DUSTRIAL EDITION AUGUST, 1943

INDUSTRIAL AND ENGINEERING CHEMISTRY

/B

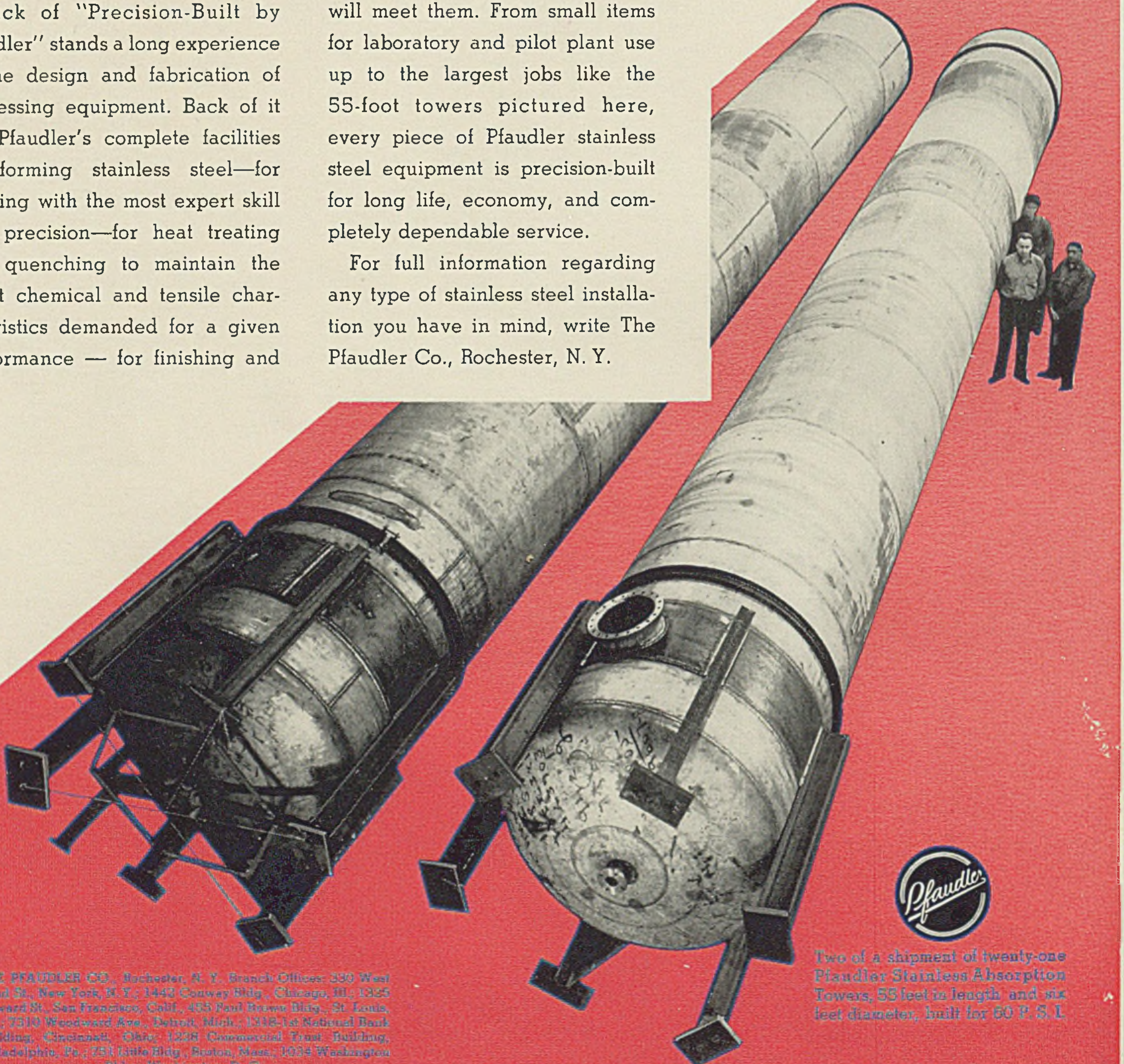
WHAT PFAUDLER *Precision-Built* STAINLESS STEEL EQUIPMENT COULD MEAN TO YOU

When you buy Stainless Steel Processing Equipment, "Precision-Built" is a lot more than a phrase. "Precision-Built" is your assurance hat the equipment will stand up n service.

Back of "Precision-Built by Pfaudler" stands a long experience n the design and fabrication of processing equipment. Back of it are Pfaudler's complete facilities or forming stainless steel—for welding with the most expert skill and precision—for heat treating and quenching to maintain the exact chemical and tensile characteristics demanded for a given performance — for finishing and polishing to the exact demands of specific applications.

If units in Pfaudler's standard lines do not meet your exact requirements, Pfaudler engineers are ready to design special units that will meet them. From small items for laboratory and pilot plant use up to the largest jobs like the 55-foot towers pictured here, every piece of Pfaudler stainless steel equipment is precision-built for long life, economy, and completely dependable service.

For full information regarding any type of stainless steel installation you have in mind, write The Pfaudler Co., Rochester, N. Y.



Pfaudler

Two of a shipment of twenty-one Pfaudler Stainless Absorption Towers, 55 feet in length and six feet diameter, built for 60 P. S. I.

THE PFAUDLER CO., Rochester, N. Y. Branch Offices: 330 West 42nd St., New York, N.Y.; 1442 Conway Bldg., Chicago, Ill.; 1325 Howard St., San Francisco, Calif., 455 Paul Brown Bldg., St. Louis, Mo.; 7310 Woodward Ave., Detroit, Mich.; 1318-1st National Bank Building, Cincinnati, Ohio; 1228 Commercial Trust Building, Philadelphia, Pa.; 751 Little Bldg., Boston, Mass.; 1034 Washington Bldg., Washington, D. C.

PFAUDLER

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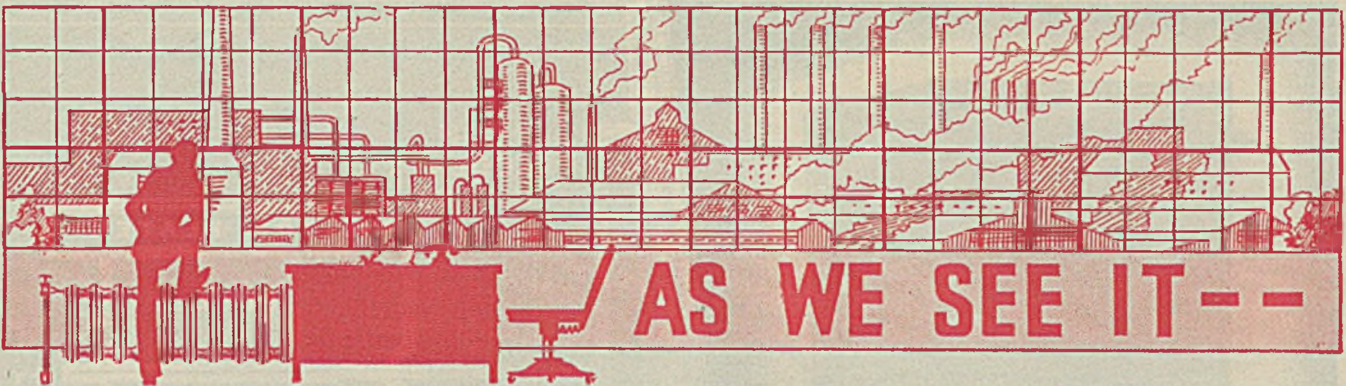


▶ SULFONAMIDE compounds, through their almost miraculous effectiveness against infectious diseases, have had an enormous amount of well deserved attention focused on their medical aspects. Equally interesting is the chemical side of the production of huge quantities of these invaluable materials. Northey (page 829) gives us this phase of the story and some of its side lights in so far as they can be discussed under present conditions.

▶ IONIC EXCHANGE, by which both anions and cations can be removed from solution, provides a new and valuable method of accomplishing many useful tasks. The new phase of this subject is the use of resinous agents to replace mineral zeolites, and it opens new and important fields for the technique. Myers (page 858) describes the functioning of the new compounds and their applications, many of them novel.

▶ POWER CONSUMPTION of propeller agitators, widely used in mixing, has been determined by Stoops and Lovell (page 845) and reduced to an equation for calculating this factor in designing installations.

▶ COUNTERCURRENT HEAT EXCHANGERS can be designed by several methods of varying degrees of accuracy and of convenience. Larian (page 840) compares the various methods to supply a basis of choice between them.

▶ HEATS OF VAPORIZATION can be determined graphically by using values for a reference substance. Gordon (page 851) presents a simplified method of doing this.

▶ ABSORPTION AND STRIPPING of hydrocarbons into and out of solutions are common operations of growing importance. Edmister (page 837) provides a short method of calculating the design of equipment for these purposes.

▶ RUBBER AND SYNTHETIC RUBBERS are useful only within specific and characteristic limits of temperature, both high and low. Morris, James, and Werkenthin (page 864) have determined the brittle points (i. e., the limiting low temperatures) of a number of commercial stocks made of both plantation and synthetic rubbers, using a modified method believed to be superior.

▶ PLASTICIZERS modify materially the properties of resins containing them, and much of the versatility of synthetic resins depends upon the proper choice and use of a plasticizing agent. Reed (page 896) has investigated the effects on vinyl chloride-acetate copolymers of some forty-six plasticizers by methods developed for the purpose.

▶ SOYBEAN MEAL produces important changes in the characteristics of phenolic resins into which it is incorporated, according to McKinney and his co-workers (page 905), and by proper consideration of these modifying effects plastics can be made to meet requirements more closely. Effects on flow, light stability of colors, and reduced cost without sacrifice of mechanical strength or moisture resistance are described.

▶ SEPARATION OF PURE HYDROCARBONS from mixtures assumes continually greater importance in petroleum technology. Griswold, Van Berg, and Kasch (page 854) have separated the constituents of a commercial hexane and describe both the method and the results.

▶ WATER TREATMENT produces a number of crystalline compounds whose compositions and characteristics affect steam boiler operation. Imhoff and Burkardt (page 873) have applied x-ray diffraction methods to their identification and give the conditions under which each is formed.

▶ WOOD'S CHEMICAL CONSTITUTION has been investigated by Coppick and Jahn (page 890) by direct nitration and by subsequent study of the products formed. Differences in solubility of nitration products are used to separate them for examination. Spruce and white pine are the woods studied.

▶ INSULATING OILS must be stable over long periods of use to be fully satisfactory. Assaf and Balsbaugh (page 909) have determined the effects of a number of additives and oxidation inhibitors on the electrical and chemical stability of mineral insulating oils.

▶ COTTONSEED, PEANUT, AND SOYBEAN MEALS, after the removal of their oil content, are important sources of edible protein and B vitamins which have been neglected in the American dietary. Zucker and Zucker (page 868) have investigated both nutritive aspects of these incompletely utilized products, already available in large quantities from oil mills, and find them good.

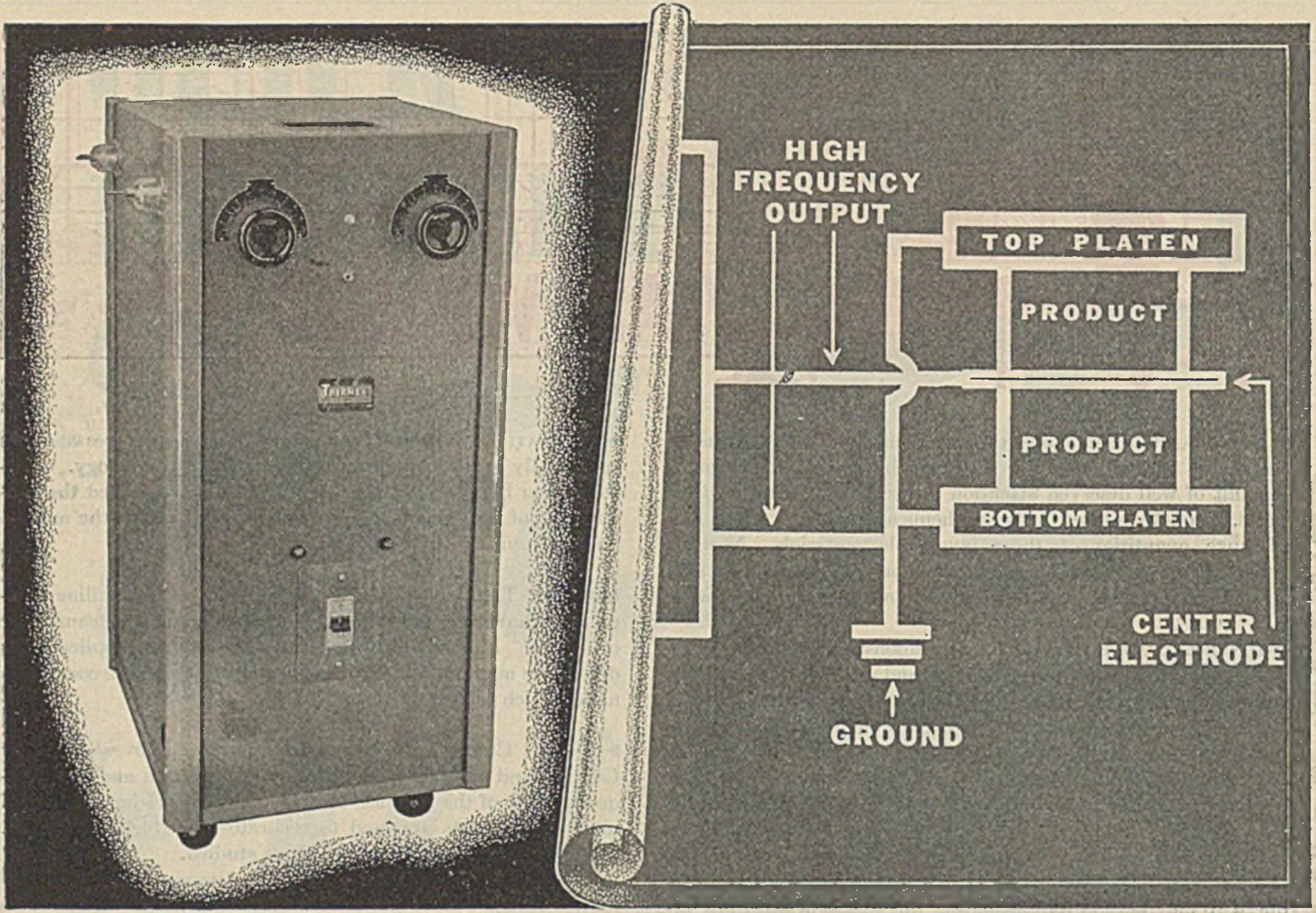
▶ SOYBEAN LECITHIN is a useful stabilizing and inhibiting additive for mineral lubricating oils, according to Jacobs and Othmer (page 883). A cheap, plentiful commercial lecithin was tested in a variety of lubricating oils with good results as compared with other synthetic commercial additives.

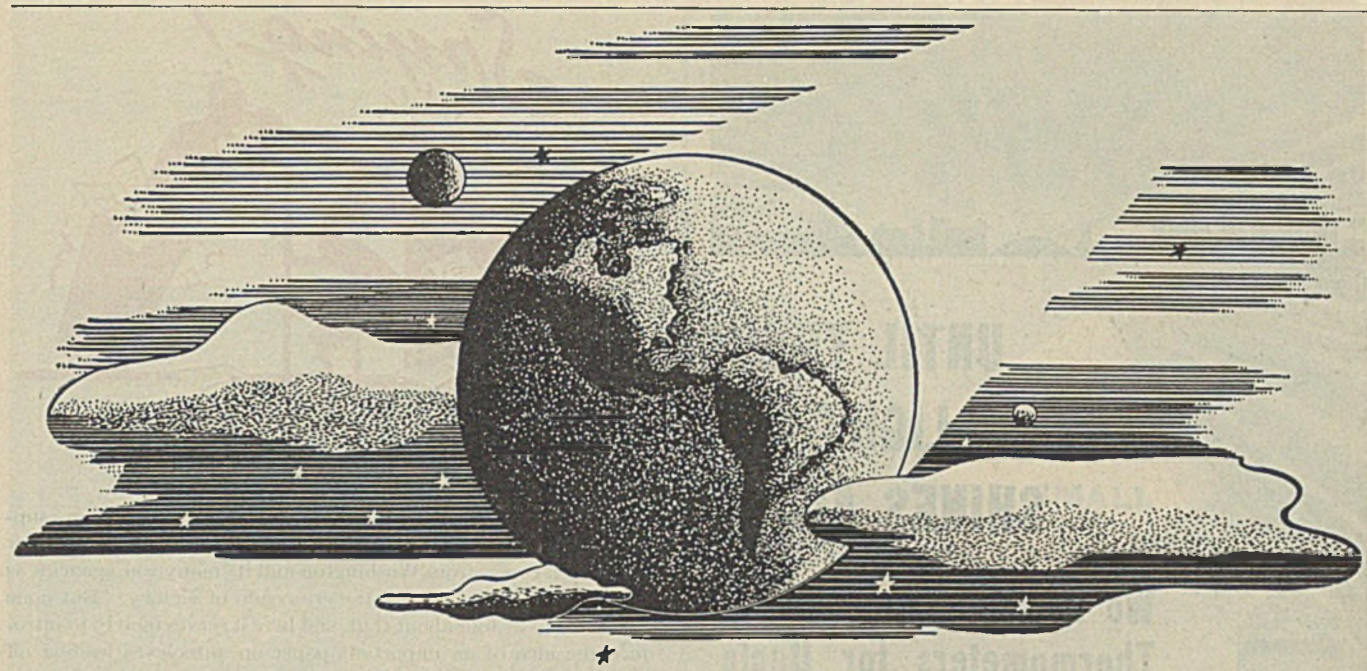
▶ METHANE'S VOLUME-PRESSURE characteristics have been determined at pressures up to 15,000 pounds per square inch and over the temperature range from −13° to 392° C. by Sage, Lacy, and their co-workers (page 922).

▶ SOAP–WATER–SALT SYSTEMS are shown by the phase rule studies of McBain and Lee (page 917) to involve a subwaxy soap phase, which is grained out in soap making.

▶ SOYBEAN MEAL produced commercially contains lipoid oxidase capable of enzymic destruction of vitamin A and carotenoids only if the temperature reached in processing is too low to denature the oxidase, according to Sumner and Tressler (page 921).

D H Killeffer


THERMEX
HIGH FREQUENCY OUTPUT
TOP PLATEN
PRODUCT
PRODUCT
BOTTOM PLATEN
CENTER ELECTRODE
GROUND



DAY BEGINS AT MIDNIGHT

NIGHT changing into day is a gradual process . . . not like the snapping on of a light. Likewise, the change from war to peace is a long transition. Right now, at the height of our war activities, the shape of the post-war industrial world is being determined by the events of each passing day. Therefore, it is imperative that management observe and utilize the lessons being taught by war-accelerated production . . . for example, the proved power of machinery to aid in world-wide economic development by bringing more things within the reach of more people.

Ingenious conveying systems, through spectacular performance in war plants, have forcefully demonstrated their vital importance in post-war production plans. They regulate the flow of materials and parts, securing the most efficient movement between processes and operations; they conserve space, eliminate wasted effort and multiply the productiveness of man power. Thus, they give to industrial management the means for expanded activities . . . for broader markets . . . for accelerated development of new products . . . in short, for sound, constructive progress.

As specialists in designing and building mechanical-handling machinery for all industry, Link-Belt engineers have learned how to apply an extensive knowledge and experience, effectively, to the solution of all kinds of materials-handling problems. Because Link-Belt makes all types of conveyors and power transmitting machinery, we can be of incalculable service in recommending the type, form, speed and drive most certain to aid you in attaining streamlined production. Submit your materials-handling problems to Link-Belt—our engineers will carefully analyze your requirements and make impartial, constructive recommendations. Write us — today!

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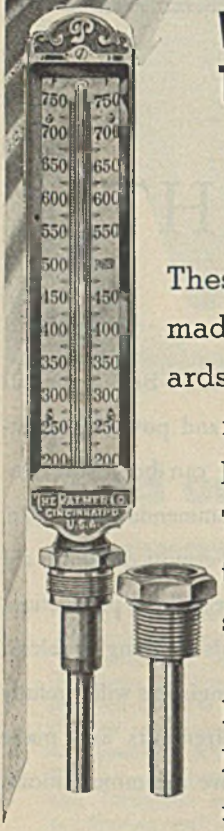
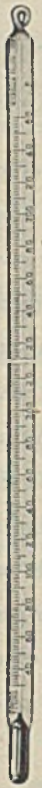
"THE BACKBONE OF MASS PRODUCTION"

LINK-BELT

CONVEYORS...CHAINS
and POWER TRANSMISSION EQUIPMENT





HEAT and pressure characterize these dog days. Nature supplies the heat, and an increasing amount of pressure for production comes from Washington and its many war agencies as our offensives build toward the crescendo of victory. But none of us need to be told about that, and here it serves merely to introduce the idea of an important paper on autoclaves leading off our September contents. It is hardly necessary to go beyond that to suggest the value of more information about these versatile and essential tools of all chemical industry.

Synthetic rubber continues our No. 1 problem. With the basic problems of production now well on the way to solution on a huge scale, those of utilizing our several new elastomers to best advantage become dominant. Just as duplication of the output of plantations achieved through decades has been accomplished in months that are only now growing into years, so will the century-long development of rubber technology be quickly reoriented and amplified to fit the new materials. Heat generation and dissipation are yet crucial problems whose solutions must precede the full utilization of synthetics. They receive first attention, and other papers will discuss Thiokol blends, heat resistance of neoprene, sulfur vulcanizates of styrene-butadiene polymers, carbon black in Butyl, and effect of petroleum products on neoprene compounds. To complete this group will be a paper on molecular weights of high polymers. That should provide food for thought and action in plenty even though we may not be coming back from our accustomed vacations.

Pickling liquors, especially obnoxious in sluggish midsummer streams, present a continuing problem to the steel industry. We shall learn something about the possibilities of getting value from them by recovering free acid.

Aging of whisky, another continuing problem, is the principal activity of distillers now that war has stopped their normal production. The phenomena connected with aging and maturing will be discussed for us in the light of new evidence.

Glutamic acid, lately coming into growing prominence as a condiment, attracts renewed attention. Sugar beet wastes generally are now shown to contain glutamic acid in recoverable quantities in addition to the customary source, Steffen wastes. Here, again, appears an opportunity to build for ourselves an industry to replace one which we formerly promoted for Japan.

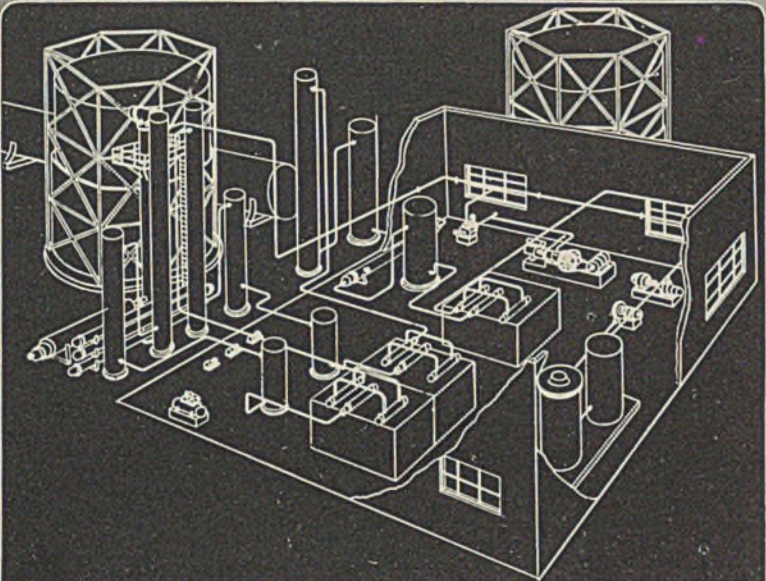
Not too remote from this subject is the industrial development of soybean lecithin, this time employed usefully in printing inks.

Phosphates, normally considered plant foods through fertilizer, will be discussed for us in their relation to animal feeding, also a vital function.

That, of course, is by no means all, but at least it is enough to prove our September issue a "must".

YOUR HUMBLE SPY

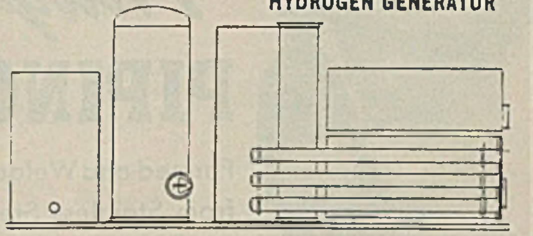
See Girdler for low-cost HYDROGEN plants



PERSPECTIVE VIEW OF LARGE GIRDLER HYDROGEN MANUFACTURING PLANT

LARGE OR SMALL

SIDE VIEW OF PORTABLE GIRDLER HYDROGEN GENERATOR



OTHER GIRDLER PROCESSES

Production, Purification, Separation, Reforming or Dehydration of

HYDROGEN SULFIDE
CARBON MONOXIDE
BLUE WATER GAS
ORGANIC SULFUR
CARBON DIOXIDE
HYDROCARBONS
HYDROGEN
NITROGEN
OXYGEN
and various mixtures.

WHETHER your hydrogen gas requirements are 500 cubic feet per hour or a million cu. ft. per hour, there is a Girdler Hydrogen Plant to meet your requirements.

These range in size from portable units which can be installed in trucks, trailers or boats to giant permanent plants.

Excellent purity of gas, extremely low operating cost, flexibility and practically automatic operation characterize all Girdler hydrogen producing plants.

Girdler plants operate in a continuous manner and are economical and efficient even if operated at only 20% of the rated capacity.

You are urged to send for further details describing Girdler hydrogen plants. If you will indicate your approximate requirements, a more specific reply can be given. No obligation, of course. Write today!

Buy another War Bond this week!

The GIRDLER CORPORATION

Specialists in Better Gas Processes

Gas Processes Division • LOUISVILLE, KENTUCKY

THE GIRDLER CORPORATION
202 E. Broadway, Louisville, Ky.
Please send further information on Girdler Hydrogen Manufacturing Plants.

Name...Title.....................
Firm..
Address..
City...State.....................

DID YOU SEE?

A NEW development is described in this month's ad of the Brown Fintube Co. It is cut and twisted Fintubes, and by their use, says the ad, the heat transfer capacity of certain heat exchangers is increased by a full 50 per cent. The conventional Fintube is cut at certain intervals and the ends are twisted. This gives greater turbulence to the liquid or gas on the shell side which, in turn, gives more efficient heat transfer. Also, says the Brown message, there are still further savings in shell size, weight, and shipping and manufacturing costs.

Why plastics? asks the Bakelite Corporation, and then proceeds to give an answer by listing all the desirable properties that plastics have. The ad contains valuable tidbits of information, such as the fact that the Navy is using plastic bayonets for training purposes, and that engine cowlings are now being made of plastic rather than metal because the plastic construction is stronger and lighter. Says Bakelite, "Hardly a day passes but another new industrial development is made possible through plastics."

To this ad commentator, the H. M. Harper Company brings out a vital message this month. It's an analogy on the old "my kingdom for a horse" plea of the old king who lost everything for the want of a horseshoe nail. The Harper Company says that often an investment of 2 cents more for a nonrusting bolt may save thousands of dollars later through the prevention of a breakdown. They say they have 4320 stock items of bolts, nuts, screws, washers, and other accessories in the nonferrous and stainless alloys.

The Philadelphia Quartz Company offers a special bulletin about silicate of soda, its brands, properties, and applications. Some of the applications are illustrated in the ad. They range over the most varied fields. One concerns the reconditioning of metal workers' files and another, quick setting inks. No matter what your status as a user of silicate, says the ad, the new bulletin will be stimulating.

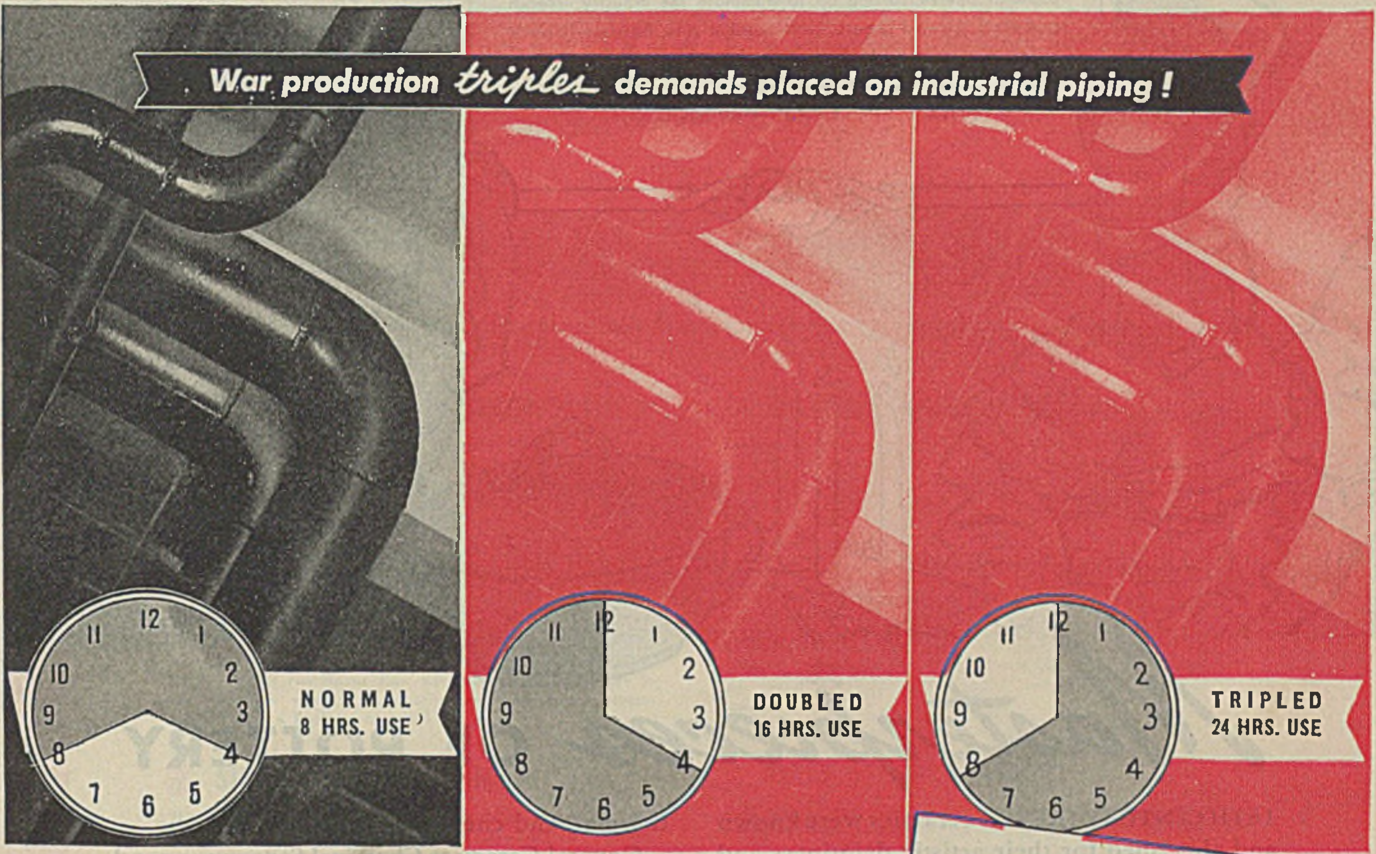
The Goodyear Tire and Rubber Co. call their ad an "expression of faith in America". It concerns, not so much a product, but the dedication of a new research laboratory devoted to the idea that "the best is yet to come". They have faith that America is going ahead and will continue to do so.

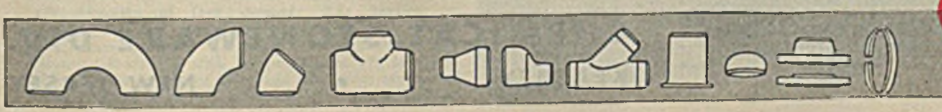
Bartlett-Snow claims that powdery materials can now be dried with almost no loss at all. Bartlett-Snow engineers, they say, keep loss of fines at minimum levels. "In one case a dryer 84 inches in diameter and 40 feet in length is drying 720 pounds an hour of a fine 57 per cent wet organic material with almost no loss at all." Long experience, they say, enables the correct selection of dryer, breechings, air ducts, and cleaners.

The Thiokol Corporation tells how concrete underground storage tanks, thought unfit for storage of high-octane gasoline, were made suitable containers through the use of a protective coating of Thiokol sheet welded to the wall and floors of the tank with a special synthetic rubber cement.

The Mixing Equipment ad this month is a particularly good example, in this writer's opinion, of an engineering ad. After reading it one feels that he has obtained some information to be used the moment he enters the plant. The points about mixing of miscible liquids are well taken and important.

T. M. PRATURE


War production triples demands placed on industrial piping!
NORMAL 8 HRS. USE
DOUBLED 16 HRS. USE
TRIPLED 24 HRS. USE



18th CENTURY FRENCH PORCELAIN

Under the régimes of Louis XV and XVI, France dominated Europe economically, politically and artistically. It was during this glittering era that the secrets of Chinese porcelain making were rediscovered, and French plants, led by the Royal plant at Sèvres, sprang up to dominate the industry. French porcelain showed superb workmanship and flawless finishes. Colored enamel, gold leaf and dainty scenic panels were often used for decoration—reflecting the grandeur and artificial elegance of 18th century French nobility.

Masterpieces **OF POTTERY**

18TH CENTURY FRENCH ceramics were known and cherished for their artistic daintiness and ornate decoration. In contrast to these characteristics, General Ceramics Chemical Stoneware is known and valued for its strength, durability and functional design. It is built for but a single purpose—to serve you, industrially, well and long. There is nothing pretty or dainty about a stoneware pump, for instance, yet, in the handling of strong chemicals and corrosive liquids, its stoneware lining assures long life to the pump itself and insures personnel and property against hazardous leakage. General Ceramics Chemical Stoneware is acid-proof throughout and is built to meet mechanical, thermal, and chemical requirements.

General Ceramics Chemical Stoneware products include acid-proof pipe, valves, fittings, kettles, jars, pots, pumps, exhausters, coolers, condensers, acid elevators, towers, filtering equipment and tourills.

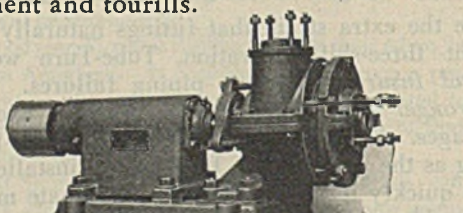


FIG. 420
ARMORED STONEWARE CENTRIFUGAL PUMP

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

3950

8 ways VOTATOR is better for continuously heating or cooling liquids and viscous materials!

Votator is the ideal heat transfer equipment for practically all liquids or viscous materials. It is especially suitable for RESINS, AVIATION GASOLINE, PETROLEUM PRODUCTS, VEGETABLE OIL PRODUCTS, and CHEMICALS. Below are some of Votator's key features that offer unusual advantages for these and many other applications.

1 HEAT TRANSFER IN SECONDS!

The rate of heat transfer is extremely fast, due to the unique principle of passing a very thin film of product over a relatively large heat transfer surface. Heating or cooling is instantaneous, requiring seconds instead of minutes, even through wide temperature ranges.

2 CONTINUOUS FLOW OF MATERIAL!

The Votator is continuous in operation. The product is pumped in at one end, heated or cooled to a uniform temperature, and discharged at the other end at the temperature desired. This continuous flow advantage likewise applies to the operation where *both* heating and cooling are accomplished with a hook-up of two Votators.

3 SIMULTANEOUS MIXING!

High speed agitation under pressure in the enclosed Votator assures thorough and intimate mixing. With a Votator, mixing, emulsifying or aerating may be accomplished at the time of heat transfer, which often results in product improvements and decided production economics.

4 EASILY INSTALLED!

Votator units are available in standard sizes and designs that fit easily into many processes. Low temperature refrigerants or high temperature steam may be used as the heat transfer medium. Inlet and outlet connections for both the product and refrigerant or heating medium are arranged so the Votator can easily be hooked into almost any plant process.

5 UNIFORM TEMPERATURE!

Uniform heating or cooling of the product is assured at all times for two reasons. First, because only a small quantity of the product is in the Votator at any one time. Second, effective insulation reduces the heat or cold loss to a minimum, and controls regulate the entire operation accurately.

6 ACCURATE CONTROL AT ALL TIMES!

A Votator is extremely simple to operate. Adjustments in operating conditions can be made quickly, and the results are immediate. Automatic controls and regulators protect against carelessness or negligence.

7 FULLY ENCLOSED UNIT!

With the Votator, liquids or viscous materials are heated or cooled without contacting the atmosphere. All air and moisture can be excluded. However, if desirable, any predetermined amount of inert gas may be incorporated uniformly in the product with a Votator.

8 MORE ECONOMICAL!

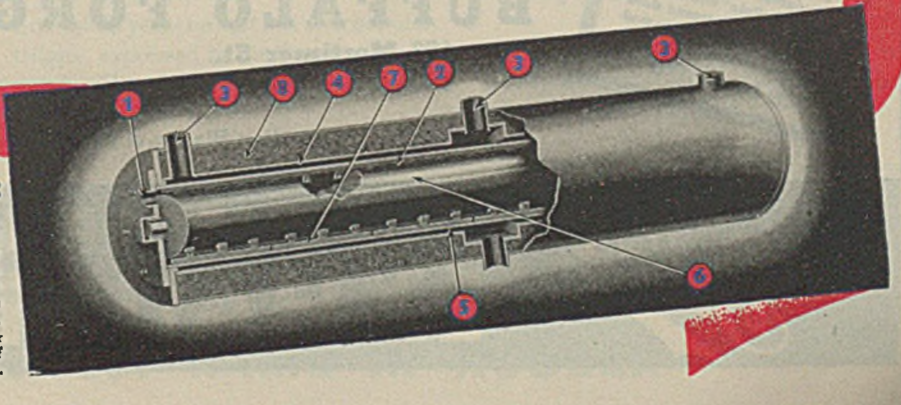
The speed of heat transfer, accurate temperature control, rapid, continuous flow, and the fully enclosed unit are factors that enable Votator equipment to be operated much more economically than ordinary types of heat exchange equipment. The added advantage of simultaneous mixing or emulsifying also may reduce processing costs and save time.

Write today for further information and illustrated booklet.

The GIRDLER CORPORATION
VOTATOR DIVISION **LOUISVILLE, KENTUCKY**

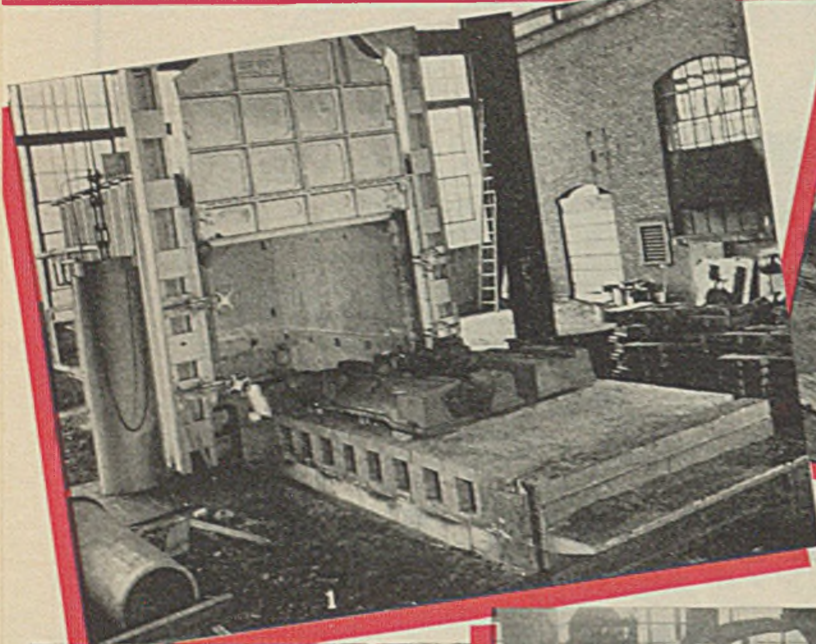
HOW THE VOTATOR WORKS:

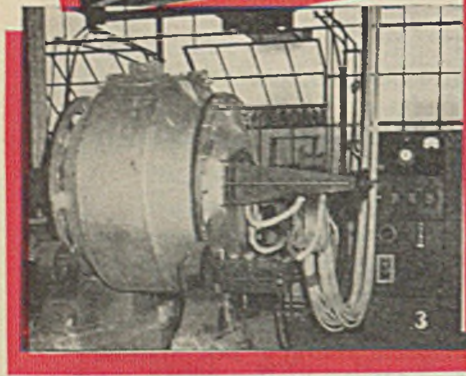
The heart of the Votator, the heat transfer cylinder, illustrates at the right how the product is pumped in connection (1) thru annular space (2) and out connection (1) at the opposite end, depending upon the direction of flow desired. The heating or cooling medium enters at connection (3), passes thru annular space (4) and out connection (3). Mutator shaft (6) with scraper blades (7) is motor driven, causing blades to scrape film from surface of heat transfer tube (5) hundreds of times a minute.

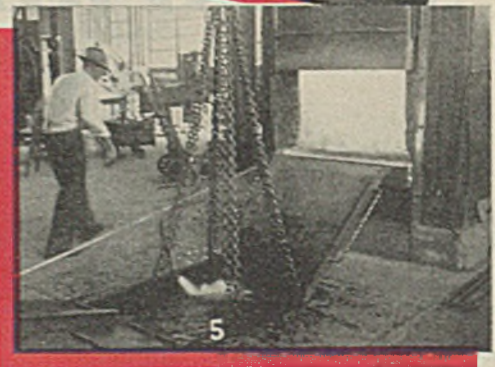



"THE BEST IS YET TO COME"

AVAILABLE CAPACITY
PROMPT DELIVERY







1 One of several 8'x12' car type annealing furnaces. Smaller sizes also available.

2 Electric induction melting furnaces — 2400 lb., 1200 lb., 650 lb., 400 lb. and 150 lb. units.

3 Indirect arc melting furnace.

4 Sand preparation equipment. All our foundries have accurate sand control.

5 Quench-anneal operation for austenitic alloys. No delay in this quench.

Do you need alloy iron or stainless steel castings (heat or corrosion resisting) of high quality, accurate analysis, for either high pressure or normal pressure service?

ALLOY IRONS, such as —
- Duriron or Durichlor (high silicon irons)
- Ni-Resist No. 1 (15% Ni, 6% Cu)
- Ni-Resist No. 2 (20% Ni, Cu free)
- 30% or 35% nickel cast iron
- 2½% Ni, 1% Cr Cast iron
- Or other alloys to your specifications.

STAINLESS STEELS, such as —
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- Monel metal
- 12% Cr; 18% Cr; or 28% Cr
- 18% Cr, 8% Ni, (18-8S) low carbon, with or without Columbium
- 18% Cr, 8% Ni, 2½% Mo, (18-8SMo)
- 25% Cr, 12% Ni
- 20% Cr, 25% Ni
- 35% Ni, 15% Cr
- Or other special analyses.

CAPACITY AVAILABLE — THREE large foundries well-equipped for producing special castings, and two large machine shops for finishing products.

FOUNDRY FACILITIES —
- Electric Induction, Indirect Arc, Powdered Fuel Air } Melting Furnaces
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HEAT TREATING FACILITIES
- Car type and smaller annealing and hardening furnaces
- Oil and water quench
- Draw furnaces, accuracy ± 1° F.

EXPERIENCE — Thirty years exclusively in the manufacture of alloys and corrosion-resisting equipment. Highest type of supervision, experienced foundry men, capable of handling to completion the pattern design and technique of making special and intricate castings.

PROMPT DELIVERIES — Capacity is now available for additional rush orders. Submit your requirements to us for quotation or for the advice and assistance of our Engineering and Metallurgical Departments.

ARMY E NAVY

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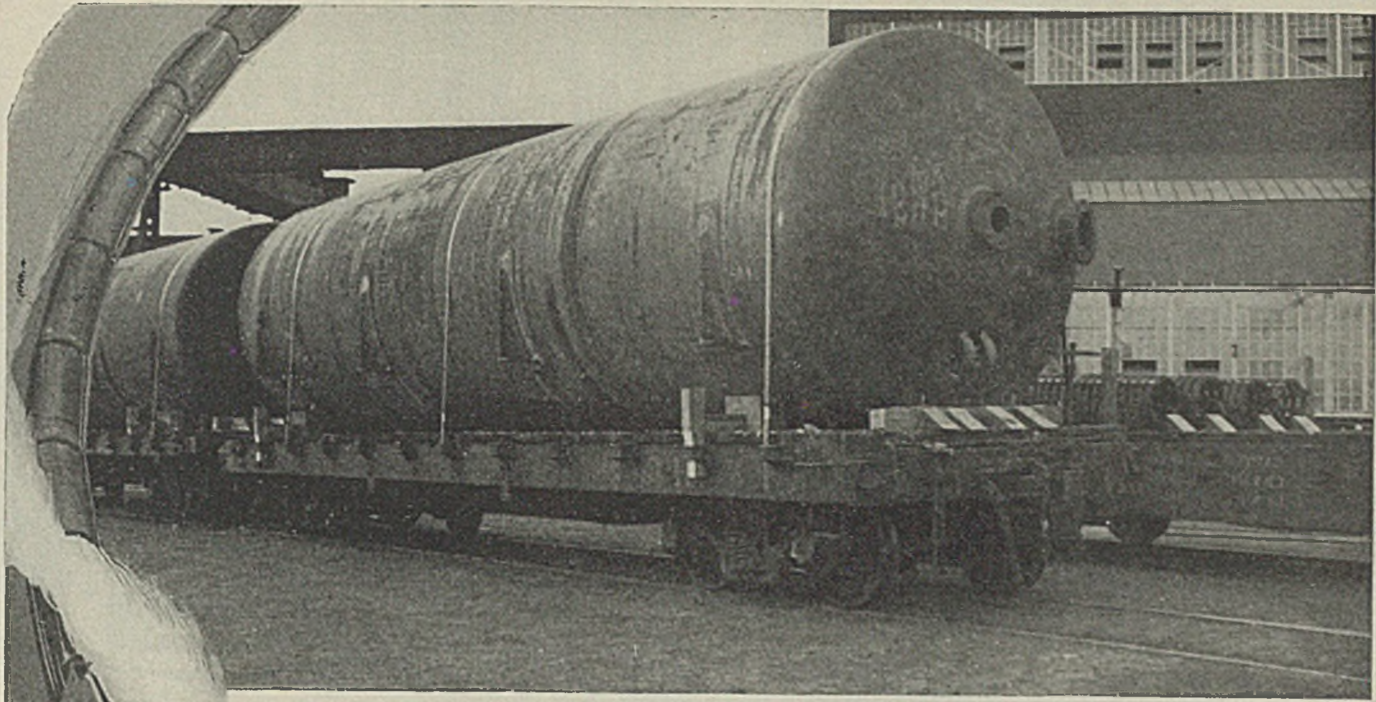

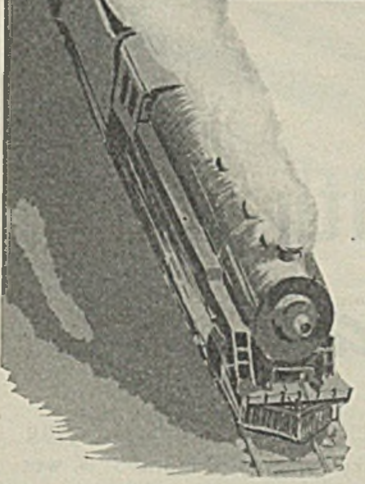

Digesters TO AID PRODUCTION AT A NEW ALUMINUM PLANT

VIRTUALLY a whole trainload of these horizontal digesters were fabricated recently at our Birmingham works and shipped to a new aluminum plant. This particular installation, only one of many, merely serves to indicate the important role that welded steel pressure vessels are playing in the nation's war effort. Chemical plants, the synthetic rubber industry, and the petroleum industry are demanding welded steel pressure vessels of various types for their "production lines."

The fabricating of such pressure vessels has long been a specialty at our plants. Complete facilities are available at our Birmingham plant for x-raying and stress-relieving. Vessels up to 13 ft. 2 in. in diam. and as long as can be shipped can be handled in the stress-relieving furnace. Those 80 ft. or less in length are stress-relieved at one time. Vessels built to API-ASME specifications not requiring stress-relieving are fabricated at our other plants.

The digesters shown above were stress-relieved before being shipped from Birmingham. They measure 9 ft. 3 in. in diam. and 35 ft. long, and are designed for 200 lbs. per sq. in. pressure.

ARMY E NAVY

The Army-Navy "E" flag now flies over two of our shipyards . . . Eureka, California and Seneca, Illinois.

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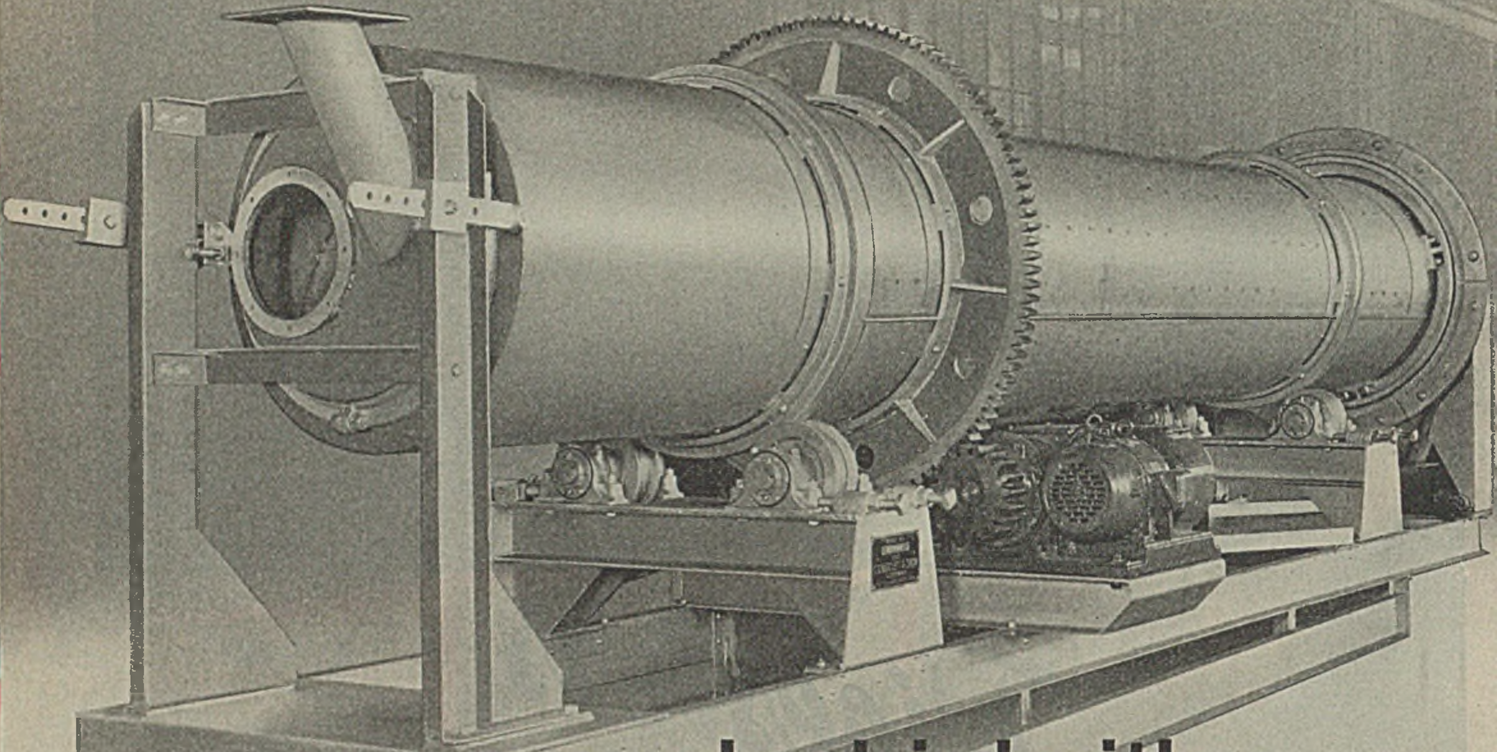
POWDERY MATERIALS



can now be dried with *almost no dust loss at all*

● That the carrying or entraining power of an air stream varies as the square to fifth power of the linear air velocity, is of small importance when drying granular or heavy bulk materials. But take the powdery ones, cellulose acetate, paint pigments, lignin or activated carbon. With these and other products whose value is computed in dollars to a pound, loss of fines in the discharged air or vapor is of great importance.

With the ability that comes from only long experience in selecting just the size and type of dryer . . . in building breechings, air ducts and cleaners, Bartlett-Snow engineers keep loss of fines at minimum levels. In one case, a Bartlett-Snow Style J Dryer, 84 inches in diameter and 40 feet in length, is drying 720 pounds an hour (dry weight) of a fine 57% wet organic material with almost no loss at all.

Cut down your product losses with Bartlett-Snow equipment. Wide customer experience, an intimate background of chemical engineering and "TECHNICAL APPROACH," the formulas developed and used only by Bartlett-Snow heat engineers, that determine with mathematical precision the drying condition best suited to the product . . . will help you solve your problems, too! What are your problems?

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U.S.I. CHEMICAL NEWS

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

U. S. Industrial Alcohol Co. Merged Into U. S. Industrial Chemicals, Inc.

New Acetone Uses Developed Covering Many Varied Fields

Importance of Chemical Shown By Study of Recent Patents

Although generally considered a staple chemical with a fairly limited although important field of utility, acetone is finding many new uses in a wide variety of processes. As an indication of the unexplored possibilities of this highly reactive chemical, a study of recent patents reveals many such applications. A few of the more interesting are outlined in the following paragraphs as described by their inventors.

In the rubber compounding field, for example, a typical new use for acetone is in condensation with aryl amide to produce an age resistor for rúbber which is particularly effective at elevated temperatures.

For inhibiting oxidation in rubber, another inventor recommends incorporating about 0.1% or more of a product of thermal reaction of a ketone such as acetone, an aliphatic "hydrocarbon alcohol" such as isopropanol, and a secondary di-aromatic amine such as diphenylamine in the presence of an acidic catalyst, with elimination of water.

One use for acetone in the metal-working field is its use in combination with boron trifluoride. An organic flux for soft soldering metals is obtained which is described as non-corrosive when left in contact with the metal being soldered and yet which mildly, but uniformly, attacks the metal surface during the soldering operation.

To produce a solvent for dewaxing mineral oils, acetone is recommended in combination with amyl mercaptan. Certain treated waxy lubricating oil stocks of 70 seconds Saybolt universal viscosity when mixed with such a

(*Continued on next page*)

Composition Developed for Treating Plastic Materials

BURBANK, Calif. — A patent has been awarded to an inventor here for a composition suitable for use in the treatment of cellulose derivatives, such as photographic film, which is claimed to be effective either to prevent shrinkage and deterioration or to restore the normal characteristics of such materials after having undergone a loss of their volatile constituents.

The composition comprises an azetropic mixture of one or more volatile organic solvents, such as dibutyl phthalate, and one or more volatile plasticizing agents such as ethanol, isopropanol, butanol, and ethyl acetate,

New Name Signifies Increasing Interest in Growing Chemical Field

Effective at the close of business on July 16th, U. S. Industrial Alcohol Co. has been merged with, and into, U. S. Industrial Chemicals, Inc., in line with the Company's increasing interest and growing activities in the broader field of industrial chemicals — and consistent with the present trends in the research and development of U.S.I. products.

Originally organized in 1906 under the name of U. S. Industrial Alcohol Co. for the express purpose of manufacturing industrial alcohols, the Company has gradually increased its activities in alcohol-derived solvents, chemicals and intermediates.

U.S.I. Activities Increase

Interest in the development of related alcohol-chemical products has continued until today U.S.I. offers a most complete line of these products for applications and for organic syntheses in new fields of endeavor.

Among important recent additions to the U.S.I. line are a number of new acetoacetarylides, developed in recognition of the growing importance of yellow pigments and dyestuffs, and ethyl benzoylacetate, an intermediate useful in the manufacture of dyes and the synthesis of many chemical compounds. U.S.I. has also recently manufactured quantities of Indalone, insect repellent outstanding for slow-evaporating and film-forming characteristics, and ethyl sodium acetone-oxalate, a highly reactive chemical.

New Glycerol Method

Another significant contribution made by U.S.I. during the past year was the development of a commercially practical method for producing glycerol by fermentation of molasses which is expected to alleviate the cri-

(*Continued on next page*)

By constant research and development, U.S.I. has expanded its activities until it is not only one of the largest industrial alcohol manufacturers, but a major producer of chemicals and solvents derived from alcohol.

High Bactericidal Properties Claimed for New Compound

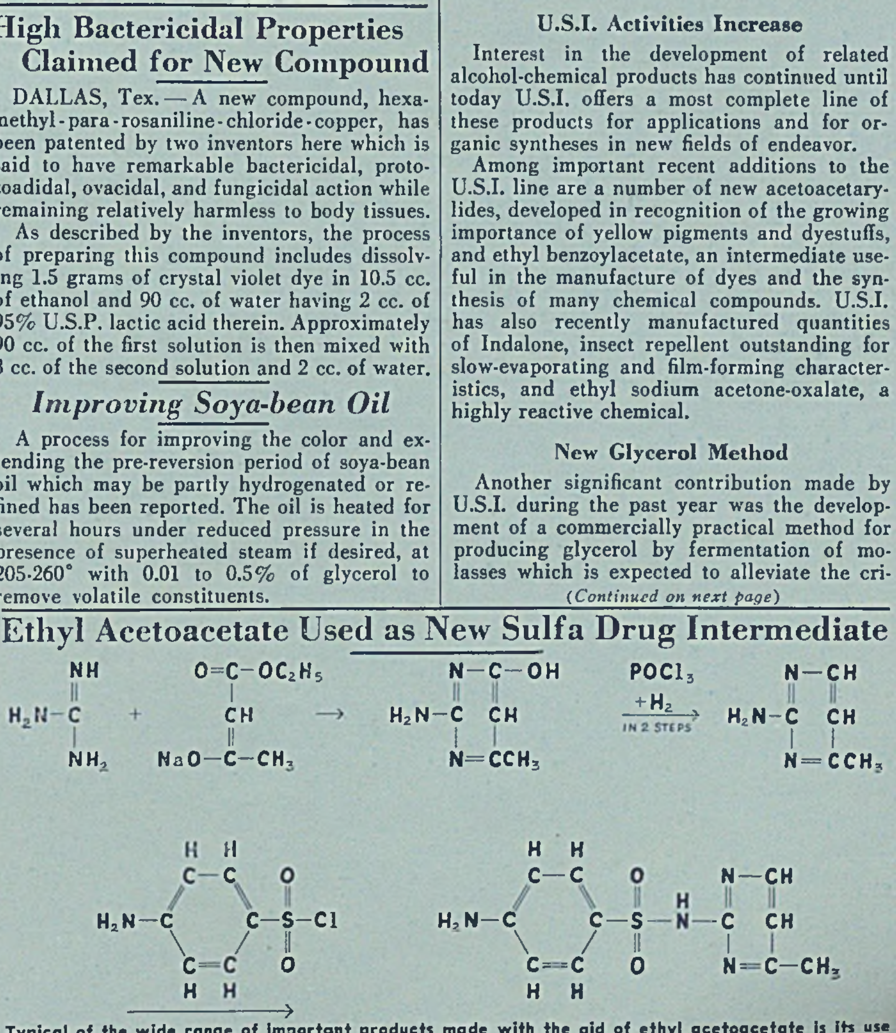
DALLAS, Tex. — A new compound, hexamethyl-para-rosaniline-chloride-copper, has been patented by two inventors here which is said to have remarkable bactericidal, protozoadidal, ovacidal, and fungicidal action while remaining relatively harmless to body tissues.

As described by the inventors, the process of preparing this compound includes dissolving 1.5 grams of crystal violet dye in 10.5 cc. of ethanol and 90 cc. of water having 2 cc. of 95% U.S.P. lactic acid therein. Approximately 90 cc. of the first solution is then mixed with 8 cc. of the second solution and 2 cc. of water.

Improving Soya-bean Oil

A process for improving the color and extending the pre-reversion period of soya-bean oil which may be partly hydrogenated or refined has been reported. The oil is heated for several hours under reduced pressure in the presence of superheated steam if desired, at 205-260° with 0.01 to 0.5% of glycerol to remove volatile constituents.

Ethyl Acetoacetate Used as New Sulfa Drug Intermediate



Typical of the wide range of important products made with the aid of ethyl acetoacetate is its use as an intermediate for the new sulfa drug sulfamerizine, which is reported to be more powerful than sulfadiazine and less liable to cause damage to the kidneys. Sulfamerizine can be produced in accordance with sequence shown above.

U.S.I. Merger

(Continued from preceding page)

tical demand for this war-important material.

Intermediates Developed

One of the major undertakings of U.S.I.'s laboratories at the present time is the development of new chemical intermediates for use in the manufacture of hormones, amino acids, vitamins, insecticides, and chemo-therapeutics.

To exploit further uses for the staple products and develop new ones, a Technical Sales Development Department was established by U.S.I. with headquarters in a newly constructed laboratory building.

A significant step in the widening of U.S.I.'s chemical activities was its entrance into the field of synthetic resin manufacture with a fairly complete line which includes modified and pure phenolics, alkyds, urea-formaldehydes and ester gums. A line of natural resins was added a short time later.

Two new plants have been built to increase U.S.I.'s resin manufacturing capacity. Both the manufacture and sale of these materials are now conducted by U.S.I.'s Stroock & Wittenberg Division.

Through an active research and development program, coupled with the maintenance of high standards of purity and uniformity, U.S.I. has been able to serve not only virtually every important industry, but to make a substantial contribution to America's fight for freedom as well.

Patent Awarded for Process To Separate Fatty Acids

A method for obtaining fatty-acid fractions relatively rich in stearic and palmitic acids from mixtures such as tallow and garbage grease is the subject of a recent patent.

The method comprises dissolving the fat in a solvent such as 90% methanol, and establishing in the solution a quantity of neutral fat amounting to about 0.5 to 3.5% of the weight of the fatty acids. The solution is then chilled to provide a fraction purer in stearic than in palmitic acid. After this fraction has been removed by filtration, the solution is again chilled to effect crystallization of an eutectic mixture of stearic and palmitic acids. This fraction is also removed by filtration and the solution again chilled to precipitate a fraction richer in palmitic acid than in stearic acid. This final fraction is also removed by filtration.

New Acetone Uses

(Continued from preceding page)

solvent are claimed to produce a dewaxed oil with a pour point of 5° F.

A recent pharmaceutical application of acetone is in dissolving the salt of calabash-curare as a preliminary step in purifying toxiferine. The patent also outlines subsequent steps in the process.

Another new pharmaceutical use for acetone is in the extraction of stings and poison glands of bees. The extract is then evaporated in vacuum at 20° and extracted first with a concentrated alcohol, such as ethanol or methanol, and with 55-65% aqueous alcohol.

New uses for acetone are discovered frequently in the paint, varnish and lacquer industries where this chemical has long been one of the most useful solvents. One recent application is found in a process for a drying oil composition claimed to possess improved hardness and adhesion, as well as greatly reduced wrinkling tendencies. It comprises an unsaturated ketone condensation product of acetone in which tung oil is dissolved.

A rapid, uniform method of producing a luminous coating for electric lamps was discussed recently in which luminescent particles are dissolved in a medium of acetone, nitrocellulose and dimethyl phthlate. Another inventor recommends the addition of colloidal graphite dissolved in acetone and aluminum to lacquer that is to be used on aircraft.

Among the new uses for acetone in organic synthesis is one in which it is used in preparing a pure grade of hydroxylamine hydrochloride. Acetone is reacted with a mixture of nitric acid and hydrochloric acid to produce chloroisonitrosoacetone, which is dissolved in water and reacted with chlorine gas, then hydrolyzed in dilute hydrochloric acid.

The preparation of new emulsifying agents which disperse calcium soap also involves the use of acetone. Lauryl chloride is condensed with a sulphonic acid of para-toluidine or para-chloroaniline in the presence of caustic soda ash or other alkalies and acetone.

An improved method of manufacturing vinyl crotonate makes use of acetone. Acetylene is brought into contact with crotonic acid in the presence of acetone and in the presence of a catalyst at a temperature not exceeding about 50° C.

One of the foremost producers of this basic chemical for many years, U.S.I. offers acetone of highest purity to meet essential needs.

TECHNICAL DEVELOPMENTS

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

A textile sample dryer is offered which is claimed to perform both drying and conditioning operations on samples of materials in from one to two minutes. Swatches are placed on a wire screen on the disc or rotor attached to the inside of the door of an insulated cabinet, and rotated first with door closed, then opened. **(No. 720)**

U S I

A portable parts-testing unit has been developed which the maker says can subject specimens to any temperature between 165° F. and 100° below zero. Using carbon dioxide as refrigerant, the unit may be attached to a small enclosure built around test parts. A small electric heater provides heat. **(No. 721)**

U S I

A moisture-resistant white pencil tracing cloth has been put on the market which is said to guard against spots from perspiration or moist hands and climatic conditions. It is described as having glass-like transparency and a fine-tooth surface. **(No. 722)**

U S I

A floor cleaning and disinfecting powder is offered which is said to form a non-caustic solution that is effective on floors of wood, tile, terrazzo, cork, linoleum, and rubber. The maker says it rinses readily, does not turn rancid, and is harmless to the skin. **(No. 723)**

U S I

A resin-base paint has been developed which is said to protect the surfaces of metal, wood, and concrete against attack by organic and inorganic acids, alkalis, salts, alcohol, gasoline, oils, and moisture. It is applied by brushing, spraying or dipping. **(No. 724)**

U S I

A salve for treating burns has been developed which is claimed to offer ease of application, relief of pain, acceleration of rate of healing, shortening of disability period, and the prevention of disfiguring scars in many cases. **(No. 725)**

U S I

An acid rust solvent and metal cleaner has been developed for ferrous metals and galvanized sheets. The maker says it will remove oxides quickly in cold solutions without attacking the metal, and that it is fumeless and will not damage clothing, shoes, or hurt hands in any way. **(No. 726)**

U S I

A paint-type marking crayon is offered for use on cold surfaces of steel, lumber, rubber, stone, glass, porcelain and plastics. Colors include white, black, red, blue, green, and yellow. **(No. 727)**

U S I

A flame-proofing material is offered for cloth and fabric that is said to prevent them from igniting even when exposed to actual flames. The maker says it is non-injurious to woolens, cotton or rayon, non-injurious to the skin, and non-poisonous and odorless. **(No. 728)**

How Calgon helps speed America's war effort:

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THE nation's priceless steel-making equipment must be kept in good condition at all costs. Unfortunately, the water necessary for cooling, which is usually taken for granted, sometimes can do a surprising amount of damage.

When hard, high-bicarbonate water must be used for cooling, blast-furnace jackets and open-hearth doors clog up with scale, overheat and often burn out, causing frequent repairs. Heat exchangers, furnace cooling coils, and all kinds of water-cooled rolls have similar scale trouble.

Everywhere, but particularly where water is too soft, equipment and pipe lines suffer from corrosion —sometimes rusting through in a few months. This trouble is even more deadly as repair parts are increasingly difficult to get.

Fortunately, scale can be prevented, corrosion controlled with a simple treatment using only a few parts per million of Calgon*. Heat-exchanger equipment can be kept on the job with no down time for cleaning. Gas coolers, air coolers retain their full capacity; even ammonia scrubbers stay in service much longer.

Wherever industry is troubled with problems of scale and corrosion, the chances are that Calgon can be of immediate service. No elaborate equipment is needed to start the treatment. Get in touch with us at once for complete details.

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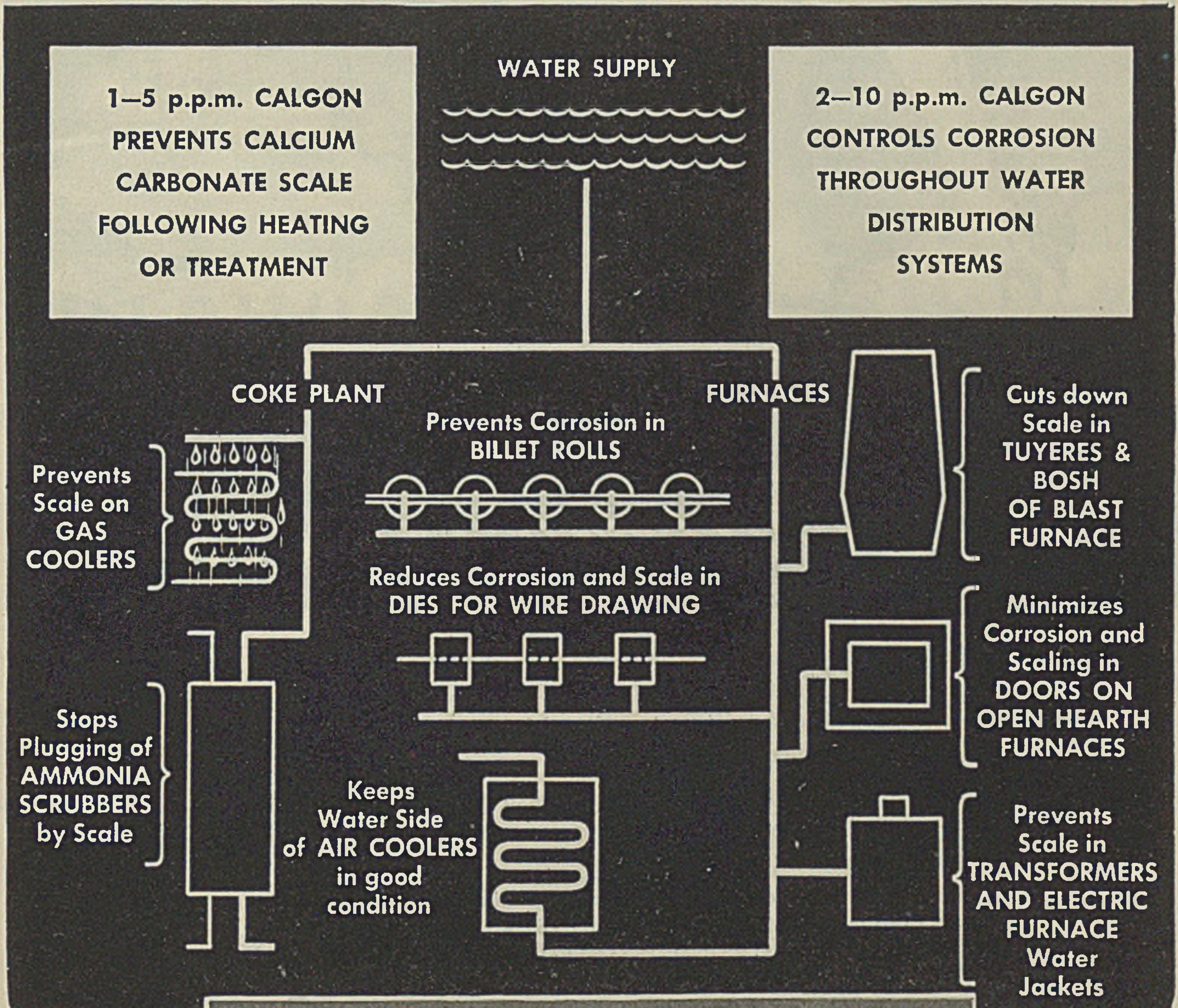
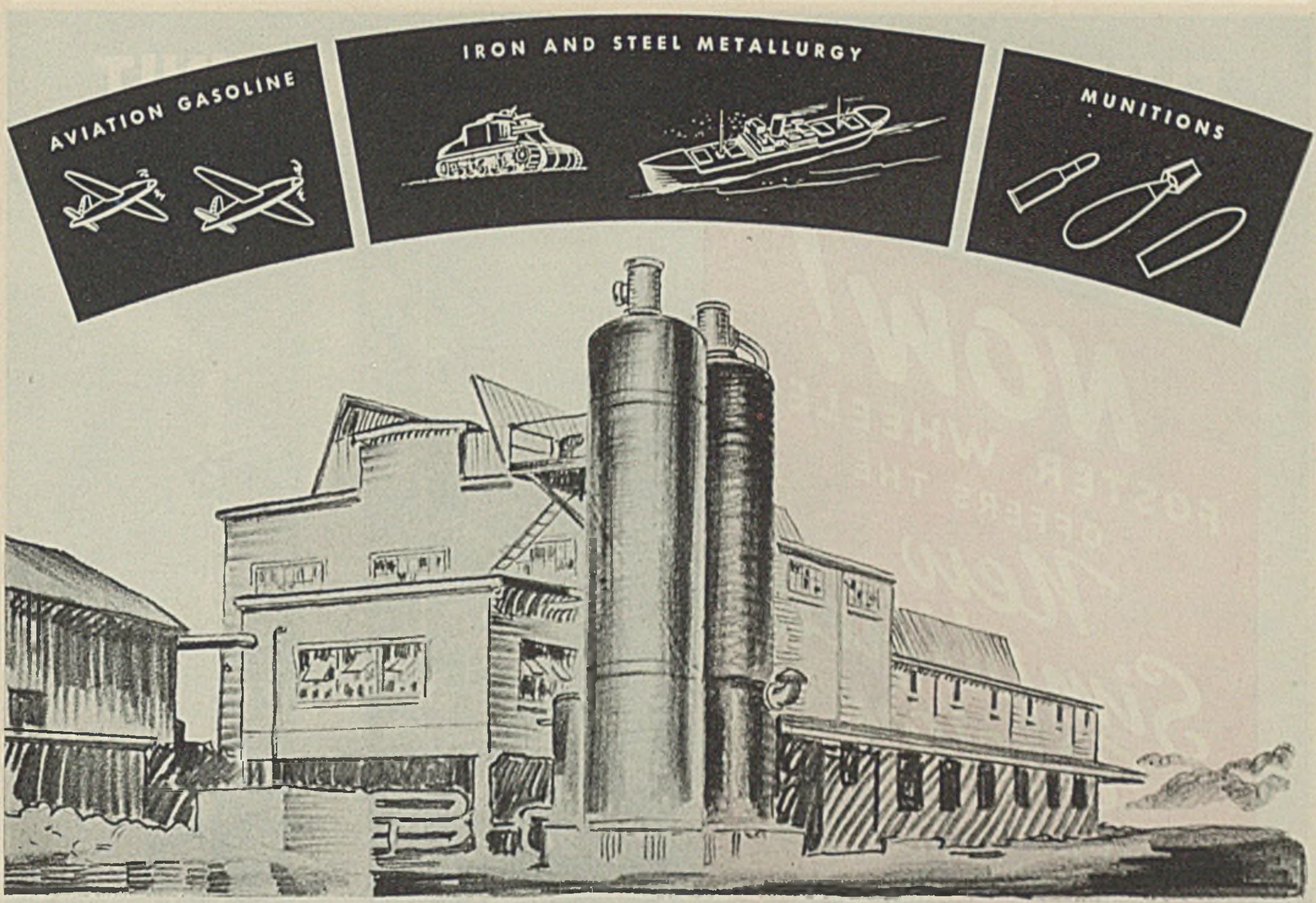
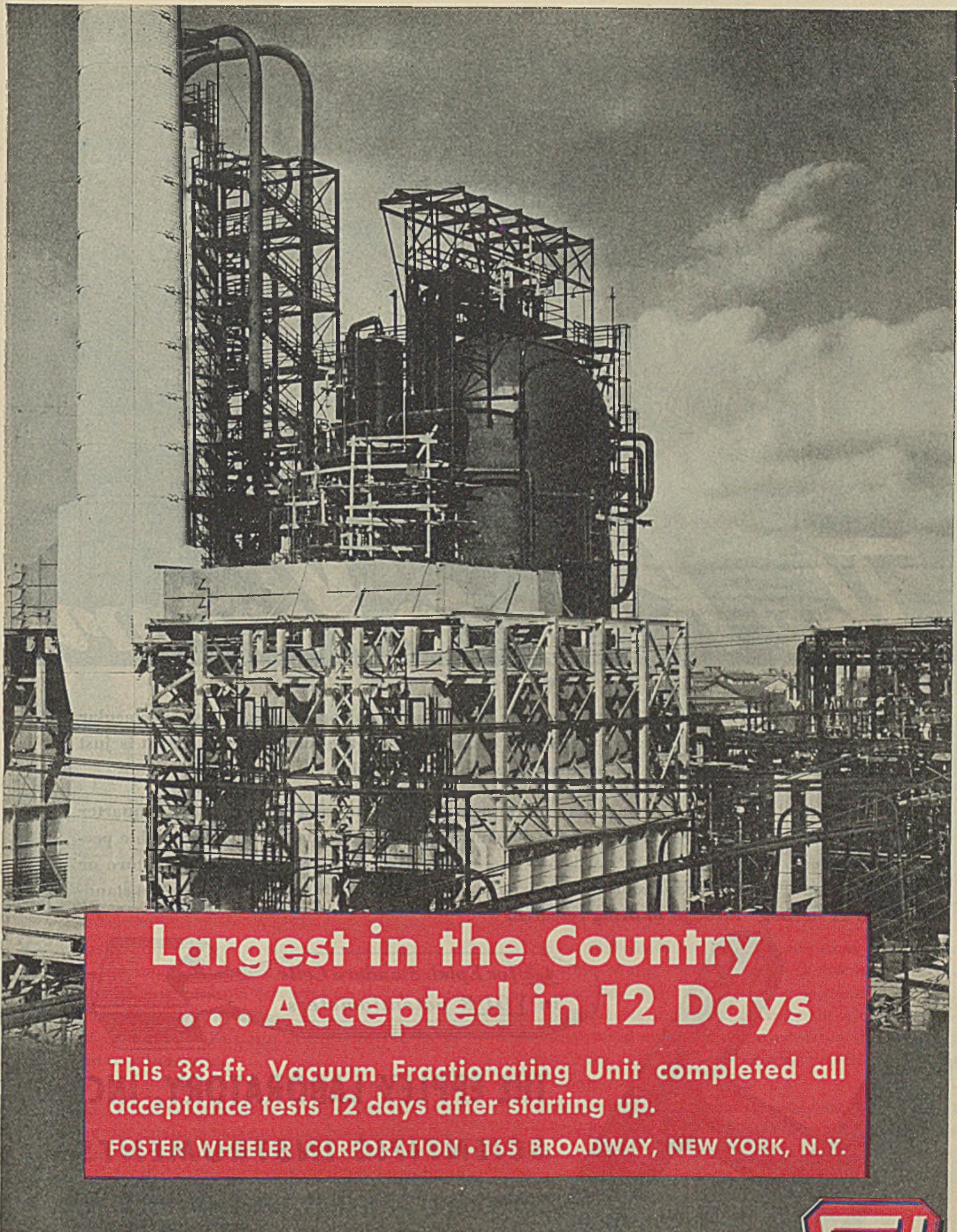


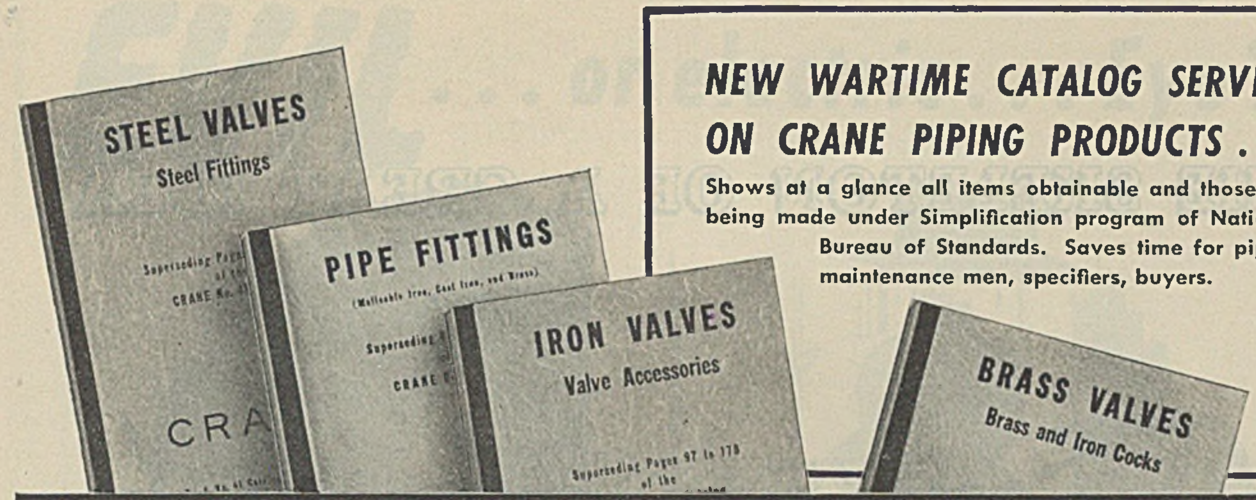
calgon, inc.

HAGAN BUILDING PITTSBURGH, PA.


Electrons ARE COMING


AVIATION GASOLINE
IRON AND STEEL METALLURGY
MUNITIONS

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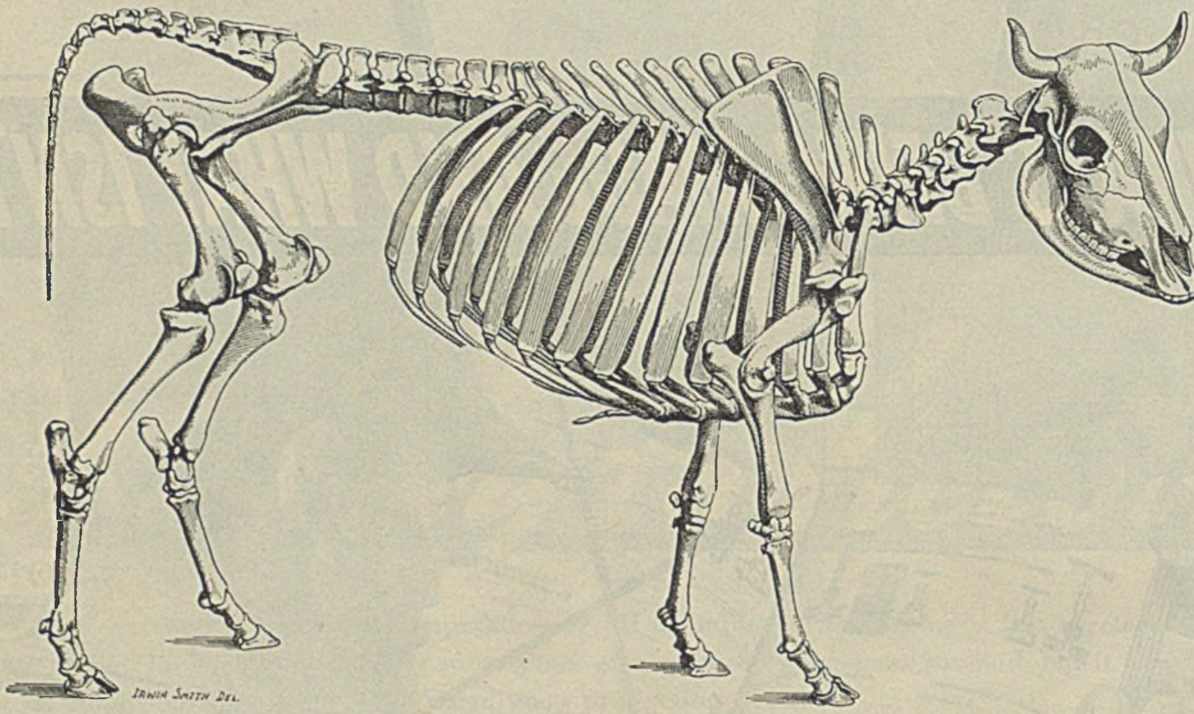
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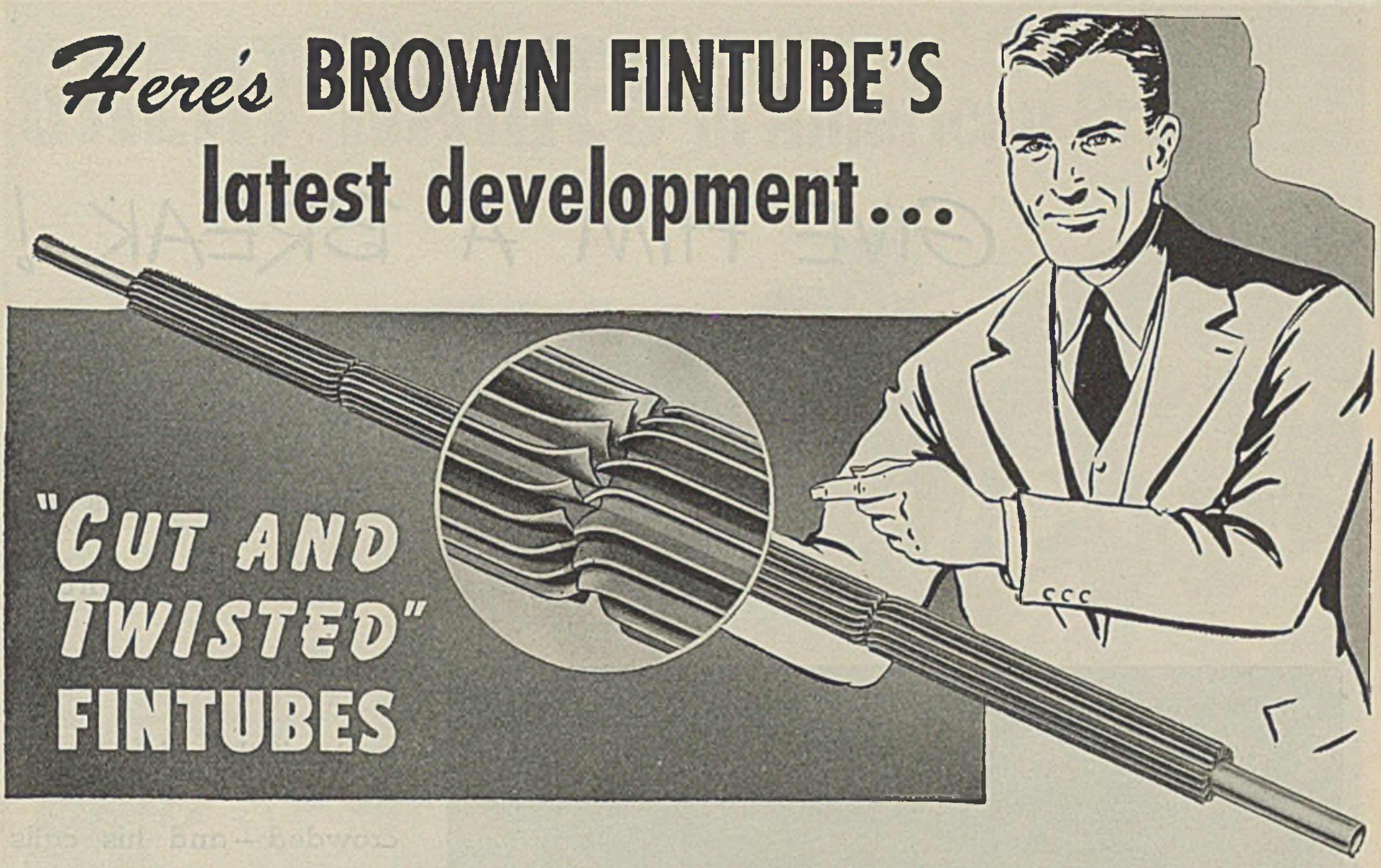

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Brown "longitudinal" and "cut and twisted" Fintubes are available in 6 standard—and many special types—of Brown Fintube Heat Exchangers —one or another of which will meet practically every requirement for effecting heat transfers between liquids and gases, or other commodities having unequal transfer co-efficients . . . Also in exchangers built by a considerable number of other concerns who regularly employ Brown Fintubes as the heat transfer medium in their exchangers. Let us quote on your requirements.

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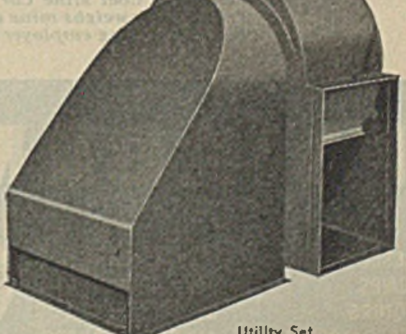

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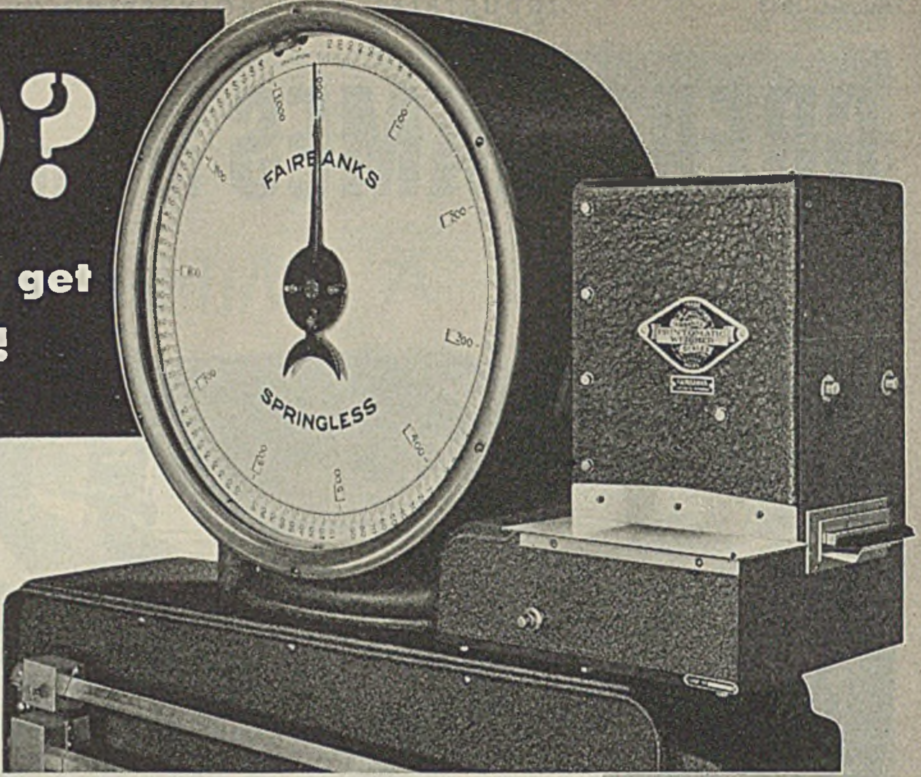

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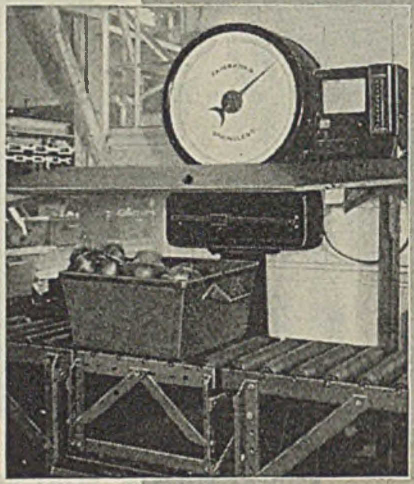
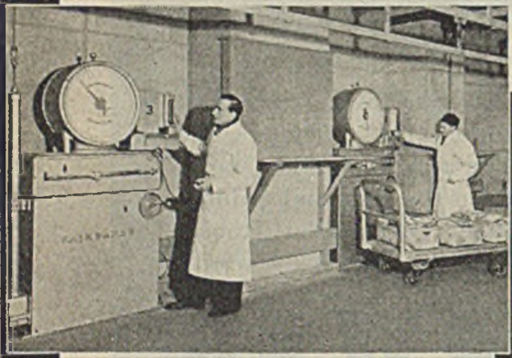
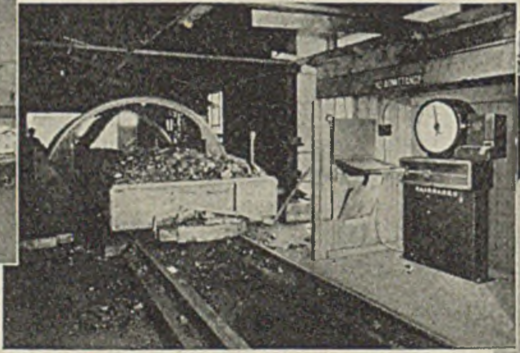


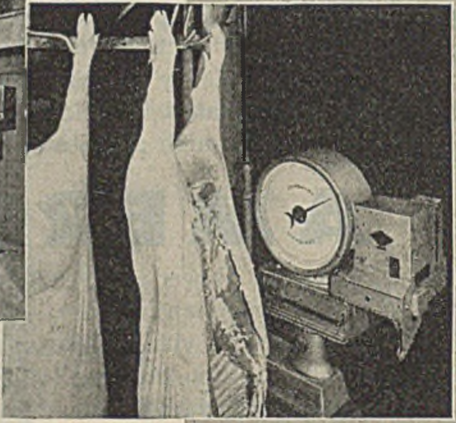
Fairbanks Printomatic Conveyor Scale ➔ keeps printed record of piecework in foundry.



↑ Fairbanks Printomatics recording meat shipments to retailers. Each of 221 different kinds of meat is given a designating number.



↑ Fairbanks Coal Mine Car Scale with Printomatic weighs mine cars in motion, protecting employer and miner.



Fairbanks Portable Dial ➔ Scale with Printomatic weighing and printing records of meat to retailers.

FAIRBANKS-MORSE

FAIRBANKS SCALES

Scales

DIESEL ENGINES
PUMPS
MOTORS
GENERATORS
SCALES

WATER SYSTEMS
FARM EQUIPMENT
STOKERS
AIR CONDITIONERS
RAILROAD EQUIPMENT

ARMY
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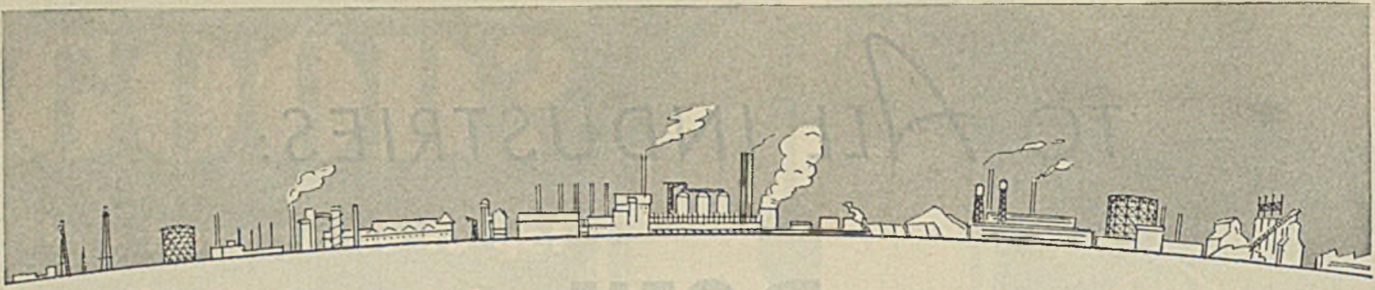
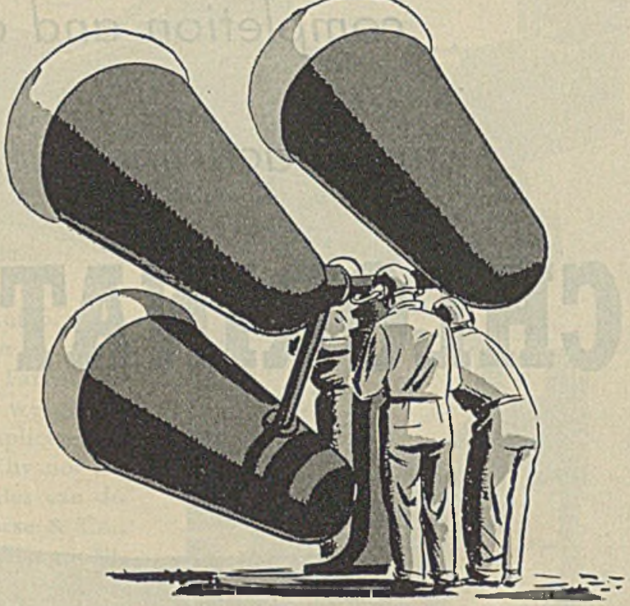




LISTENING IN ON INDUSTRIAL AMERICA

WITH "ears" as big as those of a listening post at the battle front we are catching sounds of a stirring, restlessly active industry—the sounds of plan making for the world stimulating changes of the coming post war era.

New processes, new materials and new equipment are already being developed and perfected to provide for a far higher standard of living. Many of these will be out-growths of developments born of war's necessities in which specialized refractories by Carborundum have played such an important part.

Take synthetic rubber for example. In certain processes "Carbofrax," with its high refractoriness, low spalling tendency and high thermal conductivity has helped to make higher production possible.

The unusual properties of "Carbofrax" are likewise utilized to excellent advantage in the manufacture of some of the materials required in synthetic rubber products to give them the desired characteristics.

In one method by which magnesium is produced, the highly corrosion resistant refractory "Monofrax" plays a vital role. Another magnesium process requires the use of "Carbofrax" because of its high strength at elevated temperatures and rapid heat conductivity.

In the production of zinc and molybdenum the unique properties of "Carbofrax" are again of tremendous importance in increasing output—reducing operating costs.

Thus, it is by no means surprising that we have our ears tuned to the plans for tomorrow—listening for word of new processes in which the use of Carborundum Brand Super-Refractories will undoubtedly prove of great value.

If your process—either present or planned—presents a refractory problem, we would welcome an opportunity of discussing it with you.

REFRACTORY
CARBORUNDUM
PRODUCTS

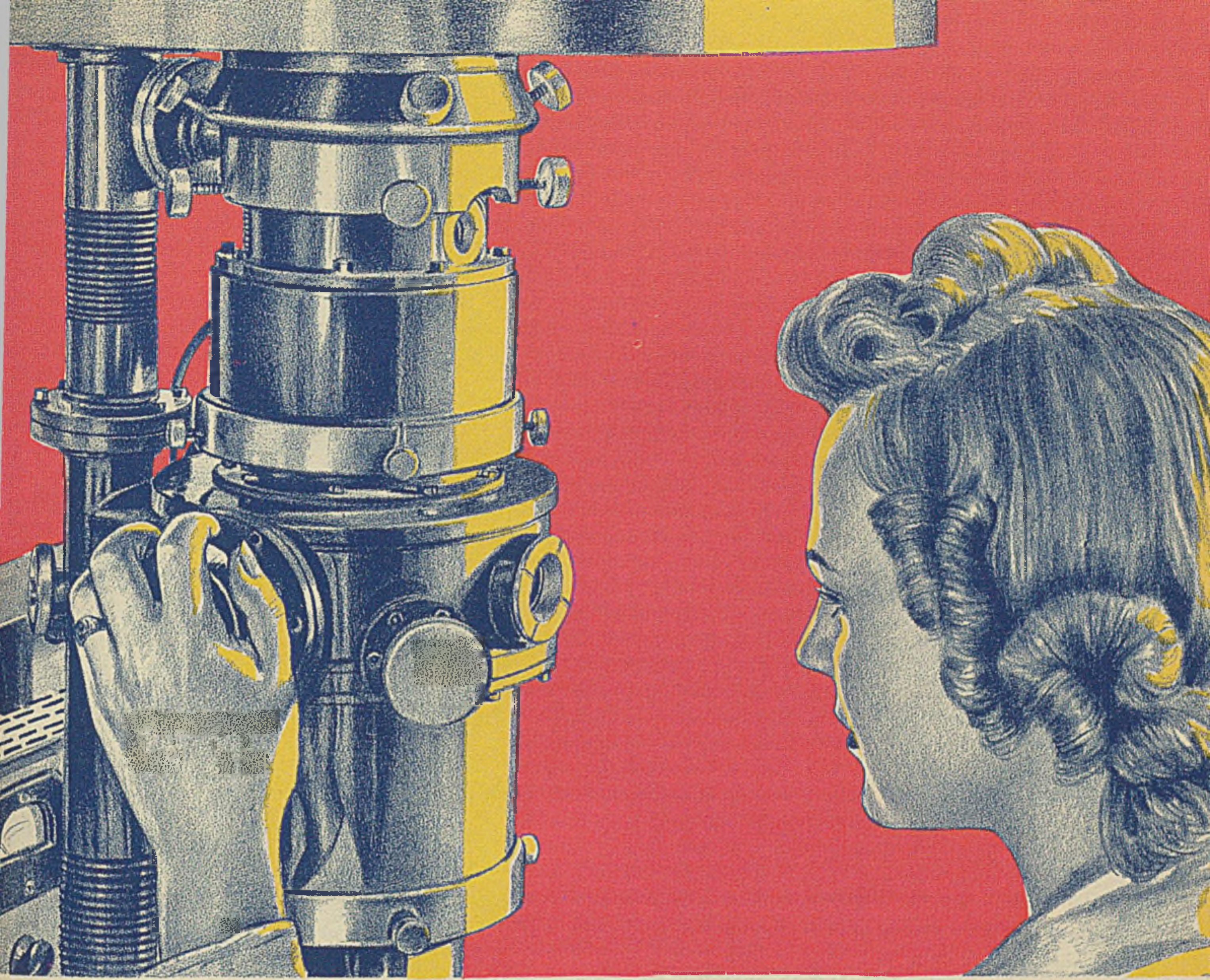
THE CARBORUNDUM COMPANY • PERTH AMBOY, N. J.

REG. U. S. PAT. OFF.

Refractory Division

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

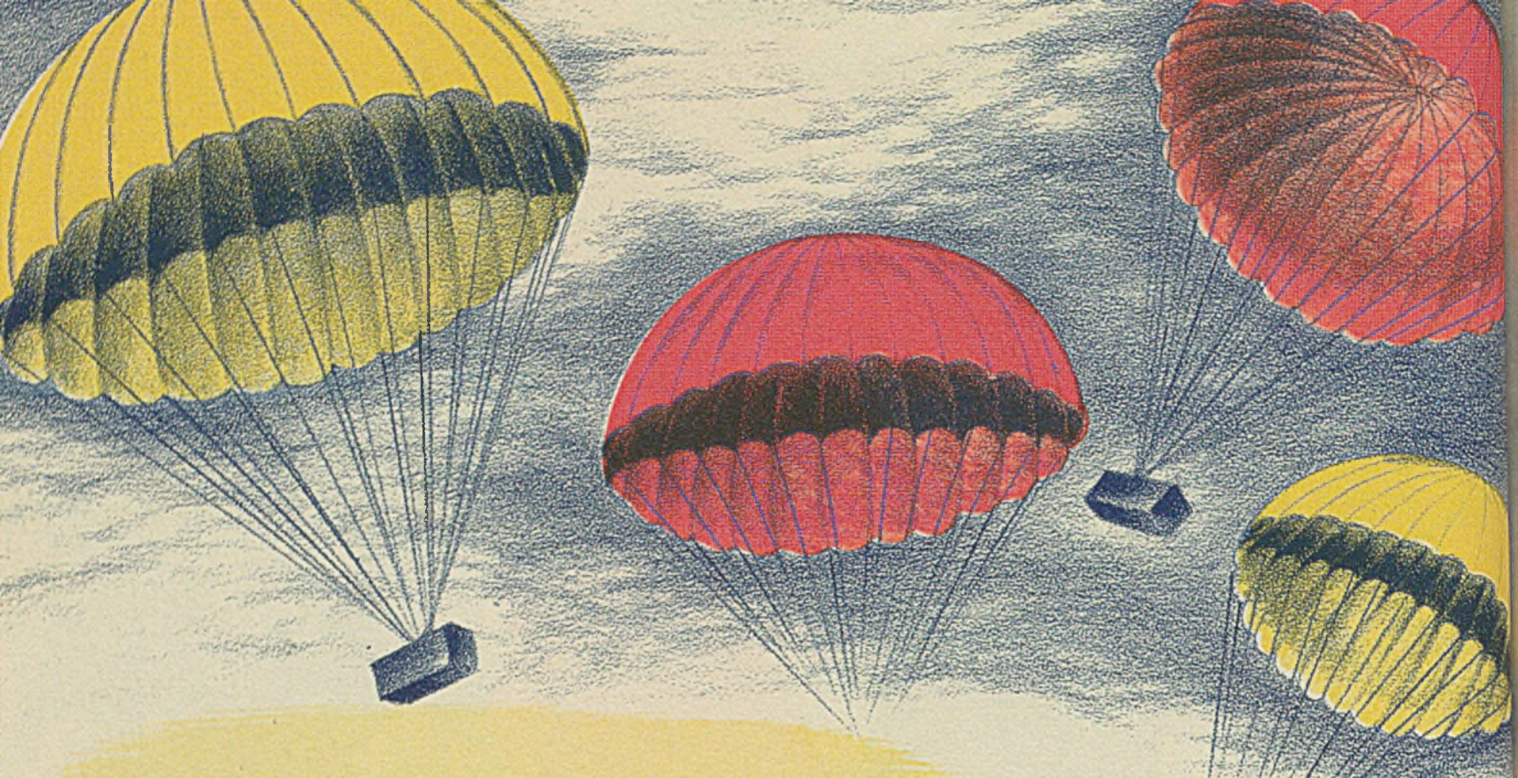
(Carborundum, Carbofrax and Monofrax are registered trade-marks of and indicate manufacture by The Carborundum Company)



Chemical Riddle-Buster

TODAY, this electron microscope at the Hercules Experiment Station is helping to broaden the horizons of chemical knowledge. With super-revealing power, it brings into sharp definition a completely new realm of chemical and physical phenomena.

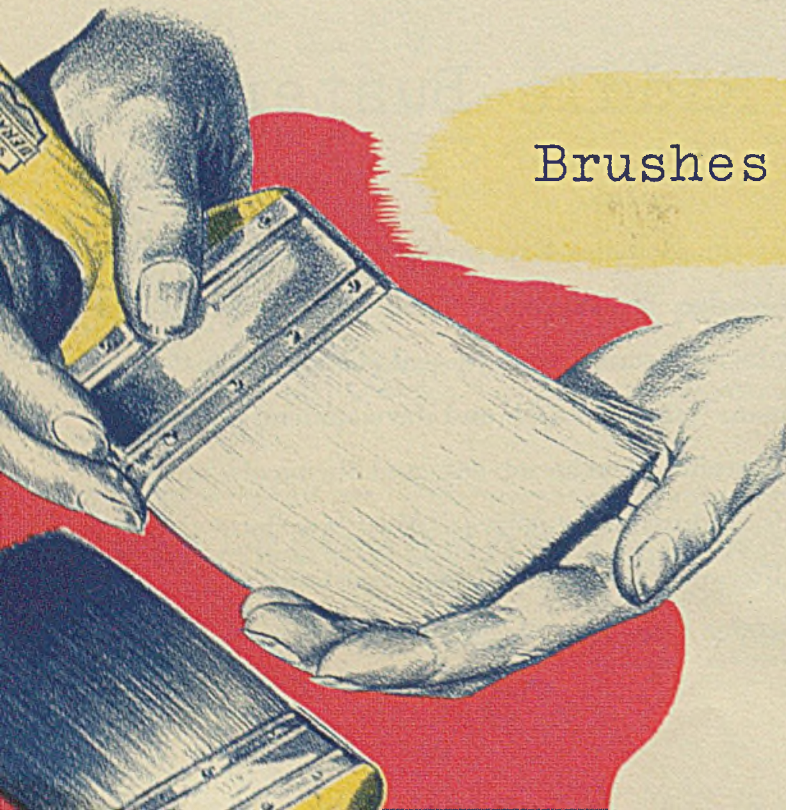
This work, correlated with our many other research and development projects, is improving all of our products—rosins, resins, terpene solvents and chemicals, cellulose derivatives, paper-making chemicals, industrial explosives. May we share these improvements with you? For literature, information, and assistance on specific problems, write Hercules Powder Company, Wilmington, Delaware.



Parachutes of Rayon!

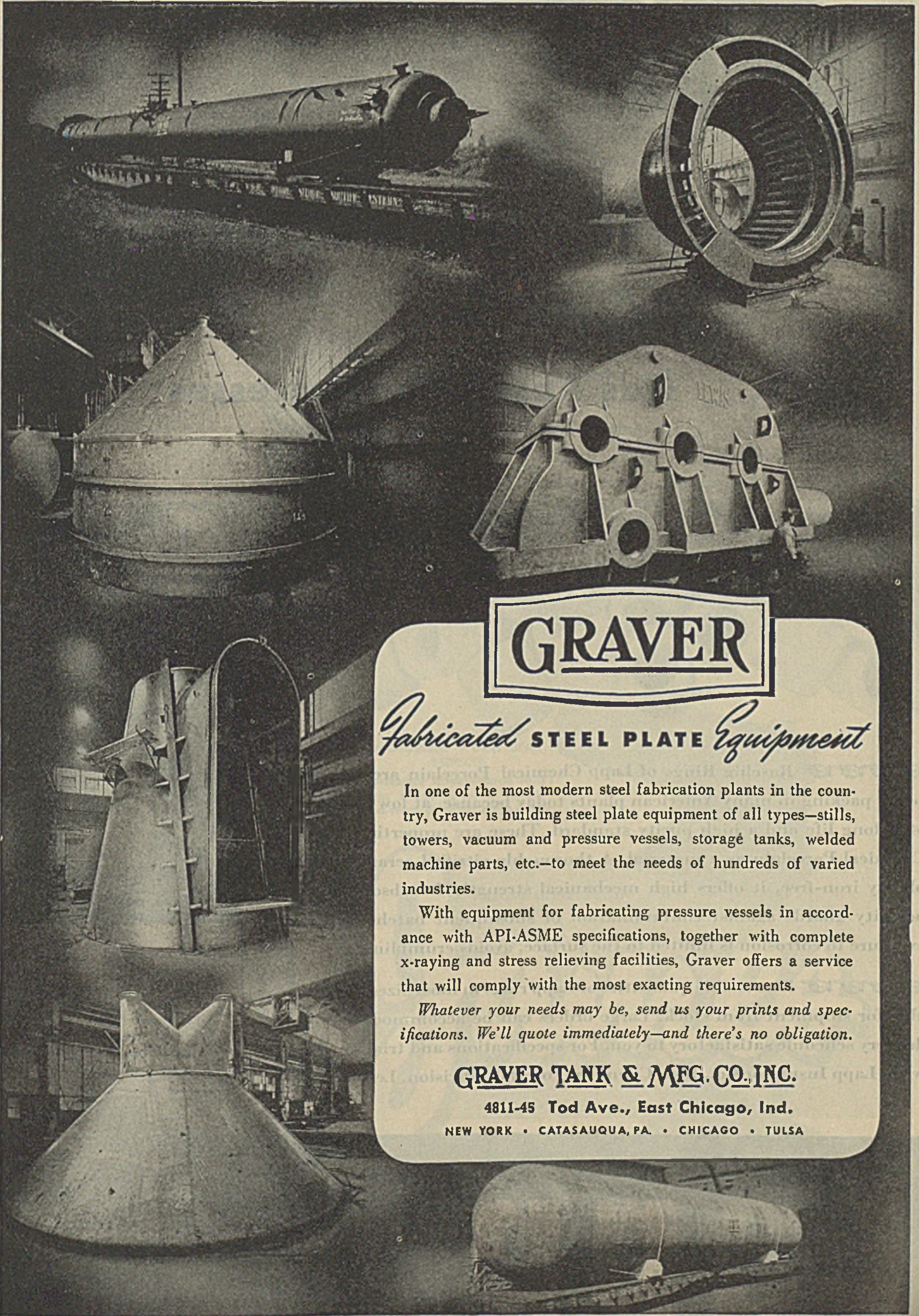
Aerial delivery parachutes, capable of transporting loads as heavy as 300 pounds, are now being made of a new-type, extra-strength rayon. The parachutes are of different colors . . . each color denoting the contents of the cargo, such as food, fuel, water, clothing, medicine, or other vital supplies. The finished rayon used in many of these parachutes is made from Hercules Chemical Cotton and has the unusual property of increasing its strength in direct proportion with the suddenness of the applied load. This unique property is invaluable, also, in the production of the Army's famous tires for combat vehicles and airplanes. Additional development work is now being conducted for other war uses. Further data are available on request.

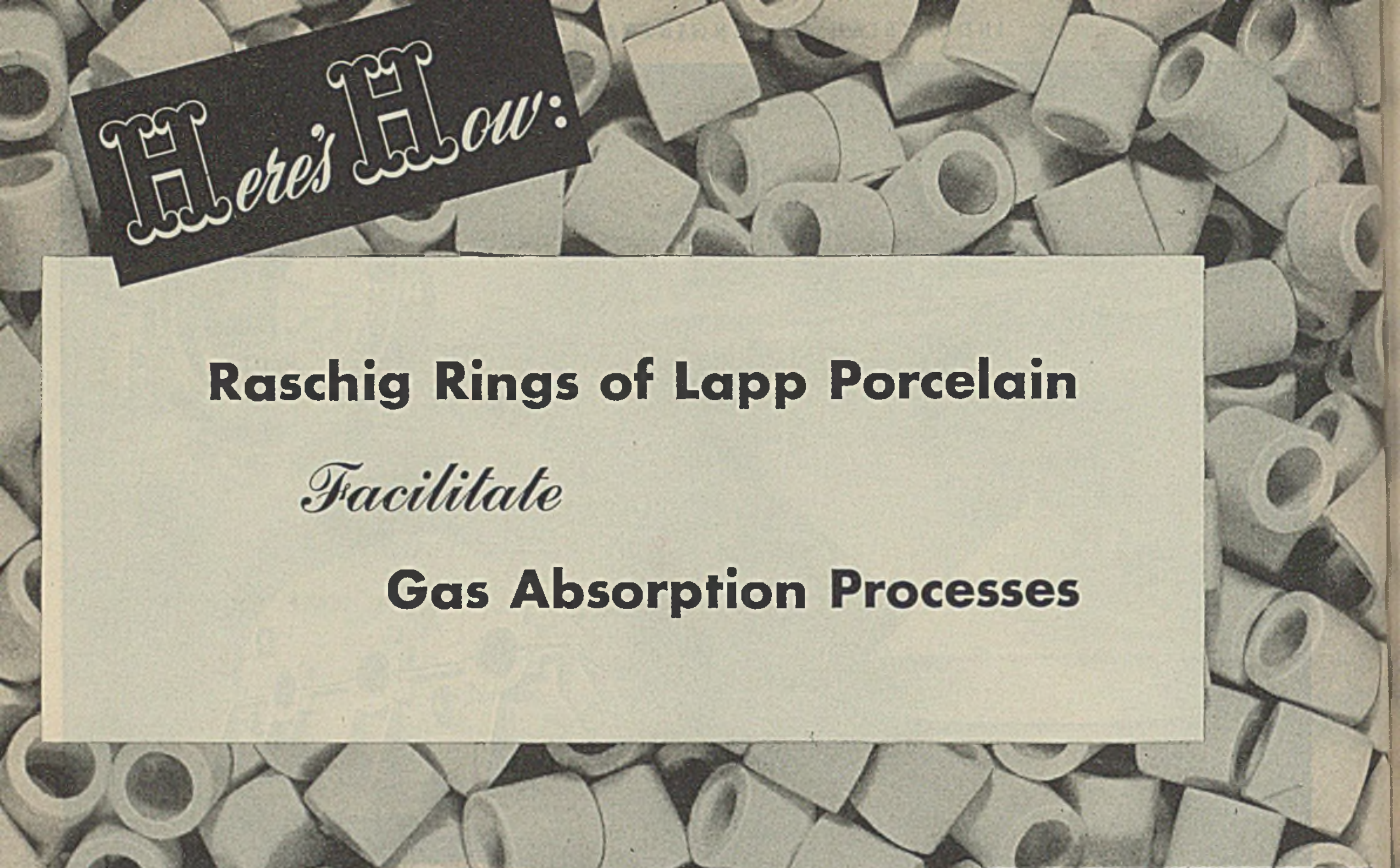
Brushes with Chemical Bristles

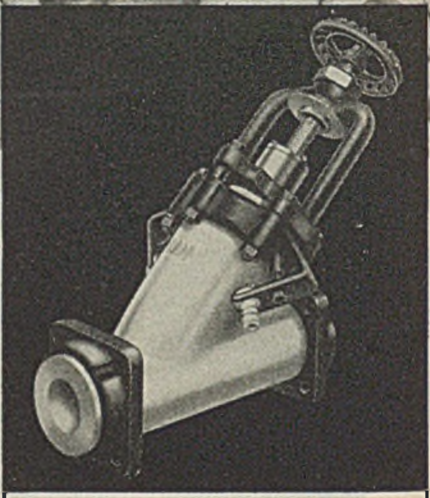


To replace the time-honored hog bristles in paint brushes, bristles of rayon threads coated with cellulose acetate are being used.

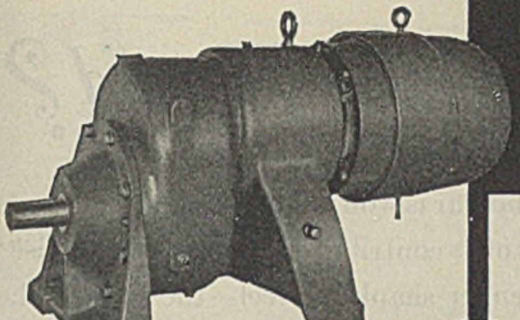
Resistance to oils, flexibility, and toughness are important virtues cellulose acetate offers to paint brush bristles. These features plus economy, lightweight, stability, clarity, and ease of fabrication may suggest that cellulose acetate is a material you should investigate now. Write to Cellulose Products Department, Hercules Powder Company, Wilmington, Delaware.







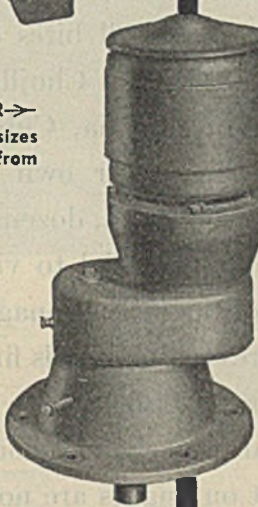
MOTORIZED HELICAL REDUCER
Horizontal drive—made in 13 sizes in ratios of 1¼ to 9½:1 and from ¾ to 50 horsepower.



D.O.JAMES MOTORIZED SPEED REDUCERS

ARMY E NAVY

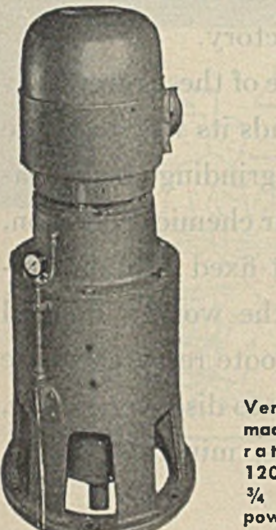
MOTORIZED HELICAL REDUCER→
Vertical drive—made in 13 sizes in ratios of 1¼ to 9½:1 and from ¾ to 50 horsepower.



SAVE ESSENTIAL AND VALUABLE SPACE

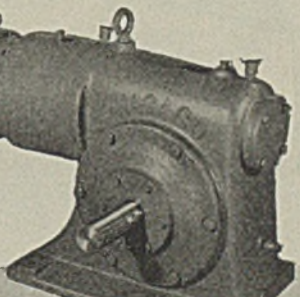
War time requirements make the D.O.James Motorized Reducers a very important *Must* in solving and meeting the power-saving needs of modern industry. Their accessibility and compactness make them most desirable when floor space is limited. Their soundness of design and manufacture insures maximum efficiency with minimum maintenance.

D.O.JAMES MANUFACTURING CO.
1140 W. Monroe Street Chicago, U. S. A.



