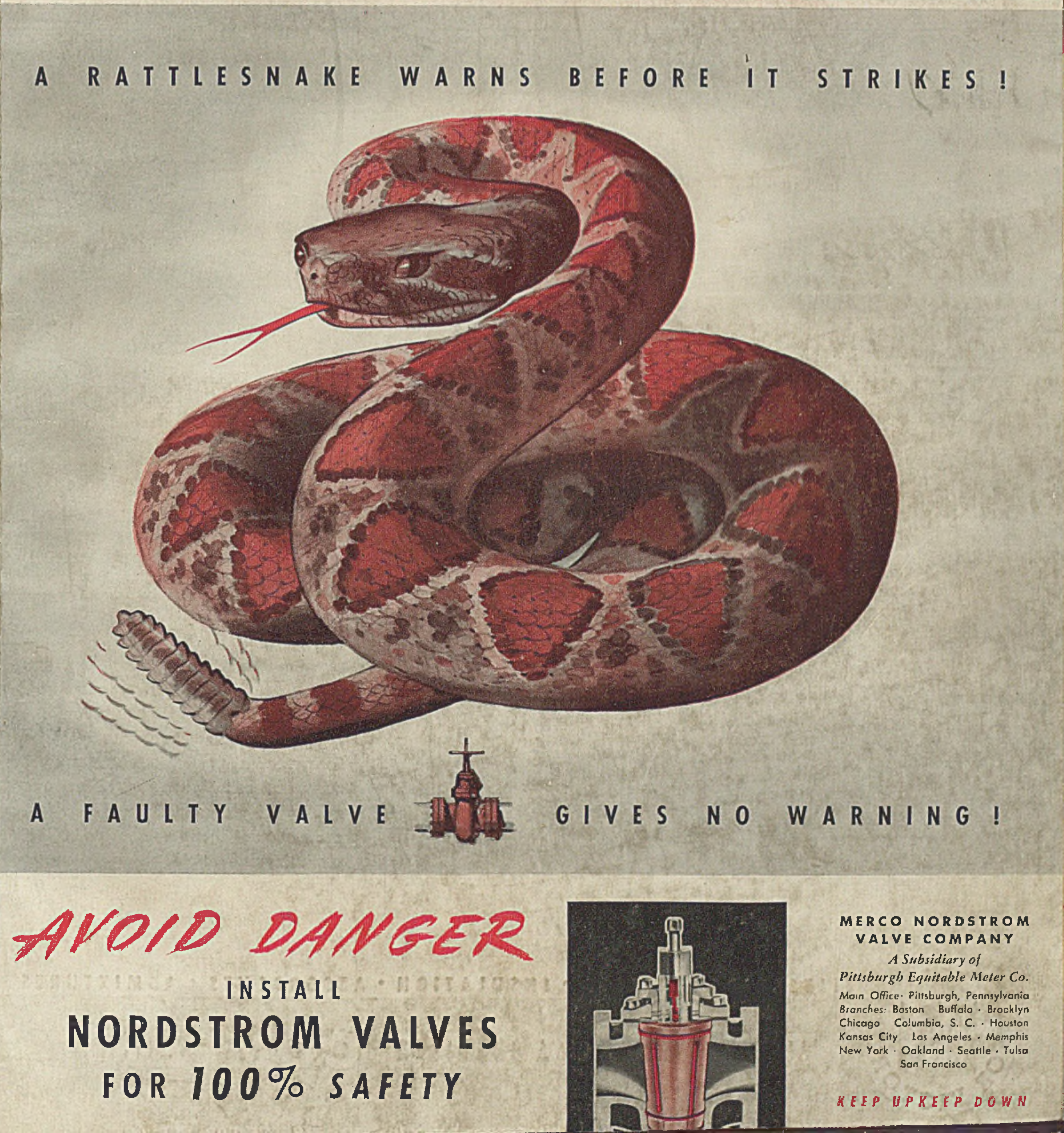
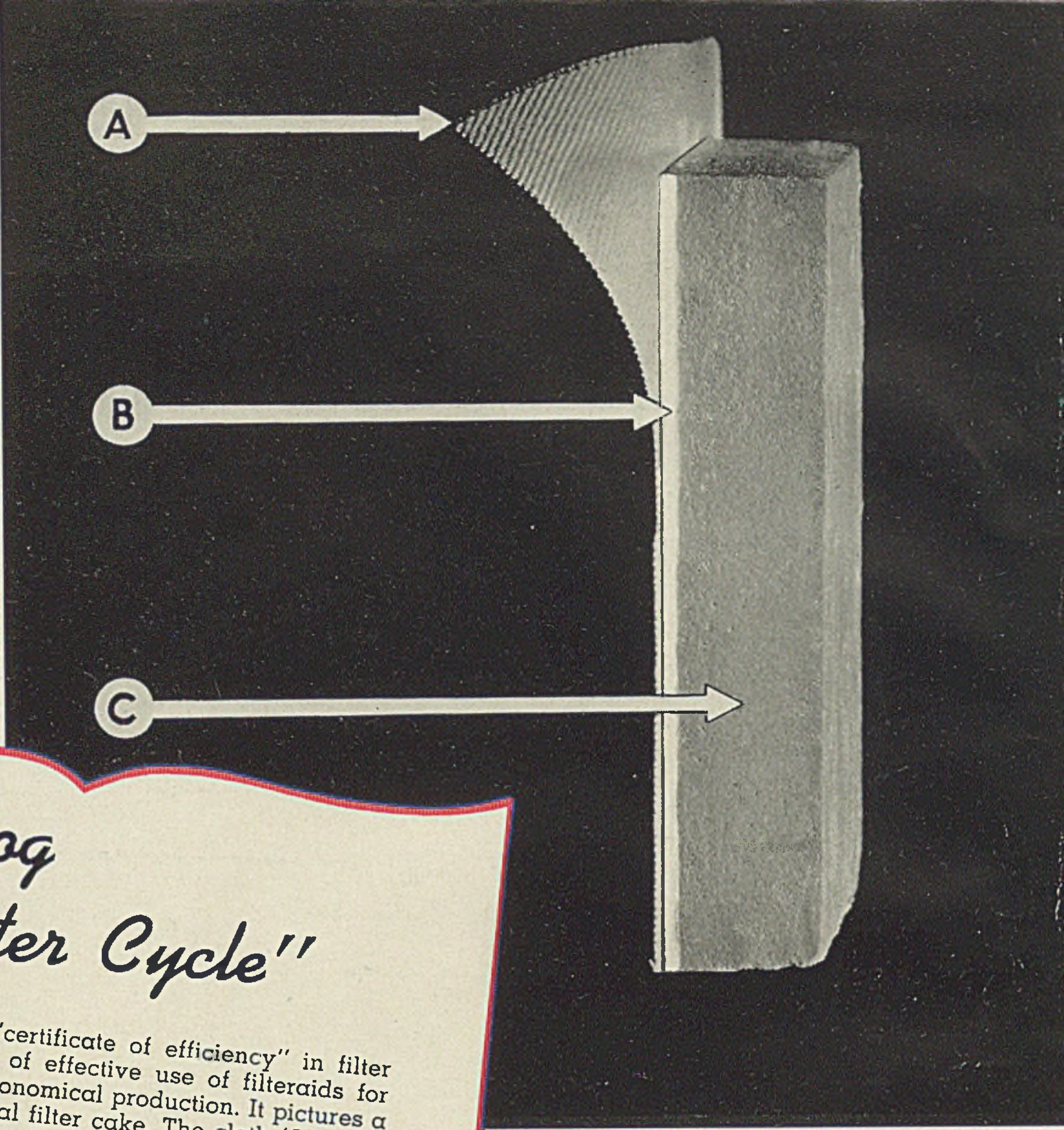
INDUSTRIAL AND ENGINEERING CHEMISTRY

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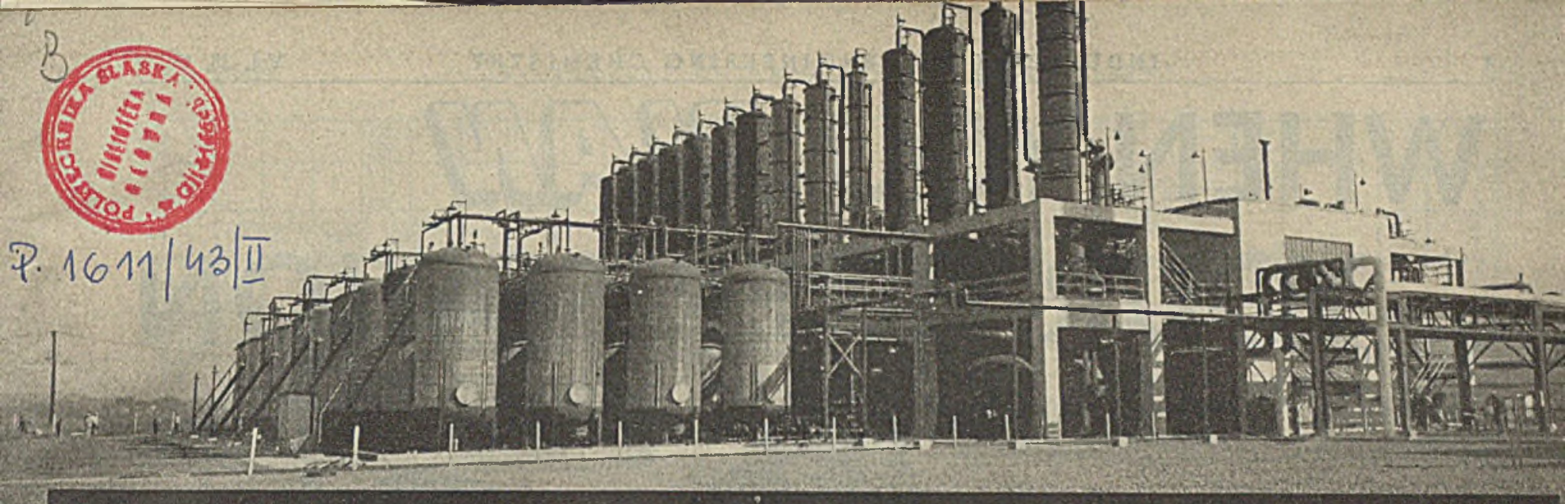

INDUSTRIAL AND ENGINEERING CHEMISTRY • INDUSTRIAL EDITION

30,300 copies of this issue printed

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The photograph shows one of the butadiene units at Institute, W. Va., operated for the Government by Carbide and Carbon Chemicals Corporation.

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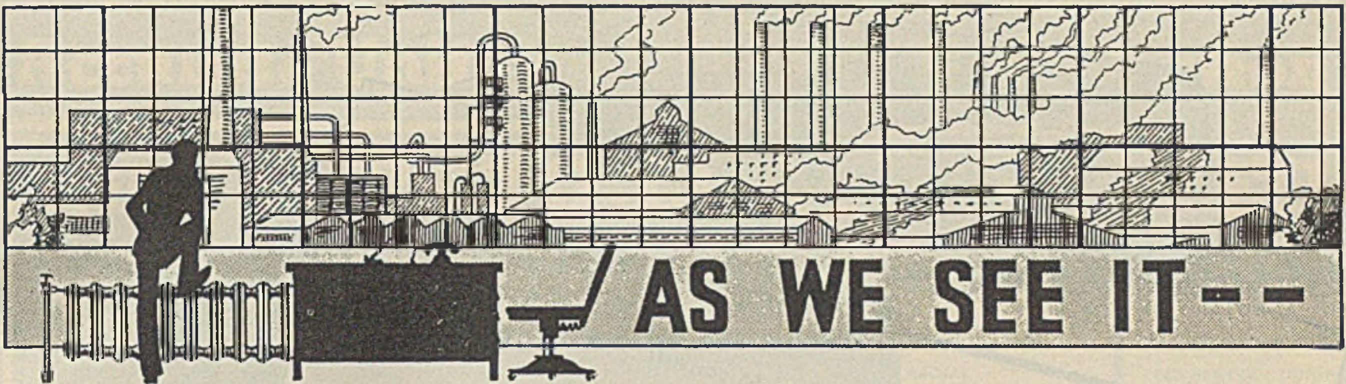


AS WE SEE IT- -

▶ **Synthetic Rubbers** of several varieties offer new materials to meet a variety of needs for which their properties particularly fit them. Sebrell (page 736), in his Charles Goodyear Memorial Lecture, examines these synthetics both broadly and in detail, pointing out their various applications and the directions in which they can be improved for useful futures in industry.

▶ **Catalysis**, particularly of reactions of hydrocarbons, has assumed immense and growing importance in industry. Grosse (page 762) examines this field and proposes with excellent reason that catalytic chemistry be considered a separate branch cognate with classical organic and inorganic chemistry. Such special emphasis, he suggests, is likely to accelerate development in this field.

▶ **Fluid Catalyst**, designating solid material maintained in flowing condition, has been the means of revolutionizing the technique of petroleum cracking, according to Murphree and his collaborators (page 768). The entire matter is discussed in as much detail as necessary censorship permits, as it relates to catalytic cracking to produce high-octane motor fuel. Other applications of the basic technique in widely diverse fields are suggested.

▶ **Rubber's Electrical Conductivity** can be controlled between wide limits by selection of both the quantity and quality of the carbon with which it is compounded. Cohan and Mackey (page 806) describe the effects of various loadings with different types of carbon in producing tread stocks of high conductivity, valuable in dissipating static charges through tires, floor coverings, and shoe soles.

▶ **Sulfamide** is produced in good yield by the method proposed and described in detail by Degering and Gross (page 751). The reaction is between sulfuryl chloride and ammonia. The product is an approximate sulfur analog of urea.

▶ **Hydrocarbons** of the aromatic series and containing eight carbon atoms are produced easily and in comparative abundance by new methods now used in the petroleum industry. Hammond and McArdle (page 809) examine the solvent properties of these xylenes as one of the steps toward their utilization by industry after the war.

▶ **Solvent Extraction** as a method of concentrating desired volatile products from dilute solutions is compared with distillation processes by Othmer and Ratcliffe (page 798). Alcohol and acetone are the compounds studied, and the conclusion reached from experiments is that substantial savings can be effected by extraction and rectification as compared with usual distillation methods.

▶ **Densities** of aliphatic hydrocarbons in the critical region, important data in the design of many high-pressure processes, have been correlated by Stevenin and Allen (page 788) to simplify necessary calculations.

▶ **Soap's Sorption** of water depends on which of several hydrated phases are present, according to McBain and Lee (page 784).

▶ **Molds** supply amylases which are effective agents for converting the starch of corn to sugar for fermentation. Hao, Fulmer, and Underkofler (page 814) have examined the activities for this purpose, of twenty-seven strains of molds. A new technique of growing molds is described and results are presented. *Aspergillus oryzae* gave alcohol yields of 95 per cent under optimum conditions.

▶ **Viscosities** of methane, propane, and their mixtures have been determined by Bicher and Katz (page 754) over a range of temperatures and pressures.

▶ **Coffee's Quality** deteriorates under many conditions of storage. Shuman and Elder (page 778) have investigated the effects of various factors involved, and find oxidation of aromatic constituents to be more important in staling than evaporation in containers or moisture content.

▶ **Phosphoric Acid** in rock phosphate can be efficiently and economically converted to available form by fusing the rock with olivine, according to Walthall and Bridger (page 774). The abundance and cheapness of olivine near phosphate deposits and the simplicity of the treatment suggest wide usefulness of the process.

▶ **Degradation of Cellulose Acetate** by light has been followed by Montonna and Winding (page 782), using a new modified method of determining copper numbers.

▶ **Meta-, Pyro-, and Tetraphosphates**, widely used to control corrosion and the deposit of scale from water, have been studied by Morgen and Swoope (page 821) to determine their rates of hydration in aqueous solution under various conditions, and hence their useful lines.

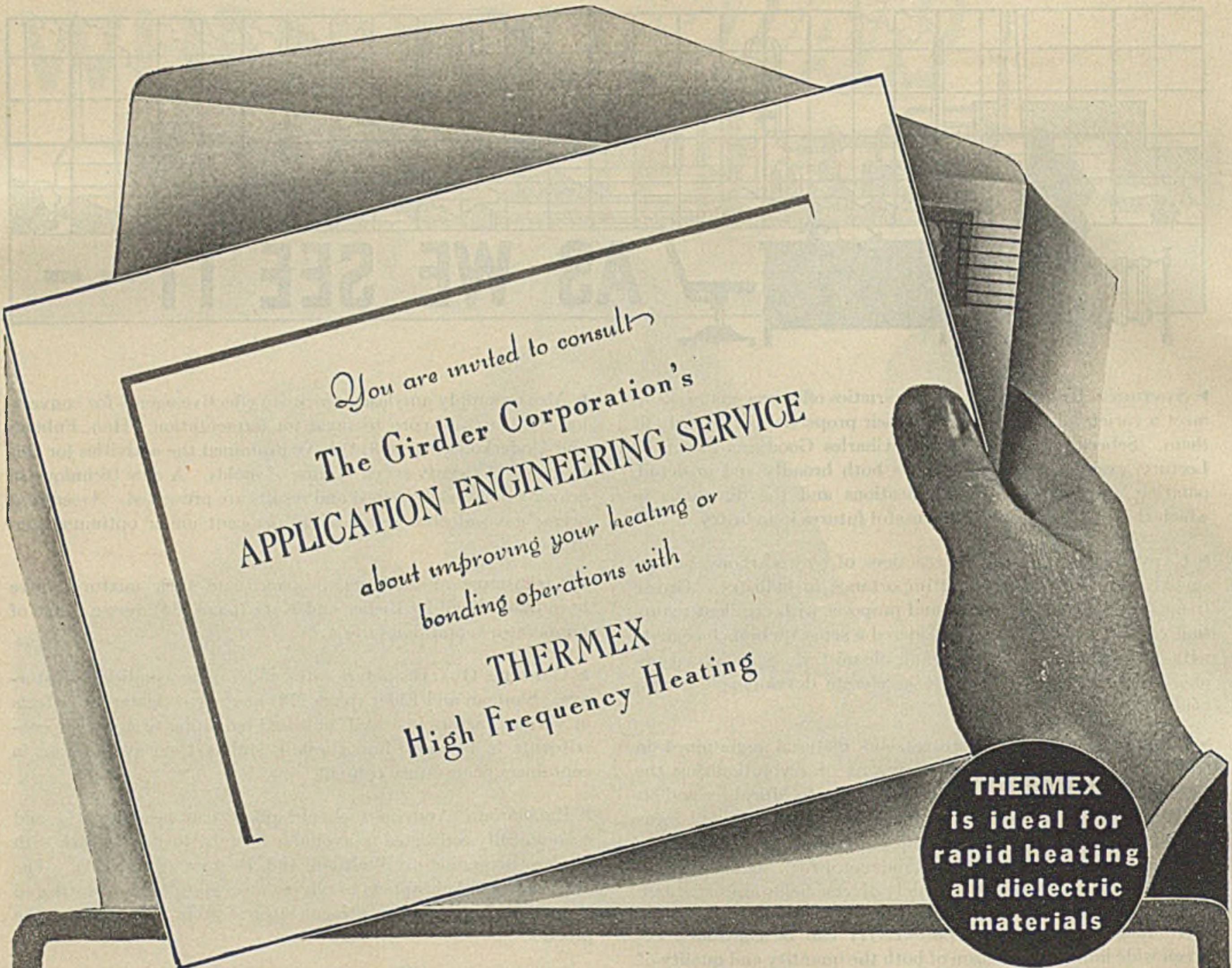
▶ **Water Clarification** by the use of activated silica sol with copperas offers important advantages. Hirsch (page 811) presents results of tests on Mississippi River water and a graphical method of arriving at economical proportions in treatment. The activated silica sol is produced by partially neutralizing sodium silicate with sulfuric acid.

▶ **Shellac** can best be stored dry, according to McCulloch (page 825), lost moisture being restored before use.

▶ **Stability of Vitamins**, under conditions of use to fortify foods, is vital to their effectiveness. Morgal, Byers, and Miller (page 794) provide data on the stability of carotene in various food products.

▶ **Dew Points** of ethane-water mixtures have been determined by Reamer, Olds, Sage, and Lacey (page 790).

D H Killeffer



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High Frequency Heating

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Heat processing or bonding at a *speed* never before attained!

May be used with most known *non-conducting* materials!

Product is heated *uniformly* thruout the entire mass!

Great flexibility. Thermex may be used to supply heat for a variety of consecutive operations

Heating capacity continuously adjustable from practically zero to maximum rating of equipment.

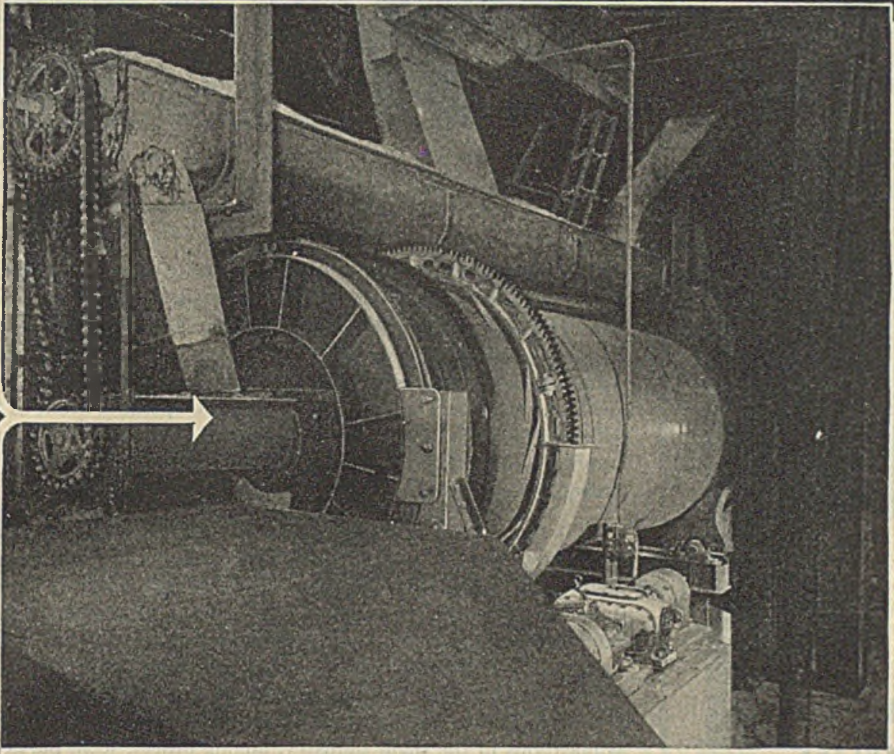
Sizes available for *all* requirements.

The GIRDLER CORPORATION

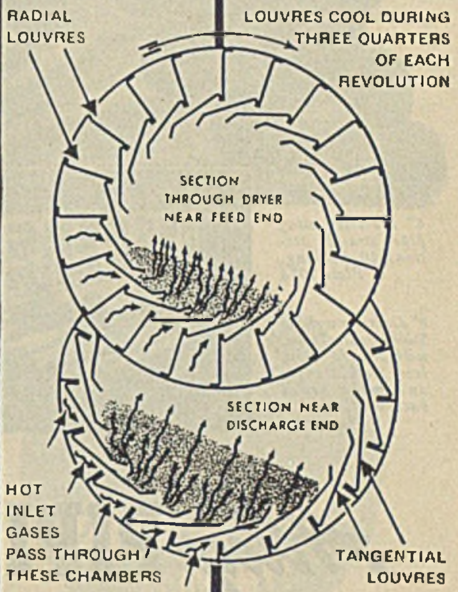
Pioneers in the Development of Industrial High Frequency Heating Equipment

THERMEX DIVISION • LOUISVILLE, KENTUCKY

Accurate Uniform Drying... Dehydration With the ROTO-LOUVRE DRYER



Link-Belt Roto-Louvre Dryer, now doing very satisfactory job of dehydrating soy bean meal prior to extraction of oil. Products previously dried in this machine include copra meal, ground apricot kernels, and mustard seed.



A large volume of dry hot air easily penetrates the relatively thin bed of material near the feed end of the dryer for maximum heat transfer where greatest evaporation can take place. As the material moves forward the bed becomes thicker and the air passages get smaller so that a reduced volume of heated air will penetrate the bed—thus preventing overheating.

DRIES UNIFORMLY—every particle of material is subjected to the same uniform treatment, eliminating "spotty" results.

HANDLES GENTLY—the Roto-Louvre design entirely eliminates cascading and avalanching—gentle rolling action preserves the desired form of material.

MINIMIZES "DUSTING"—the Roto-Louvre Dryer gives you "continuous aerated mass drying" which retains material in a compact bed yet exposes every particle to intimate contact with the transfer medium.

BUILT FOR SERVICE—no moving parts within the dryer shell—nothing to get out of order—longer service life—keeps maintenance and repair costs low.

NO OVERHEATING—highly heat-sensitive materials are exposed to an efficient high-temperature transfer medium without overheating—thermal input is reduced automatically to prevent a surplus of heat from raising the temperature.

HIGH EFFICIENCY—you get maximum vaporization and prompt removal of the moisture-laden exhaust gases.

OCCUPIES SMALL SPACE—often less than 50% of the floor space is needed over that of conventional-type drying equipment of comparable capacity.

SEND FOR THIS BOOK!

This informative Engineering Data Book, No. 1911, has been prepared by engineers who know drying problems such as yours. Address:

LINK-BELT COMPANY
300 W. Pershing Road, Chicago
Indianapolis, Philadelphia, Atlanta, Dallas
San Francisco, Toronto

9195

LINK-BELT ROTO-LOUVRE HEAT DRYER

Most subjects connected with war possess immense interest, but few of them can be discussed with any reasonable degree of freedom. The outstanding exception is to be found in the sulfa drugs, whose already great importance has soared following their miraculous successes in all theaters of war. We shall learn much on this timely subject from a chemist's point of view, as to both the basic chemistry involved and the problems solved in building production in priority-ridden war times. This is a "must" for everyone.

As if that were not enough meat for an issue in dog days, it will be followed by a highly provocative discussion of applications of the resinous ion-exchange agents. Our thinking about these synthetic resins has naturally been linked with water softening as accomplished by their zeolite predecessors. That is all very well, but the removal of both anions and cations to yield the virtual equivalent of distilled water is only a small beginning of what appear to be important new developments now possible. Applications in the sugar industry, among others, seem particularly promising.

Heat exchanger design, now diligently exercised in the creation of new industries for war, will be discussed with a view to improved performance and economy of materials.

Mixing, also a virtually universal operation, receives attention this time on the problem of power consumption of propellers.

Absorption and stripping of hydrocarbons form a basic pair of operations of greatest significance in the swift striding advances of the petroleum industry. On them we shall receive new and important design data and methods for their application to current and future problems in this essential industry. Not, be it noted, that absorption and stripping are important only in this field. Far from it!

Also in the petroleum field are papers on cyclopentane and hexane from natural gasoline.

In the plastics field, new work on plasticizers and on soybean-modified phenolics will be described.

An investigation of applications of the phase rule to soap boiling sheds new light on this old process.

New information will be forthcoming on crystalline compounds formed in water treatment (that damage high-speed equipment) and on the treatment of brandy with charcoal in manufacture.

And there will be more, much more, to help keep you up to date on things, even in the season once devoted to vacations.

Your Humble Spy

A Girdler plant produces HYDROGEN at lower cost than any other process!

Practically automatic! Continuous in operation! Actually pays for itself! Sizes for all needs!

Users of hydrogen gas in quantities from approximately 1,000 to 1,000,000 cubic feet per hour will find the Girdler Hydrogen Manufacturing Process provides H_2 at considerably less cost than heretofore possible. Savings are such that a Girdler plant often will pay for itself in less than three years.

Operating costs of a Girdler plant are usually from 30c to 50c lower per 1,000 cubic feet of hydrogen than any other process. This saving, of course, is contingent upon and varies with utility costs in different sections of the country.

A Girdler hydrogen plant is semi-automatic, and operates in a continuous manner. It is extremely flexible; may be run from 20% to 100% of rated maximum capacity.

Carbon dioxide is a valuable by-product of this process. It may be used for fire protection, prevention of oxidation and many other uses.

Write for free illustrated bulletin No. 103, giving description and data on the Girdler Hydrogen Manufacturing Process.

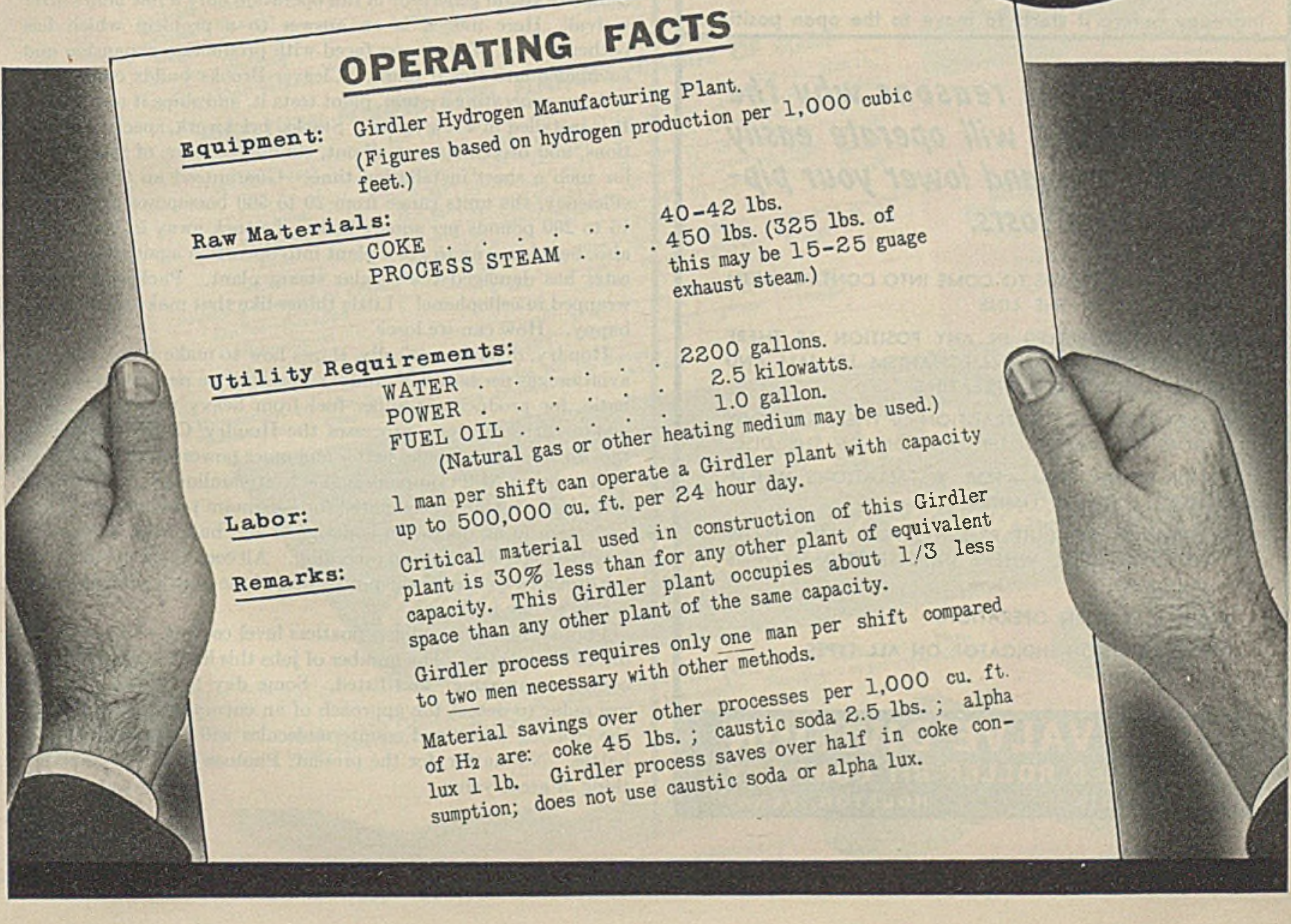
The GIRDLER CORPORATION

GAS PROCESSES DIVISION LOUISVILLE, KENTUCKY

Do you use CARBON MONOXIDE?

Girdler offers several processes for manufacturing, purifying, dehydrating, separating or reforming various gases or mixtures. The Girdler Carbon Monoxide Manufacturing Process is one such process. It produces CO at an extremely low cost by utilizing stack, kiln or similar waste gases. The resulting carbon monoxide is pure and moisture-free. Write for illustrated bulletin No. 102.

OPERATING FIGURES PROVE *unusual* ECONOMY!



OPERATING FACTS

Equipment: Girdler Hydrogen Manufacturing Plant. (Figures based on hydrogen production per 1,000 cubic feet.)

Raw Materials:
COKE . . . . . . 40-42 lbs.
PROCESS STEAM . . . 450 lbs. (325 lbs. of this may be 15-25 guage exhaust steam.)

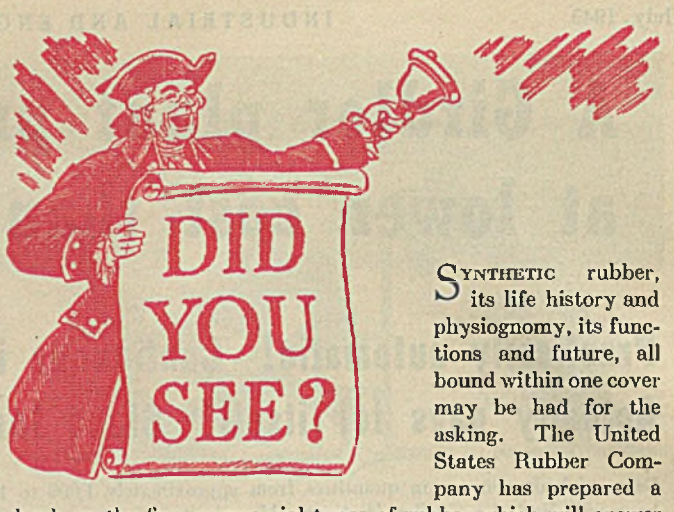
Utility Requirements:
WATER . . . . . . 2200 gallons.
POWER . . . . . . 2.5 kilowatts.
FUEL OIL . . . . . 1.0 gallon.
(Natural gas or other heating medium may be used.)

Labor: 1 man per shift can operate a Girdler plant with capacity up to 500,000 cu. ft. per 24 hour day.

Remarks: Critical material used in construction of this Girdler plant is 30% less than for any other plant of equivalent capacity. This Girdler plant occupies about 1/3 less space than any other plant of the same capacity.

Girdler process requires only one man per shift compared to two men necessary with other methods.

Material savings over other processes per 1,000 cu. ft. of H_2 are: coke 45 lbs.; caustic soda 2.5 lbs.; alpha lux 1 lb. Girdler process saves over half in coke consumption; does not use caustic soda or alpha lux.



Synthetic rubber, its life history and physiognomy, its functions and future, all bound within one cover may be had for the asking. The United States Rubber Company has prepared a book on the five commercial types of rubber which will answer most of the questions usually asked about these products. And, as they say, questions will be asked as our supply of natural product diminishes and more and more mechanical goods are made from the polymerized products of man-made rubber trees.

Reed Valves list a number of important features which make their valves well worth investigation by the whole clan of "pipe fitters". No stem threads, quarter-turn operation, nonrising stem for close quarter spots, and unrestricted flow are some things mentioned. Instant operation of the valve spots it as being of great usefulness in many chemical plant processes.

An exciting vista has been opened up by the new ion exchangers. Through their use de-ionized water is being produced which in many cases is replacing distilled aqua. The Illinois Water Treatment Company tells of treating 10,000 gallons of water for less than a dollar, and with dissolved solid content of less than 1 to 5 p. p. m. Though they don't mention ion exchangers, we are guessing the process is just that; but to make certain, send for their literature.

Cleaver-Brooks Company comes out with a pipin of an ad. A complete steam generator in full operation only a few hours after arrival! Here indeed is an answer to a problem which has bothered a lot of engineers faced with production expansion and an inadequate steam plant. Cleaver-Brooks builds completely a steam generating system, plant tests it, and ships it out to you. It is installed in a few hours. Stacks, brickwork, special foundations, and breechings are all out, eliminated—one of the reasons for such a short installation time. Guaranteed an 80 per cent efficiency, the units range from 20 to 500 horsepower, pressures 15 to 200 pounds per square inch. To tuck away in your mind also, here is a way to get a plant into operation again after a disaster has damaged the regular steam plant. Packaged steam, wrapped in cellophane! Little things like that make an engineer happy. How can we lose?

Houdry, diagrammatically, shows how to make more catalytic aviation gas per barrel of crude. They have a new process, adiabatic, for producing a super fuel from heavy naphthas. This makes three catalytic processes the Houdry Company has on tap, all working to make better and more powerful fuel.

Sturtevant Mill Company is able to streamline process units by grouping machines coordinated for maximum production. Thus each item in an operation is designed and built with a capacity equal to that following and preceding. All conveyors, spouts, etc., are designed to handle the production of the unit, and everything is sold as one package.

Photoswitch is showing a floatless level control which owes its life to electronics. The number of jobs this little instrument can control is amazing—and listed. Some day they will probably use radar to detect the approach of an enemy molecule through the reacting mass, and countermolecules will be sent out to do battle. No matter, for the present, Photoswitch has here something of great value.

Cal Sine

90° SHORT RADIUS ELBOW

90° LONG RADIUS ELBOW

45° LONG RADIUS ELBOW

STRAIGHT TEE

REDUCING OUTLET TEE

CONCENTRIC REDUCER

ECCENTRIC REDUCER

TUBE-TURN WELDING FITTINGS—RANGE OF SIZES

Type of Fitting	Description	Standard Weight	Extra Strong	Schedule 160	Double Extra Strong	Light Gauge Nominal Pipe Size	Light Gauge Iron Pipe Size
Elbows	90° Long Radius	½"-24"	¾"-24"	1"-14"	1"-8"	4"-24"	3"-12"
Elbows	90° Short Radius	1"-30"	1½"-30"				
Elbows	45° Long Radius	½"-30"*	¾"-30"*	1"-14"	1"-8"	4"-24"	3"-12"
Returns	180° Long Radius	½"-24"	1"-24"	1"-14"	3"-8"	4"-24"	3"-12"
Returns	180° Short Radius	1"-30"	1½"-30"				
Returns	180° Extra Long Radius	1"-2½"	1"-2½"				
Tees	Straight	½"-24"	½"-24"	1"-12"	1"-8		
Tees	Reducing Outlet	¾x⅜-24x20	¾x⅜-24x20	¾x⅜-12x10	1x⅜-8x6		
Reducers	Concentric & Eccentric	1x⅜-24x20	1x⅜-24x20		1x⅜-8x6		
Caps		¾"-24"	¾"-24"		1"-8"		
Stub Ends	Lap Joint	¾"-24"	¾"-24"				
Nipples	Shaped, 90° to Header	1¼"-12"	1¼"-12"				
Nipples	Shaped, 45° to Header	1¼"-12"	1¼"-12"				
Saddles		2"-24"					
Laterals	Straight	1¼"-24"	1¼"-24"				
Laterals	Reducing	1¼"-24"	1¼"-24"				
Crosses	Straight	¾"-24"	¾"-24"				
Rings	Welding	¾"-12"	¾"-12"				
Sleeves	Welding	2"-24"					

*30" size short radius.

SUPER Tube-Turn 45° long radius elbows, 90° long radius elbows, and 180° long radius returns available in both Standard weight and Extra Strong in sizes from 3" to 12".

Tube-Turn welding fittings and flanges conform to applicable ASA and ASTM Standards. For further details please refer to Tube Turns catalog and data book No. 111.

180° LONG RADIUS RETURN

LAP JOINT STUB END

CAP

STRAIGHT LATERAL

45° SHAPED NIPPLE

90° SHAPED NIPPLE

TUBE-TURN FORGED STEEL FLANGES—RANGE OF SIZES

	150 Lb.	300 Lb.	400 Lb.	600 Lb.	900 Lb.	1500 Lb.	2500 Lb.
Welding Neck	½"-24"	½"-24"	½"-24"†	½"-24"	½"-24"*	½"-24"	½"-24"
Slip-On	½"-24"	½"-24"	½"-24"†	½"-24"	½"-24"*	½"-24"	½"-24"
Lap Joint	½"-24"	½"-24"	½"-24"†	½"-24"	½"-24"*	½"-24"	½"-24"
Threaded	½"-24"	½"-24"	½"-24"†	½"-24"	½"-24"*	½"-24"	½"-24"
Blind	½"-24"	½"-24"	½"-24"†	½"-24"	½"-24"*	½"-24"	½"-24"
Socket Type	¼"-24"	¼"-4"		¼"-3½"			
Reducing-threaded or slip-on	¾"-24"	¾"-24"	¾"-24"	¾"-24"	¾"-24"	¾"-12"	¾"-12"
Orifice—threaded		1"-24"	4"-12"	4"-12"	3"-12"	1"-12"	
Orifice—slip-on		1"-24"					
Orifice—welding neck		1"-24"	4"-12"	1"-12"	3"-12"	1"-12"	
Long Welding Neck	1"-24"	1"-24"	1"-10"	1"-10"	1"-10"	1"-10"	

†Dimensions on sizes thru 3½" same as for 600 lb. flanges.
*Dimensions on sizes thru 2½" same as for 1500 lb. flanges.

WELDING RING

SADDLE

STRAIGHT CROSS

BLIND FLANGE

TUBE-TURN

TRADE MARK

Welding Fittings and Flanges

★ The ★ FIRST
WELDING FITTINGS
1ST
AND STILL THE BEST

TUBE TURNS (Inc.) Louisville, Ky. *Branch offices*: New York, Chicago, Philadelphia, Pittsburgh, Cleveland, Dayton, Washington, D. C., Houston, Los Angeles. *Distributors in principal cities.*

WELDING NECK FLANGE

LAPPED FLANGE

SLIP-ON FLANGE

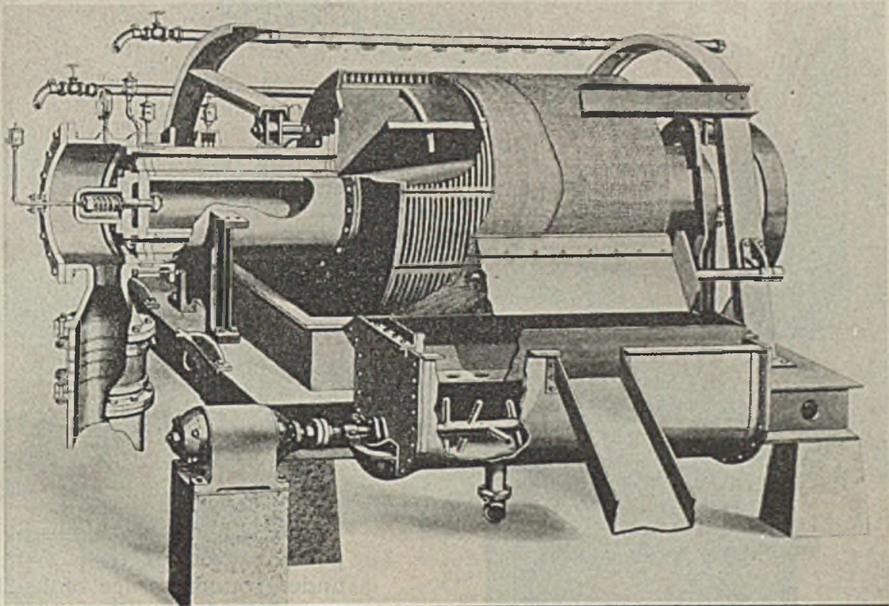
SCREWED FLANGE

SWENSON FILTERS are engineered to meet individual requirements.

Optimum efficiency in filtration is obtained only with equipment that meets the specific conditions of the operation. Swenson filters are giving excellent service in many different applications, because in each case design has been based on careful analysis of individual needs.

The engineers who design Swenson filters also supervise their construction. Having their own manufacturing facilities, they can make sure that every production detail conforms to all requirements.

Swenson engineering insight and skill are the result of nearly sixty years' experience. Through observations of filter performance under all sorts of operating conditions—as well as through scientific research—Swenson engineers are constantly developing improvements in design and enhancing the functional efficiency of chemical equipment.



SWENSON ROTARY DRUM VACUUM FILTER

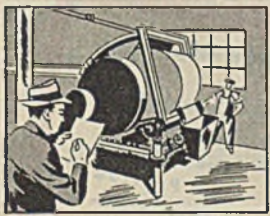
If you have a filtration problem, bring it to Swenson. Competent engineers are prepared to give you practical assistance.

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

The Rotary Drum Vacuum Filter is suited to filtration of solids that are easily kept in suspension by a mechanical agitator.

Extensively used for Glauber's salt, lime sludge, zinc sulphate, copperas, starch, cement, and similar materials.

ONLY SWENSON PROVIDES THIS FIVE-WAY SERVICE

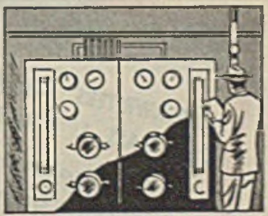


1. Analysis of Requirements

2. Design and Layout

3. Manufacture of Equipment

4. Test Operation



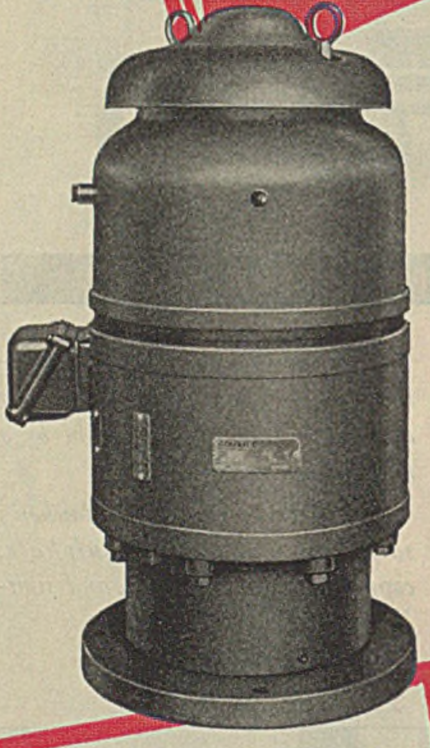
5. Periodic Check-ups

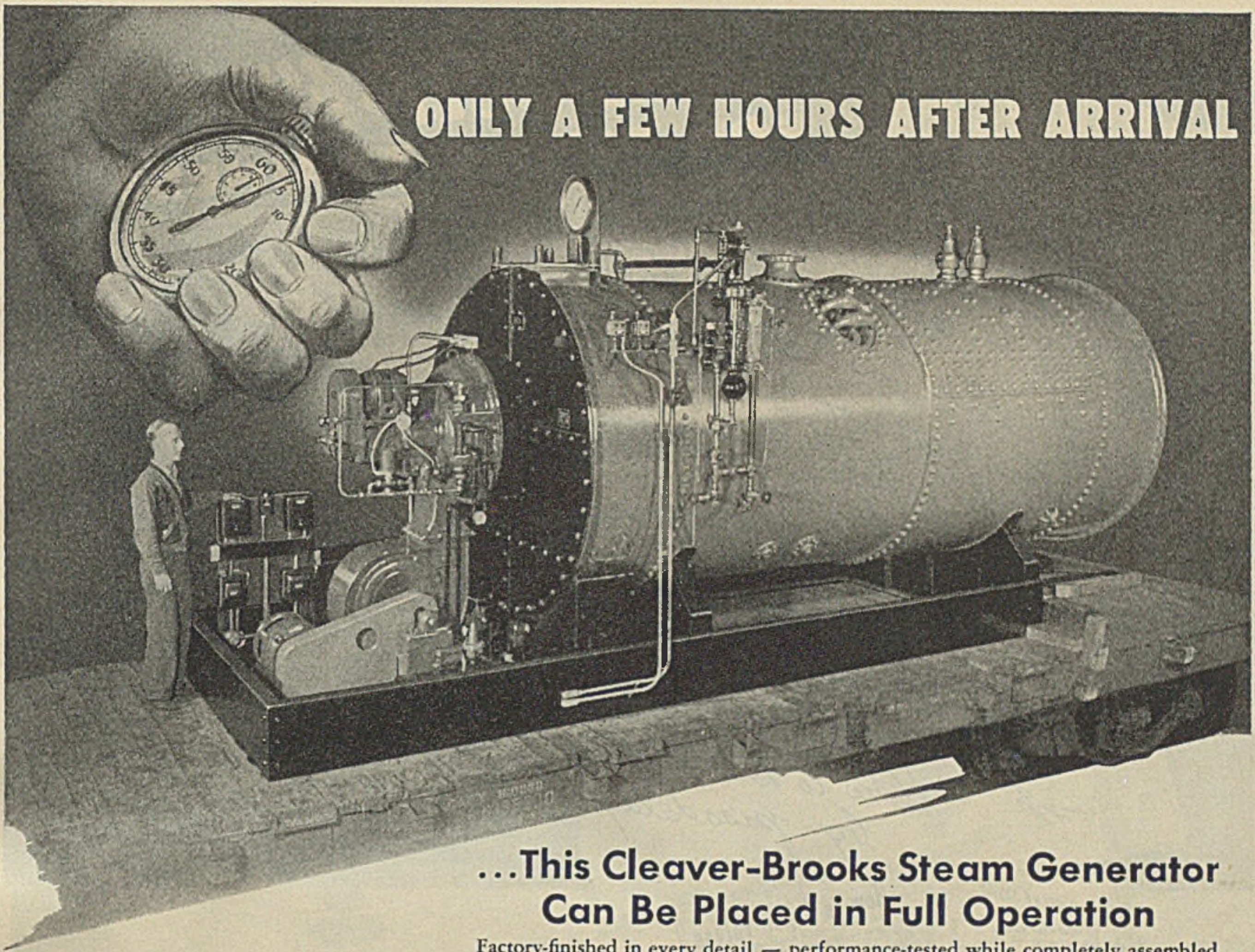
SWENSON

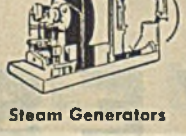
ARMY E NAVY

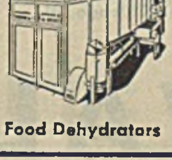
EVAPORATORS · FILTERS · CRYSTALLIZERS


EXPLOSION-PROOF
FOR PUMPING
FROM
UNDERGROUND TANKS!




