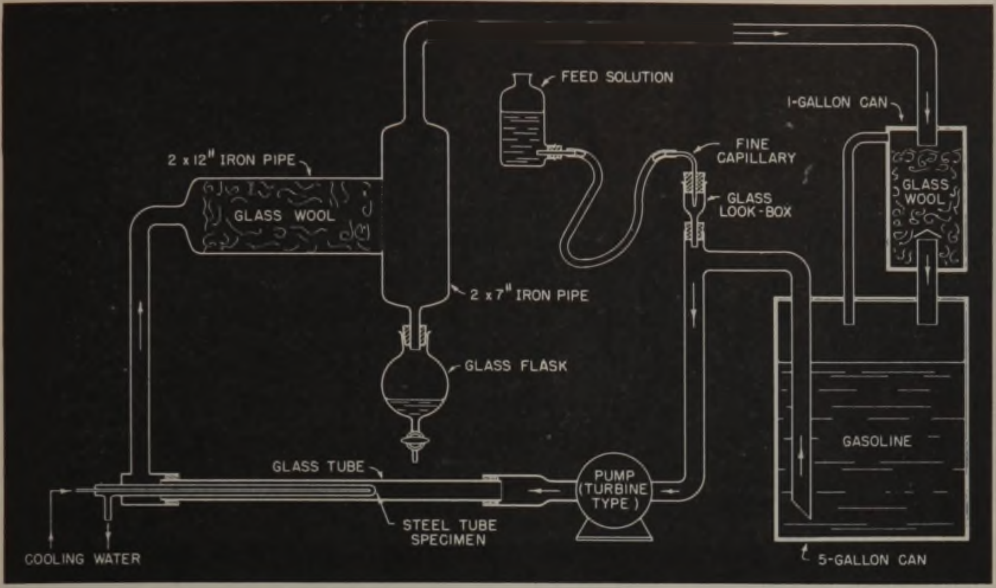

Figure 3. Apparatus for Experiments with Flowing Gasoline and Injected Solutions

process. This is indicated by results of electrochemical experiments of the type described by Chyzewski and Evans (*3*). Since nitrite salts of iron are soluble in water, it is not unlikely that the protective film formed at the anodic areas consists of ferric oxide, especially since the solutions are alkaline and nitrite will oxidize ferrous to ferric compounds. It is unlikely that oxygen enters into the mechanism of action of the sodium nitrite since alkaline solutions of sodium nitrite react extremely slowly, if at all, with oxygen from the air at room temperature.

Table XII. Effectiveness of Sodium Nitrite at High Volume Ratios of Gasoline to Water

(Regular-grade gasoline containing dispersed droplets of water flowing over a polished 1/4-inch steel tube at a linear velocity of about 4.5 ft./sec., at about 70° F.)

Solution	Volume Ratio, Gasoline to Water	Time to Start Steel Rusting	Condition after 2 Days	Subsequent Treatment and Observations
Tap water	200,000	<10 min.	95% rusted	None
0.1% $NaNO_2$	200,000	>4 days	No change	No change after 19 days more with tap water, no $NaNO_2$
2.0% $NaNO_2$	280,000	>4 days	No change	Terminated at 4 days
0.05% NaCl	183,000	3 min.	95% rusted	None
0.05% NaCl 0.1% $NaNO_2$	144,000	2.5 hr.	50% rusted	None
0.05% NaCl 0.1% $NaNO_2$	41,400	24 hr.	0.3% rusted	2% rusted after 2 days more with 0.05% NaCl, no $NaNO_2$
0.05% NaCl 1.0% $NaNO_2$	196,000	24 hr.	0.7% rusted	No change after 2 days more with 0.05% NaCl, no $NaNO_2$

Effect of Sodium Nitrite on Refined Petroleum Products

An essential requirement of an inhibitor for products pipe line was mentioned earlier: The inhibitor must have no adverse effects on the quality of the refined petroleum products which may be pumped through the line. Laboratory experiments (Table XIII) showed that no changes in the properties of common refined products result from contact with sodium nitrite under conditions which in several respects are more severe than are likely to be encountered in pipe line operation. Also, no change of nitrite concentration could be found by analysis of the aqueous phases used in many of these tests. Even more convincing is the fact that, in about 2-year operation of 450 miles of a products line with sodium nitrite inhibition, no adverse effect on any product has been observed which could be attributed to the use of the inhibitor.

Solubility of Sodium Nitrite in Gasoline

Although it was known that sodium nitrite is practically insoluble in gasoline, the possibility of minute solubility was examined. The gum content data for gasolines which had been shaken with excess quantities of anhydrous sodium nitrite and with aqueous solutions of the nitrite (compare Tables XIII and XIV) indicate that the solubility of the salt in gasoline is less than 0.002 per cent, the limit of experimental precision of the method.

A cumulative type experiment was made in which a given volume of gasoline was circulated by thermosiphon action, first over a solution of sodium nitrite and then over distilled water. The apparatus is illustrated in Figure 4. A transfer of all the gasoline was completed in this apparatus in about 5 minutes. The lower bulb contained 100 ml. of 3 per cent sodium nitrite solution, the upper contained 100 ml. of distilled water, and 560 ml. of regular-grade gasoline filled the rest of the apparatus. After 7 days the water in the upper bulb was drained and analyzed for nitrite content. No nitrite was found greater than the limits of precision of the analytical method. A duplicate experiment with anhydrous crystals of sodium nitrite in the lower bulb gave the same negative result. In view of these results, it was estimated that the solubility of sodium nitrite in gasoline is less than 0.00001 per cent.

It seems clear, therefore, that no significant concentration of the inhibitor would be carried in solution in gasoline through a pipe line.

Consumption of Sodium Nitrite

A large pipe line system may have sections extending for 100 miles or more between pumping stations. A line this long has a considerable total internal surface area, and a given small volume of sodium nitrite

Table XIII. Effect of Sodium Nitrite on Gasoline, as Shown by One Group of Experiments

(400 ml. of premium-grade gasoline, containing about 2 ml. $PbEt_4$/gal., in a pint bottle, rotated end over end at 60 r. p. m. at room temperature for 11 days)

Material Added to Gasoline	Air-Jet Gum (A. S. T. M. D381-36), Mg./100 Ml.	Octane No., A. S. T. M. Motor Method
None	0.6	82
50 ml. 10% $NaNO_2$, aq.	0.7	82
5 g. $NaNO_2$ crystals	0.6	82

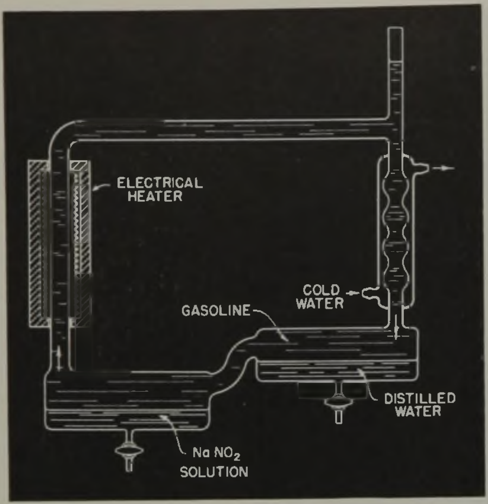

Figure 4. Thermosiphon Apparatus for Detection of Trace Solubility

solution injected into one end may come into contact with practically all of this surface. The possibility of adsorption of the inhibitor by the steel wall or by rust therefore becomes important.

To test the adsorptive capacity of clean steel for sodium nitrite, 100 grams of cleaned steel wool with an estimated surface area of 14.2 square feet were left in contact with 100 ml. of 0.1 per cent sodium nitrite solution for 2 days. No change, within experimental error, was found in the nitrite content of the solution. On the basis of estimated experimental error it was calculated that not more than 0.003 gram of nitrite could have been adsorbed, which corresponds to maximum adsorption of 210 grams on 1,000,000 square feet of clean steel. Apparently adsorption of the inhibitor by clean steel does not occur to any significant extent.

That sodium nitrite in solution is not oxidized by air was shown by shaking a sample of 0.10 per cent solution (pH 9.1) with air for 14 days. No change in nitrite content was found.

Fresh rust was found to react with sodium nitrite, the ferrous oxide being oxidized to ferric oxide and the nitrite being reduced to ammonia. The following equation expresses the over-all reaction:

$$NO_2^- + 6Fe(OH)_2 + 5H_2O = NH_3 + 6Fe(OH)_3 + OH^-$$

This reaction is not instantaneous; a complex is formed first between the nitrite and ferrous oxide or hydroxide, and relatively slow decomposition of the latter gives the end products indicated. Apparently a steady state is reached in this reaction. The higher the concentration of nitrite and the relative amount of ferrous hydroxide present, the more rapid the initial reaction rate and the greater the percentage decrease of nitrate concentration in reaching the steady-state value.

No reaction with or adsorption of nitrite by ferric hydroxide could be detected.

Therefore, full benefits along the entire length of a line cannot be expected immediately following the start of continuous injection of sodium nitrite solution if ferrous rust is distributed along the inner pipe wall. The attainment of full inhibition should progress along the pipe as rapidly as the ferrous rust is oxidized. Owing to the relatively large quantity of ferrous rust which will react with a given amount of sodium nitrite (7.8 pounds ferrous hydroxide with 1 pound sodium nitrite), the attainment of inhibition at the end of each injection section of line (usually 50 to 100 miles) probably would not be delayed beyond a month or two following the start of inhibitor injection into an old line.

Sodium Nitrite in Products Pipe Lines

Sodium nitrite is being used successfully for prevention of internal corrosion in three products pipe lines. It has been in use for over 2 years in a 450-mile line. In a 266-mile line, operated as a crude oil line for about 11 years, its use was started 8 months after the line was converted to gasoline transportation about 2 years ago. In a 90-mile line sodium nitrite has been employed from the start of operations following construction in the early part of 1941. The inhibitor is to be used also in a 1200-mile pipe line recently completed and has recently been started in 370 miles of an old gasoline line. Additional applications are in prospect.

In essence, the application of the inhibitor to gasoline pipe lines involves continuous injection of a 5 to 30 per cent solution of sodium nitrite at the rate of 5 gallons per day into the pipe at the beginning of each station-to-station length of line. The need for injection at each station on a long line arises from the fact that sediment and water separators are usually built into the end of the section of line bringing gasoline into a station. Since the water at all points in the pipe line must be alkaline for the inhibitor to be effective, sodium hydroxide is added to the inhibitor solution when the pH of the effluent water falls below 8.

Although there is some evidence that the inhibitor tends to loosen rust scale from the pipe wall, the removal of the accumulated scale during inhibition with sodium nitrite is more rapidly accomplished by mechanical scraping. In preventing steel from rusting, the inhibitor indirectly aids in the removal of scale under pipe line conditions, inasmuch as the cementing action of further rusting on somewhat loosened scale particles is prevented between scraper runs. A cumulative effect in scale removal is probably derived in this way.

Considerably less difficulty with line sediment in the gasoline is experienced after sodium nitrite inhibition is started than before. The average quantity of sediment

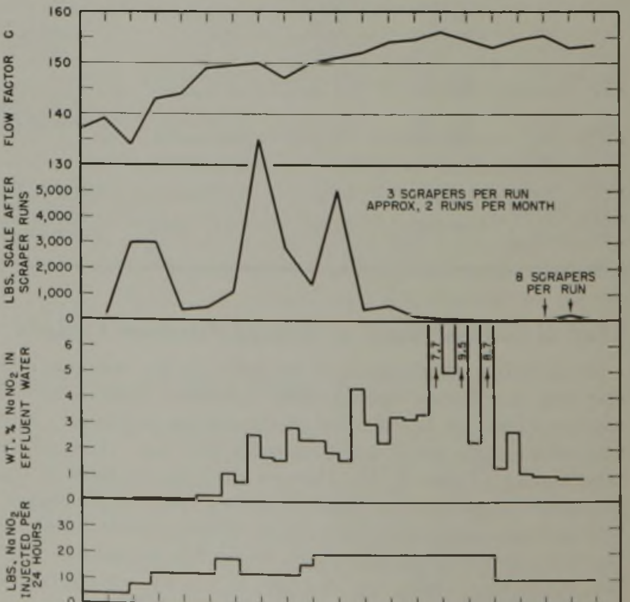

Figure 5. Inhibition Results on the First 55 Miles of a 450-Mile Products Pipe Line (8-Inch Pipe)

Table XIV. Corrosion Tests with Effluent Pipe Line Water Samples after Start of Inhibition

(Rotating bottle tests with 20 ml. of pipe line water and 70 ml. of regular-grade gasoline, for 14 days)

Section No.	Sample No.	$NaNO_2$ Concn. in Effluent, %	Area of Steel Rusted,[a] %	Time after Taking Sample A, Mo.
1	A	0.001	100	...
	B	0.89	0	4
2	A	0.04	0	...
	B	0.08	0	1
3	A	0.25	0	...
4	A	0.000	100	...
	B	0.21	0	6
5	A	1.85	0	...
6	A	0.000	100	...
	B	0.28	0	2.5

[a] The specimens for which 0% area rusted is indicated were bright all over without a single rust spot or any tarnish or discoloration at the end of the tests.

brought into a station between scraper runs is much greater with than without inhibition, but the sediment is associated with the water and is easily removed in the station separator rather than suspended as fine particles in the gasoline. During the early stages of inhibition, therefore, the mechanical scraping program is intensified as much as possible while avoiding serious interference with the normal functions of a line; the object is to remove old scale accumulated on the pipe wall. The time to remove old scale will vary considerably for different lines, perhaps from a few months to a year, but eventually the condition will be reached when only trivial quantities of scale are found in the effluent after a scraper run, and only occasional precautionary scraper runs need be made.

The results obtained with the use of sodium nitrite in a 450-mile pipe line which has been in operation since April, 1938, are summarized for the first 55 miles in Figure 5. The experience is similar for succeeding sections of line. Flow factor C is calculated by the modified Hazen-Williams formula from operating data obtained on the pipe line. The formula is

$$Q = \frac{C\, d^{2.63}\, P^{0.54}}{66\, g^{0.54}}$$

where Q = flow rate, barrels/hour
C = flow coefficient
d = inside diameter of pipe, inches
P = friction loss, lb./sq. in. per 1000 ft. of pipe
q = specific gravity of gasoline

Since C is directly proportional to throughput, it is commonly used as a measure of pipe line flow efficiency. For design purposes 8-inch-diameter pipe in gasoline service is generally considered to have a flow factor of about 140, since most 8-inch lines do not exceed this value in flow efficiency. For the reasons discussed earlier, measurement of flow factor on new line which has been in service from a few weeks to several months will probably give values indicating that the rusting process is already well underway.

The flow factor curve of Figure 5 shows an improvement from a level of about 137 before inhibition to about 155 after inhibition, with corresponding increase in throughput capacity.

The quantity of scale removed by scraping increased markedly for a time during heavy inhibitor input and then decreased to very small amounts, the major part of the old scale in the line having presumably been removed.

The delay in the appearance of the inhibitor in the effluent water (Figure 5) is ascribable to consumption of the nitrite by the ferrous rust in the line. The total quantity of inhibitor consumed in this and succeeding treated sections of the same line is about 18 pounds per mile of 8-inch pipe.

Although the opportunities for inspection of the internal surface of an operating gasoline line are rare, the few which have been possible from time to time have shown a practically clean steel surface free from rust scale and blisters in pipe treated for some time with sodium nitrite.

Additional confirmation of the efficacy of sodium nitrite in preventing steel rusting by water in a pipe line is shown (Table XIV) by corrosion tests with effluent waters from various sections (40 to 100 miles long) of line treated with the inhibitor. Water containing nitrite did not rust steel in these tests, as determined by analysis.

Conclusions

The practical benefits which can be derived from the inhibition of corrosion by sodium nitrite in products pipe lines may be summed up as follows: Maximum flow efficiency of the pipe is achievable, and significantly greater quantities of gasoline can be pumped through a line with existing equipment and power consumption; alternatively, the power required for reduced flow throughput is significantly lower than in a rusted line. Once mechanical scraping has removed pre-existing rust from a line, the frequency of scraping runs can be materially reduced. Maintenance operations on machinery which operates at stations in contact with the gasoline are materially reduced because of the reduced quantity of abrasive fine particles carried by the gasoline stream. For the same reason the accuracy of metering, a vital consideration in long products lines which have intermediate take-off points, is materially improved. The color, gum, and oxidation stability of transported products are not subject to the deteriorating influence of large quantities of rust. Trouble with sediment in the gasoline is avoided. The loss of pipe wall thickness from internal corrosion is stopped.

Acknowledgment

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COLORING MATERIALS FOR COPOLYMER

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Properties of the vinyl chloride–vinyl acetate copolymer resins are discussed relative to their effect on the choice of coloring materials. Tests for bleeding characteristics, light stability, and heat stability of colors in these resins are outlined. Tabular results are given for a number of specific

THE development of the conjoint polymer of vinyl acetate and vinyl chloride to yield a thermoplastic resin has resulted in the commercial application of these materials in a wide variety of forms including lacquers, rigid sheets, injection moldings, extruded shapes, and, more recently, as flexible sheets, films, molding compounds, and electrical insulating materials. Interest in the latter types has increased because of their properties of high dielectric strength, good chemical resistance, good flame resistance, and low-temperature flexibility which are highly desirable for electrical insulating purposes.

Because copolymer vinyl resins of this type are transparent and nearly colorless, the range of colors possible is limited only by the dyestuffs and coloring materials available and suitable. A consideration of the factors governing the choice of coloring agents and their methods of evaluation is therefore believed timely since many coloring materials have been found to behave differently in copolymer resins from what would be predicted from their properties in printing inks, protective coatings, and other plastic applications. This is also desirable because of the availability of these materials for use within the consumer's plant where color compounding problems may arise which are specific to his particular usage.

Resin Properties

In the absence of stabilizers, vinyl chloride-acetate copolymers are subject to yellowing on heating and progressively darken with eventual loss in plasticity. Reed and Groff (*8*) recommended the use of calcium and lead salts as stabilizers to retard this reaction, presumably by removal of the acid formed in decomposition. Litharge, basic-carbonate white lead, and lead stearate are widely used along with other materials of that type. Stabilized compounds can be processed as high as 150° to 160° C. without color change, although the tendency for development of a yellow component is always present and enters into the problem of coloring these compounds aside from the specific behavior of the coloring ingredient itself. Even in the presence of stabilizer certain substances, such as some iron and zinc salts, act as decomposition catalysts and may cause darkening of the compound. This factor, with others subsequently discussed, frequently limits the choice of coloring materials to a few of the many types available.

The addition of liquid plasticizers to vinyl copolymers to yield flexible compositions and the solubility of many coloring materials in these plasticizers introduce the factor of color migration. In the extreme case migration results in a bloom or film of color at the surface of the compound and the possibility of objectionable transfer of that color to an adjacent contact surface.

It is therefore obvious that the selection of coloring materials is not always a matter of the simple use of one or more available coloring ingredients to produce the shade desired. In reality the following factors must be taken into consideration: specific behavior of the color in the presence of the stabilized copolymer vinyl resin, bleeding and/or blooming tendency, inherent light stability, heat stability, and covering power and dispersibility.

Tests and data presented are primarily based on experience with calendered, extruded, and molded compounds, although it is believed that many of the conclusions can be extended to vinyl resin lacquers. Particular emphasis is placed on light stability studies and on coloring materials for plasticized compounds.

Test Methods

The following procedures were used throughout this work in evaluating specific colors and their behavior in the copolymer vinyl resins.

General Procedure. All components were thoroughly preblended in a kitchen mixer and fluxed on a steam-heated, 6 × 12 inch, two-roll rubber mill. The batches were given ten passes with the rolls set to give a sheet about 0.040 inch thick. Between each pass the batch was rolled up and inserted endwise until after the tenth pass when the roll opening was changed and the batch permitted to run one minute with a small revolving bank. The batch was then sheeted off or the milling continued for deliberate increase of the thermal treatment. This rapid method has been found to yield homogeneous compounds showing good dispersion of nearly all materials. For the evaluation of specific properties the test recipes given in Table I were chosen as characteristic compounds.

Bleeding Test. For bleeding or color migration studies, recipe A was prepared using one per cent of coloring material in a 200-gram batch and was fluxed by the general procedure. A similar white recipe containing one per cent titanium dioxide was used as the reference sample against which a 1 × 1 inch square of the colored batch was attached in a cabinetmaker's clamp and stored at room temperature. Examination of the surface of the white batch, which was

Table I. Test Recipes

Recipe Test	A Bleeding	B Light stability	C Heat stability	D Resin stability
Vinyl chloride-acetate copolymer[a]	66.50	65.90	....	....
Vinyl chloride-acetate copolymer[b]	....	....	98.00	96.60
Stabilizer	1.50	1.50	2.00	2.40
Dibutyl Cellosolve phthalate	25.75	27.00	....	....
Methyl Cellosolve oleate	3.00	3.00	....	....
Raw castor oil	0.75	....	....	....
Carnauba wax	1.00	1.50	....	....
Salol	0.50	1.00	....	....
Titanium dioxide	....	0.10	....	....
Coloring material	1.00	Varies	Varies	1.00
	100.00	100.00	100.00	100.00

[a] 95% vinyl chloride, 5% vinyl acetate; mol. wt. 22,000.
[b] 86% vinyl chloride, 14% vinyl acetate; mol. wt. 10,000.

VINYL CHLORIDE-ACETATE COMPOUNDS

coloring materials by trade name and for a generalized list by chemical classes. Wide discrepancies have been found between properties of coloring materials in this copolymer resin and those in inks and surface coatings. Emphasis is placed on light stability studies.

in contact with the colored sample, for evidence of color bleeding was made at the end of 1, 5, 10, 20, and 30 days, and every 30 days thereafter to a total of 180 days. The following final ratings were applied:

A = nonbleeding in 180 days
B = slight bleeding in 180 days
C = moderate bleeding, distinct after 180 days
D = bad bleeding, distinct after 10 days
E = very bad bleeding, distinct after 1 day

Light Stability. Studies were made with recipe B. Since the light stability of a coloring material is frequently dependent upon the concentration of coloring agent present, all colors tested were rated at the same visual intensity in so far as possible rather than on the basis of equal concentrations by weight. To save testing time, only pastel tints were studied. With the intense organic colors, such as benzidine yellow, 0.005 per cent was used, while the weak hydrated chromic oxide required 0.40 per cent to yield compounds of about the same intensity. A set of standard intensities was chosen in strong pastel tints to which each color to be tested was approximately matched in intensity for light exposure tests:

Red	Lithol rubine (calcium resinated salt)	0.01%
Orange	Basic lead chromate (60% lead chromate, 40% lead oxide)	0.20
Yellow	Lead chromate (61% lead chromate, 39% lead sulfate)	0.20
Green	Chlorinated copper phthalocyanine	0.02
Blue	Copper phthalocyanine blue	0.02

Recipe B was prepared and fluxed by the general procedure mentioned except that, for convenience in weighing where 0.05 per cent and less color was required, the coloring material was added to the fluxed batch as a 1 per cent milled master batch previously prepared in recipe A for bleeding test purposes. After the standard intensity sample was matched, a second sample was prepared containing half the concentration, and this half-concentration sample became the basis for subsequent comparisons of the amount of fading produced.

To obtain samples of uniform thickness, which is particularly important in these comparisons, weighed amounts of the compound were pressed in a positive mold to a thickness of 0.015 inch, and samples were cut 2.25 × 2.25 inches for test and filing purposes. It has been found useful to mount the original and half-concentration sample of each color tested on a 3 × 5 inch file card for reference. Exposed samples were mounted in the same manner.

Light stability ratings are based on exposures in the National accelerated weathering unit, Type XV (7); an interior view is shown in Figure 1. The samples rotate about the arc once in 55 seconds at a mean distance of 10.25 inches. Sunshine carbons, operating at 28 amperes with 29 volts across the arc, burn one pair at a time. (Since these tests were started, the standard operating conditions for this machine have been set at 30 amperes, 40 volts by the manufacturer.) A Corex D filter surrounding the arc cuts off radiation below 2600 Å. No water spray was used.

As a preliminary test all color samples were exposed in the Type XV unit for 20 hours. Comparison of the exposed sample with the unexposed half-concentration sample showed in which direction to proceed for the next exposure. Time periods were 5, 10, 20, 40, 80, 160, 240, and 320 hours. Two exposed samples were finally obtained; one was less than, and one more than, one half faded. A light stability half-life rating was then estimated which served as a relative

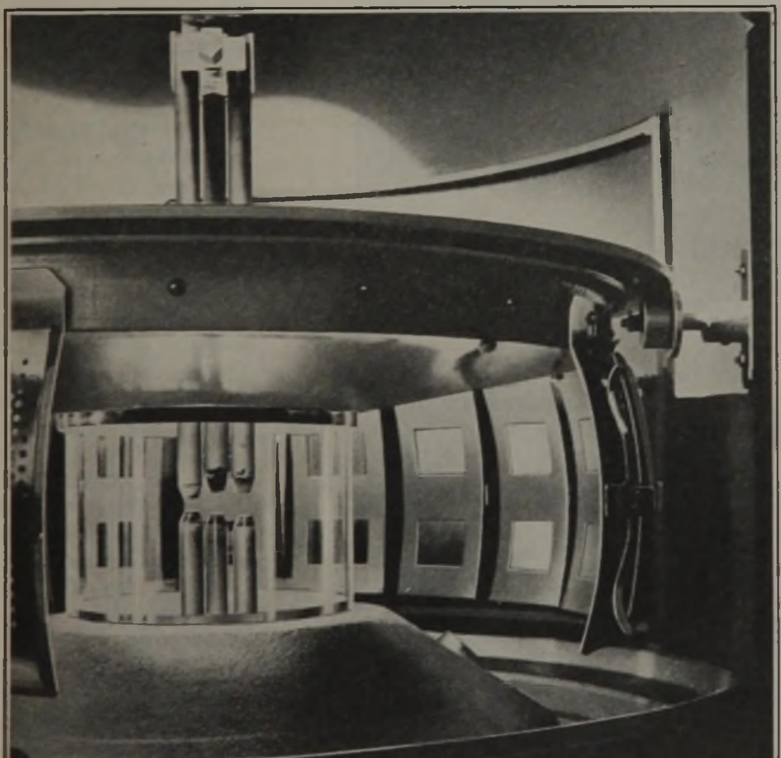

Figure 1. Interior of Type XV Accelerated Fading Unit, Showing Color Samples and Corex D Filter Surrounding the Arc

One pair of carbons burns at a time.

basis of comparison with other coloring materials. A specimen set of exposed samples compared with a strip of the half-concentration sample is shown in Figure 2. Samples which remained less than half faded in 320 hours were removed from test inasmuch as the blank compound started to yellow on longer exposures from effects not directly related to the actual coloring material.

To simplify the reporting of generalizations given in Tables III and IV, the following ratings have been assigned on the basis of "XV half-life" hours:

A	Excellent	Over 320 hours
B	Good	100 to 320
C	Fair	20 to 100
D	Poor	5 to 20
E	Very poor	Less than 5

In order to correlate the arc exposures with sun tests, a series of samples was exposed on the roof at Cleveland, Ohio, in a manner similar to the A. S. T. M. method (*1*) for textile fading tests. Duplicate series were run bare and under window glass, mounted on open racks facing south, placed at an angle of 45° with the horizontal. Exposures were made on clear days only during June, July, and August, 1941, between the hours of 9:30 A. M. and 3:30 P. M. eastern standard time. On days when it became cloudy by 12:30 P. M., the samples were removed from test.

Samples were examined at regular intervals, compared with half-concentration samples where possible, and removed from test when slightly less than half faded. The duplicate sample was then exposed for double the time of the first one removed. Comparisons of sun-exposed samples with at least two XV-arc-exposed samples for each color made possible the estimation of sun hours equivalent to XV-arc hours. A summation of results is shown in Table II.

TABLE II. CORRELATION OF SUNLIGHT ROOF TESTS WITH TYPE XV CARBON ARC EXPOSURES

	No. Samples Tested			Sun Hr. Equivalent to 1 Hr. in XV Unit	
	Bare	Under window glass		Bare	Under window glass
Coloring materials in recipe B	36	37		1.30	1.40
Miscellaneous copolymer compounds	24	22		1.58	1.91
Total	60	59	Av.	1.43	1.60
Average deviation from mean				±0.58	±0.63

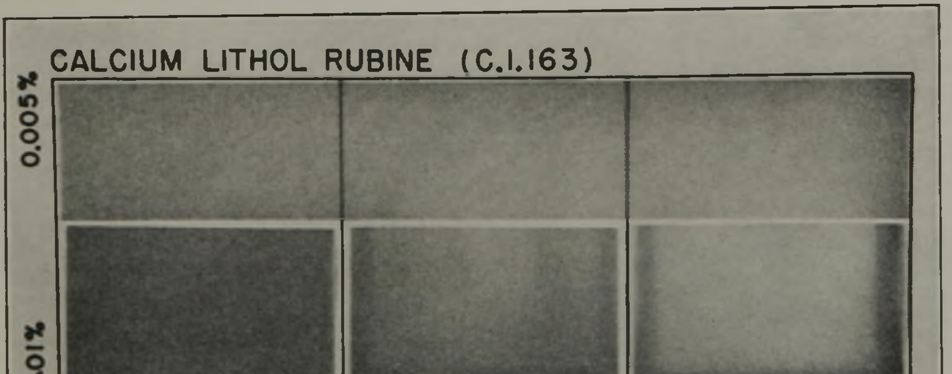

FIGURE 2. EXPOSED LIGHT STABILITY TEST SAMPLES COMPARED WITH HALF-CONCENTRATION SAMPLES FOR DETERMINATION OF HALF LIFE OF COLORING MATERIALS

A good and poor color are shown.

HEAT STABILITY. A milling test of coloring material in recipe C served to evaluate not only the heat stability of the coloring material and the effect of the color on the heat stability of the resin, but also color development.

A 300-gram batch of recipe C containing about twice the amount of color used in the standard light stability test sample was prepared and fluxed on the mill operating with 40 pounds gage steam pressure. The batch was run with a small bank, and samples were removed at 1 and 30 minutes. For comparison they were molded side by side to produce a plaque 0.070 inch thick which was examined by transmitted and reflected light for evidences of fading or color development.

In the evaluation of blacks or dark opaque colors this method is inadequate because changes due to resin degradation are obscured. For these special cases Clash (*2*) developed a test, a complete description of which is beyond the scope of this report. Briefly it consists in milling one

Table III. Properties of Coloring Materials by Trade Names Recommended for Vinyl Chloride-Acetate Copolymer Resins

Trade Name	Supplier[a]	Color	Relative Strength[b]	Bleeding[c]	Light Stability[d]	Heat Stability[e]
Red						
Ansico Red B 37B31	Ansb.-Siegle	Medium red	25	*A*	*B*	*S*
Ansico Red Y 37B32	Ansb.-Siegle	Medium red	20	*A*	*B*	*S*
Arcadia Red X-1700	Imp. P. & C.	Blue-red	100	*C*	*B*	*S*
Brilliant Lake M R-6	Harmon	Medium red	50	*D*	*C*	*S*
c. p. Cadmium Light Red #28	Harshaw	Orange-red	15	*A*	*A*	*S*
c. p. Cadmium Med. Lt. Red #29	Harshaw	Orange-red	15	*A*	*A*	*S*
Cadmium Lithopone Lt. Red #8	Harshaw	Orange-red	7	*A*	*A*	*S*
Cadmium Lithopone Med. Lt. Red #9-3	Harshaw	Orange-red	7	*A*	*A*	*S*
Cadmium Red Medium #4333	Chem. & Pig.	Medium red	7	*A*	*A*	*S*
Genoa Toner X-1180	Imp. P. & C.	Blue-red	100	*C*	*B*	*S*
Geranium Red X-1129	Imp. P. & C.	Blue-red	30	*B*	*B*	*S*
Lithol Rubine R-9	Harmon	Blue-red	100	*B*	*B*	*S*
Lithol Rubine Red Toner R-97	Harmon	Blue-red	100	*B*	*B*	*S*
Parisian Red X-1093	Imp. P. & C.	Blue-red	25	*C*	*B*	*S*
Plastic Red 3171	Brooklyn	Blue-red	50	*E*	*B*	*S*
Pure Light Red Oxide R-2899	C. K. W.	Orange-red	25	*A*	*A*	*S*
Red Lake C Toner R-1	Harmon	Medium red	50	*A*	*C*	*S*
Red Toner R-84	Harmon	Blue-red	100	*C*	*B*	*S*
Red Toner R-90	Harmon	Blue-red	100	*C*	*B*	*S*
Red Toner R-92	Harmon	Blue-red	100	*C*	*B*	*S*
Red Toner R-93	Harmon	Medium red	100	*A*	*B*	*S*
Selkirk Red X-2028	Imp. P. & C.	Blue-red	100	*B*	*B*	*S*
Solfast Red CP 663	Sher.-Will.	Blue-red	100	*C*	*B*	*S*
Special Red Toner X-1778	Imp. P. & C.	Blue-red	100	*C*	*B*	*S*
Virginia Red Toner CR 6500	Std. Ultr.	Blue-red	100	*B*	*B*	*S*
Orange						
Benzidine Orange YB-3	Harmon	Yellow-or.	100	*C*	*C*	*S*
Burnt Sienna #1118	C. K. W.	Or.-brown	10	*A*	*A*	*S*
c. p. Deep Orange A-4337	Imp. P. & C.	Red-or.	5	*A*	*A*	*S*
Gold Paste F-45	Harmon	Amber	3	*A*	*A*	*S*
Hoover Brown #7764	Hoover	Yel.-brown	...	*A*	*A*	*S*
Mandarin Orange 68-T-01	Ansb.-Siegle	Red-or.	20	*A*	*A*	*S*
Rex Orange A-4403	Imp. P. & C.	Red-or.	20	*A*	*A*	*S*
Yellow						
Benzidine Yellow D-2472	Sher.-Will.	Green-yel.	200	*C*	*C*	*S*
Benzidine Yellow YB-1	Harmon	Green-yel.	200	*D*	*C*	*S*
Benzidine Yellow YB-2	Harmon	Green-yel.	200	*B*	*C*	*S*
Benzidine Yellow YB-22	Harmon	Green-yel.	200	*D*	*C*	*S*
Benzate Yellow YB-27	Harmon	Green-yel.	100	*C*	*D*	*S*
Canary Toner X-786	Imp. P. & C.	Green-yel.	50	*D*	*C*	*S*
Ceylon Yellow X-1934	Imp. P .& C.	Green-yel.	100	*D*	*C*	*S*
Fanchon Yellow YH-1	Harmon	Green-yel.	50	*D*	*C*	*S*
Fanchon Yellow YH-2	Harmon	Green-yel.	50	*D*	*C*	*S*
Fanchon Yellow YH-4	Harmon	Green-yel.	50	*E*	*C*	*S*
Horicon Yellow X-1351	Imp. P. & C.	Green-yel.	50	*E*	*C*	*S*
Mapico Yellow Lemon	Bin. & Smith	Or.-yel.	...	*A*	*A*	*S*
Osaka Yellow Lake X-1630	Imp. P. & C.	Medium yel.	5	*C*	*C*	*S*
Perfect Yellow 65-T-95	Ansb.-Siegle	Green-yel.	1.5	*A*	*A*	*S*
c. p. Primrose Yellow A-3042	Imp. P. & C.	Medium yel.	5	*A*	*A*	*S*
Yellow Toner YB-17	Harmon	Medium yel.	100	*C*	*C*	*S*
Green						
Chromic Oxide Green	Harshaw	Yel.-green	5	*A*	*A*	*S*
Doco Permanent Green #1	Stan.-Dogg.	Medium green	2.5	*A*	*A*	*S*
Opaline Green G-1	Harmon	Medium green	50	*A*	*A*	*S*
Permanent Green X-1010	Imp. P. & C.	Medium green	2.5	*A*	*A*	*S*
Sherwood Green A-4436	Imp. P. & C.	Medium green	50	*A*	*A*	*S*
Viridine Green 62-A-11	Ansb.-Siegle	Medium green	50	*D*	*C*	*S*
Blue						
Blue Toner B-3	Harmon	Medium blue	50	*A*	*A*	*S*
Cobalt Blue #221	Shepherd	Red-blue	3	*A*	*A*	*S*
Fastolux Blue 43-8013	Ansb.-Siegle	Medium blue	50	*B*	*A*	*S*
Franconia Blue A-4431	Imp. P. & C.	Medium blue	50	*A*	*A*	*S*
Laconia Blue A-4432	Imp. P. & C.	Medium blue	50	*A*	*A*	*S*
Luna Blue B-36	Harmon	Medium blue	50	*A*	*A*	*S*
Marine Blue Toner A-8021	Imp. P. & C.	Medium blue	100	*D*	*C*	*S*
Ultramarine Blue #1401	Calco	Red-blue	5	*A*	*B*	*S*
Ultramarine Blue #2136	Calco	Red-blue	5	*A*	*B*	*S*
White						
Antimony Oxide	Harshaw	White	20	*A*	*A*	*S*
Rayox YCR	R. T. Vand.	White	100	*A*	*A*	*S*
Titanox A #168 M. O.	Titan. Pig.	White	100	*A*	*A*	*S*
Ti-Pure R-110	Krebs	White	100	*A*	*A*	*S*
Black						
Excello 2X Carbon Black	Imp. Oil & Gas	Black	...	*A*	*A*	*S*
P-33 Thermatonic Black	R. T. Vand.	Gray-black	...	*A*	*A*	*S*
Super-Spectra Carbon Black	Bin. & Smith	Black	...	*A*	*A*	*S*

[a] Ansb.-Siegle = Ansbacher-Siegle Corp.; Bin. & Smith = Binney and Smith Co.; Brooklyn = Brooklyn Color Works; Calco = Calco Chemical Div. American Cyanamid Co.; Chem. & Pig. = Chemical and Pigment Co.; Harmon = Harmon Color Works; Harshaw = Harshaw Chemical Co.; Hoover = C. E. Hoover; Imp. Oil & Gas = Imperial Oil and Gas Products Co.; Imp. P. & C. = Imperial Paper and Color Corp.; Krebs = Krebs Pigment and Color Corp.; Shepherd = Shepherd Chemical Co.; Sher.-Will. = Sherwin-Williams Co.; Std. Ultr. = Standard Ultramarine Co.; Stan.-Dogg. = Stanley Doggett, Inc.; Titan. Pig. = Titanium Pigment Corp.; R. T. Vand. = R. T. Vanderbilt Co.; C. K. W. = C. K. Williams and Co.