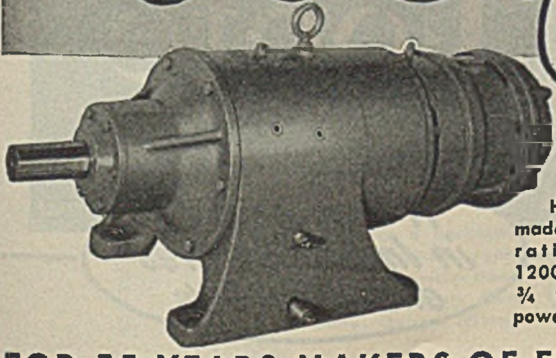
MOTORIZED PLANETARY REDUCER
Vertical drive — made in 35 sizes in ratios of 10 to 1200:1 and from ¾ to 75 horsepower.

MOTORIZED WORM GEAR REDUCER
Horizontal drive—made in 11 sizes in ratios of 6 to 80:1 and from ⅛ to 50 horsepower.



Established 1888

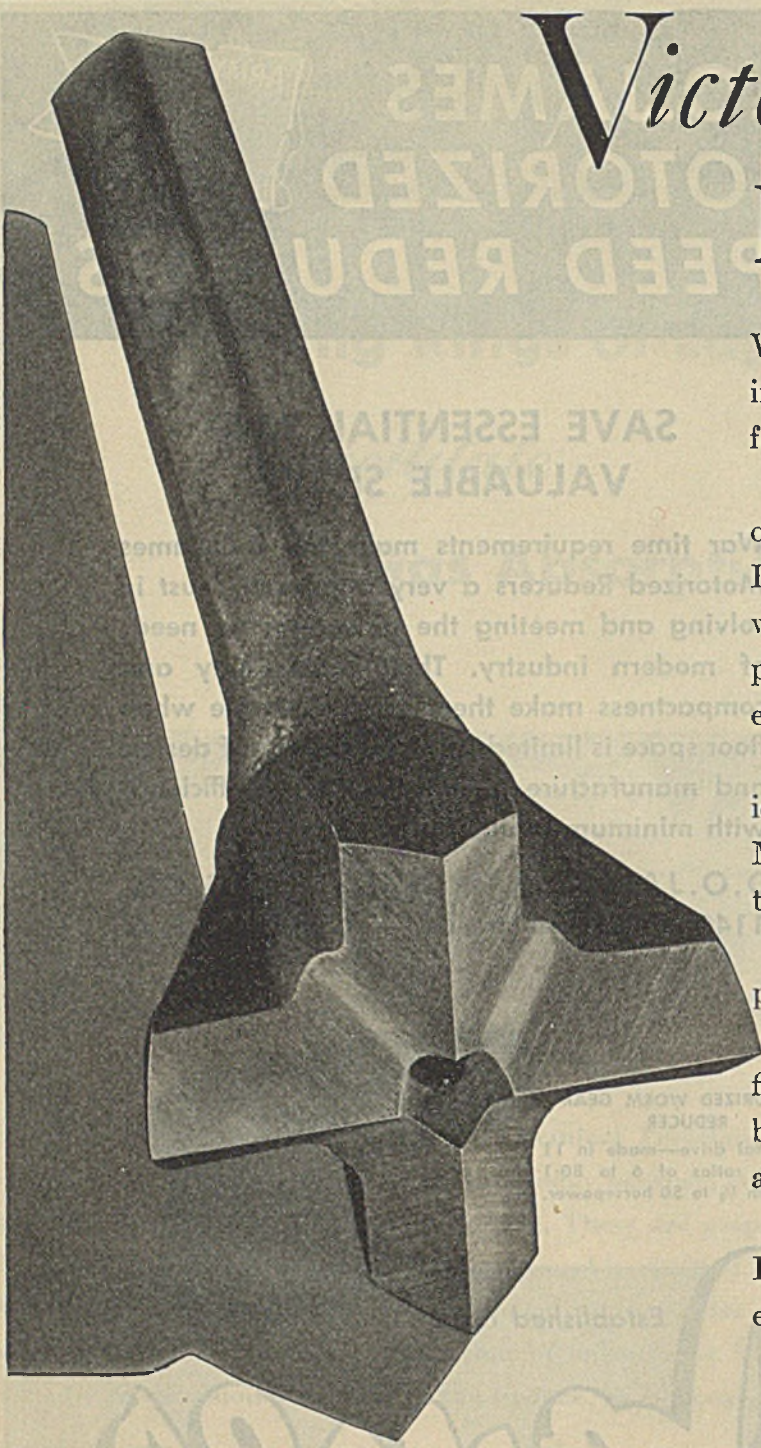
D.O.James



MOTORIZED PLANETARY REDUCER
Horizontal drive, made in 35 sizes in ratios of 10 to 1200:1 and from ¾ to 75 horsepower.

MOTORIZED WORM GEAR REDUCER
Vertical drive — made in 11 sizes in ratios of 6 to 80:1 and from ⅛ to 50 horsepower.

FOR 55 YEARS MAKERS OF EVERY TYPE OF GEAR AND GEAR REDUCER



Victory's ...— Magic Wand?

When the war is won, and victory is reckoned in terms of its contributors, save a pat of praise for a slender shank of steel—the rock drill.

The rock drill bites off the tungsten-tin ores of Bolivia's Chojlla region, chews out Brazilian zirconia, Cuban manganese, and wrests from our own and many another picturesque land, dozens more of the earth's elements essential to victory.

A considerable tonnage of these rarer, critical ores and minerals finds its way to Foote Mineral Company for grinding, beneficiation, or processing by our chemical division.

Yet our sights are not fixed only on supplying and improving the world's mineral treasures. Every day Foote researchers are finding, or helping others to discover, newer, better ways to put ores, minerals, metals and chemicals to work.

If you are interested to know whether Foote products, processes or research can benefit you, make a point of writing to us today.

WILL STRONTIUM SALTS ANSWER YOUR $64 QUESTION?

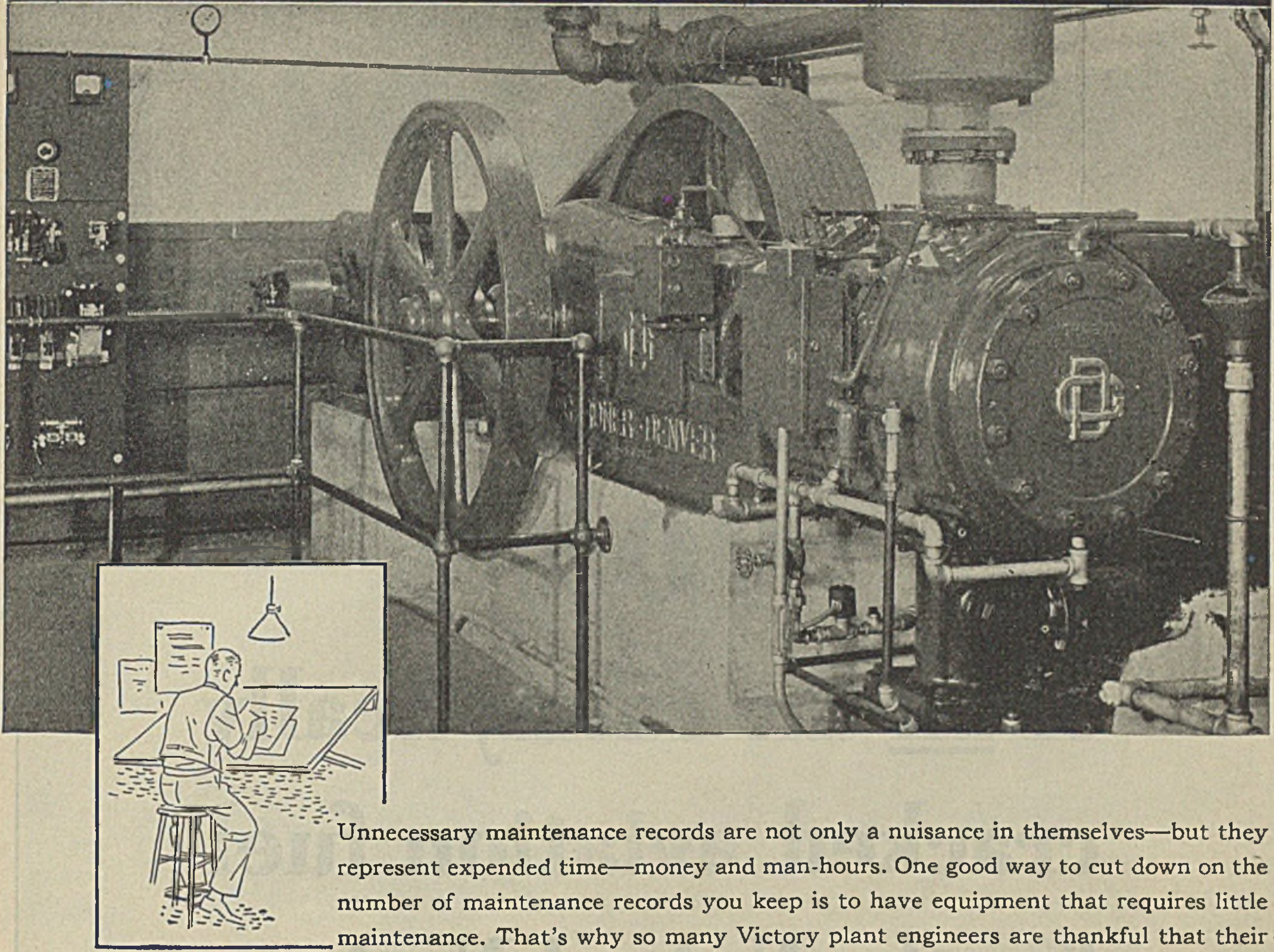
If you should ask your non-technical friends what strontium salts are, you would probably draw a blank expression. They aren't well known; not nearly as well as they should be *and will be* after the war. It's no military secret that strontium is an essential ingredient of tracer bullets. But persistent investigators are finding it will also answer their $64 questions. For instance, strontium chromate is the basis of a new metal inhibitor, strontium salts forecast better ceramic glazes and glasses, strontium sulphate reduces iron and manganese content of sodium hydroxide in the purification of caustic soda. It may answer an important question of yours. If you think so, we're willing to help you find out. Inquiries about the uses or possibilities of strontium salts are invited.

PHILADELPHIA • ASBESTOS • EXTON, PENNSYLVANIA
Home Office: 1616 SUMMER STREET, PHILADELPHIA, PA.
West Coast Representative: GRIFFIN CHEMICAL CO., San Francisco, California
English Representative: ERNEST B. WESTMAN, LTD., London, England

Foote
MINERAL COMPANY

A Step Ahead
in Industrial Ores
and Chemicals

One Good Way to Simplify MAINTENANCE RECORDS



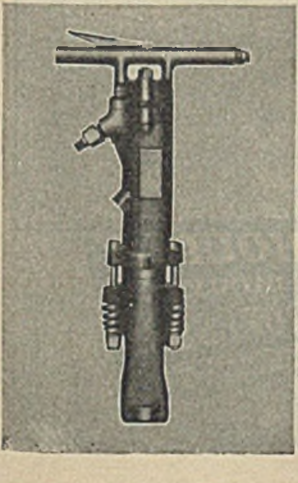
Unnecessary maintenance records are not only a nuisance in themselves—but they represent expended time—money and man-hours. One good way to cut down on the number of maintenance records you keep is to have equipment that requires little maintenance. That's why so many Victory plant engineers are thankful that their compressed air source is the rugged and reliable Gardner-Denver "RX" compressor.

"RX" single-stage horizontal air compressors are staunch machines that take the 24-hour day in stride—yet their horsepower requirements remain unusually low.

THEIR HIGHER EFFICIENCY AND EXTRA DEPENDABILITY ARE THE RESULT OF DESIGN FEATURES LIKE THESE:

1. Long service assured by rugged, dirt-free construction.
2. Increased efficiency due to large and unrestricted valve and port areas and extra large water jackets.
3. "Air-Cushioned," silent Duo-Plate valves virtually eliminate valve breakage—actually become tighter with use.
4. Air output automatically regulated to fit air needs.
5. Easily adapted to any type of drive that fits your plant conditions.
6. Built in capacities from 89 to 1292 cubic feet displacement per minute.

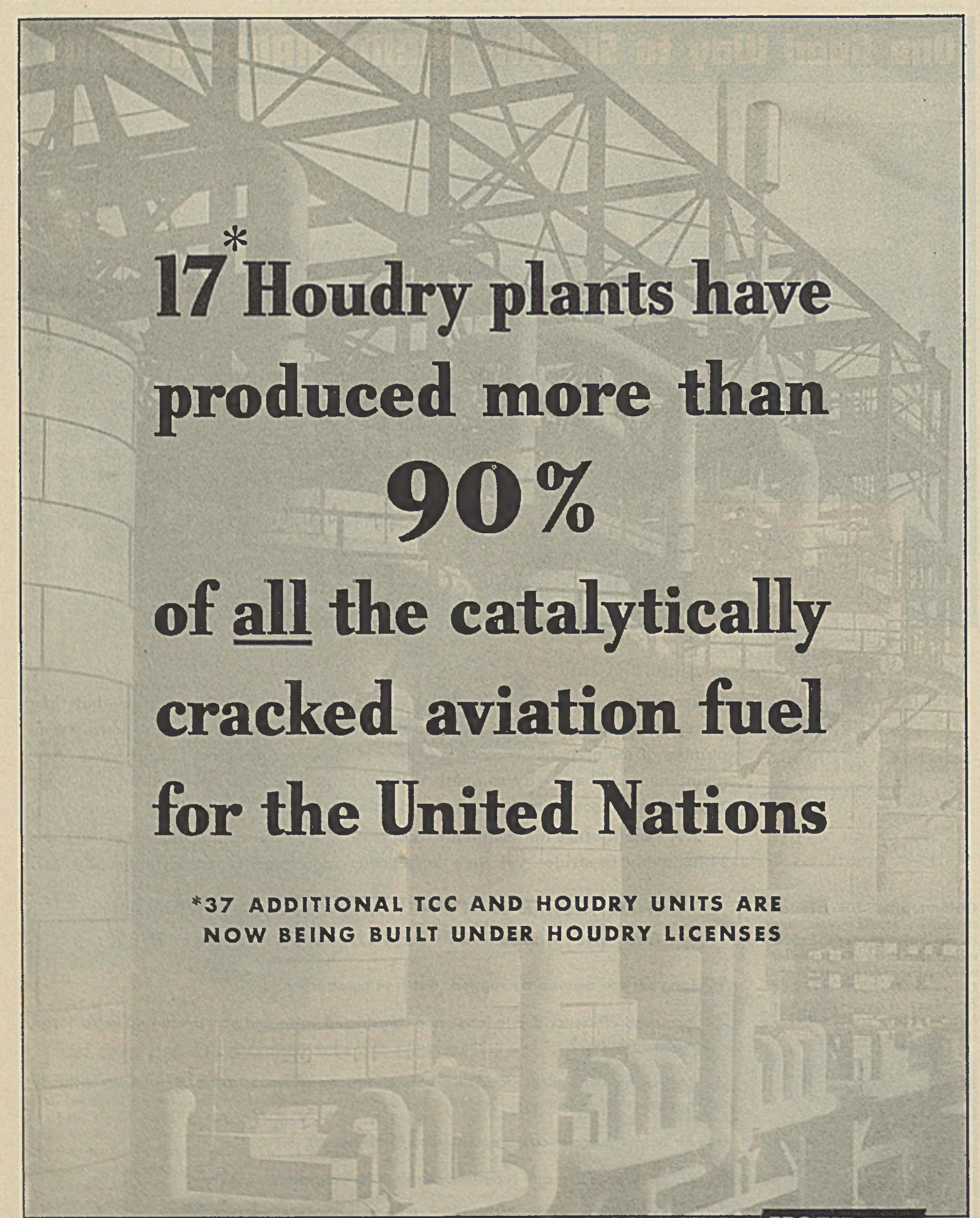
Obsolete machinery foundations — walls — etc., are more quickly demolished when the crew is equipped with powerful Gardner-Denver B-72H Paving Breakers. The B-72H is a hard-hitting tool, delivering slow, heavy blows.

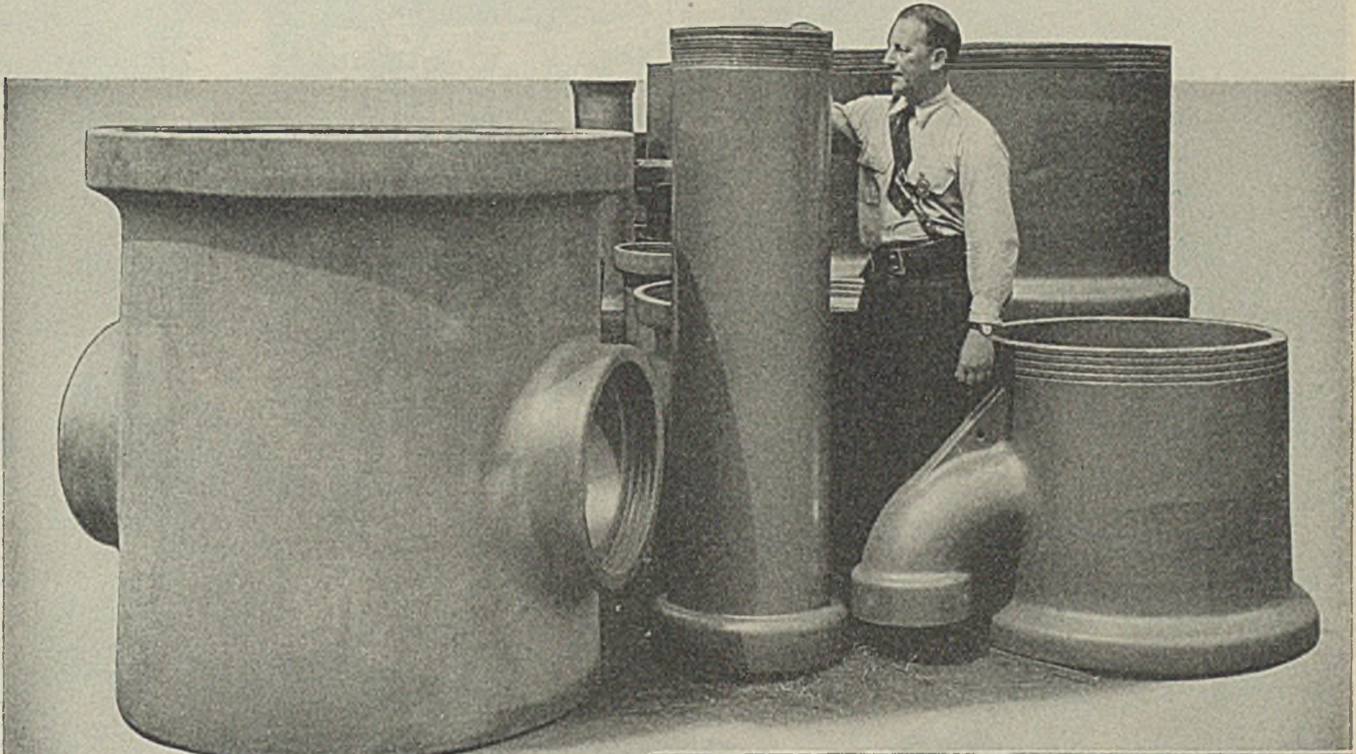


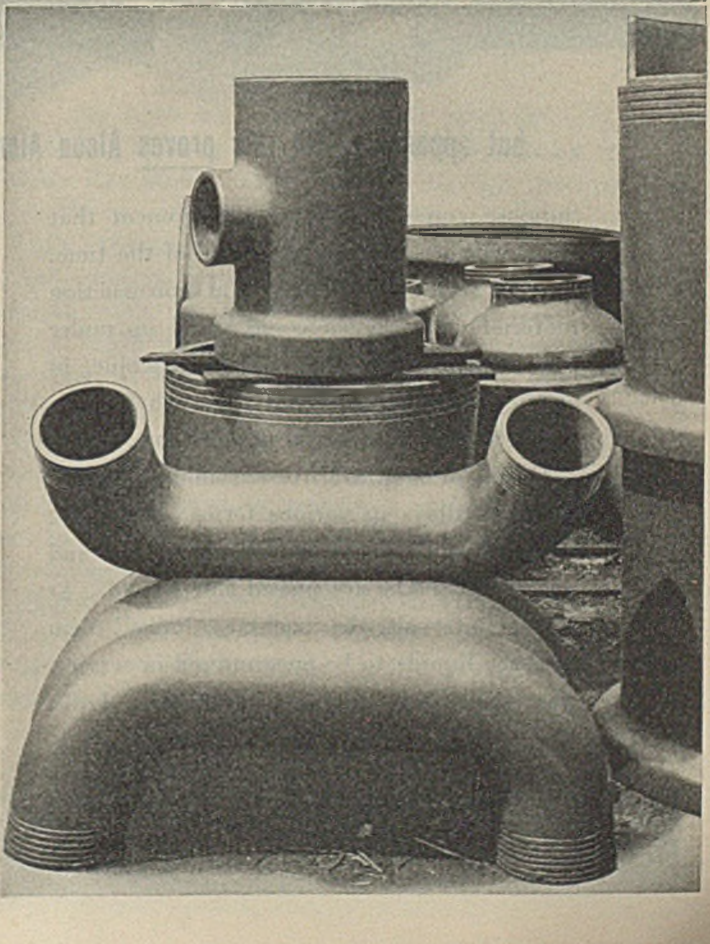
Write for a descriptive bulletin containing complete specifications. Gardner-Denver Company, Quincy, Illinois.

GARDNER-DENVER
Since 1859

GARDNER-DENVER PRODUCTS HELP SPEED VICTORY


17* Houdry plants have produced more than 90% of all the catalytically cracked aviation fuel for the United Nations
*37 ADDITIONAL TCC AND HOUDRY UNITS ARE NOW BEING BUILT UNDER HOUDRY LICENSES





. . . but apparatus like this proves Alcoa Aluminum Alloys before you put them to work

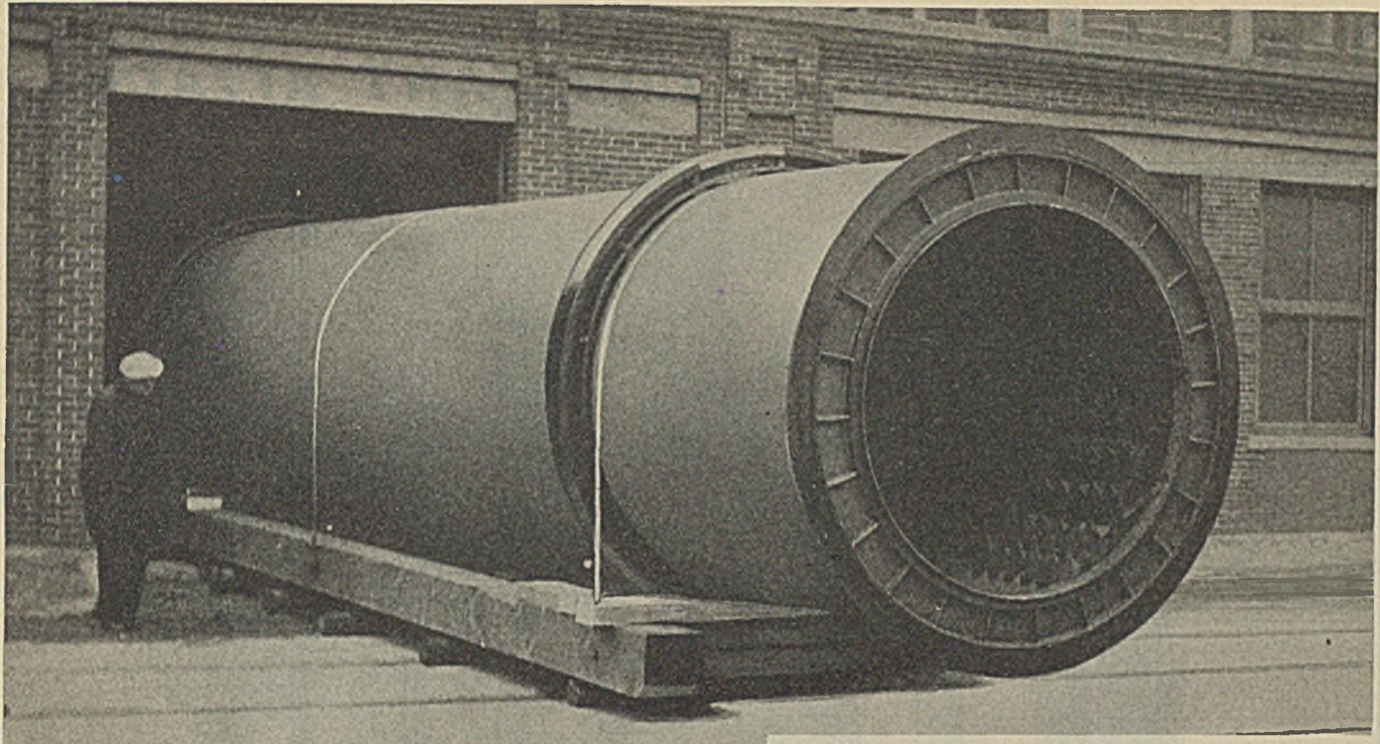
Suppose you were planning equipment that was to be wet by a liquid some of the time. You'd want to be sure the construction material you selected could stand up under such treatment. Well, here's a machine, in constant use at Aluminum Research Laboratories, which does this kind of testing.

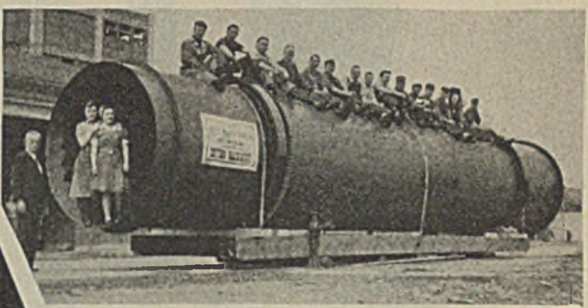
Dozens of samples are tested simultaneously; different alloys in various forms, extrusions, castings, rolled shapes and sheet. Stressed and unstressed pieces are placed side by side. At regular intervals, the machine "dunks" them into the liquids to be encountered in service, then pulls them out. A housing (not shown here) around the machine makes it possible to keep atmospheres at temperatures and humidities simulating service conditions.

Day after day this test goes on, until we can say—"There's the Alcoa Aluminum Alloy best suited to your job."

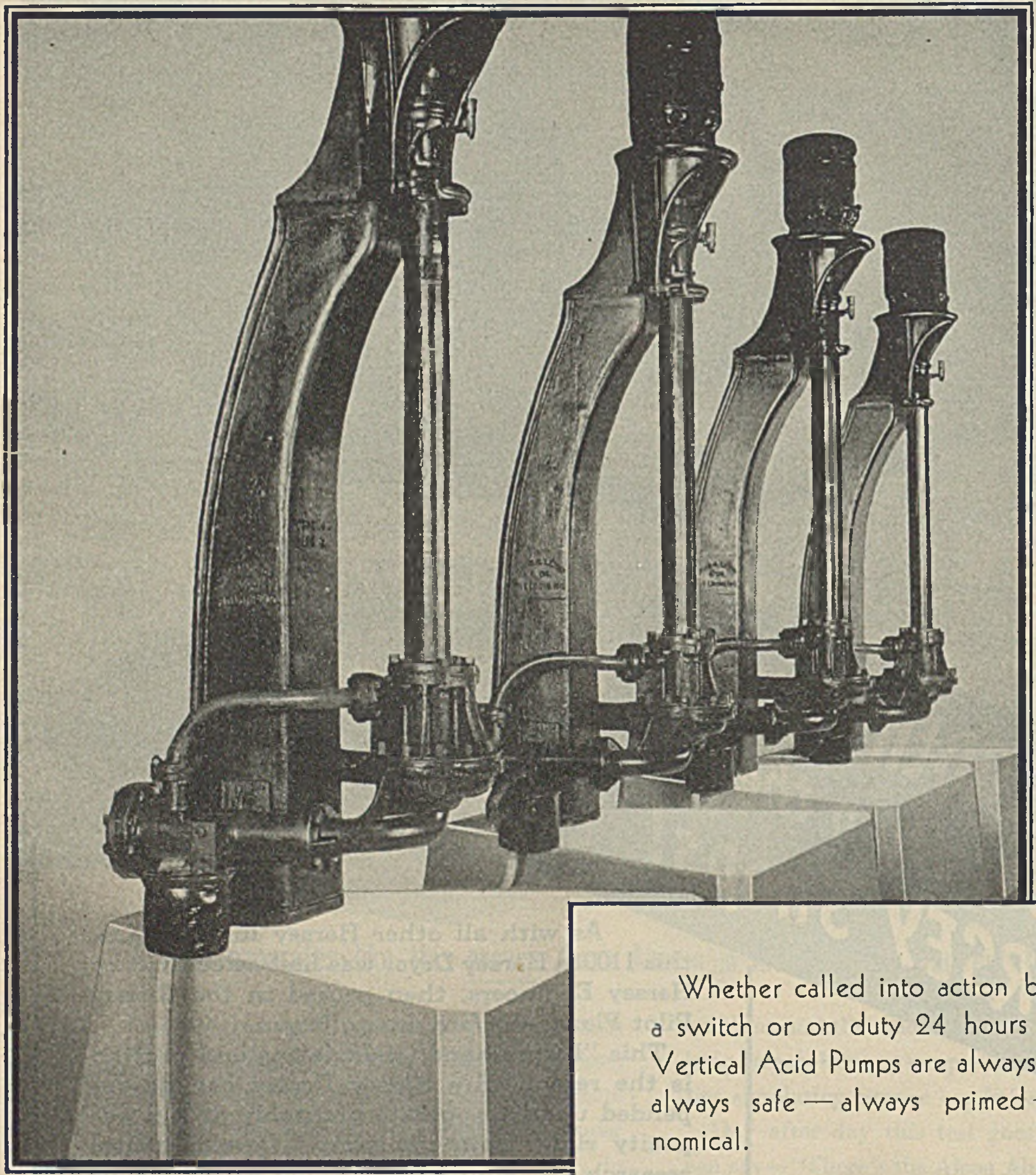
This pre-testing, like dozens of other similar services available to Alcoa's customers, helps account for the better performance of Alcoa Aluminum when it gets on a job. It's another reason why those postwar specifications you're writing should read, "ALCOA ALUMINUM". Aluminum Company of America, 2154 Gulf Building, Pittsburgh, Pa.

ALCOA ALUMINUM





Dependable UNDER CONSTANT ATTACK!



Whether called into action by the throw of a switch or on duty 24 hours a day — Lewis Vertical Acid Pumps are always dependable — always safe — always primed — always economical.

Because all Lewis Vertical Acid Pumps are designed, engineered and built for a ***specialized*** job — pumping H_2SO_4 — they deliver acid every time; they completely isolate the liquid pumped from contact with the shaft packing; they are gravity-fed; they operate on minimum power.

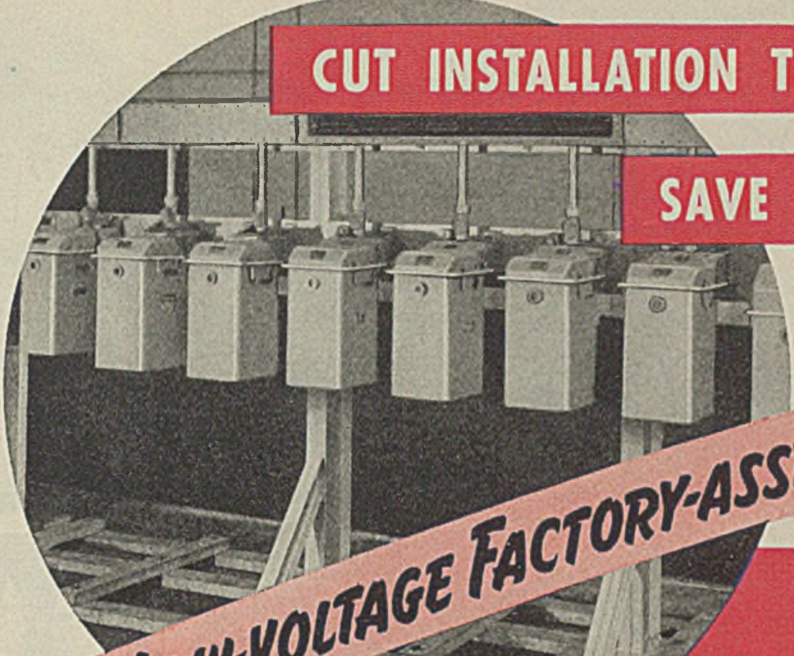
- **MOUNTING — SUBMERGED OR EXTERNAL**
- **OPERATION — INTERMITTENT OR CONTINUOUS**
- **CONTROL — MANUAL OR AUTOMATIC**

CHAS. S. LEWIS & CO., INC. ST. LOUIS, MO.

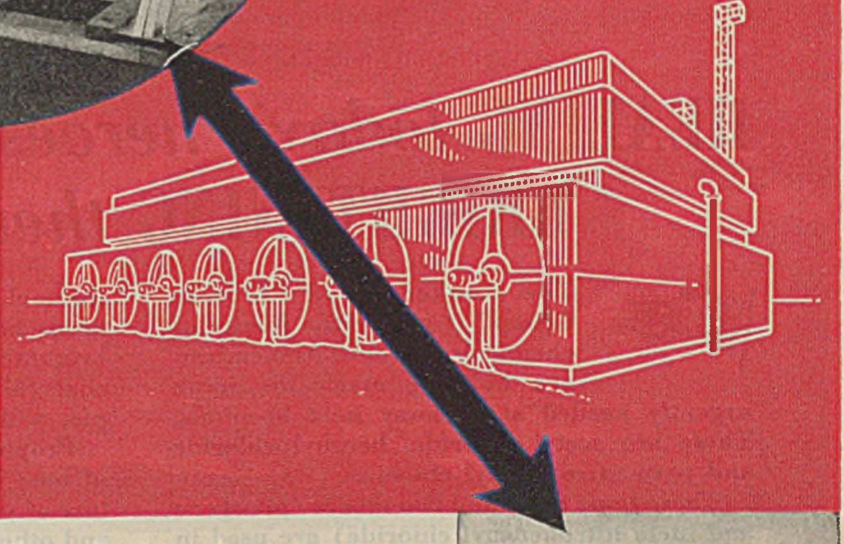
SIMPLIFY LAYOUT PROBLEMS

CUT INSTALLATION TIME

SAVE CRITICAL MATERIAL



WITH LOW-VOLTAGE FACTORY-ASSEMBLED CONTROL

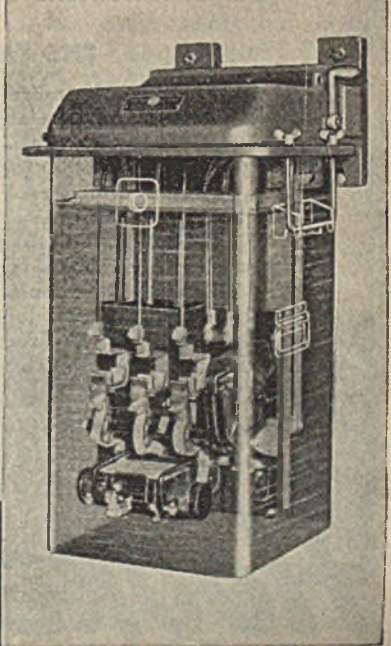


FOR CORROSIVE OR HAZARDOUS GAS LOCATIONS

- Now you can order a complete low-voltage control system as easily as you can order a magnetic switch—saving precious engineering and drafting time on problems of layout. Here's everything you need between feeder and motors in a single control unit.
- Piecemeal installations, which consume valuable time in selecting, ordering, and laying out separate controls, are eliminated with group control. These starters are factory-assembled into a group, which is wired and shipped as one complete unit. You have only to set this compact, space-saving unit in place and connect the incoming line and outgoing motor leads.
- Because they are pre-assembled into groups, these "racked-up" low-voltage controls save the critical materials required for conduit, junction boxes, and special fittings on separately-mounted devices.
- For complete details of the advantages of group controls, and specific suggestions as to where you can apply them, get in touch with our local office, or write General Electric, Schenectady, N. Y.

For cooling-tower fan motors, low-voltage group control is ideal. Other uses are: controlling motors driving blowers, transfer pumps, circulating pumps, and many other equipments used in catalytic cracking, blending and treating, fractionating, and numerous other chemical and refinery processes.

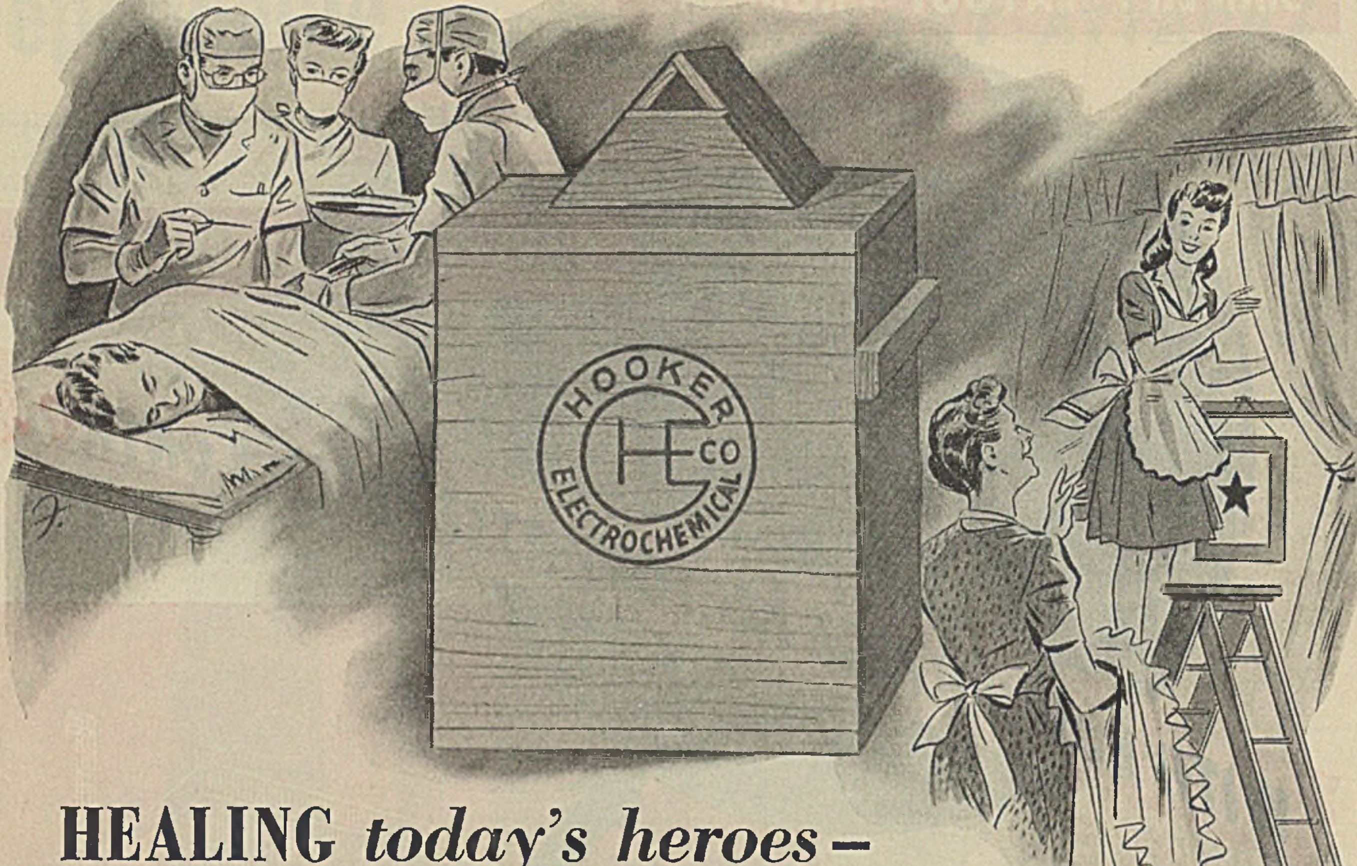
Installed indoors or outdoors, the CR7008, oil-immersed combination motor starter contains, in a single unit, the equipment required for controlling and protecting a motor: (1) A manually-operated circuit breaker for short-circuit protection and disconnecting. (2) A long-lived, dependable magnetic starter for push-button control of the motor.



GENERAL ELECTRIC

676-88-8920

Busy Chemicals for the War and After



HEALING *today's heroes*— BRIGHTENING *their homecoming*

The Hooker "Acid Chloride Group" is a versatile family of chemicals. Three of its members are helping make medicine urgently needed at far-away field hospitals. These are acetyl chloride, benzoyl chloride and para nitrobenzoyl chloride.

These same three and two others (phosgene and meta nitrobenzoyl chloride) are used in the making of synthetic dyes. After military needs have been met, they'll be ready to add brightness to the post-war picture when new, cheerful furnishings and draperies, for example, will welcome home returning soldiers.

Propionyl chloride rounds out this sextet of busy chemicals. It is used in the manufacture of propionamide, esters of propionic acid and other synthetic chemicals.

THE "ACID CHLORIDE GROUP" OF HOOKER CHEMICALS

comprises six of the more than a hundred products developed and commercially produced since the two original Hooker Chemicals. Some of the uses of each are given in tabulated form at right, graphic evidence of how busy these products are.

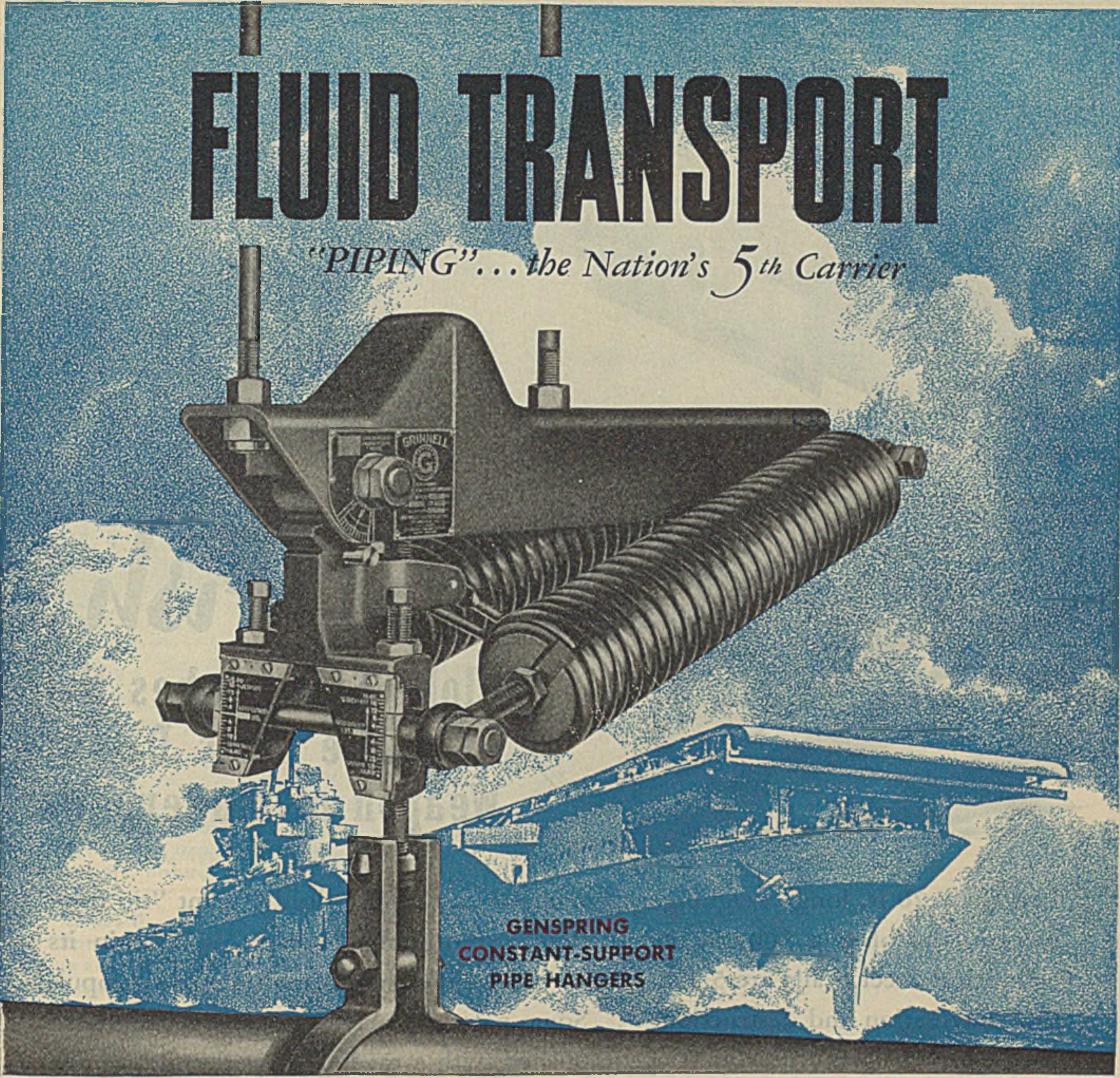
	DYES	MEDICINALS	ORGANIC SYNTHESIS	PERFUMES	PHARMACEUTICALS	WAR & POLICE GASES
ACETYL CHLORIDE	X	X	X		X	
BENZOYL CHLORIDE	X	X	X	X	X	
META NITROBENZOYL CHLORIDE	X			X		
PARA NITROBENZOYL CHLORIDE	X	X				
PHOSGENE	X		X	X	X	X
PROPIONYL CHLORIDE			X			

No table can chart *all* the possibilities the future holds for any chemical today. Research is constantly uncovering new jobs for Hooker products used directly or combined with others in organic synthesis. As new post-war conditions arise, many changes will have been anticipated by this "spadework".

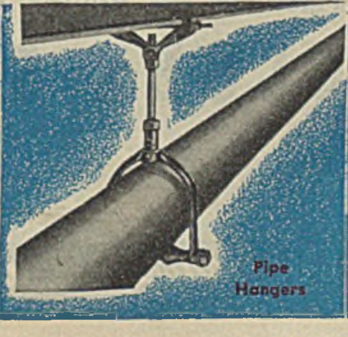
Hooker chemists may be able to combine some of their post-war thinking with the research you have been doing towards filling long-deferred civilian needs as soon as they can be met. A consultation right now will be held confidential and may prove of practical help to you. Remember that "It's never too early to tackle tomorrow".

HOOKER ELECTROCHEMICAL CO.
NIAGARA FALLS, N. Y.
New York, N. Y. Tacoma, Wash. Wilmington, Calif.

HOOKER CHEMICALS




Prefabricated Piping


Pipe Hangers


Pipe and Tube Fittings


Grinnell Saunders Diaphragm Valves

NEED MOTORS FOR Hazardous Areas?

Here's your *most complete* lineup of motors tested and listed by Underwriters' Laboratories, Inc., for service in hazardous locations.

EXPLOSION-PROOF MOTORS

	Polyphase Squirrel-cage	Polyphase Wound-rotor	Single-phase	Direct-current
RANGE OF AVAILABLE* HORSEPOWER RATINGS				
CLASS I, GROUP C For atmospheres containing ethyl-ether vapor, etc.			1/20 to 1/3 hp	1/20 to 1/2 hp
CLASS I, GROUP D For atmospheres containing gasoline, petroleum, naphtha, alcohols, acetone, solvent vapors, natural gases, etc.	1/8 to 1000 hp	1/2 to 250 hp	1/20 to 5 hp	1/20 to 30 hp
CLASS II, GROUP E For atmospheres containing metal dusts—magnesium, aluminum, etc.	1/8 to 75 hp	1/2 to 60 hp	1/20 to 10 hp	1/20 to 30 hp
CLASS II, GROUP F For atmospheres containing coal dust, coke dust, etc.	1/8 to 600 hp	1/2 to 250 hp	1/20 to 10 hp	1/20 to 30 hp
CLASS II, GROUP G For atmospheres containing grain dust, etc.	1/8 to 600 hp	1/2 to 250 hp	1/20 to 10 hp	1/20 to 30 hp

* *In addition to those listed, inert-gas-filled motors in large sizes can be supplied. On special order, we may be able to build certain types and sizes not listed. Ask us for a quotation.*

JUST NAME YOUR HAZARD—in almost every case, there's a G-E motor to meet it, as shown in the table above. In most of these groups and ratings, G.E. was *first* with U. L.-listed, explosion-proof motors. In some of them, General Electric motors are the only ones so listed. If you need a motor for war work in *any* sort of hazardous location, ask us for application aid. *General Electric Co., Schenectady, N. Y.*

GENERAL ELECTRIC

750-216-8030

INDUSTRIAL AND ENGINEERING CHEMISTRY

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

EDITORIALS

A Practical Angle of Postwar Planning

THE chemical industry, with its relatively large staffs of research workers now engaged on problems essential to the successful prosecution of the war, fully recognizes also the serious postwar responsibility it shares with other progressive industries in establishing ways and means of re-employment for the men now serving in the Armed Forces or who are engaged in turning out the sinews of war required by the Army and Navy and by our several Allies.

To do this and to meet wage increases instituted since 1940 will require a substantial increase in production estimated at 35 per cent above the 1940 level. Above all, careful planning will be required, plus considerable research, to solve the many problems of future peacetime production. Normally, chemical projects require from five to ten years from the inception of an idea and its adoption to the operation of an actual commercial-size manufacturing unit.

Planning in industry is normally a continuous process and is vital as regards future and sustained employment. Long-term planning has been slowed down during the past year or two in the interests of the immediate war effort. Practically all chemical companies have half-developed projects now at a point where semi-large-scale or pilot-plant operation is necessary to study process and engineering phases, but all such work was stopped months ago because of shortages of critical materials and personnel.

It now appears reasonable to assume that with the decline in construction of war plants and with the machine tool industry no longer wholly occupied with the task of gearing up industry for production of implements of war, some critical materials will be available and some trained personnel released to employ in postwar projects. The time is here for cooperation between government and industry to the end that a limited amount of critical materials be set aside and earmarked for use in important postwar projects which must be started now, or very soon, if we are to be prepared to employ some 55 million people when hostilities are over. The critical materials needed for such purposes would probably amount to not more than a fraction of one per cent of the United States output of such materials, yet the importance of their use now can hardly be overestimated.

Men in the fighting forces are vitally interested in knowing what constructive steps are being taken on the home front to provide jobs for them on their return. Effective efforts in this direction will stimulate their morale.

Industry is interested in knowing whether it can count on governmental cooperation in this matter of the availability of limited amounts of critical materials.

It is essential that government agencies responsible for distribution of raw materials and equipment properly appraise this situation so that the Government can do its share toward effective postwar planning without interference with the war effort.

Highly encouraging in this picture is a change in regulations agreed to by Washington under date of July 1, 1943, which will permit chemical companies wanting to build pilot plants to do so, provided they qualify under a plan designated as P-43. If firms and projects are qualified under the rules laid down by P-43, pilot plants can be built with a rating of AA-1. It is understood, of course, that this plan applies only to pilot plants and not to construction of full-scale commercial units. Momentarily it is not clear whether P-43 will facilitate not only the construction of pilot plants but also the acquisition of a small amount of chemicals required in the operation of pilot plants when such chemicals are on the critical list. But this is a relatively minor angle that undoubtedly will be quickly clarified.

Knowledge that small amounts of strategic materials are now obtainable for pilot-plant work on postwar problems will act as a distinct stimulus to many companies whose postwar product planning has been dragging because they have felt that they might as well wait until they could be certain materials would be available for such purposes. It certainly will bring no comfort to our enemies to learn that America can continue to be the "Arsenal of Democracy" and at the same time prepare in other than mere words for the postwar period.

Just Who Is Santa Claus?

AT THE moment the American public is getting a few so-called "breaks"—that is, relatively speaking. Washington has decreed that eastern motorists will not be treated as lawbreakers if they use their "A" coupons to get in a summer vacation, provided such rest or "hot" spots are remote from train and bus connections, the ladies are promised a little more rayon coverage for their lower extremities, there are inklings that John Q. Public may get a synthetic tire or two next year, and there are implied promises of less frigid climatic conditions in our homes come Jack Frost and his wintry blasts from the North.

Grown accustomed over the past year or so to government agency directives, requests, commands and countercommands, orders and disorders, the American public is inclined to forget that Washington does not make gasoline, rubber, fuel oil, or rayon—industry does. If the civilian population is about to enjoy in a small measure a few necessities and luxuries now denied them, either for good and sufficient reasons, or because of autocratic and bureaucratic bungling, it is because industry, big and small alike, has risen to the occasion and is producing enough to fill both military and civilian needs. It is industry, not Washington, that in the final analysis is largely responsible, and rightfully so, for the appearance of what might be called the beginning of a "guns and butter" era.

There should be and is sufficient glory for all—Washington, industry, and labor—in the job that is being done to supply our heroic men and women of the Armed Forces and our Allies with the tools of modern warfare and in such tremendous quantities as to strike terror in the hearts of our enemies.

Unfortunately, it has become necessary to place the spotlight of public opinion on the "slide-rule" boys—theorists and left-wingers who are determined to employ the most critical period in American history to revamp the basic structure and political philosophy of this country. As chemists and chemical engineers we are fully acquainted with the limitations of the slide rule.

But Washington is not entirely populated by "slide-rule" boys. The results we are getting in the field and in industrial output are proof of this. Literally there are thousands of sincere and thoroughly capable individuals working most efficiently in the service of their country, men and women who were in government service prior to the war, executives from private industry, scientists, college professors, and lawyers. Many departments and agencies are functioning as smoothly as anyone can reasonably expect under the terrific stresses and strains of all-out war and it is unnecessary to go beyond one group, the Chemicals Division of WPB, with which our industry is most familiar, to find such an example. The members of this division and others like it are working without fanfare, are not interested in personal publicity, nor are they using their positions in the government service to initiate long-term economic and political programs, good, bad, or indifferent in nature. They are concentrating on one job—that of winning the war.

Let us leave the Santa Claus idea where it belongs—with the children—on December 25. Tolerance, understanding, and teamwork on the other hand are virtues to be practiced, not alone on Christmas Day but every other day of the year also. To our enemies and our Allies alike we are giving the distinct impression of being a "house divided". Indeed, this is the one thread of hope that sustains our enemies.

All Washington is not incompetent, uncooperative, and selfish, neither are industry and labor. But perusal of almost any given day's news reports would seem to so indicate. There are reasonable men in all walks of life. Unfortunately, they are not the ones who are getting the lion's share of publicity. Certainly the time has arrived when a few olive branches should be mutually extended by and to the representatives of government, industry, and labor. Name-calling is much less effective than a sincere pat on the back. Overdue, too, is an internal house cleaning by government, industry, and labor alike of those few in the ranks in these respective fields who are zealots to an extent that precludes comparatively smooth cooperation and intelligent appreciation of the many factors involved in winning a war of many fronts and the establishment of a just and lasting peace, not alone among the nations of the world but between capital, management, and labor in this country.

America will never go forward until we compose our supposed differences in the American way, free of foreign ideologies and philosophies. Within this range there is ample opportunity to achieve a glorious future for all.

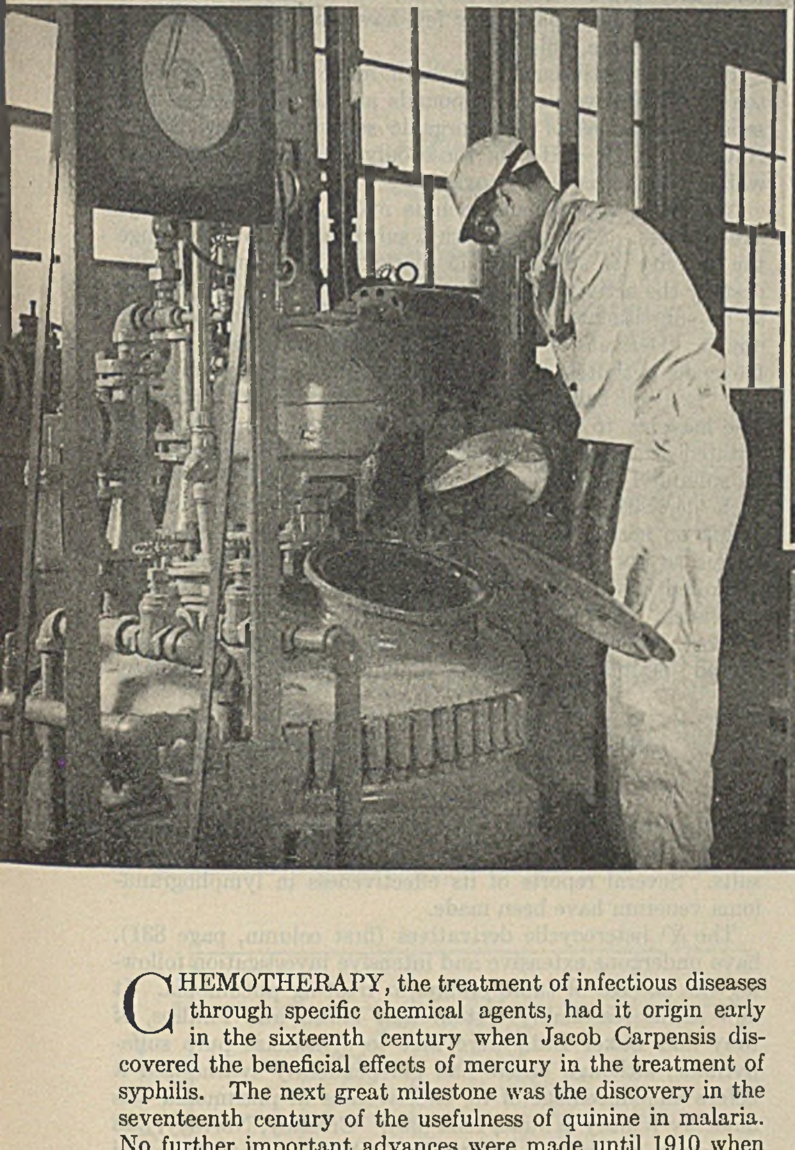
Occupational Deferments

THE attention of chemists, chemical engineers, and the employers of chemists and chemical engineers is called to the statement by the Secretary of the SOCIETY appearing in the July 25 issue of *Chemical and Engineering News* entitled "Occupational Deferment of Chemists and Chemical Engineers—Amended Data and Recommendations" (pages 1206–1209).

The Selective Service System and the National Roster of Scientific and Specialized Personnel are companion units in the War Manpower Commission and the two are cooperating most effectively. The National Roster has appointed an advisory committee with W. T. Read as Executive Officer and as principal group specialist on the staff of the Roster's professional allocation section. A workable and highly efficient procedure has been established. This is clearly explained in the statement appearing in the July 25 issue of *Chemical and Engineering News* and every chemist, chemical engineer in the draft, and all employers should read this statement.

Chemical Side of CHEMOTHERAPY

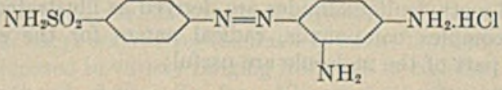
E. H. NORTHEY
Calco Chemical Division, American Cyanamid Co.,
Bound Brook, N. J.



This partial story of contributions of chemistry to chemotherapy relates, for the first time, some of the problems encountered in commercial production of sulfa drugs.

CHEMOTHERAPY, the treatment of infectious diseases through specific chemical agents, had it origin early in the sixteenth century when Jacob Carpensis discovered the beneficial effects of mercury in the treatment of syphilis. The next great milestone was the discovery in the seventeenth century of the usefulness of quinine in malaria. No further important advances were made until 1910 when the chemist, Ehrlich, developed arsphenamine for treatment of syphilis. This development, plus the new knowledge of the causative organisms responsible for many diseases, laid the groundwork for further research, which centered on finding specific chemical agents able to kill the infecting parasite without at the same time killing the host.

This research bore bitter fruit in 1911 when Morgenroth and Levy discovered that Optochin, a quinine derivative, had a curative effect on pneumonia, but the drug caused at least temporary blindness in a large proportion of the patients treated. This was the first case of antibacterial chemotherapy, the organisms of malaria and syphilis being protozoal. The selective staining of different bacteria by dyes stimulated a search to find a dye which would have the power to kill bacteria in the blood stream without harm to the patient. Eventually in 1932 Mietzsch and Klarer (*16*) working in the laboratories of I. G. Farbenindustrie, synthesized such a dye, Prontosil:



$NH_2SO_2-C_6H_4-N=N-C_6H_3(NH_2)-NH_2.HCl$

The medical world and even the Nobel Prize Committee gave Domagk credit for this epochal discovery, largely because publication of his findings on February 15, 1935 (*7*), that Prontosil was curative of streptococcal infections, opened the eyes of the scientific world and led to the avalanche of research which has now revolutionized modern medicine through use of sulfa drugs.

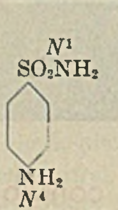
The facts seem to be as follows: After many failures and a growing belief that there was no correlation between *in vivo* and *in vitro* activity, Mietzsch and Klarer decided to insist on animal testing of all the drugs they synthesized. Theirs, also, was the program of substituting a sulfamyl group (—SO_2NH_2) para to the azo linkage in the dyes, which led to Prontosil. This was done on a chemist's hunch since there was no previous information to associate chemotherapeutic activity with this group. The author regards Domagk's role as largely that of a skillful technician carrying out more or less routine tests on the drugs submitted to him; but Mietzsch and Klarer exercised the same creative genius and patient search which had led one of them to the synthesis of Atebrin, the antimalarial, some years earlier.

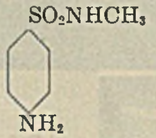
Soon after Domagk's publication, intensive work began at the Pasteur Institute in Paris under the direction of M. Fourneau. Late in 1935 Trefouel, Trefouel, Nitti, and Bovet (*20*) published the important fact that Prontosil was apparently broken down in the body to give sulfanilamide, the active part of the molecule. Subsequent chemical research has concentrated largely on derivatives of this parent compound. About 2500 such derivatives have been described and these are reviewed briefly to show the main classes of these compounds that chemists have synthesized.

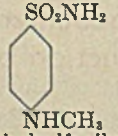
NOMENCLATURE

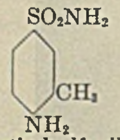
The system of nomenclature developed for sulfanilamide derivatives by the author and associates (*3*) in collaboration with Austin M. Patterson, and now in general use throughout the world, is reviewed here for clarity.

Other groups may be substituted for any of the hydrogens in sulfanilamide:

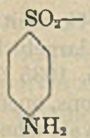

Sulfanilamide

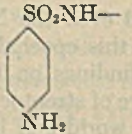

N^1-Methylsulfanilamide

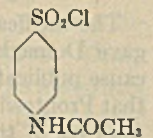

N^4-Methylsulfanilamide


3-Methylsulfanilamide

In naming simple derivatives such as substituted sulfanilamides, it is necessary to distinguish between derivatives of amide and amino nitrogens. Since the sulfamyl group ($—SO_2NH_2$) is the most important functional group, it occupies the 1 position on the ring and derivatives of the amide nitrogen are designated as N^1 substituents. Thus in the simple methyl-substituted sulfanilamides, the N^1, N^4, and 2- or 3-methylsulfanilamides are derived as illustrated. For more complex compounds, radical names for the sulfanilamide part of the molecule are useful:


Sulfanilyl—


Sulfanilamido—


Acetylsulfanilyl chloride

The compound having six benzene rings illustrates the usefulness of all three types of names. By starting with the starred ring as parent, the full name is readily derived.

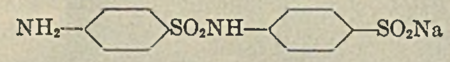
CLASSIFICATION OF SULFANILAMIDE DERIVATIVES

Sulfanilamide derivatives can be most readily classified according to the position of the substituents. Thus we have nuclear, N^1, and N^4 substituents, as well as all combinations of all three. The nuclear substituents can be passed over, since they are all nearly inactive as antibacterial agents; for this reason comparatively few have been made, and also synthesis is more difficult.

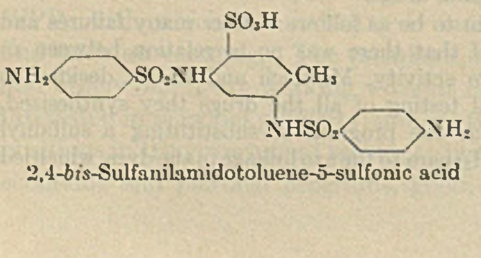
The N^1 substituents have been made in great variety; the most effective new compounds are all members of this series. Examples of N^1 inorganic substituents are HO—, NaO_3S—, and $—NH_2$; of these only the first has activity, while the latter is highly toxic.

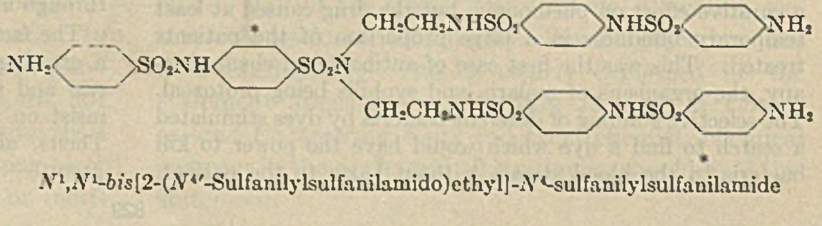
N^1 acyclic substituents include many mono- and dialkyl substituents. Methyl and ethyl substituents do not change the activity of sulfanilamide markedly, but longer chains destroy the activity, probably because of lack of absorption, as do substituents on the alkyl groups such as carboxyl or amino. Derivatives of mono- and diethanolamine have controversial activities but less than sulfanilamide, apparently.

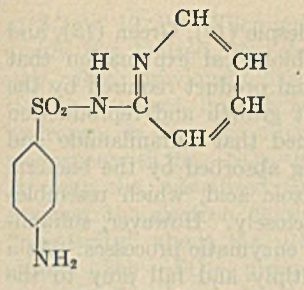
N^1 isocyclic substituents have been made in great variety. One has only to think of a substituted aniline or other substituted aromatic amine, and the chances are excellent that its sulfanilyl derivative has been made. At last count, 180 such derivatives had been described. Conflicting statements on activities have been made for these compounds. As far as the author is aware, none of them is now being marketed, although pharmacological and clinical research continues. N^1-(4-aminophenyl)sulfanilamide was used for a short period in Europe but was withdrawn because it caused peripheral neuritis. Sodium sulfanilylsulfanilate, was thought by Dochez and Slantez to be effective against dog distemper; however, others could not duplicate the results. Several reports of its effectiveness in lymphogranuloma venerum have been made.



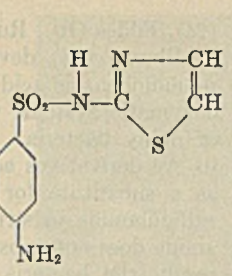
The N^1 heterocyclic derivatives (first column, page 831), have undergone extensive and intensive investigation following the success of sulfapyridine in treating pneumonia. It now seems reasonably certain that Ewins and Phillips, of May and Baker Ltd., were first to synthesize pure sulfapyridine, although others had independently synthesized it before announcement of its effectiveness in pneumonia was made by Whitby in June, 1938 (*22*). Crossley, Northey, and Hultquist (*5*) in this country and Goldirev and Postovski (*12*) in Russia published the fact that they independently synthesized the compound. Still others have been involved in the patent interference which has now been settled with issuance of the United States patent to May and Baker (*9*).


2,4-*bis*-Sulfanilamidotoluene-5-sulfonic acid

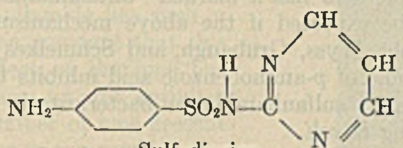

N^1,N^1-*bis*[2-($N^{4'}$-Sulfanilylsulfanilamido)ethyl]-N^4-sulfanilylsulfanilamide



Sulfapyridine



Sulfathiazole



Sulfadiazine

Sulfathiazole was first described by Fosbinder and Walter (*11*) but it was independently synthesized by at least ten others both here and abroad. The United States patent has not yet issued. Synthesis of sulfadiazine involved considerably more difficulty. Roblin, Williams, Winnek, and English first described the compound (*18*). It has proved to be practically the equal of sulfathiazole in potency while involving fewer toxic reactions. The armed forces have adopted it as the drug of choice (*21*) for treatment of most of the common diseases caused by streptococcus, staphylococcus, pneumococcus, and gonococcus, and for oral treatment in preventing or curing infections of wounds and burns. It is also used for application to burns as an ointment, by spraying its triethanolamine solution, or by use of a methylcellulose film containing a high percentage of sulfadiazine.

Many derivatives of these parent ring structures have been made by substitution of various groups and by shifting the point of attachment of the sulfanilamido group on the ring. The following is a list showing the number of offspring in various family trees:

42	sulfanilamido derivatives of pyridine
25	sulfanilamido derivatives of quinoline
38	sulfanilamido derivatives of pyrimidine
83	sulfanilamido derivatives of thiazole, thiazoline, and thiazolidone
18	miscellaneous sulfanilamido derivatives of heterocycles containing one heterocyclic nitrogen
39	miscellaneous sulfanilamido derivatives of heterocycles containing two or more heterocyclic nitrogens

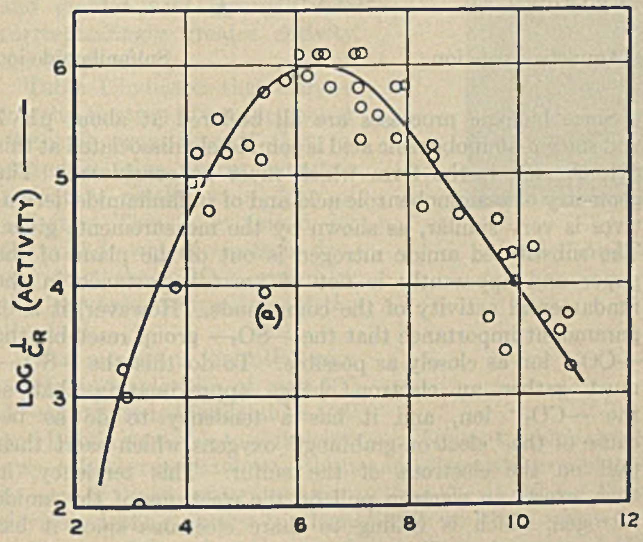
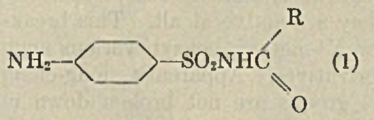
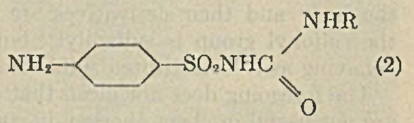


Figure 1. Dependence of Activity on Acid Dissociation Constants of Substituted Sulfanilamides

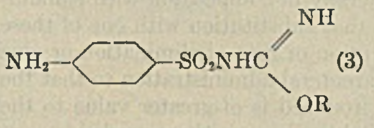
The following are six general types of N^1-acylsulfanilamides:



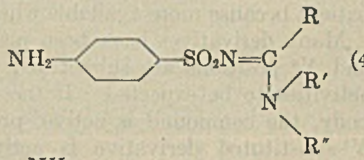
(1)



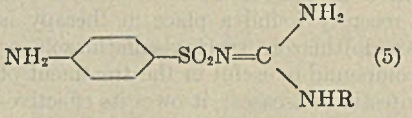
(2)



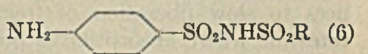
(3)



(4)



(5)



(6)

The N^1-acyl derivatives of sulfanilamide have been well explored. Of these, the derivatives of carbonic acid are most numerous; they include sulfanilyl derivatives of substituted ureas, isoureas, urethanes, thioureas, isothioureas, guanidines, guanylureas, biguanides, etc. (formulas 2, 3, and 5 above)—thirty-five compounds in all. The only commercial product of this group is sulfanilylguanidine, or sulfaguanidine (formula 5 where R = H), first synthesized by Winnek (*23*); it was found by Marshall (*15*) at Johns Hopkins to be poorly absorbed in oral dosages and therefore capable of being given in sufficient quantity to combat bacterial infections of the intestine, particularly bacillary dysentery. This disease has always been the scourge of armies fighting in tropical countries, which makes sulfaguanidine a drug of great importance to our armed forces. The withdrawal of the Japanese from the advance on Port Moresby in New Guinea was blamed on dysentery.

The N^1-acyl derivatives (formula 1) of the fatty acids have been prepared in variety ranging from two to eighteen carbon in length of chain. So far, N^1-acetylsulfanilamide, also known as sulfanilylacetamide, Sulamyd, Albucid, Sulfacet, and Sulfacetamide, is the only one of commercial importance. This is used mainly for treatment of gonorrhea and other urinary infections where its very low toxicity is an advantage.

N^1-Benzoylsulfanilamide is a possible rival of sulfaguanidine, which has received a few favorable clinical reports. In all, fifty-one N^1-acyl derivatives have been described.

Sulfanilylamidines (formula 4) have been made in some variety. Thirty-six have been described, but what little is known of their activity is not promising (*17*).

N^1-Sulfonylsulfanilamides have been synthesized, where the R group is either alkyl (two to twelve carbons), cycloalkyl, or variously substituted aryl (*6*). Most of them are completely inactive. True disulfanilamide has had a number of conflicting reports of its activity, but is probably almost inactive (*4*).

Many N^4-substituted derivatives of sulfanilamide have been made, at last count 534. They follow the same classes as the N^1 substituents, with the addition of azo and anil derivatives. As a result of the study of these compounds, it is now generally agreed that none of them are more potent than sulfanilamide and are, in fact, broken down in the body to give sulfanilamide if they are active at all. This breakdown has been verified for N^4-methyl, benzyl, various acyl, azo, anil, and sugar derivatives. Apparently long-chain alkyl groups and sulfonyl groups are not broken down in the body and their derivatives are inactive, except where the sulfonyl group is sulfanilyl; but these compounds are behaving as N^1-substituted sulfanilamides.

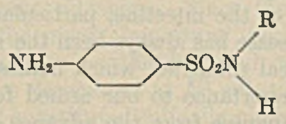
The foregoing does not mean that compounds of this type are not useful in chemotherapy in competition with sulfanilamide, since it is possible that substitution with one of these groups may modify adsorption or rate of elimination or give solubility properties for parenteral administration so that the sulfanilamide ultimately produced is of greater value to the patient because more available when or where needed.

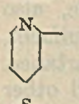
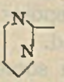
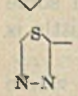
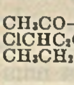
Many derivatives have been made in which both the N^1 and N^4 positions are substituted. In general these follow activities to be expected. If the N^4 group is labile in the body, the compound is active, provided the corresponding N^1-substituted derivative is active. A N^1,N^4-substituted derivative which has recently found a place in therapy is 2-(N^4-succinylsulfanilamido)thiazole, succinylsulfathiazole, or Sulfasuxidine. This compound is useful in the treatment of dysentery and other intestinal diseases; it owes its effectiveness to slow liberation of free sulfathiazole in the lower intestine where absorption is poor so that toxic blood levels of sulfathiazole are not attained.

THEORY OF ACTION

There has been much speculation on how sulfanilamide compounds accomplish their miracles and what physical or chemical characteristics are essential to activity. A theory is now available and has sufficient experimental backing to be widely accepted. The English workers Woods (*24*), Fildes (*10*), Rubbo and Gillespie (*19*), Green (*13*), and McIllwain (*14*) developed the biological explanation that *p*-aminobenzoic acid is an essential product required by the enzymatic systems which permit growth and reproduction of many bacteria. They reasoned that sulfanilamide and its N^1 derivatives acted by being absorbed by the bacteria as a substitute for *p*-aminobenzoic acid, which resembles sulfanilamide in structure very closely. However, sulfanilamide does not substitute in the enzymatic processes. As a result, the bacteria cannot multiply and fall prey to the normal defenses of the body. It has been found that *p*-aminobenzoic acid has a marked "antisulfanilamide" effect as would be expected if the above mechanism were true. For example, Wyss, Grubaugh, and Schmelkes (*25*) showed that one mole of *p*-aminobenzoic acid inhibits the action of 3330 moles of sulfanilamide in bacteriostatic experiments *in vitro* using *E. coli.*

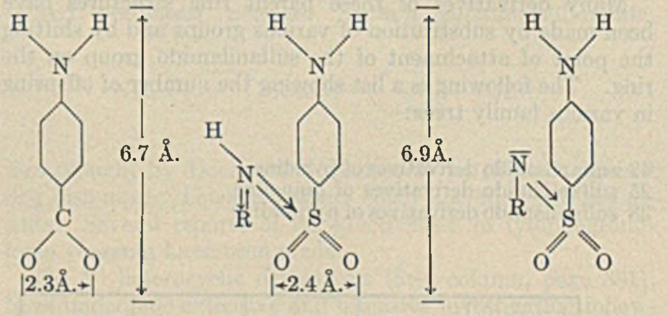
Table I. Effect of Group Substitution on Activity of



R	*Ka*	% Ionized at pH 7	Activity, $C_R \times 10^6$
H—	3.7×10^{-11}	0.03	20.0
CH_3—	1.7×10^{-11}	0.01	30.0
C_6H_5—	2.5×10^{-10}	0.25	3.0
	3.7×10^{-9}	3.5	0.6
	7.6×10^{-8}	43.0	0.08
	3.3×10^{-7}	77.0	0.08
	1.7×10^{-5}	99.0	0.6
CH_3CO—	4.2×10^{-6}	98.0	0.7
$ClCHC_2O$—	1.6×10^{-4}	100.0	10.0
$CH_3CH_2SO_2$—	7.9×10^{-4}	100.0	1000.0

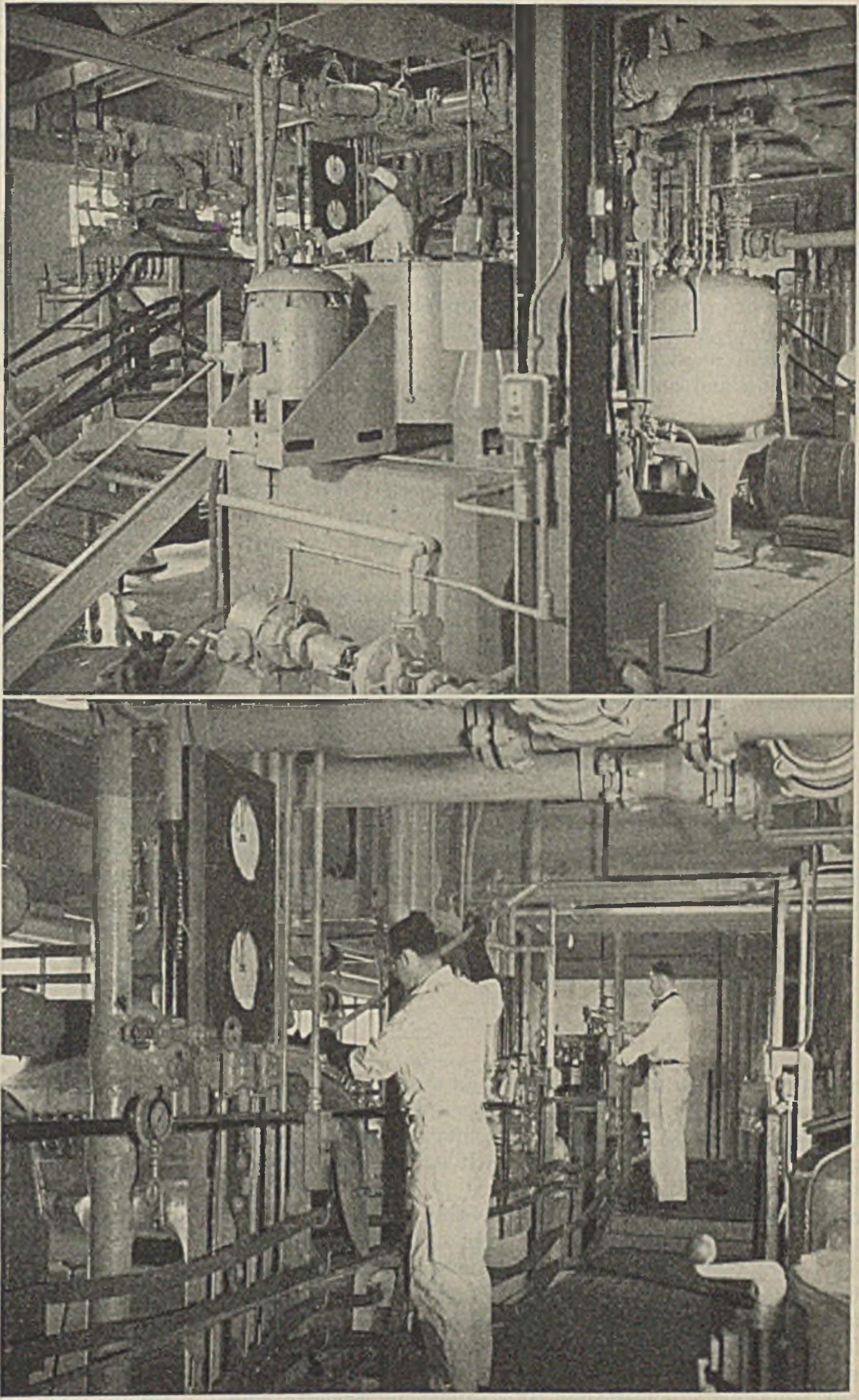
Bell and Roblin (*2*) combined this theory with physicochemical and molecular structural considerations out of which has come the first rational explanation of the relation of structure to sulfanilamide-type chemotherapeutic action. In order to collect data on activities that were as free as possible from misleading factors, *in vitro* tests were made of the minimum molar concentration (C_R) of the sulfonamide required to produce bacteriostasis of *E. coli* grown in a synthetic culture medium. These concentrations are very low for highly active compounds. For example, one gram mole of sulfadiazine will prevent growth of *E. coli* in 1,250,000 liters of culture medium.

This theory can be simply stated by saying that the most active sulfanilamide derivatives are those which approach most closely to the molecular structure and state of distribution of electric charge of the *p*-aminobenzoate ion:



p-Aminobenzoate ion Sulfanilamide ion

Since biologic processes are all buffered at about pH 7 and since *p*-aminobenzoic acid is completely dissociated at this pH, the ion is the form which must be considered. The geometry of *p*-aminobenzoic acid and of sulfanilamide derivatives is very similar, as shown by the measurements given. The substituted amide nitrogen is out of the plane of the paper and apparently is not of great importance in the fundamental activity of the compounds. However, it is of paramount importance that the —SO_2— group resemble the —CO_2^- ion as closely as possible. To do this the —SO_2— must gather an electron charge approximating that of the —CO_2^- ion, and it has a tendency to do so because of the "electron-grabbing" oxygens which exert their pull on the electrons of the sulfur. This tendency, in turn, exerts an electron pull on the electrons of the amide nitrogen, which is willing to share electrons since it has an extra pair. This withdrawal of electrons from the nitrogen means that the nitrogen does not attract the proton as strongly, and as a result sulfanilamide is a weak acid which has an acid dissociation constant, *Ka*,



Small Unit Used in the Manufacture of Sulfa Drugs at the Calco Chemical Division of American Cyanamid Company

◆

of 3.7×10^{-11}. When sulfanilamide has ionized, the electron pair, which previously has been tied in covalent linkage to the hydrogen, is free to enter into resonance with the —SO$_2$— group. It may be visualized as increasing the electron density or "negativity" about the —SO$_2$— group. The —SO$_2$— group then approximates the electrical setup of the —CO$_2^-$ ion. Unfortunately, sulfanilamide has such a low ionization constant that this increased effect of the ions has little influence on its activity, since the number of ions present at pH 7 is low as compared to the un-ionized molecules.

By substituting a group on the amide nitrogen which attracts electrons, two conflicting effects result. Competition is set up for the free electron pair of the amide nitrogen between the —SO$_2$— group and the entering group. It might be predicted that this would lower the electron density about the —SO$_2$— group and decrease the activity. This takes place when the hydrogen on the amide nitrogen has been replaced by another group so that ionization is impossible. However, this effect is overshadowed by the effect of ionization when the hydrogen is present, because the increased competition for electrons of the amide nitrogen means less pull on the proton and a resulting ease of ionization. Thus, by substitution of groups of increasing electronegativity or electron attracting power, derivatives of greater and greater acid strength and correspondingly greater activity are obtained.

Table I indicates that increasing the electron attracting power of the R group beyond that required to give nearly complete ionization results in a drop of activity. This is explained by the withdrawal of electron density from the —SO$_2$— group by the increased competition of the R group.

After measuring ionization constants and activities of over 100 N^1-substituted sulfanilamides, Bell and Roblin were able to plot the curve of Figure 1, which shows a remarkable correlation of activities and dissociation constants in view of the experimental error in $\log 1/C_R$ of ± 0.3. They developed their theory mathematically so that, when the electronegativity of an R group is known, the activity of the compound *in vitro* can be predicted.

It appears that at last a theory is available which permits prediction of the activities of new sulfanilamide derivatives before they are synthesized. This should help channel research into the most promising lines of attack. The fact that a maximum appears in the curve suggests that the maximum activities to be found in sulfanilamide derivatives have already been uncovered. What remains to be done, therefore, is to so modify existing structures as to cut down on undesirable side effects. Unfortunately, these effects are not yet predictable. Sulfadiazine is on the peak of activity curve and exhibits less toxic effects than any other sulfonamide drug of comparable activity, yet it is far from perfect. Its most apparent defect is lack of solubility. This is not important from the standpoint of absorption, which is good but involves complications in elimination of the drug. In people with impaired kidney function, those whose urine is acid, or those who do not have sufficient urinary output, the drug is apt to crystallize in the kidney and cause moderate to severe kidney trouble. This is a particular disadvantage for troops in desert fighting where water supplies are limited and urinary output very low because of surface evaporation. Recent work indicates that solubility troubles may be largely eliminated by adequate dosage of sodium bicarbonate so as to maintain a slightly alkaline urine. The solubility of sulfadiazine and sulfathiazole increases rapidly with pH above 6.5.

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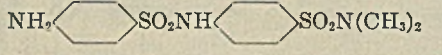

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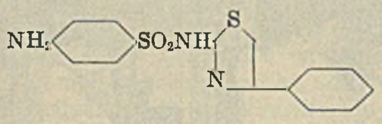
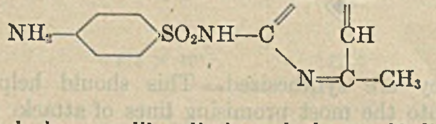


which contains no methyl groups, is an even worse offender.

Acute toxicities are not a good basis for comparison of these drugs because the lethal dose is fifty to a hundred times greater than the therapeutic dose. It is rather the chronic toxicity which counts, and on this basis Sulfamethazine compares much more favorably. Possibly it will prove more useful in tropical countries because of its greater solubility. There are two schools of thought on this point, however. One holds to drugs of low solubility and slow elimination so as to permit maintenance of adequate and constant blood levels of the drug with infrequent dosage; the other, to the more soluble drugs involving less risk of kidney damage, but requiring administration at frequent intervals to give the patient adequate protection from the disease.

Adherents of the first school are intensely investigating sulfamethyldiazine, or Sulfamerazine,



This drug is less readily eliminated than sulfadiazine and appears to be equally active. It seems possible to maintain equivalent blood levels of the drug with half the dosage or twice the interval between doses. With only half as much drug to be eliminated from the body, kidney damage should be less, according to its proponents.

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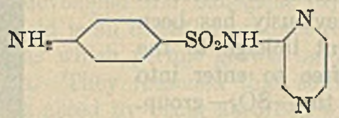

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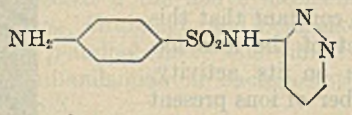

synthesized by Roblin's group (*1*), is highly active *in vitro* on *E. coli* (as active as sulfadiazine), but it has no activity *in vivo* in spite of being well absorbed. This does not contradict Bell and Roblin's theory, which applies quantitatively only to *in vitro* activities measured on *E. coli* grown in a synthetic medium; but it does raise a large question as to why it is not active *in vivo*. This, of course, means that after the chemist figures out just what compounds to synthesize on theoretical grounds, he still has to make them and have the pharmacologist test them thoroughly before he knows they will actually be useful in treating more than theoretical diseases.

The fact that sulfapyrazine has been tested and found as good as sulfadiazine raises the question of why it is not available to the public. The shocking fact is that no one has succeeded in synthesizing it at a reasonable cost. This introduces a phase of chemotherapy which is so obvious that it is often overlooked; that is, someone has to develop the processes and manufacture the drugs before they do the patient any good. The cheaper they can be manufactured, the more good they do, because then more patients can afford to use them.

PRODUCTION PROBLEMS

The author wishes to pay tribute to some of his colleagues for having succeeded in making a number of sulfa drugs, particularly sulfadiazine and sulfaguanidine, available to the public and armed forces in increasing quantities and at lower prices, in the face of serious problems and difficulties. The management is to be congratulated on having had sufficient faith to gamble large sums of money on the extensive research and development which led to proof of the value of sulfadiazine. They then had to invest an even greater sum in the plant to make the drug; this was done in the face of the imminent possibility that a new drug might enter the field which would be even better and could be made for a fraction of the cost of sulfadiazine. Even today sulfadiazine has to go through many costly steps in synthesis.

Praise is due the engineers and construction men who built the plant and have continued to expand it through the trying conditions faced by all wartime construction and multiplied in this case by constant changes in plan; between the time the original plans were made and construction of the first unit was completed, the production demanded of the plant increased fourfold and a fundamental change in process was made. The superintendents and foremen who have borne the burden of 168-hour-a-week production under a backlog of unfilled orders ever since the plant started, deserve special praise for their endurance and for their skill in training new men while constantly increasing production. This has all been done under the adverse conditions of wartime man-power shortages, which are now better stated as women-power shortages. The chemical problems which were solved are perhaps of most interest. Because of government secrecy orders on the more recent developments, only part of the story can be told now.

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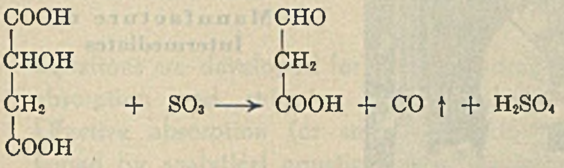
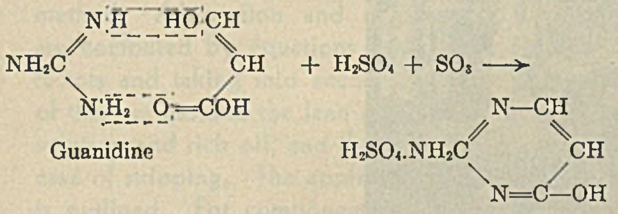


$$\begin{array}{l}COOH\\ |\\ CHOH\\ |\\ CH_2\\ |\\ COOH\end{array} + SO_3 \longrightarrow \begin{array}{l}CHO\\ |\\ CH_2\\ |\\ COOH\end{array} + CO\uparrow + H_2SO_4 \quad (7)$$

Malic acid Formylacetic acid



Guanidine (8)

Isocytosine acid sulfate in sulfuric acid solution

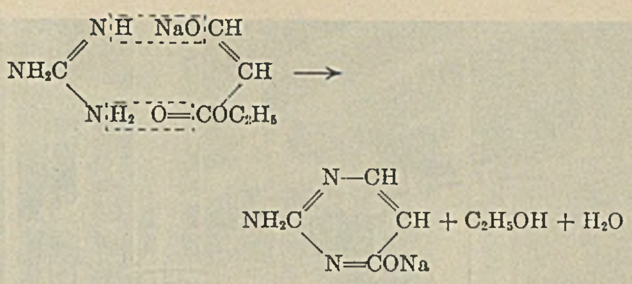
$$\xrightarrow[\text{with ammonia}]{\text{neutralization}} \text{isocytosine} \downarrow \quad (9)$$

This process required large amounts of oleum, low-temperature refrigeration for the initial reaction, and large amounts of ice to drown the reaction mixture. The neutralization with ammonia also required refrigeration, since the isocytosine was unstable in the presence of weak sulfuric acid. The high dilution of the neutralized solution led to serious solubility losses, so that the yield was poor but apparently very much better than any other scheme for making isocytosine then known. The sensational properties of sulfadiazine put extreme pressure on producing it as soon as possible. It was necessary for expediency to do what could be done quickly with the existing process and then push it into production, rather than take time to search for the best ultimate process. A major yield and quality improvement was worked out in the laboratory by drowning the reaction mixture in methanol instead of water. Isocytosine acid sulfate was almost insoluble in methanol so that it could be recovered by filtration.

Construction of the sulfadiazine plant based on this process had advanced to partial completion when the sole supplier of malic acid reported a failure of the autoclave used in its synthesis. Replacement of the autoclave, which was made of a special alloy on high priority, was out of the question for many months. This crisis forced investigation of other processes. After a few hectic days important improvements were discovered; the oldest process reported in the literature, which consisted of reacting ethyl formate, sodium ethylate, and ethyl acetate to form sodium formylacetic ester, was developed into a usable process. This had the decided advantage that it could be carried out in steel:

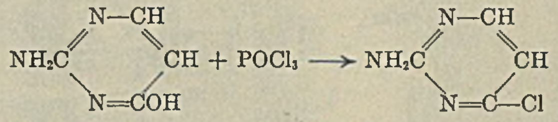
$$HCOOC_2H_5 + CH_3COOC_2H_5 + NaOC_2H_5 \longrightarrow NaOCH{=}CHCOOC_2H_5 \quad (10)$$

Sodium formylacetic ester



Sodium isocytosine (11)

The next step in the process involved conversion of isocytosine to 2-amino-4-chloropyrimidine by reaction with phosphorus oxychloride:



Laboratory experiments showed that much better yields were obtained if, instead of isocytosine, its sulfate or bisulfate were used. The reaction seemed satisfactory in the laboratory so was tried in large pilot plant equipment; however, when a temperature of 80° C. was reached, a violent exothermic reaction occurred which foamed most of the charge out of the vent, plugged it, and opened joints in the vent system which permitted enough phosphorus oxychloride to escape to drive everyone out of the shop. Needless to say, the pilot plant run was not repeated until large laboratory experiments had demonstrated how to control the reaction. It developed that sulfuric acid and phosphorus oxychloride reacted vigorously under the conditions, and that only a small fraction of the stoichiometric amount of sulfuric acid was required to give good yields of 2-amino-4-chloropyrimidine. Various improvements have been made since, but that solved the immediate problem.

As originally developed at Stamford, the only satisfactory method of replacing the chlorine with hydrogen to give 2-aminopyrimidine was by catalytic reduction with hydrogen in the presence of barium hydroxide, using a palladium catalyst. This worked well in the laboratory, but when the first pilot plant batch of 2-amino-4-chloropyrimidine was made, all attempts to reduce by this method failed to give more than traces of 2-aminopyrimidine. Obviously some impurity was poisoning the catalyst, but attempts to purify were of no apparent avail. The literature indicated that dechlorination was possible with zinc dust, but the yields were almost microscopic. This was verified when the reduction was carried out either neutral or acid. It was found that moderately good yields could be obtained if reduction was in the presence of a base. By further experimentation, including addition of ammonia to the reduction mixture, further improvements in yields were made. Much of this work was purely Edisonian, since there was little background of experience and theory to draw on. Isolation of the very soluble 2-aminopyrimidine from the zinc-reduction mother liquors introduced further problems.

The conversion of 2-aminopyrimidine by reaction with acetylsulfanilyl chloride and then hydrolysis to sulfadiazine was done by methods previously worked out in manufacture of sulfapyridine and sulfathiazole. The nature of these heterocyclic bases requires that the condensation with acetylsulfanilyl chloride be done in dry pyridine if reasonable yields are to be obtained. Hydrolysis of the acetyl group of the intermediate 2-(N^4-acetylsulfanilamido)pyrimidine is best curve and exhibits less toxic effects than any other sulfonamide drug of comparable activity, yet it is far from perfect. Its most apparent defect is lack of solubility. This is not important from the standpoint of absorption, which is good but involves complications in elimination of the drug. In people with impaired kidney function, those whose urine is acid, or those who do not have sufficient urinary output, the drug is apt to crystallize in the kidney and cause moderate to severe kidney trouble. This is a particular disadvantage for troops in desert fighting where water supplies are limited and urinary output very low because of surface evaporation. Recent work indicates that solubility troubles may be largely eliminated by adequate dosage of sodium bicarbonate so as to maintain a slightly alkaline urine. The solubility of sulfadiazine and sulfathiazole increases rapidly with pH above 6.5.

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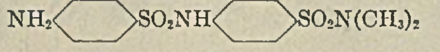

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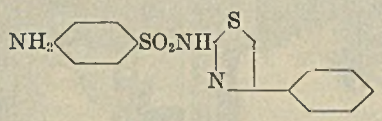

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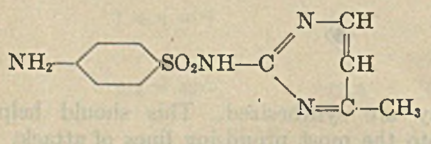

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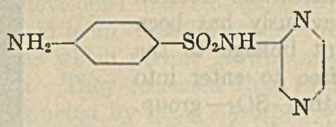

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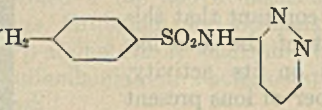

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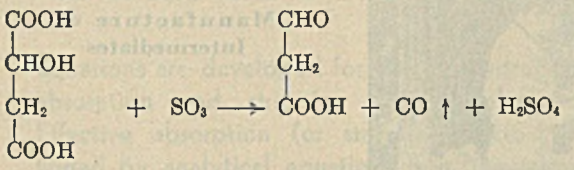
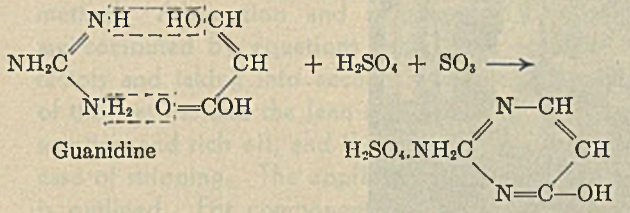


$$\mathrm{COOH{-}CHOH{-}CH_2{-}COOH} + \mathrm{SO_3} \longrightarrow \mathrm{CHO{-}CH_2{-}COOH} + \mathrm{CO}\uparrow + \mathrm{H_2SO_4} \qquad (7)$$

Malic acid Formylacetic acid



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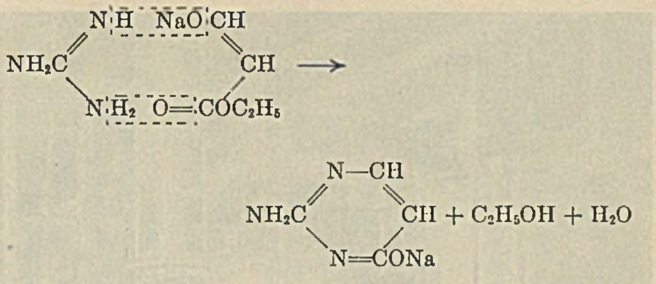

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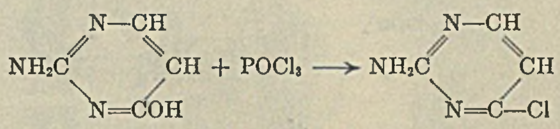
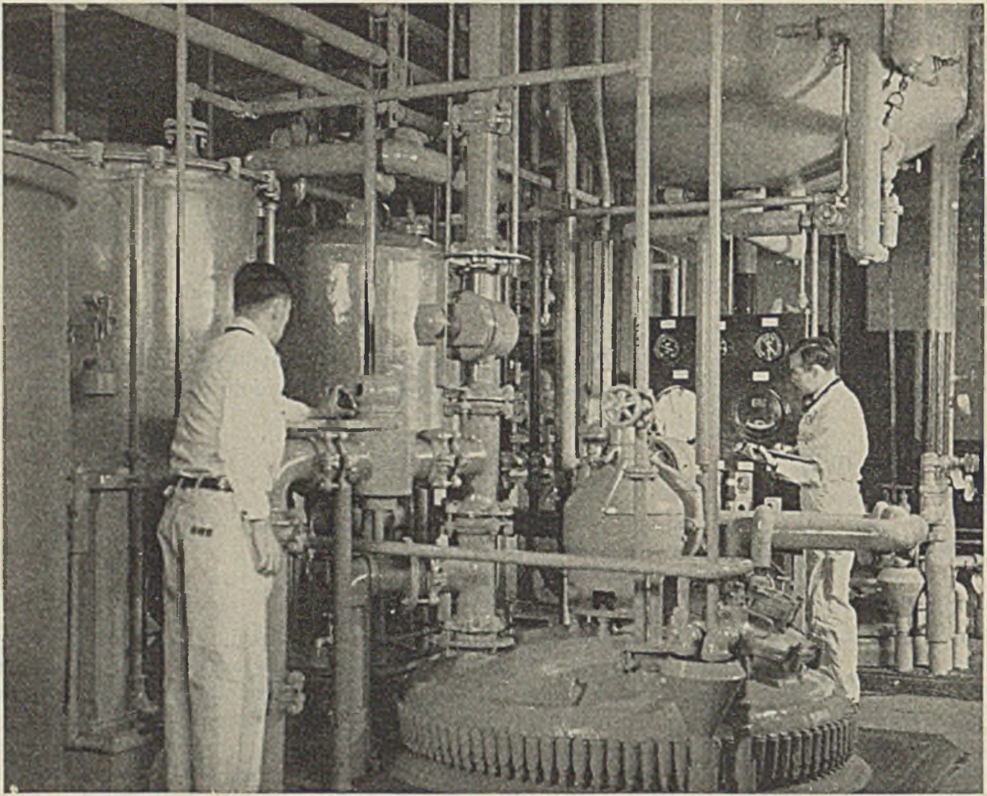


Laboratory experiments showed that much better yields were obtained if, instead of isocytosine, its sulfate or bisulfate were used. The reaction seemed satisfactory in the laboratory so was tried in large pilot plant equipment; however, when a temperature of 80° C. was reached, a violent exothermic reaction occurred which foamed most of the charge out of the vent, plugged it, and opened joints in the vent system which permitted enough phosphorus oxychloride to escape to drive everyone out of the shop. Needless to say, the pilot plant run was not repeated until large laboratory experiments had demonstrated how to control the reaction. It developed that sulfuric acid and phosphorus oxychloride reacted vigorously under the conditions, and that only a small fraction of the stoichiometric amount of sulfuric acid was required to give good yields of 2-amino-4-chloropyrimidine. Various improvements have been made since, but that solved the immediate problem.

As originally developed at Stamford, the only satisfactory method of replacing the chlorine with hydrogen to give 2-aminopyrimidine was by catalytic reduction with hydrogen in the presence of barium hydroxide, using a palladium catalyst. This worked well in the laboratory, but when the first pilot plant batch of 2-amino-4-chloropyrimidine was made, all attempts to reduce by this method failed to give more than traces of 2-aminopyrimidine. Obviously some impurity was poisoning the catalyst, but attempts to purify were of no apparent avail. The literature indicated that dechlorination was possible with zinc dust, but the yields were almost microscopic. This was verified when the reduction was carried out either neutral or acid. It was found that moderately good yields could be obtained if reduction was in the presence of a base. By further experimentation, including addition of ammonia to the reduction mixture, further improvements in yields were made. Much of this work was purely Edisonian, since there was little background of experience and theory to draw on. Isolation of the very soluble 2-aminopyrimidine from the zinc-reduction mother liquors introduced further problems.

The conversion of 2-aminopyrimidine by reaction with acetylsulfanilyl chloride and then hydrolysis to sulfadiazine was done by methods previously worked out in manufacture of sulfapyridine and sulfathiazole. The nature of these heterocyclic bases requires that the condensation with acetylsulfanilyl chloride be done in dry pyridine if reasonable yields are to be obtained. Hydrolysis of the acetyl group of the intermediate 2-(N^4-acetylsulfanilamido)pyrimidine is best



Glass-Lined Equipment Used in the Manufacture of Intermediates

carried out with sodium hydroxide, since hot mineral acids cleave the sulfonamide linkage to give sulfanilic acid and the salt of the heterocyclic base.

Success in overcoming obstacles can be gaged by the fact that production is now at a rate forty times that contemplated when a sulfadiazine plant was first planned a little over two years ago.

FUTURE DEVELOPMENT

The future of chemotherapy appears very bright. The essential metabolite theory of chemotherapeutic action is not limited to drugs in which *p*-aminobenzoic acid is the essential growth factor. Already pantoyltauramide, in which the carboxyl group of pantothenic acid has been replaced by the sulfamyl group, has been shown to inhibit the growth of organisms requiring pantothenic acid for their metabolic processes. 3-Sulfamylpyridine has also been found to inhibit organisms requiring nicotinic acid. Careful study of essential materials required for the growth of pathogenic bacteria not now successfully treated by sulfa drugs is almost certain to suggest new compounds which may prove effective in combating these infections. The requirements of bacteria need not be the sole application of the theory, since there is no apparent reason why it should not be successfully applied to protozoal diseases as well. The virus diseases are another matter but may eventually be susceptible to chemotherapy.

Meanwhile much research is being devoted to a whole new line of chemotherapeutic agents—the metabolic products of various molds which are extremely bactericidal and yet comparatively harmless to man. Penicillin from the mold *Penicillium notatum* is the most successful of these to date and is said to be bactericidal in dilutions of 1 part in 30,000,000. Many difficulties in isolation of these products are being encountered, but the hope remains that these compounds can be identified chemically and eventually be synthesized. Intensive work is being done, but government secrecy has withheld publication of results so that it is impossible to say how soon the public can enjoy the benefits of these remarkable compounds.

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PRESENTED before several of the southwestern sections of the AMERICAN CHEMICAL SOCIETY.

Design for Hydrocarbon
ABSORPTION AND STRIPPING

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Equations are developed for making hydrocarbon absorption and stripping design calculations. Effective absorption (or stripping) factors, obtained by analytical equations from the terminal (top and bottom tray) conditions, are used in this method. Absorption and stripping efficiencies are computed by equations using these effective factors and taking into account the compositions of the wet gas and the lean oil in the case of absorption and rich oil, and the stripping gas in the case of stripping. The application of the method is outlined. For components appearing in both wet and gas and lean oil, it is frequently necessary to apply both the absorption and stripping equations. A comparison of this and other methods with plate-to-plate calculations indicates that this provides an accurate and rapid short cut.

THE recovery of valuable hydrocarbons from multicomponent gaseous mixtures by absorption, followed by steam stripping of the enriched solvent, is an important process in the petroleum industry. A simplified flow diagram of this process is given in Figure 1. This system consists of an absorber, stripper, and auxiliaries. In spite of the importance of these operations, no rapid accurate method of design has been proposed. Such a method is presented in this paper.

If the number of theoretical plates are known or assumed, the required lean oil rates for absorption and the steam quantities for stripping may be found by plate-to-plate calculations involving heat and material balances and phase equilibria at each theoretical contact of vapor and liquid, a tedious and slow method. By the Kremser-Brown method, which involves the use of absorption and stripping factors, originally proposed by Kremser (*2*) and later improved by Souders and Brown (*4*), design calculations of this kind may be made more rapidly. However, the simplifying assumptions made in the development of the Kremser-Brown method often lead to serious errors, particularly in the design of absorbers treating rich gases. The leaner the gas and the greater the solvent quantity, the more reliable is the Kremser-Brown method.

A more accurate method of making absorption and stripping calculations is the rigorous graphical treatment of Sherwood (*3*). The theoretical plates are stepped off between operating and equilibrium lines on an X-Y plot for the key component in determining the proper relation between number of plates, recovery, and solvent or steam rate. For this plot the operating line is made straight and the equilibrium line curved to fit the equilibrium relations at both ends of the column. The Kremser-Brown absorption factor method is frequently used in making first approximations before applying this graphical method. Nevertheless, the construction of an X-Y plot of sufficient accuracy for process design calculations is frequently too tedious and time consuming to be practical for most design problems.

Recently Horton and Franklin (*1*) proposed two design procedures for predicting absorber performance. Their first method, which is the longer and more accurate, involves the use of separate absorption factors for each component on each plate throughout the absorber, and the calculation of the absorption efficiency by a general equation. Their second and shorter method involves the use of an effective absorption factor for each component, and the calculation of absorption efficiency by the Kremser-Brown equation. In this method the effective absorption factor for the more volatile components is the L/KV ratio near the bottom of the absorber, and for the less volatile components it is the L/KV ratio near the middle of the tower. An empirical rule for locating and evaluating these effective absorption factors is proposed by Horton and Franklin. Briefly, their procedure is (*a*) to assume the total amount of gas absorbed, (*b*) estimate the L/V ratio and the temperature at various points in the column, (*c*) evaluate the effective absorption factors by the proposed method, (*d*) calculate the absorption efficiency by the Kremser-Brown equation, and (*e*) revise the assumption of total gas absorbed and repeat the above steps. Horton and Franklin recommend this second and shorter method as a first trial, and their first and more rigorous method as the final trial in the solution of absorption problems.

A new method of making absorption and stripping design calculations by the use of effective absorption or stripping factors, which are obtained from an analytically derived equation, is presented in this paper. Plate-to-plate calculations were made up to eight equilibrium stages, and for practical purposes the assumption could be made that the effective absorption factor was independent of the number of plates.

EQUATIONS

An algebraic solution of a plate-to-plate calculation for an absorber of n plates (Figure 1) is represented by the following equation, which involves only the assumption of equilibrium between vapor and liquid on each theoretical plate, where the plates are numbered from top to bottom:

$$\frac{Y_{n+1}-Y_1}{Y_{n+1}} = \left(\frac{A_1A_2A_3\ldots A_n + A_2A_3\ldots A_n + \ldots + A_n}{A_1A_2A_3\ldots A_n + A_2A_3\ldots A_n + \ldots + A_n+1}\right) - \frac{L_oX_o}{V_{n+1}Y_{n+1}}\left(\frac{A_2A_3\ldots A_n + A_3\ldots A_n + \ldots + A_n + 1}{A_1A_2A_3\ldots A_n + A_2A_3\ldots A_n + \ldots + A_n+1}\right) \quad (1)$$

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The derivation of Equation 1 was presented by Horton and Franklin (*1*). It is an exact expression for the efficiency of an absorber of n plates; the term to the left of the equality sign is the absorption efficiency E_a, the first term to the right gives the absorption efficiency for a denuded lean oil, and the second term to the right is a correction for the presence of solute in the lean oil. An analogous equation may be written for stripping.

Using average effective absorption factors instead of values for each plate makes it possible to express Equation 1 in the following simplified manner:

$$E_a = \frac{Y_{n+1} - Y_1}{Y_{n+1}} = \left[1 - \frac{L_o X_o}{A' V_{n+1} Y_{n+1}}\right]\left[\frac{A_e^{n+1} - A_e}{A_e^{n+1} - 1}\right] \quad (2)$$

where A_e and A' are defined by the following relations:

$$\left[\frac{A_e^{n+1} - A_e}{A_e^{n+1} - 1}\right] = \left[\frac{A_1A_2A_3\ldots A_n + A_2A_3\ldots A_n + \ldots + A_n}{A_1A_2A_3\ldots A_n + A_2A_3\ldots A_n + \ldots + A_n + 1}\right] \quad (3)$$

$$\frac{1}{A'}\left[\frac{A_e^{n+1} - A_e}{A_e^{n+1} - 1}\right] = \left[\frac{A_2A_3\ldots A_n + A_3\ldots A_n + A_n + 1}{A_1A_2A_3\ldots A_n + A_2A_3\ldots A_n + A_n + 1}\right] \quad (4)$$

In a similar manner the following analogous expression is written for the stripping efficiency:

$$E_s = \frac{X_{n+1} - X_1}{X_{n+1}} = \left[1 - \frac{V_o Y_o}{S' L_{n+1} X_{n+1}}\right]\left[\frac{S_e^{n+1} - S_e}{S_e^{n+1} - 1}\right] \quad (5)$$

where S_e and S' are defined in the same way A_e and A' are defined in Equations 3 and 4.

Reference to Figure 1 will make the significance of the terms in Equations 2 and 5 more clearly understood.

Simple and direct equations or correlations for predicting the average effective absorption and stripping factors appearing in Equations 2 and 5 are desired. These relations have been developed by analyzing plate-to-plate calculations and test data for absorbers and strippers. From this study it was found that A_e and A' are essentially independent of n, and can be expressed as functions of A_1 and A_n, the terminal values of A, for practical design calculations with very little sacrifice in accuracy. If A_e and A' are independent of n, Equations 3 and 4 may be written for any number of plates and useful equations developed. Rewriting Equations 3 and 4 for a two-plate absorber gives:

$$\left(\frac{A_e^3 - A_e}{A_e^3 - 1}\right) = \frac{A_n(A_1 + 1)}{A_n(A_1 + 1) + 1} \quad (6)$$

$$\frac{1}{A'}\left(\frac{A_e^3 - A_e}{A_e^3 - 1}\right) = \frac{A_n + 1}{A_n(A_1 + 1) + 1} \quad (7)$$

Equation 6 may be written

$$A_e^3 - A_e[A_n(A_1 + 1) + 1] + A_n(A_1 + 1) = 0 \quad (8)$$

Factoring out $[A_e - 1]$,

$$[A_e - 1][A^2 + A_e - A_n(A_1 + 1)] = 0 \quad (9)$$

$A_e = +1$ is always a solution to this equation but is of no interest. The other positive root is the one desired; hence,

$$A_e^2 + A_e - A_n(A_1 + 1) = 0 \quad (10)$$

from which

$$A_e = \sqrt{A_n(A_1 + 1) + 0.25} - 0.5 \quad (11)$$

Equation 11 gives values of A_e for use with Equation 2. An analogous equation is written by inspection for stripping:

$$S_e = \sqrt{S_n(S_1 + 1) + 0.25} - 0.5 \quad (12)$$

Equation 12 gives values of S_e for use with Equation 5.

An expression for A' is derived by combining Equations 6 and 7 as follows:

$$\frac{1}{A'}\left[\frac{A_n(A_1 + 1)}{A_n(A_1 + 1) + 1}\right] = \left[\frac{A_n + 1}{A_n(A_1 + 1) + 1}\right] \quad (13)$$

from which

$$A' = \frac{A_n(A_1 + 1)}{A_n + 1} \quad (14)$$

Equation 14 gives values of A' to use with Equation 2. An analogous equation is written for stripping:

$$S' = \frac{S_n(S_1 + 1)}{S_n + 1} \quad (15)$$

Equation 15 gives values of S' to use with Equation 5.

APPLICATION OF METHOD

Equations 2, 5, 11, 12, 14, and 15 constitute the absorption and stripping design method proposed in this paper. These equations have been derived mathematically and are based on two fundamental assumptions: (*a*) Equilibrium exists between vapor and liquid on each theoretical plate, and (*b*) effective absorption and stripping factors are functions of terminal conditions only and independent of the number of theoretical plates.

The above equations are not limited to the ideal cases of perfectly denuded lean absorption oil or stripping gas but may even be used to predict the performance of absorbers and strippers where overlapping occurs—e. g., where the same components appear in both the lean oil and wet gas. Unless a perfectly denuded and nonvolatile lean oil is used in absorbers, lean oil will be lost into the off gas due to stripping the more volatile components of the lean oil. An analogous situation exists for strippers. Unless a perfectly inert and condensable free stripping gas is used in strippers, there will be absorption of the less volatile components of the stripping gas. Thus absorption and stripping may both occur simultaneously in the same absorber or stripper. Accordingly, both the absorption Equation 2 and the stripping Equation 5 must frequently be used in designing an absorber; the former equation is applied to all the components in the wet gas, and the latter to all components in the lean oil.

In applying Equations 2 and 5, it is convenient to have the last terms plotted graphically as a function of A_e or S_e and n. Such a plot is easy to construct and therefore not presented in this paper.

For components that appear in both the wet gas and lean oil to an absorber, either absorption or stripping may take place or absorption may prevail on some and stripping on the others, depending upon the concentrations and operating conditions. It is usually possible to tell at a glance which operation prevails for the various components in this overlapping region. If such is not the case, the first term in brackets to the right of the equality sign in either Equation 2 or 5—i. e., $(1 - L_oX_o/A'V_{n+1}Y_{n+1})$ or $(1 - V_oY_o/S'L_{n+1}X_{n+1})$—may be applied to the components in question. One of these expressions will be negative and one positive for each of the overlapping components. The positive expression indicates the proper equation for that component.

In calculating the effective absorption or stripping factors (A_e and A', or S_e and S') by Equations 11, 12, 14, and 15, care should be taken to use the proper values of L, V, and K for computing A or S at the top and bottom plates. The liquid and vapor quantities leaving the plate (top or bottom) and K at the condition of the plate in question should be used. These liquid and vapor quantities, which are not known accurately until the solution is complete, may be estimated by assuming the total absorption and prorating this to obtain the quantities absorbed on the top and bottom plates. This proration may be done by the equations presented below.

The vapor contraction across any plate in an absorber is approximately represented by the following relation:

$$\frac{V_m}{V_{m+1}} = \left(\frac{V_1}{V_{n+1}}\right)^{\frac{1}{n}} \tag{16}$$

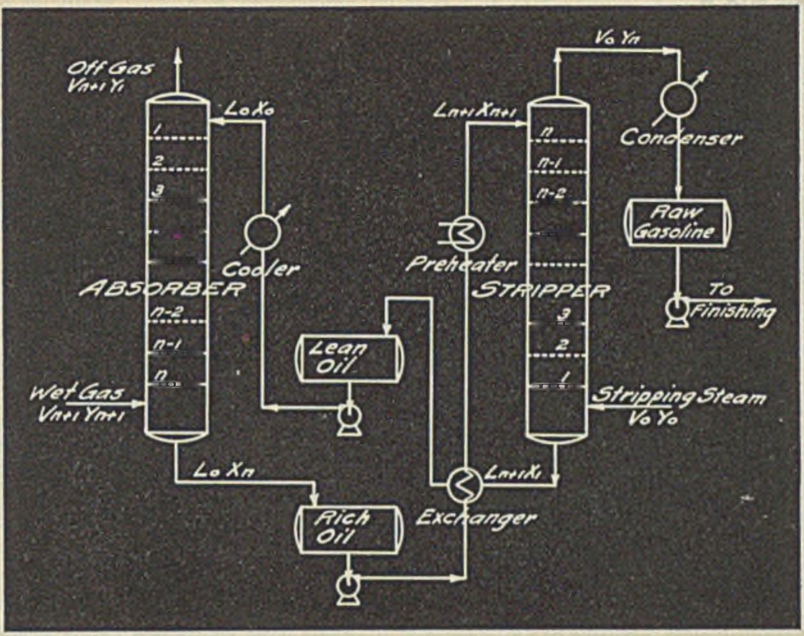

Figure 1. Flow Diagram for Absorbing-Stripping System

This equation says that the vapor contraction per plate is the same percentage of the vapor to the plate in question for all plates in an absorber. Applying Equation 16 to the top plate gives the following expression for the vapor leaving the second plate:

$$V_2 = V_1\left(\frac{V_{n+1}}{V_1}\right)^{\frac{1}{n}} \tag{17}$$

Applying Equation 16 to the bottom plate gives the following expression for the vapor leaving the bottom plate:

$$V_n = V_{n+1}\left(\frac{V_1}{V_{n+1}}\right)^{\frac{1}{n}} \tag{18}$$

Equations 17 and 18 plus material balances around each plate will give the approximate L and V quantities for each plate.

Temperatures on the top and bottom plates may be estimated by heat balances and the assumption that the temperature change per plate is proportional to the gas contraction.

The accuracy of any method of making absorption and stripping design calculations is dependent upon the estimation of temperatures and liquid and vapor quantities. The initial assumption of total absorption for the liquid and vapor quantities and the heat balances for temperatures can be checked after the calculations of the absorption of each component are complete. It is frequently necessary to make a second set of calculations in order to bring the initial estimates and the final results into closer agreement. With experience these items may be estimated closely enough so that a second trial is unnecessary.