ONLY A FEW HOURS AFTER ARRIVAL






MORE SELF-HELPS FOR PIPING TRAINEES
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Keep this one in mind
Saving with
How to beat by-pass delays


TIPS ON VALVE TRIM TO HELP KEEP PIPING ON THE JOB
How to Repair Valves TO GET RENEWED LIFE FROM GATE AND GLOBE VALVES TO CONSERVE CRITICAL METALS
11 SIMPLE WAYS TO GET BETTER SERVICE FROM PIPING EQUIPMENT
Short-Cuts to Faster Piping Jobs
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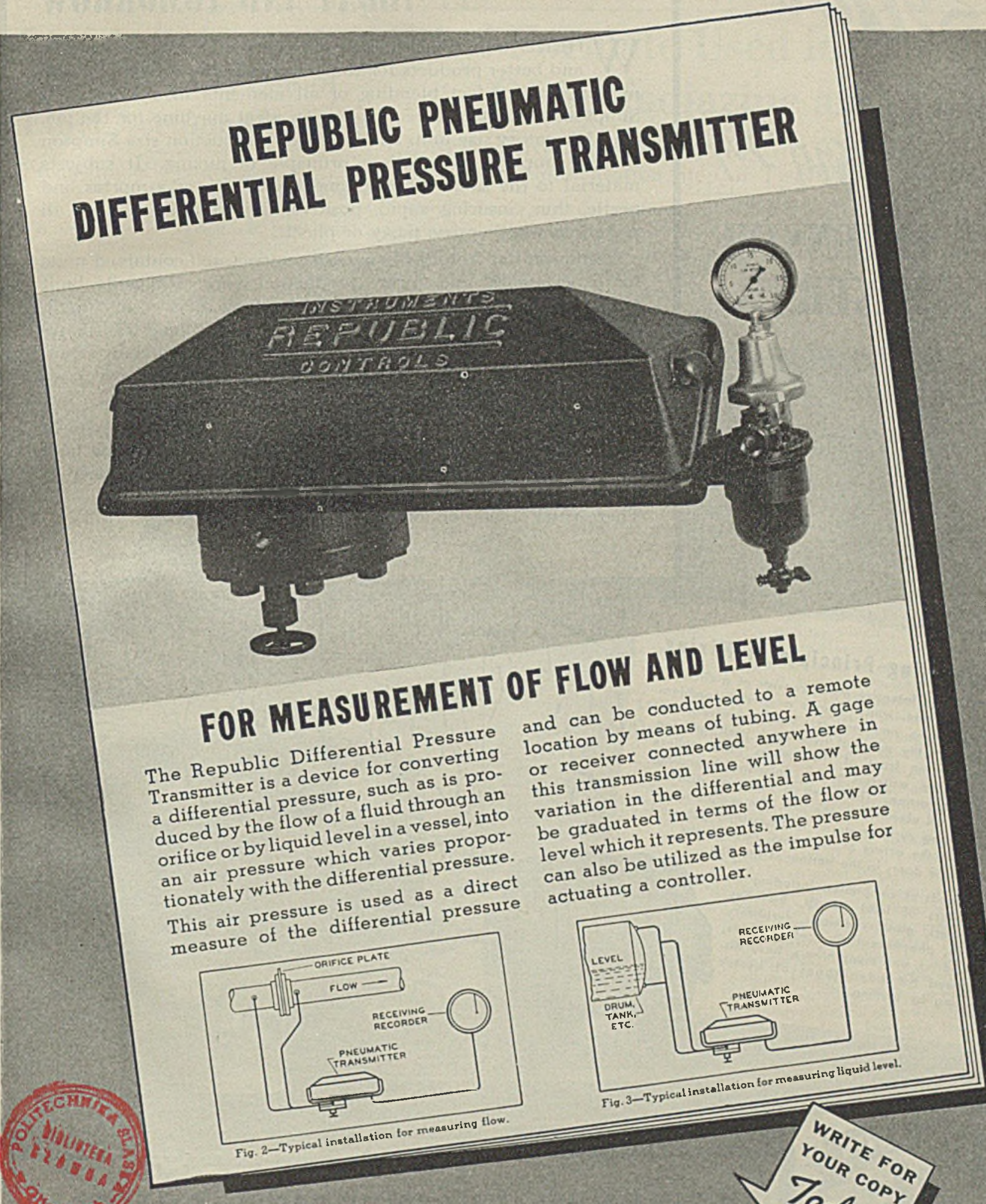
HOW TO KEEP YOUR PLANT GOING WITHOUT INTERRUPTION!
HELPFUL HINTS ON CHOOSING VALVES FOR BETTER PIPING SERVICE

A NEW BULLETIN ON A NEW METER



REPUBLIC PNEUMATIC DIFFERENTIAL PRESSURE TRANSMITTER

FOR MEASUREMENT OF FLOW AND LEVEL

The Republic Differential Pressure Transmitter is a 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 variation in the differential 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.

Fig. 2—Typical installation for measuring flow.

Fig. 3—Typical installation for measuring liquid level.

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BULLETIN No. 43-4

REPUBLIC FLOW METERS CO.

2234 DIVERSEY PARKWAY • CHICAGO, ILLINOIS

Better Mixing FOR BETTER PRODUCTS TODAY AND TOMORROW

SIMPSON *Laboratory Size* INTENSIVE MIXERS

WHERE improving today's products and developing new and better products for tomorrow requires rapid, intensive mixing with perfect blending of all elements in the "mix", a Simpson Laboratory Size Mixer is an ideal machine for the job. This laboratory size unit, like the larger production size Simpson Mixers, employs the mulling principle of mixing. It subjects material to the same rubbing, smearing action as a mortar and pestle, thus, insuring rapid, positive, uniform blending of all materials, whether dry, pasty or plastic.

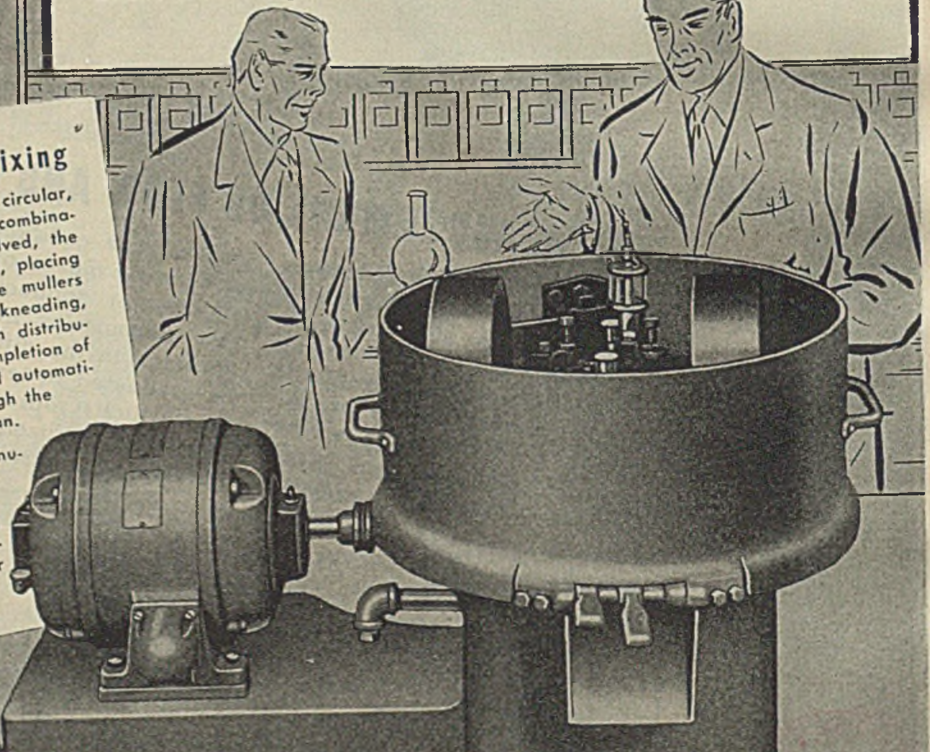
Simpson Laboratory Mixers are compact, self contained units for experimental and "light" production work. Ruggedly built to exacting specifications, they will give long service, with minimum maintenance. Available in two sizes: 18″ and 24″ diameter pan, they can be supplied with jackets for water or steam —for mixing in vacuum or under pressure—with dust covers or cooling hoods—or to meet most any special requirements.

To help you solve your mixing problems and to achieve better, faster mixing at less cost, National Engineering and Laboratory Service is available. Ask a National Engineer to go over your mixing problems with you. There is no obligation, of course.

The Mulling Principle of Mixing

THE Simpson Intensive Mixer consists of a circular, stationary pan, which mounts a special combination of plows and mullers. When revolved, the plows turn the material over upon itself, placing it directly in front of the mullers. The mullers subject the material to an intensive kneading, smearing action. The result is thorough distribution of all elements in the mix. On completion of the mixing cycle, material is discharged automatically by the action of the plows, through the discharge doors in the bottom of the pan.

Hundreds of companies, including manufacturers of lead pencils, batteries, ceramics, glass, chemicals, fertilizers, feeds, pharmaceuticals, refractories, foundries, and many others, have discovered the advantages of better mixing by mulling.



SIMPSON
INTENSIVE MIXERS
Built in 10 Sizes

NATIONAL ENGINEERING COMPANY

MACHINERY HALL BUILDING • CHICAGO, ILLINOIS

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

U.S.I. CHEMICAL NEWS

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

Vitamin B_6 Synthesis Requires the Use of Ethyl Acetone-Oxalate

Production of Pyridoxin Aided by U.S.I. Compound

A new synthesis of Vitamin B_6 (pyridoxin) that has just been published requires the use of ethyl acetone-oxalate (ethyl acetyl-pyruvate — $CH_3COCH_2COCOOC_2H_5$), a compound which offers many interesting possibilities for experimental work.

The ammonium derivative is first prepared according to the method of Mumm and Bergell [*Berichte* **45**, 3041 (1912)] and this is then combined with cyanoacetamide according to the method of Bardhan (Journal of the Chemical Society, page 2227 (1929)) to give ethyl 2-methyl-5-cyano-6-hydroxy-pyridine-4-carboxylate. Ammonia in methanol gives the amide which is reacted with phosphorus oxychloride to give 2-methyl-4, 5-dicyano-6-hydroxy-pyridine. By means of nitric acid, the 3-nitro derivative is obtained which is reacted with phosphorus pentachloride to give 2-methyl-3-nitro-4, 5-dicyano-6-chloro-pyridine. Hydrogen reduction converts the 3-nitro compound to the 3-amino from which is obtained, by reacting hydrochloric acid in methanol, 2-methyl-3-amino-4,5-diaminomethyl-pyridine-trihydrochloride. Sodium nitrite with hydrochloric acid gives the hydrochloride of Vitamin B_6.

Sample quantities of ethyl sodium acetone-oxalate may be obtained by writing U.S.I.

Emulsifying, Foaming Agents Produced from Soybean Oil

A new method for producing emulsifying and foaming agents, together with phosphatides, from soybean oil was described in a recent patent.

The inventor suggests that compounds containing phosphorous be removed from the soybean oil by passage through an absorbent such as silica gel. The absorbent may then be (a) extracted with acetone and evaporated, the sterols removed, and the residual oil again passed through the absorbent, or (b) the absorbent extracted with acetone and then with diethyl ether, giving a good grade of phosphatide. The residue is next extracted with 99-99.5% ethanol, giving a sterol glucoside, and the remainder extracted with 20-70% ethanol to produce a foaming agent soluble in dilute aqueous alkali and precipitated by aqueous hydrochloric acid or aqueous sulfuric acid. Phosphatide-rich material (an oil-free viscous liquid soluble in diethyl ether, ethanol and acetone and insoluble in water-ethanol) is obtained from this last step by evaporating the water-ethanol extract to quarter bulk and skimming off the floating gum.

Ethyl Chloride Recovery

According to a new method recently patented, ethyl chloride can be recovered from the eutectic mixture of ethyl chloride-butane obtained in the manufacture of tetraethyl lead upon treatment under pressure at —10° to 30° with an aqueous solution of an alcohol such as 70% ethanol.

Ethyl Formate Used in Synthesis Of Sulfadiazine and Thiamin

Highly Reactive Ester Produced by U.S.I. Employed In Condensation Step of Two War-Important Products

Ethyl formate, a very reactive ester which heretofore has been used chiefly in the production of fumigants, is now being employed in substantial quantities for the synthesis of thiamin (Vitamin B_1) and sulfadiazine, one of the newer sulfa drugs. Both of these products, now filling vital war needs, will undoubtedly play an increasingly important part in the advancement of peacetime medicine.

The extensive use of thiamin in supplying certain body deficiencies is well known and its importance is becoming more apparent each day. It is, for example, an ingredient of the concentrated chocolate bars issued to soldiers as part of their emergency rations.

Sulfadiazine, while exhibiting the same bacteria-killing action of the other sulfa drugs, has been found to cause less reaction than some of the others. Tablets of sulfadiazine are included in soldiers' first aid packets.

Synthesis Is Similar

The synthesis of thiamin and sulfadiazine follows a similar pattern. In the synthesis of the pyrimidine part of thiamin, ethyl formate is condensed with ethyl beta-ethoxy propionate. This is a typical Claisen condensation with sodium which gives ethyl beta-ethoxy sodium formylpropionate. This product on condensation with acetamidine hydrochloride, yields 2-methyl-4-hydroxy-5-ethoxy-methyl-pyrimidine. The hydroxyl group in the 4- position is converted to the chloride by phosphorus oxychloride, and finally into the amino group by ammonia in alcohol. After replacement of the ethoxy group with bromine by action of hydrobromic acid, the pyrimidine part is condensed with the thiazole part to give thiamin.

The synthesis of sulfadiazine actually requires another U.S.I. product, ethyl acetate, as well as ethyl formate. The first step here again involves a Claisen condensation. The ethyl formate is condensed with ethyl acetate in the presence of sodium ethoxide to produce ethyl sodium formylacetate. The remainder of this synthesis consists of condensing the ethyl sodium formylacetate with guanidine to the hydroxypyrimidine, which is then treated with phosphorus oxychloride and hydrogen in order to substitute hydrogen for the hydroxyl group. In the last step, the pyrimidine is

(*Continued on next page*)

Reducing Compounds Detected Rapidly with Spot Tests

A test for the rapid detection of reducing compounds which can be carried out with small amounts of material in the form of spot reactions was described in a recent issue of "The Chemist Analyst."

The following procedure is recommended: place one drop of the solution, or several granules of the solid substance, in one of the cavities of a spot plate and add one drop of an approximately 5% solution of phosphomolybdic acid in water or ethanol. In the case of difficult soluble compounds, a drop of dilute sulfuric acid can be added if necessary. In the presence of reducing compounds there is formed, in proportion to their amount, a blue or green coloration. A blank test is required only when very small amounts of the reducing substance are present.

New Process Patented for Paper, Cloth Coating Material

EAST ORANGE, N. J. — A patent has been awarded to an inventor here for a method of preparing paper and cloth coating materials from cashew nut shell liquid said to produce resistant, infusible and insoluble films. A suggested use is for coating paper to be used as liners for the caps and covers of containers for food, cosmetics and paints.

A typical coating is prepared by heating together about three parts by weight of cashew nut shell liquid and one part of hexamethylene tetramine to about 250° F. After holding at that temperature for about thirty minutes, two parts of a fifty per cent solution of an organic solvent soluble urea-formaldehyde resin in equal parts of butanol and xylol, and four parts of a petroleum spirits are added.

Photo by U. S. Army Signal Corps

Thiamin and sulfadiazine, which are being synthesized with U.S.I.'s ethyl formate, guard the health of soldiers at the front. Shown at left are emergency field rations for the Army, included among which is a concentrated chocolate bar (Ration D) containing thiamin. At right is a front line first aid station where sulfadiazine is administered to prevent infection.

July ★ U.S.I. CHEMICAL NEWS ★ 1943

Ethyl Formate Uses

(Continued from preceding page)

combined with sulfanilyl chloride to give 2-sulfanilamido-pyridine (sulfadiazine).

These uses of ethyl formate again show the diversified applications for such organic chemicals, and the typical reactions in which they are used. The impetus of war needs is resulting in many new synthetic chemicals, especially for medicinal purposes. As illustrated here, the Claisen condensation reaction is extremely important in many of these syntheses. U.S.I. has had years of experience with this reaction in the production of ethyl acetoacetate and ethyl sodium oxalacetate. This company is undertaking the development of other chemicals for similar syntheses which will undoubtedly find a role in the manufacture of hormones, amino acids, vitamins, insecticides and new chemo-therapeutics. U.S.I.'s technical staff will collaborate with any organization whose products call for intermediates obtained by the Claisen type reaction.

Describe Method for Making Air-Drying Ink Vehicle

DOVER, Del. — A patent has been awarded to a company here for a non-oily air-drying vehicle to be used in the formulation of vitrifiable inks that is claimed to offer many advantages over oil vehicles.

The following mixture is recommended:

	Parts
Copaiba resin	32
Venice turpentine	16
Molasses	4
Dammar (crystal dammar varnish)	4
Dibutyl phthalate	1/32

The vehicle is prepared by mixing together and stirring slowly the copaiba resin, Venice turpentine and dibutyl phthalate. To this mixture is added the molasses and dammar. The powdered solids are then added and mixed to produce a finished ink or color.

New Formula Devised For Topical Anesthetic

The following formula has been suggested for a topical anesthetic:

Benzocaine	7.5
Oil of peppermint	6.0
Phenol crystals	3.5
Ethylene glycol, q.a.	50.0

The inventor suggests that the benzocaine, oil of peppermint and phenol crystals be mixed in a flask and heated until the benzocaine dissolves, and sufficient ethylene glycol be added to make 50 cc.

Butanol, Glycerine Mixture Declared Best Soap Solvent

A mixture of 56% of glycerine and 44% of butanol was found to be the most effective solvent for soap, following recent tests in which the solubility of sodium stearate was determined at 25° C. in various mixtures of ethylene glycol with different monohydric alcohols; of butanol with different glycols and glycerine; of chloroform with glycols, and of acetone with ethylene glycol.

It was discovered that for the same glycol, the percentage of different alcohols required to produce maximum solubility is between 40 and 45, except for methanol which was 60%. For a single solvent or mixture to be a good soap solvent, the experimenters say it must have two adjacent hydroxy groups and a hydrocarbon-dissolving portion.

Purification Advised for Use Of Fibrous Sodium Pectate

Recently developed as a substitute for agar in bacteriological gels, fibrous sodium pectate is claimed to be more satisfactory for such use when purified. To achieve purification, it is suggested that the material be suspended in 60% ethanol and pH adjusted to 7.5. The pectate is then filtered and dried in a vacuum at 60° C.

Transparent Sheet Materials Made With Aid of Acetone

A new method has been patented for the manufacture of transparent or translucent sheet materials. An open-work fabric — wire netting, woven-wire fabric, knitted or leno fabric of organic derivatives of cellulose — is wetted with a mobile, volatile liquid such as acetone. It is then treated with a dope compatible with acetone and containing a lacquer base. The solvent is removed by evaporation and the product calendered.

Chloroformic Esters Used To Treat Cellulosic Fabrics

A process for permanently imparting water repellency to cellulosic fabrics was recently patented which comprises reacting a chloroformic ester of ten carbon atoms or more with hexamethylenetetramine directly on the fabric in the presence of heat and an inert solvent. A number of chloroformic esters have been produced by U.S.I.

TECHNICAL DEVELOPMENTS

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

An organic alkyl peroxide is offered for use as a catalytic agent in one or two phase polymerizations, as an oxidation agent for laboratory use, as a drying accelerator, and as a bleaching agent. Described as comparatively stable, it is standardized at concentration of 50 to 60% with more than 10% available oxygen. **(No. 710)**

U S I

A grinding, mixing or compounding mill has been developed for relatively small or moderate size batches of wet or dry material. **(No. 711)**

U S I

A photoelectric gloss meter has been developed for measuring the reflecting ability of a finished surface in terms of per cent of an arbitrary standard such as a mirror. It consists of a galvanometer with connection switches and adjusting controls and a photoelectric search unit. **(No. 712)**

U S I

Deodorant oils are offered which the maker says can be readily mixed with formaldehyde and water in proved proportions. It is claimed that deodorants so made will kill all tobacco, cooking, theatre and tavern odors. **(No. 713)**

U S I

A line of paints for machinery and building interiors is offered that can be applied by brush or spray on wood, brick, plaster and metal surfaces. Included are a mill white flat, a mill white gloss enamel, commercial interior gloss and semi-gloss enamel, commercial interior flat, dado enamel, machine enamel, a primer, an undercoat and a thinner. **(No. 714)**

U S I

Direct current resistance decades have been developed with ranges of 0.9 to 999.999 ohms total and accuracy of plus or minus 1% and 0.1% respectively. Switches are described as having self-cleaning, multi-bladed phosphor bronze spring wipers. **(No. 715)**

U S I

Tempered glass tubing is offered which is said to be suitable for handling all types of corrosive fluids except hydrofluoric acid and strong, hot caustic soda solution. **(No. 716)**

U S I

A strainer for handling highly viscous liquids or liquids that are solid at room temperatures has been announced. Maximum operating pressure is 50 psi at temperature of 600°F. The bottom and sides are completely enclosed in a steam jacket suitable for 125 pounds pressure. **(No. 717)**

U S I

Two water and stain-repellent materials are available to treat clothes by dipping after washing or dry cleaning. One is an emulsion that is diluted with water, the other a solvent type. **(No. 718)**

U S I

Skin-protecting creams are offered which are described as non-clogging, non-toxic, and non-irritating. One is recommended for protection against skin absorption of paints, lacquers, tars, resins, glues, graphite and other materials. The second is insoluble in cutting oils or soluble oil emulsions. It is said to afford protection against strong or dilute acids and alkalis, metallic salts, dyes and coal tar distillates. **(No. 719)**

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

OXALIC ESTERS
- Butyl Oxalate
- Ethyl Oxalate

PHTHALIC ESTERS
- Amyl Phthalate
- Butyl Phthalate
- Ethyl Phthalate

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

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

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ETHERS
- Ethyl Ether
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OTHER PRODUCTS
- Acetone
- Collodions
- *Curbay B-G
- *Curbay Binders
- *Curbay X (Powder)
- Ethylene
- Ethylene Glycol
- *Indalone
- Nitrocellulose Solutions
- Potash, Agricultural
- Urethan
- *Vacatone

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TYPICAL ANALYSIS OF MALLINCKRODT STANDARD STEARATE PRODUCTS

Name	Bulk in Fl. Oz. per Lb.	Metallic Oxide	*Extractable Acid	Softening Point
Aluminum Stearate Technical M	52	15%	6%	170° C.
Aluminum Stearate Technical D	54	8.4%	7%	157° C.
Aluminum Stearate Technical D 5-47	58	8.7%	4.8%	160° C.
Aluminum Stearate Technical D Fluffy	70	8.2%	8%	148° C.
Flatting Agent No. 22	70	8%	7.5%	....
Aluminum Stearate Technical T D (Formerly named No. 1-49)	80	7.7%	15%	130° C.
Aluminum Stearate Technical T	48	6%	25%	109° C.
Aluminum Stearate Technical T for Paint & Varnish Manufacture	76	6%	24%	115° C.
Calcium Stearate Technical	35	9%	1.5%	125° C.
Calcium Stearate Impalpably Powd.	125	9%	1.5%	146° C.
Zinc Stearate U.S.P. XII	160	14%	2%	118° C.
Zinc Stearate U.S.P. XII "S"	160	14%	2%	120° C.
Magnesium Stearate Technical	40	6.8%	2.5%	125° C.
Magnesium Stearate Impalpably Powd.	140	6.8%	2.5%	125° C.

The water content of stearates is limited to 1%. In most cases the actual amount is less.
The water-soluble material is also limited to 1% and is usually less.
**The "Extractable Acid" is determined by extraction with boiling Acetone.*

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or to modify the properties of other colloidal systems.

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Standardized Stearates of Aluminum, Calcium, Magnesium, and Zinc are now available. Special applications of the soaps of many other metals have been studied in our laboratories. We invite you to draw on our extensive experience in the application of the Standardized Stearates, or to confer with us on your particular needs for other metallic soaps. Call our representative or write us today for the New Product Data Booklet on Stearates.

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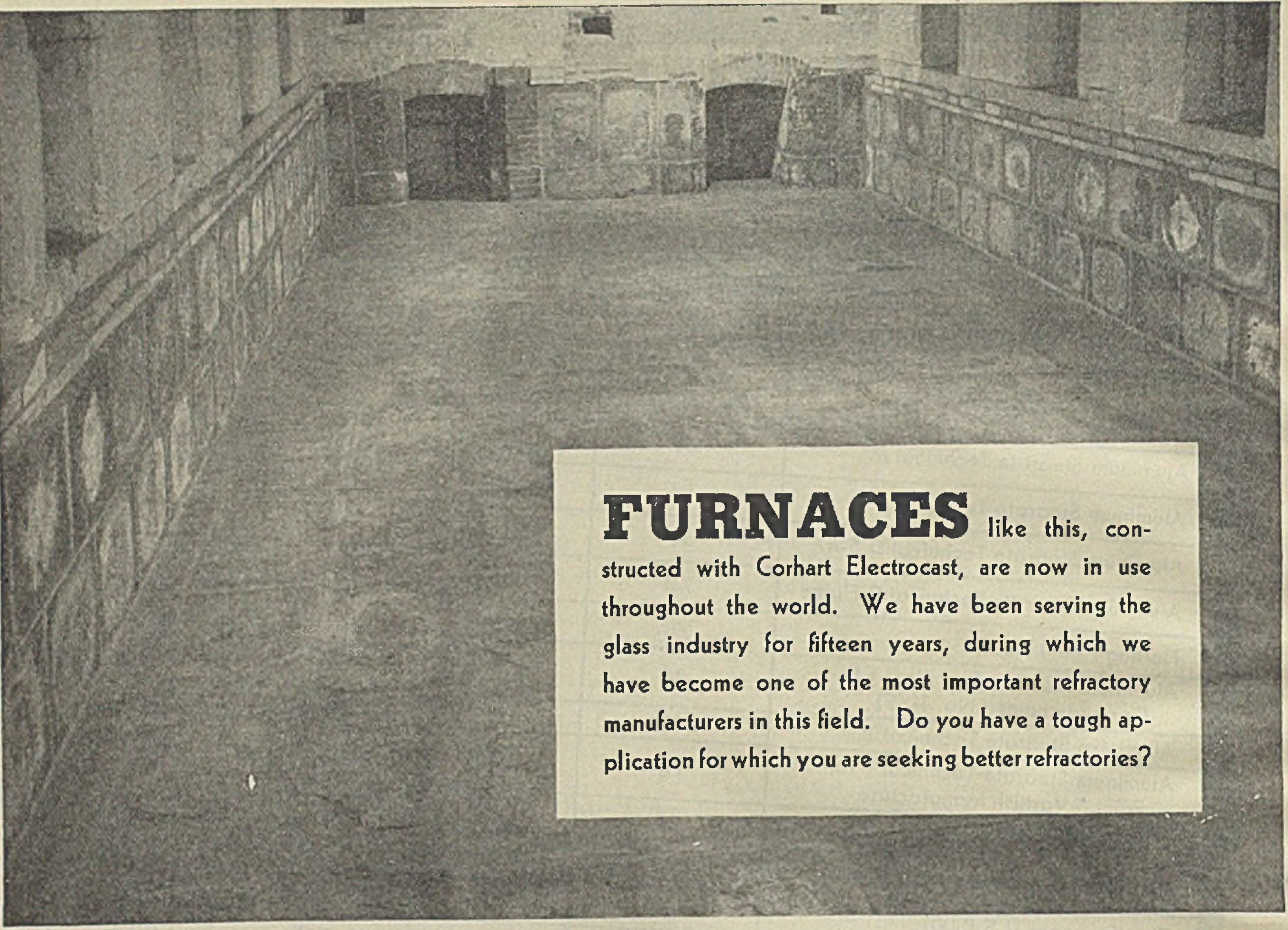

FURNACES like this, constructed with Corhart Electrocast, are now in use throughout the world. We have been serving the glass industry for fifteen years, during which we have become one of the most important refractory manufacturers in this field. Do *you* have a tough application for which you are seeking better refractories?

The entire flux walls and bottom of this 16′ x 56′ glass furnace are constructed of Corhart Electrocast blocks.

Now Still Another Corhart* Uninsulated Bottom!

HERE'S another item to add to your "mental file" on Corhart* Electrocast bottoms.

In March, 1942, a well-known glass manufacturer installed his first uninsulated Corhart Electrocast melting-end bottom. On the strength of its performance, this customer has now installed another uninsulated Corhart bottom in another of his tanks. Both are of 12″ Corhart Standard Electrocast.

But these two tanks are by no means the only ones in which uninsulated Corhart bottoms are now being used.

In addition to numerous insulated bottoms, there are now at least THIRTY-EIGHT uninsulated Corhart bottom installations in glass tanks in North and South America. . . .

We knew you'd like to have these facts.

Corhart Refractories Company, Incorporated, Sixteenth & Lee Streets, Louisville, Kentucky.

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*Not a product, but a registered trade-mark.

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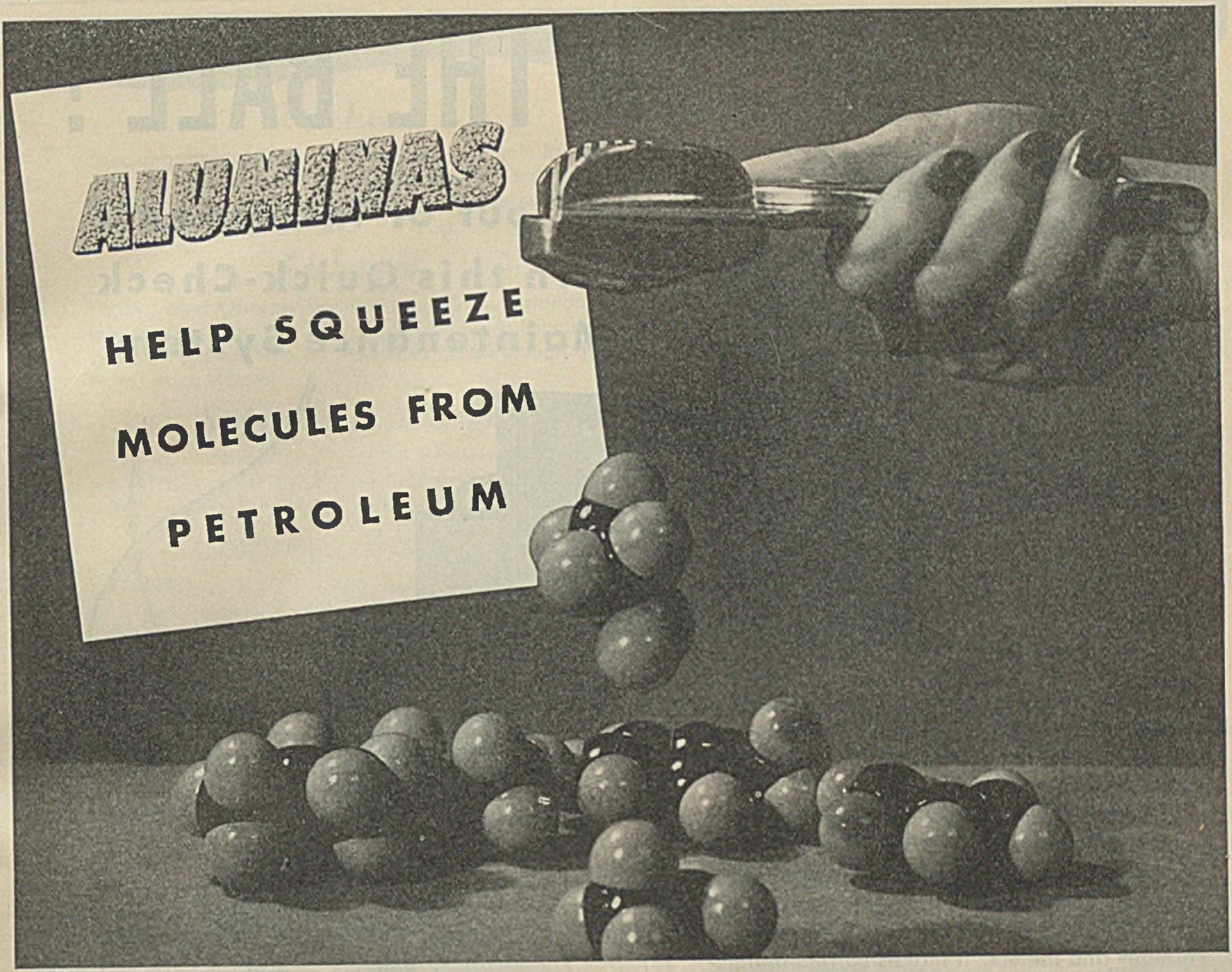
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Special grades of Eagle Red Lead are available for the paint, storage battery, ceramic and varnish industries. Pb_3O_4 content accurately maintained to meet exact requirements of each industry.

Litharge

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

Sublimed Litharge

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

Orange Mineral

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

Zinc Oxide

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

Leaded Zinc Oxides

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

White Lead Carbonate

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

Sublimed White Lead

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

Lithopone

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

Titanated Lithopone

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

Lead Silicate

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

* * *

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

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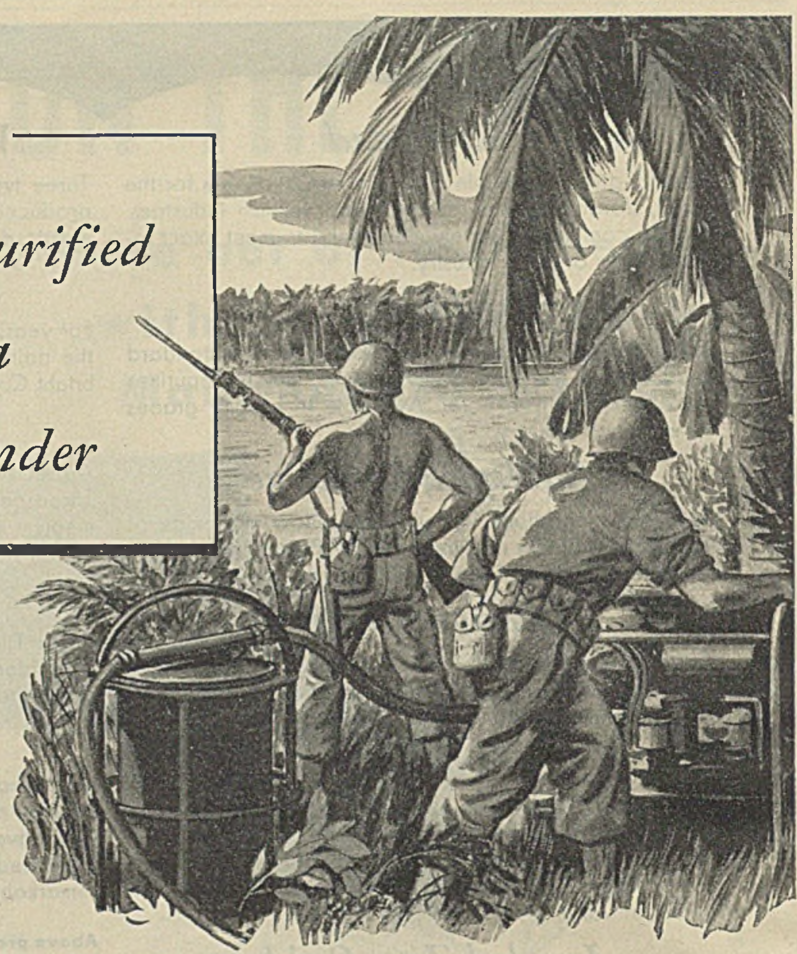


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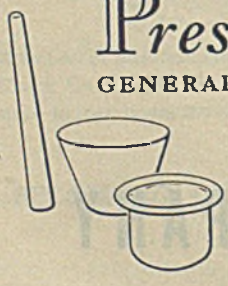

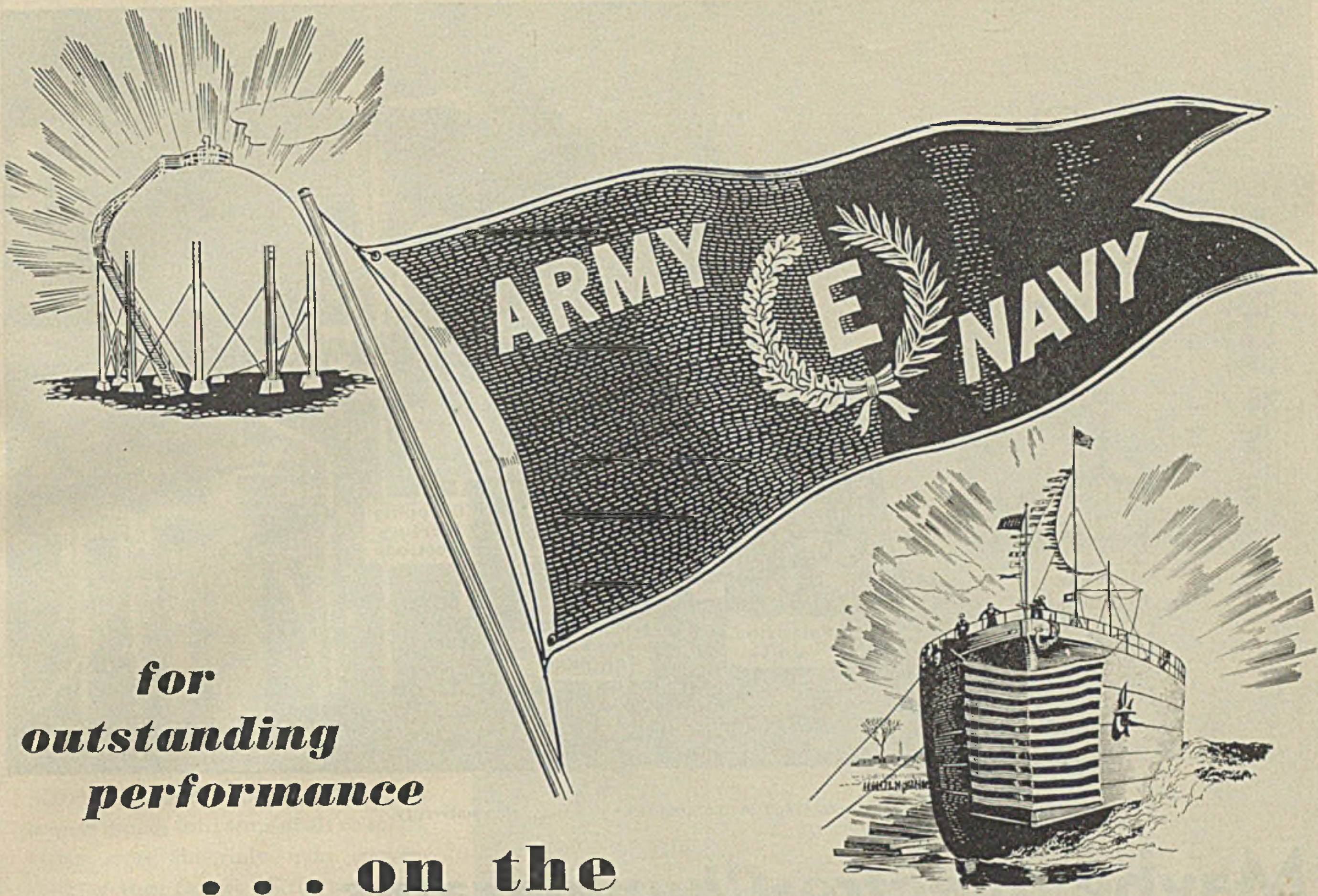
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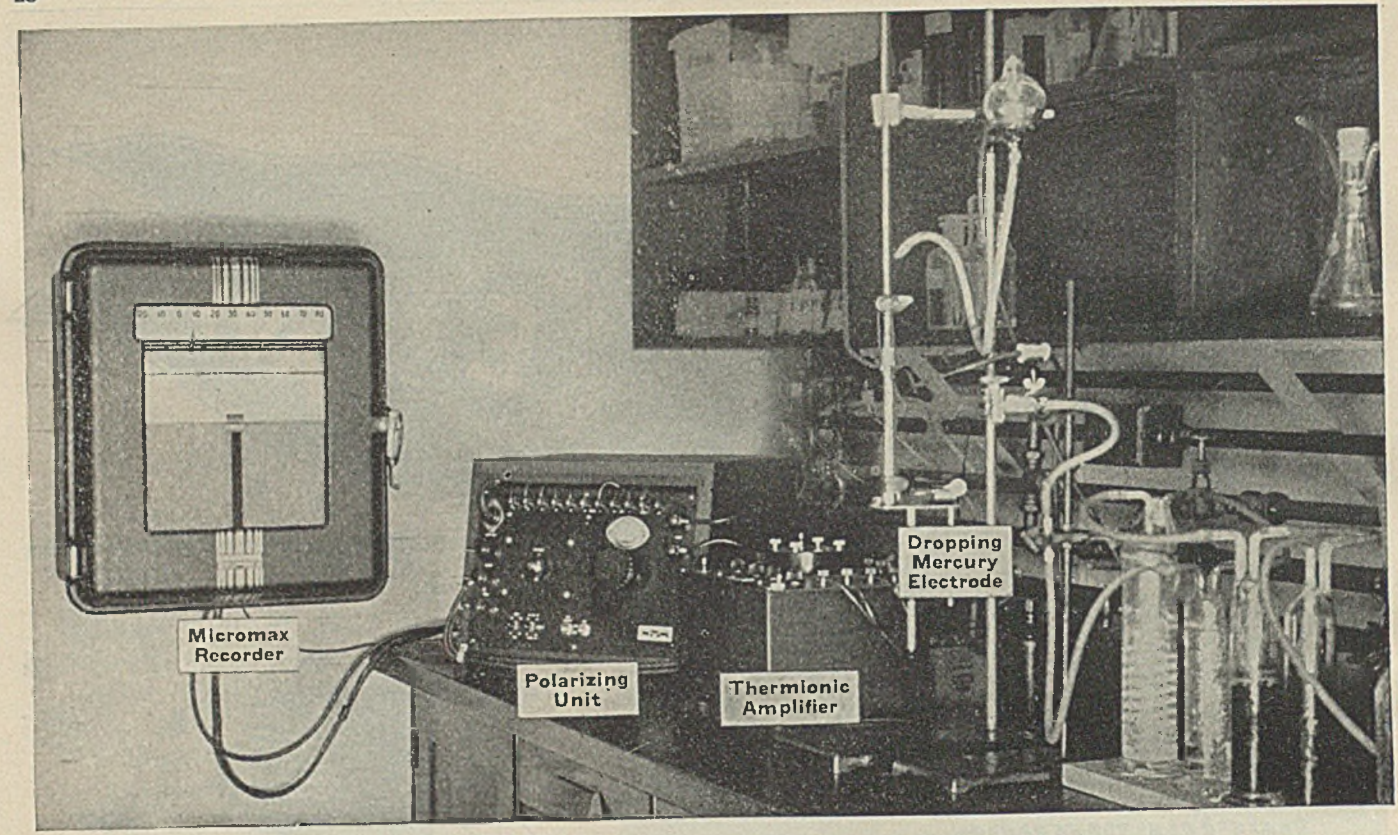
NAVY



Electro-Chemograph in the graduate aboratory of a university.

Maybe *Electro-Chemograms* Can Help You Analyze Faster

An Electro-Chemogram is the record supplied by the Micromax Recorder which is a part of the L&N Electro-Chemograph. It is an ink-recorded chart which shows the current and potential curves of a dropping-mercury electrode. It records the progress of an electro-analysis while the analysis is still proceeding; and when the analysis is finished, the record is finished simultaneously. An Electro-Chemogram thus relieves the chemist of the necessity for first completing his work, then developing a photographic chart, before he knows his results. The usefulness of the entire dropping-mercury electrode method of analysis is thus increased in two fields:

1. In process control, the time which an Electro-Chemogram saves in analyses is passed on directly to the process and may be of great additional benefit in improving the operation.

2. In exploratory or experimental analysis, the Electro-Chemogram helps the chemist to see and correct any faults in technique as he proceeds. Since the user of the dropping-mercury electrode method must, at present, nearly always develop his own calibration of the current/potential curves, he finds this feature extremely valuable.

A complete Electro-Chemograph equipment is shown above. The Polarizing Cell and Electrodes are simple, sturdy and adapted to a wide range of analyses. The Polarizing Unit makes available four "programs" of applied potential: For cathodic polarization, 0 to −3 v or +1 to −2 v; for anodic polarization, 0 to +3 v or −1 to +2 v. The complete range of 3 volts is covered in approximately 25 minutes, but an analysis may be started or ended at any desired potential within the range.

The time constant of the current-measuring system is equivalent to that of a galvanometer having a period of approximately 8 seconds. The full-scale current range of the equipment can be varied by the user in 8 steps from 2×10^{-6} ampere to 100×10^{-6} ampere; at the lowest value the approximate total concentration of the substance to be determined is 0.0005 gram equivalents per liter, and at the highest current this value is 0.025.

The amplifier is fully shielded and well insulated. The Micromax Recorder is, in general, our standard design, widely used for electrical measurement.

For further particulars of the Electro-Chemograph, see Bulletin E-94(1), which will be sent on request.

Jrl. Ad E-94(7)

ARMY E NAVY
V depends on me!
A Slogan for All Americans

LEEDS & NORTHRUP COMPANY, 4920 STENTON AVE., PHILA., PA.