[b] Lithol rubine = 100.

[c] *A* = nonbleeding; *B* = slight; *C* = moderate; *D* = bad; *E* = very bad.

[d] *A* = excellent; *B* = good; *C* = fair; *D* = poor; *E* = very poor.

[e] *S* = satisfactory; *F* = fair; *U* = unsatisfactory.

per cent of the material being tested into recipe D. A small sample is then sealed in a glass tube connected to a mercury reservoir and a capillary tube. By immersing the sample tube in an oil bath, pressure is built up that can be read by the mercury level in the capillary. The pressure increases slightly at first, then falls gradually until the decomposition point is reached, whereupon it rises steadily, a fact attributed to the evolution of decomposition gases. By running a blank control simultaneously, it is possible to determine a heat stability index which is the ratio of the time to the decomposition point (heat stability) of the mix containing one per cent color to the heat stability of the uncolored mix. The test serves to eliminate dark coloring materials which markedly lower the stability of the resin.

RESULTS. Table III lists the coloring materials by specific trade names. To test all the coloring materials on the market would be impossible and futile, since there are more than a hundred manufacturers of dyes and dry colors in the United States. Hence, a generalized summation by chemical classes is included in Table IV from which a coloring material may be selected and ordered from any manufacturer with a reasonable assurance that the properties will be similar to those given

Interpretation of Bleeding Tests

Some interpretation of the bleeding test results on the basis of experience must be made before the suitability of a chosen color is decided upon for a given application. Recipe A was chosen as a typical plasticized composition which would exhibit moderate bleeding tendencies in the compound if there were any. The degree of bleeding permissible depends upon the application; e. g., colors for a highly plasticized strap to be used on a white sheeting for a lady's purse would require a definitely nonbleeding color. On the other hand, a cable coating composition might tolerate a coloring material rated *C* or *D* by this test. The degree of bleeding is dependent upon the plasticizer content and, to some extent, on the particular plasticizer used.

In general, from a bleeding standpoint all types of coloring materials, including dyes, lakes, and toners, can be used in unplasticized or rigid compounds provided the other properties are satisfactory. Coloring materials with bleeding ratings of *A* to *C* are required for most plasticized compounds containing 10 per cent or more liquid plasticizer.

In case of doubt with an unknown color, a brief test of 5 days in the composition under consideration is sufficient to eliminate most colors which are undesirable from a bleeding standpoint.

Since dyes and colors partially soluble or extractable in plasticizers cannot be used in flexible compounds, inorganic pigments and certain organic toners and lakes are indicated. Exclusion of dyes also limits the range of clarity of flexible compositions because most of the organic lakes and toners are clear only in low concentrations. The production of nonbleeding, dull, opaque stocks is relatively easy inasmuch as inorganic pigments can be used, virtually all of which are nonbleeding.

For the more transparent bright colors the organic pigments are required. Of these, the aluminum hydroxide lakes possess the best clarity because aluminum hydroxide has an index of refraction close to that of the copolymer vinyl resins. Many other organic nonbleeding colors are clear in low concentrations. In general, resinated colors have been found to possess some advantage in transparency and are claimed to have some other minor advantages (*10*). Certain ultramarine blues are exceptions in the inorganic field and yield clear stocks even in high concentrations of color.

Interpretation of Light Stability Tests

To avoid misinterpretation in the application of test results, the half-life results in Tables III and IV are expressed in general terms of *A*, *B*, *C*, etc., covering exposure ranges. The numerical half-life ratings have been found satisfactory for detecting differences between the members of the same class of colors when samples were exposed simultaneously. Some errors are introduced, however, by comparing half-life samples exposed at widely different times of the year. The location of the arc unit was such that the room temperature varied from a low of 16° in winter to 31° C. in midsummer, at the extremes, and this affected the temperatures of the samples in the unit—hence the rate of fading. The effect has not been quantitatively evaluated although it has been taken into account by running check samples throughout the year. The effect of temperature was minor in comparison with the differences found among the various chemical classes of coloring materials tested.

TABLE IV. GENERAL CLASSIFICATION OF PROPERTIES OF COLORING MATERIALS IN VINYL CHLORIDE-ACETATE COPOLYMER RESINS

	Relative Strength	Bleeding	Light Stability	Heat Stability[a]
RED				
Alizarin lakes	25	D	D	U
Burnt siennas	10	A	A	F
Cadmium reds	15	A	A	S
Cadmium red lithopones	10	A	A	S
Chloronitraniline reds	100	E	D	S
Hansa rubine G	25	A	B	S
Indanthrene pinks	50–100	C	E	F
Lithol reds	100	C	D	S
Lithol rubines	100	A–C	B	S
Madder lakes	25	D	D	U
Para reds	100	E	C–D	S
Pigments scarlets	100	B–C	B	S
Red iron oxides (natural)	25	A	A	F
Red iron oxides (synthetic)	25	A	A	F
Red lake C lakes	50	A	C	S
Red lake R lakes	50	C–D	C	S
Red lead oxide	5	A	A	S
Rhodamines	..	E	D	U
Spanish oxides	10–30	A	A	F
Thioindigos	25	C–D	E	F
Toluidine toners	100	E	D	S
ORANGE				
Benzidine oranges	100	C–D	C	S
Cadmium oranges	..	A	A	S
Chrome oranges	5	A	A	S
Chrome-molybdate oranges	20–30	A	A–B	S
Nitraniline oranges	50–100	D–E	D	S
Persian orange lakes	25	D	D	..
YELLOW				
Benzidine yellows	200	B–D	C–D	S
Cadmium yellows	..	A	A	F
Chrome yellows	5	A	A	S
Hansa yellows	50	E	C–D	S
Iron oxides (natural)	..	A	A	F
Iron oxides (synthetic)	..	A	A	F
Zinc chromates	2	A–B	A	U
GREEN				
Brilliant green crystals	..	E	..	U
Chlorinated copper phthalocyanine	50	A	A	S
Chrome greens	..	A	A	S
Chromic oxides	5	A	A	S
Hydrated chromic oxides	2	A	A	S
BLUE				
Copper phthalocyanines	50	A	A	S
Indanthrene blues	25–50	A–B	C	F
Iron blues (ferrocyanides)	..	..	..	U–S
Ultramarine blues	2–5	A	A–B	U–S
Victoria blue (PTA lake)	100	D	C	S
WHITE				
Antimony oxides	20	A	..	S
Titanium dioxides	100	A	..	S
Zinc oxides	..	A	..	U
Zinc sulfides	..	A	..	S
BLACK				
Bone blacks	..	A	A	S
Carbon blacks	..	A	A	S
Iron oxide black (synthetic)	..	A	A	S
Nigrosines	..	E	..	U

[a] Compounds containing iron oxides vary widely; synthetic oxides are best.

A few samples changed in dominant wave length as they faded, but even in these cases an estimation of a half life was possible.

The correlation of XV-arc exposures with sun tests (Table II) shows a value of 1.60 hours of sunlight equivalent to 1 hour in the XV unit for samples exposed under glass, and the type of change closely simulated that found in sunlight. For the sun tests the average percentage sunshine for the entire days when samples were exposed was 88.2 per cent of that possible, based on Weather Bureau reports (*9*). It should be remembered that the period during which the outdoor comparisons were made was one in which the actinic value of the sunlight was very high.

Recipe B contains salol (phenyl salicylate). This and a number of other substances (*3*) act as light stabilizers for the vinyl copolymer resins and retard the yellowing action of light. The effect of salol as a light stabilizer for coloring materials was briefly investigated, using salol in amounts up to 5 per cent. Additions up to 1 per cent had some stabilizing effect, while further additions were ineffective. It was concluded that, although the addition of salol retarded fading, colors which were rated as poor without salol were still rated poor with salol present. Its use as a color stabilizer is therefore not recommended except for special cases where it is proved desirable.

The light stability ratings given here represent the minimum ratings because the color concentrations are so low. A number of coloring materials falling in the poorer classifications can be used satisfactorily in high concentrations with adequate light stability.

Some rather striking results are evident when the light stability ratings in the vinyl copolymer resins are compared with results of ratings in inks and surface coatings. Several examples may be noted. Toluidine red toner, here rated poor, is generally considered one of the best in light fastness in other media (*6*); lithol rubine, normally rated fair, is here rated good. One toluidine toner tested had a half life of 10 hours; a lithol rubine calcium salt rated 120 hours under the same conditions. Rhodamines, found very poor in vinyl resins of this type, are considered permanent in tints for inks (*6*).

A few of the anthraquinone and vat colors have been tested, with unusually poor light stability found for all except an indanthrene blue which had poor heat stability. As a class these are usually "very permanent and durable" (*5*).

Other discrepancies will be obvious to those familiar with the organic pigments without discussing each in detail.

Interpretation of Heat Stability Tests

With processing temperatures in the range 130° to 160° C., the question of heat stability of coloring materials is of special importance in copolymer vinyl compounds, just as in the case of colors for lacquers which must withstand baking temperatures.

The comparison of sample plaques in recipe C prepared from samples milled 1 and 30 minutes showed five types of results:

Bad Fading. Rated unsatisfactory. They cannot be used for any purpose.

Slight Fading. Rated fair. Colors of this rating should be avoided wherever possible, although occasionally they have to be used because of some other outstanding property such as brightness.

Unchanged. Rated satisfactory.

Increased Intensity. May be caused by initial poor dispersion or by chemical action. If the other properties of the material are favorable, further tests may be run to improve the dispersion. A few colors such as rhodamine B act as indicators and increase in intensity, presumably upon reaction with acid liberated in the resin by the heat treatment.

Blackened. Rated unsatisfactory. These are colors which cannot be used for any purpose because they act as decomposition catalysts. In general, compounds of iron and zinc have this tendency.

A few generalizations can be made regarding the last classification listed and the specific offenders mentioned:

Iron Compounds. No comprehensive general rules can be given for the effect of iron coloring materials on resin stability, although the synthetic iron oxides are more apt to be satisfactory than the natural oxides and earth pigments. More work remains to be done before the ferrocyanides can be recommended. Some of the latter appeared to be heat stable, others faded.

Zinc Compounds. Most zinc compounds, including zinc oxide and zinc chromate, have been found very active decomposition catalysts. A number of samples of zinc sulfide, however, has been found satisfactory.

Miscellaneous. Several outstandingly bad colors should be mentioned. The rhodamines, brilliant green crystals, and the nigrosine blacks have a deleterious effect and must be avoided.

Relative Strength

In the preparation of light stability samples, all colors were matched to approximately the same intensity; hence the amount used is an indication of the tinting strength of the material. The relative strength figures in Tables III and IV are the reciprocals of the concentrations used in the standard light stability samples. For example, lithol rubine required 0.01 per cent color, hence its relative strength is 100; madder lake used 0.04 per cent, and its relative strength is therefore 25.

Dispersion Problems

With unplasticized compounds very little difficulty is encountered with dispersion of coloring materials added as dry powders prior to fluxing. The shearing forces encountered in fluxing and mixing these relatively stiff compounds are sufficient to break up agglomerates and disperse practically all types of coloring materials. The plasticized stocks present a very different problem, however. In this case bleeding requirements limit the choice to pigments (inorganic and organic) which, in general, are more difficult to disperse than dyes.

Two solutions are possible for dispersion problems. The first is to grind the pigment with plasticizer into a thick paste on a three-roll paint mill. This is highly satisfactory for most pigments. Specifically, dibutyl Cellosolve phthalate and di-(2-ethylhexyl) phthalate have been successfully utilized. The latter is superior in wetting characteristics and produces easy-grinding pastes. For the organic pigments, 30 to 50 per cent of pigment by weight generally produces a paste of suitable consistency. Considerable work has been done on the use of wetting agents in conjunction with pigment grinding for the printing ink and paint industry which can be of value here. Addition of a wetting agent results in more highly viscous pastes with some pigments (*4*) for a given pigment-plasticizer ratio.

Another solution to the dispersion problem for organic pigments is by the use of flushed colors prepared by the color manufacturer. These are colors which are wet with plasticizer, for example, after precipitation of the coloring material from water solution and prior to drying. In this way the formation of agglomerates is largely eliminated, which results in a more readily dispersible paste.

Color Master Batches

In the procedure for the preparation of light stability test samples, the use of a one per cent milled master batch was mentioned as an aid to weighing the small quantity of color required. Powder master batches have been found useful in increasing accuracy and facilitating weigh-up procedures, wherever small quantities are involved, by eliminating the necessity of using an analytical balance. Concentrations of 0.1, 1.0, and 10 per cent color in dry copolymer resin powder are commonly used.

Homogeneous batches are obtained by ball milling the dry color and resin powder in a pebble mill for several hours. Iron mills or balls should be avoided because of the possibility of contamination. Some grinding action results from this treatment, which may increase the ease of dispersion of a few pigments although the method is not nearly so effective as grinding the pigment into paste on a three-roll paint mill, as previously discussed above. The primary object is the production of a uniform dilution.

Acknowledgment

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CREEP AND CREEP RECOVERY

In Plasticized Polyvinyl Chloride

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Time effects play an important part in the mechanical behavior of plastics and textile fibers at room temperature. In many cases these time effects are due mainly to the existence of a delayed elasticity superimposed upon Hooke's law or instantaneous elasticity, the delayed component of the deformation being a function of the previous loading history.

Methods are discussed of investigating the delayed elastic behavior in the light of Boltzmann's superposition principle. It is shown that this principle is obeyed by plasticized polyvinyl chloride specimens under small longitudinal deformations.

IN THE development of plastics and synthetic fibers attention has been concentrated in the past on the attainment of satisfactory strength without undue brittleness. Consequently, mechanical tests were limited to the measurement of strength and ultimate deformation. There are, however, many technologically important mechanical properties of plastics—fatigue, impact strength, damping or internal friction, and the so-called cold flow—which bear little relation to strength and extensibility. Load-deformation tests yield little information concerning these properties. In the mechanical behavior of high polymers a marked time effect exists, and a study of this effect is likely to lead to a better understanding of the mechanism of deformation as related to constitution.

Primary Creep

Under certain circumstances irreversible flow phenomena in high polymers can be eliminated. The time effect may then be described as a delayed elasticity superimposed upon Hooke's law or instantaneous elasticity. At any instant the deformation of a body thus consists of an instantaneous component, proportional to the load acting at that instant, together with a delayed elastic component which is a function of the previous loading history. This delayed elasticity will be denoted by the term "primary creep".

Let us suppose first that a constant load is applied to a body at zero time and left in position for 24 hours; at the end of the period the load is removed, as in the load-time diagram in Figure 1.

In general, we may represent the corresponding deformation-time diagram by Figure 1(a). While the body is under the load, the deformation increases continuously; i. e., creep takes place. Following load removal, the residual deformation is not constant but decreases gradually with time; i. e., creep recovery takes place, after which a permanent set remains. If this experiment is repeated, it may often be found, if the load is not too large, that the behavior represented by Figure 1(b) is obtained. In this case the body eventually regains the form it possessed at the beginning of the test, and further permanent deformation in similar subsequent tests under the same or smaller load will be absent. Under these circumstances the body is said to be "mechanically conditioned", and the creep and creep recovery are then of the nature of the delayed elasticity described above. This paper

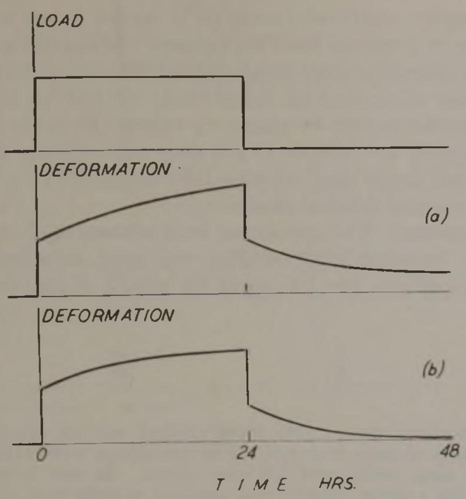

FIGURE 1. CREEP AND CREEP RECOVERY

is concerned with the laws governing such delayed elastic behavior and with an investigation of the nature of this behavior in a series of plasticized polyvinyl chloride specimens.

The Superposition Principle

The problem of the delayed elastic behavior of bodies such as glass and silver filaments was important about ninety years ago (*4–7*). These bodies were useful as the suspensions of electrical and magnetic measuring instruments, and it was necessary to know to what extent the elastic behavior of the suspensions was affected by the previous deformation history. Boltzmann (*1*) advanced a hypothesis which gave a general relation between load, time, and deformation for materials such as glass which manifest delayed elasticity at room temperature. This hypothesis, called the "superposition principle" of Boltzmann, appears to be in agreement with the experimental data on glass. It is reasonable, therefore, to use this principle as a basis for the study of the primary creep properties of high polymers, bearing in mind that in the latter case the range of reversible elasticity is much greater than for glass.

The superposition principle may be stated as follows: We assume that when a load, P, is applied at zero time to a previously unloaded body, an instantaneous deformation occurs first, proportional to load P. This subsequently increases by the delayed deformation, which is assumed to be again proportional to load P and to a function, $\psi(t)$, of the time under load t. Thus if F is a form factor and E is the appropriate instantaneous modulus, the instantaneous deformation is given by (FP/E) and the deformation, x_t, at time t by:

$$x_t = (FP/E)\,\{1 + \beta\psi(t)\} \tag{1}$$

where β = a constant
$\psi(t)$ = the creep function

Now let us assume that various loads, P_θ, are applied at times θ previous to a given instant, t. According to Boltzmann's principle, the deformation at time t due to the several previously applied loads is assumed to be equal to the simple summation of the deformations which would have been observed at that instant if each of the loads had been independently applied. The deformation x_t at time t due to all the previously applied loads is thus assumed to be given by

$$x_t = \sum_{\theta = -\infty}^{\theta = t} (FP_\theta/E)\,\{1 + \beta\psi(t - \theta)\} \tag{2}$$

Equation 2 is one form of the superposition principle.

The problem is now to devise experiments by means of which the validity of Equation 2 can be demonstrated. Two methods of test have been used in the investigations on plasticized polyvinyl chloride and other materials; these tests will be called the "long-duration creep and recovery test" and the "superposition test", respectively.

Long-Duration Test

Let us suppose that, to a body manifesting only primary creep, a constant load is applied at zero time, as shown by the load-time diagram in Figure 2(*a*), and that the corresponding deformation-time diagram is given by curve *abc* in 2(*b*). The deformation at time t will be denoted by d_c. Let us suppose alternatively that the load is removed at some time, T, at which the deformation is proceeding very slowly; the course of the deformation after removing the load will be given by a curve such as *bde* in Figure 2(*b*). According to the superposition principle, we may determine the course of the creep recovery by assuming that the original load applied at zero time continues indefinitely, and that a negative load of equal magnitude is applied at the instant T. Consequently at time $(T + t)$ the deformation is that due to the first load diminished by that due to the negative load—i. e., by d_c.

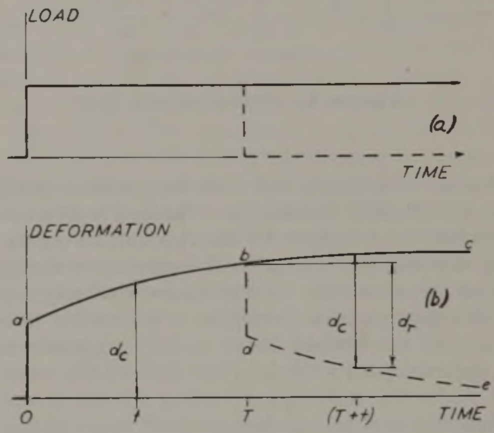

FIGURE 2. LONG-DURATION CREEP AND RECOVERY TEST

Following removal of load at time T, the (negative) deformation due to load removal, d_r, as a function of recovery time is nearly the same as the deformation due to load application d_c as a function of creep time, since we have assumed that at instant T the deformation is increasing only slowly with time. According to the superposition principle, therefore, in such a test d_r and d_c should be nearly the same for small values of creep or recovery time t; thereafter d_r should be progressively less than d_c as t approaches the value of the total time under load T. Furthermore, the value of the deformation at any particular instant should be proportional to the load used in the test.

The Superposition Test

In this type of test much less time is required than in the previous test. This test does not give so much information concerning the nature of the creep function $\psi(t)$; on the other hand, it is a more rigorous test of the superposition hypothesis than is the simple long-duration creep and recovery experiment. Let us suppose that a constant load is applied to a previously unloaded body, as shown by the broken line in Figure 3(*a*), and that the corresponding deformation as a function of time under load is as given by the broken line in 3(*b*). Now let us suppose alternatively that the load is re-

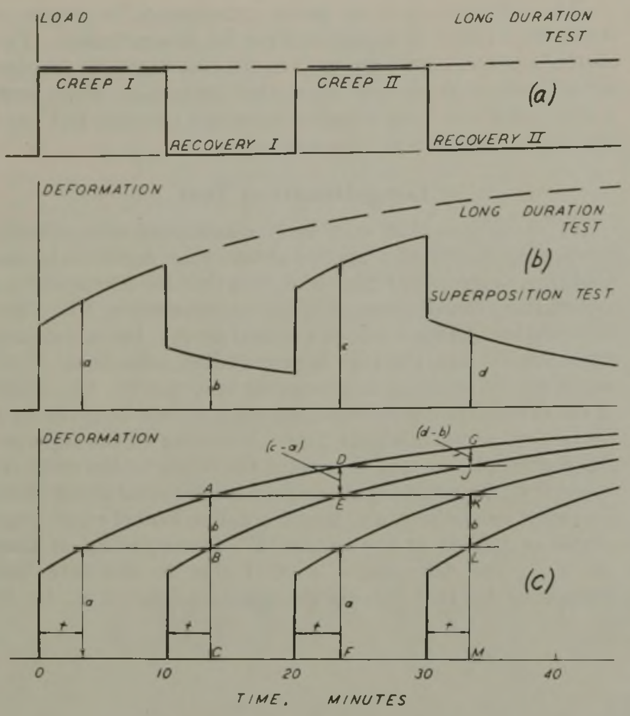

Figure 3. Superposition Test

moved after 10 minutes, and that the specimen is allowed to recover for a further 10 minutes. The load is then assumed to be reapplied for a further 10 minutes and so on, as in 3(*a*). During this test the change in deformation with time is observed, as shown in 3(*b*). If the delayed elasticity of the body obeys the superposition principle, it is possible to compute, for example, the broken curve in 3(*b*)—representing creep under uninterrupted loading—from data on the creep and recovery under the interrupted loading scheme shown by the unbroken line in 3(*b*). If data on both types of test for the same material under the same load are available, then it is possible to determine whether the principle gives a valid description of the creep and recovery behavior under the complex loading history of the superposition test.

Let us suppose in the superposition test of Figure 3 that the deformations at corresponding times, t, after the commencement of each creep or recovery stage is given by a, b, c, and d, respectively. The geometrical construction in 3(*c*) shows that the deformations at the corresponding instants in a simple creep test under uninterrupted loading should be equal to a, $(a+b)$, $(b+c)$, and $(c+d)$, respectively. In this way it is again possible to demonstrate whether the delayed elasticity of a body obeys the superposition principle.

Plan of the Tests

Materials. Experiments were carried out according to the above two schemes on the longitudinal creep and creep recovery properties of three specimens of polyvinyl chloride plasticized with tricresyl phosphate. Unplasticized polyvinyl chloride is normally "glassy" at room temperature. In such materials the time effect is not very marked in the sense that, if a constant load is applied to a specimen, the deformation increases relatively slowly with time. When this material is highly plasticized, it becomes rubberlike; again in this material time effects are comparatively small. If the unplasticized material is heated beyond a certain ill-defined transition temperature, it becomes rubberlike; on the other hand, if the highly plasticized material is cooled below room temperature, it becomes hard and glassy. Materials with intermediate degrees of plasticization are either somewhat leathery or possess what may be called "lazy rubberlike elasticity". In contradistinction to glassy or rubberlike materials, time effects (creep and recovery) are very noticeable in these materials, and hence they are especially suitable for studying the phenomenon of delayed elasticity.

Procedure. The specimens were lettered A, B, and C and had the following compositions, expressed as weight of tricresyl phosphate per 100 parts by weight of polyvinyl chloride:

A	40
B	50
C	110

Longitudinal creep tests were carried out on specimens cut from sheets of each material. The specimens were about 13 cm. long, 25 mm. wide, and 0.8 mm. thick. In the long-duration creep tests a given weight was applied rapidly but carefully at zero time to the lower end of the specimen, the upper end of

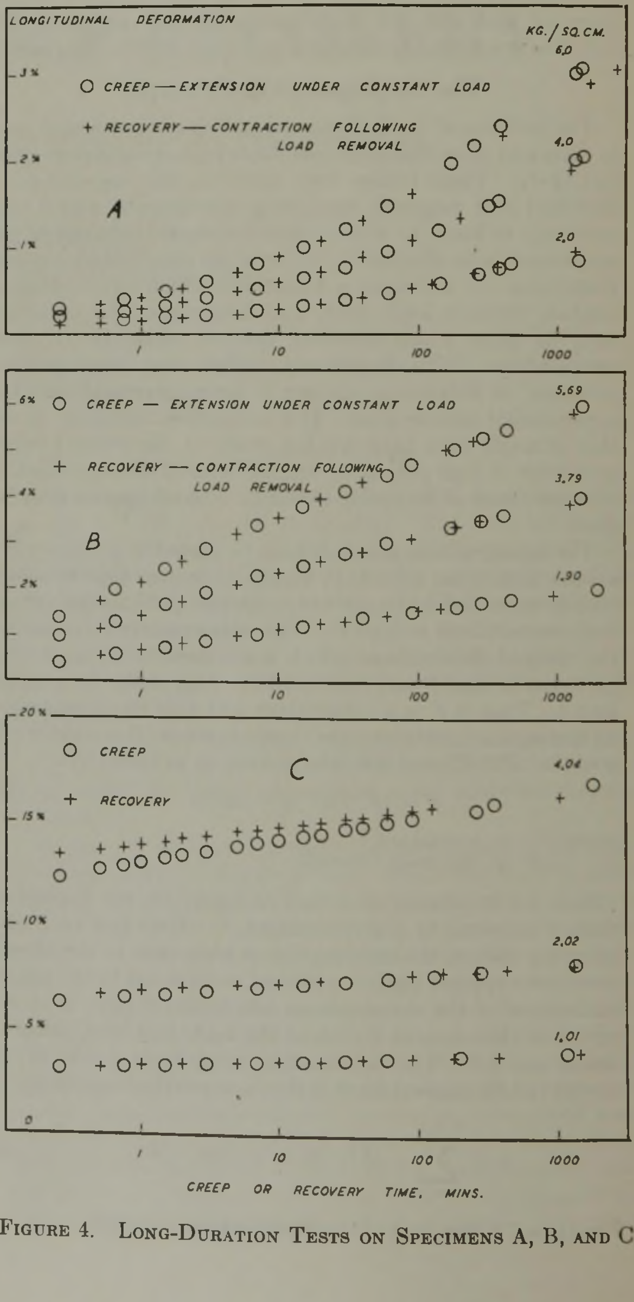

Figure 4. Long-Duration Tests on Specimens A, B, and C

which was fixed. The changes in length with time were observed by a cathetometer reading to 0.01 mm. In the long-duration creep tests the load was left in position for about 24 hours; observations were made at 15, 30, 45 seconds, and 1, 2, 3, 5, 7, 10, 15, 20, 30, 40, 60, 90 minutes after the instant of application of load, and at convenient times thereafter. After about 24 hours the load was removed, and the change in length was observed similarly for 24–48 hours. From the initial observations just before load application or removal, the extension under load as a function of creep time and the contraction due to load removal as a function of recovery time could be determined. The experiments were carried out in a room in which the temperature was held nearly constant at 21.5° C. and the relative humidity at about 62 per cent.

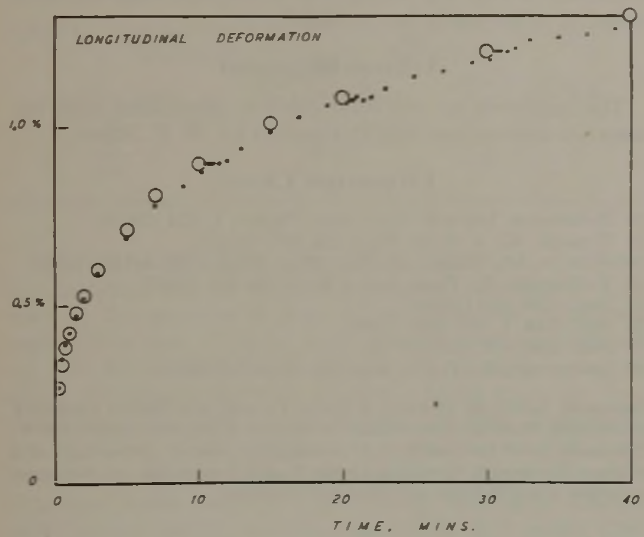

Figure 5. Creep Behavior of Specimen A

Circles, observed deformations; dots, computed from superposition test data.

The general procedure in the long-duration tests was as follows. A long-duration test was carried out on a specimen as described above, with the largest load to be used for the given specimen. Recovery was allowed to take place in each case for about 48 hours. Apparently by this time the creep recovery had reached completion, and there was a slight permanent deformation. A second long-duration test was performed with the smallest load used on the specimen, this time allowing only 24 hours for recovery. The long-duration test was subsequently repeated at successively larger loads. After the first, or mechanical conditioning, test there was in general no further evidence of nonrecoverable deformation; hence the data refer only to the instantaneous and delayed elasticity of the specimens. With this procedure interference on the data of any one experiment due to residual effects of previous experiments was minimized.

Results of Long-Duration Creep and Recovery Tests

Figure 4 shows the behavior following mechanical conditioning of plasticized polyvinyl chloride specimen A in a series of long-duration creep and recovery tests under constant loads corresponding to stresses of 6.0, 4.0, and 2.0 kg. per sq. cm. The extension under each load is shown as a function of time under load, and the contraction due to removal of load as a function of recovery time. For times up to about 200 minutes the corresponding extensions and contractions in each test are nearly the same; thereafter the contractions in the recovery test are slightly smaller than the corresponding extensions. Furthermore, at any given time value the longitudinal deformation is closely proportional to the load used in the test. These results are thus in agreement with the superposition principle. The curves in Figure 4 for specimen A are, in general, concave upward on the logarithmic time plot; this is characteristic of unplasticized or slightly plasticized resins. The deformation after 24 hours under load is about nine times that observed 15 seconds after the instant of load application. This large increase in deformation with time cannot be attributed to the existence of cold flow, since subsequent to removal of load the specimen regained its original length. Presumably, in an unplasticized specimen of polyvinyl chloride a similar but less marked creep behavior would be observed.

The behavior in long-duration creep and recovery tests following mechanical conditioning of specimen B is also shown in Figure 4. In this case the same general behavior regarding the agreement of creep and recovery deformation holds; the curves are, however, slightly concave upward at first and thereafter slightly concave downward, and the deformation after 24 hours under load is only about four times that observed 15 seconds after the instant of load application.

Similar tests on specimen C, which has a rubberlike behavior, show that time effects are much less marked than for specimens A and B (Figure 4). Under small deformations the behavior is consistent with the superposition principle. In tests under loads corresponding to large deformations, there is a systematic deviation from the behavior observed in the less plasticized specimens; at corresponding instants of time the contraction following load removal is greater than the extension under load. This departure from the behavior discussed previously is attributed to the increase in stress on the specimen and in the orientation of the molecular chains while the specimen is extending under load. These curves are, in general, concave downward, and seem to be characteristic of the creep and recovery behavior of rubberlike materials. The creep curve for the highest load used tends to be slightly concave upward towards the right-hand end, suggesting that there is superimposed upon the delayed elastic deformation a slight nonrecoverable flow.

Superposition Test Behavior of Specimen A

A superposition test following the scheme of Figure 3 was carried out on specimen A; from the observations, by means of the superposition principle, the anticipated creep behavior was computed for a simple creep test under the same load These computed deformations as a function of time under load are represented by the dots in Figure 5. The circles represent the observed deformations in a simple creep test carried out after the superposition test, using the same load. The close agreement between these observed deformations and those predicted from the superposition test data suggests that the delayed elastic behavior obeys the superposition principle.

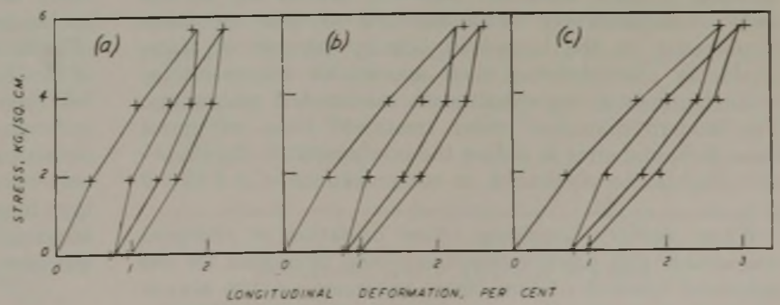

Figure 6. Load-Deformation Behavior of Specimen B

(a) 30-second loading interval
(b) 1-minute loading interval
(c) 2-minute loading interval

Load-Deformation Tests on Specimen B

Figure 6 represents the behavior in load-deformation tests of specimen B. The load was applied in three equal steps over equal intervals of time and removed in the same fashion. The extension of the specimen was observed at the mid-point of each loading interval. On completion of the cycle, a second cycle was traced by the same procedure. Following the last removal of load, the specimen was allowed to rest; after some time it had restored itself nearly to its original length. The tests were carried out with time intervals of 30 seconds, 1 minute, and 2 minutes between each load application or removal. The crosses represent the observations. The effect of increase in loading interval is to shear over the load-deformation loops, a geometric change in time-interval causing an arithmetic displacement in the loops.

Since after each test the specimen recovered to its original length, the load-deformation loops in these tests must be due to the existence of delayed elasticity superimposed upon instantaneous elasticity. From the creep data on specimen B (Figure 4) the load-deformation loops were computed for each test by the superposition principle. The computed deformations are joined by straight lines in Figure 6. The agreement between the observed and computed deformations indicates that in this case the load-deformation loops are due solely to the existence of a delayed elasticity obeying the superposition principle.