COMPARISON OF METHODS

Absorption efficiencies computed by this method are compared with those obtained by other methods in the following tabulation of "fraction absorbed" which means the amount of the component in the wet gas:

		Horton and Franklin		This
	Plate-to-Plate	Method 1	Method 2	Method
Methane	0.0336	0.0328	0.0327	0.033
Ethane	0.125	0.122	0.127	0.125
Propane	0.506	0.501	0.509	0.506
n-Butane	0.9185	0.916	0.921	0.918
n-Pentane	0.9568	0.956	0.9588	0.956

This comparison shows that the proposed method is almost as good as plate-to-plate calculations for a four-plate absorber. This proposed method is shorter than Horton and Franklin's Method 1 and of comparable accuracy (*1*), although not more accurate. The method is more rapid and more accurate than Horton and Franklin's Method 2. A comparison for absorbers containing more plates would be desirable.

NOMENCLATURE

A = absorption factor = L/VK
A_e = effective absorption factor
A' = effective absorption factor
S = stripping factor = VK/L
S_e = effective stripping factor
S' = effective stripping factor
L = moles of liquid
V = moles of vapor
X = moles of any component in the liquid phase per mole of liquid entering absorber or stripper
x = mole fraction of any component in liquid
Y = moles of any component in liquid phase per mole of vapor entering absorber or stripper
y = mole fraction of any component in vapor
K = phase equilibria constant = y/x
E_a = absorption efficiency = $(Y_{n+1} - Y_1)/Y_{n+1}$
E_s = stripping efficiency = $(Y_{n+1} - X_1)/X_{n+1}$

Subscripts
o = conditions at top of absorber or bottom of stripper—i. e., reference to lean oil for absorbers and to stripping medium for stripping
$1,2,3 \ldots n$ = plate numbers, top to bottom for absorbers, bottom to top for strippers
m = any plate
$n + 1$ = conditions at bottom of absorber or at top of stripper—i. e., reference to entering wet gas for absorbers and to entering rich oil for strippers

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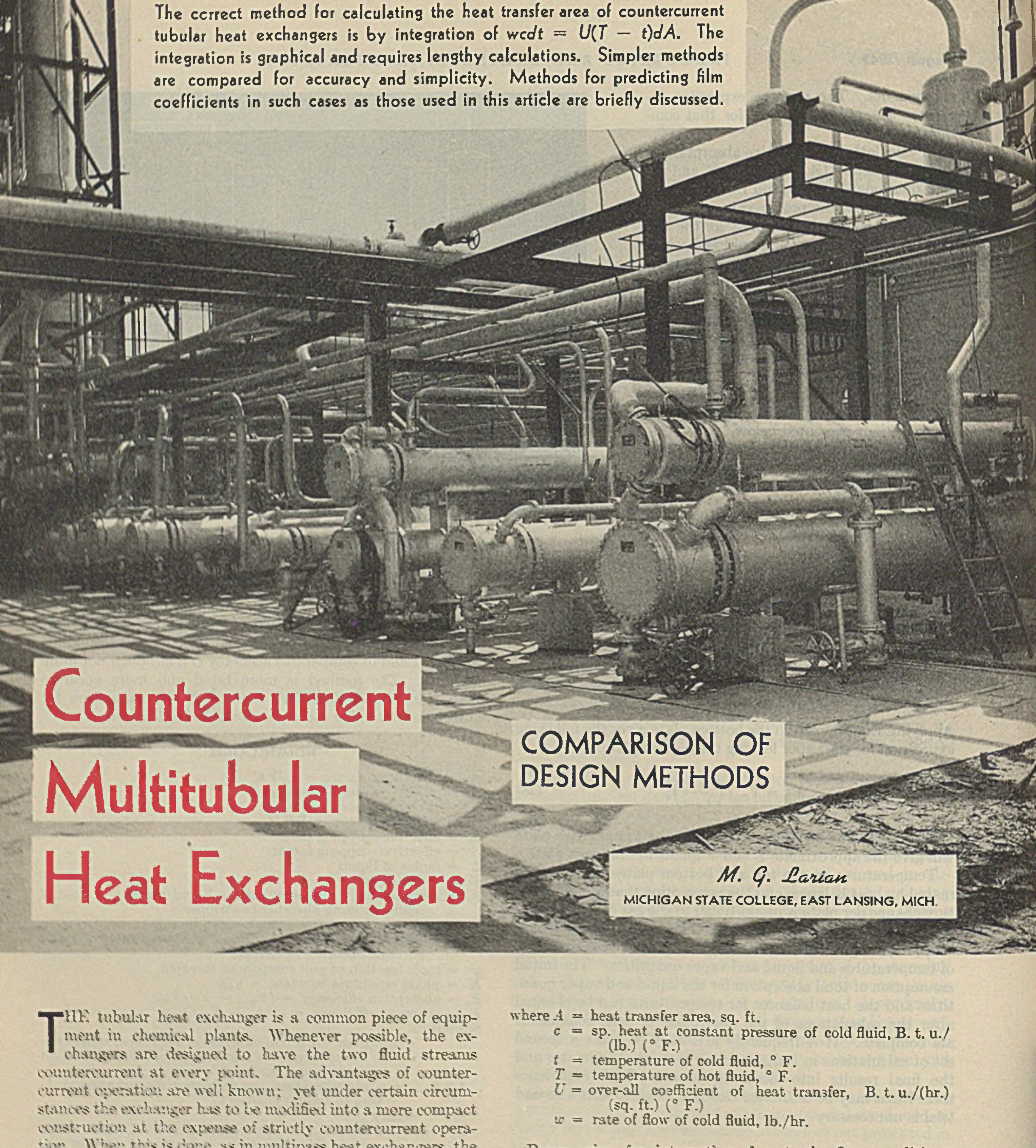
The correct method for calculating the heat transfer area of countercurrent tubular heat exchangers is by integration of $wcdt = U(T - t)dA$. The integration is graphical and requires lengthy calculations. Simpler methods are compared for accuracy and simplicity. Methods for predicting film coefficients in such cases as those used in this article are briefly discussed.



Countercurrent Multitubular Heat Exchangers

COMPARISON OF DESIGN METHODS

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THE tubular heat exchanger is a common piece of equipment in chemical plants. Whenever possible, the exchangers are designed to have the two fluid streams countercurrent at every point. The advantages of countercurrent operation are well known; yet under certain circumstances the exchanger has to be modified into a more compact construction at the expense of strictly countercurrent operation. When this is done, as in multipass heat exchangers, the streams are no more strictly countercurrent. Along certain paths they flow countercurrent, and along others, parallel. It is up to the designer to make the choice between the two types of exchangers. However, for the purpose of this article, it is justified to state the problem as if the exchanger were to be strictly countercurrent.

In heat exchanger design the most important quantity to be calculated is the heat transfer area. It can be shown that for adiabatic (well insulated) heat exchangers, the heat transfer area is calculated from the equation

$$wcdt = U(T - t)dA \tag{1}$$

where A = heat transfer area, sq. ft.
c = sp. heat at constant pressure of cold fluid, B. t. u./(lb.) (° F.)
t = temperature of cold fluid, ° F.
T = temperature of hot fluid, ° F.
U = over-all coefficient of heat transfer, B. t. u./(hr.) (sq. ft.) (° F.)
w = rate of flow of cold fluid, lb./hr.

Rearranging for integration, for steady flow conditions Equation 1 is written:

$$\int_1^2 \frac{c\,dt}{U(T - t)} = \frac{1}{w}\int_1^2 dA = \frac{A}{w} \tag{2}$$

Equation 2 is integrated best by the graphic method. When t is plotted against $c/U(T - t)$, the area under the curve between the limits t_1 and t_2 is equal to A/w (Figure 1).

The relation between $c/U(T - t)$ and t is not represented by a straight line on ordinary graph paper, and even though the form of the curve may suggest that it is on log-log or semilog scale paper, it is not. Therefore, it is necessary to calculate the ordinates of several points.

At any given cross section where the temperature of the cold fluid is t and that of the hot fluid is T, the over-all coefficient is calculated from the following formula:

$$U = \frac{1}{\frac{1}{h_1} + \frac{1}{h_{s1}} + \frac{L}{k} \cdot \frac{D_1}{D_m} + \frac{1}{h_{s2}} \cdot \frac{D_1}{D_2} + \frac{1}{h_2} \cdot \frac{D_1}{D_2}} \tag{3}$$

where D_1 = outside diameter of tubes
D_2 = inside diameter of tubes
D_m = log mean diameter, or for $D_1/D_2 \leq 2$, arithmetic mean diameter
h_1 = film coefficient of outer fluid, B. t. u./(hr.) (sq. ft.) (° F.)
h_2 = film coefficient of inner fluid, B. t. u./(hr.) (sq. ft.) (° F.)
$1/h_{s1}$ = fouling factor for tube outer surface
$1/h_{s2}$ = fouling factor for tube inner surface
L = thickness of tube metal wall, ft.
k = heat conductivity of tube metal, B. t. u./(hr.) (ft.) (° F.)

The over-all coefficient, as calculated from Equation 3, is for a square foot of tube outside area, and for this reason the heat transfer area, A, in Equation 2 is based on the tube outside area.

It is evident that a long time is needed to complete the calculations necessary for the integration of Equation 2. For this reason other simpler methods have been suggested in the literature for calculating the heat transfer area. Naturally these simpler methods are based upon one or more assumptions. The desire to simplify calculations is always justified, provided the assumptions made do not lead to serious errors; if they do, the resultant final error and its sign must be known so that the necessary correction can be made after the completion of the calculations. The purpose of this article is to compare these methods as to simplicity and accuracy. It is somewhat supplementary to the paper on the same subject by Friend and Lobo (*4*), but the present article is justified because: (1) Friend and Lobo compared the simpler methods with one another on the basis of the implied assumption that one of them (listed as method 2 in the present article) gave the correct answer; the comparison should have been made with the answer obtained by integration of Equation 2. (2) For reasons not stated Friend and Lobo used the Sieder-Tate (*7*) graphic correlation for calculating the film coefficients. The Sieder-Tate correlation is based upon plotting DG/μ against $(hD/k)/(c\mu/k)^{1/3}(\mu_a/\mu_w)^{0.14}$ on log-log scale. The physical properties of the fluid,

k = heat conductivity, B. t. u. /(hr.) (ft.) (° F.)
μ = viscosity, lb./(hr.) (ft.)
c = sp. heat at constant pressure, B. t. u./(lb.) (°F.)

in the Reynolds, Prandtl, and Nusselt groups are taken at the main-stream temperature. In μ_a/μ_w, μ_a is the viscosity of the fluid at the main-stream temperature, and μ_w at the temperature of the tube wall. For strictly turbulent flow (in the sense of heat transfer)—i. e., for Reynolds number greater than 8000—a single straight line is obtained which can be represented by the equation (*5*):

$$\frac{hD}{k} = 0.027 \left(\frac{DG}{\mu}\right)^{0.8} \left(\frac{c\mu}{k}\right)^{1/3} \left(\frac{\mu_a}{\mu_w}\right)^{0.14} \tag{4}$$

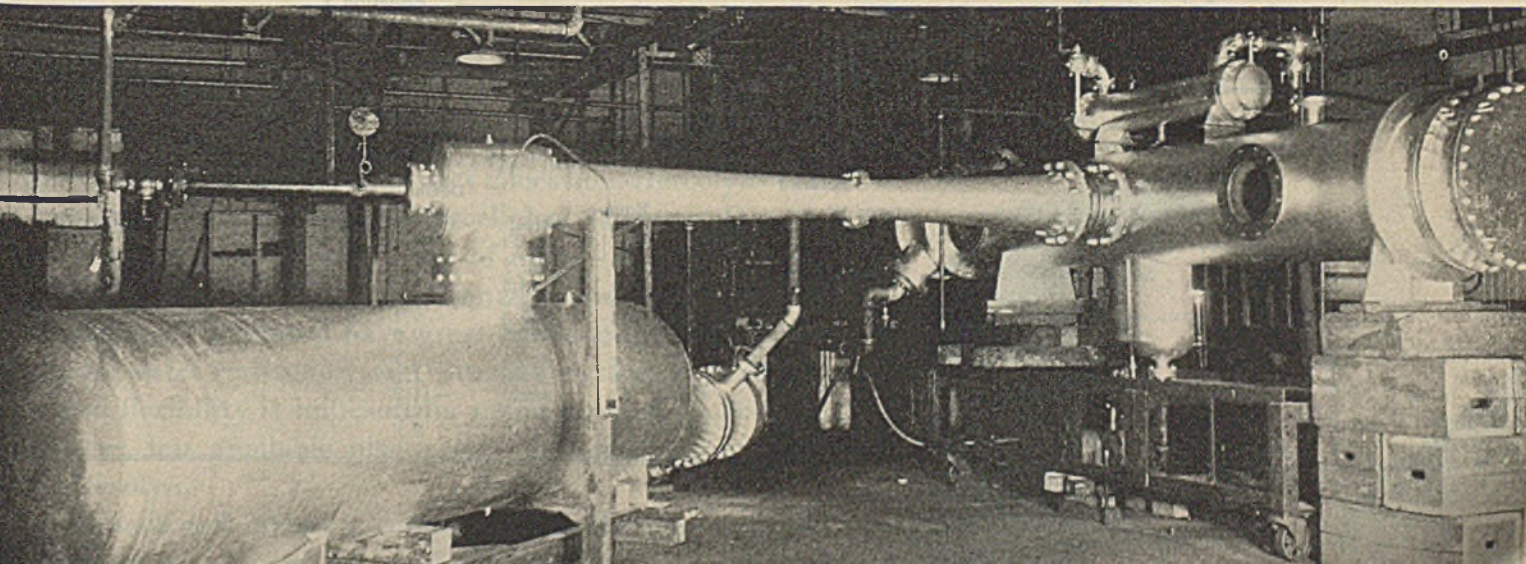
For Reynolds numbers less than 8000, the ratio of length to diameter, L/D, enters the picture as an important factor. Previous to Sieder and Tate (1936), for strictly turbulent flow inside pipes, the Dittus-Boelter (*3*) equation (1930),

$$\frac{hD}{k} = 0.0225 \left(\frac{DG}{\mu}\right)^{0.8} \left(\frac{c\mu}{k}\right)^{1-n} \tag{5}$$

was considered the best general correlation. Sherwood and Petrie (*6*) also found that their data could best be correlated by Equation 5 with a coefficient equal to 0.024. The physical properties of the fluid are taken at the main-stream temperature. Equation 5 represents a straight line on log-log scale when DG/μ is plotted against $(hD/k)/(c\mu/k)^{1-n}$, where n = 0.6 for heating and n = 0.7 for cooling. It is evident that the Sieder-Tate correlation offers an advantage in the sense that heating and cooling data are brought into agreement. On the other hand, to calculate the ratio μ_a/μ_w, it is necessary to know the tube wall temperature. The tube wall temperature can be calculated from the data already given in the problem, but more time will be required to calculate the film coefficients from the Sieder-Tate correlation than from that of Dittus-Boelter. The time needed to calculate tube wall temperatures can be shortened by estimating the over-all and film coefficients as Friend and Lobo have done. An experienced designer can roughly estimate these coefficients. In any event, there should be some reason other than bringing heating and cooling data into agreement to justify the introduction of the factor $(\mu_a/\mu_w)^{0.14}$. If the two correlations give the same answer, it is natural that the simpler of the two, the Dittus-Boelter equation, should be preferred. On the other hand, if the answers differ, the question to be settled is: Which is the more accurate? Before answering the question, it is desirable to review the various equations, proposed on account of their simplicity, for calculating the heat transfer area.

Heat Exchangers Are of Myriad Design, Depending upon the Task to Be Performed

Courtesy, The Lummus Company



If U and c were constant, Equation 2 combined with $q = wc(t_h - t_c)$ would reduce to the simple form,

$$A = q/U\Delta_m \tag{6}$$

where

q = heat transfer capacity of exchanger, B. t. u./hr.

Δ_m = log mean over-all temperature difference, or for $\Delta_h/\Delta_c \leq 2$, arithmetic mean. Subscripts h and c refer to hot and cold ends, respectively, of the exchanger.

The conditions stated above are obtained only when the fluids undergo small changes in temperature, such as when they pass through the exchanger at very rapid rates. Such rates are not practical. However, in its general form, Equation 6 is still useful provided the change in U is taken into account in one way or another. This is done in methods 1, 2, and 3.

COMPARISON OF METHODS

METHOD 1. Using an over-all coefficient U_a which is calculated using film coefficients at the arithmetic mean mainstream temperatures of the fluids—i. e., at $T_a = (T_h + T_c)/2$ for the hot fluid and $t_a = (t_h + t_c)/2$ for the cold fluid. The equation is:

$$A = q/U_a\Delta_m \tag{7}$$

METHOD 2. The arithmetic mean temperatures, T_a and t_a, are appreciably higher than the integrated mean temperatures. For instance, in problem 1 referred to below, T_a = 400° F. and t_a = 95° F., while the integrated mean temperatures are 356° and 88° F., respectively. The film coefficients calculated at the arithmetic mean temperatures are higher than when calculated at the integrated mean temperatures; correspondingly, the over-all coefficient is higher in the former than in the latter case. In order to determine the integrated mean temperatures, it is necessary to know the temperatures of the fluids at various points along the length of the exchanger. Such data are available only after the calculations for the integration of Equation 2 are completed. Therefore the suggestion of using the integrated mean temperatures is of no practical value. However, temperatures T_x and t_x, approximately equal to the integrated mean temperatures (compare T_x = 344° F. with integrated mean temperature of 356° F., and t_x = 88° F. with integrated mean temperature of 88° F.), can be calculated from $T_x = F(T_h - T_c) + T_c$ and $t_x = F(t_h - t_c) + t_c$. The factor F is obtained from a chart originally prepared by Colburn (*2*) on the basis of the assumption that the relation between U and T, or t, is linear. When the chart is not available, F is calculated using

$$F = \frac{\frac{1}{C} + \frac{1}{R-1}}{1 + \frac{\log (C+1)}{\log R}} - \frac{1}{C} \tag{8}$$

where $R = \Delta_c/\Delta_h$

$C = (U_h - U_c)/U_c$

subscripts c, h = cold and hot ends of exchanger, respectively

Using T_x and t_x in calculating the over-all coefficient U_x, the equation for method 2 is

$$A = q/U_x\Delta_m \tag{9}$$

METHOD 3. Assuming that the over-all coefficient and temperature relation is linear, and using the arithmetic average of the coefficients at the hot and cold ends of the exchanger

$$A = 2q/(U_h + U_c)\Delta_m \tag{10}$$

METHOD 4. Making the same assumption as in method 3 and, in addition, assuming c constant and the exchanger adiabatic, Colburn (*2*) integrated Equation 2 and, combining it with $q = wc(t_h - t_c)$, derived the equation

$$A = q\left[\frac{2.303 \log (U_h\Delta_c/U_c\Delta_h)}{U_h\Delta_c - U_c\Delta_h}\right] \tag{11}$$

COMPARISON. Three problems were selected. The first is for cooling oil and is the same as that used by Friend and Lobo (*4*). The second problem is for cooling aniline: An exchanger is to be designed for 21,000 pounds of aniline per hour which is to be cooled with clean cooling water. The exchanger is a double-pipe arrangement; for the inner a standard 2-inch pipe and for the outer a standard 3-inch pipe are used. It is assumed that a coefficient of 1000 will take care of the

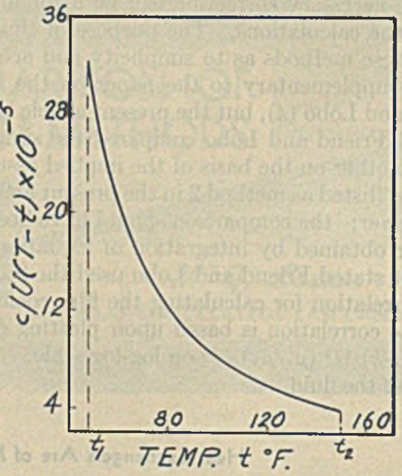
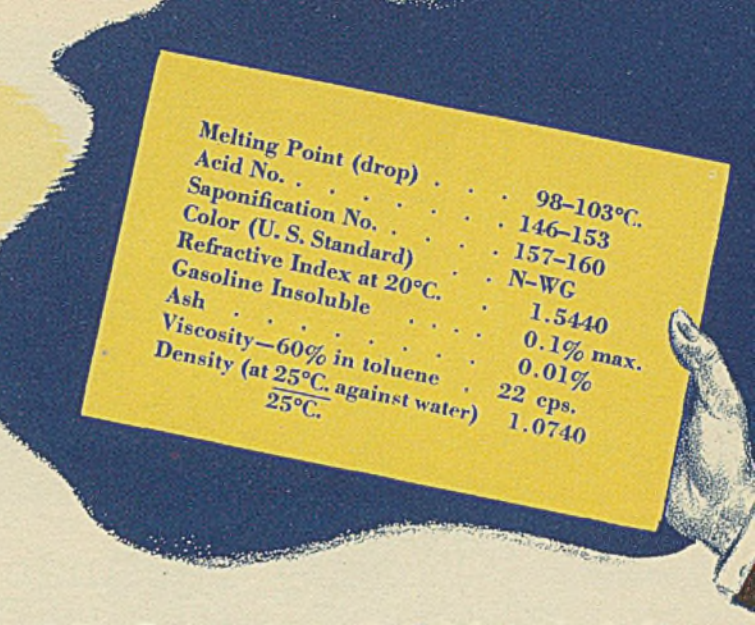


Figure 1. Graphic Integration of Equation 2

TABLE I. VALUES OF HEAT TRANSFER AREA FOR COOLING OIL, BASED ON OUTSIDE PIPE AREA, CALCULATED BY DIFFERENT METHODS AND FOR DIFFERENT OVER-ALL TEMPERATURE DIFFERENCES OF THE HOT AND COLD ENDS OF THE EXCHANGER

Temperature, ° F. Oil In, T_1	Temperature, ° F. Oil Out, T_2	Temperature, ° F. Water In, t_1	Temperature, ° F. Water Out, t_2	Over-All Δ Δ_c, $T_2 - t_1$	Over-All Δ Δ_h, $T_1 - t_2$	Method No.	Equation No.	Area, Sq. Ft.	Deviation from Correct, %	Results of Friend and Lobo
600	200	70	120	130	480	1	7	186.7	− 2.5	173.9
						2	9	198.5	3.7	187.0
						3	10	195.0	1.8	...
						4	11	209.0	9.1	197.0
						5	2	191.5	0.0	...
600	100	70	120	30	480	1	7	385.5	−18.7	...
						2	9	480.0	1.3	...
						3	10	422.0	−11.0	...
						4	11	531.5	12.1	...
						5	2	474.0	0.0	...

New things have happened with Rosin



Melting Point (drop)	98–103°C.
Acid No.	146–153
Saponification No.	157–160
Color (U. S. Standard)	N–WG
Refractive Index at 20°C.	1.5440
Gasoline Insoluble	0.1% max.
Ash	0.01%
Viscosity—60% in toluene	22 cps.
Density (at $\frac{25^\circ C.}{25^\circ C.}$ against water)	1.0740

In the past year-and-a-half new rosin modifications have opened up many new applications. An outstanding example is Hercules Poly-pale* Resin. This polymerized rosin offers all the good qualities of natural rosin plus many extra advantages. It extends critical supplies of glycerin, phenol-aldehyde condensates, and maleic anhydride. It eliminates rosin's tendency to crystallize in solution. It has a 15° to 20° higher melting point than rosin. It is pale in color and is widely soluble. For complete technical data, check the coupon block numbered "1" on the next page.

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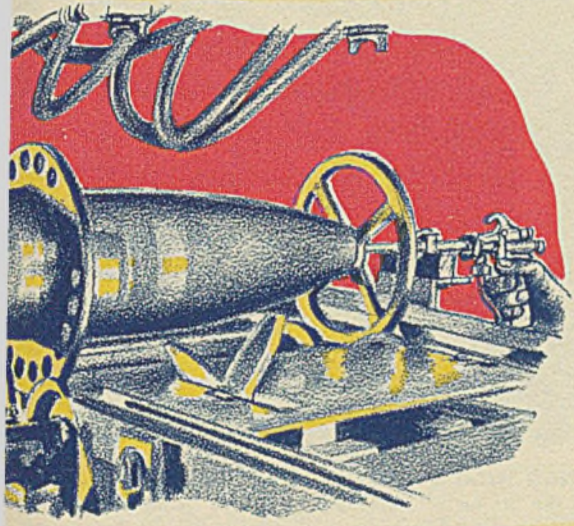

Nitrocellulose lacquers have long been recognized as the fastest-drying finishes known. (Applications air-dry in from 5 to 10 minutes.) In addition, nitrocellulose lacquers provide one of the toughest finishes known—finishes incorporating flexibility, durability, and resistance to water and chemicals.

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Timely Technical Information

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CELLULOSE ACETATE ... Just off press, lists properties and uses of cellulose acetate in plastics and lacquers. Charts, tables, formulation directions. (*Check No. 2 below.*)

STABLE ROSIN DERIVATIVE...Properties and uses of Staybelite*—Hercules' hydrogenated rosin—which combines color and clarity of Hercules Pale Wood Rosins with greatly increased resistance to oxidation and action of light. (*Check No. 3 below.*)

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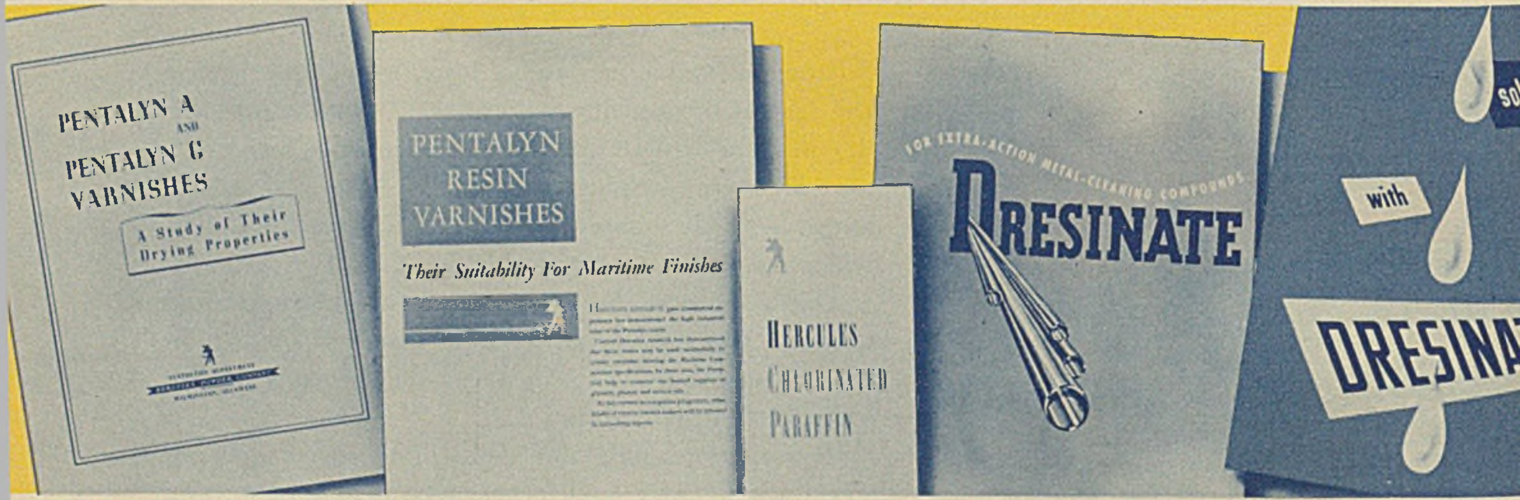

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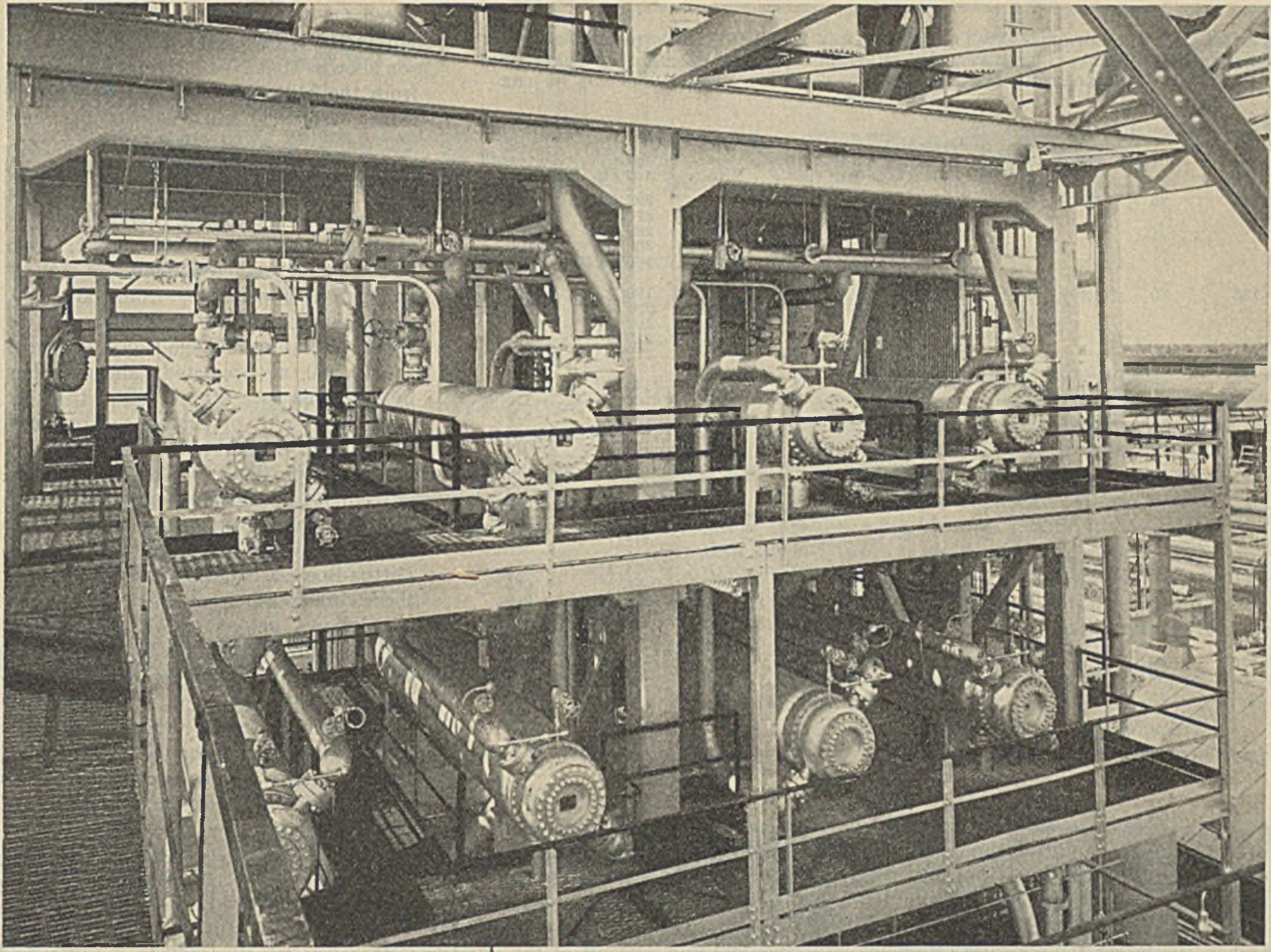

Courtesy, The Lummus Company

Conservation of Heat Energy through the Use of Heat Exchangers Is an Integral Part of Chemical Engineering Design. Shown Above Is a Bank of Heat Exchangers in a Recently Built Defense Plant.

resistances of the pipe metal and of any deposit collecting thereon. The third problem is for heating oil of the same physical properties as that in problem 1. Heating is to be in a double-pipe heat exchanger. The oil flows inside a standard 2-inch pipe at the rate of 3 feet per second at the cold end. Saturated steam condenses on the outside. The steam-side temperature is assumed to be constant at 227° F. along the entire length of the outer jacket. The film coefficient for the steam side is assumed to be 2150.

The terminal operating conditions are listed in Tables I, II, and III. The temperature of the oil or aniline was kept the same at the inlet and varied at the outlet. The temperature of the cooling water was varied at both ends. This approach offers an opportunity for comparing each method with the integration method for different over-all temperature differences at the hot and cold ends of the exchanger.

The film coefficients were calculated from the Dittus-Boelter Equation 5 with $n = 0.7$ for cooling and $n = 0.6$ for heating. The tables show the calculated results. Those calculated by Friend and Lobo (*4*) are included as the last column of Table I.

DISCUSSION

Of the five methods listed in the tables, the fifth is the correct method for calculating the heat transfer area of countercurrent tubular heat exchangers. The calculations are, however, lengthy. Of the remaining four methods, No. 1 is the simplest. It requires about half as much time as the others to complete the calculations. However, when the larger over-all temperature difference is at the hot end (i. e., when $\Delta_h > \Delta_c$) it gives a low answer, and there is the possibility that the deviation from the correct answer will be appreciable and greater than the accuracy required would permit (Tables I and II). The accuracy of the method improves as the over-all temperature at the cold end, Δ_c, is increased. There is no way of predicting offhand the deviation to be expected for a given combination of operating conditions specified in the problem. As Friend and Lobo (*4*) pointed out from practical experience, in most commercial design problems a deviation of −10 to −15 per cent may be expected from method 1. Therefore, using this method and adding about 11 to 18 per cent to the answer may prove satisfactory. This will be the case, for instance, when, as in problem 1 on the cooling of oil, the exchanger is to be assembled in sections of specified length. For greater accuracy and for reliability in accuracy, method 2 appears to be the most satisfactory as long as $\Delta_h > \Delta_c$. The deviation from the correct value is small in all cases listed in Tables I and II, and will possibly be so in other cases. In other words, method 2 gives a result within the accuracy required in such problems. When the larger over-all temperature difference is at the cold end (i. e., $\Delta_c > \Delta_h$) the accuracy of method 1 is as good as that of 2 and is better when Δ_h is de-

TABLE II. VALUES OF HEAT TRANSFER AREA FOR COOLING ANILINE, BASED ON OUTSIDE PIPE AREA, CALCULATED BY DIFFERENT METHODS AND FOR DIFFERENT OVER-ALL TEMPERATURE DIFFERENCES OF THE HOT AND COLD ENDS OF THE EXCHANGER

Temperature, ° C. Aniline		Temperature, ° C. Water		Over-All Δ					
In, T_1	Out, T_2	In, t_1	Out, t_2	Δ_c, $T_2 - t_1$	Δ_h, $T_1 - t_2$	Method No.	Equation No.	Area, Sq. Ft.	Deviation from Correct, %
125	25	20	65	5	60	1	7	298.0	−18.6
						2	9	370.0	1.1
						3	10	289.0	−21.0
						4	11	360.0	−1.6
						5	2	306.0	0.0
125	25	8	65	17	60	1	7	199.2	−10.5
						2	9	231.0	3.8
						3	10	192.5	−13.5
						4	11	223.0	0.1
						5	2	222.6	0.0
125	35	8	65	27	60	1	7	144.6	−6.5
						2	9	156.0	1.0
						3	10	140.8	−8.9
						4	11	156.7	1.4
						5	2	154.5	0.0
125	45	8	65	37	60	1	7	109.7	−4.6
						2	9	116.0	1.1
						3	10	107.8	−6.0
						4	11	114.5	−0.2
						5	2	114.7	0.0
125	60	8	65	52	60	1	7	74.5	−2.2
						2	9	76.6	0.5
						3	10	74.0	−2.9
						4	11	76.1	−0.1
						5	2	76.2	0.0
125	60	8	75	52	50	1	7	83.0	−1.2
						2	9	85.0	1.1
						3	10	82.6	−1.8
						4	11	84.5	0.5
						5	2	84.1	0.0

creased (Table III). It is interesting to observe the deviation signs (Table III) and to compare them with those of the preceding cases (Tables I and II). When $\Delta_c > \Delta_h$, method 1 appears to be the best of the simpler methods. This observation is supported by the statement from Friend and Lobo (*4*) that "when the larger temperature difference is at the cold end, method 1 gives more nearly correct results".

Table I shows that the author's results are higher than those of Friend and Lobo. This is due to the fact that the former values are based upon film coefficients calculated from the Dittus-Boelter Equation 5, the latter from the Sieder-Tate correlation (*7*). The film coefficients calculated from the Dittus-Boelter equation are lower than those from the Sieder-Tate correlation. For instance, the film coefficient of the cooling oil in problem 1 at 400° F. is 326 when calculated from the Dittus-Boelter equation, and is 378 (according to Friend and Lobo) when calculated from the Sieder-Tate correlation. It is difficult to explain this difference as both equations are based upon experimental data. Boelter, Martinelli, and Jonassen (*1*) and others before them recognized the need of an analytical approach to heat transfer by conduction-convection in the turbulent region. Using the analogy of heat and momentum transfer, they analytically correlated the Nusselt, Prandtl, and Reynolds moduli. While their correlation is too complicated to be of practical value to designers, it serves an excellent purpose as a reference or standard equation. Thus, experimental Nusselt values, taken from the literature, were compared with those predicted from the analytical equation and were found to agree within ±20 per cent. The same experimental Nusselt values were compared (*1*) with those predicted from the Dittus-Boelter equation. This comparison showed that Nusselt values predicted from the Dittus-Boelter equation varied from −20 to as much as +60 per cent. The comparison covered a range of experimental Nusselt values from about 15 to 500. To be more specific, for Nusselt values from 15 to 50, all predicted values are high by as much as 15 per cent; from 50 to 100, all predicted values are high by as much as 60 per cent; from 100 to 180, the predicted values gradually shift to lower values and change sign; and from 180 to 500, all predicted values are low by as much as −20 per cent. In other words, the plot of experimental against predicted Nusselt values showed a "bumped" portion. Whether this nature of the plot is significant is not now known. For the present, the important fact is that film coefficients predicted from the Dittus-Boelter equation are lower than those predicted from the Sieder-Tate correlation; yet as shown above, they may be high by as much as 60 per cent when compared with experimental values. It is evident that there is a great need for examining anew all available data for the purpose of recommending a correlation which is simple enough to be acceptable and still compares favorably with the analytical equation. Until then it is left to the individual designer to make the choice between the Dittus-Boelter equation and the Sieder-Tate correlation, when the Reynolds number is greater than 8000. For a Reynolds number less than 8000, the use of the Dittus-Boelter equation is out of the question; therefore the Sieder-Tate graphic correlation which extends to include the transition and the viscous flow regions should be used.

TABLE III. VALUES OF HEAT TRANSFER AREA FOR HEATING OIL, BASED ON OUTSIDE PIPE AREA, CALCULATED BY DIFFERENT METHODS AND FOR DIFFERENT OVER-ALL TEMPERATURE DIFFERENCES OF THE HOT AND COLD ENDS OF THE EXCHANGER

Temperature, ° F. Steam		Temperature, ° F. Oil		Over-All Δ					
In, T_1	Out, T_2	In, t_1	Out, t_2	Δ_c, $T_2 - t_1$	Δ_h, $T_1 - t_2$	Method No.	Equation No.	Area, Sq. Ft.	Deviation from Correct, %
227	227	80	200	147	27	1	7	107.0	3.1
						2	9	101.8	−1.9
						3	10	106.0	2.1
						4	11	102.2	−1.5
						5	2	103.8	0.0
227	227	80	220	147	7	1	7	186.0	1.1
						2	9	174.6	−5.1
						3	10	187.2	1.7
						4	11	171.5	−6.8
						5	2	184.0	0.0

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Power Consumption of PROPELLER-TYPE AGITATORS

C. E. Stoops[1] and C. L. Lovell

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The power consumed by certain propeller-type agitators has been studied. The dynamometer used to measure the shaft power is described. The data are correlated by dimensional analysis. The following equation, in consistent units, gives the best correlation of the data:

$$P = 0.56\rho^{0.8}\mu^{0.2}N^{2.8}L^{3.7}D^{0.9}$$

Attention is called to the fact that no critical value is found for the modified Reynolds number, $\rho NL^2/\mu$.

MIXING is an engineering operation which has probably received less quantitative study than any other operation in the process industries. There are several reasons. A mixing job can be performed in almost any type of equipment, from an old broomstick and a tin bucket to huge vats with side-entering propellers. So many variables are involved and a rational correlation of them seems so difficult that most workers have turned to more profitable fields.

If, however, an engineer wishes to estimate or design a mixer with any degree of accuracy, a method must be devised whereby he can calculate the necessary power and the time to achieve the desired results for any one of several types of agitators. In spite of the apparent similarity, the interrelation between the various objectives of agitation and the variables is such that each objective must be studied separately. For example, if in dissolving a solid, the rate of solution is known as a function of several variables and if the power consumption of the agitator is known, it should be comparatively simple to calculate the energy that will be consumed in dissolving the material. The same consideration holds for the heating of a liquid. Yet there is no reason to suppose that the rate of solution and the rate of heat transfer (not to mention the maintenance of a suspension, production of an emulsion, etc.) would obey the same laws. The use, without further proof, of one objective as a general criterion of the effectiveness of a mixer would be illogical.

A sound, long-range program must devote itself to a study of the power consumption for many varied types of equipment, to their effectiveness in accomplishing the varied desired results, and to a correlation of these and all the variables involved. The magnitude of such a program may be judged by consulting Valentine and MacLean's summary (*6*) of the available types of equipment and their uses. Hixson and co-workers (*1–5*) have done considerable work on the solution of solids, wall friction of a propeller-type agitating system, and the power consumption of turbine-type agitators. White and co-workers (*7*, *8*, *9*) have studied the power consumption of paddle-type agitators.

This investigation is concerned with only one aspect of the general problem—a study of the power necessary to turn certain propeller-type agitators under varying conditions.

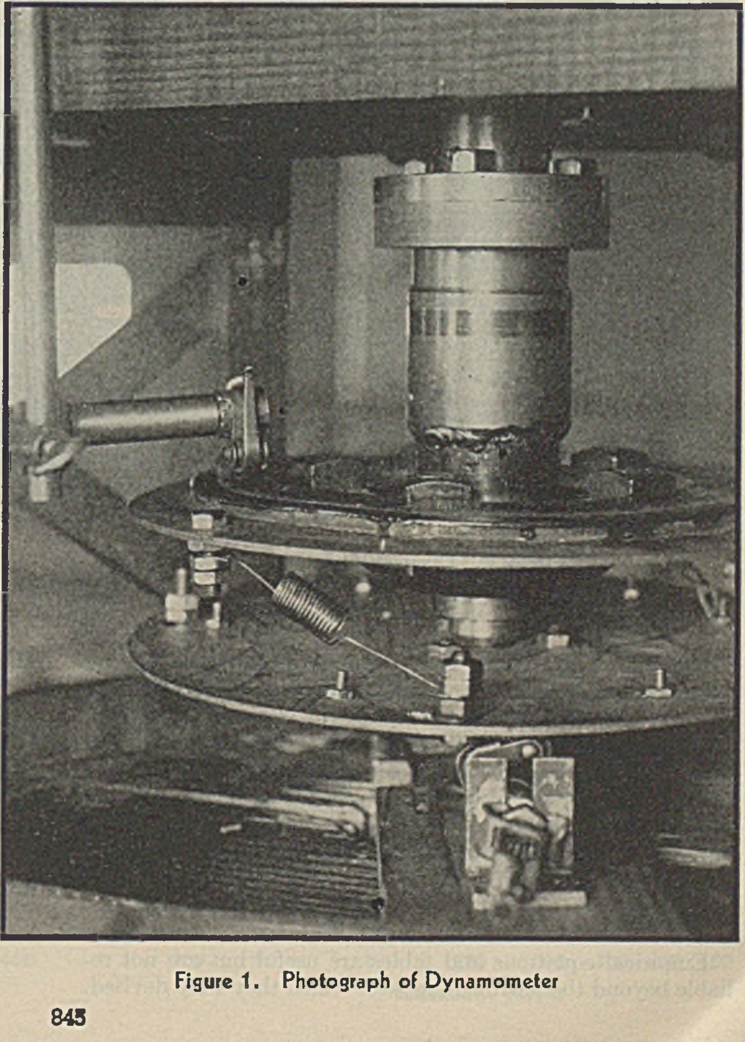

Figure 1. Photograph of Dynamometer

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[1] Present address, Lehigh University, Bethlehem, Penna.

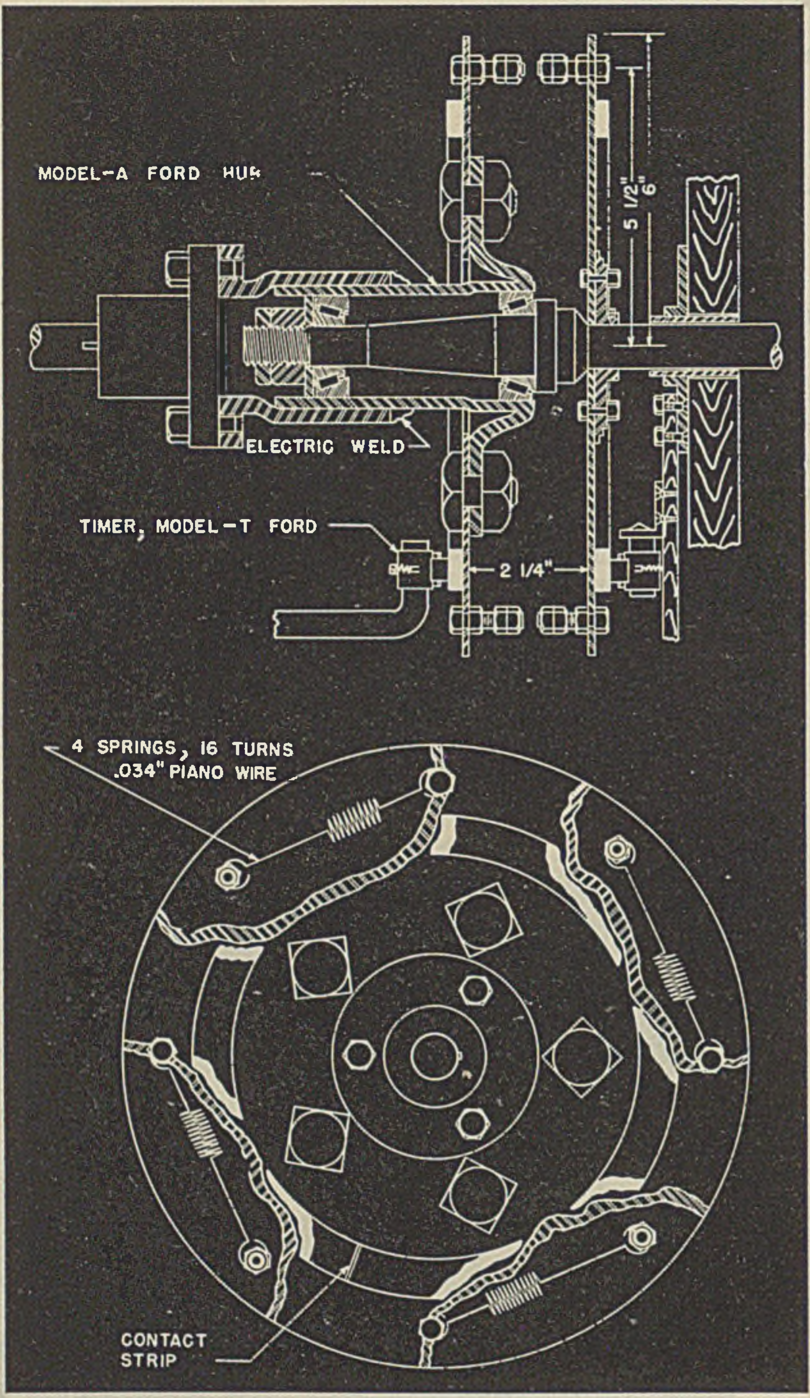

Figure 2. Diagrams of Torsional Dynamometer

Data can be correlated by: (*a*) analytical equations based on scientifically accepted theories and laws of physics and chemistry, (*b*) empirical equations, (*c*) equations based on dimensional analysis and the theory of models, and (*d*) equations based on semianalytical consideration. Although the first is probably the ultimate goal, it can be for the present pigeonholed. In spite of the amount of work done in fluid flow, no universally applicable analytical method has been developed in that field. The research engineer can expect to do no better in this field of mixing which is so intimately connected with that of fluid flow.

Empirical equations and tables are useful but are not reliable beyond the narrow ranges for which they were devised. They tend to lead to erroneous conclusions by lumping together or ignoring certain variables. A report on work performed by a commercial testing laboratory and accepted by a manufacturer of mixing equipment illustrates this tendency. The experimenter tried to correlate power consumption and viscosity. The correlation was poor because it ignored the change of other properties of the liquid when the viscosity was changed. Extrapolation from the data to liquids of the same viscosity but different densities would be almost worthless. Nevertheless, power corrections are found based on nothing but the difference in viscosity of the reference liquid (usually water) and the liquid to be mixed.

The methods of dimensional analysis and the theory of models combined with analytical approaches offer the best method of attacking the problem. If an exponential function is assumed, the following dimensionless equation can be written:

$$\frac{P}{\mu N^2 L^3} = K\left(\frac{\rho N L^2}{\mu}\right)^a \left(\frac{g}{N^2 L}\right)^b \left(\frac{D}{L}\right)^c \left(\frac{H}{L}\right)^d \left(\frac{W}{L}\right)^e \left(\frac{X}{L}\right)^f \quad (1)$$

where K, a, b, c, d, e, f = dimensionless constants to be determined experimentally

ρ = density of fluid
μ = viscosity of fluid
P = power consumed by agitator
N = propeller speed
L = diameter of agitator
D = tank diameter
H = height of liquid
W = width of agitator
g = acceleration of gravity
X = height of propeller above tank bottom

The theory of models states that, if two systems are geometrically similar, they are dynamically similar when the ratios of the various forces acting on one system are equal to the same ratios on the other system. $\rho N L^2/\mu$ can readily be recognized as the Reynolds number and is the ratio of the inertia force to the viscous force; in fluid flow work it is considered to measure turbulence. g/N^2L is Froude's number, named after the naval architect who first used it in ship design, and is the ratio of inertia force to gravity force. It is considered to measure the power consumed in wave formation. If the significant physical quantities have been chosen properly, these terms will determine the dynamic similarity of two systems. The other terms on the right-hand side of the equation are obviously geometrical terms. This analysis does not include certain geometric factors such as the propeller blade angle, baffling the tank, etc.

White and Brenner (*7*), ignoring the power consumption of wave formation (which is justified), gave a slightly different form:

$$\frac{P}{\rho N^3 L^5} = K\left(\frac{\mu}{L^2 N \rho}\right)^a \left(\frac{W}{L}\right)^b \left(\frac{H}{L}\right)^c \left(\frac{D}{L}\right)^d$$

Their evaluation of the constants for a simple paddle agitator gave:

$$P = 0.000129\, L^{2.72} Z^{0.14} N^{2.86} \rho^{0.86} D^{1.1} W^{0.3} H^{0.06}$$

White and Summerford (*9*), from the same data, found a critical value for the Reynolds number. Hixson and Luedeke (*4*), studying wall friction for a simple agitating system with propellers, found:

$$P = \alpha \rho^{0.78} \mu^{0.20} n^{2.79} d^{3.58}\, (d + 4h) \sin (1.13\theta - 12)$$

Hixson and Baum (*3*), in an extensive study of turbine agitating systems, obtained for standard design:

$$P = 1.50 \times 10^{-10} n^{2.88} d^{4.76} \gamma^{0.88} \mu^{0.12}$$

They also found a critical range for the Reynolds number.

GENERAL METHODS OF MEASURING POWER

In the design of mixing equipment, it is almost obvious that the energy absorbed by the driving mechanism and the energy absorbed by the fluid system must be considered separately. The study of losses in the electrical or mechanical driving systems more properly belongs in other provinces.

The following methods suggest themselves:

1. Calibrate an electrical drive by means of a Prony brake and correlate the mechanical power output with the electrical power input.
2. Connect the driving shaft with the driven shaft by means of a fluid or magnetic drive, and determine the power by the slip and the speed of the shaft.
3. Place the mixing vessel on a turntable and then determine the torque necessary to prevent rotation of the tank.
4. Connect the driving shaft to the driven shaft by a spring system, and measure the torque by the displacement of the two shafts.

The first method seemed the most practical. It apparently would require simple equipment and expedite the taking of data. Several trials showed that this was not true. The

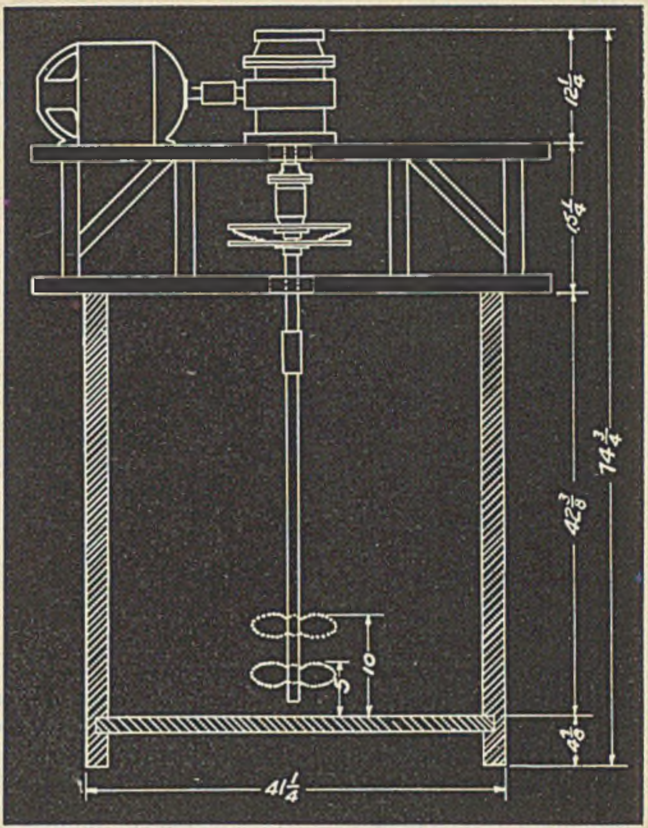

Figure 3. Agitator Assembly (Dimensions in Inches)

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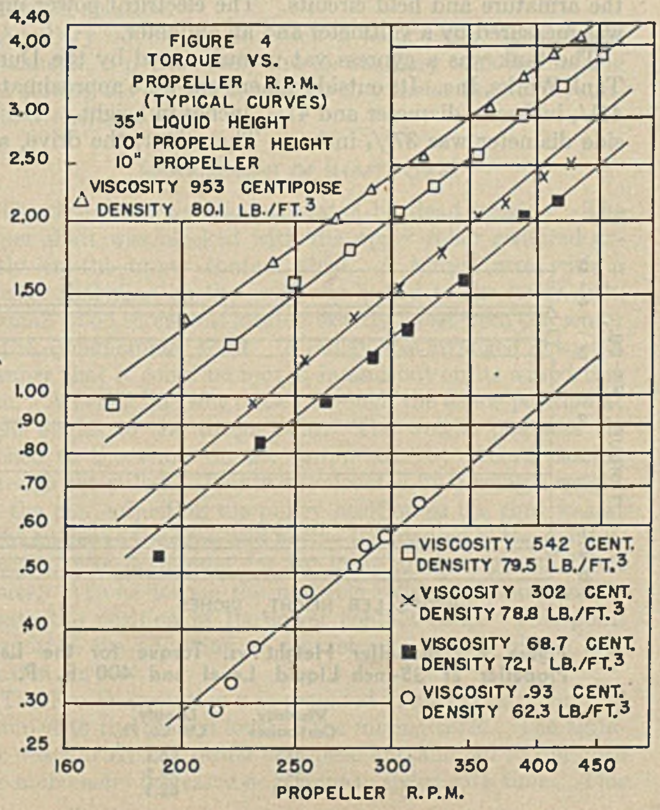
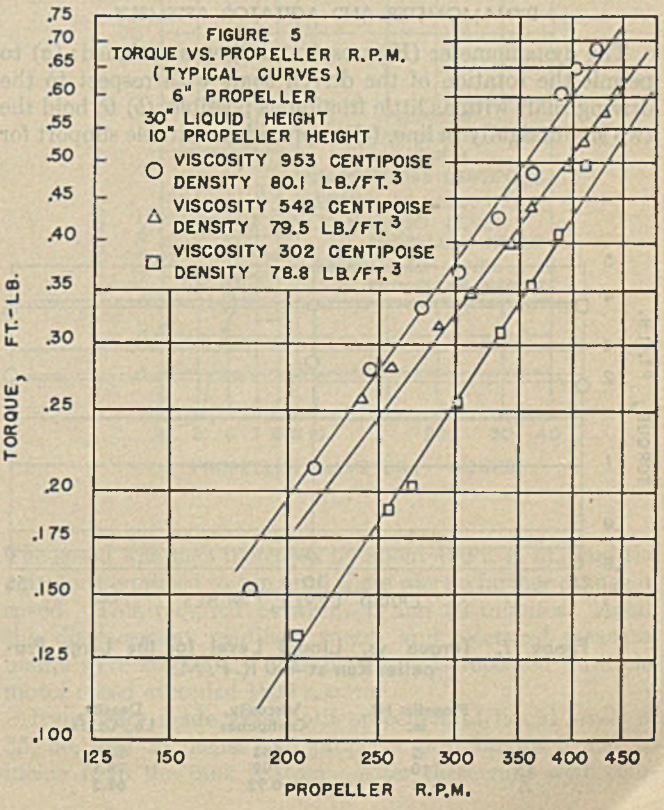
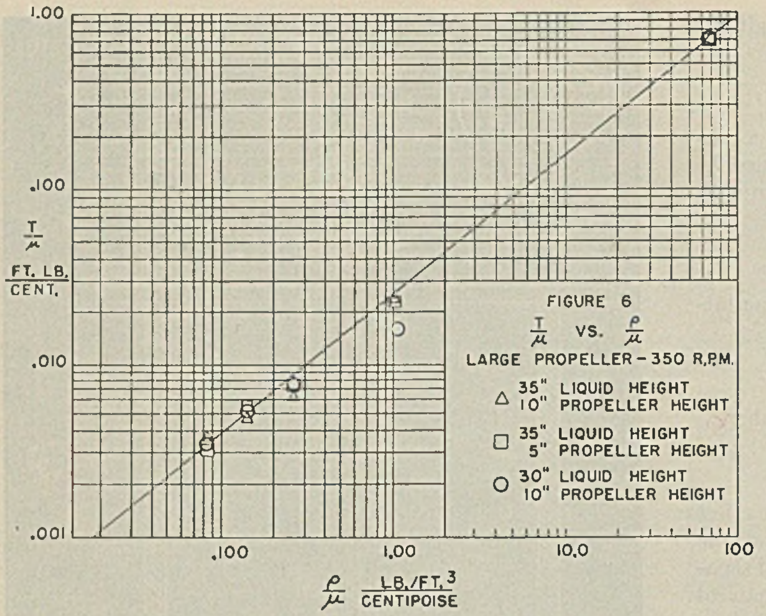






mechanical energy was very small compared to the electrical energy, and such items as hysteresis and resistance change with temperature became so important that no reasonable correlation could be made.

The second method would require such careful design and extraordinary shop facilities that it was not even considered.

The third method has been used successfully by White and Brenner (*7*). Hixson and co-workers (*3, 4*) employed a similar piece of equipment for measuring wall friction in a cylindrical agitation system and in their power study of turbine type agitation. This method was considered impractical because of the difficulty and expense of constructing a turntable large enough for the tank to be used.

The fourth method was considered feasible and such a dynamometer was built.

DYNAMOMETER AND AGITATOR ASSEMBLY

The dynamometer (Figures 1 and 2) was designed: (*a*) to permit the rotation of the driven shaft with respect to the driving shaft with as little friction as possible, (*b*) to hold the two shafts rigidly in line, (*c*) to provide a suitable support for easily changed springs, and (*d*) to provide a suitable method for measuring the angular displacement of the two shafts.

The first two considerations were solved by means of tapered roller bearings. The front wheel housing of a Model-A Ford supplied both the bearings and outer support. The propeller (driven) shaft was machined to conform to the dimensions of the spindle and fitted to the bearings. A coupling adapter was roughly machined from a piece of 4-inch cold-rolled shafting and welded to the housing. The dynamometer was then assembled, and the adapter machined accurately. Two $^1/_4 \times$ 12 inch sheet metal disks were cut out. One was attached to the housing and the other to the propeller shaft. Suitable spring mounts were provided on the disks. A snub chain was attached to disks to prevent excess torque from stretching the springs beyond their elastic limit.

The angular-displacement measuring device consisted of two contact strips set in plywood insulator rings and roller contacts from a Model-T Ford timer. One roller was mounted in a fixed position and the other attached to a movable arm. The arm turned about the shaft center but did not touch the shaft. A pointer was attached to the arm so its position could be read on the scale. The relative position of the contact strips was determined by using earphones to detect the closing of a 45-volt direct-current circuit when the movable roller was in the proper position.

Eight springs were wound on the lathe. Four were wound of 18-gage piano wire and four of 16-gage. They were a half inch in diameter and had sixteen turns. The number and size could be adjusted to meet the torque range.

The agitator drive was a fully enclosed, four to one, worm-gear reduction unit (Model WT 11) manufactured by the New England Tank and Tower Company. It was powered by a one-horsepower, shunt-wound, 220-volt, d. c. motor. The motor speed was controlled by variable resistances in the armature and field circuits. The electrical power input was measured by a voltmeter and an ammeter.

The tank was a cypress vat manufactured by the Dunck Tank Works, Inc. Its outside dimensions were approximately $41^1/_4$ inches in diameter and $47^1/_4$ inches in height. The inside diameter was $37^3/_4$ inches. The motor, the drive, and

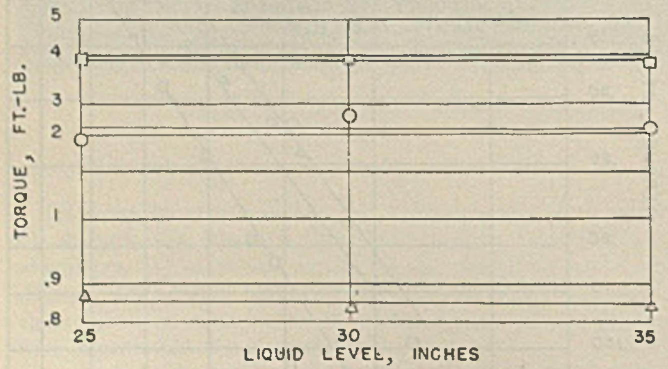


Figure 7. Torque vs. Liquid Level for the Large Propeller Run at 400 R. P. M.

	Propeller Ht., In.	Viscosity, Centipoises	Density, Lb./Cu. Ft.
□	5	953	80.1
○	10	302	78.1
△	5	0.93	62.3

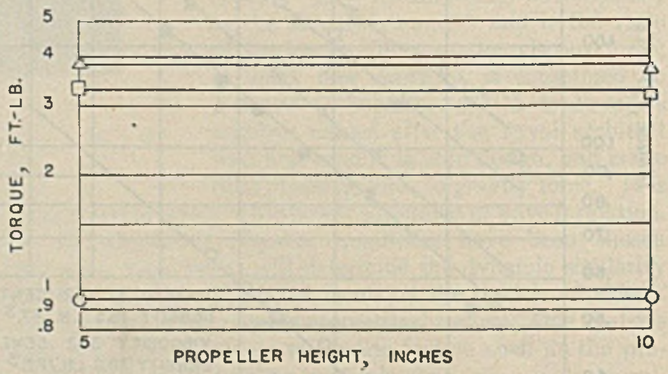


Figure 8. Propeller Height vs. Torque for the Large Propeller at 35-Inch Liquid Level and 400 R. P. M.

	Viscosity, Centipoises	Density, Lb./Cu. Ft.
△	953	80.1
□	542	79.5
○	0.93	62.3

Table I. Typical Runs with Propeller Height of 5 Inches, Liquid Viscosity of 953 Centipoises, and Density of 80.1 Pounds per Cubic Foot

Scale Deflection	Av. Propeller Speed, R. P. M.	Armature		Torque, Ft.-Lb.	Mechanical Output, Watts	Electrical Input, Watts	$\frac{\rho N L^2}{\mu}$	$\left(\frac{\rho N L^2}{\mu}\right)^{0.7}$	$\frac{P}{\mu N^2 L^3}$	$\left(\frac{D}{L}\right)^{0.8}$	$\left(\frac{D}{L_i}\right)^{0.8}\left(\frac{\rho N L^2}{\mu}\right)^{0.7}$
		Voltage	Amperage								
6-Inch Propeller, 25-Inch Liquid Height, One Spring; $\rho NL^2/\mu = 0.521\ N$; $P/\mu N^2L^3 = 154{,}000\ (T/N)$											
3.1	179	79	1.30	0.150	3.9	102	93	23.9	128	4.35	103.5
4.1	212	95	1.38	0.195	5.9	131	111	27.1	142	4.35	118
5.5	244	108	1.40	0.260	9.0	151	122	29.0	164	4.35	126
6.1	272	119	1.48	0.285	11.0	176	142	32.2	162	4.35	140
7.5	304	131	1.50	0.350	15.1	196	159	34.8	177	4.35	151.5
8.4	331	141	1.52	0.395	18.6	214	173	36.9	183	4.35	160.5
9.5	355	151	1.58	0.450	22.7	239	185	38.8	195	4.35	169
11.3	379	160	1.45	0.535	28.8	232	198	40.5	217	4.35	176
12.1	396	167	1.50	0.560	31.5	250	207	41.9	217	4.35	182
13.9	420	177	1.55	0.605	36.1	274	219	43.4	222	4.35	189
14.9	436	184	1.55	...	..	285	228	44.8	...	4.35	195
10-Inch Propeller, 30-Inch Liquid Height, Three Heavy Springs; $\rho NL^2/\mu = 1.448\ N$; $P/\mu N^2L^3 = 1.985\ T/N$											
3.5	183	88	1.52	1.15	29.9	134	265	49.8	207	2.90	144
4.1	215	104	1.70	1.15	40.3	177	311	56.0	203	2.90	162
5.9	250	119	1.80	1.32	66.4	204	362	62.0	248	2.90	180
7.1	280	123	1.90	1.87	87.5	234	405	67.0	261	2.90	194
8.5	309	142	2.10	2.20	113.2	298	447	72.0	277	2.90	209
9.1	340	160	2.28	2.58	132.3	365	492	77.0	257	2.90	223
11.5	364	170	2.40	2.74	169.0	408	527	80.0	302	2.90	232
13.0	389	179	2.50	3.27	198.9	448	562	84.0	307	2.90	244
15.3	411	192	2.71	3.60	234.6	520	594	87.5	325	2.90	254
17.6	435	202	2.90	4.02	...	586	630	91.0	...	2.90	264
18.0	451	215	3.00	..	...	645	652	93	...	2.90	270

the tank were mounted as shown in Figure 3 and placed on a wooden platform. The propeller shaft was vertical and located in the center of the tank. The propellers were three-bladed, made of stainless steel, and manufactured by the Mixing Equipment Company, Inc. The small propeller was 6 inches in diameter and $1^1/_8$ inches thick; the large propeller was 10 inches in diameter and $1^7/_8$ inches thick. The propeller shaft was $^7/_8$ inch in diameter. The shaft was split and connected by a coupling to facilitate changing the propellers.

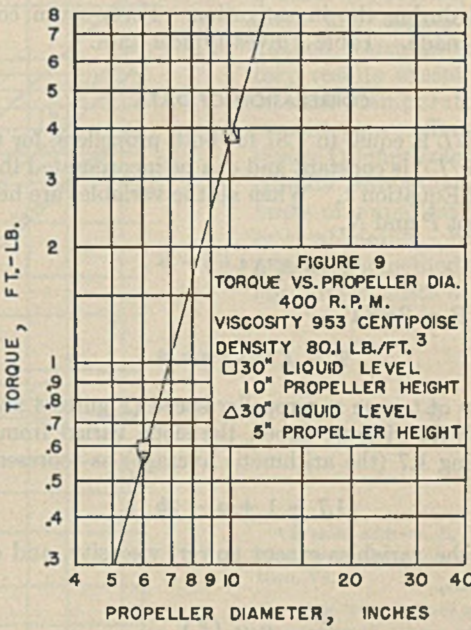
The liquid media were water and a series of solutions of Fro-Dex, a corn sirup solid manufactured by the American Maize Products Company. This material offered the advantages of being readily available and of having a viscosity which could easily be changed by dilution. The most concentrated solution contained 1700 pounds of Fro-Dex in 230 gallons of solution.

Auxiliary equipment included a tachometer, an Ostwald viscometer, a pycnometer, and an auxiliary tank for making and storing the solutions, a pump to transfer the liquid, suitable wrenches, etc.

MEASUREMENT OF SHAFT POWER

The dynamometer was calibrated by dead weights. The upper shaft was blocked with the upper roller centered exactly on the upper contact strip. A torque arm with a pointer that read on the scale was bolted to the lower disk. A small wood screw was located exactly 2 feet from the center of the dynamometer shaft. A pulley was arranged in such a manner that it could be moved in and out on its supporting arm. A pencil line was drawn through the screw position at right angles to the torque arm. The weight pan was attached to the screw on the torque arm by a cord passing through the pulley. Points were located by placing a weight on the pan, adjusting the pulley position so the cord was at right angles to the arm, and noting the reading of the pointer. Friction was accounted for by locating the right and left limits. At one torque the movable roller arm was used to locate the position of the lower contact strip. This point permitted the adjusting of contact strip points to the calibration curve.

The Fro-Dex solution was prepared in an auxiliary vat and pumped to the desired level in the mixing tank. The agitator was started at a rather low speed and allowed to run until the tachometer indicated no change in speed with time. This required from about 15 minutes to an hour, more often the latter. The voltage, amperage, and motor speed were recorded. The roller arm was adjusted until clicks could be heard in the earphones. The right and left limits of this range were recorded. (At moderately high speeds the lower shaft oscillated with respect to the upper. This period never exceeded 30 seconds. Under these conditions and starting from the clicking range, the outer limit was determined by the point at which no clicks could be heard for at least 30 seconds.)



The speed was then increased by about 100 r. p. m., and the agitator permitted to run until there was no further change in speed. This required between 10 and 30 minutes. Again the displacement readings, speed, and electrical measurements were recorded. This process was repeated until the motor speed exceeded 1800 r. p. m.

Runs were made with both propellers at liquid levels of 35, 30, and 25 inches and propeller positions of 5 and 10 inches from the tank bottom. After these runs were com-

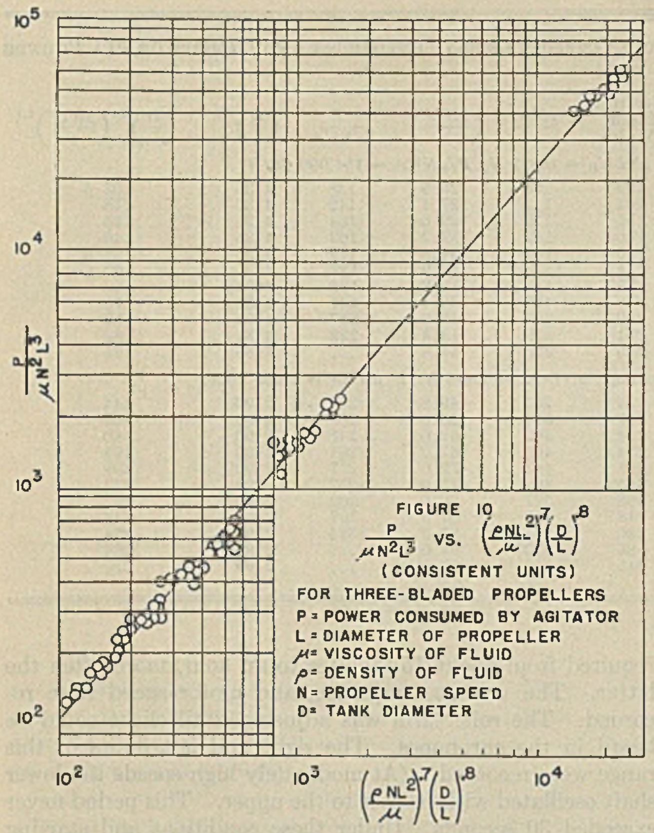


FIGURE 10
$\frac{P}{\mu N^2 L^3}$ VS. $\left(\frac{\rho N L^2}{\mu}\right)^{.7}\left(\frac{D}{L}\right)^{.8}$
(CONSISTENT UNITS)
FOR THREE-BLADED PROPELLERS
P = POWER CONSUMED BY AGITATOR
L = DIAMETER OF PROPELLER
μ = VISCOSITY OF FLUID
ρ = DENSITY OF FLUID
N = PROPELLER SPEED
D = TANK DIAMETER

pleted, the material was diluted and another series of runs performed. Four different Fro-Dex solutions and tap water were used during the investigation. Forty-seven complete runs were made. Table I gives typical data.

CORRELATION OF DATA

Since W/L is equal to 1.87 for both propellers, for this set of data $(W/L)^e$ is constant and can be incorporated into constant K of Equation 1. When all the variables are held constant except P and N,

$$P = K'N^{2+a-2b} \tag{2}$$

But since $P = 2\pi NT$,

$$T = K''N^{1+a-2b} \tag{3}$$

From plots of torque *vs.* propeller speed (Figures 4 and 5 are typical) on logarithmic paper, the slope varied from 1.6 to 1.9. Taking 1.7 (the arithmetic average) as representative,

$$1.7 = 1 + a - 2b \tag{3A}$$

When all the variables except power, viscosity, and density are constant,

$$\frac{P}{\mu} = K'''\left(\frac{\rho}{\mu}\right)^a \tag{4}$$

Expressing the equation in terms of torque rather than power,

$$\frac{T}{\mu} = K''''\left(\frac{\rho}{\mu}\right)^a \tag{5}$$

A plot of (T/μ) *vs.* (ρ/μ) on logarithmic paper is shown in Figure 6. The slope is 0.7; therefore a has a value of 0.7. Substituting in Equation 3A and solving, b has a value of 0. This would indicate that Froude's number has little effect and is tentatively dropped from the equation. Within the accuracy of this set of experimental data, the liquid depth (Figure 7) and propeller position (Figure 8) have a negligible effect on power consumption. The equation then simplifies to:

$$\frac{P}{\mu N^2 L^3} = K'''''\left(\frac{\rho N L^2}{\mu}\right)^{0.7}\left(\frac{D}{L}\right)^c \tag{6}$$

or

$$\frac{2\pi NT}{\mu N^2 L^3} = K'''''\left(\frac{\rho N L^2}{\mu}\right)^{0.7}\left(\frac{D}{L}\right)^c \tag{7}$$

If all factors except T and L are constant,

$$T = K''''''L^{4.4-c} \tag{8}$$

The slope of torque *vs.* propeller length plotted on logarithmic coordinates (Figure 9) is 3.6; then c has a value of 0.8, and

$$\frac{P}{\mu N^2 L^3} = K'''''\left(\frac{\rho N L^2}{\mu}\right)^{0.7}\left(\frac{D}{L}\right)^{0.8} \tag{9}$$

All the dimensionless ratios were calculated in consistent units, and $P/\mu N^2L^3$ was plotted against $(\rho NL^2/\mu)^{0.7} \times (D/L)^{0.8}$ on logarithmic paper. For clarity only every fourth or fifth point is shown in Figure 10. If the exponents had been chosen properly, the best line drawn through the points would have a slope of 1. But evaluation of the best line through this set of points gave the equation:

$$\frac{P}{\mu N^2 L^3} = 0.56\left[\left(\frac{\rho N L^2}{\mu}\right)^{0.7}\left(\frac{D}{L}\right)^{0.8}\right]^{1.16} \tag{10}$$

or

$$\frac{P}{\mu N^2 L^3} = 0.56\left(\frac{\rho N L^2}{\mu}\right)^{0.81}\left(\frac{D}{L}\right)^{0.93} \tag{11}$$

This indicates that the representative slope for the plots of torque *vs.* propeller speed should be 1.8 rather than 1.7. Since the value of c is based on a limited number of points, there is little choice between values of 0.8 and 0.9. The data are probably best represented by the following exponential equation (in consistent units):

$$P = 0.56\rho^{0.8}\mu^{0.2}N^{2.8}L^{3.7}D^{0.9} \tag{12}$$

The exponent of 0.8 for the Reynolds number is in agreement with previous work. Perhaps coincidentally, this is the same value given in many heat transfer equations. Although the physical appearance of the liquids varied from very turbulent to very placid, there seems to be no evidence of a critical range for this ratio. This may not be what would be expected, particularly since evidence of critical ranges has been reported (*3*, *4*, *8*). Yet the placid appearance and the apparent continuity of the function can be readily rationalized by the assumption of a turbulent core in the immediate vicinity of the propeller at all the speeds employed.

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Based on a Ph.D. thesis by Charles E. Stoops, Purdue University.

HEATS OF VAPORIZATION from REFERENCE SUBSTANCE PLOT

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A plot of the vapor pressure of a substance against the vapor pressure of a reference substance at the same values of reduced temperature gives a straight line whose slope is equal to $(T'_c/T_c) \times (L/L')$, where T_c and L represent the critical temperature and the molal latent heat of vaporization, respectively, and the primes indicate a reference substance. This is true because of the relative constancy of the ratio L/L' when both are taken at the same value of reduced temperature. From the slope of the line, from the critical temperatures of the substance in question and of the reference, and from the latent heat of vaporization of the reference substance, the latent heat of vaporization of the substance in question can be calculated at any temperature.

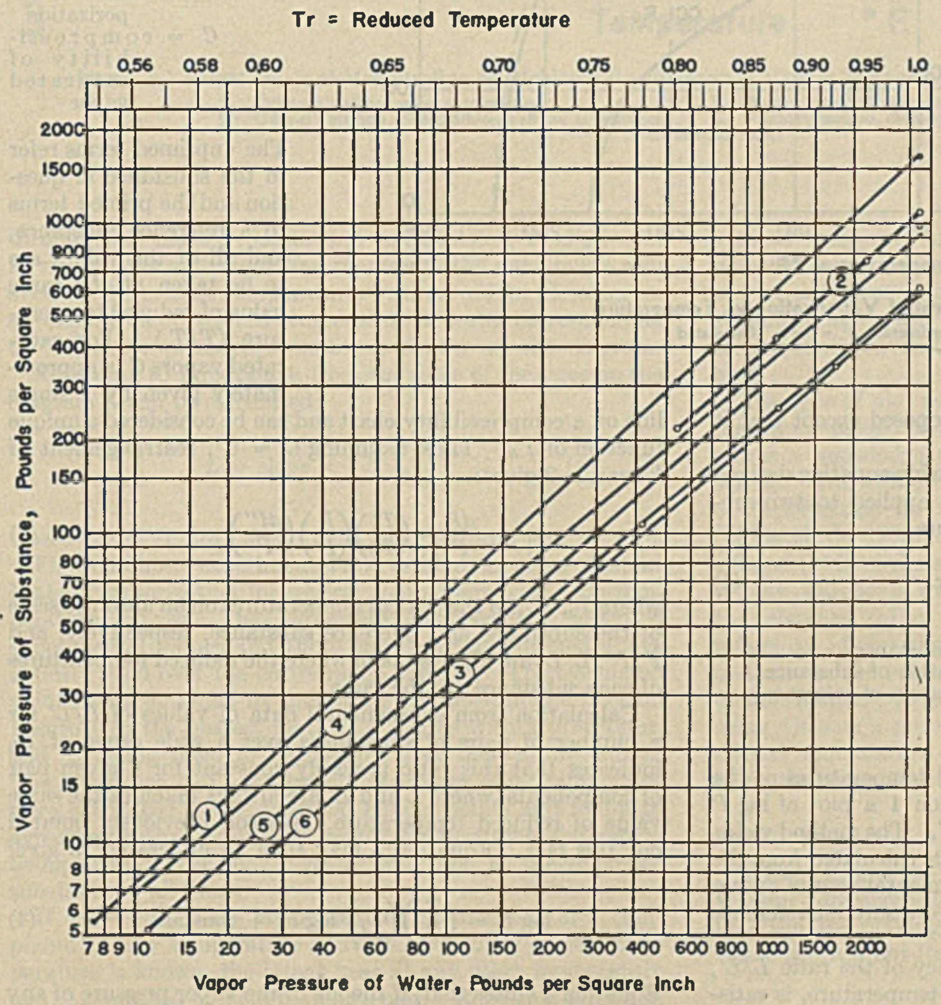

Figure 1. Plot of Various Substances against Water as Reference

1. Ammonia
2. Carbon dioxide
3. Propane
4. Methyl chloride
5. Dichlorofluoromethane
6. Dichlorodifluoromethane

SEVERAL methods for estimating latent heats of vaporization from reference-substance vapor pressure plots are available. Othmer (*1*) recently reviewed these and suggested a new method which gives satisfactory results except near the critical temperature. The present paper offers modification to Othmer's method which permits estimation of latent heats of vaporization to the critical point. Watson (*2*) presented a method of estimating latent heats of vaporiza-

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EDITOR'S NOTE. Since material complementing that here presented was published earlier [D. F. Othmer, IND. ENG. CHEM., 34, 1072 (1942)], it should be pointed out that this article in substantially its present form was first received in the editor's office on March 10, 1942. An unusual combination of circumstances originating in the editorial offices has been responsible for delay in publication. This fact is mentioned that the author may receive due credit for his contribution where the question of priority is involved.

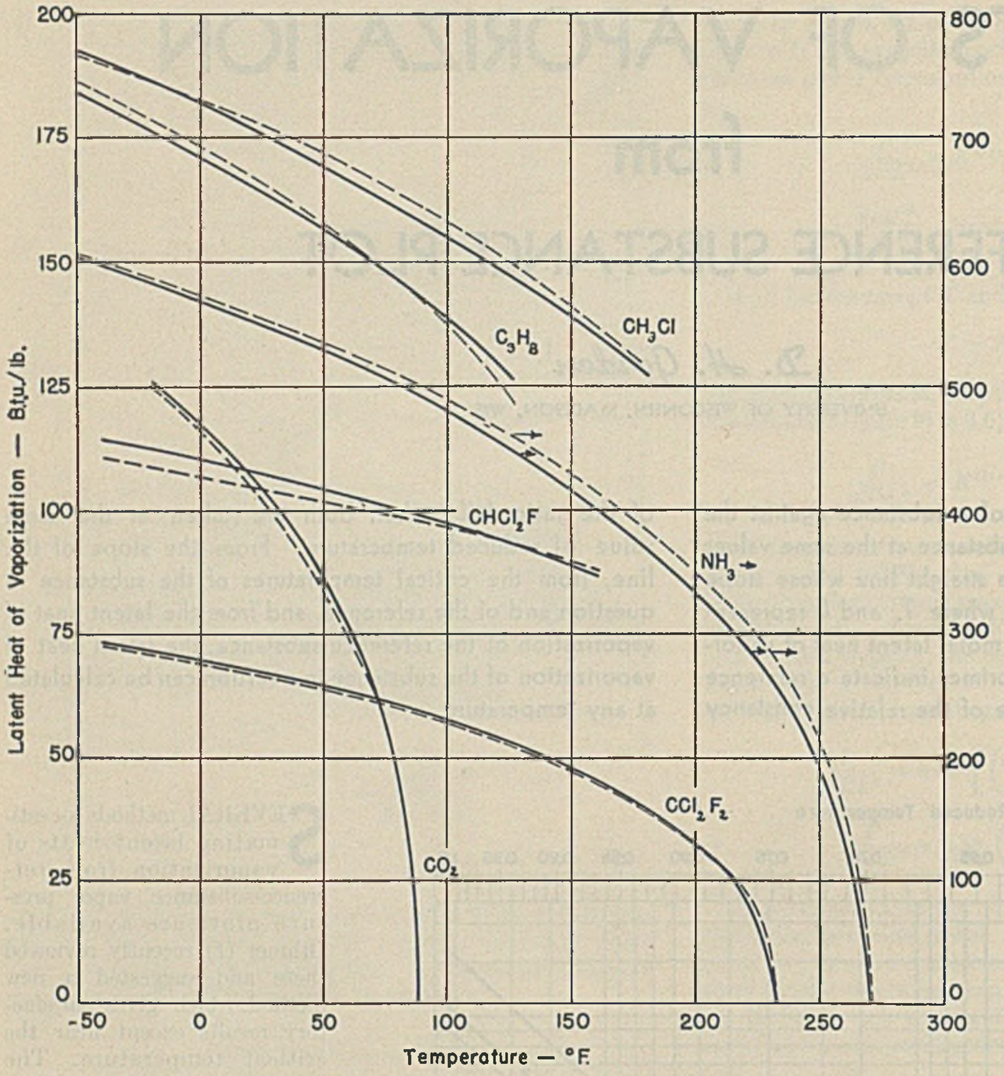

Figure 2. Latent Heat of Vaporization *vs.* Temperature

——— Experimental - - - - Calculated

tion which is similar to the one here proposed except that it is not based on a vapor pressure plot.

Othmer's method is based on the following equation derived from the Clausius-Clapeyron equation applied to two substances at the same absolute temperature:

$$\log P = \frac{L}{L'} \log P' + c \tag{1}$$

where P = vapor pressure of substance
P' = vapor pressure of reference substance
L = molal latent heat of vaporization of substance
L' = molal latent heat of vaporization of reference substance
c = constant

The above values are taken at equal temperatures of the two substances. According to Equation 1 a plot of log P *vs.* log P' gives a line whose slope is L/L'. The method yields essentially straight lines, and latent heats calculated from the slope agree reasonably well with experimental results over a considerable temperature range, provided a suitable reference substance is used.

While the assumption of the constancy of the ratio L/L', where L and L' are taken at the same temperature, is satisfactory over a short temperature interval, it cannot hold at temperatures near the critical for either the substance in question or the reference substance, unless they have the same critical temperature. This suggests that latent heats of vaporization should properly be compared at the same reduced temperatures. Othmer pointed out the restriction of his method to temperature ranges removed from the critical of either substance.

Following a derivation similar to Othmer's, but introducing a generalized expression in terms of compressibility for the vapor volume in the Clapeyron equation and using reduced temperatures throughout,

$$\left(C\frac{T_c}{L}\right)\left(\frac{dP}{P}\right) = \left(C'\frac{T'_c}{L'}\right)\left(\frac{dP'}{P'}\right) \tag{2}$$

where T_c = critical temperature
P = vapor pressure
L = molal latent heat of vaporization
C = compressibility of saturated vapor

The unprimed terms refer to the substance in question and the primed terms to a reference substance, and all of the values are to be taken at the same value of reduced temperature (T/T_c). For saturated vapors C is approximately given by a single line on a compressibility chart and can be considered a unique function of T_R. Thus, assuming $C = C'$, rearrangement of Equation 2 gives:

$$\frac{dP}{P} = \left(\frac{T'_c}{T_c}\right)\left(\frac{L}{L'}\right)\left(\frac{dP'}{P'}\right) \tag{3}$$

where T_c, T' are the critical temperatures on an absolute scale of the substance and reference substance, respectively, and P, P', L, L' are always taken where the reduced temperatures of each substance are the same.

Calculation from experimental data of values of L/L' for a number of pairs of substances over a wide range of T_R indicates that this ratio is nearly constant for a given pair of components, where L and L' are always taken at the same value of reduced temperature. Watson previously pointed out this fact. Equation 3 may then be integrated to give:

$$\log P = \left(\frac{T'_c}{T_c}\right)\left(\frac{L}{L'}\right) \log P' + \text{constant} \tag{4}$$

Equation 4 states that, if the log of the vapor pressure of any substance is plotted against the log of the vapor pressure of any other substance at the same reduced temperature, a line will result whose slope is equal to $(T'_c/T_c) \times (L/L')$. The line will be straight if the assumptions made in the derivation of Equation 4 are permissible. Figure 1 is an example of such a plot. Vapor pressures of several substances are plotted on log scales against the vapor pressure of water at equal reduced temperatures. Straight lines are drawn through the plotted points and extrapolated to $T_R = 1$. In most cases a straight line represents the data fairly well even to the critical temperature. As an aid to plotting, an abscissa scale of reduced temperature of water corresponding to the vapor pressure of water is drawn on the diagram.

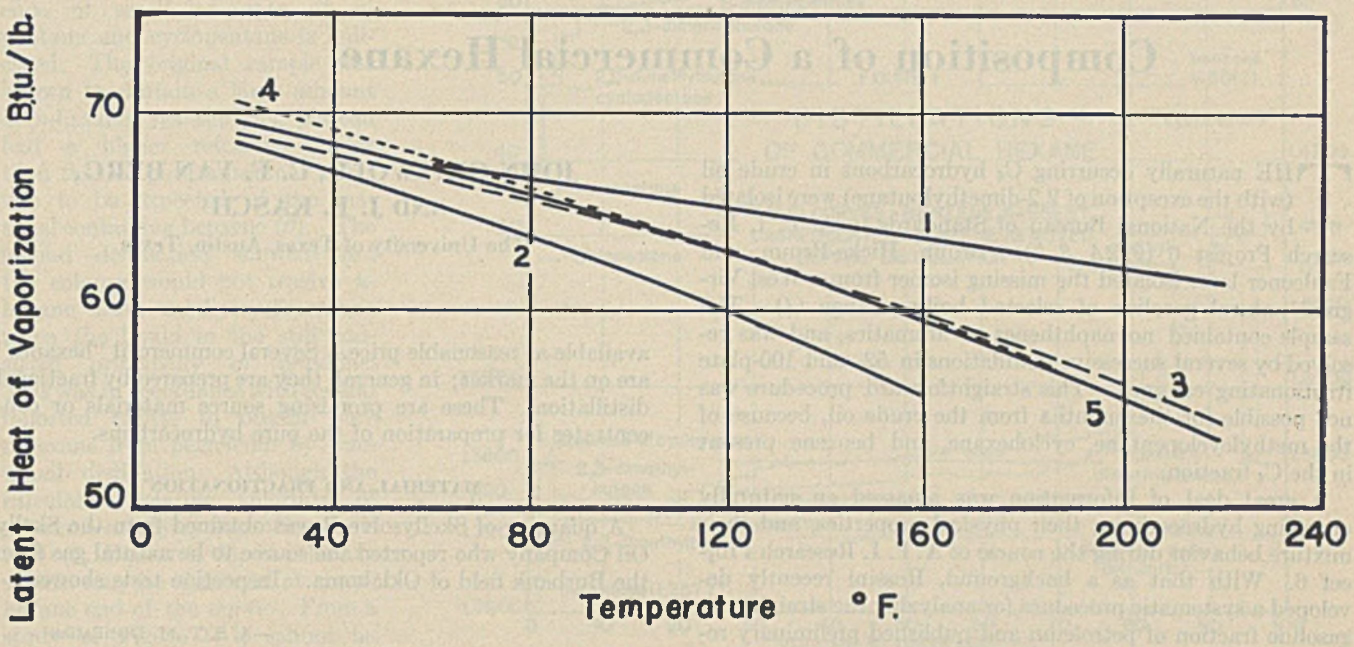

Figure 3. Latent Heats of Vaporization of Trichlorotrifluoroethane at Various Temperatures as Estimated by Several Methods

1. Othmer's method, water as reference
2. Othmer's method, dichlorofluoromethane as reference
3. Author's method water as reference
4. Author's method, dichlorofluoromethane as reference
5. Experimental values

According to Equation 4, from the slope of the lines on the diagram L can be calculated:

$$L = \text{slope} \times \left(L' \frac{T_c}{T_c'}\right) \tag{5}$$

where L and L' are taken at the same reduced temperature.

Figure 2 shows experimental and estimated values of latent heats of vaporization for several compounds over wide temperature ranges. The agreement between the accepted experimental values and those calculated as outlined above is fairly good over the entire range covered. The calculated values were obtained by measuring the slope of the lines on Figure 1 to the nearest tenth of a degree with a protractor, and assuming them to be straight over their entire length. The latent heats of vaporization of twenty other compounds were calculated at their normal boiling points and found to agree well with experimental values, the maximum differences being about 5 per cent. Water was used as the reference substance in all cases.

If one value of the latent heat of vaporization of a compound at any temperature is available and its critical temperature is known, the latent heat at any other temperature can be estimated without making a plot. Rewriting Equation 5 as

$$L = kL' \tag{6}$$

where L and L' are taken at the same reduced temperature and k, equal to slope × (T_c/T_c'), is a constant to be evaluated from the one known value of L, gives a simple relation whose validity is indicated by the curves on Figure 2. Watson's method uses a chart based on Equation 6. Water is a convenient reference substance, since its properties are accurately known and widely tabulated. Values of latent heats of vaporization estimated using water as the reference substance agree well for a variety of compounds so its use seems justified even though it has an abnormally high latent heat.

The type of plot used here is not so convenient for obtaining vapor pressures as Othmer's plot and, in addition, requires a knowledge of the critical temperature of the substance. The utility of the chart is in calculating latent heats of vaporization up to the critical temperature. Figure 3 compares the latent heats of trichlorotrifluoroethane as calculated (*a*) by Othmer's method using water as the reference, (*b*) by Othmer's method using dichlorofluoromethane as the reference, (*c*) by the author's method using water as the reference, (*d*) by the author's method using dichlorofluoromethane as the reference with (*e*) experimental values. The greater influence of the nature of the reference substance when using Othmer's method is apparent. Water has a higher critical temperature than trichlorotrifluoroethane, and dichlorofluoromethane has a lower critical temperature.

ACKNOWLEDGMENT

Acknowledgment is due to O. A. Hougen and K. M. Watson for suggestions concerning this paper, to Harold Peterson for making some of the calculations, and to the Wisconsin Alumni Research Foundation for financial support.

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PURE HYDROCARBONS from PETROLEUM

Composition of a Commercial Hexane

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THE naturally occurring C_6 hydrocarbons in crude oil (with the exception of 2,2-dimethylbutane) were isolated by the National Bureau of Standards in A. P. I. Research Project 6 (*2*, *2A*, *3*, *7*). Bruun, Hicks-Bruun, and Faulconer later isolated the missing isomer from a West Virginia natural gasoline of selected boiling range (*4*). The sample contained no naphthenes or aromatics, and was resolved by several successive distillations in 52- and 100-plate fractionating columns. This straightforward procedure was not possible for the naphtha from the crude oil, because of the methylcyclopentane, cyclohexane, and benzene present in the C_6 fraction.

A great deal of information was amassed on naturally occurring hydrocarbons, their physical properties, and their mixture behavior during the course of A. P. I. Research Project 6. With that as a background, Rossini recently developed a systematic procedure for analyzing the straight-run gasoline fraction of petroleum and published preliminary results on East Texas and Oklahoma samples (*10*). The method consists of separating the aromatics by adsorption on silica gel, then performing an "analytical distillation" upon the separated portions. While a single distillation upon each portion resolved them sufficiently for accurate analysis, the distillations must be carried out in a low-capacity column and under very high reflux ratio. The time required is from many hours to as long as several months. One of the purposes of this paper is to show that, by a further initial separation of the sample into essentially paraffinic and naphthenic portions, the analytical distillations are greatly expedited.

Pure C_6 hydrocarbons are not now being separated from petroleum in commercial quantity, although an immediate demand for them is anticipated as soon as they become available at reasonable price. Several commercial "hexanes" are on the market; in general, they are prepared by fractional distillation. These are promising source materials or concentrates for preparation of the pure hydrocarbons.

A quantitative analysis for the hydrocarbons present in a narrow-boiling mid-continent hexane fraction (from natural gas) was obtained by nitrating out the benzene, separating the aromatic-free mixture into essentially paraffinic and naphthenic portions, and then fractionating each portion in a Podbielniak Heli-Grid column. In contrast to reports on other straight-run hexane fractions, its 3-methylpentane content was too small for identification of this hydrocarbon.

MATERIAL AND FRACTIONATION

A quantity of Skellysolve B was obtained from the Skelly Oil Company who reported the source to be natural gas from the Burbank field of Oklahoma. Inspection tests showed:

		A. S. T. M. Distillation	
Gravity, ° A. P. I.	74.9	Initial B. P.	148° F.
d_4^{20}	0.6814	5% over	150
n_D^{20}	1.3840	10%	150
Aniline point, ° C.	59.2	20%	151
Bromine No., mg./g.	0.7	30%	151.5
		40%	152
		50%	152.5
		60%	153
		70%	153.5
		80%	154
		90%	155
		95%	156
		End point	165
		Recovery	99.0%
		Residue	0.2
		Loss	0.8

As a preliminary analysis, samples of the material were carefully fractionated in a Podbielniak column with an 11-mm. distilling tube equipped with 36 inches of Heli-Grid packing (*8*). A specially constructed head consisting of a total condenser and variable-volume sample trap was installed for use with low-boiling naphthas; it also permitted observation of the condensation rate and withdrawal of as little as one drop of liquid for refractive index determination. The head had a minimum liquid holdup of 1.2 cc.

Two preliminary distillations were made—the first upon the stock as received, and a second upon the stock from which the benzene had been removed by nitration (*2A*). Charges of 200 cc. were used; the boiling rate averaged 330 cc. per hour, and the operation was conducted at total reflux with intermittent sample take-off. Calculated as over-all averages, the ratios of reflux to product were 61 for the first run and 102 for the second. Under these conditions, the column efficiency was about 55 equivalent theoretical plates. In the first run the sample size was 4.65 cc.; in the second, 3.85 cc. The time between samples varied from 20 to 90 minutes, depending upon the trend of the overhead temperature. The first run required 37 hours and the second, 62 hours. Boiling points of samples were determined with an apparatus containing a four-junction thermocouple (*14*) and were corrected to 760 mm. Refractive indices were determined at

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20° C. with a Bausch & Lomb Precision oil refractometer. Results of these distillations are plotted on Figure 1. A considerably better separation is evident for the nitrated, benzene-free material than was obtained on the untreated stock. The presence of small amounts of *n*-pentane and cyclopentane is indicated. The original sample was known to contain a large amount of *n*-hexane, yet the long plateau had a higher refractive index than that of pure *n*-hexane. This was to be expected of the material containing benzene (*6*). The second distillation showed that the column would not resolve *n*-hexane from methylcyclopentane when the liquid in the still consisted principally of paraffins. This was in accordance with several reported efforts to obtain pure *n*-hexane from petroleum by fractional distillation. Although the calculated relative volatility of *n*-hexane-methylcyclopentane is 1.10 (*5*, Equation 5), the binary system may be abnormal at the *n*-hexane end of the curve. From a study of Figure 1, it cannot be concluded that any of the hexane isomers are absent. Likewise, no dependability can be placed upon an analysis of the stock as calculated from that plot.

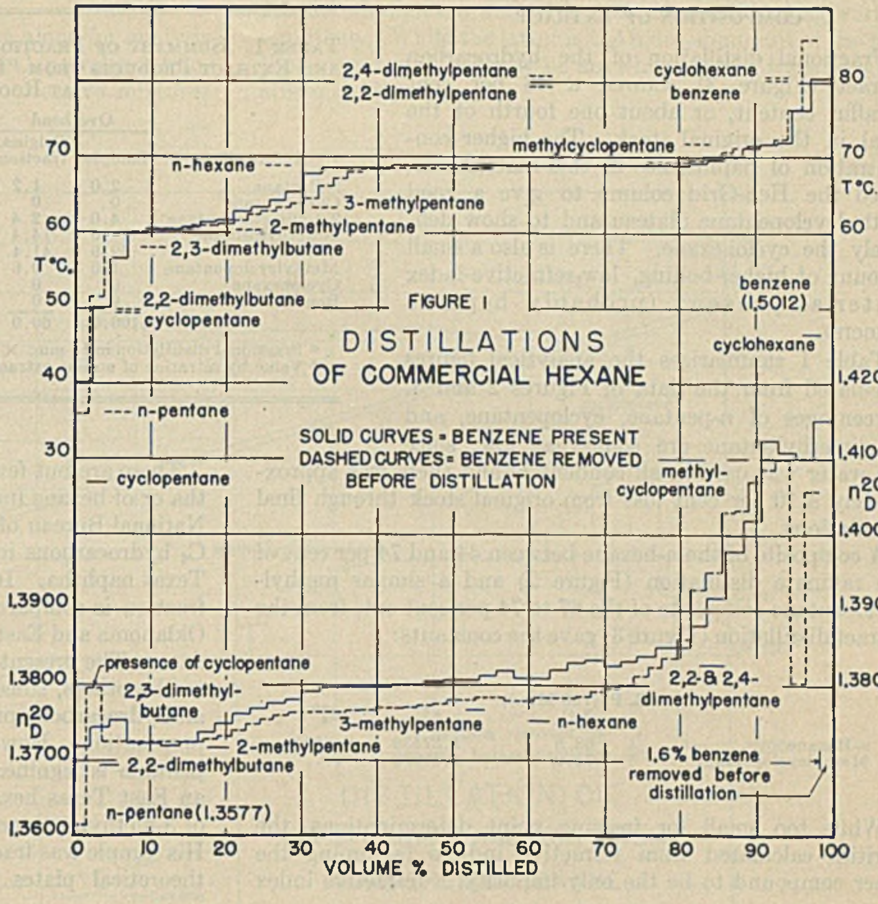


FIGURE 1
DISTILLATIONS OF COMMERCIAL HEXANE

PARAFFINIC AND NAPHTHENIC-AROMATIC PORTIONS

To obtain a satisfactory fractionation analysis, a fresh sample was separated into two portions, one essentially paraffinic, the other essentially naphthenic and aromatic, by countercurrent treatment with aniline. Bruun and Hicks-Bruun (*2A*) describe an extraction apparatus and procedure for separation of *n*-hexane from benzene. In this work, a simpler apparatus was used which consisted of a vertical 1-inch standard steel pipe solvent column, packed with 48 inches of single-turn Nichrome helices. Aniline was fed to the top of the column through a small tube, and the aniline extract was similarly removed from the bottom. The hydrocarbon feed was introduced near the bottom of the column and the paraffinic raffinate removed at the top. Most of the overhead product was mixed with the incoming aniline before introduction to the column. This procedure gave the effect of refluxing the hydrocarbons (*13*). The approximate flow rates as cc. per minute were: hydrocarbon feed 1.8, aniline feed 87, hydrocarbon reflux 24, and overhead product 1.2.

The treatment separated the hydrocarbon stock into a 60 per cent paraffinic overhead and a 40 per cent extract. The extracted hydrocarbons were distilled out of the solvent and then nitrated to remove the benzene. Separate fractional distillations were made upon both hydrocarbon products with the Heli-Grid column. The charge of raffinate was 172 cc., and that of the extract was 90 cc. Treatment to remove last traces of aniline was unnecessary, and 100 cc. of pure aniline were added to provide adequate still bottoms for each distillation.

Total reflux with intermittent take-off and the same boiling rates were maintained as before, but the sample size was reduced to 1.4 cc. in both runs. Samples were removed at intervals of 10 to 20 minutes. Calculated average reflux ratios were approximately 25 on the plateaus and 50 at the temperature breaks. Temperature and refractive index curves for the two fractions are plotted as Figures 2 and 3. Refractive indices were determined as before, but the boiling point curves are the column overhead temperatures. Boiling points of several cut composites checked the overhead temperatures.

COMPOSITION OF RAFFINATE

The paraffins present (Figure 2) consisted of *n*-pentane, 2,3-dimethylbutane, 2-methylpentane, and *n*-hexane. Less than 1 per cent of 2,2-dimethylbutane was present, and it is improbable that the original sample contained as much or more than 1 per cent of 3-methylpentane. The final analysis is in marked contrast to the conclusion which could easily be drawn from Figure 1 that all isomers were present in appreciable quantity. A small amount of methylcyclopentane is evident, but there are no indications of cyclopentane, cyclohexane, or benzene in this material. The virtual absence of 3-methylpentane was unexpected since the compound has been isolated from West Virginia (*4*) and Oklahoma (*2*, *7*) samples. However, the presence of 3-methylpentane has not been proved in all Pennsylvania and East Texas samples (*11*, *12*). It is interesting to note that fractionation of a sample containing 2-methylpentane, *n*-hexane, and methylcyclopentane in a column having 50 or 60 equivalent theoretical plates may produce overhead cuts having the boiling point, refractive index, and density of 3-methylpentane.

COMPOSITION OF EXTRACT

Fractional distillation of the hydrocarbon extract (Figure 3) showed a 48 per cent paraffin content, or about one fourth of the total in the original stock. The higher concentration of naphthenes in this material enabled the Heli-Grid column to give a good methylcyclopentane plateau and to show definitely the cyclohexane. There is also a small amount of higher-boiling, low-refractive-index material present (probably heptane isomers).

Table I summarizes the analytical figures calculated from the data of Figures 2 and 3. Percentages of *n*-pentane, cyclopentane, and 2,3-dimethylbutane are somewhat low, since tap water was used in all condensers and there was approximately a 10 per cent loss from original stock through final distillations.

A composite of the *n*-hexane between 44 and 74 per cent of the raffinate distillation (Figure 2) and a similar methylcyclopentane composite of the 67 to 74 per cent cuts from the extract distillation (Figure 3) gave the constants:

	B. P. (760 Mm.), ° C.	n_D^{20}	d_4^{20}
n-Hexane	68.8	1.37536	0.6600
Methylcyclopentane	71.9	1.40973	....

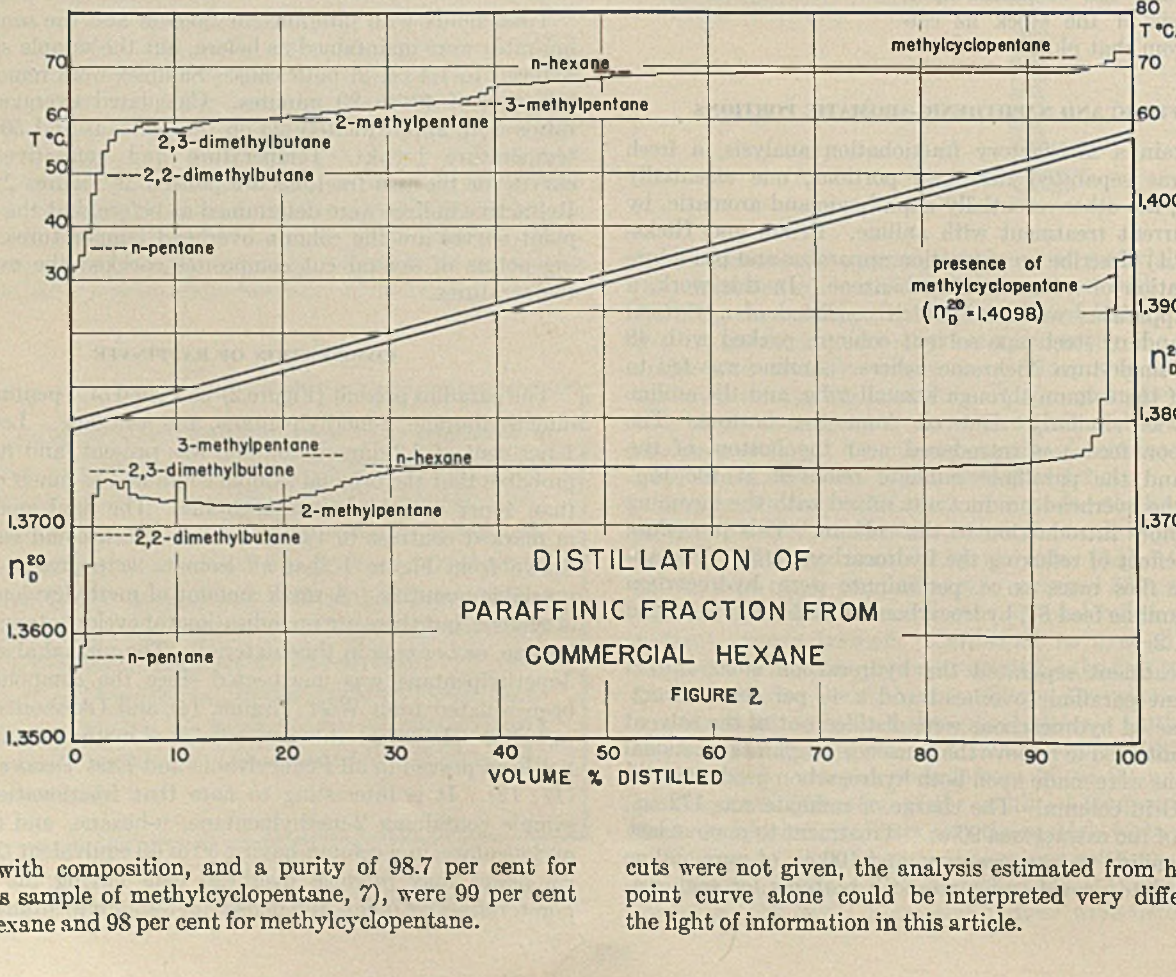
While too small for freezing point determinations, the purities calculated from refractive indices (assuming the other compound to be the only impurity, a refractive index linear with composition, and a purity of 98.7 per cent for Bruun's sample of methylcyclopentane, 7), were 99 per cent for *n*-hexane and 98 per cent for methylcyclopentane.

Table I. Summary of Fractional Distillation[a] of Aniline Raffinate and Extract Products from "Hexane" Fraction (in Volume Per Cent at Room Temperature)

Hydrocarbon	Overhead		Bottoms		Total Individual Component in:		Final Analysis
	Sample	Original fraction	Sample	Original fraction	Raffinate	Extract	
n-Pentane	2.0	1.2	0	0	100	0	1.2
Cyclopentane	0	0	0.6	0.2	0	100	0.2
2,3-Dimethylbutane	4.0	2.4	0	0	100	0	2.4
2-Methylpentane	24.0	14.4	4.0	1.6	87	13	16.0
n-Hexane	69.0	41.4	43.4	17.4	70	30	58.8
Methylcyclopentane	1.0	0.6	39.5	15.8	3.5	96.5	16.4
Cyclohexane	0	0	8.0	3.2	0	100	3.2
Benzene	0	0	4.5[b]	1.8[b]	0	100	0.
	100.0	60.0	100.0	40.0			100.0

[a] Fractional distillation in 11 mm. × 36 inch Podbielniak column with Heli-Grid packing.
[b] Value by nitration of aniline extract before fractional distillation.

There are but few complete quantitative analyses of naphtha or of hexane fractions to be found in the literature. The National Bureau of Standards has reported percentages of all C_6 hydrocarbons in an Oklahoma crude oil and in an East Texas naphtha. In Table II the composition of the present fraction is compared to the C_6 fractions calculated for these Oklahoma and East Texas samples from Bureau of Standards' data. The present fraction is not quantitatively comparable to the others, since it did not contain the total quantity of all hydrocarbons present in the crude, due to the method of preparation. However, the virtual absence of 3-methylpentane is significant. Bates (1) published an analysis of an East Texas hexane fraction, reporting a large proportion of 3-methylpentane and not more than traces of naphthenes. His sample was fractionated in columns having 50 equivalent theoretical plates or less. While refractive indices of his cuts were not given, the analysis estimated from his boiling point curve alone could be interpreted very differently in the light of information in this article.



DISTILLATION OF PARAFFINIC FRACTION FROM COMMERCIAL HEXANE

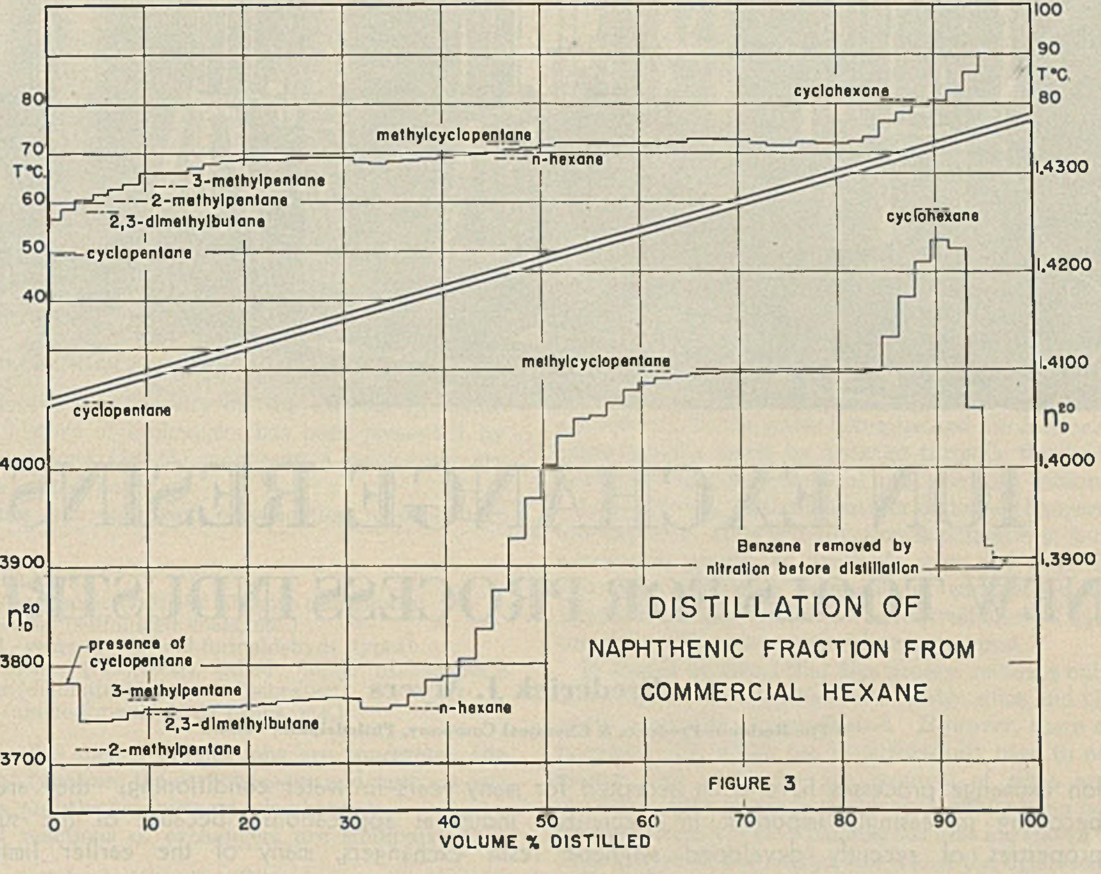
FIGURE 2

SUMMARY

The inadequacy of fractional distillation alone for analysis and separation of pure hydrocarbons from C_6 petroleum fractions is confirmed. The operation cannot resolve mixtures containing benzene, and as ordinarily carried out, it may give misleading results on paraffin-naphthene mixtures.

The complete analysis of a commercial "hexane" fraction is presented. Apparently, methylcyclopentane is of widespread occurrence in virgin naphthas and is more difficult to separate quantitatively from *n*-hexane than has been generally appreciated.

There appears to be no regularity in the abundance of 2,2-dimethylbutane and of 3-methylpentane among various naphthas. While the latter is the more abundant of the two, the amount of either may be anywhere from a trace to a sizable quantity.



DISTILLATION OF NAPHTHENIC FRACTION FROM COMMERCIAL HEXANE

FIGURE 3

TABLE II. COMPARATIVE ANALYSES OF "HEXANE" FRACTIONS

Hydrocarbon	Pure Compounds		Vol. % at Room Temp.		
	B. P., ° C.	n_D^{20}	Oklahoma fraction[a]	E. Texas fraction[b]	Present fraction[c]
n-Pentane	36.0	1.3577	..	..	1.2
Cyclopentane	49.5	1.4098	..	..	0.2
2,2-Dimethylbutane	49.7	1.3691	0	0	0
2,3-Dimethylbutane	58.0	1.3749	3.3	2.3	2.4
2-Methylpentane	60.3	1.3712	6.6	15.5	16.0
3-Methylpentane	63.3	1.3765	13.8	11.6	Trace[d]
n-Hexane	68.7	1.3750	38.8	31.0	58.8
Methylcyclopentane	71.8	1.4098	13.8	23.3	16.4
Benzene	80.1	1.5012	4.3	0.8	1.8
Cyclohexane	80.8	1.4263	19.4	15.5	3.2
Olefins	..	....	0	..	0[e]

[a] From data by Rossini (*9*) on C_6 hydrocarbons in an Oklahoma crude oil converted to basis of 100.

[b] From data by Rossini *et al.* (*10*) on C_6 hydrocarbons in an East Texas naphtha converted to basis of 100.

[c] Commercial product (Skellysolve B).

[d] Presence confirmed by Research Department of Skelly Oil Company.

[e] Bromine number, 0.7 mg./gram.

ACKNOWLEDGMENT

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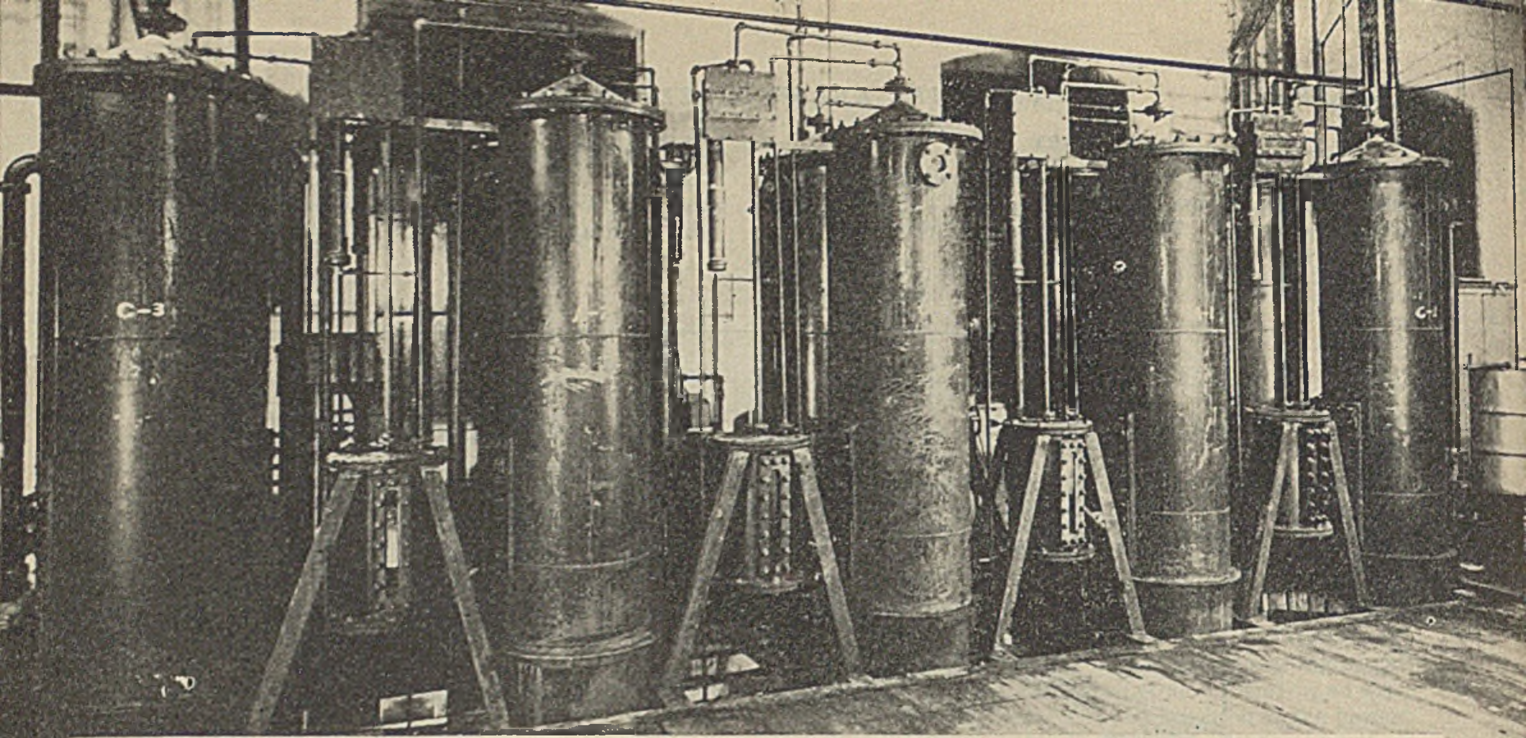

ION EXCHANGE RESINS

NEW TOOLS FOR PROCESS INDUSTRIES

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Ion exchange processes have been accepted for many years in water conditioning; they are now becoming increasingly important in specialized industrial applications. Because of the superior properties of recently developed synthetic resin exchangers, many of the earlier limitations have been overcome. Applications of the deionizing process, acid removal, and metal ion removal or substitution appear to offer many possibilities. Despite the newness of this field of resin technology, valuable data have been accumulated; some of them are presented here.