L&N LEEDS & NORTHRUP

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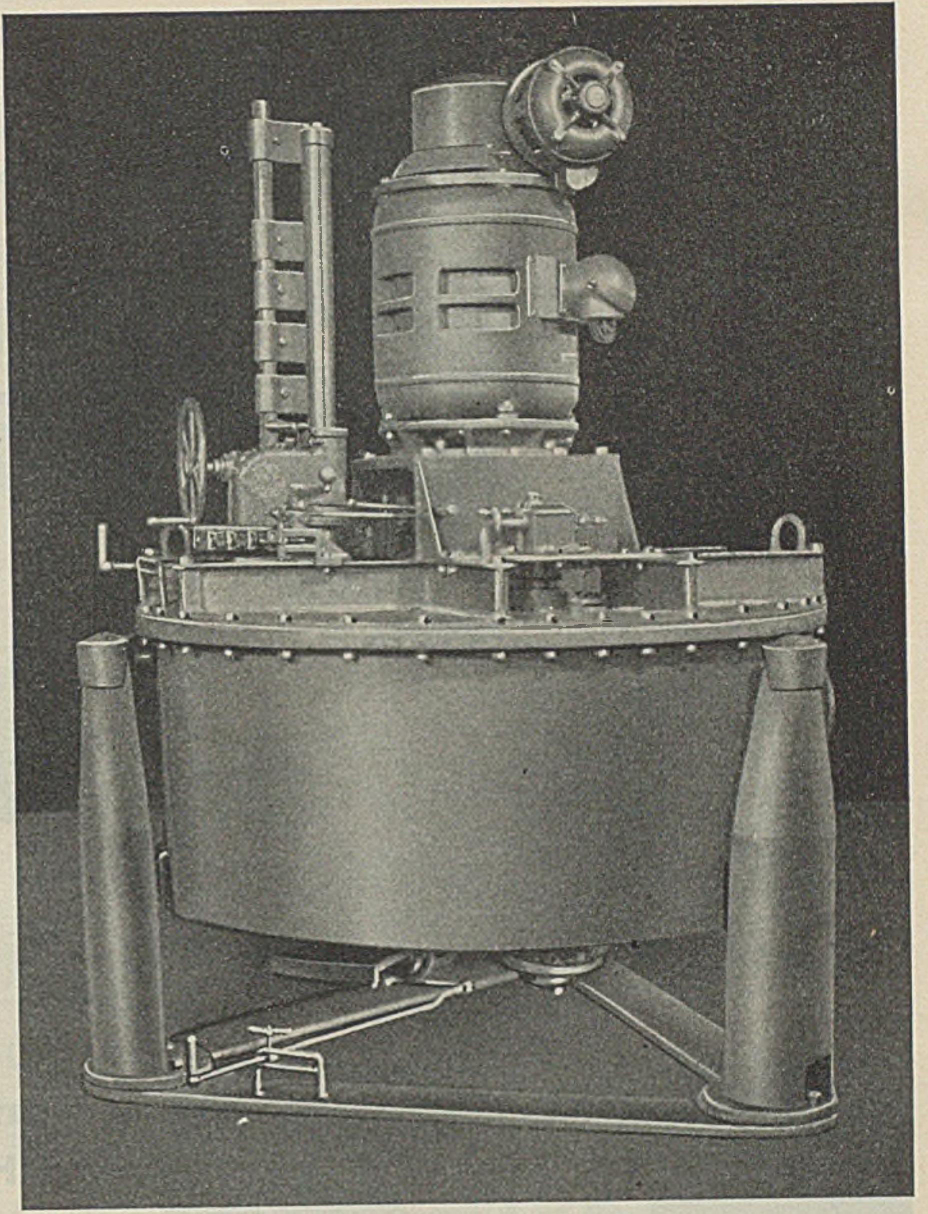

TO MAKE YOUR "CHANGE-OVER" A CHANGE FOR THE BETTER

Reconversion — America's post-war challenge to Industry — *can* be an unparalleled opportunity to improve your process and product, with the help of AT&M centrifugals.

"Change-over" from filters. In some instances, filters have been found hard-to-clean and wasteful of fine substances. A change-over to AT&M centrifugals has saved production time, loss of materials and floor space . . . in one case saving 25 to 40 percent of a scarce chemical.

"Change-over" from tanks, kiers, or autoclaves. In impregnation, also, AT&M-engineered centrifugal force now presses liquids into semi-solids or solids, faster, more uniformly, more conveniently — then throws off the surplus in the same swift, space-saving operation. Today, nitrating and final wringing of cotton for war explosives is speeded up by AT&M centrifugals.

"Change-over" from settling tanks. In precipitation of particle-sized substances, or slimes from suspension, advantages of change to AT&M centrifugals have included immediate precipitation, finer degree of clarity, dryer cake. Floor space saved, of course.

"Change-over" from ovens, squeeze rolls, boxes. In dehydration, AT&M centrifugals whirl out H_2O in a hurry — in one case 70% faster than an expensive machine formerly used for drying. Savings over other equipment also include cost of power, time of supervision, factory footage.

After the war, AT&M centrifugals, now heavily engaged in war production, will be available in all machinable metals and coatings . . . link-suspended . . . suspended . . . base-bearing . . . with additional time-and-space-saving advances stimulated by war.

Now is the time, as national needs permit, to plan with us how you can get the most out of your re-conversion dollars, or solve the special problems which AT&M engineers are accustomed to deal with . . . in strict confidence. Write American Tool & Machine Co., 1421 Hyde Park Avenue, Boston, — or 30C Church Street, New York, N. Y.

AT&M Centrifugals Save Time and Space in —

EXTRACTION
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FILTRATION
PRECIPITATION
IMPREGNATION
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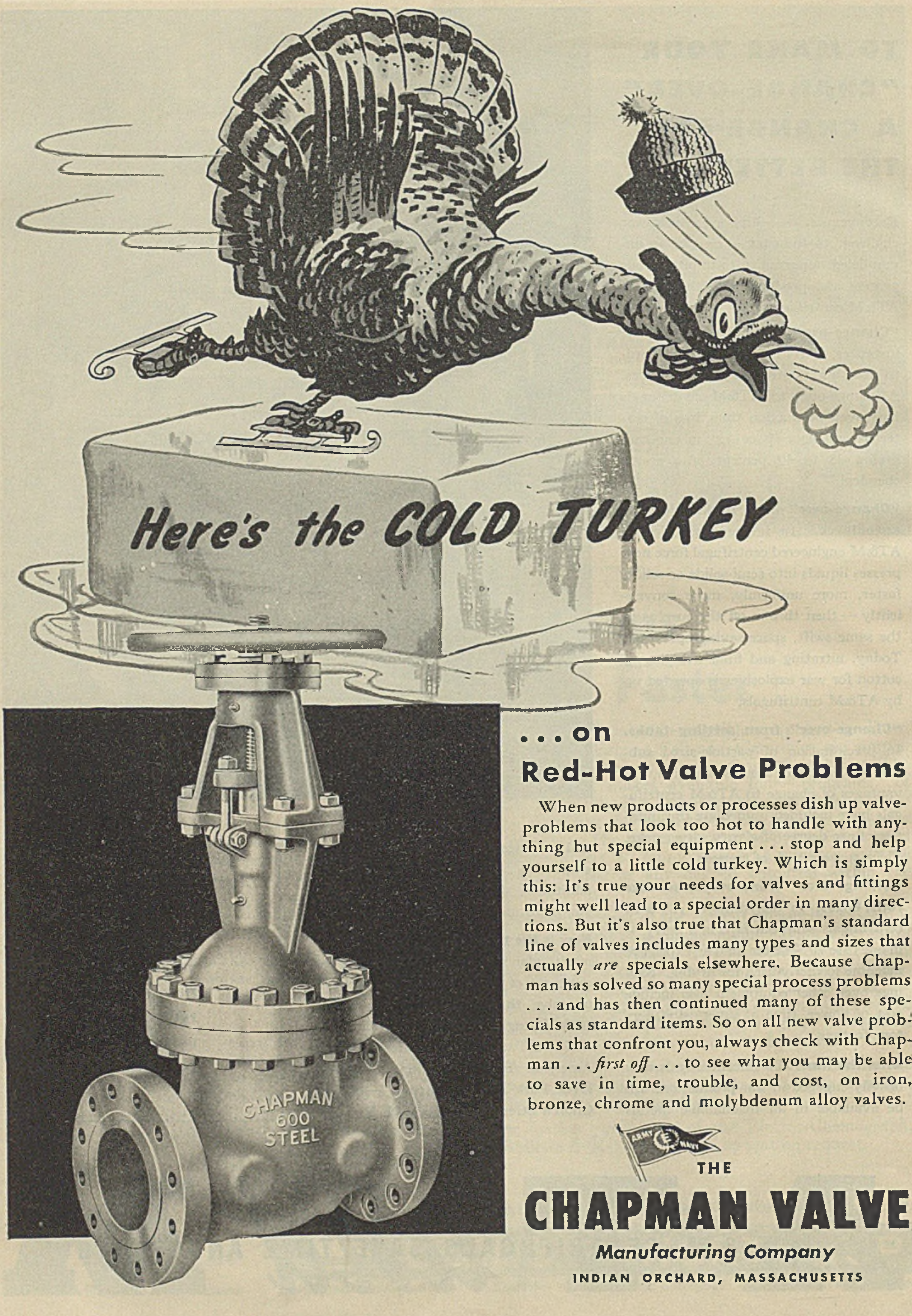
AT and M

A T & M CENTRIFUGALS SAVE TIME AND SPACE


Here's the COLD TURKEY
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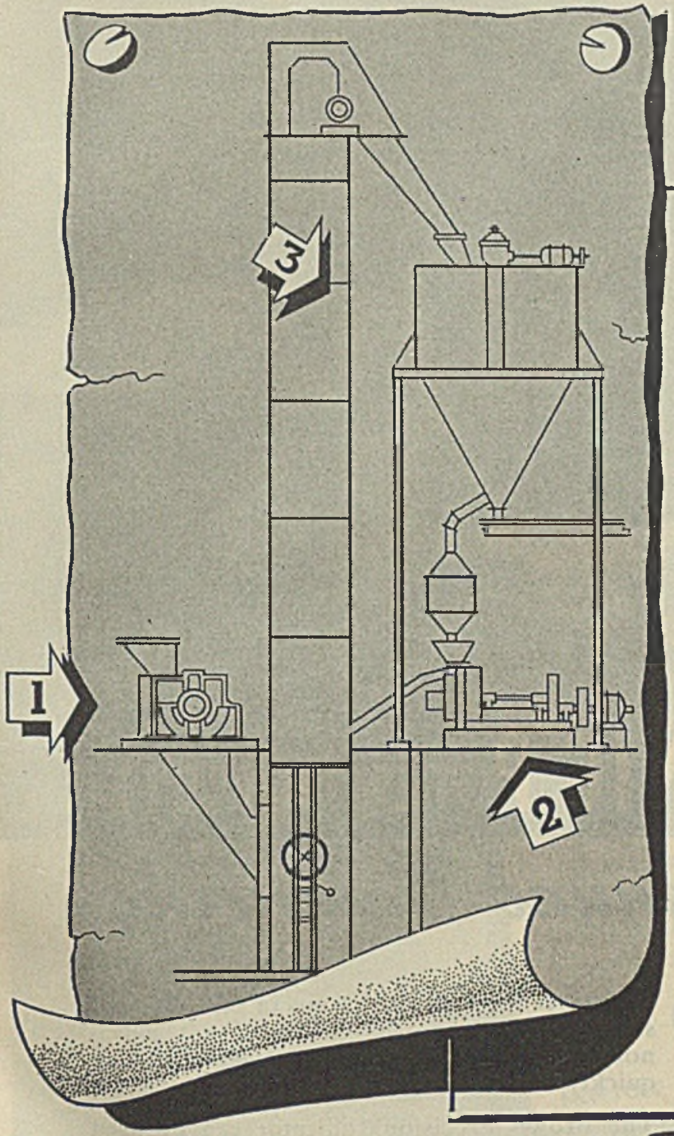
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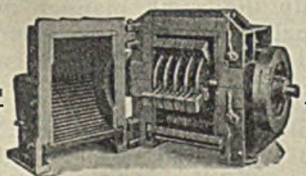
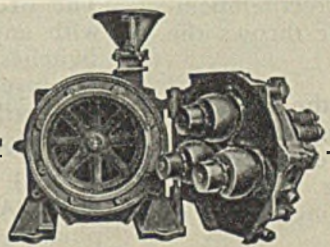
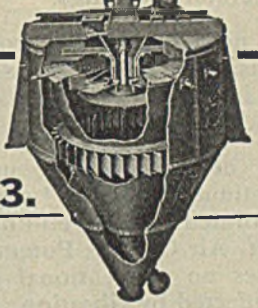
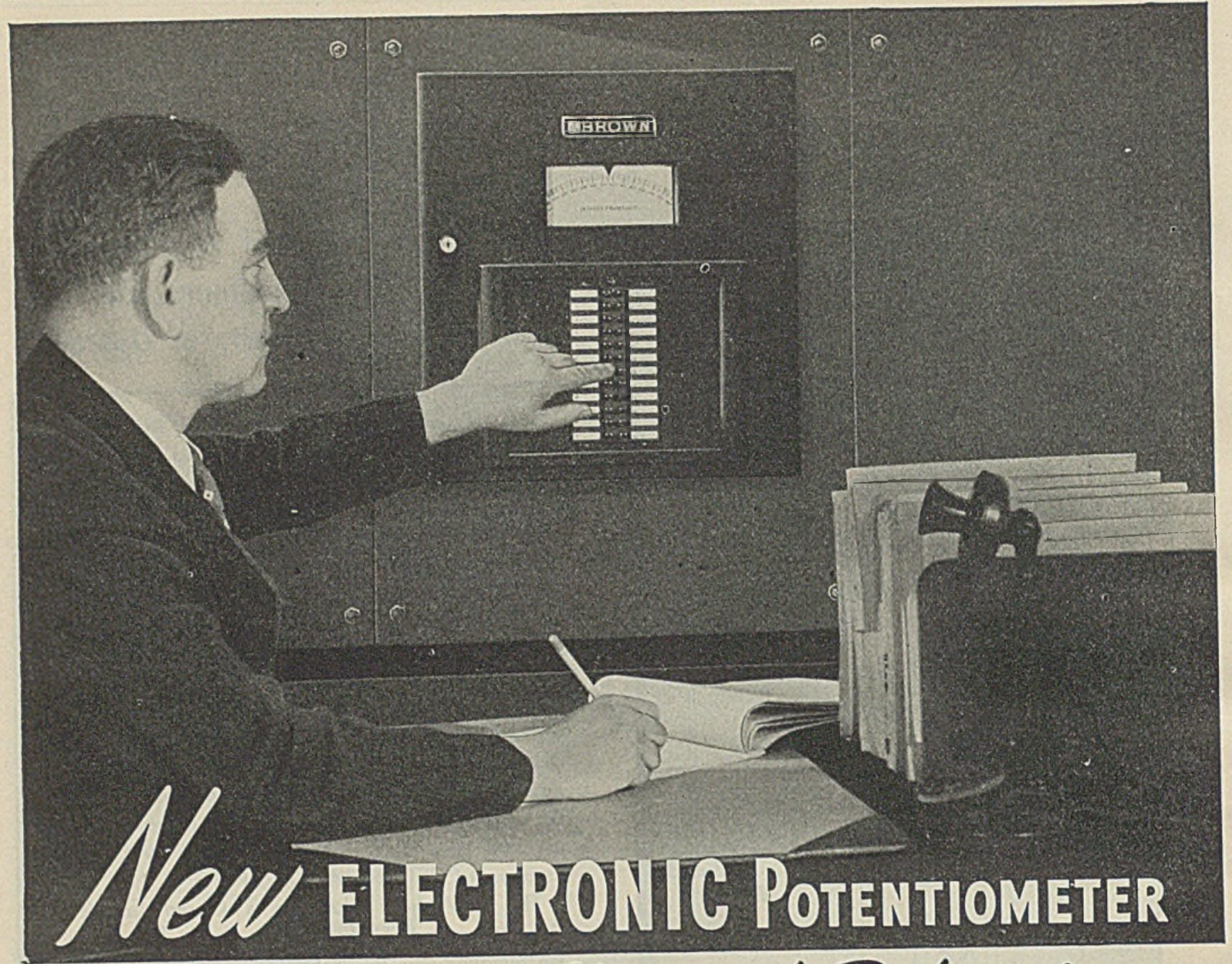




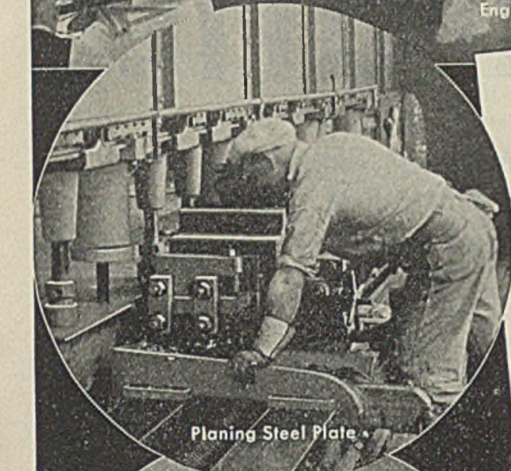



BROWN
New ELECTRONIC POTENTIOMETER

From Laboratory to Working Unit...


Engineering Department


Chemical Laboratory


Planing Steel Plate

Graver Does The Whole Job

All Graver Water Conditioning Equipment is completely Graver-built from start to finish. There is no "jobbing out" of work. No sub-contractors enter into the picture. The service is complete and the responsibility is undivided.

- **Your raw water supply is given a thorough study and analysis in Graver laboratories.**
- **The proper equipment to meet your specific requirements is designed by Graver engineers alone or in cooperation with your engineers.**
- **The equipment is built in Graver plants by Graver workmen under the supervision of Graver engineers.**
- **And the installation is made under Graver supervision or by your contractor with such help from Graver engineers as he may desire.**

That's what we mean by complete service and undivided responsibility.

If you are planning to invest in water conditioning equipment of any type, bear these facts in mind — and consult Graver. We'll gladly discuss your problems with you and submit quotations without obligation.

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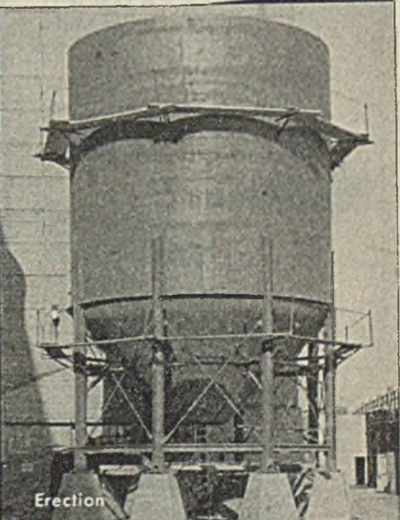
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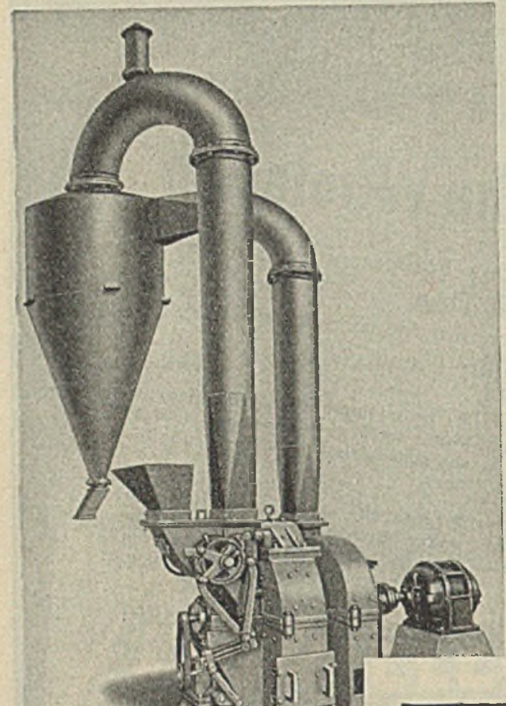
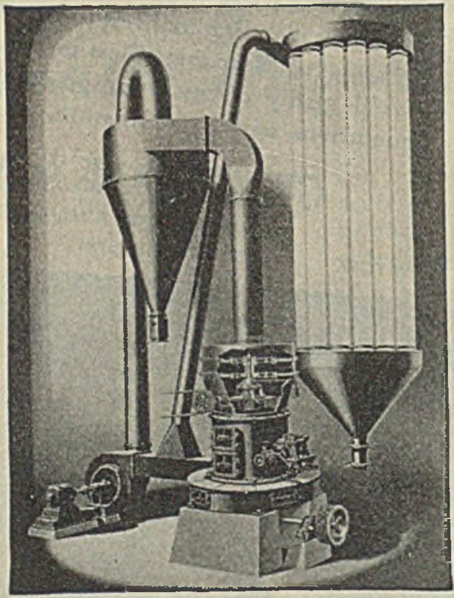
PRODUCING... *Intimate* MIXTURES

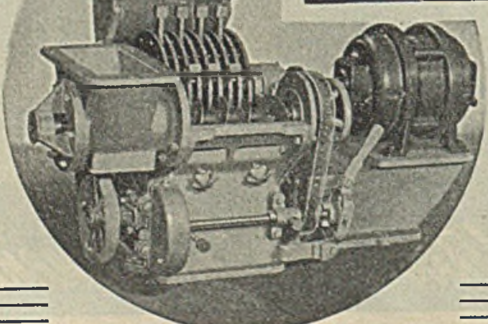
RAYMOND Mills with Air Separation provide a positive method of obtaining a complete and thorough intermixture of ingredients in finely powdered form.



RAYMOND
Imp Mill



RAYMOND
Roller Mill



RAYMOND
Screen Mill

The Roller Mills, Imp Mills and Screen Pulverizers have been used as standard equipment for years in blending operations on various materials. With suitable feeders for proportioning the several ingredients to the mill, the finished product is delivered with an intimate dispersion of the particles, in the proper proportions and to specified fineness.

The Raymond system both with and without air separation is successfully used in blending the various ingredients used in face powders . . . mixing of conditioning and wetting agents when grinding sulphur for insecticide spray purposes . . . blending pigments . . . making food product mixtures . . . introducing flavoring media, extenders and free flowing admixtures.

Other recent applications include grinding of coal and salt mixtures, coal and pitch, and other combinations. If you have a special problem in grinding and blending, let Raymond engineers aid you in getting accurate and economical results.

RAYMOND PULVERIZER DIVISION
COMBUSTION ENGINEERING CO., INC.
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Sales Offices in all Principal Cities
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Hastelloy High-Strength Alloys Resist These Corrosive Media

Hastelloy alloys were developed in four types—A, B, C, and D—to withstand certain severe conditions of chemical corrosion more adequately than most other commercially available materials, and thus to minimize the tremendous losses from corrosion in the chemical and process industries. In addition to outstanding corrosion resistance, these alloys have excellent physical properties, are available in a variety of forms, and can be readily fabricated by the usual metal-working methods.

Some of the common corrosive media for which these alloys are especially suited are indicated below.

FOR VICTORY BUY UNITED STATES WAR BONDS AND STAMPS

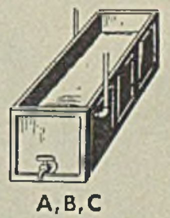
Hydrochloric Acid—Hastelloy alloy A is very resistant to all concentrations of hydrochloric acid at temperatures up to 70 deg. C. (158 deg. F.). Hastelloy alloy B has an unusually high resistance to hydrochloric acid in *all concentrations* and at *temperatures* up to and including the boiling point. Hastelloy alloy C resists all concentrations of hydrochloric acid at temperatures up to 50 deg. C. (122 deg. F.). Near this limiting temperature, however, Hastelloy alloy A is the better choice of material, except where salts or traces of free chlorine are present.

Sulphuric Acid—Hastelloy alloy A is suitable for equipment handling sulphuric acid in concentrations up to 50 per cent and at temperatures up to the boiling point. It is resistant to concentrations over 50 per cent up to 70 deg. C. (158 deg. F.). Alloy B is more resistant to boiling sulphuric acid than Hastelloy alloys A, C, and D at concentrations up to about 60 per cent; above that figure, Hastelloy alloy D is more resistant, and is, in fact, employed in equipment used to concentrate sulphuric acid. Hastelloy alloy C is recommended for boiling sulphuric acid only up to 50 per cent concentration; in concentrations from 50 to 100 per cent it can be used up to a maximum temperature of 70 deg. C. (158 deg. F.).

Nitric Acid and Oxidizing Acid Mixtures—Alloy C resists dilute nitric acid at temperatures up to about 65 deg. C. (149 deg. F.), and nitric acid of over 40 per cent concentration at room temperature. In addition, alloy C is resistant to oxidizing acid mixtures such as nitric and sulphuric; chromic and sulphuric; sulphuric and copper sulphate; sulphuric and dichromates, permanganates or persulphates; and similar combinations.

Organic Acids—Penetration tests show that Hastelloy alloys are highly resistant to acetic and formic acids. They also resist many other organic acids. These alloys are especially valuable for linings in equipment for extrusion and injection molding of plastics containing chlorides. They are also recommended for the handling of organic chlorides, such as ethyl and methyl chlorides, carbon tetrachloride, and similar compounds which hydrolize to form acids.

Chlorine and Hypochlorites—Hastelloy alloy C is one of the few metallic materials possessing adequate resistance to hypochlorites and other solutions containing free chlorine in appreciable concentrations. However, at temperatures over 40 deg. C. (104 deg. F.), even Hastelloy alloy C may be attacked.



Salts—Hastelloy alloys A, B, and C are highly resistant to acid chlorides, such as ammonium or zinc chloride. Hastelloy alloys C and D resist acid sulphates, such as aluminum or ammonium sulphate, and acid phosphates. Hastelloy alloy C possesses unusual resistance, at temperatures up to 70 deg. C. (158 deg. F.), to such strongly corrosive oxidizing media as solutions of ferric chloride and ferric sulphate.

Wet and Dry Gases—Hastelloy alloys A, B, and D are resistant to progressive atmospheric oxidation and to oxidizing and reducing flue gases, carbon monoxide, carbon dioxide, and hydrocarbons at temperatures up to about 800 deg. C. (1,470 deg. F.). Hastelloy alloy C is resistant at temperatures up to 1,000 deg. C. (1,830 deg. F.). All four Hastelloy alloys resist ammonia, wet or dry. Types C and D are highly resistant to wet hydrogen sulphide or sulphur dioxide up to about 70 deg. C. (158 deg. F.).

For More Information on Hastelloy alloys, including results of penetration tests, available forms, and methods of fabrication—write for the 40-page booklet, "Hastelloy High-Strength Alloys."

HASTELLOY
TRADE MARK

HAYNES STELLITE COMPANY
Unit of Union Carbide and Carbon Corporation
New York, N. Y. UCC Kokomo, Ind.
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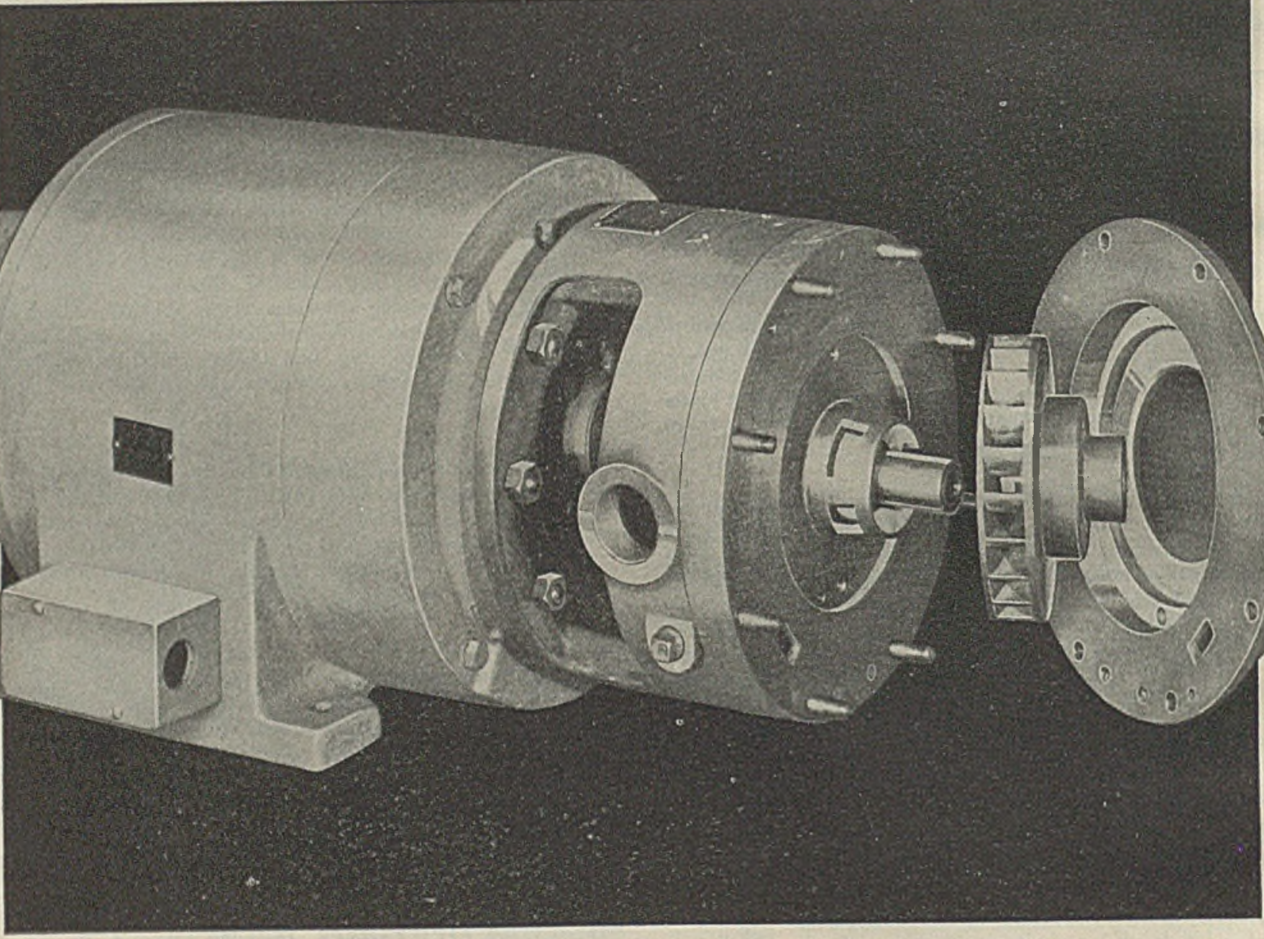
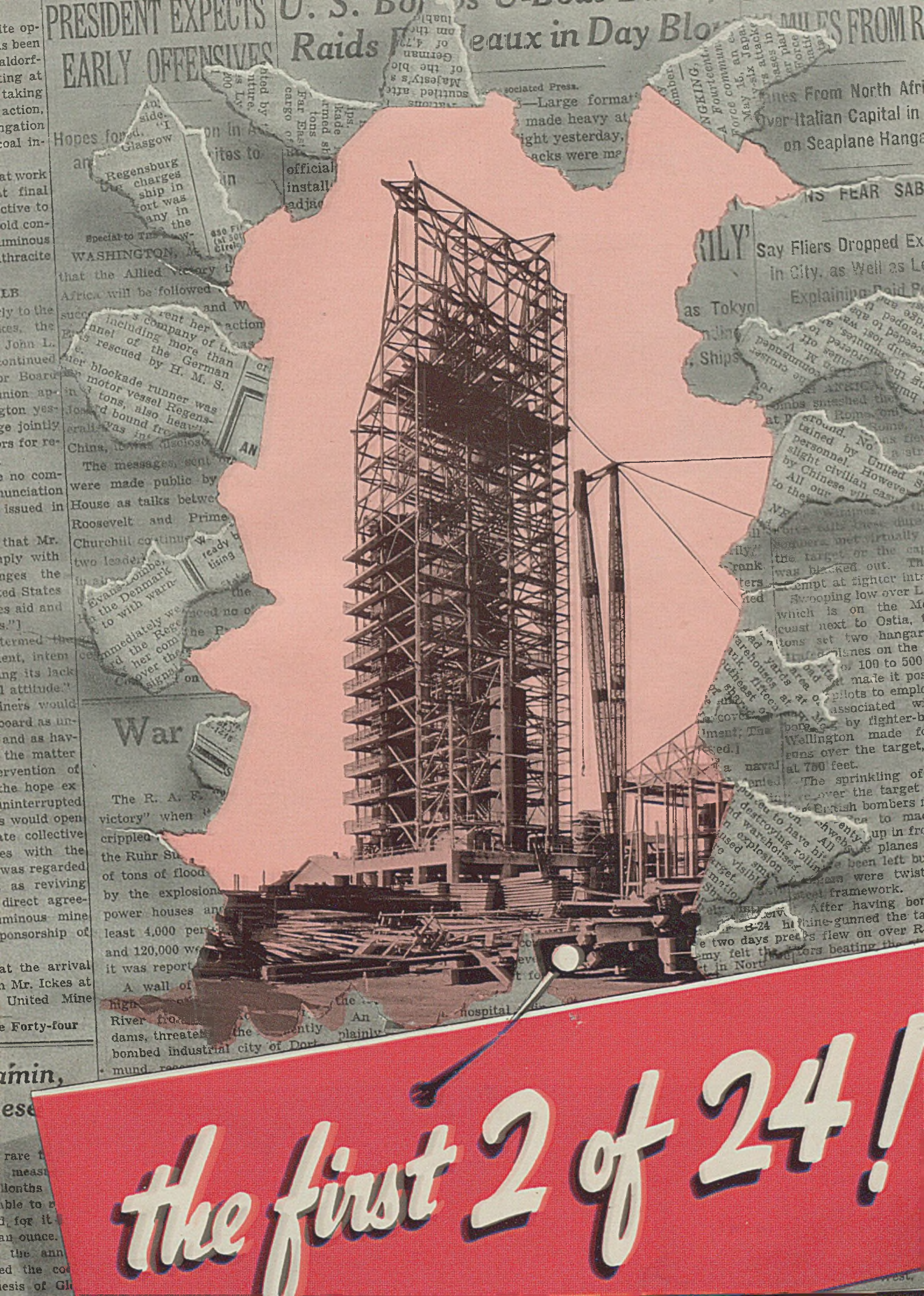
HIGH-STRENGTH NICKEL-BASE ALLOYS FOR CORROSION RESISTANCE

The word "Hastelloy" is a registered trade-mark of Haynes Stellite Company.

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Explaining Raid R
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the first 2 of 24!

24

TCC

UNITS

NOW UNDER CONSTRUCTION

all designed and
being built by LUMMUS

DESIGNED to produce more . . . and higher quality . . . source materials for 100 octane gasoline, requiring less strategic materials, particularly less alloy requirements in the handling of corrosive stocks . . . the twenty-four T.C.C.* units designed and now under construction by Lummus are an important part of America's 100 octane gasoline program.

They will be a mighty important factor in America's post-war program, too, for the Thermofor Catalytic Process with the new synthetic bead catalyst shows lowest cost of operation . . . improved performance beyond any catalytic operation known to date and high yields of post-war quality motor gasoline.

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FLOATLESS LEVEL CONTROL

On the industrial front . . . as on the battle front . . . the electron tube, miracle of modern science, is today accomplishing the impossible — with precision, speed, efficiency. It has eliminated from the field of level control the need for complicated mechanical devices. It has made available to industry PHOTOSWITCH . . . the modern floatless level control.

THESE ARE THE AMAZING FINGERS OF PHOTOSWITCH — *electronic* fingers that actually "feel" liquids or powders — operate Photoswitch Level Controls. Today, in hundreds of industrial and chemical plants, modern Photoswitch installations . . .

- **Control pumps to maintain constant liquid level.**
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- **Maintain interface between two liquids.**
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There is a Photoswitch Level Control to meet ***every*** need . . . for use with ***all*** types of liquids and powders. ***Write for complete catalogue information.***

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PHOTO-ELECTRIC & ELECTRONIC CONTROLS FOR EVERY INDUSTRIAL PURPOSE

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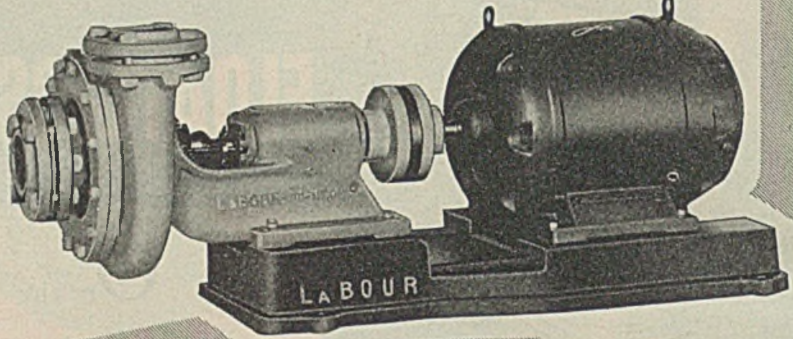
GETTING *Sustained Efficiency* IN CHEMICAL PUMPS



FREE THIS HANDY FLUID FLOW CALCULATOR

We have available for distribution to engineers and pump buyers a limited number of LaBour Fluid Flow Calculators. Greatly facilitates figuring of elements entering into the pumping of most industrially used chemicals at various temperatures and specific gravities.

When writing for your free Calculator, please use company letterhead.

The surest way to get sustained efficiency in your chemical pumps is to use pumps whose efficiency is not materially affected by the inevitable wear and corrosion accompanying chemical service.

That was a large order until the advent of the LaBour Type Q, a high efficiency centrifugal having an open impeller and using no sealing rings. The Type Q does not depend on close clearances to secure hydraulic efficiencies comparable to those of most closed impeller pumps.

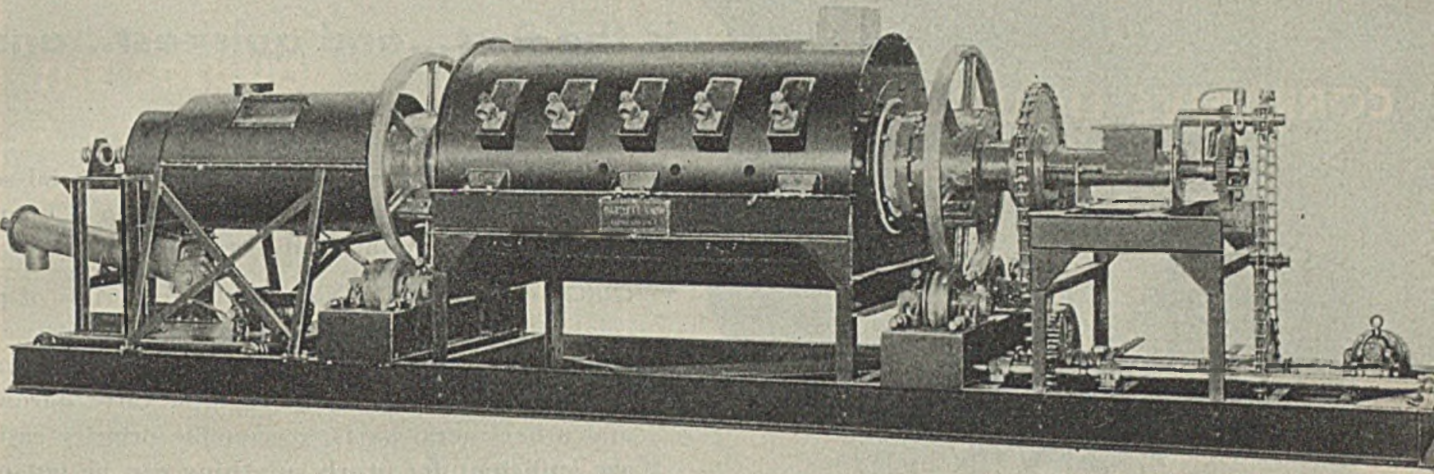
Exclusive design features, born of LaBour's field-secured knowledge of process industry pumping problems, are responsible for the Type Q's high efficiency. That these features enable the Type Q to *maintain* unusually high efficiency even after long service, has been demonstrated time after time by countless installations in process industries.

Full information about the Type Q or other LaBour centrifugal pumps for chemical service is yours for the asking.

THE LaBOUR COMPANY, Inc.
Elkhart, Indiana, U. S. A.

LaBOUR PUMPS

THIS CALCINER



translates *theory into practice*

● To take an inexpensive organic material specified by the customer . . . to calcine it at high temperatures in a reducing atmosphere . . . to get the required product with just the yield desired . . . seemed possible in theory, although it had never been done before, but

Bartlett-Snow did it with 100% Results

Based on Bartlett-Snow theoretical calculations, Bartlett-Snow design and heat engineering, and constructed in Bartlett-Snow's completely equipped machine and structural shops, this indirect heat calciner has met every operating condition. Every prediction and every expectation has been entirely fulfilled.

Special Construction

From the receiving hopper the material is passed by a motor driven, but instantly variable and volumetrically exact screw feeder, capable of handling from 29 to 745 pounds per hour, into a specially cast high nickel-chrome tube, guaranteed to withstand temperatures of 2000°F., when in continuous use. In the reducing atmosphere of this air tight, gas tight chamber, the material is broken down . . . gaseous products are released through a water-jacketed outlet, and the solid material, first cooled to normal temperatures, is discharged continuously at the desired rate per hour.

Use Bartlett-Snow Experience

Equipped with auxiliary manual driving mechanism, to insure the safety of the calcining tube in case of current failure, with spidery air-cooled riding rings and with discharge equipment mounted on a traveling and counterweighted frame, that compensates the 1⅛-inch expansion of the nickel-chrome calcining tube . . . this installation proves again the ability of Bartlett-Snow engineers to master even the most severe heat engineering problems . . . What is your problem?

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

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DRYERS • CALCINERS • COOLERS • KILNS

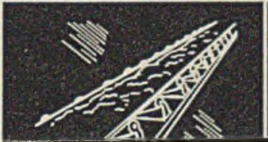
Also complete materials handling facilities to meet any requirement
One contract • One guarantee of satisfactory performance • Unit responsibility

Screw Feeders

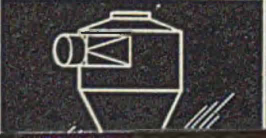
Rotary Crushers

Bucket Elevators

Belt Conveyors



Dust Collectors

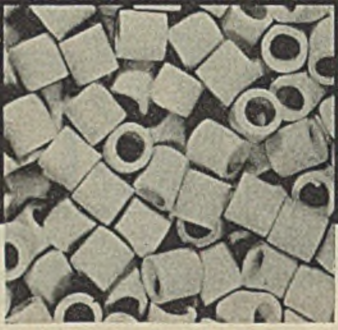


Pressure Ves

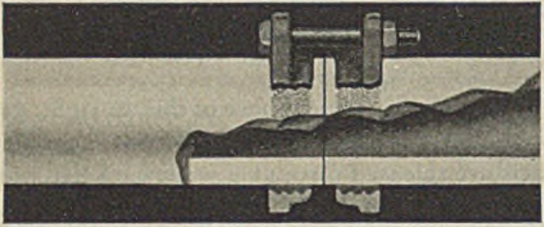
WHEN BIG PRODUCTION INVOLVES EFFICIENT HANDLING OF CORROSIVE LIQUIDS

Lapp Chemical Porcela

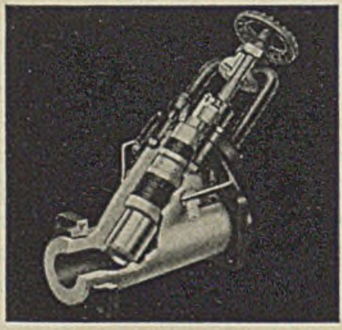
is the first...and quickest...answ



Raschig rings of Lapp Porcelain facilitate gas absorption processes by prohibiting contamination, and by standing up without crumbling under longest, most severe duty.



Lapp Chemical Porcelain Pipe is available in all standard sizes up to 8" inside diameter. Its ground ends permit installation with thin hard gaskets, eliminating at its source the chief cause of trouble in most corrosion-free pipe.



The Lapp Valve is designed to bring liquids into contact only with porcelain. Fine grinding, polishing and lapping of bearing surfaces—and a unique spring washer arrangement—assure smooth action, and a permanently maintained seal, even under vibration and thermal change.

☞☞☞☞ To installations for industrial-scal processing of corrosive liquids, Lapp Chemica Porcelain offers notable advantages:

QUICK AVAILABILITY. None of the materials of por celain itself is on the critical list. Lapp facilities ar adequate for the production of a large volume o porcelain pieces. For pipe flanges, valve hardwar and other metal parts, reasonable priority rating are sufficient for nearly anything can be put on delivery schedule to fit any construction program

CHEMICAL PURITY. As a material of construction Lapp Porcelain brings the purity always associate with laboratory porcelain to industrial processing Completely iron-free, it is a dense, thoroughly vitrified non-porous body, smooth and corrosion-free

STRENGTH AND LONG LIFE. The fragility which th word "porcelain" sometimes suggests is not property of Lapp Porcelain. This material is remark ably rugged, able to withstand mechanical shoc of surprising intensity. As a major contributin factor in its purity and long life both, is its com plete non-porosity—it does not absorb the liquid exposed to it. The only exposure is on the surface . . the body cannot be weakened by the capillar forces of penetrating liquids.

☞☞☞☞ A phone call or letter will bring quick answer as to how Lapp Porcelain can hel you meet your processing problem, quickly an with top production performance. Lapp Insulat Co., Inc., Chemical Porcelain Division, LeRoy, N.

Lapp *Chemical Porcelain*

Valves • Pipe • Raschig Rin

No. 1 in a series of case studies on dust and fume conditions in the process industries.

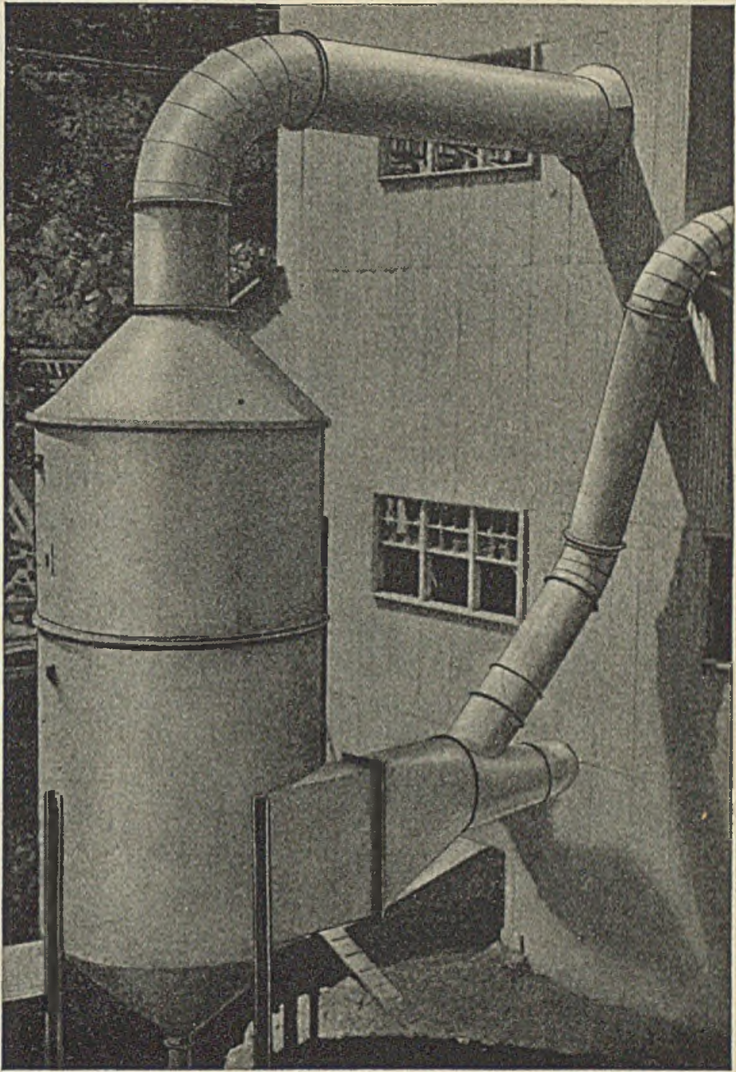
THE PROBLEM

Controlling bleaching powder dust.

THE SOLUTION

A 6,000 c.f.m. Schneible Senior Multi-Wash Collector of standard steel construction, using only water as the collecting medium, was installed for handling the exhaust from all dust-creating operations.

The air in these working zones is now free of dust. The morale of the workers has improved, and production has increased.



What Is Your Dust and Fume Problem?

Many contaminated air conditions found in the process industries have been overcome by standard Schneible Multi-Wash Dust Collectors. Collector towers are built of the metal most resistant to the dust and fumes handled, in capacities up to 30,000 c.f.m., in multiple unit installations and self-contained units. Settling and dewatering equipment provides for water or other cleansing liquid being used over and over again. Where valuable dusts are collected, they can be easily recovered.

Write us about your dust and fume problems.