Conclusions

Except for the mechanical conditioning tests and possibly the test under the largest load used on specimen C, nonrecoverable flow is absent, and therefore the change of deformation with time under constant load is of the nature of delayed elasticity. Such behavior is not unexpected in, for example, Glyptal resin at elevated temperatures (*2*, *3*, *8*) since in this material chemical cross bonds link the primary valence chains. It must be assumed that in the plasticized polyvinyl chloride, points of entanglement exist between the chains which are sufficiently strong to prevent any observable slippage under the conditions of test. The creep and creep recovery must be due to the straightening and refolding of the chains between the points of entanglement. Such straightening and folding of the primary valence chains is presumably retarded by the existence of secondary forces between the chains. These secondary forces are diminished when the temperature is raised or when plasticizer is added.

Acknowledgment

The specimens of polyvinyl chloride plasticized with tricresyl phosphate were kindly supplied by W. F. Busse.

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PRESENTED before the Division of Paint, Varnish, and Plastics Chemistry at the 104th Meeting of the AMERICAN CHEMICAL SOCIETY, Buffalo, N. Y. This paper gives the results of an investigation carried out as part of a program of research, sponsored by the Textile Foundation, on the creep properties of textile fibers and other high polymers.

Removal of Iron from Water

Use of Carbonaceous Ion Exchangers

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THE presence of iron in water has long been considered both an industrial and domestic problem. In textile dyeing, the beverage industry, ice making, food canning, as well as many other industrial processes, the removal of any iron present in the current water supply is considered essential. It requires less than 1.0 part per million of iron in water to stain household bathroom fixtures and kitchen sinks. Comparatively small amounts of iron are more troublesome in the household laundry because of stain-producing characteristics than appreciable concentrations of the hardness-giving constituents, calcium and magnesium. The modern municipal water treatment plant recognizes these facts and aims to reduce the iron present in the supply delivered to the consumers to concentrations of 0.1 to 0.2 p. p. m.

While methods involving either oxidation or chemical coagulation and precipitation have been developed for the industrial removal of iron, these processes are not always satisfactorily applicable to the problem at hand. Wherever it is more convenient to keep the water under pressure at all times, the above mentioned procedures are not easily applied. With the extension of electric power and the building up of suburban communities, thousands of homes are dependent on private wells for their water supply. Many of these wells contain soluble iron. These domestic supplies have not been satisfactorily treated by aeration or coagulation.

The zeolite method of water softening has long been recognized as a satisfactory method for domestic water softening. Since the introduction of the newer organic types of ion exchangers which can be regenerated with either sodium chloride or dilute acid, the industrial applicability of products of this type has been greatly increased. While considerable has been written (*1*, *2*, *3*) regarding the application of the carbonaceous exchangers to the removal of hardness and the reduction of bicarbonate alkalinity in water, minor references only have appeared relative to the ability of products of this type to remove iron. It is fortunate that these carbonaceous exchangers are inherently iron removers as well as water softeners.

Mechanism of Iron Removal

When it was found that carbonaceous exchangers would remove iron from water as well as calcium and magnesium, a series of tests was made to determine the mechanism by which the removal was obtained. A quantity of commercially available carbonaceous exchanger (Nalcite AX) was regenerated with sodium chloride and thoroughly washed to remove excess regenerant. Samples (5.3 grams) of the exchanger were added to 100-ml. samples of water containing varying concentrations of soluble iron. The samples were agitated for 30 minutes, after which the residual soluble iron was determined in each sample. A plot of the data obtained made on log-log paper gives a straight line which follows the Freundlich adsorption isotherm (Table I).

TABLE I. ADSORPTION OF IRON BY 5.3 GRAMS OF CARBONACEOUS EXCHANGER IN 100 ML. OF SOLUTION

Mg. Fe in Soln.	Mg. Fe in Soln. after Adsorption	Mg. Fe Adsorbed/Gram Adsorbent
40	2.4	7.1
60	8.4	9.7
80	21.6	11.0
100	31.2	13.0

Other investigators have revealed that the removal of ions by adsorption and by ion exchange are closely allied. Our work in the removal of iron by carbonaceous exchangers verified this fact. Typical ion-exchange columns were set up, and the carbonaceous material was regenerated as in zeolite softening with dilute sodium chloride solution. Exchanger capacity tests were carried out on pure solutions of ferrous sulfate. The solutions varied in iron content from 5 to 48 p. p. m. of iron expressed as Fe. All synthetic solutions used in the laboratory were freshly made several times daily, excess carbon dioxide was added, and added precautions were taken to prevent oxidation of the iron by air contact. As the exchanger beds remained free of precipitated iron and the results obtained were found to be reproducible, it was felt that the precautions taken to eliminate oxidation were adequate for all practical purposes. Table II indicates that the capacity of the material for the removal of iron from pure solutions is comparable to its capacity for hardness removal. It also indicates that appreciable iron concentration is required to affect removal capacity adversely.

TABLE II. CAPACITY OF MATERIAL FOR IRON REMOVAL

Hardness Present[a] as $CaCO_3$, P. P. M.	Iron Present as Fe, P. P. M.	Exchange Capacity as $CaCO_3$, Grains/Cu. Ft.
85	0	7200
171	0	6800
0	5	5900
0	10	6230
0	15	6500
0	48	4930

[a] Two thirds calcium salts, one third magnesium salts.

After proving definitely that the tubes could be regenerated with sodium chloride and the above results obtained on cycle after cycle, regeneration of the tubes was carried out with calcium chloride and magnesium chloride.

TABLE III. REPLACEMENT OF CALCIUM AND MAGNESIUM BY IRON

Regenerant Used	Iron Influent: As Fe, p. p. m.	Iron Influent: $CaCO_3$, grains/gal.	Hardness Effluent as $CaCO_3$, Grains/Gal.	Iron Removal Capacity as $CaCO_3$, Grains/Gal.
NaCl	15	1.57	0	6500
$MgCl_2$	15	1.57	1.5	6000
$CaCl_2$	15	1.57	1.5	3450

Table III indicates that the Fe^{++} ion will displace the calcium ion and also the magnesium ion. These ions are not displaced so readily as the sodium ion, however, particularly in the case of calcium. The initial capacity of the calcium regenerated material is not so high, and its capacity is not maintained on repeated regeneration.

The presence of iron compounds in many water supplies presents a problem comparable in importance to that of hardness-forming constituents, the salts of calcium and magnesium. The application of a typical carbonaceous ion exchanger to the removal of iron from public water supplies is discussed. The mechanism of iron removal is explained. Comparative capacity data covering the removal of iron, calcium, and magnesium from pure solutions are given, together with tables on the effect of varying concentrations of iron on the capacity of the exchanger for its removal.

Data on the influence of varying concentrations of calcium and magnesium salts on the capacity of the exchanger for iron removal are given. Examples are cited illustrating industrial and domestic applications of the carbonaceous exchangers to this problem.

The ion replacement characteristics of the carbonaceous material revealed in Table III were further verified in a series of tumble tests. Samples of the exchanger were regenerated with sodium chloride, magnesium chloride, and calcium chloride. Excess regenerant was eliminated from each of the three samples by washing with distilled water. The samples were then "tumbled" for a 30-minute period with 100 ml. of distilled water containing 40 mg. of iron as Fe. At the end of the contact period, the water from each sample was analyzed for soluble cations. In each case the quantity of cation displaced from the exchanger bed was practically equivalent to the amount of iron picked up by the exchanger bed (Table IV).

TABLE IV. RESULTS OF TUMBLE TESTS ON SAMPLES CONTAINING 40 MG. IRON

Regenerant Used	Final Iron, Mg. Fe	Iron Removed, Mg. Fe	Ions Displaced from Bed, Mg. Fe
NaCl	1.6	38.4	Na, 39.5
$MgCl_2$	7.0	33.0	Mg, 35.5
$CaCl_2$	9.8	30.2	Ca, 27.9

Removal from Natural Waters

In the removal of iron from natural water supplies, the problem is somewhat complicated by the presence of calcium and magnesium salts. Because the Fe^{++} ion can displace the calcium and magnesium ions, the removal of the iron will continue after the hardness (calcium and magnesium) removal capacity of the sodium chloride regenerated carbonaceous exchanger has become exhausted (Table V, examples 2, 3, 5, and 6).

Table V. Removal of Iron from Natural Water Supplies

No.	Hardness as $CaCO_3$, P. P. M.	Iron as Fe, P. P. M.	Gallons per Cubic Foot: Hardness-free water	Gallons per Cubic Foot: Iron-free water	Gallons per Cubic Foot: Iron-free water obtained beyond softening cycle
1	0	5	..	11,814	..
2	120	5	1000	5,260	4260
3	120	10	1000	2,400	1400
4	120	20	1000	1,000	None
5	510	5	210	4,920	4710
6	510	10	210	2,300	2090
7	510	20	210	210	None

Because the replacement of the calcium and magnesium ions does not proceed so readily as the replacement of the sodium ions, the capacity of the exchanger for the removal of the iron in the presence of the calcium and magnesium is not so great as indicated above from pure iron solutions (Table V, examples 1 and 2).

When the concentration of iron- and hardness-giving constituents are both appreciable, the characteristics of the exchanger for the removal of iron are modified (Table V, examples 4 and 7). While the exchanger will continue to remove a large percentage of the influent iron after its capacity for hardness removal has become exhausted, the residual iron in the treated water will be too high (above 0.3 p. p. m.) to make the water satisfactory for use. Results to date indicate, therefore, that when the concentration of iron in the raw water approaches 20 p. p. m., the iron-removal cycle must be terminated at the same time as the hardness-removal cycle.

In all cases investigated to date, the complete removal of the iron present continued at least throughout the entire hardness-removal cycle. This is important in domestic water treatment as the treated water is not of satisfactory quality if it contains either appreciable hardness or soluble iron. In the examples shown having hardness concentrations of 120 and 510 p. p. m., where the iron present was 10 p. p. m. or less, the removal of iron took place without regard for the concentration of hardness present and continued beyond the hardness-removal cycle.

Indications are, therefore, that with a water having 10 p. p. m. of iron and a very low hardness concentration (10–20 p. p. m.), the amount of iron-free water obtained beyond the softening cycle would be very small, but the capacity for iron removal would approach that obtained on hardness-free water. It would also appear that on an extremely hard water with the same iron content (10 p. p. m.) the amount of iron-free water obtained beyond the softening cycle would increase to approximately 2200 gallons per cubic foot. Inasmuch as the large majority of municipal and industrial iron-bearing water supplies contain concentrations of less than 5 p. p. m. of iron as Fe, the carbonaceous ion exchanger can be satisfactorily used for the removal of the iron from these supplies and will turn out high-capacity cycles of iron-free water as above indicated (Table V).

Table VI gives analyses of four natural waters which are being satisfactorily treated by the carbonaceous ion exchanger, Nalcite AX, regenerated in each case by sodium chloride. The analyses of the effluent waters are also listed. Sample 4 shows that manganese also can be satisfactorily removed (Table VI).

While working on this investigation, it became apparent that the pH of the iron-bearing water had considerable influence on the removal capacity of the carbonaceous exchanger. In most of the laboratory tests the pH of the water was adjusted to 5.8. Field tests conducted on supplies having a pH of 6.8 or above revealed the possibility of higher exchange capacities than those given in the attached tables.

Table VI. Analyses of Four Natural Waters

	Constituents Present as $CaCO_3$, P. P. M.: Supply 1 Raw	Supply 1 Softened	Supply 2 Raw	Supply 2 Softened	Supply 3 Raw	Supply 3 Softened	Supply 4 Raw	Supply 4 Softened
$Ca(HCO_3)_2$	252	0	340	0	170	0	258	0
$Mg(HCO_3)_2$	136	0	58	0	0	0	34	0
$NaHCO_3$	0	387	0	398	0	170	0	292
$CaSO_4$	0	0	0	0	39	0	0	0
$MgSO_4$	109	0	95	0	94	0	41	0
Na_2SO_4	29	138	95	190	0	133	24	65
NaCl	8	8	17	17	12	12	16	16
Fe[a]	12	0 to 0.2	17	0 to 0.2	23	0 to 0.2	9.6	0
Mn[b]	0	0	0	0	0	0	3.4	0

[a] Expressed as p. p. m. of Fe.
[b] Expressed as p. p. m. of Mn.

In the field the test units were connected directly to the source of supply so that water contact with the exchanger was obtained before oxidation and subsequent precipitation could take place, as the exchanger particles remained clean and free of oxidized iron at all times. In this same connection, it became evident that the use of a neutralizing material placed ahead of the carbonaceous exchanger to react with high concentrations of free carbon dioxide would be an aid to higher capacity attainment as well as a help in corrosion control. While it is planned to carry out further field work, focusing the attention on the pH of the iron-bearing water, the work carried out thus far indicates that the carbonaceous ion exchanger is very applicable to the removal of iron from both industrial and domestic water supplies.

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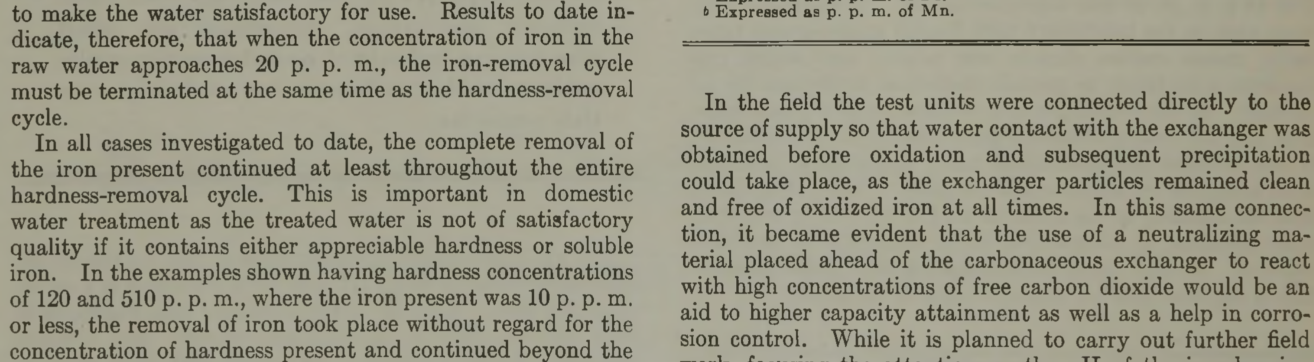
Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 103rd Meeting of the American Chemical Society, Memphis, Tenn.



STARCH STUDIES

Possible Industrial Utilization of Starch Esters[1]

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The properties of starch triesters which might make them industrially useful are discussed. Because of the molecular shape of starch, its esters will probably never produce molded articles of great strength. In molding their use will be confined to that of a diluent and plasticizer for other thermoplastic materials.

Definite possibilities do exist, however, for these esters in the coating, sizing, and adhesive industries. The starch esters will perhaps find their greatest usefulness in two relatively new but important fields—the preparation of aqueous emulsions or suspensions of high polymers and the compounding of soft rubberlike plastics.

THE large quantity of starch available and the low price at which it can be obtained have resulted in considerable research for derivatives with industrially utilizable properties. Reference is made only to some of the more recent work (*1*, *2*, *5*, *6*, *8-11*). Many uses have been suggested for these starch derivatives, including application as thermoplastic moldings, coatings, films, adhesives, sizing and stiffening agents for paper and textiles, and even as flotation agents in ore and mineral recovery processes. The purpose of this paper is to discuss the properties of the starch esters prepared by the process already described (*6*), and to see if these properties are favorable for commercial utilization of the esters. These derivatives are the full triesters; they are characterized by high molecular weight (from about 500,000 for the acetate to well over 1,000,000 for those containing larger acyl groups) which is due to the freedom from degradation of the native starch under the conditions of the process. In consequence of these high molecular weights the esters form only colloidal solutions, the ease of dispersion being different for different esters. The viscosities of these ester "solutions" are considerably higher than those for the corresponding cellulose esters, especially at higher concentrations. The viscosity relations were fully discussed in the previous paper (*6*). Melting takes place over a range of about 100° C. Within this range the esters are plastic and workable.

How the properties of the esters vary from species to species was shown previously (*6*), and this point will not be stressed further.

Properties of Starch Esters

FATTY ACID ESTERS. The triacetate, tripropionate, tributyrate, and tricaproate of starch are all white powders (Figure 1). On application of heat they soften at progressively lower temperatures with increasing size of the acyl group. The caproate is puttylike at room temperatures, whereas the acetate softens just under 200° C. The melting range is wide for all these esters, covering nearly 100° from the softening point to the formation of a clear melt. They are all insoluble in water. The acetate is insoluble in the lower alcohols and ether, but the other members of the series tend to become gummy in these solvents. Practically all of the ordinary organic solvents swell or colloidize these esters. Dispersion is perhaps best in the aromatic or the halogenated hydrocarbons and in the tertiary organic bases. Ease of dispersion in these solvents decreases with increasing molecular weight (i. e., increasing size of the acyl group) as well as with the natural increase in molecular weight which was observed (*6*) to parallel increase in granule size from species to species. These "solutions" are very viscous, a 10 per cent solution of acetate in acetone showing practically no tendency to flow. However, it must be noted that the viscosity of these "solutions" depends somewhat upon the length of time they have been allowed to stand after dispersion. For example, immediately after removal from the colloid mill, the 10 per cent solution is viscous but still fluid. After 48 hours the "solution" has set to an immobile gel. This gel may then again be redispersed. Such behavior is due entirely to aggregation phenomena.

ESTERS OF DIBASIC ACIDS. When the anhydride of a dibasic acid (e. g., phthalic anhydride) is reacted with an alcohol, one carboxyl group is set free. The preparation of such esters involving cellulose as the alcohol was discussed by Malm and Fordyce (*3*). Such esters prepared from starch cannot be precipitated from their pyridine reaction jelly by addition of excess water, since their pyridine salts, formed between the pyridine and the three free carboxyl groups present on each six-carbon unit, are water soluble. The precipitation must be carried out by the addition of the calculated amount of dilute acid.

The triphthalate and the trisuccinate of starch are both white powders, insoluble in water of pH 7 or less but dissolving in dilute alkalies. They are soluble in methyl and ethyl alcohol. In the molten state they have strong adhesive properties.

If the succinate is dissolved in absolute methyl alcohol and a few drops of sulfuric acid added, a white precipitate

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[1] For the first two papers in this series, see literature citations *5* and *6*.

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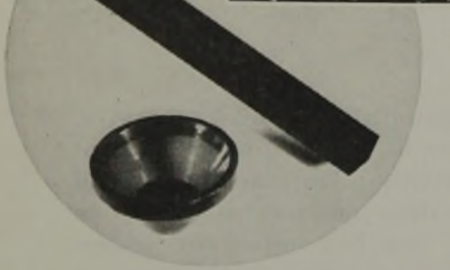
→ FIGURE 1. CORNSTARCH TRIPROPIONATE IN THE FORM OF A WHITE POWDER



← FIGURE 2. BAR AND SMALL CUP MOLDED FROM CORNSTARCH TRIPROPIONATE, PLASTICIZED WITH 10 PER CENT DIBUTYL PHTHALATE

is thrown down in a short time. This is the methyl ester of the starch trisuccinate. A similar reaction is obtained with the phthalate.

STARCH TRIBENZOATE. This is one of the few esters which may be prepared from the acid chloride via the pyridine method using no other diluent. The pure ester is white, but as usually prepared it retains a trace of color from the deep orange reaction mixture. Its properties resemble those of the lower fatty acid esters. Most notable is the strong adhesive bond which it forms with metals. If some of the molten benzoate is pressed between two blocks of steel and allowed to cool, it becomes exceedingly difficult to break the steel blocks apart. This bond is even stronger after the ester has been suitably plasticized.

ESTERS OF ROSIN ACIDS. The rosin acids (e. g., abietic) contain a conjugated double-bond system to which may be added maleic anhydride. This adduct, possessing an anhydride grouping, may then be used to esterify starch. Actually they were obtained by partial esterification of starch with the adducts of methyl abietate and diethylene glycol diabietate. Though only partially esterified, the products resembled the original rosin derivatives, and their properties scarcely revealed the starch which they contained. Such high molecular weight "rosins" might find application in the varnish industry.

Molding Starch Esters

An attempt was made to use the starch esters as thermoplastic molding compounds. The work was carried out in a small cylinder mold, a small cup mold, and a $^1/_2 \times {^1/_2} \times 5$ inch bar mold. The molding operation (compression molding) was performed at about 200° C. and 5000 pounds per square inch pressure.

Of all the esters molded in the unplasticized state, the butyrate and caproate had the best properties in that they were not brittle. They pared but did not chip when cut with a knife. Their surface hardness was, however, low. The results of molding the unplasticized esters are given in Table I.

The plasticized esters showed more promise. The results of the plasticized cornstarch moldings are given in Table II. Dibutyl phthalate was more effective than any of the other plasticizers tried. All the esters were molded with this plasticizer. Results are given in Table III. Little if any difference was observed between the properties of the plasticized acetates of potato, tapioca, wheat, corn, and rice starch.

Meyer (*4*) reported the triacetate of amylose to form much stronger films and fibers than the triacetate of amylopectin. This is to be expected if the amylose is a straight-chain compound, free from branching. It would resemble cellulose in behavior in that chains lying alongside of one another could form the strength-giving micellar bonds. The molding of amylose acetate prepared by a previously described method (*7*) was no different in properties from the molding made from total starch acetate. This observation is, however, based on only one experiment, involving an amylose sample of doubtful purity.

Two of the molded articles are shown in Figure 2. The strength of the bars molded from starch acetate was considerably less than that of similar bars of cellulose acetate. All in all, the molding of the starch esters was unsatisfactory. This fact is no doubt due to the roughly spherical shape of the major component (amylopectin) of starch. The evidence for this was previously discussed (*6*). Spherical molecules (highly branched "clumps") would not form the large number of secondary bonds, the existence of which is responsible for the strength characteristic of strictly linear polymers.

TABLE I. PROPERTIES OF MOLDED STARCH ESTERS

ESTER	COLOR	TRANSPARENCY	TACKINESS	SURFACE	HARDNESS	TOUGHNESS
Cornstarch acetate	Yellow-green	Clear	None	Glossy	Hard	Very brittle
Cornstarch propionate	Amber	Clear	None	Glossy	Hard	Fairly brittle
Cornstarch butyrate	Rosin	Clear	Stuck to mold	Glossy	Fairly hard	Slightly brittle
Cornstarch caproate	Rosin	Clear	None	Glossy	Fairly hard	Very slightly brittle
Cornstarch benzoate	Orange	Clear	None	Glossy	Hard	Very brittle
Cornstarch phthalate	Tan	Opaque	Stuck to mold	Gummy (water sol.)	Soft (hardens in air)	Tough, sticky
Cornstarch methyl abietate–maleic anhydride adduct ester[a]	Rosin	Dark	None	Glossy	Hard	Very brittle
Cornstarch diethylene glycol diabietate–maleic anhydride adduct ester[a]	Rosin	Dark	None	Glossy	Hard	Very brittle
Cornstarch β-amylose acetate	Rosin	Clear	None	Glossy	Hard	Very brittle
Tapioca starch acetate	White	Opaque	None	Smooth	Soft	Brittle

[a] These two esters contain only one or less than one hydroxyl substituted per C_6 unit.

Additions of cellulose acetate were found to improve the strength of the starch esters tremendously. In fact, when the starch esters were used as a diluent for cellulose acetate, even up to 75 per cent of the total weight, the moldings turned out to be quite satisfactory.

In the above discussion the usual rigid type of plastic has been considered; today, however, soft, rubberlike plastic compositions are becoming of increasing importance (*12*). Such compositions find use as aircraft sealing compounds, as adhesives, and as substitutes for natural rubber in certain specialty items. The starch esters, suitably plasticized, either as such or compounded with other plastic materials, may become of considerable value in this new development. In support of this statement it is to be noted that starch butyrate, containing 25 per cent dibutyl phthalate, is quite soft and possesses a relatively high tack. Starch caproate, even without plasticizer, is puttylike at room temperature.

Table II. Effect of Plasticizers (20 Per Cent) on Molded Cornstarch Acetate

No.	Plasticizer	Color	Transparency	Tackiness	Surface	Hardness	Toughness
1	Dibutyl phthalate	Yellow-green	Clear	None	Glossy	Medium	Tough
2	Phthalic anhydride	Yellow-green	Opaque	Stuck to mold	Gummy	Soft	Fairly tough
3	Equal parts of 1 & 2	Yellow-green	Murky	Stuck to mold	Smooth	Soft	Fairly tough
4	Diethylene glycol diabietate (20% plasticizer incompatible)	Green-gray	Opaque	Slight	Smooth	Medium	Very tough, at first, brittle on standing
5	Equal parts of 1 & 4	Tan	Murky	None	Glossy	Hard	Brittle
6	Camphor	Olive green	Clear	None	Glossy	Hard	Tough
7	10% No. 1 + 1% No. 6	Olive green	Clear	None	Glossy	Hard	Fairly tough, cracks on standing

Fibers

Exactly the same shortcomings that exist for the starch ester moldings also limit the usefulness of the fibers formed from them. As long as the fiber is in a hot semimolten state, it is tough, flexible, and elastic; on cooling, however, it becomes very brittle, especially the acetate. Plasticizers remedy this condition but little.

Extrusion of the fibers under tension does not result in a great increase in tensile strength. This is to be expected since there can be no axial orientation of a "spherical" molecule, as is the case with fibers made up of long-chain molecules (e. g., rayon fibers).

Coatings and Adhesives

Although the unsupported films formed both by evaporation of the solvent from a solution of the ester and by extrusion of the molten ester are brittle when unplasticized and weak when plasticized, the behavior of the starch esters as coatings was far more gratifying. Colloidal solutions of the esters were prepared in the usual commercial lacquer thinners. These solutions were quite viscous so that those containing more than 5 per cent solid matter could not be sprayed. Freshly prepared solutions containing more material could be applied with a brush. It would, however, be necessary to lower the viscosity of the ester solutions by some degradative process in order to increase the concentration.

When no plasticizer is added to the solution, the coatings formed from the acetates check on standing. Those formed from the propionate and butyrate show less tendency to check. Plasticizers, however, improve them all. Dimethyl, diethyl, and dibutyl phthalates were found to be most efficient. Tricresyl phosphate is apparently incompatible with the starch esters.

The coatings of these esters resemble clear varnishes when applied to wood. Their surfaces are quite glossy. The hardest surface is formed by the acetate, the softest by the butyrate.

Paper and cloth coated with the plasticized esters may be crumpled without cracking the coating. This resistance to cracking is impressive.

These starch ester coatings adhere well to glass and metals, and seem subject to considerably less shrinkage on drying than similarly applied coatings of cellulose acetate.

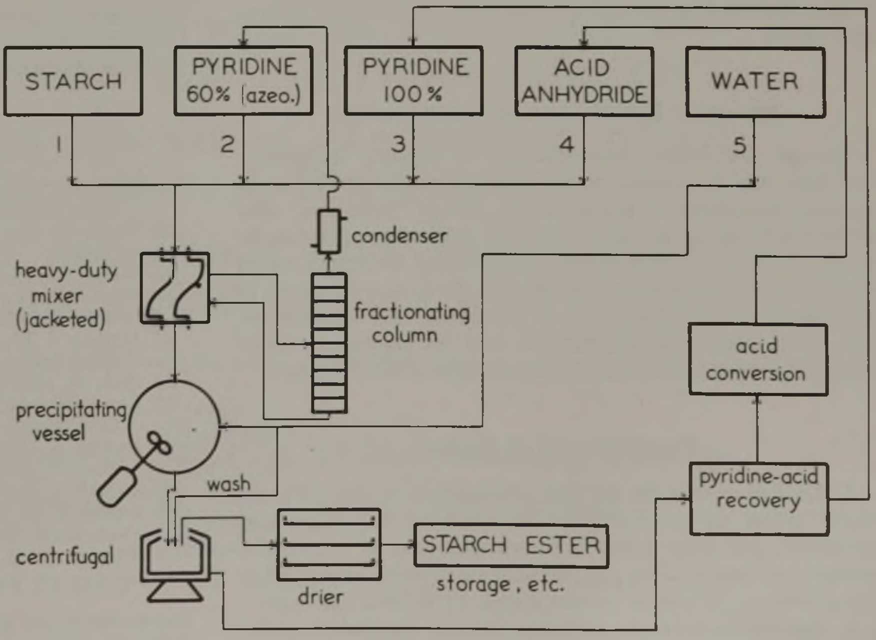


Figure 3. Flow Sheet for Starch Ester Preparation

Table III. Properties of Starch Esters Plasticized with Approximately 5 Per Cent Mixed Camphor and Dibutyl Phthalate

Ester	Color	Transparency	Tackiness	Surface	Hardness	Toughness
Cornstarch acetate	Olive green	Clear	None	Glossy	Hard	Fairly brittle
Cornstarch propionate	Olive green	Clear	None	Glossy	Medium	Fairly brittle
Cornstarch butyrate	Amber	Cloudy	None	Glossy	Medium	Tough
Cornstarch caproate	Dark amber	Dark	Stuck to mold	Smooth	Soft	Tough
Cornstarch benzoate	Orange	Clear	Stuck to mold	Glossy	Hard	Brittle
Tapioca starch acetate	Lemon	Clear	None	Glossy	Hard	Very slightly brittle

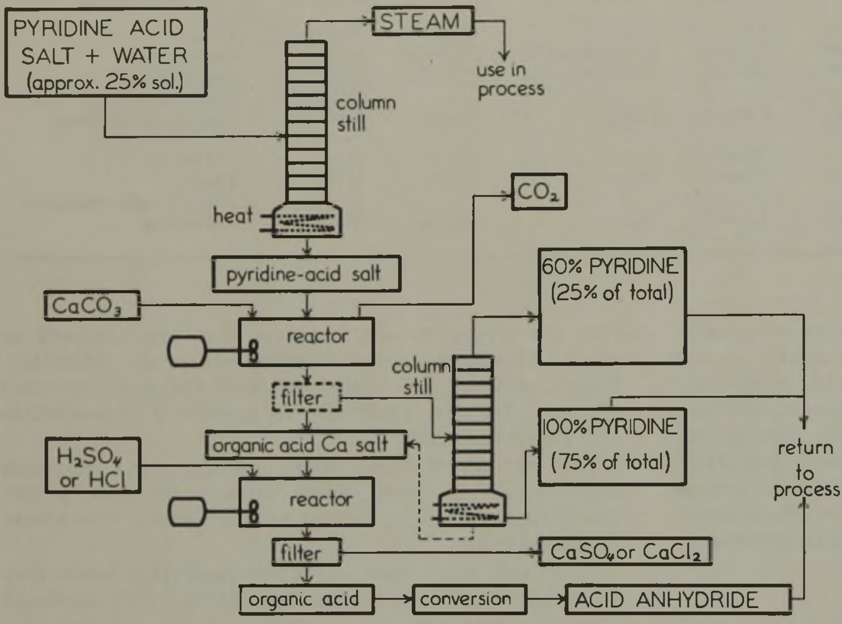


Figure 4. Flow Sheet for Pyridine-Acid Recovery

The bond formed between certain of these esters and pieces of steel, wood, glass, or paper, is quite strong. Most noteworthy in this respect are the benzoate and the dibasic acid esters.

Aqueous Emulsions or Suspensions

One of the newer developments in plastics technology has been the incorporation of high polymeric materials in aqueous emulsions or suspensions. These "solutions" find widespread use (e. g., adhesives and sealing compounds, to name but two). The molecular structure of the starch esters which results in poor moldings and fibers should show to advantage in the preparation of emulsions and suspensions, the forces producing aggregation and its resultant colloid instability being lower than in long straight-chain polymers.

Preparation of Esters

A detailed procedure for the preparation of the different starch esters by precipitation in water of the respective pyridine-starch ester jellies is shown in Figure 3. As to the recovery of the pyridine and the acid anhydrides employed in the procedure, it can be accomplished by several methods—e. g., distillation, solvent extraction, ternary distillation of the pyridine azeotrope with benzene, etc. One of these pyridine-acid recovery procedures, based on distillation of the aqueous pyridine-acid solution treated with calcium carbonate and then with mineral acid, is illustrated in Figure 4.

Conclusions

Any hope for the industrial development of the starch esters seems to lie in their use:

1. As coatings.
2. As adhesives.
3. As diluents for other plastics.
4. In the compounding of soft rubberlike plastics.
5. In the preparation of aqueous emulsions or suspensions.
6. In some heretofore unsuspected use stemming from their possession of high molecular weights and shapes which are definitely nonlinear.

Acknowledgment

We gratefully acknowledge the financial assistance given by the Research Corporation, of New York, which made this investigation possible. We wish to thank Stein, Hall & Company, Inc., and the Corn Products Refining Company for their generous supply of starches.

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Abstracted from a thesis presented by James W. Mullen II to the faculty of Princeton University in partial fulfillment of the requirements for the degree of doctor of philosophy.

Competing with the enemy

There's a new kind of competition in the oil industry today It isn't a race for more customers—it's a race to serve to the limit the enormous wartime needs of one big, preferred customer—Uncle Sam

American refiners are competing with the enemy Every one is seeking his right place in the production battle line Universal's exclusive job now is to help refiners produce to their utmost capacities for war and Universal is doing it

Here are U.O.P. processes that are helping to win the war:

- Catalytic cracking
- Catalytic reforming
- Alkylation
- Polymerization
- Isomerization
- Cyclization
- Aromatization
- Hydrogenation
- Dehydrogenation
- Dubbscracking
- Pyrolytic reforming

By these processes the constituents of 100-octane aviation gasoline are produced in ever increasing volume as well as butadiene and styrene for synthetic rubber and toluene for TNT

The processes are all at the service of all refiners under license from Universal

And all the experience and know-how of Universal refining specialists goes with them

OIL IS AMMUNITION—USE IT WISELY

Universal Oil Products Co
Chicago, Illinois

Dubbs Cracking Process
Owner and Licensor

THE REFINERS INSTITUTE OF PETROLEUM TECHNOLOGY

Perhaps REVERE can help you with your

NON-FERROUS

Reactor vessels
Storage tanks
Catalyst tubes
Pressure vessels
Mixers
Heat Exchanger shells
Fractionating columns

Revere is trying in every way to help iron out kinks in war production problems for old and new users of copper and copper alloys. We may be able to give first aid to you in one or more of four ways:

1. Revere copper and copper-base alloys... sound, superior metals produced in a range of compositions and forms meeting the special requirements of war processes.
2. Revere Bimetal... where war requirements and service conditions demand, Revere can supply bonded Bimetal sheets and plate of S.A.E. 1010 carbon steel clad on one or both sides with copper as well as with certain other metals and alloys.
3. Welding technique . . . *practical* assistance which will aid in the completion of equipment *when* needed and insure uninterrupted service.
4. Revere Engineering Service . . . to help Revere customers in the selection of metals and in methods of fabrication so as to save time, increase output and reduce costs wherever possible.

If you have special problems, send us specifications and full details of your requirements. We will endeavor to supply an answer promptly. Get in touch with Revere today.