MATERIALS capable of ion exchange have been in commercial use for many years, but these zeolites and related products have generally been considered as water treating chemicals, and have found relatively little use in fields not related to the conditioning of water supplies. Originally this was due mainly to the limitations imposed by the general properties of siliceous exchangers. They tended to disintegrate both physically and chemically when used under alkaline or acid conditions, and were thus limited to a very narrow pH operating range. As a result they could not be converted to their hydrogen form, and thus only sodium cycle operation was possible.

With the advent of the carbonaceous or sulfonated coal type of cation exchanger, hydrogen cycle operation became possible, and some specialized uses were developed. However, until the resinous exchangers became available in 1935, as a result of the work of Adams and Holmes (*2*), little progress was made in the adaptation of exchange materials to special processes other than water conditioning.

EXCHANGER TYPES AND REACTIONS

A comprehensive bibliography on the existing literature and the past history of exchangers has been presented by Myers and co-workers (*12–15*), and only a brief summary will be included in this paper.

The following is a simplified classification of exchanger types:

1. Cation exchangers
   a. Zeolites (natural or synthetic siliceous compounds)
   b. Carbonaceous (sulfonated coals, etc.)
   c. Resinous (generally phenol-formaldehyde types)
2. Acid adsorbents (incorrectly called "anion exchangers")
   a. Inorganic (dolomite, heavy metal silicates)
   b. Organic (amine-formaldehyde resins, etc.)

In so far as the special applications are concerned, the most important types are the carbonaceous and resinous cation exchangers, and the organic acid adsorbents.

The typical reactions of exchangers are summarized as follows:

SODIUM CYCLE CATION OPERATION. Regeneration is effected by an excess of sodium salt:

$$\mathrm{NaR} + \mathrm{MX} \rightleftharpoons \mathrm{NaX} + \mathrm{MR}$$

HYDROGEN CYCLE CATION OPERATION. Regeneration is effected by an excess of acid:

$$\mathrm{HR} + \mathrm{MX} \rightleftharpoons \mathrm{MR} + \mathrm{HX}$$

ACID ADSORPTION:

$$\mathrm{RNH_2} + \mathrm{HX} \longrightarrow \mathrm{RNH_2.HX}$$

ANION EXCHANGE:

$$\mathrm{RNH_2.HX} + \mathrm{HY} \rightleftharpoons \mathrm{RNH_2.HY} + \mathrm{HX}$$

WATER CONDITIONING

Prior to the advent of satisfactory ion exchange resins, only two water conditioning exchange processes were being widely used. They were the softening of water (sodium cycle operation) and the reduction of alkalinity by the use of a cation exchanger operating in the hydrogen cycle. These processes have been described in detail elsewhere (*3, 4*). It should also be noted that the resinous cation exchangers have proved eminently suitable for use in both of these well-established processes (*12, 13*).

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Photographs on the Opposite Page Show Top and Bottom of Semicommercial-Scale Amberlite Sugar Purification Unit at Burley Plant of the Amalgamated Sugar Company.

A third exchanger process for water conditioning is now available, and its success has been proved on a commercial scale. This process has been variously referred to as deionizing, demineralizing (*18*), or merely two-step exchange.

DEIONIZING. It was generally recognized that the only method of producing very pure water was by distillation, whether in specifically designed stills or by the use of industrial condensate. In many cases, however, it was realized that the degree of purity was greater than necessary, and that costs were invariably high. Furthermore, throughput per unit of equipment necessary was low, and if the quality of the raw water was poor, scaling and priming would occur to such an extent that still capacity was appreciably reduced or the purity of the water produced was seriously affected.

Deionizing processes now available are proving to be a valuable addition to distillation as a method of producing very pure water. Although fundamentally simple and discussed in detail by Adams and Holmes (*2*) in 1935, only recently has the process been adopted on a large scale. The soluble salts in the water being treated are converted to their corresponding acids by passage through the hydrogen exchanger, and the acids thus produced are removed by the acid adsorbent. Although earlier cation exchangers exhibited low capacity, they did function satisfactorily, but the acid adsorbents previously available were not physically stable and were invariably incapable of complete acid removal. Recent synthetic acid adsorbents, resinous in nature, overcome the difficulties previously encountered.

It should be noted that this process removes only the salts and other ionic impurities, and soluble silica and nonionic organic impurities are unaffected. However, there are several processes (*20*) which can be successfully used to pretreat deionizer feed water for the removal of silica and organic matter, so that a very pure deionizer effluent can be obtained. Analyses from a typical commercial unit are shown in Table I. The analysis of the condensate which the deionized water replaced is given for comparison.

TABLE I. COMPARISON OF RAW AND DEIONIZED WATERS AND CONDENSATE

	Raw Water	Deionized Water	Condensate
Total dissolved solids, p. p. m.	117.9	6.9	3.9
Volatile matter, p. p. m.	39.6	2.5	2.6
Inorganic material, p. p .m.	78.2	4.4	1.3
Iron, p. p. m.	0.07	0.01	0.25
Silica, p. p. m.	2.0	2.0	0.25
pH	6.9	6.7	6.3
Conductivity, reciprocal ohms	..	3×10^{-6}	7×10^{-6}

The purity of deionized water, in so far as U. S. Pharmacopoeia specifications are concerned, was discussed in detail by Harrison, Myers, and Herr (*10*). They found that resinous exchanger systems would produce water equal in quality to that required by U. S. P. specifications, and biological tests proved that the pyrogen content of the water was unaffected by the exchange process.

The success of this process for the economical production of large quantities of very pure water appears to be assured, and its adoption has solved many industrial water conditioning problems.

SPECIALIZED DEIONIZING PROCESSES

Deionizing is now being used in other fields. Rawlings and Shafor (*16*) summarized the application of this process in the sugar industry. Because the nonsugar constituents of the

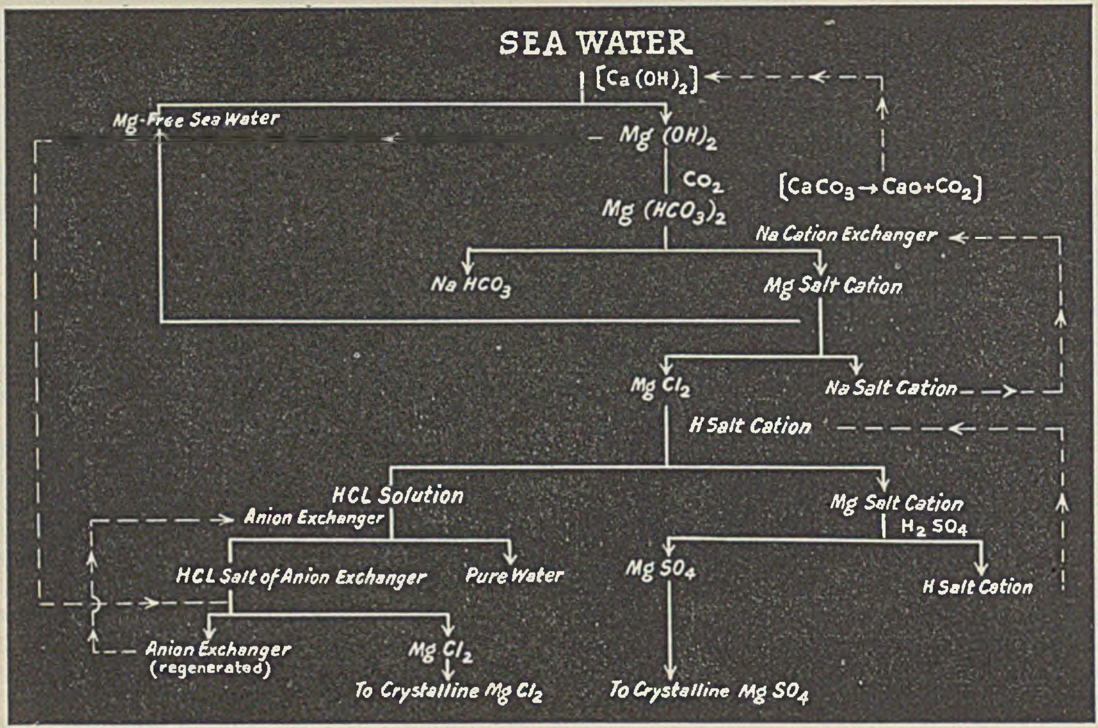


Figure 1. Flow Sheet of Exchange Process for Recovering and Concentrating Magnesium in Sea Water

Raw materials: sea water, $CaCO_3$ [$Ca(OH)_2$ and CO_2], H_2SO_4; products: $MgSO_4$, $MgCl_2$, $NaHCO_3$, pure water.

juice retard the crystallization of sucrose with subsequent loss in yield, many means of removing these nonsugar impurities prior to crystallization have been studied so that purer sugar would result, and less sucrose would be retained in the low-price molasses.

Rawlings and Shafor developed a resinous exchanger process which treats the partially purified beet or cane juice (approximately 12–14 per cent sucrose) prior to evaporation and crystallization. This process has shown as high as 98 per cent removal of inorganic salts ("ash"), organic impurity removal up to 83 per cent, color removal from 50 to over 90 per cent, and a high degree of colloid elimination from the sugar juice as determined by the ultramicroscope.

The degree of impurity removal can be controlled by varying the operating conditions of the process and by changes in the regeneration steps. The extent to which impurities are removed is governed by economic considerations which are dictated by local operating costs and prevailing sugar prices. On a semicommercial scale the exchange process of sugar juice treatment has proved completely satisfactory; it has the advantages of increased yield of sugar, appreciable elimination of scaling, reduction in the amount of low-purity products to be reboiled, reduction in fuel consumption, and increased production of sugar without increase in evaporation or crystallization equipment.

Although similar in theory to deionizing as used in water purification, the application of the process to the sugar industry is further complicated by the numerous varieties of impurities present, the susceptibility of sucrose to hydrolysis at low pH, and many other peculiar limitations. Treatments for cane, beet, and refinery sugars present distinctive problems which are being actively investigated.

Weitz (*19*) recently described the large-scale operation of an exchanger sugar purification plant; on the basis of all data obtained to date, it appears that the exchange process represents a real advance in sugar technology.

Englis and Fiess (*8*) evolved a similar process in a related field. In the production of a palatable levulose sirup from Jerusalem artichokes, their original process consisted in the acidification of the polysaccharides (predominantly inulin) with hydrochloric acid, hydrolysis, and salt and acid removal by dialysis or electrodialysis. However, as a result of the buffering action of the salts present, large quantities of acid were necessary for hydrolysis, and the purification of the hydrolysate was tedious and expensive. They found that treatment of the polysaccharide solution with a cation exchanger operating in the hydrogen cycle resulted in the production of sufficient acid to make hydrolysis possible without the use of additional acid. After autoclaving, the acidic levulose solution was treated with Amberlite IR-4 to effect acid removal. The expensive acid addition was avoided, and as a result of conversion of the salts, a quick and simple purification process could be substituted for dialysis. Furthermore, because of removal of organic acids, not removed by dialytic procedures, the exchanger-treated product was superior in quality and flavor to sirups produced by the earlier process. In this study complete elimination of nonsugar impurities was not attempted. However, further work on this problem is being conducted with the aim of effecting crystallization of levulose from highly purified sirups.

A modification of the deionizing process, in which it is desired to recover the valuable acidic constituents removed, was developed by Matchett (*11*). The recovery of tartrates from wine residues has long been practiced, but the process was inefficient, and residues with low tartrate content were not amenable to treatment. The newly developed process is applicable to either distillery slops or grape waste extracts. The aqueous extract, following clarification, is passed through a bed of Amberlite IR-1 (hydrogen form) which frees the tartaric acid. This tartaric acid is subsequently adsorbed and concentrated in the Amberlite IR-4 bed. The acid is flushed from the bed with sodium carbonate and purified by precipitation as the calcium salt. Beginning with an initial tartrate concentration of 0.25–0.30 per cent, a twelve to fifteen fold concentration of the tartaric acid is being effected. At present in the pilot plant stage, commercial scale application is planned if preliminary results are substantiated by further operation. Adoption of this process by domestic wineries alone could add several million pounds of tartaric acid to the present annual production. Further, the Amberlite process makes possible the recovery of this valuable chemical which is being wasted at present.

No discussion of the deionizing process would be complete without a consideration of the effects obtained at very high salt concentrations. In so far as maximum concentrations are concerned, there are two main limitations—chemical inhibiting effect and economics, which are in some cases of secondary importance. Considering the former, the limiting factor is the lowest pH at which the particular cation exchanger being used will effect exchange. Studies on Amberlite IR-1 (hydrogen cycle) indicate that the lowest pH at which exchange will occur is approximately 0.85. The following data were obtained on treating sodium chloride solutions of varying concentrations with Amberlite IR-1-H:

Initial Salt Concn. %	pH of Effluent	Salt Concn. of Effluent, %
10.28	0.85	4.60
4.91	0.90	1.50
2.00	0.86	0.59
0.99	0.87	0.05
0.75	1.05	0.03
0.40	1.35	0.00

As a result of these studies, it appears that the critical concentration at which sodium chloride is completely converted to hydrochloric acid by Amberlite IR-1 is approximately 0.5 per cent (5000 p. p. m.). However, it is obvious that complete salt removal from more concentrated solutions may be effected by stepwise treatment with cation and anion exchangers which can be carried out by a recycling process or multiple bed operation.

Studies have also been conducted on the desalting of sea water. Although work on combinations of chemical and exchange processes continues, it does not appear at present that any unmodified exchange process is the answer to the problem.

ACID REMOVAL

The development of acid adsorbents which are physically and chemically stable, and will effect complete removal of acid traces, has made another valuable unit process possible. Admittedly the use of an acid adsorbent eventually involves neutralization, but the neutralization is effected independently of the solution being treated for acid removal, and contamination of the product is thus avoided. Furthermore, the neutralized acids are handled separately, and can be purified or further treated if desired.

Considering the acid-binding capacities of acid adsorbents, it would be expected that the capacity would depend on the chemical composition and molecular configuration of the exchanger being studied. This is true, but many other factors also influence capacity, and the relative importance of all are by no means clearly understood. Thus degree of ionization of the acid, basicity, influent concentration, molecular size, operating and regenerating conditions, etc., all have their effect; and capacity values should be accompanied by a description of the conditions under which they were determined. Typical capacities of Amberlite IR-4 are shown in Table II.

Table II. Acid-Binding Capacity of Amberlite IR-4

Acid	Influent Concn., P. P. M.	Capacity at Break-through[a]: Grains (as $CaCO_3$) per cu. ft.	Lb. (as acid) per cu. ft.	Lb. acid per lb. dry resin
HCl	400	30,000	3.13	0.174
HNO_3	372	49,500	8.91	0.495
H_2SO_4	500	50,000	7.00	0.389
H_3PO_4	1500	98,000	9.15	0.508
H_3BO_3	64	117	0.007	0.0004
$HCOOH$	500	12,000	1.58	0.088
CH_3COOH	2000	24,200	4.15	0.231
C_3H_7COOH	2140	21,300	5.35	0.298

[a] Break-through capacity as given is acid-binding capacity until first appearance of acid in effluent; total acid-binding capacity (complete saturation of resin) is in all cases appreciably higher. In all cases regenerant used was approximately three times theoretical requirement; normal operating rates were in the range of 3–5 gallons per square foot per minute.

A well-established use of the exchanger acid removal process is in the deacidification of formaldehyde. Most formaldehyde produced today is obtained by the catalytic oxidation of methanol, and may contain as much as 0.05–0.08 per cent formic acid. In many of the uses of formaldehyde this impurity is objectionable; it is particularly so if the formaldehyde is to be used for the production of synthetic resins. Neutralization of the acid is laborious, and the salts are as objectionable as the free acid. Removal of the acid can be effected with activated carbon, but the process is cumbersome and expensive. Passage of acidic formaldehyde through a bed of Amberlite IR-4 effects complete and rapid removal of the acid, and high throughput is possible. Typical data on a commercial size Amberlite IR-4 unit follow:

Diameter of resin unit, ft.	5.0
Surface area, sq. ft.	19.6
Bed depth, ft.	3.0
Bed volume, cu. ft.	59.0
Acid concentration (in formaldehyde)	
Per cent	0.05
Lb./gal.	0.0045
Capacity of IR-4, lb. formic acid per cu. ft.	1.58 (equivalent to 351 gal. formaldehyde)
Total bed capacity (between regeneration), lb. formic acid	93.1 (equivalent to 20,700 gal. formaldehyde)
Throughput, gal./hr.	Approx. 2350

REMOVAL OF METALLIC IONS

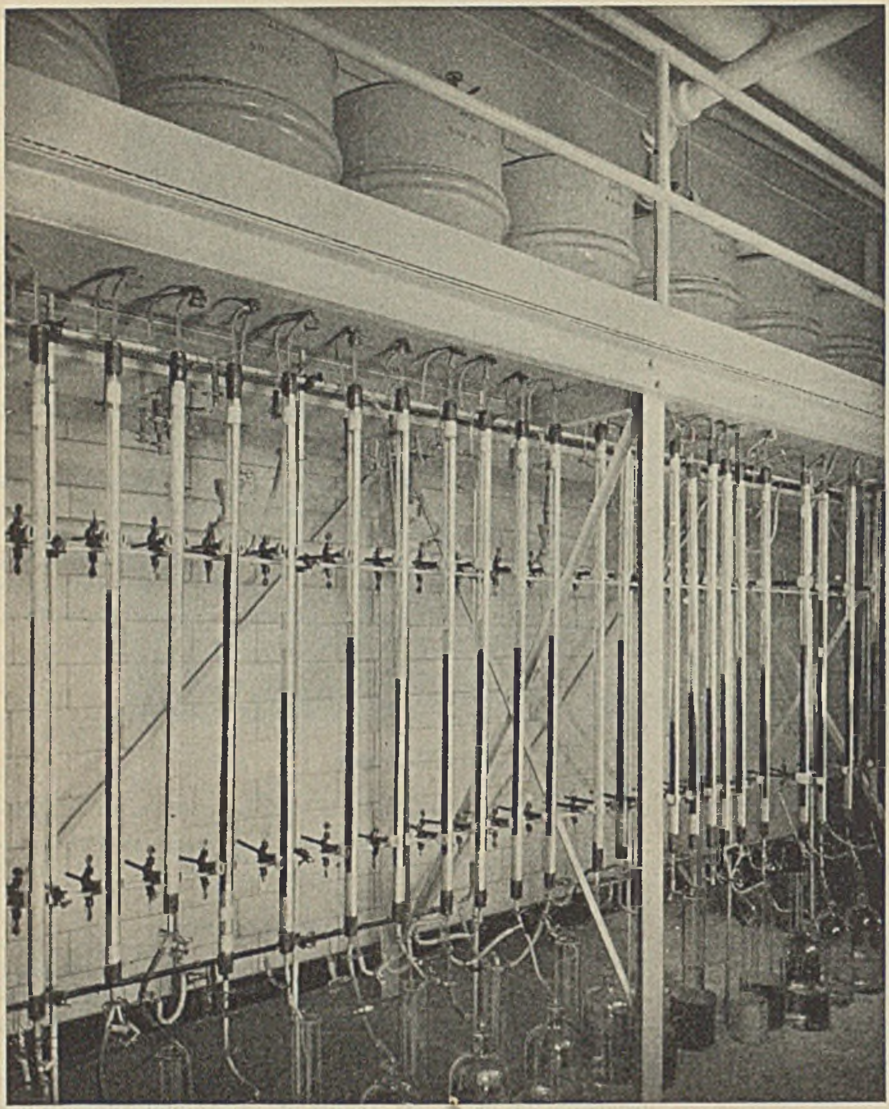
The removal of metallic ions may be desired because they constitute objectionable impurities, or because they are sufficiently valuable to be recovered. In certain applications, both factors enter into consideration.

The exchange process adopted for metal ion removal depends on the particular conditions. If sodium salts are not objectionable in the effluent, then sodium cycle operation will be satisfactory, and in unusual cases, salts other than sodium have been used as regenerant. Generally, however, more complete removal of cations is effected by the use of the cation exchanger in the hydrogen form.

Beaton and Furnas (*5*), in applying exchangers to the purification of brass mill pickling liquor wastes and to the recovery of valuable constituents therefrom, have presented an excellent study of the Cu^{++}–hydrogen cation exchanger system. The value of cation exchangers as a means of concentrating metallic ions is clearly shown, and in the recovery of copper from a dilute copper sulfate solution (0.005 *N*), concentration increases of over 220 fold were obtained. They further determined that one pound of sulfuric acid used for the regeneration of a cation exchanger could effect a concentration increase equivalent to the evaporation of 4200 pounds of water.

With many special chemicals, heavy metal tolerances are low, and in some cases repeated recrystallization or distillation was the only method of purification possible. It has been found that resinous exchangers are unique in the completeness with which they remove traces of ions and are thus applicable to these special problems. The removal of calcium, iron, copper, and lead from organic acids (*7*), glycerol, carbohydrates, and wines are typical commercial applications.

The experimental data on the removal of iron from aluminum sulfate solutions are as follows: A tower was charged with 800 grams Amberlite IR-1 (sodium form) and flushed with dis-



Typical Test Columns for Studying Special Exchanger Applications, for Evaluation of New Types, and for Production Control

tilled water. After backwashing to classify the bed, a 33° Baumé alum solution (approximately 25 per cent aluminum sulfate) containing 125 mg. ferric oxide per 100 ml. was allowed to flow through the column at the rate of 50 ml. per minute. A total of 3300 ml. was passed through the bed before the experiment was discontinued. The first 250-ml. portion of the effluent contained no alum, since it was required to convert the sodium derivative of the resin to the aluminum salt. The course of the iron removal is summarized as follows:

Sample No.	Total Vol. Treated, Ml.	°Baumé	Fe_2O_3, Grams per 100 Ml.
1	214	18.5	0.060
2	448	31.6	0.063
3	662	32.4	0.074
4	872	32.6	0.071
5	1520	33.0	0.077
9	1958	33.0	0.106
11	2398	33.0	0.112
13	2838	33.0	0.117
15	3298	33.0	0.120

This experiment clearly shows the efficiency of the iron removal, unusual when the concentration of aluminum ion is considered.

Adams (*1*) discloses a novel exchange process for recovering and concentrating the magnesium in sea water; flow sheet of the process is shown in Figure 1. Closer consideration of the process suggests that there are many details to be clarified, and it is not known whether this process, or a modification thereof, is in actual commercial use. However, investigation of exchange processes in connection with the recovery of magnesium from sea water is under way in this country.

PREFERENTIAL ADSORPTION

Preliminary data on this subject were presented by Myers, Eastes, and Urquhart (*15*), and the use of exchangers for the separation of sulfuric acid from hydrochloric acid and copper ion from zinc ion was clearly demonstrated. Further studies have been conducted; although additional data are available, all the factors which govern ion separation are not clearly understood and much work still remains to be done.

A typical problem is the removal of copper from rayon wastes, in which the concentration of ammonium salts is high. The composition of the waste was as follows:

Copper (as CuSO), p. p. m.	4.8
Ammonia (as $NH_4)_2SO_4$, p. p. m.	2750
pH	5.02

Amberlite IR-1 was used, and the static adsorption technique rather than column operation was employed. Removal of copper was effected to a residual of approximately 2.00 p. p. m. even in the presence of this high ammonium ion concentration. However, the capacity of the resin for copper under these conditions was only one third of that obtained when the concentration of other salts is negligible. As would be expected, a 50 per cent reduction in the concentration of copper and ammonium ions in the original solution increased the efficiency of removal as well as the total capacity for copper. Further column studies have shown that copper removal from a waste such as this is entirely practical.

A study of the recovery of zinc from mine waters has also been made. The mine water studied had the following composition (in parts per million): zinc 137.0, calcium 147.7, magnesium 17.7, iron and aluminum 8.0, copper <0.1, and lead <0.1. Column studies with Amberlite IR-1-H showed that, although there was a slight preferential adsorption of calcium over zinc, the difference in adsorption was not sufficient to make separation possible, and the economics of the process were not favorable. A typical calcium-zinc chromatogram as obtained in this study is shown in Table III. The solution used was the mine water described above, and a column of Amberlite IR-1-H, 1 inch in diameter and 20 inches long, was employed. Flow rate was 5 gallons per square foot per minute. The column was then cut into six equal sections, and the resin analyzed for calcium and zinc.

TABLE III. AMBERLITE IR-1-H CHROMATOGRAM FOR CALCIUM-ZINC SYSTEM

Section	Per Cent Ca	Per Cent Zn
1	3.76	3.21
2	3.77	2.37
3	3.73	1.66
4	3.18	1.92
5	1.98	..
6	1.16	1.46

Recovery of magnesium from sea water was mentioned earlier in the paper, but the process described consisted of a combination of chemical and exchange processes. Experiments have been conducted on sea water to determine whether preferential adsorption of magnesium over calcium would be obtained. In the first portion of the column effluent there was a definite enrichment of magnesium, and indication of preferential adsorption of calcium. Using a synthetic sea water, the magnesium calcium ratio was originally 5.48. The magnesium-calcium ratio in the first portions of the effluent was 9.0. However, the actual volume of enriched effluent was very small per unit of exchanger necessary, and on the basis of present findings this process does not appear to be economically feasible.

REACTIONS IN NONAQUEOUS MEDIA

As the reactions of the ion exchange resins in aqueous media became more clearly understood and the industrial use of the products became more widespread, it was natural that consideration should be given to applications in nonaqueous media. Although it was not to be expected that the cation exchangers would function in a nonionizing solvent, it was possible that acid adsorption could occur in any solvent in which the particular acids being considered were soluble, inasmuch as the net result of the acid adsorbing reaction is the reversible binding of an acid molecule. Static equilibrium experiments were therefore conducted, using fatty acids in various solvents, and both "wet" and dry Amberlite IR-4 (*17*). The results appear in Table IV, and it is concluded that an ionizing medium is necessary for this particular type of acid adsorption. A small amount of acid adsorption did occur in anhydrous benzene (dry resin) in the acids lower than valeric in the series, but further work has indicated that this adsorption differed from the normal acid adsorption exhibited by Amberlite IR-4.

TABLE IV. ADSORPTION OF ACIDS

	In Anhydrous Benzene by Anhydrous IR-4		In "Wet" Benzene by "Wet" IR-4		In Anhydrous Dioxane by Anhydrous IR-4	
Acid	Original concn., g./l.	Meq. acid adsorbed, g. dry resin	Original concn., g./l.	Meq. acid adsorbed, g. dry resin	Original concn., g./l.	Meq. acid adsorbed, g. dry resin
Propionic	5.11	0.30	7.40	7.10	13.61	1.08
Valeric	6.33	0.01	...	...	...	...
Lauric	10.66	0.00	9.00	3.10	20.35	1.26
Stearic	16.10	0.00	14.48	2.18	30.07	1.25
Oleic	13.53	0.00	12.70	1.57	28.19	0.90

Experiments have been completed using "wet" acetone, ethanol-water mixtures, "wet" chlorinated hydrocarbons, etc., and all results prove that the presence of a small amount of water will permit acid binding to occur. It is sometimes noted, however, that the capacity of the acid adsorbent is somewhat lower when used in "wet" nonaqueous solvents than in aqueous solutions.

The industrial application of these ideas is already underway, and the use of Amberlite IR-4 to remove residual acids from fine chemicals, from dry cleaning solvents, etc., shows promise in early experiments.

The resinous cation exchangers have also been employed in similar nonaqueous media, and again it has been found that some water (or other strongly ionizing solvent) is required. Typical of such experiments was work on the removal of copper compounds from wet gasoline. Both IR-1 and IR-100 exhibited a low but definite capacity for copper, but analyses indicated that much of the copper was present in a nonionic form, apparently as a nonionic organic copper complex. Further studies of special resinous exchangers resulted in the development of a new type of cation exchanger which would reduce the copper content of gasoline from 12.0 to 0.2 p. p. m. Further modifications of this product are under study at the present time.

MISCELLANEOUS USES

Resinous exchangers are rapidly finding increasing use as research and analytical tools. The use of a "salt machine" for determining salt concentrations of solutions was suggested in 1941 (*13*). The apparatus consists of a column of hydrogen exchanger; the solution to be analyzed is passed through this column, and the titratable acidity of the effluent determined. Because of the stoichiometric relation which exists between the original salt concentration and the concentration of acid in the effluent, this method of analysis is very accurate, checking remarkably well with gravimetric procedures.

Gaddis (*9*) describes an unusual application for acid adsorbents. Using Amberlite IR-4, he found that a stable addition compound was formed with hydrogen sulfide, and that the resin would absorb 12 per cent of its weight of hydrogen sulfide. This addition compound is used in the analysis of Group II ions in the place of gaseous hydrogen sulfide. Results are claimed to be excellent, and the analytical scheme is simplified.

Block (*6*) utilized resinous exchangers in a process for the large scale production of arginine, histidine, and lysine. Work in our laboratories has shown that thiamine hydrochloride is adsorbed quantitatively and reversibly by Amberlite IR-100. A comprehensive study of the application of cation exchangers and acid adsorbents in the isolation, purification, and recovery of physiologically active materials is underway.

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BRITTLE POINTS of Natural and

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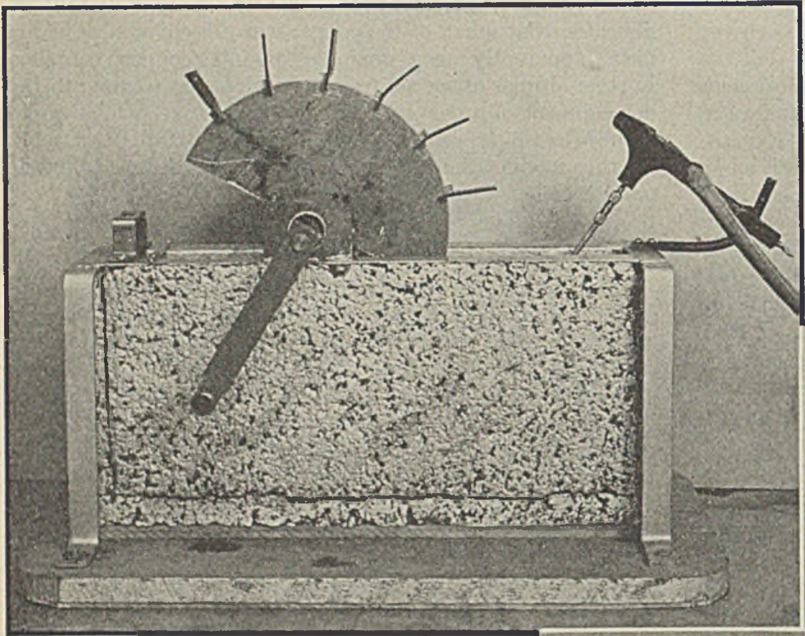

Figure 1. Brittle Point Apparatus

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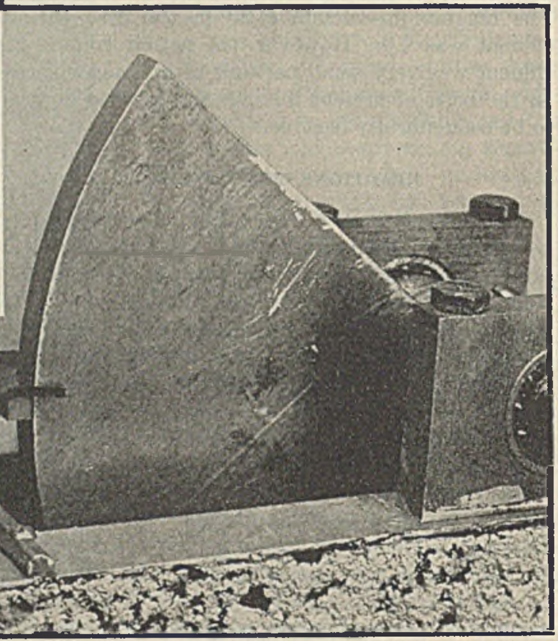

Figure 2. Close-up of Specimen Striking the Rod

BECAUSE of the present interest in the cold resistance of natural and synthetic rubber vulcanizates, data are presented here which may help compounders in selecting the correct synthetic rubber for specific applications.

A comparatively simple apparatus for determining the brittle points of plastic and elastic materials was developed by Selker, Winspear, and Kemp of the Bell Telephone Laboratories (*4*). While determining the suitability of this apparatus for specification tests, the authors had occasion to determine the brittle points of similar vulcanizates prepared from Hevea rubber, guayule rubber, and a wide variety of synthetic rubbers. A description of this apparatus (including the modifications in the original design made by the authors), the recipes of the stocks tested, and the brittle points of the stocks are given here. In addition, a test for brittle point under less severe bending stress is described, and data obtained by this test are included for some of the same stocks.

SIGNIFICANCE OF BRITTLE POINT

The word "brittle" means "easily broken". Kemp, Malm, and Winspear (*2*) showed that the ease with which natural and synthetic vulcanizates can be broken by bending depends not only upon the temperature, but also upon the rate and radius of bending. Increasing the rate or decreasing the radius of bending enhances the possibility of breakage at a given temperature. In other words, rubber vulcanizates behave at low temperatures like the so-called plastics at normal temperatures.

To compare vulcanizates from the standpoint of brittleness, it is necessary to define at least two of these variables and use the third as a criterion of brittleness. For example, the temperature and the rate of bending may be maintained constant in all determinations, and the radius of bending required to fracture the specimens may be considered a measure of brittleness. However, for convenience in measurement and because of closer agreement with many service conditions, the brittle point is generally defined as the temperature at which fracture occurs, assuming that the rate and radius of bending have been established. This is the case with the experiments reported here.

TESTING METHOD

Brittle Point Apparatus. The apparatus was constructed essentially as described by Selker, Winspear, and Kemp. It consisted of an insulated steel tank, 18 × 2 × 8 inches. Seven inches from one end on the top was mounted a brass semicircle, 4.87 inches in radius and 0.50 inch thick, keyed to a shaft. Six notches, 0.25 inch deep and 0.075 inch

Synthetic Rubber Stocks

wide, were spaced at 2-inch intervals on the rim of the semicircle. Each notch was backed with a block extending 0.25 inch above the rim. A stiff $^1/_4$-inch round rod was fixed across the tank exactly 0.5 inch from the rim of the semicircle. The shaft upon which the sample-holding fixture was mounted had a crank which, on rotation, immersed the specimens in the tank. The shaft was supported on ball bearings.

Methyl alcohol was used as the immersion medium and solid carbon dioxide as the cooling medium. The alcohol was circulated by an air-driven stirring motor. The temperature of the alcohol was determined with a thermocouple. The temperature of the alcohol was raised rapidly when desired by adding warm alcohol or inserting a 500-watt immersion heater in the bath.

Photographs of the apparatus appear as Figures 1 and 2. Figure 1 shows the insulated tank, the brass semicircle with six specimens in position for breaking, the crank, and the air-operated stirring motor. Figure 2, a close-up view of the specimen striking the round rod, shows the support for a thermometer although, as mentioned above, the authors preferred to use a thermocouple for measuring the temperature of the alcohol.

A close-fitting sheet metal hood was placed over most of the tank after insertion of the specimen in order to prevent splashing of the alcohol when the crank was turned rapidly. This hood is not shown in the photographs.

The brittle point apparatus used in these tests deviated from the design proposed by Selker, Winspear, and Kemp in in the following respects: The insulated steel tank was 4 inches longer to accommodate the air stirrer. Ball bearings were used on the crankshaft in order to reduce rotational friction and thus obtain a greater velocity of impact. A $^1/_4$-inch round rod mounted across the tank was used instead of an arm mounted in the side of the tank because the former arrangement was believed to be more stable and reproducible. A bracket was provided for supporting a thermometer in the bath.

Testing. Specimens, 1 × 2 inches, were died from test sheets 0.08 inch thick. One end of the specimens was inserted in a notch on the rim of the semicircle by grasping the corners with pliers and stretching the rubber so as to decrease its thickness and allow it to slip freely into the notch. When the tension was relaxed, the rubber fit snugly in the notch and overlapped $^1/_4$ inch on each side of the semicircle. It was found advisable to insert and test only one specimen at a time on the rim of the semicircle in order to obtain maximum velocity of impact.

Table I. Composition, Cure, and Properties of Vulcanizates from Natural Rubbers and Butadiene-Styrene Copolymers

	Smoked Sheet	Deresinated Guayule	Buna S	Buton S	Chemigum IV	Hycar OS-10	Hycar OS-20
Composition							
Smoked sheet	100.0	....	....	....	....	....	....
Deresinated guayule	....	100.0	....	....	....	....	....
Buna S	....	....	100.0	....	....	....	....
Butaprene S	....	....	....	100.0	....	....	....
Chemigum IV	....	....	....	....	100.0	....	....
Hycar OS-10	....	....	....	....	....	100.0	....
Hycar OS-20	....	....	....	....	....	....	100.0
Semireinforcing carbon black	75.0	75.0	75.0	75.0	75.0	75.0	75.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	....	....	....	....	....
Phenyl-α-naphthylamine	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Dibenzothiazyl disulfide	0.8	0.8	....	....	....	....	....
Zinc dimethyl dithiocarbamate	0.1	0.1	....	....	....	....	....
Tetramethylthiuram monosulfide	....	....	0.5	0.5	0.5	0.5	0.5
Sulfur	2.5	2.5	2.0	2.0	2.0	2.0	2.0
Cure							
Temperature, ° F.	260	260	287	287	287	287	287
Time, minutes	20	25	20	20	20	20	20
Tensile strength, lb./sq. in.	2840	2010	1890	1790	2100	2090	2060
Ultimate elongation, %	450	360	230	220	320	240	310
Shore hardness (after 10 sec.)	68	72	67	70	62	69	61
Brittle point, ° F.	−71	−56.5	−68	−56	−71	−4.5	−63

Table II. Composition, Cure, and Properties of Vulcanizates from Chloroprene and Isobutylene Polymers and Copolymers

	Neoprene E	Neoprene FR	Neoprene GN	Neoprene ILS	Vistanex Medium	Butyl B
Composition						
Neoprene E	100.0	....	....	....	....	....
Neoprene FR	....	100.0	....	....	....	....
Neoprene GN	....	....	100.0	....	....	....
Neoprene ILS	....	....	....	100.0	....	....
Vistanex Medium	....	....	....	....	50.0	....
Smoked sheet	....	....	....	....	50.0	....
Butyl B	....	....	....	....	....	100.0
Semireinforcing carbon black	75.0	75.0	75.0	75.0	75.0	75.0
Zinc oxide	10.0	....	5.0	10.0	5.0	5.0
Light-calcined magnesia	10.0	....	4.0	10.0	....	....
Litharge	....	10.0	....	....	....	....
Stearic acid	0.5	1.0	0.5	0.5	2.0	1.5
Wood rosin	5.0	....	....	....	....	....
Di-o-tolylguanidine salt of dicatechol borate	....	....	....	1.0	....	....
Phenyl-α-naphthylamine	2.0	2.0	2.0	2.0	....	....
Dibenzothiazyl disulfide	....	....	....	....	0.8	....
Mercaptobenzothiazole	....	....	....	....	....	0.5
Zinc dimethyl dithiocarbamate	....	....	....	....	0.1	....
Tetramethylthiuram disulfide	....	....	....	....	....	1.0
Sulfur	1.0	1.0	....	....	2.0	1.5
Cure						
Temperature, ° F.	307	287	287	307	287	307
Time, minutes	40	40	40	40	20	90
Tensile strength, lb./sq. in.	2250	2420	2550	2590	1300	1290
Ultimate elongation, %	210	190	260	160	390	650
Shore hardness (after 10 sec.)	75	73	81	86	55	62
Brittle point, ° F.	−29	−41	−31	+22.5	−57	−33

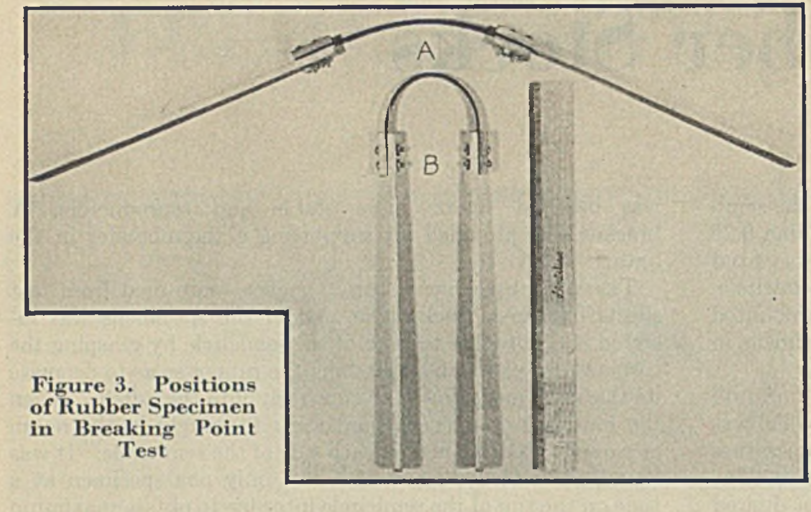

Figure 3. Positions of Rubber Specimen in Breaking Point Test

The tank was filled to within 3 inches of the top with methyl alcohol, which was cooled to the desired temperature by chunks of solid carbon dioxide. The cooled alcohol was circulated by the stirring device. When the alcohol had arrived at the desired temperature, the semicircle was turned so that the specimen was immersed in the cold alcohol. Exactly 2 minutes after immersion of the specimen, the crank was turned rapidly in a clockwise direction so that the specimen struck the horizontal bar just as it rose from the alcohol. The temperature at which the specimen was cracked by this treatment was considered to be the brittle point of the rubber. The brittle points of different specimens of the same stock generally agreed within 0.5° F.

Rubbers Tested. Similar stocks were prepared from the following rubbers for the brittle point tests:

Natural: smoked sheet, deresinated guayule (2.7 per cent acetone-extractable remaining).
Chloroprene polymers and copolymers: Neoprene E, Neoprene FR, Neoprene GN, Neoprene ILS.
Butadiene-styrene copolymers: Buna S (Naugatuck GR-S), Buton S (Firestone GR-S), Chemigum IV (Goodyear GR-S), Hycar OS-10 (styrene content higher than GR-S), Hycar OS-20 (stearic acid content lower than GR-S).
Buna N type copolymers: Butaprene NXM, Butaprene NM, Butaprene NX, Chemigum I, Chemigum X, Hycar OR-15, Hycar OR-25, German Perbunan, Stanco Perbunan, Thiokol RD.
Isobutylene polymer: Vistanex Medium (blended 50-50 with smoked sheet in order to vulcanize).
Isobutylene copolymer: Butyl B.
Organic polysulfides: Thiokol F, Thiokol FA.

Results. The formula, cure, tensile strength, ultimate elongation, hardness, and brittle point of the vulcanizates prepared from the above rubbers are given in Tables I to IV. It is apparent that the GR S stocks (Table I) were the only synthetic vulcanizates with brittle points as low as the smoked sheet stock. Hycar OS-10, although a butadiene-styrene copolymer, gave a stock with a much higher brittle point than the GR S stocks. The guayule stock (Table I) and the Vistanex–smoked sheet blend (Table II) had quite low brittle points, but not so low as the GR S or smoked sheet stocks. It is interesting to note that the GR S stocks differed among themselves with respect to brittle point by as much as 15° F.

The brittle points of the neoprene stocks (Table II) varied widely, depending upon the type of neoprene. The brittle point of the Neoprene FR stock was fairly low; that of the Neoprene ILS stock was high.

The stocks prepared from the Buna N type rubbers (Tables III and IV) had brittle points ranging from a very high value for the Thiokol RD to a fairly low value for the German Perbunan stock. The Butaprene NM stock had the lowest brittle point of the domestic Buna N type stocks.

The stocks prepared from the true Thiokols (Thiokol F and Thiokol FA, Table IV) had surprisingly low brittle points, considering the semiplastic nature of these synthetic rubbers.

EFFECT OF ESTER TYPE SOFTENERS

Ester type softeners improve the cold resistance of Hycar OR-15 and Stanco Perbunan vulcanizates (*1*, *3*). Ester type softeners are also of value for improving the processing of these synthetic rubbers and all other Buna N type copolymers. To determine the effect of these softeners on the brittle points of typical Buna N type stocks, the Thiokol RD, Hycar OR-15, Stanco Perbunan, Butaprene NM, and Chemigum I stocks were recompounded with 10 parts dibutyl sebacate, 10 parts dibutyl phthalate, and 10 parts diisobutyl adipate. The addition of these softeners made the uncured stocks practical for factory processing. Esterlike softeners have also been shown to improve the cold resistance of Neoprene FR vulcanizates (*6*). Therefore, the Neoprene FR stock was also recompounded with the same softeners in the same proportions.

The stocks containing the softeners were given the same cure as formerly. The tensile properties, hardnesses, and brittle points are given in Table V. The data show that the inclusion of the softeners in the recipes resulted in a pronounced drop in the brittle points of the stocks. The Thiokol

Table III. Composition, Cure, and Properties of Vulcanizates from Buna N Type Copolymers

	Chemigum I	Chemigum X	Hycar OR-15	Hycar OR-25	German Perbunan	Stanco Perbunan
Composition						
Chemigum I	100.0	.....	.....	.....	.....	.....
Chemigum X	.....	100.0	.....	.....	.....	.....
Hycar OR-15	.....	.....	100.0	.....	.....	.....
Hycar OR-25	.....	.....	.....	100.0	.....	.....
German Perbunan	.....	.....	.....	.....	100.0	.....
Stanco Perbunan	.....	.....	.....	.....	.....	100.0
Semireinforcing carbon black	75.0	75.0	75.0	75.0	75.0	75.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0
Phenyl - α - naphthylamine	1.0	1.0	1.0	1.0	1.0	1.0
Dibenzothiazyl disulfide	1.75	1.75	1.75	1.75	1.75	1.75
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75
Cure						
Temperature, ° F.	274	274	274	274	274	274
Time, minutes	60	60	60	60	60	60
Tensile strength, lb./sq. in.	2790	2850	2630	2560	3040	2540
Ultimate elongation, %	230	150	290	310	300	300
Shore hardness (after 10 sec.)	76	84	72	70	73	70
Brittle point, ° F.	−11	+36.5	+5	−18	−35.5	−29

Table IV. Composition, Cure, and Properties of Vulcanizates from Organic Polysulfides and Buna N Type Copolymers

	Thiokol F	Thiokol FA	Thiokol RD	Butaprene NXM	Butaprene NM	Butaprene NX
Composition						
Thiokol F	100.0	....	.....	.....	.....	.....
Thiokol FA	.....	100.0	.....	.....	.....	.....
Thiokol RD	.....	....	100.0	.....	.....	.....
Butaprene NXM	.....	....	.....	100.0	.....	.....
Butaprene NM	.....	....	.....	.....	100.0	.....
Butaprene NX	.....	....	.....	.....	.....	100.0
Semireinforcing carbon black	75.0	75.0	75.0	75.0	75.0	75.0
Zinc oxide	10.0	10.0	5.0	5.0	5.0	5.0
Stearic acid	0.5	0.5	1.0	1.0	1.0	1.0
Phenyl - α - naphthylamine	.....	....	1.0	1.0	1.0	1.0
Dibenzothiazyl disulfide	0.35	0.3	1.75	1.75	1.75	1.75
Diphenylguanidine	0.1	0.1	.....	.....	.....	.....
Sulfur	.....	....	1.75	1.75	1.75	1.75
Cure						
Temperature, ° F.	298	298	274	274	274	274
Time, minutes	50	40	60	60	60	60
Tensile strength, lb./sq. in.	1490	1390	2260	2370	2160	2950
Ultimate elongation, %	240	190	170	320	260	230
Shore hardness (after 10 sec.)	82	81	87	71	69	75
Brittle point, ° F.	−19	−26	+50	+1	−31	−3.5

Table V. Effect of Ester Type Softeners on Physical Properties and Brittle Points of Vulcanizates Containing Softeners

Synthetic Rubber Type	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore Hardness (after 10 Sec.)	Brittle Points, ° F.		
				With softeners	Without softeners	Lowering due to softeners
Thiokol RD	2140	300	65	−20	+50	70
Hycar OR-15	1990	440	55	−41	+ 5	46
Chemigum I	1900	310	56	−63	−11	52
Stanco Perbunan	1790	470	50	−70	−29	41
Butaprene NM	1710	380	47	−79	−31	48
Neoprene FR	1470	270	52	−82	−41	41

Table VI. Comparison of Brittle Points Determined with Rapid and with Slow Bend

Vulcanizate	Brittle Point, ° F.		
	Slow bend	Rapid bend	Difference
Chemigum IV	< −106.5	−71	35.5
Smoked sheet	−96.5	−71	25.5
Stanco Perbunan	−71	−29	42
Neoprene E	−64	−29	35
Neoprene GN	−60.5	−31	29.5
Hycar OR-15	−37.5	+ 5	42.5

RD stock exhibited the greatest lowering in brittle point, but the Butaprene NM and Neoprene FR stocks had the lowest brittle points. The softeners likewise had an effect on tensile properties and hardness; the tensile strengths were decreased, the ultimate elongations were increased, and the hardnesses were decreased.

DETERMINATION OF BRITTLE POINTS UNDER LESS SEVERE BENDING STRESS

The foregoing experiments gave data on brittle points when the specimens were subjected to a rapid rate of bending and an acute radius of bending. The work of Kemp, Malm, and Winspear (*2*) indicates that, when the rate of bending is decreased and the radius of bending is increased, the brittle points of natural and synthetic vulcanizates are lowered. The present authors have also conducted experiments with a low rate and a large radius of bending. These experiments were carried out in a simple fashion but gave quite consistent results.

The procedure employed was as follows: A strip, 6.0 inches long, 0.25 inch wide, and 0.08 inch thick, was cut from a cured tensile sheet. The strip was clamped at each end to wooden sticks as shown in Figure 3*A*. The strip was maintained in this slightly bent condition and immersed in acetone at the test temperature. After 2-minute immersion, the strip was slowly bent while still immersed until the sticks were parallel (Figure 3*B*). If the strip broke during this operation, the temperature of the acetone was raised slightly and the test repeated with a new specimen. The highest temperature at which the strip broke was considered to be the brittle point of the stock. This temperature was found to be the same within 0.5° F. for different specimens of the same stock. A Scott T-50 apparatus (*5*) was used to provide the cold acetone bath for this brittle point test. This apparatus afforded a convenient means of cooling the specimens because of its shallow cooling tray and easy temperature regulation.

The results of these brittle point tests with low rate of bending and large radius of bending are given in Table VI. Included are the corresponding rapid-bend brittle points obtained with the Bell Telephone Laboratories apparatus for comparison. The slow-bend brittle points are 25° to 45° F. lower than the corresponding rapid-bend brittle points. Of particular interest is the very low brittle point of the Chemigum IV stock when determined by the slow-bend test; it was below the lowest temperature obtainable in the Scott T-50 apparatus with solid carbon dioxide in acetone as the cooling medium.

CONCLUSION

The slow-bend brittle point test does not have the same practical significance as the Bell Telephone Laboratories brittle point test because most rubber articles which are exposed to low temperatures in service are required to withstand fairly rapid flexing. If the slow-bend brittle point test were used as a criterion of the cold resistance of these rubber articles, it might qualify the rubbers for a lower temperature than they could safely withstand in service. The brittle point test developed by the Bell Telephone Laboratories is simple and sensitive. It is believed that this test may advantageously be used to study all cold resistance problems where damage to the rubber itself and not increase in stiffness is the first consideration.

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The opinions or assertions in this paper are those of the authors, and are not to be construed as official or reflecting the views of the Navy Department or the naval service at large.

Nutritive Value of COTTON, PEANUT, and SOY SEEDS

In contrast to cereal grain milling, the process applied to oil-bearing seeds conserves the vitamin B complex values in the same edible milling fraction with the protein. The hull is the only waste product as far as food uses are concerned. Judging by comparison of assays on seed and seed flour, the removal of the oil leaves the cake with an increased concentration of water-soluble vitamins. From a food standpoint the oil has calorie and culinary value with little if any known specific nutritional properties. Flours of cottonseed, peanut, and soybean are concentrated sources of high quality protein especially suitable for supplementing white flour. Results so far obtained indicate moderate differences in amounts of the three seed flours required for producing normal growth. Soybean flour is superior in protein quality, cottonseed flour in riboflavin content; assays on peanut flour indicate an outstanding nicotinic acid value. As substitutes for both the protein and the vitamins of meat, a mixture of the three seed flours offers possibilities.

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AMONG the available materials high in protein and vitamin B complex which have not yet been utilized to more than a fraction of their possibilities are the seeds of cotton, peanut, and soybean. Peanuts and certain varieties of edible (i. e., directly edible) soybeans make up a very small part of the American diet. All three seeds are the basis of large industrial operations for vegetable oils. The press cake or expeller residue from such operations yields enormous amounts of practically dehydrated, low-fat concentrates of protein. Its use in the past has been principally as animal feed and to some extent as fertilizer. Improvements in process have in recent years yielded products quite palatable and adequately sanitary for consumption as wholesome food for man. In the form of flour and grits they are now available in commercial quantities for use in the human dietary. A general description of properties and process has been given for cotton by McMath (*16*) and Council on Foods (*3*), for peanut by Harrell (*8*) and Payne (*18*); for soybeans by the Soybean Nutritional Research Council (*9*). The latter discusses the feeding of various farm animals but as yet has no section on application to the nutrition of man.

As early as 1910 Fraps (*6*) used cottonseed flour as an enriching component in bread making, and Johns and coworkers have published studies of the nutritional quality of bread made with supplements of peanut flour (*12*) and soybean flour (*11*). Soybean preparations (curd) as well as the beans themselves have been used as human food in the Far East for centuries. Adaptations to western food habits are discussed in detail by Schroeder (*19*). A synopsis (*7*) of the German Army Soya Cook Book 1938 indicates further developments. The soybean curd used in China and other eastern countries is apparently the only instance of an oilseed product, including the protein fraction, being used as such for food. All other uses employ the product as a supplement in some other food article. Two plans may be followed: Fraps, Johns *et al.*, and others utilize large amounts in baked goods (25 per cent is apparently the highest amount that can be used without disturbing the baking quality of ordinary flour); the German Army Cook Book and Schroeder recommend the incorporation of small amounts of soybean flour in almost every article of the menu.

The present report is aimed at showing the effect of graded amounts of the seed flours as supplements to white flour. Suitable salt mixtures and adequate supplies of the fat-soluble vitamins are incorporated in the diets so that the variables are reduced to protein and the vitamins of the B complex. The ability of the diet to support the maximal growth rate in rats is used as criterion, since deficiency in any of the nutritional factors under question results in a reduced growth rate. The method used is more nearly related to the determination of protein requirement than to biological value technique. Maynard (*17*) discusses and illustrates the various methods of protein investigation, and McCollum *et al.* (*15*) discusses the difficulties in interpreting biological values. The criterion employed has the advantage over others in current use that it allows data to be collected at the level of nutrition which is approximately optimal for the test animal, and this is the nutritional level at which we wish to operate in human feeding. An important requirement is a well defined growth standard which will not be exceeded by dietary means and to which the degree of adherence on any diet to be tested can be quantitatively determined.

GROWTH STANDARDS

As shown elsewhere (*23*), all the carefully recorded growth data on healthy albino rats, both large and small strains, indicate that when they are put on well chosen liberal diets, there is an upper limit to the growth process. This optimal growth can be put into straight line form if the log of the weight is plotted against the reciprocal of age in any appropriate units. Means for strains of different characteristic body sizes come out in such a plot as parallel straight lines with slope determined by sex, intercept by inherent size. Dietary deficiencies result in suboptimal growth curves which, by their shape, are frequently characterisic of the type of deficiency. For instance, with a moderate protein deficiency the curvilinear log reciprocal plot tends to ap-

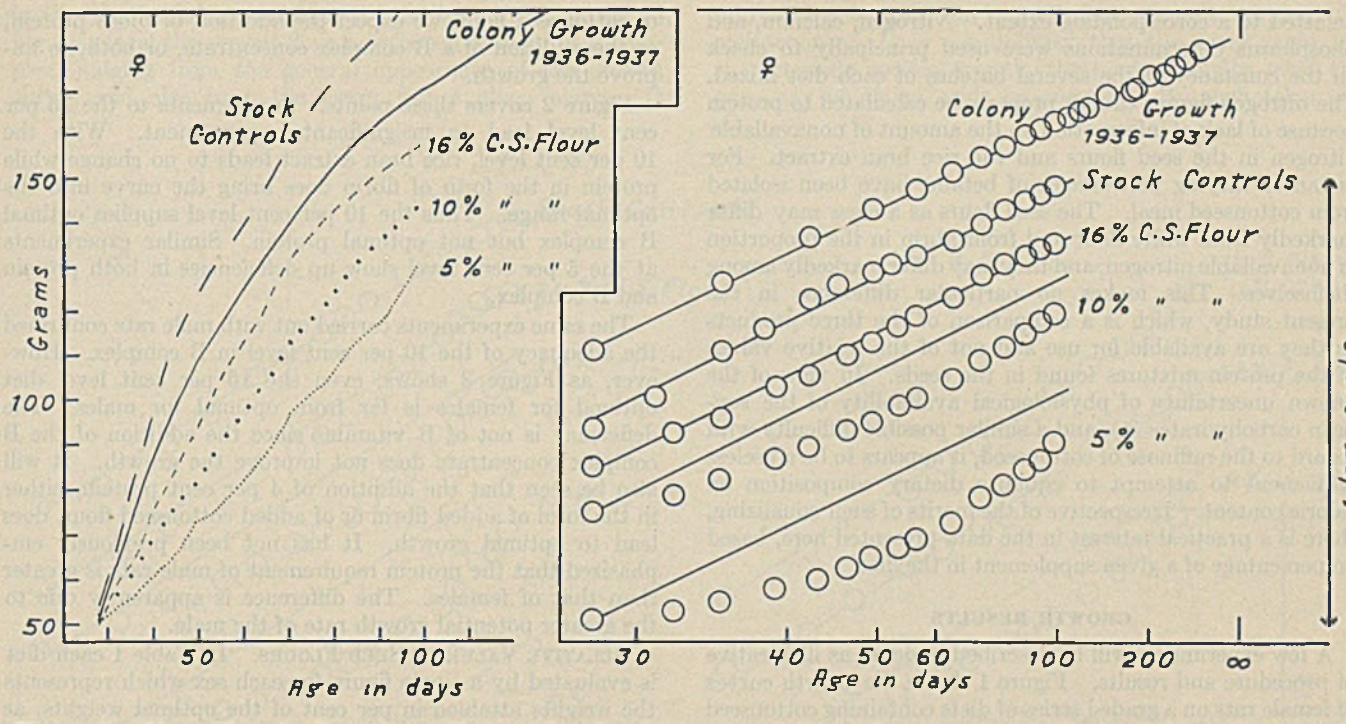

Figure 1. Mean Female Growth on Various Levels of Cottonseed Flour Compared with Optimal Growth of Stock Diet Controls and the Previously Published Colony Average for 1936–37 on Some 600 Animals

In the log reciprocal plot the reference points for the log scale have been arbitrarily shifted to separate the various curves. The 5 and 10 per cent cottonseed flour diets are clearly deficient; the 16 per cent curve shows a slight tendency towards a growth deficit which may or may not be real.

proach the straight line optimal growth as time goes on (spontaneous realimentation). This can be attributed to a decreasing protein requirement as the animal grows older. In contrast, dietary essentials whose requirement increases with age, such as thiamine, cause an increasing departure from the growth norm as time goes on.

EXPERIMENTS WITH RATS

Young rats from the stock colony weaned at 4 weeks were selected for the experiments on the basis of meeting set standards of weight and growth rate in the 3–4 week age period. Such selection is indispensable for obtaining consistent results (compare Eppright and Smith, *5*). Experimental groups initially comprised twelve animals, half of each sex, but some groups as finally reported are a little smaller owing to the elimination of rats showing respiratory involvement with consequent erratic growth. The diets were fed ad libitum from 4 to 14 weeks of age when the experiment was terminated. Weighings were made to the nearest gram at biweekly and later at weekly intervals.

Common to all the seventeen diets was the addition of 5.5 per cent of a salt mixture (*21*) modified to give, respectively, 0.6 and 0.4 gram of added calcium and phosphorus per 100 grams of diet. A uniform addition of the fat-soluble vitamins gave each diet at least 50 U. S. P. units of D in 0.2 gram of cod liver oil and 750 units of A activity in 0.1 gram of carotene solution. A stock solution of these two factors in cottonseed oil was made up so that 2 grams of the solution could be weighed out per 100 grams of diet. Each of the seed flours was studied at levels of 5, 10, and 16 per cent in the diet; with cottonseed flour a 24 per cent level was also introduced. In each case the diet was made up to 100 per cent with white flour. To test for adequacy of B complex factors, additional groups were run with the addition of 4 per cent of rice bran extract. To test for adequate protein, check experiments were conducted with the addition of blood fibrin to make the total estimated protein content approximately constant; this required 4, 7, and 10 per cent of added fibrin, respectively, in the diets containing 16, 10, and 5 per cent cottonseed flour.

The products used were from the following sources: cottonseed flour, McMath process Proflo, Traders' Oil Mill Company; peanut flour, McMath-Howard process PDP, from the same source; soybean flour, No. 1, A. E. Staley Manufacturing Company; rice bran extract, Vitab type II, National Oil Products Company; white flour, Power Plus, a standard patent flour made from spring wheat, Techanny Milling Corporation; crude blood fibrin, Armour Glue Works, ground in a hammer mill and repeatedly extracted with hot 95 per cent ethanol.

Assay values for certain vitamin B factors as provided by the manufacturers follow:

	Thiamine	Riboflavin	Nicotinic Acid	Pantothenic Acid	Pyridoxin
			Micrograms per gram		
Cottonseed flour	10.4	10.2	85	25.5	
Soybean flour	5.4	4.1	29	15.0	6.4
Peanut flour	6.0	3.0	High (ca. 200)		
			Micrograms per cc.		
Rice bran extract	150	10	2000	275	150

The peanut values refer to the product used in this work. The difference between these figures and those of 12 and 5, respectively, for thiamine and riboflavin cited by Payne (*18*) is accounted for by the absence or presence of the skins which are known to be high in these factors. The product with skins has apparently been discontinued on account of flavor difficulties. The description as otherwise given by Payne refers to the product without skins.

Various analytical figures obtained in this laboratory on some of the diet constituents may be of interest:

	% P	% Ca	% Mg	P. P. M. Mn	% N (Kjeldahl)	% H_2O	% Ash
White flour	0.130	0.014	0.039	..	2.47	9.5	...
Cottonseed flour	1.26	0.20	0.65	15	9.0	6.3	6.1
Peanut flour	0.56	0.070	0.36	45	9.7	7.6	3.6
Soybean flour	0.58	0.24	0.25	32	6.8	8.6	4.8
Fibrin	0.096	0.18	0.015	3	13.7	7.1	3.4
Rice bran ext.	0.54	0.03	0.16	18	1.60	37	4.9

The soybean flour was higher in fat than the other two; a higher nitrogen content would be found in a soybean flour defatted to a corresponding extent. Nitrogen, calcium, and phosphorus determinations were used principally to check on the constancy of the several batches of each diet mixed. The nitrogen figures cannot properly be calculated to protein because of lack of information on the amount of nonavailable nitrogen in the seed flours and the rice bran extract. For instance, varying percentages of betaine have been isolated from cottonseed meal. The seed flours as a class may differ markedly from white flour and from fibrin in the proportion of nonavailable nitrogen, and they may differ markedly among themselves. This makes no particular difference in the present study, which is a comparison of the three products as they are available for use and not of the relative values of the protein mixtures found in the seeds. In view of the known uncertainty of physiological availability of the soybean carbohydrates (*1*), and a similar possible difficulty with regard to the raffinose of cottonseed, it appears to be a useless refinement to attempt to equalize dietary composition on calorie content. Irrespective of the merits of such equalizing, there is a practical interest in the data presented here, based on percentage of a given supplement in the diet.

GROWTH RESULTS

A few experiments will be described in detail as illustrative of procedure and results. Figure 1 shows the growth curves of female rats on a graded series of diets containing cottonseed flour at levels of 5, 10, and 16 per cent, compared with the colony growth standard established some years ago and with a contemporary small group of controls run on the same stock diet. In the plots made on ordinary cross section paper (left-hand side of the figure), there is apparently as much difference between the two groups of animals on the stock diet as between any other two neighboring groups. In the log reciprocal plot of the same data (right-hand side), it is clear that the two stock diet groups differ only in inherent size, both lying on straight lines of the same slope. Also, the 16 per cent level diet seems to be practically optimal and will not be materially improved by either more protein, more B complex, or a higher level of cottonseed flour. With the lower levels of cottonseed flour, we expect the addition of more protein, or the addition of a B complex concentrate, or both, to improve the growth.

Figure 2 covers these points. Supplements to the 16 per cent level lead to insignificant improvement. With the 10 per cent level, rice bran extract leads to no change while protein in the form of fibrin does bring the curve into the optimal range. Thus the 10 per cent level supplies optimal B complex but not optimal protein. Similar experiments at the 5 per cent level show up deficiencies in both protein and B complex.

The same experiments carried out with male rats confirmed the adequacy of the 10 per cent level in B complex. However, as Figure 3 shows, even the 16 per cent level diet optimal for females is far from optimal for males. The deficiency is not of B vitamins since the addition of the B complex concentrate does not improve the growth. It will also be seen that the addition of 4 per cent protein, either in the form of added fibrin or of added cottonseed flour, does lead to optimal growth. It has not been previously emphasized that the protein requirement of male rats is greater than that of females. The difference is apparently due to the greater potential growth rate of the male.

Relative Value of Seed Flours. In Table I each diet is evaluated by a single figure for each sex which represents the weights attained in per cent of the optimal weights, as an average of the percentage at each weighing day. The values for comparable diets range fairly consistently so as to make soybean a little better than cotton, and cotton a little better than peanut. A more highly defatted soybean preparation could be expected to increase the difference somewhat. The superiority of the soybean is attributable to protein quality. As a general B complex source, the cottonseed flour is superior, since it provides optimal B complex at the 10 per cent level whereas the soybean flour (on the basis of experiments just now terminating) is definitely below B complex requirements when fed at the 10 per cent level (approximately 5 per cent soybean protein). Hayward *et al.* (*10*) state that soybean flour providing 18 per cent of protein

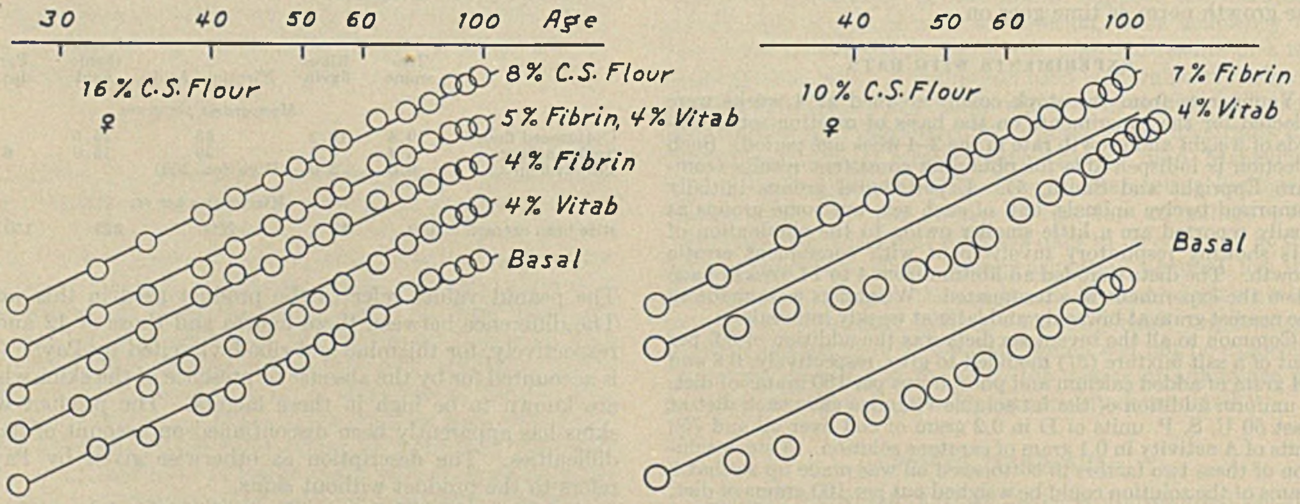

Figure 2. Mean Female Growth on Protein and B Complex Supplements at Two Cottonseed Flour Levels

The protein supplement definitely improves the growth at the 10 per cent cottonseed flour level; at both levels the B complex supplement makes the growth slightly worse, if anything. The 4 per cent Vitab substitutes for 4 per cent flour and thereby lowers the protein by about 0.6 per cent; the Vitab itself contributes some nitrogen which is probably largely nonprotein. If this is a valid interpretation, it contributes more evidence that the 16 per cent level is just border line as far as protein is concerned.

in the diet furnishes adequate B complex. Even at the 16 per cent level the peanut flour may be suboptimal in B complex, judging from the general appearance of the growth curves and also from the assay values given above. It should be noted, however, that peanut flour is an unusually rich source of nicotinic acid, an essential factor in human nutrition. Unfortunately the rat does not require an external source of nicotinic acid, and nicotinic acid thus comes outside of the scope of this investigation.

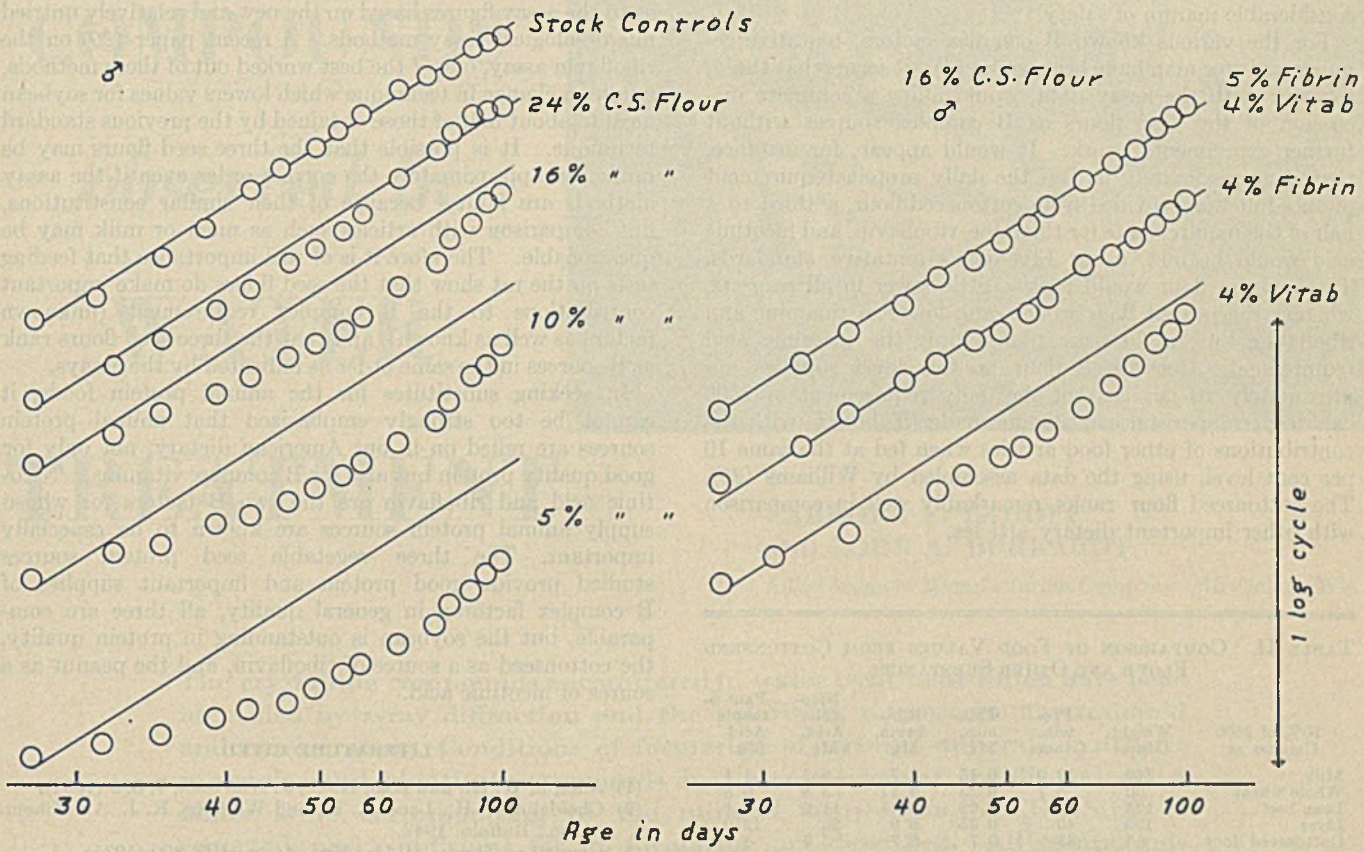

Figure 3. Mean Male Growth on Some of the Cottonseed Flour Diets

The normally much greater growth rate of the males (*cf.* Figure 1), which is not accompanied by any greater food intake in comparison with that of a female of the same body weight, results in the male having a higher requirement of protein on a percentage basis in the diet. The 16 per cent level is definitely inadequate.

Recent experiments of Jones *et al.* (*13*) place the three seed flours in the same order with regard to quality of protein. In his experiments the protein quality is the only variable, adequate B complex being supplied from other sources.

HUMAN NUTRITION

Usually it is stated that the protein requirement of man (including infancy) is satisfied when 10 per cent of the calories are derived from a good quality protein. More rapidly growing animals, such as the rat and the chick, require about double this amount when young. Differences in total amount of protein required may appear to obscure the problem of protein quality when we compare one species with another.

The greatest demand for amino acids is for tissue building. Older rats (*14*) do just as well on 8 per cent protein in the diet as on larger amounts. Later in life the requirements are also less exacting with regard to the essential amino acids. This is exemplified by the fact that certain amino acids are said to be essential for growth but are not required for maintenance. It is not unlikely that the more rapid the characteristic species growth, the more carefully must the adequacy of amino acids be guarded. By such token we may be bending over backward in using the rat as a test object in discussing human requirements, but we are playing safe.

Table I. Diet Evaluation

Per Cent	Females Soybean	Females Cottonseed	Females Peanut	Males Soybean	Males Cottonseed	Males Peanut
24		100.0			97.0	
16	96.8	97.7	90.0	86.0	86.3	79.9
10	88.7	82.5	82.4	78.1	72.7	69.1
5	79.8	73.2	72.2	64.9	63.8	62.1

Cottonseed level, %	16		10		5	
Sex	F	M	F	M	F	M
Basal	97.7	86.3	82.5	72.7	73.5	63.8
Basal + Vitab	95.6	85.3	82.5	74.7	80.4	69.0
Basal + fibrin	100.7	99.5	100.0	97.3	100.3	94.7
Basal + fibrin + Vitab	99.4	99.4				

	F	M
Stock controls	101.1	99.1
No growth (initial wt. just maintained)	46.2	37.3

With regard to the amino acid distribution in the diets of young rats, containing mixtures of wheat and seed protein, at levels of total protein comparable with those required with high quality single proteins (egg protein or casein) all the amino acid requirements are fully met, provided the seed protein represents about half the total. Probably the conclusion stated in this way is directly applicable to man with a considerable margin of safety.

For the various known B complex factors, tentative requirements for man have been set up (*4*); it seems that these, together with the assay data, would allow a complete discussion of the seed flours as B complex sources without further experimental work. It would appear, for instance, that if approximately half of the daily protein requirement of an adult was provided from cottonseed flour, a third to a half of the requirements for thiamine, riboflavin, and nicotinic acid would be met, using Elvehjem's tentative standards. The soybean flour would rank a little lower in all respects, whereas the peanut flour would rank lower in thiamine and riboflavin, but would more than supply the nicotinic acid requirement. Cottonseed flour at this level supplies approximately 10 per cent of the daily requirement of 2500 calories; comparison can also be made (Table II) with the contributions of other food articles when fed at the same 10 per cent level, using the data assembled by Williams (*22*). The cottonseed flour ranks remarkably well in comparison with other important dietary articles.

TABLE II. COMPARISON OF FOOD VALUES FROM COTTONSEED FLOUR AND OTHER SUBSTANCES

10% of 2500 Calories as:	Weight, Grams	Protein, Grams	Thiamin, Mg.	Riboflavin, Mg.	Nicotinic Acid, Mg.	Pantothenic Acid, Mg.
Milk	360	12.0	0.15	0.7	0.2	1.1
Whole wheat	60	6.7	0.33	0.11	3.8	0.8
Lean beef	125	25	0.08	0.45	11.0	1.1
Liver	195	40	0.35	5.0	25	12.0
Cottonseed flour	65	35	0.7	0.7	5.7	1.7

The procedure by which cottonseed flour becomes available is of interest on several scores. Originally cotton was grown simply for the fiber. When it was found that a valuable oil could be obtained from the seed, the press cake at first was a waste product which soon, however, was utilized in stock feeding as a source of protein. By careful control of the process (*3*, *8*, *16*), a wholesome food product high in protein and B complex vitamins was prepared. In a sense, grain milling and oil seed milling are complementary processes. Both grains and oil seed store a large nonprotein energy content, in the one case as carbohydrate and in the other as fat; and in the separations involved in milling, the water-soluble vitamin potency goes with the protein fraction. From wheat the principal edible portion is used for its calorie value and contains a relatively low amount of protein of not particularly good quality; little of the B complex contained in the grain accompanies this fraction. In cottonseed milling, a large yield of oil is first expressed and marketed as such. The remainder contains large amounts of relatively good quality protein together with nearly all the water-soluble vitamin fraction. Through the removal of the oil, both protein and vitamins are concentrated in comparison to their content in the seed. The vitamin assay figures for whole cottonseed as determined by Cheldelin and co-workers (*2*) are, in micrograms per gram, 3.2 of thiamine, 2.3 of riboflavin, 11 of pantothenic acid, and 16 of nicotinic acid. The cottonseed flour represents 15 per cent by weight of the cottonseed.

There are several reasons for questioning the completeness and correctness of the above discussion of the B complex factors in the seed flours in relation to human requirements. The human requirement figures are not only tentative, but also do not include all the known B complex vitamins. They cannot cover any unidentified factors whose importance is indicated by recent rat work. Some question can be raised as to the assay figures based on the new and relatively untried microbiological assay methods. A recent paper (*20*) on the riboflavin assay, one of the best worked out of these methods, studies a change in technique which lowers values for soybean meal to about half of those obtained by the previous standard technique. It is possible that the three seed flours may be ranked in approximately the correct order even if the assay methods are faulty, because of their similar constitutions, but comparison with articles such as meat or milk may be questionable. Therefore it is of real importance that feeding tests on the rat show that the seed flours do make important contributions to the B complex requirement (unknown factors as well as known), and that the three seed flours rank as B sources in the same order as indicated by the assays.

In seeking substitutes for the animal protein foods, it cannot be too strongly emphasized that animal protein sources are relied on in our American dietary, not only for good quality protein but also for B complex vitamins. Nicotinic acid and riboflavin are the two B factors for whose supply animal protein sources are known to be especially important. The three vegetable seed protein sources studied provide good protein and important supplies of B complex factors; in general quality, all three are comparable, but the soybean is outstanding in protein quality, the cottonseed as a source of riboflavin, and the peanut as a source of nicotinic acid.

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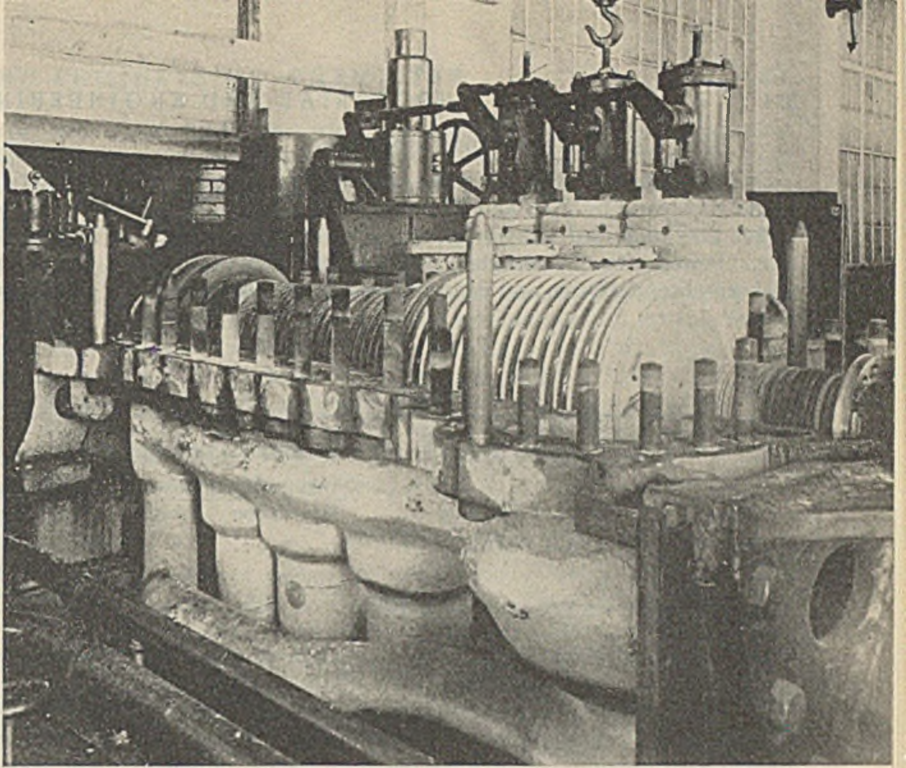
CRYSTALLINE COMPOUNDS *observed in* WATER TREATMENT



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The crystalline compounds encountered in water treatment which have been identified by x-ray diffraction and the polarizing microscope are reviewed and enumerated. Conditions of formation of natural minerals, synthetic minerals, and identical compounds in water treatment are discussed. A boiler scale corresponding to the mineral acmite ($Na_2O.Fe_2O_3.4SiO_2$) is reported, and conditions for its formation are described. All compounds identified by the authors have been by the x-ray powder diffraction method.

MANY types of solid compounds are encountered in various phases of water treatment. Some of them are desirable and some undesirable. In either case it is necessary to know the exact nature of these compounds in order to facilitate or hinder their formation, as may be desired. The first step in a study of the compounds is an accurate analysis, both as to chemical composition and crystalline modification. In the case of a single compound, chemical analysis is often sufficient; however, in a majority of cases, precipitates and deposits are mixtures, and chemical analyses must be supplemented by other methods of examination to identify the different crystalline species properly. Physicochemical methods can be applied to equilibria calculations only when identification is complete, for the solid phases in contact with solutions must be definitely known.

Most of the solid compounds in water treatment may be classed as crystalline, and therefore crystal methods may be applied to their identification.

The impurities in water are of mineral origin, and the products formed from these impurities are synthetic minerals of the same kind as were originally leached from the earth's crust, or they may be other minerals produced by different arrangements of the ions comprising the original solution. The mineralogist has long used the microscope for identification purposes and more recently the x-ray diffraction method. With the polarizing microscope such characteristics as refractive index, optic sign, extinction, and birefringence can be determined. By referring to tables of physical and optical properties of minerals, the crystals can be properly identified. The x-ray diffraction method gives patterns which are characteristic for each mineral. The simplest technique is to make visual comparisons by placing known patterns beside unknown patterns and observe whether the lines of the known come into coincidence with those of the unknown. This method is satisfactory for most mixtures also. The distances between atomic planes can also be calculated, and these are constant for each mineral or crystalline compound. A method of analysis is based on this principle by comparing interplanar spacings in an unknown pattern with previously determined interplanar spacings for various compounds (*17*).

The petrographic microscope is useful in observing the "texture" of deposits; that is, occlusions may be distinguished from the main crystal growth. In certain cases nonopaque amorphous material can be identified. On the other hand, the x-ray diffraction method can be used for identification of crystals too small to be resolved by the microscope and also of materials which are opaque to light. The x-ray method is useful in studying thin layers at different depths in a deposit. This paper reviews the compounds previously reported by either of the above mentioned methods and includes identifications made by the authors by x-ray diffraction.

SUMMARY OF IDENTIFICATIONS

One of the first studies of a series of boiler sludges and deposits was made by Hall and Merwin (*15*); by microscopic means they identified anhydrite, calcite, brucite, and aragonite. Powell (*29, 30*) reported analcite, anhydrite, calcite, opal, noselite, natrolite, and dendritic copper with the petrographic microscope. Clark and co-workers (*3–6*) used x-ray diffraction to find hydroxyapatite, calcium hydroxide, xonotlite, pectolite, and calcium aluminate. Brines (*2*) by x-ray identification lists calcite, hydroxyapatite, magnetite, hematite, serpentine, and anhydrite. By x-ray Corey and Finnegan (*8*) found magnetite in corrosion deposits. Imhoff and

Table I. Crystalline Constituents Identified in Water Treatment

Name	Formula	Means of Identification		Occurrence in Water Treatment	Some Conditions of Deposit Formation
		Microscope	X-ray		
Acmite	$Na_2O.Fe_2O_3.4SiO_2$	.....	[a]	Boiler scale Superheater Turbine deposits	400–1200 lb./sq. in. (steam pressure) 400 lb./sq. in. 1250 lb./sq. in.
Analcite	$Na_2O.Al_2O_3.4SiO_2.2H_2O$	(*20*)	(*20*)	Boiler scale and sludge	400–900 lb./sq. in.; excess alumina in water
Anhydrite	$CaSO_4$	(*15, 29*)	(*2, 20*)	Boiler scale	Up to 600 lb./sq. in.; excess calcium in boiler water
Aragonite	λ-$CaCO_3$	(*15*)	(*20*)	Feed lines and pumps	Thermal decompn. of bicarbonates; pptn. with alkali
Bayerite	α-$Al_2O_3.3H_2O$	.....	[a]	Corrosion deposit	Hot condensate in contact with aluminum
Böhmite	γ-$Al_2O_3.H_2O$	.....	(*40*)[a]	Oil filter floc	Pptn. of alum above pH of 5.5
Brucite	$Mg(OH)_2$	(*15*)	(*20*)	Boiler scales, softener sludges, feed line deposits	Pptn. of sol. magnesium at high pH
Bunsenite	NiO	.....	[a]	Turbine blade corrosion	....
Burkeite	$Na_2CO_3.2Na_2SO_4$	.....	[a]	Superheater deposit Turbine blade deposit	150 lb./sq. in. 400 lb./sq. in.
Calcite	β-$CaCO_3$	(*15, 29*)	(*2, 20*)	Boiler scale and sludge, softener sludge, feed line deposits	Pptn. of $CaCO_3$ with lime; high-temp. pptn. of carbonate
Calcium aluminate	$3CaO.Al_2O_3.6H_2O$	.....	(*3*)	Softener in chem. tank	Reaction between lime and sodium aluminate
Calcium hydroxide	$Ca(OH)_2$	.....	(*6*)[a]	Boiler scales	400 lb./sq. in.
		.....	.....	Superheater deposit	400 lb./sq. in.
Cancrinite	$4Na_2O.CaO.4Al_2O_3.$- $2CO_2.9SiO_2.3H_2O$	.....	[a]	Superheater deposit	400 lb./sq. in.
Chalcocite	Cu_2S	.....	[a]	Turbine deposit	H_2S in steam
Cristobalite	SiO_2	.....	[a]	Ignited turbine blade deposit	
Cuprite	Cu_2O	.....	[a]	Preheater corrosion product	
Ferrous oxide	FeO	.....	[a]	Superheater tube, boiler tube	Excessive overheating of metal
Forsterite	$2MgO.SiO_2$	.....	[a]	Domestic hot water heater	....
Gypsum	$CaSO_4.2H_2O$	.....	[a]	Evaporator scale	Low-temp. evapn. of calcium sulfate soln.
Halite	$NaCl$	.....	(*20*)	Turbine blade deposits	500–250° C.
Hematite	Fe_2O_3	.....	(*2, 20*)	Boiler scale, corrosion deposits	Highly oxidizing environment
Hemihydrate	$CaSO_4.{}^1/_2H_2O$	.....	(*28*)	Boiler scale	....
Hydroxyapatite	$Ca_{10}(OH)_2(PO_4)_6$	.....	(*2, 5, 20*)	Boiler scale, boiler sludge	Moderate excess of sodium phosphate and high alkalinity favor formation
Magnetite	Fe_3O_4	.....	(*2, 8, 20*)	Corrosion deposits, superheater deposits	Corrosion in absence of oxygen; high-temp. reaction of steam and iron
Metallic copper	Cu	(*29*)	(*20*)	Boiler scale, boiler sludge	Most troublesome in low-make-up stations
Metallic iron	Fe	.....	[a]	Superheater corrosion	Inversion product from ferrous oxide
Natrolite	$Na_2O.Al_2O_3.SiO_2.2H_2O$	(*30*)	(*30*)	Boiler scale	....
Noselite	$4Na_2O.3Al_2O_3.6SiO_2.SO_4$	(*30*)	(*30*)	Boiler scale	....
Opal	SiO_2 (amorphous)	(*29*)	.....	Feed line scale	....
Pectolite	$Na_2O.4CaO.6SiO_2.H_2O$	.....	(*4*)	Boiler scale	....
Phosphorite	$Ca_3P_2O_8.H_2O$	.....	[a]	Hot phosphate softener	About 5 p. p. m. excess phosphate in softener effluent
Quartz	SiO_2	.....	(*20*)	Boiler scale, turbine blade deposits	High silica concn. in boiler water and high steam generation rates in stages at 280° C. to exhaust
Serpentine	$3MgO.2SiO_2.2H_2O$	(*2*)	[a]	Boiler scale	150–900 lb./sq. in.
Tenorite	CuO	.....	[a]	Ejector	Highly oxidizing conditions for copper
Thenardite	Na_2SO_4 (V)	.....	[a]	Boiler scale superheater	Dry tubes, high pressure; carry-over of high-sulfate boiler water
Whitlockite	β-$Ca_3P_2O_8$	.....	[a]	Ignited phosphate sludge; deposit from phosphate line to boiler	....
Wollastonite	$CaSiO_3$		(*31*)[a]	Boiler scale xonotlite ignited at 950° C.	Extremely high tube temp.
Xonotlite	$5CaO.5SiO_2.H_2O$	.....	(*4, 20, 31*)	Boiler scale	Deficiency of phosphate in high-pressure boilers being fed water containing calcium and silica

[a] Additional compounds identified by the authors by x-ray diffraction patterns.

Burkardt (*20*) reported analcite, anhydrite, aragonite, brucite, calcite, hematite, hydroxyapatite, magnetite, metallic copper, quartz, sodium chloride, and xonotlite by x-ray identification.

Table I lists the compounds identified by either x-ray diffraction patterns or the petrographic microscope with references to the reports. The information regarding conditions under which each species is formed is not meant to indicate the limits for the compound formation, but rather to describe conditions under which these compounds have been found. The letter *a* marks additional compounds which have been identified by the authors by x-ray diffraction patterns. The last column refers to specific deposits.

In the following discussion, the compounds encountered in water treatment are considered from the standpoint of their relation to natural minerals, mode and conditions of formation or synthesis, and occurrence in practice.

TABLE II. CONDITIONS FOR FORMATION OF HYDROUS ALUMINUM OXIDES

Name	Formula	Conditions of Alumina Formation
Gibbsite	γ-$Al_2O_3.3H_2O$	Pptd. with long aging
Bayerite	α-$Al_2O_3.3H_2O$	Pptd. and aged in cold
Böhmite	γ-$Al_2O_3.H_2O$	Pptd. and aged in hot
Diaspore	α-$Al_2O_3.H_2O$	
Basic aluminum sulfate	$Al_2O_3.SO_3.1^1/_2\ H_2O$	Pptd. from alum below pH 5.5

ALUMINUM OXIDES

Aluminum oxides occur in nature in several hydrated forms and in several modifications of each hydrate. Bauxite ore is a mixture of various hydrous aluminum oxides. Weiser and Milligan (*38*) studied the conditions under which the various forms of hydrous oxides could be precipitated. Variables affecting the crystal forms of the precipitate are temperature of aging, time of aging, rate of hydrolysis, and hydrogen ion concentration. Some of the forms of alumina and conditions of formation are given in Table II. Only bayerite and böhmite have been found in water treatment deposits so far.

The composition of the floc formed in coagulation has long been thought to be a basic aluminum sulfate of variable composition depending upon the pH value at the time of coagulation (*25*). In very dilute solutions, alum forms a floc most readily at a pH of about 5.5 (*34*). The composition of the floc at this point corresponds to an empirical formula of $5Al_2O_3.3SO_3.XH_2O$. Weiser, Milligan, and Purcell (*39*, *40*), by means of x-ray and electron diffraction, studied the composition of the alum floc in the pH range between 3.97 and 10.50. They could find only two crystalline forms. Working with alum flocs precipitated from dilute solutions, they found γ-$Al_2O_3.H_2O$ (böhmite) was formed above a pH of 5.5, and below that value, a basic aluminum sulfate corresponding to the formula $Al_2O_3.SO_3.1^1/_2H_2O$.

The authors have studied some alum flocs taken from coagulation basins and filter backwashings to determine what crystalline species could be found. The pH range in this study was between 4.5 and 8.0. A floc formed at a pH of 4.5 gave a pattern which was neither böhmite nor basic aluminum sulfate ($Al_2O_3.SO_3.1^1/_2H_2O$). It has not been determined whether this was another crystal form of the alum floc or resulted from impurities. Several samples gave patterns of quartz only, and these were definitely due to the coagulated suspended matter brought down by the floc.

Böhmite was identified in an oil filter floc using alum at a pH of 6.5–7.0, but no basic aluminum sulfate could be found in several alum flocs formed below a pH of 5.5. Bayerite (α-$Al_2O_3.3H_2O$), a trihydrate, was found in a corrosion product taken from condensate returns of an air conditioner unit using aluminum cooling coils. Figure 1 shows the diffraction patterns of the two forms of hydrated aluminum oxide thus far identified.

Closely allied to the alum floc is the aluminate floc. The composition has been studied from chemical analyses, but it is difficult to study by x-ray diffraction for it is always heavily contaminated with softening precipitates and for this reason is greatly diluted. A calcium aluminate ($3CaO.Al_2O_3.6H_2O$) has been identified (*3*), however, in chemical solution tanks where sodium aluminate and lime are mixed together. This aluminate is reported to have a fundamental structure which is constant over a range of compositions in which the $CaO:Al_2O_3$ ratios vary from 4:1 to 1:1.

CALCIUM CARBONATE

Calcium carbonate exists in one stable form, β-$CaCO_3$ (calcite), and two unstable forms, λ-$CaCO_3$ (aragonite) and μ-$CaCO_3$, in the temperature range 0–970° C. (*24*). Above 970° C. and under a carbon dioxide pressure of one atmosphere α-$CaCO_3$ is the stable form.

Calcite generally results from slow precipitation. It may be obtained under conditions which usually produce the unstable forms. If either of the unstable forms is left in contact with water, it will invert to calcite. The speed of the inversion is dependent on the temperature. The presence of calcite particles in a liquid containing either of the unstable forms will facilitate inversion to calcite. Inversion of the dry unstable forms at room temperature is very slow; at temperatures above 400° C., inversion of the dry unstable forms is rapid.

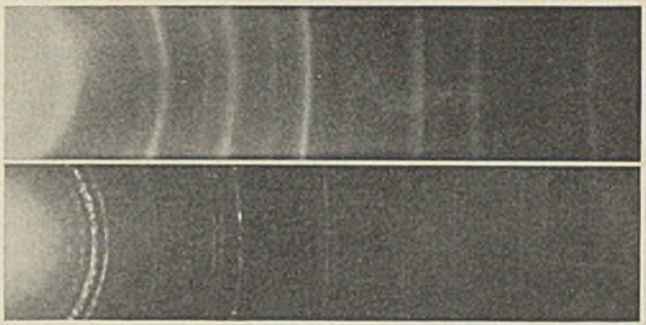


Figure 1. X-Ray Diffraction Patterns of Hydrated Aluminum Oxides

The upper pattern is a böhmite (γ-$Al_2O_3.H_2O$) floc from an oil filter using alum and caustic for coagulation at a pH value of 6.5–7.0. The lower is a bayerite (α-$Al_2O_3.3H_2O$) corrosion product from an air conditioner using aluminum cooling coils.

Aragonite is formed if precipitation is carried out at a temperature approaching the boiling point of water, or in the presence of an isomorphous carbonate such as that of lead, barium, or strontium. Johnston, Merwin, and Williamson (*21*) studied formation of the various forms of calcium carbonate by precipitation and state that their best preparation of aragonite was obtained by dropping equivalent amounts of calcium chloride and potassium carbonate solutions from burets into hot water (85–90° C.) which is being stirred.

μ-$CaCO_3$ may be obtained in the same fashion as aragonite except that the temperature is maintained at 60° instead of 90° C.; under this condition a mixture of aragonite and μ-$CaCO_3$ results. The mixture may be separated by flotation in a liquid of specific gravity 2.6, the density of μ-$CaCO_3$ being 2.54 against 2.93 for aragonite and 2.71 for calcite. At temperatures below 60° C. a mixture of μ-$CaCO_3$ and calcite results, except in the presence of sulfate ions in which case aragonite containing a small amount of sulfate is obtained.

At temperatures below 20° C. a hexahydrate of calcium carbonate may be obtained. At higher temperatures this is converted to calcite.

Hall (*14*) states that aragonite is prevalent in feed line deposits. Except in feed pump and condenser deposits of aragonite, the authors have found only calcite in calcium carbonate deposits. This does not exclude the possibility that calcium may be originally precipitated in an unstable form which then undergoes conversion to the stable calcite form. The temperature, the length of time in contact with the solution from which the deposit is forming, and the presence of calcite grains tend to make the conversion rapid and complete. The authors have attempted to check this point by examining precipitates from a hot-process softener in the initial stages of precipitation. In the samples so far examined, only calcite has been observed. In dried precipitates from cold-process softening, at temperatures as low as 1° C., calcite was the only form found. It appears that calcium carbonate formed from the reaction of hydrated lime produces calcite whereas calcium carbonate precipitated through the action of sodium hydroxide or carbonate or by the thermal decomposition of calcium bicarbonate may form aragonite.

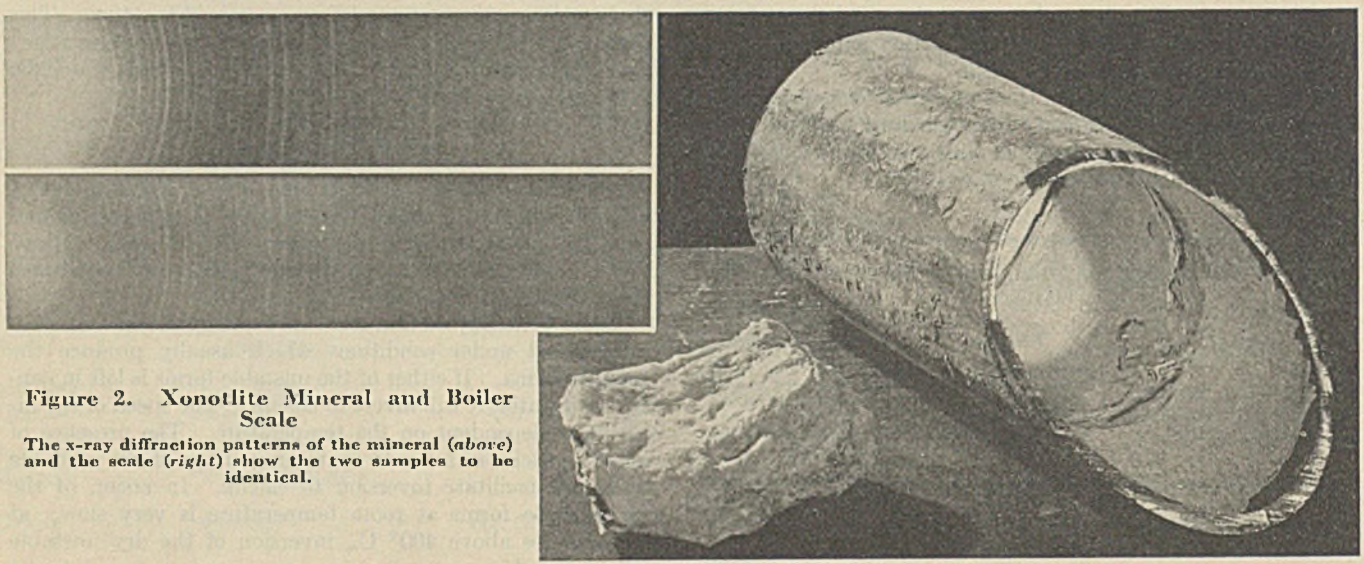


Figure 2. Xonotlite Mineral and Boiler Scale

The x-ray diffraction patterns of the mineral (*above*) and the scale (*right*) show the two samples to be identical.

CALCIUM HYDROXIDE

Calcium hydroxide was reported as a constituent of boiler scale by Clark and Gerrard (*6*). It was identified by the x-ray method. They believe that calcium hydroxide is sufficiently insoluble at boiler temperatures to crystallize in a manner similar to anhydrite. The authors found calcium hydroxide as the principal constituent of a superheater deposit. This came from a central station boiler operating at 400 pounds per square inch. The boiler was not treated with phosphate during that time.

CALCIUM PHOSPHATES

The stable form of the basic calcium phosphates is apatite. This is the normal form in which it is found in natural deposits and is the stable form toward which synthetic precipitates from water solutions tend to go. Apatites are somewhat flexible with regard to chemical composition and may vary considerably with respect to certain constituents without appreciable changes in the crystal structure or lattice constants. The general formula is $Ca_{10}X_2(PO_4)_6$ in which X may be F, Cl, OH, $^1/_2CO_3$ or $^1/_2O$. These are known as fluorapatite, chlorapatite, and hydroxyapatite according to the constituent represented by X in the general formula. Fluorapatite is the most abundant. Teeth and bones are composed mainly of hydroxyapatite and carbonatoapatite. A rather rare calcium phosphate called "phosphorite" is represented by the formula $Ca_3(PO_4)_2.H_2O$ but is a true apatite.

When physicochemical principles were first applied to equilibria in softening reactions, tricalcium phosphate was assumed to be the reaction product between soluble calcium and soluble phosphate (*16*). Water softening calculations involving phosphate requirements for precipitating calcium are still based on this assumption. It has been found, however, that the composition of a calcium phosphate precipitate will depend on the conditions of temperature and alkalinity and the manner of adding one to the other. If soluble calcium is added to soluble phosphate, the initial precipitate is high in P_2O_5 and will closely conform to the composition of tricalcium phosphate (*19*). However, if soluble phosphate is added to soluble calcium, the precipitate will be lower in P_2O_5 than tricalcium phosphate. Larson (*24*) described methods of preparing the mono-, di-, and tricalcium phosphates. The method for tricalcium phosphate requires the dripping of calcium chloride into a solution of disodium phosphate. The composition of this precipitate corresponds to the mineral phosphorite. Both phosphorite and hydroxyapatite give the characteristic apatite diffraction pattern. Differentiation between the two is made by examination of diffraction patterns of ignited samples. Samples having the composition of phosphorite change over to β-$Ca_3P_2O_8$. The authors have found β-$Ca_3P_2O_8$ to be identical with the non-apatite mineral, whitlockite (*13*). Samples corresponding to hydroxyapatite undergo no transformation upon ordinary ignition.

There has been much confusion and difference of opinion in regard to the basic calcium phosphates, mainly because the ratio of P_2O_5 to CaO is not constant for different methods of precipitation (*35*). Precipitated calcium phosphate may contain a greater percentage of P_2O_5 than is allowed by the formula $Ca_3P_2O_8$ or it may, under special conditions, contain a greater percentage of CaO than is allowed by the formula $Ca_{10}(OH)_2(PO_4)_6$ (*10*). This suggests that hydroxyapatite can form a continuous series of solid solutions with CaO and P_2O_5. X-ray studies show practically no change in the lattice dimensions of the apatite crystal within the limits of these solid solution concentrations. Hydroxyapatite is the stable form of all the basic calcium phosphates, however, for it is always the end product if the solid is permitted to come to equilibrium in an aqueous solution. Precipitates such as dicalcium and tricalcium phosphate give up phosphate ions and become more basic. Precipitates having a higher CaO percentage than the formula $Ca_{10}(OH)_2(PO_4)_6$ will lose $Ca(OH)_2$ in contact with water.

The apatites are formed in water treatment in phosphate softeners and within steam boilers when phosphates are used to prevent scale formation. An x-ray diffraction study was made by Clark and Gerrard (*5*) of a number of deposits from boilers employing phosphate treatment; they found that the hydroxyapatite pattern was obtained from a number of samples in which the P_2O_5:CaO ratios were variable. The authors have examined a number of calcium phosphates, and found both hydroxyapatite and phosphorite in boiler deposits. Both hydroxyapatite and phosphorite have appeared in hot phosphate softener sludges. In general, hydroxyapatite is found in softeners operated with little or no excess phosphate in the effluent. An excess of 5 p. p. m. PO_4 seems sufficient to form phosphorite at 212° F. All the calcium phosphates give rather weak and diffuse patterns which suggest small particle size. Hydroxyapatite has been found in boilers up to 1400 pounds per square inch, in feed lines, feed pumps, evaporators, and filters. From the hypothetical equation for the hydrolysis of phosphorite, it is evident that composition is dependent upon alkalinity and excess phosphates:

$$10Ca_3(PO_4)_2.H_2O + 6NaOH \leftrightarrows 3Ca_{10}(OH)_2(PO_4)_6 + 2Na_3PO_4 + 10H_2O$$

Sodium hydroxide favors the formation of hydroxyapatite by forcing the reaction toward the right while sodium phosphate favors the formation of phosphorite by forcing the reaction toward the left. It is, therefore, to be expected hydroxyapatite would form in a highly alkaline boiler water and phosphorite in a softener operated with an excess of phosphate and low caustic alkalinity.

CALCIUM SILICATES

Calcium silicate exists as a number of different minerals having a wide range of composition. The $CaO:SiO_2$ ratios vary from 0.5 to 2.0; many of them have been synthesized in water solution using high-pressure bombs. Table III shows the temperature ranges under which these silicates have been synthesized by Flint, McMurdie, and Wells (*11*).

Synthesis is usually accomplished by heating in water a mixture of the oxides in appropriate ratios, a precipitate of the proper composition, or a glass of the proper composition, in a bomb to the required temperature. The composition of the final product is influenced by the composition of the initial mixture, temperature, and the presence of impurities.

Table III. Temperature Ranges for Synthesis of Calcium Silicates

Mineral	Formula	$CaO:SiO_2$ Ratio	Temp., ° C. Min.	Temp., ° C. Max.
Okenite	$CaO.2SiO_2.2H_2O$	0.5	...	...
Gryolite	$2CaO.3SiO_2.2H_2O$	0.67	150	450
	$4CaO.5SiO_2.5H_2O$	0.80	150	275
Crestmoreite	$2CaO.2SiO_2.3H_2O$	1.00	...	...
Pseudowallastonite	α-$CaO.SiO_2$	1.00	450	...
Wollastonite	β-$CaO.SiO_2$	1.00	400	...
	$CaO.SiO_2.H_2O$	1.00	150	...
Xonotlite	$5CaO.5SiO_2.H_2O$	1.00	175	390
Afwillite	$3CaO.2SiO_2.3H_2O$	1.50	...	...
Foshagite	$5CaO.3SiO_2.3H_2O$	1.67	300	350
Hillebrandite	$2CaO.SiO_2.H_2O$	2.00	...	...
	$10CaO.5SiO_2.6H_2O$	2 00	100	200
	$3CaO.SiO_2.2H_2O$	3.00	200	450

From the data of Flint, McMurdie, and Wells on the preparation of a number of hydrated calcium silicates, it is apparent that xonotlite is the mineral most readily obtained when the $CaO:SiO_2$ ratio in the starting materials is 1:1, and gyrolite is most readily obtained when the ratio is between 1:1.3 and 1:2. In a boiler, however, conditions seem to be more favorable for the formation of xonotlite. This is true in spite of the fact that the soluble silica concentration is usually many times greater than that of the soluble calcium.

Clark and Bunn (*4*) identified with x-ray patterns the presence of xonotlite in boiler scales obtained at pressures of 180 to 350 pounds per square inch. It has been identified by the authors in scales from boilers varying in pressure from 250 to 450 pounds. It has occurred in boilers with a feed-water silica content as low as 3 p. p. m. It has formed from both hot-process and zeolite-softened feed water. A common factor in all instances, however, was a low phosphate content of the boiler water. Xonotlite has occurred in all locations in steam boilers. It is always slow in crystallization and is hardest when formed in tubes generating the greatest amount of steam. It also forms, however, in areas of relatively low steam generation rates. It has been found in steam drums and mud drums as continuous layers. Often on cooling a boiler, this type will come off in sheets like wallpaper. When appearing this way in tubes farthest removed

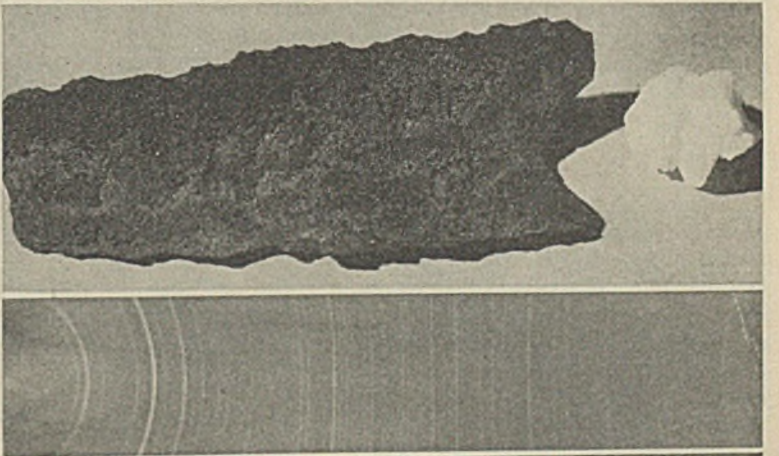


Figure 3. Analcite Boiler Scale and Mineral

In spite of the great differences in color, the x-ray diffraction patterns of the scale (*above*) and the mineral (*below*) are the same.

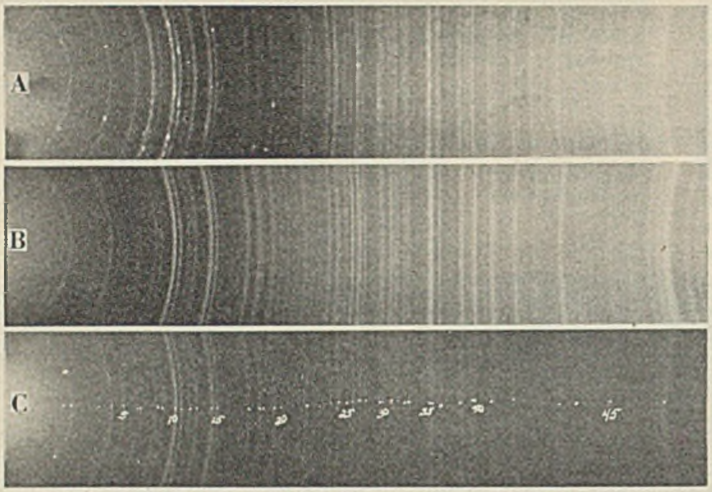


Figure 4. X-Ray Diffraction Patterns of Norwegian Acmite (*A*), Acmitic Boiler Scale (*B*), and Synthetic Acmite (*C*) Prepared in the Laboratory

from the furnace fire, it may curl up and break away from the tubes in small flakes.

A xonotlite scale in a boiler tube is shown in Figure 2. The hardness and brittleness of the scale are indicated by the manner in which it broke away when the tube section was sawed. The mineral xonotlite is also very hard and ranks close to quartz in this respect.

Another calcium silicate in which the CaO:SiO$_2$ ratio is 1:1 is wollastonite. In nature it occurs mainly as a product of contact metamorphism. Xonotlite scale when ignited at 950° C. will invert to wollastonite, and upon ignition at 1200° C. will again invert to a still higher temperature form known as pseudowollastonite.

Reinhard, Brandenberger, and Oesterheld (*31*) found wollastonite in a boiler scale along with xonotlite. However, this scale was taken from a boiler which had exploded, and it is not clear whether the scale had originally deposited as xonotlite and inverted to wollastonite after the explosion or whether the primary crystallization was wollastonite.

Pectolite ($Na_2O.4CaO.6SiO_2.H_2O$), a sodium calcium silicate, was reported by Clark and Bunn (*4*) in a scale from a boiler operating at 180 pounds per square inch. They also synthesized this mineral by heating a mixture of silica and calcium oxide with sodium hydroxide at 180° C.

CALCIUM SULFATES

Calcium sulfate mineral deposits are usually the result of precipitation from the concentration of sea water. Gypsum ($CaSO_4.2H_2O$) and anhydrite ($CaSO_4$) are the stable forms. Gypsum mineral may be formed as an alteration product of anhydrite when underground water comes into contact with a bed of anhydrite, or it may precipitate as gypsum when the temperature is below 42° C. (*18*). An intermediate form called "hemihydrate" ($CaSO_4.{}^1/_2H_2O$) may be prepared synthetically. Partridge (*28*) reported it in scale from an experimental boiler, although it is rarely found in industrial boiler deposits.

Since the stable form of calcium sulfate above 42° C. is anhydrite, this is the form found in boiler scale. It has been observed in boilers operating at steam pressures as high as 650 pounds per square inch. Since it is one of the more soluble of the common scale-forming salts, the boiler water must contain a measurable amount of soluble calcium for its formation. It always forms in the areas of highest steam generation and is characterized by a needle-like appearance.

Gypsum was found by the authors as the main constituent of an evaporator scale.

SODIUM ALUMINUM SILICATES

Among the complex silicates formed in boiler scales are those of the zeolite type. The corresponding natural minerals are classified as secondary minerals in that they have been formed in nature by alteration from some other mineral. The alteration is caused by the action of hot circulating waters carrying relatively large amounts of soluble silica. They occur chiefly in cavities of igneous and volcanic rocks.

The complex sodium aluminum silicates thus far identified in boiler scales are analcite ($Na_2O.Al_2O_3.4SiO_2.2H_2O$) (*29*), natrolite ($Na_2O.Al_2O_3.3SiO_2.2H_2O$), and noselite ($4Na_2O.3Al_2O_3.6SiO_2.SO_4$). The first two are easily synthesized; however, there are few references on the hydrothermal synthesis of noselite.

Analcite has been synthesized at temperatures as low as 100° C. (*22*) and as high as 395° C. (*27*). The tendency at the higher temperatures is to go over into an anhydrous mineral called "nepheline". Straub (*33*) studied the apparent solubility of analcite between 182° and 282° C. in various concentrations of sodium hydroxide. The analcite was previously synthesized from sodium silicate and sodium aluminate at 282° C.

Natrolite has been synthesized at temperatures as low as 90° C. (*9*) and as high as 510° C. (*12*). Doelter (*9*) found that concentrated solutions having the theoretical composition of natrolite crystallized to natrolite at 90° but at 190° analcite was formed. This indicates that there is a close relation between analcite and natrolite, and conditions for their formation may be similar.

Analcite has been observed most frequently in boilers operating between 400 and 900 pounds per square inch. Conditions necessary for its formation are the presence of

Table IV. Patterns of Acmite

Natural Acmite (*1*)		Synthetic Acmite		Acmitic Scale	
d	*I*	*d*	*I*	*d*	*I*
6.54	4	6.46	6	6.52	6
4.50	4	4.44	6	4.46	6
4.05	1	4.06	6	...	..
3.68	1	3.69	2	...	..
3.01	10	3.00	10	3.01	10
2.92	7	2.90	8	2.93	8
...	..	2.70	6	2.73	1
2.55	10	2.54	8	2.55	8
2.48	6	2.47	6	2.49	6
2.29	1	...	..	...	..
2.21	4	2.20	4	2.21	3
2.12	4	2.12	2	2.13	2
2.03	4	2.02	4	2.04	2
1.942	1	1.950	2	1.941	1
1.900	1	...	..	...	..
1.820	1	...	..	1.810	1
1.729	3	1.727	2	1.734	2
...	..	1.693	4	1.693	1
...	..	1.658	2	1.662	1
...	..	1.634	4	1.637	2
...	..	1.609	4	1.615	3
...	..	1.586	2	1.594	2
1.562	4	...	..	...	..
...	..	1.539	2	1.537	1
1.521	4	1.529	1	1.531	1
1.497	4	1.503	2	1.503	1
...	..	1.485	2	1.485	1
1.468	1	1.463	2	1.467	1
...	..	1.398	4	1.399	6
1.385	4	1.371	4	1.376	1
1.327	2	1.327	2	1.328	2
1.294	2	1.296	2	1.300	2
1.261	2	1.264	2	1.268	1
1.227	2	1.227	2	1.228	1
1.194	1	...	..	...	..
1.154	1	1.160	2	1.160	1
1.136	1	1.139	1	...	..
1.062	2	...	..	1.067	1
...	..	1.052	4	1.053	2
1.030	1	...	..	...	..

soluble silica and soluble alumina in the boiler feed water. The concentration of alumina seems to be more critical than that for silica, for analcite has been formed from feed water containing as little as 0.3 p. p. m. of aluminum.

Analcite has a hardness of 5 and often may be obtained in large pieces after a boiler in which it has been formed is cleaned. Such a piece is shown in Figure 3 along with the pure mineral. Iron oxide and organic matter have imparted a dark color to the scale.

The report of the identification of natrolite (*30*) and noselite in scale does not give any conditions of formation, but they were probably similar to those for analcite formation, especially the presence of soluble alumina.

Cancrinite ($4Na_2O.CaO.4Al_2O_3.2CO_2.9SiO_2.3H_2O$) is another complex sodium aluminum silicate containing calcium and carbon dioxide. It has been observed in a superheater deposit which formed from the reaction of boiler water salts which had been entrained in the steam.

ACMITE

The authors have found a new complex silicate not previously reported but observed in deposits from boilers operating between 400 to 1200 pounds per square inch. The x-ray pattern of this silicate is identical with that of acmite ($Na_2O.Fe_2O_3.4SiO_2$). Figure 4 compares the x-ray diffraction patterns of three forms of acmite. The mineral contains some hematite as an impurity and accounts for the extra lines not common to all three patterns.

It has been found in rope scale, in boiler tubes in which proper water circulation was highly questionable, in superheater deposits, and in turbine blade deposits. It can be prepared (*36*) easily in nonaqueous conditions by fusing an intimate mixture of the proper molecular amounts of precipitated silica, ferric oxide, and sodium carbonate monohydrate with twice as much sodium chloride. Both the mode of occurrence in scales and the method of synthesis suggest that high temperature and dryness are necessary for its formation in boiler scale. It is likely to be formed from a boiler water having soluble silica and sodium hydroxide if some of the steaming tubes are sufficiently "steam-bound" to allow the formation of magnetic oxide. The exact mechanism of formation is not entirely understood, but it seems that the iron oxide in acmite formed in boilers can have its source in magnetic oxide.

Acmite scale exists as a hard, dense, compact deposit due to the fusion conditions present during its formation. This is demonstrated in the photographs of sectioned boiler tubes in Figure 5.

Table IV compares patterns of natural acmite, synthetic acmite, and acmitic scale. The *d* values represent the interplanar spacings calculated from x-ray lines. The term *I* designates the estimated intensity of the x-ray lines on a scale where 10 represents the intensity of the strongest line. Synthetic acmite was made by the method of Washington and Merwin (*36*); ferric oxide, silica, and $Na_2CO_3.H_2O$ are taken in the proper molecular amounts and fused in sodium chloride. The sodium chloride was leached out of the fusion product with hot distilled water before a diffraction pattern was made. The scale sample was taken from a central boiler operating at 1400 pounds per square inch with evaporator make-up.

COPPER COMPOUNDS

Copper minerals found in scales include cuprite (Cu_2O), tenorite (CuO), chalcocite (Cu_2S), and metallic copper (Cu). Copper is usually present in boiler sludges and scales in the metallic form. Powell (*29*) observed it microscopically as dendrites in boiler sludges. It is found frequently in central station boilers where the feed water is largely condensate returns which have had intimate contact with a large amount of metallic copper as in copper condenser tubes. Metallic copper has also been found as the principal constituent in a deposit from the steam trap of a coil using high-pressure steam for process purposes.