CLAUDE B. SCHNEIBLE COMPANY
3959 Lawrence Ave. Chicago, Ill.
Engineering Representatives in Principal Cities

SCHNEIBLE

DUST, ODOR AND FUME CONTROL EQUIPMENT

D.O.JAMES MOTORIZED SPEED REDUCERS

ARMY E NAVY

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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.

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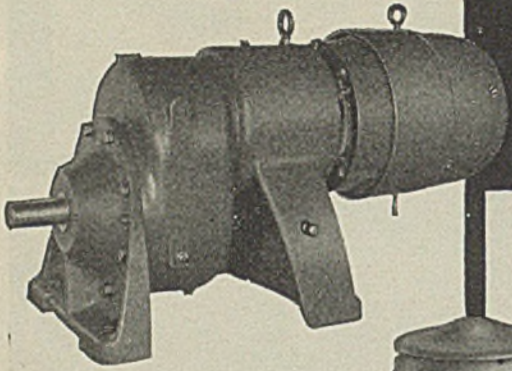
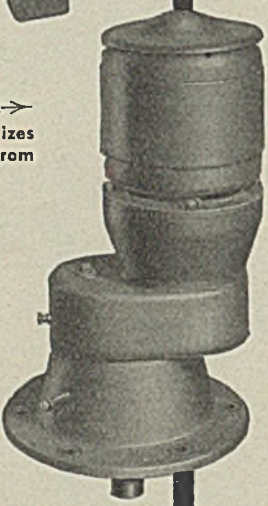


MOTORIZED HELICAL REDUCER
Horizontal drive—made in 13 sizes in ratios of 1¼ to 9½:1 and from ¾ to 50 horsepower.



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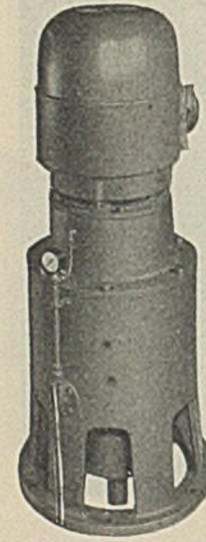
Vertical drive—made in 13 sizes in ratios of 1¼ to 9½:1 and from ¾ to 50 horsepower.



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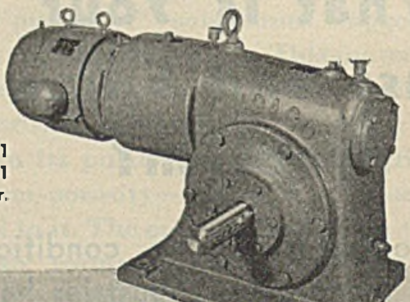

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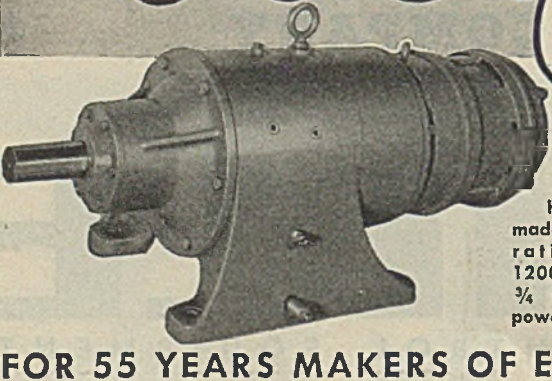

MOTORIZED PLANETARY REDUCER
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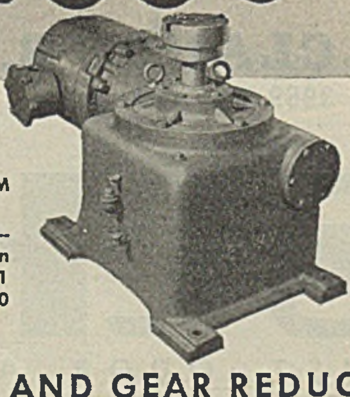

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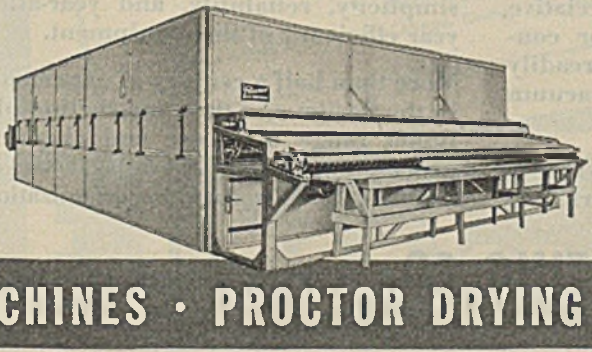

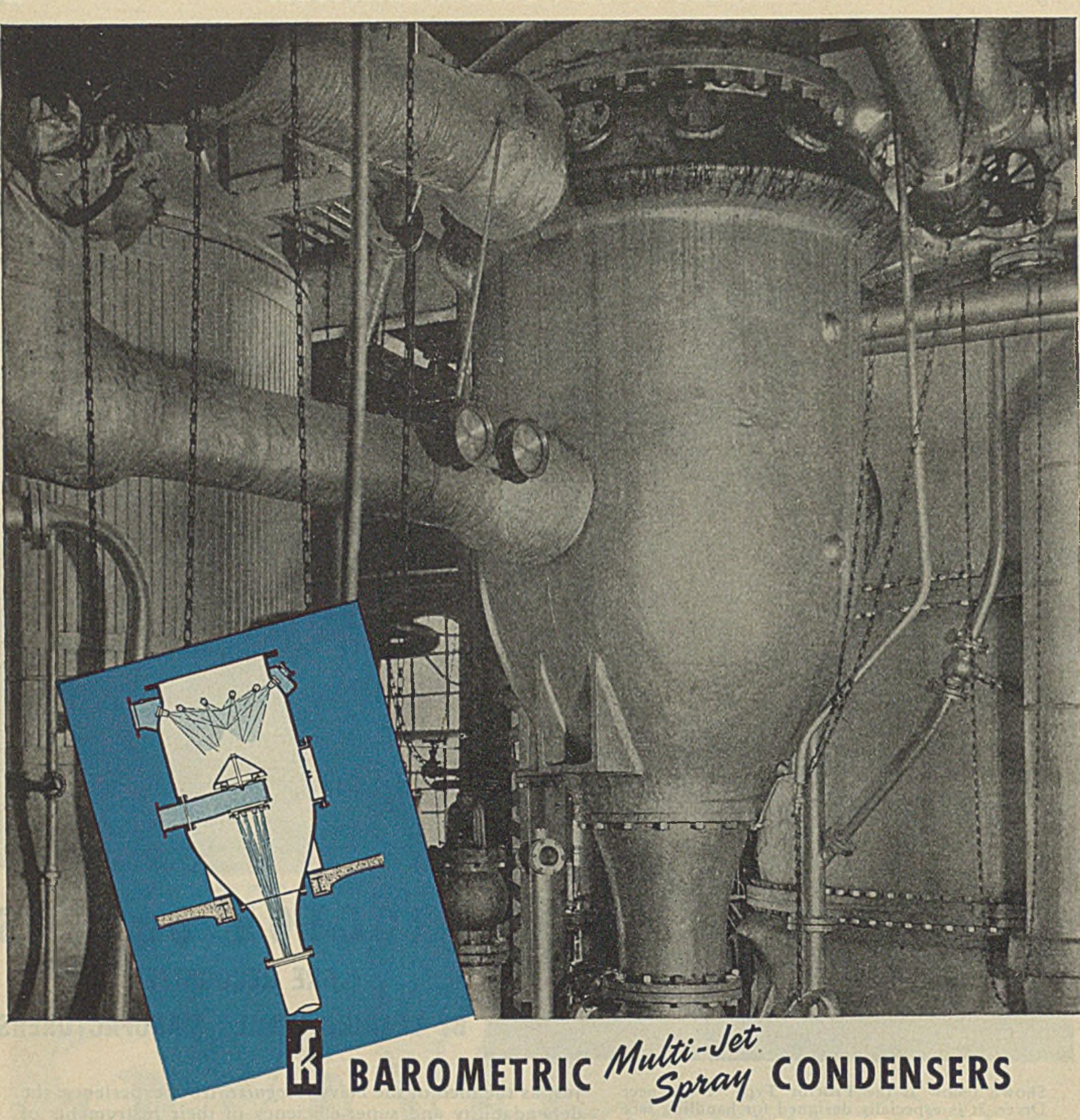

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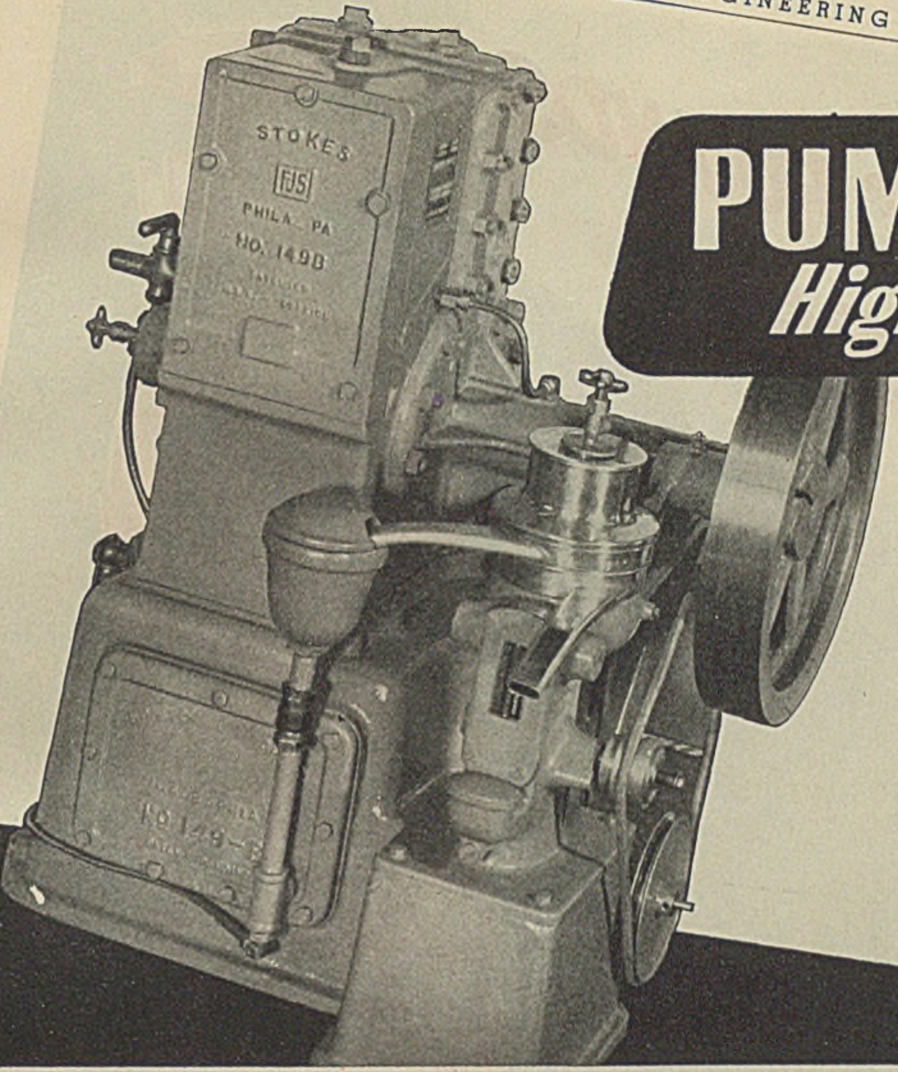

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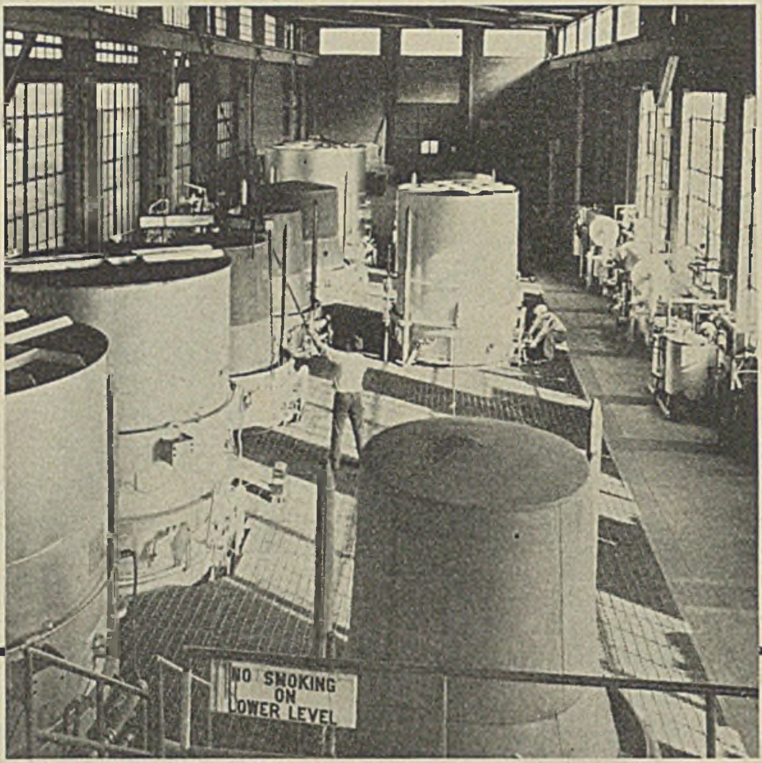

Two Lectrodryers DRY deoxidizing gas, produced in generators, for these heat-treating furnaces

Perhaps this use of Lectrodryers by Atlantic Wire Company will suggest some way you can profitably employ DRYing—

Controlled atmosphere in these furnaces—DRY deoxidizing gas—prevents decarburization of the steel wire being annealed here. Properties of the steel are held uniform, its high quality maintained. The requirement that the furnace atmosphere be DRY is taken care of by Lectrodryers, which remove moisture to a very low dew point.

This example of a manufacturing process being dependent upon accurate control or complete removal of moisture is repeated hundreds of times throughout many industries. Lectrodryers are removing moisture from air, gases and liquids to dew points below −110° F. Charged with Activated Aluminas as their DRYing agents, they are easily maintained at high efficiency.

DRYing service provided by Lectrodryers has enabled manufacturers to standardize and simplify their processes. Our engineers will gladly advise you on the possibility of using Lectrodryers in your processes. Pittsburgh Lectrodryer Corporation, 305 32nd Street, Pittsburgh, Pa.

LECTRODRYERS DRY WITH ACTIVATED ALUMINAS

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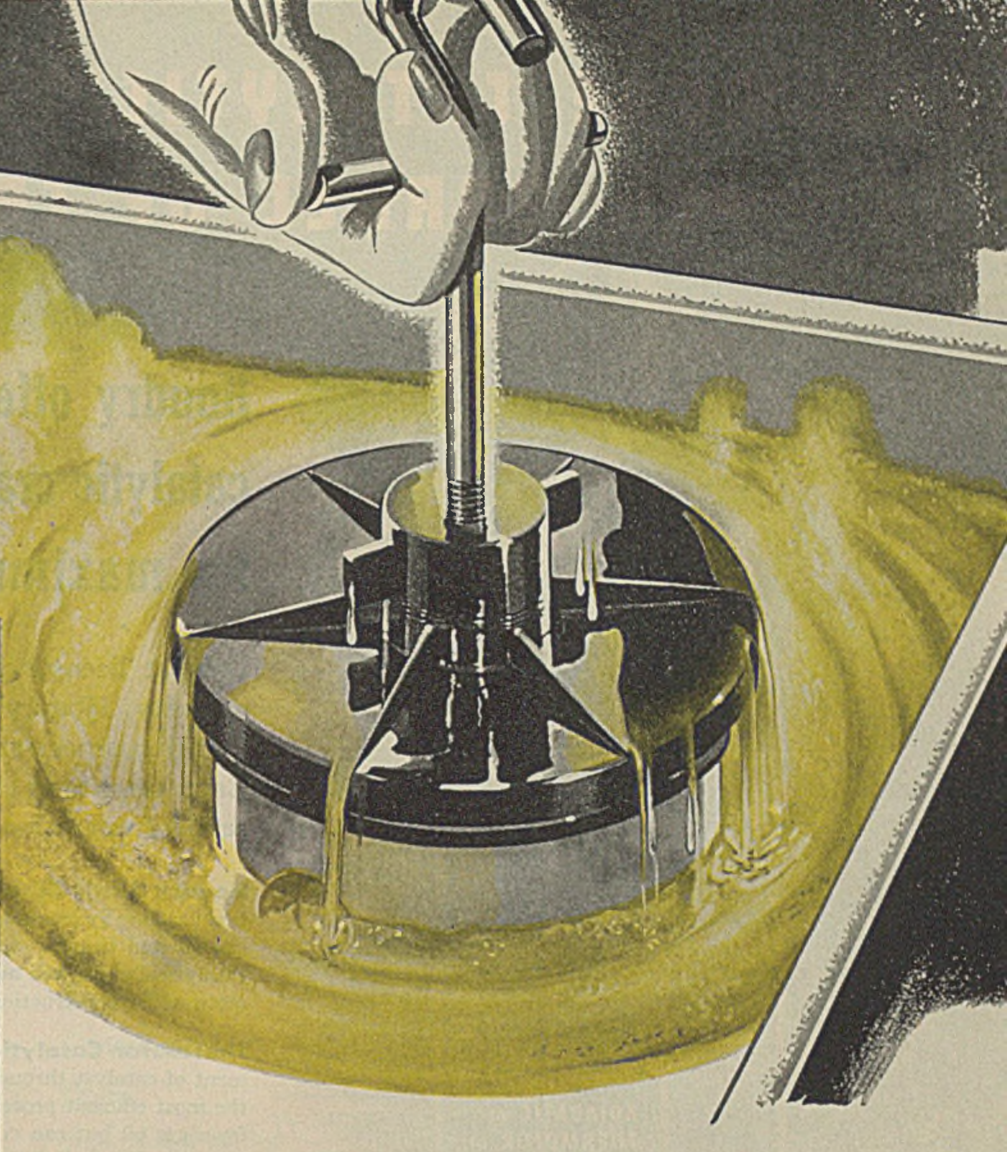

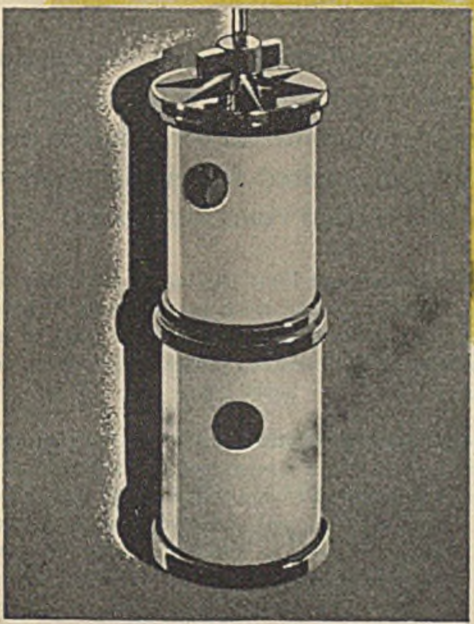

MASKING PARTS FOR PLATING OPERATIONS

Saran masking parts help speed production of cylinders used in airplane motors. The entire outside diameter of the cylinder, illustrated here, is nickel plated with the exception of one-half inch on top and bottom. Snug-fitting top, center and bottom saran masking plates, into which two sleeves are placed, provide complete protection. As a result, valuable time and material are conserved by this newest contribution of a superior plastic material.

SARAN PLASTIC—

For Uses Requiring High Chemical Resistanc

Saran's high degree of resistance to a broad range of chemicals is dem strated by its successful use in plating masks and fixtures. This diffic application emphasizes saran's distinctive position among plastic materi For, in a series of exhaustive tests in many plating solutions and over norr operating temperature ranges, saran proved its superiority.

Saran advantages go far beyond exceptional chemical resistance to inclu such important properties as excellent dimensional stability, resistance moisture and heat, and resiliency and durability. These factors mark sa for many new uses—extending from the electroplating industry to a w variety of industrial applications.

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SARAN

DOW PLASTICS

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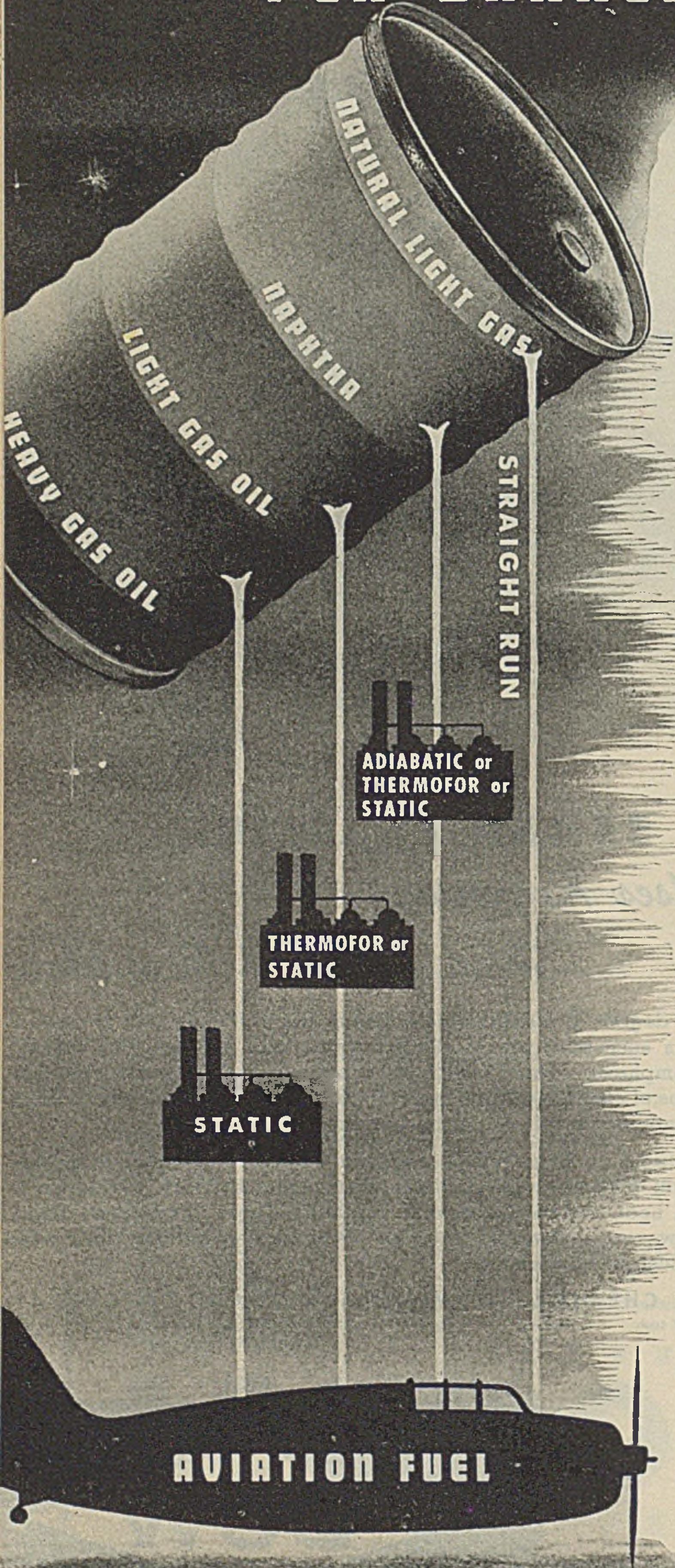
CHEMICALS INDISPENSABLE

MAKE MORE CATALYTIC AVIATION GAS PER BARREL OF CRUDE



Houdry offers licenses for <u>all</u> the catalytic cracking processes needed for maximum yield and quality

Largest licensor in the industry, based on refining capacity, Houdry offers not one but *three* catalytic cracking processes for the production of aviation fuel. Each process is especially suited to certain types of refinery operation and certain charging stocks.

Houdry Static Catalyst Process: First process to produce aviation gasoline by cracking. Highly versatile, it efficiently cracks naphtha, gas oil and heavier oils. Last year produced more than 90% of *all* catalytically cracked aviation fuel. Seventeen plants in operation, ten more under construction.

Thermofor Catalytic Cracking: Embodies the continuous movement of catalyst through a reactor and a regenerator. Unquestionably the most efficient process of its type. Provides particularly high yields from gas oil but can crack naphtha as well. Adaptable to almost any size of refinery. T.C.C. makes available to small and large refiners a catalytic cracking process requiring low amounts of critical construction materials, low operating cost, and is highly economical for the production of catalytically cracked aviation base stocks of superior quality. Twenty-two plants now in various stages of construction.

Houdry Adiabatic Process: Latest Houdry development can produce a *super* aviation fuel incomparably superior to present aviation fuels. Uses as charging stock heavy naphthas heretofore almost useless for aviation gasoline, thus substantially increasing total possible yield per barrel of crude. Semi-commercial unit, now in operation, indicates Adiabatic plants will cost less to build and operate than static catalyst plants.

These Houdry-licensed processes assure maximum production of high-octane aviation fuel from crude, with minimum materials required for construction and operation of plants. Houdry offers these outstanding processes to all American refiners without restriction, under license arrangements subject to approval by the U. S. Government.

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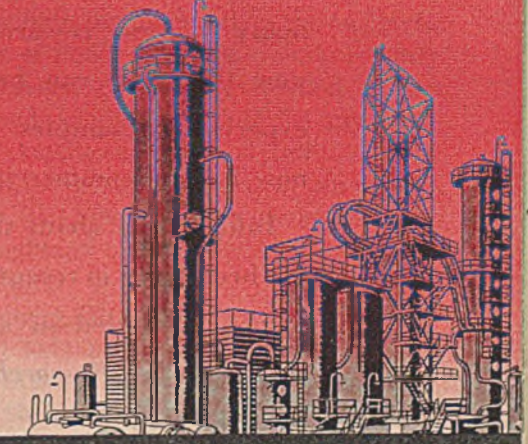

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Information about these new chemicals has been given in recent advertisements and is now compiled in a leaflet, *Chemicals Available in "Research" Quantities.* Send for your copy.

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- Ethyl Morpholine
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INDUSTRIAL AND ENGINEERING CHEMISTRY

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

EDITORIALS

The Patent Report

THE long-awaited report of the National Patent Planning Commission has been sent to Congress by President Roosevelt and it is highly significant that the group has failed to find "any serious instances in which the patent system has interfered with the prosecution of the war". Thus the contention of Thurman Arnold and his former coterie of workers in the Department of Justice that international cartels involving patent agreements have hampered the war program to a serious degree is refuted by such men as Charles F. Kettering, Chester C. Davis, Francis P. Gaines, Edward F. McGrady, and Owen D. Young.

Few defenders of the American patent system (which the commission termed "the best in the world") go so far as to insist that no abuses exist and that changes and improvements are undesirable. It is hardly necessary to burn down or tear down a house in order to make structural improvements.

Chairman Kettering and his co-workers on the commission have taken a very realistic and enlightened viewpoint in the recommendations suggested. To minimize abuses and make them readily detectable, the commission suggests legislation compelling the recording in the United States Patent Office of:

> All existing agreements to which one of the parties is a citizen of a foreign country, all agreements regardless of the citizenship of the parties which include any restrictions as to price, quantity of production, geographical areas or fields of use, and all future agreements regardless of restrictions or citizenship of the parties.

Three or four other suggestions are noteworthy. The report calls attention to one serious weakness—the Patent Office lacks the power to withdraw or cancel a patent inadvertently granted. It also recommends that any person be given the right to challenge the validity of a patent within six months after it has been granted. It is suggested that patents be held to a life of twenty years based on the date of application for the patent, and the commission approves a single court of patent appeals.

The Kettering group has performed a signal service in calling attention to the present chaotic condition which has arisen as a result of a lack of a uniform test or standard for determining what really is a patentable idea and proposes that Congress lay down a reasonable, understandable test by legislation.

Perhaps it is unlikely that the commission's proposals will meet with unanimous approval even among those who staunchly support the American patent system, but it is very definitely a constructive step forward. Intelligent leadership and vigorous initiative will provide a satisfactory solution. Let those who understand and appreciate the benefits of the American patent system unite now to modernize it properly.

Let's Look at the Record

> "THE Congress hereby recognizes that the full development and application of the Nation's scientific and technical resources are necessary for the effective prosecution of the war and for peacetime progress and prosperity, and that serious impediments thereto consist in—
>
> The unassembled and uncoordinated state of information concerning existing scientific and technical resources; the lack of an adequate appraisal, and the unplanned and unprovident training, development, and use of scientific and technical personnel, resources, and facilities in relation to the national need; the consequent delay and ineffectiveness in meeting the urgent scientific and technical problems of the national defense and essential civilian needs . . ." (From Senate Bill 702 not yet even favorably reported on by the subcommittee of the Senate Committee on Military Affairs.)

Anyone fortunately able to learn at first hand of the enormous feats of production achieved in many varied fields sees a totally different picture than the one given in the Declaration of Policy of S. 702. Visits recently made to widely diverse chemical production centers provide a ready and complete antidote for any pessimism concerning America's industrial front. Flaws, if indeed they exist in chemical production, can only be detected by those who look down on accomplishment from the dizzy heights of uncontrolled expectations of the wholly impossible.

A realistic summary of the goals achieved reveals that we have not only performed industrially as requested, but that in many instances we have surpassed by a wide margin the production requested.

Most exciting and inspiring are plants grown huge almost overnight, busy turning out synthetic rubber, aviation gasoline, toluene, aluminum, magnesium, and hundreds of other strategic and critical materials.

For the record of the future let us summarize briefly but a few of these accomplishments. The Japanese felt they were dealing us a mortal blow when they cut us off from sources of supply of quinine and natural rubber. What does the record show? To protect our men and women assigned to tropical posts we will produce 2,500,000,000 antimalarial tablets in 1943, yet in 1939 production was less than 5,000,000 tablets.

In the place of natural rubber American chemists and chemical engineers were assigned the intricate problem of providing some 800,000 long tons of synthetics annually, an amount greatly in excess of our imports prior to Pearl Harbor. By the end of 1943 we will have ready the necessary plants and today synthetic rubber of excellent compounding qualities is being produced in sizable quantities. Twenty months ago our annual output was less than 4000 tons annually.

To prevent the spread of infection in wounds we will manufacture over 10,000,000 pounds of sulfa drugs, as compared with a peacetime output of 1,000,000 pounds.

What is the picture in high-octane gasoline? Six years ago the petroleum industry's production was a mere 800 barrels per day. In 1943 more than thirty companies will be in production and one plant alone is now producing more than the projected requirements cited as late as March of 1941 by a representative of the Joint Aeronautical Board. Present production figure is a military secret, but several months ago we were producing 3800 per cent more than the 1937 output.

Projected capacity for production of light alloys is now 1,500,000 tons, consisting of 1,200,000 tons of aluminum and 300,000 tons of magnesium. By 1944 we will have increased production of the former seven times and the latter one hundred times.

The story of production successes is the same for dehydrated and compressed foods, vitamins, explosives, nitrogen, plastics, industrial alcohol, toluene.

One exceptionally well-informed executive and technologist recently stated in a meeting in Washington that he knew of no single instance where the war production program had been seriously delayed for lack of necessary chemicals. Later we shall learn, as our enemies now know, that America's chemical forces have fully met the supreme test.—The defense rests!

The Sirocco and the Straw

SCIENCE has been blamed for countless things, not the least of which is war. It seems to please magniloquent politicians to bait scientific industries and modern inventions, to denounce in bombastic specious terms, the munitions maker and the heartless scientist. Even sincere thinkers have, with less oratory, attacked our scientific progress as a bringer of unrest, unemployment, and war. They have suggested moratoria on invention or a freezing of technical progress. Their thought is that it is necessary to give the souls of men an opportunity to catch up with progress, to become acclimated to changed conditions—an internal evolution to godliness as it were.

At present no one is attacking science. It is being given every encouragement possible, even to the eager suggestion that we become as efficient as politicians by getting ourselves thoroughly mobilized and entangled in red tape and federal finance.

But men of science have long memories. They, as is their wont, plan ahead and try to see what the future will bring, and in such a mental projection they use experience as their guide. They remember the vicious attacks on industry and science in the former period of peace. They remember their relative unpreparedness and unwillingness to defend themselves against untruths. Like little children, they were hurt and puzzled by the charges, and stung into retort semioccasionally. But during that same period interest began to stir in our economic and political life. Thought was consolidated, concerted drives were advocated on pending harmful legislature, original thinkers arose, science was urged to awaken and extend its penetrating analytical concepts to mankind and its mode of life. There are signs that such groundwork is bearing fruit. Science refuses to accept the blame for world conditions. The challenge will be hurled back. A straw in the wind (sirocco is a better description at present) was the speech of Willard Dow in accepting the Chandler Medal in New York in which he said:

> We are in the midst of a holocaust of destruction in which apparently nothing is sacred or inviolate. The war, if it demonstrates anything, demonstrates that mankind as a whole is morally and politically unfit to apply the knowledge which science has placed at its command. Indeed the thin veneer of civilization is easily rubbed off. Are we not today applying against mankind nearly all the forces and laws of Nature which science has uncovered for the making of a better and happier living?

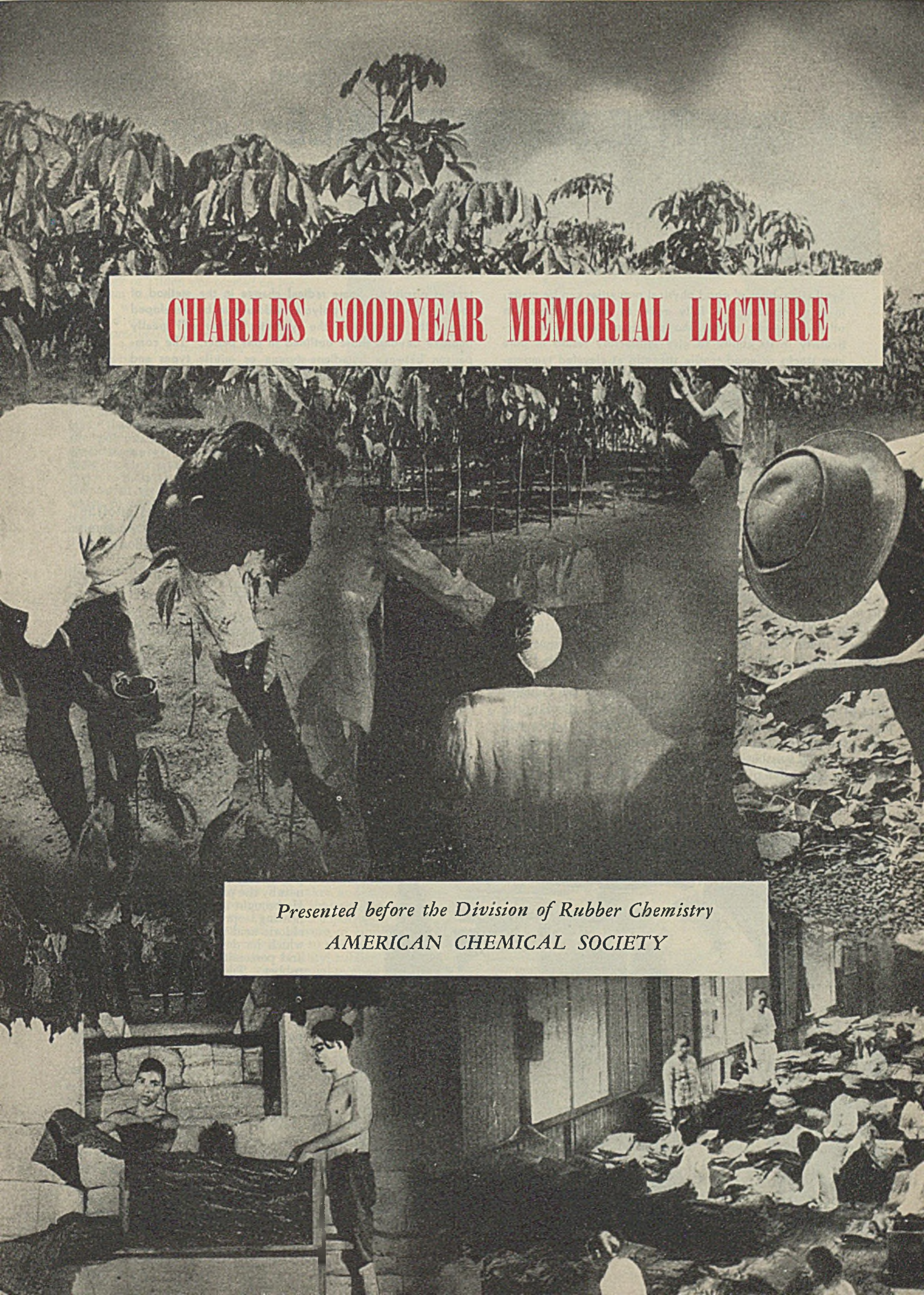
Or as C. C. Williams, president of Lehigh University, said recently:

> The recent brutal aggressions of dictator nations are recrudescences of the tribal barbarities and perfidies depicted in the Iliad, the Aeneid, Caesar's Commentaries, the Book of Judges, the Nibelungenlied.

The fault lies with man and his inhumanity to man. Science and politics are both to blame, but of the two, our political dishonesty bears the greater share by far. This time, for the first time in history, we expect to see the peace influenced by scientific truths. It may even be that science will be given a voice. At least we can hope for such, and if the recent straws are an indication, we know that science will be far more vociferous and forceful in presenting and defending our case.

The McKellar Bill S. 575

WHILE the ire of certain elements in Congress over the legions of bureaucrats who have fastened their tentacles on the government payroll and brazenly propose to remain indefinitely is quite understandable, nevertheless the McKellar Bill is definitely not the corrective measure needed. The proposed measure is an out-and-out attempt at patronage grabbing and deserves to be defeated. Congress has more important things to do with a war on than to concern itself with passing upon the qualifications of Civil Service employees who happen to be in salary brackets of $4500 and over. The bill is an attack on the rights of thousands of efficient government workers. It is a threat to the whole merit system.



CHARLES GOODYEAR MEMORIAL LECTURE

Presented before the Division of Rubber Chemistry

AMERICAN CHEMICAL SOCIETY

THE SECOND MILE

L. B. SEBRELL
Goodyear Tire and Rubber Company, Akron, Ohio

Synthetic rubber of good physical properties can be made; in many respects it is fully equal to natural rubber; in others, synthetic rubber shows serious deficiencies, particularly in its ability to give satisfactory results in pure gum stocks or good tensile strengths at elevated temperatures. While there is considerable work to be done in improving synthetic rubber, the dangers arising from a lack of rubber may be considered largely removed. An accurate plan of attack to improve synthetic rubber must consist of the removal of cross linkages to as great an extent as possible. Some radical change in the method of forming the rubberlike polymer will have to be developed before the qualities of the synthetic rubber will greatly improve beyond those outlined in this paper. The comparison between butadiene-styrene or -nitrile types and the Butyl type of rubber is interesting. While Butyl is inferior in several respects to the other synthetics it excels them in other respects. Since it is generally assumed to be more nearly a straight-chain polymer, further development along this line would seem to be in order.

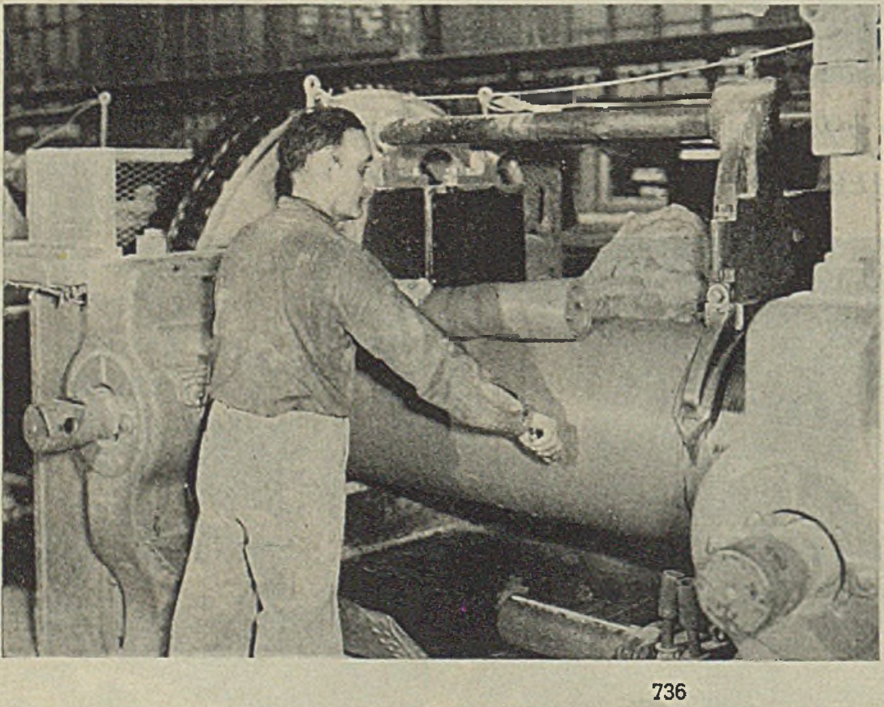
THE title "The Second Mile" was inspired by an address given by W. E. Wickenden, of the Case School of Applied Science, upon an entirely different subject. Since this title seemed to suit the synthetic rubber situation as it now exists, Wickenden's permission was secured to use the title in connection with this lecture. In its broader aspects, the paper purports to cover the present status of the synthetic rubber situation. Natural rubber will be compared with the copolymers made from butadiene and styrene, butadiene and acrylonitrile, and the copolymers generally known as Butyl rubber. These three materials were chosen for the comparative study because they are the materials which the Government proposes to use in the largest quantities to alleviate the present shortage of rubber. It is hoped that the data will give a fairly accurate picture of the comparative or relative values of these synthetic rubbers and natural rubber. There will be no discussion of the methods of manufacture which are still more or less secret. It is also proposed to go into the probable structure of these polymers and to indicate some trends of research which might profitably be followed in order to improve them.

Polymerization

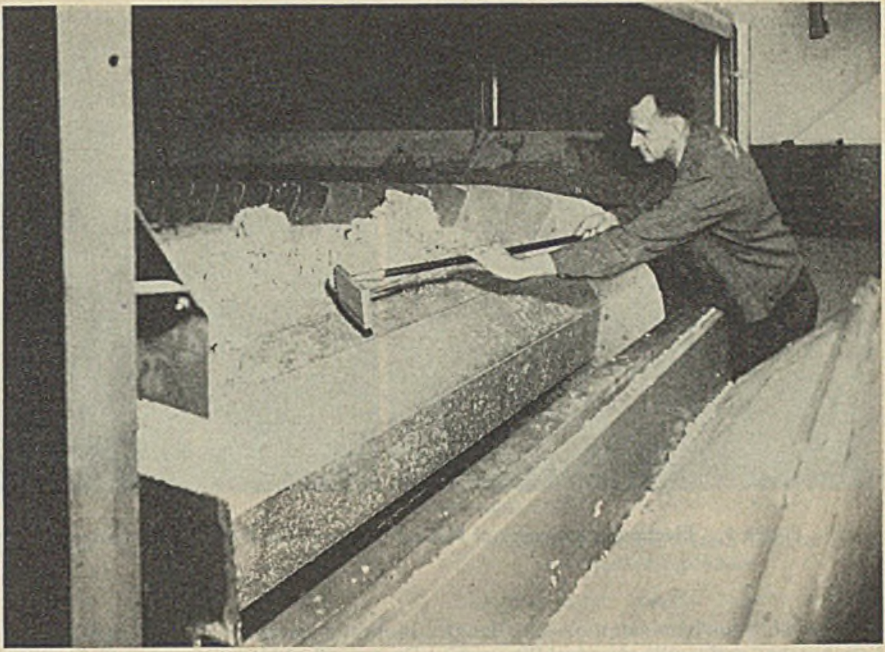
The polymerization of organic substances has been known for considerably more than a hundred years. Berzelius (*2*) was the first to use the term "polymerization" and to define it as indicating those compounds which possess the same properties but have a different total number of atoms. Williams (*23*) is generally credited with the first preparation of isoprene when he separated this material from the products of destructive distillation of rubber. However, Himly (*10*), while investigating the fractional distillation of rubber, isolated a distillate which he called "Faradayin". He also coined the term "Kautchin" (now known as dipentene) for one of the higher boiling fractions. However, these investigators did not again polymerize these rubberlike products to any compounds of a higher molecular weight.

Bouchardat (*3*) is usually given the credit for first synthesizing a rubberlike material from a liquid of low molecular weight. In 1875 he advanced the idea that isoprene is a primary unit of natural rubber and succeeded in producing a rubbery polymer from the distillation products by the process of polymerization. He brought about this conversion by heating isoprene with fuming hydrochloric acid and obtained a product which he described as being elastic and possessing the characteristics of rubber. Tilden (*19, 20*) then showed that isoprene could be obtained by the pyrolysis of turpentine, and that by treatment with hydrochloric acid it would also undergo spontaneous polymerization. He also polymerized isoprene by the use of nitrosyl chloride.

★



(Left)
Rolling Mill for Crude Dry Chemigum, Synthetic Rubber Made by Goodyear Tire and Rubber Company



(Right)
Chemigum Emerging from a Dryer Which Removes Water Collectted during the Process of Coagulation

* * *

The work of Tilden was carried on by Hofmann (*11*) in Germany. In connection with Coutelle (*1*), Hofmann obtained the earliest German patent on the production of synthetic rubber by the heat polymerization of isoprene with or without polymerizing agents.

In 1910 Matthews and Strange (*15*) in England and Harries (*9*) in Germany reported almost simultaneously that metallic sodium catalyzes the polymerization of isoprene to synthetic rubber. The claims of these early patents specify subjecting isoprene to metals of the alkali or alkaline earth groups, their mixtures, alloys, or amalgams in such a manner that the metals are wholly or largely in contact with the vapor of the hydrocarbon.

The story of synthetic rubber manufacture in Germany during the First World War is well known. A derivative of butadiene (2,3-dimethylbutadiene) was polymerized by means of sodium to give methyl rubber. During 1914–18 some 2400 tons were said to have been manufactured. One or two different grades of this type of synthetic rubber were prepared at that time; almost all of the dimethylbutadiene was made from acetone.

After the First World War several attempts were made to carry on the development of synthetic rubber in various laboratories, both in the United States and abroad. It can safely be said that not until it was generally known in the United States that the Germans were again devoting serious attention to the synthetic rubber problem was concerted effort put forth here to produce a good synthetic rubber.

In Italy the polymerization of butadiene and related hydrocarbons by the sodium method has been fairly well developed, and samples received in this country have been of a relatively high quality.

However, only after the general application of the emulsion technique of manufacturing synthetic rubbers did they begin to assume an important role in supplying large quantities of material. One of the first patents on the emulsion polymerization of synthetic rubber was granted to Dinsmore (*5*) in 1929. This was followed in 1930–33 by patents on the emulsion polymerization of butadiene-styrene and butadiene-acrylonitrile mixtures, issued to the German chemists Tschunker and Bock (*21*, *22*), Konrad (*14*), and other investigators in that country. From the basic foundation of these emulsion type copolymers and variations in this technique, our entire picture of synthetic rubber has been built up. Perhaps exceptions to this statement should be made, since the polymerization of Butyl rubber does not follow this technique, and in this case a special method of polymerization has been applied, the exact nature of which has not been publicized.

Latex

There is an outstanding difference in the particle size of natural latex and the synthetic latex of any of the copolymers made by the emulsion processes above referred to. Figure 1 represents natural and synthetic latex, respectively. The synthetic latex, when examined with the ordinary microscope, is of so small a particle size as to be almost invisible. The electron microscope shows the presence of particles, but these particles may be merely aggregations of larger clumps of molecules.

In discussing the difference in particle size with A. R. Kemp, of the Bell Telephone Laboratories, he pointed out that possibly the particle size of the synthetic latex might be directly connected with the physical properties to be obtained from synthetic rubbers. It is common knowledge that the present types of synthetic rubber do not give as good results when vulcanized in pure gum stocks as they do when substantial quantities of carbon black are added.

This brings up the question of whether or not carbon black, being of submicroscopic size, acts as a grinding medium; and whether, upon being milled with the synthetic rubber, it has a pronounced surface effect upon the particles of synthetic latex or acts as a shearing medium to break them down and reveal less highly polymerized rubber in the interior of these small particles. This assumption is based upon the fact that, in milling, the original latex particles are disintegrated; it has long been known that the outer shells of these particles possess a somewhat higher degree of polymerization than the interior of the natural latex particle. Further studies with the ultramicroscope may disclose additional data of value in determining the difference in particle size between natural and synthetic latex and supply the reason for the differences and the possible significance of such variations.