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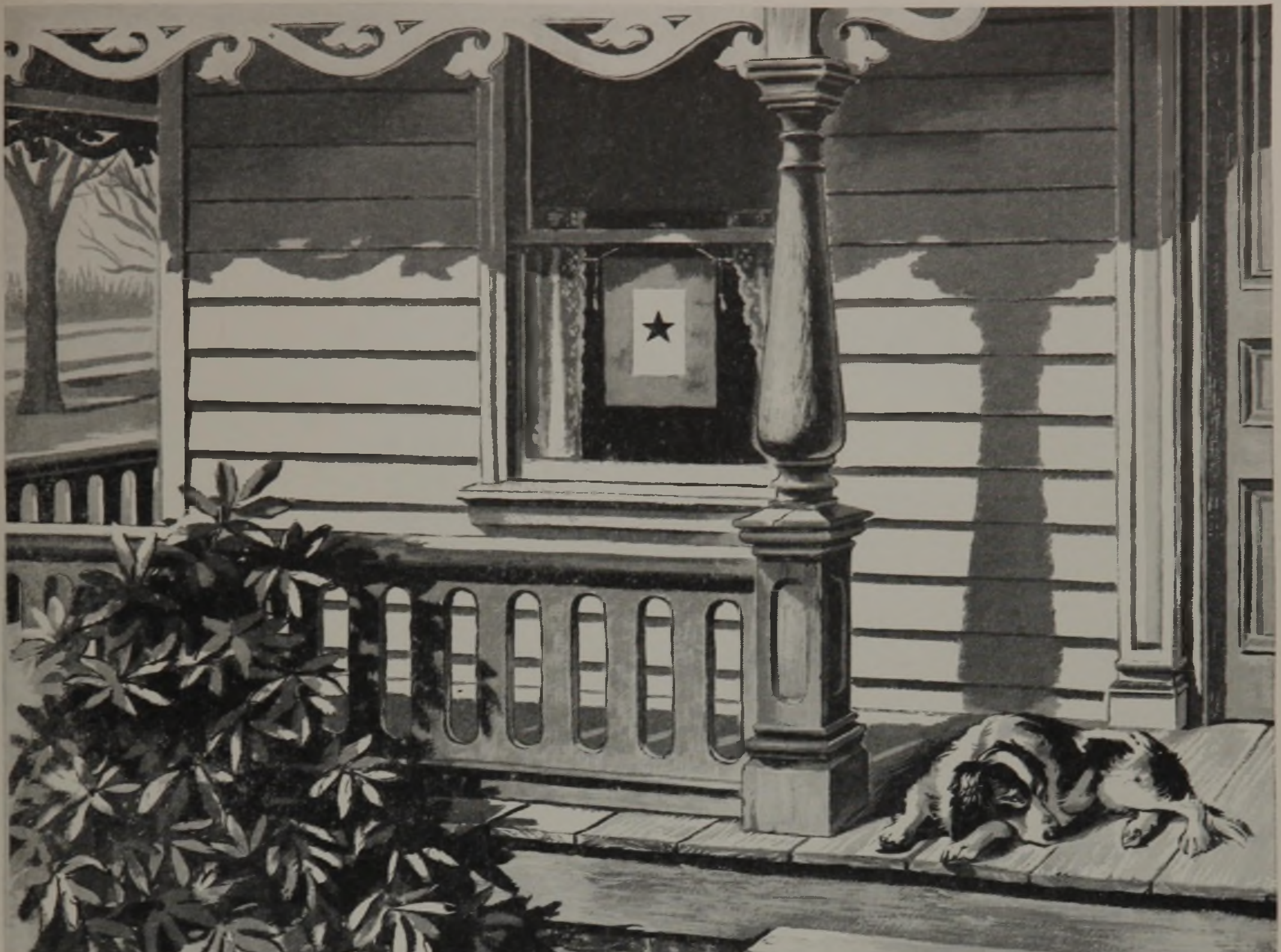
COPPER AND BRASS INCORPORATED
Founded by Paul Revere in 1801
Executive Offices: 230 Park Avenue, New York
Sales Offices and Distributors in Most of America's Major Cities




ARMY
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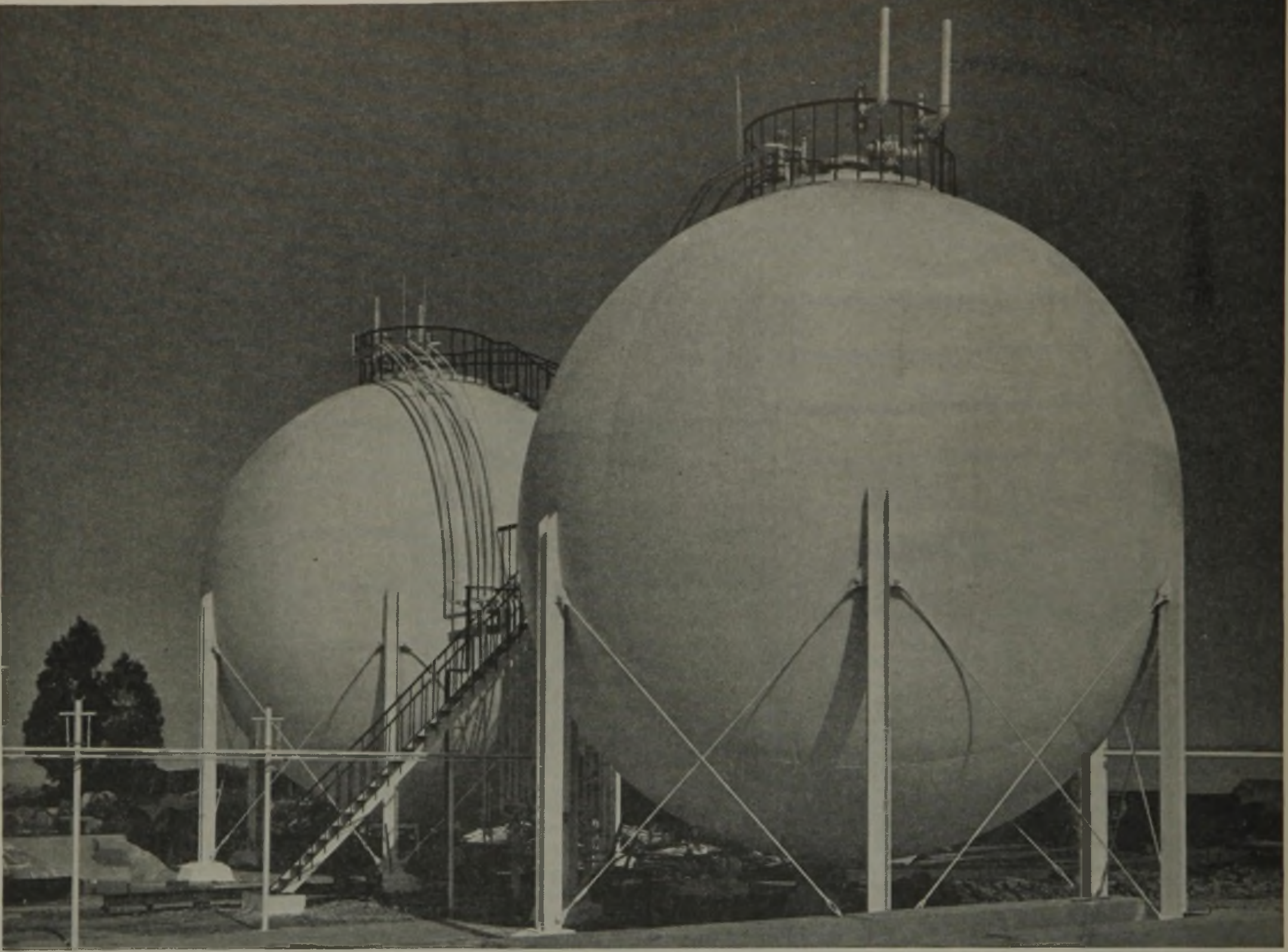
NAVY


FOR VICTORY
BUY
UNITED STATES WAR BONDS AND STAMPS



Guardians OF ANHYDROUS AMMONIA

AS THE nation lengthens its stride to meet faster wartime production schedules the Hortonsphere becomes a more familiar sight throughout many types of industry. At first these steel spheres were used to store volatile liquids in the oil industry to prevent excessive evaporation loss. Then they became popular as an economical means of storing gases under pressure.

Today Hortonspheres for liquids and gases are being used in a wide range of sizes to solve an almost infinite number of pressure storage problems encountered in handling chemicals, petroleum products, as well as industrial gases and sewage gas at disposal plants.

The two Hortonspheres shown above were installed at a chemical plant for the pressure storage of anhydrous ammonia. Designed for an operating pressure of 50 lbs. per sq. in. these spheres reduce the amount of vaporization that takes place from the liquid ammonia. They have a capacity of 2,500-bbls. each.

HORTONSPHERES

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Plants in BIRMINGHAM, CHICAGO and GREENVILLE, PA. *In Canada:* HORTON STEEL WORKS, LIMITED, FORT ERIE, ONTARIO

Looking ahead from a long way back

From the early days of "Colonel" Drake and "Coal Oil Johnny," the chemistry of oil has been destined for great things. Greater even than the high-octane gasoline which today is propelling planes across the sky at 400 miles per hour. Greater than butadiene and toluene.

So, too, with the chemistry of alcohols, phenols, esters, ketones and other organic compounds.

The greater things are sure to come. Many are already germinating—secretly in some instances—and inevitably heading toward enriching the world of tomorrow.

It takes background and experience to put into successful production the products chemical research has perfected. It takes far-reaching facilities to design and build processing equipment that can be expected to operate efficiently.

Badger perspective looks through four generations toward process engineering and plant construction in many future fields. Though busy on gasoline, rubber, T.N.T. and other war-aid projects, Badger is nevertheless preparing for post-war undertakings. . . . Manned with engineers, designers and draftsmen to convert the new miracles of science into realities. . . . Equipped to plan, build, and to supervise the initial operations of complete manufacturing units.

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ZIRCONIUM

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Today, war and non-war manufacturing has emphasized the ever-increasing uses and possibilities of the element ZIRCONIUM and its compounds in industry. TAMCO Zirconium compounds are being used successfully in the manufacture of Refractories, Electrical Resistors, Resins, Dye Extenders, Water Repellents, Catalysts, Abrasives, and Ceramics.

TAMCO'S development engineers and research laboratories have long been cooperating with the industry. Write today, for a TAM resident field engineer to call at your plant and discuss the potential use of Zirconium Compounds with you.

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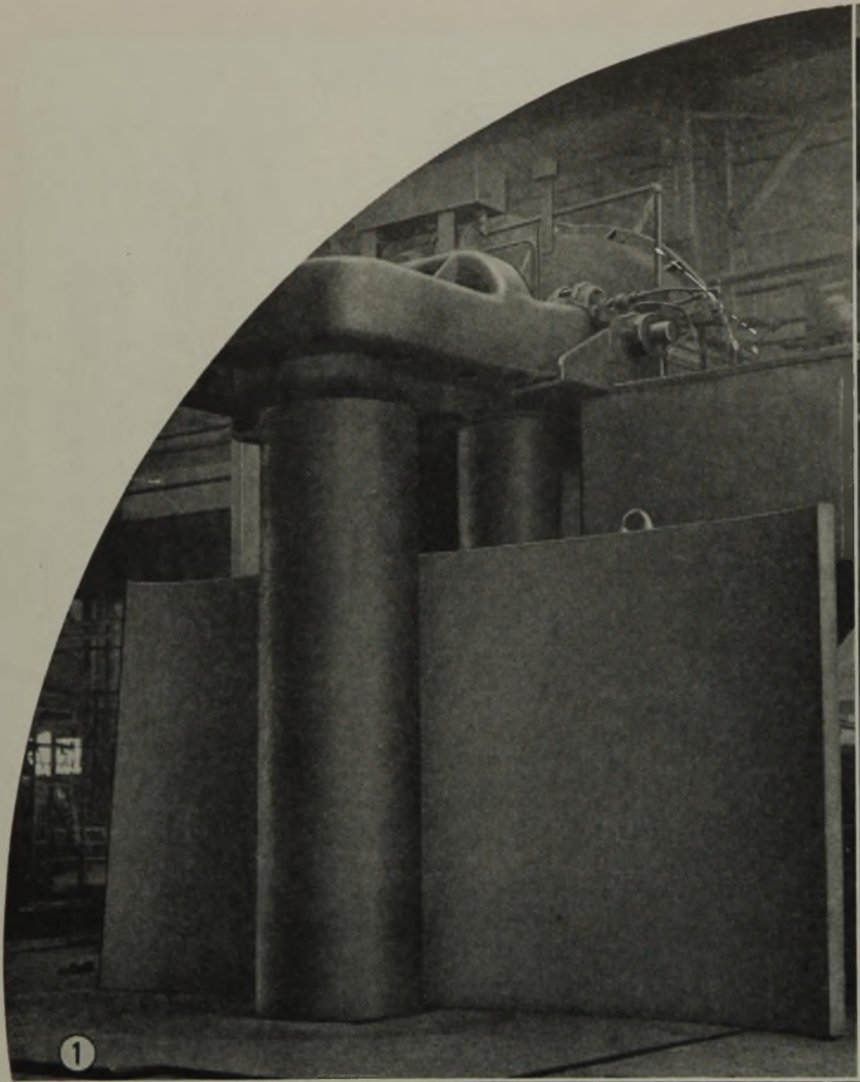

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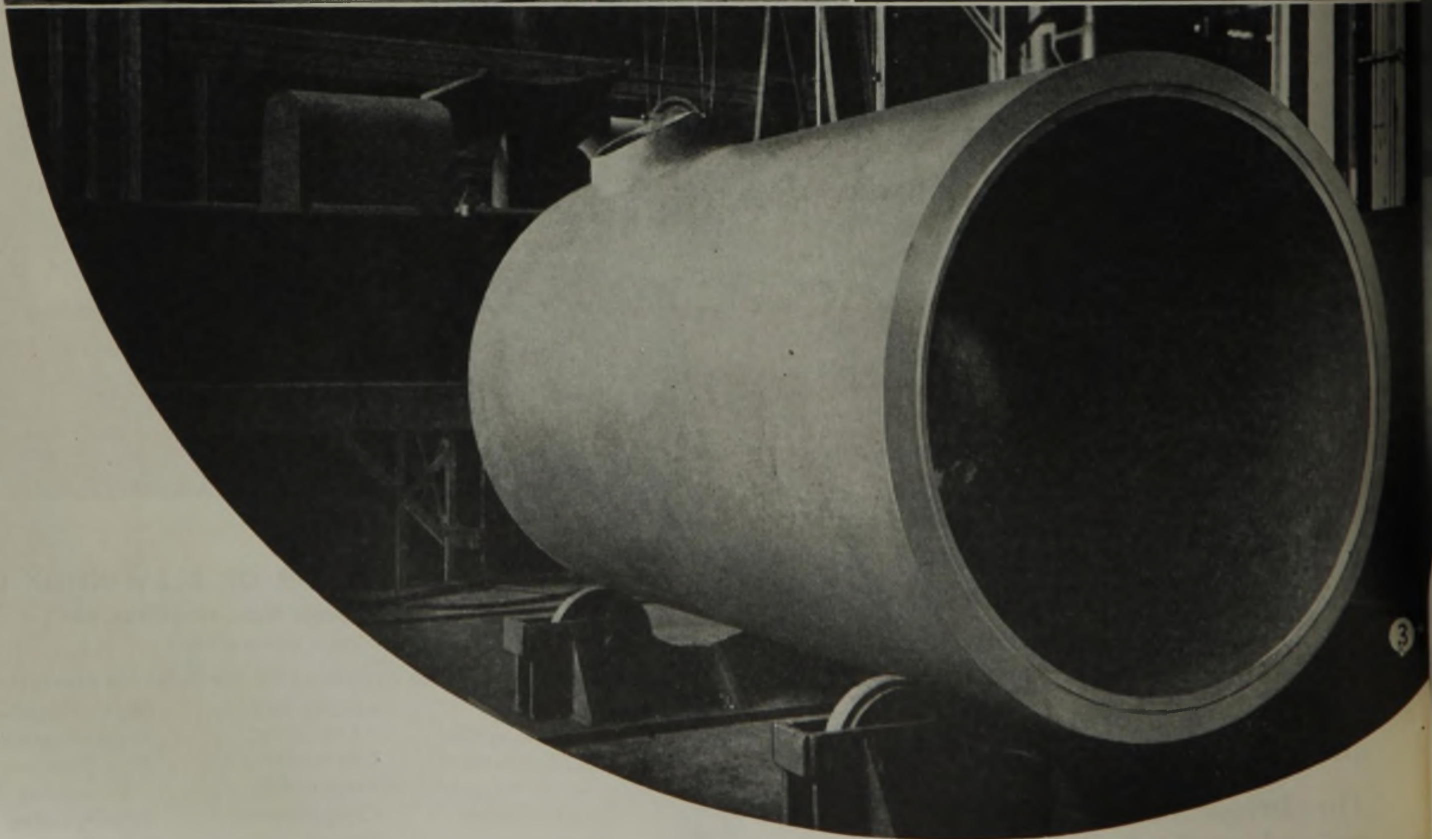

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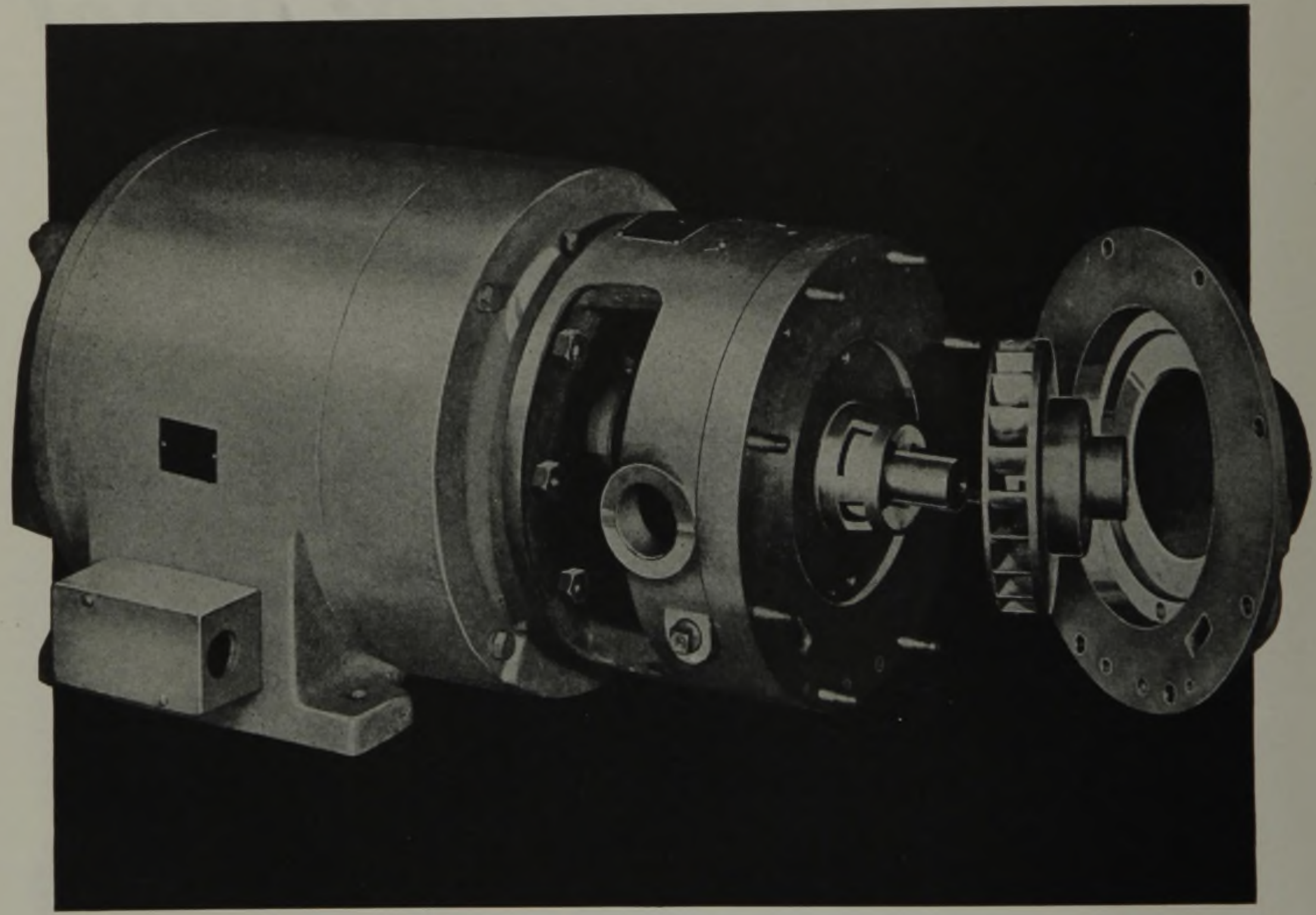
Nash Clean-Air Compressors

(TRADE-MARK REG.)

are Long Life compressors, because they have no internal wearing parts.



The Nash Clean-Air Compressor has but one moving part, cast in one piece and rotating in the pump casing without metallic contact. No internal lubrication is necessary; therefore air or other gas compressed with a Nash is entirely free from oil contamination.

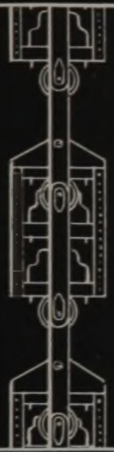
Dust and heat are removed from the air, or gas compressed, by the unique Nash "Liquid Piston". Air from a Nash Compressor is therefore delivered free from dust, heat, or oil, without supplementary filters or air washers, in a perfected mechanical structure with no internal wearing parts.

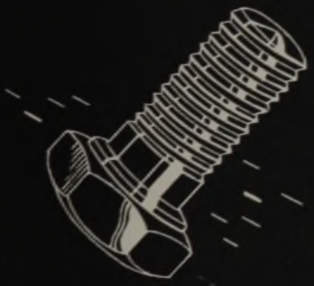
Air or gas from a Nash Compressor may be used for agitating, blending, maintaining pressure on storage tanks, or moving liquids and materials by pressure displacement, in connection with the most delicate food, beverage, or chemical process, without danger of contamination.

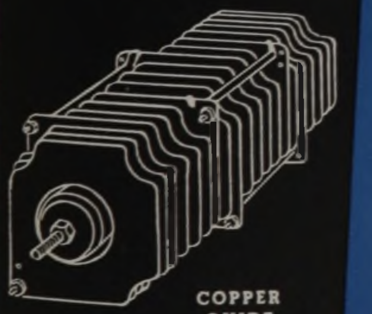
Bulletin D-252 tells all about Nash Clean-Air Compressors, and it is free on request.

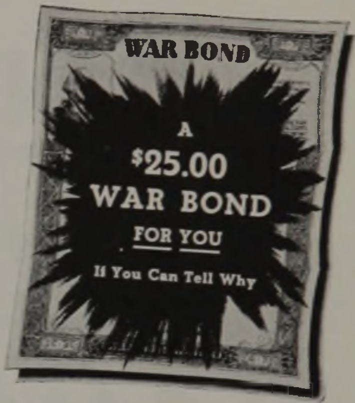
THE NASH ENGINEERING COMPANY

220-AS WILSON ROAD, SOUTH NORWALK, CONNECTICUT, U. S. A.





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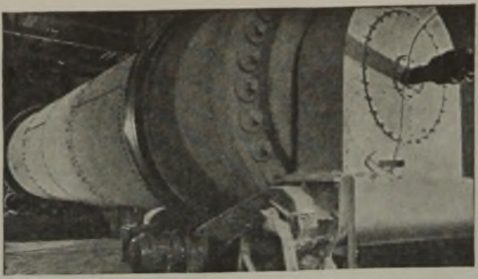

LOUISVILLE SYNTHETIC-RESIN DRYER SAVES $15,500 ANNUALLY!

Today when the words "continuous, automatic" are practically synonymous with *efficiency*, it's hard to believe that so many old-fashioned batch-type dryers are still being allowed to waste space, time, money, and productive capacity for manufacturers in America. . . . The case at the right is typical. . . . By replacing *one* tray-type machine with a modern Louisville Rotary Dryer, a manufacturer of synthetic resins is eliminating product-contamination, and is now drying in 20 minutes instead of 4 hours. In addition, he is saving $15,500 annually, in operating costs!

FORMER DRYER
(Tray Type)

Annual Production	2,880,000 lbs.
Space Required	1900 sq. ft.
Drying Time	about 4 hours
Drying Cost	$0.63 per 100 lbs.
Installed Cost	$70,000.

LOUISVILLE DRYER
(Warm Air Rotary Type)

Annual Production	4,325,000 lbs.
Space Required	900 sq. ft.
Drying Time	20 minutes
Drying Cost	$0.27 per 100 lbs.
Installed Cost	$35,000.

Louisville Dryer increases output 50%, saves space, saves drying time, and then pays its own cost in 27 months!

Incidentally — this Louisville Dryer, originally guaranteed to produce the same output as the old batch dryer formerly used, is actually delivering about 50% more than that!

Maybe a Louisville Dryer could produce some such results for *you*. Maybe not. If you'll give us brief answers to questions about your product, we'll be able to tell you almost exactly what a modern Louisville Dryer could do. Want the questions? *Address:* Louisville Drying Machinery Co., *Incorporated*, 433 Baxter Avenue, Louisville, Kentucky.

This Year Rubber Is Tapped from Test Tubes

Synthetic Rubber Already Is Working for Users of Mechanical Rubber Goods

War production is up threefold. But the vital rubber stock pile is dwindling fast. This is the year of crisis in rubber.

There is only one solution . . . the production of synthetic rubber in steadily increasing tonnages . . . synthetic rubber to take over jobs once handled by natural rubber . . . to perform new tasks, serve in new applications created by wartime need.

One of the first synthetic rubber plants in the Government's program was built and is being operated by United States Rubber Company . . . another soon will be in production.

Our engineers have been working with synthetic rubber since 1921. During this period they have learned that no one synthetic should be used for all types of mechanical rubber goods. They have found where and how synthetic is superior to natural rubber, where it is equally as good, where it falls short. They know what uses each of the five basic commercial types of synthetic rubber is best suited for — Neoprene, Buna-S, Buna-N, Butyl, or Thiokol—and how to compound the specific synthetic rubber for the specific task. U. S. Rubber has used all five types and knows which one to select for the performance required.

Information based on the results of vast experiments and practical applications of synthetic rubber has been incorporated in a new comprehensive book, *The Five Commercial Types of Synthetic Rubber.*

This informative book traces the history of synthetic rubber from the earliest experiments of Michael Faraday to the present. It discusses each of the basic types of synthetic rubber, tells where it has been used successfully in United States Rubber Company products, and compares its properties with natural rubber. It tells how synthetic rubber is made. It is a detailed answer to the most vital question of the day.

We feel that *The Five Commercial Types of Synthetic Rubber* is a publication of real importance to men of industry. Requests made by them on their company letterhead will be filled promptly.*

The successful use of synthetic rubber in mechanical rubber goods and the insurance of fully dependable service depend largely upon the skill of the manufacturer and compounder. Each of the five basic commercial types of synthetic permits a myriad of variations.

The United States Rubber Company has been developing and improving rubber products for one hundred years. Today, the same vast resources for research and development that resulted in some of the most spectacular achievements in the rubber industry are being devoted to the problem of synthetic rubber. A great backlog of knowledge already has been built. More is being constantly added.

**Requests for this Synthetic Rubber Book should be addressed to Department 30, Mechanical Goods Division, United States Rubber Company, Rockefeller Center, N. Y. C.*

UNITED STATES RUBBER COMPANY

Mechanical Rubber Goods Division • Rockefeller Center • New York

In Canada, Dominion Rubber Co., Ltd.

HYDROFLUORIC ACID

for CLEANING
ETCHING
CATALYTIC PROCESSES
BLEACHING

Seven Strengths Available

Anhydrous HF
80%
71-75%
60%
52%
48%
30%

● Specify Penn Salt hydrofluoric acid for cleaning stainless steel—for etching and polishing of fine glass—for catalytic process requiring such a reagent—for frosting electric light bulbs—as an aid in straw bleaching processes—and for any of many other industrial uses.

Depend upon Penn Salt hydrofluoric acid to meet your most exacting requirements. It can be supplied in six strengths for domestic users—30%, 48%, 52%, 60%, 80%, and Anhydrous HF. For export, there is 71-75% acid. In strengths up to and including 60%, hydrofluoric acid is shipped in rubber drums. In strengths of 60% to and including 80%, it is shipped in steel drums. Anhydrous HF is shipped in cylinders and tank cars.

ANHYDROUS HF—We are pioneer manufacturers of Anhydrous HF. This acid is used in the alkylation process for the manufacture of high octane gasoline and in many other new catalytic processes.

PENNSYLVANIA SALT MANUFACTURING COMPANY
Chemicals
1000 WIDENER BUILDING, PHILADELPHIA, PA.

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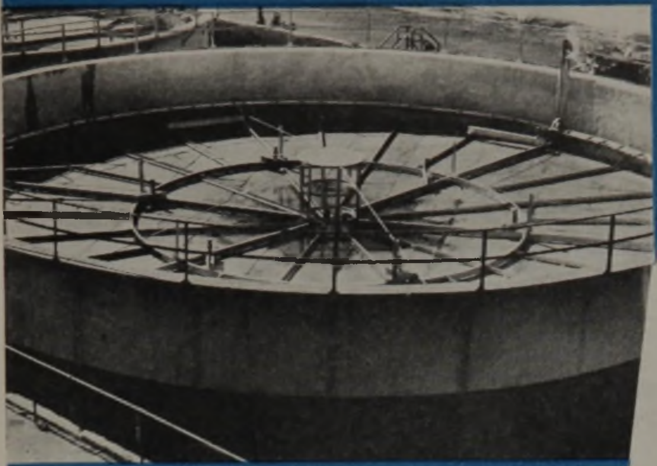
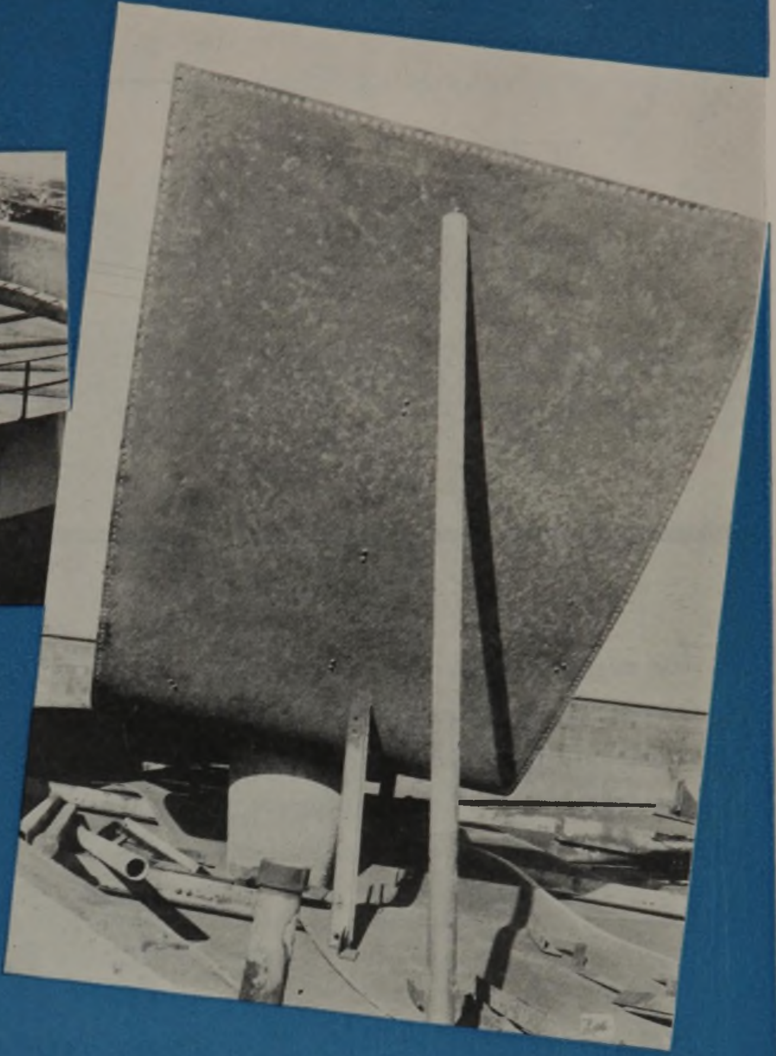




LIFTED FROM A SCRAP PILE TO TELL YOU IT'S HISTORY

Long ago, this aluminum alloy roof of an oil storage tank left the scrap pile for points unknown . . . The tank was torn down to make way for plant expansion, but the aluminum told an interesting story of endurance under trying conditions.

The sour distillate which had been stored in this tank destroys *ordinary* tank roofs in a surprisingly short time. But not so with this aluminum alloy roof! Though the outside was very dirty and the inside was coated with a thick, crusty deposit, removal of these coatings showed the aluminum to be sound.

That aluminum roof had been on this job over nine years. It had years and years of service left in it.

In planning for the future, keep the performance of this aluminum roof in mind. Think of Alcoa Aluminum Alloys as a means of combating corrosion and protecting your products. Aluminum Company of America, 2154 Gulf Building, Pittsburgh, Pennsylvania.

ALCOA ALUMINUM

He gets his second breath from a deep-drawn cylinder

The oxygen cylinder shown below is another example of the way the Hackney deep-drawing process is conserving materials, man-hours and equipment—and is producing improved products.

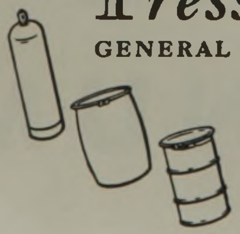
High above the clouds, deep-drawn cylinders containing oxygen aid pilots to breathe easily. To meet the necessarily stringent requirements, these cylinders must be light in weight and have high tensile strength.

Hackney Cylinders, Drums and Barrels

Products like the one described above keep rolling out of Pressed Steel Tank Company's factory. Today, all of Hackney's facilities are pledged to the making of products for Victory. Hackney cylinders, drums and barrels are now in service for hundreds of war plants—helping to solve transportation and storage problems for vital chemicals. Thus, they are hastening the day when their advantages can be available to all businesses.

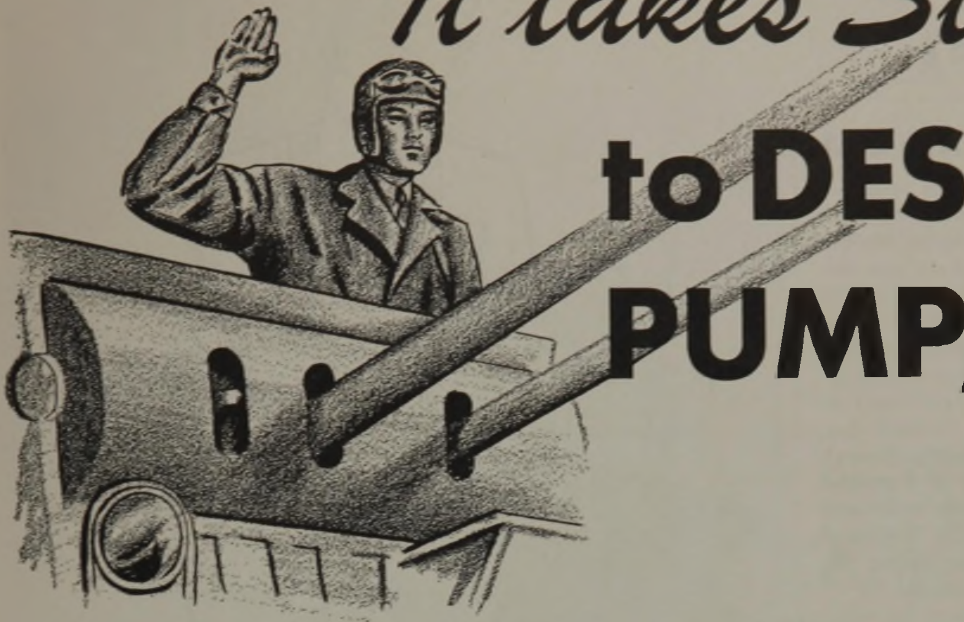
When that day arrives, the vast knowledge and research of Hackney's wartime experiences will be available to all industry. It is your assurance that Hackney will continue to make improved containers for gases, liquids and solids.

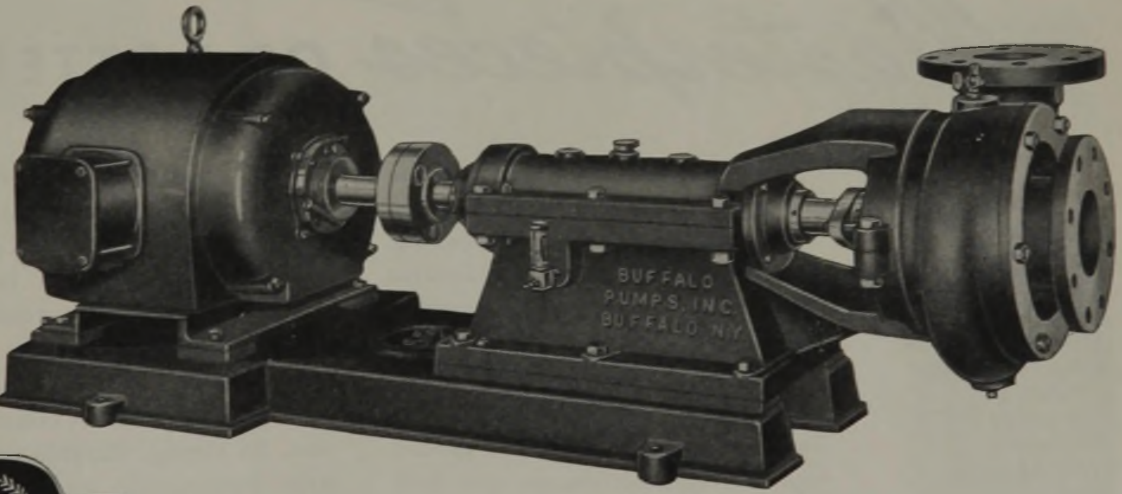
Pressed Steel Tank Company



GENERAL OFFICES AND FACTORY • 1451 SOUTH 66th STREET
Milwaukee, Wisconsin

CONTAINERS FOR GASES, LIQUIDS AND SOLIDS

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PUMPS, INC.
BUFFALO, N.Y.