Cuprite and tenorite are found mainly in corrosion deposits, the former in weakly oxidizing environments such as in preheaters and the latter under more strongly oxidizing conditions as in ejector traps. Figure 6 shows the x-ray diffraction patterns of two such examples.

Chalcocite was found in several corrosion deposits from low-pressure steam turbine blades. The steam contained no superheat and variable amounts of hydrogen sulfide up to 2 p. p. m. The pH value averaged around 5.0.

IRON OXIDES

As a result of the use of iron and steel for powerhouse equipment, some iron, primarily in the form of oxides, occurs in all deposits. The amounts of iron observed may range from a few per cent up to practically pure iron oxides, the

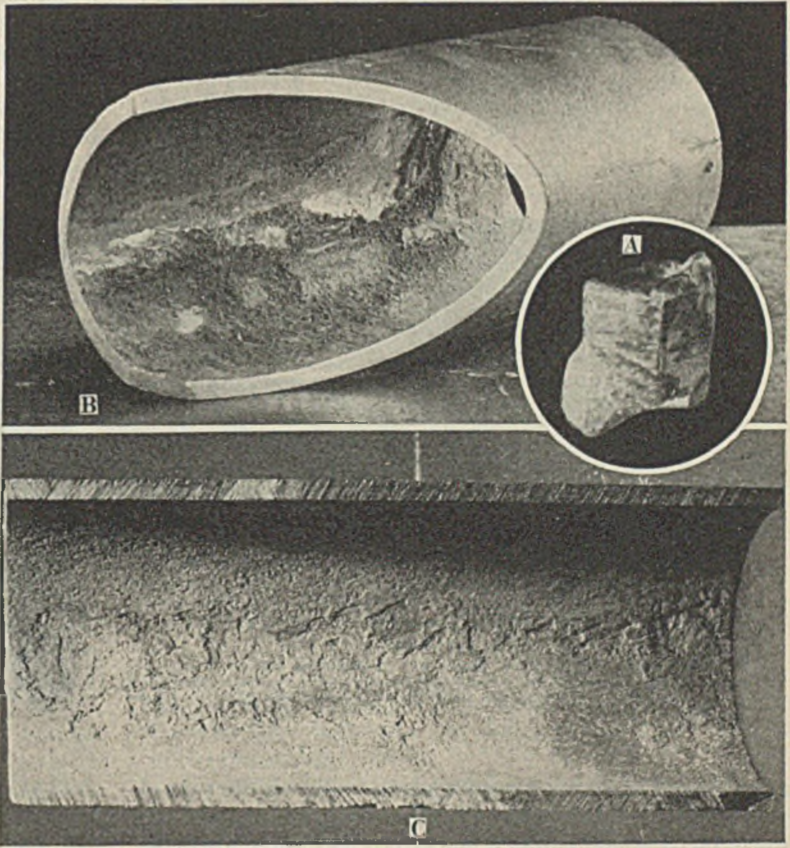


Figure 5. Monoclinic Crystal of Acmite Mineral from Eker, Norway (*A*); Acmite as a Constituent of "Rope" Scale (*B*); Dense Adherent Scale (*C*), Much Less Thick and Relatively Pure

latter being primarily corrosion deposits. The various iron oxides are indicated in the following table; the mineralogical name is given for those occurring naturally (*7*):

Name	Formula	Name	Formula
Hematite	α-Fe_2O_3	Lepidocrocite	γ-$Fe_2O_3.H_2O$
	γ-Fe_2O_3		FeO
Goethite	α-$Fe_2O_3.H_2O$		$Fe(OH)_2$
	β-$Fe_2O_3.H_2O$	Magnetite	Fe_3O_4

Magnetite is the commonest iron oxide encountered in feed water treatment. It has been identified as the end product of corrosion between iron and pure water in the absence of oxygen (*8*). This holds true for steam also below 570° C. Above this temperature ferrous oxide may be formed, provided there is a highly reducing atmosphere present.

The presence of magnetic iron oxide in superheater tube deposits usually indicates overheating of the metal to the temperature at which the steam-iron reaction occurs. Ferrous oxide is also occasionally found in such deposits and indicates that a temperature of at least 570° C. has been reached for ferrous oxide is metastable below 570°.

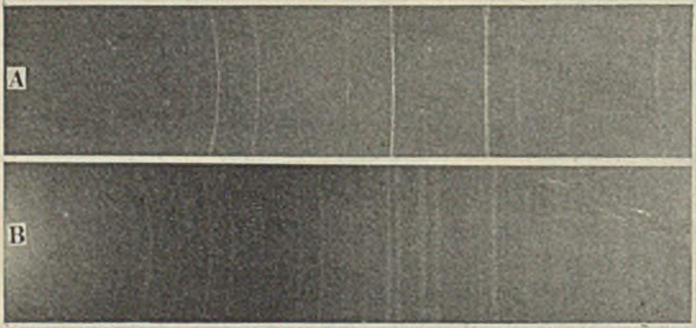
Hematite is the ordinary form of iron oxide in the complete stage of oxidation and may be found in deposits formed at room temperatures or in boilers operating at pressures as great as 1200 pounds per square inch.

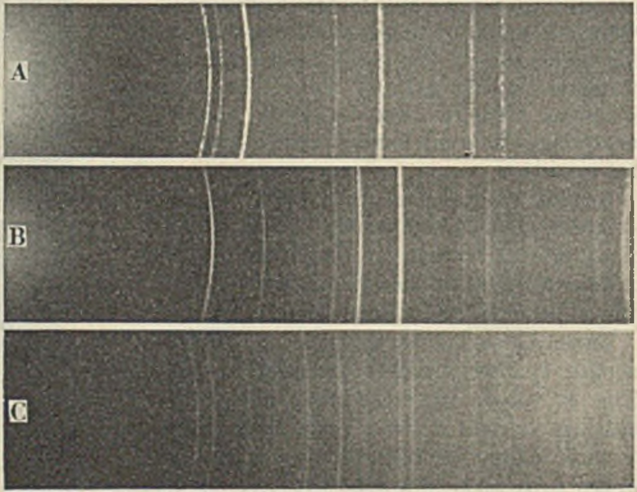
X-ray diffraction patterns for the three iron oxides appear in Figure 7.

MAGNESIUM COMPOUNDS

Insoluble magnesium compounds formed in the treatment of water include brucite [$Mg(OH)_2$], serpentine ($3MgO.2SiO_2.2H_2O$), and forsterite ($2MgO.SiO_2$). Most of them give rather weak diffraction patterns due to the low atomic weight of the magnesium atom.

Brucite is found in nature associated with other magnesium minerals as a decomposition product of magnesium silicates, especially serpentine. It may be readily obtained synthetically by the slow addition of alkali to a soluble magnesium salt. Brucite was previously reported in boiler scale and sludges (*2*, *15*, *29*). The authors have found it in a wide range of particle sizes, depending principally on the rate of precipitation. Particle size is smallest in hot process sludges, where precipitation is rapid, and largest in locations such as feed lines and feed troughs where precipitation is slow. Some feed trough deposits have been found to contain crystals of brucite large enough to be seen by the naked eye.





↑ **Figure 6. X-Ray Diffraction Patterns for Copper Oxide**

Cuprite (Cu_2O) corrosion deposit from a preheater (*A*) and tenorite (CuO) corrosion deposit from an ejector trap (*B*)

Figure 7. X-Ray Diffraction Patterns of Iron Oxide Formations

Ferrous oxide (FeO) scale from an overheated boiler tube (*A*), magnetite (Fe_3O_4) deposit from a superheater (*B*), and hematite (Fe_2O_3) sample from a cold water line (*C*) →

Serpentine is formed in nature by the reaction of steam and water on some other magnesium silicate mineral. In water treatment it forms slowly, and the mechanism of formation seems to be first by the formation of brucite followed by adsorption of silica and consequent recrystallization to serpentine. Figure 8 compares the patterns of serpentine mineral and a boiler scale containing serpentine.

Brines (*2*) had reported the presence of a serpentine in five scale samples. The authors have observed serpentine in a number of samples of deposits in boilers operating at pressures up to 900 pounds per square inch. It has been found with calcite and hydroxyapatite. A number of patterns from other scales known to contain appreciable amounts of silica and magnesium indicate the presence of an altered serpentine. Further study is required to identify this group completely.

A magnesium orthosilicate identical with the mineral forsterite was found as the principal constituent of a deposit from a domestic hot water heater. The service water was from city mains and had previously been submitted to lime softening.

NICKEL OXIDE

Nickelous oxide occurs rarely as the mineral bunsenite (NiO). It can be produced artifically by the oxidation of metallic nickel. It has been identified as one of the corrosion products in a high-pressure Monel turbine blade deposit. In this instance steam purity was very high in that soluble solids were very low. Traces of ammonia were found, however.

SILICA

Silica occurs in nature in three crystalline forms—quartz, tridymite, and cristobalite. It also appears in amorphous form as opal. The three crystalline forms are anhydrous, but opal contains an indefinite quantity of water. Quartz is by far the most common form and, next to the feldspars, is the most abundant mineral in the crust of the earth. Tridymite and cristobalite are rare except in siliceous volcanic rock.

An examination of the stable phases of silica shows that quartz is the stable phase at room temperature. The high-temperature form is cristobalite. The inversion temperatures may be represented as follows (*32*):

$$\alpha\text{-quartz} \xleftrightarrow{573^\circ\text{ C.}} \beta\text{-quartz} \xrightarrow{870^\circ\text{ C.}} \alpha\text{-tridymite} \xrightarrow{1470^\circ\text{ C.,}} \alpha\text{-cristobalite}$$

These inversions are very sluggish, however, and cristobalite may exist below 1470° C. for long periods even though it is metastable.

Quartz has been synthesized from amorphous silica at temperatures between 100° (*26*) and 650° C. (*37*) in aqueous solutions. Small traces of alkali were needed to serve as mineralizer. Morey and Fenner (*26*) produced quartz in the range between 200° and 600° C. while studying the system H_2O–K_2SiO_3–SiO_2 from 200° to 1000° C. Numerous other investigators have accidentally synthesized quartz when attempting to synthesize some other silicate, and invariably small amounts of alkali have served as the mineralizer (*11*, *23*).

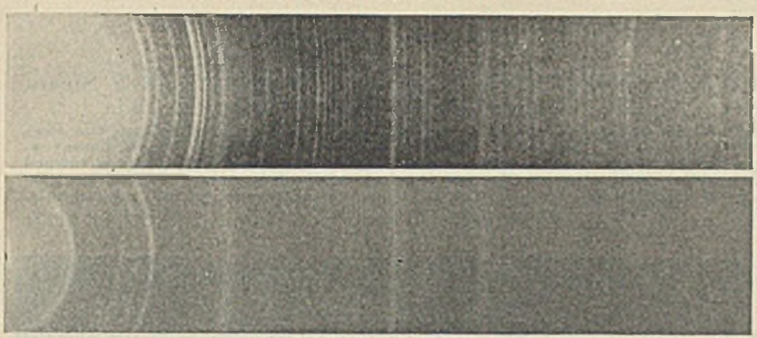


Figure 8. X-Ray Diffraction Pattern of a Boiler Scale Containing Serpentine

Serpentine associated with hydroxyapatite in a high-pressure boiler gives the upper pattern; the serpentine lines may be recognized by comparison with the lower pattern for serpentine mineral.

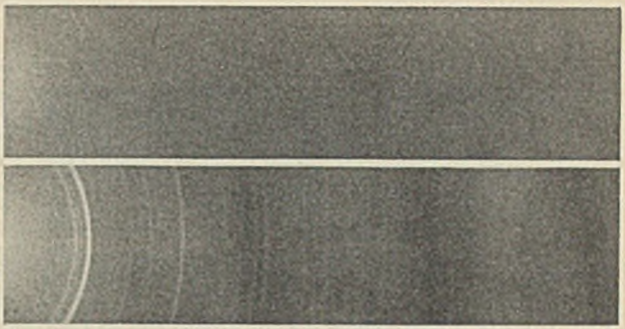


Figure 9. X-Ray Diffraction Pattern of a Turbine Blade Deposit of Amorphous Silica

The upper pattern indicates absence of crystalline compounds; the lower cristobalite pattern, after ignition of same sample, shows that the original composition was largely amorphous silica.

Tridymite and cristobalite have been synthesized in the same manner as quartz, but higher temperatures are necessary. Higher alkali concentrations favor the production of quartz. It would be expected, therefore, that wherever crystalline silica would be encountered in water treatment, quartz would be the most likely form, for temperatures as high as the quartz-tridymite inversion point are not reached.

The authors have found quartz in both boiler scales and turbine blade deposits. An x-ray study of a boiler scale showed that only the portion of the scale adjacent to the tube contained quartz. The remainder was mainly hydroxyapatite. This particular quartz formation probably resulted from an alteration of a previously deposited calcium silicate scale.

Amorphous silica has been found in boiler scales in rather indirect ways. A number of patterns have been taken of scale and sludge samples which are rather high in silica, yet evidence of crystalline silica is entirely lacking in the diffraction pattern. Chemical analysis shows that silica was present in high enough percentages to have given strong lines in the pattern if it had existed in the crystalline state. This type of evidence is used reservedly for the presence of amorphous silica. It is probable that in these cases the silica has been adsorbed on other scale constituents and exists homogeneously throughout the scale instead of in clumps or amorphous aggregates.

An indirect identification of amorphous silica in a turbine blade deposit is shown in Figure 9. The upper x-ray pattern is that of a turbine blade deposit as removed from the turbine; there are practically no diffraction lines. The lower pattern is one of the same sample after ignition at 950° C. for one hour. The latter is a strong pattern of cristobalite. Ignition caused the amorphous silica to crystallize.

The most perfectly crystallized quartz is to be found on high-pressure steam turbine blades. Intensity of pattern does not seem to bear a relation to hardness or compactness, for strong patterns have been obtained from soft, easily ground samples as well as from hard, dense samples.

Quartz is often found in the last stages of back-pressure steam turbines. Figure 10 shows patterns from a badly fouled turbine in which the last two stages are plugged with pure quartz. The rows ahead of these stages, also colored white, are coated with halite (NaCl). The sequence halite-quartz is quite universal, with the halite depositing in the zones of higher temperature.

SODIUM SALTS

In spite of the fact that sodium salts are highly soluble in water, they are found as solid deposits under special conditions. For these salts to come out of solution requires extremely high concentration by evaporation or even evaporation to dryness. These conditions may obtain in superheaters, in boilers of faulty water circulation, and within steam turbines.

Halite occurs naturally as deposits formed through the evaporation of saline solutions. In feed-water treatment, salt is found mainly in steam turbine deposits in the higher temperature stages. It is found in greatest percentages in the range between 450° and 300° C.

Thenardite (Na_2SO_4), anhydrous sodium sulfate, is found in saline residues and is one of the constituents of evaporated sea water. There are five different forms (*24*) of anhydrous sodium sulfate; they may all be formed by heat treatment of thenardite, the low-temperature type. The inversion proceeds as follows:

$$\underset{\substack{\text{orthorhombic}\\ \text{thenardite}}}{Na_2SO_4(V)} \xrightarrow{160\text{–}180^\circ\text{ C.}} \underset{\text{monoclinic}}{Na_2SO_4(IV)} \xrightarrow{185^\circ\text{ C.}}$$

$$Na_2SO_4(III) \xrightarrow{241^\circ\text{ C.}} \underset{\substack{\text{hexagonal}\\ m\text{-thenardite}}}{Na_2SO_4(I)} \underset{\longrightarrow}{\xleftarrow{236^\circ\text{ C.}}} Na_2SO_4(II)$$

$Na_2SO_4(V)$ and $Na_2SO_4(III)$ are stable at room temperatures; the others are unstable. On cooling they will revert to one of the two stable forms.

Thenardite has been identified by the authors as the main constituent in a boiler scale formed at 900 pounds per square inch. The location was in a main steam-generating tube, but water circulation was faulty and boiler water concentrations reached a very high value. The scale was quite hard and its rate of solution in water extremely slow. Chemical analysis, however, indicated a sodium sulfate content of over 85 per cent. An x-ray diffraction pattern of the sample in Figure 11 showed the crystalline species to be thenardite, the low-temperature form of sodium sulfate.

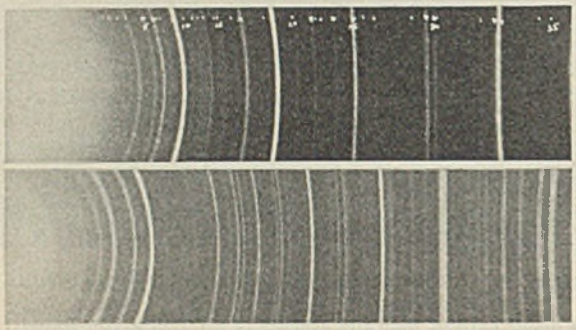


Figure 10. X-Ray Patterns of Blade Deposits from a Steam Turbine (Shown on Page 873)
←

The turbine was taken out of service to remove blade deposits from the low-pressure half of the machine. Although there is no noticeable line of demarcation, the last two rows of blading are coated with α-quartz (SiO_2) and those toward the middle, with halite (NaCl); loss in capacity was 30 per cent. Diffraction patterns of middle and rear deposits are those of halite and quartz, respectively.

↓Figure 11. X-Ray Diffraction Pattern of Thenardite Boiler Scale

In addition to thenardite deposits, the authors have examined a number of superheater and turbine blade deposits containing sodium sulfate in other forms. One form is burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$). It has been found in superheaters of boilers operating at 150 pounds per square inch and in blade deposits of turbines operating at 400 pounds. A number of blade deposits containing sodium silicate and sodium sulfate give patterns which are not yet identified, but there is a suggestion that a series of compounds may be formed from these two salts.

ALKALINE SALTS

A number of alkaline turbine blade deposits have been examined by x-ray diffraction patterns, and in many cases identification has been incomplete. Chemical analysis would indicate sodium hydroxide carbonate, and silicate. The complex patterns in these instances were probably due to solid solutions, hydrates, or double salts for which standards and x-ray data were not available.

SUMMARY

The first step in the solution of any problem is to define the different elements of the problem. The more completely this can be done, the greater are the chances of a successful solution. By using the x-ray diffraction and microscopic methods of identification to supplement chemical analyses, the problems involving crystalline precipitates or deposits in water treatment are greatly clarified. It is often not enough to determine what compounds are present, but the crystal and mineral forms should be known in order to understand the chemical and physical properties of the deposit. The discussion reviews the crystalline species which have been found in water treatment and steam production, to give some conditions of formation in nature and in laboratory synthesis and conditions of formation in water treatment.

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Deterioration of Lubricating Oils

SOYBEAN LECITHIN AS AN INHIBITOR

With the advent of modern high-compression engines, the natural stability of mineral lubricating oil has not been enough to withstand the severe operating conditions. The necessity for using additives to impart the required stability has caused the development of addition agents. Since many of these synthetics contain critical materials, the possibility of using a natural product was investigated. Commercial soybean lecithin is an oil-soluble material containing phosphorus and nitrogen, two elements claimed to have desirable properties in additives. The optimum concentration of this cheap, readily available material was determined by the Sohio oxidation test. A comparison with other commercial additives and the effectiveness of the lecithin in different base stocks and oils of different viscosities was made. Some observations of the effect of method of refining on the stability of oils were noted.

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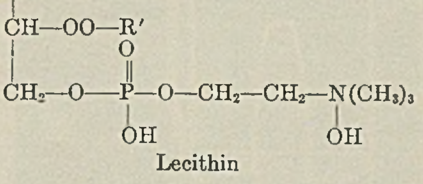
LUBRICATING oils must do more than lubricate modern engines. They must also seal piston rings, carry away carbon and soot, and cool the engine. To fulfill these requirements, oils must have a property for which there is no standard laboratory test—stability in use. The major reason that vegetable oils were discarded as industrial lubricants was that they broke down in use and produced gums, sludge, and corrosive acids. For many years mineral oils served satisfactorily because of their resistance to breakdown. However, the low clearances, high bearing loads, and excessive temperature of modern high-compression engines have increased the tendency to break down, particularly in high-speed Diesels where piston temperatures are especially high.

The breakdown is due primarily to oxidation (*6*) and, secondarily, to cracking and polymerization. The products of the deterioration are deposited in the piston grooves (*14*), where they bake to hard lacquerlike cement which may even freeze the rings and cause scoring of the cylinder walls.

Furthermore, bearing corrosion is increased greatly (*15*) when the oil is badly oxidized to give corrosive acids. The formation of these acids has been a strong deterrent in the utilization of the new high-strength alloy bearings, such as copper-lead or cadmium-silver, even in automobiles where the duty is relatively mild. Many other effects have been attributed to degradation of the oil, such as piston skirt varnish, undercrown deposits, increased engine wear, and power loss due to the increased viscosity of the oil.

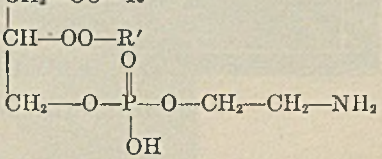
While it is possible to increase the stability of lubricating oils considerably by careful selection of base stocks and application of modern refining methods, there is a limit to the benefits which can be so derived. The petroleum industry has thus turned more and more to the use of additives to impart certain additional properties to lubricating oils. It is sometimes possible to obtain certain properties more cheaply by the use of additives than by refining, even when they may be so obtained. Many hundreds of patents have been granted on the use of different additives, including (*a*) various types of phenols, (*b*) sulfur-bearing compounds, (*c*) phosphorus compounds, and (*d*) amines (*4*). The antioxidant properties of lecithin phosphatides were shown by Olcott and Matill (*12*); recently a patent was issued to Hall and Towne (*8*) claiming the use of lecithin as an inhibitor. It has also been used to prevent cloud and storage tank corrosion in gasoline (*13*).

Until recently lecithin, the pure phosphatide from which the commercial product gets its name, was obtained from egg yolk and brain substance, and was a laboratory curiosity. However, methods for recovering it from soybean oil have made it a cheap article of commerce. It is widely used in the food and edible fat field (*5*). The commercial preparation is obtained by blowing steam into solvent-extracted soybean oil. The phosphatide materials hydrate and are removed by centrifuging. The wet mass is then dried under vacuum to produce the crude mixture known under the trade name "Gliddol" and containing approximately 30 per cent lecithin, 40 per cent cephalin (an alcohol-insoluble phosphatide), and 30 per cent of adhering soybean oil which tends to stabilize the product against aging. The formulas for lecithin and cephalin are:



$$\begin{array}{l} \mathrm{CH_2{-}OO{-}R} \\ | \\ \mathrm{CH{-}OO{-}R'} \\ |\qquad\qquad \mathrm{O} \\ |\qquad\qquad \| \\ \mathrm{CH_2{-}O{-}P{-}O{-}CH_2{-}CH_2{-}N(CH_3)_3} \\ \qquad\qquad | \qquad\qquad\qquad\qquad | \\ \qquad\quad \mathrm{OH} \qquad\qquad\qquad\quad \mathrm{OH} \end{array}$$

Lecithin



$$\begin{array}{l} \mathrm{CH_2{-}OO{-}R} \\ | \\ \mathrm{CH{-}OO{-}R'} \\ |\qquad\qquad \mathrm{O} \\ |\qquad\qquad \| \\ \mathrm{CH_2{-}O{-}P{-}O{-}CH_2{-}CH_2{-}NH_2} \\ \qquad\qquad | \\ \qquad\quad \mathrm{OH} \end{array}$$

Cephalin

where R and R′ are fatty acids such as oleic, stearic, palmitic, etc.

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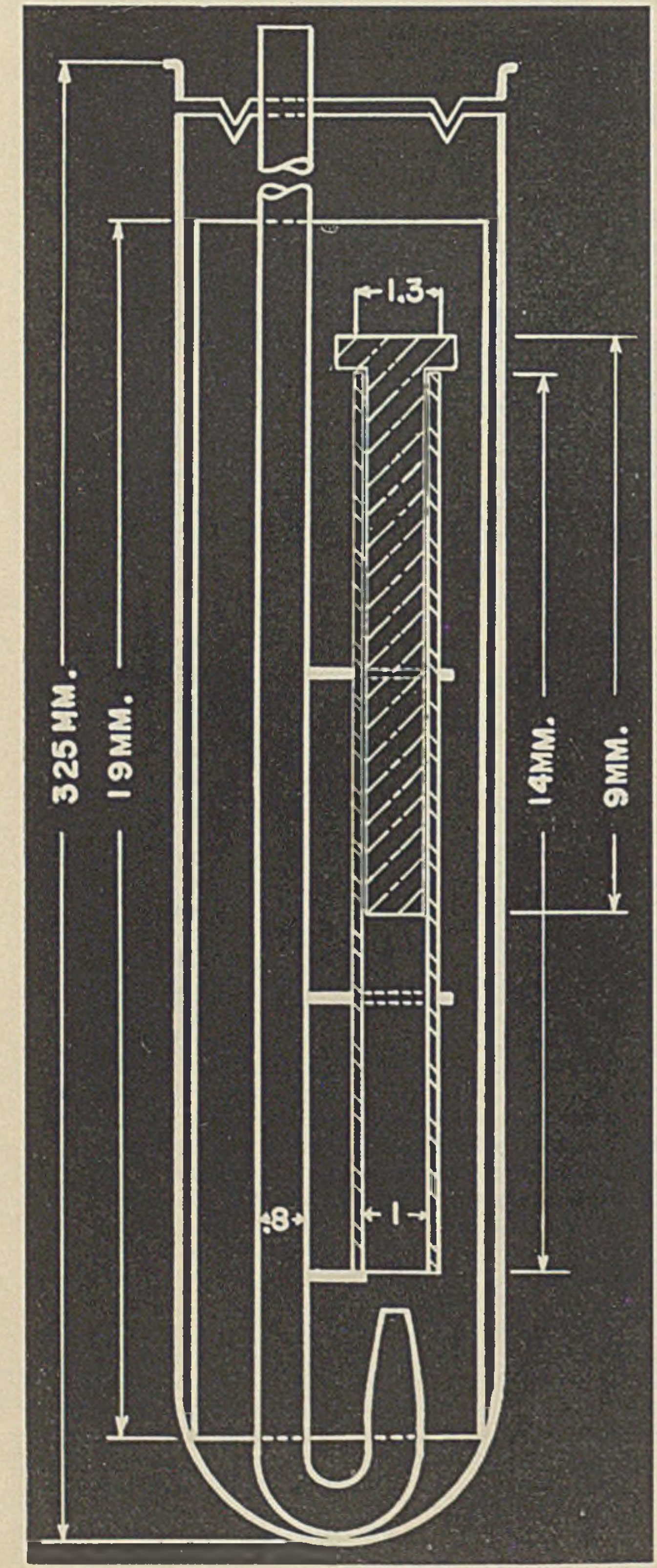

Figure 1. Oxidation Cell

Since the phosphatides contain phosphorus and nitrogen in oil-soluble form, it appeared that the possibilities for a lube oil additive should be investigated.

EFFECT OF GLIDDOL ON INSPECTION TESTS

The usual inspection tests give, in most cases, little indication as to the behavior of oils in use; but they are used to specify lubricating oils. An additive might be an excellent antioxidant and still affect the inspection tests adversely so that the oil would be rejected. Accordingly, samples of a highly refined Pennsylvania oil of high viscosity index and containing 0.05, 0.1, 0.2, 0.5, and 1.0 per cent of Gliddol R were prepared and tests were run on them. The data in Table I indicate that there is little effect on the inspection tests of oils as determined by Standard A. S. T. M. practice except for the slight increase in neutralization number and naphtha insolubles (as a result of the insolubility of traces of Gliddol R). The small increase in neutralization number may be attributed to hydrolysis of the phosphatides under the conditions of test.

VISCOSITY INDEX IMPROVEMENT

A mid-continent solvent-refined oil with a viscosity index of 82 was treated with 0.5, 1.0, and 2.0 per cent Gliddol R and tested in a kinematic viscometer. The values were checked in the laboratory of an independent oil company, and the improvement is shown in Table II.

LABORATORY OXIDATION TESTS

A standard laboratory method for determining oil deterioration is not available (*3*). The following factors affect the choice of a method: (*a*) The test must be simple; (*b*) it must give reproducible results (i. e., the variables which are not easily controlled must be kept to a minimum); (*c*) probably most important, the test must simulate as closely as possible oil deterioration under actual service conditions in an engine. It should, therefore, include those factors which had previously been shown to affect oil breakdown in an engine—for example, the presence of a metal catalyst. Lamb, Loane, and Gaynor (*9*) showed that the use of a sulfurized additive, which had been shown to be a good additive on the basis of engine tests, gave contrary results in the Indiana oxidation test. This has been attributed to the effect of sulfurized additive as a catalyst poison and a lack of catalyst in the laboratory test.

Taking these factors into account, it was decided to use the Sohio test (*2*), an improvement over the Indiana test. The breakdown of the oil is catalyzed by a steel sleeve and a copper strip immersed in the oil. Air is admitted through a specially designed jet below a narrow steel tube, in which the copper strip is hung. The position of this jet is such that an air lift pumping action takes place. This test seems to have all of the elements necessary for correlation with engine tests. It contains catalysts in the same approximate ratio of metal surface to oil as exists in an automobile engine. There is a violent scrubbing action of changing oil against metal. The contacting of oil and air to allow oxidation is excellent; and, owing to the long passage of oil and air through the air lift tube, there is the necessary good contacting of volatile oxidation products with the metal surfaces (*2*). On the other hand, the oil is well ventilated and the artificial condition of condensing volatile products and returning them to the oil is avoided. The design of the oxidation cell is shown in Figure 1, and a photograph of six cells mounted in an oil bath, in Figure 2.

After considerable variation in test conditions, the procedure which follows was standardized.

Table I. Inspection Tests on Pennsylvania S. A. E. 30 Lube Oil Containing Various Percentages of Gliddol

Gliddol R Concn., %	0.0	0.05	0.1	0.2	0.5	1.0
Gravity, ° A. P. I.	28.3	28.3	28.3	28.3	28.3	28.2
Viscosity, Saybolt Universal sec.						
100° F.	547.9	....	547.0	547.0	547.0	548.9
210° F.	67.8	....	67.8	67.8	67.9	68.0
Viscosity index	103.0	....	103.1	103.1	103.5	103.7
Flash point[a], ° F.	440.0	440.0	440.0	440.0	445.0	445.0
Fire point[a], ° F.	500.0	500.0	500.0	500.0	500.0	500.0
Neutralization No.	0.05	0.04	0.06	0.07	0.09	0.13
Naphtha insol., mg./10 g. oil	1.8	1.5	2.3	2.5	2.7	4.7
Pour point, ° F.	0	0	0	0	0	−5
Carbon residue (Conradson)	0.52	0.57	0.50	0.52	0.52	0.57

[a] Cleveland open cup.

Table II. Inspection Tests on Mid-continent Solvent-Refined Oil Containing Gliddol

Gliddol R Concn., %	0	0.5	1.0	2.0
Kinematic viscosity				
100° F.	114.6	114.6	114.4	115.0
210° F.	10.78	10.82	10.9	11.01
Viscosity, Saybolt Universal sec.				
100° F.	530.0	529.0	528.0	531.0
210° F.	62.0	62.1	62.4	62.8
Viscosity index	82.0	83.0	85.0	86.0

The two steel tubes were polished to a high luster on a lathe with No. 0 emery cloth. Considerable care was taken to remove small amounts of impurities from previous runs which might influence the rate of oxidation. The copper strip was washed and then polished thoroughly with emery cloth. The glassware was cleaned with hot cleaning solution before each run. The oxidation cell was then assembled, the oil sample placed in the cell, and the whole assembly hung in the oil bath which had previously been brought to the right temperature. The air lines were connected and the air rate was adjusted. Time was measured from this point. Summarizing, the general conditions of the test were: 325° F., 50–84 hours, air flow rate of 30–125 liters per hour, 300 sq. cm. steel area, 20 sq. cm. copper area, and 250 cc. oil volume.

At the end of the test the air lines were disconnected, and the units were immediately removed. The bubbler assembly and the large steel tube were removed; and the hot oil was allowed to drain off. After cooling, they were wiped with a soft cloth and the copper strips were put into a bottle containing chloroform. The hot oils were poured into sample bottles, care being taken to remove all adhering solids from the test tubes.

EXTENT OF OIL DETERIORATION

In the oxidation of lubricants, the reaction mechanisms are so complex and the products formed are so varied that chemical analysis is of little value. Consequently, the only method for measuring the breakdown is by determining the change in certain over-all physical properties rather than in any single chemical compound. The action of an oil in the engine is directly attributable to the following physical values which were therefore measured both on the original and the oxidized oils:

Gravity was measured directly as A. P. I. degrees. This test is not so significant in laboratory oxidations as it is in engine tests where it is an indication of crankcase dilution. No dilution is obtained in the laboratory test.

Viscosity was measured in a Fenske viscometer. In the case of oxidized oils, the samples generally contained oil-insoluble materials which tended to clog the capillary. Consequently, the oxidized samples were first filtered through 100-mesh and then 200-mesh stainless steel screens on a Büchner funnel. An attempt was made to filter the viscous oxidized oils through a thick asbestos mat. In those cases anomalous results were obtained, probably due to the adsorption of the resinous oil-soluble materials on the surface of the naphtha insolubles. These resinous materials are generally conceded to be the cause of viscosity increase. In the case of the screen filtration there was no adsorption, and the viscosities were consistent. Measurements of viscosity were made at both 100° and 210° F., and the percentage increase was noted.

Naphtha Insolubles. Ten grams of oxidized oil were weighed out accurately into a 250-cc. Erlenmeyer flask to which was added 100 cc. of 86° A. P. I. precipitation naphtha, prepared according to A. S. T. M. method D-91-40. The solution was allowed to stand for 3 hours in a dark cabinet and then filtered through a

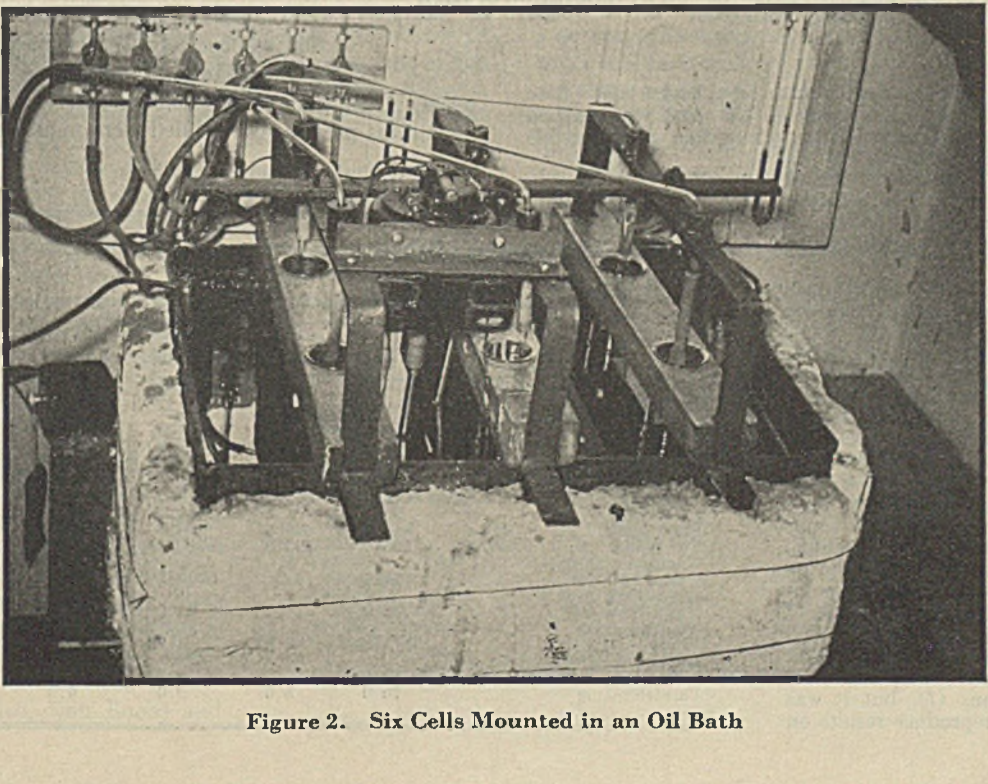

Figure 2. Six Cells Mounted in an Oil Bath

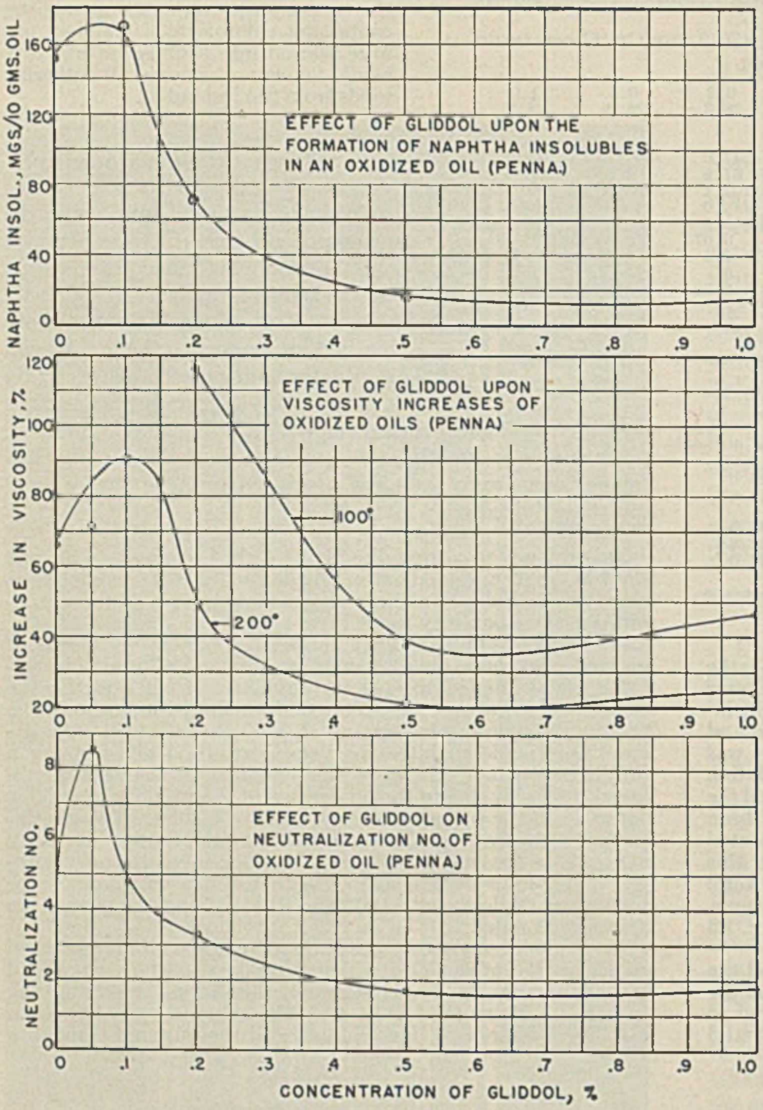

Figure 3. Effect of Gliddol Concentration on Deterioration of High Viscosity Index Oil

dried and weighed Gooch crucible with an asbestos mat 1/4 to 1/2 inch. The precipitate remaining on the pad was washed thoroughly with an additional 100 cc. of naphtha. The crucible was then placed in an oven at 110° C. for 3 hours, cooled in a desiccator, and finally weighed. The increase in weight represented the naphtha insolubles, expressed in milligrams per 10 grams of oil.

Chloroform Solubles. The crucible containing the naphtha insolubles was washed with a total of 100 cc. of chloroform, dried, and weighed as before. The loss in weight was considered to be chloroform solubles. Naphtha precipitates certain of the less highly polymerized oil-soluble resinous materials as well as the oil-insoluble material; and the chloroform-soluble material is generally thought to be a rough measure of the amount of naphtha-insoluble which is oil-soluble. The results are expressed either as chloroform solubles or chloroform insolubles in milligrams per 10 grams of original oxidized oil.

Neutralization Number. This test was first carried out by the A. S. T. M. specifications (*1*), but it was found difficult to reproduce results on highly oxidized oils as a result of inability to observe the end point of phenolphthalein in the dark oil. A revised method suggested by the A. S. T. M. was used. This procedure was to dissolve 10 grams of oil in 100 cc. of 95 per cent ethyl alcohol which was boiled. The cooled mixture was titrated with standard potassium hydroxide almost to the end point, 50 cc. of water were added, and a milk-white emulsion formed. Titration was continued to the end point of phenolphthalein. The pink color was easily observed against the background of the white emulsion. This method gave consistent results. Neutralization number is expressed in milligrams of potassium hydroxide required for 10 grams of oil.

Loss in Weight of Copper Strip. The copper strip was polished and weighed before use. After completion of the run the strip was removed, soaked in chloroform for one day, and wiped thoroughly with a dry cloth. The strip was weighed and the loss in weight recorded in milligrams. Since the amount of surface was constant (20 sq. cm.) in each case, the results are comparable. It was found that in some cases a coating was formed on the copper strip which was insoluble in chloroform. This was either a highly polymerized lacquer or an inorganic coating such as an oxide. Consequently, weighings gave the difference of two opposing effects—corrosion loss and coating deposition. In some later runs it was found that the copper strips had actually gained in weight. As a result little stress was laid upon this determination.

Varnish Rating was a measure of the detergent effect of an oil. The small steel tubes which were mounted in the center of the oxidation cell were removed and wiped free of adhering oil with a soft cloth. The tubes were then given an arbitrary rating on a scale ranging from 0 to 10, depending upon the amount of lacquer or varnish formed and its quality factors, such as color, hardness, ease of removal, etc. A rating of 0 is a clean tube and a rating of 10 signifies a completely varnished tube with a hard and gritty black or deep brown lacquer. Ratings were not made in all cases.

OPTIMUM PERCENTAGE OF GLIDDOL

Five samples of a pure Pennsylvania stock S. A. E. 30 lubricating oil, containing 0.05, 0.1, 0.2, 0.5, and 1.0 per cent commercial soybean lecithin, respectively, were prepared. These samples and the same oil containing no additive were tested in the individual oxidation cells in the oil bath. The conditions previously outlined were maintained for 48 hours

Table III. Optimum Percentage of Gliddol in a Pennsylvania Oil of High Viscosity Index

(Oil A of 100 viscosity index, time 48 hours, air rate 125 liters per hour, temperature 325° F.)

	Unoxidized Oil	Oxidized Oils					
		Oil alone	+ 0.05% Gliddol	+ 0.1% Gliddol	+ 0.2% Gliddol	+ 0.5% Gliddol	+ 1.0% Gliddol
Gravity, ° A. P. I.	28.3	27.5	27.5	27.5	27.5	28.0	28.0
Viscosity, Saybolt Universal sec.							
100° F.	547.0	1320.0	....	1690.0	1180.0	750.0	800.0
210° F.	67.0	111.0	115.0	128.0	100.0	81.0	83.0
Increase in viscosity, %							
100° F.	...	141.0	....	206.0	116.0	37.3	46.4
210° F.	...	65.7	71.1	91.0	49.0	21.0	24.0
Flash point, ° F.	440.0	445.0	445.0	450.0	455.0	445.0	445.0
Fire point, ° F.	500.0	505.0	495.0	500.0	500.0	500.0	495.0
Naphtha insol., mg./10 g. oil	...	151.4	....	170.2	71.7	16.1	14.5
Chloroform insol., mg./10 g. oil	...	72.0	....	91.0	31.0	5.1	4.2
Neutralization No.	...	5.13	8.61	4.83	3.32	1.73	1.84
Loss in wt. of Cu strip, mg.	...	16.0	....	9.2	6.2	3.1	6.0
Varnish rating	...	10.0	8.0	9.0	6.0	0	1.0

Table IV. Optimum Percentage of Gliddol in a Mid-continent Oil of Medium Viscosity Index

(Solvent refined oil B of 82 viscosity index, time 64 hours, air rate 125 liters per hour, temperature 325° F.)

	Un-oxidized Oil	Oxidized Oils					
		Oil alone	+ Inhibitor I	+ 0.2% Gliddol	+ 0.3% Gliddol	+ 0.4% Gliddol	+ 0.5% Gliddol
Gravity, ° A. P. I.		24.2	27.4	25.2	27.0	27.8	27.8
Viscosity, Saybolt Universal sec.							
100° F.	529.0	1210.0	736.0	994.0	724.0	583.0	598.0
210° F.	62.0	94.0	77.7	89.8	70.1	66.4	66.5
Increase in viscosity, %	...						
100° F.	...	129.0	39.0	88.0	37.0	10.4	13.0
210° F.	...	51.5	25.3	44.0	13.0	7.1	7.3
Naphtha insol., mg./10 g. oil	...	460.0	235.0	511.0	13.0	8.0	15.0
Chloroform insol., mg./10 oil	...	53.0	4.0	...	8.0	...	2.0
Neutralization No.	...	8.4	2.9	8.1	3.9	1.7	1.5
Loss in wt. of Cu strip, mg.	...	34.0	8.6	11.9	17.3	2.3	8.9
Varnish rating	...	10.0	8.0	6.0	5.0	1.0	1.0

Table V. Effect of Base Stock

(Time 64 hours, air rate 100 liters per hour, temperature 325° F.)

	Oil B[b]	B + 0.4% Gliddol	B + Inhibitor I	Oil A[a]	A + 0.4% Gliddol	Oil C[c] + Inhibitor R
Gravity, ° A. P. I.	26.0	27.0	27.2	25.6	28.0	24.2
Viscosity, Saybolt Universal sec.						
100° F.	829.0	579.0	689.0	981.0	623.0	847.0
210° F.	...	62.7	70.1	89.8	73.9	70.1
Increase in viscosity, %						
100° F.	57.0	9.4	30.2	82.5	13.8	...
210° F.	...	1.1	13.0	32.0	8.5	...
Naphtha insol., mg./10 g. oil	193.0	15.4	88.0	61.0	9.9	120.0
Chloroform insol., mg./10 g. oil	0	12.0	30.0	0	8.0	17.0
Loss in wt. of Cu strip, mg.	67.3	3.0	11.8	4.3	16.9	...
Varnish rating	9.0	1.0	6.0	2.0	2.0	3.0

[a] 100 viscosity index Pennsylvania.
[b] 82 viscosity index mid-continent, solvent refined.
[c] California.

except for a high air rate of 125 liters per hour, as shown in Table III. The effect of the concentration of Gliddol on the various physical properties is represented in Figure 3. In this case Gliddol was demonstrated to have a marked inhibiting effect upon oxidation, especially when used to the extent of 0.5 per cent.

Samples were next run on a mid-continent, solvent-refined 82 viscosity index lube oil of S. A. E. 30 viscosity range with 0.2, 0.3, 0.4, and 0.5 per cent Gliddol, no Gliddol as a blank, and the same oil containing a standard inhibitor. The composition of the latter was not known, but it was supplied by the producer of the base oil. The data are shown in Table IV and Figure 4. This oil shows an optimum in the effectiveness of Gliddol as an inhibitor somewhere between 0.4 and 0.5 per cent concentration, or in the same range as that for the Pennsylvania oil.

This laboratory test lays stress primarily upon oxidation resistance; and the optimum concentration might be considerably different for uses in which other factors were more important. Thus, in a Diesel lubricant, where detergency is a vital necessity for a compounded lubricating oil, the addition of higher percentages of Gliddol may be efficacious.

EFFECT OF BASE STOCKS AND REFINING METHOD

Oils from different base stocks and refined by different methods vary considerably in their stability against deterioration in use. Thus it has been stated that naphthenic oils are preferable as Diesel lubricants because of superior heavy-duty performance; von Fuchs and Diamond (7) showed the desirability of a high aromatic content for good stability in lube oils.

The effect of different base stocks and various refining methods on oil oxidation as well as the effect of Gliddol addition on these oils, was determined in a series of runs. In run 6 (Table V) a comparison was made between Pennsylvania oil A, mixture of 60 per cent bright stock and 40 per cent neutral with a high viscosity index (103), and mid-continent oil B, a solvent-refined oil of 82 viscosity index. Both of these oils were also inhibited with Gliddol. Together with oil B, containing a commercial inhibitor designated as I, and a California oil (oil C), containing another commercial inhibitor R, all six samples were run simultaneously. Consideration of the viscosity increases alone shows that the Pennsylvania oil is less stable than the mid-continent oil. This is in agreement with the data of von Fuchs and Diamond (7).

Considering the naphtha insolubles, however, the situation is reversed; mid-continent oil B has a much higher naphtha insoluble content than the Pennsylvania oil. This would seem to indicate that the oxidation of paraffin type oils tends to give high concentrations of resinous materials rather than naphtha insolubles. In other words, paraffinic oils increase in viscosity more than solvent-refined mid-continent oils, whereas the amount of sludge formed is considerably less. This seems to be somewhat characteristic, as will be pointed out later.

Consideration of run 6 shows that the naphtha insolubles of both the untreated oils are wholly chloroform soluble, whereas the sludge from the Gliddol-treated oils is probably a decomposition product of the Gliddol itself; after this initial precipitation the oil is quite stable. The Gliddol-treated oils are the most stable.

Run 14 (Table VI) compares two oils from the same source and treated by the same refining methods, but of different viscosity ranges. These oils, E and F, were mid-continent

Table VI. Effect of Viscosity

(Time 65 hours, air rate 30 liters per hour, temperature 325° F.)

	Unoxidized Oils		Oxidized Oils					
	E[a]	*F*[b]	Oil E	E + 0.5% Gliddol	E + 1.0% Gliddol	Oil F	F + 0.5% Gliddol	F + 1.0% Gliddo
Gravity, ° A. P. I.	...	...	26.7	27.1	26.8	24.2	24.7	25.0
Viscosity, Saybolt Universal sec.								
100° F.	205.6	608.0	273.2	234.1	229.1	903.0	770.0	684.0
210° F.	45.9	64.4	47.4	46.4	50.7	73.1	69.9	67.7
Increase in viscosity, %								
100° F.	...	...	32.9	13.9	11.5	48.6	26.7	12.5
210° F.	...	...	3.3	1.1	10.5	13.5	8.5	5.1
Naphtha insol., mg./10 g. oil	...	...	126.0	55.3	84.7	134.5	80.7	40.1
Chloroform insol., mg./10 g. oil	...	...	0	17.7	37.3	1.1	14.2	12.3
Neutralization No.	...	...	1.7	1.1	0.9	1.6	0.9	0.5
Varnish rating	...	...	9.0	5.0	6.0	9.0	6.0	4.0

[a] S. A. E. 10 mid-continent, conventionally refined.
[b] S. A. E. 30 mid-continent, conventionally refined.

oils prepared by conventional refining methods—i. e., acid treating, neutralizing, and clay contacting. Two samples of each were treated with 0.5 and 1.0 per cent Gliddol, respectively. The heavier grade (oil F) is oxidized to a greater extent than the lighter oil. This is implied in the work of Larsen, Thorpe, and Armfield (*10*). Comparison of the chloroform solubles with the naphtha insolubles in this run shows that the untreated oils give naphtha insoluble material which is almost wholly soluble in chloroform; this was to be expected. However, in the case of the Gliddol-treated oils, there is an appreciable and constant difference between the two. This is probably the precipitate caused by the presence of Gliddol. There is not so great a difference between the neutralization numbers of the two oils as might be expected from a consideration of the other data. As a matter of fact, the heavier oil in this case had a slightly lower neutralization number.

In run 25 (Table VII) three different type oils of S. A. E. 30 viscosity range were considered. N was a mid-continent conventionally refined oil, O was a mid-continent oil from the same or similar stock which was solvent-refined, M was the previously mentioned California oil. The conventionally refined stock N gave a considerably higher yield of naphtha insoluble material than the other oils. However, comparison of oil N and solvent-refined oil O confirms a previously noted difference. Oil O shows a considerably greater increase in viscosity than N, whereas the naphtha insolubles are much lower. This would seem to indicate a much higher resin content. In filtering the naphtha insolubles from oil O, the same effect was noted as was observed with Pennsylvania oils; i. e., the precipitate was soft, sticky, and difficult to filter. This, together with the high viscosity increase, leads to the conclusion that the oxidation in the case of paraffinic constituents (the viscosity index of oil O was 100, and consequently it can be considered essentially paraffinic in nature) tends toward the formation of intermediate, oil soluble oxidation products rather than the more highly oxidized oil and naphtha insoluble materials. Mougey's statement (*11*) that solvent refining tends to increase the varnish-forming propensities of an oil and at the same time reduce sludge is thus corroborated. However, whether the effect is due to removal of inhibitors or merely to the fact that paraffins tend to give more resinous oxidation products than naphthenes or aromatics is debatable. If it is considered that these intermediate oxidation products or resins are the materials from which lacquer and varnish are formed, the reasons are indicated for the selection of naphthenic base oils as recommended lubricants by many Diesel manufacturers. It has been shown that naphthenic oils (*10*) tend to give less varnish in engine testing than paraffinic oils. As a possible explanation it has been stated that the lacquer-forming materials were more soluble in the naphthenic oils and thus would not precipitate out readily on the piston. The evidence here seems to contradict the latter theory. It is more probable that the varnish is formed by the polymerization of partially oxidized bodies which are dissolved in the oil. Otherwise it would be hard to explain how these materials are carried to the various parts of the engine and why they should precipitate out only on the hottest portions—i. e., the piston skirt, undercrown, and ring grooves. It would be expected that the solubility of these materials would increase rather than decrease at the higher temperature if it is presumed that there is no polymerization.

COMPARISON OF GLIDDOL WITH OTHER ADDITIVES

Several runs were made to compare Gliddol and other additives. Data were also obtained from other runs to emphasize the conclusions. In run 4 (Table VIII), oil B was treated with the following inhibitors:

INHIBITOR O is an additive made by a company whose major business is the development and sale of inhibitors for lubricating oil. No composition is given.

INHIBITOR P is marketed by an oil company as having over-all antioxidant, detergent, and anticorrosion properties. It is probably a metal salt of an alkylphenol.

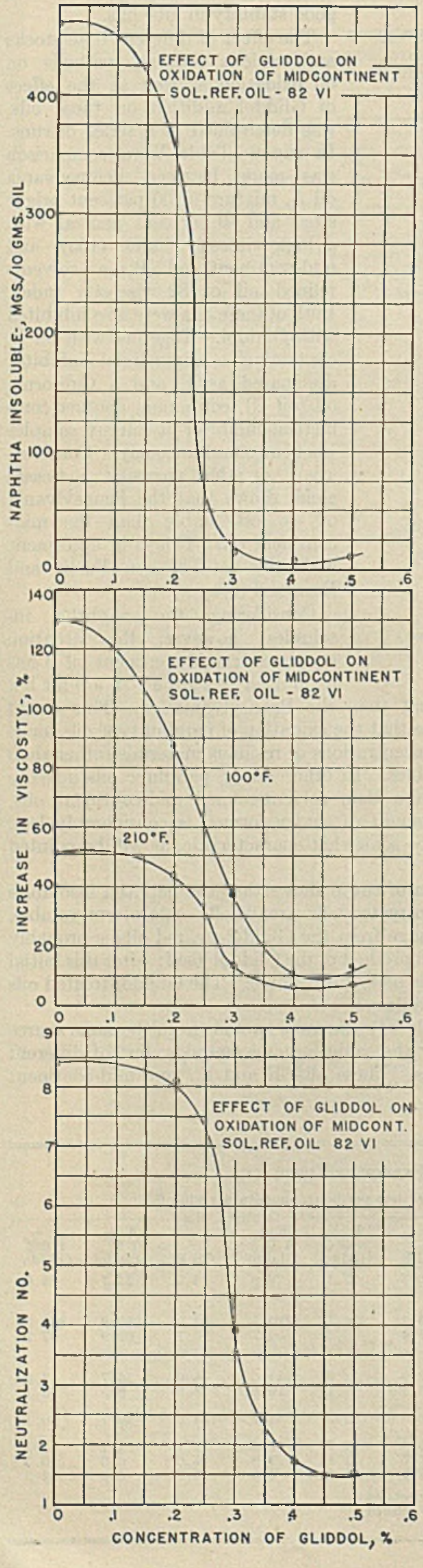

Figure 4. Effect of Gliddol Concentration on Deterioration of Medium Viscosity Index Oil (Mid-continent)

Inhibitor T is the standard inhibitor recommended by the company who supplied the base oil. Nothing was known of its composition.

Inhibitor A is marketed primarily as an oiliness agent, for reduction of friction in moving parts, but it is claimed to have some value as an antioxidant. It is essentially a petroleum fraction which has been oxidized under controlled conditions to produce a complex mixture of phenols, aldehydes, esters, etc.

TABLE VII. EFFECT OF REFINING METHOD

(Time 75 hours, air rate 30 liters per hour, temperature 325° F.)

Oxidized oil	N[a]	N + 0.5% Gliddol	O[b]	O + 0.5% Gliddol	M[c] + 0.5% Gliddol	M + Inhibitor R
Gravity, ° A. P. I.	22.4	24.3	24.0	24.6	26.8	26.8
Viscosity, Saybolt Universal sec.						
100° F.	1085.0	867.0	1330.0	1310.0	665.0	680.0
210° F.	78.7	76.2	110.2	109.9	71.14	71.4
Increase in viscosity, %						
100° F.	75.0	39.7	118.0	114.0	34.3	19.4
210° F.	15.8	12.0	43.0	42.8	12.5	10.3
Naphtha insol., mg./10 g. oil	435.3	211.2	154.5	112.1	109.1	59.0
Chloroform insol., mg./10 g. oil	348.1	112.0	146.1	82.8	31.5	8.5
Neutralization No.	2.8	1.5	2.5	1.6	1.2	1.0
Varnish rating	10.0	7.0	9.0	4.0	4.0	5.0

[a] S. A. E. 30 mid-continent, conventionally refined.
[b] S. A. E. 30 mid-continent solvent refined.
[c] S. A. E. 30 California.

The percentages of inhibitors used were recommended by the manufacturers; since in some cases the material was supplied as a concentrate, it would be difficult to determine the actual percentage of active material. Gliddol was used in optimum amount, 0.5 per cent.

Gliddol appears to be the most effective inhibitor of this particular group, which were, however, chosen at random, and may not be the best available. Inhibitor P is the only one of comparable effectiveness. The differences between Gliddol and inhibitor P are not to be overemphasized, since the variations noted are not much greater than the accuracy of the experimental data. Furthermore, the determinations used are highly empirical and are influenced by many variables. However, the differences between these two additives and the others, especially the improvement over the blank, are great enough to conclude that they were effective. On this basis, a choice would probably rest on cost per gallon of oil treated.

Gliddol is a fairly cheap material (about 30 cents a pound) and is less costly than any of the synthetic materials. Furthermore, it is essentially a by-product material in the manufacture of soybean oil, and the possibilities are that it may become even cheaper as demand for it increases. Another important factor at this time is its availability. The amount of soybean oil produced in this country is large, and the amount of phosphatide which could be produced is far above present demands. On the other hand, most of the synthetic materials contain such constituents as tin and chlorine which are difficult to obtain at present. On the basis of this laboratory work and considering primarily the resistance to oxidation, there seems to be a place for commercial soybean lecithin as an inhibitor for lubricating oils.

The selection of a good inhibitor depends as well upon other properties, such as prevention of the related gummy deposits in vital portions of the engine and the reduction of varnish deposition. The so-called detergency is a vital function of an additive, although it is more important in Diesel than in automotive engines; other work, to be reported later, indicates that Gliddol adds to the detergent properties of lubricating oils.

CONCLUSIONS

Gliddol has been shown by laboratory tests to be an oxidation inhibitor. It reduces the amount of naphtha insolubles formed, the viscosity increase, and the neutralization number. It is effective in oils from widely varying base stocks and in oils refined by widely varying methods. It is effective in oils of different viscosity indices. It compares well with several commercially accepted inhibitors.

TABLE VIII. COMPARISON OF ADDITIVES

(Mid-continent solvent-refined oil B, time 64 hours, air rate 125 liters per hour, temperature 325° F.)

	Unoxidized Oil	Oxidized Oils					
		Oil alone	+Inhibitor O	+Inhibitor P	+Inhibitor T	+Inhibitor A	+0.5 % Gliddol
Viscosity, Saybolt Universal sec.							
100° F.	529.0	1120.0	760.0	640.0	710.0	770.0	590.0
210° F.	62.0	90.1	86.0	77.0	71.0	74.0	68.0
Increase in viscosity, %							
100° F.	....	112.0	43.5	21.0	34.2	45.5	11.5
210° F.	....	45.5	38.8	24.2	14.5	19.2	9.2
Flash point, ° F.	445.0	440.0	440.0	445.0	445.0	450.0	445.0
Fire point, ° F.	505.0	500.0	495.0	495.0	500.0	505.0	495.0
Naphtha insol., mg./10 g. oil	....	721.7	190.1	89.8	271.0	152.3	31.8
Chloroform insol., mg./10 g. oil	....	180.9	50.5	0.8	72.2	67.3	16.1
Neutralization No.	0.05	5.2	3.1	1.3	3.14	2.2	1.14
Loss in wt. of Cu strip mg.	....	2.3	6.0	3.1	0.6	9.2	0.2
Varnish rating	....	10.0	7.0	2.0	8.0	9.0	0

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The photograph shows molding powders, films, lacquers, molded products, lacquer-finished articles, etc., prepared from nitrated sawdust.

NITRATED WOOD

FRACTIONATION AND MOLECULAR MAGNITUDES

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THE exact nature of the chemical components of wood and their relation to one another as they exist in the woody tissue is unknown. Wood is not a uniform mixture of cellulose, hemicelluloses, and lignin, since these substances are distributed in varying proportions in the different morphological parts of the tissue. Physical means of separating the cell wall components, such as extraction or solution and fractionation, are not possible. Chemical methods of isolating any of the constituents of wood are all drastic, and it is apparent that they result in isolated compounds which are altered from their original condition in the tissue. Chemical changes may be brought about in the structure by hydrolytic or oxidative effects on certain groups and by cleavage of chain length; decreased molecular magnitude is the result. Lignin appears to be particularly sensitive to chemical changes which vary with the method of isolation used, and cellulose is susceptible to degradation of chain length. For example, treatment of cellulose with dilute chlorine water or calcium hypochlorite is reported to decrease greatly the degree of polymerization (*6*) unless the bleaching treatments are carefully controlled as in optimum commercial practice. It is probable that any of the methods for isolating the wood components would also cleave the weak linkages which are postulated by several investigators to exist between lignin and the hemicelluloses.

A previous paper (*2*) showed that nitrated wood is almost completely soluble in acetone and other simple solvents, and that the nitrated wood lends itself to fractionation on the basis of solubilities in acetone and water. This offers a new approach to the study of the chemical relation of the woody constituents to one another and to the study of the molecular magnitude of the components and chemical complexes in wood.

MATERIAL AND METHODS

Various woody tissues were nitrated as previously described (*2*). These included groundwood, mechanical pulp, raw sulfate pulps, and bleached sulfate pulps. For viscosity studies the nitrated products were purified by hot water extraction, alcohol extraction, reprecipitation from acetone with water, or bleaching with calcium hypochlorite or sodium chlorite (*7*).

Viscosity was determined in values designated as "effective viscosities". This term indicates the viscosity at a given concentration, neglecting the small amount of material insoluble in the solvent.

The nitrated products were fractionated by a combination of solution and precipitation methods (*3*) as shown in Figure 6.

Chlorine consumptions during bleaching were measured by titrating the excess bleach with standard sodium thiosulfate. The "brightness" or light reflectance for blue light of the various products were compared on the Higgins reflection meter (*8*). The ester nitrogen analysis was conducted by the Schultz-Tieman method (*1*).

VISCOSITY AND MOLECULAR MAGNITUDE

The viscosities of the nitrated lignocelluloses examined do not differ greatly (Figure 1), despite the fact that considerable amounts of lignin have been removed in the case of the very raw sulfate pulps.

On the basis of Staudinger's theory (*4*),

$$\underset{c \to 0}{\text{limit}} \left[\frac{\eta_{sp.}}{c_{g.\,d.\,m.}}\right] = K_m M \qquad (1)$$

when $\eta_{sp.}$ = specific viscosity of a long-chain polymer
$c_{g.\,d.\,m.}$ = concentration, primary moles/liter
K_m = a constant
M = molecular weight of long chain

Because of its solubility in acetone and other simple organic solvents, nitrated wood provides a new approach to the chemistry of woody constituents *in situ*. Nitrated spruce and white pine contain considerable amounts of ligneous material; most of it may be removed by alcohol extraction to yield a product which appears to contain 5 per cent lignin and has a high viscosity. The average molecular size of nitrated spruce and white pine woods is equivalent to that of the nitrate from moderately bleached cotton linters. However, the distribution of molecular sizes seem to be much wider than that of nitrated cotton linters or pulp. Evidence points to the existence of large amounts of material in wood, having exceptionally large molecular size. It appears that nitration does not reduce the chain length of the cellulose in the wood to the extent that cooking and bleaching processes for isolating cellulose do. Evidence is obtained for the existence in nitrated wood of easily severed linkages; the result, upon fission, is a decrease in viscosity. The behavior of nitrated wood to bleaching and to hot water and hot alcohol extraction suggests that these are lignin-carbohydrate linkages. However, pending further evidence, the possibility that these easily cleaved linkages connect other residues or are of some other type, such as ester cross linkages or glucosidic linkages connecting furanose rings in hemicelluloses, cannot be excluded.

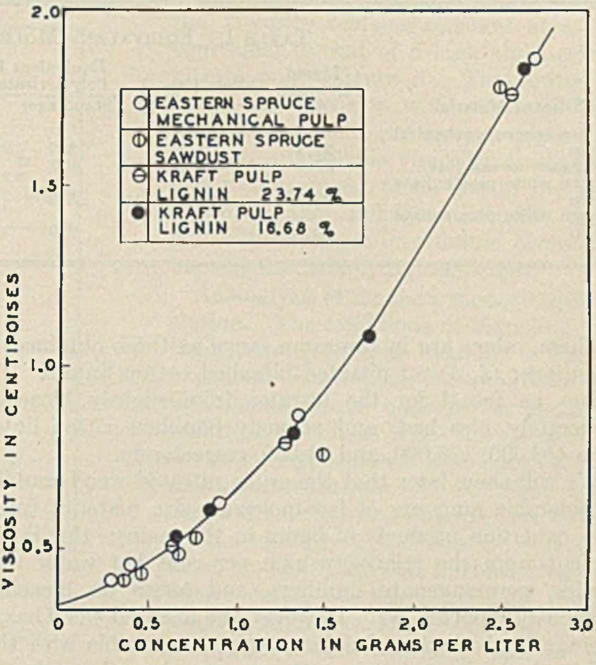

Figure 1. Relation of Viscosity to Concentration in Acetone Solution for Nitrated Lignocelluloses

Equation 1 may be written:

$$\text{D. P.} = \underset{c \to 0}{\text{limit}} \left[\frac{\eta_{sp.}}{c}\right] 1/10K_m \qquad (2)$$

where D. P. = degree of polymerization
c = concentration of polymer, grams/100 cc.

If the constant $K_m = 10 \times 10^{-4}$ is substituted[1], Equation 2 becomes:

$$\text{D. P.} = \underset{c \to 0}{\text{limit}} \left[\frac{\eta_{sp.}}{c}\right] 100 \qquad (3)$$

From which M = D. P. × m, where m is the weight of the repeating unit. Similarly, Kraemer's intrinsic viscosity,

$$[\eta] = \underset{c \to 0}{\text{limit}} \left[\frac{\ln \eta_r}{c}\right] = \underset{c \to 0}{\text{limit}} \left[\frac{\eta_{sp.}}{c}\right]$$

where ultracentrifuge measurements have calibrated the viscosity equation such that D. P. = 270 $[\eta]$.

Since nitrated wood is not a purified chemical compound, the above theory cannot be applied to its viscosity in acetone solutions without the following restriction: The molecular weight calculated will not be the average molecular weight of the compounds in solution, but will represent that average molecular weight of purified cellulose nitrate which will give the same viscosity relation—i. e., the "equivalent molecular weight".

By plotting the reduced viscosity ($\eta_{sp.}/c$) against c (concentration in grams per 100 cc.) and extrapolating the straight line obtained to infinite dilution, the value of the function, $\underset{c \to 0}{\text{limit}} \left[\frac{\eta_{sp.}}{c}\right]$, is determined. These values for the different materials investigated, as well as the calculated values for equivalent degrees of polymerization and equivalent molecular weights, are shown in Table I. The equivalent molecular weights for the different nitrated lignocelluloses are of the same order of magnitude.

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[1] More recent work by Staudinger and co-workers (*5*) gives a K_m value of 11 × 10^{-4} for cellulose nitrate. However, since the exact value of K_m is still questioned, the original value is used here and is satisfactory for comparative purposes.

Table I. Equivalent Molecular Size of Crude Nitrated Wood

Nitrated Material	Lignin Content, %	Limit $c \to 0 \left[\frac{\eta_{sp}}{c}\right]$	Equivalent Degree of Polymerization, D. P.		Nitrogen, %	NO_2, %	Wt. of Repeating Unit, m	Equivalent Mol. Wt., M	
			Staudinger	Kraemer				Staudinger	Kraemer
Eastern spruce mechanical pulp	27.1	6.2	620	1670	10.0	32.8	238	147,500	398,000
Eastern spruce sawdust	27.6	4.0	400	1080	10.3	33.8	242	96,700	262,000
Eastern white pine sulfate pulp	23.74	5.8	580	1560	11.6	37.9	258	149,000	403,000
Eastern white pine sulfate pulp	16.68	6.1	610	1640	12.1	39.7	266	162,000	438,000

These values are in the same range as those obtained by Staudinger (*4*, *5*) for nitrated bleached cotton linters. The values he found for the nitrates from slightly bleached, moderately bleached, and strongly bleached cotton linters were 443,000, 176,000, and 81,000, respectively.

We will show later that the crude nitrated wood contains considerable amounts of low-molecular-size material (probably oxidation products of lignin in the main); this is also evident from the relatively high per cent hot water solubilities, permanganate numbers, and losses on bleaching previously reported (*2*). However, the nitrated wood has an average equivalent molecular weight comparable with that of bleached cotton linters. It appears, then, that nitration does not reduce the chain length of the cellulose in the wood to the extent that cooking and bleaching processes for isolating cellulose do; also, nitrated lignocelluloses seem to have a much wider distribution of molecular sizes than do nitrated cotton linters, and must therefore contain larger quantities of material of relatively high molecular size than do bleached cotton linters.

The results indicate that little difference in yield or degree of esterification is obtained by varying the particle size of the spruce sawdust nitrated. Viscosities are fairly constant, but some abnormal values are obtained for the very fine mesh sizes. Extracting and bleaching the nitrated wood result in higher nitrogen content and viscosity, which was to be expected since previous evidence indicated that the extractives are composed of material of small molecular dimensions (*2*).

Precipitation of acetone solutions of nitrated spruce wood in water and then bleaching show that a fairly good yield of very white material can be obtained. The bleach consumptions are low. Precipitation from acetone followed by bleaching or by stabilization by boiling in water results in products of much higher viscosities than the original crude material; this again confirms the previous data that a considerable low-molecular-weight fraction is removed.

Although purification of nitrated wood by precipitation from acetone followed by bleaching gives a bright white material, bleaching alone fails to remove all color; the products show a shade of yellow. For example, a consumption of 11.3 per cent chlorine resulted in a brightness of 22.5, and a consumption of 22.6 per cent chlorine gave a product with a brightness of 38.5. Similar results were obtained by bleaching nitrated spruce wood which had previously been stabilized by hot water extraction. The per cent of original wood lost by bleaching the crude wood nitrate increases with increased bleach consumption; there is about 5 per cent loss with 2.8 per cent chlorine consumed and 10 per cent loss with 22.6 per cent chlorine consumed (Figure 4). However, by varying the chlorine consumed in bleaching the stabilized wood nitrate from 6.0 to 22.7 per cent, no significant difference in yield was obtained; the bleaching loss was about 3 per cent in all cases.

The viscosity of the nitrated products uniformly decreases in all cases with increased chlorine consumption within the limits examined—namely, 0 to 23 per cent chlorine consumed (Figures 2 and 3). Extraction with hot water does not affect the viscosity of the crude nitrate appreciably, but lowers the viscosity of the bleached nitrate somewhat (Figures 2 and 4), presumably due to some hydrolysis of the oxidized product. But extraction with alcohol increases the viscosity of both the crude and bleached nitrate to a considerable extent (Figures 2, 3, and 4). The alcohol-extracted residues are also susceptible to the hydrolytic action of boiling water, since their viscosities are less after hot water extraction (Figure 2).

The action of alcohol extraction in removing low-molecular weight material is again demonstrated in the case of nitrated spruce wood which was subjected to stabilizing in boiling water prior to bleaching. Here again the viscosities are higher (Figure 3).

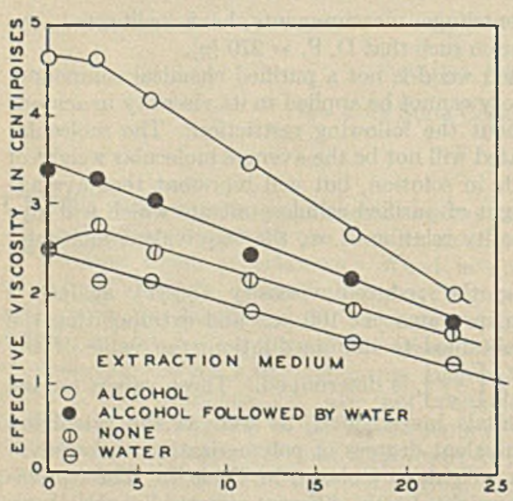


Figure 2. Changes in Viscosity of Nitrated Spruce Wood Caused by Bleaching and Extraction

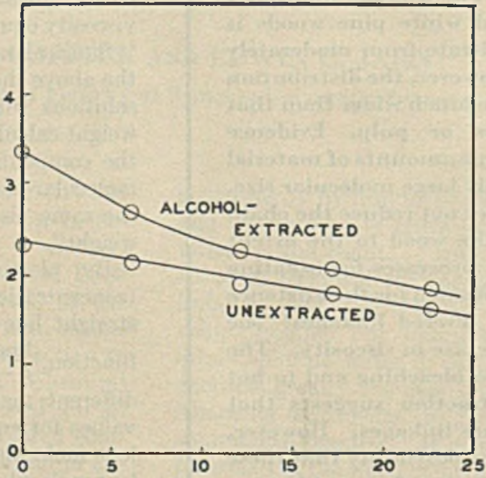


Figure 3. Changes in Viscosity of Stabilized Nitrated Spruce Caused by Bleaching and Alcohol Extraction

Viscosity at 15° C. in 1 alcohol-2 benzene-7.5 acetone, 2.85 grams per liter

These phenomena are summarized in Figure 4; it is apparent that, regardless of the order followed in purification of crude wood nitrate

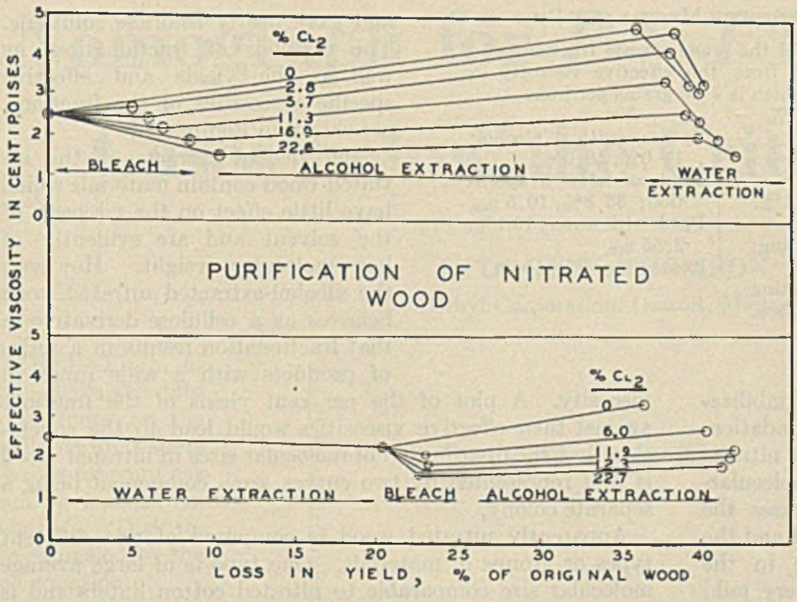


Figure 4. Relation of Viscosity of Nitrated Spruce Wood with Loss in Yield by Purification Treatments

by bleaching, stabilizing, and alcohol extracting, approximately the same values for viscosity and yield are obtained.

Since hot water extraction appears to remove considerable material of low molecular weight and yet decreases the viscosity, it must also cause some hydrolysis of that portion of the nitrate which constitutes the high-molecular-weight fraction. On the contrary, alcohol extraction apparently removes material of small molecular sizes without appreciable action on the long chains. Bleaching gives a product of lower molecular size, owing either to a degradative action on the long chains of the nitrated polysaccharides or to the decomposition of a possible lignin-carbohydrate compound.

Alcohol extraction removes most of the ligneous material from the crude nitrated wood, and the amount remaining in the extracted residue is evidently low, since delignification of the residues by the Cross and Bevan method removes only 5–6 per cent of material. Furthermore, the alcohol-benzene and water extractions prior to chlorination remove 2–3 per cent of material, so that the amount of lignin in the alcohol-extracted nitrates may be as low as 2–3 per cent. Degradation of chain length by the chlorination procedures is severe, as indicated by the large decrease in viscosity (Table II).

Removal by bleaching of the small amount of ligneous material present in the alcohol-extracted nitrated spruce wood is accompanied by a decided drop in viscosity. However, on stronger bleaching with either calcium hypochlorite at pH 11.3 for 0.5 to 3 hours or with sodium chlorite at pH 4.5 for 1 hour, the viscosity remains constant at a value equivalent to that of a high alpha-cellulose nitrate pulp (Figure 5). This initial decrease in viscosity with increased bleach consumption, followed by a leveling off at such an appreciable viscosity, is significant and would appear to be due to the breaking of weaker linkages than the normal glucosidic linkages in cellulose chains, perhaps lignin-carbohydrate linkages.

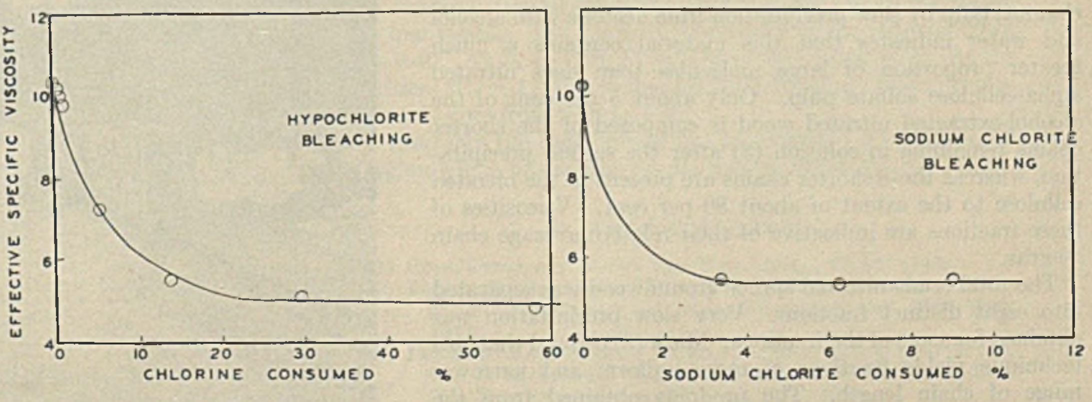


Figure 5. Effect of Bleaching with Calcium Hypochlorite and Sodium Chlorite on the Viscosity of Alcohol-Extracted Nitrated Spruce Wood

Viscosity at 15° C. in 1 alcohol–2 benzene–7.5 acetone, 2.85 grams per liter

An analysis of the data supports this conclusion. The conditions of bleaching (short time, very weak acid medium in the case of sodium chlorite) are such that the cellulose chains should undergo very little degradation. It has been shown that well controlled hypochlorite bleaching causes no serious degradation (*6*) and that weakly acid sodium chlorite solutions have no effect on the viscosity of cellulose (*7*). Hence, it must be concluded that the bleaching treatments employed have, at most, only a slight degradative effect on the cellulose chains, but that bleaching cleaves some of the more easily split linkages in large molecules and brings about a drop in viscosity which remains constant once these easily broken bonds are severed.

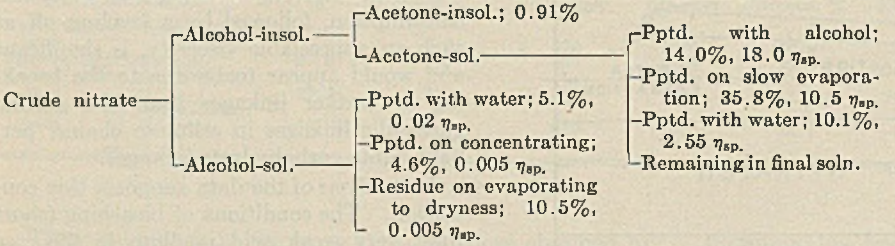
Table II. Delignification of Alcohol-Extracted Nitrated Spruce Wood

Treatment	Loss during Treatment, %	Effective Sp. Viscosity (Calcd. from 2.85 G./L.)
None	0	10.3
Alcohol-benzene and water extns.	2.74	8.90
10 chlorinations and Na_2SO_3 digestions	4.92	2.6
10 chlorinations and cold dil. NH_4OH extns.	2.22	1.45
6 chlorinations and hot dil. NH_4OH digestions	6.47	0.2

The behavior of nitrated wood to hot alcohol and hot water extraction lends further support to the above probability (Figure 2). Although hot water extraction removes over 20 per cent of low-molecular-size material, it does not raise the viscosity of the residue; in fact, the latter may even

FIGURE 6. FRACTIONATION OF NITRATED EASTERN SPRUCE MECHANICAL PULP

The first number after the fraction is the per cent yield of the crude nitrate fractionated; the second number is the specific viscosity calculated from the effective viscosity in 1 alcohol–2 benzene–7.5 acetone solvent at 15° C. which is 2.85 grams per liter.



drop slightly. This is significant in that hot water stabilization of cellulose nitrates causes no appreciable degradation. On the other hand, hot alcohol extraction of wood nitrate, which removes about the same amount of low-molecular-weight material as does hot water, greatly increases the viscosity of the residue. Both the alcohol-extracted and the bleached residues are still somewhat susceptible to the hydrolytic action of hot water. Apparently the very mild hydrolytic effect of hot water is sufficient to bring about the cleavage of some large-molecular-weight material. The viscosities of the alcohol-extracted nitrated spruce wood and mechanical pulp are much higher than that of the highest grade of cellulose pulp examined (Table III). The constant viscosity which alcohol-extracted nitrated spruce maintains on excessive bleaching is equivalent to that of a cellulose nitrate prepared from pulp having a cuprammonium viscosity of about 20 centipoises, which is a high-grade alpha-cellulose pulp (*8*).

TABLE III. VISCOSITIES OF CELLULOSE AND WOOD NITRATES IN CUPRAMMONIUM AND IN 1 ALCOHOL–2 BENZENE–7.5 ACETONE SOLVENT

Material Nitrated	Pulp Viscosity[a] in Cuprammonium (*8*), Centipoises	Effective Sn. Viscosity (Calcd. from 2.85 G./L.)
Bleached kraft	5.07	1.67
Bleached kraft	11.83	2.98
Bleached kraft	15.6	4.39
Bleached kraft	17.74	4.15
Bleached kraft	28.0	7.38
Eastern spruce mechanical pulp	...	10.85
Eastern spruce sawdust	...	10.3

[a] Determined by C. P. Donofrio, New York State College of Forestry.

FRACTIONATION OF NITRATED WOOD

Fractionation of alcohol-extracted nitrated spruce mechanical pulp by slow precipitation from acetone with alcohol and water indicates that this material contains a much greater proportion of large molecules than does nitrated alpha-cellulose sulfate pulp. Only about 5 per cent of the alcohol-extracted nitrated wood is composed of the shorter chains remaining in solution (*3*) after the second precipitation, whereas these shorter chains are present in the nitrated cellulose to the extent of about 80 per cent. Viscosities of these fractions are indicative of their relative average chain lengths.

The total crude nitrated spruce groundwood was separated into eight distinct fractions. Very slow precipitation was obtained for some of the fractions; Mark (*3*) showed that this technique yields fractions of more uniform and narrower range of chain length. The products obtained from the alcohol extracts were orange or brown powders which gave dark solution. The fractions precipitated from the acetone solution of the alcohol-extracted residues were light in color and gave nearly colorless solutions. The methods of fractionation, as well as the yields and effective specific viscosities of the fractions, are shown in Figure 6.

The alcohol extracts of the nitrated wood contain materials which have little effect on the viscosity of the solvent and are evidently of low molecular weight. However, the alcohol-extracted nitrated wood behaves as a cellulose derivative in that fractionation results in a series of products with a wide range in viscosity. A plot of the per cent yields of the fractions against their effective viscosities would lead to the conclusion that the distribution of molecular sizes in nitrated wood is best represented by two curves, each component being a separate colony.

Apparently nitrated wood is composed of two different types or groups of materials. One type is of large average molecular size comparable to nitrated cotton linters and is probably mainly carbohydrate in nature. This group has a wide distribution of molecular weights. The second type has a narrow distribution of molecular sizes which are not in the form of long-chain molecules. This group is probably a mixture, for the most part, of various degradation and nitration products of lignin and other noncellulosic materials.

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Hauling Old Growth Spruce

Nomograph for *P-V-T* Relations of Gases below the Critical Point

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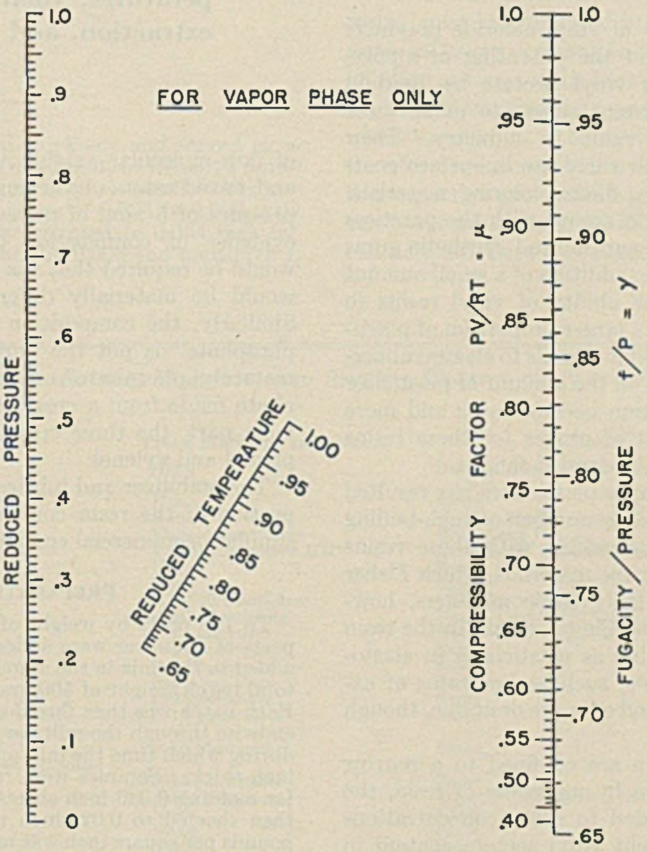

A CORRELATION of the available data for hydrocarbons on the compressibility of vapors below the critical point has been made by Cope, Lewis, and Weber (*1*). Their results are expressed by the following equation:

$$\mu \log \mu = -P_r f_{10} \qquad (1)$$

where $\mu = PV/RT$
P_r = reduced pressure
f_{10} = a function of reduced temperature only

The values of f_{10} for various values of the reduced temperature were presented in their paper. A direct solution for μ is not possible from Equation 1 because of its transcendental nature, but a nomograph may be simply constructed which obviates the tedious interpolation between curves necessary in a graphical solution. Although the nomograph shown gives an accurate solution of Equation 1, it is not recommended for a μ value closer than ±0.01 because of the uncertainties in the basic correlation.

The activity coefficient, f/P, equal to the ratio of fugacity to pressure, may be obtained by integration (*6*), as shown in Equation 2:

$$\ln f/P = -\int_0^{P_r} \frac{(1-\mu)}{P_r}\, d\,P_r \qquad (2)$$

The relation between f/P and μ can be expressed by Equation 3, obtained by substituting the value of P_r from Equation 1 into Equation 2:

$$\ln f/P = -\int_1^{\mu} \frac{(1-\mu)\,(1+\ln \mu)}{\mu \ln \mu}\, d\mu \qquad (3)$$

It is to be noted that the function of the reduced temperature, f_{10}, has been eliminated, so that Equation 3 represents a unique relation between f/P and μ below the critical point. The integral cannot be evaluated without the use of series, although a direct solution can be obtained by using tables of the exponential integral (*2*), as shown in Equation 4:

$$\ln f/P = \mu - \ln \mu - \ln(-\ln \mu) + Ei\,(\ln \mu) - 1.577216 \qquad (4)$$

The term $Ei\,(\ln \mu)$ is conveniently obtained by entering the tables (*2*) of $-Ei(-t)$ with $t = -\ln \mu$. The simple parabolic equation below gives a satisfactory fit to the values and is much easier to use than Equation 4:

$$f/P = 0.7 - 0.4\mu + 0.7\mu^2 \qquad (5)$$

A useful relation between f/P and P_r was obtained by plotting f/P against $\mu \log \mu$. The resulting equation,

$$f/P = 1 - 2.181\, f_{10} P_r \qquad (6)$$

fits the f/P values from Equation 4 to within ±0.003.

The f/P values shown on the same axis on the nomograph as the μ values were obtained from Equation 4. They are a little higher than the values in the chart presented by Newton (*4*) and are in good agreement with the charts of Lewis and Kay (*3*) and Weber (*5*).

Extrapolation of the nomograph beyond the ranges shown is inadvisable. For example, the μ scale shown extends down to 0.40. At $T_r = 1.00$, $P_r = 0.98$ at this value of μ. At the critical ($P_r = 1.00$), μ is about 0.26, indicating a rapid drop in μ as P_r goes from 0.98 to 1.00.

Similarly the data should not be extended into the liquid region where misleading results may be obtained.

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Behavior of Plasticizers in

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Methods for the evaluation of plasticizers for use in vinyl chloride-acetate copolymers are described; forty-six different plasticizers have been evaluated. Elongations at 1000 pounds per square inch at three temperatures, volatility, water extraction, oil extraction, and flex temperature are tabu-

FOLLOWING the discovery of vinyl chloride polymers by Regnault in 1838 (*7*) and the patenting of copolymers of vinyl chloride and vinyl acetate by Reid in 1933 (*8*), there have been consistent efforts to make these potentially low-cost resins of value in industry. Their chemical inertness suggested their early use in surface coatings, and to this end plasticizers, fillers, coloring materials, and other modifiers were added in accord with the practices well established with other hard natural and synthetic gums and resins. It was found that the addition of a small amount of plasticizer would improve the ability of vinyl resins to bend without checking, and that a larger proportion of plasticizer would change them from rigid materials to elastic rubber-like solids or soft gels, depending on the amount of plasticizer used. Thus this plasticizing action became more and more important with the development of usages for these resins in rolled, calendered, molded, and extruded shapes.

The search for better and cheaper plasticizers has resulted in the availability of a considerable number of high-boiling liquids which are sufficiently compatible with these resins to convert them from rigid to flexible materials, which Fisher (*3*) has termed "elastomers". Only those modifiers, however, which are sufficiently nonvolatile to remain in the resin permanently are of practical value as plasticizers in elastomeric vinyl resins. Other factors, such as low rates of extraction and freedom from color and odor are desirable, though not essential in all applications.

While the data presented here are confined to a narrow range of plasticizer concentration in one grade of resin, the main conclusions may be extended to other concentrations and to similar resins with different vinyl acetate content in so far as the specific and relative behavior of the plasticizing component is concerned.

MATERIALS USED

The resin used in this investigation was made by copolymerizing 95 parts of vinyl chloride and 5 parts of vinyl acetate. The apparent molecular weight was approximately 22,000 as determined by measuring the specific viscosity in cyclohexanone. It was compounded in the following proportions:

	Per Cent by Weight		
Resin	66.97	62.21	57.42
Lubricant	1.01	0.93	0.86
Stabilizer	2.02	1.86	1.72
Plasticizer	30.00	35.00	40.00
	100.00	100.00	100.00

The plasticizers (Table I) were obtained from various manufacturers and are believed to be substantially as represented. In the case of mixed esters, however, the composition is sometimes a matter of conjecture. A material made by esterifying two moles of phthalic anhydride with one mole of ethylene glycol and subsequently reacted with two moles of butanol would be labeled dibutyl ethylene glycol diphthalate. The probability is that it would be a mixture of low-molecular-weight alkyd resins, dibutyl phthalate, and mixed esters of varying compositions. Distillation at a pressure of 5 mm. of mercury would not reveal satisfactory evidence of composition because such high temperatures would be required that the mixture of the fractions obtained would be materially different from the starting material. Similarly, the composition of the material called "tricresyl phosphate" is not the pure substance properly called "trimetatolyl phosphate" or a mixture of its isomers, but a phosphate made from a cresylic acid fraction containing, for the most part, the three cresol isomers and smaller amounts of phenol and xylenol.

The stabilizer and lubricant were added as a constant proportion of the resin component to facilitate processing and simulate commercial compounds of this type.

PREPARATION OF SAMPLES

To 100 parts by weight of resin, 1.5 parts of lubricant and 3 parts of stabilizer were added and dry-blended. Plasticizer was added to this mix in the amounts of 30, 35, and 40 per cent of the total batch weight of 500 grams and blended in a kitchen mixer. Each batch was then fluxed on a hot two-roll mill, rolled, passed endwise through the mill ten times, and milled one minute longer during which time the mill opening was set to make a sheet 0.045 inch thick. Samples were removed for heat stability tests and for molding 0.040-inch sheets, and the balance of the batch was then sheeted to 0.025-inch thickness. A steam pressure of 50 pounds per square inch was maintained in the rolls, yielding a roll surface temperature of 138° to 145° C.

A part of the 0.025-inch sheet was then used for molding 0.020-inch sheets, and the balance was calendered to a thickness of 0.003 to 0.006 inch.

Sheets for the stress-strain test were pressed in a flash mold, 6 × 6 × 0.020 inch, using an 8-minute heating cycle attaining a maximum temperature of 167° C. Samples cut longitudinally with the direction of milling were laid on the surface of a molten alloy at 170° C. for one minute and showed less than 6.0 per cent reduction in length. Calendered sheets usually ranged from 14 to 20 per cent shrinkage. These molded sheets were therefore considered to be sufficiently strain-free for the tests where that property might affect the results.

Samples for the flex temperature test were molded 0.040 inch thick in a similar flash mold using the same molding cycle.

Specimens were not conditioned with respect to humidity, but no elongation or flex temperature tests were made before the material had aged at least 40 hours subsequent to the last heating process.

Specimens for the stress-strain test were cut 4.75 × 0.25 inch longitudinally with grain, by means of a special jig. Specimens for the flex temperature test were cut in the same manner, the ends were trimmed off to make a length of 2.5 inches, and holes were punched 2 inches apart for mounting. The film specimens for volatility and extraction tests were died out as 3.5-inch disks. All thicknesses were measured by a dial gage having a flat circular foot 0.25 inch in diameter and a load of 3 ounces, and otherwise conforming to the A. S. T. M. method of measuring the thickness of rubber specimens (*1*).

The thicknesses of the disks were then calculated from the specific gravity and the original weight. The calculated thick-

VINYL CHLORIDE-ACETATE RESINS

lated for a series of elastomeric compounds containing 30 to 40 per cent of plasticizer, and these data are interpolated to a percentage yielding a standard flexibility. A special oven has been built for volatility tests, and the amount of ventilation required has been calculated.

ness agreed well with the measured thickness and served as a check on experimental procedure. On account of the large number of small batches it was not practical to sheet all stocks accurately to 0.004 inch; therefore a range of 0.003 to 0.006 inch was permitted, and all results were corrected to 0.004 inch by dividing the actual thickness in inches by 0.004 and multiplying by the found loss in per cent. The error resulting from this correction was found to be small when the loss amounted to less than half of the original plasticizer content, which was generally the case.

PLASTICIZER CHARACTERISTICS

There are several bases on which a plasticizer for these resins must be evaluated in order to arrive at logical conclusions as to its permissible use. Not all the properties contributed are important for every application, but a knowledge of them is important to permit of the optimum compromise which usually has to be made. The data accumulated should therefore be interpreted in terms of the relative differences in the respective properties which each plasticizer contributes to the resultant compound, and for that purpose the following characteristics are considered to be dominant (page 899, etc.).

TABLE I. SOURCE, VISCOSITY, AND SPECIFIC GRAVITY OF PLASTICIZERS

No.	Plasticizer	Trade Mark or Trade Name	Supplier	Viscosity (20° C.), Centipoises	Sp. Gr., d_{20}^{20}
1	Methyl cyclohexyl lactate[a]	None	Barrett Div., Allied Chem. & Dye Corp.	19.3[b]	...
2	Methyl cyclohexyl stearate[a]	None	Same	21.5	0.886
3	Methyl pentachlorostearate	None	Hooker Electrochemical Co.	1250	1.202
4	Methyl Cellosolve oleate	Kapsol plasticizer	Ohio-Apex Inc.	10.2	0.902
5	Triethylene glycol di-2-ethyl hexoate	Flexol plasticizer 3GO	Carbide & Carbon Chemicals Corp.	16.1	0.970
6	Ethylene glycol dipelargonate	None	Exptl. sample	...	0.932
7	Triethylene glycol dipelargonate	None	Same	...	0.963
8	Methyl Cellosolve acetyl ricinoleate	KP-120 plasticizer P-4C plasticizer	Ohio-Apex Inc. Baker Castor Oil Co.	68.9	0.970
9	Methyl acetyl ricinoleate	P-4 plasticizer	Baker Castor Oil Co.	23.1	0.938
10	Ethyl acetyl ricinoleate	P-5 plasticizer	Same		0.931
11	Butyl acetyl ricinoleate	P-6 plasticizer	Same	35.3	0.929
12	Acetylated castor oil	P-8 plasticizer	Same	271	0.964
13	Acetylated polymerized castor oil	P-9 plasticizer	Same	457	0.961
14	Methyl ester of polymerized ricinoleic acids	P-11 plasticizer	Same	29.4	0.930
15	Methyl ester of acetylated polymerized ricinoleic acids	P-14 plasticizer	Same	27.6	0.931
16	Butyl ester of acetylated polymerized ricinoleic acids	P-16 plasticizer	Same	29.8	0.922
17	Glycol oxopentanoate	S-454 plasticizer	Glyco Products Co., Inc.	54.1	1.113
18	Di-2-ethyl hexyl fumarate	None	Exptl. sample	24.4	0.941
19	Di-2-ethyl hexyl acetyl malate	None	Same	42.0	0.981
20	Dibutyl Cellosolve sebacate	None	Same	18.2	0.972
21	Tri-2-ethyl butyl ester of tricarboxymethylamine	None	Same	...	0.982
22	Tri-2-ethyl hexyl ester of tricarboxymethylamine	None	None	...	0.963
23	Di 2-ethyl hexyl ester of 2,3-dicarboxy $\Delta^{5,6}$-norcamphene	None	Same	86.7	0.993
24	Di-2-ethylhexyl ester of 2,3-di-carboxynorcamphane	None	Same	81.0	1.051
25	Di-2-ethyl hexyl-$\Delta^{4,5}$-tetrahydrophthalate	None	Same	45.7	0.967
26	Dicapryl phthalate	None	Resinous Products and Chemicals Co., Inc.; Amecco Chemicals, Inc.	69.1	0.970
27	Di-2-ethyl hexyl phthalate	Flexol plasticizer DOP	Carbide & Carbon Chemicals Corp.	81.1	0.984
28	Dimethyl Cellosolve phthalate	Methox	Ohio-Apex, Inc.	53.3	1.17
29	Dibutyl Cellosolve phthalate	Kronisol plasticizer	Same	32.4	1.063
30	Methyl phthalyl ethyl glycolate	Santicizer plasticizer M-17	Monsanto Chemical Co.	185	1.227
31	Butyl phthalyl butyl glycolate	Santicizer plasticizer B-16	Same	64.9	1.103
32	Di(chloroethoxy ethyl) phthalate	Flexol plasticizer 2GCP	Carbide & Carbon Chemicals Corp.	312	1.274
33	Tributyl glycerol triphthalate	None	American Cyanamid & Chemical Corp.	110	1.101
34	Mixed phthalic and fatty acid esters	KP-150 plasticizer	Ohio-Apex Inc.	11.8	0.955
35	Mixed phthalic and fatty acid esters	KP-61 plasticizer	Same	12.7	1.010
36	Tri-2-ethyl hexyl phosphate	None	Exptl. sample	13.8	0.925
37	Tributyl Cellosolve phosphate	KP-140 plasticizer	Ohio-Apex Inc.	20.1	1.022
38	Tricresyl phosphate	Kronitex AA plasticizer Lindol plasticizer None	Same Celanese Celluloid Corp. Monsanto Chemical Co.	120	1.165
39	Aromatic phosphate	M-179 plasticizer	Celanese Celluloid Corp.	124	1.155
40	Aromatic phosphate	M-142 Celluflex plasticizer	Same	500	1.120
41	Isopropylated *o*-tolyl phosphate[c]	M-180 plasticizer	Same		1.084
42	*N*-*n*-butylbenzene sulfonamide	Santicizer plasticizer 127	Monsanto Chemical Co.	162	1.148
43	Coal tar oil	Bardol plasticizer	Barrett Div., Allied Chem. and Dye Corp.	25.0	1.11
44	....	SC plasticizer	E. F. Drew & Co., Inc.	16.5	0.971
45	Pine tar	None	Wishnick-Tumpeer, Inc.	...	...
46	Methylamyldihexylcyclohexenone	C-24 plasticizer	Resinous Products & Chemicals Co.	70.6	0.879

[a] Pilot plant products.
[b] Kinematic viscosity in centistokes.
[c] Not available commercially.

Table II. Properties of Compounds with Varying Amounts of Single Plasticizers

No.	Plasticizer	% by Weight	% Elongation			% Lost in 10 Days from 0.004-In. Film			Heat Stability, Hr. at 160° C.	Flex Temp., ° C.	Sweat-Out
			10° C.	25° C.	40° C.	Air, 60° C.	Water, 25° C.	Oil, 25° C.			
1	Methyl cyclohexyl lactate[a]	30	19	48	127	11.0	3.8	2.5	9.0	+6.0	No
		35	10	42	123	7.8	1.5	1.7	6.0	+1.0	No
		40	21	67	159	12.6	2.9	2.8	9.0	−1.0	No
2	Methyl cyclohexyl stearate	Incompatible									
3	Methyl pentachlorostearate	30	12	43	112	0.6	....	2.8	1.0	−0.5	No
		35	22	63	150	0.4	0.5	4.7	0.5	−4.0	No
		40	45	103	200	0.4	0.4	10.1	0.5	−19.0	No
		39.6	44	100	196	0.4	0.4	9.5	0.5	−14.5	No
4	Methyl Cellosolve oleate	Incompatible									
5	Triethylene glycol di-2-ethyl hexoate	30	48	88	159	8.4	2.0	15.3	4.0	−31.5	No
		35	81	135	225	10.1	2.6	21.2	5.0	−44.5	No
		40	118	175	289	6.2	2.7	26.4	5.0	−58.0	Yes
		31.2	55	100	175	8.4	2.0	17.2	4.5	−34.5	No
6	Ethylene glycol dipelargonate	30	54	98	170	12.5	1.4	21.2	8.0	....	No
		35	97	130	224	12.8	1.3	25.5	8.0	....	No
		40	135	170	265	15.9	1.8	29.4	8.0	....	No
		30.4	56	100	175	12.5	1.4	21.5	8.0	....	No
7	Triethyleneglycol dipelargonate	30	55	99	169	2.3	1.4	19.5	8.0	−37.5	No
		35	91	140	235	2.7	1.9	24.8	8.0	−52.0	No
		40	124	182	279	2.1	3.0	29.4	8.0	−68.0	No
		30.1	56	100	171	2.3	1.4	19.8	8.0	−38.0	No
8	Methyl Cellosolve acetyl ricinoleate	30	40	81	151	2.8	0.8	11.5	1.5	−23.0	No
		35	69	120	198	2.2	1.6	16.9	1.5	−37.0	No
		40	109	178	290	2.2	2.2	22.3	1.5	−49.5	No
		32.6	54	100	172	2.4	1.3	14.5	1.5	−30.5	No
9	Methyl acetyl ricinoleate	30	35	80	165	8.9	8.8	9.9	1.0	−23.0	No
		35	82	145	239	8.7	12.1	14.5	1.0	−38.0	No
		40	108	182	285	11.2	11.6	20.4	1.0	−48.0	Yes
		31.3	50	100	186	8.8	9.6	11.0	1.0	−28.3	No
10	Ethyl acetyl ricinoleate	30	32	72	127	7.4	5.7	16.0	5.0	−20.0	Yes
		35	59	108	180	5.9	5.1	22.5	5.0	−41.5	Yes
		40	94	157	237	7.6	5.8	30.7	5.0	−52.5	Yes
		34.1	53	100	168	7.1	5.6	21.0	5.0	−38.5	Yes
11	Butyl acetyl ricinoleate	30	28	71	127	[b]			1.0	−33.5	Yes
		35	58	103	168				4.0	....	Yes
		40	100	175	269				4.0	....	Yes
		34.6	55	100	164				4.0	....	Yes
12	Acetylated castor oil	Incompatible									
13	Acetylated polymerized castor oil	Incompatible									
14	Methyl ester of polymerized ricinoleic acids	Incompatible									
15	Methyl ester of acetylated polymerized ricinoleic acids	30	18	50	116	6.5	4.0	10.0	0.5	−8.5	Yes
		35	41	85	152	8.9	6.4	12.8	0.5	−18.0	Yes
		40	85	140	226	7.1	6.7	19.4	0.5	−33.5	Yes
		36.4	52	100	170	8.2	6.6	14.6	0.5	−21.5	Yes
16	Butyl ester of acetylated polymerized ricinoleic acids	30	25	63	128	6.0	3.4	13.0	1.0	−31.5	Yes
		35	60	101	168	11.3	4.7	16.2	1.0	−34.5	Yes
		40	98	155	231	10.2	5.5	22.2	1.0	−44.0	Yes
		34.8	58	100	166	10.9	4.6	16.1	1.0	−34.0	Yes
17	Glycol oxopentanoate	Incompatible									
18	Di-2-ethyl hexyl fumerate	30	28	79	121	7.1	0.7	12.8	9.0	−25.0	No
		35	59	104	184	9.6	1.0	19.7	8.0	−43.5	Yes
		40	75	132	233	10.3	0.9	26.3	8.0	−50.0	Yes
		34.1	55	100	182	9.4	1.0	18.1	8.0	−42.5	Yes
19	Di-2-ethyl hexyl acetyl malate	30	35	72	145	....	....	....	9.0	−18.0	No
		35	64	122	208	2.6	0.3	13.5	10.0	−29.5	No
		40	115	198	278	3.2	0.3	17.6	10.0	−41.5	No
		33.3	50	100	186	....	....	....	9.5	−26.0	No
20	Dibutyl Cellosolve sebacate	30	58	108	179	1.5	2.0	22.3	5.0	−39.5	No
		35	79	135	202	2.0	3.5	21.5	3.5	−46.0	No
		40	128	198	302	2.5	3.3	24.0	3.5	−56.0	No
		30.5	57	100	174	1.6	2.1	22.2	5.0	−37.0	No
21	Tri-2-ethyl butyl ester of tricarboxymethylamine	30	52	102	170	2.4	1.1	12.8	2.0	....	No
		35	78	138	220	2.2	1.8	20.4	2.0	....	No
		40	95	153	230	2.6	1.5	17.7	2.0	....	No
		30.0	51	100	170	2.4	1.1	12.8	2.0	....	No
22	Tri-2-ethyl hexyl ester of tricarboxy methylamine	30	22	68	115	1.6	1.2	10.6	2.0	−12.5	No
		35	50	98	163	2.0	1.3	22.1	2.0	−29.0	No
		40	84	145	233	1.8	1.4	27.1	2.0	−41.5	No
		35.1	50	100	165	2.0	1.3	22.5	2.0	−29.0	No
23	Di-2-ethyl hexyl ester of 2,3-dicarboxy-$\Delta^{5,6}$-norcamphene	30	30	77	145	5.6	0.7	8.5	6.0	−16.0	No
		35	57	118	215	6.6	1.2	16.6	7.0	−29.0	No
		40	104	172	278	13.3	1.4	23.2	8.0	−37.0	No
		33	45	100	190	5.8	1.0	13.6	6.5	−24.3	No
24	Di-2-ethyl hexyl ester of 2,3-dicarboxynorcamphane	30	21	55	119	2.1	0.1	7.8	10.0	−6.0	No
		35	58	98	175	1.4	0.2	20.2		−23.0	No
		40	74	142	232	2.2	0.1	28.1	8.0	−34.0	No
		35.1	60	100	175	2.0	0.2	20.4		−23.0	No
25	Di-2-ethyl hexyl-$\Delta^{4,5}$-tetrahydrophthalate	30	31	80	150	2.2	0.1	8.8	6.0	−19.5	No
		35	60	128	197	2.0	0.1	19.1	6.0	−25.5	No
		40	109	172	250	3.1	0.1	17.3	6.0	−43.5	No
		32.3	43	100	171	2.1	0.1	10.5	6.0	−21.5	No
26	Dicapryl phthalate	30	20	54	116	1.0	0.1	6.9	8.0	−7.5	No
		35	50	95	181	1.4	0.2	15.4	7.0	−21.0	No
		40	81	150	249	1.1	0.4	27.9	7.5	−31.0	No
		35.6	53	100	189	1.2	0.2	16.9	7.5	−22.0	No

TABLE II (*Continued*)

No.	Plasticizer	% by Weight	% Elongation			% Lost in 10 Days from 0.004-In. Film			Heat Stability, Hr. at 160° C.	Flex Temp., ° C.	Sweat-Out
			10° C.	25° C.	40° C.	Air, 60° C.	Water, 25° C.	Oil, 25° C.			
27	Di-2-ethyl hexyl phthalate	30	29	70	149	0.7	0.3	5.3	8.0	−10.5	No
		35	57	115	208	0.8	0.2	10.0	10.0	−19.5	No
		40	100	175	288	1.4	0.2	16.5	10.0	−34.5	No
		33.5	47	100	187	0.7	0.3	8.2	9.5	−16.0	No
28	Dimethyl Cellosolve phthalate	30	35	95	192	6.4	4.4	3.2	6.0	− 1.0	No
		35	75	145	265	10.3	11.4	9.0	6.0	−15.1	No
		40	110	205	345	10.7	19.2	17.6	6.0	−25.7	No
		30.5	44	100	200	6.6	4.6	3.7	6.0	− 1.0	No
29	Dibutyl Cellosolve phthalate	30	32	90	171	2.1	4.8	7.3	5.0	−12.7	No
		35	68	135	258	2.0	4.9	14.7	3.0	−22.1	No
		40	117	210	338	..	5.2	18.5	2.0	−33.4	No
		31.3	42	100	193	2.1	4.8	11.4	4.5	−15.0	No
30	Methyl phthalyl ethyl glycolate	30	11	67	147	15.2	2.4	2.6	4.0	+ 1.5	No
		35	38	104	217	17.7	6.5	6.2	4.0	− 7.5	Yes
		40	73	152	278	20.4	10.2	10.1	4.0	−15.0	Yes
		34.6	36	100	215	17.5	6.1	5.9	4.0	− 7.0	Yes
31	Butyl phthalyl butyl glycolate	30	28	89	180	3.5	1.7	3.0	3.0	− 2.0	No
		35	68	138	262	2.8	1.6	10.7	4.0	−13.0	No
		40	120	215	361	3.7	1.9	14.0	4.0	−25.0	No
		31.5	38	100	201	3.3	1.7	4.3	3.5	− 5.0	No
32	Di(chloroethoxy ethyl) phthalate	30	12	50	125	1.2	2.6	2.1	5.0	+ 7.5	No
		35	29	72	150	2.0	6.5	5.5	3.0	− 8.5	Yes
		40	51	103	187	4.4	12.0	8.1	3.0	−13.5	Yes
		39.7	50	100	185	4.1	11.6	8.0	3.0	−13.5	Yes
33	Tributyl glycerol triphthalate	30	11	57	150	14.6	2.0	3.1	8.0	+ 1.0	No
		35	48	114	218	19.2	3.4	7.4	8.0	− 8.5	No
		40	80	172	322	22.8	3.9	15.2	8.0	−20.5	No
		34.0	43	100	204	18.5	3.2	6.2	8.0	− 7.0	No
34	Mixed phthalic and fatty acid esters (KP-150)	30	44	99	188	16.9	1.2	12.5	5.0	−22.0	No
		35	86	178	282	18.6	1.2	17.0	5.0	−41.5	No
		40	128	228	345	22.0	1.9	25.5	5.0	−52.0	No
		30.1	46	100	188	16.9	1.2	12.5	5.0	−23.0	No
35	Mixed phthalic and fatty acid esters (KP-61)	30	47	92	155	10.3	3.5	9.8	7.0	−21.0	No
		35	81	143	235	13.4	2.8	22.5	7.0	−40.0	No
		40	128	199	335	20.3	3.4	26.1	7.0	−47.5	No
		30.9	53	100	168	10.4	3.3	13.0	7.0	−25.5	No
36	Tri-2-ethyl hexyl phosphate	30	38	80	152	1.9	0.3	16.3	3.0	−41.0	No
		35	70	128	208	2.5	0.4	23.0	3.0	−55.0	No
		40	124	189	271	3.6	0.4	29.3	3.0	−62.0	No
		32.3	50	100	178	2.2	0.3	19.5	3.0	−49.5	No
37	Tributyl Cellosolve phosphate	30	53	105	195	1.1	14.5	13.9	0.5	...	No
		35	105	179	278	1.2	20.0	21.4	0.5	−39.5	No
		40	162	248	370	1.5	23.9	25.0	0.5	−53.0	No
		29.5	54	100	185	1.1	14.2	13.5	0.5	−25.0	No
38	Tricresyl phosphate	30	10	45	148	0.2	0.1	0.4	1.5	+13.0	No
		35	19	95	211	0.5	0.9	1.4	1.5	+ 5.0	No
		40	49	156	320	0.6	2.1	4.2	1.5	− 6.0	No
		35.3	20	100	218	0.5	1.0	1.5	1.5	+ 4.2	No
39	Aromatic phosphate (M-179)	30	10	29	118	1.3	0.5	0.3	1.0	+12.0	No
		35	18	75	171	2.0	2.1	1.2	1 0	0.0	No
		40	52	130	253	1.3	1.9	5.5	1.0	− 8.0	No
		37.4	33	100	206	1.7	2.0	3.8	1.0	− 4.3	No
40	Aromatic phosphate (M-142)	30	11	19	87	1.0	0.5	0.6	1.0	+15.5	No
		35	11	60	165	0.9	0.7	0.3	1.0	+ 5.5	No
		40	28	111	238	0.6	0.9	1.5	1.0	− 2.0	No
		39.0	25	100	224	0.8	0.9	1.1	1.0	− 1.0	No
41	Isopropylated *o*-tolyl phosphate (M-180)	30	11	12	68	1.5	0.2	0.5	1.0	+19.5	No
		35	12	21	115	1.8	0.3	0.8	1.0	+11.0	No
42	*N*-*n*-butylbenzene sulfonamide	30	14	62	148	18.6	6.7	5.0	2.0	− 0.5	No
		35	31	87	175	25.4	12.0	9.6	2.0	−10.5	No
		40	60	127	250	23.3	20.3	17.7	1.0	−21.0	No
		36.8	40	100	197	23.9	13.9	11.2	2.0	−14.0	No
43	Coal tar oil	35	8	9	179	4.8	....	....	....	+15.0	No
		40	8	86	295	11.3	....	....	....	+ 5.0	Yes
44	SC plasticizer	30	72	117	188	5.1	8.8	20.0	5.0	−39.0	Yes
		35	96	153	251	4.7	9.1	25.0	5.0	−52.0	Yes
		40	143	209	310	4.8	11.4	30.0	5.0	−62.5	Yes
		29.3	54	100	177	4.1	8.2	20.0	5.0	−36.0	Yes
46	Methylamyldihexylcyclohexenone	Incompatible									

[a] Volatility so high that concentration was much lower than specified.
[b] Too incompatible to calender.

SPECIFIC GRAVITY AND VISCOSITY

Where available, the specific gravity was taken from data furnished by the supplier; otherwise it was determined by a hydrometer or pycnometer. Viscosity was determined by a Saybolt Universal viscometer at 20° C. and in most instances also at 1° and at 40° C. Results were converted to centipoises by the equation (*4*):

$$\text{cp.} = \left(0.0022\,t - \frac{1.8}{t}\right)(100\ d)$$

where t = time, seconds; d = specific gravity

COMPATIBILITY

Since variations in gloss of the various sheets obscured the appearance of liquid exudate or waxy surface, a more sensitive test for incompatibility was required. The sheet was laid on a flat surface and a clean cigaret paper was drawn across the sheet under the pressure of the finger. If any evidence of oil showed on the paper or if any bloom was apparent, the sheet was recorded as having a positive sweat-out.

Some of these materials with limited compatibility, nevertheless, impart very desirable properties to copolymer vinyl resins when used as extenders for more compatible liquids. In order to evaluate these incompatible liquids, 10, 15, and 20 parts were combined with 20 parts of tricresyl phosphate and used in the same resin composition employed with the more compatible plasticizers. In general, the properties obtained with these mixtures deviated in a normal manner from these obtained with tricresyl phosphate alone.

These plasticizers with limited compatibility may also be combined with other plasticizers, but tricresyl phosphate was used because it is usually employed when a low burning rate is essential; since it is a common plasticizer for these resins, it serves as a basis for comparison.

HEAT STABILITY

Long periods of heating at high temperatures produce a darkening of the resin. While this discoloration is not always detrimental, it serves as a danger signal to warn of more serious degradation coincident with the liberation of acid and loss of plasticity which eventually follows discoloration. Pieces approximately 0.75 inch square were placed on thin aluminum strips and heated in an oven at 160° C. until a dark brown or dark gray color developed. The time for darkening is listed in Tables II and III and may be regarded as roughly indicative of the effect of these plasticizers on the tendency of the plasticized compound to discolor during processing.

ELONGATION AND EFFECTIVENESS

Elongation tests were made on an autographic stress-strain tester similar to the one described by Williams and Sturgis (*10*). The application of this machine to the measurement of vinyl elastomers was discussed by the author (*6*) in a previous publication. The tester is of the constant-rate-of-loading type, applying a load of 1000 pounds per square inch in 74 seconds. Specimens 4.75 × 0.25 × 0.020–0.025 inch were stretched under water which was maintained at the specified temperature, ±0.2° C. Elongations were measured at 10°, 25°, and 40° C. and plotted against temperature and against plasticizer concentration.

The relative efficiency of several plasticizers in converting rigid vinyl copolymer resin to elastomeric compounds may be demonstrated by a comparison of the elongations of batches containing a like amount of different plasticizers. For example, those materials (Table II) which yield the highest elongations at 25° C. when used in 35 per cent concentration have the highest plasticizing efficiency under those conditions. Since the amount of plasticizer used in any technical compound is based on the amount required to achieve the desired properties rather than on any preconceived stipulation regarding the composition, it seems more advantageous to compare the amounts of different modifiers required to obtain a standard flexibility. For materials of this type, extensibility at constant load is an accurate measure of flexibility, and in this study an elongation of 100 per cent at 25° C. with a load of 1000 pounds per square inch was chosen as the standard flexibility. The amount of plasticizer required to yield this elongation is shown in Tables II and III. This is approximately the median range of the commercial vinyl elastomeric compounds and serves as a convenient reference point. The smaller the amount required to yield 100 per cent elongation, the more efficient is the plasticizer.