X-Ray Structure of Synthetic Rubber

A considerable amount of attention has been given to the x-ray diagrams of various synthetic rubbers, but it has not been possible to apply the results of such studies directly to the process of improving the copolymer types of synthetic rubber now under consideration.

The general character of the x-ray diffraction results with synthetic rubbers was discussed in a previous paper (*16*). The copolymers of butadiene and styrene and of butadiene and acrylonitrile are amorphous under all conditions. Polyisobutylene and polychloroprene, on the other hand, develop a crystalline structure upon stretching. Stretched Butyl B rubber shows the same crystalline structure as polyisobutylene. Thiokol has a somewhat crystalline structure, both stretched and unstretched.

In the cases where crystalline structures are obtained, it is evident that the x-ray patterns can be used to secure information on the chain form. They can be used to evaluate in various indirect ways the strength of the intermolecular forces

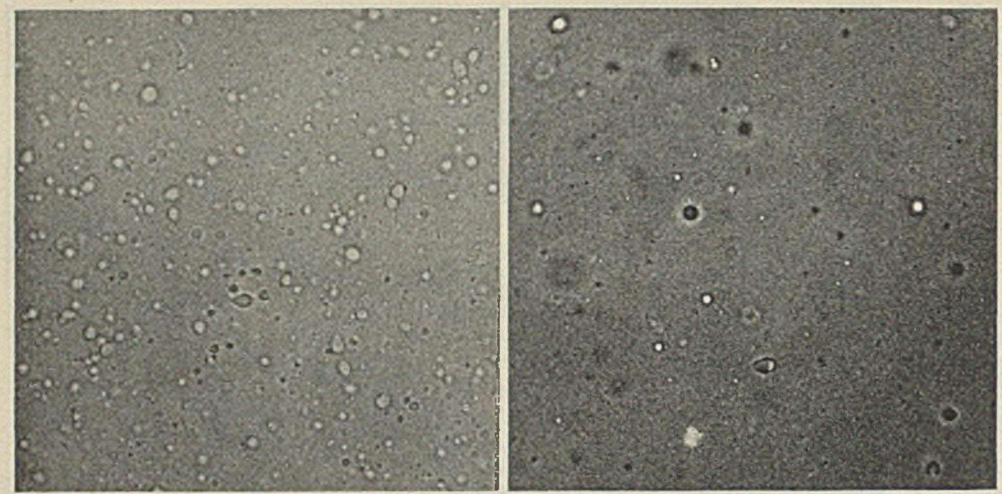


Figure 1. Electron Micrograms of Natural (*left*) and Synthetic (*right*) Latices (X 1300)

and the relations between molecular length, molecular length distribution, and molecular mobility, which in turn finds its reflection in the plastic properties.

The x-ray diffraction results with Butyl B rubber are especially interesting when correlated with stress-strain curves. Figure 2 shows the amorphous pattern for unstretched Butyl rubber and the crystalline pattern which develops upon stretching. Unlike Hevea and GR-S, Butyl rubber does not show very marked improvement in tensile strength due to incorporation of gas black, although typical reinforcement occurs for such properties as abrasion, tear, and modulus. Since the tensile strength is closely connected with the crystallinity at high elongations, x-ray diffraction results might be expected to throw some light on this apparently contradictory result.

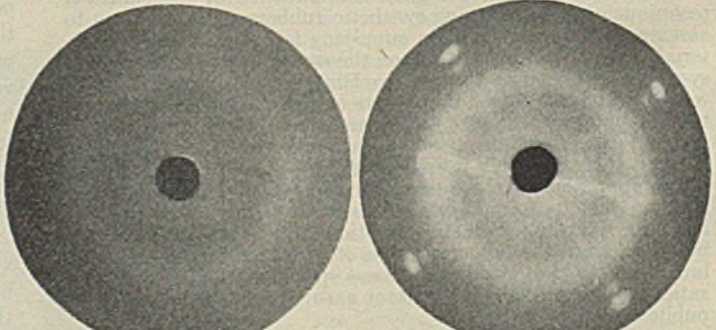
It was found that the crystallization phenomena in loaded and unloaded Butyl rubber stocks were analogous to those with Hevea (7). Evidence of crystallization began to appear at about 500 per cent elongation for the gum stock and at about 200 per cent for a compound loaded with 60 parts of gas black. Spreading of the diffraction spots into longer arcs for the loaded stock indicated that the alignment of the crystallites in the direction of stretching was less perfect than for the gum stock. Thus, although higher elongations are required for crystallization in Butyl rubber as compared to Hevea, the effect of carbon black on the patterns is similar.

The stress-strain curves in Figure 3 indicate that there may be a simple explanation of the apparent lack of tensile reinforcement. Between 800 and 900 per cent elongation, the stress-strain curve for the Butyl rubber gum stock rises abruptly, reflecting the onset of a highly crystalline structure which is also indicated by the sharp, intense diffraction pattern. The fact that crystallization sets in at higher elongations when the molecules are already well aligned probably contributes to this perfection, as does the simple and regular chain form of the Butyl rubber molecules. Thus, in the gum stock, the ultimate tensile strength of the material is nearly realized due to its own crystal reinforcement. The black can contribute little further in this respect, and its interference in the alignment of the crystallites may actually work against a higher tensile strength. For Hevea, on the other hand, the onset of crystallization is more gradual and the resulting structure less regular. The black can furnish effective anchorage points to prevent failure from starting between the crystallites, and a large improvement in tensile strength results.

For copolymers, which invariably show amorphous structures, the use of x-ray diffraction as a means for investigating the molecular structure is severely limited. It is true that, even in the case of liquids, the x-rays reveal a fundamental type of molecular structure which consists of a statistical space distribution of neighboring molecules. The only information to be obtained directly from the analysis of such patterns is the average distance of atom neighbors. A comparative study of these amorphous patterns for copolymers has been found to yield some interesting results, even without carrying through the involved mathematical analysis required for their exact interpretation.

The patterns shown in Figures 4, 5, and 6 were taken by J. E. Field, using strictly monochromatic CuKα radiation securedby reflection of the x-ray beam from a rock salt crystal.

The polybutadiene pattern (Figure 4) is a broad halo, indicating an amorphous structure. In contrast, the pattern for polyacrylonitrile shows a sharp diffraction ring, proving the existence of small crystalline regions in random orientation. The pattern for polystyrene indicates that, in addition to the usual halo for liquids, there is an inner ring corresponding to a larger molecular spacing. Thus, these three polymers give patterns which are readily distinguishable. We wished to know to what extent these structures occurred in copolymers.



Unstretched Stretcned

Figure 2. X-Ray Patterns of Butyl Rubber

Figure 5 shows the pattern for an emulsion copolymer with a 75–25 starting ratio of butadiene to acrylonitrile. This appears to be the pattern of a homogeneous structure. When the starting ratio was 50–50, the crystalline ring of polyacrylonitrile became plainly evident. Two conclusions can be drawn. Either some or all of the acrylonitrile units of the chain molecules were sufficiently numerous and flexible to come within their normal range of action and assume the same

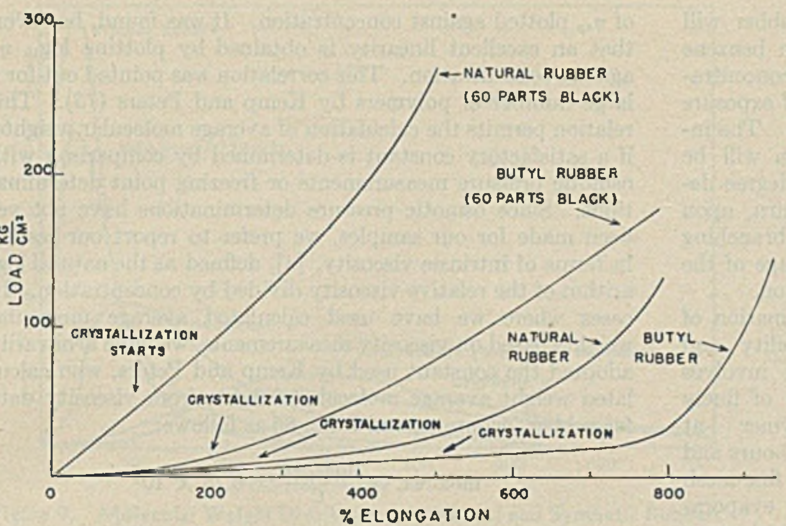


Figure 3. Stress-Strain Curves

structural relations as for polyacrylonitrile, or the polymer was not entirely a true copolymer and some polyacrylonitrile was formed during the polymerization.

The pattern from a copolymer made with a 50–50 starting ratio of butadiene to styrene (Figure 5) does not show any evidence of the inner polystyrene ring and hence of the polystyrene structure. The presence of the inner polystyrene ring could not be detected until the styrene component was about 70 per cent. Estimating from the completeness of the copolymerizing reaction, this starting ratio was also the composition of the product. Since the molecular weight of styrene is about twice that of butadiene, this is approximately the composition for which the number of molecules of each component would be the same.

Control patterns were run for products coagulated from mixtures of polybutadiene and polystyrene latices. Thirty per cent of polystyrene could be readily detected by the presence of the inner ring. Although this method of x-ray analysis is not so sensitive as might be desired, it shows that for copolymerization of either acrylonitrile or styrene with butadiene, the structure of polyacrylonitrile and of polystyrene, respectively, tends to make its appearance when the number of molecules approximates the number of butadiene molecules.

In an experiment with a three-component system, with starting ratios of 50, 25, and 25 of butadiene, acrylonitrile, and styrene, respectively, the pattern of Figure 6 was obtained. The presence of polystyrene structure is plainly shown by the inner halo, indicating a different character of reaction for this system as compared to the two-component system.

To what feature of the polystyrene structure the inner ring is related is not definitely known. Katz (*12*) ascribed it to a large spacing of parallel molecular chains brought about by the attached benzene rings. To test this idea, we determined the effect of the polystyrene temperature on the relative intensity of the inner and outer halos of the polystyrene pattern. The results are shown in the microphotometer curves of Figure 7. Curiously enough, the pattern does not approach that of monomeric styrene (a single halo) as the temperature is raised; on the contrary, the relative intensity of the inner ring is increased. At 195° C., for which a microphotometer curve is shown, the polymer had actually melted and become a viscous fluid. Thus the inner ring represents some statistical molecular configuration which is not necessarily associated with the solid state.

Molecular Weight Determinations of Synthetic Rubbers

The molecular weight of the butadiene copolymer with styrene was determined and compared with that of natural rubber, obtained by the same method, in the hope that this information will be of value in the preparation of an improved type of synthetic rubber. Viscosity measurements, described by Staudinger (*18*), were used for this purpose. The molecular weight of the butadiene copolymer was also determined by the ultracentrifuge method.

Benzene Solublity and Swelling Indices. One of the readily observed differences between synthetic butadiene rubbers is their degree of solubility and swelling in solvents, such as benzene, which are good solvents for the polymer if no considerable degree of cross linking has taken place. If the degree of polymerization, reaction temperature, or other conditions have caused appreciable cross linkage, however, a por-

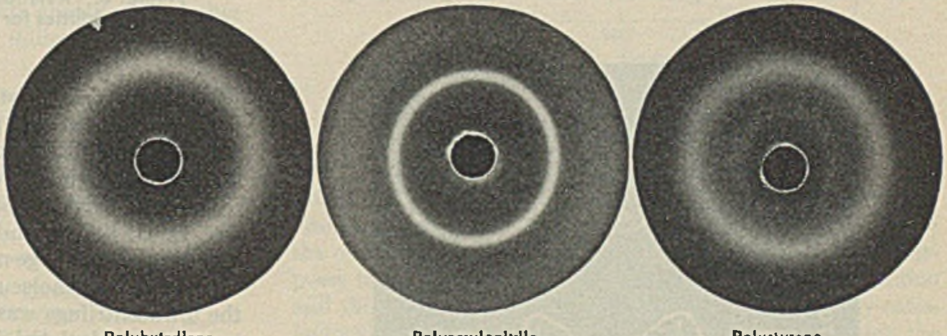

Polybutadiene Polyacrylonitrile Polystyrene

Figure 4. X-Ray Patterns of Polymers

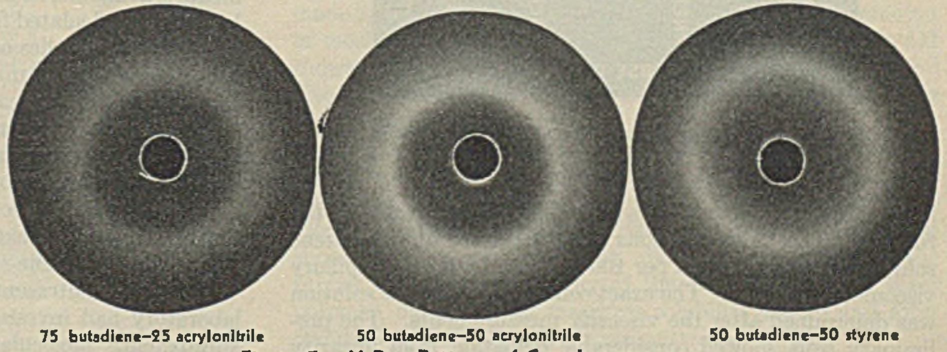

75 butadiene–25 acrylonitrile 50 butadiene–50 acrylonitrile 50 butadiene–50 styrene

Figure 5. X-Ray Patterns of Copolymers

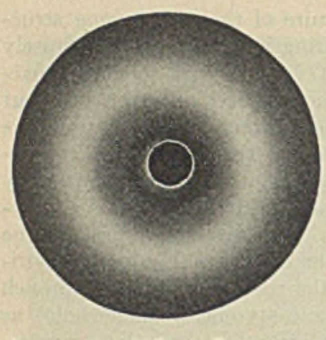


Figure 6. X-Ray Pattern of 50 Butadiene–25 Acrylonitrile–25 Styrene

tion of the rubber will be insoluble in benzene regardless of concentration or time of exposure to the solvent. The insoluble portion will be swollen to a degree dependent, in turn, upon the degree of branching and cross linkage of the insoluble fraction.

The determination of benzene solubility and swelling index involves the extraction of finely divided polymer at 35° C. for 16 hours and separation of the sol and gel phases with a fine-mesh Monel screen. The solubility is determined by evaporation of an aliquot portion of the filtrate and is expressed as per cent of the original rubber soluble in benzene.

The swelling index is defined as

$$\frac{\text{cc. of solution retained by swollen gel}}{\text{grams undissolved rubber}}$$

and is calculated by subtracting from the original volume of the solvent the volume of the filtrate and dividing by the weight of undissolved polymer.

The swelling indices were determined for a large number of butadiene-styrene rubbers of varying benzene solubilities. A good correlation was found for these values as Figure 8 shows. As would be expected, the insoluble portions of highly insoluble rubbers are less swollen than the insoluble fractions of rubbers which are almost completely benzene soluble. The correlation of these values of swelling indices and benzene solubilities has been close enough so that the swelling index is no longer measured.

VISCOSITY MEASUREMENTS AND CALCULATED AVERAGE MOLECULAR WEIGHTS. Viscosity measurements were made of the benzene-soluble portions of butadiene-styrene polymers in an attempt to determine average molecular weights of the rubbers. The determinations were made in dilute benzene solution (0.1 to 0.3 gram per 100 cc.) in an Ostwald capillary viscometer at 25° C. The exact concentration of the solution was determined after the viscosity measurements. The preliminary tests showed considerable deviation from linearity of η_{sp} plotted against concentration. It was found, however, that an excellent linearity is obtained by plotting $\log_{10} \eta_R$ against concentration. This correlation was pointed out for a large number of polymers by Kemp and Peters (*13*). This relation permits the calculation of average molecular weights, if a satisfactory constant is determined by comparison with osmotic pressure measurements or freezing point determinations. Since osmotic pressure determinations have not yet been made for our samples, we prefer to report our results in terms of intrinsic viscosity, $[\eta]$, defined as the natural logarithm of the relative viscosity divided by concentration. In cases where we have used calculated average molecular weights based on viscosity measurements, we have arbitrarily adopted the constant used by Kemp and Peters, who calculated weight average molecular weights from viscosity data for rubber, neoprene, and Buna 85 as follows:

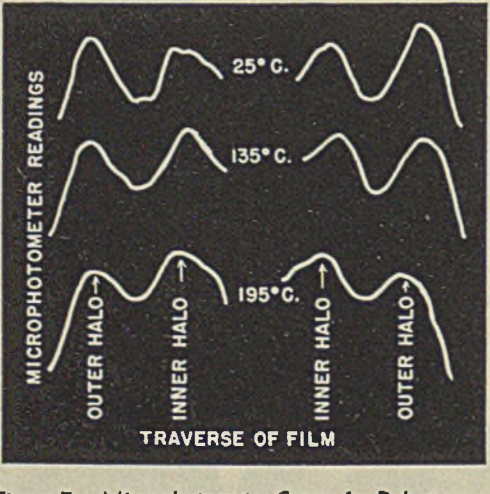


Figure 7. Microphotometer Curves for Polystyrene

$$\text{mol. wt.} = \frac{\log_{10} \eta_R}{C} \times 0.75 \times 10^4$$

where C is expressed in unit moles per liter. Their constant was based on cryoscopic measurements for various fractions of natural rubber. Although its use for the synthetics is not rigidly justified, the values used in our work serve the purpose of expressing relative molecular weights. Calculated on this basis, the average molecular weights for completely benzene-soluble butadiene-styrene rubber of good quality are in the range 40 to 50,000.

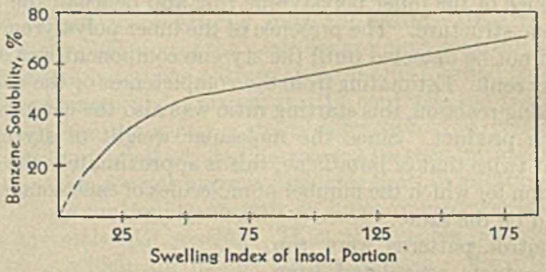


Figure 8. Relation of Swelling Indices to Benzene Solubilities for 75 Butadiene–25 Styrene Rubber

A sample of completely benzene-soluble butadiene-styrene (75–25) made in our pilot plant was checked by viscosity measurements and then submitted to the laboratories of E. I. du Pont de Nemours & Company, Inc., for ultracentrifuge tests. Through the courtesy of Cole Coolidge, G. D. Patterson, E. D. Bailey, and J. B. Nichols, molecular weight distribution and average molecular weights were obtained.

The average molecular weight found for this sample by the ultracentrifuge was 92,500. This value is approximately twice that calculated from relative viscosity determinations using the formula and constant referred to above. This value was 44,000. Until a check against osmotic pressure measurements is available, no absolute value is attached to the molecular weights calculated from viscosity values. Since the Staudinger relation applies only to linear molecules, its application to a polymer which may be considerably branched would be expected to give low calculated molecular weights.

MOLECULAR WEIGHT DISTRIBUTION. The molecular weight distribution obtained at the du Pont laboratories by ultracentrifuging a chloroform solution of butadiene-styrene rubber is shown in Figures 9 and 10. This particular sample is somewhat richer in extremely low-molecular-weight material than other butadiene-styrene rubbers tested.

Before the ultracentrifuge data had been obtained, our laboratory had investigated available methods of obtaining approximate molecular weight distributions. Our object

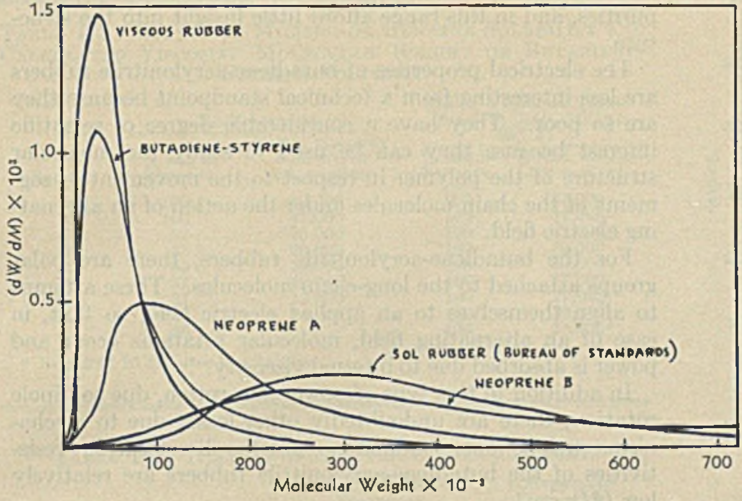


Figure 9. Molecular Weight Distributions of Natural and Synthetic Rubbers

was not to obtain precise distribution curves, but to develop a rapid convenient procedure which would permit a study of the changes in relative amounts of low-, intermediate-, and high-viscosity fractions with change of polymerization conditions and of mechanical treatment of the rubber.

The following method was adopted: A sample is extracted (by the same method described for benzene solubilities) with a poor solvent, and the amount and relative viscosity of the extracted polymer are determined. This extraction is then repeated on the undissolved polymer, using progressively richer blends of the poor solvent with a good solvent. The solvents for the butadiene-styrene polymers are petroleum ether (30–60° C.) and benzene. As Table I shows, it is sometimes necessary to use alcohol–petroleum ether blends for the first fractions if the sample is especially rich in low-molecular-weight polymer. The data for polymer A in Table I and Figure 11 indicate the results of our fractionation of a portion of the batch from which the sample submitted to du Pont was taken. Similar fractional extraction data are shown for other butadiene-styrene rubber samples to indicate the different types of distribution obtained.

In the cases where high-viscosity fractions were found, no fraction of intermediate average viscosity was found. These data do not indicate that the intermediate material was absent, but that the solvent blends, sufficiently rich in benzene to dissolve the intermediate portion, also extract the very highest. That is, the sensitivity of the fractionation is less than in the low-molecular-weight range. Since this method of fractionation gives cuts which are still quite heterogeneous, the data are to be used only for comparative purposes. The separation is not sufficiently precise to warrant drawing complete distribution curves.

Table I. Successive Fractional Extractions of Butadiene-Styrene Polymers

Polymer	Solvent Blend[a], Vol. %		% of Total Rubber Hydrocarbon	Intrinsic Viscosity	Calcd. Viscosity Mol. Wt.
A (9% nonrubber)	80/20	P. E./EtOH	5.1	0.33	6,500
	100	P. E.	15 2	0.46	9,000
	95/5	P. E./benzene	26.3	0.92	18,000
	93/7	P. E./benzene	13.0	1.53	30,000
	91/9	P. E./benzene	24.4	3.92	77,000
	90/10	P. E./benzene	14.6	4.85	95,000
B (6% nonrubber), 50% insoluble	100	P. E.	7.8	0.42	8,000
	95/5	P. E./benzene	10.8	0.56	11,000
	91/9	P. E./benzene	16.1	1.23	24,000
	89/11	P. E./benzene	9.9	1.75	34,000
	86/14	P. E./benzene	5.0	3.74	73,500
C (9% nonrubber)	100	P. E.	7.7	0.49	9,500
	95/5	P. E./benzene	9.6	0.52	10,000
	91/9	P. E./benzene	29.3	1.28	25,000
	89/11	P. E./benzene	11.1	2.47	48,000
	86.5/13.5	P. E./benzene	29.5	6.05	118,500
	38/62	P. E./benzene	12.0	6.24	122,000

[a] P. E. = Petroleum ether.

Since the successive extraction of the polymer samples by several solvent blends is time consuming (about a week for each complete determination), a rapid method has been tested by which a fractionation is completed in less than 24 hours. It had been observed that the viscosities for the fractions of butadiene-styrene rubbers were additive, and that good agreement was found between the intrinsic viscosity (or calculated molecular weight) calculated from the amount and viscosity of the separate fractions, and the value obtained by a viscosity determination of the solution of the entire unfractionated rubber. This relation suggested fractional extraction by the following method: Several duplicate samples of the rubber are extracted for 16 hours with a series of petroleum ether–benzene blends of the compositions used in successive extractions. The amount and viscosity of the rubber extracted by each blend is determined, and the amounts and viscosities of the individual fractions calculated from those of the combined fractions are actually measured. For our purposes the agreement between this "simultaneous" extraction and the more valid "successive" extraction was highly satisfactory. The agreement is shown in Table II in which the various fractions are combined as shown.

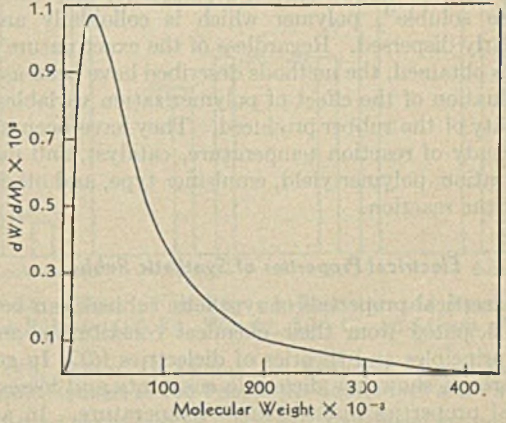


Figure 10. Molecular Weight Distribution of Butadiene-Styrene Polymer

Effect of Milling on Solubility and Viscosity Molecular Weight. The tests of solubility and viscosity must be made upon a sample of known history in regard to the amount of mechanical working the sample has received. Table III shows the effect of milling upon the benzene solubility and viscosity of butadiene-styrene rubbers of varying solubilities in the unmilled condition.

All samples tested could be milled to complete solubility, but the viscosity of the rubber after milling to complete solubility is lowest for polymers of low original solubility. The viscosity of rubbers originally 100 per cent soluble is likewise shown to be lowered by milling. Since any application of the rubber must involve milling of the crumb or massed sheet polymer, our test now measures solubility before and after standardized milling and the viscosity after milling.

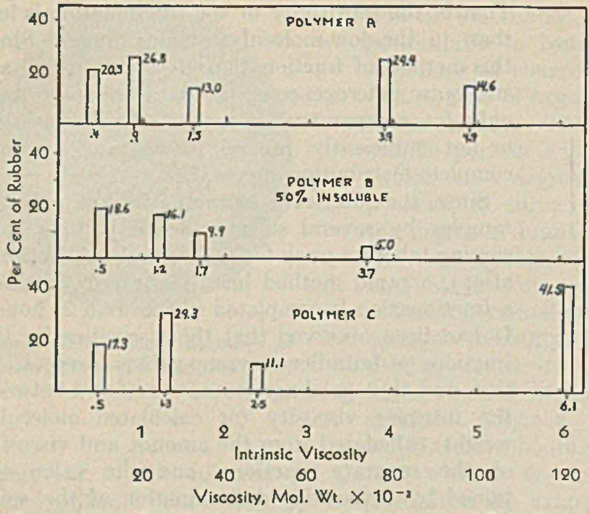


Figure 11. Results of Fractional Extraction of Butadiene-Styrene Rubbers

Interpretation of Tests. It has recently been pointed out by W. O. Baker of the Bell Telephone Laboratories that the described method of determining polymer solubilities (which has been used in several laboratories) may include as "benzene soluble", polymer which is colloidally and not molecularly dispersed. Regardless of the exact nature of the solutions obtained, the methods described have been useful in the evaluation of the effect of polymerization variables upon the quality of the rubber produced. They have been applied to the study of reaction temperature, catalyst, and modifier concentration, polymer yield, emulsifier type, and other variables of the reaction.

Electrical Properties of Synthetic Rubber

The electrical properties of synthetic rubbers can be fairly well anticipated from their chemical constitution and the known principles and theories of dielectrics (*6*). In general, hydrocarbons show low dielectric constants and losses, with electrical properties insensitive to temperature. In accordance with this, butadiene-styrene rubbers, polyisobutylene, and Butyl rubber have excellent properties as electrical insulators. Any electric power absorption observed for these uncompounded rubbers can almost certainly be attributed to traces of impurities or moisture absorption due to impurities. To this extent there is a field of application here for synthetic rubber in which it is not fundamentally at any disadvantage to natural rubber.

For compounded stocks of these hydrocarbon rubbers, the electrical properties will be almost entirely determined by the ingredients which it is found necessary to add to secure desirable physical properties. Since these hydrocarbon rubbers are so inactive electrically, at least for frequencies up to a few megacycles, electrical measurements on them require the highest degree of precision, are influenced by traces of impurities, and in this range afford little insight into the structure.

The electrical properties of butadiene-acrylonitrile rubbers are less interesting from a technical standpoint because they are so poor. They have a considerable degree of scientific interest because they can be used to study the molecular structure of the polymer in respect to the movement of segments of the chain molecules under the action of an alternating electric field.

For the butadiene-acrylonitrile rubbers, there are polar groups attached to the long-chain molecules. These attempt to align themselves to an applied electric field, so that, in case of an alternating field, molecular rotations occur and power is absorbed due to internal viscosity.

In addition to this type of power absorption, due to dipole rotation, there are undoubtedly other losses due to mechanisms such as ionic conduction since the direct-current resistivities of the butadiene-acrylonitrile rubbers are relatively low (*24*).

Table IV gives typical results of electrical measurements on gum stocks of natural rubber, several hydrocarbon synthetic rubbers, and a nitrile rubber. The measurements were made in the Goodyear laboratories by R. B. Stambaugh, using General Radio audio- and radiofrequency bridges.

Table II. Comparison of Successive and Simultaneous Methods of Fractional Extraction of Butadiene-Styrene Polymers

Calcd. Viscosity Mol. Wt.	% of Total Rubber Hydrocarbon	
	Successive method	Simultaneous method
< 12,000	20.3	17.2
12,000–30,000	26.8	30.8
30,000–60,000	13.0	15.9
60,000–85,000	24.4	24.6
> 85,000	14.6	10.9

Comparison of Synthetic Rubbers in Vibration

In a paper from our research laboratories, given before the Society of Automotive Engineers in Detroit in 1941, a method of determining the hysteresis and internal friction of rubber stocks was described. The application of this method to synthetic rubber has been extended to give the comparison between natural rubber and the synthetic rubbers which are under discussion in this paper. The measurement of synthetic rubbers when subjected to a vibratory driving force of known magnitude offers a convenient and accurate method of evaluating the stiffness and resilience for small deformations such as occur in many important applications. The technique has been described (*8*, *16*, *17*).

Although general practice in testing the physical properties of synthetic rubber is to use a test formula containing gas black, it seemed worth while to determine whether vibration

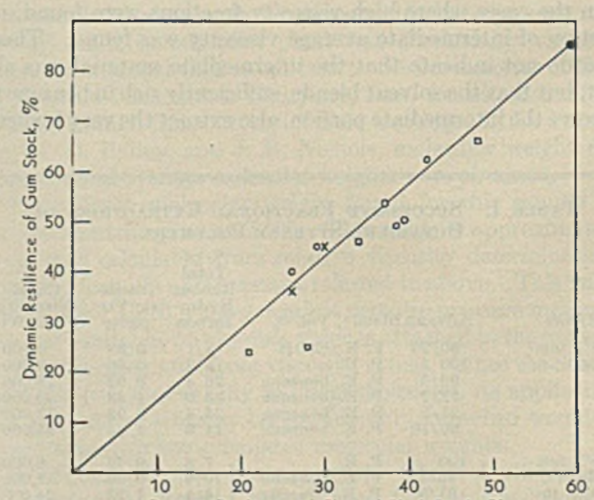


Figure 12. Relation in Dynamic Resilience between Channel Black and Gum Stocks

	Starting Ratio for Polymer	
	Butadiene	Acrylonitrile
□	50	50
○	70	30
	Butadiene	Styrene
×	75	25
●	Natural Rubber	

Table III. Effect of Milling on Benzene Solubility and Calculated Viscosity Molecular Weight of Butadiene-Styrene Polymers

	No Treatment		Milled 5 Min. on Tight-Set 6-In. Lab. Mill at 80° F.	
Sample	% sol. in benzene	Calcd. viscosity mol. wt. of sol. portion	% sol. in benzene	Calcd. viscosity mol. wt.
A	100	50,000	100	37,000
B	100	47,000	100	39,000
C	67	20,000	100	31,000
D	55	20,000	100	39,000
E	59	19,000	100	38,000
F	37	19,000	100	32,000
G	31	15,000	100	27,000
H	43	14,000	100	29,000
I	20	....	100	25,000[a]

[a] Required 15 minutes to solubilize.

Table IV. Results of Electrical Measurements

	1-Kilocycle Frequency		1-Megacycle Frequency	
Type of Rubber	Dielectric constant	Power factor, %	Dielectric constant	Power factor, %
Natural	2.69	0.271	2.52	0.695
Butyl	2.38	0.302	2.20	....
Butadiene-styrene	2.70	0.342	2.49	1.02
Butadiene-acrylonitrile	12.65	5.73	11.0	25.9

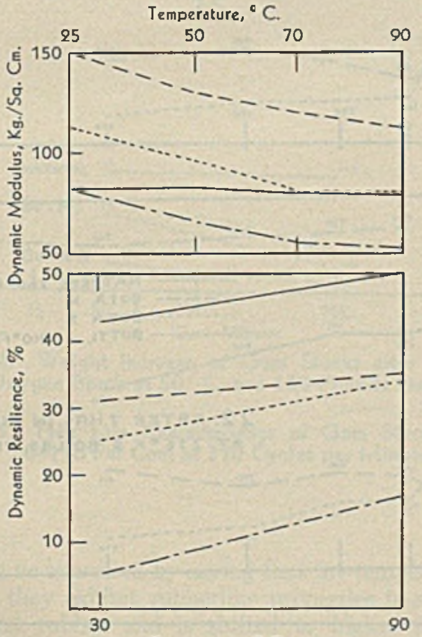
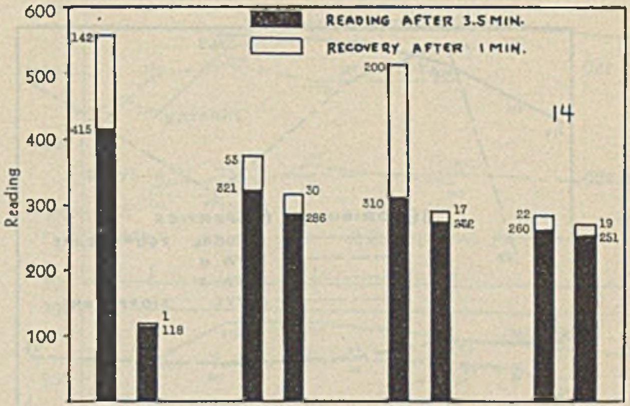


Figure 13. Effect of Temperature on Dynamic Modulus and Dynamic Resilience of Various Channel Black Stocks

——— Natural rubber -------- Buta S
— — — Buta N —·—·— Butyl



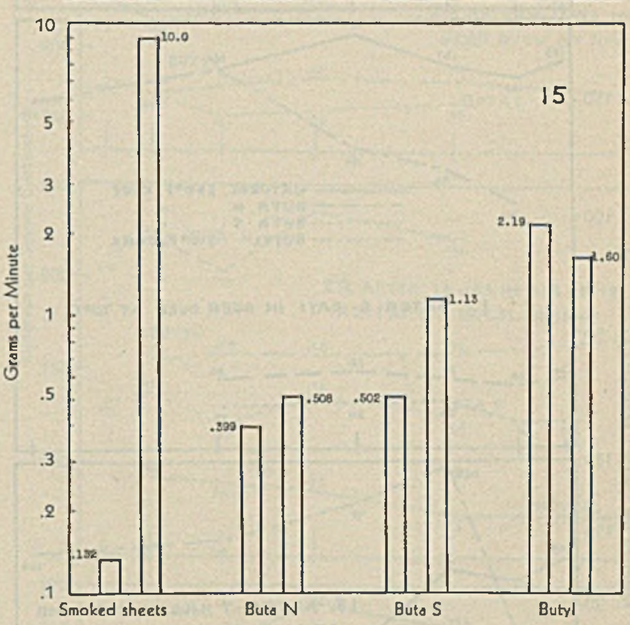


Figure 14. Effect of Milling on Plasticity and Recovery of Various Rubbers (10 Kg. Weight, 70° C., 15-Minute Preheat)

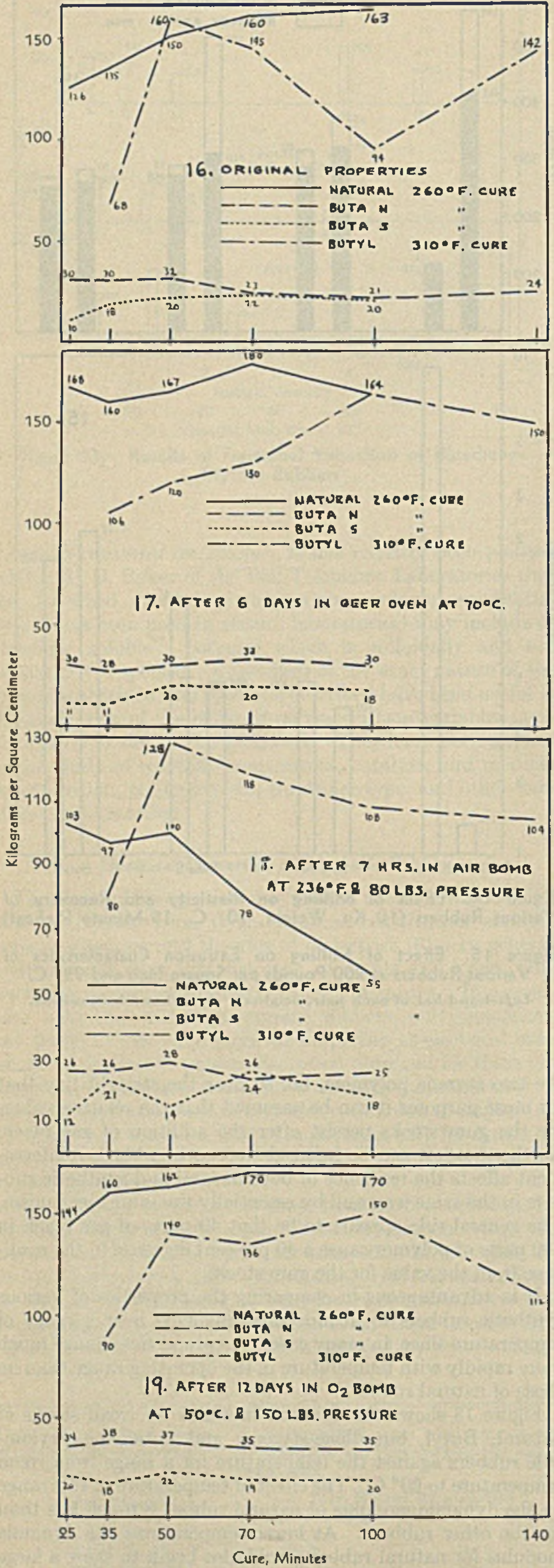
Figure 15. Effect of Milling on Extrusion Characteristics of Various Rubbers at 200 Pounds per Square Inch and 92° C.

Left-hand bar of each pair, original; right-hand bar, milled.

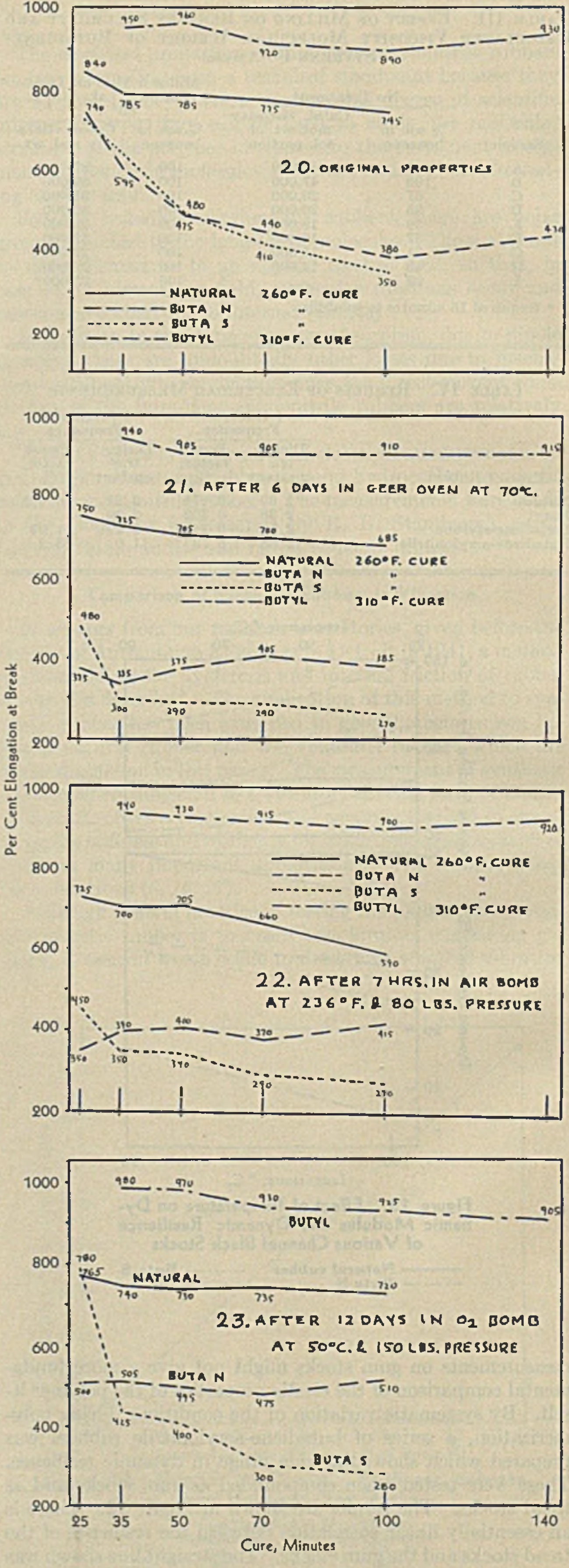
measurements on gum stocks might not give a more fundamental comparison of the elastic properties of the polymer itself. By systematic variation of the conditions during polymerization, a series of butadiene-acrylonitrile rubbers was prepared which showed a wide range in dynamic resilience. These were tested when compounded as gum stocks and as tread stocks. The results are shown in Figure 12. There is an essentially linear correlation between the resilience of the tread stocks and the gum stocks. The straight line shown was drawn between the origin and the point for natural rubber. The points, especially those for the 70/30 nitrile polymers and the two styrene polymers, fall so near the straight line that for most purposes it can be assumed that the relative values for the gum stocks persist after the addition of gas black. Furthermore, it can be inferred that carbon black reinforcement affects the resilience of both natural and synthetic rubbers in the same way and by essentially the same mechanism. The general rule appears to be that 40 parts of gas black in 100 parts of polymer cause a 40 per cent decrease in the resilience from the value for the gum stock.

It is advantageous in comparing the properties of various synthetic rubbers to include measurements over a range of temperature since, in many cases, the properties change much more rapidly with temperature in the operating range than do those of natural rubber.

Figure 13 shows the dynamic modulus for tread stocks of natural, Butyl, butadiene-styrene, and butadiene-acrylonitrile rubbers against the temperature for a range from room temperature to 90° C. The effect of temperature in this range on the dynamic modulus of natural rubber is much less than for the other rubbers. At lower temperatures the dynamic modulus for natural rubber would also begin to show a large temperature dependence. The curves illustrate a fundamental difference between these synthetic rubbers and natural rubber



Figures 16 to 19. Tensile Characteristics of Gum Stocks



Figures 20 to 23. Elongation Characteristics of Gum Stocks

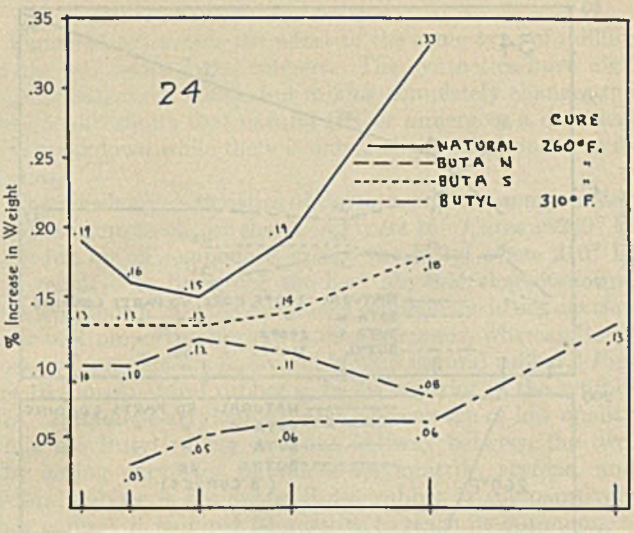


Figure 24. Weight Increase of Gum Stocks after 12 Days in Oxygen Bomb at 50° C. and 150 Pounds Pressure

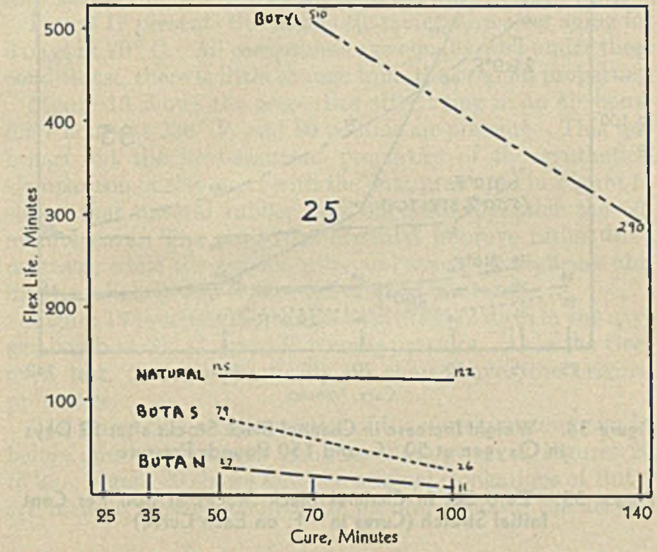
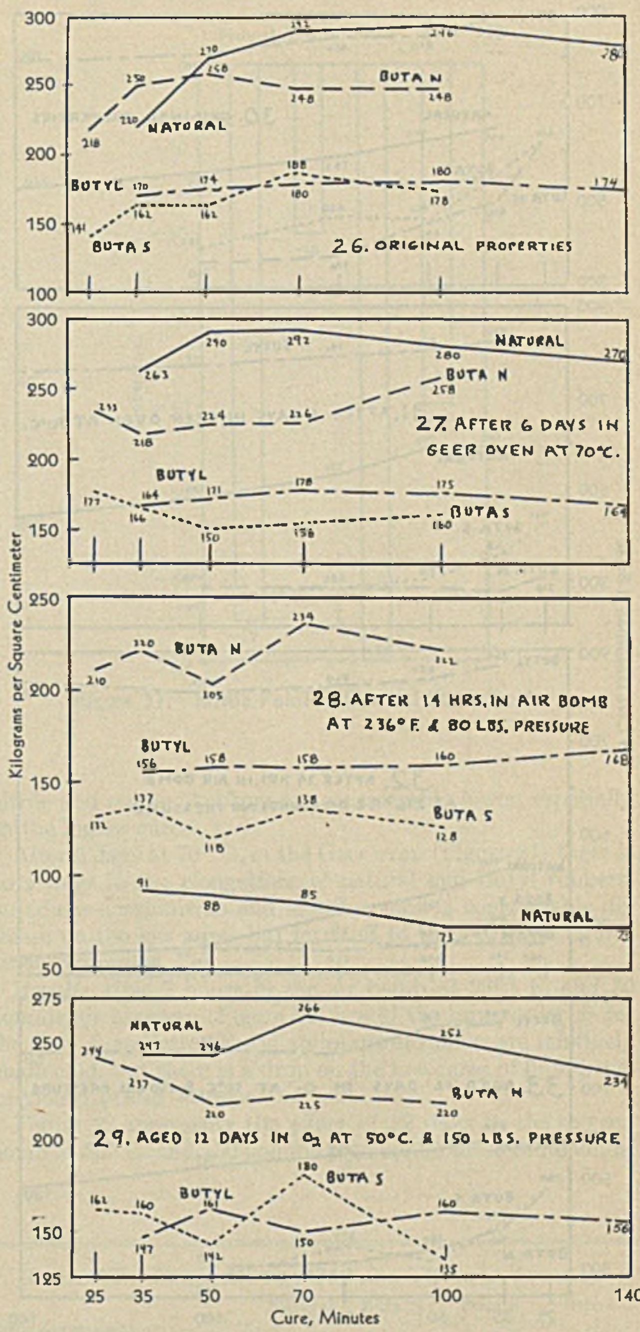


Figure 25. Flex Life Characteristics of Gum Stocks Stretched 0–116 Per Cent at 370 Cycles per Minute



Figures 26–29. Tensile Characteristics of Channel Black Stocks

Natural	260° F. cure	50 parts loading
Buta N	260° F.	50 parts
Buta S	290° F.	50 parts
Butyl	310° F.	60 parts

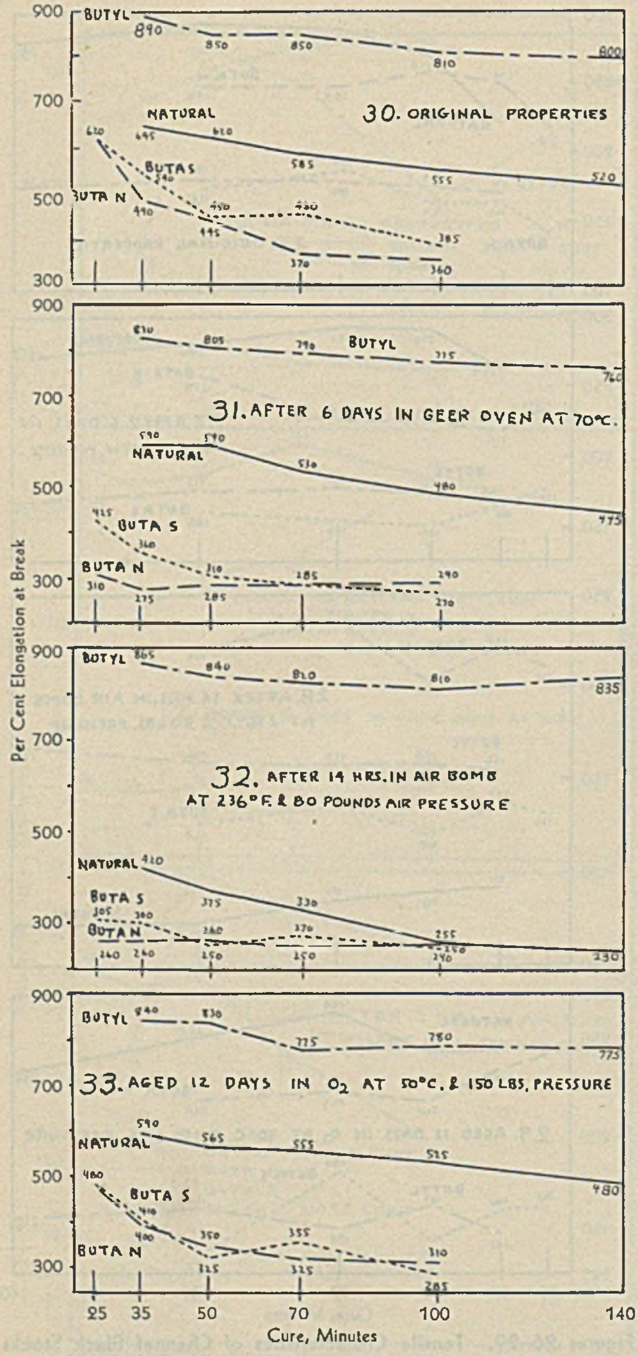
which can be expressed by saying that the temperature range in which they exhibit rubberlike properties is shorter than for natural rubber and is shifted to higher temperature. There are some reasons for supposing that this is analogous to the difference between rubber and gutta-percha, and is related to an essentially *trans* form of the chain molecules for synthetic rubbers as compared to the *cis* form for natural rubber.