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Pressed Steel Tank Company

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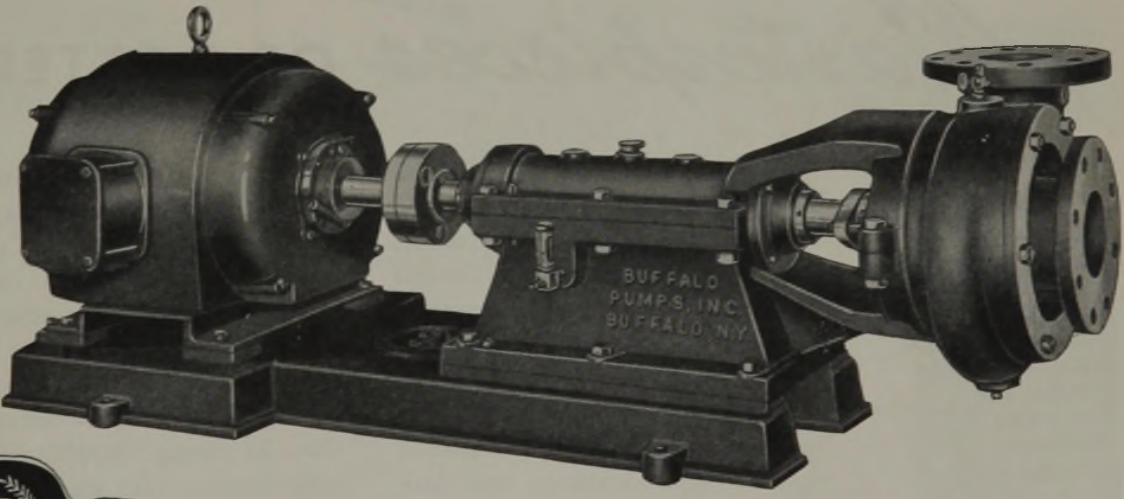
CONTAINERS FOR GASES, LIQUIDS AND SOLIDS



BUFFALO
PUMPS, INC.
BUFFALO, N.Y.

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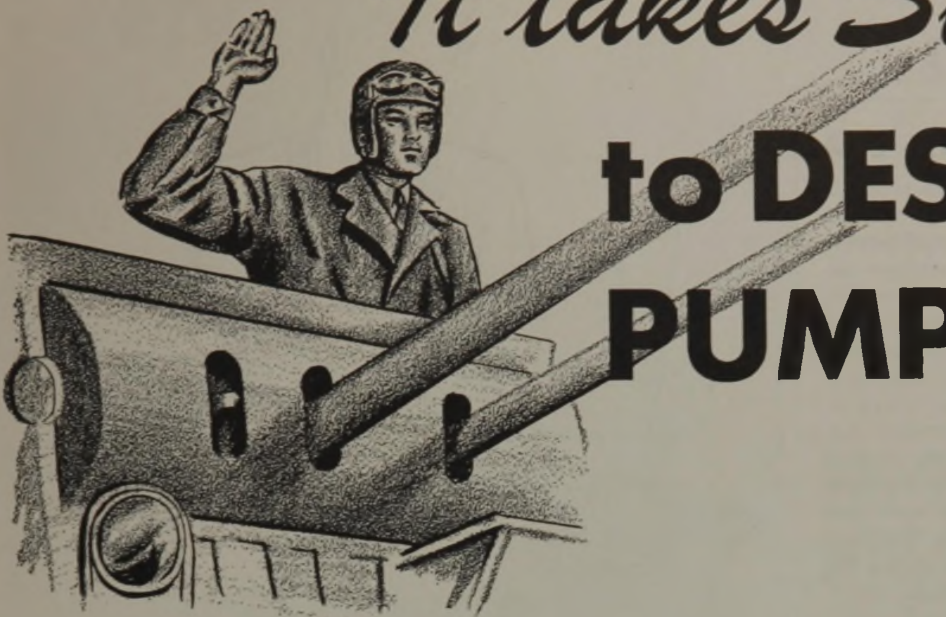
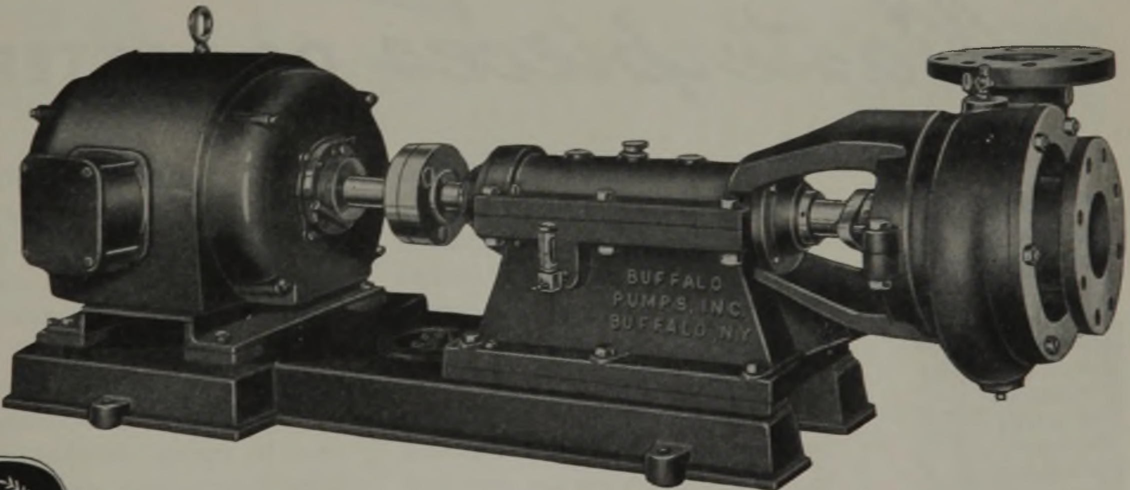



BUFFALO
PUMPS, INC.
BUFFALO, N.Y.

THE GRECIAN ERA

In ancient Greece the scope of ceramics was greatly widened. The potter's art created humble kitchen utensils and storage vessels, yet soared to new heights in exquisitely designed ornamental vases admired for their beauty down to the present day.

Ceramic tile for roofs was an innovation of the Hellenic Era. However, it was chiefly through fine craftsmanship and careful selection of different kinds and colors of clay that the Greeks of old took their place among the fine potters of the world.

Masterpieces OF POTTERY

Chemical Stoneware Cooling Coil

THE SAME PAINSTAKING selection of the finest clays, the same careful molding and baking that made Grecian pottery famous and time enduring, is being carried on today by General Ceramics. Unlike the pottery of the Greeks, however, distinction in General Ceramics Chemical Stoneware is gained not through decoration and delicacy, but through tested quality and adaptable utility. In order to handle the strong chemicals used in industry today, General Ceramics Chemical Stoneware is carefully processed to make it acid-proof through and through. Its glazed surface is easy to keep clean, thus eliminating product contamination. Its strong, durable, seamless body construction guards against hazardous leakage.

Other products include Steatite Insulators made by General Ceramics & Steatite Corp., Keasbey, N. J.

General Ceramics Co.

GENERAL CERAMICS COMPANY
CHEMICAL STONEWARE

CHEMICAL STONEWARE DIV.
KEASBEY • NEW JERSEY

3565

The familiar bomber nose is a *PLEXIGLAS* nose

PLEXIGLAS, the crystal-clear acrylic plastic which made possible the familiar bomber nose, as well as other transparent parts aboard every type of Army and Navy plane, was developed in Rohm & Haas laboratories, first brought to commercial production in Rohm & Haas plants.

There the first transparent plastic bomber nose was built, and the method for mass production of these curved sections was developed. Formed from "aviation's standard transparent plastic," the now famous PLEXIGLAS "greenhouse" is one of numerous examples of a chemical development begun in peace which is now meeting the needs of war.

TEGO...AND PLYWOOD PLANES

Five years before the war began the manufacture of plywood was literally revolutionized when our associate, The Resinous Products & Chemical Co., introduced a new resin adhesive in sheet form—TEGO. Bonded with this resin, veneers became a "wonder-wood," weight for weight stronger than steel, weatherproof, fungus-proof. Today practically all aircraft plywood is TEGO bonded plywood.

LETHANE... AND INSECTS

As a result of prewar research, LETHANE, the first synthetic organic insecticide was developed in Rohm & Haas laboratories. LETHANE is the killing agent in leading agricultural, household, livestock and industrial insect sprays. When war sharply curtailed imports of rotenone and pyrethrum, LETHANE, made from American materials, stood ready to relieve this shortage of botanical toxicants.

ONE ORGANIZATION'S PART

The chemical companies most active in research before Pearl Harbor are today the ones most helpful in prosecuting the war. The Rohm & Haas Company and its associates are giving effective aid to the war effort as a result of their peacetime research.

PLEXIGLAS, TEGO *and* LETHANE
are trade-marks Reg. U. S. Pat. Off.

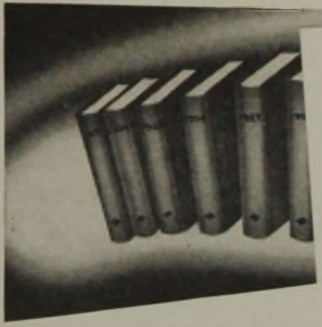
ROHM & HAAS COMPANY

AND ASSOCIATES:

THE RESINOUS PRODUCTS & CHEMICAL COMPANY • CHARLES LENNIG & COMPANY

WASHINGTON SQUARE, PHILADELPHIA, PA.

Manufacturers of Plastics, Insecticides and Fungicides, Coating Resins, Plywood Adhesives, Ion Exchange Resins and Chemicals for the Leather, Textile, Enamelware and Other Industries.



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which produced the
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ing problems when
pumps.

THE LaBO
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LaBOU

ACE Hard Rubber helps safeguard America on land...on sea ...in the air

•

Rugged, precision parts of Ace hard rubber—all with these advantages: Acid and Alkali Resistant . . . Dependable . . . Economical . . . Non-Hygroscopic . . . Adaptable for integrally molded metal parts...Easily machined, turned and finished.

Ace hard rubber Rotary Gear Pump
a range of uses from laboratory
problems, Capacity 9 gallons per
ber Centrifugal, Single Acting and

AC

In Active Duty!

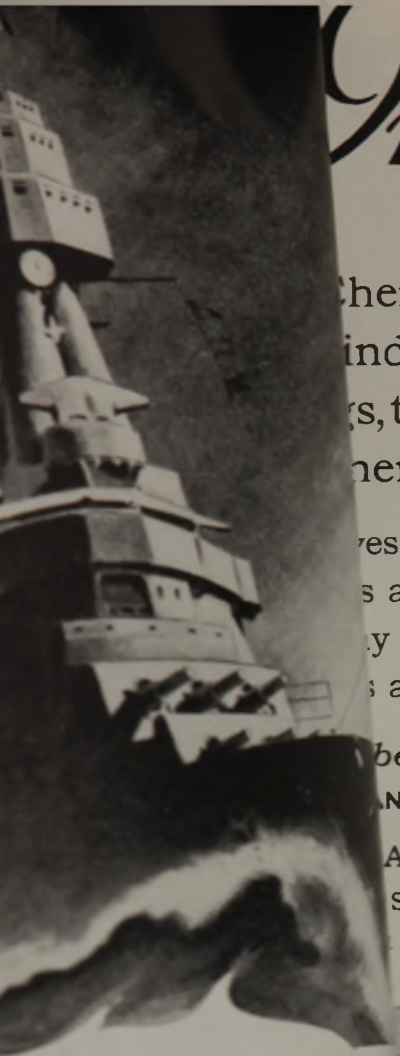
hemical Process Industries ACE rubber lining is a stra- indispensable material for tanks, pumps, pipe, valves, s, tank cars, etc. ★ Engineers responsible for safeguard- nent against corrosion know that ACE rubber lining

ves complete, positive protection against corrosion and contamination
s a wide temperature range
y be compounded to meet specific requirements of service
s a non-porous surface, smooth, easy to clean

ber linings, including Thiokol, Neoprene, etc., are also available

N Pipe and Fittings, iron pipe sizes; Injection Moldings; Thin Wall Tubing and Fittings

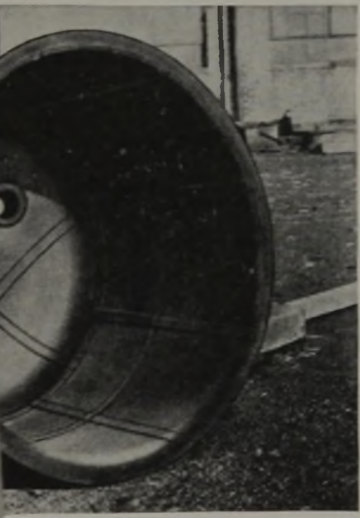
ARD RUBBER COMPANY
STREET, NEW YORK, N. Y.
W. WASHINGTON ST., CHICAGO, ILL.



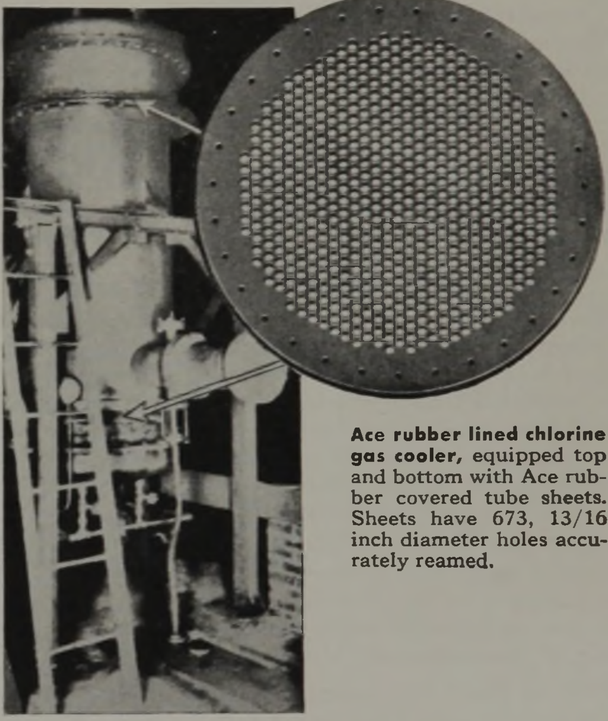
d Rubber helps
uard America
land...on sea
...in the air

•

ugged, precision parts of Ace hard rubber—all with these advantages: Acid and Alkali Resistant ... Dependable ... Economical ... Non-Hygroscopic ... Adaptable for integrally molded metal parts...Easily machined, turned and finished.



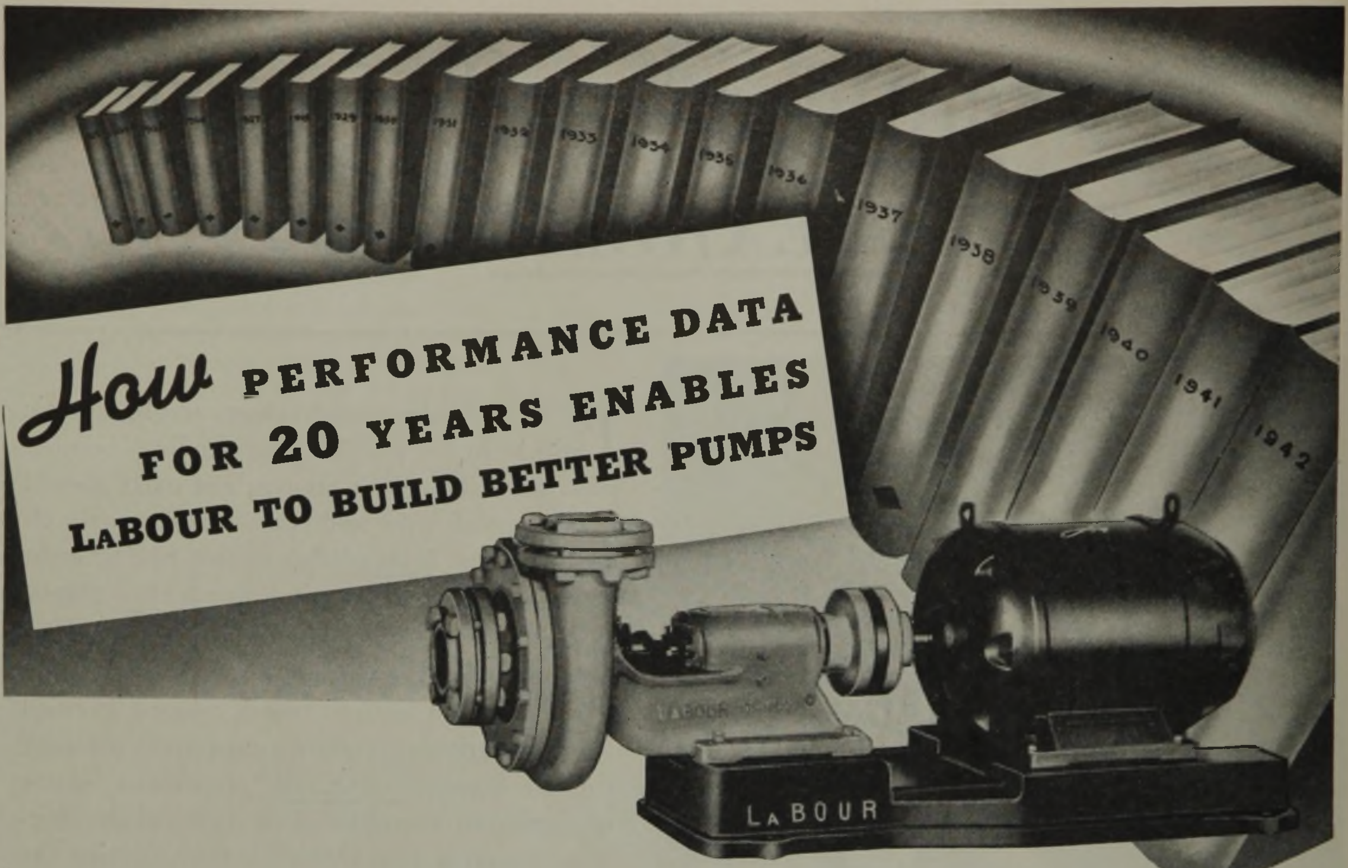
ined Evaporator Head



Ace rubber lined chlorine gas cooler, equipped top and bottom with Ace rubber covered tube sheets. Sheets have 673, 13/16 inch diameter holes accurately reamed.

BER PROTECTION

fense against Corrosion



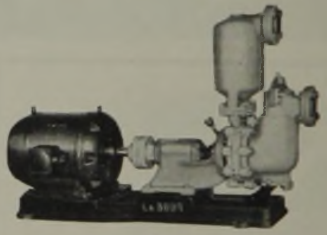
How PERFORMANCE DATA FOR 20 YEARS ENABLES LaBOUR TO BUILD BETTER PUMPS

Only continuous fact-finding and record-keeping can furnish answers to the multitude of liquid chemical handling problems encountered in the process industries.

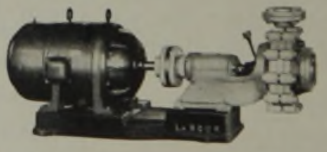
That's why LaBour started to record, more than 20 years ago, accurate metallurgical data on every heat poured in our own foundries. Each chrome alloy casting carries an identifying mark and performance data on any LaBour pump can then be correlated with recorded information to point the way to constant improvement, and better pump service for every LaBour user.

Today LaBour has in these "case histories" an invaluable source of the facts required to build pumps best suited to any particular chemical pumping service. These methods, plus the engineering skill which produced the first practical self priming centrifugal pump, go to work on your chemical pumping problems when you order or specify LaBour pumps.

THE LaBOUR COMPANY, Inc.
Elkhart, Indiana, U. S. A.



LaBour Type DPL—This centrifugal pump primes itself without the use of valves or any auxiliary priming mechanism. Capacities range from 10 GPM to 1500 GPM.



LaBour Type DZ — A non-priming pump especially designed for conditions of high head where relatively low capacity is required.

Every LaBour pump undergoes elaborate running tests to insure its ability to meet operating conditions which will be encountered in use.

LaBOUR PUMPS

LaBour

Air Conditioning gives it OOMPH!

This war is being fought with *explosions.* All kinds...from block-busters to hand grenades. And don't forget the explosions in the barrels of guns that propel bullets and shells toward the enemy.

It takes a lot of skill to make a good explosion. Air conditioning helps.

The rate at which powder *dries* determines the way it explodes. It must not explode too soon or too late. Hence, special air conditioning . . . with temperature and humidity controlled precisely . . . is used for the drying of powder.

Also, air conditioning protects the lives of workers in munitions plants by providing the safest temperature and humidity conditions.

General Electric is an outstanding supplier of the new improved kind of air conditioning equipment needed for these wartime requirements. It has developed equipment more flexible, more compact than ever before . . . with more accurate temperature and humidity control.

Today this equipment is being devoted to winning the war. After the war, a far better air conditioning will be made available for offices and factories, stores and theatres; homes, hospitals and hotels . . . from General Electric.

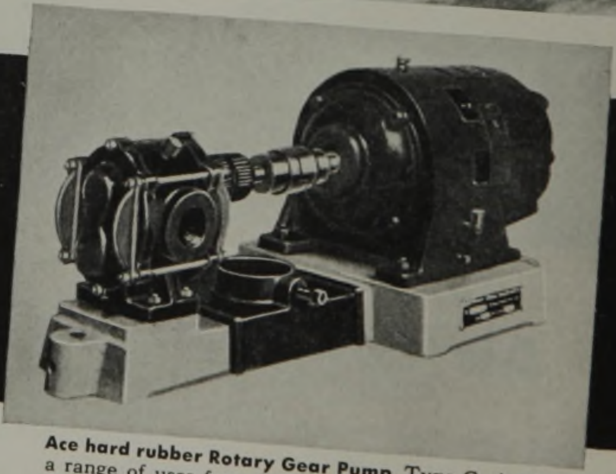
Air Conditioning and Commercial Refrigeration Department, Division 433, General Electric Co., Bloomfield, N. J.

Air Conditioning by **GENERAL ELECTRIC**

ACE Hard Rubber helps safeguard America on land...on sea ...in the air

•

Rugged, precision parts of Ace hard rubber—all with these advantages: Acid and Alkali Resistant . . . Dependable . . . Economical . . . Non-Hygroscopic . . . Adaptable for integrally molded metal parts...Easily machined, turned and finished.



Ace hard rubber Rotary Gear Pump, Type G. Applicable to a range of uses from laboratory work to factory pumping problems, Capacity 9 gallons per minute. Also Ace hard rubber Centrifugal, Single Acting and Double Acting pumps.

ACE

On Active Duty!

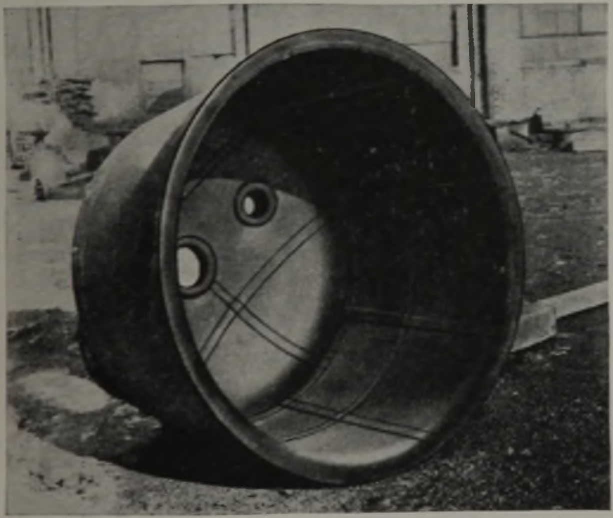
★ In the Chemical Process Industries ACE rubber lining is a strategic and indispensable material for tanks, pumps, pipe, valves, pipe fittings, tank cars, etc. ★ Engineers responsible for safeguarding equipment against corrosion know that ACE rubber lining

- . . . gives complete, positive protection against corrosion and contamination
- . . . has a wide temperature range
- . . . may be compounded to meet specific requirements of service
- . . . has a non-porous surface, smooth, easy to clean

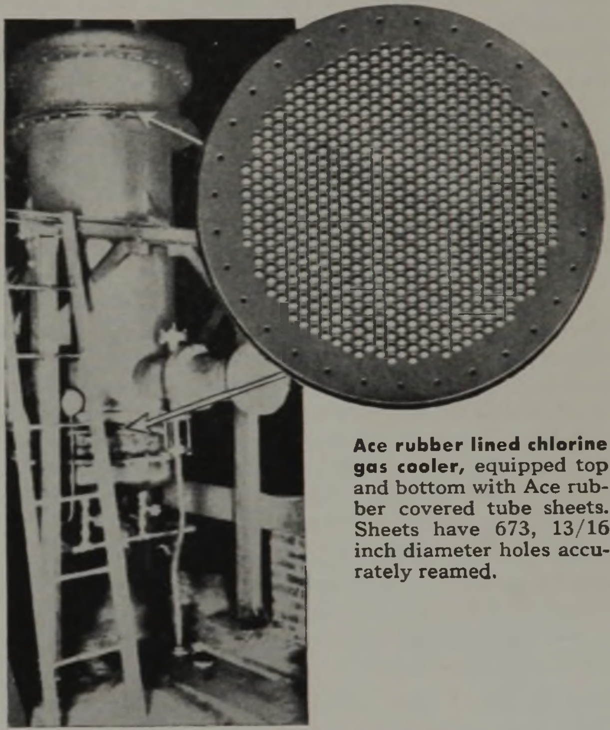
Synthetic rubber linings, including Thiokol, Neoprene, etc., are also available

Ace plastic SARAN Pipe and Fittings, iron pipe sizes; Injection Moldings; Thin Wall Tubing and Fittings

AMERICAN HARD RUBBER COMPANY
11 MERCER STREET, NEW YORK, N. Y.
AKRON OHIO 111 W. WASHINGTON ST., CHICAGO, ILL.



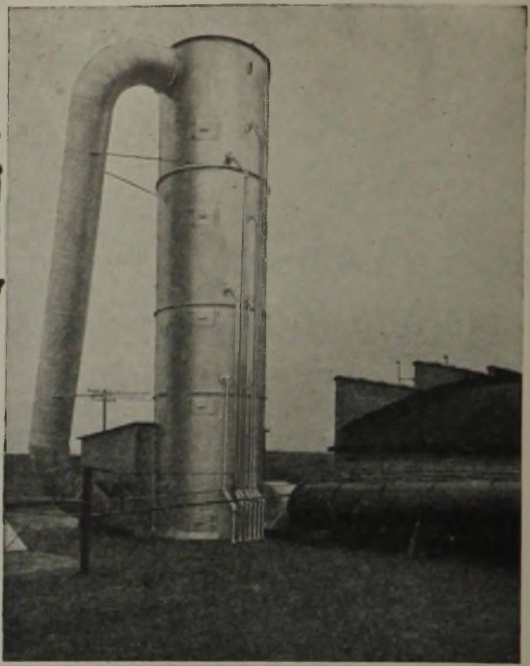
Neoprene lined Evaporator Head



Ace rubber lined chlorine gas cooler, equipped top and bottom with Ace rubber covered tube sheets. Sheets have 673, 13/16 inch diameter holes accurately reamed.

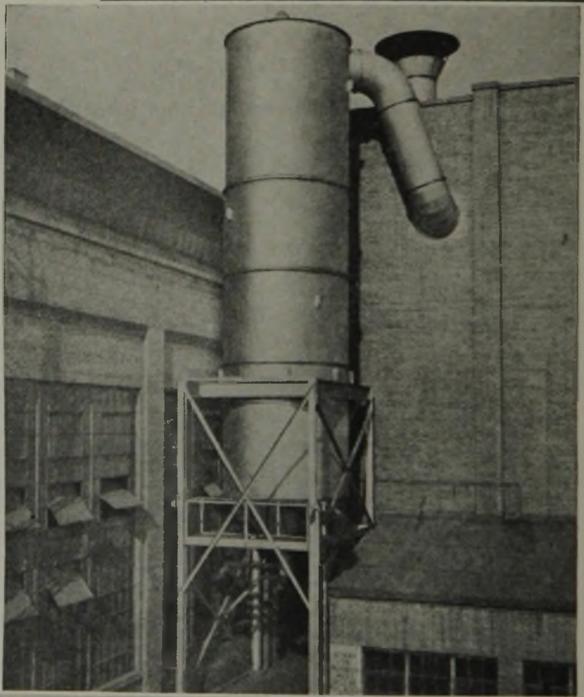
RUBBER PROTECTION
for Defense against Corrosion

Solving Three Tough Process Problems



Schneible Equipment is doing its part in the war effort by keeping the air in busy process plants clean and by salvaging valuable by-products. Schneible installations result in improved working conditions and higher human efficiency, which is all important in the face of today's maximum production demands.

Whatever your dust or fume problem may be, dependable Multi-Wash Equipment has coped with similar conditions or our engineers will recommend an installation consisting of standard units to meet your special needs.



1. Controlling Obnoxious Fumes and Nuisance

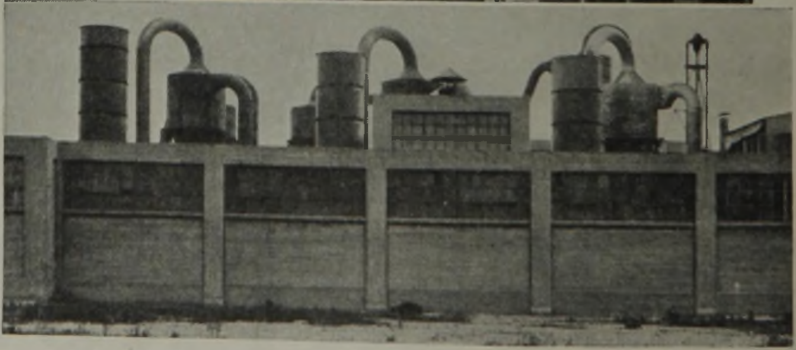
For several years, this 12,000 c.f.m. Schneible Special Multi-Wash Collector has been effectually removing hydrogen sulphide, ammonia and other obnoxious fumes exhausted in manufacturing a specialized viscous product in a large Wisconsin processing plant. What was formerly a neighborhood nuisance has been permanently abated.

2. Controlling Acid Fumes in a Refinery

This 3,000 c.f.m. Schneible Senior Multi-Wash Collector has proved highly effective in removing acid fumes from the air exhausted from reaction vessels in an Illinois plant engaged in refining rare metals for use in high speed cutting tools.

3. Controlling Dust and Waste

This multiple installation of Schneible Senior Multi-Wash Collectors with copper towers in a large Illinois processing plant is used to remove and recover corn sugar from the air exhausted from dryers and from handling and packaging operations. Multi-Wash Equipment with towers of cast iron and steel are used in the corn starch division of the same company. The salvage value, alone, of the products recovered quickly paid for these installations.



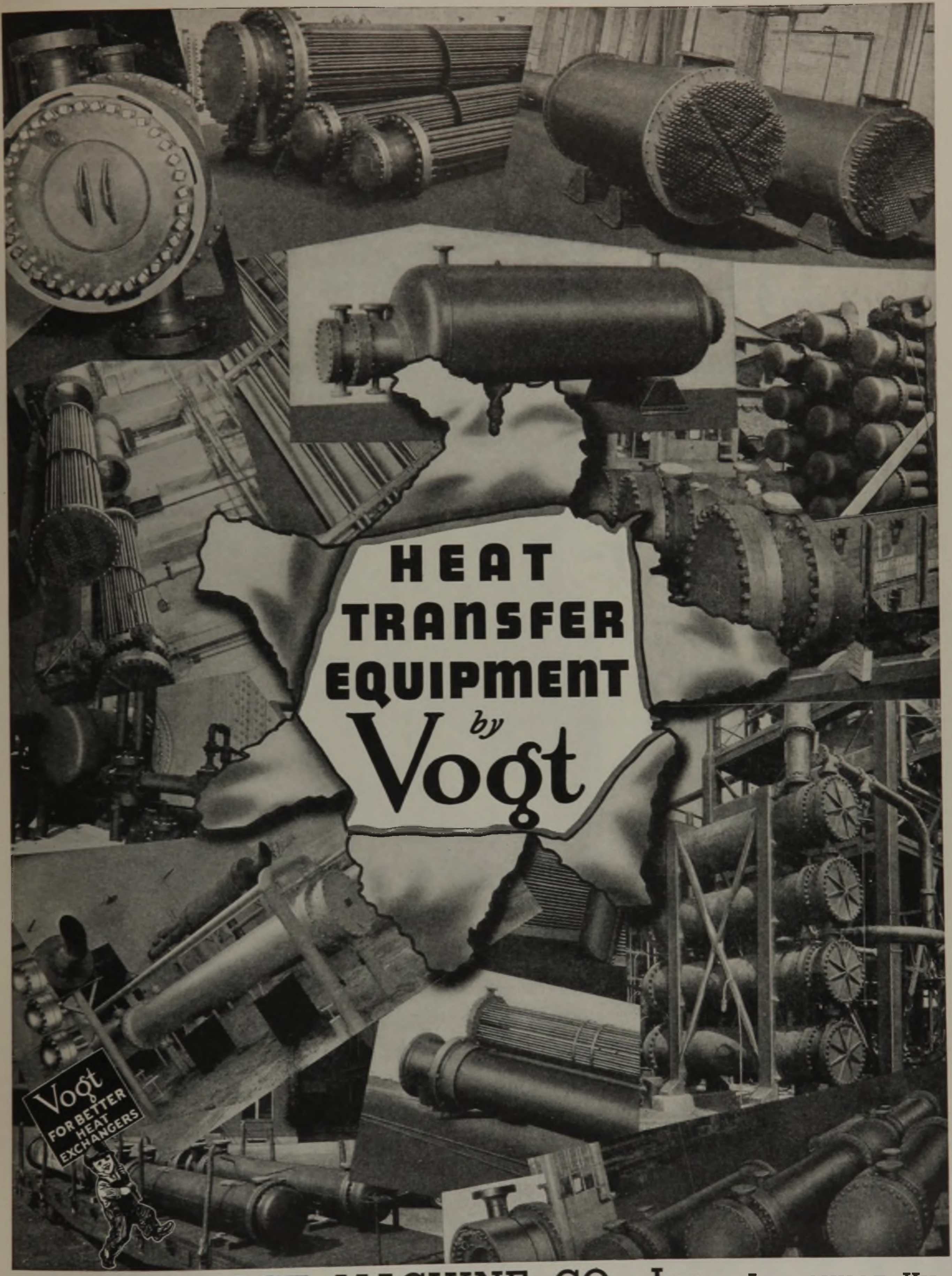
If Old Man Atmosphere is robbing you of valuable material or product, we may be able to recover it for you. The case cited above is but one of a number where product recovery paid for the equipment.

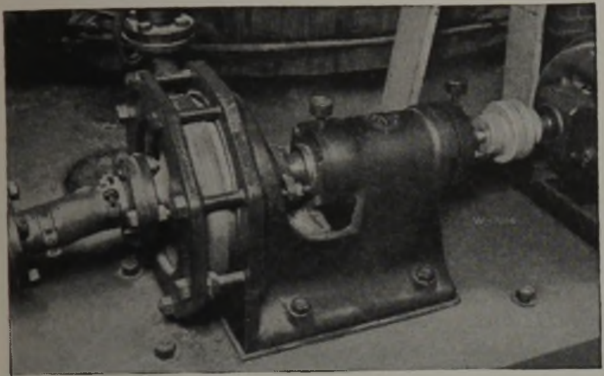
Write us about your problem — whether it affects your entire plant or a single isolated operation.