The objective in this investigation was to answer two questions relative to a group of materials suggested as ingredients in vinyl elastomers: (1) How much of a given plasticizer is required to produce a standard flexibility? (2) What are the properties of a compound so formulated? Since our interest is not confined to compositions with only one degree of flexibility, the properties of the compounds with 30, 35, and 40 per cent plasticizer are included in Table II along with those having the standard flexibility as determined by graphical interpolation.

Since copolymer vinyl elastomers are thermoplastic materials, they are much more sensitive to temperature than butadiene copolymers and rubber, and the type of plasticizer has a great effect on the way the stiffness of vinyl elastomers varies with temperature changes. For this reason it cannot be assumed that if one compound has adequate cold flexibility, another compound with the same stiffness at room temperature will also be sufficiently flexible when cold. Approximately 35 per cent of either dicapryl phthalate or of tricresyl phosphate yields an elongation of 100 per cent at 25° C. However, at 10° C. these compounds show elongations of 53 and 20 per cent, respectively. Likewise, the flex temperature for the former is −22° C. and for the latter is +4° C. The minimum temperature at which these materials could be bent slowly without shattering would also be interesting, but that property was not studied. Increased amounts of plasticizer improve flexibility at low temperatures but with some sacrifice in tensile strength and stiffness at room temperature and above.

LOW-TEMPERATURE FLEXIBILITY

The instrument used for this work was described by Clash and Berg (*2*). It consists of a device for applying a torsional stress to a rectangular strip immersed in a coolant and measuring the amount of deflection. The flex temperature is defined as the temperature at which a specimen 0.25 × 0.040 inch in cross section mounted in clamps 1.5 inches apart will yield a rotation of 200° of arc when a torque of 5.68×10^5 dyne-cm. is applied for 5 seconds. This is an empirical definition of the lower temperature limit of the elastomeric range.

On account of the difficulty encountered in accurately measuring elongation at low temperatures, this torsional method was employed. It is apparent from Tables II and III that this test does not parallel the elongation test. Thus it may be concluded that the decrease in flexibility from 25° to 10° C. is not a satisfactory index of the lowest temperature at which a compound will remain flexible. It is characteristic of some plasticizers that they produce compounds which show a sharp decrease in flexibility with temperature decrease at some range below 0° C. In the case of a material which must be used at very low temperatures, there is no alternative to making a trial compound and testing it at this temperature, and for this work the flex temperature test has been useful. The data in the tables may be used to select those plasticizers most likely to produce elastomers which will exhibit the desired low-temperature flexibility behavior.

VOLATILITY

This property is subject to erroneous interpretation if factors such as plasticizer-resin attraction, rate of diffusion, and plasticizer concentration are neglected. Several types of ovens were tried and found to be unsatisfactory because of lack of temperature uniformity or inadequate ventilation. The requirements for ventilation were then calculated from the best data available on vapor pressure and rate of volatilization from film with a volatile plasticizer and with one that was relatively nonvolatile. The amount of air required to ensure a low vaporized plasticizer concentration was surprising.

Assuming that a plasticizer has a vapor pressure of 1.6×10^{-5} mm. of mercury at 60° C. and evaporates at a rate of 10.84 mg. per square meter per hour from a film (based on the area of one side of the sheet), 1.56 minutes would be required for one square meter of film to saturate one cubic meter of air. It was assumed that the plasticizer vapor must be kept

Table III. Properties of Compounds with 20 Per Cent Tricresyl Phosphate and Varying Amounts of Other Plasticizers

No.	Plasticizer	% by Weight	% Elongation			% Lost in 10 Days from 0.004-In. Film			Heat Stability, Hr. at 160° C.	Flex Temp., ° C.	Sweat-Out
			10° C.	25° C.	40° C.	Air, 60° C.	Water, 25° C.	Oil, 25° C.			
2	Methyl cyclohexyl stearate	10	17	51	120	2.2	2.1	3.3	1.0	0.0	Yes
		15	25	71	150	2.7	3.1	6.4	1.0	− 5.0	Yes
		20	38	88	175	2.1	3.0	10.5	1.0	−14.0	Yes
		23.0	49	100	193	2.6	3.6	13.0	1.0	−21.0	Yes
4	Methyl Cellosolve oleate	10	28	75	148	3.8	2.1	9.1	1.0	− 8.5	No
		15	67	130	238	3.5	3.4	12.0	2.0	−23.5	No
		20	112	194	302	3.2	3.8	16.0	2.0	−32.0	No
		12.6	50	100	200	3.6	3.0	10.3	1.5	−18.0	No
5	Triethylene glycol di-2-ethyl hexoate	10	27	74	139	3.0	2.7	4.5	1.0	− 7.5	No
		15	60	125	205	2.6	3.7	15.7	1.0	−18.5	No
		20	109	199	312	3.2	4.5	17.8	1.0	−27.5	No
		13.0	47	100	175	2.7	3.3	12.7	1.0	−15.0	No
9	Methyl acetyl ricinoleate	10	29	70	140	3.0	2.7	4.8	1.0	− 6.5	Yes
		15	63	117	223	3.9	2.6	9.8	3.0	−20.5	Yes
		20	110	178	287	3.3	2.9	15.3	2.0	−35.0	Yes
		13.3	48	100	193	3.3	2.7	7.2	2.0	−15.5	Yes
10	Ethyl acetyl ricinoleate	10	25	73	150	2.7	2.6	4.2	2.0	− 3.5	No
		15	58	120	220	4.5	2.4	10.6	2.0	−22.0	No
		20	104	168	305	4.1	3.0	14.9	2.0	−37.0	No
		13	44	100	191	3.6	2.6	7.8	2.0	−14.5	No
11	Butyl acetyl ricinoleate	10	16	53	123	1.3	2.2	3.4	1.0	− 2.0	No
		15	48	108	189	1.9	2.6	9.3	1.0	−20.5	No
		20	97	177	292	2.4	2.9	18.0	2.0	−31.5	Yes
		14.4	44	100	177	1.8	2.5	8.4	1.0	−18.5	No
12	Acetylated castor oil	10	12	45	116	1.3	1.5	2.1	2.0	+ 1.0	No
		15	28	78	160	1.5	2.4	5.9	3.0	−12.0	No
		20	60	115	209	1.3	2.6	13.5	3.0	−25.5	No
		18.0	46	100	189	1.4	2.5	9.5	3.0	−20.0	No
13	Acetylated polymerized castor oil	10	12	29	118	1.2	0.8	0.7	3.0	+ 9.0	No
		15	18	65	158	1.1	2.1	3.0	3.0	− 4.5	No
		20	40	110	205	1.7	3.0	13.8	4.0	−19.0	No
		18.8	34	100	195	1.5	2.8	9.4	3.0	−15.5	No
14	Methyl ester of polymerized ricinoleic acids	10	13	51	124	2.0	2.3	3.0	2.0	− 4.0	No
		15	47	98	195	4.4	3.7	9.8	2.0	−17.5	No
		20	68	130	250	6.0	5.3	15.3	2.5	−29.0	Yes
		15.1	47	100	196	4.4	3.7	10.0	2.0	−17.5	No
15	Methyl ester of acetylated polymerized ricinoleic acids	10	21	63	140	2.7	1.9	4.0	2.0	− 9.0	No
		15	48	107	207	3.7	2.5	10.3	2.0	−25.5	No
		20	96	181	305	4.1	3.0	18.8	3.0	−36.5	No
		14.4	45	100	199	3.6	2.4	9.5	2.0	−23.5	No
16	Butyl ester of acetylated polymerized ricinoleic acids	10	18	60	137	1.5	2.0	3.2	2.0	− 3.5	No
		15	56	112	221	2.9	2.9	8.3	2.0	−21.0	No
		20	95	162	282	3.1	2.6	13.8	2.0	−36.5	No
		13.7	46	100	204	2.7	2.7	6.9	2.0	−16.5	No
17	Glycol oxopentanoate	10	25	69	155	4.1	3.7	3.2	2.0	− 1.0	No
		15	58	118	220	4.6	8.8	8.9	2.0	−14.0	No
		20	91	165	282	5.1	15.3	17.3	2.0	−27.5	Yes
		13.4	47	100	196	4.5	7.2	7.9	2.0	− 9.0	No
25	Di-2-ethyl hexyl-$\Delta^{4,5}$-tetrahydrophthalate	10	12	60	138	2.5	1.4	1.9	0.5	+ 5.0	No
		15	43	110	204	2.7	1.9	6.3	0.5	−12.0	No
		20	87	179	293	3.7	1.7	14.9	0.5	−26.5	No
		14.2	36	100	192	2.6	1.8	5.5	0.5	−10.3	No
27	Di-2-ethyl hexyl phthalate	10	11	58	133	1.5	1.3	1.0	0.5	− 2.5	No
		15	41	108	197	1.6	1.6	6.9	0.5	−11.5	No
		20	82	170	275	2.4	2.2	15.2	0.5	−35.0	No
		14.2	35	100	182	1.6	1.6	5.8	0.5	− 9.0	No
43	Coal tar oil	20	38	118	263	9.7	2.7	2.4	...	0.0	No
44	SC plasticizer	10	22	68	158	6.6	2.3	2.8	3.0	+ 2.0	No
		15	41	93	198	7.8	6.1	6.5	3.0	−10.0	No
		20	72	138	248	7.7	11.9	11.7	3.0	−23.5	Yes
		16.2	46	100	205	7.8	7.3	7.3	3.0	−13.5	No
45	Pine tar	10	14	12	98	4.5	1.1	1.1	...	+21.0	No
		15	13	35	150	8.5	2.4	1.2	...	+14.0	No
		20	12	58	174	8.1	....	....	...	+ 8.0	No
46	Methylamyldihexylcyclohexenone	10	11	57	122	2.2	1.6	1.9	1.0	+ 3.0	No
		15	38	102	192	3.0	1.9	7.3	2.0	− 9.5	No
		20	71	139	253	3.9	2.3	15.9	2.0	−25.5	No
		14.8	36	100	188	2.9	1.9	7.2	2.0	− 8.8	No

below 20 per cent saturation to prevent volatile plasticizers from being absorbed by films containing less volatile plasticizers. Ten 3.5-inch (8.89-cm.) disks would require 13.2 cubic feet (0.37 cubic meter) of air per minute to keep the vapor concentration below this level. Experiments carried out in an ordinary type of laboratory oven actually showed a weight loss for some specimens and a gain for other specimens placed in the oven at the same time. With the present oven no weight gains have been encountered.

The oven used for the volatility tests in this study is shown in Figure 1.

It consists of twelve cells or individual ovens in which the samples are held, a radiator, a blower, a plenum chamber with one tube to each cell and a flue for removal of the hot air to the outside. Each cell is 12 inches square in horizontal plan and 12 inches high from the screen to the top of the partitions. The whole oven is insulated with soft pulp board one inch thick, except for the sliding doors on the cells. Each cell is provided with three rods on which samples may be hung. Each rod has six notches to accommodate the sample hangers and to prevent the samples from shifting. A spreader holds each sample so that it will not fold and reduce air contact. Twelve disks, 3.5 inches in diameter, may be suspended in each cell, or six larger samples may be suspended using only the center rod. In this work not more than ten disks were used in any one cell.

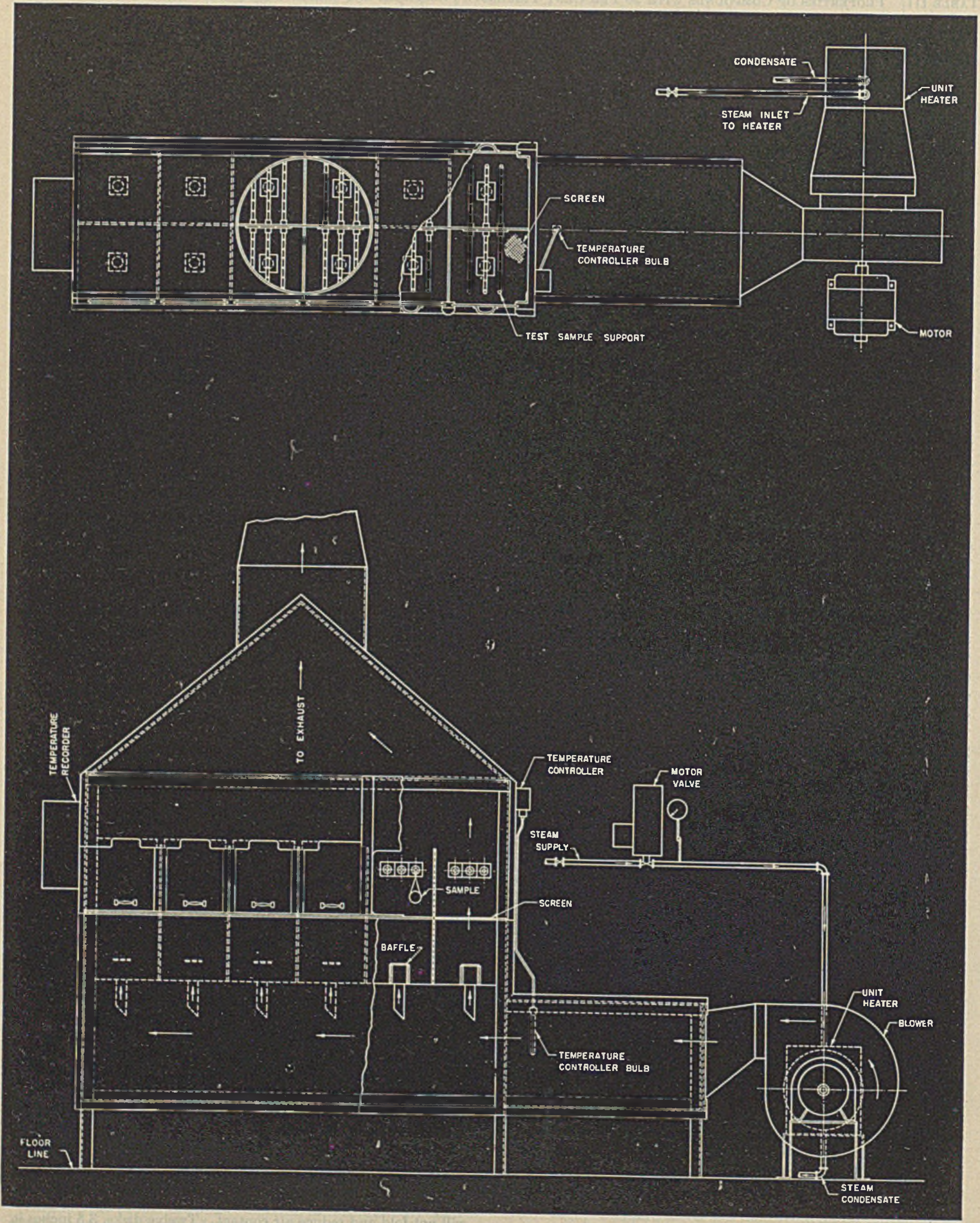

Figure 1. Top and Side Views of the Oven Used for the Volatility Tests

One re-entrant tube for each cell was adopted as a means of maintaining a positive pressure in the plenum chamber and of equalizing the flow to all cells. These conditions were checked, and the behavior of all cells was balanced before the tests were started. A steam pressure regulator reduces the line pressure to a value slightly greater than required, and the final regulation is accomplished by means of an electrically actuated thermoregulator with a bulb located near the blower outlet.

A steam pressure of approximately 40 pounds per square inch is required in the unit heater when the room temperature is 25° C. and the oven is maintained at 60° C. A recording potentiometer is provided with a thermocouple junction in each cell and a switch enables selecting any one of the cells for a record. The temperature is easily maintained within 1° of the desired value. The upper limit of temperature is approximately 50° above room temperature, using an air velocity of 20 feet per minute across the specimens or 240 cubic feet per minute through the entire oven. The air velocity was fixed by a damper ahead of the unit heater.

Duplicate disks, 3.5 inches in diameter and 0.003–0.006 inch thick, were suspended on the racks for 10 days at 60° ± 1° C. The disks were weighed before being placed in the oven and were put into a desiccator on removal from the oven and weighed within 24 hours. Results were calculated in per cent weight loss based on the original weight and then corrected for thickness as described above.

The upper limit of volatility permissible for plasticizers in vinyl copolymer resins depends on the application in question. Articles of clothing, curtains, and other objects fabricated from thin films present a large surface for the escape of volatile constituents, yet they must maintain flexibility over an extended period. Plasticizers for these applications must have a low rate of volatile loss. The requirements for metal-covered cable, for instance, would be less rigid.

A word of caution at this point is in order. A loss of one per cent in 10 days does not necessarily mean that, on continued exposure, this rate of loss would be maintained. In some cases a plasticizer has a small fraction of very volatile material which is lost rapidly, after which the rate of loss is greatly diminished. There is also some evidence that the thermal abuse encountered in mixing, calendering, or extruding converts a small part of some esters to more volatile compounds. While very small differences in volatility as shown by this method may not be substantiated in practical experience, it is apparent from Tables II and III that many of the materials suggested for use in copolymer vinyl resins are far too volatile. Materials having a volatile loss greater than 3 per cent by this test have only limited applicability in these resins.

In general, the higher the boiling point of a plasticizer, the lower is the rate of volatile loss, but until more data are available, boiling range alone cannot be considered a sufficient basis for prediction of volatility from these elastomers.

Verhoek and Marshall (*9*) concluded that the vapor pressure of plasticizer in a polyvinyl chloride–trimetacresyl phosphate composition appears to be equal to the vapor pressure of the pure plasticizer for all concentrations above 15 per cent of plasticizer. Liebhafsky, Marshall, and Verhoek (*5*), however, conclude that "a plastic under our experimental conditions tends to seal itself against further loss as plasticizer disappears". These observations, based on high vacuum technique, would appear to parallel the practical experience that, when fugitive plasticizers are used, the surface of the plastic mass hardens in service more than the interior. The similarity of evaporation rates of dibutyl phthalate and tricresyl phosphate observed by Liebhafsky, Marshall, and Verhoek does not agree with practical experience with these plasticizers, which shows that dibutyl phthalate is very volatile whereas tricresyl phosphate is one of the most permanent of the commercial plasticizers.

EXTRACTIONS

One disk, 3.5 inches in diameter and 0.003–0.006 inch in thickness, was placed in an 8-ounce bottle filled with deaerated tap water and allowed to stand for 10 days at 25° ± 2° C. On removal from the water, the disk was placed in an oven at 60° C. for 3 hours to dry out any absorbed water, put into a desiccator over calcium chloride, and weighed within 24 hours. Thickness, weight loss, and per cent weight loss calculated to 0.004 inch thickness were determined in the same manner as in the volatility test. All tests were run in duplicate and the water was changed every day, Saturdays and Sundays excluded.

The amount of water used to extract the plasticizer from the film (approximately 1800 ml. per gram of specimen) was estimated to be adequate to prevent any retardation of extraction due to partial saturation of the water. The effect of more frequent water changes or of immersing the film in a stream of water so as to increase the rate of removal of the sparingly soluble plasticizer was not determined. It is believed, however, that these results, showing variations from negligible loss to almost complete extraction in 10 days, will serve to indicate those materials unsuited to uses involving frequent contact with water. In a few instances the films blushed when immersed in water, but this was observed only with plasticizers showing high extraction values.

Oil extraction was determined in a similar manner, using a water-white mineral oil with a specific gravity of 0.860 at 20° C. The oil was changed twice during the test, and at the end of the test it was washed off by quickly immersing the sheet in four rinses of petroleum ether having a distillation range of 60° to 70° C., and the disks were dried 3 hours at 60° C. The rate of extraction by mineral oil was usually more rapid than by water. The increase in rate of oil extraction with increase in plasticizer concentration was in many cases very steep. There is no close parallel between solubility of plasticizer in oil and rate of extraction by oil. Neither can it be inferred that a high rate of oil extraction is associated with a low rate of water extraction. It is significant that these plasticized films did not gain weight in mineral oil.

Results obtained by others in this laboratory show that gasoline and alcohol extract plasticizer more rapidly than does mineral oil.

EFFECT OF CHEMICAL COMPOSITION

The plasticizers in the tables are arranged according to chemical classification so as to display the effect of functional groups on behavior in vinyl resins. Few generalizations may be stated without exceptions, but several interesting trends are apparent.

The most successful plasticizers now known for copolymers of vinyl chloride and vinyl acetate are esters. The esters having low molecular weight are usually compatible and have high plasticizing efficiency but are too volatile. Aliphatic alcohols having more than eight carbon atoms usually make incompatible esters. Therefore, it is necessary to have more than one solubilizing group in the molecule to realize both low volatility and good compatibility. Polybasic acids such as sebacic, phthalic, and phosphoric produce valuable plasticizers when esterified with octyl alcohols. Hydroxy acids may be acetylated and esterified to increase the number of active groups. Dibutyl phthalate is too volatile, but butyl phthalyl butyl glycolate and dibutyl Cellosolve phthalate are sufficiently permanent for some purposes.

The esters of monobasic acids and ethylene glycol are either too volatile or are insufficiently compatible. The substitution of polyethylene glycols for monoethylene glycol increases compatibility and reduces volatility. The substitution of butoxyethanol for butanol in phthalic esters also reduces volatility but increases water extraction. Dibutyl Cellosolve phthalate has moderately low volatility but a high rate of water extraction.

Usually, plasticizers having high viscosity produce poor flexibility at low temperatures. Whether this poor flexibility is a result of high viscosity or high molecular weight cannot be adequately established on the basis of the limited number of materials available. Most substances which are solid at room temperature have a limited temperature range of flexibility in these resins. Camphor, triphenyl phosphate, and hexaethylbenzene reduce processing temperatures and act like ordinary liquid plasticizers at high temperatures but yield very low elongations at 10° C.

Phosphate esters are characterized by good flame resistance and are widely used for this reason. The aromatic phosphates also exhibit very low water extraction, moderately low oil extraction, very low volatility, and poor cold flexibility. All of the phosphates tested produced poor heat stability. The aliphatic phosphates exhibit high rates of oil extraction and good cold flexibility.

A few nonester plasticizers have been tested, but none has been satisfactory in all respects. Camphor, aromatic-aliphatic ketones, chlorinated hydrocarbons, and polymers of coumarones and indenes are useful as extenders in some applications but are not applicable where low volatility and good flexibility at low temperatures are essential. Developments in this field of plasticizers depend largely on the progress of organic chemistry to produce a plentiful supply of materials of diverse types with effective solubilizing groups at a cost comparable to esters commonly used for this purpose.

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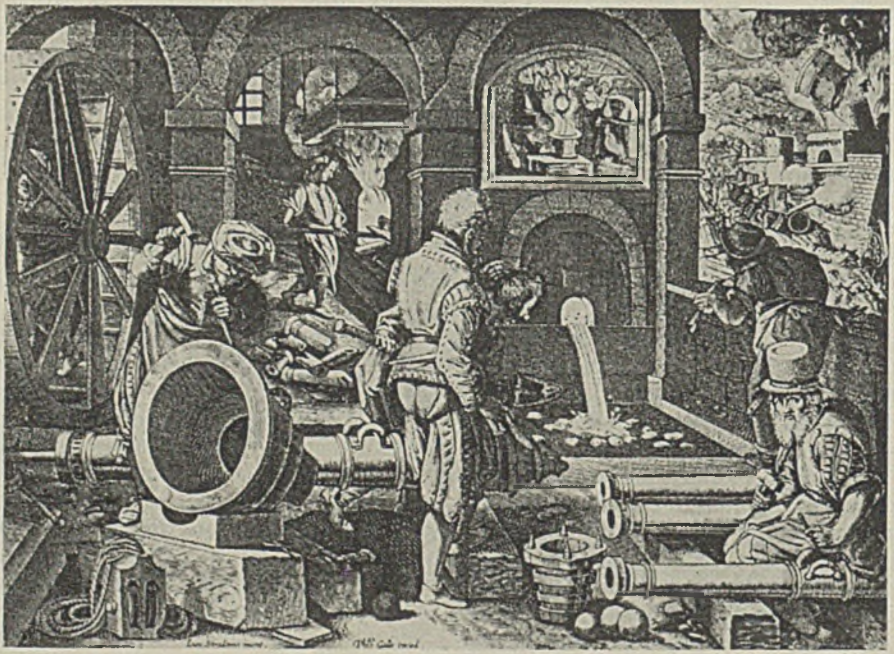
CANNON FOUNDRY

By Giovanni Stradano (1536-1605)



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Soybean-Modified Phenolic Plastics

L. L. McKINNEY[1], RUDOLPH DEANIN[2],
GLEN BABCOCK, AND A. K. SMITH
U. S. Regional Soybean Industrial Products Laboratory[3], Urbana, Ill.

The wet and dry mix methods for incorporating modified soybean meal into phenolic resins are described. The replacement of wood flour in phenolic plastics by soybean meal causes a rapid increase in flow while the addition of increasing amounts of soybean meal to constant ratios of phenolic resin and wood flour results in a gradual decrease in flow. These two effects can be balanced against each other to produce plastics having either higher flow or lower percentage of resin or both. The curing time increases with increasing content of thermoplastic soybean protein. This effect can be diminished in practice by longer periods of rolling the plastic before molding, use of paraformaldehyde accelerator, or preheating the molding powder. The water absorption of soybean-modified plastics is held within practical limits by a preliminary leaching and heat denaturation of the meal and by preparing the plastics by the wet mix instead of the dry mix method. The flexural strength varies slightly, and the impact strength decreases with increasing content of soybean meal; loss of impact strength is less for the wet method than for the dry method. Colored soybean-modified phenolics may be produced with organic dyes; they have a greater depth of color and are more stable to light than standard phenolics.

FOR several years soybean meal has been incorporated to a limited extent in phenolic plastics. When this practice was started, no data were available to show how soybean meal or protein might be expected to modify the properties of the plastic, but the practice began in the hope that the cost of the molding powder would be reduced without degrading the product. Continued research, however, has demonstrated that heat-denatured soybean meal, from which the water-soluble fraction has been removed, can be used to replace part of the resin and wood flour; this makes possible the production of plastics having greater flow, colors better in light stability than are possible with standard phenolic resins, and a lower percentage of resin without loss of moisture resistance or mechanical strength. In the present paper the methods used for making soybean-modified phenolic resins are illustrated, and the effect of the added meal on the properties of the plastic are shown. Because of the complexity of the system, there is no fundamental chemistry which will serve as a guide in this type of investigation, and the study is of necessity empirical. The formulas used are illustrative and the technique is for the specific equipment at hand. It is therefore anticipated that for commercial production some adjustment in the procedure will be necessary.

One of the disadvantages of the use of proteinaceous materials in plastics has been high water absorption and the resulting blistering, leaching, and cracking. It is now known that there are two factors in the reduction of the moisture absorption of soybean-modified phenolic plastics—namely, treatment of the meal before use and protection of the meal by phenolic resin. Leaching the meal at the isoelectric point of the protein (pH 4.0–4.6) to remove water-soluble materials, followed by heat denaturation, lowers the water absorption considerably. This method of preparing the soybean meal was adopted in the present work to replace the earlier method of treating it with formaldehyde (*3*). By this method the water absorption results are as satisfactory as for the formaldehyde method, and flow properties are better. The soybean meal used in the experimental work was approximately 50 per cent protein and 50 per cent water-insoluble material, largely carbohydrates.

MIXING METHODS

There are two general procedures for introducing the soybean meal into the plastics molding powder. The "dry mix" method is the simpler and easier to control; it consists in mechanically mixing the prepared soybean meal with the resin and wood flour. In the experimental work with the dry mix method, mixing is carried out in a ball mill followed by the calender rolls. In the "wet mix" method phenol and formaldehyde are condensed directly in the presence of soybean meal, using an alkaline catalyst, and the resulting two-stage resin is mixed with filler, lubricant, dye, and accelerator. The dry mix method is satisfactory for incorporating small amounts of soybean meal (up to 10 per cent), but it does not give the intimate combination of meal and resin obtained by the wet mix method, and the moisture resistance is less satisfactory. While the wet mix method is the more difficult to control, it offers the opportunity for using larger percentages of soybean meal and a correspondingly larger number of modifications. On the other hand, for the experimenter it complicates the calculations used in determining the amount of resin produced in the reaction, with a corresponding difficulty in estimating precisely the composition of the molding powder.

From the simplest theoretical consideration it might be expected that phenol and formaldehyde would react in the mole ratio of 1:1.5 to give 1.19 parts of resin per part of phenol by weight. In commercial practice the amount of formaldehyde combined in the phenolic resin is probably less. On the other hand, the soybean-modified plastic is improved by using 2 moles of formaldehyde, including the accelerator, per mole of phenol. Whether this is due to a reaction of formaldehyde with the soybean protein in the meal or to a modifica-

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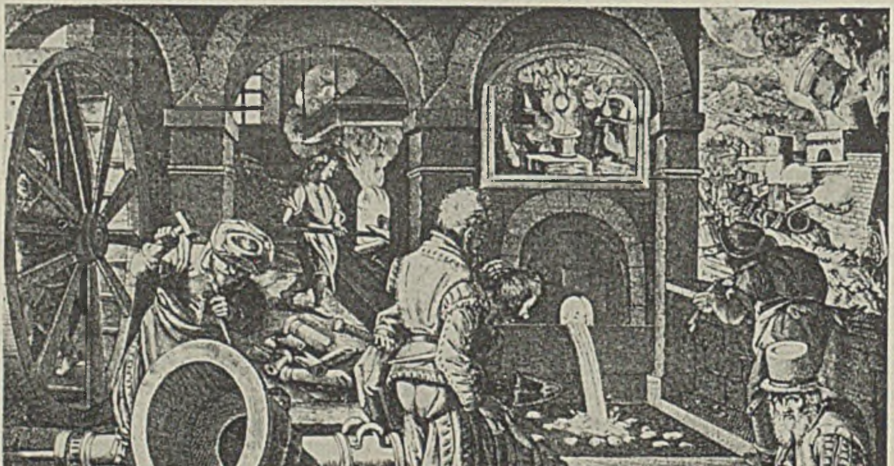

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TABLE I. BALL MILL PLASTICS SERIES

Batch No.	Composition, % Resin[a]	Wood flour[b]	Soybean meal[c]	Flow, In.[d]	Water Absorbed[e], % 24 hr.	48 hr.	Flexural Strength, Lb./Sq. In.	Impact Strength, Ft.-Lb./In.
1	50	50	..	1.10	0.48	0.60	9,200	0.37
2	50	45	5	1.08	0.48	0.63	9,000	0.32
3	50	40	10	1.33	0.68	0.92	8,800	0.32
4	50	30	20	1.60[f]	0.97	1.34	9,400	0.30
5	50	20	30	2.10[f]	1.13	1.70	10,200	0.28
6	50	10	40	1.62[f]	1.73	3.03	9,200	0.22
7	50	..	50	2.00[f]	4.20	7.91	9,600	0.22
8	45	55	..	0.40	0.48	0.68	9,000	0.37
9	45	50	5	0.40	0.57	0.80	8,700	0.37
10	45	45	10	0.45	0.73	0.92	8,800	0.28
11	45	35	20	0.65	1.05	1.88	8,600	0.26
12	45	25	30	0.82	1.34	2.37	9,400	0.24
13	45	15	40	0.82	2.55	4.65	9,100	0.23
14	40	60	..	0.15	0.62	0.85	8,600	0.38
15	40	50	10	0.26	0.74	0.99	8,500	0.28
16	40	40	20	0.27	1.04	1.41	7,900	0.35
17	40	30	30	0.32	2.02	3.37	8,600	0.25
18	40	20	40	0.38	3.30	5.84	8,400	0.23
19	40	10	50	0.40	4.36	7.31	8,800	0.26
20	40	..	60	0.40	6.13	10.57	8,900	0.25
21	35	35	30	0.10	2.33	3.26	8,417	0.20

[a] Including phenolic resin, accelerator, catalyst, and lubricant.
[b] Including 2 per cent dye.
[c] Leached, heat-denatured soybean meal.
[d] At 500 lb./sq. in. and 150° C., on composition rolled 3 min.
[e] Standard disks molded 5 minutes from composition rolled 3 minutes.
[f] Approximate values, obtained by estimation where curve left graph.

tion of the phenol-formaldehyde condensation product in the presence of the soybean meal or to some other effect is not known. Consequently, the amount of resin present, and therefore the percentage composition of the plastic, cannot be accurately determined. From these considerations one must allow for a deviation of several per cent in calculations of the resin composition of the molding powder.

DRY MIX METHOD. A series of plastics was prepared in which the ratio of resin, wood flour, and soybean meal was varied stepwise (Table I). The resin component had the following composition: 100 parts two-stage phenolic resin (Monsanto 827 resin compound, serial No. 731), 10 parts hexamethylenetetramine, 2 parts lime, and 3 parts stearic acid. These components were mixed with the indicated proportions of wood flour and soybean meal in a ball mill for 24 hours.

WET MIX METHOD. To illustrate the wet mix method, the following is a typical formula (in grams) used successfully for a molding powder containing approximately 40 per cent phenolic resin, 40 per cent wood flour, and 20 per cent soybean meal:

400	soybean meal
762	phenol
100	barium hydroxide hydrate
986	37% formaldehyde
800	wood flour
10	stearic acid
10	calcium stearate
50	zinc sulfide
50	dye
94	hexamethylenetetramine

Formulas of the wet mix method used here are based on the proportions of phenol in this formula.

The actual preparation of soybean-modified phenolic plastics by the wet mix method is carried out in the following manner: The soybean meal is mixed with the phenol and the alkaline catalyst, so that the particles of meal may become thoroughly permeated. Aqueous formaldehyde (1.5 moles per mole of phenol) is then added and the mixture is heated in a closed steam-jacketed mixer, 15 minutes at 15 pounds per square inch gage steam pressure in the jacket (250° F.) to start the reaction and one hour at a jacket temperature of 190° F. and inside temperature of 175–185° F. to complete the formation of a two-stage resin. The wood-flour filler, stearic acid lubricant, dye, and pigment are added; the mixture is cooled and the accelerator, either hexamethylenetetramine or paraformaldehyde (equivalent to 0.5 mole formaldehyde per mole phenol), is added in concentrated aqueous solution with thorough mixing. The batch is dried to a moisture content of 3–6 per cent and is then suitable for treatment on the calender rolls.

The resulting powdered mixtures, prepared by either the dry or wet method, are worked on the calender rolls, with the cold roll at 150° and the hot roll at 200° F. Small portions of each batch are first rolled for various times and tested on a Rossi-Peaks flowmeter to determine the variation of flow and of curing time with length of rollings. The main portion of each batch is then rolled sufficiently to give the optimum flow and curing time; for standard molding powders and for most of the tests the flow chosen was 1.0 inch at 500 pounds pressure and 150° C., or 1.5 inches at 700 pounds pressure and 150° C.

FLOW CHARACTERISTICS

REPLACEMENT OF RESIN AND WOOD FLOUR BY SOYBEAN MEAL. The effect on the flow of a molding powder of substituting soybean meal for part of the resin or wood flour by the dry mix method is illustrated in Table I.

For these and subsequent flow tests, the moisture content was reduced to a value below 1 per cent. This is done by drying the molding powder to about 5 per cent moisture before working it on calender rolls; the heated rolls have been shown by the Bidwell-Sterling moisture method to reduce the moisture further very rapidly to a value of 1 per cent or lower. Under these conditions the soybean meal has practically no flow in the Rossi-Peaks flowmeter. However, the phenolic resin appears to plasticize the soybean meal and thus its flow properties become a substantial factor in the flow properties of the molding powder as a whole.

The flowmeter has been tested at regular intervals with a standard phenolic resin and gives a flow of 0.55 inch at 800 pounds per square inch pressure and 150° C. for Baketal 120.

The data in Table I show that, when the resin is held constant and the wood flour is replaced stepwise by soybean meal, a rapid increase in flow properties is observed. The data given by Brother and McKinney (*2*) indicate that this effect is not nearly so pronounced when formaldehyde-hardened meal is used instead of the leached, heat-denatured meal of this investigation.

Examination of batches 1, 10, 16, and 21 (Table I) shows that, when the ratio of resin to wood flour is held constant and soybean meal is added stepwise, the plastic flow decreases gradually. If we assume that the flow properties of the meal are due to its protein fraction, then we may say that the ratio of total flow component (resin plus protein fraction of meal) to total filler (wood flour plus nonprotein in meal) remains nearly constant. The effect probably should be ascribed to the fact that protein plasticized by phenolic resin has less flow than the resin itself. Furthermore, the plasticizing effect of the resin upon the protein may be expected to decrease also.

TABLE II. EFFECT OF HEAT DENATURATION OF SOYBEAN MEAL UPON FLOW (DRY MIX METHOD)

Resin, %	Wood Flour, %	Heat-Denatured Soybean Meal, %	Leached Meal, %	Flow, In[a]
47.5	47.5	5	..	1.15
47.5	47.5	..	5	1.70[b]
45.0	45.0	10	..	1.10
45.0	45.0	..	10	1.30

[a] At 700 lb./sq. in. and 150° C., on composition rolled 3 minutes.
[b] Approximate value, obtained by estimation where curve left graph.

If ordinary leached meal is used in place of the leached, denatured meal, the decrease in flow is less pronounced; the data of Table II indicate that heat denaturation slightly decreases the flow of the protein.

If the percentage of wood flour is held constant and the resin is replaced stepwise by soybean meal or protein, the flow decreases although not so rapidly as when the resin is replaced by wood flour. This is because the soybean meal is approximately half carbohydrates and other substances which

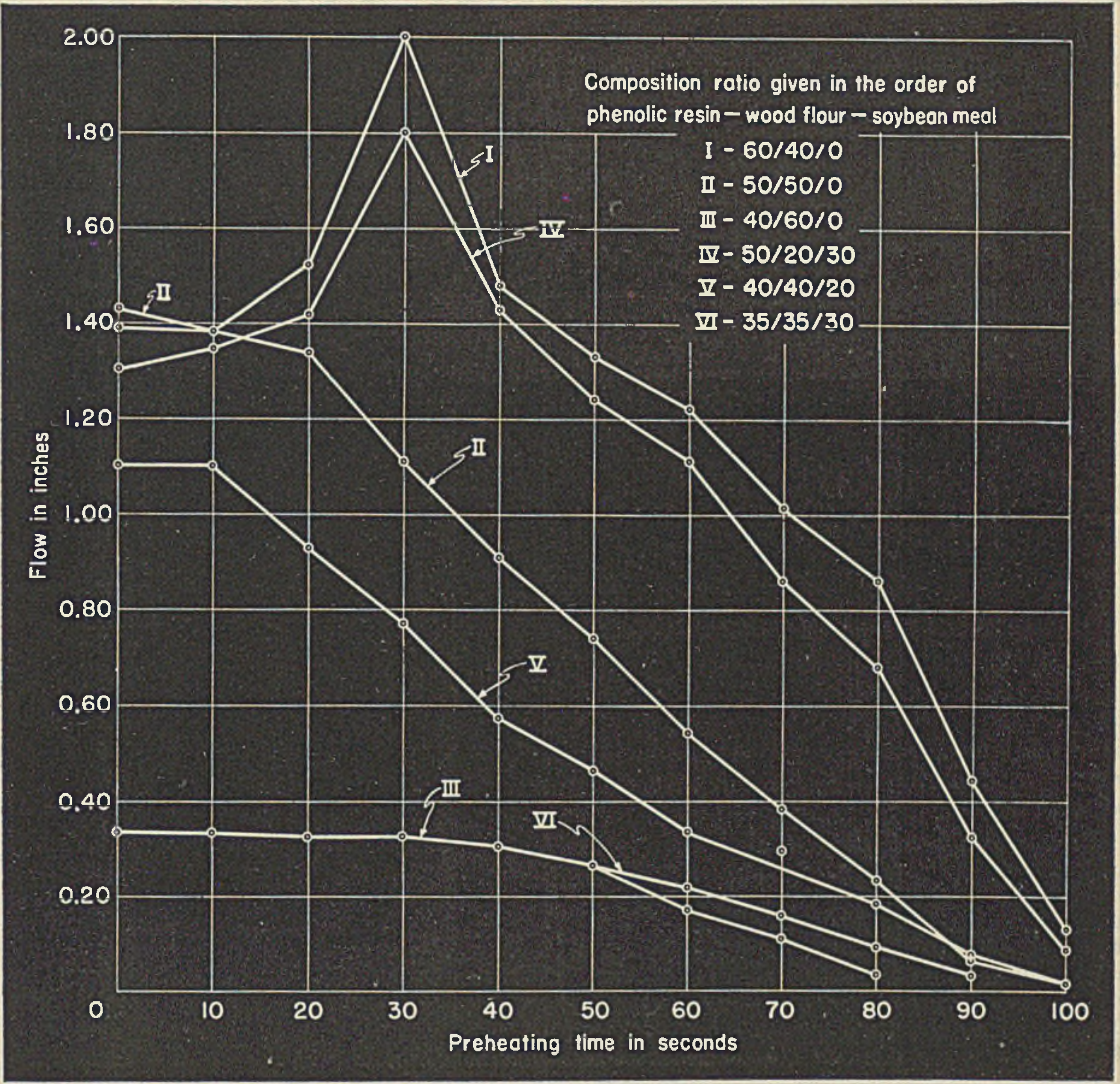

Figure 1. Effect of Preheating upon Flow

Curves I, II, and III are for high-flow, standard, and low-flow phenolic resins; IV, V, and VI are the corresponding types of soybean-modified phenolics.

have no appreciable flow, and half protein which has somewhat less flow than the resin. These effects may be observed partially in the flow data of Table I and are clearly demonstrated in Table III.

Effect of Rolling. The effect of rolling upon plastic flow is especially important. Some representative data are shown in Table IV.

Effect of Preheating. Also of considerable interest is the effect upon flow of preheating the molding powder immediately before molding. The Rossi-Peaks flowmeter was used for preheating the preformed plastic being held in the heated cavity at 150° C. and 700 pounds per square inch pressure for a predetermined time preceding the flow test. The results are shown in Figure 1. The flow values above 1.5 inches are obtained by estimation.

High-flow plastics show a marked increase in flow at 10 to 40 seconds of preheating; in standard and low-flow plastics this effect diminishes to mere constancy of flow at 10 to 30 seconds of preheating or even to an immediate decrease of flow with small amounts of preheating.

CURING AND SETTING TIME

The molding time required to cure completely a thermosetting plastic is not readily defined, and standards for its measurement are somewhat arbitrary. Appearance and finish of the molded piece and its resistance to moisture absorption after various molding times are considered the best criteria of cure. Two other methods which, strictly speaking, refer to setting time but for relative values may be used to compare curing time, are the time required for the flow curve of the molding powder to become parallel to the time axis and the complete loss of flow by preheating of the molding powder.

Composition and Plastic Flow. Whatever standard is chosen, two observations have been made: The curing time increases with increasing per cent of soybean meal, and the curing time increases somewhat with increasing flow, regardless of whether the increased flow is caused by a higher percentage of resin or soybean meal. The data in Tables V and VI illustrate the determination of curing time by two of the

Table III. Effect upon Flow of Replacing Resin by Wood Flour, Meal, or Protein (Dry Mix Method)

Resin, %	Wood Flour, %	Soybean Meal, %	Protein[a], %	Flow, In.[b]
50	50	..	..	1.50
45	55	..	..	0.90
45	50	5	..	1.10
45	50	..	5	1.40
40	60	..	..	0.28
40	50	10	..	0.40
40	50	..	10	0.50

[a] A low-viscosity type commercial protein.
[b] At 700 lb./sq. in. and 150° C., on composition rolled 1 minute.

Table IV. Change of Flow with Rolling Time (Dry Mix Method)

Compn., Resin/Wood Flour/Meal	Flow[a] after Rolling Time of: 0 min.	1 min.	2 min.	3 min.	5 min.
50/50/0	1.45	1.70[c]	1.49	1.31	....
50/40/10	High[b]	1.50	1.45	1.28	1.50
45/45/10	1.30	1.30	1.30	1.15	....
40/50/10	0.47	0.50	0.56	0.52	....
40/60/0	0.28	0.42	0.47	0.47	....

[a] In inches at 700 lb./sq. in. and 150° C.
[b] Curve off graph; flow 0.60 inch at 300 lb. and 150° C.
[c] Approximate value, obtained by estimation where curve left.

Table V. Curing Time Determined by Appearance of Molded Piece[a] (Wet Mix Method)

Resin, %	Wood Flour, %	Soybean Meal, %	Curing Time, Min.
50	50	..	1.5
40	40	20	2.0
40	30	30	3.0
40	20	40	3.0

[a] Test cup molded at 300° F.

above-mentioned methods, and show clearly the effects of soybean-meal content and plastic flow upon cure.

Accelerators. The use of paraformaldehyde in place of hexamethylenetetramine as an accelerator decreases the curing time markedly but also decreases the flow. A practical objection, however, to the use of paraformaldehyde is the tendency of molding powders containing it to "set up" on standing and to lose their flow completely in several months.

RESISTANCE TO MOISTURE

Table II shows that, although a moderate amount of heat denaturation does decrease the flow of the resin-plasticized protein somewhat, it does not destroy or produce any drastic change in the flow value. Further studies along the line of heat denaturation of the protein should prove profitable in the continued development of soybean meal to plastics.

The resin used in the plastic reduces the moisture absorption by coating or impregnating the meal particles, and the wet mix method does a more thorough job than the dry mix (Table VII).

STRENGTH

Flexural Strength was measured according to A. S. T. M. standards (*1,4*). The results for the dry mix method are given in Table I. The data indicate that flexural strength depends primarily upon the percentage of resin, and does not vary greatly with the ratio of wood flour and soybean meal. Generally, when wood flour is replaced stepwise by soybean meal, the flexural strength first decreases slightly to a minimum at 10 to 20 per cent soybean meal and then increases to its original value or higher. Although flexural strength results are not shown for the wet mix method, they are not substantially different.

Impact Strength was determined by the Izod notched-bar method, according to A. S. T. M. specifications (*1*). The data are given in Table I for the dry mix method; they indicate that the impact strength gradually decreases with increasing content of soybean meal. While similar results are not shown for the wet mix method, the loss with increased amounts of soybean meal is appreciably less.

COLOR

The incorporation of soybean meal into phenolic plastics provides a protein base for organic dyes; thus a wider variety of bright stable colors can be produced than when standard phenolics are used. It is possible to prepare various shades of orange, red, green, and blue plastics as well as browns and blacks by the use of compatible organic dyes. For example, Phenoform Red (General Dyestuff Corporation) and 2 per cent zinc sulfide or other white pigment give a highly satisfactory red. A rich orange is produced with Sherwin-Williams Toluidine Red No. 10189. Two per cent of Kohnstamm Green A6318 with white pigment or chromic oxide forms satisfactory greens. Pastel shades fail because of the darker color of the original plastics. Most blues fail because of the yellow-brown color of the original plastic or because of the decomposition of the dye, but one per cent of Federal Color Laboratories Duratint Blue No. 1001 with 2 per cent white pigment produce a good blue plastic, provided paraformaldehyde is used in place of hexamethylenetetramine for the curing agent. Good browns are formed by Reichard-Coulston brown and burnt umber pigments, with or without brown dyes. Black is obtained with one per cent of nigrosine dye. These colors are unharmed by molding temperatures of 300–320° F. and are stable to light. Thus there is a definite color advantage for the phenolic resin by combining it with soybean meal.

Table VI. Curing Time Determined by Preheat Flow Curves (Dry Mix Method)

Resin, %	Wood Flour, %	Soybean Meal, %	Flow, In.[a]	Curing Time, Sec.[b]
40	60	..	0.45	70
50	50	..	1.30	90
47.5	47.5	5	1.10	90
50	45	5	1.20	95
45	45	10	1.15	90
50	40	10	1.80[c]	100
40	40	20	1.00	90
50	30	20	1.80[c]	95
35	35	30	0.20	90
50	20	30	1.50[d]	105

[a] At 700 lb./sq. in. and 150° C.
[b] Determined by preheat time necessary to cause complete loss of flow.
[c] Approximate value, obtained by estimation where curve left graph.
[d] Flow at 500 lb. and 150° C.

Table VII. Comparison of Water Absorption of Plastics Prepared by Wet and Dry Mix Methods

Compn., Resin/Wood Flour/Meal	Method of Preparation	Molding Time for Disks, Min.	Moisture Absorption %	Hr.
40/40/20	Dry mix	5	1.41	48
40/40/20	Wet mix	1	0.97	96
40/30/30	Dry mix	5	3.37	48
40/30/30	Wet mix	2	1.42	96
40/20/40	Dry mix	5	5.48	48
40/20/40	Wet mix	2	1.65	96

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(1) Am. Soc. for Testing Materials, D 256-41T.
(2) Brother, G. H., and McKinney, L. L., Ind. Eng. Chem., 32, 1002 (1940).
(3) Brother, G. H. and McKinney, L. L., *Plastics* (London), 4, 93–5 (1940).
(4) Brother, G. H., Suttle, W. C., and McKinney, L. L., *A. S. T. M. Bull.* 109, 13–16 (1941).

MINERAL INSULATING OILS

Effect of Additives on Electrical and Chemical Stability

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CUSTOMARY procedure in studying the electrical and chemical stability of mineral oils is to oxidize the samples at elevated temperatures (with or without catalysts) with air (*6*) or oxygen (*4*). Recent publications (*3*), however, have demonstrated that small amounts of oxygen in the order of what may feasibly be contained in oils in service could produce relatively high electrical losses. It has been found that copper is necessary to produce these losses. Apparently, compounds already present in a refined oil (although in relatively small quantities) react with or are catalyzed by copper to produce these loss components. The addition of increasing amounts of oxygen alters these losses to varying degrees, depending on the oil tested.

The source of these losses has been a matter of speculation. Clark (*6*) found dielectric deterioration of commercial importance in oil-treated kraft paper insulation, even under the most carefully maintained oxygen-free conditions. This may presumably be caused by "impurities" or nonhydrocarbon constituents which cannot be removed from a mineral oil without the danger of overrefining it. Evans and Davenport (*7*) reported the formation of a strong acid during the oxidation of a mineral insulating oil, probably from some sulfur complex originally contained in the oil.

As a result of these findings, the authors studied the effect of some of the nonhydrocarbon constituents normally found in commercially refined oils—namely, the sulfur compounds. Representative samples of thioethers, disulfides, mercaptans, and a few special samples were investigated. At the same time it was thought desirable to study the effect of oxidation inhibitors on the electrical losses produced during a limited oxidation. Consequently a group of six oxidation inhibitors was added to the list of additives studied.

DETERIORATION TESTS

OILS AND ADDITIVES. The experimental oils and additives were supplied by the Gulf Research and Development Company; G-10 is a light cable oil and GS-1338, a transformer oil. The physical properties are given in Table I.

TABLE I. PHYSICAL PROPERTIES OF OIL SAMPLES

Sample G-10		Sample GS-1338	
Viscosity at 100° F.		Gravity, ° A. P. I.	27.5
(approx.)	100	Sp. gr. (60° F.)	0.8899
Density, 20° C.	0.9036	Flash point, ° F.	280
Refractive index, n_D^{20}	1.4979	Fire point, ° F.	315
Sp. dispersion (20° C.)		Cloud point, ° F.	−60
× 10⁴	117	Pour point, ° F.	−60
Aniline point, ° C.	74.0	Viscosity at 100° F., Saybolt	
Waterman analysis, %		Universal sec.	55
Aromatics	11.6	Cu strip (3 hr.)	Passes
Naphthenes	38.0	Cu strip (12 hr.)	Passes
Paraffins	50.4	Combined S, %	0.11
		Sulfur No.	0.01

The sulfur compounds (Table II) consisted of mercaptans, thioethers, disulfides, ring sulfur compounds, crystalline sulfur, and a sulfur compound preparation. The oxidation inhibitors were selected at random and are listed in Table II.

PROCEDURE AND APPARATUS. The procedure and apparatus have already been described (*1*, *4*). The oil samples were deteriorated with and without copper wire (5-mil wire wound into coils $^1/_4$ inch in diameter) at 85° C. and a gas pressure of 760 mm. mercury. In limited oxidations in which specific amounts of oxygen were made available to the oil, the oxygen was introduced into the evacuated deterioration cell through a control stopcock. The final pressure of 760 mm. was obtained with dry, oxygen-free nitrogen. Figure 1 shows the deterioration cell; Figure 2 is a type of limited-oxidation cell which was used extensively. It consists of a Ŧ19–22 female joint with a side tubulation to which is attached a 4-mm. slant-bore stopcock and a Ŧ10–30 female joint. Approximately 13.5 grams of sample may be used with as high a copper-oil ratio as 16 sq. cm. per gram of oil. The oil was degassed into the cell through the stopcock, and the initial electrical properties of the oil were measured under vacuum. The desired volume of oxygen was then introduced by a gas pipet which consisted of a calibrated tube included between two

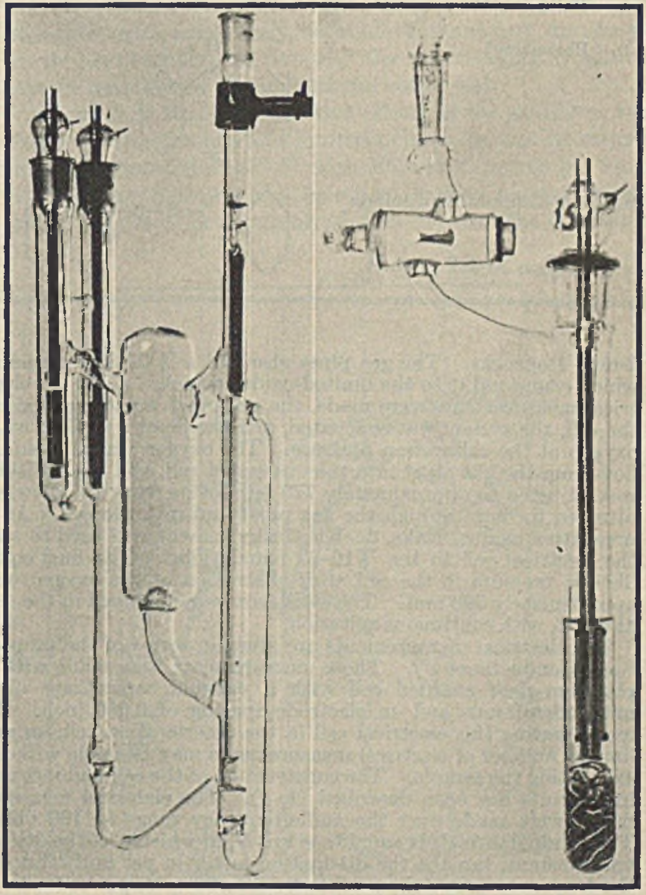
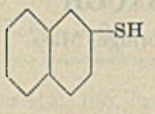
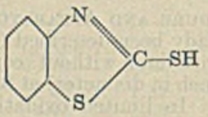
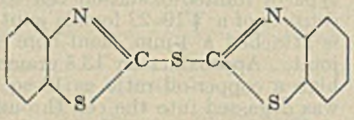
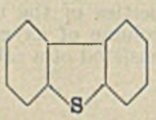
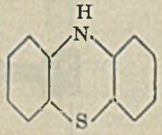
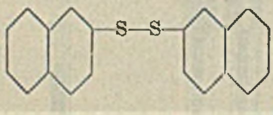
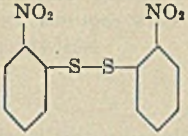
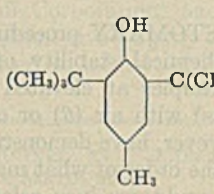
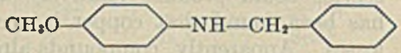
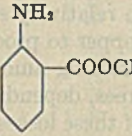
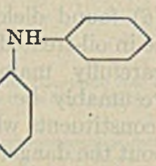
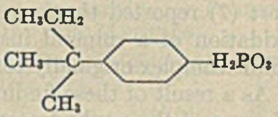
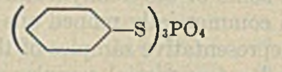


Figure 1 (*Left*). Deterioration Cell for Continuous or Limited Oxidation
Figure 2 (*Right*). Limited-Oxidation Cell

TABLE II. ADDITIVES STUDIED

Sulfur Compound	Formula
1. *p*-Thiocresol[a]	
2. Thio-β-naphthol[a]	
3. Mercaptobenzothiazole[a]	
4. Cetyl mercaptan	$CH_3(CH_2)_{14}CH_2SH$
5. Thioether A[a]	.....
6. 2,2′-Dibenzothiazyl sulfide	
7. Dibenzothiophene	
8. Thioether B	.....
9. Phenazine[a]	
10. β,β′-Dinaphthyl disulfide	
11. Di-*o*-nitrophenyl disulfide[a]	
12. Disulfide A	.....
13. Sulfur compound preparation	.....
14. Crystalline sulfur	.....

Inhibitor	
1. 2,6-Di-*tert*-butyl-4-methylphenol	
2. *N*-Benzyl-*p*-anisidine	
3. Methyl anthranilate	
4. *N*-Phenyl-α-naphthylamine	
5. *tert*-Amyl phenyl phosphite	
6. Trithiophenyl phosphate[a]	

[a] Eastman Kodak product.

2-mm. stopcocks. The gas pipet also had a ₸10-30 male joint which connected it to the limited-oxidation cell. After the electrical measurements were made, the gas pipet was connected to the cell, the system was evacuated, and the pipet was filled with oxygen at the calibration pressure. The oxygen was allowed to flow from the gas pipet into the evacuated cell, and the pressure was adjusted to approximately 770 mm. of mercury by allowing nitrogen to flow through the gas pipet and into the cell. As a precaution against leaks, de Khotinsky cement was used to seal the electrical cell to the ₸19-22 female joint. The final equilibrium pressure in the cell after absorption of the oxygen was approximately 700 mm. The additives were dissolved in the oils at 85° C. with continuous agitation.

The electrical measurements are given in terms of the proportional conductance $\epsilon''f$. These measurements were made with a platinum-glass guarded cell with a vacuum capacitance of 4 micromicrofarads and an electrode spacing of 0.050 inch. By incorporating this electrical cell in the deterioration cell, an unlimited number of electrical measurements may be made without exhausting the sample. The construction of the cell and measuring circuits has been described (*1*, *5*). The electrical measurements were made over the audiofrequency range at 100 volts. The conductance $\epsilon''f$ is equal to $\epsilon' \tan \delta f$, in which ϵ' is the dielectric constant, $\tan \delta$ is the dissipation factor in per unit, and f is the frequency in cycles per second. The 60-cycle power factor is equal to $\cos (90\ \delta)$ and, therefore, in the low ranges is practically equal to the dissipation factor. Since ϵ' of the oils is approximately 2 at a frequency of 60 cycles per second,

$$\epsilon''f = \epsilon' \tan \delta f = 120 \tan \delta$$

and, therefore, $\epsilon''f$ is approximately equal to the 60-cycle dissipation factor (or the 60-cycle power factor up to approximately 20 per cent) in per cent.

EFFECT OF INHIBITORS

Figure 3 shows the results on the rate of oxidation of oil G-10 containing the various inhibitors in a concentration of 0.3 per cent by weight. The samples were oxidized at 85° C. with copper equivalent to 1.6 sq. cm. per gram of oil. Apparently three types of mechanisms were involved. Sample G-10 exhibited an autoinhibited or autoretarded oxidation mechanism, presumably because of the conversion of some of the hydrocarbons to inhibitors (*9*). Methyl anthranilate and trithiophenyl phosphate retarded the oxidation still more. *N*-Phenyl-α-naphthylamine, *tert*-amyl phenyl phosphite, and *N*-benzyl-*p*-anisidine not only retarded the oxidation, but apparently changed the mechanism of reaction. On the other hand, 2,6-di-*tert*-butyl-4-methylphenol inhibited the oxidation. Methyl anthranilate apparently was not effective in decreasing the oxidation of G-10, possibly because of chelation; the other nitrogen compounds were much more effective. Trithiophenyl phosphate retarded the oxidation, presumably because of a decrease in the available copper surface. At the end of the oxidation the copper sur-

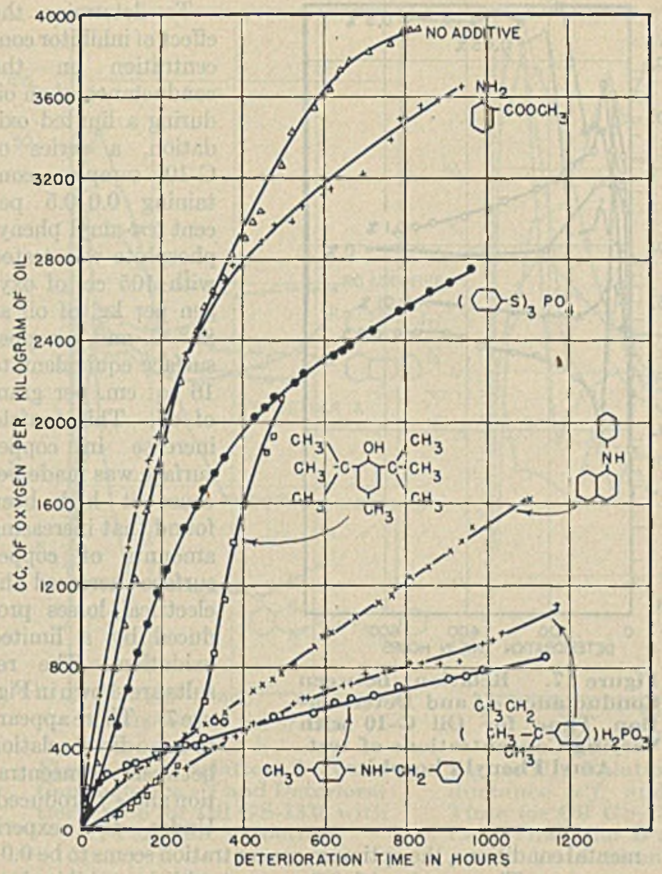


Figure 3. Oxidation-Time Curves for Oil G-10 with 0.3 Per Cent Oxidation Inhibitors

Continuous oxidation, 1.6 sq. cm. copper per gram oil, 85° C.

face was badly tarnished. However, *tert*-amylphenyl phosphite is also a metal corrosive, yet its ameliorating effect is much more marked. It may be that the rate of corrosion with the latter is much greater than that with the former, if we recognize that these two phosphorus compounds may have different chemical effects on the mechanism of oxidation of the oil.

Table III. Comparison of $\epsilon''f$ of G-10 with Inhibitors during Continuous and Limited Oxidation after 400 Hours

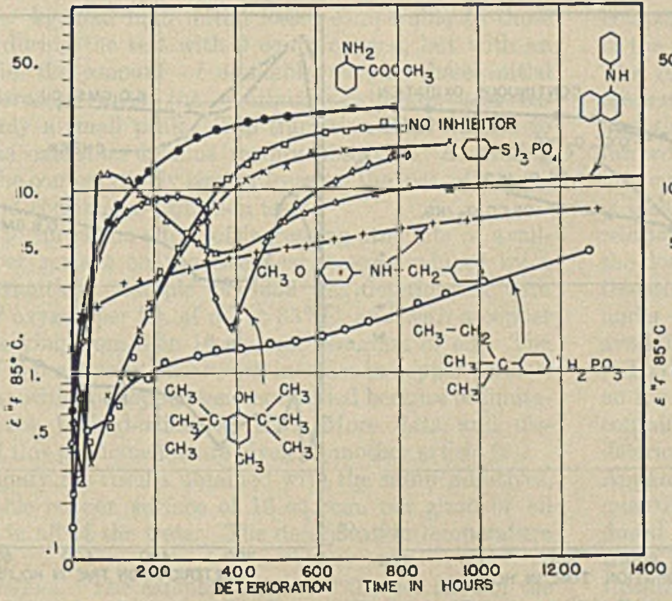
(0.3% inhibitor, 85° C., 1.6 sq. cm. copper per gram oil)

Inhibitor No.	Continuous Oxidation		Limited Oxidation	
	Cc. O_2/kg.	$\epsilon''f$	Cc. O_2/kg.	$\epsilon''f$
None	2950	12.7	105	8.4
3	2770	22.5	105	14.0
4	650	4.8	105	14.0
1	1600	1.9	105	7.0
2	500	4.3	105	34.0
6	1950	10.0	105	5.6
5	490	1.4	105	1.5

Figure 4 shows the electrical properties of oil samples as a function of time. Figures 3 and 4 reveal that, with the exception of methyl anthranilate and *n*-benzyl-*p*-anisidine, the $\epsilon''f$ curves fall in the same order as their oxidation-time curves. Also, the sample containing 2,6-di-*tert*-butyl-4-methylphenol attained its highest loss ($\epsilon''f$ of 9) during the induction period; then with increased oxidation the loss dropped and again increased to values corresponding to those obtained by the continuous oxidation of the blank oil. This phenomenon was observed previously (*3*). It also substantiates the hypothesis that a normal inhibitor merely postpones a reaction (or series of reactions) but does not change its fundamental character. Apparently the other additives decreased the number of loss components which would otherwise have been formed and thereby decreased the electrical loss.

Figure 5 shows the reproducibility of the electrical measurements. It also demonstrates the large number of electrical measurements which may be made without any diminution in the test sample; in this way the experimental conditions can be maintained throughout the entire test.

In order to study the relative effects of the additives with respect to continuous and limited oxidations, similar samples were deteriorated at 85° C. with 105 cc. of oxygen per kg. of oil. Figure 6 shows the electrical results plotted against time. There is no apparent relation between the continuous



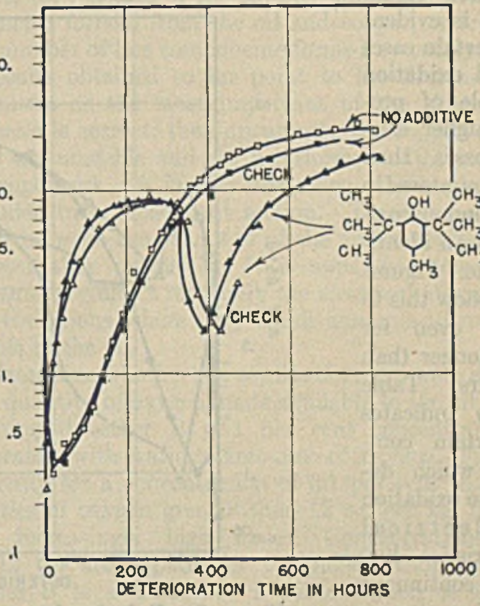


Figure 4 (*Left*). Relation between Conductance $\epsilon''f$ and Deterioration Time for Oil G-10 with 0.3 Per Cent Oxidation Inhibitors

Continuous oxidation, 1.6 sq. cm. copper per gram oil, 85° C.

Figure 5 (*Right*). Reproducibility of Electrical Measurements

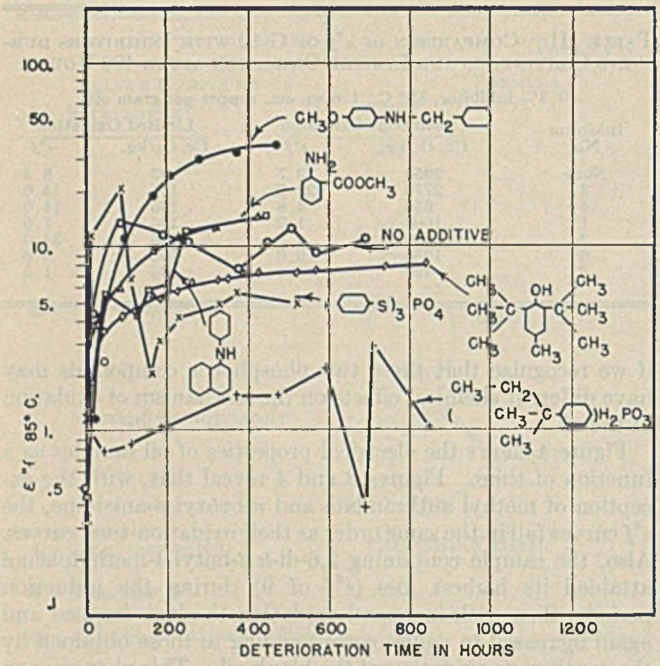


Figure 6. Relation between Conductance ε″f and Deterioration Time for Oil G-10 with 0.3 Per Cent Oxidation Inhibitors

Limited oxidation, 105 cc. oxygen per kg. oil, 1.6 sq. cm. copper per gram oil, 85° C. (applies to both figures)

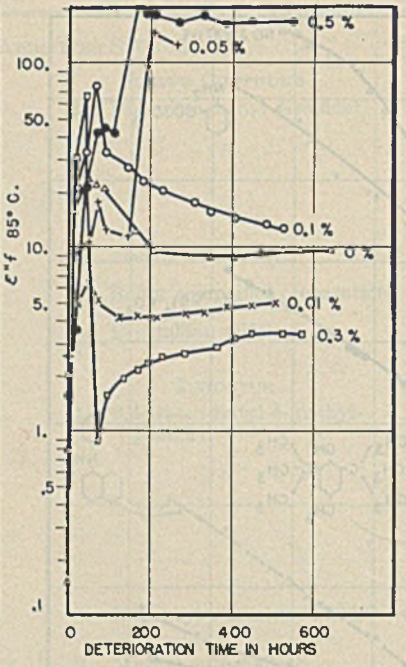


Figure 7. Relation between Conductance ε″f and Deterioration Time for Oil G-10 with Varying Concentrations of *tert*-Amyl Phenyl Phosphite

and limited oxidations. *N*-Benzyl-*p*-anisidine which produced a comparatively low conductance during continuous oxidation produced the highest ε″f values during limited oxidation; the two phosphorus compounds gave the lowest losses. Only after 90 hours did the trithiophenyl phosphate exert any appreciable influence, when it brought the conductance from 20 down to 2. *tert*-Amyl phenyl phosphite acted after only 18 hours when it abruptly changed the initial rapid increase of ε″f at the relatively low value of 1. Table III compares ε″f of the inhibited samples after 400 hours of continuous and limited oxidation. It is evident that in certain cases a limited oxidation is capable of producing higher electrical losses than those encountered in the continuous oxidation of an identical sample. Figures 4 and 6 show this to be true even for periods longer than 400 hours. Table III also indicates that certain compounds which decrease the oxidation and electrical characteristics during a continuous oxidation may increase them during a limited oxidation.

To determine the effect of inhibitor concentration on the conductance of an oil during a limited oxidation, a series of G-10 samples containing 0.0–0.5 per cent *tert*-amyl phenyl phosphite was tested with 105 cc. of oxygen per kg. of oil at 85° C. and a copper surface equivalent to 16 sq. cm. per gram of oil. This tenfold increase in copper surface was made because it had been found that increasing amounts of copper surface increased the electrical losses produced by a limited oxidation. The results are shown in Figure 7. There appears to be no direct relation between concentration and ε″f produced. Under the experimental conditions, the optimum concentration seems to be 0.01 per cent. The sample with 0.3 per cent additive exhibited an initially high peak which disappeared rapidly. The difference between this curve and that shown in Figure 6 can undoubtedly be attributed to the increase in available copper surface.

EFFECT OF SULFUR ADDITIVES

The sulfur additives were dissolved in oil GS-1338. A short study of the oil was made preparatory to introducing the sulfur compounds. Figure 8 shows the effect of varying

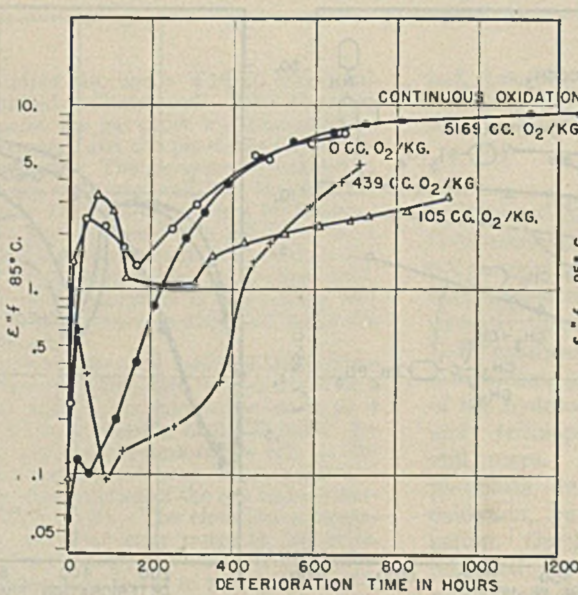


Figure 8. Relation between Conductance ε″f and Deterioration Time for Oil GS-1338 with Varying Oxygen Concentration

1.6 sq. cm. per gram oil, 85° C.

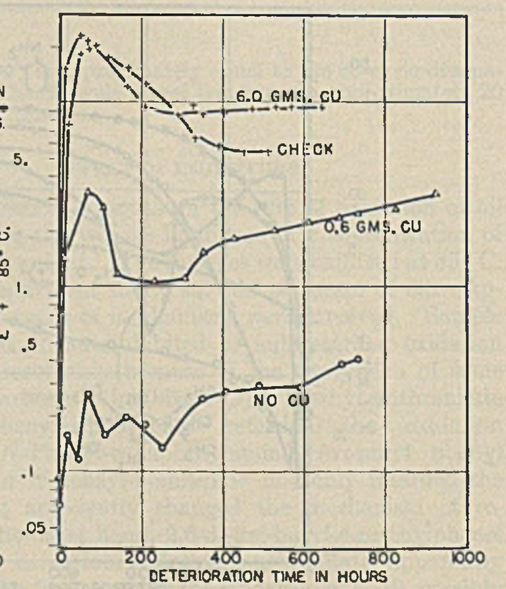


Figure 9. Relation between Conductance ε″f and Deterioration Time for Oil GS-1338 with 0, 1.6, and 16 Sq. Cm. Copper per Gram Oil

Limited oxidation, 105 cc. oxygen per kg. oil, 85° C.

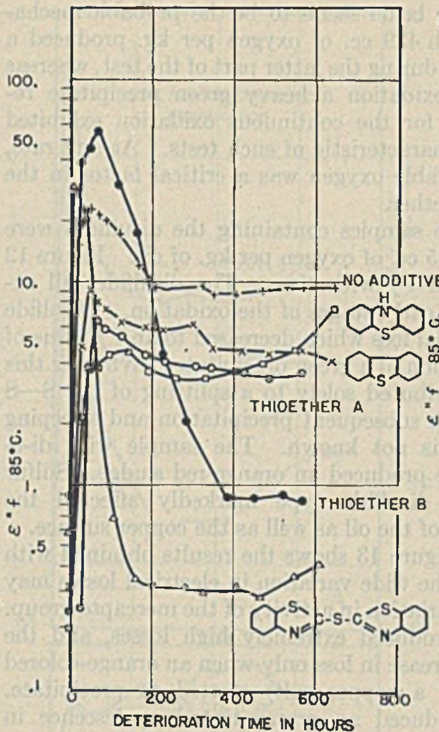


Figure 10. Relation between Conductance ε"f and Deterioration Time for Oil GS-1338 with 0.1 Per Cent Thioethers

Limited oxidation, 105 cc. oxygen per kg. oil, 16 sq. cm. copper per gram oil, 85° C.

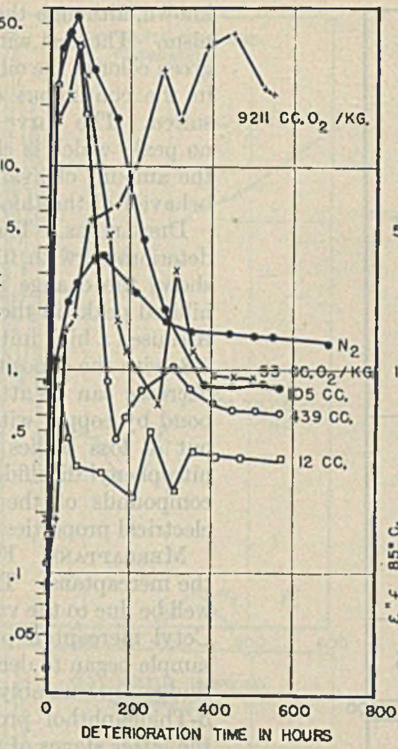


Figure 11. Relation between Conductance ε"f and Deterioration Time for Oil GS-1338 with 0.1 Per Cent Thioether B at Varying Oxygen Concentrations

16 sq. cm. copper per gram oil, 85° C.

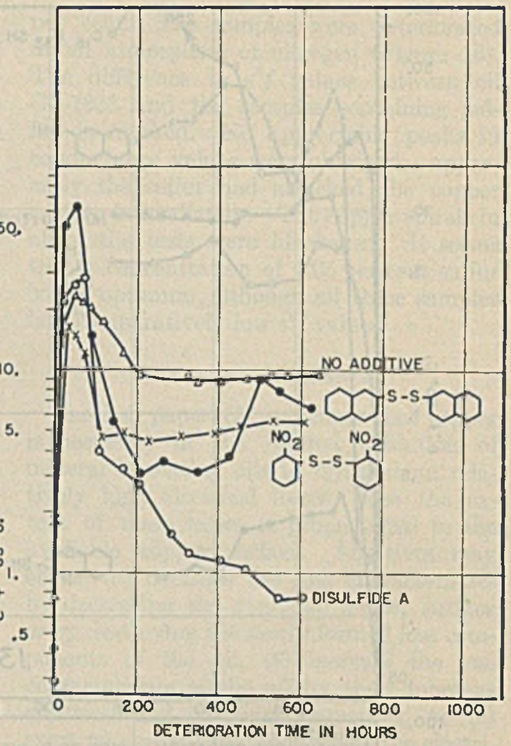


Figure 12. Relation between Conductance ε"f and Deterioration Time for Oil GS-1338 with 0.1 Per Cent Disulfide

Limited oxidation, 105 cc. oxygen per kg. oil, 16 sq. cm. copper per gram oil, 85° C.

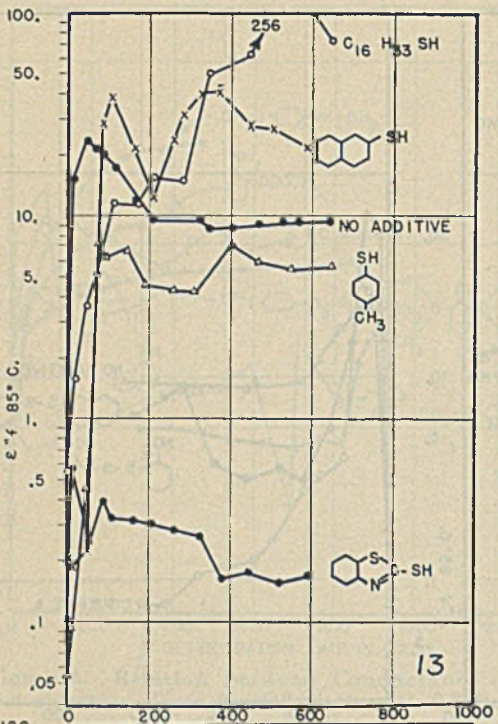
concentrations of oxygen on the loss characteristics of GS-1338 at 85° C. and with 1.6 sq. cm. of copper surface per gram of oil. In an atmosphere of nitrogen the oil produced initial losses higher than those obtained under conditions of continuous oxidation. After 400 hours of testing, the ε"f values were approximately equal to those produced by continuous oxidation, yet the two methods and mechanisms of deterioration were entirely different. The test run with 105 cc. of oxygen per kg. had high initial losses comparable to those obtained during the test with 0 cc. of oxygen, but with an increase in the amount of available oxygen these initial losses decreased until the continuous-oxidation test exhibited only a small peak. The transition from limited to continuous oxidation is thus readily observed. A striking result is the comparatively similar losses of the 0 cc. of oxygen per kg. and continuous-oxidation tests.

Figure 9 shows the effect of increasing amounts of available copper surface on the electrical losses produced by a limited oxidation. Sample GS-1338 was deteriorated with 105 cc. of oxygen per kg. of oil at 85° C. and with a copper surface varying from 0 to 16 sq. cm. per gram of oil. The rise in ε"f is practically linear with increase in copper surface. Larger quantities of copper were not added because of limitations in the limited-oxidation cell. More data and discussion of this phenomenon are given in another article (*2*).

To magnify the results obtained with the sulfur additives, an available copper surface of 16 sq. cm. per gram of oil was used in all of the tests. The deterioration temperature was 85° C.

Thioethers. The samples contained 0.1 per cent of the respective thioethers and were oxidized with 105 cc. of oxygen per kg. of oil. Figure 10 shows the electrical results plotted against time. Three of the compounds produced losses similar to those encountered with the oil itself, although at a lower level. These compounds presumably decreased the number of loss components formed and thereby decreased the final equilibrium value of ε"f. Two of the thioethers, however, produced relatively high initial losses followed by a sharp decrease to relatively low values. This behavior may be explained by three possible mechanisms: (*a*) reaction of the sulfur compound with copper to form additional loss components, (*b*) reaction of the sulfur compounds with the loss components formed from the oil and copper, or (*c*) increase in the number of loss components formed by catalytic action. The results obtained so far point to the first and second mechanisms as the most important of the three. If this hypothesis is correct, then apparently the copper complexes formed are unstable and are transformed with time to low-loss components. A further discussion of this phenomenon is included in a subsequent section. There is no apparent relation between the structure of the added compounds and the losses they produced. It is apparent, however, that thioethers may affect markedly the electrical losses of an oil under conditions where only small amounts of oxygen are available to the oil.

To determine whether the results obtained were dependent on the quantity of oxygen made available to the oil, a sample containing thioether B (0.1 per cent concentration) was deteriorated with various amounts of oxygen (Figure 11). Apparently for a concentration of 0.1 per cent thioether B, quantities of oxygen greater than 12 cc. per kg. of oil produced increasingly high losses. Concentrations greater than 12 cc. are capable of completely transforming the thioether B to a sulfoxide; a concentration of 439 cc. of oxygen per kg. of oil is capable of transforming it completely to a sulfone. Whether this mechanism is solely responsible for the losses indicated or whether a combination of this and other complex reactions with copper is the cause, is not



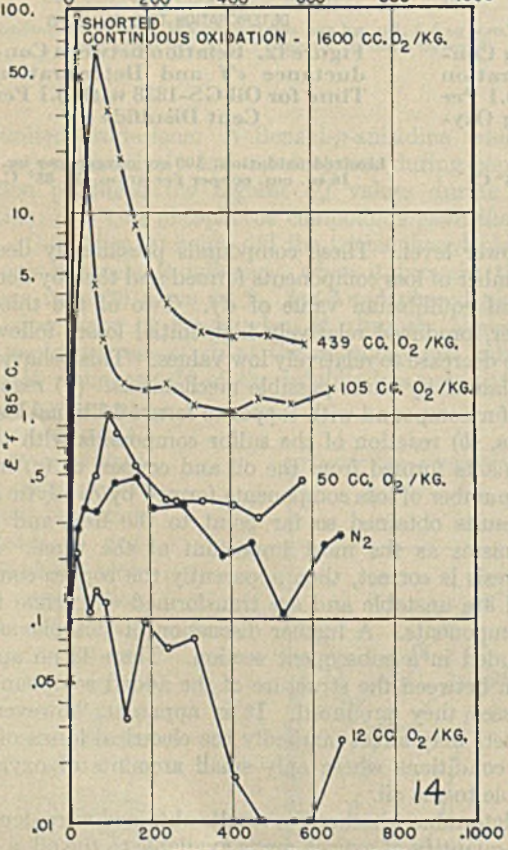


Figure 13. Relation between Conductance $\epsilon''f$ and Deterioration Time for Oil GS-1338 with 0.1 Per Cent Mercaptans

Limited oxidation, 105 cc. oxygen per kg. oil, 16 sq. cm. copper per gram oil, 85° C.

Figure 14. Relation between Conductance $\epsilon''f$ and Deterioration Time for Oil GS-1338 with 0.05 Per Cent Mercaptobenzothiazole at Varying Oxygen Concentrations

16 sq. cm. copper per gram oil, 85° C.

known, although the latter seems to be the probable mechanism. The test with 439 cc. of oxygen per kg. produced a green color in the oil during the latter part of the test, whereas in the continuous oxidation a heavy green precipitate resulted. The curve for the continuous oxidation exhibited no peak, which is characteristic of such tests. At any rate, the amount of available oxygen was a critical factor in the behavior of the thioether.

Disulfides. The samples containing the disulfides were deteriorated with 105 cc. of oxygen per kg. of oil. Figure 12 shows the change in $\epsilon''f$ with time. The disulfides all exhibited peaks in the early stages of the oxidation. Disulfide A caused a high initial loss which decreased to an $\epsilon''f$ value of 0.8, with the deposition of a green precipitate. Whether this decrease can be attributed solely to a splitting of the S—S bond by copper with subsequent precipitation and sweeping out of loss bodies is not known. The sample with di-*o*-nitrophenyl disulfide produced an orange-red sludge. Sulfur compounds of the disulfide type markedly affected the electrical properties of the oil as well as the copper surface.

Mercaptans. Figure 13 shows the results obtained with the mercaptans. The wide variation in electrical losses may well be due to the variation in activity of the mercapto group. Cetyl mercaptan produced extremely high losses, and the sample began to decrease in loss only when an orange-colored sludge (presumably a copper salt) started to precipitate. β-Thionaphthol produced an orange-tinted opalescence in the latter stages of the test. The oil remained clear and the copper untarnished in the *p*-thiocresol test, while mercaptobenzothiazole tarnished the copper surface but kept the oil clear. To determine the effect of varying amounts of available oxygen on the electrical losses, samples containing 0.05 per cent mercaptobenzothiazole were oxidized over a wide range of oxygen concentrations. The results are shown in Figure 14. Here again as in the case of the thioethers (Figure 10), a small amount of oxygen decreased the loss, and the $\epsilon''f$ values remained relatively small, even with 50 cc. of oxygen per kg. of oil. However, above that concentration, values of $\epsilon''f$ increased rapidly to approximately 60 and then decreased again. A continuous oxidation test shorted the electrical cell after a consumption of only 1600 cc. of oxygen per kg. of oil. Evidently mercaptobenzothiazole accelerated the oxidation and electrical deterioration of sample GS-1338 for the initial conductance values are higher than those obtained with a limited oxidation. The curve (Figure 14) obtained from the test with 50 cc. of oxygen per kg. is analogous to that with 105 cc. in Figure 13, in that the concentration of mercaptan to available oxygen is practically the same. Here too, apparently, the concentration of oxygen is important.

Table IV. Comparison of $\epsilon''f$ of GS-1338 with Various Concentrations of Sulfur Compound Preparation after 400 Hours

	Concn. of Preparation, %			
Cc. O_2/Kg.	0.01	0.05	0.1	0.3
0.0	0.16	0.21	0.011	0.034
23	1.3	0.57	0.10	1.8
105	2.0	22.7	0.94	1.2

Sulfur Compound Preparation. A sulfur compound preparation consisting of sulfur compounds normally found in oils was added to oil GS-1338 in concentrations of 0.01, 0.05, 0.1, and 0.3 per cent, and deteriorated with 0, 23, and 105 cc. of oxygen per kg. of oil (Figure 15). In concentrations up to 0.1 per cent the conductance decreased with an increase in concentration in the nitrogen and 23 cc. oxygen

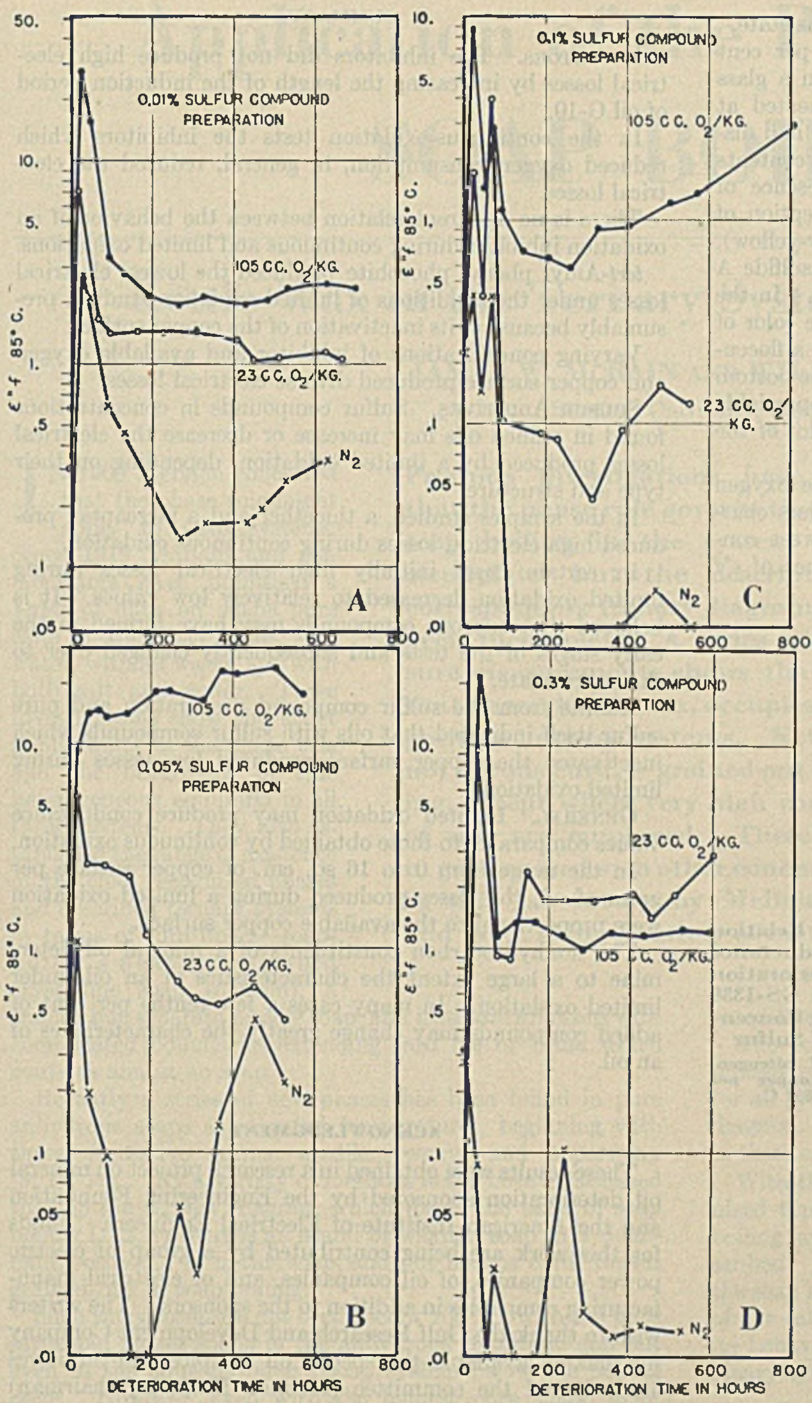


Figure 15. Relation between Conductance $\epsilon''f$ and Deterioration Time for Oil GS-1338 with Varying Concentrations of Sulfur Compound Preparation at 0, 23, and 105 Cc. Oxygen per Kg. Oil

Limited oxidation, 16 sq. cm. copper per gram oil, 85° C.

tests. Table IV shows $\epsilon''f$ values after 400 hours for each test; 0.1 per cent concentration seems to be the optimum. In general, the samples produced peaks in the conductance values before stabilizing at lower equilibrium values. The copper surface was blackened considerably at the end of the tests.

Sulfur. Since the results indicated that copper surface plays a large part in the magnitude of the losses produced during limited oxidations, it was decided to determine the effect of a metal corrosive in the oil. Pure sulfur was dissolved in GS-1338 in concentrations of 0.01, 0.05, and 0.1 per cent. The samples were deteriorated in an atmosphere of nitrogen (Figure 16). The difference in $\epsilon''f$ values between oil GS-1338 and the samples containing sulfur is marked. No appreciable peaks in conductance values were obtained; apparently the sulfur had attacked the copper surface immediately. The copper spirals in all of the tests were blackened. It seems that a concentration of 0.05 per cent sulfur is the optimum, although all three samples had comparatively low $\epsilon''f$ values.

ELECTRICAL LOSSES

Another paper (*2*) indicates that copper is necessary in the limited oxidation of mineral insulating oils to bring about relatively high electrical losses; also the extent of these losses is proportional to the available copper surface. Additives may either (*a*) decrease the loss characteristics by decreasing the available copper surface or by destroying the newly formed loss components of the oil, (*b*) increase the loss characteristics of the oil by their inherent electrical and chemical properties, or (*c*) exert no appreciable influence on the electrical losses by virtue of their inactivity.

Sulfur and its products are known to be corrosive to metals. The more reactive of these components are found mostly in the mercaptans and in sulfur itself. The marked effect of sulfur on the electrical loss (presumably because of the decrease in copper surface) is evident in Figure 16. Whether sulfur also eliminates any loss components that may have formed in the oil is not known. The sulfur compound preparation presumably contained sulfur as well as its derivatives, and it too lowered the loss characteristics (Figure 15). In both cases the copper surface was blackened. Mercaptobenzothiazole was the only sulfur compound used which appreciably tarnished the copper surface. In general, the other sulfur compounds did not seem to affect the appearance of the copper surface. In certain cases (Figures 12 and 15) the sulfur compounds raised and then lowered the electrical loss to less than 1 for $\epsilon''f$. In the presence of oxygen the following reaction may take place between copper and mercaptans (*11*):

$$2Cu + O_2 + 4HSR \longrightarrow 2CuSR + RSSR + 2H_2O$$

The cuprous salt and the disulfide formed may or may not be soluble in the oil. It has been found that cuprous salts in mineral oils produce high losses, and upon their oxidation to the green cupric salts there is a marked decrease in the electrical loss (*12*). When thioether B, dibenzothiazyl sulfide, and disulfide A were used as additives (Figures 10 and 12), the $\epsilon''f$ values increased above those obtained in the blank test but then fell to less than 1.0. Piper, Fleiger, Smith, and Kerstein (*10*) made tests on the insulation of badly deteriorated oil-filled cables and stated: "It seems probable that under conditions of service where the amount of air coming into contact with the oil is at a minimum, the stable state of copper compounds in oil is the cuprous state." They also described experiments in which a 0.5 per cent solution of cupric stearate in paraffin was sealed in a glass tube, and the tube was evacuated, sealed, and heated at 90° C. After 88 days the original blue-green color had disappeared and left a yellow sol. Upon testing the contents of the tube with phosphomolybdic acid, the presence of cuprous compounds was confirmed. With the exception of dibenzothiazyl sulfide (whose test sample was straw-yellow), the color of the oils containing thioether B and disulfide A deposited a green residue on the bottom of the cell. In the test using di-*o*-nitrophenyl disulfide (Figure 12), the color of the oil at the end of the test was orange-brown, and a flocculent precipitate of the same color was observed at the bottom of the cell. The remaining tests showed no appreciable change either in the surface of the copper or the color of the oils.

In general, the oxidation inhibitors lowered the oxygen consumption of base oil G-10 and also lowered its loss characteristics. Those inhibitors which caused the lowest consumption of oxygen also brought about lower values of $\epsilon''f$ (Figures 3 and 4).

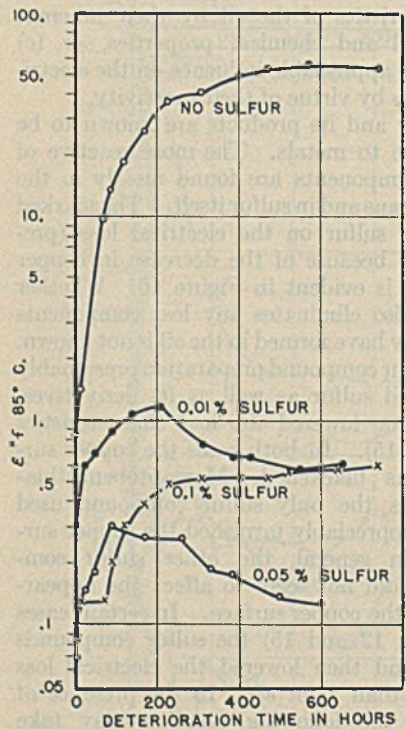


Figure 16. Relation between Conductance $\epsilon''f$ and Deterioration Time for Oil GS-1338 with Varying Concentrations of Sulfur

Atmosphere of nitrogen, 16 sq. cm. copper per gram oil, 85° C.

In view of previous results (*3*) it was thought that the increase in induction period caused by inhibitors might increase the electrical losses. However, apparently the type of "limited" oxidation brought about by inhibitors is different from that in which only small amounts of oxygen are made available to or are consumed by the sample.

In the limited-oxidation tests the nonphosphorus inhibitors had no appreciable effect on the electrical losses, with the exception of *N*-benzyl-*p*-anisidine which gave losses higher than the blank oil (Figure 6). The phosphorus-containing compounds lowered the loss characteristics of the oil. Organophosphates and -phosphites normally are metal corrosives (*8*), and the low losses obtained may have resulted from the subsequent decrease in available copper surface, although no appreciable surface corrosion could be observed.

SUMMARY

Inhibitors. The inhibitors did not produce high electrical losses by increasing the length of the induction period of oil G-10.

In the continuous-oxidation tests the inhibitors which reduced oxygen consumption, in general, reduced the electrical losses.

There is no apparent relation between the behavior of an oxidation inhibitor during continuous and limited oxidations.

tert-Amyl phenyl phosphite produced the lowest electrical losses under the conditions of limited oxidation studied, presumably because of its inactivation of the copper surface.

Varying concentrations of inhibitor and available oxygen and copper surface produced diverse electrical losses.

Sulfur Additives. Sulfur compounds in concentrations found in refined oils may increase or decrease the electrical losses produced by a limited oxidation, depending on their type and structure.

In the samples studied, a thioether and a mercaptan produced high electrical losses during continuous oxidation.

In certain cases initially high electrical losses during limited oxidation decreased to relatively low values. It is believed that cuprous compounds may have formed in the early stages of the tests and subsequently changed over to the cupric state.

Results from the sulfur compound preparation and pure sulfur itself indicated that oils with sulfur compounds which inactivated the copper surface produced low losses during limited oxidation.

General. Limited oxidation may produce conductance values comparable to those obtained by continuous oxidation.

In the range from 0 to 16 sq. cm. of copper surface per gram of oil, the losses produced during a limited oxidation were proportional to the available copper surface.

The nonhydrocarbon constituents of a mineral oil determine to a large extent the characteristics of an oil under limited oxidation. In many cases a few tenths per cent of added compounds may change greatly the characteristics of an oil.

ACKNOWLEDGMENT

These results were obtained in a research project on mineral oil deterioration sponsored by the Engineering Foundation and the American Institute of Electrical Engineers. Funds for this work are being contributed by a group of electric power companies, of oil companies, and of electrical manufacturing companies in addition to the sponsors. The writers wish to thank the Gulf Research and Development Company for making available the special oil samples and additives studied, and the committee (Herman Halperin, chairman) for their cooperation and interest in the work.

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Application of the Phase Rule to SOAP BOILING

Kettle Wax in the Ternary System Soap–Water–Salt

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Previous investigations have established that the phase rule governs the processes of soap boiling in the system soap–water–electrolyte, but the description of the corresponding ternary diagrams has always been incomplete. A series of vapor pressure measurements shows that an important phase, kettle wax, occupies a dominant position in these systems. Kettle wax, and not fibrous curd, is grained out in soap boiling, except where very high concentrations of salt are employed. These results are in good accord with other concurrent studies in this laboratory by McBain, Gardiner, and Vold, using a variety of methods.

IN 1906 Merklen conceived that the phase rule might apply to soap systems. Since 1919 McBain and collaborators have published a series of data on single pure salts of the fatty acids with water, without water, and with both salt and water. These investigations show the strict applicability of the phase rule and the occurrence of true heterogeneous equilibria in all these systems. They also established the range of existence of the chief recognized phases and described ternary systems in terms of curd fibers—soap-boiler's neat soap (liquid crystalline soap solution), a similar but separate middle soap, and isotropic solutions with complicated boundaries extending into lye or brine which contains almost no soap.

Recently a series of new phases has been found in pure anhydrous soaps at elevated temperatures, beginning with three successive forms—waxlike, waxy, and superwaxy (*9*, *11*, *12*). By a variety of methods it has been established that, in the ternary diagram which forms the basis of soap boiling (*1*, *2*, *8*) there is an island of waxlike soap in a dominant position. It is this soap, and not fibrous curd, that is grained out in soap boiling.

Such waxy forms do not occur below 100° C. with the pure saturated higher soaps in the anhydrous condition, and not even in the aqueous binary soap system below the boiling point. However, even with the highest pure single soap, the stearate, the usual ternary phase diagram exhibits a tongue reaching down from higher temperatures and appearing as this island, above and to the right of soap-boiler's neat soap; that is, it contains a somewhat higher concentration of soap and much more salt.

The evidence for the existence of this kettle wax island in pure and commercial soap boiling systems has been obtained by varied experiments and is now published for the first time. Previous publications demonstrated that with anhydrous sodium oleate (*9*, *10*, *11*) the subwaxy form exists between 66° and 115° C., and indicated that with a mixture of sodium laurate, sodium palmitate, and salt (*6*) a waxlike form exists at 90° C.

The present communication is confined to a vapor pressure study, using the McBain-Bakr sorption balance for determining the amount of water vapor taken up by different mixtures of sodium stearate and sodium chloride over a long series of vapor pressures at 90° C. In this way it has been possible to determine the amount of water vapor sorbed by curd fibers of sodium stearate at low relative pressures in the presence of sodium chloride, and the maximum amount of hydration of the curd fibers before another phase appears. A well defined flat of constant pressure follows across the diagram throughout the three-phase region curd–salt–saturated aqueous salt solution. As soon as the salt crystals are dissolved, the pressure rises steadily as more water is put into the system, so that the lye is less than saturated but still in equilibrium with the curd.

The position and existence of the waxy island is best exhibited by plotting and connecting the points of equal pressure for all proportions of salt to sodium stearate in the ternary diagram. The island is shown as a decided dip or minimum in these curves where the kettle wax phase is being traversed.

With this important addition to the five previously recognized typical phases, we believe that the behavior of soap boiling systems can be quantitatively and definitely described. It should be remembered that the final process in the soap kettle is to separate out nigre and thus remove most of the salt; only the soap-boiler's neat soap is left behind; its behavior has been outlined in previous descriptions of binary systems (*7*).

VAPOR PHASE MEASUREMENTS

Samples were made up by weight from pure dry sodium stearate (*5*) and Kahlbaum's sodium chloride for analysis. They were placed in a McBain-Bakr sorption balance, consisting of a platinum bucket suspended from a fused silica spring whose increase in length is proportional to the weight of any water taken up by the mixture. The sealed, evacuated tubes surrounding the springs and buckets were maintained at 90° C. side by side in one thermostat, while pure water in the bottom of the tubes was adjusted to various temperatures in a lower thermostat to produce definite vapor pressures. These are recorded as per cent relative humidity, compared with the vapor pressure of water at 90° C.

Since one vapor phase is always present in a closed system of soap–salt–water, according to the phase rule three liquid or solid phases must coexist at equilibrium when a flat appears

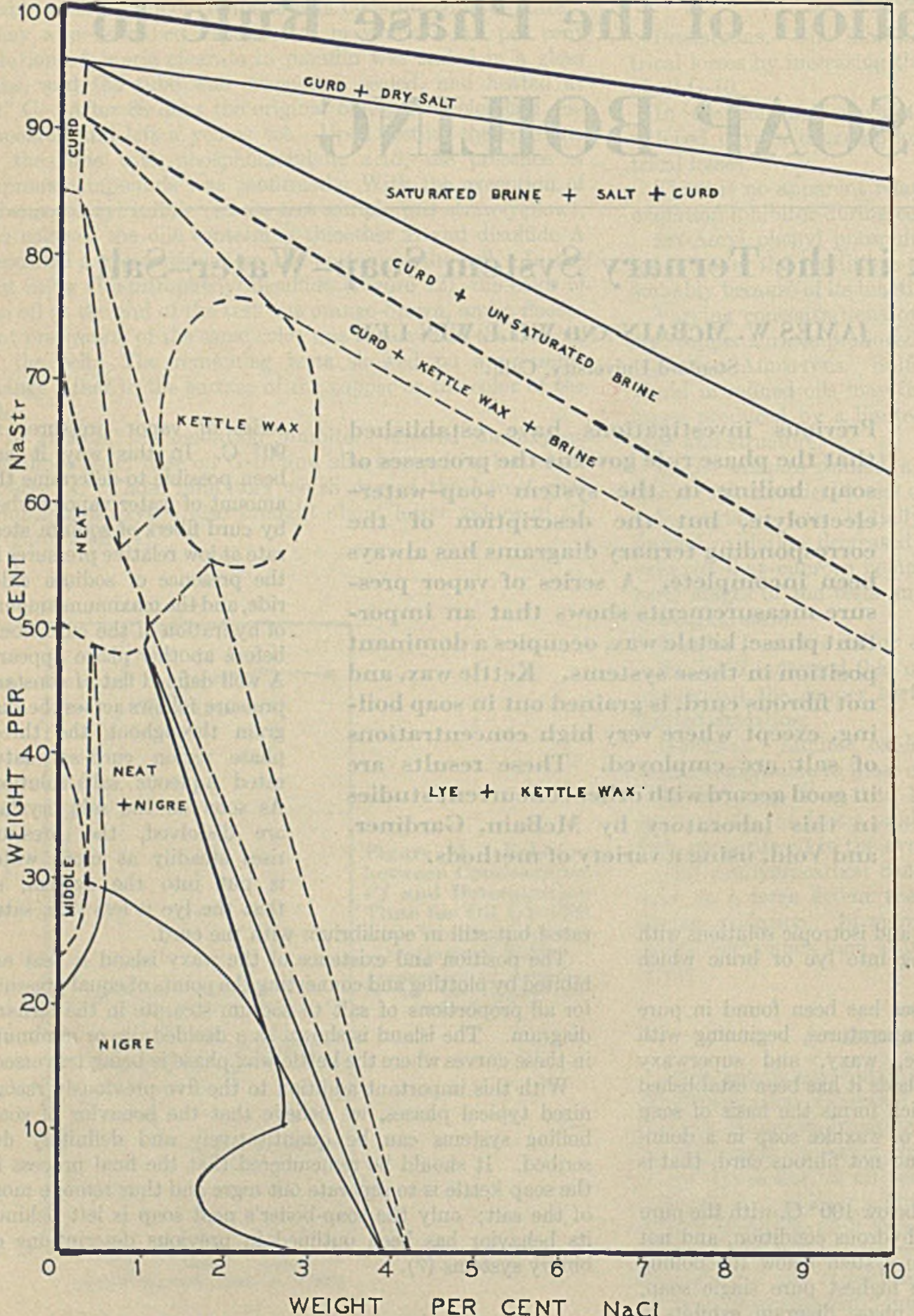

Figure 1. Proposed Phase Diagram for Sodium Stearate–Sodium Chloride–Water at 90° C., Showing Five Homogeneous Fields

The triangles indicate heterogeneous equilibria between the three condensed phases at the apexes of the triangle. The regions between the triangles should be filled with tie lines, each connecting two condensed phases, the tie lines nearest any triangle being almost parallel to the nearest boundary of that triangle.

in the curve of vapor pressure plotted against composition of the mixture in the bucket. As soon as one disappears, the system is bivariant instead of univariant, and the vapor pressure alters continuously at constant temperature. The diagrams are shown in Figures 1 to 3. Figure 1 is the phase diagram itself; it is a right-angle triangle whose ordinates show the weight per cent sodium stearate, and abscissas, the weight per cent sodium chloride. Per cent water is obtained by difference from 100. Figures 2 and 3 are similar diagrams upon which are superimposed isotherms, labeled A_1 to A_3 and C_1 to C_6, respectively. The experimental points are represented by circles.

The isotherms begin at the top of the diagram at 0 per cent humidity and 0 per cent water in the system. All the isotherms begin with the taking up of 1 per cent or so of water in continuous fashion up to about 63 per cent relative humidity; then there is a break and a flat corresponding to a transition to a hemihydrate of composition Na stearate.-$^1/_2H_2O$—that is, about 3 per cent water. This again is stable as it takes up about 1 per cent more water until at 74 per cent relative humidity there is another break. Typical isothermal curves are given in two other communications (*3*, *4*).

This flat at 74 per cent relative humidity corresponds to the vapor pressure of saturated sodium chloride solution (28.4 per cent) at 90° C. Up to this point the sodium chloride had remained solid and inert, and the systems had behaved as if only soap and water were present.

Now that saturated brine is present, the vapor pressure remains constant until enough water is added to dissolve all the salt, and the width of the flat depends upon the amount of salt present. For example, for the three tubes of salt, series *A*, containing as original dry weight 0.5, 1.5, and 3.2 per cent of salt, the flats extend, respectively, from 4.0 to 5.0, from 4.0 to 7.5, from 4.5 to 11.0 per cent by weight of water; or from 95.5 to 94.5, from 94.5 to 91.1, from 93.4 to 86.1 per cent by weight of sodium stearate.

Beyond the right-hand end of the flat, where the salt has all dissolved, the vapor pressure goes up as the brine becomes more dilute. Later we shall see that the other phase (the curd) is also variable in composition. At about 94 to 95 per cent relative humidity the white curd changes to a clear gel. Upon dehydration of the system, the isotherms are found to be reversible and reproducible. However, the exact ratio between salt and soap in the small samples taken (20 mg.) is subject to some error on account of the difficulty of mixing the solids and adequately sampling such small quantities. Hence, there is a lack of complete coincidence between series *A* and *C*, although both yield substantially the same result.

The surest way to interpret the data is to plot all the points on the standard triangular phase diagram shown in Figure 1. Then all points of equal pressure can be connected to give a series of isobaric curves, because all the sealed and evacuated tubes of each of the series of experiments *A* and *C* were in the same thermostats and were read at the same pressures.

TERNARY DIAGRAMS

Figure 1 indicates approximately the phases occurring in the ternary system soap–water–salt and their approximate positions. Tie lines are not drawn between the pairs of phases in equilibrium with each other, but their direction is evident from the boundaries of the six triangular fields drawn to show where three solid or liquid phases are present in equilibrium. The proportions of such phases are given by the inverse of the distances from any given point within the triangle to its three respective corners. The newly recognized kettle wax phase occupies a dominant position in the diagram and shows that, as salt is added in the soap kettle over a wide range, the kettle wax and not curd is first salted out. Only when the lye is really concentrated can curd exist in contact with lye.

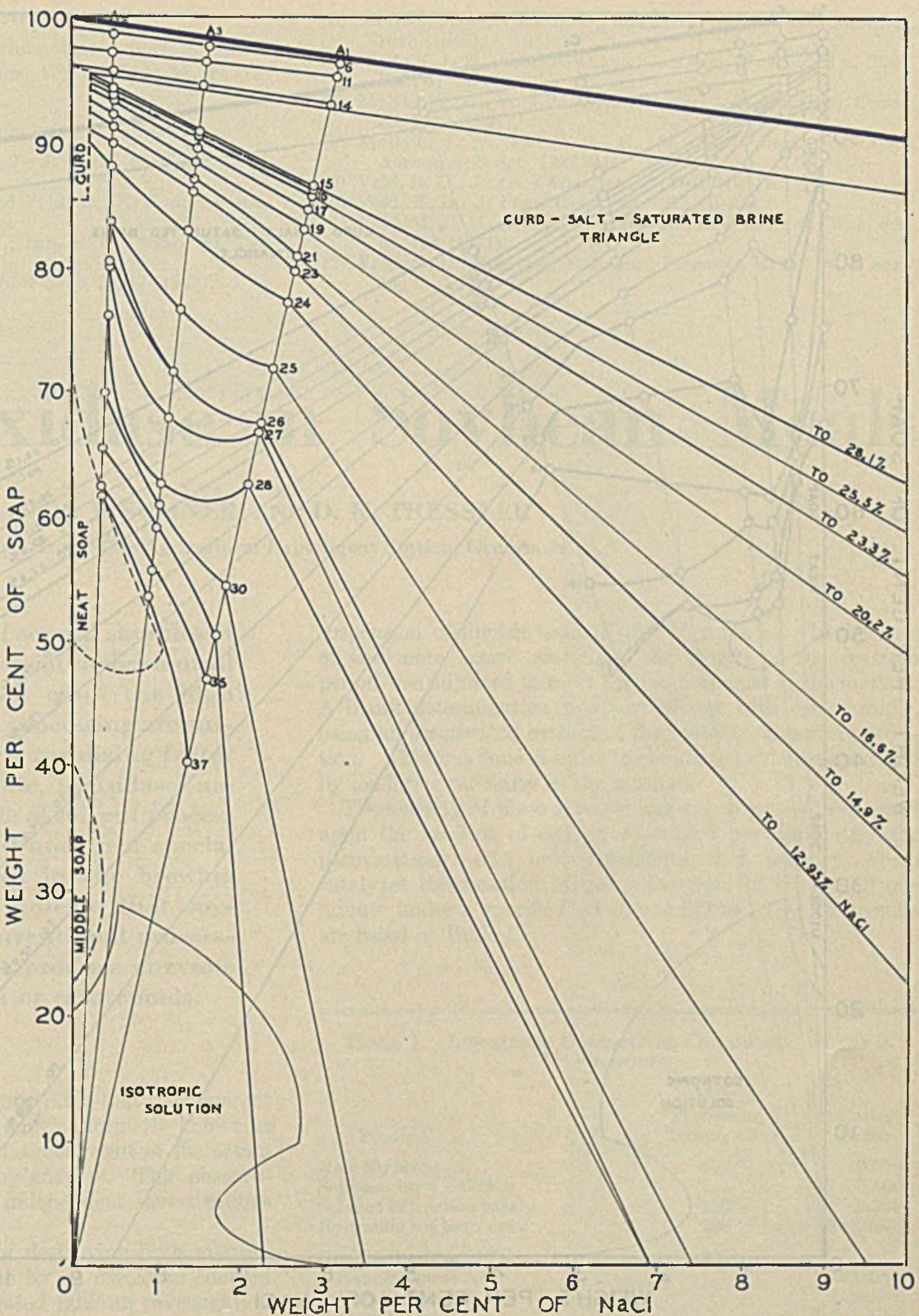

Figure 2. Isobars Connecting Points of Equal Relative Humidity Superimposed upon a Phase Diagram

The points on straight lines A_1, A_2, A_3 running to the water corner of the triangle represent the observations of relative humidity as successive amounts of water are added to the anhydrous compositions at A_1, A_2, and A_3.

The decision on how to place the boundary of the curd region at 90° C. in the absence of salt has to be made arbitrarily. The point is that the curd fibers themselves consist of hemihydrate (Na stearate.$^1/_2H_2O$) containing only 3 per cent combined water. At high humidities, however, there is actually more water in the felted mass of interlacing fibers. Some of this additional water is sorbed, and at highest humidities a progressively larger amount is present simply as capillary liquid in the pores or interstices. Thus, at highest humidities the curd mass contains perhaps as much as 15 or 16 per cent water. Probably it is fairest to present the gross composition of the curd mass as is done in the present diagrams.

Similarly, there is some uncertainty about the uppermost part of the curd region, because we have no means of knowing whether dry salt is sorbed by curd fibers containing sorbed water, although sorption certainly occurs as soon as the saturated brine is present at 74 per cent relative humidity.

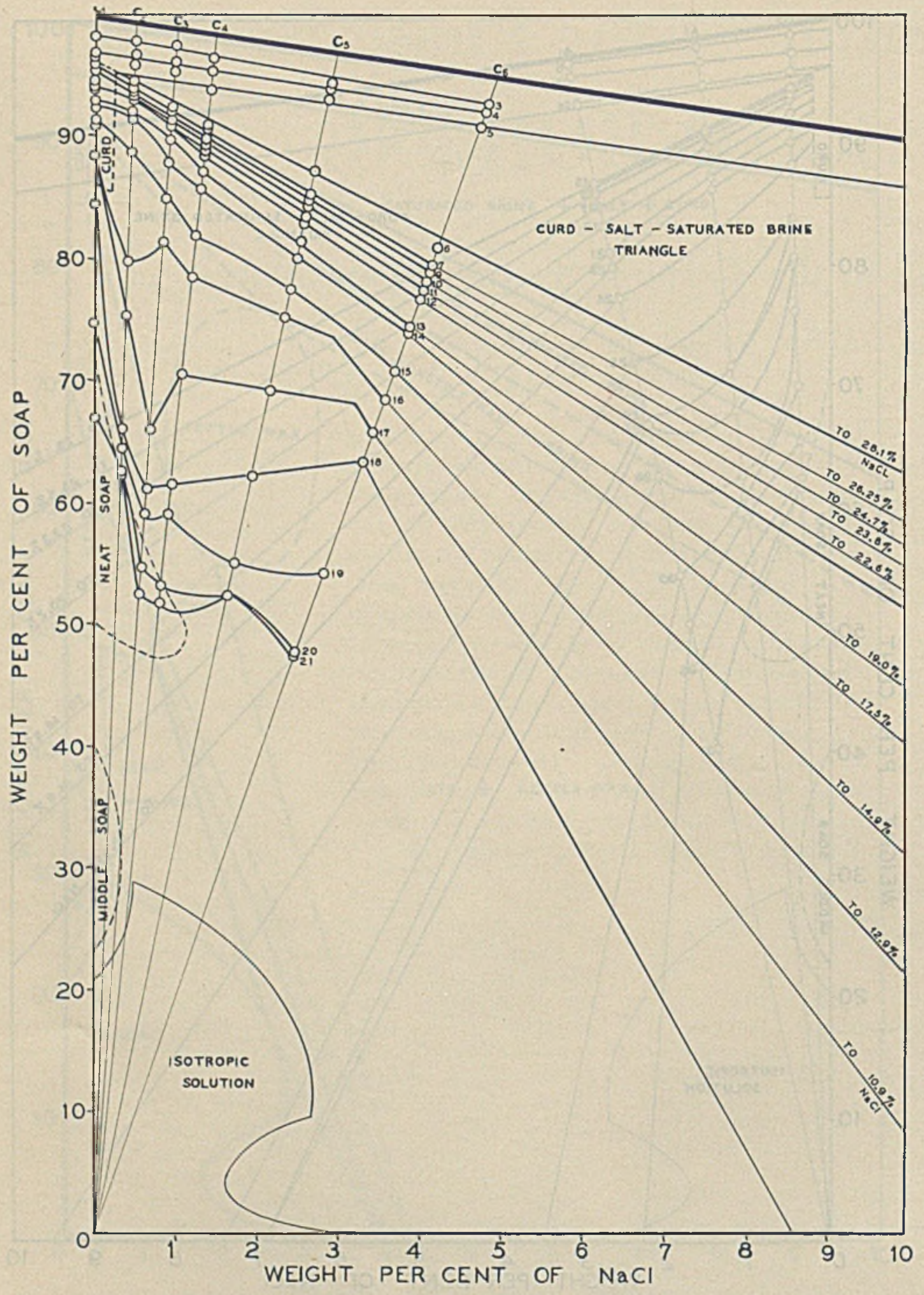

Figure 3. Isobars Connecting Points of Equal Relative Humidity Superimposed upon a Phase Diagram

The points on straight lines C_1, C_2, C_3, C_4, C_5, C_6 running to the water corner of the triangle represent the observations of relative humidity as successive amounts of water are added to the anhydrous compositions at C_1, C_2, C_3, C_4, C_5, and C_6. Lines within curd region are not tie lines but merely connect isobaric points.

Therefore, instead of connecting the pure anhydrous soap directly by a dotted line with the apex of the saturated brine triangle, it may be more correct to represent the composition as proceeding, without salt, down the ordinate until 4 per cent of water has been taken up, and then suddenly breaking over to the apex of saturated brine triangle, where for the first time there is liquid in the system. This has been done in the diagrams.

The triangle uppermost in the diagram is well established at 74 per cent relative humidity. It consists of solid sodium chloride, its saturated aqueous solution (28.4 per cent), and a curd containing 3.85 per cent water, 0.15 per cent salt, and 96 per cent sodium stearate.

The important criterion in looking at the isobars on Figures 2 and 3 is to see how far they extend as straight lines. As long as they are straight lines, they must be tie lines, with no intervening phases between the two ends of the straight part of the lines. With equal cogency, it follows that, where they are not straight and yet are in equilibrium with the same vapor, there cannot be tie lines between two phases. Hence, wherever there is a marked change in direction in the isobars, there is a change in the number of phases or in the kind of equilibrium caused by the intervention of a new phase.