Figure 13 shows the dynamic resilience of the same tread stocks *vs.* temperature. The superior resilience of natural rubber is plainly shown. The nitrile and styrene rubbers had about the same resilience, which was considerably lower than for natural rubber. The Butyl rubber stock was lower still.

Measurements were made by a thermocouple of the temperature rise in the center of 1 × 1 × 2 inch blocks of these stocks when subjected to 60-cycle-per-second vibrations of fixed amplitude in the lengthwise direction, using a large flexometer operating on the same principle as the small vibrator employed for the previous measurements. The results are shown in Table V. Again, the superiority of natural rubber is plainly evident. The lower dynamic modulus of Butyl rubber helps counteract the effect of its low resilience in this test so that the observed temperature rise is not so much greater than for the other synthetic rubbers.

Table V. Comparison of Synthetic Rubbers in Flexometer Test (Static Compression, 6 Per Cent)

Type of Rubber	Temp. Rise, ° C., at Amplitude of: $^1/_{16}$ in.	$^3/_{32}$ in.
Natural	49.5	70.5
Butyl	78.5	102.5
Butadiene-acrylonitrile	77.0	96.0
Butadiene-styrene	71.5	90.5



Figures 30–33. Elongation Characteristics of Channel Black Stocks

Natural	260° F. cure	50 parts loading
Buta N	260° F.	50 parts
Buta S	290° F.	50 parts
Butyl	310° F.	60 parts

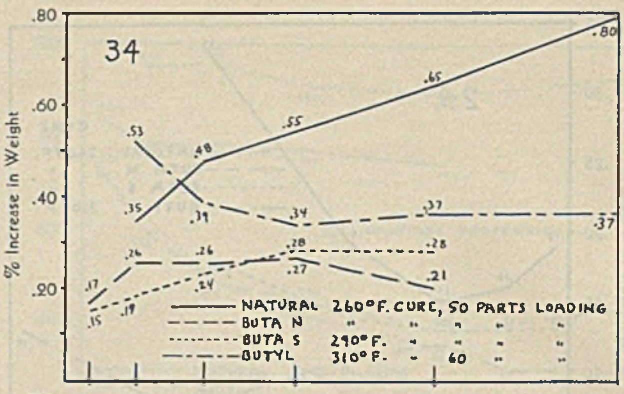


Figure 34. Weight Increase in Channel Black Stocks after 12 Days in Oxygen at 50° C. and 150 Pounds Pressure

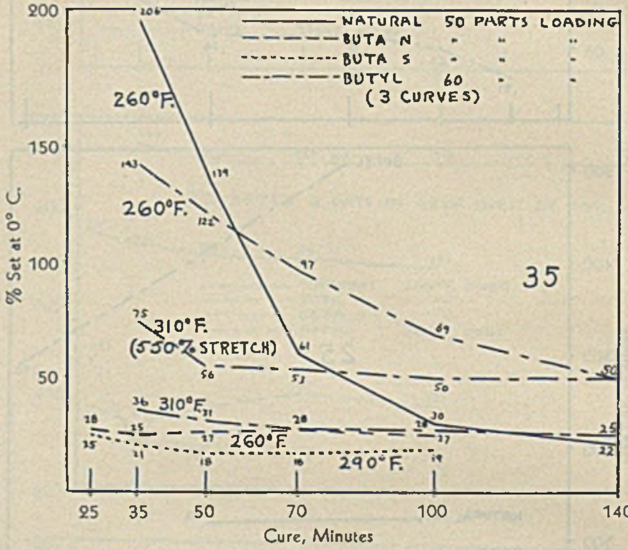


Figure 35. Zero Set in Channel Black Stocks at 300 Per Cent Initial Stretch (Cures in ° F. on Each Curve)

Chemical Unsaturation

Cheyney (4) has set forth his findings regarding chemical unsaturation. Briefly, he found that the unsaturation as measured by the iodine chloride method gave approximately 90 per cent of the amount which would be expected of a straight lineal copolymer, rubber being considered as 100 per cent on the same basis.

Practical Aspects

Turning now from the purely scientific aspects of the synthetic rubber problem to the more practical aspects of commercial utilization of the various types of synthetic rubbers, the comparative physical properties in a standard series of formulas will be discussed.

Formulas for the three synthetic rubbers compared with natural rubber are given in Table VI, both for compounds containing no carbon black and for those containing substantial amounts of black. We do not contend that these formulas represent the maximum properties to be obtained with the synthetic rubbers, since there may be various opinions as to what constitutes the best type of compounding. However, it is believed that the results outlined in the succeeding pages are substantially representative of the general properties of the rubbers under consideration.

Properties of Gum Compounds

Figure 14 represents the effect of milling on the plasticity and recovery of the various rubbers. Two determinations were made: original, after one pass through a tight cold mill; milled, after ten passes through the same mill. While the original plasticity-recovery data show but little difference between the rubbers, the milled data show that the natural rubber becomes much more plasticized than the synthetics. The latter give plasticities of the same order under this treatment; all are considerably stiffer than natural rubber. It should be noted that, while the drop in plasticity between one and ten passes is about 75 per cent for natural rubber, there is only a 10 per cent decrease for the synthetics.

Figure 15 represents the effect of the same type of milling on the extrusion of the rubbers. The synthetics have high original extrusion values, but milling completely changes the picture and shows that natural rubber undergoes a considerable breakdown while there is only a slight effect on the synthetics.

The tensile characteristics of the four rubbers, compounded in a pure gum stock, are shown in Figure 16. Cures at 260° F. were run on all compounds except the Butyl where 310° F. was required to bring out the best physical characteristics. It is well known that the butadiene copolymers do not develop their best properties in pure gum compounds, whereas Butyl does not compare too unfavorably with natural rubber. Figure 16 shows natural rubber to be far superior to the synthetics. Butadiene-acrylonitrile and -styrene are of low quality while the Butyl rubber is about halfway between the two. The curing curve for butadiene-acrylonitrile, styrene, and natural rubber is flat while Butyl rubber is comparatively slow curing; it required 50 minutes to reach its optimum.

Figure 17 presents the tensile characteristics after aging for 6 days at 70° C. All compounds age equally well under these conditions; there is little change from the original properties.

Figure 18 shows the properties after aging in an air bomb for 7 hours at 236° F. and 80 pounds air pressure. This test brings out the heat-resistant properties of the synthetics. Comparison of this chart with the data presented in Figure 16 shows that natural rubber falls off decidedly after the 50-minute cure. The properties of Butyl improve rather than decrease, while the acrylonitrile- and styrene-butadienes also increase slightly and do not fall off over the range.

Figure 19 presents the tensile data after 12 days in the oxygen bomb at 50° C. and 150 pounds pressure. As in the Geer oven test, there is practically no change over the original properties.

The elongation characteristics of the pure gum compounds, before and after various aging tests are given in Figures 20 to 23. Figure 20 shows that the original elongations of Butyl are highest, closely followed by natural rubber; the acrylonitrile and styrene rubbers are considerably lower, especially on the higher cures.

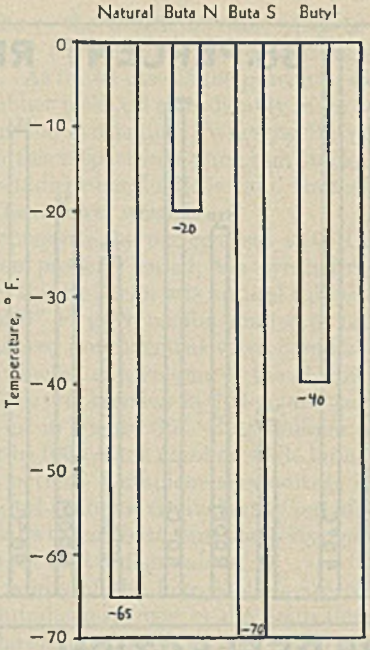


Figure 37. Brittle Point of Channel Black Stocks

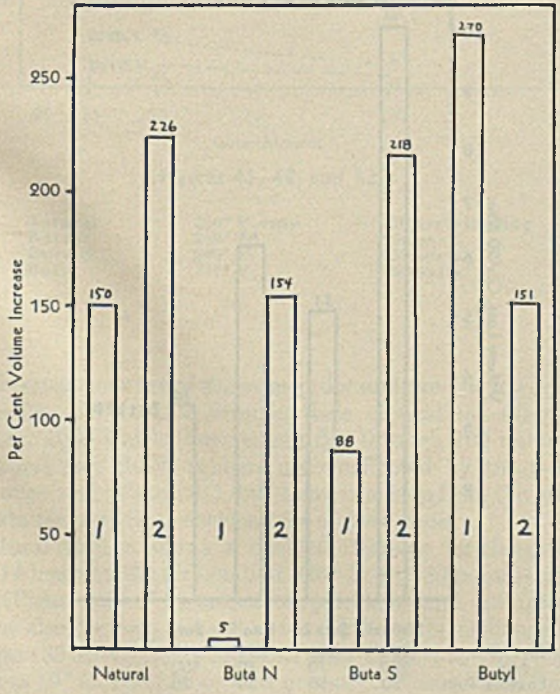


Figure 36. Volume Increase of Channel Black Stocks after 7-Day Swelling in (1) 100-Octane Gas and (2) Benzene

After 6 days at 70° C. in the Geer oven (Figure 21) there is no change in the elongations of natural and Butyl rubbers; butadiene-acrylonitrile and -styrene show a considerable decrease on the low cures but level off to their original figures after 35 minutes.

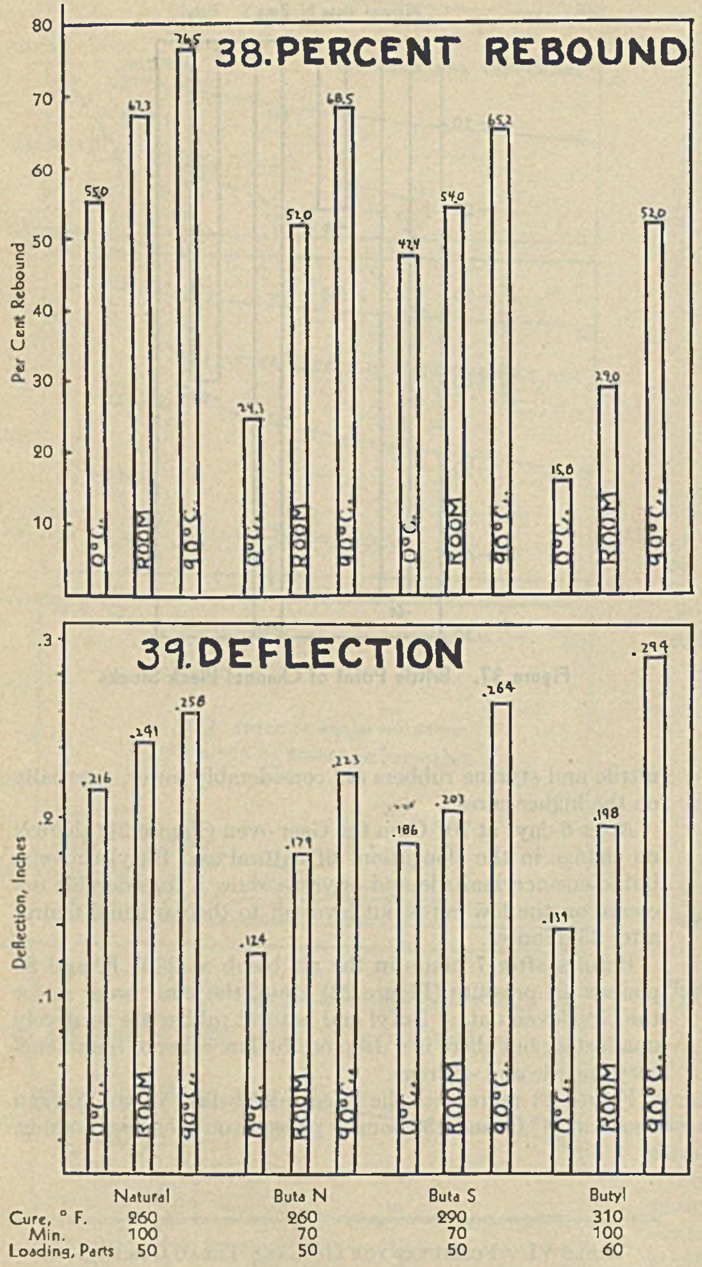
Results after 7 hours in the air bomb at 236° F. and 80 pounds air pressure (Figure 22) are of the same order as for the Geer oven data. Butyl and natural rubber are relatively unaffected, but there is a drop on the low cures of butadiene-acrylonitrile and -styrene.

Figure 23 represents the effect of 12 days in the oxygen bomb at 50° C. and 150 pounds pressure on these compounds.

Table VI. Formulas for Gum and Tread Compounds

	Natural	Buta N	Buta S	Butyl
Gum compounds				
Smoked sheets	100.0	....	....	....
Buna N	.....	100.0	....	....
Buna S	.....	....	100.0	....
Butyl B	.....	....	....	100.0
Captax	0.5	1.0	1.0	....
Tuads	.....	....	....	1.0
Sulfur	3.0	2.0	2.0	1.5[a]
Zinc oxide	5.0	5.0	5.0	5.0[a]
Stearic acid	1.0	1.0	1.0	3.0
Phenyl-α-naphthylamine	.....	1.5[a]	1.5[a]	....
Phenyl-β-naphthylamine	.....	1.5[a]	1.5[a]	....
	109.5	112.0	112.0	110.5
Tread compounds				
Smoked sheets	100.0	....	....	....
Buna N	.....	100.0	....	....
Buna S	.....	....	100.0	....
Butyl B	.....	....	....	100.0
Captax	1.25	1.5	1.5	....
Tuads	.....	....	....	1.0
Sulfur	3.0	2.0	2.0	1.5[a]
Zinc oxide	5.0	5.0	5.0	5.0[a]
Channel black	50.0	50.0	50.0	60.0
Stearic acid	3.0	2.0	2.0	3.0
Phenyl-α-naphthylamine	.....	1.5[a]	1.5[a]	....
Phenyl-β-naphthylamine	1.0	1.5[a]	1.5[a]	....
Pine tar	3.0	....	....	....
Barrett No. 10	.....	3.0	3.0	....
Medium process oil	.....	....	....	3.0
	166.25	166.5	166.5	173.5

[a] Included in the polymer.



Figures 38 and 39. Rebound and Deflection of Channel Black Stocks

There is no change in natural, Butyl, and butadiene-styrene rubbers over the originals, while butadiene-acrylonitrile shows an increase in elongation on the high cures.

Figure 24 represents the weight increase by the four gum stocks after 12 days in the oxygen bomb at 50° C. and 150 pounds pressure. Natural rubber absorbs considerably more weight, due to oxidation under the conditions of test, than any of the synthetics. Of the latter, Butyl rubber is least affected.

Figure 25 shows the relative flexing of the natural and synthetic rubbers in a pure gum stock. The standard punched-hole flexing test was used. This was run at 0–116 per cent stretch at the rate of 370 cycles per minute. Although falling off considerably over the range, Butyl rubber is still outstanding as compared to the others of this group. Natural rubber is superior to the butadiene-acrylonitrile and -styrene, both of which give poor results.

Properties of Tread Compounds

Thus far we have considered the rubbers in pure gum compounds (that is, without loading). The following data show the effects of channel black loading on the rubbers. Original data for channel black loaded stocks are presented in Figure 26. Butyl and butadiene-styrene are of the same order and give lower results than butadiene-acrylonitrile and natural rubber, the latter of which is slightly higher. All compounds have approximately the same rate of cure and, after the optimum is reached, remain flat curing over the range.

Comparison of Figures 26 and 16 illustrates the effect of channel black in these synthetics. Butadiene-acrylonitrile and -styrene and Butyl rubber show a large increase in tensile, and the Butyl range of cures is smoothed out. There is some increase in the tensile of natural rubber but it is not nearly so great as for the synthetics.

Tensile aging data for the channel black loadings are presented on Figures 27, 28, and 29. Figure 27 represents the Geer oven aging for 6 days at 70° C. It shows no great change for any of the rubbers over the originals.

Figure 28 presents data on air bomb aging, run for 14 hours at 236° F. and 80 pounds pressure. Natural rubber has decreased considerably over the originals, while Butyl and butadiene-acrylonitrile show increases. Butadiene-styrene is unchanged.

All the rubbers decrease correspondingly in tensile after 12 days in the oxygen bomb at 50° C. and 150 pounds pressure (Figure 29).

Original and aging characteristics of the elongations on the channel black loadings are given in Figures 30 to 33. The original data on Figure 30 show Butyl to have the highest elongation, followed by natural rubber. Both of them are comparatively flat over the range. Butadiene-acrylonitrile and

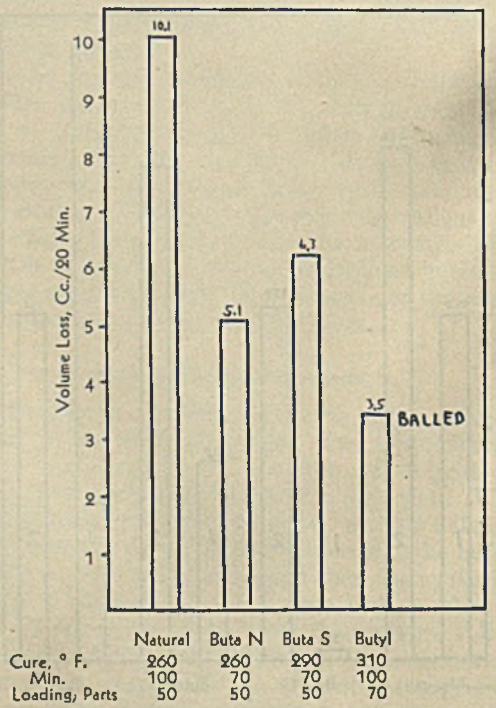
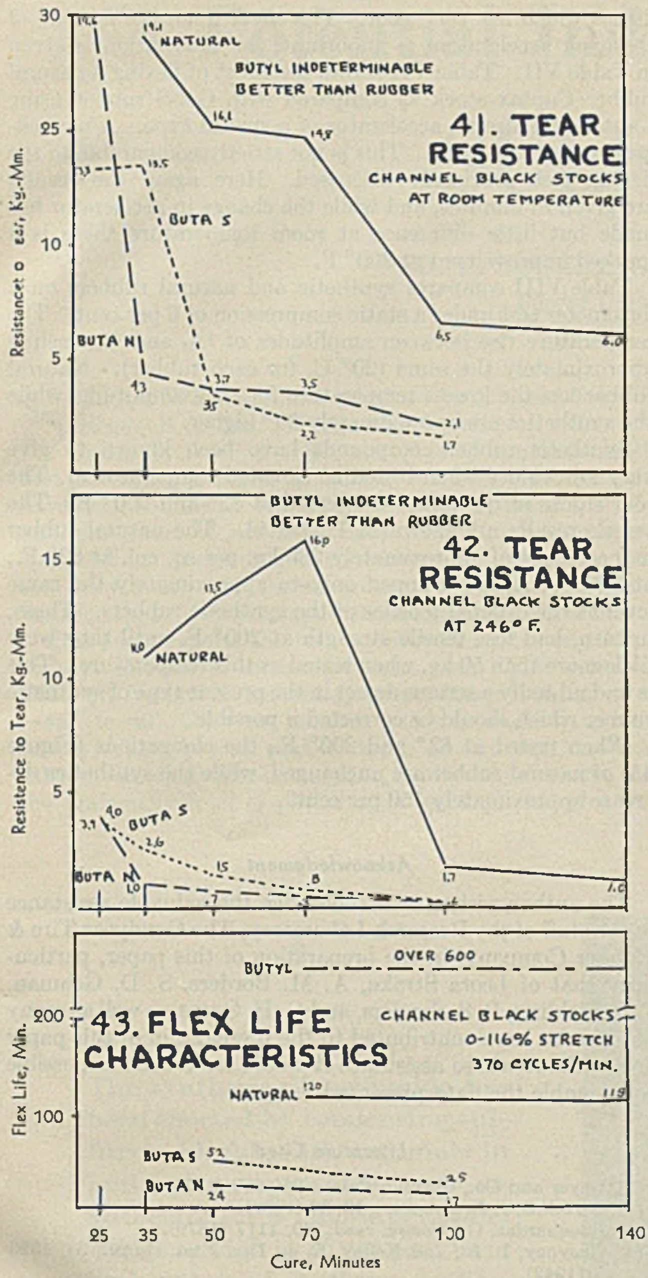


Figure 40. Angle Abrasion of Channel Black Stocks



Figures 41, 42, and 43

Natural	**260° F. cure**	**50 parts loading**
Buta N	**260° F.**	**50 parts**
Buta S	**290° F.**	**50 parts**
Butyl	**310° F.**	**60 parts**

butadiene-styrene are of the same order and are the lowest of this series. There is a drop in their elongations after 25 minutes, after which they remain flat through 100 minutes.

Natural and Butyl rubbers are unaffected by the 6-day Geer oven test (Figure 31), but there is a drop from the original data for butadiene-acrylonitrile and -styrene.

Natural rubber shows a decided decrease in elongation after 14 hours in the air bomb at 236° F. and 80 pounds pressure (Figure 32). Butadiene-acrylonitrile and butadiene-styrene also decrease but not so much; Butyl is unchanged.

Figure 33 shows the elongations after 12 days in the oxygen bomb at 50° C. and 150 pounds pressure. Natural and Butyl rubbers are unaffected, while there is a slight decrease in acrylonitrile- and styrene-butadienes.

Figure 34 shows the weight increase after 12 days in the oxygen bomb of the channel-black-loaded rubbers over a range of cures. As in the case of the pure gum stocks (Figure 24), natural rubber picks up considerably more weight due to oxidation than the synthetics. Whereas Butyl rubber was outstanding in this respect in a pure gum stock, it is now replaced by butadiene-acrylonitrile and butadiene-styrene, both of which have lower weights.

Figure 35 represents the per cent set at 0° C. of the four rubbers. When properly cured, the synthetics were much less affected by this test than was natural rubber Butyl rubber cured at 260° F. gave results similar to natural rubber but showed marked improvement when cured at 310° F.

The per cent increase in volume of the channel black compounds after 7-day immersion in 100-octane gasoline and in benzene is given in Figure 36. Butyl rubber is inferior to natural rubber in 100-octane gasoline while butadiene-styrene is 50 per cent better. Butadiene-acrylonitrile is best of the synthetics. Butyl rubber is equivalent to butadiene-acrylonitrile in benzene, whereas both butadiene-styrene and natural rubber give 70 per cent higher values.

The brittle points of the four rubbers are represented in Figure 37. Butadiene-styrene is the equivalent of natural rubber from the standpoint of flexibility, whereas butadiene-acrylonitrile is much less able to withstand low temperatures. Butyl rubber falls midway between the two extremes.

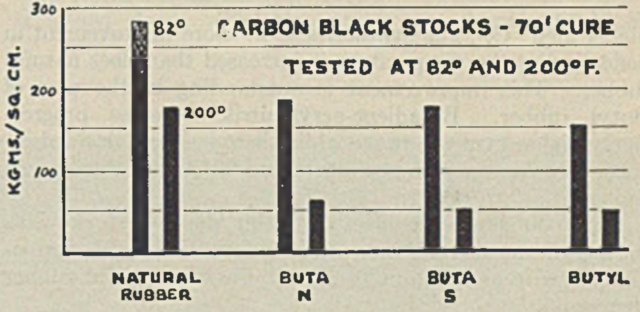


Figure 44. Effect of Temperature on Tensile Strength

Figures 38 and 39 illustrate the rebound and deflection of the channel black stocks at 0° C., room temperature, and 90° C. Natural rubber shows the highest rebound values over the range, and Butyl the lowest. Butadiene-acrylonitrile and butadiene-styrene give equivalent values at room temperature and at 90° C., but the styrene rubber is considerably

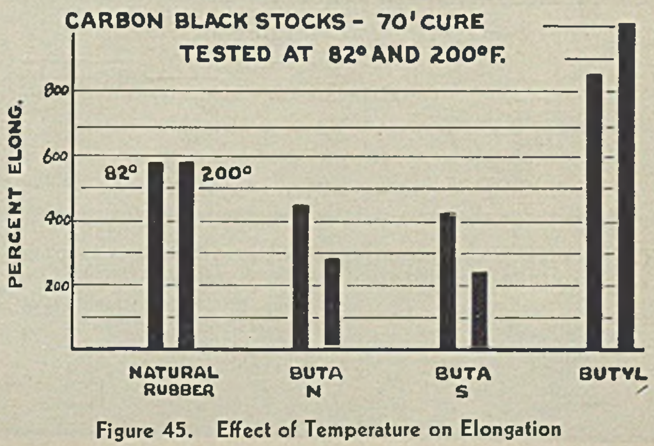
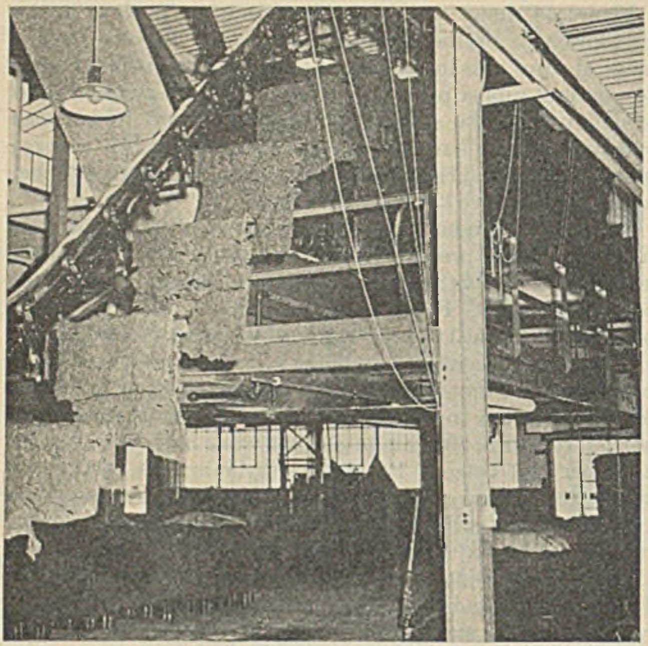


Figure 45. Effect of Temperature on Elongation



Chemigum Leaving the Tanks and Reactors on a Conveyor Line, Ready to Be Converted into Tires for Military Vehicles

higher at 0° C. The synthetics show more improvement in deflection as the temperature is increased than does natural rubber. This improvement is outstanding in the case of Butyl rubber. Butadiene-acrylonitrile becomes progressively higher over the range while there is also a decided increase between room temperature and 90° C. for the styrene rubber.

Figure 40 shows the effect of testing the four stocks with the angle abrasion machine. All of the synthetics are approximately twice as resistant to abrasion as the natural rubber compound.

Figures 41 and 42 illustrate the tear resistance of the channel black stocks at room temperature and at 246° F. In both cases natural rubber is superior to the acrylonitrile and styrene rubbers, and Butyl rubber is superior to natural.

Figure 43 represents the flex life of the channel black compounds as determined by standard punched-strip tests; 370 cycles per minute at 0–116 per cent stretch were run. The superiority of Butyl rubber is outstanding, and natural rubber shows up much better than the acrylonitrile- or styrene-butadienes which are very poor. The effect upon the flex life of changing acceleration is important; an illustration is given in Table VII. Table VII shows the effect of flexing a natural rubber–Captax stock as compared with GR-S rubber using Captax and also an accelerator of a special type. A pierced-groove test was made. This is not strictly comparable to the flexing test previously discussed. Here again the results are given in minutes, and while the change in accelerator has made but little difference at room temperature there is a marked improvement at 200° F.

TABLE VII. COLD *vs.* HOT FLEX TEST

		Flex Life, Min.		
		Natural rubber–Captax	GR-S	
			Captax	S-2164
Room temp.	70/275° F.	400	25	25
	140/275° F.	400	15	35
200° F.	70/275° F.	600	2.3	4.0
	140/275° F.	450	1.8	8.0

TABLE VIII. COMPARISON OF SYNTHETIC RUBBERS IN FLEXOMETER TEST (STATIC COMPRESSION 6 PER CENT)

Type of Rubber	Temp. Rise, ° C. at Amplitude of: $^1/_{16}$ in.	$^3/_{32}$ in.
Natural	49.5	70.5
Butyl	78.5	102.5
Nitrile	77.0	96.0
Styrene	71.5	90.5

Table VIII compares synthetic and natural rubbers on a flexometer test under a static compression of 6 per cent. The temperature rise between amplitudes of $^1/_{16}$ and $^3/_{32}$ inch is approximately the same (20° C. for each rubber). Natural rubber has the lowest temperature for each amplitude, while the synthetics are approximately 20° higher.

Synthetic rubber compounds have been known to give very low values when tested at elevated temperatures. The four stocks in question were tested at 82° and 200° F. The tensile results are shown in Figure 44. The natural rubber had a tensile of approximately 280 kg. per sq. cm. at 82° F.; at 200° F. it had dropped only to approximately the same level as the original tensiles of the synthetic rubbers. These, in turn, had lost tensile strength at 200° F. until they were little more than 50 kg. when tested at this temperature. This is undoubtedly a serious defect in the present type of synthetic rubber which should be corrected if possible.

When tested at 82° and 200° F., the elongations (Figure 45) of natural rubber are unchanged, while the synthetics decrease approximately 150 per cent.

Acknowledgment

The author wishes to acknowledge the valuable assistance of the staff of the Research Laboratory, The Goodyear Tire & Rubber Company, in the preparation of this paper, particularly that of Leora Straka, A. M. Borders, S. D. Gehman, J. E. Fielding, R. S. Sanders, and G. H. Gates, as well as many others who have contributed to the preparation of this paper and without whose assistance it would have been impossible to assemble the data presented.

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PRESENTED before the Division of Rubber Chemistry at the 105th Meeting of the AMERICAN CHEMICAL SOCIETY, Detroit, Mich

A Potential Industrial Process for
SULFAMIDE

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SULFAMIDE was first prepared in impure form by Regnault (*1*) and subsequently by others (*2–9*). It is believed, however, that the present synthesis is the first in which appreciable amounts of relatively pure sulfamide have been obtained. An extensive review of the preparation and properties of sulfamide and related compounds was compiled by Audrieth and co-workers (*1*). Because of its similarity to urea and the importance of the latter, sulfamide has been the subject of an appreciable amount of research.

This paper reports the results obtained by the reaction of sulfuryl chloride in an inert solvent with liquid ammonia. Different variables, including temperatures ranging from −45° to 40° C., were studied. The interaction between sulfuryl chloride and such reagents as aqueous ammonia, calcium chloride octa-ammoniate, and sodium amide, and the ammonolysis of *N*-phthalimide sulfonyl chloride, were also studied but with unsatisfactory results. Under proper conditions sulfuryl chloride and ammonia react principally in accordance with the equation:

$$Cl.SO_2.Cl + 4NH_3 \longrightarrow H_2N.SO_2.NH_2 + 2NH_4^+Cl^-$$

By-products of the reaction are $H_2N.SO_2.NH.SO_2.NH_2$ and $H_2N.SO_2.(NH.SO_2)_n.NH_2$ or the salts of these imidosulfamides.

LABORATORY SYNTHESIS

Liquid ammonia (75 ml.) is placed in the reaction flask (Figure 1), which is surrounded by a solid carbon dioxide–chloroform–carbon tetrachloride bath. To the liquid ammonia is added slowly a solution of 20 ml. of sulfuryl chloride

The synthesis of sulfamide has been effected by condensing sulfuryl chloride with ammonia in both glass apparatus and an autoclave on a laboratory scale. Yields as high as 86 per cent have been obtained in these studies. Low temperature, vigorous agitation, and a diluent favor increased yields of the sulfamide and correspondingly decreased amounts of the imidosulfamides. Methyl acetate and acetone are satisfactory solvents for the extraction and purification of the sulfamide.

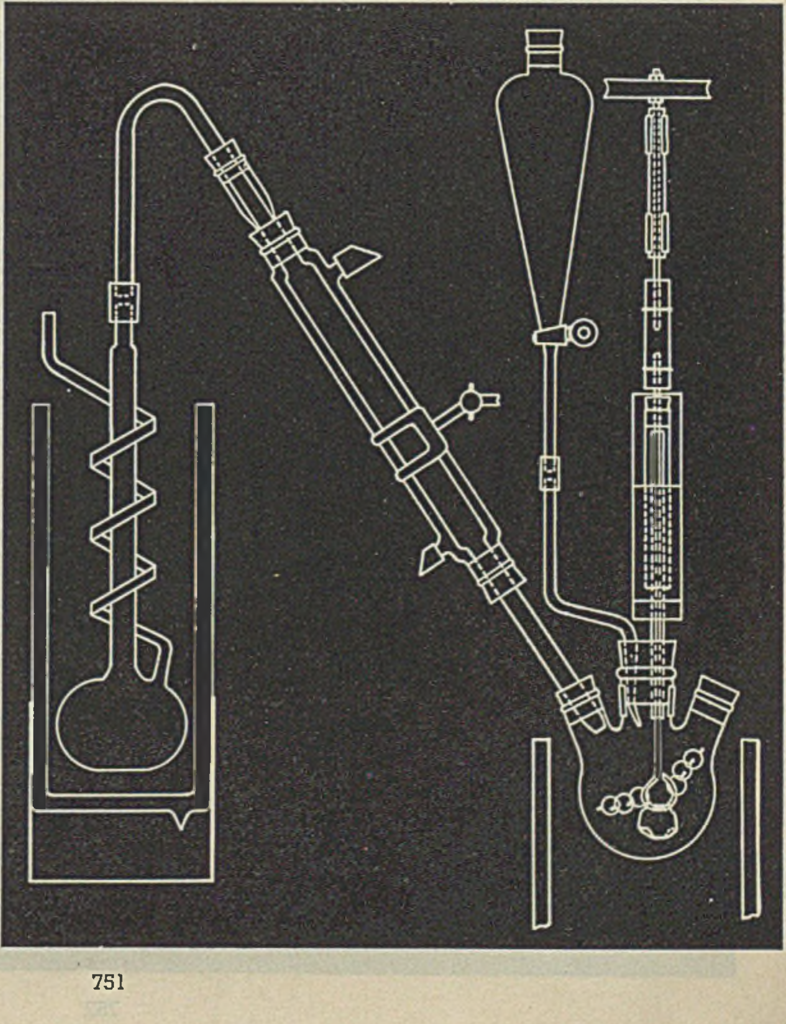

Figure 1. Glass Apparatus

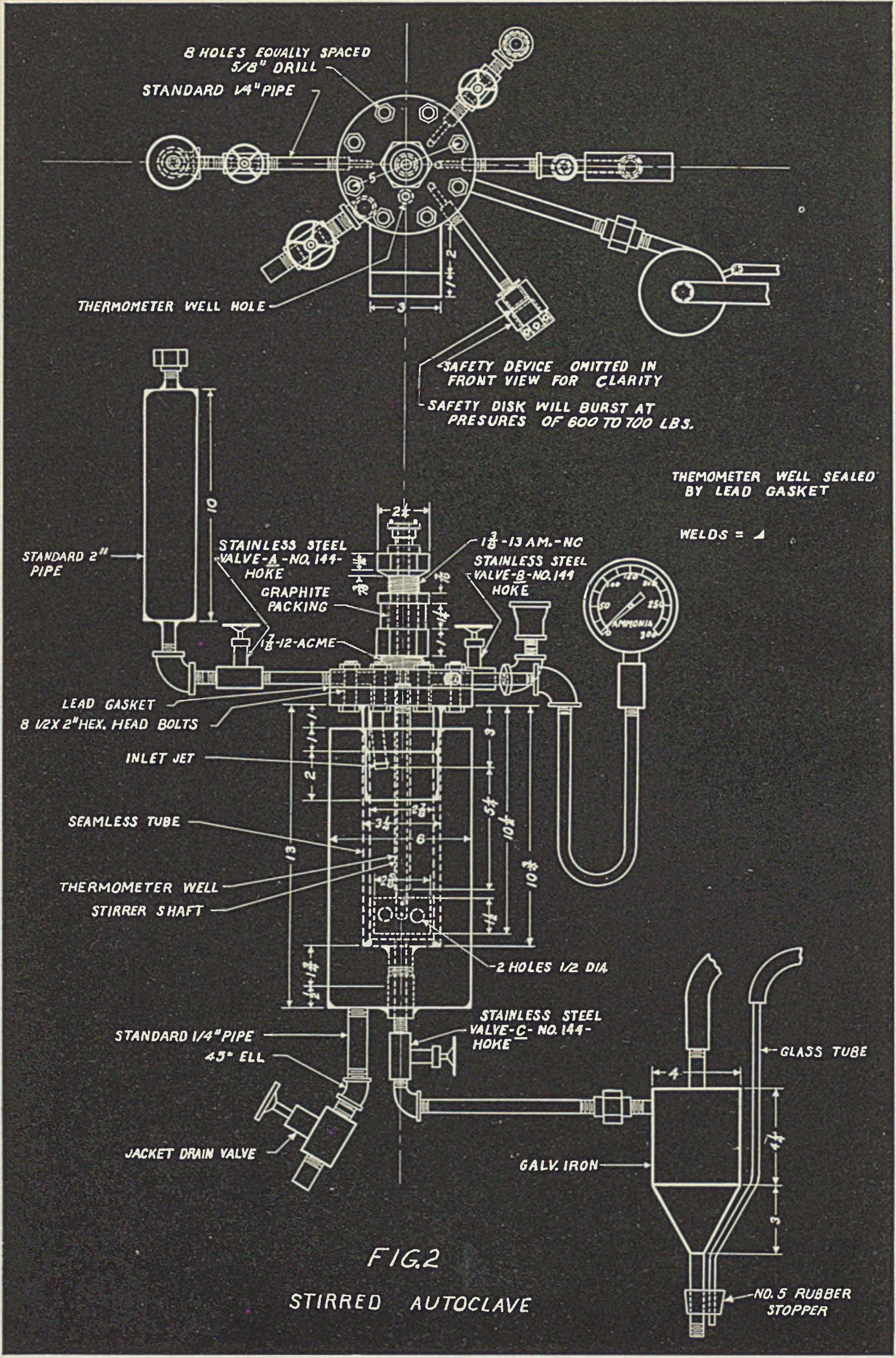

FIG. 2

STIRRED AUTOCLAVE

in 210 ml. of dry petroleum ether. During the introduction of the latter, the reaction mixture is stirred vigorously (1000 r. p. m.), and the reactant is added at such a rate that there is a slight mist in the lower part of the condenser. The addition requires from 20 to 40 minutes. The cooling bath is then removed, and the excess ammonia is allowed to distill off. The residual inert diluent is decanted. The last traces of the ammonia and of the diluent are removed from the product by warming under vacuum. The dry, white, solid residue is extracted for 2 or more hours in a Soxhlet extractor with methyl acetate. The extract is evaporated under vacuum on a steam bath, and the residue is allowed to crystallize. The product is ground up, dried under reduced pressure, and recrystallized from water. The sulfamide thus obtained is a white solid which melts at 91–93° C.

TABLE I. CRUDE YIELDS OF SULFAMIDE OBTAINED IN GLASS APPARATUS FROM 75 ML. OF AMMONIA AND 20 ML. OF SULFURYL CHLORIDE

Expt. No.	No. of Runs	Diluent[a]	% Yield
1	6	80 ml. p. e. (petroleum ether)	51–64
2	4	80 ml. p. e. + Na_2CO_3 (or $CaCO_3$) added slowly	47–70
3	8	80 ml. p. e. + 1–18 grams Filter-Cel in 120 ml. p. e.	38–77
4	5	200 ml. p. e.	64–81
5	1	80 ml. *n*-heptane	66
6	2	80 ml. chloroform	51–55
7	2	80 ml. CCl_4	55–62
8	3	No diluent	28–38
9	5	60–20 ml. p. e.	34–60
10	6	100–210 ml. p. e.	52–74
11	3	80 ml. p. e., stirring rate decreased to 450 r. p. m.	43–63
12	7	80 ml. p. e., stirring rate increased to as much as 1750 r. p. m.	56–87

[a] All runs made at temperature of chloroform–CCl_4–CO_2 bath. Unless otherwise indicated, the stirring rate was 1000 r. p. m. Numerous additional preliminary runs were made, but the results are not included.

The yield may be increased (10 to 15 per cent) by dissolving the reaction mixture in water before extraction, acidifying, allowing the solution to stand a week at room temperature, evaporating to dryness on a steam bath under diminished pressure, and extracting the residue. This increased yield is a consequence of the fact that the imidosulfamides are hydrolyzed to give one equivalent of sulfamide and one or more equivalents of sulfamic acid (*1, 4, 5*).

Acetone, ethyl acetate, ethyl methyl ketone, or methyl acetate may be used for the extraction. The use of methyl acetate gives both a better quality product and slightly higher yields.

Inert solid diluents such as Filter-Cel (Table I, experiment 3) and basic chemicals (experiment 2) tone down the violence of the reaction without appreciably affecting the yield. An inert solvent likewise decreases the violence of the reaction, but the choice of the solvent seems relatively unimportant (Table I). Efficient agitation prevents localized overheating.

Sulfamide starts to decompose at about 90° C. The use of a diluent, efficient agitation, and a low temperature all tend to prevent localized overheating. This, in turn, prevents the decomposition of the sulfamide *in situ* and/or its condensation to give imidosulfamides.

AUTOCLAVE SYNTHESIS

In order to operate on a larger scale, and to make a further study of the effect of the variables on the reaction, experiments were carried out in a stirred jacketed autoclave with a discharge valve at the bottom and a reservoir at the top to hold the sulfuryl chloride. Figure 2 is a detail drawing of the autoclave, one-sixth actual size. The autoclave was fitted with a gas release valve, safety disk, pressure gage, and thermometer well. The sulfuryl chloride reservoir was connected to a cylinder of nitrogen. The inlet tube for the sulfuryl chloride was fitted with a nipple of $^1/_8$-inch pipe and a cap. The use of caps with different size holes determined the size of the inlet jet.

The jacket was half filled with carbon tetrachloride–chloroform mixture and chilled with solid carbon dioxide. Then 400 ml. of liquid ammonia were drawn directly from the cylinder into the reaction chamber and allowed to cool. The top of the autoclave was lowered and bolted down. Eighty-one ml. (1 mole) of sulfuryl chloride, dissolved in 210 ml. of petroleum ether, were then placed in the reservoir through the male end of the union. The union was connected to the nitrogen cylinder and the pressure adjusted to 300 pounds per square inch. In runs made at 0° C. or above, the cooling was effected by ice or an ice-salt mixture. The stirrer was started and the sulfuryl chloride mixture allowed to flow in at a rate that maintained the temperature in the desired range. The cooling bath was also stirred during the entire run.

When all of the sulfuryl chloride had been added, stirring was continued until the mixture had warmed up to 0–10° C. The bottom valve was then opened slowly to transfer the solution to a 500-ml. flask. The solution, slightly colored by iron salts, was warmed under reduced pressure on a steam bath to remove the excess ammonia. The residue was ground and then extracted for 2 hours in a Soxhlet extractor with methyl acetate. After removal of the solvent from the extract, the residue was dissolved in 200 ml. of water, heated, filtered, acidified, and allowed to stand a week. The solution was then evaporated to dryness under vacuum on a steam cone. The dry solid was re-extracted, the solvent removed, and the residue allowed to solidify. The solid was then ground to a powder, dried in a desiccator over sulfuric acid, and weighed (Table II).

TABLE II. CRUDE YIELDS OF SULFAMIDE OBTAINED IN AN AUTOCLAVE FROM 400 ML. OF LIQUID AMMONIA AND 81 ML. OF SULFURYL CHLORIDE

Expt. No.	No. of Runs	Jet, Inch	Temp., ° C.	% Yield
1	8	0.0625	0 to 25	40 to 63
2	2	0.0625	−15 to −18	56 to 61
3	2	0.0625	−42 to −45	66 to 70
4	6	0.0325	18 to 25	52 to 68
5	6	0.0325	−15 to 10	50 to 77
6	4	0.0325	−42 to −40	78 to 86
7	4	0.0177	0 to 20	50 to 69
8	4	0.0177	−40 to −20	74 to 77
9	4	0.0097	0 to 20	57 to 61
10	4	0.0097	−45 to −20	70 to 75

No appreciable corrosive effect of the reactants and products on the reaction chamber was observed. The technical sulfamide thus obtained may be decolorized, when necessary, with activated carbon.