CLAUDE B. SCHNEIBLE COMPANY
3959 Lawrence Avenue Chicago, Illinois
Engineering Representatives in Principal Cities

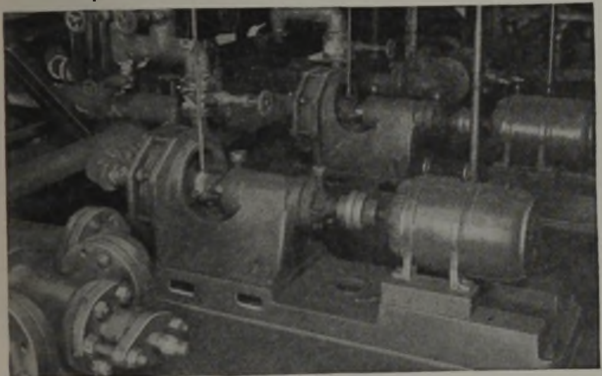
SCHNEIBLE

DUST, ODOR AND FUME CONTROL EQUIPMENT

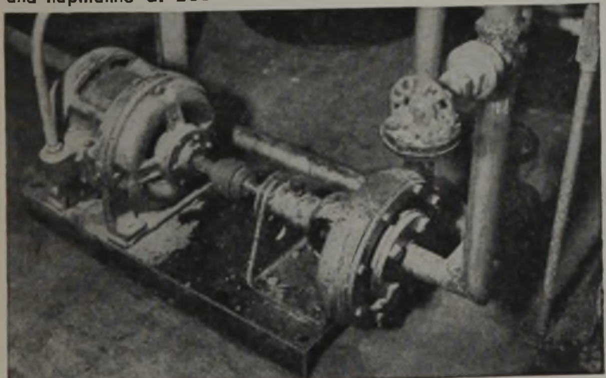

HEAT
TRANSFER
EQUIPMENT
by
Vogt
Vogt
FOR BETTER
HEAT
EXCHANGERS



Worthite pump handling vinegar in a food products plant



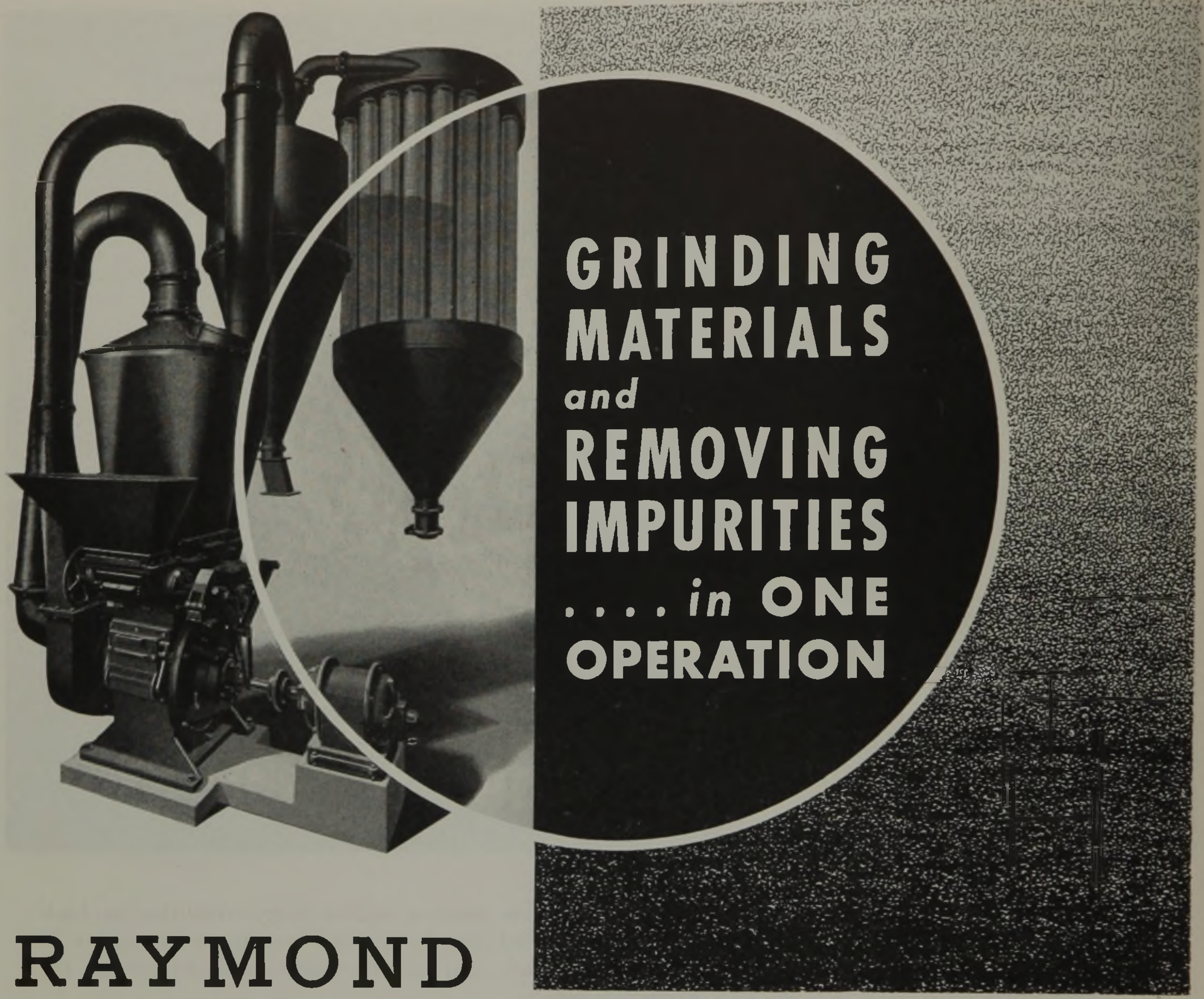
Worthite pumps handling tar acids and napthaline at 200° — 230° F



Worthite pump handling sulfuric acid and sulphurated oil


PLEASE NOTE AND PASS ON
Short-Cuts to Faster Piping Jobs
..FOR SPECIFIERS
..FOR PIPEFITTERS
POST ON SHOP BULLETIN BOARD
HELPS IN MEETING PIPING MATERIAL SHORTAGES
A FEW EXAMPLES OF WARTIME PIPING INGENUITY
CRANE Piping Pointers for Peak War Production!
"PIPING POINTERS" BULLETIN NO. 6


Treat it Right
for
PRODUCT QUALITY
PRODUCTION EFFICIENCY
OPERATING ECONOMY



RAYMOND

SINCE 1887

AUTOMATIC PULVERIZER

In making powdered products, you can often simplify methods of operation and maintain uniform quality in the finished material by the use of Raymond equipment.

For example, with the Automatic Pulverizer, you can completely process difficult materials that usually require several units of equipment. This machine disintegrates the product, cleans it of impurities, and classifies it to desired fineness by air separation. It is a single cycle operation, dustless and automatic throughout.

The throw-out attachment, a Raymond feature, is useful in such operations as: Pulverizing litharge and rejecting the free lead . . . separating granular impurities from extreme fines . . . eliminating sand from ochres or pigments . . . removing unburnt lime from chemical hydrate . . . cleaning kaolin and clays from impurities.

For further details, see Raymond Catalog #37.

RAYMOND
PULVERIZER DIVISION
Combustion Engineering Company, Inc.
1313 North Branch Street
CHICAGO

Sales Offices in Principal Cities

Canada: Combustion Engineering Corp., Ltd. Montreal

GET THIS NEW VALVE CATALOG

32 PAGES OF VALUABLE REFERENCE DATA ON CORROSION-RESISTANT VALVES

WHAT YOU CAN GET IN Duriron and Durichlor Valves

- Y Valves
- Duriron-Nordstrom Valves
- Plunger-Release Valves
- Bottom-Lubricated Valves
- Gate and Straightway Valves
- 3-Way, Foot and Check Valves
- Mechanically Operated Valves
- Angle, Relief and Float Valves
- Three-Quarter Inch Valves

DURIRON is a corrosion-resisting alloy universally known and used. DURICHLOR is for hydrochloric acid and other chlorine solutions.

WHAT YOU CAN GET IN Durco Stainless Steel Valves, Durimet, KA2S, KA2SMo, etc.

- Y Valves
- *Plain Plug Valves
- *Plunger-Release Valves
- *Lubricated Plug Valves
- *Combination P-R and Lubricated Valves
- *Mechanical Lift Plug Valves
- Three-Way Valves

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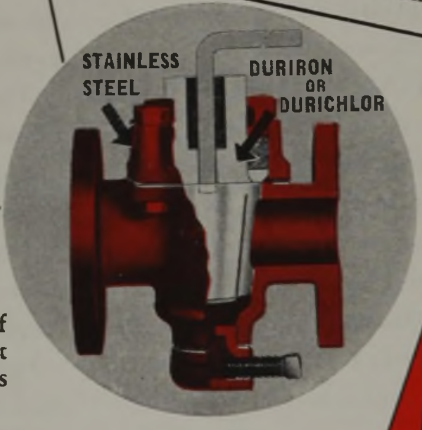
*These valves are furnished with Stainless Steel bodies and Stainless Steel plugs, *and also with DURIRON or DURICHLOR plugs.* This exclusiye feature provides great strength and resistance to abrasion and scouring.



Type 602 Valve

Here is a reference book that should be in the hands of everyone using acids. In it are shown the latest and best metallurgical and engineering developments in valves for handling corrosive solutions.

WHAT YOU WILL FIND IN THIS BOOK

- Cross-sectional views of all principal valve types.
- Sizes and dimensions of 24 types of valves, in many different capacities.
- Parts lists.
- Installation photos.
- Information as to the proper application of DURIRON, DURICHLOR, DURIMET and DURCO STAINLESS STEELS.

THE DURIRON CO., INC. • DAYTON, OHIO

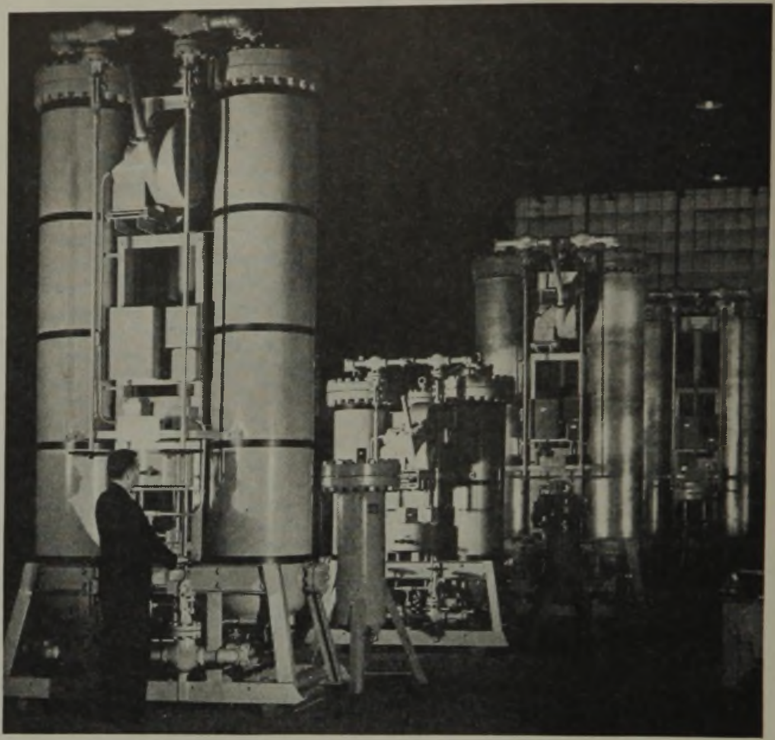
ARMY E NAVY

DURIRON · DURICHLOR
CORROSION-RESISTING
DURCO
ALLOYS & EQUIPMENT
THE DURIRON CO., INC.
DAYTON, OHIO
DURIMET · DURCO STAINLESS STEELS

CLIP this coupon. Attach it to your letterhead.

The DURIRON CO., Inc. DAYTON, OHIO.
Send Valve Bulletin No. 605-E to:

Name____________________
Address____________________



THIS LINE OF
Lectrodryers
CARRIES A
PROMISE
for the
Future

These Lectrodryers were photographed as they left for points best known to the censors. Like hundreds of others, they are now at work on synthetic rubber production, in oxygen plants, and on dozens of other processes vital to the war effort.

Lectrodryers are DRYING MACHINES. They control humidity. They dry air and gases to extremely low dew points, at either atmospheric pressure or compressed to 3,000 pounds per square inch. They dry many of the organic liquids so important today. Although engineered for every installation, each is a standard, proved design.

Lectrodryers are speeding war production. Work is now done in atmospheres of definite humidity, with gases and liquids of known dryness. Materials contain only the water that is wanted there. Because Lectrodryers use Activated Aluminas as their drying agent, you can dry liquids and gases DRY, to dew points below −110°F.

This experience with controlled humidity and dryness spells the doom of hit-or-miss methods of production. Postwar industry is going to demand the same independence of outside weather conditions, the same sureness of quality and speed of production. Lectrodryer engineers will gladly help shape your thinking on these problems.

Pittsburgh Lectrodryer Corporation, 305 32nd Street, Pittsburgh, Pennsylvania.

LECTRODRYERS DRY WITH ACTIVATED ALUMINAS

PITTSBURGH
LECTRODRYER
CORPORATION
Reg. U.S. Pat. Off.

TYPICAL ANALYSIS OF MALLINCKRODT STANDARD STEARATE PRODUCTS

Name	Bulk in Fl. Oz. per Lb.	Metallic Oxide	*Extractable Acid	Softening Point
Aluminum Stearate Technical M	52	15%	6%	170° C.
Aluminum Stearate Technical D	54	8.4%	7%	157° C.
Aluminum Stearate Technical D 5-47	58	8.7%	4.8%	160° C.
Aluminum Stearate Technical D Fluffy	70	8.2%	8%	148° C.
Flatting Agent No. 22	70	8%	7.5%	....
Aluminum Stearate Technical T D (Formerly named No. 1-49)	80	7.7%	15%	130° C.
Aluminum Stearate Technical T	48	6%	25%	109° C.
Aluminum Stearate Technical T for Paint & Varnish Manufacture	76	6%	24%	115° C.
Calcium Stearate Technical	35	9%	1.5%	125° C.
Calcium Stearate Impalpably Powd.	125	9%	1.5%	146° C.
Zinc Stearate U.S.P. XII	160	14%	2%	118° C.
Zinc Stearate U.S.P. XII "S"	160	14%	2%	120° C.
Magnesium Stearate Technical	40	6.8%	2.5%	125° C.
Magnesium Stearate Impalpably Powd.	140	6.8%	2.5%	125° C.

The water content of stearates is limited to 1%. In most cases the actual amount is less.
The water-soluble material is also limited to 1% and is usually less.
**The "Extractable Acid" is determined by extraction with boiling Acetone.*

This Simple Care
ADDS YEARS OF LIFE
TO STAINLESS STEEL EQUIPMENT

Certainly, stainless steel is tough and strong. It resists hard wear and abuse—resists corrosion and oxidation. Normally, it will last longer than most other materials —even in the most severe service.

And it could last even longer—if certain precautions were taken and care exercised in cleaning.

Are you doing everything possible to get every available day of service from your stainless steel equipment? Remember—when your present equipment is worn out, you probably will not be able to replace it during wartime, unless you have an extremely high priority.

Here's what to do. Write and tell us the nature of your operations, and we'll send you a poster-size wall card (several if you need them) giving suggestions for lengthening service life and detailed information on cleaning. Individual cards are available for the following types of equipment: (1) Process and Chemical, (2) Pulp and Paper, (3) Textile, (4) Food and Beverage Processing—meat packing, canning, etc., (5) Food Handling and Serving —restaurant, hotel, hospital and institutional kitchen and service equipment, and (6) Dairy.

This information—prepared by Republic metallurgists from their *UNEQUALLED* experience in the development and application of Republic ENDURO* Stainless Steel—may be the means of adding years to the life of your priceless equipment.

REPUBLIC STEEL CORPORATION
Department EC
Alloy Steel Division
Sales Offices: Massillon, Ohio
GENERAL OFFICES • • CLEVELAND, OHIO
Berger Manufacturing Division • Culvert Division
Niles Steel Products Division • Steel and Tubes Division
Union Drawn Steel Division • Truscon Steel Company
Export Department: Chrysler Building, New York, N. Y.

• • •

TO ENDURO FABRICATORS: *Tell us how many of these conservation cards you would like for distribution to your customers. We'll gladly furnish them already imprinted with your name and address.*

*Reg. U. S. Pat. Off.

CONSERVE STAINLESS STEEL
Process and Chemical Equipment
IT'S EASY . . . HERE'S HOW

Republic ENDURO Stainless Steel is the nearest approach to the perfect metal for equipment of many kinds in many industries. It withstands corrosive attack and wear far better than most other metals. However, proper care requires only a little time. Give your stainless steel equipment regular, systematic care and you will be repaid in maximum service life.

Follow These Suggestions for Longer Service Life . . .

1 **Cleanliness is of utmost importance.**

2 **Remove materials and deposits that tend to adhere to the surface**

3 **Use same types of metals together where possible. Work for uniformity in regard to solutions, temperatures, agitation, concentrations and surface conditions.**

4 **Avoid prolonged standing of chlorides, bromides, thiocyanates and iodides in stainless steel equipment,**

5 **Be sure the chemicals you employ are recommended for use with stainless steel.**

6 **Avoid corrosion fatigue.**

* HOW TO CLEAN ENDURO STAINLESS STEEL EQUIPMENT *
Cleansers and Their Reactions to Stainless Steel

REPUBLIC
Enduro STAINLESS STEEL

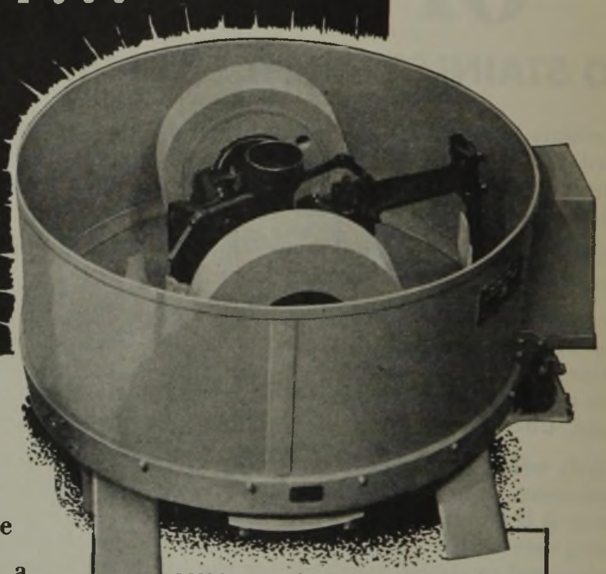
Pipe and Sheets—Upson Quality Bolts, Nuts and Rivets—Berger Lockers and Shelving

. . . for mixing plastics?——Yes!

WHEREVER THOROUGH-UNIFORM MIXING IS IMPORTANT . . .

SIMPSON INTENSIVE MIXERS do it

Better-Faster-for Less



JUST as in 101 other applications, the Simpson mulling principle of intensive mixing has proved advantages to offer in mixing plastics. One of them is the ability to thoroughly impregnate a filler with the binder *in a minimum of time.* Another is flexibility in handling dry powders — semi-dry materials, or a heavy pasty mass. Simpson Mixers may be equipped with water and steam jackets — with covers to control dust or special hoods for vacuum operation, as in the case where volatiles may be reclaimed. They are virtually self cleaning.

If you have dry, semi-dry or plastic materials to mix thoroughly and uniformly—you will find a Simpson Mixer will do the job better, faster and at less cost.

Write for details or ask to have a National mixing specialist go over your problem with you. No obligation, of course.

BUILT IN 10 SIZES

MIXING by MULLING

The mulling action employed by Simpson Intensive Mixers is comparable to the rubbing, kneading and smearing action of the mortar and pestle. A special combination of mullers and plows revolve in a circular, stationary pan. Mullers, mounted on rocker arms, are adjustable, and are free to float on material being mixed. They create pressure and an intensive rubbing action as they revolve, but do not cause grinding. The plows exert a shoveling action to the material being mixed, turning it over upon itself and directing it in front of the mullers.

Liquids may be introduced through a funnel mounted in the center of the mixer. On completion of the mixing cycle, action of the plows automatically discharges the material through a door in the bottom of the pan.

SIMPSON APPLICATIONS

Simpson Intensive Mixers are successfully serving in hundreds of plants in the chemical and process industries. They are mixing plastics, soaps, cosmetics, drugs, storage battery paste, graphite products, welding rod coatings, ceramic clays, refractory cements, asphaltic compounds, fertilizers, sand, paste powder, boiler compounds, food, feed, crayon stock, paper coatings, putties, roofing materials, and many other dry, semi-plastic and pasty products.

SIMPSON INTENSIVE MIXERS

NATIONAL ENGINEERING COMPANY

MACHINERY HALL BUILDING • CHICAGO, ILLINOIS

Manufacturers and Selling Agents for Continental European Countries:—The George Fischer Steel & Iron Works, Schaffhausen, Switzerland. For the British Possessions, Excluding Canada and Australia—August's Limited, Halifax, England. For Canada—Dominion Engineering Co., Ltd., Montreal, Canada. For Australia and New Zealand—Gibson, Battle & Co., Pty., Ltd. Sydney, Australia


HOOKER ELECTROCHEMICAL COMPANY
NIAGARA FALLS, NEW YORK
ALUMINUM CHLORIDE

How Calgon helps speed America's war effort:

6. IN THE PULP AND PAPER INDUSTRY

THE pulp and paper industry is making the greatest effort in its history to adapt itself to war-time conditions and to make its products conform to the requirements of war industries and the armed services. In this connection Calgon is contributing to the solution of many of the problems arising from water.

In the washing of chemical pulps the calcium and magnesium salts in water set coloring matter, making subsequent bleaching difficult. Calgon used in the water to wash pulp inhibits this action and saves chlorine, thus increasing the strength of the paper.

In the sizing of pulp in the beater the addition of 10-25 ppm. of Calgon improves the sizing through better dispersion.

In the coating of paper Calgon improves the homogeneity of the coating mix, through better dispersion of the pigment, and increases the bonding action of the coating to the paper stock.

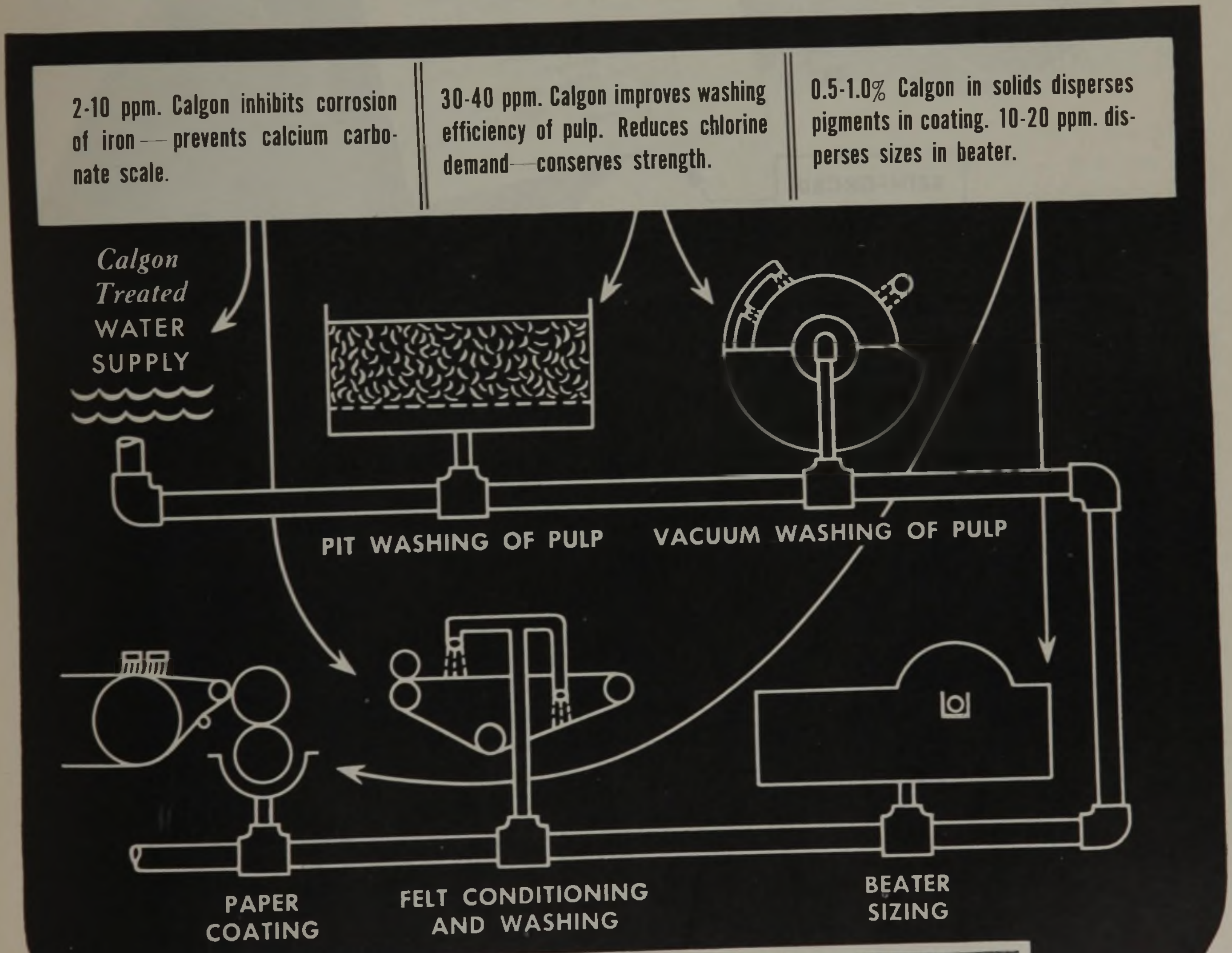
Calgon is used in the conditioning of felts to keep the felts more open, and is also used in the washing of felts for better removal of the impurities present.

Another important use of Calgon is in the treatment of the mill supply water to inhibit corrosion of the pipe lines and reduce the iron content of the water. This requires only from 2-10 ppm. of Calgon in the water. Corrosion of calendar rolls in wet finishing has been inhibited with Calgon.

Similar treatment when applied to high bicarbonate waters, inhibits scale deposition in alkaline pulp washers, vacuum pumps, condensers, heaters and suction pipes, and keeps the felts more open.

If you have a water problem we may be able to help you. Write us for complete information. We will be glad to show you what Calgon* will do.

**Calgon is the registered trade-mark of Calgon, Inc. for its glassy sodium phosphate products.*



2-10 ppm. Calgon inhibits corrosion of iron — prevents calcium carbonate scale.

30-40 ppm. Calgon improves washing efficiency of pulp. Reduces chlorine demand — conserves strength.

0.5-1.0% Calgon in solids disperses pigments in coating. 10-20 ppm. disperses sizes in beater.

HAGAN
HALL
BUROMIN
CALGON

calgon, inc.

A SUBSIDIARY OF
HAGAN CORPORATION

HAGAN BUILDING
PITTSBURGH, PA.

WeldELLS *have everything*★

The amount by which stress is greater at the crotch in a fitting having uniform wall thickness depends only on its radius. Mathematical analysis (specifically the Lorenz formula) shows the stress at the crotch to be:

$$S = \frac{pr\,(2R - r)}{2t\,(R - r)}$$

Where:

S = Bursting stress, lbs. per sq. in.

p = Internal pressure, lbs. per sq. in.

r = ½ inside diameter of fitting (O.D. if Barlow's formula is desired).

t = Wall thickness in inches.

R = Center line radius of fitting, inches.

FULL WALL THICKNESS HERE

REINFORCED HERE

It's a feature that tells the whole story . . .

TO the kind of engineer we're thinking about, *nearly right* is not right enough. He's the kind of fellow who makes sure that the strength of every part is as nearly proportionate to the stress imposed on it as exacting calculation can make it. To him, nothing less is *right*.

The feature of WeldELLS, pictured above, is certain to strike a responsive chord in such a man. It is based on mathematical calculations and practical tests which prove that the bursting stresses in an elbow are greatest at the crotch or inner wall—and show just how much greater.

In keeping with this finding, WeldELLS are given extra reinforcement in this region of greatest stress. To us, as to you, nothing less would be right!

We are not implying that welding fittings which lack this feature are bursting right and left. We are simply showing that in this, as in other features listed opposite, we have gone the engineering limit to make WeldELLS the fittings that have *EVERYTHING*.

Don't you agree that nothing less is right for *your* piping job.

★ No other fittings for pipe welding combine the features found in WeldELLS. In addition to that described, they include:

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

PRODUCTS VITAL TO MODERN WARFARE

WeldELLS are only one of many Taylor Forge contributions to the war effort. One of many examples is Taylor Corrugated Marine Furnaces, essential to many merchant and fighting ships.

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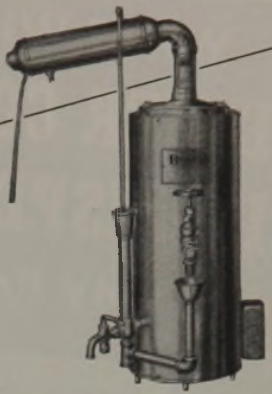
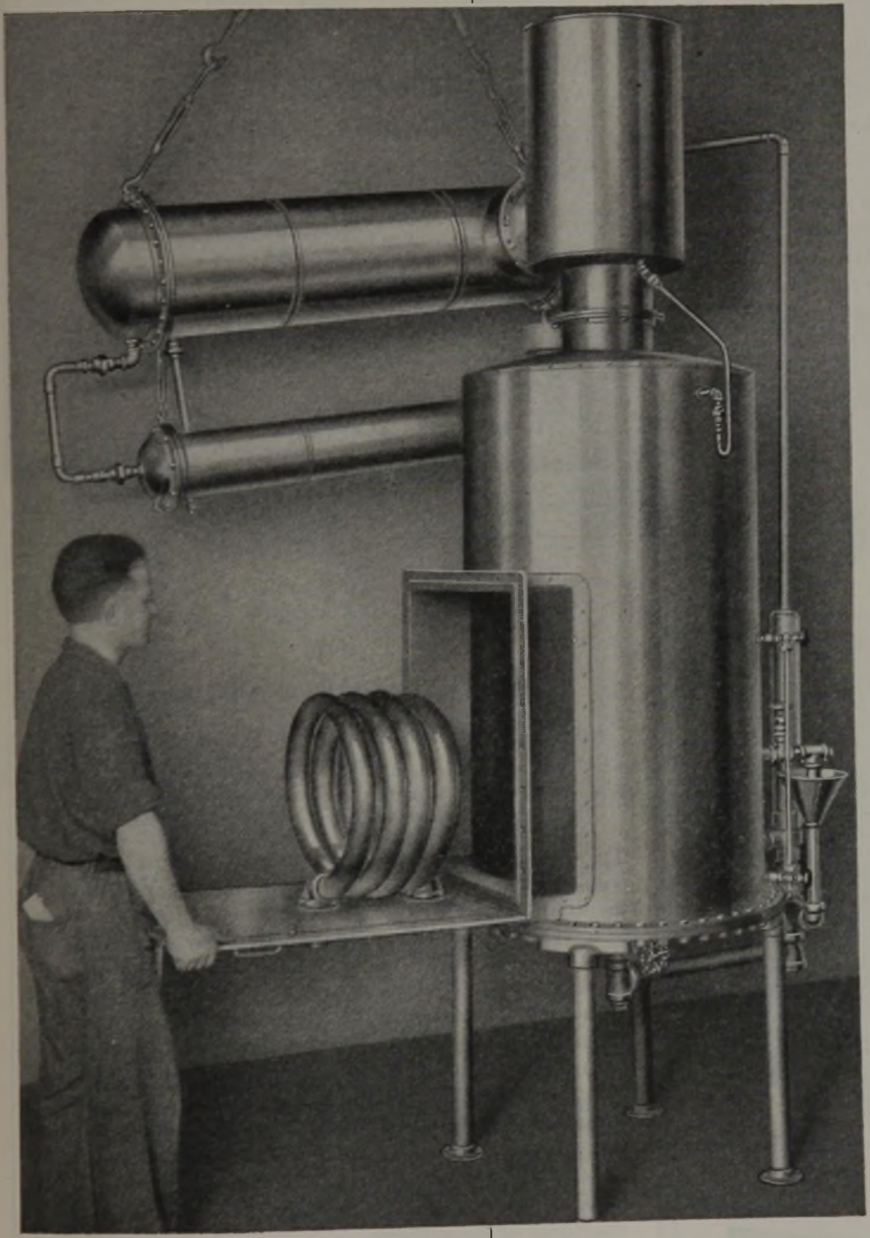
FROM EITHER ONE





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Take the distillates of a ½ gallon per hour Barnstead Water Still and of a 500 gallon per hour Barnstead Still and compare them. You'll find no difference at all in quality. Both are of the same consistent, high grade of purity.

This works to your advantage. You can standardize on the quality of your water in both your laboratory and plant. And, if you have to step up your production of pure distilled water, you can add another Barnstead Water Still and be sure of avoiding variables. Age makes no difference with Barnstead Stills. Units in use many years produce water that is just as pure as the new stills.

Type of operation makes no difference either. Barnstead gas, steam, or electric operated stills all produce the same quality of pure distilled water.

It all boils down to this—when you want to be surest of getting purest distilled water—regardless of amount—use Barnstead Water Stills.

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STILL & STERILIZER CO. Inc.
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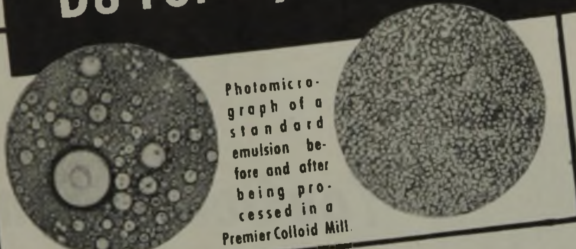

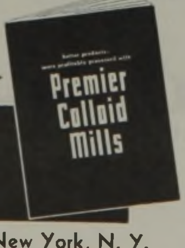
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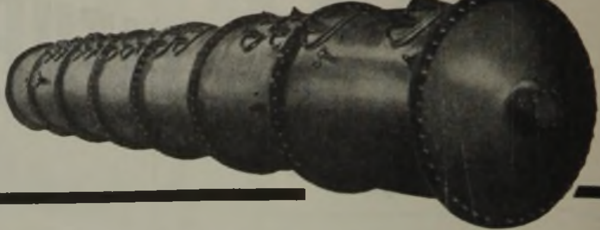

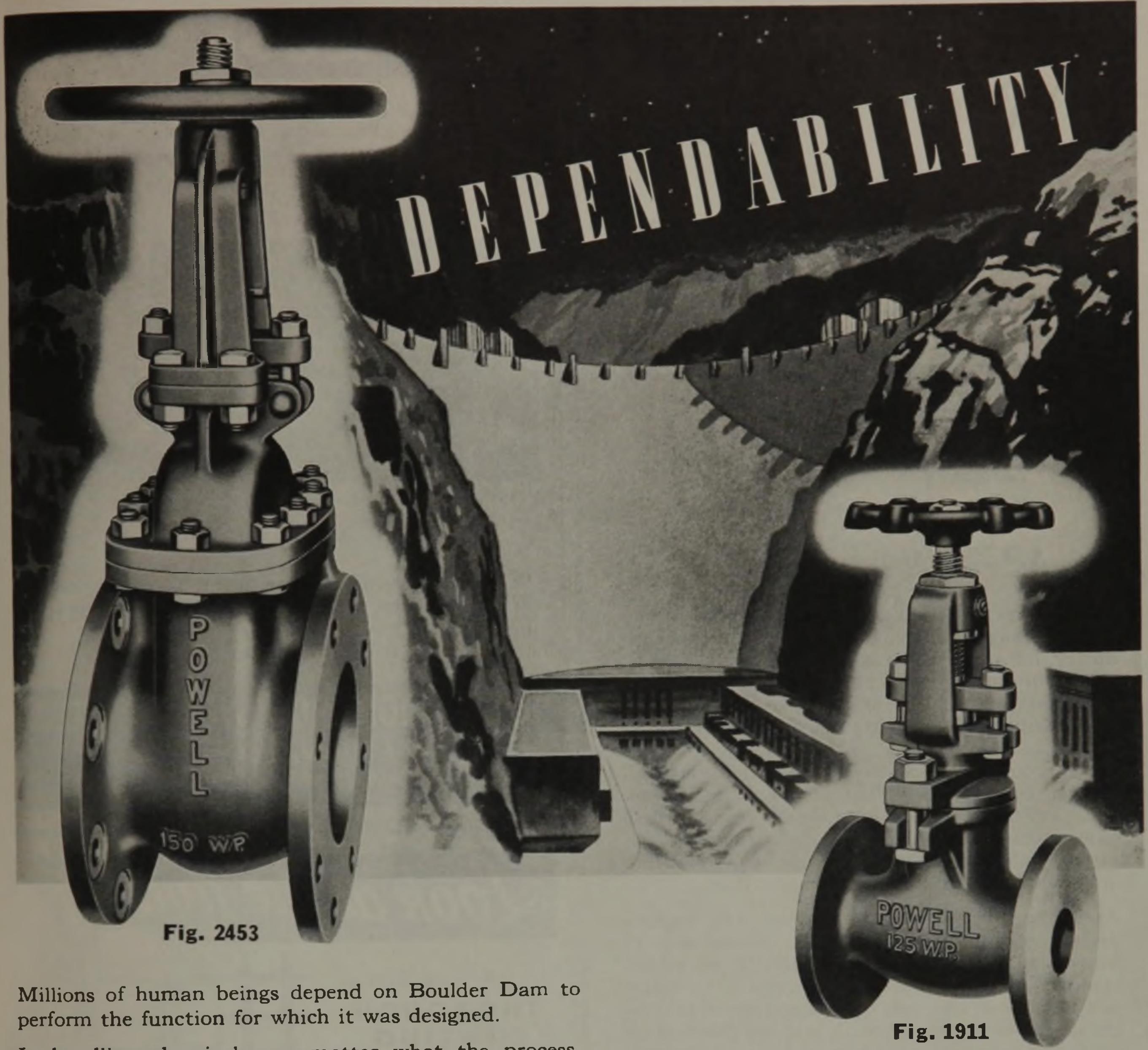

Fig. 2453

Fig. 1911

Millions of human beings depend on Boulder Dam to perform the function for which it was designed.