The most important single result in these two figures is that some new phase must have intervened between lye and curd to have made it impossible for a straight tie line to be drawn at constant vapor pressure from lye to curd. The new island of kettle wax soap must have its site in the region of the phase diagram where this complication of the tie lines is definitely found to occur.

The validity of the data is attested by the regions where the isobars or tie lines are actually straight and by the fact that they were reproduced when the system was brought back to any former composition after having passed through the more complicated part of the diagram. The delimitation of the kettle wax island can be made only approximately from the number of isobars available, but the right-hand boundary of the island phase must lie where these bend away from straight lines. Similarly, the upper left-hand boundary of the island phase can be approximately inferred from the forms of the isobars in the region of very low salt concentration and moderately high humidity.

ACKNOWLEDGMENT

The experimental work upon which this report is based was carried out by K. W. Gardiner, W. W. Lee, M. E. L. McBain, and R. D. Vold.

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Lipoid Oxidase in Soybean Meals

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The lipoxidase content of several samples of the three types of commercial soybean meal is investigated. In most cases the high temperatures reached in processing are sufficient to inactivate the peroxidizing factor completely. Considerable lipoxidase activity is found in a sample of solvent process meal extracted at 150°F. and in a special enzyme preparation used in the brewing industry. The results indicate that soybean meals made by conventional processing methods should not produce enzymic destruction of vitamin A or carotenoids.

SUMNER and Sumner (*2*) demonstrated that the apparent oxidation of carotene by the enzyme formerly known as carotene oxidase is in reality an indirect result of the action of an unsaturated fat-peroxidizing enzyme. This observation was later confirmed by the independent investigations of Tauber (*4*).

Since this enzyme is capable of destroying both vitamin A (*1*) and provitamin A pigments by an oxidation coupled with the peroxidation of unsaturated fats, an investigation of the enzymic activity of the various types of commercial soybean meals was undertaken. These meals are used extensively in livestock feeds as a source of protein, so that any possible vitamin A destruction assumes immediate importance.

The soybean meals available commercially are products of the expeller process, the solvent process, or the hydraulic process. Samples of each of these types were procured from manufacturers. They were examined for lipoxidase activity by observation of their effect upon an aqueous suspension of linoleic acid (*3*). Also tested were raw soybeans and a soybean enzyme preparation used in the brewing industry.

The samples of soybean meal were finely ground in a glass mortar and pestle, 0.5 gram of each was extracted with water, and the extracts were made up to 25 cc. volume. One cc. of each extract was allowed to act on a standard suspension of linoleic acid (*3*) for 15 minutes. In the case of the more active materials, the length of the reaction period was adjusted to meet the requirements of the method. A blank determination was carried out with each sample, using an inactivated extract of the material under investigation. This was done in order to eliminate any error produced by oxidative rancidity in the samples.

The activity of these extracts was expressed in units based upon the amount of oxygen consumed per minute by the peroxidation; one unit represents that activity which catalyzes the reaction of one microgram of oxygen in one minute under a specified set of conditions (*3*). The results are listed in Table I.

TABLE I. LIPOXIDASE CONTENT OF COMMERCIAL SOYBEAN PRODUCTS

Product	Max. Processing Temp., ° F.	Units/ Gram
Raw soybeans	...	12,650
Soybean brew flakes	...	9,400
Solvent extraction meal	150	6,800
Hydraulic soybean meal	230	Inactive
Expeller soybean meal	300	
Expeller meal A		Inactive
Expeller meal B		Inactive
Expeller meal C		Inactive
Expeller meal D		Inactive
Expeller meal E		Inactive
Solvent extn. soybean meal	220	
Solvent meal A		Inactive
Solvent meal B		Inactive
Solvent meal C		Inactive
Solvent meal D		Inactive

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Approved by the Station Director. Paper 511.

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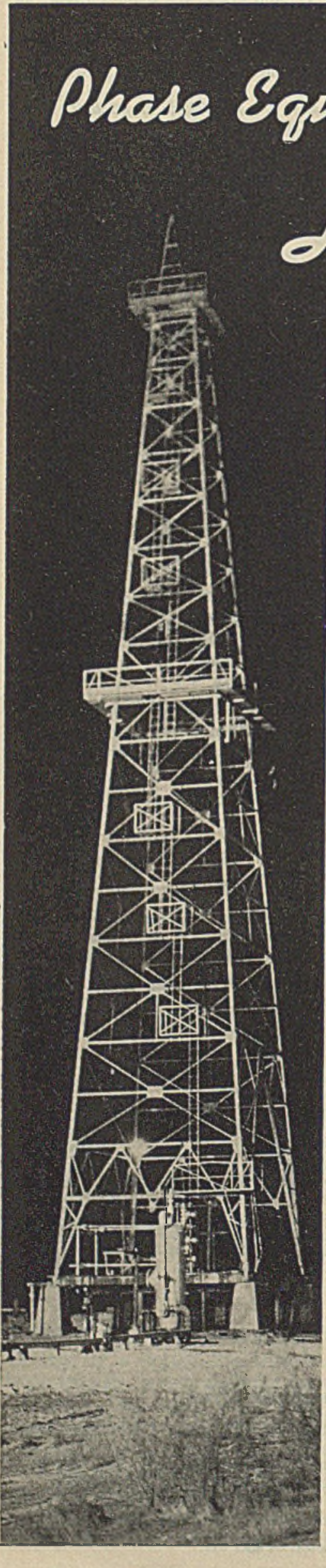
Phase Equilibria in Hydrocarbon Systems



VOLUMETRIC BEHAVIOR OF METHANE

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The volumetric behavior of methane was investigated at pressures up to 10,000 pounds per square inch in the temperature interval between 100° and 460° F. The results of the experimental work are presented in tabular form, and are compared with values obtained in earlier investigations.

THE volumetric behavior of methane was investigated in some detail by Kvalnes and Gaddy (*2*) at pressures up to 15,000 pounds per square inch between −13° and 392° F. Somewhat earlier Keyes and Burks (*1*) studied the volumetric behavior of this gas with some accuracy. The measurements of Michels and Nederbragt (*3*) represent one of the most recent and accurate studies of the behavior of methane. Owing to the importance of this substance in natural hydrocarbon gases and to its frequent use as a component of binary and ternary hydrocarbon systems studied in the laboratory, it appeared desirable to compare measurements obtained with apparatus at the authors' laboratory with those obtained by other investigators. For this reason the volumetric behavior of methane was determined at pressures from above atmospheric to 10,000 pounds per square inch at seven temperatures from 100° to 460° F.

The equipment and methods have already been described (*4*), and no particular modifications were necessary. The equipment for the establishment of the primary variables (weight, temperature, and pressure) was calibrated before the study by comparison with accurate secondary standards. These comparisons permitted corrections to be made for the deviation of the platinum resistance thermometer from the thermodynamic scale of temperature. The volume of the working chamber was large enough so that adsorption did not play a significant part in the uncertainty of measurement.

The gas from a field in the San Joaquin Valley, Calif., was used as the source of methane. This gas consists essentially of methane with water vapor and a small amount of carbon dioxide. The gas as received at the laboratory was passed over granular calcium chloride, sodium hydroxide, activated charcoal, magnesium perchlorate, an ascarite at pressures in excess of 1000 pounds per square inch before introduction into the apparatus. Gas, purified as described above, was subjected to a partial condensation analysis carried out under such conditions that the hydrocarbons heavier than methane were separated quantitatively. The results of these measurements showed that the quantity of ethane and heavier hydrocarbons was less than 0.0002 mole fraction. The specific weight of the purified gas, as determined gravimetrically at atmospheric pressure, agreed with that for pure methane, after correction for the deviation from the perfect gas laws, within 0.1 per cent. Combustion analyses showed that the quantity of nitrogen and other inert gases was less than 0.001 mole fraction. These analytical procedures indicated that the purified material could be expected to contain not more than 0.001 mole fraction of material other than methane.

The smoothed experimental results presented in Table I show the compressibility factor as a function of pressure and temperature. The average deviation of experimental values from the smoothed data was less than 0.1 per cent. The compressibility factor is defined by the following equation:

$$Z = PV/bT \tag{1}$$

In carrying out the calculations necessary to arrive at the values recorded in Table I, the molecular weight of methane, M, was taken as 16.042, and the value of the universal gas constant, R, was taken to be 10.732 (lb./sq. in.) (cu.ft./lb. mole)/° Rankine.

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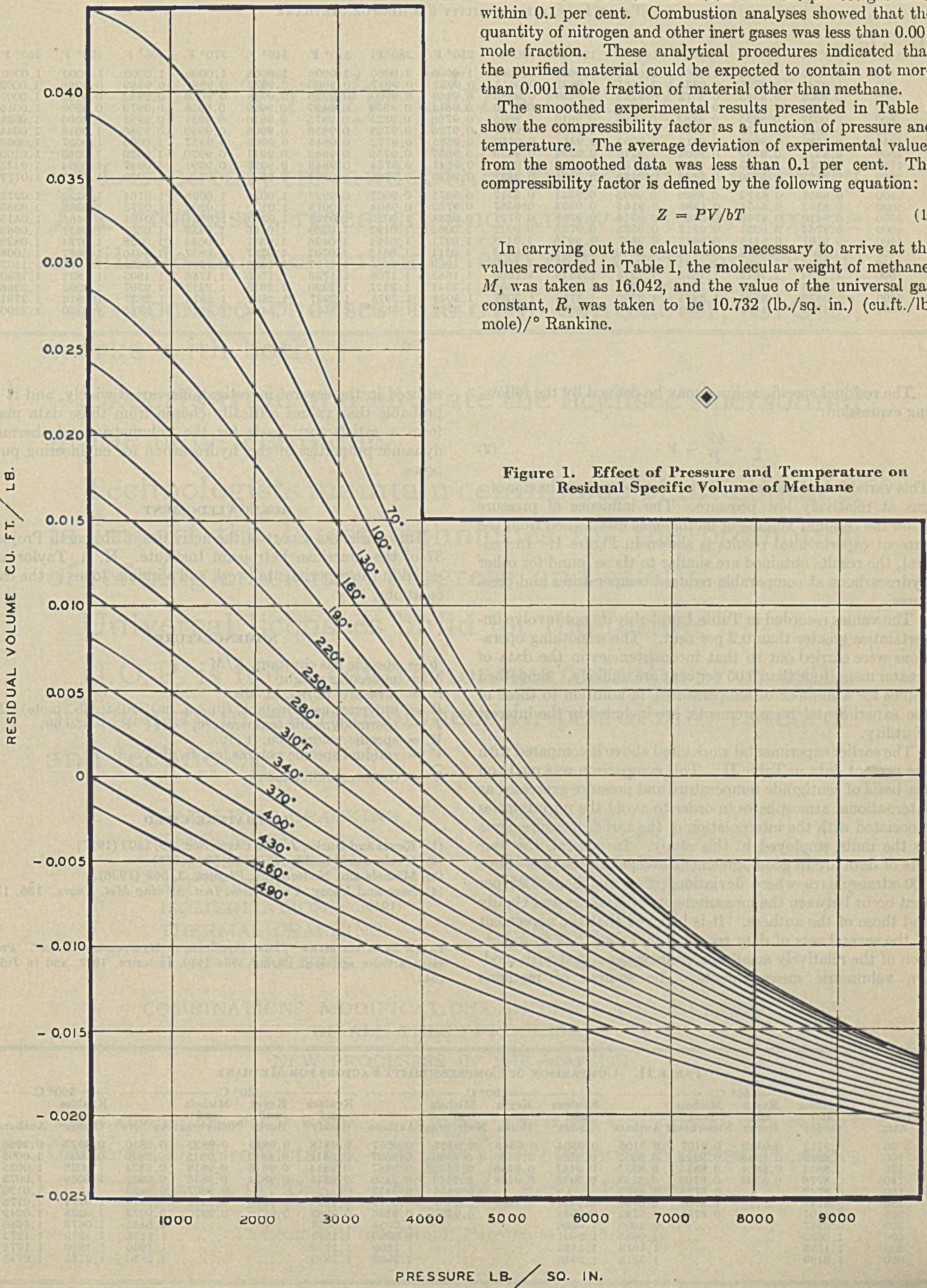

Figure 1. Effect of Pressure and Temperature on Residual Specific Volume of Methane

Table I. Compressibility Factor for Methane

Pressure, Lb./Sq. In. Abs.	70° F.	100° F.	130° F.	160° F.	190° F.	220° F.	250° F.	280°F.	310° F.	340° F.	370° F.	400° F.	430° F.	460° F.
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.9749	0.9795	0.9833	0.9865	0.9891	0.9913	0.9932	0.9947	0.9960	0.9972	0.9981	0.9989	0.9996	1.0002
400	0.9503	0.9598	0.9673	0.9736	0.9789	0.9833	0.9869	0.9900	0.9926	0.9948	0.9966	0.9982	0.9995	1.0007
600	0.9264	0.9410	0.9522	0.9617	0.9695	0.9760	0.9814	0.9859	0.9897	0.9929	0.9956	0.9979	0.9999	1.0016
800	0.9037	0.9235	0.9383	0.9508	0.9610	0.9695	0.9766	0.9825	0.9875	0.9916	0.9951	0.9981	1.0006	1.0028
1000	0.8823	0.9072	0.9257	0.9410	0.9535	0.9639	0.9725	0.9798	0.9858	0.9908	0.9950	0.9986	1.0018	1.0044
1250	0.8582	0.8892	0.9119	0.9303	0.9456	0.9582	0.9685	0.9772	0.9845	0.9905	0.9957	1.0000	1.0037	1.0069
1500	0.8378	0.8739	0.9004	0.9216	0.9394	0.9539	0.9657	0.9758	0.9842	0.9911	0.9970	1.0020	1.0063	1.0100
1750	0.8222	0.8615	0.8913	0.9152	0.9349	0.9510	0.9641	0.9754	0.9848	0.9927	0.9991	1.0047	1.0094	1.0135
2000	0.8122	0.8526	0.8849	0.9109	0.9321	0.9497	0.9639	0.9760	0.9864	0.9950	1.0019	1.0079	1.0131	1.0177
2500	0.8059	0.8471	0.8809	0.9095	0.9321	0.9512	0.9671	0.9807	0.9923	1.0020	1.0098	1.0164	1.0222	1.0272
3000	0.8163	0.8554	0.8886	0.9165	0.9393	0.9587	0.9752	0.9894	1.0018	1.0120	1.0204	1.0273	1.0333	1.0385
3500	0.8410	0.8758	0.9060	0.9316	0.9535	0.9721	0.9884	1.0025	1.0148	1.0250	1.0334	1.0404	1.0465	1.0515
4000	0.8764	0.9054	0.9312	0.9535	0.9735	0.9912	1.0062	1.0192	1.0308	1.0406	1.0489	1.0558	1.0617	1.0663
4500	0.9191	0.9415	0.9622	0.9807	0.9979	1.0138	1.0271	1.0391	1.0496	1.0587	1.0664	1.0728	1.0784	1.0829
5000	0.9650	0.9813	0.9968	1.0119	1.0266	1.0395	1.0511	1.0612	1.0707	1.0787	1.0857	1.0916	1.0967	1.1008
6000	1.0610	1.0681	1.0761	1.0840	1.0925	1.1000	1.1069	1.1134	1.1197	1.1253	1.1297	1.1335	1.1371	1.1402
7000	1.1624	1.1612	1.1613	1.1615	1.1628	1.1650	1.1682	1.1708	1.1739	1.1765	1.1786	1.1803	1.1822	1.1830
8000	1.2664	1.2555	1.2480	1.2425	1.2384	1.2355	1.2341	1.2327	1.2320	1.2315	1.2312	1.2307	1.2303	1.2296
9000	1.3673	1.3508	1.3365	1.3250	1.3158	1.3084	1.3029	1.2975	1.2937	1.2898	1.2870	1.2837	1.2813	1.2791
10000	1.4713	1.4470	1.4259	1.4080	1.3937	1.3822	1.3722	1.3635	1.3554	1.3490	1.3425	1.3375	1.3330	1.3290

The residual specific volume may be defined by the following expression:

$$\underset{\sim}{V} = \frac{bT}{P} - V \qquad (2)$$

This variable is of special utility in describing the behavior of a gas at relatively low pressure. The influence of pressure upon the residual volume of methane as established from the present experimental results is shown in Figure 1. In general, the results obtained are similar to those found for other hydrocarbons at comparable reduced temperatures and pressures.

The values recorded in Table I probably do not involve uncertainties greater than 0.2 per cent. The smoothing operations were carried out so that inconsistencies in the data of greater magnitude than 0.05 per cent are unlikely. Smoothed values for a number of temperatures, in addition to those of the experimental measurements, are included in the interest of utility.

The earlier experimental work cited above is compared with the present data in Table II. This comparison was made on the basis of centigrade temperature and pressure expressed as international atmospheres in order to avoid the uncertainties associated with the interpolation of the earlier measurements to the units employed in this study. In general, the four sets of data are in good agreement except at pressures above 300 atmospheres where deviations of as much as 0.25 per cent occur between the measurements of Kvalnes and Gaddy and those of the authors. It is believed that the agreement of the several sets of data recorded in Table II is an indication of the relatively small uncertainty associated with modern volumetric measurements. The sources of methane utilized in the several investigations varied widely, and it is probable that values critically chosen from these data may form a satisfactory basis for the volumetric and thermodynamic properties of this hydrocarbon for engineering purposes.

ACKNOWLEDGMENT

This work was a part of the activities of Research Project 37 of the American Petroleum Institute. H. A. Taylor assisted in the experimental work and Virginia Jones in the calculations.

NOMENCLATURE

b = specific gas constant, R/M
M = molecular weight
P = pressure, lb./sq. in. abs.
R = universal gas constant, (lb./sq. in.) (cu. ft./lb. mole)/°R.
T = thermodynamic temperature, ° R. (° F. + 459.69)
V = specific volume, cu. ft./lb.
$\underset{\sim}{V}$ = residual specific volume, cu. ft./lb.
Z = compressibility factor

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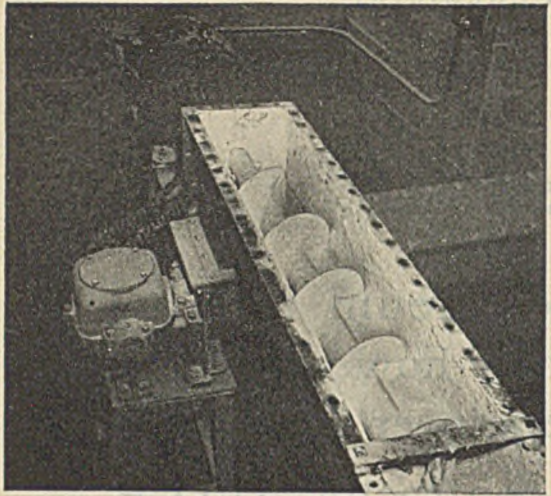
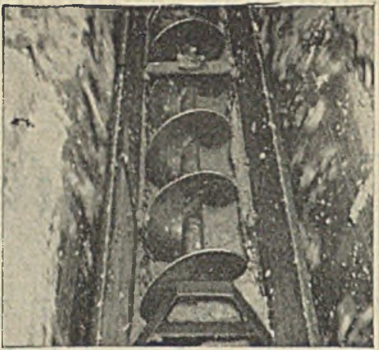
Paper 39 in the series "Phase Equilibria in Hydrocarbon Series". Previous articles appeared during 1934–1940, inclusive, 1942, and in July, 1943.

Table II. Comparison of Compressibility Factors for Methane

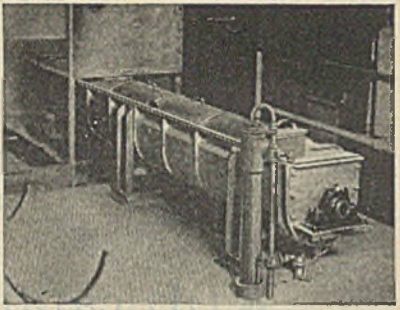
Pressure, Atm.	50° C.				100° C.				150° C.				200° C.	
	Kvalnes and Gaddy	Keyes and Burks	Michels and Nederbragt	Authors	Kvalnes and Gaddy	Keyes and Burks	Michels and Nederbragt	Authors	Kvalnes and Gaddy	Keyes and Burks	Michels and Nederbragt	Authors	Kvalnes and Gaddy	Authors
80	0.9112	0.9110	0.9107	0.9106	0.9564	0.9565	0.9567	0.9567	0.9818	0.9819	0.9827	0.9830	0.9975	0.9986
100	0.8969	0.8948	0.8952	0.8952	0.9506	0.9506	0.9506	0.9507	0.9811	0.9812	0.9816	0.9820	0.9995	1.0005
120	0.8852	0.8834	0.8835	0.8835	0.9467	0.9468	0.9466	0.9467	0.9814	0.9815	0.9819	0.9824	1.0028	1.0035
140	0.8776	0.8761	0.8760	0.8758	0.9448	0.9449	0.9449	0.9450	0.9834	0.9834	0.9836	0.9842	1.0069	1.0073
160	0.8742	....	0.8728	0.8725	....	....	0.9454	0.9452	....	....	0.9867	0.9873	....	1.0120
180	0.8747	....	0.8739	0.8735	0.9499	0.9493	0.9482	0.9479	0.9914	0.9916	0.9912	0.9916	1.0174	1.0176
200	0.8801	....	0.8791	0.8786	0.9548	....	0.9530	0.9526	0.9983	0.9979	0.9970	0.9973	1.0228	1.0242
300	0.9517	....	....	0.9500	1.0066	....	....	1.0054	1.0453	....	....	1.0432	1.0673	1.0680
400	1.0632	....	....	1.0635	1.0901	....	....	1.0900	1.1119	....	....	1.1118	1.1279	1.1272
500	1.1895	....	....	1.1918	1.1885	....	....	1.1890	1.1939	....	....	1.1930	1.1980	1.1971
600	1.3199	....	....	1.3218	1.2946	....	....	1.2962	1.2836	....	....	1.2830	1.2745	1.2745



Reclaiming Hydrated Lime



Handling Paper Pulp



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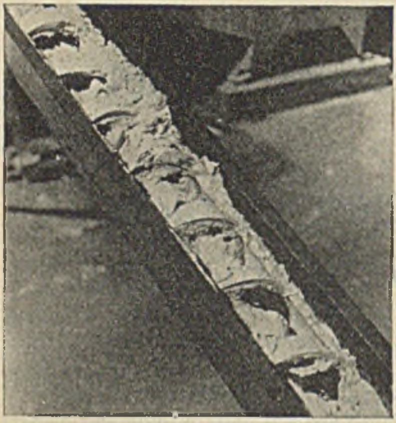
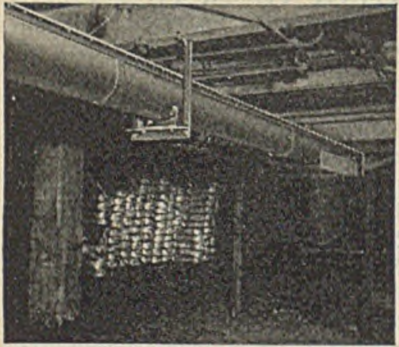
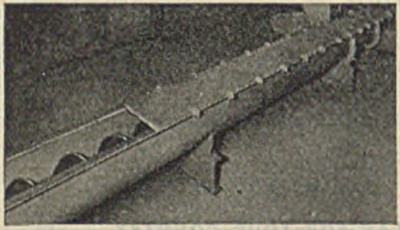


Conveying Wet Silica Sand



Handling Carbon Black



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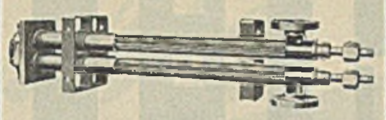
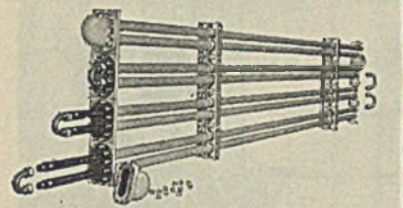
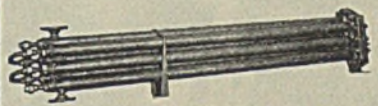
FOR VICTORY BUY UNITED STATES WAR BONDS AND STAMPS








WeldELLS
have everything★
6" STD. TAYLOR FORGE WELDELL

Struthers Wells

EVAPORATORS-CRYSTALLIZERS

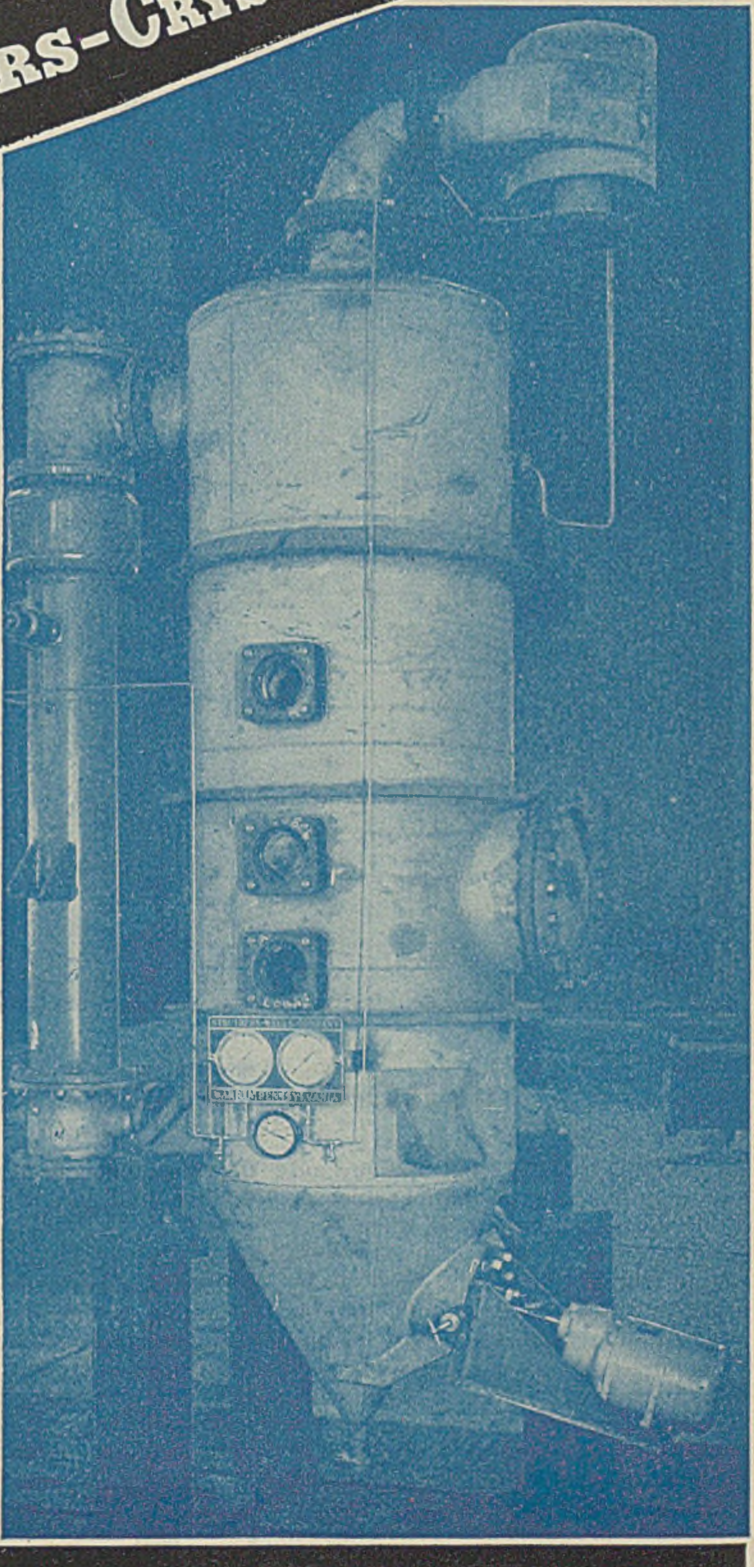


Illustration shows a Struthers Wells evaporator-crystallizer used in recovery of acid solution in a large steel plant. Part of a new system recently installed, which will save a large quantity of a strategic metal for war use. A number of similar units are in service in four other plants.

The unit shown is constructed of stainless steel; similar units have been made of Monel and nickel clad construction.

Struthers Wells specializes in evaporation and crystallization work involving acid solutions and other corrosive fluids. Units of nickel, Monel, stainless, lead, rubber lined, Hastelloy and Karbate are under construction at this time in our shops.

ARMY E NAVY

For outstanding production, the Army-Navy "E" Flag proudly flies over all of three plants.

STRUTHERS WELLS CORPORATION

WARREN, PENNSYLVANIA

***Plants at Titusville,* Penna. and Warren, Penna.**

Where will help come from...?

NO MATTER what foreign land a man fights in, no matter which of the farthest seas he sails, there's one direction—and only one direction—he can look to, for the aid he needs in fighting. That direction is *homeward.*

In no other war in history has the man at home played such an important part. The arms to fight with, *enough in time* to give our men a fighting chance, must be produced at home. The ships to carry them, and naval craft to guard them adequately, must be produced at home. This is a total war, and that is why it is vital that each man at home produce as much as he can, *without interruption or slow down.*

There is one kind of industrial slow down that we can and should prevent . . . the slow down caused by failure of the valves that control power and production fluids in a plant.

The way to prevent such a slow down is to *avoid valve trouble before it starts.* Keep the valves in your plant operating continuously, by inspecting them regularly. Renew worn parts before a valve can destroy itself. When valves must be replaced, have the new valves selected and installed by experienced men. Above all, train new workers to operate and maintain valves properly.

Jenkins Engineers are ready to assist any management in developing a practical program of valve conservation.

Reprints of this advertisement are available for display in your plant.

Jenkins Bros., 80 White Street, New York, N. Y.; Bridgeport, Conn.; Atlanta, Ga.; Boston, Mass.; Philadelphia, Pa.; Chicago, Ill. Jenkins Bros., Ltd., Montreal; London, Eng.

TRADE JENKINS MARK

Jenkins Bros

JENKINS VALVES

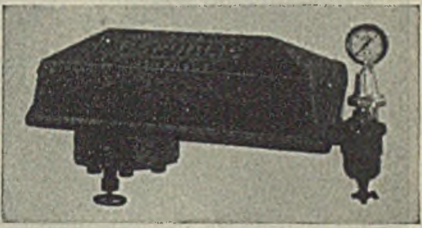
SINCE 1864

For every industrial, engineering, marine and power plant service . . . in Bronze, Iron, Cast Steel and Corrosion-Resisting Alloys . . . 125 to 600 lbs. pressure.

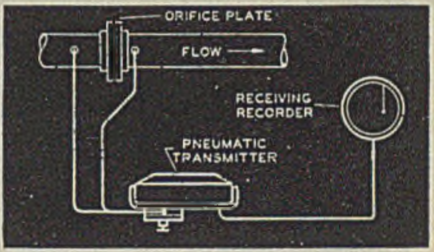
A COMPLETELY NEW PNEUMATIC TRANSMITTER

For Measuring Flow and Level

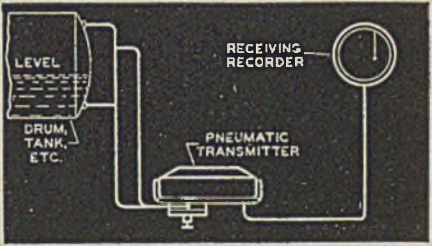
A new metering device operating on the Force-Balance Principle



The Republic Differential Pressure Transmitter.



Typical installation for measuring flow.



Typical installation for measuring liquid level.

Republic announces an entirely new type of pneumatic meter which has been thoroughly field tested during the past two years. The Republic Differential Pressure Transmitter is a simple pneumatic device for converting a differential pressure, such as is produced by the flow of a fluid through an orifice or by liquid level in a vessel, into an air pressure which varies proportionately with the differential pressure.

This air pressure is used as a direct measure of the differential pressure and can be conducted to a remote location by means of tubing. A gage or receiver connected anywhere in this transmission line will show the variations in the differential pressure and may be graduated in terms of the flow or level which it represents. The pressure can also be utilized as the impulse for actuating a controller.

RANGES—standard ranges are available from 0.9 in. to 25 in. of water differential, for working pressures up to 15 psi.; 7 in. to 50 in. of water for working pressures up to 25 psi.; and 13 in. to 800 in. of water for working pressures up to 600 psi. Special heads can be provided for working pressures up to 2000 psi.

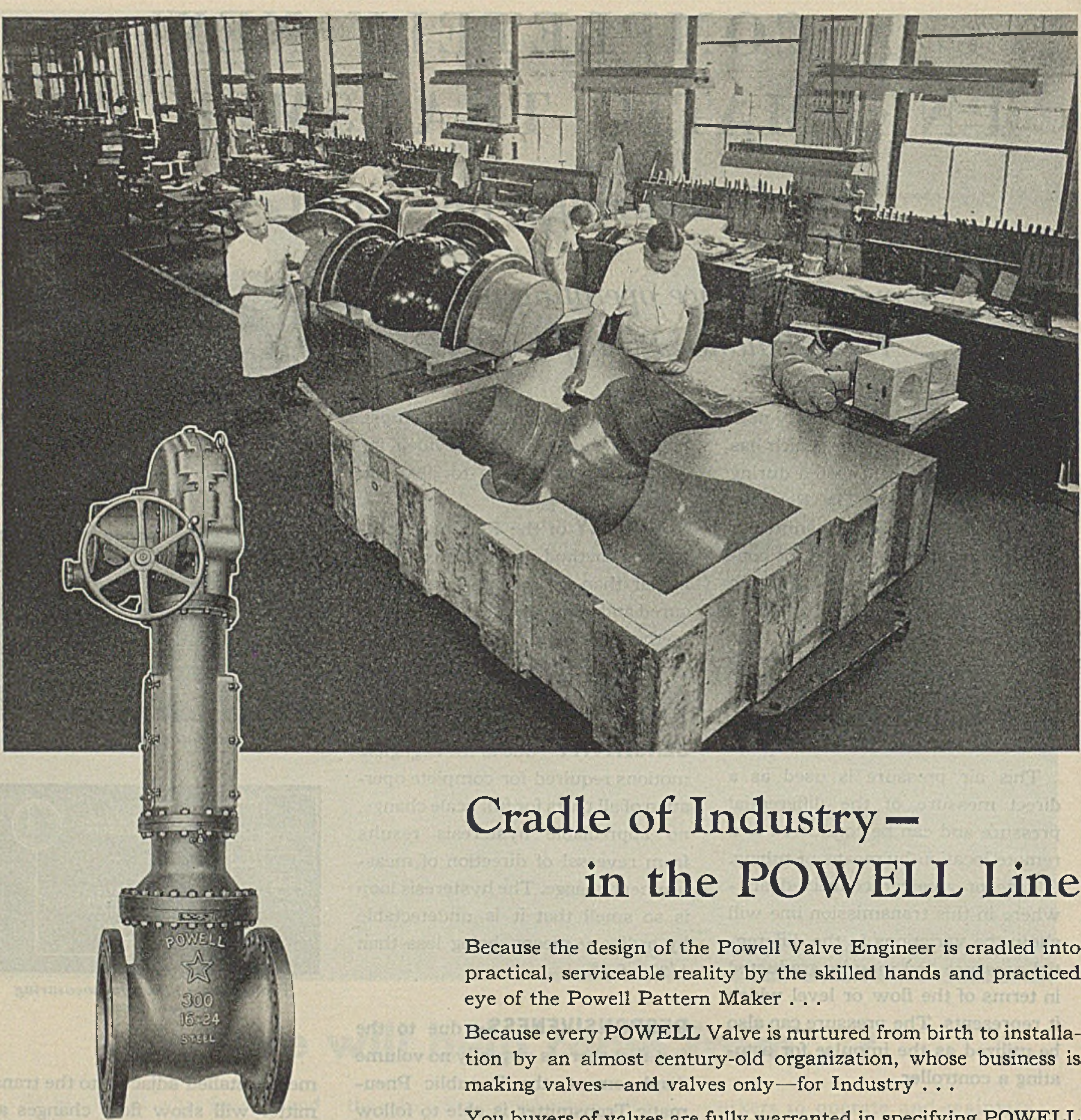
ACCURACY of the Republic force-balance method of measurement is higher than can be consistently secured and maintained with any other method. Transmitting pressure vs measured differential is guaranteed within ½ of 1% of meter range.

SENSITIVITY—due to the negligible motions required for complete operation of all parts for full scale change, no appreciable hysteresis results from reversal of direction of measurement change. The hysteresis loop is so small that it is undetectable by ordinary means, being less than 1/20 of 1%.

RESPONSIVENESS—due to the fact that there is virtually no volume displacement, the Republic Pneumatic Transmitter is able to follow flow changes almost instantaneously. The time required to produce full output pressure at the transmitter is in the nature of fractions of a second, after the differential is imposed. Therefore a receiving instrument installed adjacent to the transmitter will show flow changes almost instantly. With 500 feet of ¼ in. O.D. tubing, the full value of the change will have registered on a Republic receiver in 15 seconds. This is the overall lag in the system not merely, the transmission lag.

For complete data write for Bulletin No. 43-4

REPUBLIC FLOW METERS CO.
2212 Diversey Parkway, Chicago, Illinois



POWELL
300
16-24
STEEL

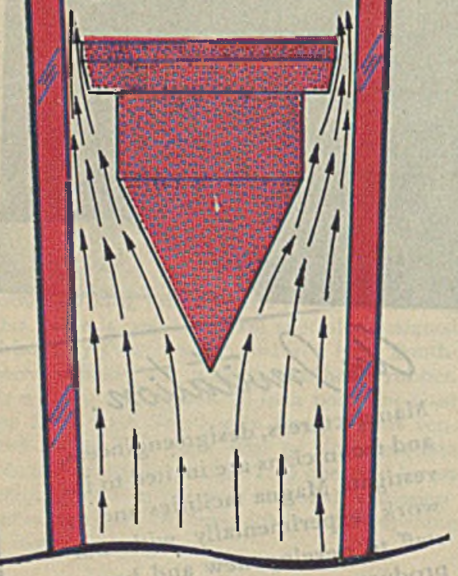

Today... IT'S LIGHT
TO WIN THE FIGHT

The **ROTAMETER**

has these advantages over head-type meters for flow rate measurement and control

8 BASIC ADVANTAGES

1. Metering elements and fluid being metered clearly visible
2. Wide flow range—20-to-1 easily obtained
3. Evenly spaced scale divisions—no compression of scale at low flows
4. Low, constant pressure drop—reduces pumping costs
5. New Stabl-Vis rotameter compensates for viscosity and density variations
6. 10" to 24" travel of metering float—accuracies correspondingly high
7. Instantaneous response to flow change—no friction or hysterisis
8. Measures corrosive gases, liquids and slurries that no other meter will handle accurately



DURING the last two years a definite reversal of trend in the development of meters for rate of flow measurement has become noticeable in industry. The area-type flow meter, in the form of the rotameter sight flow meter, has steadily and surely elbowed its way to the front. Already it has completely replaced the head-type meters (orifices, flow nozzles, venturis, weirs, capillaries) for many important applications and the process of replacement is still going on.

The inherent theoretical advantages of the area-type flow meter have always been recognized, and equally obvious were the several limitations of the head-type meter. Yet for a long time the area-type meter was mainly a curiosity, used only for unusually difficult applications. Not until Fischer & Porter Company in 1937 announced the availability of precision-bore, interchangeable transparent metering tubes for rotameter sight flow meters, did the area meter start to progress.

In Toricelli's equation $Q = CA\sqrt{2gh}$, the area-type meter (rotameter) obtains measurement by varying the value of "A" (area of flow passage) whereas head meters vary the value of "h" (head producing flow). Thus the rotameter "gets out from under the square-root sign," which results in a linear calibration scale instead of a square root scale crowded at the lower end. The range of flows which can be accurately metered with the rotameter is thereby tremendously increased.

Furthermore, the visibility in the rotameter of the fluid being metered and of the metering elements eliminates errors due to fouling or corrosion. Likewise, the pressure drop through the rotameter is low and constant because the flow area enlarges as the float rises in the tapered tube with flow increase. Thus the rotameter may be used where low initial pressures only are available, and at all times the rotameter reduces the pressure required to pump fluids through the lines. In remote recording and controlling rotameters, another outstanding advantage is the ability to visually check the readings of the primary instrument against the readings of the secondary instrument while in operation.

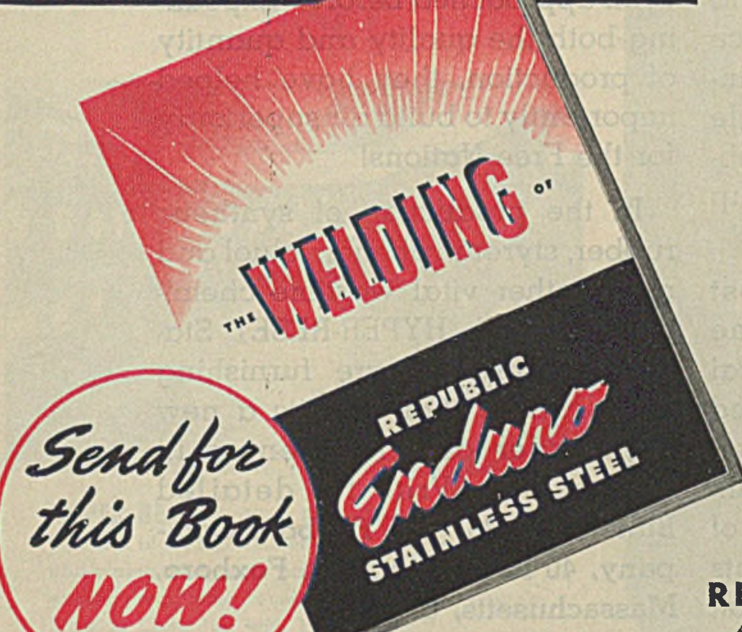
Possibly you have used the rotameter sparingly, or not at all, because you have not realized its basic worth. The further one delves into the details of the rotameter functioning, the more advantages come to light. Modern instrumentation is characterized by an acknowledgment of these advantages through the increasing use of the rotameter for flow rate measurement and control. Our bulletin #10-A entitled "A New Trend in Flow Rate Measurement" describes the rotameter clearly and concisely. It contains free, valuable information — why not write for it? We will gladly send it to you without any obligation whatsoever.

FISCHER & PORTER CO.
348 County Line Road, Hatboro, Pa.

FISCHER & PORTER CO.

F-P ROTAMETERS

RATE OF FLOW INDICATING, RECORDING OR CONTROLLING ROTAMETERS FOR ANY LIQUID OR GAS



TO HELP YOU *get best results in* WELDING STAINLESS STEEL

Republic metallurgists and engineers prepared this book for YOU—to help you weld Republic ENDURO Stainless Steel soundly and economically on a steady production basis.

It contains twenty pages of useful information based on Republic's many years of pioneering stainless steel and wide experience in the production and fabrication of this metal. It covers electric arc, spot, projection, atomic hydrogen, gas, flash and seam welding.

It discusses the various analyses, their relative welding qualities and precautions to exercise. It contains diagrams of joint set-ups. It includes brazing and silver soldering. And it contains a two-page chart showing physical, electrical, mechanical, heat-treating, heat-resisting, machining and drawing or stamping properties of the popular analyses.

This book has proved a very useful and valuable aid to thousands of users of stainless steel—and will do the same for you. Write us for a copy—and, if you are interested in other methods of fabrication (stamping, drawing, machining, forming, etc.), ask also for a copy of "The Fabrication of Republic ENDURO Stainless Steel". Either or both books will be sent promptly.

REPUBLIC STEEL CORPORATION
Alloy Steel Division, Dept. EC
Sales Offices • Massillon, Ohio
GENERAL OFFICES • CLEVELAND 1, 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 17, N. Y.

REPUBLIC
*Enduro** **STAINLESS STEEL**
*Reg. U. S. Pat. Off.

Other Republic products include Pipe, Sheets, Upson Quality Bolts and Nuts, Electrunite* Condenser and Heat Exchanger Tubes

Behind Our Growing

AN IMPORTANT DEVELOPMENT IN PROCESS CONTROL!

Warplanes weren't the only things required to establish the United Nations' present mastery of the skies above both friendly and enemy territories. The importance of aviation gasoline, as well, is indicated by the fact that a single raid in today's "saturation" bombing of European cities burns up 500,000 to 1,000,000 gallons!

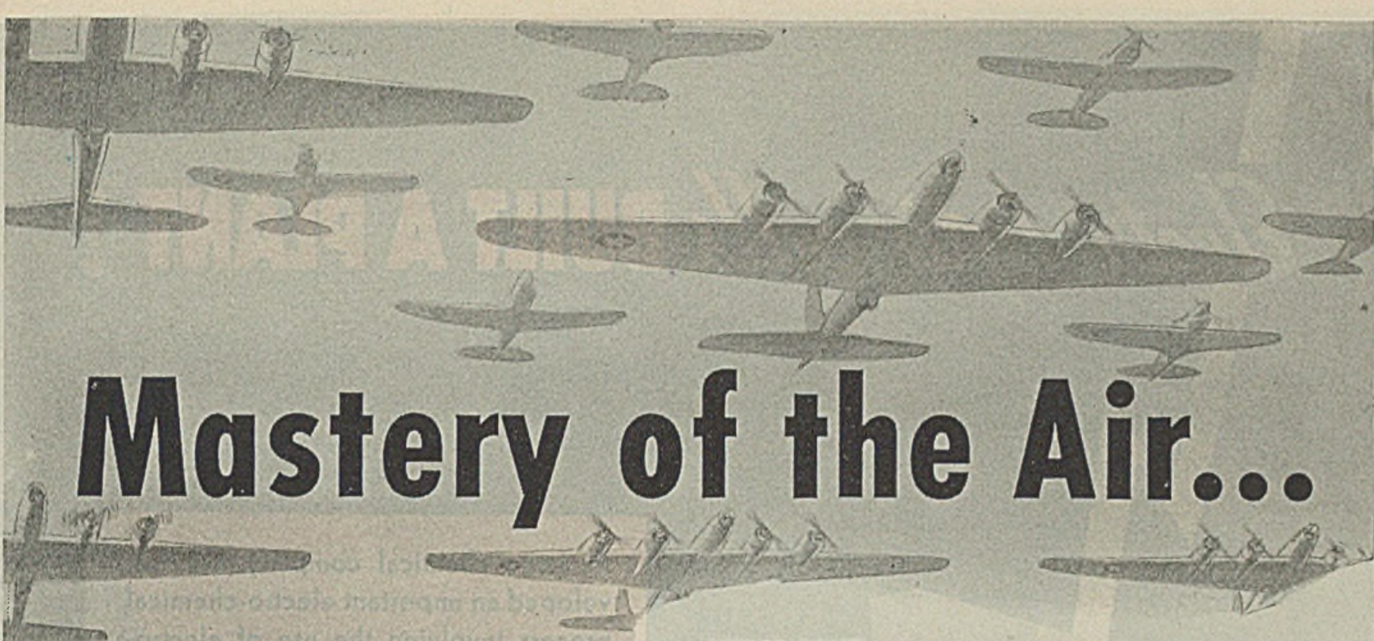
Just in time to help boost America's 100-octane gasoline production to meet this colossal war demand, Foxboro developed HYPER-RESET . . . a new advanced control function that enabled fullest and most efficient utilization of 100-octane units. At critical points in the majority of today's aviation gasoline plants, Stabilog Controllers with this exclusive function are furnishing *process stability never even approached before!* Expediting both the quality and quantity of production, they have helped importantly to build air superiority for the Free Nations!

In the production of synthetic rubber, styrene, phenol, toluol and many other vital wartime chemicals, as well, HYPER-RESET Stabilog Controllers are furnishing super-control that permits a new high order of selectiveness in processing. Write for detailed Bulletin A-330. **The Foxboro Company, 40 Neponset Ave., Foxboro, Massachusetts, U. S. A.**

Stabilog

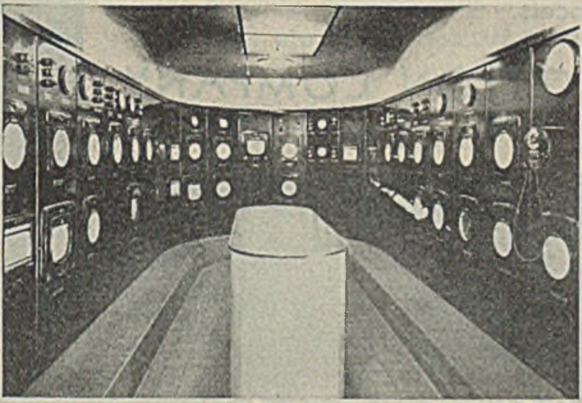
REG. U.S. PAT. OFF.

Controllers with HYPER-RESET

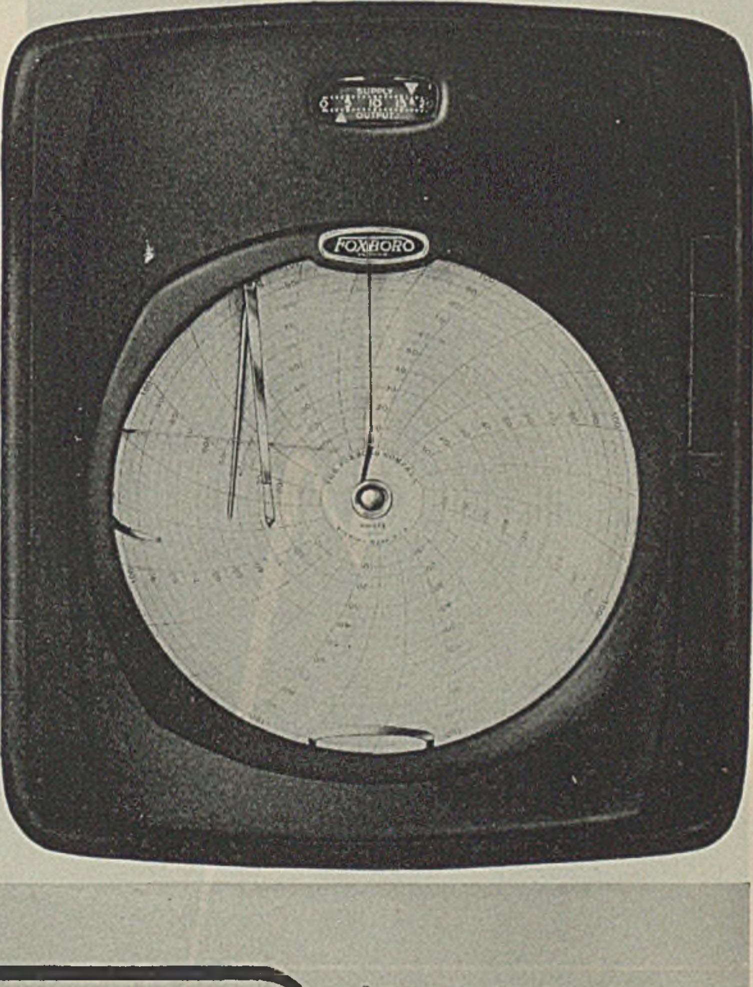


Mastery of the Air...

HYPER-RESET Stabilog Controllers set a new precedent for stability in process control! They automatically evaluate the maximum of every disturbance by accurately measuring the *rate of change* at the start. Then, they instantly apply hyper-corrective action to suit. The result is radically smoother recovery . . . in as little as ¼ the usual time . . . with as much as 50% reduction in the amount of upset!



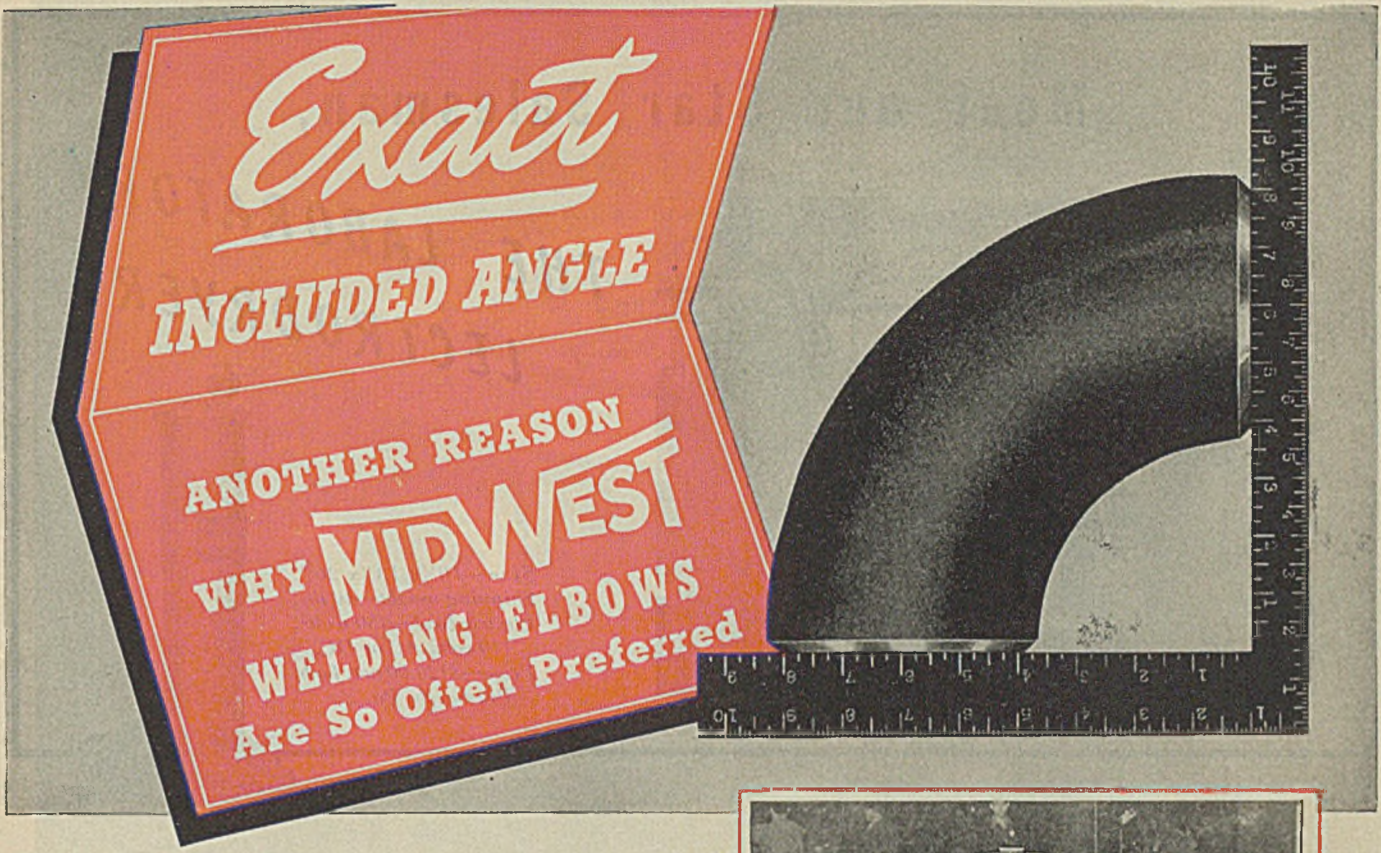
HYPER-RESET Stabilog Controllers in new polymer unit of a large refinery. Newest-type alkylate and casinghead plants also have found their most exacting requirements uniquely fulfilled by today's Stabilog Controller with HYPER-RESET.

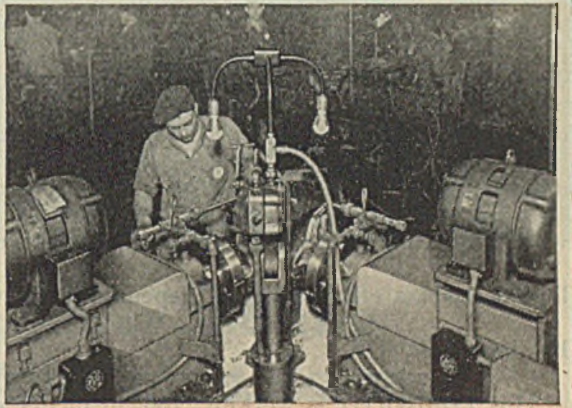


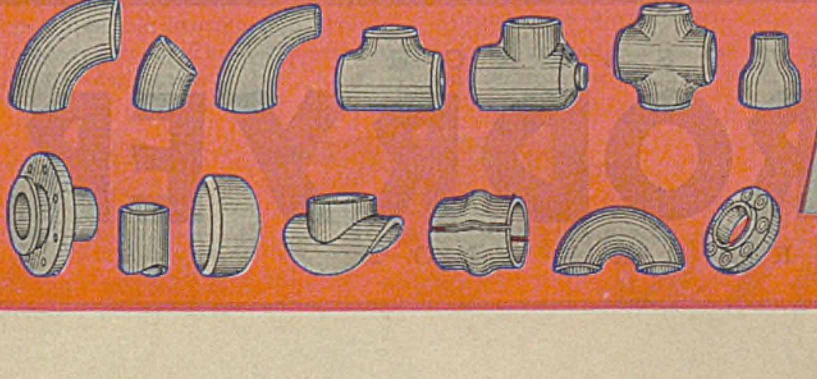
by FOXBORO

REG. U. S. PAT. OFF.

ARMY E NAVY

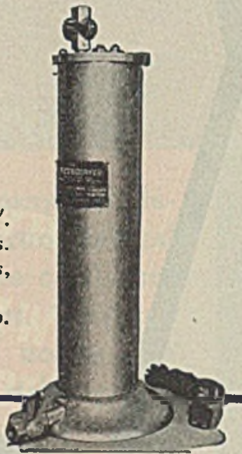

Exact
INCLUDED ANGLE
ANOTHER REASON
WHY MIDWEST
WELDING ELBOWS
Are So Often Preferred





Meet our Star Salesman,

THE LABORATORY LECTRODRYER



Size—10″x 13″x 26″.
Shipping weight—40 lbs.
Electric load—450 watts,
110 volts AC or DC.
Price—$120.00 net, f.o.b.
Pittsburgh, Pa.

The "Laboratory model" Lectrodryer is on dozens of important production jobs. The work can't be described here—Censors say "No", for it is war work—but each machine is DRYing air, gases or liquids just as efficiently and dependably as its big brothers.

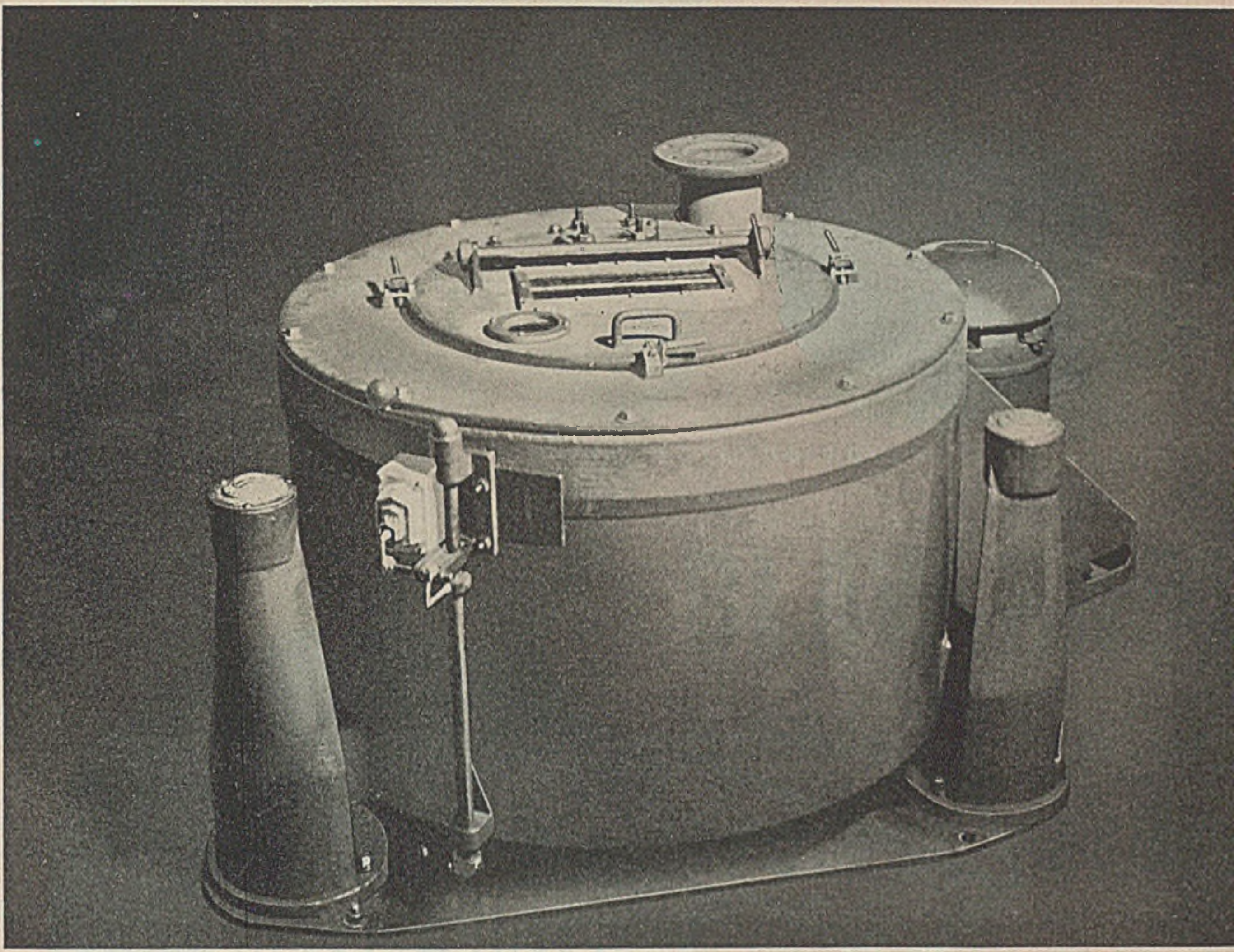
This Lectrodryer is working, too, in plenty of laboratories throughout the country. It is teaching students the difference between old-fashioned hit-or-miss methods and the modern way of working with materials of definite dryness. The war effort is aided as these students carry this knowledge into industry.

And the Laboratory Lectrodryer is serving in many pilot plant operations, helping researchers perfect their products. It points the way for speeding production, standardizing manufacturing methods and maintaining constant quality. Hundreds of standard Lectrodryers have been installed as pilot plant findings were shifted to full scale production.

Laboratory Lectrodryers can be shipped from stock with suitable priority. Pittsburgh Lectrodryer Corporation, 305 32nd Street, Pittsburgh, Pennsylvania.

LECTRODRYERS DRY WITH ACTIVATED ALUMINAS

PITTSBURGH
LECTRODRYER
CORPORATION
Reg. U.S. Pat. Off.



To Find More Jobs for Johnny When He Comes Marching Home

Problems of unemployment after the war can be largely met by the ability of our industries to widen markets and increase sales — hence make new jobs — by increasing *efficiency in production.*

How time-savings in production — far from limiting employment — actually *create* new jobs for thousands . . . is well illustrated by the case of one A T & M customer whose costs of production were preventing the broad distribution of his product.

A T & M engineers, by combining two slow, costly operations in one swift, space-saving centrifugal, saved so much process time that an extensive and profitable sales effort could be made in a lower-price, broader market.

Only one case among many! In the past, hundreds of manufacturers, consulting with A T & M engineers have been able to eliminate the costly, unwieldly equipment — kiers, tanks, autoclaves, filters, drying machinery — formerly used in extracting, precipitating, dehydrating and coating processes.

Today, A T & M standard centrifugals, link suspended, suspended, or base-bearing, in all machinable metals and coatings, are available only as national needs permit; and A T & M engineers, experienced in unusual centrifugal problems, are also — like yourself — working primarily to win the war.

And yet, peace tomorrow will present many problems which A T & M engineers may help you solve today, in consulta tion with you without cost or obligation Write us. We keep strict confidence American Tool and Machine Co., 1421 Hyde Park Avenue, or 30 C Church St. New York, N. Y.

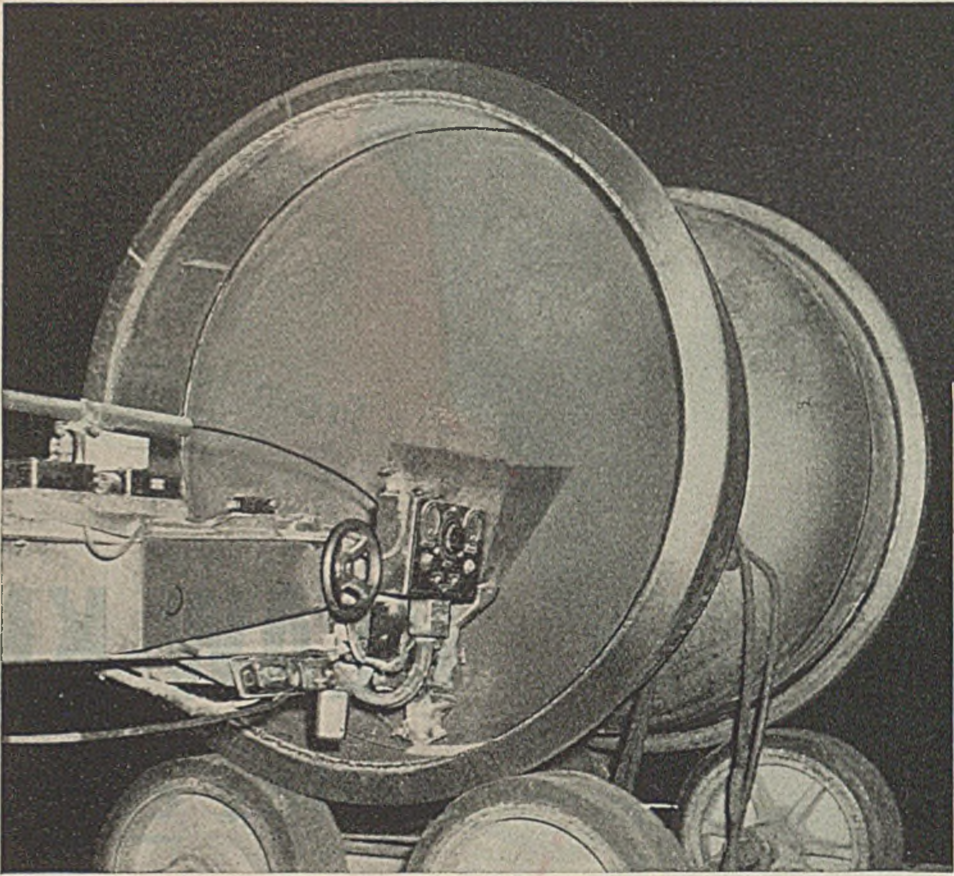
PREPARE NOW
TO "WIN THE PEACE"
by more efficient

EXTRACTION	PRECIPITATION
DEHYDRATION	IMPREGNATION
FILTRATION	COATING

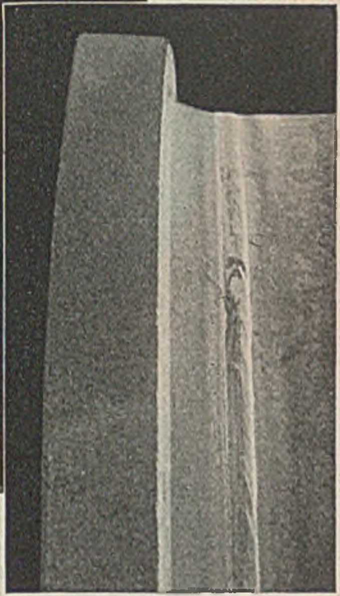
WITH AT&M CENTRIFUGALS

A T *and* M

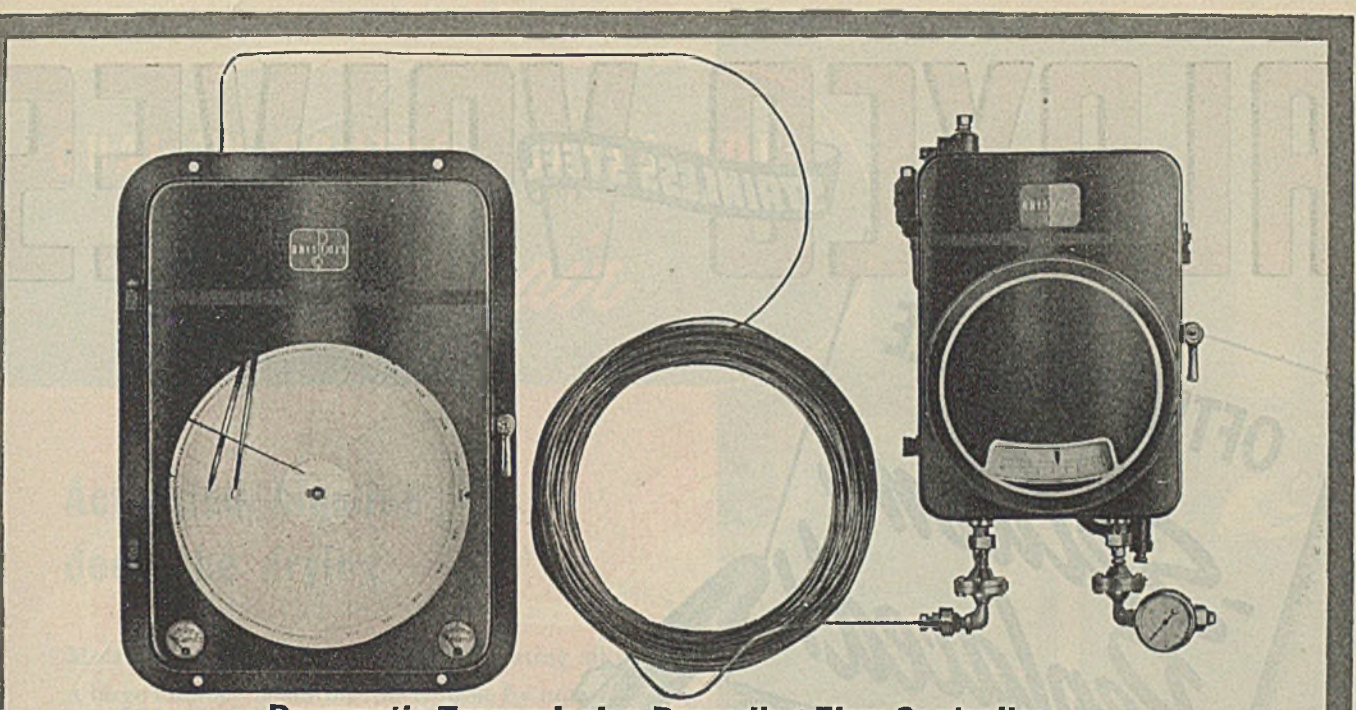
A T & M CENTRIFUGALS SAVE TIME AND SPACE



Automatic Welding of 60" Shell Covers



Typical Girth Weld
(Unretouched)



Pneumatic Transmission Recording Flow Controller

PROMPT DELIVERY SCHEDULES

ON FLOW METERS AND FLOW CONTROLLERS

For High Octane Gasoline, Synthetic Rubber and Chemical Programs

The Bristol Company, after making a careful study of probable requirements for flow meters and controllers, has expanded its manufacturing facilities and has set up a planned production schedule which will greatly facilitate delivery.

Models now being produced on a new delivery schedule, include recording flow meters, recording flow controllers and pneumatic transmission flow meters — both recorders and controllers. You can now be more certain of getting these models *in time* to break that meter-bottleneck in your plant!

These models are briefly described in Bulletin F 1601, a data sheet for your files. Write us for complete information.

Bristol instrument application engineers are available, without obligation, to assist in planning proposed installations. This service is particularly helpful during the war period because correct planning and accurate specifications save delivery and installation time and make for successful operation.

THE BRISTOL COMPANY, WATERBURY, CONNECTICUT

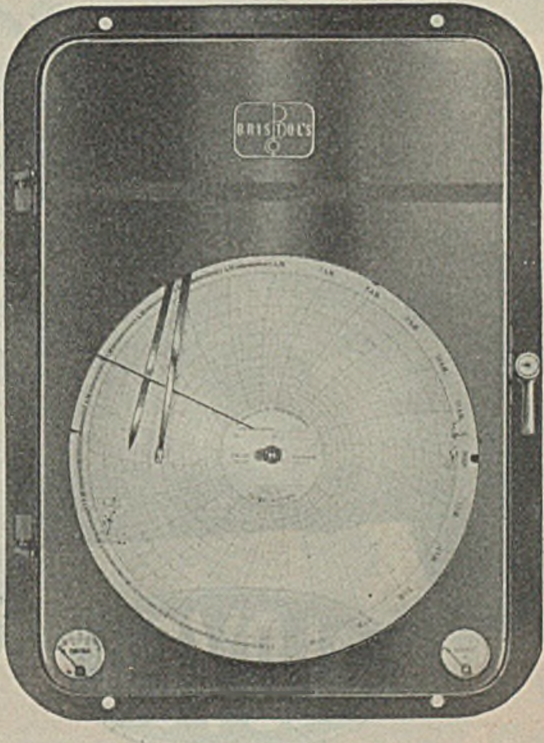
The Bristol Co. of Canada, Ltd.
Toronto, Ontario

Bristol's Instrument Co., Ltd.
London N. W. 10, England

BRISTOL

Engineers Process Control for Better Products and Profits

AUTOMATIC CONTROLLING AND RECORDING INSTRUMENTS



Mechanical Recording Flow Controller

FLOW METERS — QUICK DELIVERY COUPON

THE BRISTOL COMPANY
110 Bristol Road, Waterbury, Conn.

Please send me information about Bristol Recording Flow Meters and Flow Controllers on improved delivery schedule plan.

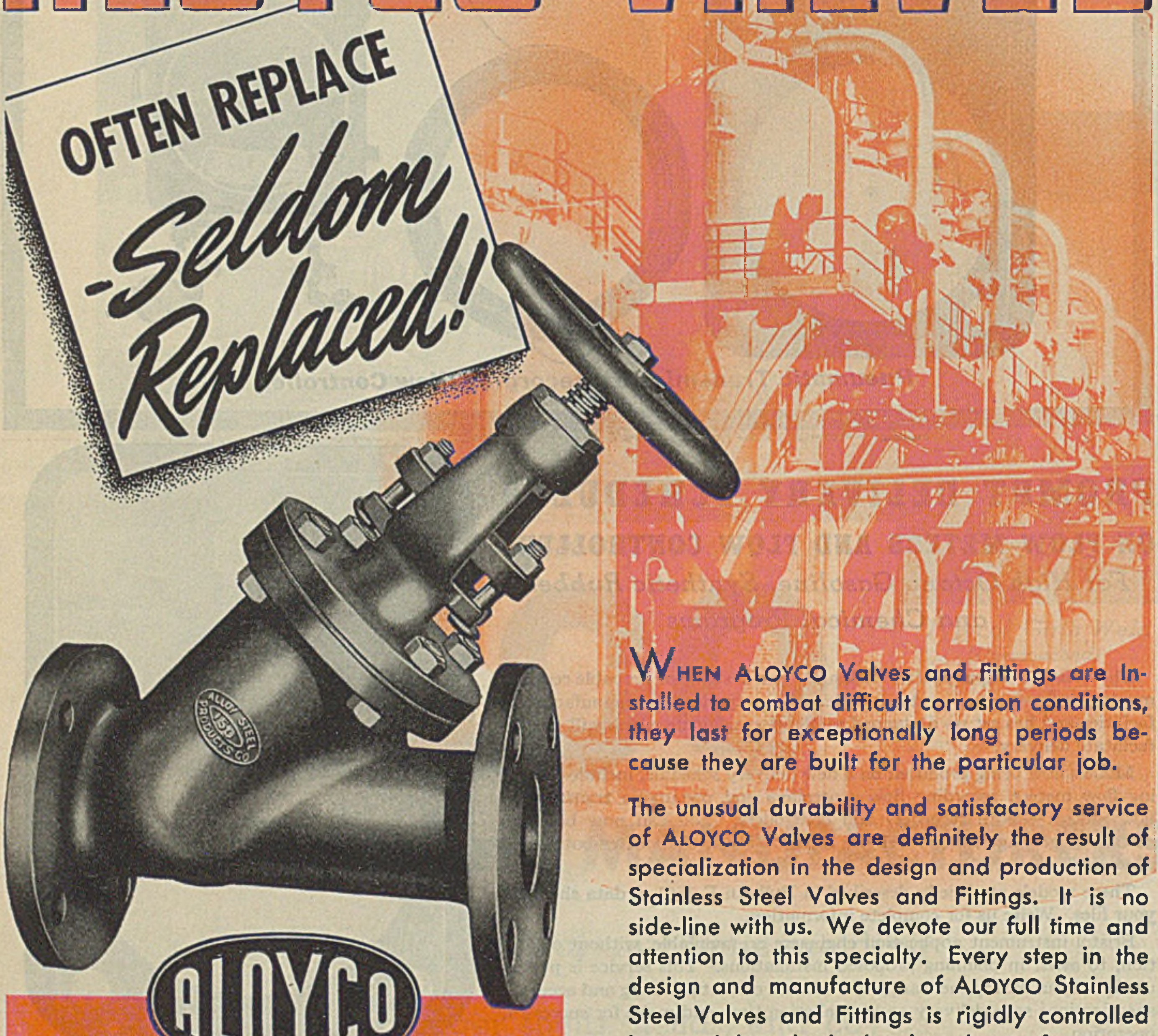
NAME..........

COMPANY..........

ADDRESS..........

....

ALOYCO STAINLESS STEEL VALVES



WHEN ALOYCO Valves and Fittings are Installed to combat difficult corrosion conditions, they last for exceptionally long periods because they are built for the particular job.

The unusual durability and satisfactory service of ALOYCO Valves are definitely the result of specialization in the design and production of Stainless Steel Valves and Fittings. It is no side-line with us. We devote our full time and attention to this specialty. Every step in the design and manufacture of ALOYCO Stainless Steel Valves and Fittings is rigidly controlled by special methods developed out of our concentrated experience.

It is natural, therefore, that engineers and plant executives in the explosives, chemical, food, textile, pharmaceutical, petroleum, and other process industries, turn to ALOYCO for authorative information and dependable service in problems of corrosion, stain or contamination in pipe lines. Write or telephone and we will be glad to serve you, also.

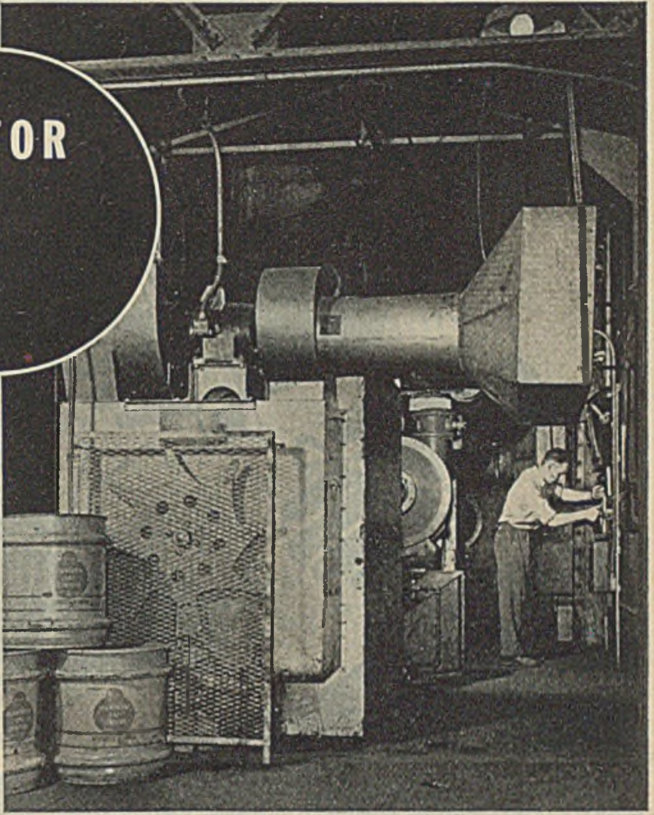
ALOYCo

Stainless Steel
VALVES and FITTINGS

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

Alloy Steel Products Company, Inc., 1300 West Elizabeth Avenue, Linden, N. J.

QUALITY CONTROL CALLS FOR *Dry air*



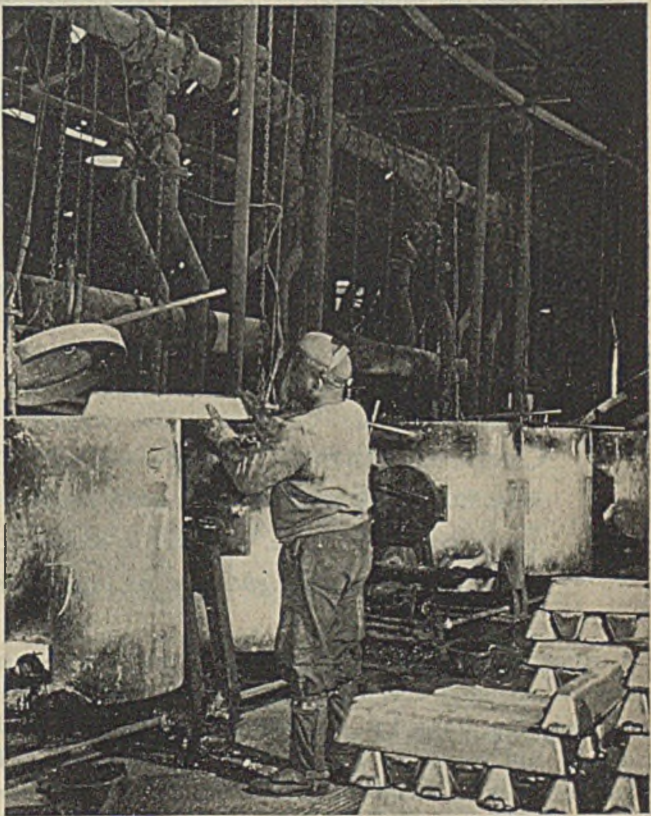
Activated Alumina does the drying

Moisture causes porosity in certain casting alloys. A large foundry heads off this trouble by maintaining a blanket of dry air over the metal in these melting furnaces; another phase of the control responsible for the higher quality of castings. Alorco Activated Alumina dries this air.

Out of sight of this foundryman are two Lectrodryers charged with Alorco Activated Alumina. They take the air from out of doors, filter, dry, and feed it into ducts. As part of this man's share in control of quality, he keeps this dry air flowing over the surface of the molten metal.

When the humidity is high, two Lectrodryers work in series; when the humidity is normal, one machine carries the load and cuts operating costs. As the beds of Activated Alumina become laden with moisture, they are automatically taken out of service for reactivation and reactivated beds take their places. Thus the Activated Alumina always works at top drying efficiency, and only the filters have to be replaced.

Have you a need for an efficient drying agent like Alorco Activated Alumina? We'll gladly help you examine its possibilities. Write ALUMINUM COMPANY OF AMERICA (*Sales Agent for* Aluminum Ore Company), 1911 Gulf Building, Pittsburgh, Pennsylvania.



"ALORCO" ALORCO PRODUCTS
Reg. U.S. Pat. Off.

ACTIVATED ALUMINAS

"too many cooks..."

"CENTRALIZATION"—*"unified command"*—*"co-ordinated management."... Call it what you may, apply it where you will, it is the best way to* get things done. *Whether in economic, military or industrial sense, appointing the right head or organization is half the battle.*

A HUGE chemical-ordnance works was constructed recently under a unified plan devised to standardize design and to utilize the facilities and abilities of various groups.

As architect-engineer-manager, E. B. Badger & Sons Company were charged with the responsibility of co-ordinating and directing *all activities* in the building of this plant. Today it stands as a shining example of co-operation and efficient handling—resulting in a substantial saving in manpower and critical materials over the expected requirements which had been determined as normal for this type of plant.

Throughout a long career, Badger has built or supervised the building of many chemical, petroleum and petro-chemical plants—large and small . . . with creditable records for speed, efficiency and successful final results. Badger understanding and facilities for designing complete plants, specifying and buying materials, assembling units, and handling labor are thorough.

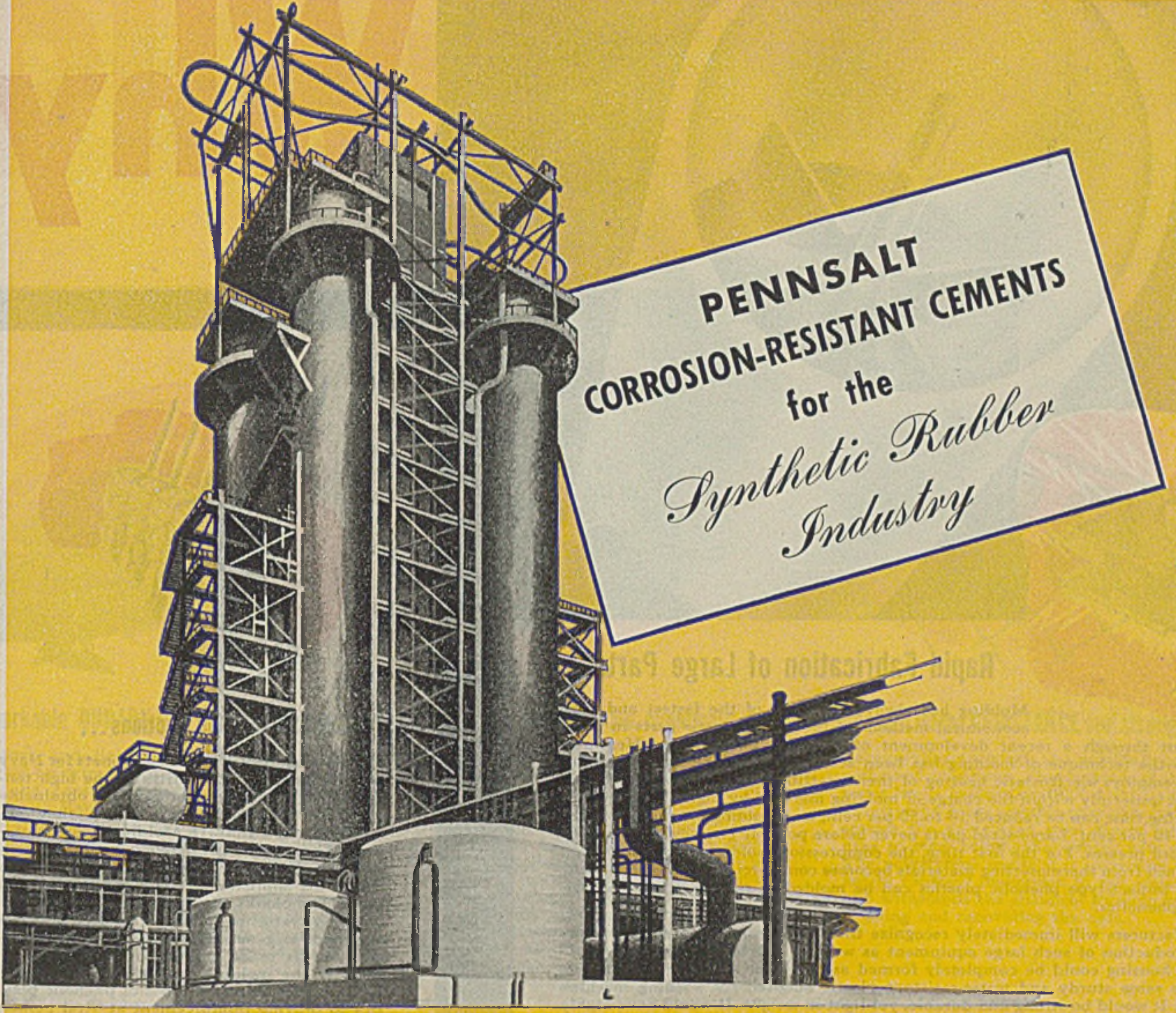
Parceling out contracts among "too many cooks" often means "spoiling the broth." On your next new-plant, conversion or modernization undertaking, consider *unifying* the job, through to initial operating, under Badger process and construction engineering.

E. B. Badger & SONS CO.

BOSTON . . . . EST. 1841

NEW YORK • PHILADELPHIA
SAN FRANCISCO • LONDON

PROCESS ENGINEERS AND CONSTRUCTORS FOR THE CHEMICAL, PETROLEUM AND PETRO-CHEMICAL INDUSTRIES



PENNSALT CORROSION-RESISTANT CEMENTS for the *Synthetic Rubber Industry*

Right on the job, contributing to the success of one of the nation's most important new industries you'll find Pennsalt corrosion-resistant cements—*Penchlor**, *Asplit**, and *Causplit**.

Penchlor is the quick-setting, self-hardening sodium silicate cement that saves time in construction—stands up under punishing duty—and serves long and well under severe acid conditions.

Asplit and Causplit are resin cements, extraordinarily strong, abrasion-resistant and easy to handle. Use Asplit where conditions are always acid . . . Causplit where conditions are alternately acid and alkali.

A leading oil company with a large synthetic rubber plant makes extensive use of Asplit and Causplit for binding brick and tile for use in both concentrated and weak hydrochloric and sulphuric acid service at ordinary temperatures and at their boiling points.

In addition, Asplit is used for sealing joints in carbon pipe spools—on the joints of a redwood tank in acid service—and in patching leaks in carbon and copper pipe lines.

What are *your* acid or alkali handling problems? Penn Salt technicians have had a wealth of experience in this field—consult them without obligation. Write fully or use the coupon.

We can supply you with Penchlor without restriction . . . Asplit and Causplit are available only for essential service.

*Trade-marks Reg. U. S. Pat. Off.

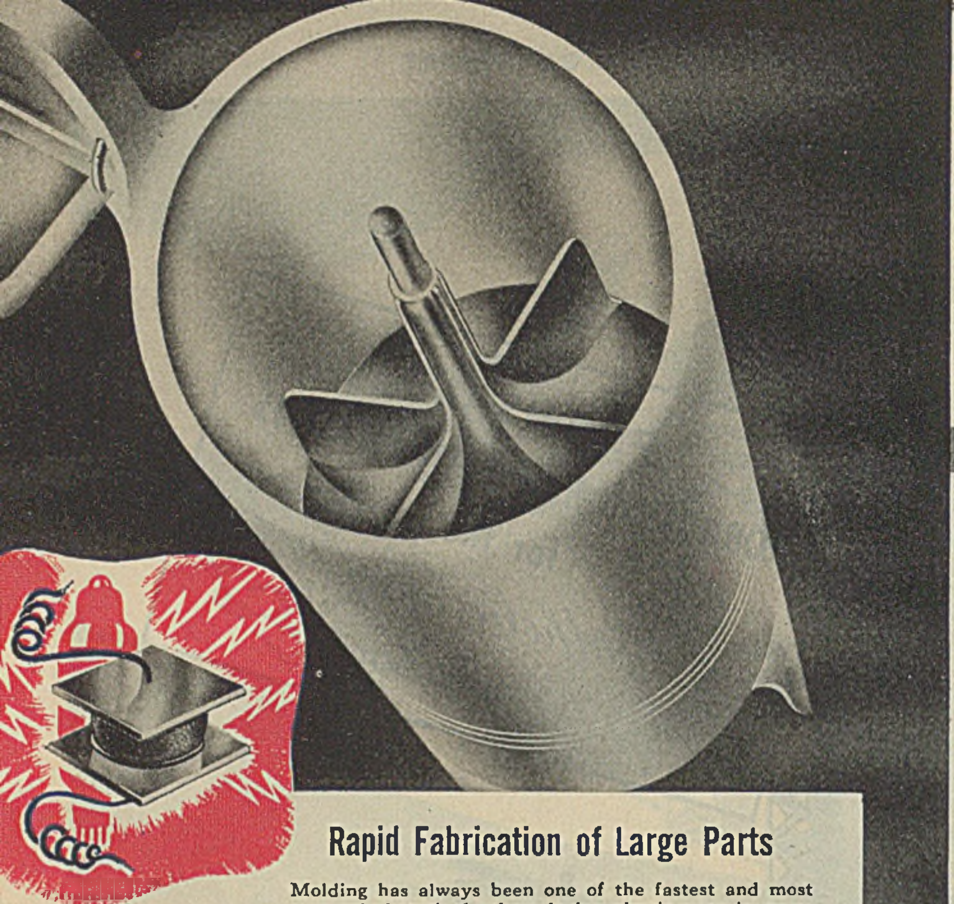
PENNSYLVANIA SALT MANUFACTURING COMPANY
Dept. IEC, 1000 Widener Bldg., Philadelphia 7, Pa.

I would like to have a free copy of your new booklet No. 6 on Penchlor Acid-Proof Cement.

NAME____________________
TITLE____________________
COMPANY____________________
ADDRESS____________________

PENNSYLVANIA SALT MANUFACTURING COMPANY
Chemicals
1000 WIDENER BUILDING, PHILADELPHIA 7, PA.
New York • Chicago • St. Louis • Pittsburgh • Minneapolis • Wyandotte • Tacoma

Why



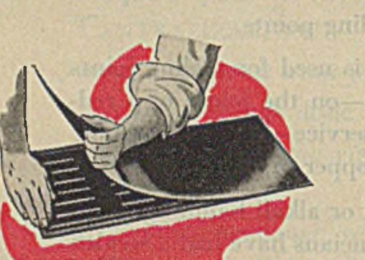
Rapid Fabrication of Large Parts

Molding has always been one of the fastest and most economical methods of producing plastic parts in quantities. But through a recent development of Bakelite Laboratories—Heatronic Molding—the technique of molding has been accelerated still further. Heatronic Molding employs electrostatic heating of thermosetting materials, so that heat is generated uniformly *within* the charge of molding material by high-frequency current. Curing time can be reduced 10 to 50 per cent, and molding pressures lowered by 30 to 40 per cent. Large-sized parts never before possible can now be produced on standard presses. For the first time, the compression molding of pieces thicker than 3/8 inch from thermosetting materials becomes commercially practicable. And, now, the impact-type phenolic plastics can be molded as readily as the general-purpose phenolics.

Manufacturers will immediately recognize the opportunities this process offers in the production of such large equipment as washing machines. The entire tub-and-gear housing could be completely formed as one unit, in a single operation, using the same sturdy and water-resistant plastic adopted for washing machine agitators. It would be strong and durable, yet light in weight. It would have highly desirable heat-insulating characteristics, and would be inert to caustic solutions.

TOUGHNESS for thin sections...

The development of plastic bayonets for Navy training purposes demonstrates the high tensile strength and flexural strength obtainable even for thin-walled parts when they are molded from BAKELITE Molding Board Materials. These impact-resistant plastics are supplied in sheets of various sizes, or in shapes cut to the approximate design of the finished parts. The blanks, as they are then called, are virtually preforms, which can be used in molds designed for general-purpose phenolics. Products can be made entirely from these materials, or the molding boards and blanks can be used with standard types of phenolic plastics to provide reinforcement at vital points.



LOW-COST metal replacement...

By adapting the plastic printing plate development of Bakelite Laboratories to the production of instrument control panels, one manufacturer is conserving impressive quantities of precious sheet aluminum and even more precious man-hours. A matrix of BAKELITE Phenolic Material is made from an etched copper plate, which serves as the original pattern. Any number of VINYLITE Plastic panels can be molded in this matrix, complete in every detail, and ready for subsequent curving to final shape by heat treatment. The combined use of these two materials assures faithful reproduction in one operation of not only the intaglio lettering, but also the hundreds of through-holes in the panel. It eliminates many operations necessary with metal plates, such as drilling, engraving, slotting, forming, anodizing, and polishing. *(Panels molded by Theo. Moss & Co., Inc.)*

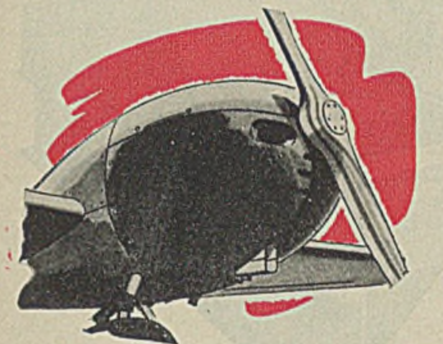
DURABLE coatings that dry in minutes..

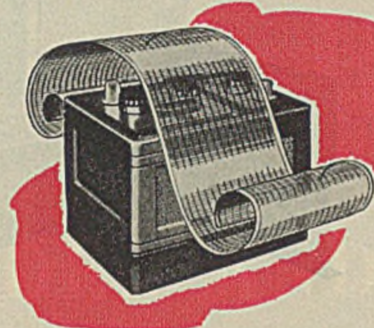
By the addition of BAKELITE Dispersion Resins to paint and varnish formulations, drying time can be reduced from hours to minutes. Such coatings, used by the Navy for more than 8 years as anti-corrosive aircraft primers, air-dry in 1 to 5 minutes without blistering or wrinkling, but nevertheless exhibit remarkable durability. Primers based on these resins and exposed, without top coat, for 2½ years on steel panels, revealed no checking or rusting. They have withstood 1,080 hours in a 3 per cent salt solution spray test, while other high-quality primers failed in 90 hours. They have shown no blistering, pimpling, or rusting after 8,000 hours of continuous immersion, whereas other primers failed in 300 hours.

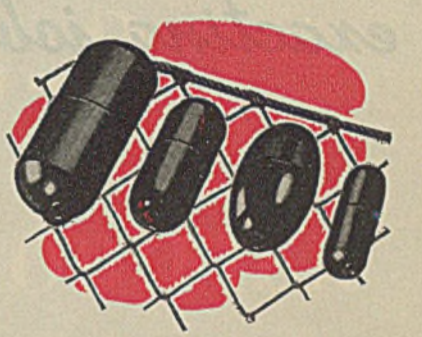
Helpful Literature on Plastics

These are a few of the valuable guidebooks you can obtain by writing to Department 27. "A Simplified Guide to Bakelite Plastics" is a 16-page summary of the principal BAKELITE Plastics now available. It describes each type briefly, and illustrates typical applications. "Bakelite Molding Plastics," a 32-page booklet, provides further information, and ASTM data, on moldable plastics. "Molding Technic for Bakelite and Vinylite Plastics," price $3.50 postpaid, is a 224-page manual on the art of molding plastics—contains comprehensive data that the designer, engineer, molder, and user should have on the design and fabrication of hot-set and cold-set molding materials. Additional pamphlets and booklets describing other types of BAKELITE Plastics are also available.

Plastics ?







Remarkable DURABILITY for wood...

Stronger and lighter than metal, yet unaffected by extremes of heat or cold, oil, gasoline, and constant vibration, wood impregnated with BAKELITE Resins and molded into three-dimensional forms has become a most valuable structural material in the building of aircraft. Engine cowlings that resist high heat are representative of the many large shapes now molded from wood impregnated with BAKELITE Resin. Entire fuselages and wings can be formed. Sections as long as 84 feet have been successfully produced in torpedo boat construction.

RESISTANCE to corrosive chemicals...

BAKELITE Polystyrene Plastics, in the form of flexible sheeting, are now employed as storage battery separators. Like all other forms of this amazing plastic—molding materials, extruded rods, tubes, and filaments, and resins for surface coatings—the flexible film is unexcelled in its resistance to both alkalies and non-oxidizing acids. Other outstanding advantages of BAKELITE Polystyrene Plastics include: extreme lightness in weight with good mechanical strength characteristics, superior electrical insulating qualities particularly at high frequencies, and high index of refraction when crystal-clear types are employed.

Unusual water RESISTANCE and strength...

Because they are tough and flexible enough to withstand pressures encountered at underwater levels as deep as 1,000 feet, BAKELITE Polystyrene floats are able to release for other service the galvanized steel sheets formerly used to buoy commercial fishing nets at sea. The polystyrene material is extremely resistant to constant immersion in salt water, and also withstands the chemical solution used in cleaning and renovating the nets.

HARDLY A DAY PASSES but another new industrial development is made possible through plastics, or the usefulness of old, familiar products is increased by these versatile materials. Look for the reason and you'll find that the trend to plastics is much more than a matter of replacing other materials. It's because plastics frequently provide a better product, and generally one that is also more rapidly and economically fabricated.

Certain BAKELITE Molding Materials, for example, can give your products high mechanical strength approaching metals—with only a fraction of the weight of metal, and no need for time-consuming finishing. They can provide inherent corrosion resistance, electrical properties, heat resistance, color, transparency, translucency, or opacity. And a new molding technique now permits large parts to be molded at high speeds and in greatly increased sizes never possible before.

Wood becomes a stable and amazingly strong material when bonded or impregnated with BAKELITE Resins . . . releases steel in building construction . . . can be molded into heat-resistant and weather-resistant forms of varied shapes and sizes. Surface finishes fortified with one type of BAKELITE Resins dry within a minute or so, yet stand up in service far longer than many other high quality coatings that require hours to dry.

But these are only a few of the plastics developments now available to industry, and merely a suggestion of the vast opportunities they offer to designers and engineers. You can keep posted on plastics by keeping in touch with Bakelite Plastics Headquarters. Our Engineering Staff and Development Laboratories offer their full co-operation in helping you adapt a growing variety of plastics and resins to your essential needs. As a first step, write for the helpful literature shown here. Please address Department 9.

BAKELITE CORPORATION, 30 E. 42ND ST., NEW YORK
Unit of Union Carbide and Carbon Corporation

UCC

BAKELITE
TRADE MARKS

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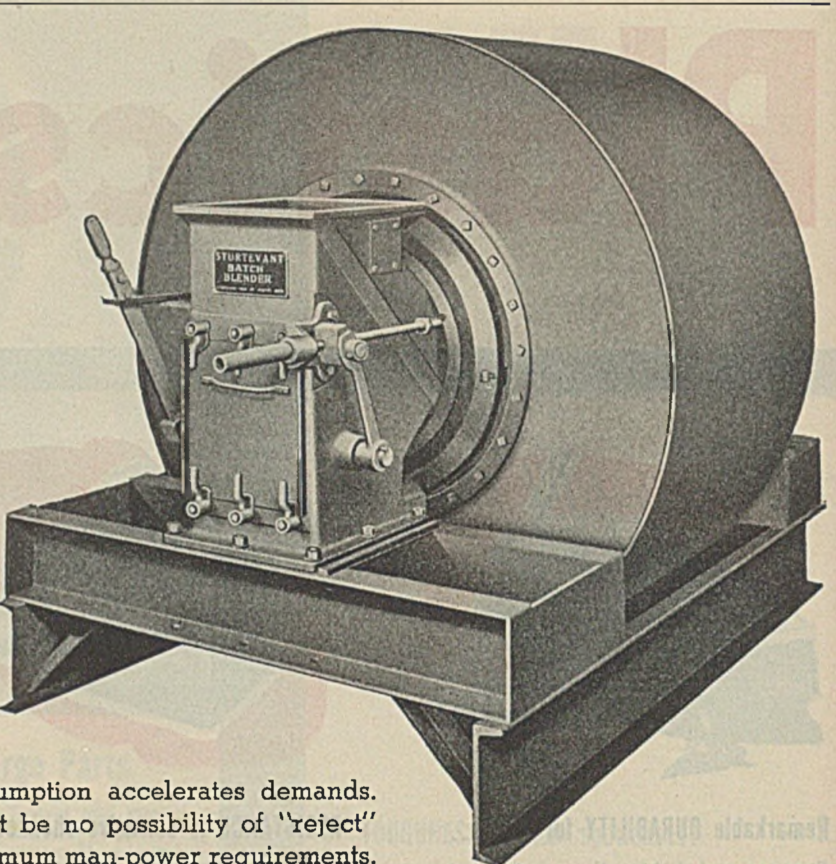
PLASTICS HEADQUARTERS

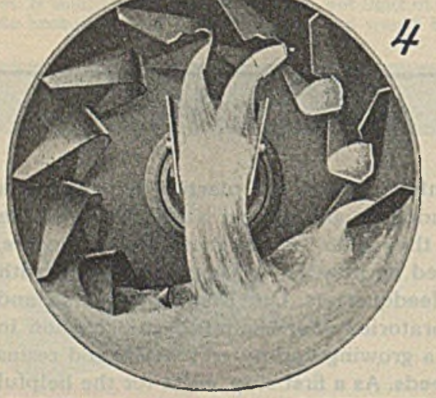
WAR-TIME MIXING *is an exacting job!*



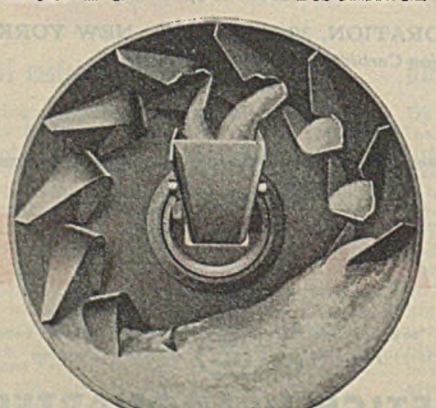
It must be fast — for accelerated consumption accelerates demands. . . . It must be thorough — for there must be no possibility of "reject" batches . . . . and it must be done with minimum man-power requirements.

Sturtevant Rotary Batch Blenders are designed to produce to just such exacting specifications. These efficient self-cleaning mixers blend any number of ingredients with varying weights, densities, fineness and other physical properties — with no loss of dust or finely ground materials. Operation is simple, automatic and fast. The drum is heavy steel, trunnion mounted. Drive shaft and rear trunnion have anti-friction bearings.

STURTEVANT
BATCH BLENDER



RECEIVING DISCHARGE



4 separate actions assure perfect blending

1 As the weighed and measured material enters the drum through the opening in the center, it is constantly lifted in a series of revolving buckets and cascaded into an intimate mix. (See illustration "Receiving.")

2 The steadily revolving action of the drum makes a continuous blend or mix of the material remaining at the bottom of the drum.

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.

●

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.

STURTEVANT MILL CO. 2 HARRISON SQUARE **BOSTON, MASS.**

ONE OF A SERIES DESCRIBING PLASTICIZERS AND MODIFIERS—FOR USE WITH NATURAL AND SYNTHETIC ELASTOMERS—PRODUCED BY THE RESINOUS PRODUCTS & CHEMICAL COMPANY

★

RESIN R6-3

AN EXTENDER AND MODIFIER FOR SYNTHETIC RUBBER

★

ESPECIALLY designed for use with the acrylonitrile-butadiene type of synthetic rubber, RESIN R6-3 is a unique modifier characterized by exceptional chemical stability. It is of particular interest where high tensile, oil insolubility, and low heat loss are primary considerations.

RESIN R6-3 can be reinforced with small amounts of a vulcanizable elastomer, yielding stocks that are of outstanding interest for gaskets, coated fabrics, and other special applications.

PHYSICAL PROPERTIES OF RESIN R6-3

Sp. gr.	1.1 (when sheeted on rolls).
Odor	Slightly sweet.
Solvent resistance	Insoluble in aliphatic hydrocarbons. Swells in aromatic hydrocarbons and solvents of the ketone or ester type. Disperses to a thick gel in chlorinated solvents.
Heat loss	0.75% (100° C. for 24 hrs.)
Thermoplasticity	Viscosity and tack change only slightly at elevated temperatures. The slight increase in tack which occurs on warming the mill produces rapid knitting of the mass.
Compatibility	Complete with Hycar OR-15, Standard Oil Perbunan, Chemigum, Neoprene, Buna S, Thiokol Type RD, Nitrocellulose, Thiokol Type FA. Limited with Vistanex (SYNTHETIC 100), natural rubber, polyvinyl chloride.

CLASSIFICATION OF SOFTENERS

FOR HIGH TEMPERATURE SERVICE. Resin R6-3, Duraplex C-50LV (100% solids), Dibenzyl Sebacate*, Plasticizer 35*.

*Excellent high temperature stability for elasticator type softeners.

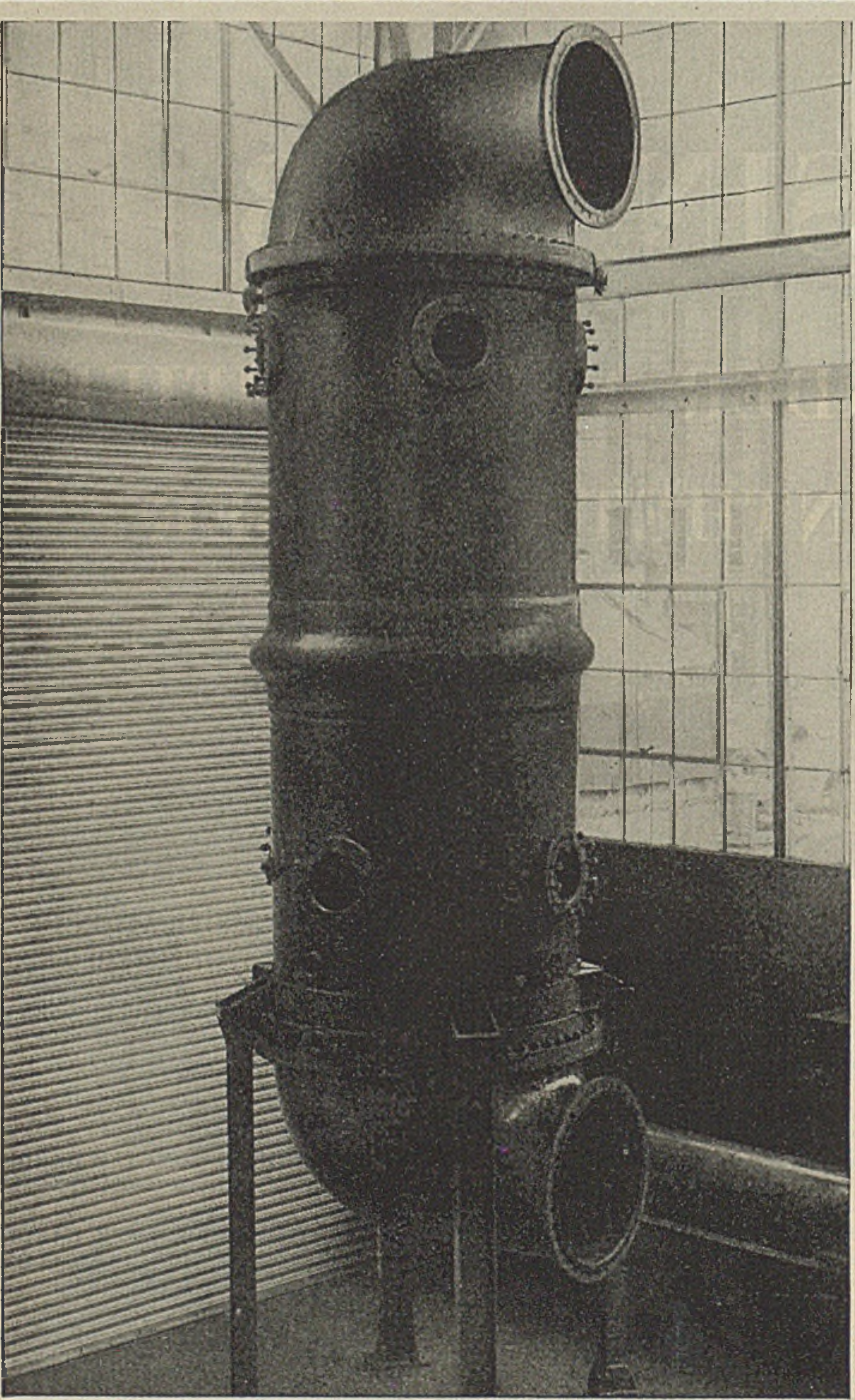
FOR HIGH DUROMETER HARDNESS. Resin R6-3, Duraplex C-50LV (100% solids).

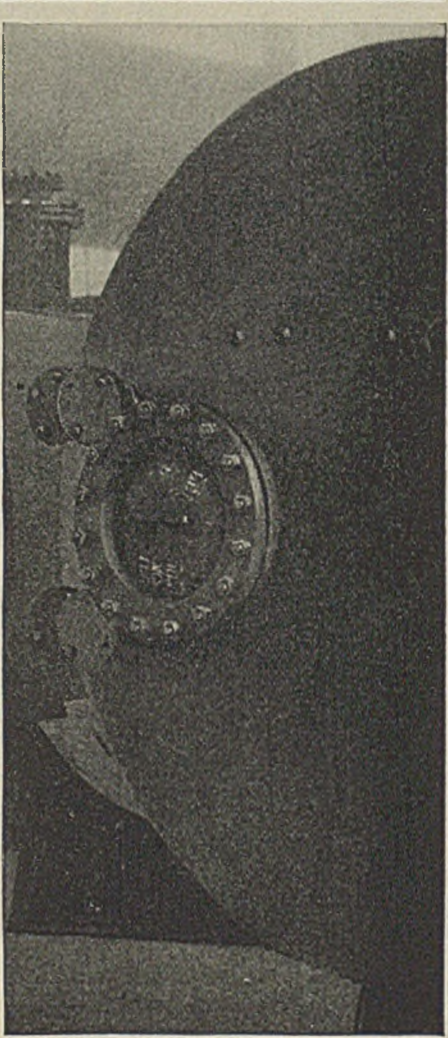
FOR LOW DUROMETER HARDNESS. Dibutyl Sebacate, Dibenzyl Sebacate, Dicapryl Phthalate, Plasticizer 35.

FOR LOW TEMPERATURE FLEXIBILITY. Dibutyl Sebacate*, Dibenzyl Sebacate*, Dicapryl Phthalate, Plasticizer 35.

*Outstanding for this specialized application.

THE RESINOUS PRODUCTS
& CHEMICAL COMPANY
WASHINGTON SQUARE, PHILADELPHIA, PA.

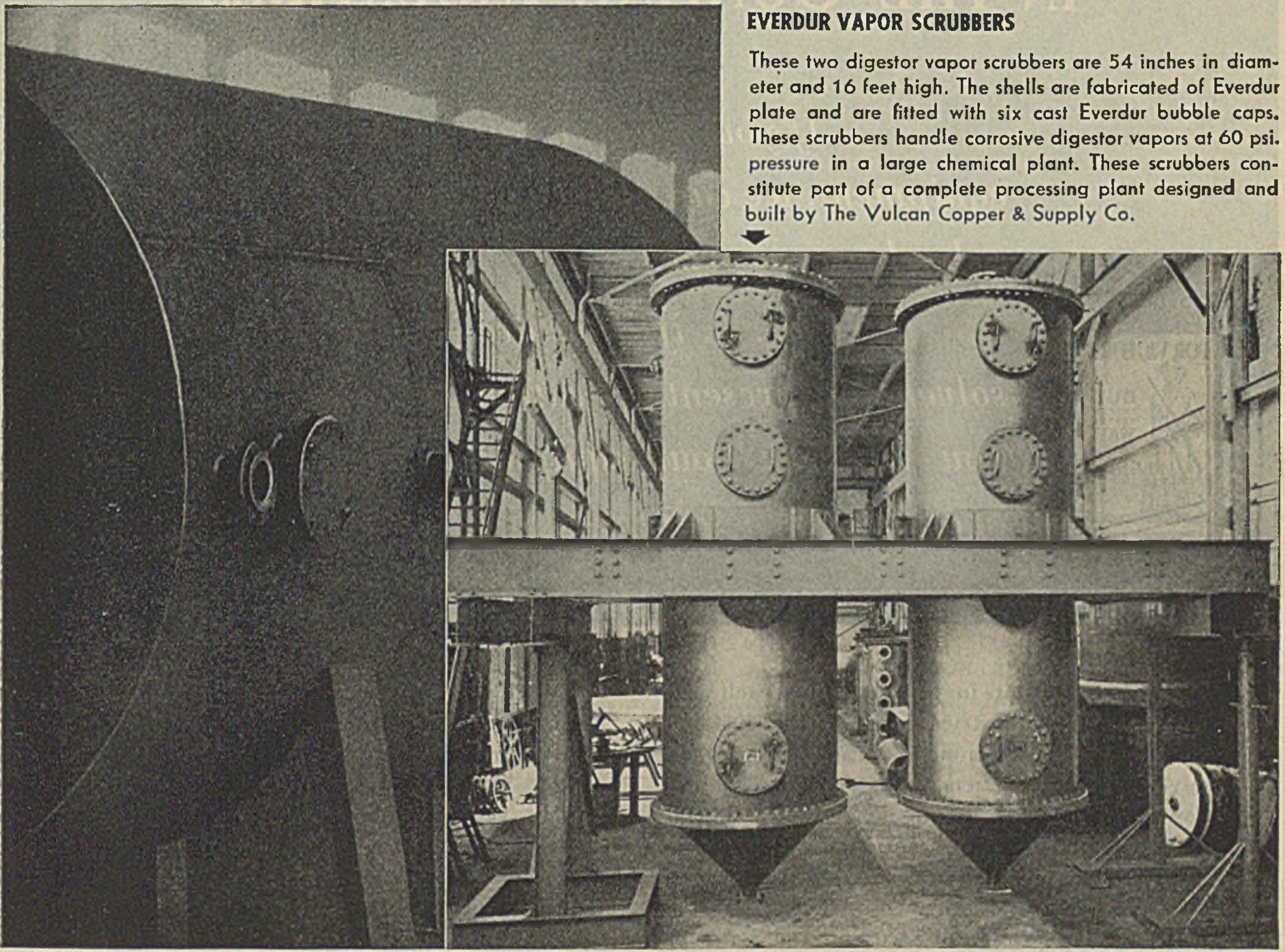




... for Victory!

EVERDUR VAPOR SCRUBBERS

These two digestor vapor scrubbers are 54 inches in diameter and 16 feet high. The shells are fabricated of Everdur plate and are fitted with six cast Everdur bubble caps. These scrubbers handle corrosive digestor vapors at 60 psi. pressure in a large chemical plant. These scrubbers constitute part of a complete processing plant designed and built by The Vulcan Copper & Supply Co.



Everdur Metal and other Anaconda Copper Alloys are serving in war-front equipment all over the globe—and in countless industrial applications behind the fighting fronts . . . meeting the performance standards that 24-hours-a-day production schedules demand.

We offer this three-fold service to those engaged in the war effort:

1. **Special Engineering Counsel** . . . cooperation in finding the solution to special metal problems involving copper, brass and other Anaconda Metals.
2. **A Laboratory You Can Call Your Own** . . . technical information plus laboratory facilities to help you fit the right metal to the job.
3. **Technical Publications** . . . up-to-the-war-minute publications containing useful technical information—available without cost. 43119

THE AMERICAN BRASS COMPANY
General Offices: Waterbury, Connecticut
Subsidiary of Anaconda Copper Mining Company
In Canada: Anaconda American Brass Ltd., New Toronto, Ont.

Made by The American Brass Company

WE OFFER HELP TO SAVE SOLVENTS IN THE COATING INDUSTRIES

If you are planning to install new coating equipment, we can help in designing it for economical solvent recovery.

Or . . . if you are not recovering your solvents in present operations, perhaps we can help you redesign your equipment to permit efficient operation of a solvent-recovery system.

FOR VICTORY BUY UNITED STATES WAR BONDS AND STAMPS

Millions of dollars in solvents are lost each year in the coating industries because many installations of coating equipment are not designed for solvent recovery. When you plan a new installation for coating fabric, paper, or other material let our engineers help in designing it for the recovery of solvents. With their co-operation, you can plan new equipment for efficient coating coupled with profitable recovery and reuse of your solvents.

COLUMBIA Activated Carbon solvent-recovery plants . . . which we design and supply . . . can be used economically for recovering as low as 50 gallons of solvent a day. These plants will recover mixtures of ketones, esters, alcohols, and hydrocarbons and the other solvents used in the application of coatings of nitrocellulose, cellulose acetate, rubber, vinyl resins, and other materials.

Since these recovery plants can efficiently recover solvents present in very low concentrations, ample air can be passed through the driers to permit rapid drying. An overall recovery of solvent vapors of over 95 per cent has been effected when driers were completely enclosed. When complete enclosure is impossible, the recovery efficiency may still be from 75 to 95 per cent—a real saving in money and material.

Efficient solvent recovery makes possible the use of a higher priced solvent to improve the quality of the coated product. Also, installation of recovery plants tends to speed up manufacturing operation and to decrease fire and health hazards.

Consult our engineers for further information on solvent-recovery plants for coating operations. Or write for our booklet, *Solvent Recovery by the Columbia Activated Carbon System.*

For information concerning the uses of COLUMBIA Activated Carbon, address:

CARBIDE AND CARBON CHEMICALS CORPORATION
Unit of Union Carbide and Carbon Corporation
30 East 42nd Street UCC New York, N. Y.