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. . . VISCOSITIES OF THE

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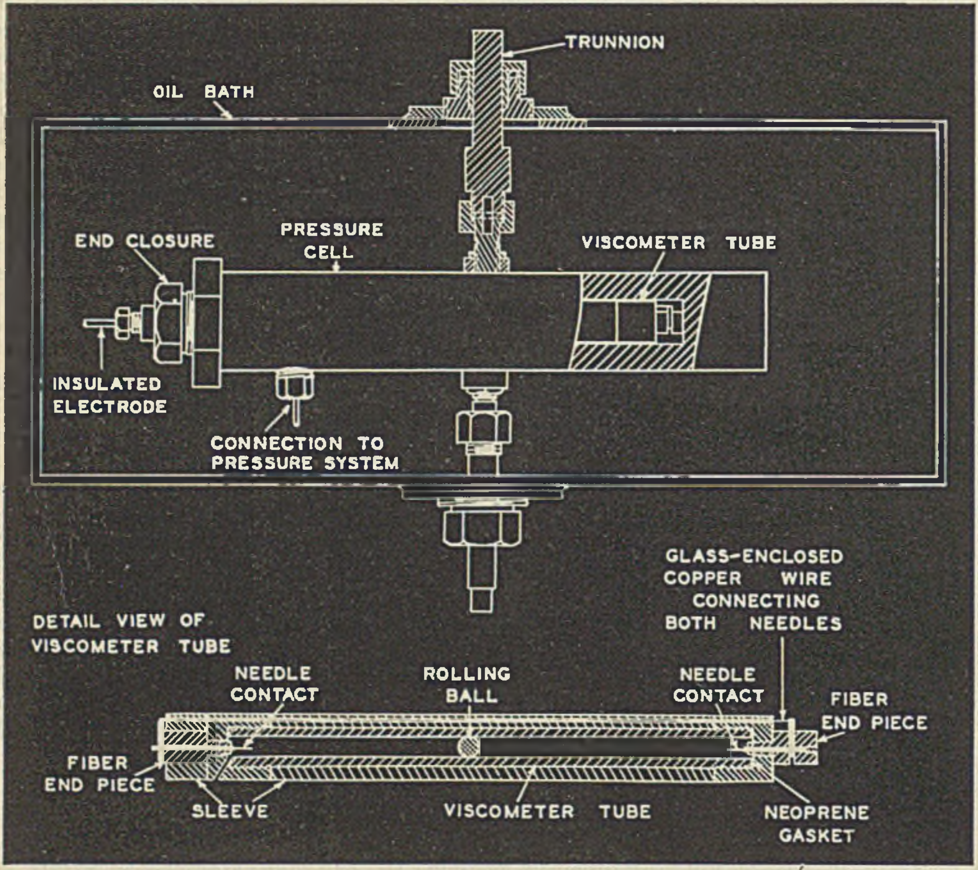

Figure 1. Viscometer Cell Assembly

In recent years there has been an increase of interest in the flow of light hydrocarbon fluids at relatively high pressures. Calculation of the energy losses in the flow of fluids requires a knowledge of the viscosity of the fluids at the pressures and temperatures involved. Although the effect of pressure upon the viscosity of several pure paraffin hydrocarbons has been reported by many investigators, as listed in Table I, there are few data on the effect of pressure upon the viscosity of low-molecular-weight hydrocarbon mixtures, especially those containing methane. Correlations based upon the viscosity studies of the pure hydrocarbons appear inadequate when applied to such mixtures.

The effects of pressure, temperature, and molecular weight upon the viscosity of light hydrocarbon fluids and the influence of critical pressure and temperature upon viscosity can best be determined by studying these variables in relation to the viscosity of a low-molecular-weight binary system whose critical properties and densities are known. The densities and critical properties of the methane-propane system were reported by Sage, Lacey, and Schaafsma (*13*), and its surface tension was given by Weinaug and Katz (*19*). In the present investigation the viscosity of methane, propane, and four of their binary mixtures (20, 40, 60, and 80 mole per cent methane) were experimentally determined at pressures from 400 to 5000 pounds per square inch and temperatures from 77° to 437° F.

APPARATUS

The apparatus is a rolling-ball inclined-tube viscometer. It was designed by Hubbard and Brown (*9*) following the principle of Flowers (*8*). They measured the viscosity of pentane at pressures up to 1000 pounds per square inch and temperatures to 482° F. The design was modified slightly by Smith and Brown (*15*), who obtained the viscosity-pressure-temperature relations of ethane and propane. This apparatus did not include equipment necessary for the introduction of mixtures into the viscometer cell. The composition of a mixture is maintained uniform by keeping the temperatures and pressures such that it is always present in a single phase.

The viscometer cell consists of a pressure vessel closed at one end and containing a steel tube shown in Figure 1. This tube is 10 inches long, drilled, reamed, and polished to an inside diameter of 0.3155 inch. The tube is closed by caps at each end, each cap being fitted with an insulated electrode. One cap is drilled

Table I. Available Data on Effect of Pressure upon Viscosity of Light Hydrocarbons

Investigator	Citation No.	Fluid Studied	Temp. Range, ° F.	Highest Pressure Lb./Sq. In.
Sage and Lacey	(*12*)	Methane	100–220	2,500
Smith and Brown	(*15*)	Ethane	59–392	5,000
		Propane	70–374	5,000
Sage and Lacey	(*11*)	Propane	100–220	2,000
Sage, Yale, and Lacey	(*14*)	*n*-Butane	100–220	2,000
		Isobutane	100–220	2,000
Hubbard and Brown	(*9*)	*n*-Pentane	77–482	1,000
Bridgman	(*3*)	*n*-Pentane	86–167	171,000
		Isopentane	86–167	171,000
		n-Hexane	86–167	171,000
		n-Octane	86–167	142,000
Dow	(*7*)	*n*-Decane	86–167	85,000
		n-Hexane–*n*-decane mixt.	86–167	57,000
Sage and Lacey	(*12*)	Lean natural gas	100–200	3,000
		Rich natural gas	160–200	2,000
Berwald and Johnson	(*2*)	Lean natural gas	60	500

METHANE-PROPANE SYSTEM

The viscosities of methane, propane, and four of their binary mixtures (20, 40, 60, 80 mole per cent methane) have been determined with an average error of 3.2 per cent at eight pressures (400 to 5000 pounds per square inch) at each of five temperatures (77° to 437° F.) in a rolling-ball inclined-tube viscometer. These data are correlated by the three variables, molecular weight, pseudoreduced temperature, and pseudoreduced pressure, with an average deviation of 2.9 per cent. This correlation may be used to obtain the viscosity of any light paraffin hydrocarbon or hydrocarbon mixture with an average error of about 3.5 per cent.

for communication with the pressure vessel. The viscosity is determined by electrically measuring the time required for a steel ball 0.3125 inch in diameter to roll 6.413 inches when the tube is at an angle of 7° 34′. The density of the steel ball is 7.758 grams per cc. The time of roll is measured by chronoscopes which are accentuated when the ball is not in contact with either of the electrodes in the viscometer tube. These electrodes are electrically connected by a wire running through a small glass tube fitted in a groove in the sleeve between the viscometer tube and the pressure cell. Outside contact is made through the insulated electrode in the closure head of the pressure vessel.

The viscometer cell is mounted to rotate on trunnions which extend through the walls of an oil bath. On one of the trunnions is attached a device to measure the angle of inclination of the viscometer tube. The oil bath is equipped with a mercury-in-glass thermoregulator. Electrical heating elements supply the heat for elevated temperatures; a copper coil through which passes refrigerated brine is used for the 77° F. measurements when necessary. Temperatures up to 230° F. are read on a calibrated thermometer with 0.1° C. divisions; temperatures up to 437° F. are read on a calibrated thermometer with 1° F. divisions.

The viscometer cell is connected to a 325-cc. charging cell (*A* in Figure 2) by a $^1/_8$-inch annealed steel tube which is coiled about the trunnion of the viscometer cell. A filter in this line consists of a small steel tube containing asbestos fibers. This filter keeps small particles such as rust and the like from entering the viscometer cell and interfering with the roll of the ball. Very fine screens at each end of the filter prevent the asbestos fibers from leaving the filter.

The fluid in the viscometer cell is in contact with mercury in charging cell *A*. The pressure in *A*, and hence the pressure in the viscometer tube, is regulated by the quantity of mercury pumped into that cell. This pressure is indicated on the calibrated Bourdon-tube pressure gages, *E* and *G*. The top of charging cell *A* is so designed that a buzzer will sound when the mercury level in the cell is near the top, to eliminate the possibility of accidentally pumping the mercury over into the viscometer cell. As fine pressure adjustment is rather difficult with the mercury plunger pump, a hydraulic screw pump is used to make small adjustments in the pressure.

Cell *B* contains pure methane, cell *C* contains pure propane, and the mixture is made up in cell *D*. Methane is pumped into *D* until the desired number of moles is obtained at the pressure,

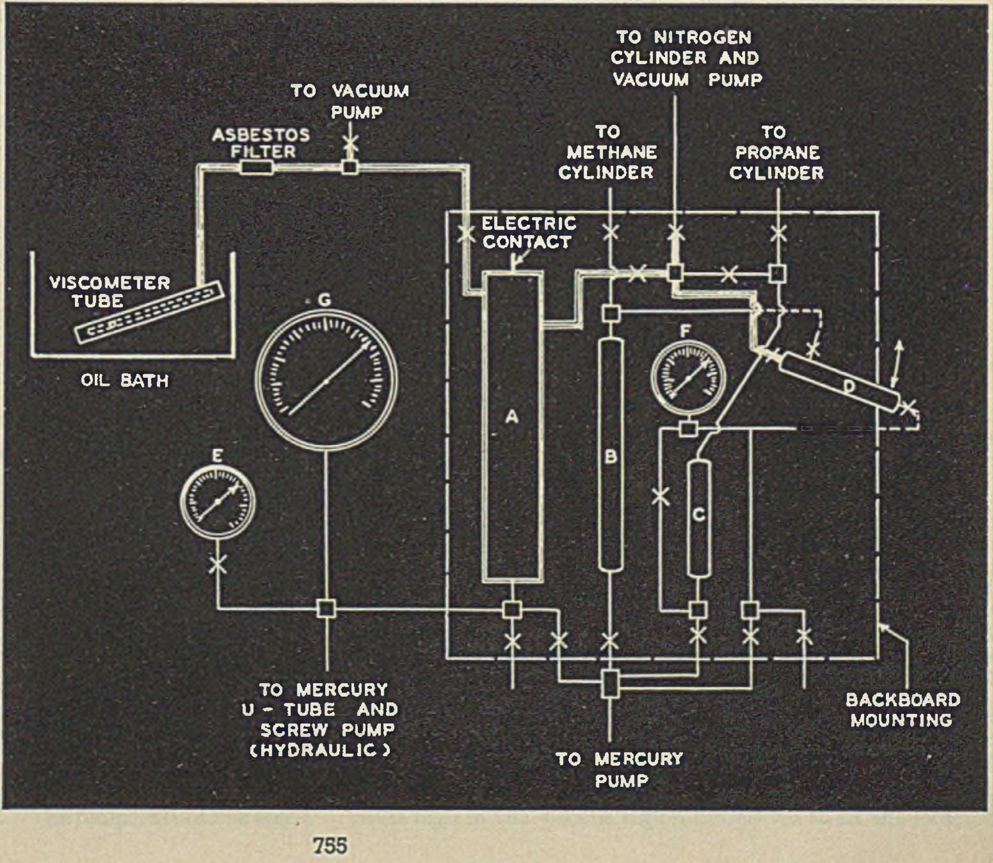

Figure 2. Pressure and Mixing System

Vol. of Cells, Cc.	Gages, Lb./Sq. In.
A (charging), 325	*E*, 1000
B (methane), 200	*F*, 3000
C (propane), 125	*G*, 5000
D (mixing), 125	

—— $^1/_8$-inch steel tubing.

- - - - Connecting lines to *D*, coiled at back to enable *D* to be rocked.

═══ Heating circuit. Charging cell *A* is covered with layer of asbestos paper, around which is wrapped No. 24 Chromel A wire and then two layers of asbestos. The connecting lines from the viscometer tube to cell *A* to cell *D* are wrapped with No. 24 Chromel A wire in asbestos tubing.

TABLE II. VISCOSITY OF 20 PER CENT METHANE–80 PER CENT PROPANE MIXTURE

Temp. ° F.	Temp. ° C.	Abs. Pressure, Lb./Sq. In.	Observed Roll Time, θ, Sec.	Fluid Density, ρ, G./Cc.	Ball − Fluid, $\rho_s - \rho$, G./Cc.	$\theta\sqrt{\frac{\rho_s - \rho}{\rho}}$	$\frac{\rho}{\eta\theta}$	Abs. Viscosity, Poises × 10^5
		N₂ Calibration[a] (Clean Tube)						
77	25	14.7	7.44	0.00111	7.757	621	0.847	176.4
167	75	515	9.65	0.0343	7.72	144.8	17.3	205.0
		3055	16.34	0.1837	7.57	105.0	46.5	241.5
		1015	11.33	0.0665	7.69	121.8	27.8	210.8
		515	9.61	0.0343	7.72	144.1	17.4	205.0
		214	8.62	0.0143	7.74	200.5	8.21	202.2
		114	8.35	0.00758	7.75	267.0	4.52	201.2
		14.7	8.16	0.00098	7.76	726.0	0.605	198.4
		14.7	8.17	0.00098	7.76	726.0	0.605	198.4
		20% CH_4–80% C_3H_8 Data (First Mixture)						
167	75	264	6.68	0.0305	7.73	106.2	42.5	107.5
		414	8.10	0.052	7.71	98.6	54.0	118.8
257	125	414	7.73	0.039	7.72	108.7	39.2	128
		2069	21.95	0.306	7.45	108.3	39.5	353
		1571	18.53	0.252	7.51	101.2	49.9	273
		1281	15.72	0.205	7.55	95.4	59.8	218
		1015	12.79	0.135	7.62	96.0	59.2	178
		718	10.03	0.076	7.68	100.8	50.1	151
		5008	31.38	0.406	7.35	133.2	21.1	613
		4039	29.10	0.389	7.37	126.5	24.9	537
		3055	26.04	0.362	7.40	117.8	30.3	458
		2069	22.02	0.306	7.45	108.8	39.1	355
167	75	3055	33.56	0.4318	7.33	138.2	19.0	677
		5008	39.14	0.4550	7.30	157.0	14.0	830
		4039	36.75	0.4452	7.31	149.0	15.8	767
		3055	33.55	0.4318	7.33	138.2	19.0	677
		2058	29.81	0.3960	7.36	128.6	23.2	572
		1561	27.50	0.365	7.39	123.8	26.1	504
		1281	25.76	0.3435	7.42	119.8	28.6	466
		915	21.42	0.2888	7.47	109.0	38.3	351
77	25	2058	41.80	0.478	7.28	163.0	12.7	899
		5008	51.71	0.5055	7.25	196.0	8.67	1129
		4035	48.61	0.4992	7.26	185.5	9.68	1060
		3045	45.26	0.4906	7.27	174.2	11.0	985
		2058	41.81	0.478	7.28	163.0	12.7	899
		1561	39.84	0.4660	7.29	157.6	13.7	853
		1015	37.47	0.4205	7.34	156.8	14.0	801
		N₂ Calibration[a]						
77	25	1015	11.44	0.080	7.68	112.0	35.5	191.5
		214	8.05	0.0170	7.74	169.8	11.73	180.0
		114	7.64	0.0095	7.75	218.0	6.96	178.8
		14.7	7.37	0.00111	7.76	616.0	0.853	176.4
257	125	14.7	8.81	0.00085	7.76	836.0	0.445	218.0
		20% CH_4–80% C_3H_8 Data (Second Mixture)						
257	125	414	7.60	0.039	7.72	107.8	40.0	127
		3055	26.10	0.362	7.40	117.8	30.2	459
		1571	18.50	0.252	7.51	101.0	50.1	272
347	175	2058	17.24	0.2208	7.54	100.8	51.3	250
		1561	14.36	0.164	7.59	97.7	56.1	204
		1015	11.11	0.0935	7.67	100.5	51.6	163
		714	9.31	0.060	7.70	105.3	44.1	146
		414	7.53	0.0323	7.73	116.4	32.6	132
		5008	26.65	0.365	7.39	120.0	29.7	461
		4035	24.35	0.3395	7.42	113.9	34.7	402
		3045	21.37	0.300	7.46	106.3	43.2	325
		2058	17.19	0.2208	7.54	100.3	51.8	248
437	225	3055	18.67	0.2463	7.51	103.2	47.5	278
		2069	15.03	0.1732	7.58	99.4	53.8	216
		1571	12.90	0.128	7.63	99.6	53.5	186
		1015	10.42	0.077	7.68	104.0	46.5	159
		718	9.05	0.0518	7.71	110.3	39.0	147
		414	7.55	0.0284	7.73	124.5	27.0	139
		5008	23.67	0.3257	7.43	113.1	35.6	386
		4039	21.42	0.293	7.47	108.1	41.3	331
		3055	18.65	0.2463	7.51	103.0	47.9	276
		N₂ Calibration[a]						
437	225	14.7	10.31	0.00068	7.76	1115	0.258	252.8

[a] Viscosity values: Michels and Gibson (*10*), Trautz and Zink (*17*).

volume, and temperature involved. The desired number of moles of propane are pumped into *D* from cell *C* by keeping the pressure on *C* constant and measuring the volume of mercury pumped into *C*. This represents the volume of propane pumped into cell *D* at that temperature and pressure. *D* is equipped for rocking to provide the agitation and mixing necessary to assure thorough mixing of the methane and propane; the result is a single-phase homogeneous mixture when the pressure is above the critical locus for that mixture. The composition of the propane-rich mixtures is checked by determining the bubble point of the mixture in cell *D*. Mercury is withdrawn from *D*, and the decrease in pressure is noted. The intersection of two straight lines when pressure is plotted against volume of mercury withdrawn gives the bubble point.

A mixture is charged into the viscometer cell in a single phase and is never permitted to go into two phases so that the composition of the mixture will remain uniform. The mixture in cell *D* is kept in a single phase by maintaining the pressure of the mixture in that cell above its bubble point pressure. The evacuated system is filled with the mixture through the slightly opened mixing cell valve at a pressure below the dew point pressure of the fluid. The fluid is therefore still in a single phase. The system is filled with the fluid and evacuated several times to reduce the impurities to a negligible amount. When increasing the pressure of the mixture to a pressure above its bubble point without going through the two-phase region, the viscometer tube, charging cell *A*, and connecting lines are heated to a temperature, above the critical locus of the mixture, at which the pressure on the fluid can be increased without going through the two-phase region.

The methane and propane used were supplied through the courtesy of the Phillips Petroleum Company. The methane, guaranteed to have a purity of 99.0 per cent and a typical purity of 99.3 per cent, was passed through a calcium chloride tube in the supply line to remove any traces of moisture. The propane was a C. P. product guaranteed to have a purity of 99.9 per cent.

DETERMINATION OF ABSOLUTE VISCOSITIES

The ball roll times as measured are only relative, and the instrument must be calibrated by measuring roll times of fluids of known viscosities. Calibration curves are drawn as suggested by Smith and Brown (*15*); $\theta\sqrt{(\rho_s - \rho)/\rho}$ is plotted against the Reynolds number, $\rho/\eta\theta$, in which θ is the roll time, ρ_s is the density of the ball, ρ is the density of the fluid, and η is the absolute viscosity of the fluid. The curve is obtained by measuring the roll times of fluids of known viscosities at various temperatures and pressures, and is used to compute the viscosities of other fluids from their measured roll times and densities.

The calibration curve is a straight line with a slope of −0.50 on a log-log plot when the flow is in the viscous region. This line is no longer straight where the flow is changing from viscous to turbulent, but curves until it reaches a slope of −0.30 in the turbulent region. Smith and Brown (*15*) showed that the calibration curve is independent of the fluid used. No corrections are necessary for the varying velocity of the ball before it reaches the terminal velocity, as they would be negligible for roll times greater than 5 seconds. Corrections for rolling length or angle of inclination need not be made since these values were kept constant for calibrations and measurements.

Temperature should have only a small effect upon the calibration of the instrument, as both the ball and the tube are made of nearly the same material. But owing to the different coefficients of expansion of the fiber end pieces and the steel tube, and the loss of the resilience of the tube gaskets at high temperatures, a slight internal leakage of fluid around the viscometer tube gives faster roll times upon cooling. Therefore, the instrument is calibrated at various temperatures and at both the initial and final temperatures of every run.

Dry commercial nitrogen is the calibrating fluid, since nitrogen is readily available and data taken with nitrogen cover

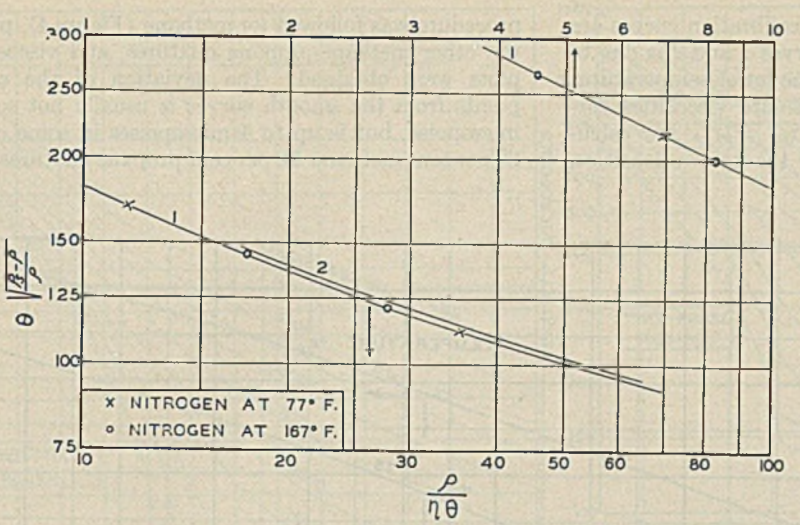

Figure 3. Calibration Curves for 20 Per Cent Methane–80 Per Cent Propane

Table III. Smoothed Viscosity Values of Methane and Propane Mixtures in Micropoises

Temp. ° F.	Temp. ° C.	Pressure, Lb./Sq. In. Abs. 14.7[a]	400	700	1000	1500	2000	3000	4000	5000
Methane										
77	25	110	119	127	137	160	182	223	256	279
167	75	125	133	139	145	159	175	207	236	261
257	125	140	147	152	157	165	176	199	226	248
347	175	154	158	162	166	174	183	201	219	235
437	225	167	170	174	178	183	189	202	213	225
80% CH_4–20% C_3H										
77	25	102	117	129	142	169	199	258	308	351
167	75	116	125	132	142	161	182	222	258	288
257	125	130	135	140	149	160	174	202	230	253
347	175	144	148	151	155	162	174	196	220	241
437	225	157	160	162	165	172	181	196	218	239
60% CH_4–40% C_3H_8										
77	25	95	108	[b]	[b]	251	320	405	472	529
122	50	105	115	127	147	190	249	336	401	458
167	75	110	120	131	146	179	213	285	343	394
257	125	123	128	134	147	167	188	235	283	322
347	175	136	140	144	152	168	186	221	259	290
437	225	149	152	155	159	172	186	216	246	276
40% CH_4–60% C_3H_8										
77	25	89.9	[b]	[b]	[b]	462	534	636	717	789
167	75	104	120	142	164	222	298	406	493	570
257	125	117	126	137	153	180	218	299	367	428
347	175	130	135	142	152	177	202	262	319	374
437	225	142	144	147	152	172	196	241	285	320
20% CH_4–80% C_3H_8										
77	25	85	[b]	763	799	846	892	978	1056	1130
167	75	99	119	[b]	393	495	561	672	760	836
257	125	112	126	148	175	257	343	452	536	612
347	175	124	133	146	162	198	242	320	397	470
437	225	136	140	146	157	177	210	273	330	384
Propane										
77	25	81	1033	1080	1121	1186	1242	1343	1445	1540
167	75	95	520	597	654	723	777	879	972	1062
257	125	107	135	164	293	420	497	619	730	818
347	175	120	125	142	182	264	340	460	561	655
437	225	131	138	150	172	218	268	366	460	540

[a] Data of Trautz and Sorg (*16*). [b] Two-phase region.

the entire calibration range required. The viscosities and densities of nitrogen reported by Michels and Gibson (*10*) are used for calibrating at temperatures up to 167° F. for pressures from 100 to 5000 pounds per square inch. Atmospheric pressure viscosities for temperatures up to 437° F. are obtained from the experimental data of Trautz and Zink (*17*).

The density of methane is taken from a compressibility factor plot reported by Brown and Holcomb (*4*). Data of Sage and Lacey (*11*) are used for low-temperature propane densities; high-temperature densities are taken from the data of Beattie, Kay, and Kaminsky (*1*). The low-temperature densities of the methane-propane mixtures are obtained from Sage, Lacey, and Schaafsma data (*13*); the high-temperature densities are taken from compressibility factor plots of ethane, natural gas, and propane with pseudo-reduced temperature and presssure lines (*4*). The computed densities of each mixture are plotted on a large scale and cross-plotted to avoid errors in extrapolation.

TYPICAL CALCULATIONS

The details of one series are given to illustrate the method of taking data, calibrating, and computing absolute viscosities. Table II contains the experimental and derived data for the 20 per cent methane–80 per cent propane mixture.

The viscometer tube was cleaned, furnished with new gaskets, and closed before being calibrated with nitrogen at 77° and 167° F. The 20 per cent mixture was charged into the instrument at 167° F. and low-pressure readings were taken at pressures below the dew point. The temperature was then increased to 257° F., where the mixture can exist only in a single phase, and readings were taken over the entire pressure range. The mixture was kept in a single phase when cooling to 167° and then to 77° F. by keeping the pressure above the critical locus of the mixture; high-pressure readings were taken at both temperatures. The mixture was discarded, and the instrument was calibrated with nitrogen at 77° and then at 257° F. A new 20 per cent mixture was charged into the apparatus at this temperature, and readings were taken at 257° F. as a check on the method of computing viscosities and on the method of making up mixtures. These readings check those of the first mixture within one micropoise. Further readings were taken at 347° and 437° F., and the instrument was calibrated with nitrogen at 437° F. before cooling. The viscosity of nitrogen at this temperature is not known at pressures other than atmospheric. This gives a calibration point high in the viscous region but serves to fix the location of the 437° F. calibration curve. The calibration curves are given in Figure 3; the difference in curves 1 and 2 is due to the internal circulation of the fluid at the lower temperatures but should not interfere with the absolute viscosities correctly computed. The values of $\theta\sqrt{(\rho_s - \rho)/\rho}$ are calculated from the measured roll times and the known densities, and the corresponding value of $\rho/\eta\theta$ is read from the calibration curve at that temperature. The absolute viscosity, η, is calculated by dividing ρ/θ by $\rho/\eta\theta$.

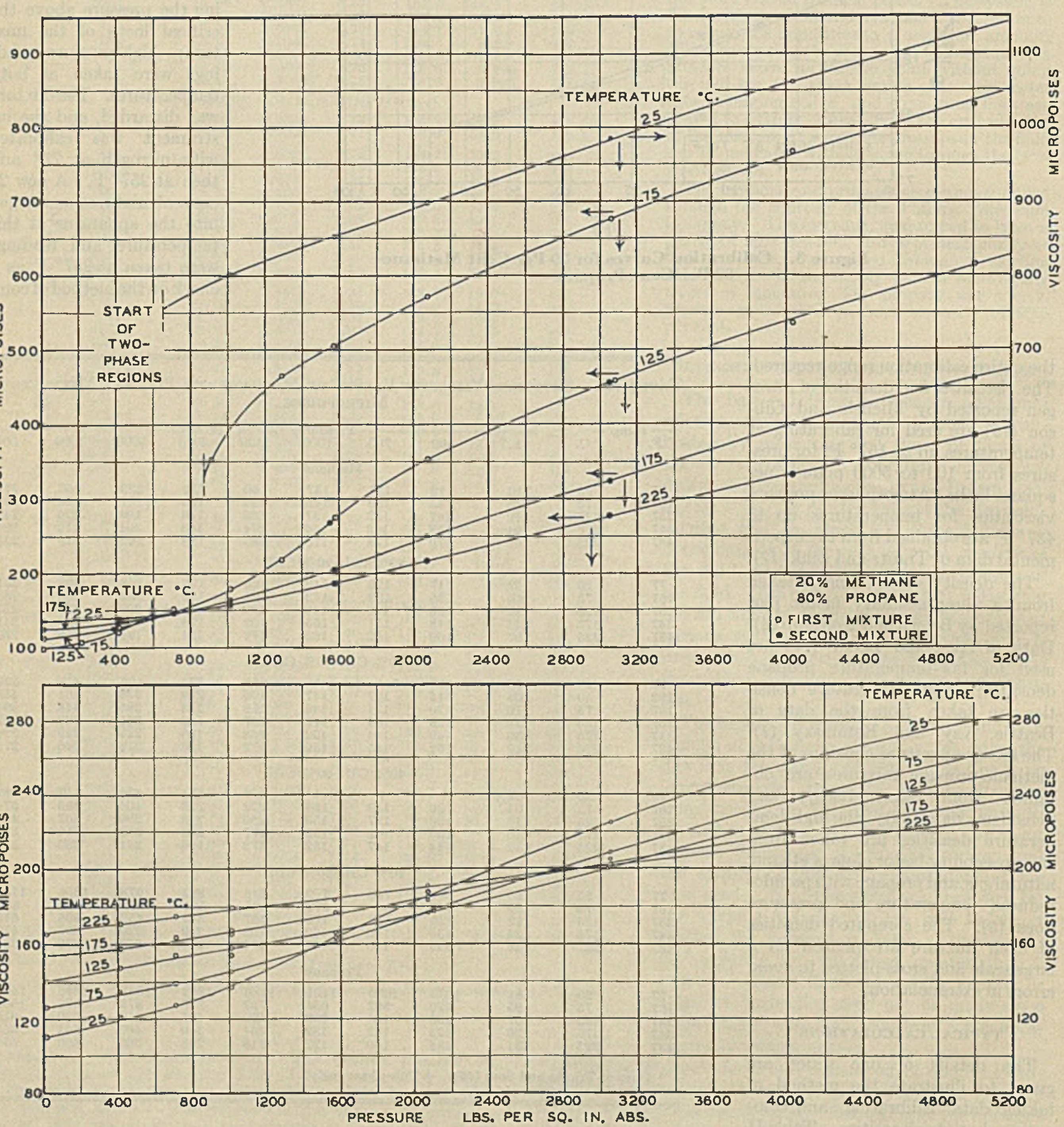

Figure 4. Viscosity of 20 Per Cent Methane–80 Per Cent Propane (*above*) and of Methane (*below*)

The experimental viscosities are plotted against pressure with lines of constant temperature in Figure 4. A similar procedure was followed for methane (Figure 4), propane, and the other methane-propane mixtures, and viscosity-pressure plots were obtained. The deviation of the experimental points from the smooth curves is usually not so much as 1 micropoise, but is up to 4 micropoises in some cases for the 80 per cent methane–20 per cent propane mixtures. Smoothed viscosity values for methane, propane, and the four methane-propane mixtures (20, 40, 60, 80 mole per cent) at temperatures from 77° to 437° F. and pressures from 400 to 5000 pounds per square inch were read from these plots and are listed in Table III. The smoothed data are plotted against

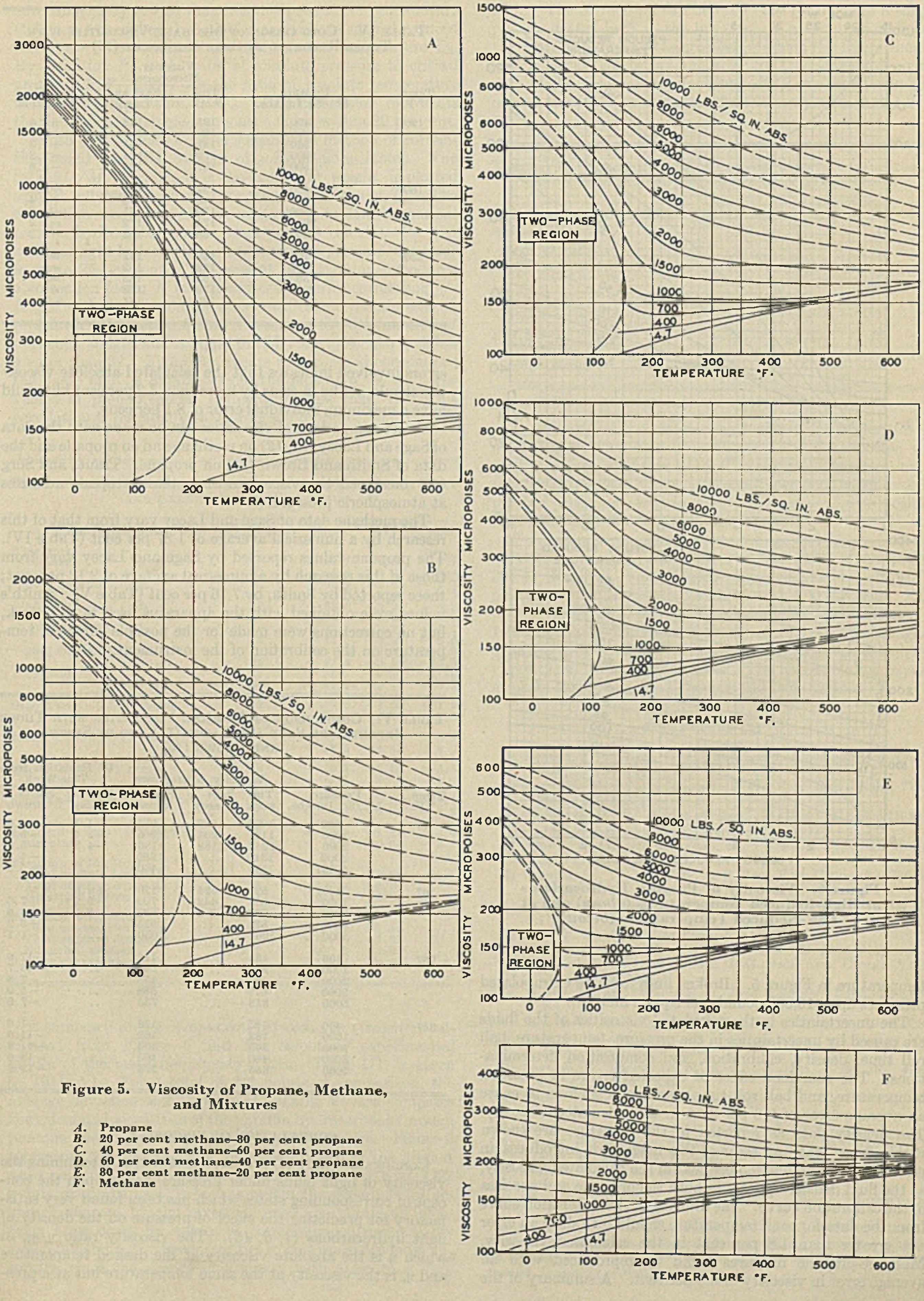

Figure 5. Viscosity of Propane, Methane, and Mixtures

- *A.* Propane
- *B.* 20 per cent methane–80 per cent propane
- *C.* 40 per cent methane–60 per cent propane
- *D.* 60 per cent methane–40 per cent propane
- *E.* 80 per cent methane–20 per cent propane
- *F.* Methane

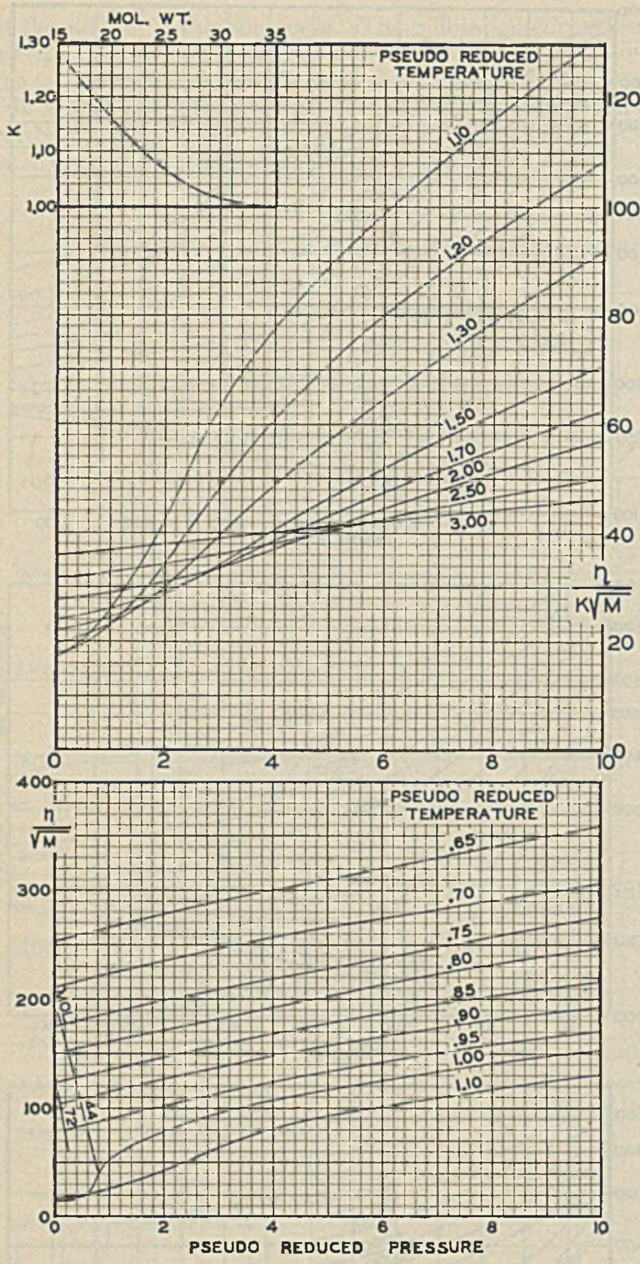

Figure 6. Viscosity of Paraffin Hydrocarbons at High-Reduced Temperatures (*above*) and at Low-Reduced Temperatures (*below*)

temperature in Figure 5. Broken lines indicate extrapolated pressures up to 10,000 pounds per square inch.

Table IV. Comparison of Methane Viscosities with Those Reported by Sage and Lacey (*12*)

Temp., ° F.	Pressure, Lb./Sq. In. Abs.	Viscosity, Micropoises: This work	Viscosity, Micropoises: Sage and Lacey	Per Cent Deviation
100	400	125	128	+2.4
	1000	139	146	+5.0
	1500	159	161	+1.3
	2000	179	174	−2.8
	2500	197	186	−5.6
160	400	134	135	+0.7
	1000	145	150	+3.4
	1500	159	161	+1.3
	2000	174	172	−1.2
	2500	188	182	−3.2
220	400	142	142	±0
	1000	152	152	±0
	1500	163	163	±0
	2000	173	173	±0
	2500	186	184	−1.1

The uncertainties in the calculated viscosities of the fluids are caused by uncertainties in the pressure, temperature, ball roll time, density, calibration, and composition determinations. The combined effect of expected errors in pressure, temperature, and ball roll time readings is such as to cause an average error of 0.6 per cent in the calculated viscosity. The density data as reported in the literature are known within 3 per cent; an error of this magnitude introduces an error of not more than 0.5 per cent in the calculated viscosity, as the fluid density appears in both the ordinate and abscissa of the calibration curve. The drawing of the calibration curve from the data for each temperature should introduce an error not greater than 1.8 per cent in the calculated viscosity. Methane-propane mixtures could be reproduced with an average error in viscosity of 0.5 per cent. A summary of the errors involved indicates that the calculated absolute viscosities should not be in error by more than 3.2 per cent but could have a maximum individual error of 8.1 per cent.

Direct comparison of viscosities can be made with the data of Sage and Lacey (*11*, *12*) on methane and on propane and the data of Smith and Brown (*15*) on propane. Trautz and Sorg (*16*) measured the viscosities of methane-propane mixtures at atmospheric pressure.

The methane data of Sage and Lacey vary from that of this research by a numerical average of 1.87 per cent (Table IV). The propane values reported by Sage and Lacey vary from those of this research by a numerical average of 2.12 per cent; those reported by Smith, by 7.76 per cent (Table V). Smith's values were obtained with the apparatus used in this work, but no corrections were made for the possible effects of temperature on the calibration of the instrument.

Table V. Comparison of Propane Viscosities with Those Reported by Sage and Lacey (*11*) and by Smith and Brown (*15*)

Temp., ° F.	Pressure, Lb./Sq. In. Abs.	Viscosity, Micropoises: This work	Viscosity, Micropoises: Sage & Lacey	Viscosity, Micropoises: Smith & Brown	% Deviation from This Work: Sage & Lacey	% Deviation from This Work: Smith & Brown
77	400	1033	1022	985	−1.1	−4.6
	1000	1121	1094	1065	−2.4	−5.0
	2000	1242	1189	1180	−4.3	−5.0
	3000	1343	...	1280	...	−4.7
	5000	1540	...	1460	...	−5.2
167	400	520	524	120	+0.8	
	1000	654	648	700	−0.9	+7.0
	2000	777	752	828	−3.2	+6.6
	3000	879	...	925	...	+5.2
	5000	1062	...	1050	...	−1.1
257	400	135	...	112	...	−17.0
	1000	293	...	244	...	−16.7
	2000	497	...	458	...	−7.8
	3000	619	...	588	...	−5.0
	5000	818	...	753	...	−7.9
347	400	125	...	123	...	−1.6
	1000	182	...	162	...	−11.0
	2000	340	...	300	...	−11.8
	3000	460	...	405	...	−12.0
	5000	655	...	575	...	−12.2

CORRELATION OF VISCOSITY

Comings and Egly (*5*) propose a method for determining the viscosity of light fluids under pressure, based upon the concept of corresponding states which has been found very satisfactory for predicting the effect of pressure on the density of light hydrocarbons (*4*, *6*, *18*). The viscosity ratio η/η_i, in which η is the absolute viscosity at the desired temperature and η_i is the viscosity at the same temperature but at a pressure sufficiently low so that it is independent of temperature (taken as atmospheric), is plotted as ordinate against reduced pressure P_R for constant values of reduced temperature T_R. By definition P_R is the ratio of absolute pressure to critical pressure, P/P_C, and T_R is the ratio of absolute temperature to critical temperature, T/T_C. This correlation represents the data of seven single-component fluids within 20 per cent.

Smith and Brown (*15*) also suggested a method of correlation based upon the concept of corresponding states. The ratio $\eta/\sqrt{M}$, in which M is the molecular weight, is plotted against reduced pressure P_R for constant values of T_R. The correlation was made on the viscosity data for the normal paraffin hydrocarbons; but when used to calculate the viscosity of light hydrocarbon mixtures under pressure, the error is up to 25 per cent. The present investigation introduces a correction factor K into the viscosity term, correlating $\eta/K\sqrt{M}$ with pseudoreduced temperatures and pseudoreduced pressures. Correction factor K is shown to be a function of molecular weight and is equal to unity for molecular weights greater than 32. Figure 6 presents the proposed correlation; the value of K is obtained from the plot of K *vs.* M. For values of pseudoreduced temperature less than 1.00, this correlation is essentially that proposed by Smith and Brown.

TABLE VI. SUMMARY OF COMPARISON BETWEEN CALCULATED AND EXPERIMENTAL VISCOSITIES

Gases Investigated	Points of Comparison	Deviation, % Total	Av.	Max.
This work				
Methane	10	+ 20.7	+2.07	+ 7.7
	27	− 54.8	−2.03	− 4.4
80% CH_4–20% C_3H_8	24	+ 95.4	+3.98	+12.7
	7	− 9.8	−1.40	− 4.9
60% CH_4–40% C_3H_8	12	+ 38.9	+3.24	+ 9.8
	14	− 55.0	−2.29	− 4.8
40% CH_4–60% C_3H_8	19	+ 43.4	+2.28	+ 6.1
	15	− 43.6	−2.90	− 6.6
20% CH_4–80% C_3H_8	13	+ 31.3	+2.40	+ 9.9
	25	− 87.6	−3.50	−13.0
Propane	25	+ 91.6	+3.66	+17.8
	20	− 49.4	−2.47	− 8.2
Sage & Lacey (*12*), methane	2	+ 2.6	+1.30	+ 1.9
	10	− 24.6	−2.46	− 5.6
Smith & Brown (*15*), ethane	6	+ 21.9	+3.65	+ 6.9
	6	− 26.5	−4.42	− 8.0
Sage & Lacey (*11*), propane	9	+ 29.7	+3.30	+ 5.3
	4	− 13.8	−3.45	−11.6
Sage, Yale, Lacey (*14*), *n*-butane	13	+128.9	+9.92	+19.1
	4	− 3.8	−0.95	− 2.3
Hubbard & Brown (*9*), Dow (*7*), *n*-pentane	16	+ 22.8	+1.43	+ 3.4
	11	− 6.9	−0.63	− 3.7
Summary of this work				
Total positive deviation	103	+321.3	+3.12	....
Total negative deviation	108	−300.2	−2.78	....
Numerical average	211	621.5	2.94	....
Summary of all values				
Total positive deviation	149	+527.2	+3.54	....
Total negative deviation	143	−375.8	−2.63	....
Numerical average	292	903.0	3.09	....
Algebraic average	292	+151.4	+0.52	....

A summary of the comparison between the viscosities calculated from Figure 6 and the smoothed experimental values of the methane-propane system (Table III) is given in Table VI. For a total of 211 points of comparison, the average deviation is 2.94 per cent. Table VI also compares the calculated viscosities of the paraffin hydrocarbons through pentane and the values reported in the literature. Figure 6 represents the data of these investigators and of the present research with an average deviation of 3.09 per cent (292 points of comparison), which is within the experimental accuracy claimed by the investigators. The points of maximum error occur for values of pseudoreduced pressure between 0.8 and 1.2. The viscosities in this range are most uncertain, since the change in viscosity with pressure is very high. The correlation can be used only for fluids in a single phase; dotted lines in the lower graph of Figure 6 indicate the limit of reduced pressures below which the figure should not be used. The maximum error for the methane-propane data of this research does not exceed 8.2 per cent for values of pseudoreduced pressure less than 0.8 or greater than 1.2.

TABLE VII. SUMMARY OF COMPARISON BETWEEN CALCULATED AND EXPERIMENTAL VISCOSITIES OF NATURAL GASES

Natural Gas Investigated	Points of Comparison	Deviation, % Total	Av.	Max.
Sage and Lacey (*12*)				
Lean (83.19% CH_4)	3	+ 2.7	+0.90	+ 1.0
	15	−106.8	−7.12	−14.5
Rich (69.74% CH_4)	4	+ 23.4	+5.85	+10.7
	6	− 24.7	−4.13	− 5.9
Berwald and Johnson (*2*), gas No. 2 (98.4% CH_4)	5	+ 38.4	+7.68	+10.7
	1	− 0.9	−0.90	− 0.9
Total positive deviations	12	+ 64.5	+5.38	....
Total negative deviations	22	−132.4	−6.02	....
Numerical average	34	196.9	5.79	....
Algebraic average	34	− 67.9	−2.00	....

A summary of the comparison between the viscosities of natural gases computed from Figure 6 and the reported viscosities is given in Table VII. The numerical average deviation for 34 points of comparison is 5.79 per cent, which is comparable with the experimental accuracy. The viscosities were computed as in the following example.

The lean natural gas reported by Sage and Lacey (*12*) has a molecular weight of 20.4, a pseudocritical temperature of 393.4° Rankine, and a pseudocritical pressure of 667.9 pounds per square inch absolute. At 100° F. and 2500 pounds per square inch, the pseudoreduced temperature is 1.423 and the pseudoreduced pressure is 3.743. From Figure 6, $\eta/K\sqrt{M}$ is read as 41.8 and K as 1.152. The calculated viscosity, η, is 217.5 micropoises. The corresponding experimental value of Sage and Lacey is 219 micropoises.