In handling chemicals, no matter what the process, valves must perform many functions. And above all they must perform these functions dependably.

For nearly a century Powell Engineering has been designing valves to meet all requirements for precise flow control of chemicals. And Powell Engineering, Powell materials and Powell workmanship have made these valves above all—*dependable*. That's probably why so many of today's leaders in the chemical field turn to Powell for today's valve engineering requirements.

The Wm. Powell Company
Dependable Valves Since 1846
Cincinnati, Ohio

Fig. 1911—Flanged End O. S. & Y. Gate Valve, with outside screw rising stem and bolted yoke bonnet. Made in sizes ¼″ to 2″ inclusive, for 125 pounds W. P.

Also available in Globe and Angle Patterns for stop or close throttling service—Figs. 1913 and 1919—sizes, ¼″ to 3″ inclusive.

Fig. 2453—Large size 125-pound O. S. & Y. Gate Valve with flanged ends, outside screw rising stem and full flanged bolted yoke bonnet. Sizes, 2½″ to 30″ inclusive.

The complete line of Powell Corrosion-Resistant Valves includes all types, in pure metals and special alloys such as stainless steel, Monel metal, nickel, aluminum, acid bronze, etc., to meet the demands of the Chemical and Process Industries for dependable, non-contaminating flow control equipment.

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NOXIOUS GASES

and the

PRINCIPLES OF RESPIRATION INFLUENCING THEIR ACTION

Second and Revised Edition

By

Yandell Henderson

and

Howard W. Haggard

Laboratory of Applied Physiology,
Sheffield Scientific School, Yale University

A. C. S. Monograph No. 35

The new revised edition of this outstandingly successful monograph has been eagerly awaited by industry for many months. In general the basic outline of the first edition has been adhered to, but the latest and most authoritative developments have been included and are described in detail. As in the previous book the gases discussed are those which occur predominantly in industrial processes; and one of the most useful features of this volume is the extensive and accurate classification of these gases according to their actions; for example, irritants, asphyxiants, volatile drugs, inorganic and organo-metallic gases.

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Foreword, General Survey of the Field, Elements of Respiration, Respiratory Functions of the Blood and Their Laws, Practical Application of the Laws of Gases and Vapors, Principles Determining Absorption, Distribution and Elimination of Volatile Substances, The Significance of Standards for Physiological Response to Various Concentrations of Gases and Vapors, Classification of Noxious Gases and Vapors, Group I. Irritant Gases, Their Action, Acute and Chronic, and Sequelae, Group I. (Continued) Special Characteristics of Various Irritant Gases, Group IIA. Asphyxiation and Simple Asphyxiants, Group IIB. Chemical Asphyxiants, Group III. Volatile Drugs and Druglike Substances, Group III. (Continued) Volatile Drugs and Druglike Substances, Group III. (Continued) Volatile Drugs and Druglike Substances, Group III. (Continued) Volatile Drugs and Druglike Substances, Group IV. Inorganic and Organometallic Gases, Methods of Resuscitation and Comparison of Various Treatments, Also First Aid, Prevention of Poisoning by Noxious Gases.

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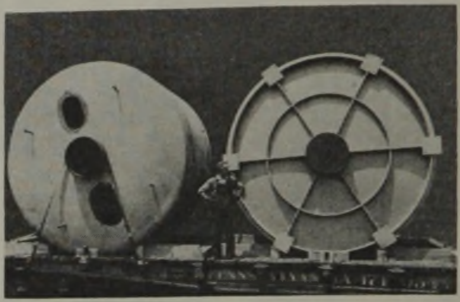

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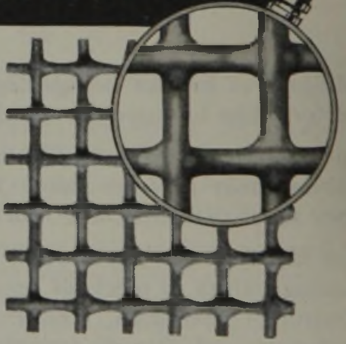

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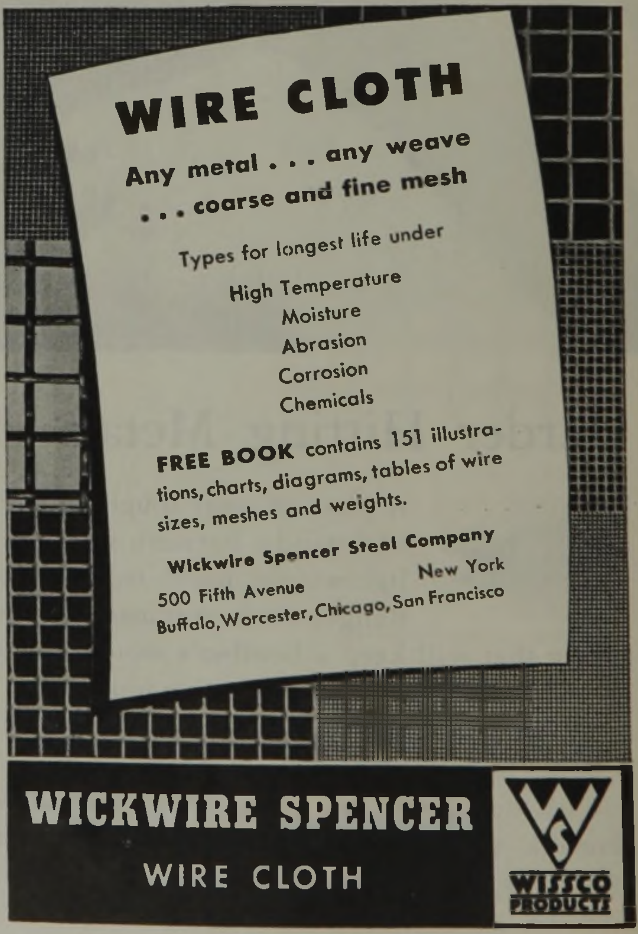

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Types for longest life under

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ON THE "LOW-TEMPERATURE" FRONT

These Micromax Features Help Win

Here are some features which make Micromax Recorders highly accurate in process-industry plants:

Operates At "Long" Distances. A Micromax may be many hundreds of feet from its Thermohm (electrical-resistance thermometer bulb) and still be as accurate and sensitive as though both were in the same room.

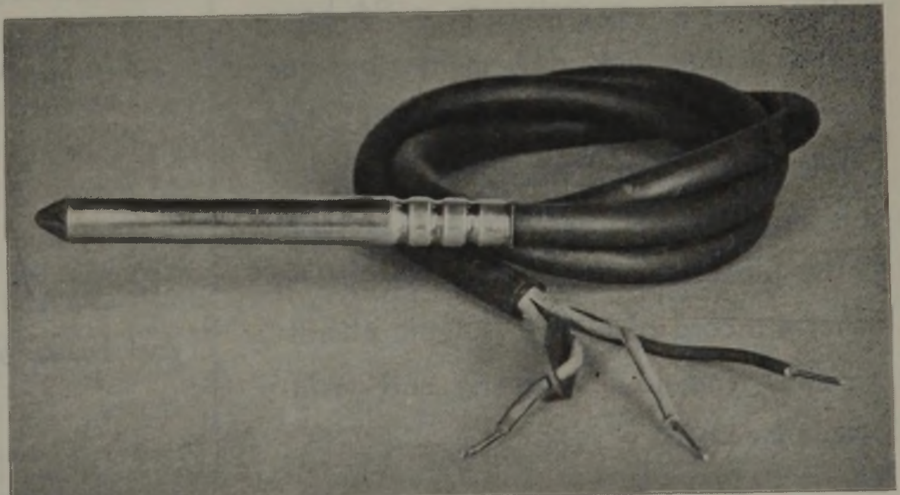
Accidents, corrosion, etc., may, of course, damage the Thermohm, but it can be replaced on the job without affecting calibration of Micromax.

Jrl Ad N-33C(2)

Motor-Driven. Taking its operating power from the plant's electric circuit, Micromax does not consume in its mechanism any of the thermal energy it measures. This not only increases accuracy but eliminates calibrated, jewelled bearings, constant-pressure springs and tubes, light, slender pen or pencil arms and delicate parts in general. Micromax sensitivity is that of a finely-fitted machine tool.

As Many as 16 Thermohms may be connected to one Strip-Chart Micromax, and their temperatures recorded in as many as 6 colors. The one-point or two-point Round-Chart Micromax can be read as far as its big dial can be seen.

Micro-Responsive Control. The Micromax Recorder's trait of showing extremely tiny changes in temperature is readily extended to automatic control, either in modern on-off applications or by full-floating, proportioning control. In the latter case, the regulated valve may be electrically driven, or may be a pneumatic diaphragm type. We will gladly help select the correct Recorder or Controller for a specific problem, or will send catalogs on request.



A Thermohm (electrical-resistance-thermometer bulb) for use with a Micromax Recorder. By an ingenious use of three leadwires instead of only two, the distance to the Recorder can be anything up to several hundred feet.

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Saves... TONS OF ORE
Thousands of Dollars

DRACCO System controls dust from conveyors, vibrating screens, dust feeders, etc.

A close-up view showing hoppers.

THE above photos were taken in a zinc smeltery where DRACCO Dust Control is doing a splendid job and has paid for itself many times over. The smeltery operates on a 24 hour basis, and each day many tons of valuable zinc ore are recovered. Only one operator working 40 hours a week is required to look after the system. The plant officials say that the system has a record of high dust control efficiency and low operating and maintenance costs.

● For Further Information Write ●

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For thorough separations of dry, powdered, granular or flaked materials
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for some of the toughest war-time sifting jobs

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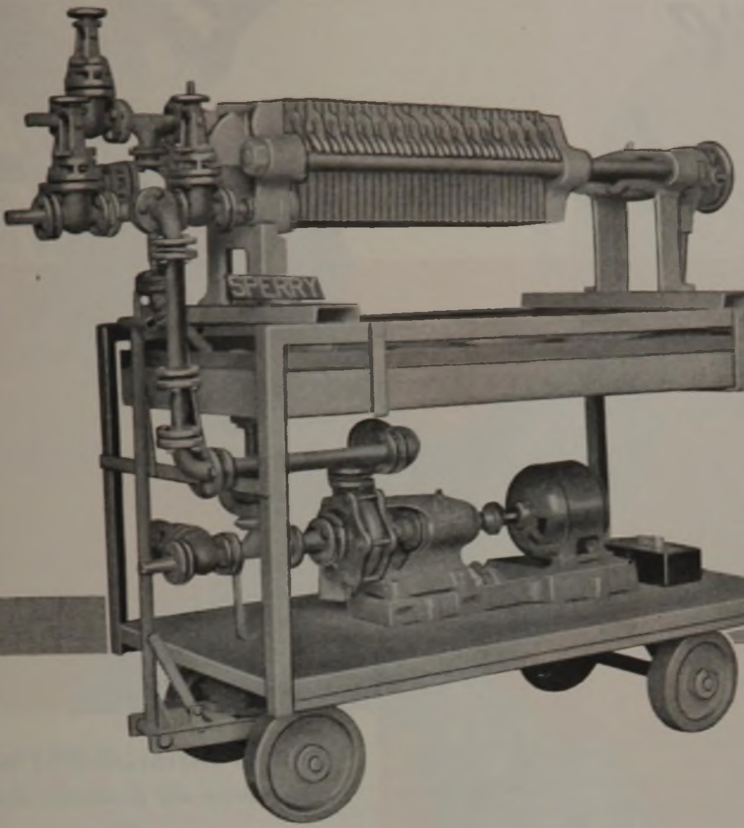

SPERRY

This Valve never had a chance!

SENTENCED TO DEATH by "Sand Blast" effect, when incorrectly chosen and installed

THIS Iron Body Globe Valve served only a few months. It was riddled by a fusillade of dirt, grit, and scale carried in the water. Throttling accelerated the flow velocity and intensified the "sand blast" effect. The seat, disc, and body were damaged beyond repair. This needless destruction could have been prevented by choosing the correct type of valve for this service.

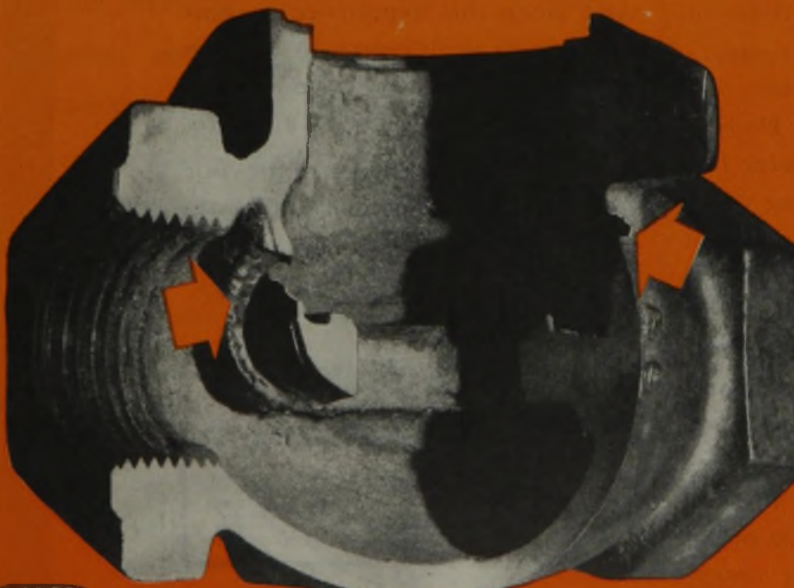
Since valve-failure often means serious interruptions in war production, and valve destruction wastes scarce metals, it is management's vital responsibility to keep valves operating efficiently.

Most valve trouble can be prevented before it starts . . . by frequent, thorough inspection . . . by repair or replacement of worn parts in time to prevent valves from destroying themselves. New maintenance workers should be taught to detect the first signs of trouble . . . to correct it without delay. Valves for new construction should be carefully selected, and properly installed.

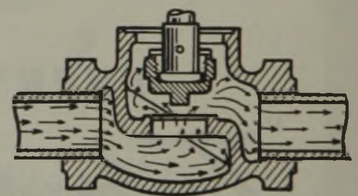
Jenkins Engineers will provide any assistance you need in developing effective valve conservation programs for your company or clients.

Jenkins Bros., 80 White Street, New York, N. Y.; Bridgeport, Conn.; Atlanta, Ga.; Boston, Mass.; Philadelphia, Pa.; Chicago, Ill. Jenkins Bros., Limited, Montreal; London, England.

Note mutilation of steel bevel disc and integral seat by wire drawing effect of the abrasive jet . . . also, perforation of body where flow impinged.

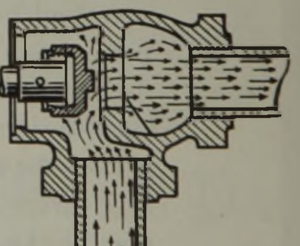


WRONG INSTALLATIONS may cause valve failure and production slow-downs



A globe valve was installed in a condensate line from a vulcanizer, carrying about 90 pounds steam pressure. See how the flow created excessive turbulence and subjected valve parts to destructive attack.

RIGHT INSTALLATIONS keep "fluid highways" serving the war effort



This is better practise for condensate discharge service: An angle valve, used in reverse position, offers less restriction to flow, decreasing turbulence. It discharges almost directly into the line; the seat acting as a funnel affords straight-down flow. Wear is reduced and service life is extended. A further improvement is the addition of a sediment trap to collect abrasive solids, and a blow-off valve to remove accumulated solids.

The angle valve is recommended for severe conditions in many services, such as continuous blow-downs, steam reducers, and soot blowers.

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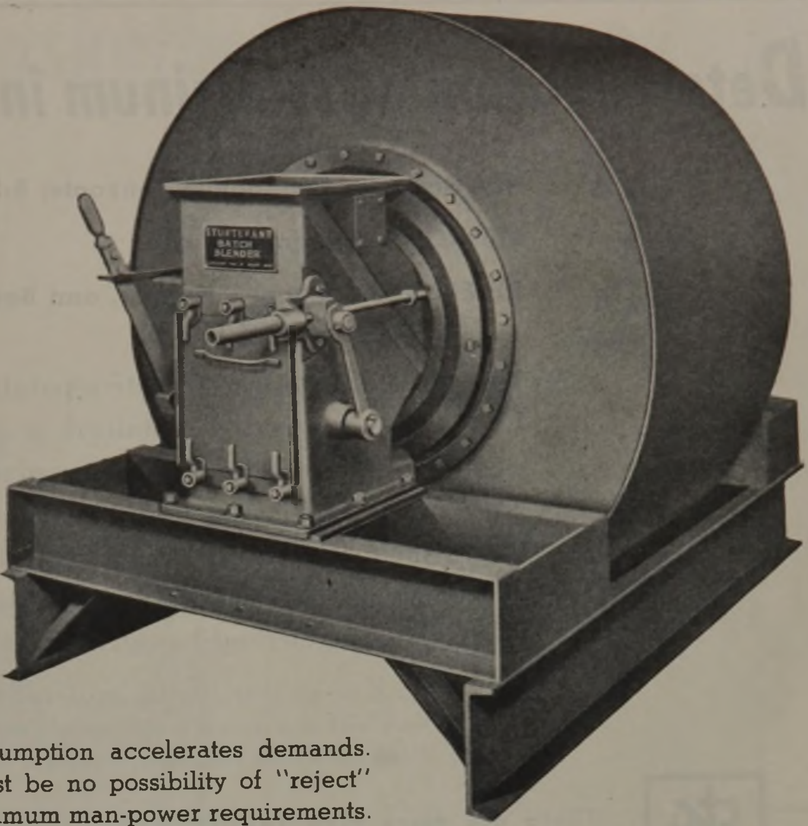

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3. A third action forces this material from both ends to the middle, adding another mixing action with no separating effect.
4. The Chute, swinging in a blending position, produces an important fourth lateral action and assures a thorough and perfect mix.

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Discharge, with the chute in the discharge position, is through the same center opening and is completely automatic. Further details on request.

Write for Bulletin 080-B.

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Determination of Aluminum in Magnesium Alloys

REAGENTS—Ammonium Benzoate; 8-Hydroxyquinoline

METHOD—Gravimetric

REFERENCE—Stenger, Kramer, and Beshgetoor, *Ind. Eng. Chem., Anal. Ed.,* 14, 797 (1942)

Rapid and virtually complete separation of aluminum from most other divalent elements is obtained in a single step by precipitation in slightly acidic solution with ammonium benzoate. The aluminum benzoate precipitate is easily soluble in warm ammoniacal tartrate solution from which the aluminum is precipitated by 8-hydroxyquinoline. None of the common alloy constituents interfere, nor is separation of silica necessary. The method has an accuracy suitable for referee work.

Write for an abstract of the article in which the determination of aluminum with ammonium benzoate and 8-hydroxyquinoline is described. . . . Eastman Kodak Company, Chemical Sales Division, Rochester, N. Y.

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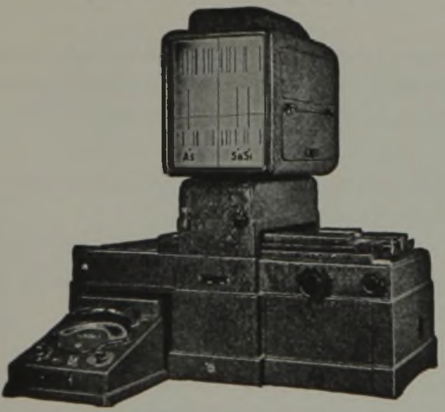

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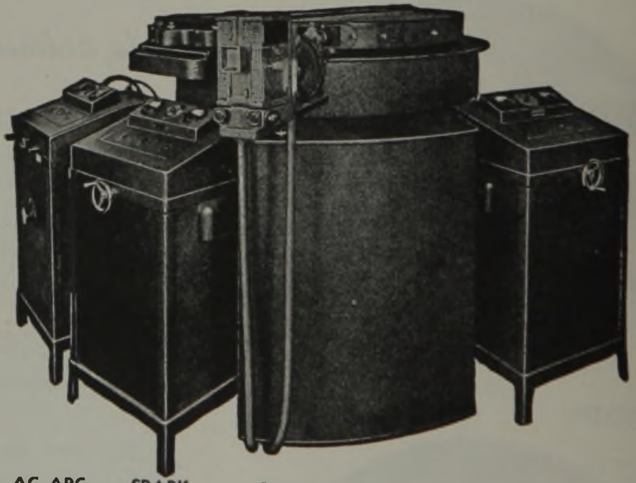

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Complete Full Vane Movement

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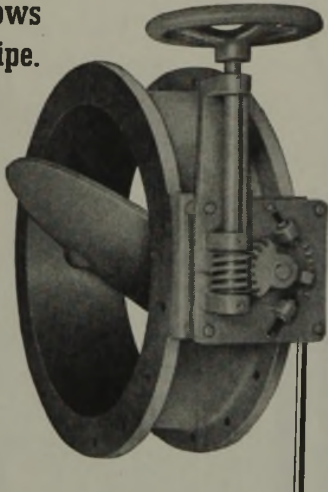

Six revolutions of the hand wheel fully open or close this R-S Butterfly Valve. Compare this quick action with that of ordinary valves. Consider, too, that R-S Valves are comparatively light in weight. They effect a considerable saving in installation costs since less space and supporting structure are required.

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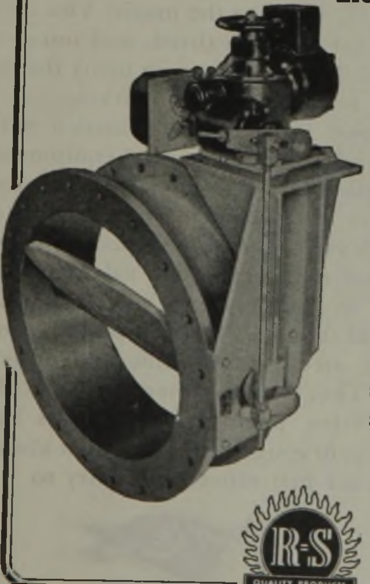

Here is a simplified, precise and entirely Automatic Butterfly Valve for the shut-off and control of liquids and gases in power plants, water works, chemical industries and refineries. Hand wheel for manual operation in case of current failure. Available in iron or steel; sizes to 84 inches.

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R-S PRODUCTS CORPORATION
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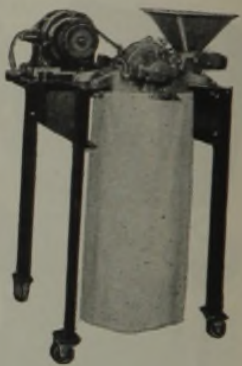

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PHILADELPHIA

"SUPERBLY ARMED"

SAID AN EARLY DISPATCH from French Morocco, describing the landing of the American forces. Never a truer word. America's Garand rifle is by far the finest infantry weapon in use today. While American tanks and Flying Fortresses have made performance records in combat service that have astounded experienced observers.

"Superbly armed," too, is the plant making war materials, where Elliott blowers are used in the process. These units, driven by Elliott motors or Elliott turbines, are engaged by hundreds in such vital production as 100 octane gasoline, magnesium, synthetic rubber materials, explosives. Their smooth, quiet, dependable operation is a direct contribution to victory.

The photo shows an Elliott blower typical of the many now used for war production. Elliott single-stage direct-connected blowers such as this are built for capacities of 5000 c.f.m. and up. Drive can be motor or turbine — both built by Elliott. Speed-increasing gears available where needed. If you have a job requiring the movement of air or gases, check on Elliott blowers.

ECo

ELLIOTT COMPANY
Centrifugal Blower Dept., JEANNETTE, PA.
DISTRICT OFFICES IN PRINCIPAL CITIES

P-1056

ELLIOTT BLOWERS
... the front line of war production

"IF YOU BURN SULFUR..

LET VIRGINIA BURN IT FOR YOU."

? Have you ever considered all of the advantages of pure, cool 100% SO_2 in the liquid or gas phase as a means of stabilizing your process . . .

? What is the SO_2 content of the burner gas supplying your process . . .

? Do the inherent impurities in the burner gas produce undesirable or unpredictable side reactions . . .

? Does the heat of the burner gas or variation in this temperature interfere with your operation or process control.

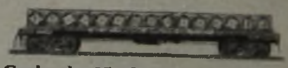
It is the job of "VIRGINIA'S" Technicians to prove the over-all economic advantages of "ESOTOO"*, to demonstrate the value of control in terms of stepped up output, simplified operation and quality production.

To the Manufacturer who desires an alternate commodity source or the assurance of a continuous supply of raw materials in these crucial days—we say again—"If you burn sulfur . . . *let Virginia burn it for you.*"

* "ESOTOO" is Virginia's Trade Name for Liquid Sulfur Dioxide

About Shipments—

Portable cylinders containing 150 lb., semi-portable drums containing 2000 lb. liquid SO_2. L. C. L. or carload.



Carload: 15 drums on multi-unit car frame; 30,000 lb. For users without storage facilities.

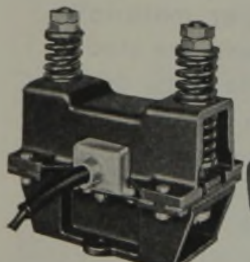
Tank car lots of 40,000 lb. for users equipped with storage facilities.

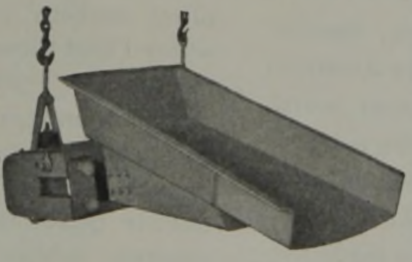
Prompt shipment from the strategically located works of the largest producer of liquid sulfur dioxide in the U. S.

V
VIRGINIA

VIRGINIA SMELTING COMPANY
WEST NORFOLK, VIRGINIA

SYNTRON



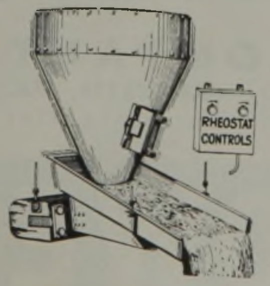


ELECTRIC VIBRATORS

VIBRATING FEEDERS

with adjustable power, on those troublesome bins and hoppers to keep their contents agitated and free-flowing.

Little 4 lb. models—up to BIG 500 lb. sizes.



Under those bins and hoppers to regulate their discharge by rheostat control of rate of flow.

Capacities of from ounces to TONS per hour.

No Motors—Gears—or other Moving, Wearing Parts
Low Initial Cost—Low Operating Cost

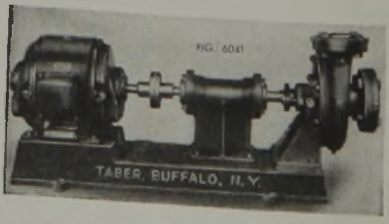
Illustrated and described in Catalog No. 429

SYNTRON CO., 415 Lexington Ave., Homer City, Pa.

TABER PUMPS

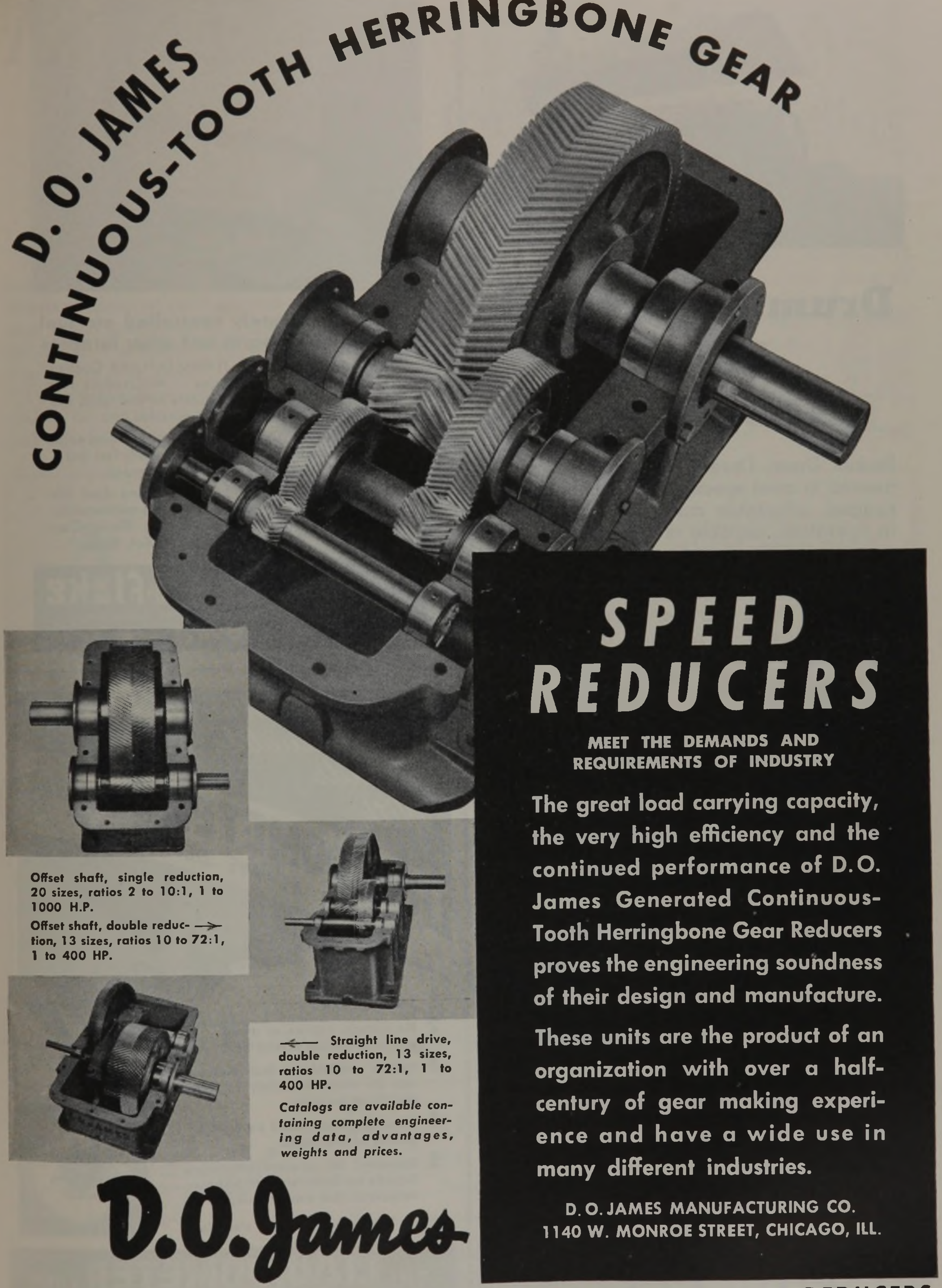
are f-l-e-x-i-b-l-e

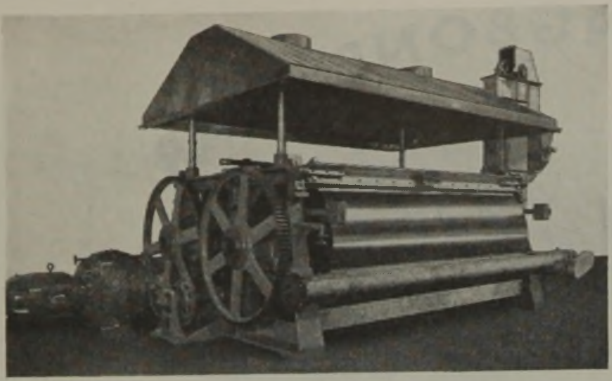
The wide adaptability of the new Taber CLVS series of "General-Use" Centrifugal Pumps makes them more suitable for the processing industry. Their design is the direct result of Taber's years of experience with some of the largest chemical plants. Two widely used pumps in this series are described below. For detailed, helpful information on Taber Horizontal Centrifugal Pumps, write for Bulletin CLVS-339.



TABER "GENERAL-USE" CENTRIFUGAL PUMP. Never obsolete. Easily adapted to many jobs. Has over-size ball bearings, extra shaft diameter, deeper stuffing box.

TABER SINGLE SUCTION CENTRIFUGAL PUMP. For Vacuum or Evaporator service. Large chamber surrounds stuffing box for a perfect [illegible]





Drum Dryers and Flakers

Atmospheric

Stokes Drum Dryers and Flakers, engineered to meet specific requirements, are rugged, adaptable machines, continuous in operation, capable of large output and requiring little operating attention.

They are efficient, economical equipment for drying thick slurries, organic and inorganic salts, food products that are not sensitive to high temperatures, pigments, oxides, insecticides, carbonates, clays, many other materials . . . also for flaking chemicals, waxes, pitch, etc.

We build this equipment in various types and capacities, with single or double drums and feed systems to suit various products. Alloy or chromium plated rolls, hoods, complete enclosures, conveyors and other accessories are supplied as needed.

Write for latest
Stokes Chemical
Equipment Catalog.

●

F. J. STOKES MACHINE COMPANY

5922 Tabor Road Olney P. O.
Philadelphia, Pa.

Representatives in New York, Chicago, Cincinnati, St. Louis Cleveland, Detroit

Pacific Coast Representative: L. H. Butcher Company, Inc.

F.J.Stokes FJS EST. 1895

Permits accurately controlled air-fuel ratios in open hearth and other furnaces

High fusion, light weight THERM-O-FLAKE Coating insulates to minimize heat losses . . . AND reduce cold air infiltration. As a result, accurate air-fuel ratios and highly efficient combustion are obtained.

THERM-O-FLAKE Coating works with surprising ease. Trowelled or gunned—it spreads unusually fast and is economical because of its greater coverage.

Find out how THERM-O-FLAKE Coating does this Double Duty as a part of regular furnace maintenance. For complete information write: The Illinois Clay Products Company, Joliet, Illinois.

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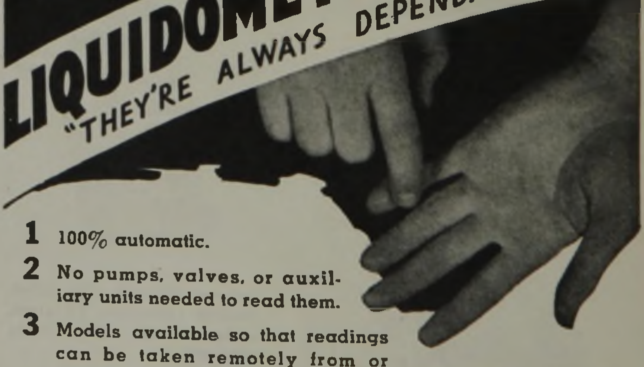
JOLIET, ILL.