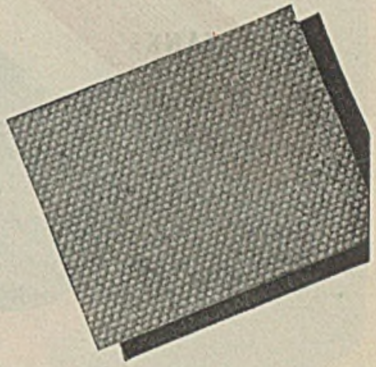
PRODUCERS OF SYNTHETIC ORGANIC CHEMICALS

"Columbia" is a registered trade-mark of Carbide and Carbon Chemicals Corporation.

Our Knowledge of FABRICS may help you out

We manufacture and distribute over 25,000 different cotton fabrics—many of which were developed especially for the Chemical Industry. Our knowledge of fabrics and their application to industrial processes has enabled us to help solve many a production problem when the proper use of fabrics was involved.

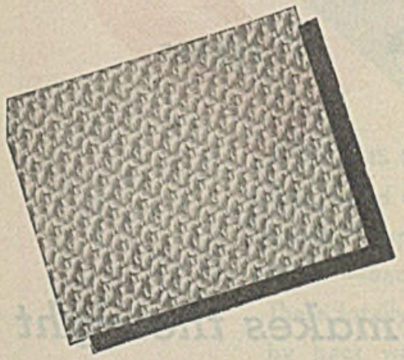
If you're working with Fabrics for Plastics—



We can offer hundreds of fabrics for test and experiment. Fabrics in a great variety of weaves, weights, strengths, and textures. Fabrics for coating—rubberizing or impregnating.

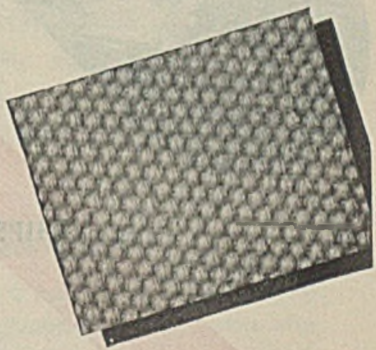
GEAR DUCK

If you're filtering mineral acids or alkalies—



VIN-28 CHAIN CLOTH

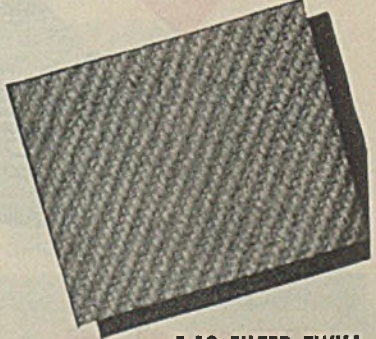
Investigate "VINYON"* the new synthetic fiber filter fabrics that are highly resistant to mineral acids and alkalies. Due to the fact that "VINYON" has definite heat limitations we suggest that our engineers be given an opportunity to discuss the application of "VINYON" fabrics to your particular filtration processes.



12/0 DUCK

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

If you're working with Cotton Filter Fabrics—



Our regular lines include over 3000 different filter fabrics ranging from heavy 12/0 duck to light and medium weight twills and chain cloths. Wellington Sears Company, 65 Worth Street, New York, N. Y.

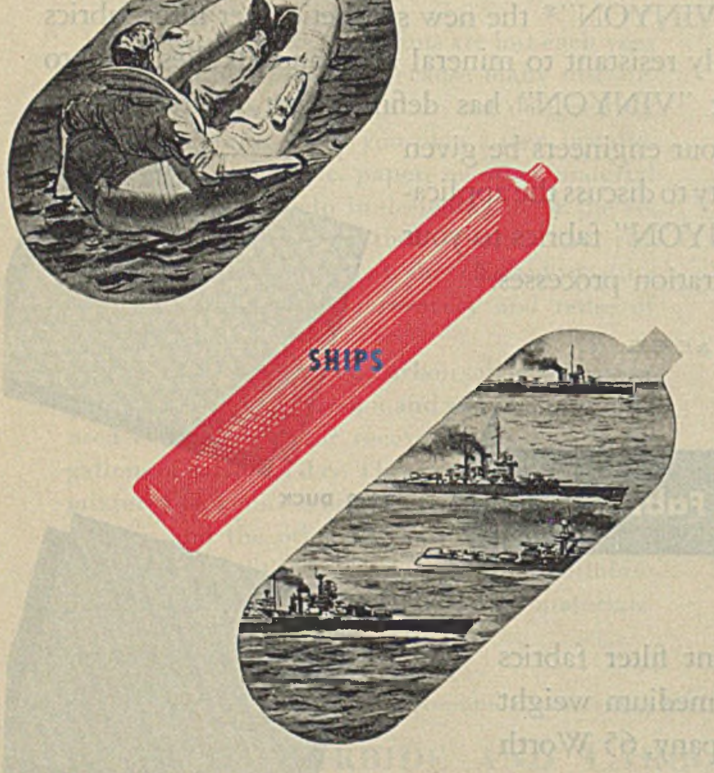
F-10 FILTER TWILL

BUY MORE WAR BONDS

SHAWMUT MILL LANGDALE MILL LANETT MILL FAIRFAX MILL RIVERDALE MILL EQUINOX MILL BROOKSIDE MILLS THE DIXIE COTTON MILLS

HIGH PRESSURE GASES

have many war jobs to do . . .



and Kidde makes the right container for each of them

★ Today there is far greater use for high pressure gases than ever before. Kidde has kept pace with this development by providing containers in an ever-widening variety of shapes and sizes. Special purpose valves and release mechanisms have been devised by Kidde engineers for proper application of the gases.

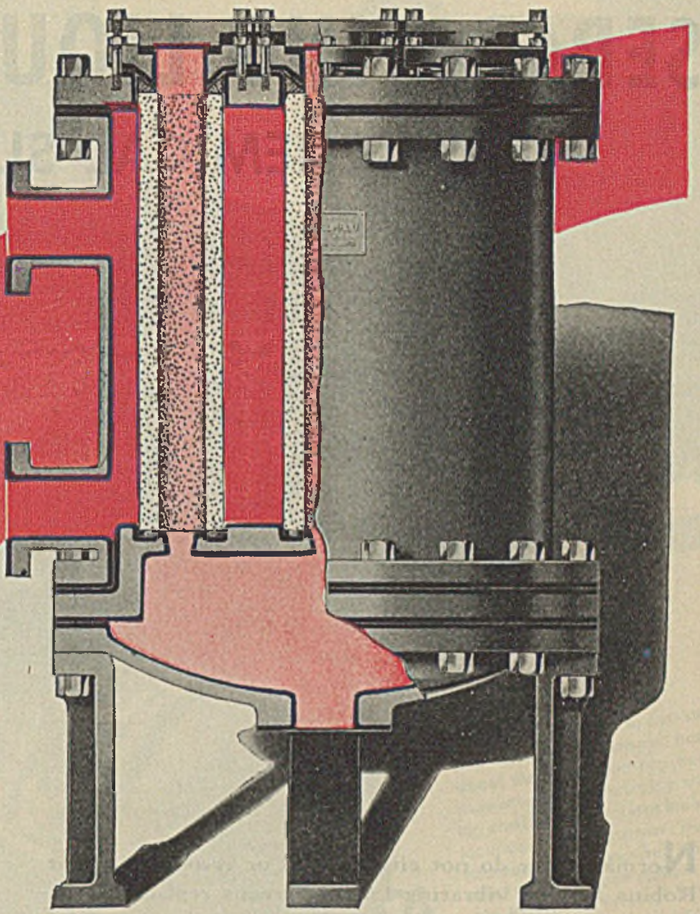
Kidde cylinders are used for storing liquefied carbon dioxide and hydraulic fluids under pressure, for oxygen, nitrogen, helium and other gases.

If *you* need help in solving a high pressure container problem, write us telling us about your requirements. Let us work with you to develop the right container for your particular needs. Walter Kidde & Company, Inc., 830 Main St., Belleville, N. J.

Kidde
PROTECTS LIVES
HIGH PRESSURE GASES • FIRE PROTECTION

PORO-STONE *Filtration for* ACIDS

...AND CORROSIVE LIQUIDS



ADAMS PORO-STONE FILTERS embody the most advanced ideas in the design and construction of pressure filter equipment for acids and corrosive liquids. Supplied in two types—the rubber-lined "CFR" and the lead-lined "CFL"—each with its specific application depending on operating conditions. These totally enclosed filter units are compact, easily installed, readily cleaned by back washing. Special construction of PORO-STONE filter medium assures long life and a minimum of maintenance time and expense. Adaptable to a wide variety of industrial applications. Write for Bulletin 302, containing full details.

CORROSION RESISTANT

Heavy duty shell and all internal parts are lead or rubber lined. Corrosion resistant porous filtering medium and bonding material.

CLEANING

The cleaning process is easily, quickly and neatly accomplished by backwashing a single tube at a time or the complete shell.

ACCESSIBILITY

Adams design permits inspection or removal of tubes without disturbing shell or piping conditions.

INSTALLATION

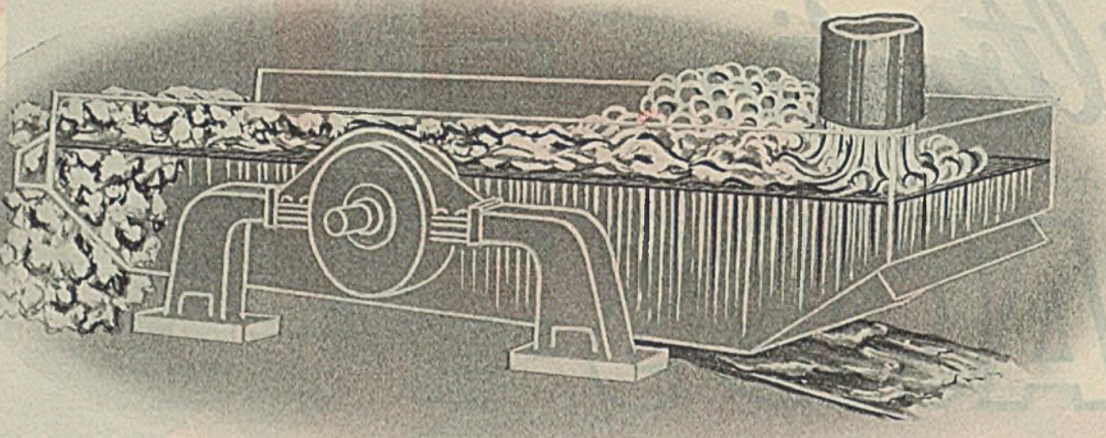
The compact, self-contained design permits installation at floor level or elevated. Only three connections required.

R. P. Adams Co. 61 Chicago St. Buffalo, N. Y.

ADAMS *Poro-Stone* ACID FILTERS

SEPARATING LIQUIDS AND SOLIDS

OF CHEMICAL SLURRY WITHOUT FILTERS



Slurry is fed under pressure to the deck of the screen which has a 4° inclination. The effluent passes through the cloth under acceleration of the vibrating action, which also progresses the solids upwards and off the discharge end.

Normally, we do not either claim or recommend that Robins *Hydrex* vibrating Liquid Screens replace filters. But one chemical plant found them entirely adequate for doing the work usually done by filters.

This plant had faced the necessity of expanding its plant rapidly to meet war-time demands. Many months would be required to manufacture and install filters as well as all the elaborate auxiliary equipment for steam pressure, air compression and piping.

Therefore, the research engineers decided to explore the possibilities of using vibrating liquid screens instead. A Robins *Hydrex* was purchased for test purposes.

In collaboration with a Robins engineer, these technicians experimented with flow, pressure, cloth openings, screen inclination, speed, throw . . . all the factors concerned with vibrating screen action and operation. After some weeks, they determined that—*for this particular purpose*—a Robins *Hydrex* vibrating Liquid Screen was able to perform the functions of filtering the chemical slurry. Records further showed that three screens turned out the same quantity as two filters with comparable quality of results. In consequence, a total of twenty Robins *Hydrex* vibrating Liquid Screens was purchased; it had been estimated that fourteen filters would have been needed. Months of valuable time were saved getting into production. The twenty screens cost about the price of two filters. No auxiliary equipment, no special piping, no elaborate foundations were necessary. Operating costs were also materially reduced since the extensive man-hours needed to change filter cloths were eliminated. (Changes of screen cloth on Robins *Hydrex* Liquid Screens are a matter of minutes.)

This instance is both unique and extraordinary. We do not claim that Robins *Hydrex* Vibrating Liquid Screens replace filters; their functions and purposes are more generally in the field of assisting filters and augmenting their capacity. These screens also accelerate productivity in chemical and process plants by introducing continuous-flow operation and reducing the static time of fluids in evaporators and settling tanks.

Have you ever considered the possibility of using liquid screens? The subject is of sufficient importance to merit investigation. Facts pertaining to applications and operations are contained in Bulletin No. 123-I8. A copy will be sent on request.

ROBINS *makes:* BELT CONVEYORS • COAL AND ORE BRIDGES • BUCKET ELEVATORS • CAR AND BARGE HAULS • CAR DUMPERS • CAR RETARDERS • CASTINGS • CHUTES • CONVEYOR IDLERS AND PULLEYS • CRUSHERS • FEEDERS • FOUNDRY SHAKEOUTS • GATES • GEARS • GRAB BUCKETS • PIVOTED BUCKET CONVEYORS • VIBRATING SCREENS • SCREEN CLOTH • SELF-UNLOADING BOAT MECHANISMS • SKIP HOISTS • STORAGE AND RECLAIMING MACHINES AND SYSTEMS • TAKEUPS • LOADING AND UNLOADING TOWERS • TRIPPERS • WEIGH LARRIES • WINCHES • WINDLASSES

FOR MATERIAL AID IN MATERIALS HANDLING . . . . . . It's ROBINS

ENGINEERS • MANUFACTURERS • ERECTORS

ROBINS
CONVEYORS
INCORPORATED
Founded in 1896 as Robins Conveying Belt Co.
PASSAIC • NEW JERSEY

MATERIALS HANDLING MACHINERY

Edward 12 in. 1500 lb cast steel stop valve with Impactor handwheel shows gamma ray negatives completely encircling welding ends. Body markings indicate locations of negatives during radiographic examination of other areas. Unique radium capsule fixtures of original Edward design facilitate production inspection.

How Radiography Protects Users of EDWARD CAST STEEL VALVES

RADIOGRAPHIC EXAMINATION is a standard inspection procedure for Edward cast steel valves. Every gamma ray negative, carefully identified with the exact area of the exact valve it pictures, is filed as a permanent case history of individual valve soundness.

Edward metallurgists pioneered the gamma ray examination of steel valve castings. Through the years they have acquired the interpretative skill that can be gained only through the experience of making and reading thousands of negatives.

The lessons they have learned are reflected in advanced foundry techniques, and progressively better valve design.

This is just one—but a very important one—of the many extra precautions that make Edward extra value valves.

THE EDWARD VALVE & MANUFACTURING CO., INC.
1210 W. 144th STREET • EAST CHICAGO, INDIANA

EDWARD
Steel CAST AND FORGED
VALVES

TWO SUPER REFRACTORIES THAT OPERATE SAFELY AT

3200° AND 4000° F

TAM Zircon (Zirconium Silicate) refractories operate safely at temperatures over 3200° F. while TAM Zirconium Oxide refractories are used in applications over 4000° F.

These two TAM super refractories resist acids and oxidizing atmospheres. They are being successfully used in the manufacture of phosphates, fused silica, aluminum melting and platinum smelting. They are also widely used as crucible backing and for various high temperature applications.

An experienced staff of field engineers located in various parts of the country are available for consultations without obligation. Write:

TAM PRODUCTS INCLUDE

Zircon bricks, special shapes and crucibles . . . Zircon insulating refractories . . . Zircon ramming mixes, cements and grog . . . Zircon milled and granular . . . Electrically Fused Zirconium Oxide Refractories . . . Electrically Fused Zirconium Oxide cements and ramming mixes . . . Electrically Fused Zirconium Oxide in various mesh sizes.

TAM ZIRCONIUM TITANIUM PRODUCTS
Registered U. S. Pat. Off.

TITANIUM
ALLOY MANUFACTURING COMPANY

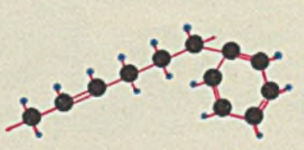
GENERAL OFFICES AND WORKS: NIAGARA FALLS, N. Y., U. S. A.
EXECUTIVE OFFICES: 111 BROADWAY, NEW YORK CITY

Representatives for the Pacific Coast States . . . . L. H. BUTCHER COMPANY, Los Angeles, San Francisco, Portland, Seattle
Representatives for Europe . . . UNION OXIDE & CHEMICAL CO., Ltd., Plantation House, Fenchurch St., London, E. C., Eng.

RUBBER TREE—*American-grow*

To the Graduate of '03 such words as butadiene, styrene and isoprene were unknown entities. Today they are firmly anchored in the lexicon of chemistry. America is growing hardy rubber trees synthetically, nurtured from oil, coal, gas, grain, guayule. In this age of miracles invention comes to necessity's aid. Laboratory curiosities bloom forth into commercial actualities. America *will* have rubber—*lots of it!*

Nordstrom Lubricated Valves are in the very vortex of synthetic rubber production. They regulate the controlled flow on vitally important lines—those handling high temperature hydrocarbons and other corrosion-forming elements as well as highly volatile and penetrating liquids. Nordstrom Valves, due to their patented lubrication system, are free from galling or sticking. They are ready for any emergency, with quick, sure quarter-turn operation providing a positive shut-off.



HAVE YOU EVER SEEN A MOLECULE?

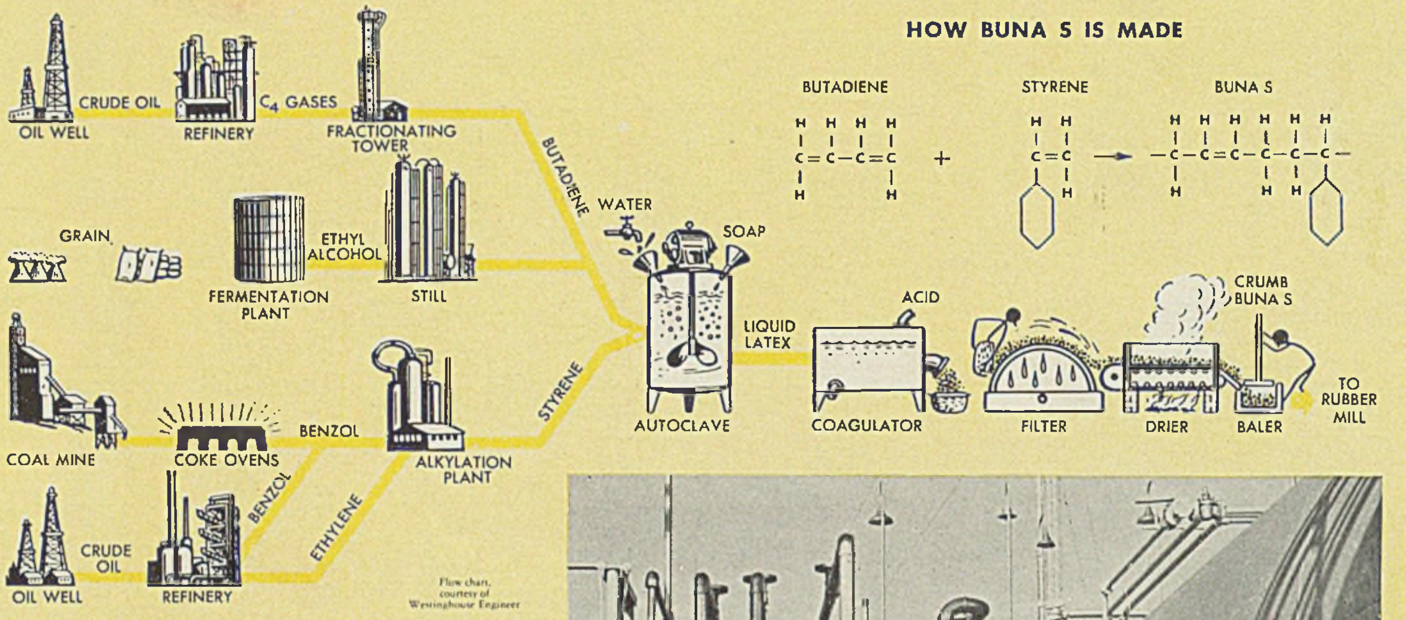
The fantastic structures of balls which give symbolism to atomic masses are chemistry's expression for unseen objects. Yet in their synthesis they impose new problems for valves never before imagined. Nordstro
Valve engineering has become, by necessit
a combined science, involving structur
design, metallurgical development, an
chemical research. But the reward for th
intensified progress is most gratifying. Th
eager acceptance of Nordstrom Valves i
practically every synthetic rubber plant i
America and the highly satisfactory servi
these valves are rendering, give us inspiratio
to continue the labors of research. By givi
outstanding service in the most difficult
applications, it is a certainty that Nordstro
Valves will best serve *your* needs for le
severe requirements on your vital flow line
It really takes a Nordstrom Lubricated Pl
Valve to give all-around, good servic

NORDSTROM VALVES

FOR ALL SYNTHETIC PROCESSE

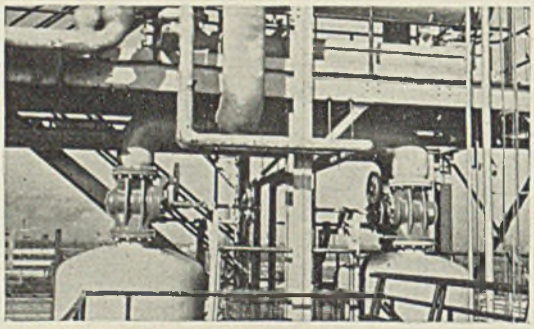
ALL ALONG THE FLOW-LINE *of synthetic rubber production*

NORDSTROM VALVES *are the vital controls*

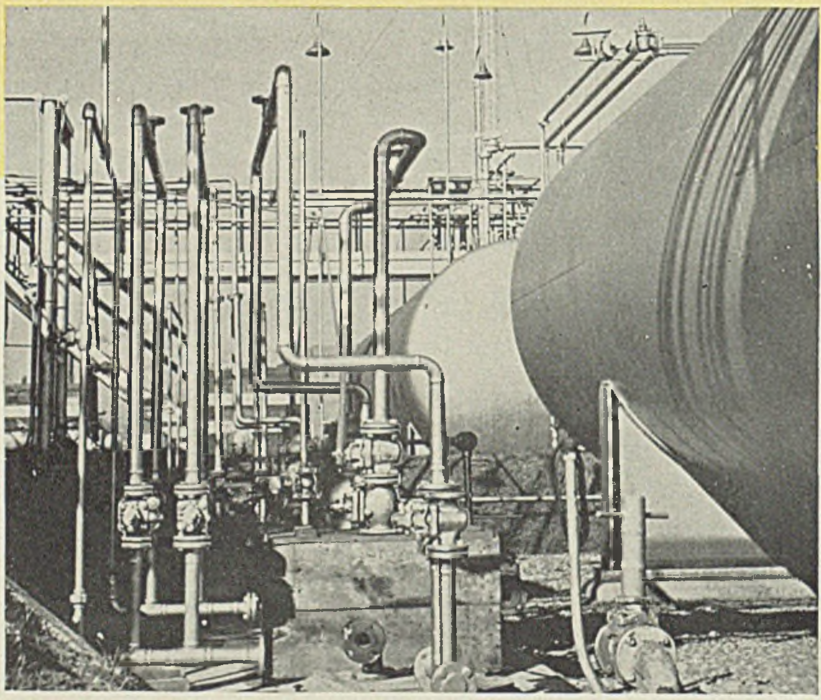


Flow chart, courtesy of Westinghouse Engineer

FROM oil or gas well, from coal mine or grain field, the use of Nordstrom Valves plays a vital part in the production of rubber. Not only are they serving oil and gas lines, but also on chemical, air and water lines. Valves of Semi-Steel, Nordco Steel, Stainless Steel and Special Alloys are used.



Two Nordstrom 14" chain operated spur gear cast steel valves installed on a recovery tower in a synthetic rubber plant.



Nordstrom Valves on raw material transfer pump lines. Nordstroms are extensively used on polymerization units and reactor chambers; also on low temperature lines and high temperature hydrocarbon lines in refineries.

Photos shown are by courtesy of Firestone Tire and Rubber Co.

Nordstrom

LUBRICATED FOR ALL-PURPOSE SERVICE VALVES

Sealdport Lubrication

MERCO NORDSTROM VALVE COMPANY – *A Subsidiary of Pittsburgh Equitable Meter Company*
WORLD'S LARGEST MANUFACTURERS OF LUBRICATED PLUG VALVES; GASOLINE, OIL & GREASE METERS
Main Offices: 400 Lexington Ave., Pittsburgh, Penna. • *Oakland (Calif.) Factory:* 2431 Peralta St.

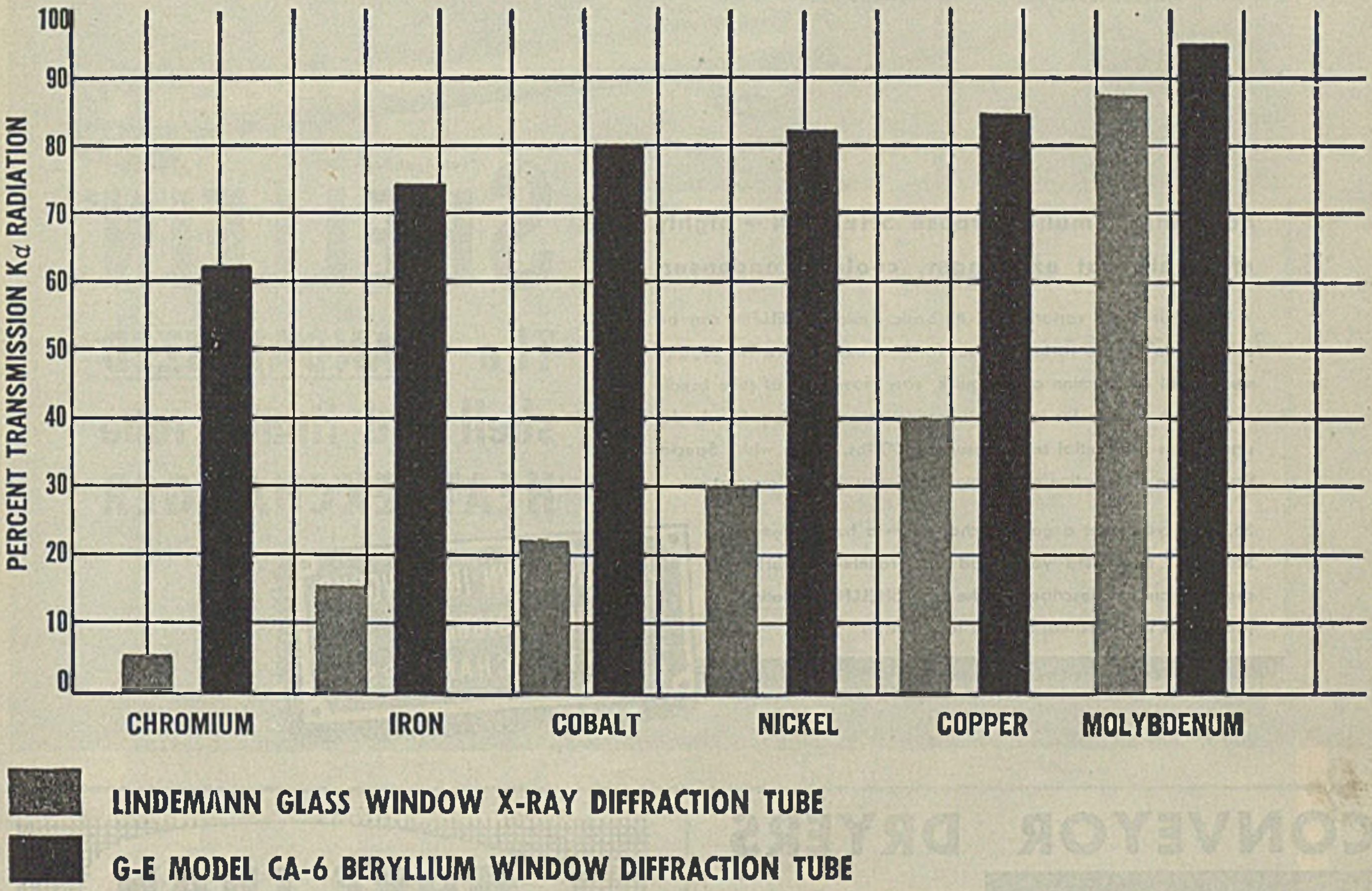
BRANCHES: Buffalo, Chicago, Columbia, Des Moines, Houston, Kansas City, Los Angeles, Memphis, New York City, Oakland, San Francisco, Seattle, Tulsa

CANADIAN Licensees: Peacock Bros., Ltd., Montreal • *EUROPEAN Licensees:* Audley Engineering Co., Ltd., Newport, Shropshire, Eng.

SOUTH AMERICAN Representative: The Armco International Corporation. *Main Office:* Middletown, Ohio

PRODUCTS: Nordstrom Lubricated Valves; Air, Curb and Meter Cocks • Nordco Valve Lubricants • EMCO Gas Meters • EMCO-McGaughy Integrators
EMCO Regulators • Pittsburgh-National Meters for Gasoline, Grease, Oil, Water and other Liquids • Stupakoff Bottom Hole Gauges

NEW G-E MODEL CA-6 BERYLLIUM WINDOW X-RAY TUBE SPEEDS UP DIFFRACTION STUDIES



THOROUGHLY TESTED—G-E perfected the Model CA-6 beryllium window x-ray diffraction tube early in 1941, and the first commercially available model was installed in the laboratory of a leading automotive manufacturer in August, 1941. The performance records of this and other CA-6 tubes back up these facts:

SPEEDS UP STUDIES—The Model CA-6 has a transmission factor, in the range of wavelengths for which these tubes are generally used, which is from six to ten times that of Lindemann glass window tubes. Typical normal exposures can be made with the CA-6 beryllium window tube in approximately one-seventh to one-tenth the time required by Lindemann window tubes.

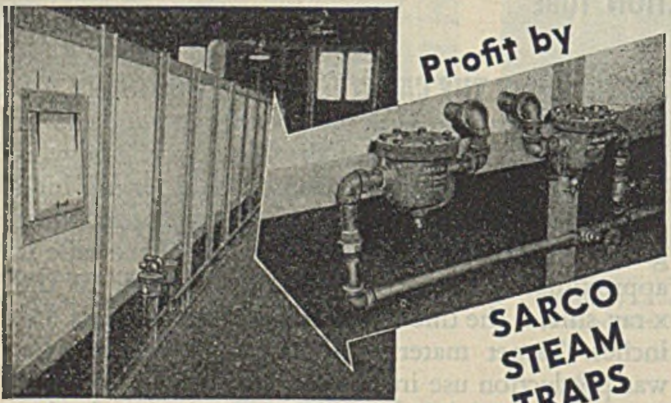
INCREASED TUBE LIFE—The increased radiation output of the CA-6 tube in itself effectively serves to lengthen tube life since it permits a greater number of exposures within a given time. In addition, its beryllium window is not susceptible to corrosion and x-ray deterioration.

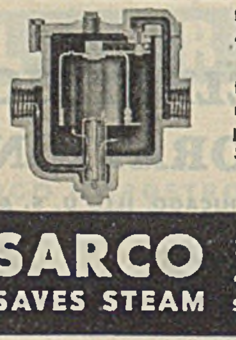
FACTS ABOUT THE CA-6 TUBE—The G-E Model CA-6 tube is constructed with two beryllium windows in line with the long axis of the focal spot. The windows are protected by a bakelite shield having high conductivity so that the shield may be operated at ground potential. The overall length of the tube is approximately 28 inches, and the diameter of the x-ray shield, the thickest portion of the tube, is 3½ inches. Target materials immediately available for war production use include copper, cobalt, iron, and chromium. Molybdenum, nickel, tungsten and other materials are available on special order.

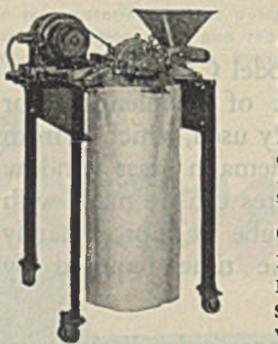
For complete information about the new G-E Model CA-6 tube, write or wire, today, to Dept. N48.

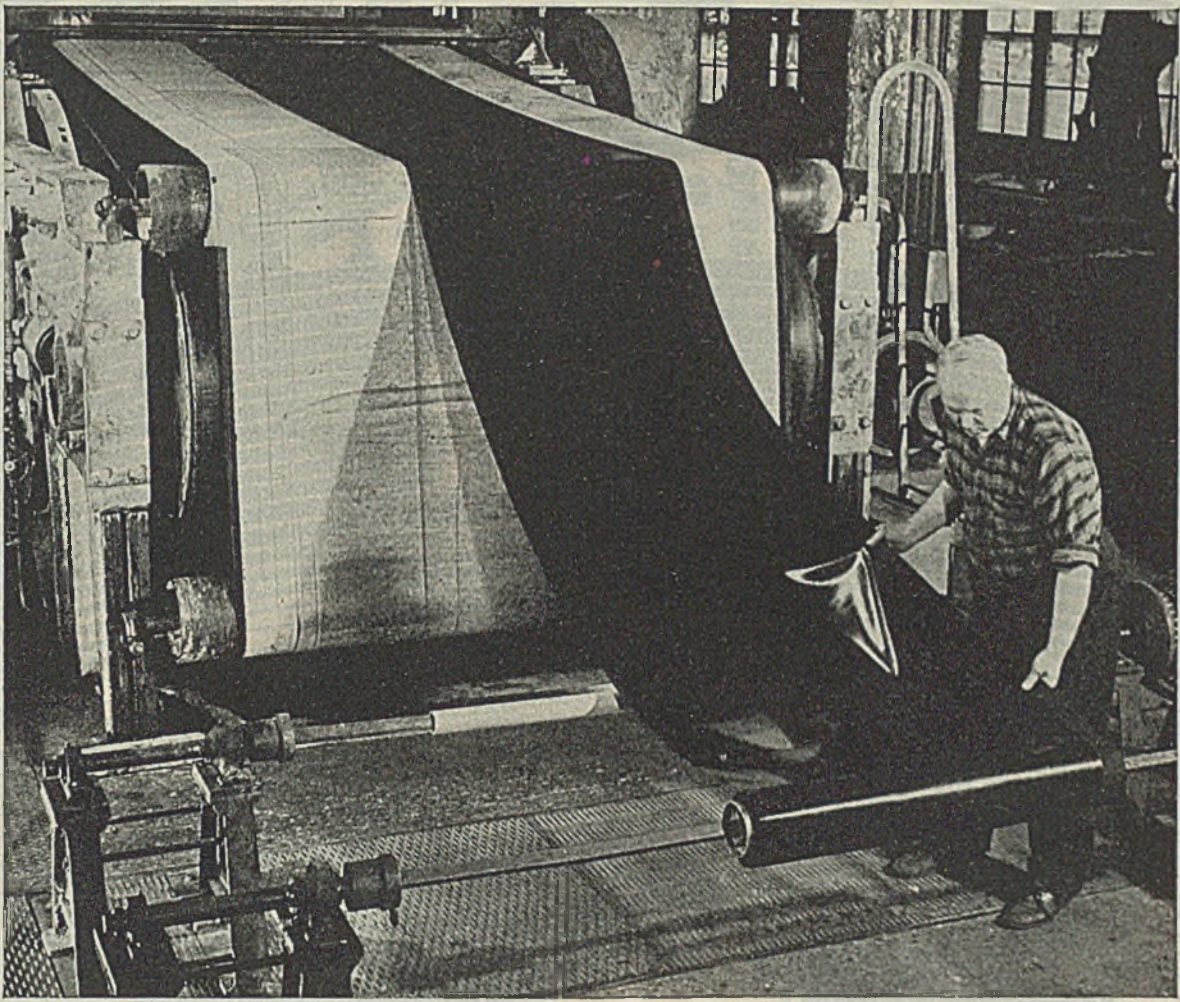
GENERAL ELECTRIC
X-RAY CORPORATION
2012 JACKSON BLVD. CHICAGO, ILL., U. S. A.

Today's Best Buy — U. S. War Bonds


Profit by
SARCO
STEAM
TRAPS







Synthetic Rubber "Wallpaper"

FOR UNCLE SAM'S UNDERGROUND OIL TREASURIES

"YOU can't store light oils and gasoline in concrete tanks," said precedent. "Oh, yes, you can," said the Navy. *And they did.*

Today, whole tank farms are now in use—underground and camouflaged. Now tremendous vaults holding as much as 100,000 gallons are storing precious fuels...all through the development of an oilproof "wallpaper" made of Thiokol* synthetic rubber.

You see, concrete is highly alkaline. In contact with aviation gasoline, these alkalies cut the fuel's all-important octane rating. Too, concrete is porous—allows precious fuel to escape.

Working closely with the Navy, the Boston Woven Hose and Rubber Company perfected a thin sheet of Thiokol synthetic rubber. This is welded to the walls and floors of the tanks with a special synthetic rubber cement. Every square inch is covered. The fuel never touches concrete. The octane rating stays up and the fuel stays in.

Valuable information on hundreds of interesting applications of Thiokol synthetic rubber is available to any American manufacturer doing war work. Ask us for it.

Thiokol Corporation, Trenton, N. J.

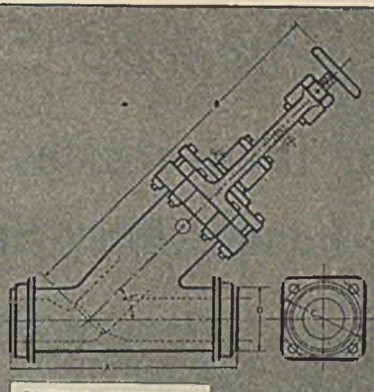
*Thiokol Corporation, Trademark Reg. U. S. Pat. Off.

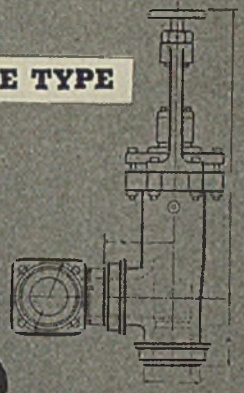
Thiokol*

SYNTHETIC RUBBER

"America's First"

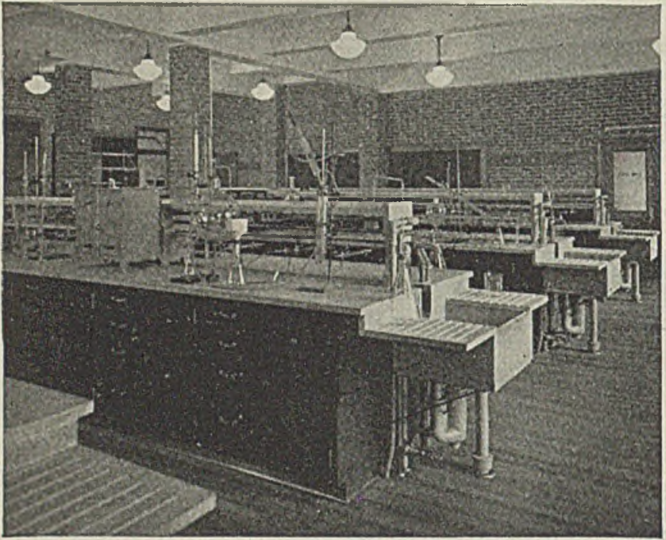

CLEAN
COMPRESSED
AIR





Prompt Service

for laboratories expanding to handle Army-Navy training



Typical Alberene-equipped college laboratory.

Currently we are active in fitting-out college laboratories to meet the influx of students under the Army-Navy war training program. Whether you require a few additional pieces of equipment, or must move to new quarters, or are planning a complete new laboratory, we are equipped to serve you. Alberene Stone's durability and economy have been proved for more than 50 years in the country's leading educational, industrial and research laboratories. Our specialized, technical experience in the design, fabrication and installation of table-tops, fume hoods, sinks, tanks, shelving, is at your immediate service. Reasonably prompt deliveries can be made.

• • •

Our engineers are experienced in designing, re-assembling and installing laboratories of every type. Call on us to do the complete job. Please address Alberene Stone Corporation of Virginia, 419 Fourth Avenue, New York, 16, N. Y. Quarries and Mills at Schuyler, Virginia. Sales offices in principal cities.

ALBERENE STONE
LABORATORY EQUIPMENT

HIGH PRESSURES
OPEN VAT APPLICATIONS
HIGH TEMPERATURES
HAZARDOUS LOCATIONS
EXTREME DIFFERENTIALS
TANK APPLICATIONS
EXPLOSIVE FLUIDS
CORROSIVE LIQUIDS

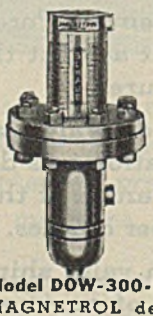
Pick Out the TOUGHEST COMBINATION of These Liquid Level Control Situations

There's a MAGNETROL Answer

● When we say "there's a MAGNETROL Liquid Level Control for *any* temperature, *any* pressure, *any* liquid, *any* differential," we mean just that. As specialists in liquid level control devices, our engineers are constantly running into unusual and difficult sets of conditions.

Their success in designing units to handle any job is written in the hundreds of custom-built MAGNETROLS now in use throughout industry. In every case, the basic MAGNETROL magnetic method of operation (eliminating all mechanical linkage between float and switch) has been a key factor in developing controls for "hard to handle" jobs. Whatever *your* liquid level control problem

Write for Information to
MAGNETROL, INC.
671 N. Orleans St., Chicago, Ill.
A Division of Fred H. Schaub Engineering Co., Inc.

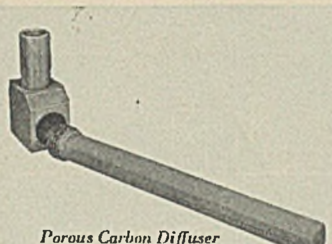


Model DOW-300-2
MAGNETROL designed for use on Dowtherm Boilers, steam and certain other high pressure and high temperature applications.

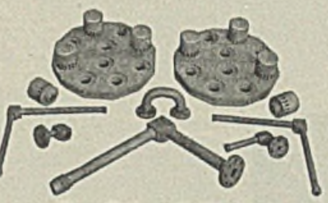
Model 750-EP
A completely welded MAGNETROL for all oil and gas piping or applications in hazardous locations. Max. Press. 750 lbs.

Model H-5000
MAGNETROL designed for extremely high pressure non-shock service for hydraulics, carbon dioxide, ethane, propane, etc.

MAGNETROL
LIQUID LEVEL CONTROLS



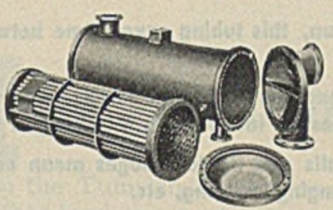
Porous Carbon Diffuser



Pipe, Fittings, Bubble Caps and Trays

Headers for heat exchanger

Sections of segmental type reaction tower



Tube and shell heat exchange unit

For Continuous and Reliable Service

NATIONAL AND KARBATE CARBON AND GRAPHITE PRODUCTS
TRADE-MARK TRADE-MARK

are extremely versatile and readily adapted to the construction of equipment of conventional design as well as special equipment of new design.

Outstanding performance and economies, along with simplification of design, are made possible by the following unique and advantageous combination of physical and chemical properties offered by these materials.

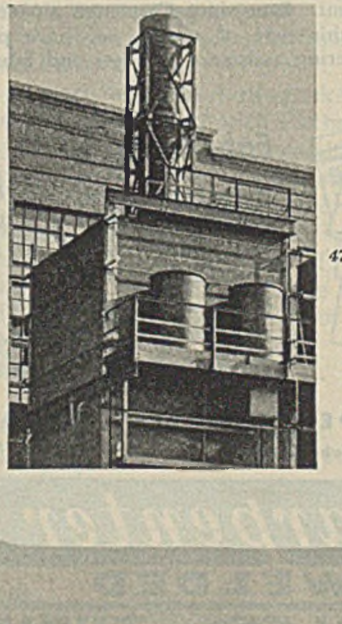
Resistance to severe thermal shock ▸ No deformation at high temperatures ▸ Not wet by molten metals – no sticking ▸ Mechanical strength maintained at high temperatures ▸ No reaction with most acids, alkalies and solvents — no contamination ▸ High rate of heat transfer (Graphite and graphite base "Karbate" products) ▸ Low rate of heat transfer (Carbon and carbon base "Karbate" products) ▸ Low thermal expansion ▸ Good electrical conductivity ▸ Self-lubricating ▸ Available in impervious grades ▸ Available in highly permeable (porous carbon and graphite) grades ▸ Easily machined and fabricated.

Practically any design can be machined or fabricated from available stock in the form of beams, blocks, slabs, brick, plates, round and rectangular rods, tubes and cylinders, pipe, fittings, valves, tower sections and tower accessories.

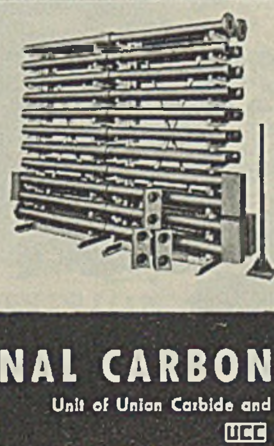
Special shapes or forms can be molded or extruded when quantity justifies.

The illustrations show only a few of the many diversified applications of these products.

Write for descriptive literature



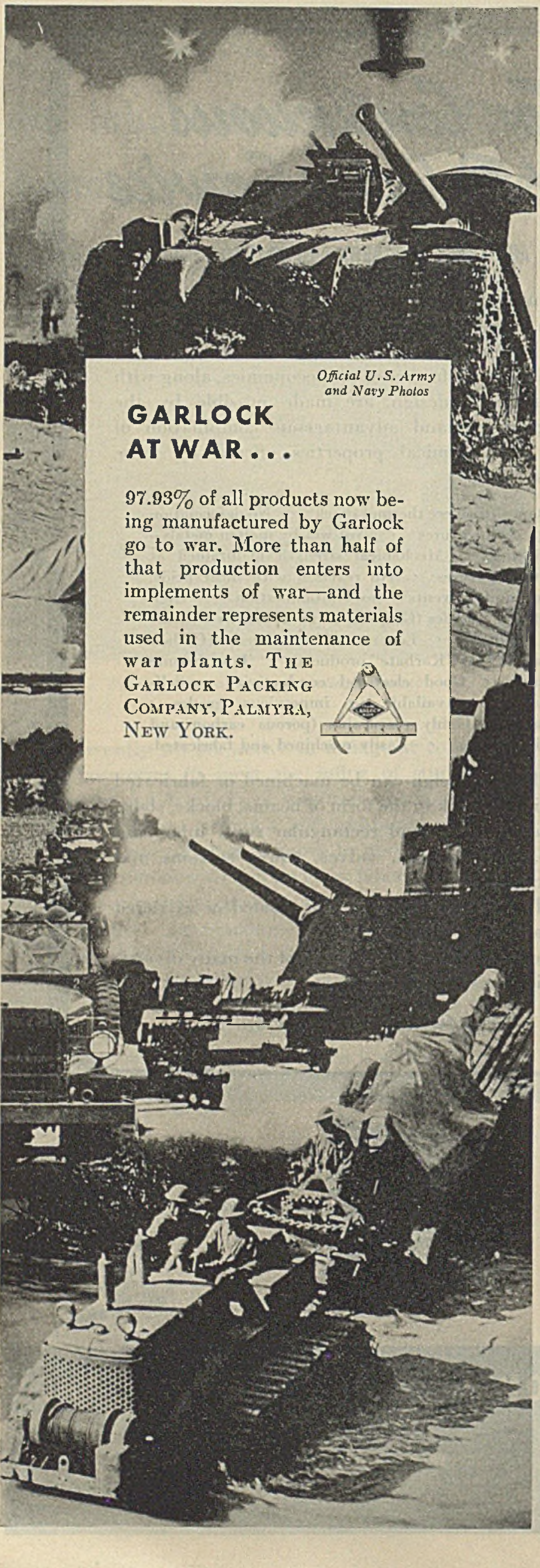
47' high all-carbon electrostatic precipitator



Return bend cooling coil

NATIONAL CARBON COMPANY, INC.

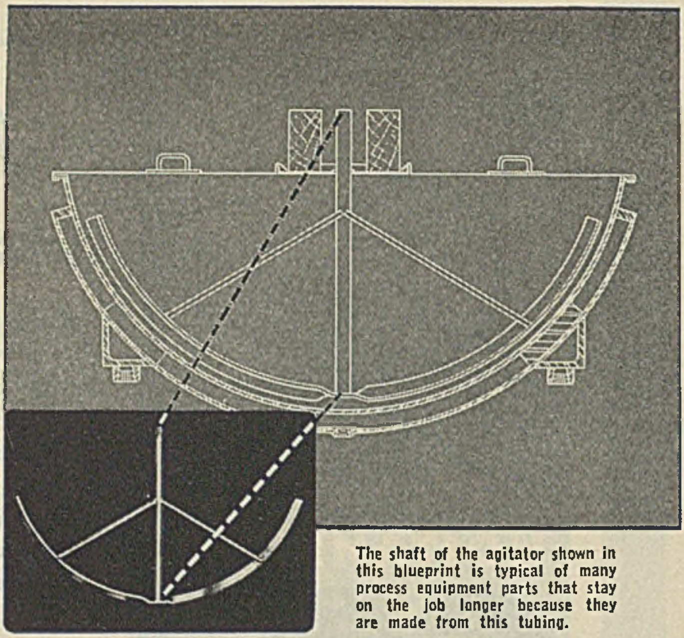
Unit of Union Carbide and Carbon Corporation
UCC
CARBON PRODUCTS DIVISION, CLEVELAND, OHIO
General Offices: 30 East 42nd St., New York, N. Y.
Branch Sales Offices: New York - Pittsburgh - Chicago - St. Louis - San Francisco



Official U. S. Army and Navy Photos

GARLOCK AT WAR . . .

97.93% of all products now being manufactured by Garlock go to war. More than half of that production enters into implements of war—and the remainder represents materials used in the maintenance of war plants. THE GARLOCK PACKING COMPANY, PALMYRA, NEW YORK.



The shaft of the agitator shown in this blueprint is typical of many process equipment parts that stay on the job longer because they are made from this tubing.

Check these 5 Advantages of this Welded Stainless Tubing!

Here are five of the reasons why more and more Carpenter Welded Stainless Tubing is used in many types of processing equipment:

1. **It provides positive protection against corrosion and heat.**
2. **It helps guard against product contamination.**
3. **Easy to clean, this tubing saves time between operations.**
4. **Its high strength-weight ratio permits the use of lighter gauges for lower costs, less weight.**
5. **Uniform walls and lighter gauges mean easier bending, flanging, welding, etc.**

For help in selecting the type of Welded Stainless Tubing best suited to your needs, get in touch with our Metallurgical Department. Ever since Carpenter pioneered the development of this type of tubing, we have provided production-engineering assistance to users and fabricators.

Fabricating Hints

in Carpenter's series of QUICK FACTS bulletins can help you get the most from Welded Stainless Tubing. A note on your company letterhead will start your series of QUICK FACTS bulletins on the way.

THE CARPENTER STEEL COMPANY
Welded Alloy Tube Division . . . Kenilworth, N. J.

Carpenter
WELDED
STAINLESS TUBING

How much coal-tar in this picture?

In the Tunisian victory, as in every other land or sea operation on America's far-flung fronts of war, coal-tar chemicals are in there fighting—co-operating inconspicuously yet effectively with American brains, brawn and bullets.

American tanks, half-tracks, trucks and jeeps, painted with Phthalic Anhydride finishes, roll forward on tires compounded with chemicals made from coal-tar. They are powered with motor fuel and lubricated with oils made better by the use of coal-tar products. In their intricate mechanisms are many parts made of Phenol plastics.

Toluol for TNT . . . Benzol for Tetryl . . . Naphthalene for smokeless powder . . . Quinoline for vitamins . . . Pyridines for sulpha drugs . . . Tar Acids for plastics, disinfectants and pharmaceuticals . . . Cumar* for waterproofing tarpaulins, tenting and other military fabrics—the list of war-time chemicals, for which Barrett is a key source of supply, is almost endless.

All Barrett's unmatched facilities and experience are today mobilized to produce these chemicals in ever-increasing quantities. And tomorrow these same chemicals will again provide the basic needs of industry to promote peacetime production and progress.

Awarded to the men and women of the Barrett Frankford Chemicals plant for excellence in the production of war materials.

THE BARRETT DIVISION
ALLIED CHEMICAL & DYE CORPORATION
40 RECTOR STREET, NEW YORK

ONE OF AMERICA'S GREAT BASIC BUSINESSES

PHENOLS
CRESOLS
CRESYLIC ACIDS
CHLORINATED TAR ACIDS
BARRETAN*
PICKLING INHIBITORS

BENZOL
TOLUOL
XYLOL
SOLVENT NAPHTHA
HI-FLASH SOLVENT
NAPHTHALENE

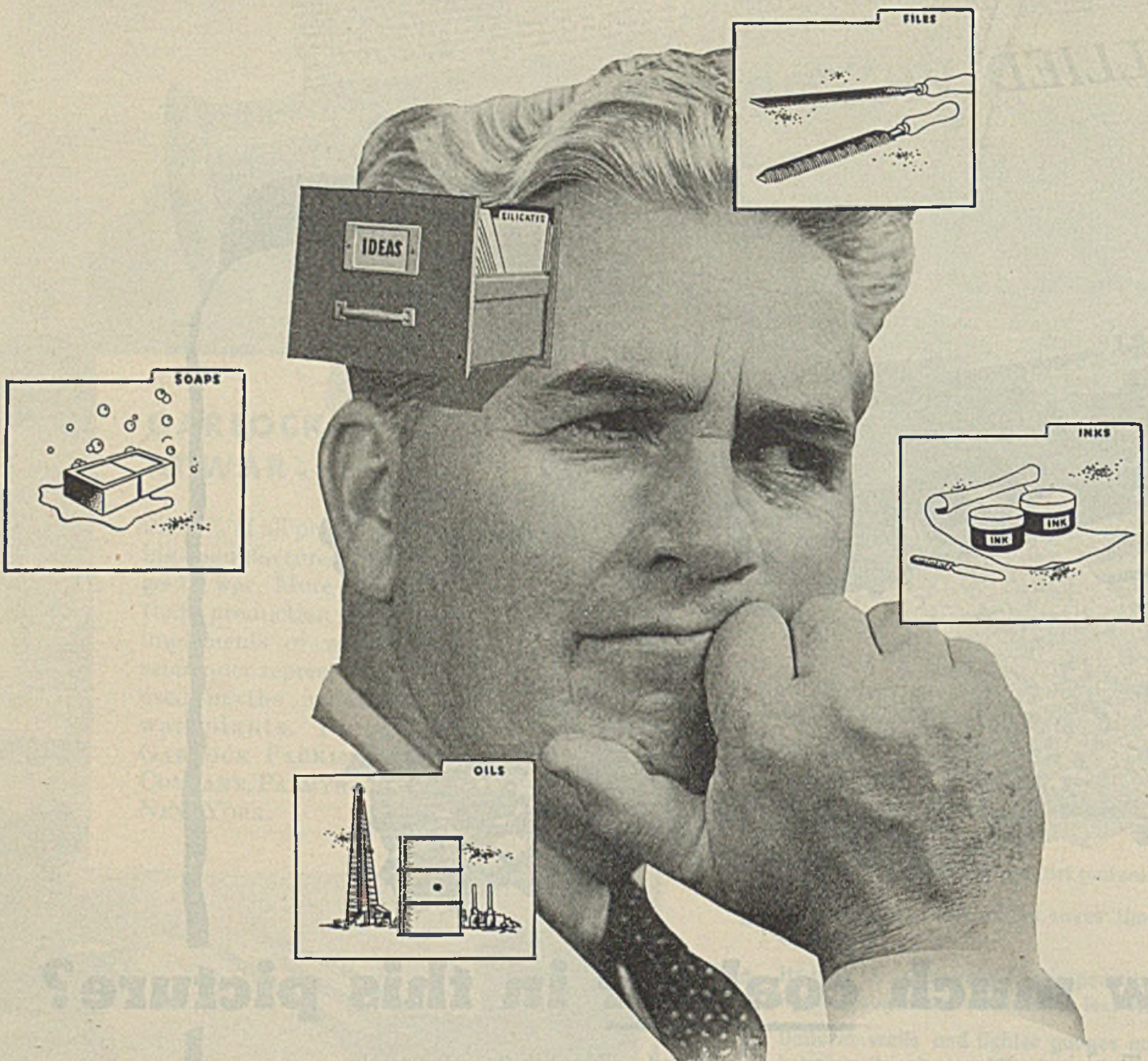
PHTHALIC ANHYDRIDE
DIBUTYL PHTHALATE
PYRIDINES
TAR ACID OILS
CREOSOTE OIL

CUMAR* (Paracoumarone-Indene Resin)
RUBBER COMPOUNDING MATERIALS
BARDOL*
HYDROGENATED COAL-TAR CHEMICALS

FLOTATION AGENTS
ANHYDROUS AMMONIA
SULPHATE OF AMMONIA
ARCADIAN* THE AMERICAN NITRATE OF SODA

*Trade-Mark Reg. U. S. Pat. Off.

IDEA STARTERS—PQ SILICATES



Perhaps silicate of soda is known to you as an ingredient of soap, which was its first important commercial use, starting back in the 1860's. Or, maybe your grandmother "put down" eggs in silicate. Whether your familiarity is limited to these or whether silicate is now used in some other way in your plant, you'll find our bulletin "Brands, Properties, Applications" stimulating. It describes over 30 brands of silicates and their uses in industry. Send for it.

Meantime, some of the current trends and developments in silicate of soda as recorded in recent patents may suggest a practical solution to one of your present problems. Write to us about any possible use of silicate that may occur to you.

Reconditioning metal workers' files: Files are degreased in boiling alkaline solution, washed by spray of water, etched in successive baths of hydrochloric, nitric and hydrochloric acids; finally rustproofed by immersing in a dilute solution of silicate of soda.

Quick-set inks: Patentee finds that if inked sheet from printing press is exposed to a mist of silicate of soda, quicker drying results. For color work, it is unnecessary to use inks with expensive volatile solvents and driers.

Removing corrosive materials from oils: Distilled petroleum oils tend to release constituents which hydrolyze to form highly corrosive acids. It has been found that 200 pounds of silicate of soda per 100 barrels of oil yields a product substantially free of corrosive materials.

PHILADELPHIA
QUARTZ COMPANY
Gen'l Offices: 125 South Third St., Phila. 6, Pa.
Chicago Sales Office: 205 West Wacker Drive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DE-ION
-IZED
WATER

COMPARABLE TO SINGLE-DISTILLED WATER . . . AND AT A FRACTION OF THE COST! — Without heat, without fuel, ILLCO-WAY De-ionizing Units are daily producing water containing less than 1 to 5 p.p.m. of dissolved solids (plus colloidal silica) . . . meeting exacting standards in outstanding war plants, chemical, pharmaceutical, industrial, etc.

10,000 GALLONS FOR LESS THAN A DOLLAR! — on average raw water supply. When water supply is low in dissolved solids, cost may be considerably less! Units have permissible flow of from 100 gallons to 50,000 gallons per hour! Send for literature.

ILLINOIS WATER TREATMENT CO.
852 CEDAR STREET • ROCKFORD, ILLINOIS

TESTED IN THE LABORATORY • ILLCO-WAY • PROVED IN THE FIELD

replaces
DISTILLED
WATER

PRECISELY ENGINEERED TO DO A *SPECIFIC* SPRAYING JOB

Spraying Systems nozzles embody knowledge and experience gained in 18 years of nozzle design and manufacture.

Suppose you need a particular type of nozzle to spray 11.6 GPM of water at 20 lbs. pressure in a full cone spray pattern. Among the thousands of nozzles available, there is one that meets exactly these specifications.

Write today — lay your spray problems before experts who have already come up with thousands of time and money-saving solutions. There's no charge for our engineers' advice.

SPRAYING SYSTEMS COMPANY
4027 W. Lake Street, Chicago, Illinois

SPECIALISTS IN THE DESIGN AND MANUFACTURE OF SPRAY NOZZLES

AMERICA'S PIONEER PRODUCER OF WIRE CLOTH

We help you get longest life, and lowest annual cost—result of 85 years' experience in manufacturing wire cloth for every use. All weaves, for screening, filtering, separating, grading, cleaning, or processing. Any metal, in types of cloth to give longest service under chemical action, corrosion, abrasion, moisture, or high temperature.

FREE BOOK contains charts, diagrams, tables of wire sizes, meshes, and weights . . . 151 illustrations. Wickwire Spencer Steel Co., 500 Fifth Avenue, New York. Or Buffalo, Worcester, Chicago, San Francisco.

WICKWIRE SPENCER
WIRE CLOTH

WS WISSCO PRODUCTS

No. 2 in a series of case studies on dust and fume conditions in the process industries.

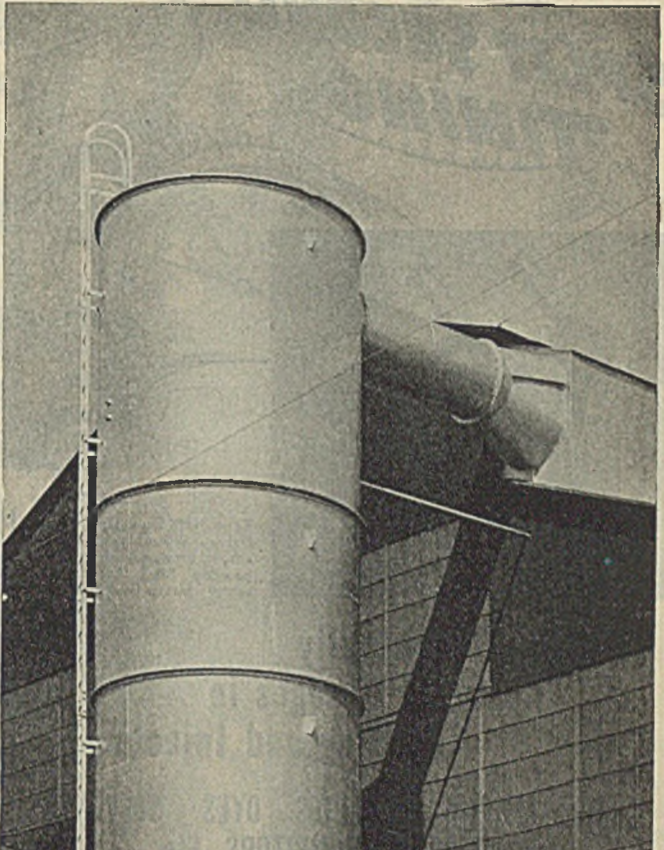
THE PROBLEM

To eliminate dust nuisance from exhaust from two multiple hearth roasters and material handling equipment operating on alumina.

THE SOLUTION

An 18,000 CFM Schneible Multi-Wash Collector, water recirculating system and Dewatering Tank for the accumulation of the collected material.

Working conditions were substantially improved, plant and neighborhood is protected against dust nuisance. As the Multi-Wash Collector is constructed of heavy gauge steel plate with no moving parts in the dust stream, it will provide many years of efficient service with a minimum of operating and maintenance cost.



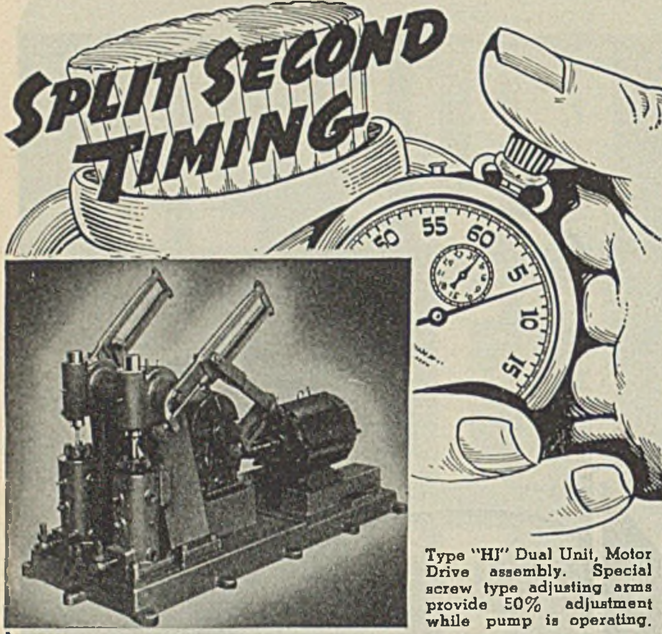
Effective for Any Dust or Fume Condition

A wide variety of dust and fume conditions are encountered in the process industries, but Schneible has the solution to most of them with standard units made of the materials to suit the requirements. The water or other suitable liquid is used as the recirculated collecting medium. Dust, odors and noxious fumes are completely and economically removed by the Schneible Multi-Wash System, which frequently pays for itself through enhanced working efficiency in many plants, and through valuable product recovery in others.

Consult us regarding your dust and fume problems.

CLAUDE B. SCHNEIBLE COMPANY
3959 Lawrence Avenue, Chicago, Ill.
Engineering Representatives in Principal Cities

SCHNEIBLE



Type "HJ" Dual Unit, Motor Drive assembly. Special screw type adjusting arms provide 50% adjustment while pump is operating.

Assures Consistently Accurate Dosages in Feeding and Injecting

ACIDS - ALKALIS - SLURRIES - DYES - SOLVENTS
EMULSIONS - INHIBITORS, Etc.

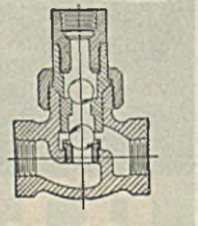
HILLS-McCANNA
Positive PROPORTIONING PUMPS
WITH POSITIVE ACTING CHECK VALVES

8 TYPES
OVER 200 SIZES

Back of these pumps stands the surety of service gained from the experience of over 70 years in single plunger pump design. This same principle, first applied to Hills-McCanna Lubricators, has been perfected in Hills-McCanna Proportioning Pumps by over 30 years of development, and thoroughly proven in service by thousands of installations.

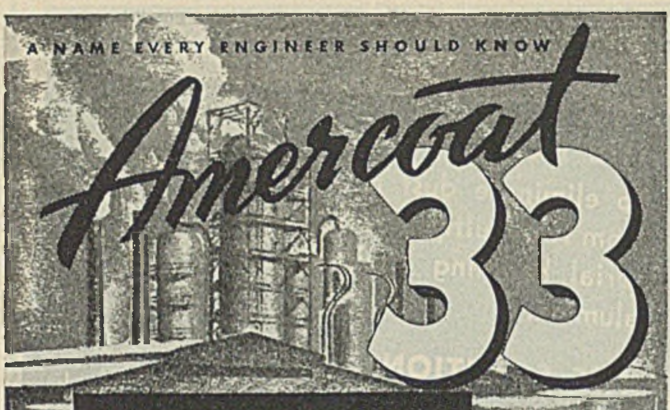
Soundly engineered—of precision manufacture—these pumps embody exclusive Hills-McCanna features to meet all needs of large or small volumes, high or low pressures—and are equipped to handle successfully the many types of chemicals used in the Processing Industries.

They are indispensable today for the positive mechanical proportioning, feeding and injecting of constituents in accurately measured dosages. Complete Catalog P-41 illustrates and describes the simple, rugged construction which permits continuous operation with minimum attention and maintenance. . . WRITE FOR YOUR COPY TODAY.



Horizontal Composite Double Ball, Cone or Disc Type Check Valves, combining suction and discharge in the same body. Automatically minimize air-binding and friction drop.

HILLS-Mc CANNA CO.
2345 NELSON STREET, CHICAGO
PROPORTIONING PUMPS • AIR & WATER VALVES • CHEMICAL VALVES
MARINE VALVES • FORCED-FEED LUBRICATORS • DOWMETAL CASTINGS



A GENERAL PURPOSE COLD-APPLIED THERMOPLASTIC COATING FOR A WIDE RANGE OF APPLICATIONS

Amercoat No. 33 Thermoplastic Coating is the result of two years of careful development and exhaustive test both in the laboratory and in the field. It meets the urgent demand for an inert, easy-to-apply protective coating for wood, metal and concrete.

Amercoat No. 33 is used as a coating for structural steel, floors, filters, tanks, concrete walls and floors, machinery, ship bottoms and boottopping, concrete urinals, shower bases, laundry tubs . . . wherever buildings and equipment are exposed to corrosive fumes or the corrosive action of salt water, fresh water or various mild acids or caustics.

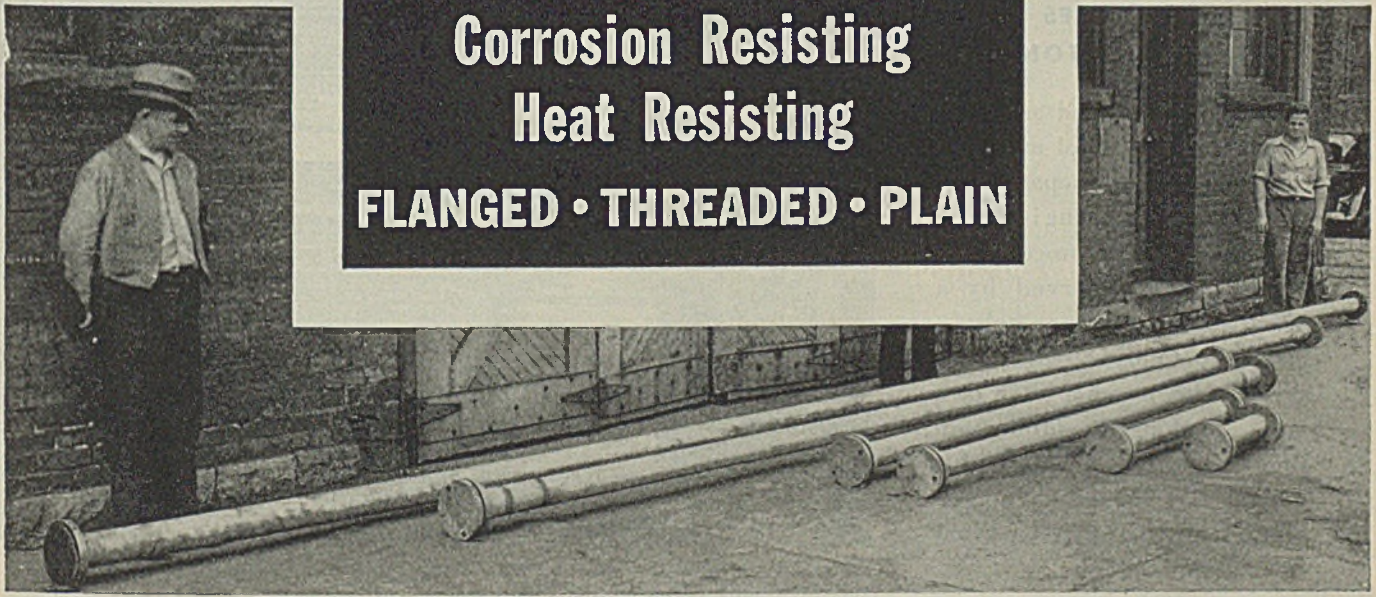
Amercoat No. 33 Thermoplastic Coating is composed of the correct combination of the most inert synthetic resins obtainable. It comes in liquid form and is easily applied with ordinary industrial paint spray equipment or by brush. It may be applied in any number of coats required for any particular condition. It is odorless, tasteless, resistant to moderate abrasion and is dielectric to a high degree.

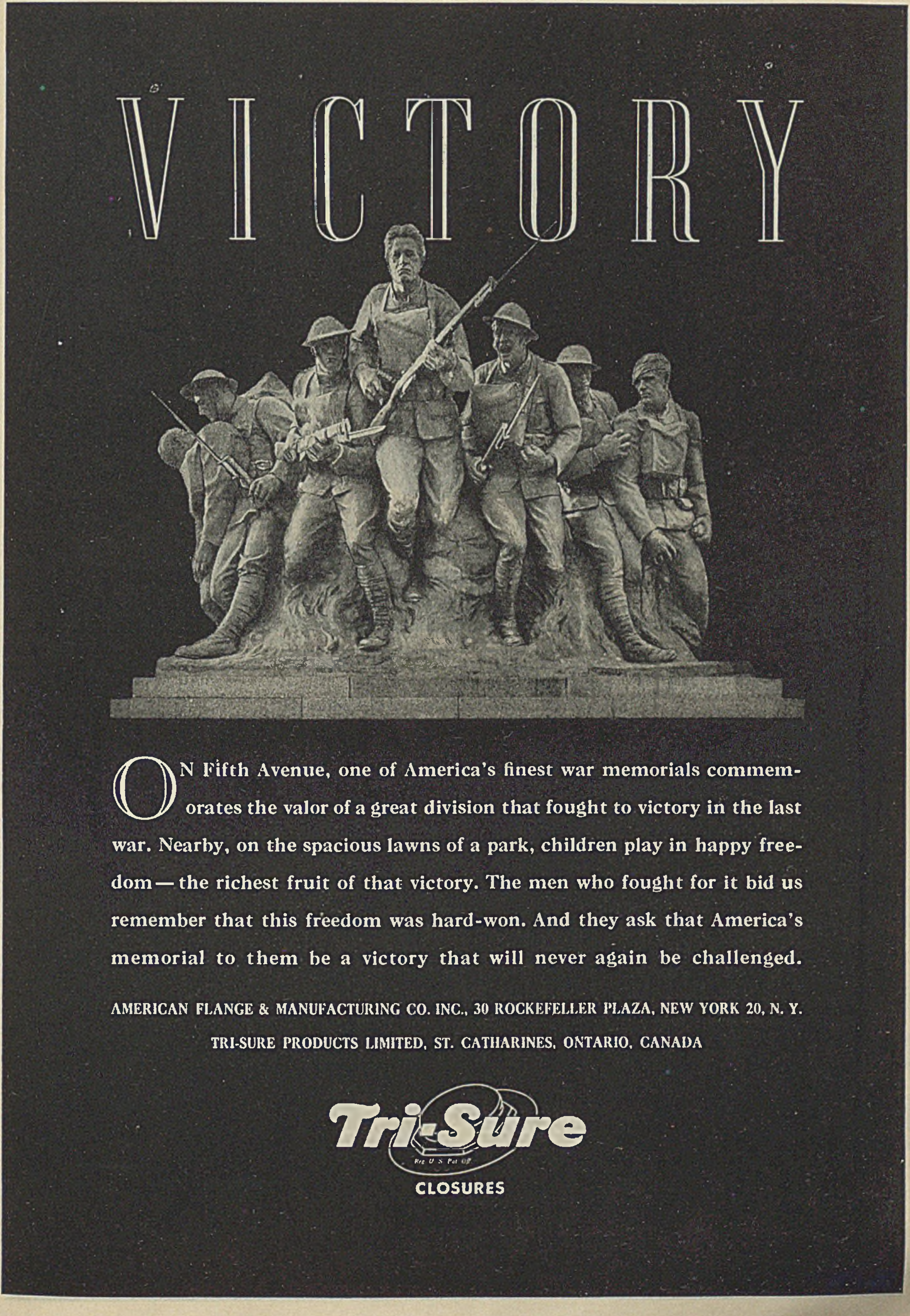
***Amercoat* No. 33 does not replace, nor is it a substitute for other *Amercoat* Compounds which have been developed for more highly specialized requirements.**

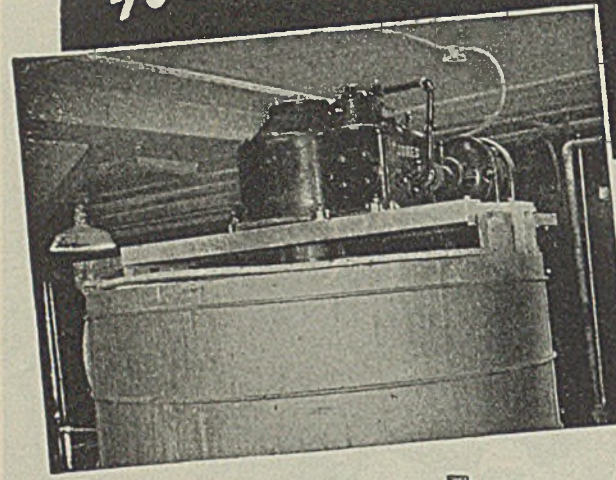
Amercoat DIVISION

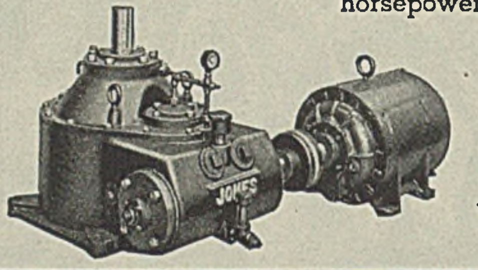
Write for Bulletin No. 33 which gives complete data on AMERCOAT No. 33 and the many uses for which it is suited

AMERICAN PIPE & CONSTRUCTION COMPANY
P.O. BOX 3428, TERMINAL ANNEX • LOS ANGELES, CALIF.
Canadian Dist: Gunite & Waterproofing, Ltd., 1538 Sherbrooke St., W.; Montreal





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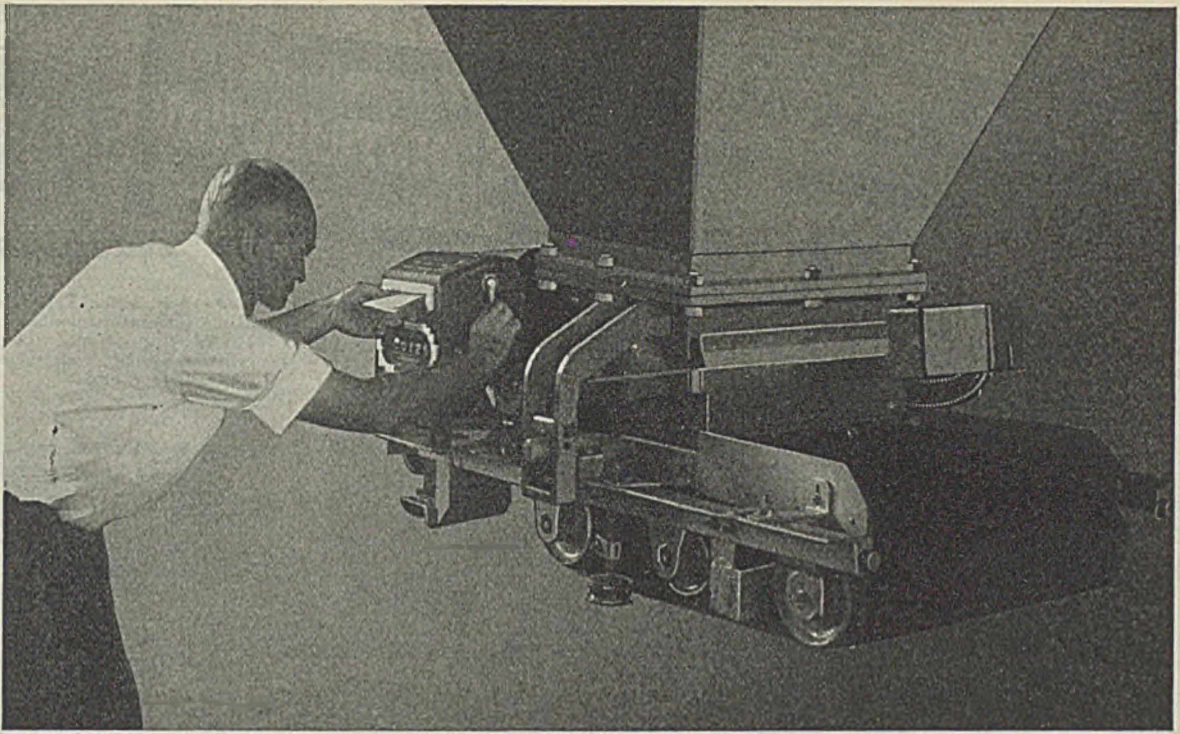


HARDINGE CONSTANT WEIGHT FEEDER

An accurate and dependable feeder for feeding by weight.

Made in five sizes with capacities from 1-lb. per hour to 1000 tons per hour. The conveyor belt is driven through a variable speed drive with a 3 to 1 variation in capacity. The counter weight on the gate arm permits considerably greater capacity range when desired.

When equipped with the no-load cut-off attachment, a signal light or bell indicates an empty bin or material hanging in bin and stops the feeder.

For proportioning two or more materials, the feeders may be interlocked. If one feeder is stopped or one bin becomes empty, all feeders stop and the warning signal operates.

The "Feedometer," a weight and rate indicating feeder, indicates the rate of feed and totalizes the amount fed. This feeder operates on the constant weight principle.

Write for Bulletins 33-C and 43

Partial List of Materials Fed with This Feeder —

- Borax
- Carborundum
- Cement Clinker
- Coal
- Coke
- Dolomite
- Ferro-Chrome
- Fertilizer
- Gypsum
- Iron Ore
- Lime
- Limestone
- Pigment
- Salt
- Silica Sand
- Soda Ash
- Sodium Silicate
- Talc

HARDINGE

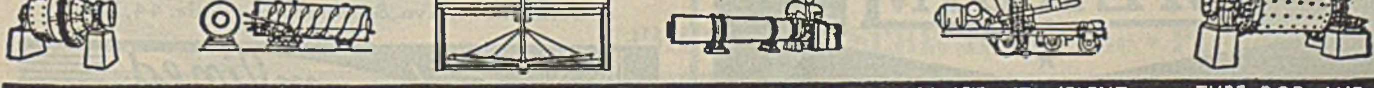
COMPANY, INCORPORATED — YORK, PENNSYLVANIA

122 East 42nd Street
New York, N. Y.

205 West Wacker Drive
Chicago, Illinois

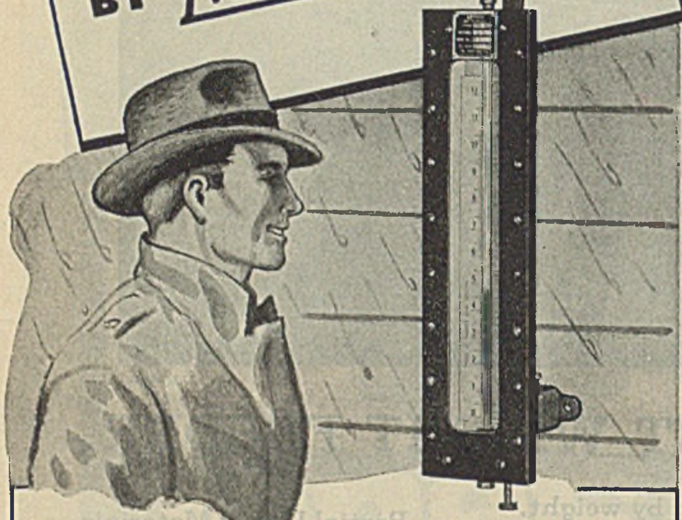
501 Howard Street
San Francisco, California

200 Bay St.
Toronto, Ontario, Canada



CONICAL MILLS | COUNTER CURRENT CLASSIFIERS | THICKENERS CLARIFIERS | RUGGLES-COLES DRYERS | CONSTANT WEIGHT FEEDERS | TUBE ROD AND BATCH MILLS

FOR OUTDOOR SERVICE WELL TYPE MANOMETER BY MERIAM



★ This manometer comes in an absolutely moisture-proof case for mounting any place outdoors.

The weather-proof feature makes it handy for a number of operations where outside reading is desirable—measuring tank liquid levels, various pressures, vacuums and differentials.

Models are available in ranges from 6″ to 100″ for use on line pressures up to 250 lbs. per sq. in. These are the well type design, direct reading, and thoroughly moisture-proof.

Write us for complete information on this convenient outdoor manometer.

THE MERIAM COMPANY

1969 West 112th Street · Cleveland, Ohio

MERIAM

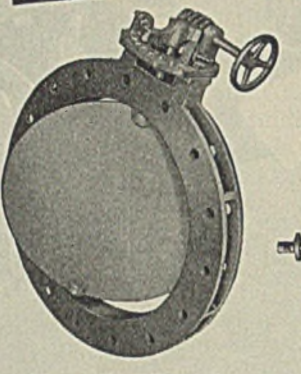
SINCE 1911

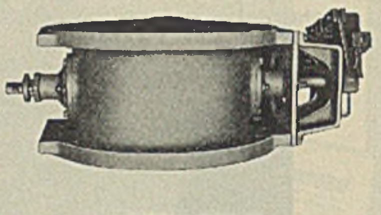
★

MANOMETERS, METERS AND GAUGES FOR THE ACCURATE MEASUREMENT OF PRESSURES, VACUUMS AND FLOWS OF LIQUIDS AND GASES

There's an R-S DISTRIBUTOR As Near as Your Telephone

Left: 15-lb Wafer Type (Narrow face-to-face construction). *Below:* 125-lb valve equipped with control cylinder. Double end stuffing box eliminates end thrust.





These R-S Distributors are valve specialists. They are experienced with the solution of problems encountered in the control and shut-off of air, gas, steam, liquids and semi-solids. Familiar as they are with the application of valves to high and low pressures, temperatures and volumes, they can frequently make suggestions that will simplify a valve installation and reduce costs.

Naturally, these local representatives are thoroughly familiar with the R-S development of special metals for resistance against heat, abrasion and corrosion.

Get acquainted. These valve experts are good men to know well.

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Columbia Bldg., Pittsburgh, Pa. Court 5362
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QUALITY PRODUCTS R-S SINCE 1908

15 to 900 psi

VALVE DIVISION

R-S PRODUCTS CORPORATION

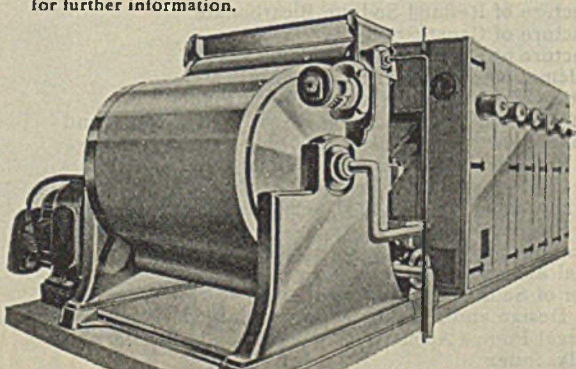
Germantown Ave. & Berkley St.; Phila. 44, Pa.

R-S *Streamlined* BUTTERFLY VALVES

CHINES · PROCTOR DRYING MACHI PROCTOR DRYING MA

PROCTOR DRYERS ARE RECOGNIZED BY LEADING SOAP MANUFACTURERS

The NEW PROCTOR FLAKE SOAP SYSTEM. Receives hot liquid soap from crutcher and delivers dried flakes in one operation. Flakes three thousandths of an inch and up to fifteen thousandths of an inch produced perfectly uniform in a much greater volume than older thick chip systems of comparative size. Cuts production costs and saves on floor space. Modern design chilling machine, carrying-in apron and dryer all in one extremely simplified unit. Write today for further information.



Just as she *recognizes* the soap that does the most for her individual complexion from among the finest products of America's leading soap manufacturers, those very manufacturers *recognize* Proctor dryers as machines of the very highest efficiency. The uniformly good quality and extremely low cost of today's soap products are dependent in a large measure on the high efficiency of modern Proctor dryers. Virtually all of the well-known brands of toilet and laundry cakes, laundry flakes and powdered and granulated soaps go through a Proctor drying machine in some stage of their manufacture. In the soap industry, as in nearly every major industry, Proctor dryers are recognized for their perfectly uniform results, high output in a minimum of floor space and low operating costs. Whether it be for soap, chemicals, plastics, food or synthetic rubber, if you have a drying problem, now is the time to have Proctor engineers consider its solution toward that day when other-than-war products can be purchased. Naturally, if your product is vital to the war effort, we can supply you with new machinery today.

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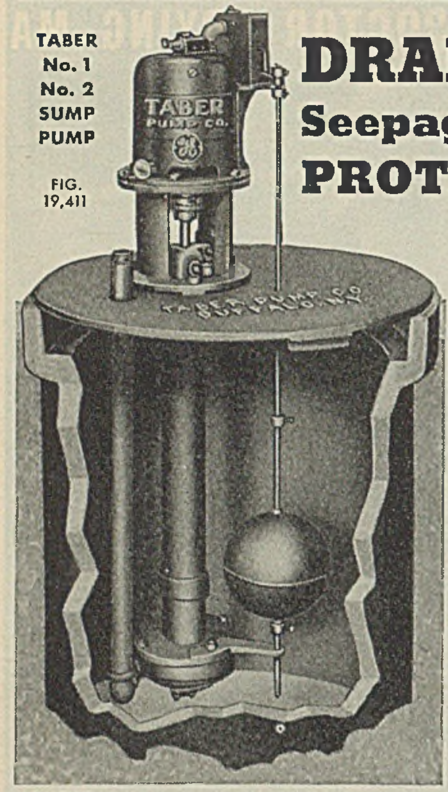
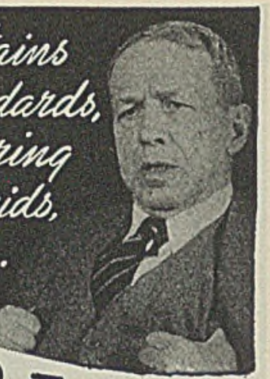

TABER PUMP CO.



A LESSON IN WATER COOLING

LESSON 4 OF A SERIES

INTERNAL "FILLING"

A prime essential to the efficient performance of many cooling towers is the wood "filling." This is the latticework arrangement of close-set horizontal slats or bars which occupies the greater portion of the tower's interior from the water distribution system at the top to the catch basin at the bottom.

The purpose of the filling is to mix mechanically the falling water with the moving air so as to facilitate the transfer of heat. In most cases the water, showered or sprayed evenly over the top level of the filling, splashes downward from one level to the next by gravity while the air moves either horizontally or vertically through the falling water by means of natural or mechanical draft.

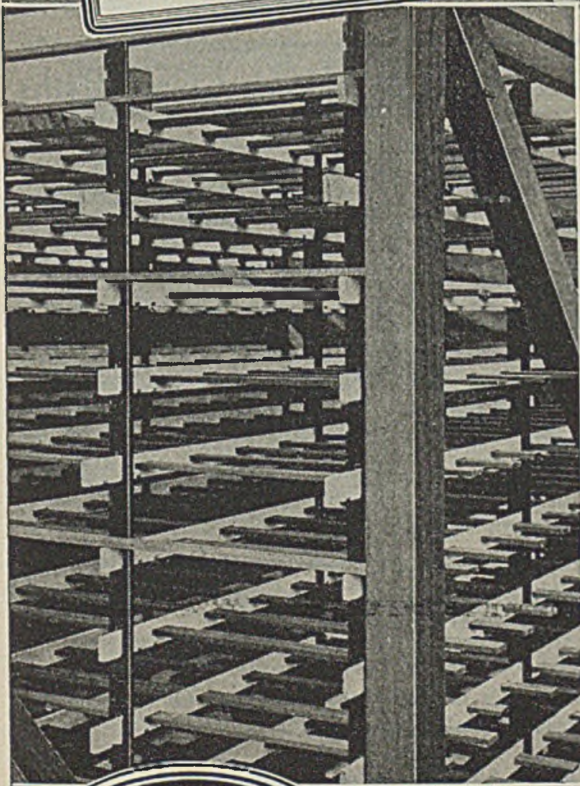
Utmost exposure of water surface to passing air is thus accomplished by repeatedly arresting the water's fall, splashing it into fine droplets, and spreading it into thin films. The filling should also maintain a uniform fall of water over the entire area at all levels and permit the free passage of adequate air volume to absorb and carry off heat rapidly.

A well-designed cooling tower filling embodies the following features in such a manner as to give optimum results:

Maximum horizontal splashing surface
Maximum active wetted surface
Minimum restriction to air flow
Freedom from warping, buckling and sagging
Maximum structural strength
Maximum ease of removing and re-installing
Minimum of nails, bolts or other metal

TOTAL HEAT CONTENT OF AIR AT VARIOUS WET BULB TEMPERATURES
at Standard Barometric Pressure

W. B. Temp. °F	BTU per Pound	W. B. Temp. °F	BTU per Pound	W. B. Temp. °F	BTU per Pound
30	**10.89**	54	22.55	78	41.42
32	11.73	56	23.77	**80**	**43.51**
34	12.56	58	25.05	82	45.72
36	13.41	**60**	**26.37**	84	48.05
38	14.28	62	27.76	86	50.47
40	**15.19**	64	29.21	88	53.02
42	16.13	66	30.73	**90**	**55.70**
44	17.11	68	32.31	92	58.52
46	18.12	**70**	**33.96**	94	61.50
48	19.16	72	35.70	96	64.62
50	**20.25**	74	37.51	98	67.92
52	21.38	76	39.42	**100**	**71.40**



MARLEY'S NEW PATENTED

MORTISLOCKED *NAIL-LESS FILLING*

A BIG FACTOR IN HIGHER COOLING TOWER EFFICIENCY

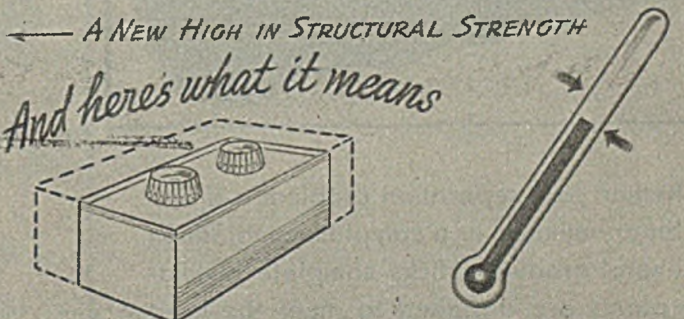
← NO NAILS, BOLTS OR OTHER METAL TO CORRODE - ALL REDWOOD PIECES INTERLOCKED BY MORTISES, SO CAN EXPAND AND CONTRACT WITHOUT STRESS

← EXTREMELY CLOSE SPACING BOTH WAYS - MORE SPLASH LEVELS, MORE WETTED SURFACE, YET OPTIMUM AIR FLOW

← SHORT SPANS PREVENT SAG - ALL BATTENS STAY LEVEL AND IN PRECISE ALIGNMENT PERMANENTLY - EVEN WATER DISTRIBUTION FROM TOP TO BOTTOM

← A NEW HIGH IN STRUCTURAL STRENGTH

And here's what it means



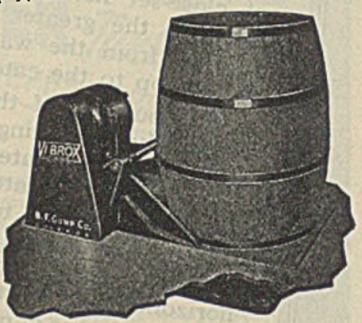
SMALLER SIZE TOWER FOR A GIVEN DUTY OR LOWER WATER TEMPERATURES FROM A TOWER OF GIVEN SIZE

MARLEY COOLING TOWERS

THE MARLEY COMPANY INC.
KANSAS CITY, KANSAS

'53-A


A+B=C


VIBROX
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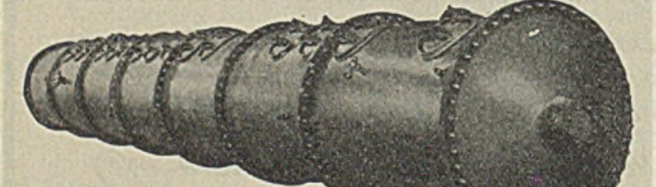
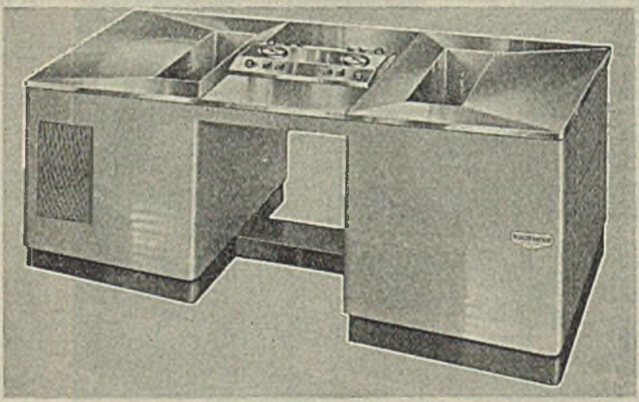




PERFORMANCE!

This is a factual recital which is typical of what we can do for you!

Emergency! *3 P.M., June 16th*—An executive of our Company received a phone call from the Engineering Department of an important industrial firm, heavily engaged in War work.

The Message! "A section of our plant has been destroyed. Eight lead lined tanks, together with piping, must be immediately replaced. You did this job about five years ago—what can you do now? We must get back in production at the earliest possible moment. We have estimated the requirement at about thirty-five tons of sheet lead and lead pipe. How many men can you put on the construction and lead burning?"

Our Answer! "The delivery of the lead represents no problem, in that the fabricating plant of Asarco can get it there almost at once. You evidently are not asking for an estimate of cost, but are concerned chiefly with getting back in production. Nevertheless, we want to estimate, and there need be no delay because of it. If your drawings will be available by tomorrow morning (*200 miles away*), I will be there to get them and go over all details. Insofar as installation is concerned, some of this work can probably be done in our lead burning plant. The larger work can be handled in the field. I do not anticipate a delay on this end of the job. If agreeable, I will see you tomorrow."

PERFORMANCE!

Thursday morning, June 17, our representative obtained blueprints and learned all details. By *Saturday, June 19th*, our engineer, with his estimate and completion schedule, was in the office of the industrial company, and secured permission to proceed. *Since then, the lead has been delivered, the lead burning completed, the tanks erected, and the unit in operation — This, two weeks from the date of the initial telephone call.*

No Promise to Accomplish, No Desire to Serve, No Hope to Achieve, Will Take the Place of Actual Performance!

THE ANDREWS LEAD CONSTRUCTION CORP.

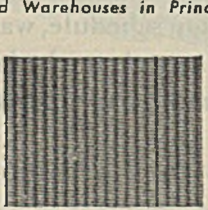
LEAD BURNING CONTRACTORS 120 BROADWAY, NEW YORK, N. Y.

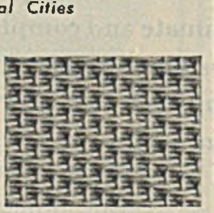
Twenty tons of roaring bomber, hitting close to 300 miles an hour, pack plenty of punch to knock out enemy factories, mix it up with intercepting fighters, *get back home* . . . And those same twenty tons, coming in for a mile-a-minute landing, still pack plenty of punch, punch that has to be absorbed and dissipated by tough brake linings. Those brake linings take terrific punishment in bringing a bomber to a gentle stop—*take* it, because they're reinforced with wire screen: a sturdy steel backbone that resists tearing and wearing of the lining.

Nor is this the only fighting job wire screen is doing today. It reinforces gaskets for high pressure lines, strengthens boiler shell insulation, guards workers from high speed machine parts . . . It filters liquid fuels, stands guard over lubricating systems, screens coal and gravel and ores . . . In all of these and many other fighting assignments, Roebling Wire Screen is serving today—from 325 mesh of .001" wire up to screen with 6-inch openings of 1-inch rod stock! Serving in steel, iron, monel, copper, brass, aluminum, stainless—name your metal. Wherever you've got a fighting job for wire screen today, Roebling has the one screen to fill that job. And Roebling makes all Wire Screen promptly available to manufacturers of essential products.

JOHN A. ROEBLING'S SONS COMPANY
TRENTON, NEW JERSEY
Branches and Warehouses in Principal Cities


OBLONG OR SQUARE MESH WIRE CLOTH


DUTCH PLAIN WEAVE FILTER CLOTH


DUTCH TWILLED WEAVE FILTER CLOTH

ROEBLING

WOVEN WIRE SCREENS

Now You Can Know...

- **That Your Vacuum Lines are Tight**
- **That They Have Sufficient Capacity**
- **That Your Pumps are Drawing Properly**

Stokes High Vacuum Gauges make it possible, for the first time, to take accurate quantitative readings of high vacuum in rapid succession with a McLeod type instrument.

They make it easy to check your vacuum systems at all points, to locate leaks, to determine pressure losses in lines, to compare efficiencies of pumps and process chambers . . . to maintain systems at maximum efficiencies, thus speeding-up production and obtaining desired results in drying, evaporating, impregnating, and other vacuum processing operations.

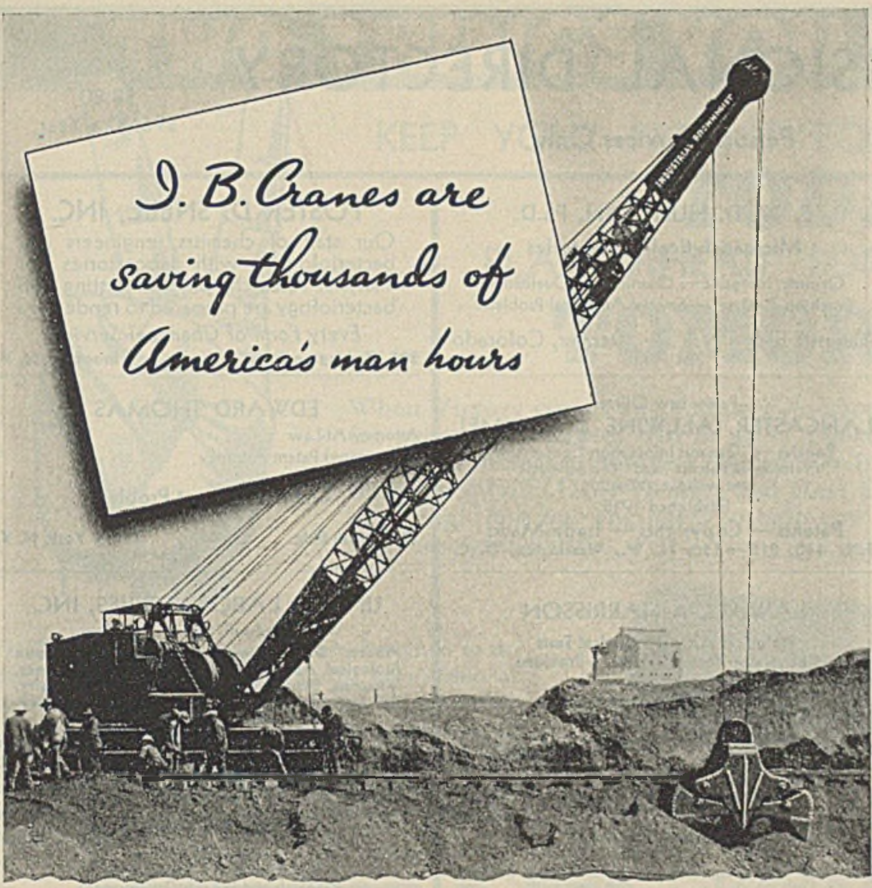
Stokes Gauges are convenient to use, either as portable instruments or on fixed mountings, in plant or laboratory. They are wide range, easily and quickly read (a few seconds only for a single reading), rugged and durable. They are carefully tested for accuracy of calibration, are widely applicable in all high vacuum processes operating within the micron and 5 mm ranges. Readings are obtainable directly, without the aid of any assisting gauge, reference vacuum, batteries or electrical connections.

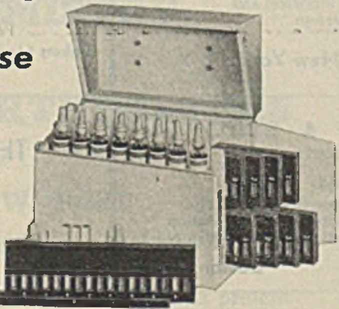
Two models, one covering entire range in moderately high vacuum operations and one for very fine readings, down to a fraction of a micro. Fully described in new Bulletin 42-G.

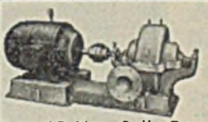
F. J. STOKES MACHINE COMPANY
5922 Tabor Road Olney, P. O. Philadelphia 20, Pa.

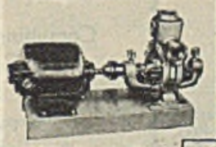
Representatives in New York, Chicago, Cincinnati St. Louis Cleveland, Detroit
Pacific Coast Representative: L. H. Butcher Company, Inc.

F.J.Stokes


I. B. Cranes are saving thousands of America's man hours







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on Water Conditioning Problems

Surveys Plant Studies Analyses

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314 West First Street Dayton, Ohio

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and Development

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F. B. Porter
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Precision Analyses — Special Analytical Problems

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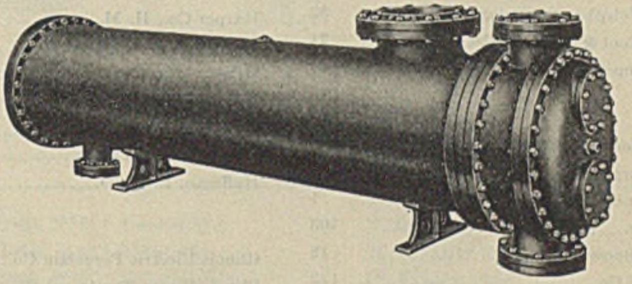

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THE CHEMISTRY
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By
HOWARD W. POST
Department of Chemistry, University of Buffalo

It is the purpose of this work to co-ordinate and present the material now to be found in the literature on the orthoesters of aliphatic carbon, namely those of orthoformic acid and its homologs and of orthocarbonic acid. Space will also be given to silicon analogs of these compounds.

The subject matter will be grouped under headings indicative of reactions rather than of compounds and under subheadings arranged in historical sequence. For instance, the preparation of orthoesters will be treated according to method, subdivided chronologically.

CONTENTS:—Introduction; Preparation and General Properties; Reactions with or Catalyzed by Inorganic Acidic Substances; Reactions with Organic Acids, Anhydrides and Halides; Reactions with Nitrogen Compounds; Reactions with Organo-Metallic Compounds; Carbohydrate Orthoesters and Orthoacids; Miscellaneous Reactions; Silicoorthoesters: Preparation and Physical Properties; Chemical Properties of Silicoorthoesters; Polyalkoxides of Other Elements of the Fourth Column; Physical Properties of Orthoesters; Author Index; Subject Index.

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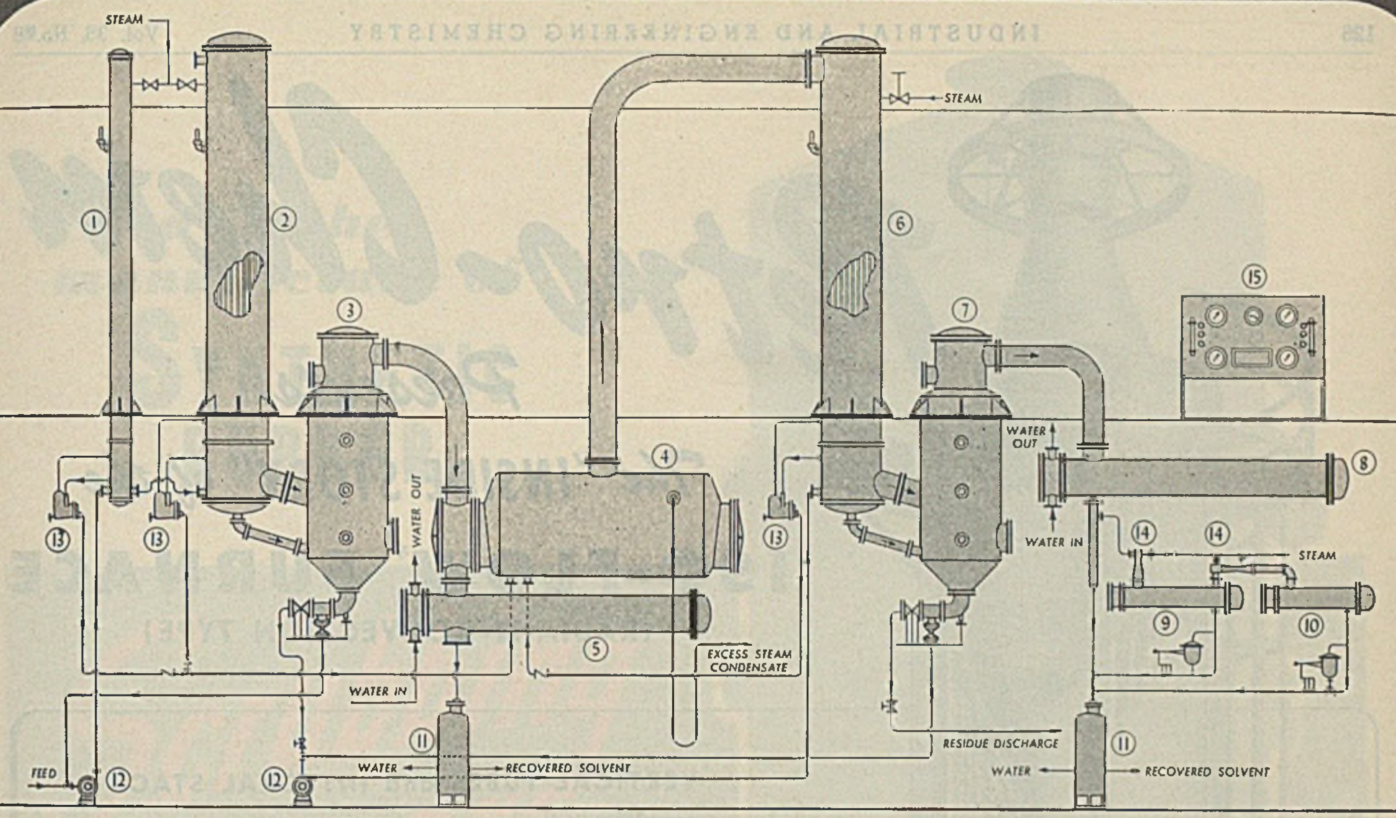
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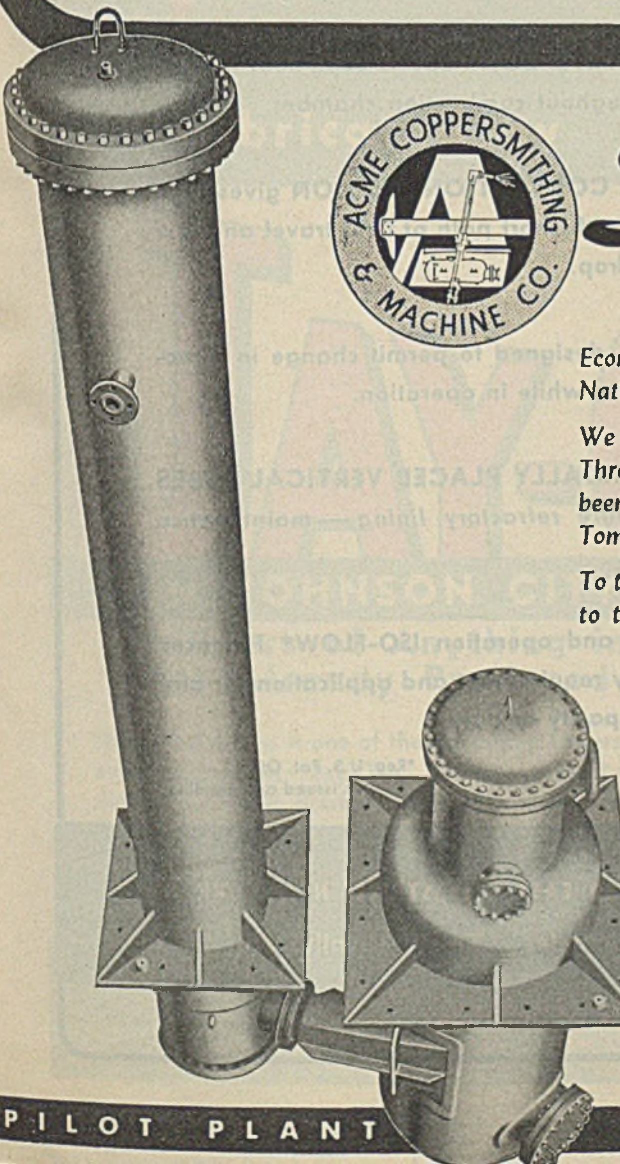

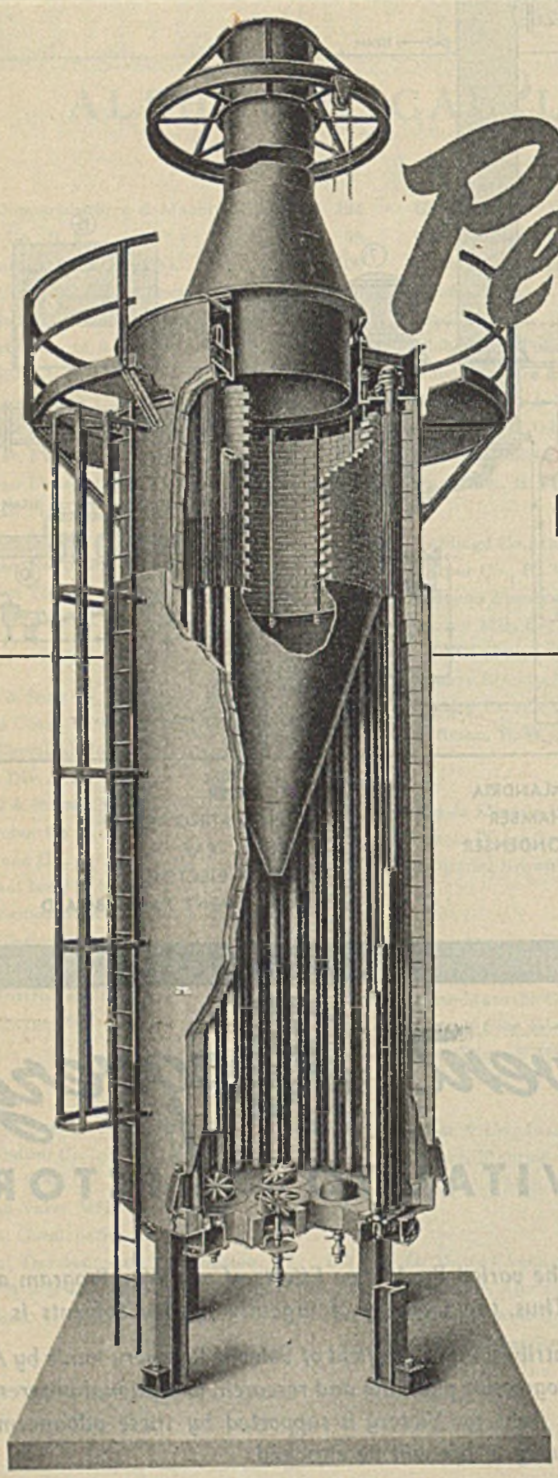

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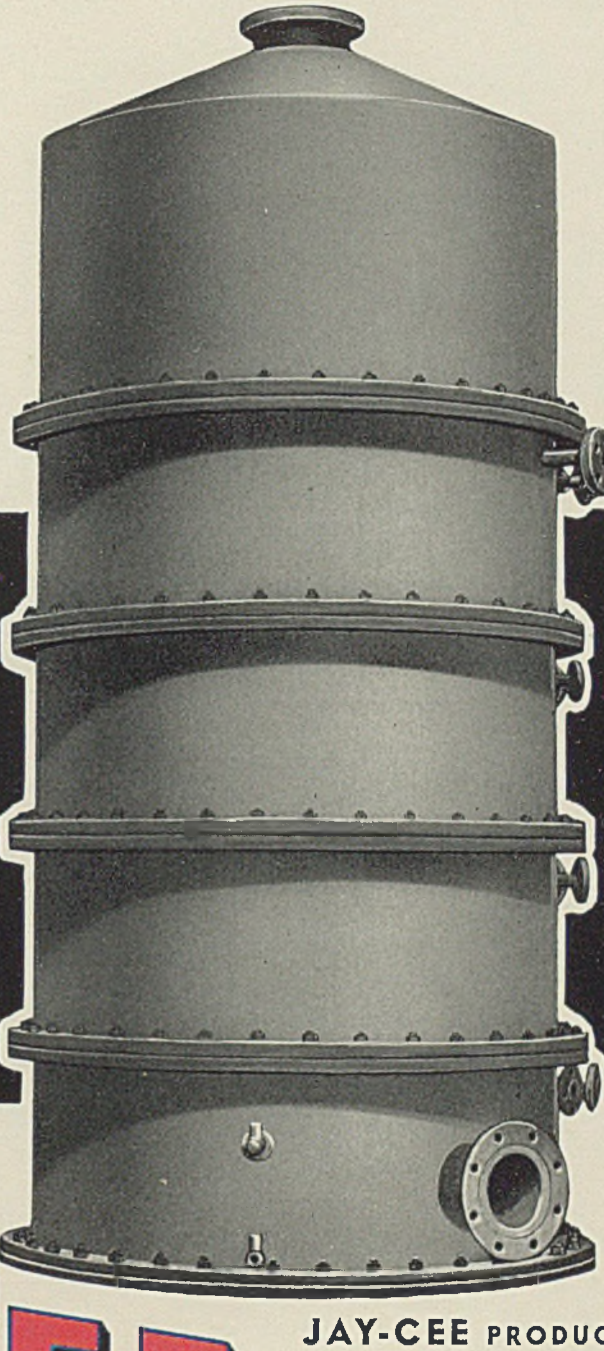

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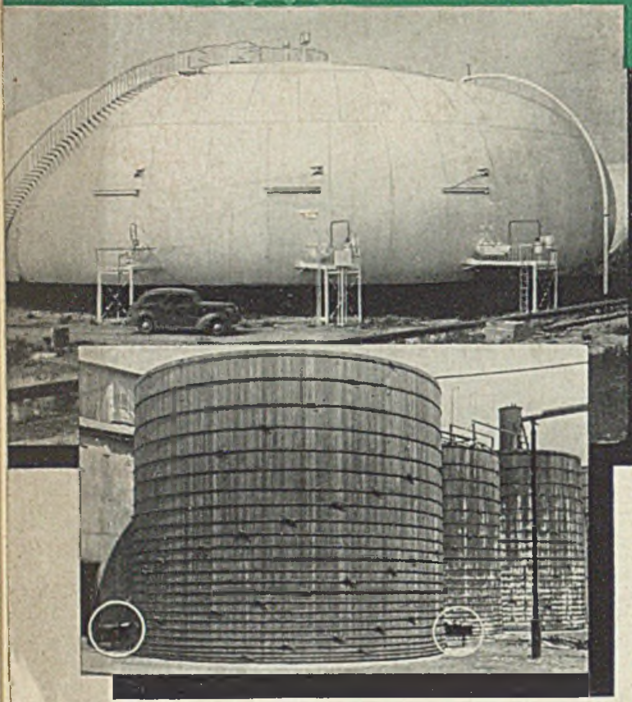

(*Upper*): *A 4,200,000 gallon motor oil tank equipped with a battery of "LIGHTNIN" Mixers.* (*Lower*): *Wooden Chemical Storage Tanks. "LIGHTNINS" do not strain tank staves, or require special fittings.*

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When miscible liquids similar in viscosity and specific gravity are put together in a vessel, they tend to diffuse. A small amount of agitation hastens this process, overcomes stratification, brings them into uniform distribution and solution. In blending miscible liquids you can substitute *time* for *horsepower*—that is, if you take a longer time to mix, you can use a smaller mixing unit. This, however, saves installed horsepower only, for the total current consumption on a given operation favors the larger mixer. Cutting the mixer size in half almost quadruples the mixing time. If a 10 H.P. mixer will do a job in two hours, power consumption of 20 H.P. hours is used. A 5 H.P. mixer requires almost eight hours time and 40 H.P. hours of current consumption. Thus, you may elect to keep installed horsepower as low as possible; or enjoy the power savings effected by the larger mixer.

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For agitation to be properly applied, many critical engineering details must be carefully observed. Here's one everyone should watch for:

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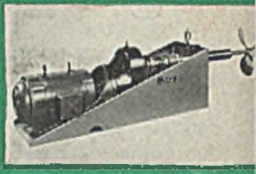

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