Therm-O-Flake
HIGH TEMPERATURE INSULATION
COATING

5 Reasons Why We Measure Our Valuable Stored Liquids With

LIQUIDOMETER *Tank Gauges*

"THEY'RE ALWAYS DEPENDABLE"



1. 100% automatic.
2. No pumps, valves, or auxiliary units needed to read them.
3. Models available so that readings can be taken remotely from or directly at the tank.
4. Accuracy unaffected by specific gravity of tank liquid.
5. Approved for gauging hazardous liquids by Underwriters' Laboratories and other similar groups.

Write for complete details

THE **LIQUIDOMETER** CORP.
38-13 SKILLMAN AVE., LONG ISLAND CITY, N.Y.

Information

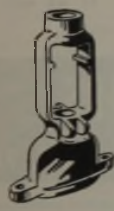
On Available forms of Hastelloy Corrosion-Resistant Alloys . . .

Hastelloy alloys are used extensively in the chemical and process industries because they resist conditions of chemical corrosion more adequately than most other commercially available materials and thus make it possible to minimize the tremendous losses from corrosion.

These nickel-base alloys are made in four types —A, B, C, and D. Alloys A and B are intended particularly for equipment handling hydrochloric acid. Alloy C withstands the action of strong oxidizing agents, and alloy D is especially suited for sulphuric acid.

Hastelloy alloys are noted not only for their outstanding corrosion resistance, but also for their excellent physical properties. In addition, these alloys are supplied in a variety of forms, some of which are described here.

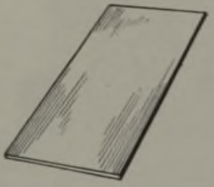
FOR VICTORY BUY UNITED STATES WAR BONDS AND STAMPS



Castings—Hastelloy alloys A, B, C, and D can all be supplied as castings—in sizes ranging in weight from 1 lb. up to 1,000 lb. or more. Patterns with the same shrinkage allowance as that customarily provided for casting steel can be used and can be furnished by the customer or will be supplied by us at cost.

Pipe and Fittings—The four Hastelloy alloys can be supplied as cast pipe in extra-heavy iron pipe sizes, or in special sizes and wall thicknesses. Screwed pipe fittings, welding bends, and welding flanges also are available. Screwed fittings are made only in the three machinable alloys—A, B, and C.

Welded Tubing — Hastelloy alloys, A, B and C can be supplied as tubing made from sheet material rolled to required diameters and welded by the atomic hydrogen process. Tubing can be furnished with a wall thickness of either 12 or 16 B.w.g. (0.109 in. or 0.065 in.), in lengths up to 10 ft.



Sheet and Plate—Alloys A, B, and C are available as standard hot-rolled sheet and plate, subject to mill limitations of a maximum weight in alloys A and B of 275 lb., and in alloy C of 200 lb. for a single plate, and a minimum sheet thickness of 27 B.w.g. (0.016 in.).

Bars, Forgings, Wire—All four alloys are made as cast bars. Alloys A and B are also furnished as bar stock in hot-rolled or hot-forged flats, rounds, squares, hexagons, and octagons. In addition, simple forgings of alloys A and B are available. Alloy A wire in a range of sizes down to 0.002 in., and alloy B wire in sizes down to 0.005 in., are available.

Welding Rod—Hastelloy alloys A and B are available as drawn welding rod in sizes 1/16, 3/32, 1/8, 5/32, and 3/16 in.; as cast rod in sizes 5/32, 3/16, and 1/4 in.; and as 1/4-in. rolled rod. Alloys C and D are made as cast welding rod in sizes 5/32, 3/16, and 1/4 in. Drawn rod of alloys A and B, and cast rod of alloy C, are furnished either bare or coated, as specified.

For complete information on available forms, penetration tests, and methods of fabrication, send for the 40-p. booklet, "Hastelloy High-Strength Alloys."

HASTELLOY TRADE MARK

HAYNES STELLITE COMPANY
Unit of Union Carbide and Carbon Corporation
New York, N. Y. UCC Kokomo, Ind.
Chicago—Cleveland—Detroit—Houston—Los Angeles—San Francisco—Tulsa

HIGH-STRENGTH NICKEL-BASE ALLOYS FOR CORROSION RESISTANCE

The word "Hastelloy" is a registered trade-mark.

What a
DESPATCH OVEN
Gives a Laboratory

UNIFORMITY IS GUARANTEED WITHIN ± 1° C
CONTROL ACCURACY ASSURED SENSITIVE TO ±1° C
OPERATING RANGE to 260° C. (500° F.)

In your laboratory you will find a Despatch Victory Oven provides the necessary flexibility to accommodate a vast number of tests with minimum time needed to come to any desired temperature. The oven will attain maximum temperature in an amazingly short time. It will usually recuperate temperature after a cold charge in from 2 to 8 minutes.

5 YEAR GUARANTEE

Despatch heating elements are guaranteed to function with normal use for five years. Many operate years over the guarantee period without replacements or repairs.

PROMPT DELIVERY — STANDARD DESPATCH VICTORY OVEN SIZES — Electrically or gas heated

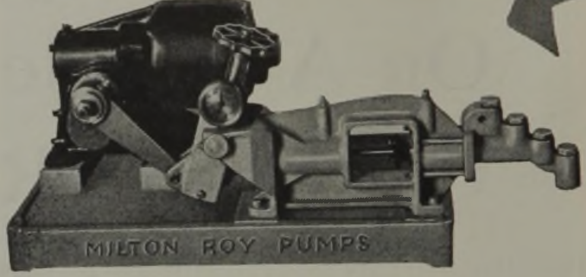
No.	Inside Sizes	No.	Inside Sizes
V-7	13″ x 13″ x 13″	V-23	37″ x 19″ x 25″
V-15	19″ x 19″ x 19″	V-29	37″ x 25″ x 37″

Temperature Range to 260° C. (500° F.)

WRITE FOR BULLETIN No. 105-N
describing many uses of the Despatch Victory Oven.

DESPATCH
OVEN COMPANY MINNEAPOLIS

High Pressure Chemical Pumps



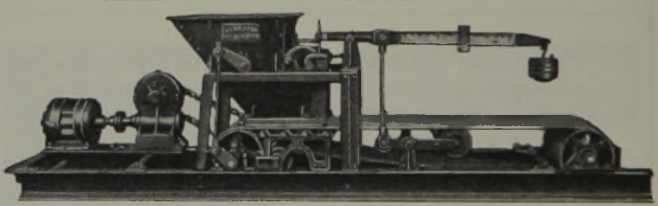
Want to Pump Salt Slurries? Liquid Latex? Fibres in Solution?

Here's the pump that can do it . . . is doing it. Many users are handling materials heretofore extremely difficult or impossible to pump . . . with Milton Roy units. The secret is in the patented Milton Roy step-valve . . . the valve that completely eliminates air-binding, is self-cleaning and non-clogging, that minimizes wire-drawing, that is furnished in metals and plastics to meet practically all corrosion problems.

You'll have to see this valve to appreciate its advantages. Catalog 941 shows it . . . tells how it functions . . . illustrates and describes the complete line of Milton Roy Pumps. Write for it.

We are still making prompt deliveries of some standard units . . . are prepared to build special Milton Roy Pumps to meet your particular requirements with all possible speed. If we can help your war effort write, wire or 'phone.

MILTON Roy PUMPS
1365 E. MERMAID AVE., CHESTNUT HILL, PHILA., PA.



When you think
WEIGHING—
Think POIDOMETER

The name "Schaffer Poidometer" has become the standard for weighing and proportioning raw and finished materials. For twenty-five years Poidometers have stood at the top for performance, reliability, accuracy and sturdiness.

It is the most accurate and durable weighing and feeding machine on the market. Buy Poidometer and you buy assured production.

GOOD EQUIPMENT *Deserves* **GOOD CARE**

To the vast number of Poidometer users we bring this message: It will more than pay you to keep your machines up to the pink of condition. Check every part of your Schaffer Poidometer. Any part that shows wear or needs replacing should be ordered now. Your Poidometer will serve you best if you keep it in top condition.

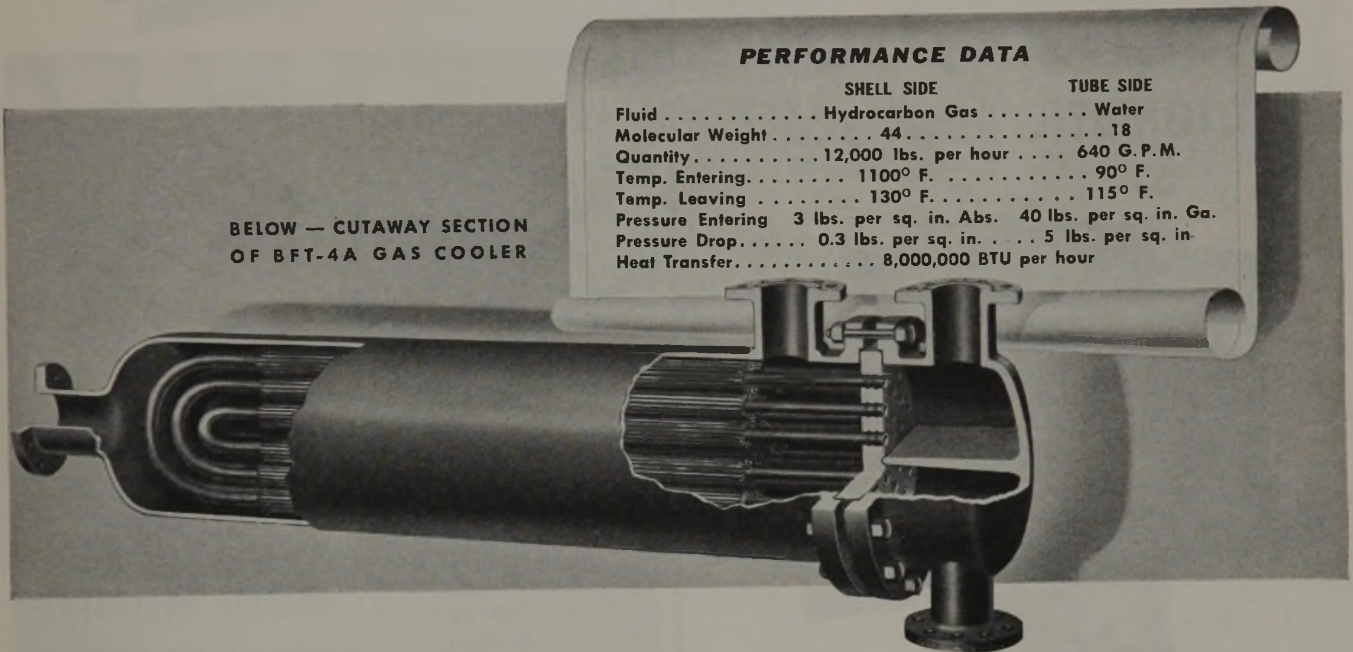
Write for Catalog No. 3

SCHAFFER POIDOMETER CO.
2828 SMALLMAN ST. PITTSBURGH, PA.

YOU TOO CAN GET MUCH INCREASED EFFICIENCY WITH

BROWN FINTUBE HEAT EXCHANGERS

29" ID x 16' Overall Type BFT-4 A Gas Cooler — in High Vacuum Service—Provides 3600 sq. ft. of Effective Surface — Transfers 8,000,000 BTU per Hour



BELOW — CUTAWAY SECTION OF BFT-4A GAS COOLER

PERFORMANCE DATA

	SHELL SIDE	TUBE SIDE
Fluid	Hydrocarbon Gas	Water
Molecular Weight	44	18
Quantity	12,000 lbs. per hour	640 G.P.M.
Temp. Entering	1100° F.	90° F.
Temp. Leaving	130° F.	115° F.
Pressure Entering	3 lbs. per sq. in. Abs.	40 lbs. per sq. in. Ga.
Pressure Drop	0.3 lbs. per sq. in.	5 lbs. per sq. in.
Heat Transfer	8,000,000 BTU per hour	

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. This avoids the necessity of using hundreds, sometimes thousands of feet of bare tubing to satisfy the requirements of the commodity having the lower heat transfer co-efficient . . . It permits a fewer number or shorter Brown Fintubes to be used in a given heat transfer service than if plain bare tubes were used . . . And results in smaller shells, less pressure drop, less back pressure, and many other important savings in manufacturing, shipping, installation and maintenance costs.

For instance, the cooler described above, which required about 1900 lineal feet of fintube, would have required more than 11,000 lineal feet of plain bare tubing—a saving of more than 6700 lbs. of steel just in the tubing alone.

Six standard and many special types of Brown Fintube Heat Exchangers meet any requirement for effecting transfers between liquids and gases, or other commodities having unequal transfer co-efficients. Engineering assistance, recommendations, estimates, and descriptive literature furnished gladly. Let us quote on your 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.

119 FILBERT STREET • ELYRIA, OHIO

MANUFACTURERS OF INTEGRALLY BONDED FINTUBES AND FINTUBE HEAT EXCHANGERS

Automatically

WEIGH MATERIALS

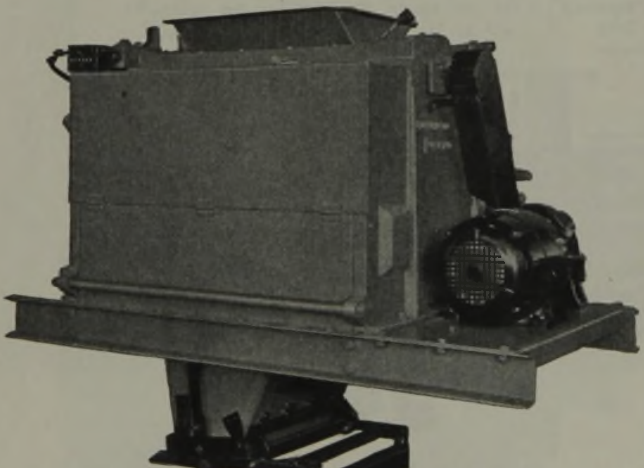
with

SPEED AND ACCURACY

with a

RICHARDSON

AUTOMATIC BULK SCALE



for weighing dry, non-flushing chemicals, granular minerals, fire clay, ilmenite ore, fluorspar, cryolite, etc.

Wherever you receive, ship, transfer, or feed bulk materials into process — a Richardson Automatic Scale will speed operations. Because it quickly and continuously weighs powdered, ground or granular chemicals with machine-perfect accuracy, month after month and year after year, the Richardson Bulk Scale brings more uniformity to your product, and steps up production. Needing no attendant, it releases labor for other tasks.

Built to last indefinitely. Operating levers are outside of the dust-proof casing — safe from clogging and wear. Weights are automatically recorded by a rust-proof counter.

Two or more units proportioning solids with consistent accuracy, result in a uniform product and avoid spoilage and waste. May be used in conjunction with a Richardson Automatic Liquid Scale to Proportion solids and liquids in exact quantities.

Gain closer control over bulk materials and reduce handling costs with a Richardson scale.

Write for bulletin IE-2140.

RICHARDSON

Atlanta Boston Chicago Minneapolis Montreal New York
Omaha Philadephia Pittsburgh San Francisco Toronto Wichita

RICHARDSON SCALE COMPANY, CLIFTON, N. J.

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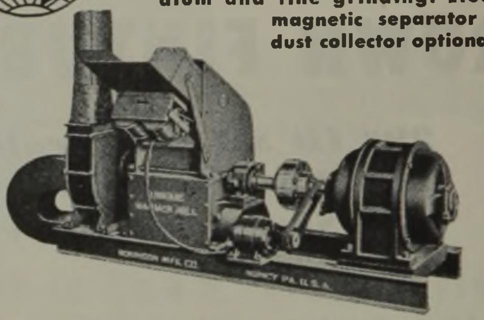
HAMMER MILLS

Many sizes. Extra heavy construction. Accurately balanced. For coarse, medium and fine grinding. Electro-magnetic separator and dust collector optional.



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Famous for over forty years, Robinson "Unique" machines today incorporate the most advanced engineering design and construction. Illustrated manuals and expert counsel are yours for the asking!

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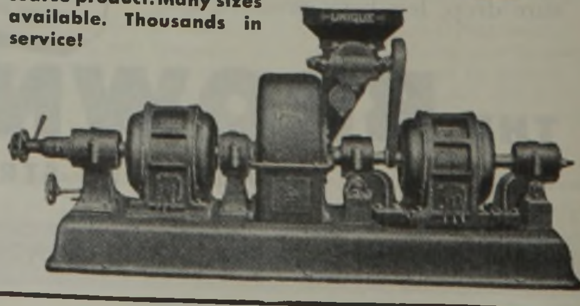
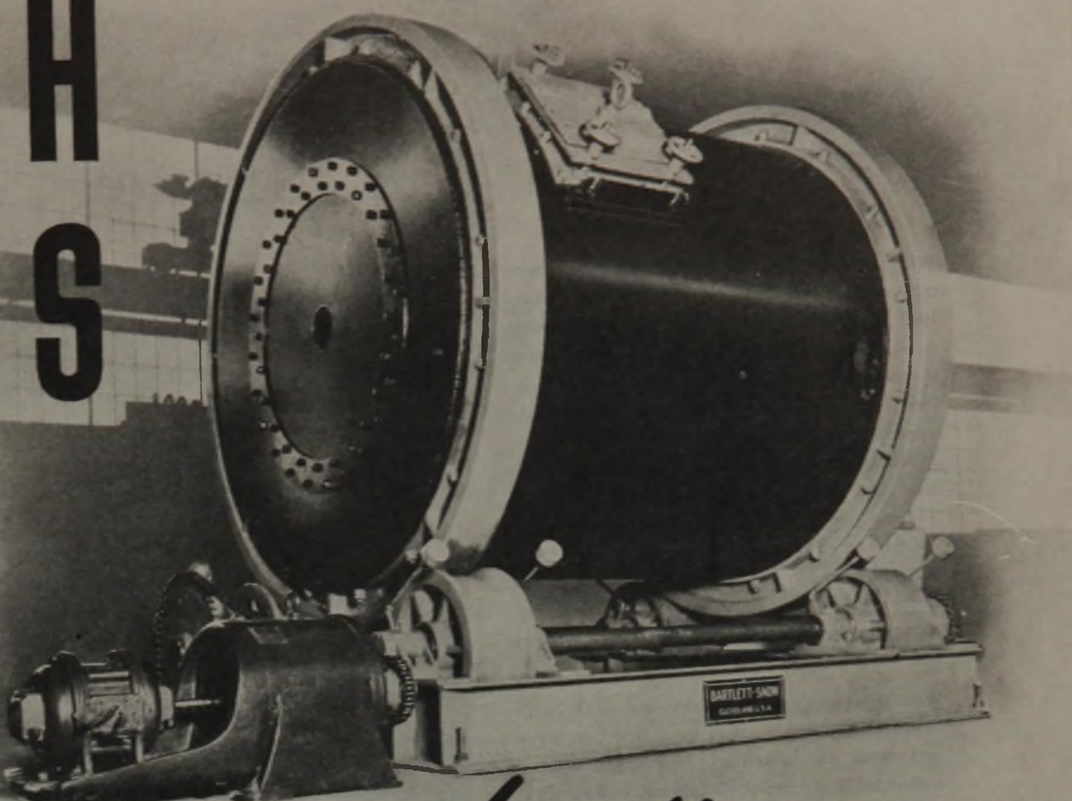
ATTRITION MILLS

TRADE UNIQUE MARK

Bosom-bodied, burr-type grinding plates produce maximum capacity. Simple adjustment provides uniform extremely fine or coarse product. Many sizes available. Thousands in service!



BATCH KILNS



....for many *heating* and *calcining* operations

● Bartlett-Snow Batch Kilns—see illustration above—are adapted to the heating of chrome ores, pebble lime, ferro chrome, fluorspar, the calcining of pigments, sludges, and many similar operations.

These kilns are mounted horizontally, and rotated with either a girt gear, or by friction through the trunnion rolls. The cylinders are closed at both ends except for the direct heat burner and spent gas discharge openings and are brick lined. Generally the net internal length is not greater than 3 times the diameter to insure good mixing, uniform heat treatment of the material, and to facilitate easy discharge.

One door centrally located, or two doors placed on opposite sides of the cylinder and approximately at quarter length, are provided. The doors are brick lined. They are forced to a tight seat in a tapered hole with hand screws, and are provided with a lifting ring to permit easy opening with a lever or small hoist. The cylinders are charged from an overhead batching hopper. After processing the kiln is stopped,—the door or doors removed and the cylinder then rotated until the processed material has been discharged.

Our recently issued Bulletin No. 89 describes Bartlett-Snow kilns, dryers, coolers, calciners, autoclaves and other heat engineering equipment in detail—discusses the fundamental principles involved—and contains much technical data of interest to every engineer and operating man . . . Send for a copy today!

THE C. O. BARTLETT & SNOW COMPANY
6207 Harvard Avenue **Cleveland, Ohio**
Engineering and Sales Representatives in the Principal Cities

BARTLETT-SNOW

DRYERS · CALCINERS · COOLERS · KILNS

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

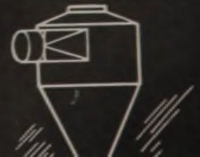
Screw Feeders

Rotary Crushers

Bucket Elevators

Belt Conveyors

Dust Collectors



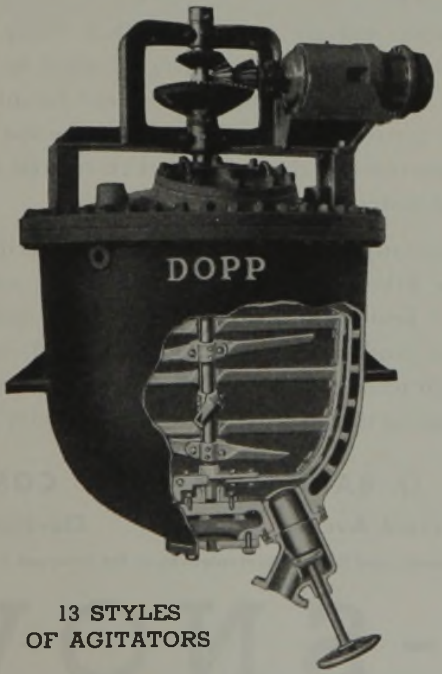
Pressure Ve

You save fuel oil with an I.B. Crane . . .

With the fuel oil shortage becoming more acute each day it is vital that every industrial plant squeeze the last drop of energy out of every drum. And that's just where Industrial Brownhoist Diesel Cranes are doing a fine job—by saving oil. One plant operating a 30 ton I. B. Crane reports an average fuel consumption of only 1.675 gallons per hour. Another reports only 1.61 gallons per hour. Both cranes were operating under fast, continuous, heavy duty service. These are not isolated cases. Those users who keep an eye on their fuel consumption invariably find that I. B. Cranes are easy on fuel.

Whether you handle heavy materials with magnet, hook or bucket you, too, can save fuel with an Industrial Brownhoist Crane. Industrial Brownhoist Corporation, Bay City, Michigan. District offices: New York, Philadelphia, Pittsburgh, Cleveland, Chicago.

INDUSTRIAL BROWNHOIST BUILDS BETTER CRANES



13 STYLES OF AGITATORS

FASTER HEATING

Users tell us that non-scraping kettle-type dryers have overall coefficients of heat transfer which are sometimes as low as about 10 and sometimes as high as about 90, but a test on a 350 gal. Dopp positive-scraping unit showed a coefficient of 139 B.t.u./hr./sq.ft./°F., as reported in Transactions of A. I. Ch. E. Details on request.

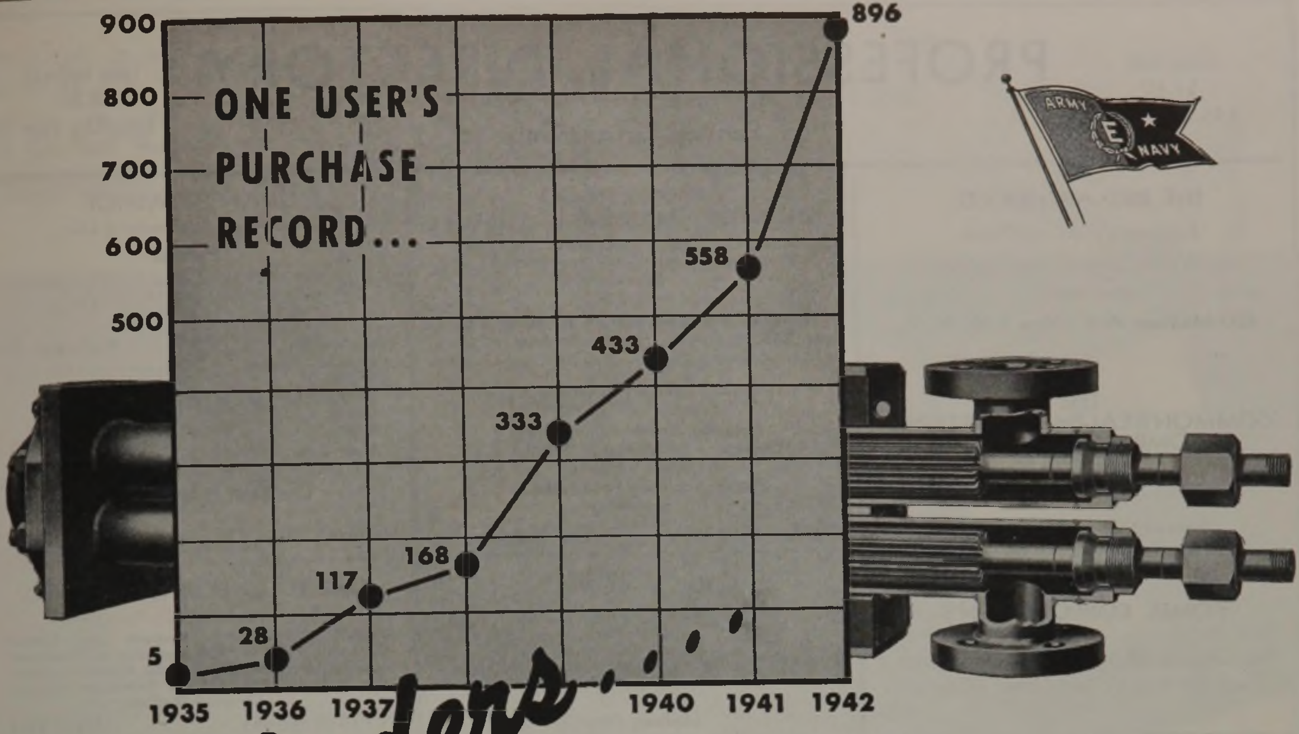
Equally faster cooling has resulted when the well established principle of Dopp-type positive-scraping has been applied to cooling materials and controlling exothermic reactions.

Higher batch temperatures are reached in a practical length of time by steam heating combined with Dopp scraping. Sometimes this has eliminated the need of direct fire heating.

What do you want to heat or cool faster? We may have applicable data in our files. If we haven't, we can develop it in our Experimental Department. What is your problem?

DOPP CAST • SEAMLESS • SCRAPED
MADE TRUE • STAY TRUE **KETTLES**
ADOPT THE DOPP

SOWERS MANUFACTURING CO., 1303 NIAGARA ST., BUFFALO, N. Y.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Consulting Chemist

153 South Doheny Drive
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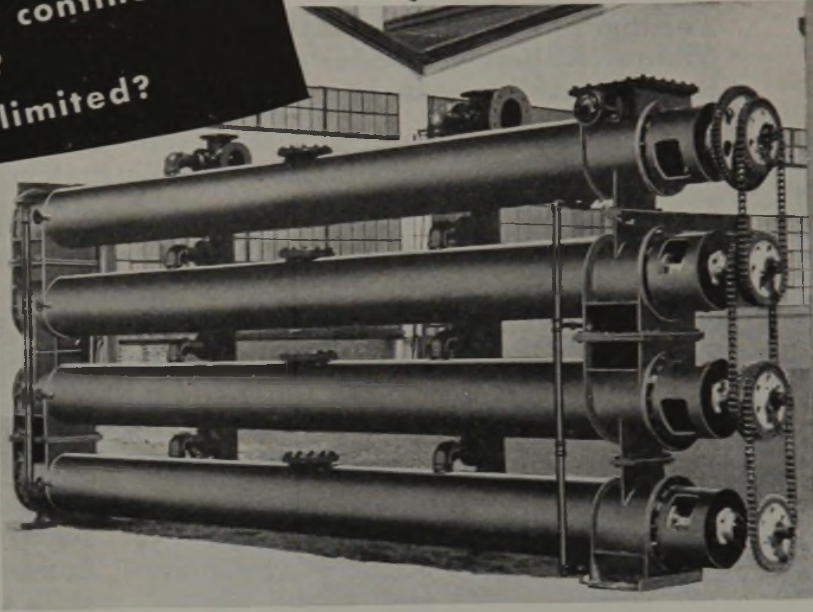


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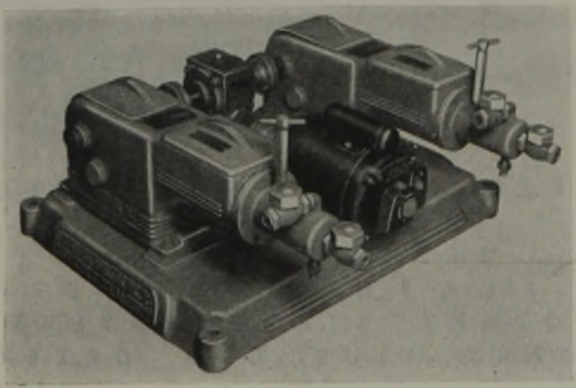

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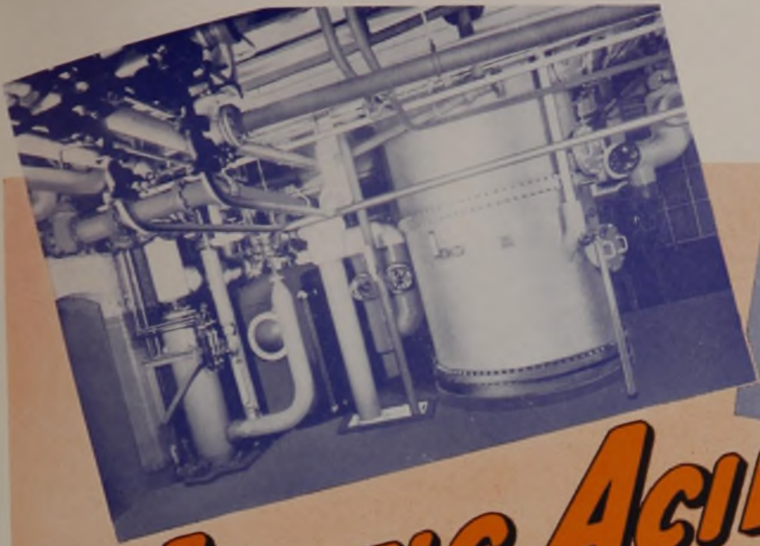
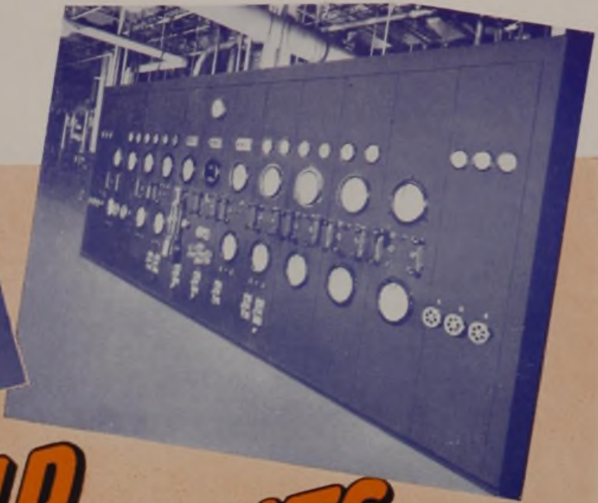

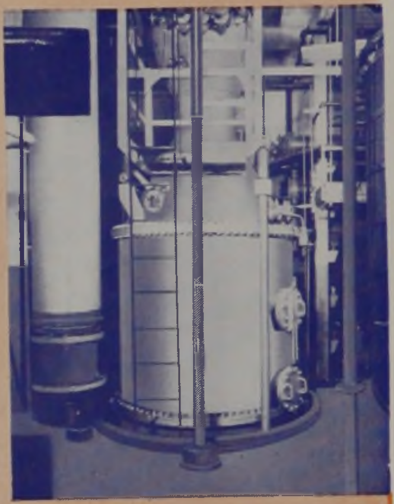

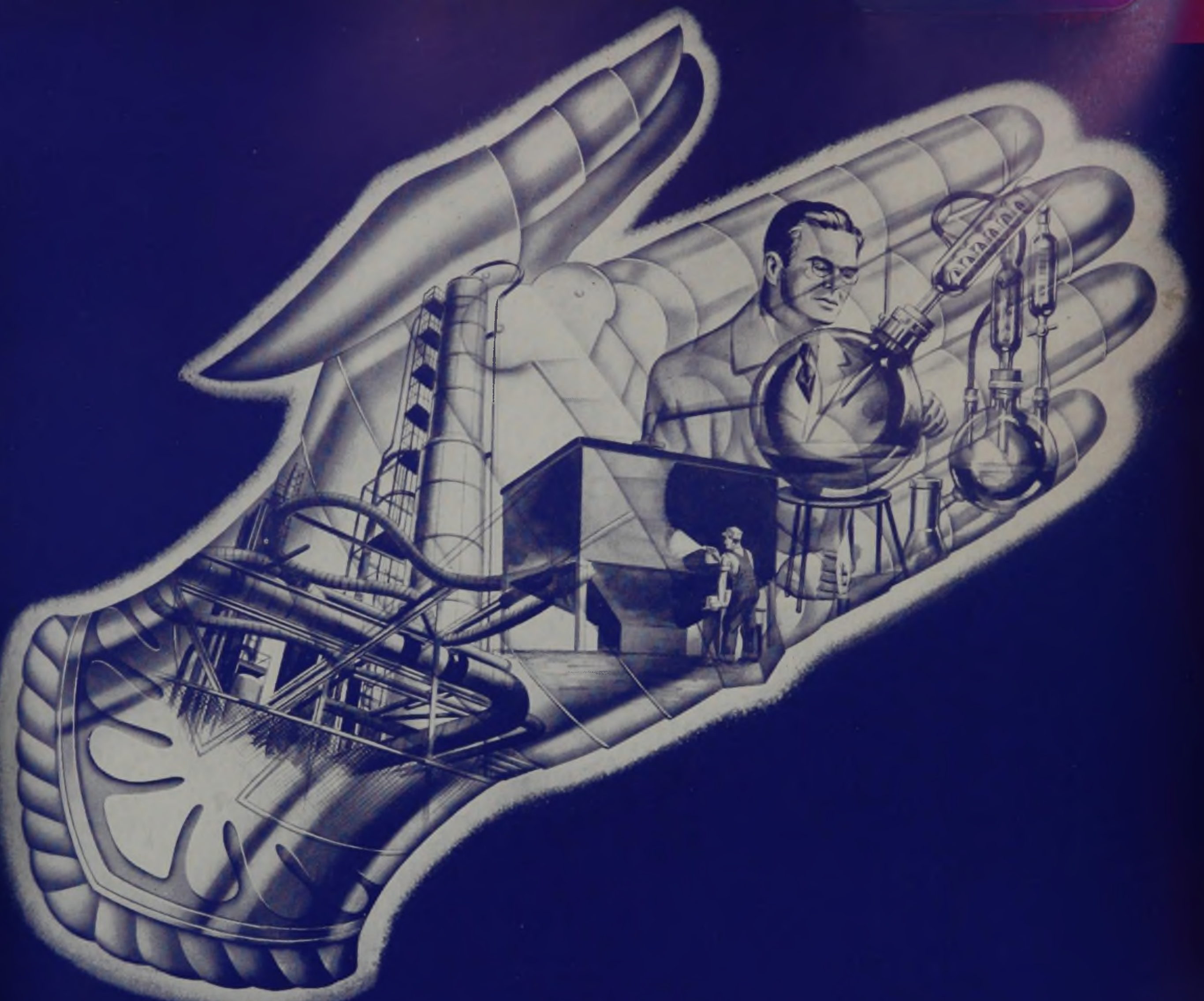

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