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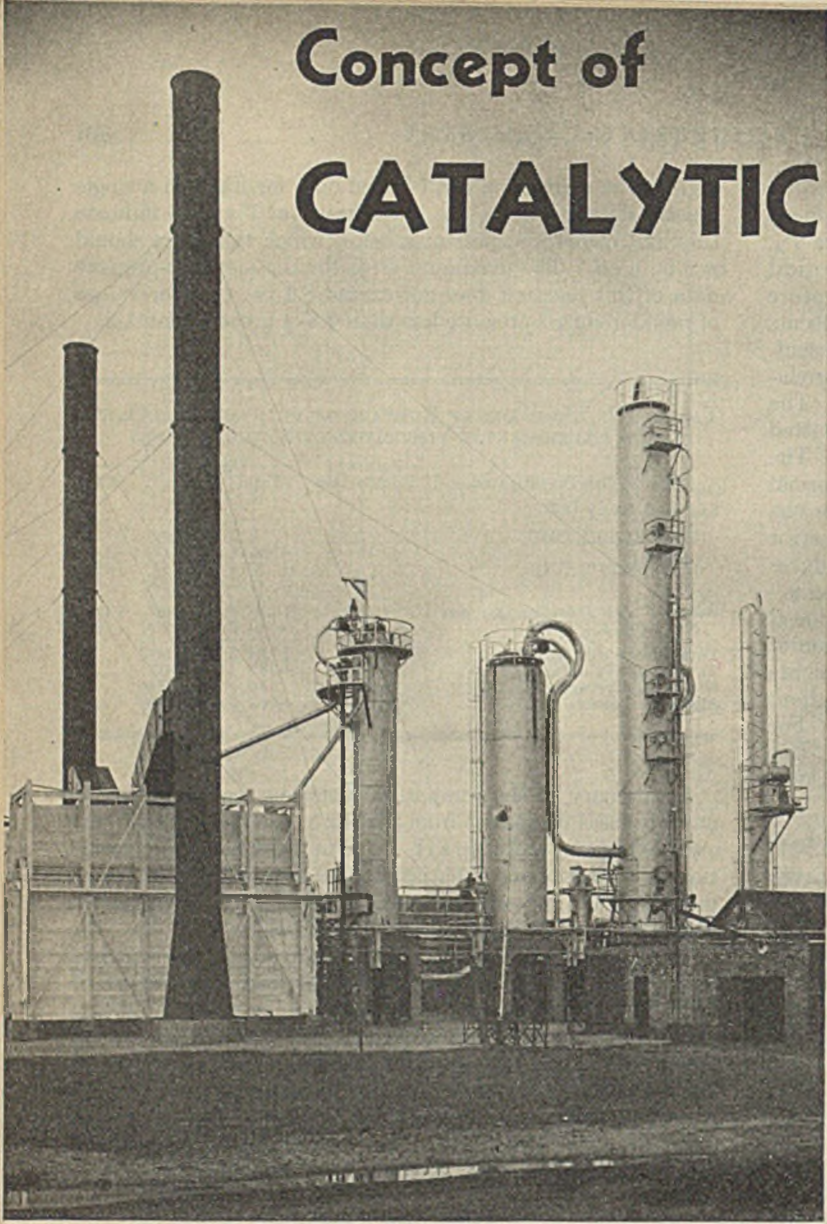
PRESENTED before the Division of Petroleum Chemistry at the 105th Meeting of the AMERICAN CHEMICAL SOCIETY, Detroit, Mich. Abstracted from the Ph.D. thesis of L. B. Bicher, Jr., Horace H. Rackham School of Graduate Studies, University of Michigan.

Concept of CATALYTIC CHEMISTRY



A Two-Coil Dubbs Cracking Unit Built by Universal Oil Products Company

Aristid V. Grosse

WAR PRODUCTION BOARD, WASHINGTON, D. C.

Fundamentally, when chemical substances are associated together and one or more of them react, two possibilities should be distinguished: In the first case one or several chemical substances react without interference or influence from the other chemical substances present. In the second case these other substances, which are not consumed in the reaction, influence the chemical behavior of the reacting substances. They may increase or decrease the velocity of the reaction and they may also change its direction. Obviously, reactions according to the first possibility form the content of classical chemistry. Reactions according to the second possibility should form the subject matter of what the author proposes to call "catalytic chemistry". The objective of catalytic chemistry is to collect, systematize, correlate, explain, and, where possible, predict the catalytic behavior of inorganic and organic substances. The explanations and predictions should be based on the known or determinable chemical properties of the reactants and catalysts involved, under the physical reaction conditions. Various deductions are made from these basic viewpoints.

WITHIN the last decade a large number of new catalytic reactions have been discovered and developed into important industrial processes. Taking the petroleum and rubber industries as an example, one need only be reminded of the following catalytic achievements: polymerization of mono-olefins to aviation gasoline (Ipatieff), of diolefins to Buna and Buna S (Tshunkur), of acetylene to vinylacetylene and further to neoprene (Nieuwland and Carothers); dehydrogenation of low-molecular paraffins to corresponding mono- and diolefins (butadiene, isoprene), of naphthenes to aromatics, of ethylbenzene to styrene; cyclization of paraffins, olefins (mono- and di-), or acetylenes containing a row of six or more carbon atoms to aromatics (toluene); alkylation of paraffins with olefins to higher paraffins; hydrogenation of carbon monoxide to hydrocarbons (Fisher-Tropsch); cracking of gas oils to aviation and motor gasoline (Houdry); and condensation of alcohol to butadiene (Lebedew).

It is safe to say that, for every new noncatalytic reaction, at least three catalytic ones are being discovered and industrially developed at present. In contrast to this amazing development in the applied field, our theoretical and scientific concepts are lagging far behind. This is due to our antiquated attitude toward catalysis.

At present, textbooks of inorganic and organic chemistry and chemical discussions talk about the "phenomenon of catalysis" and the application of this phenomenon by the chemist as a means of overcoming chemical inertia and lack of reactivity. Ostwald's physicochemical definition of catalysis has induced physical chemists for the last decade to attempt a "general explanation" of this phenomenon in terms of physical concepts.

The state of our understanding and insight into this field is closely analogous to that prevailing at the beginning of the nineteenth century in regard to organic chemistry. At that time only a small number of compounds were isolated from organic sources, and it was believed that the *vis vitalis*, a mysterious force of life, was necessary to produce them. After Woehler's synthesis of urea, these viewpoints quickly disappeared, and new discoveries soon led to the new concept that all these mysterious compounds are but compounds of carbon and form a new branch of chemistry, which we now all know as "organic chemistry".

In a similar way, it is useless now to look for a "general explanation" of the phenomenon of catalysis. From the material on hand we may conclude that we are confronted here with a new field of chemistry, which we propose to call "catalytic chemistry". It is a logical expansion of the fields of classical inorganic and organic chemistry into a new region, and we should recognize it as such.

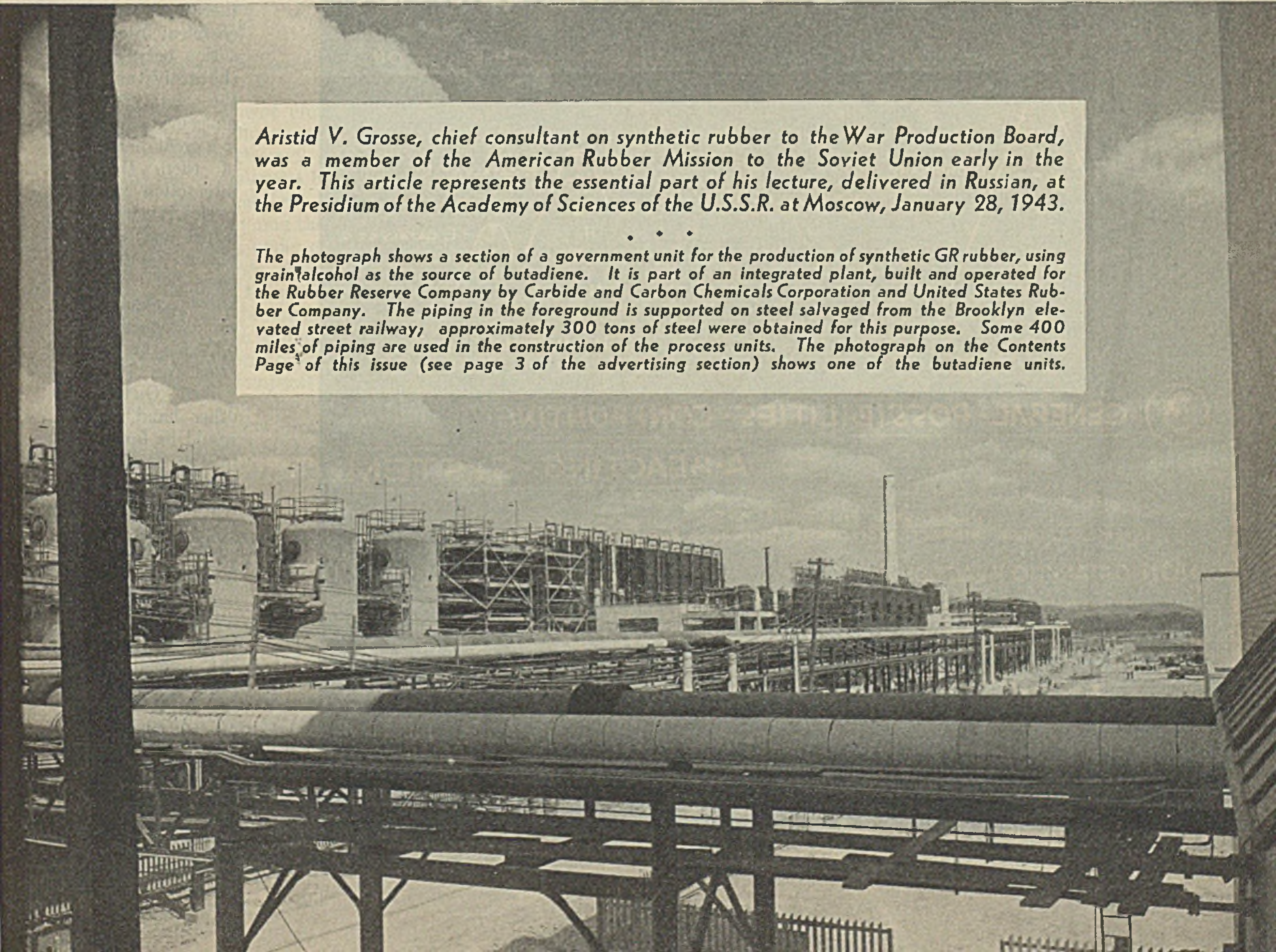
Fundamentally, when chemical substances are associated together and one or more of them react, two possibilities should be distinguished: In the first case one or several chemical substances react without interference or influence from the other chemical substances present. In the second case these other substances, which are not consumed in the reaction, influence the chemical behavior of the reacting substances. They may increase or decrease the velocity of the reaction and they may also change its direction. Obviously, reactions according to the first possibility form the content of classical chemistry. Reactions according to the second possibility should form the subject matter of catalytic chemistry.

THUS catalytic chemistry deals with the reactions of chemical substances in the presence of other chemical substances. The latter do not appear in the end products of the reaction, but do change the reaction velocity and may change its direction. In other words, it deals with the influence one chemical substance exerts on the reactions of one or many other substances without going into a stable combination with any one of them under the reaction conditions.

In contrast to noncatalytic or ordinary chemistry, every chemical substance in catalytic chemistry may play a triple role. Thus it may be catalyzed to react, under conditions where it would not react by itself; it may be a catalyst itself and promote the reaction of one or more substances; and it may prevent or "poison" the catalytic activity of another substance (or substances).

Theoretically, and in many cases practically, any given chemical reaction may be catalyzed by a large number of different substances. Thus the field or scope of catalytic chemistry is potentially much greater than that of classical organic and inorganic chemistry. In line with this the future systematic handbooks of catalytic chemistry will be many times as bulky as our present day Gmelin, Mellor, or Beilstein! The general relation between inorganic and organic chemistry to catalytic chemistry may be illustrated schematically as in Figure 1.

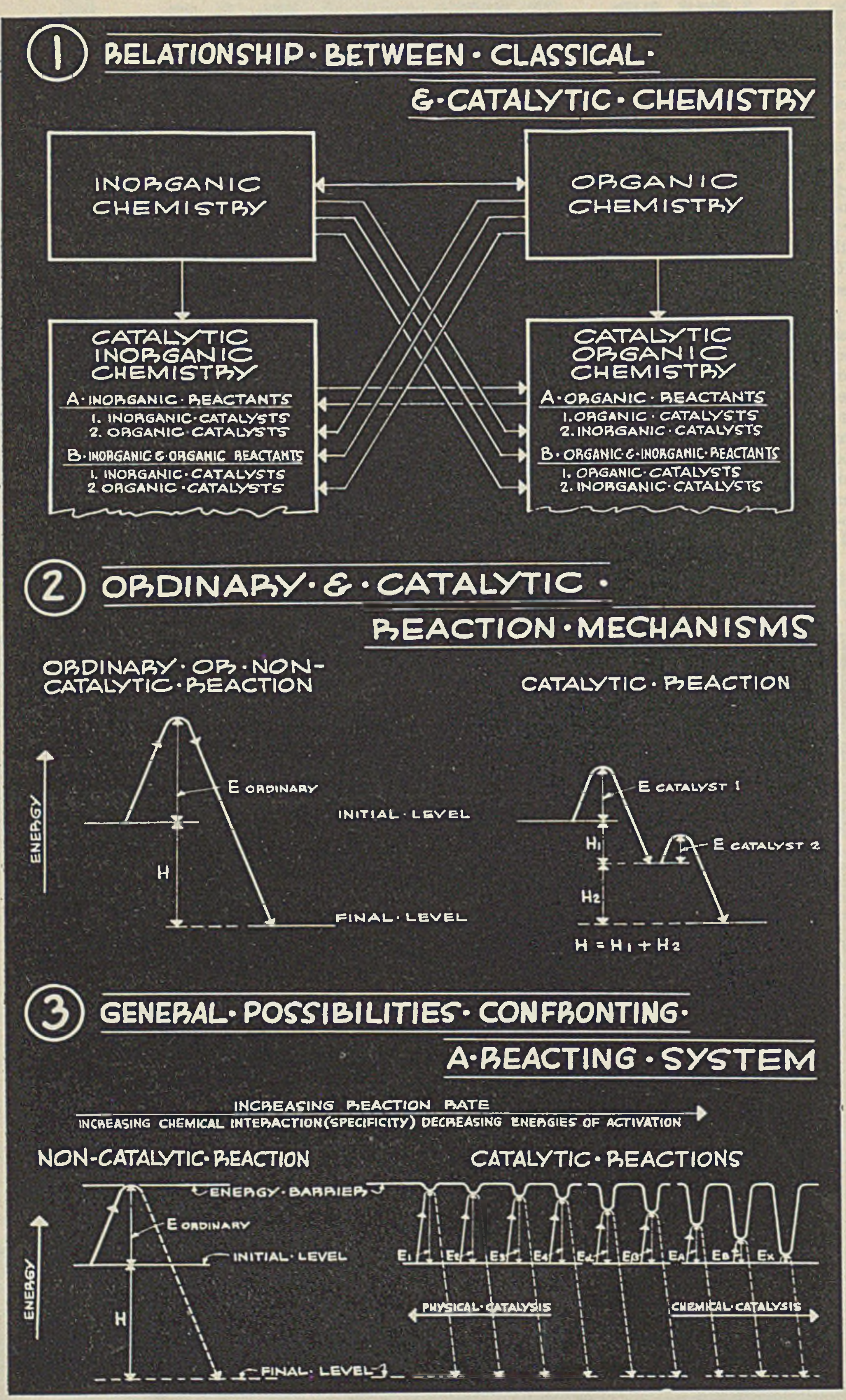
Present explanations of catalysis are adequate in some cases and fail in most others. Past attempts to develop a systematic catalytic science have never progressed far, from a chemist's point of view, because of their failure to recognize the importance of the catalytic factor of a given substance, in a given reaction, in comparing it with other substances and in attempting to classify it. Defining the catalytic factor, f, as the ratio of the rates, k, of the catalyzed and noncatalyzed reaction, $f = k_{cat.}/k_{noncat.}$ According to Ostwald's definition, a catalyst is "a substance that changes the rate of a chemical reaction". Since even very small changes in reaction rates may be measured, we have practically an



Aristid V. Grosse, chief consultant on synthetic rubber to the War Production Board, was a member of the American Rubber Mission to the Soviet Union early in the year. This article represents the essential part of his lecture, delivered in Russian, at the Presidium of the Academy of Sciences of the U.S.S.R. at Moscow, January 28, 1943.

• • •

The photograph shows a section of a government unit for the production of synthetic GR rubber, using grain alcohol as the source of butadiene. It is part of an integrated plant, built and operated for the Rubber Reserve Company by Carbide and Carbon Chemicals Corporation and United States Rubber Company. The piping in the foreground is supported on steel salvaged from the Brooklyn elevated street railway; approximately 300 tons of steel were obtained for this purpose. Some 400 miles of piping are used in the construction of the process units. The photograph on the Contents Page of this issue (see page 3 of the advertising section) shows one of the butadiene units.



Figures 1, 2, and 3

unlimited number of chemical substances that may act as catalysts for a given reaction. They will range from some that will just measurably change its rate to others that will increase it by a factor of a million and even much more.

Obviously, those substances that will change it by large factors are of immediate interest and primary concern to the catalytic chemist. In most of these cases there is a strong chemical interaction between the catalyst and the catalyzed molecules, and in a great many of them this interaction can be clearly established and explained on the basis of the known chemical properties of the substances involved. On the other hand, it would be futile in the present state of our knowledge to try to explain small changes in reaction rates and try to establish a relation between the chemical properties of the reactants and an ineffective catalyst—i.e., a substance which will accelerate their reaction rate to only a small extent.

THE objective of catalytic chemistry is to collect, systematize, correlate, explain, and, where possible, predict the catalytic behavior of organic and inorganic substances. The explanations and predictions should be based on the known or determinable chemical properties of the reactants and catalysts involved, under the physical reaction conditions. Before analyzing concrete examples of catalytic reactions, it will be appropriate to discuss them generally from the physicochemical viewpoint.

Physical chemistry teaches that the relation between reaction rate k and the energy required to overcome the chemical inertia of molecules, or the activation energy, $E_{\text{act.}}$, at absolute temperature T is expressed by the well known Arrhenius equation:

$$k = ae^{-E_{\text{act.}}/RT}$$

In view of the exponential nature of this equation, relatively small changes in activation energy will cause large differences in reaction rates.

Increases in reaction rate for given values of activation energy decrease at 100°, 300°, and 1000° K. (assuming no change in a constants) are given in Table I. For example, a 10 per cent lowering of activation energy E of 50,000 calories at 300° K. will increase the reaction rate 4400 fold, whereas even a 1 per cent lowering will more than double it.

TABLE I. INCREASES IN THE REACTION RATE FACTOR, k_1/k_2

Temperature		Decrease in Activation Energy, ΔE		
° K.	° C.	500 cal.	5000 cal.	50,000 cal.
100	−173	12	8.5×10^{10}	2×10^{109}
300	+ 27	2.3	4400	3×10^{36}
1000	727	1.3	12	8.5×10^{10}

A simple scheme illustrating the difference in mechanism between an ordinary or noncatalytic reaction and a catalytic one is given in Figure 2. In the noncatalytic case the reacting molecule or molecules have to overcome the energy barrier, $E_{\text{ord.}}$. In the catalytic case the reactants first react with the catalyst, overcoming the energy barrier $E_{\text{cat. 1}}$; in the second step they react, under regeneration of the catalyst, overcoming $E_{\text{cat. 2}}$. Since both $E_{\text{cat. 1}}$ and $E_{\text{cat. 2}}$ are smaller than $E_{\text{ord.}}$, although their sum may be larger, the catalytic reaction rate will be much faster. Obviously its rate will be governed by the rate of the slowest step or the one requiring the greatest energy of activation.

So far the temperature-independent factor, a, has been neglected. The value of a in a given reaction may be changed by a catalyst—for instance, by selective geometrical orientation of reacting groups. On the whole, since rate k changes linearly with a, the latter has a lesser significance than activation energy E.

KEEPING in mind the above-mentioned scheme, there are certain general possibilities confronting a given system of molecules, alone and in the presence of various catalysts. The general case is illustrated in Figure 3. On the left is the noncatalytic case where the reacting molecules have to overcome the highest barrier ($E_{\text{ord.}}$). For the catalytic reaction the number of possibilities is practically limitless. First there will be a large number of substances causing only a slight decrease in activation energy and a corresponding increase in rate; these substances are indicated by E_1, E_2, E_3, E_4, etc. Then there will be a lesser number of substances producing substantial decreases in the energy barrier, such as E_α, E_β, etc., or E_a, E_b, and only a few, indicated by E_x, which will produce very high increases in rate. (The effect of factor a has been neglected for simplicity. In a number of cases certain catalysts may affect it favorably and thus change the sequence of catalyst efficiency based on activation energy decreases alone.)

Thus we see a whole gamut of catalytic possibilities. The chemical interaction between reactants and catalyst will increase as we go from left to right, whereas from right to left the catalysis will assume a more physical aspect.

Thus, in general terms, on the extreme right of the diagram the catalytic mechanism will go through the formation of intermediate stoichiometric compounds of greater or lesser stability; then as we move toward the left, it will gradually change to less stable and definite surface compounds, then to activated complexes, and finally be due to mere molecular deformations caused by molecular fields of force.

Since theoretically the transition from enormous catalytic effects to none at all is continuous, there is no sharp boundary between classical and catalytic chemistry. However, in practice such a boundary has already been established and following the present tradition there should be no difficulty in maintaining it in the future.

A particular picture of a reaction and its various possible catalysts will depend on the physical reaction conditions, such as pressure, concentrations of reactants and catalyst, and particularly temperature. In making comparisons of catalytic performance of various substances, two extremes must be differentiated: (*a*) The noncatalytic reaction proceeds at a fast rate under experimental conditions; and (*b*) the catalytic reaction proceeds at a barely measurable rate only in the presence of the best catalysts. Obviously in the first case even potentially effective catalysts will not show up well, whereas in the second case medium and poor catalysts will not be noticed.

Failure to distinguish between the catalytic factor of various substances in a given reaction, failure to take due consideration of the physical conditions of the reaction, and particularly failure to compare with the rate and course of the noncatalytic reaction have been a great deterrent in chemical attempts to elucidate and classify the phenomena of catalysis in the past; generally substances of enormously varying degree of efficiency were uncritically thrown together as "catalysts".

In comparing the catalytic performance of various substances in heterogeneous catalysis, due consideration must be given to such physical factors as accessibility and availability of catalytic surface, its porosity, thermal and time stability, diffusion factors, crystalline or amorphous nature, and the effect of various substances on these factors, the size of crystals, etc.

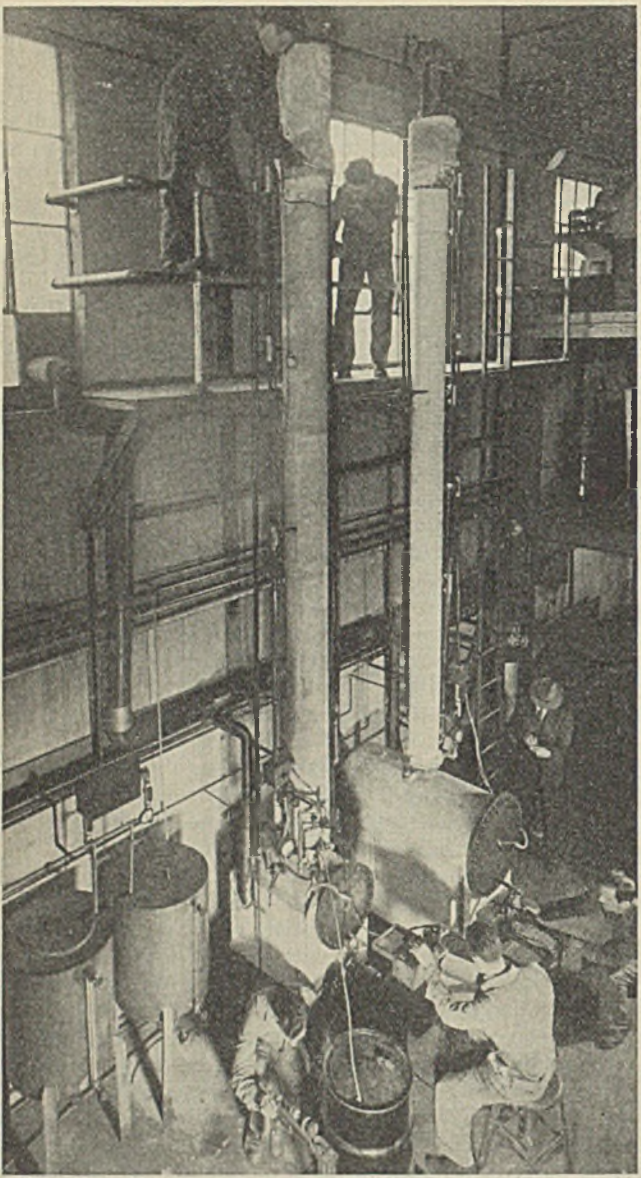
TYPICAL examples of catalytic reactions will illustrate to some extent the various points raised in the preceding paragraphs.

First is the catalytic reaction which can be fully predicted on the basis of the chemical properties of the substances involved. Such is the Squibb reaction (*8*) or the catalytic decomposition of acetic acid to acetone over calcium carbonate. Acetone was originally produced by converting acetic acid with calcium carbonate or oxide into calcium acetate, according to Equation 1. This acetate has the property of decomposing at about 400° C. into acetone, water, and carbon dioxide, following Equation 2:

$$2CH_3.COOH + CaCO_3 \longrightarrow Ca(OOC.CH_3)_2 + H_2 + CO_2 \quad (1)$$

$$Ca(OOC.CH_3)_2 \longrightarrow CaCO_3 + CH_3.CO.CH_3 \quad (2)$$

Instead of this two-step chemical process, Squibb (*8*) proposed simply to carry out the reaction in a single catalytic step, using calcium carbonate as catalyst, in line with Equation 3.



A Small-Scale Cracking Plant Used by the U. S. Bureau of Mines to Convert Medium Oil into Gasoline or Diesel Fuel

$$2CH_3.COOH \xrightarrow{CaCO_3} CH_3.CO.CH_3 + H_2O + CO_2 \qquad (3)$$

Since all carbonates may be converted into acetates by contacting them with acetic acid, it follows that any metal acetate which will decompose, under reaction conditions, into acetone and regenerate carbonate (or a metal oxide readily convertible into acetate) will act as a catalyst for this reaction. In line with this, barium, strontium, and zinc carbonates were found to be catalysts for this reaction, since their acetates on heating give acetone.

A second example is catalysis by means of surface or absorption compounds. A typical case is the well known reaction:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

This reaction does not proceed alone with any noticeable velocity at room temperature. However, at high temperatures it will proceed without a catalyst. Under such conditions practically any solid substance may measurably change the reaction rate and therefore be a "catalyst" and it would be futile for a catalytic chemist, at the present state of our knowledge, to interpret the better or lesser catalytic performance of a given substance as a function of its chemical properties.

At low temperatures this reaction is enormously catalyzed by noble metals, particularly platinum and palladium. The affinity of noble metals for both hydrogen and oxygen is well known, and the formation of unstable surface noble metal hydrides and oxides is well established. The easier oxidation or reduction, respectively, of these compounds by the reacting gases and their regeneration during the catalytic cycle as compared to direct reaction between the gases adequately explains to the catalytic chemist the chemical mechanism of this reaction and the very much faster combination of the two gases in their presence.

It does not follow that any hydrogenation catalysts will promote this reaction. The knowledge of their chemical properties, however, will permit a catalytic chemist to decide whether they are suitable or not. For instance, sodium and the other alkali metals, which readily form hydrides and may be used as high-temperature hydrogenation catalysts, will not be suitable for this reaction; for both oxygen and water, the reaction product, will convert them into stable compounds such as sodium oxide, sodium peroxide, sodium hydroxide, and others, which cannot be regenerated by hydrogen. Thus it will not be possible to establish a catalytic cycle.

TABLE II. CATALYTIC REACTIONS OF HYDROCARBONS KNOWN BEFORE 1932

	Paraffins	Olefins	Naphthenes	Aromatics
Paraffins	−	−	−	−
Olefins	−	+	−	+
Naphthenes	−	−	−	−
Aromatics	−	+	−	−

The third example is merely physical catalysis, corresponding to the region E_1, E_2, E_3, etc., of Figure 3. The catalytic cracking of hydrocarbons, pioneered by Houdry within the last fifteen years, is typical. The noncatalytic or thermal cracking takes place at a practical rate at around 500° C. A large number of inorganic substances, particularly metal oxides, will catalyze the reaction and allow it to proceed with sufficient speed at about 450° C. and even lower. Some of these substances will also appreciably change the direction of cracking—i. e., the nature of reaction products.

In view of what was said about the "physical region" of Figure 3, it is difficult at present to explain the good catalytic performance of a specific oxide mixture from its chemical nature. In this and similar cases, such factors as the size and extent of internal surface, thermal stability, lack of crystalline compound formation, etc.—in other words, factors depending on the solid chemistry of the catalyst mixture—become decisive in practice and not the chemical interrelation between the reactants and the solid catalyst.

The fourth and last example illustrates the large number of different substances that may be used to catalyze one particular reaction and also the wide range of physical conditions under which it may be accomplished. A typical case is the alkylation of paraffins by olefins (*5*). Catalysts may be (*a*) various solid metal halides, such as aluminum chloride, aluminum bromide, zirconium tetrachloride, etc. (*3*), which form solid or liquid complexes, (*b*) gaseous boron fluoride and water, with or without nickel (*5*), and (*c*) acids like sulfuric (*1*, *6*) or anhydrous hydrogen fluoride (*4*). The reaction takes place from temperatures below −50° (*7*) to about 400° C.

At these high temperatures (under pressure) no specific catalyst is required, and it becomes a pure thermal reaction (*2*).

The reaction may be carried out heterogeneously, using solid boron fluoride, nickel, water (or hydrogen fluoride) complexes, or liquid aluminum chloride or bromide complexes as catalysts. Again it may be carried out homogeneously in the liquid phase with hydrogen fluoride as catalyst. In the latter case it is necessary to use an excess of olefin over paraffin. The olefin forms an alkyl fluoride which, in turn, dissolves both the paraffin to be alkylated and the catalyst (hydrogen fluoride).

The mechanisms of these reactions, aside from the activation of the C—H bond, may be widely different, and no satisfactory explanation for any one of them has yet been proposed.

THESE examples show how the various types of catalysis (chemical and physical) form but parts of a continuous picture. The relation between various parts of this picture is established by the Arrhenius equation. The writer hopes that a more complete discussion, in book form, of the enormous volume of catalytic facts available, in the light of concepts introduced here, may be possible after this war. The enormous potential size of this new chemical field has already been stressed, although now we usually think only of inorganic and organic reactants and inorganic catalysts. The scientific vista becomes breath-taking when we begin to include organic molecules as catalysts. The conversion of the highly inert molecules of nitrogen, at room temperatures, into ammonia, nitrous acid, and nitric acid by Azotobacter bacteria is a catalytic marvel of the first order. No less so is the assimilation of carbon dioxide and elimination of oxygen by plants and the regulated oxidation of organic substances by oxygen to carbon dioxide in living bodies.

In conclusion it may be worth while to emphasize how the development of the catalytic chemistry of a particular type of compounds, such as hydrocarbons, has enlarged our general knowledge of their chemistry. Let us recall their most important classical properties. The known chemistry of paraffins is particularly brief. All textbooks stress their lack of reactivity. Sulfuric acid does not sulfonate them, nitric acid acts only with difficulty, and only halogens like chlorine attack them vigorously; of course, they burn. Olefins are characterized by addition and polymerization reaction. The aromatics, in contrast to paraffins and naphthenes, are sulfonated and nitrated.

All catalytic reactions between various classes of hydrocarbons known before 1932 are marked in Table II by plus signs. Since then systematic research, along the lines discussed in this article, has led to the discovery of all the other reactions, indicated by a minus sign, and some of them have already attained great industrial importance. Thus the volume of our knowledge of hydrocarbon chemistry has substantially increased, thanks to the development of their catalytic chemistry.

There can be no doubt that other branches of chemistry could do likewise. Their task would be simplified if textbooks would begin to give consideration to the subject of catalytic chemistry.

ACKNOWLEDGMENT

The writer had the privilege of being associated in his catalytic work over a period of years with some of the leading pioneers in this field—namely, V. N. Ipatieff (since 1926), H. Tropsch (since 1930), and in the last few years with E. Houdry and H. S. Taylor. To all of them he is indebted for many valuable discussions which gradually led him to his present viewpoint.

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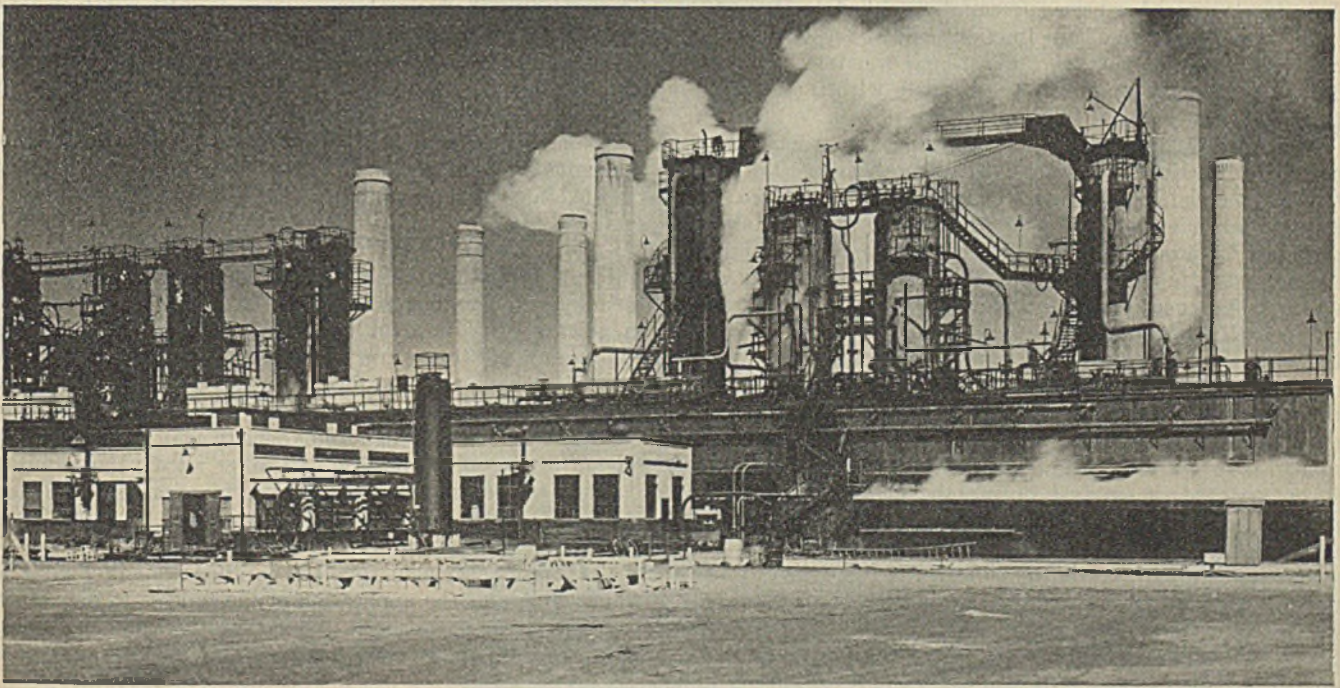
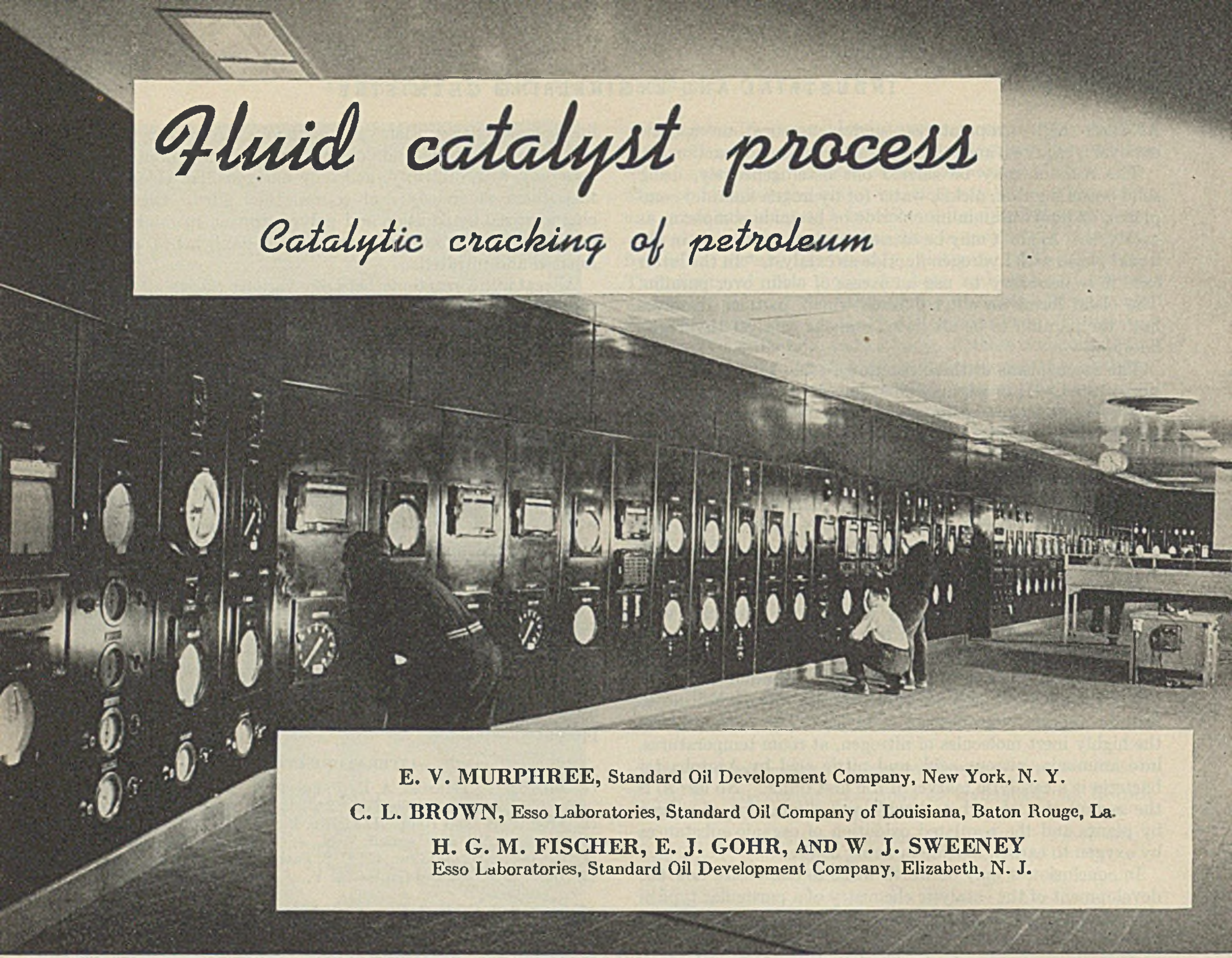


Giant "Crackers", at a Standard Oil Company of California Refinery, Convert Part of Heavier Products from Initial-Distilling into Gasoline and other Lighter Fractions

Fluid catalyst process

Catalytic cracking of petroleum



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THE Fluid Catalyst process represents a new chemical engineering technique which has wide application to industrial operations, both catalytic and noncatalytic. This development has been successfully applied to the catalytic cracking of petroleum fractions and as a result has become an essential part of the national wartime economy. The present paper is concerned primarily with this application of the fluid catalyst technique.

The oil industry's quest for more efficient utilization of petroleum fractions led to the field of catalysis in 1931 with the commercial application of hydrogenation. More recently work has centered on development of other catalytic processes for producing gasoline from petroleum. Inasmuch as the catalytic decomposition of hydrocarbons in the absence of hydrogen is accompanied by the formation of coke-like deposits on the catalytic surfaces, which in turn reduce the activity of the catalyst, the utilization of such reactions depended on the successful revivification or regeneration of the catalyst. The Houdry process, the first to be commercially applied, accomplishes regeneration with a conventional multireactor system. The oil vapors are passed through a stationary bed of catalyst during the cracking cycle. At periodic intervals the oil stream is switched from one reactor to another; the first reactor then enters into a regeneration cycle where the carbon is burned off the catalyst with air. The operation is thus continuous, but in terms of the reactors containing the catalyst, the operation is intermittent. Hydroforming is another commercial process operating in this manner.

The most recent developments in this field, the Fluid Catalyst and the Thermofor processes, are characterized by a continuous flow of both catalyst and oil. The Thermofor method circulates coarse granular catalyst continuously between separate cracking and regenerating zones by mechanical conveyors. The Fluid process also operates on the principle of continuous catalyst flow but with no mechanical handling of catalyst at any stage in the process.

Because of the vital part played by the Fluid Catalyst process in making war products, it has been necessary to omit detailed information and data at many points in the paper.

PRINCIPLES OF THE PROCESS

The Fluid Catalyst process fundamentally represents a new technique in handling solid materials. The solid material, in powder form, is maintained in a fluid or freely flowing condition at all times, and can thus be handled in much the same way as a liquid. A fluidized mass can be circulated by application of the gas lift principle—that is, by balancing a downflowing stream of high-solids density against an upflowing stream of low-solids density. In other words, the required pressure differential for circulation is obtained in much the same way as water would be transferred by balancing a column of water against a water-gas mixture.

The basic equipment involved is illustrated in Figure 1, which illustrates the application of the process to petroleum cracking. The operation is divided into two primary zones, a cracking and a regeneration zone. The principal apparatus

When oils are cracked, carbon is deposited on the catalyst, reduces its activity, and makes necessary its removal by burning with air. In the Fluid Catalyst cracking process the catalyst is handled as a fine powder and is kept in a fluidized condition so that it may be handled substantially as a liquid. The catalyst is conveyed through the reactor by the oil vapor and is separated in dust recovery equipment; then the product vapor flows to distillation apparatus. The carbonized catalyst flows down a standpipe in a high-density condition. Its pressure is thus increased sufficiently to permit injection into a stream of air, which carries it to the regenerator where the carbon is burned off. The catalyst is separated, the flue gas is vented to the atmosphere, and the regenerated catalyst passes down a second standpipe and is injected into the oil vapor going to the reactor. The process is thus completely continuous as regards oil, air, and catalyst flow. Information is available on production of motor gasoline from a variety of charge stocks. The gasoline has a clear octane number of 92–94 by the CFR Research method. Operating conditions may be adjusted to produce high-octane aviation fuel, butylenes, and toluene. Gasoline fractions from the operation may be used directly as aviation base or may be reprocessed in the fluid catalyst unit or hydrogenated. Aviation fuels produced by these methods have low alkylate requirements, and after addition of tetraethyllead, they meet the highest specifications.

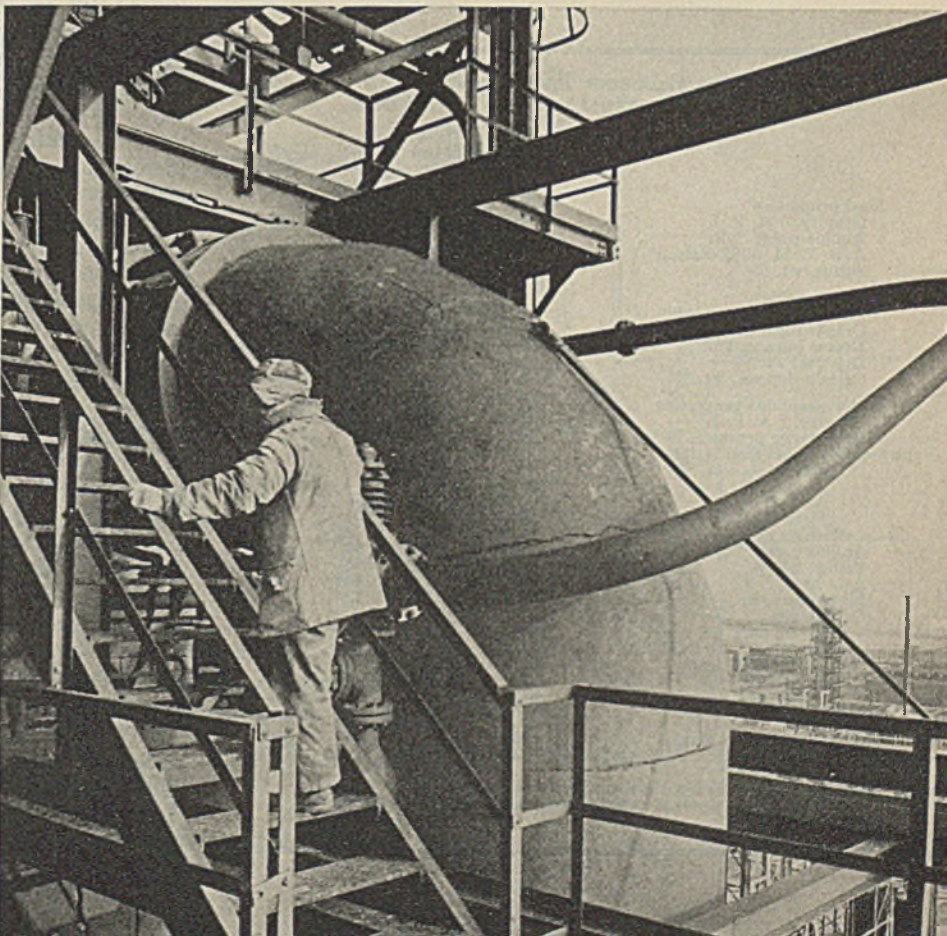
is the same in each zone—standpipe, reaction vessel, and dust separator. Oil vapor is contacted with regenerated catalyst delivered by gravity from a standpipe, and the mixture flows in suspension into the cracking reactor where the reaction occurs. The mixture of cracked products and catalyst flows through dust recovery equipment where the catalyst is recovered. The separated spent catalyst is collected in a hopper, flows at high density down a standpipe, and is injected into a stream of air used for regeneration. This air carries the spent catalyst to the regeneration vessel, and it then passes into dust collecting equipment where essentially all the catalyst is removed from the flue gas. The recovered catalyst is collected in a hopper, flows down through a standpipe, and is injected into the oil vapor stream; the cycle is thus completed.

The flow characteristics of gases carrying solid particles have been carefully investigated; it has been found possible by suitable adjustment of gas or vapor velocities to build up relatively high concentrations of solids where desirable—for example, in reaction and regeneration vessels. The densities which can be attained are functions of the solids feed rate, composition, and particle size, as well as the vapor or gas velocity. Pressure drop due to friction is quite small, the main pressure drop in the system being due to static heads.

Although high concentrations of solids may be obtained in reaction vessels, the solid-gas mixture is extremely turbulent and resembles a boiling liquid in many respects. Owing to this high turbulence with consequent rapid circulation of solids, the temperature throughout the solids mass is surprisingly uniform, varying less than 5° F. from bottom to top in large vessels in catalytic cracking. The extreme turbulence of solids in vessels of this type offers many advantages in temperature control in catalytic or other processes.

DESCRIPTION OF A CRACKING PLANT

A simplified flow diagram illustrating the first commercial design of a Fluid Catalyst cracking plant is presented in Figure 2 to show in more detail the application of the Fluid technique to the cracking of oil. (More recent designs represent definite improvement and simplification over that indicated by Figure 2.) Regenerated catalyst from a storage hopper flows by gravity through a standpipe and is injected into the fresh oil feed vapor which carries it to the cracking reactor. The velocity in the reactor is low so as to maintain a high concentration of catalyst, and cracking occurs with a subsequent deposition of carbon on the catalyst. The mixture of cracked products and spent catalyst from the cracking zone are separated in dust recovery equipment; the cracked products flow to fractionating equipment for separation into desired components. The spent catalyst drops into a storage hopper, flows down a standpipe, is picked up by an undiluted air stream, and is carried to the regenerator in which car-



bonaceous deposits are removed by combustion. The mixture of flue gas and catalyst from the regenerator are separated, the catalyst dropping into the regenerated catalyst hopper to complete its cycle.

The heat evolved in burning the carbon deposit on the catalyst is greater than can be absorbed as sensible heat by the catalyst for a reasonable temperature rise. It is therefore necessary to have an additional means of absorbing regeneration heat. This is accomplished by circulating regenerated catalyst through shell-and-tube heat exchangers, using a separate standpipe circuit as shown in Figure 2. The cooling medium applied to the heat exchangers in the unit described is fresh oil feed to the plant. However, the heat absorbed by this oil is ordinarily more than that required to bring it to proper temperature, and a further dissipation of this heat is made to produce steam.

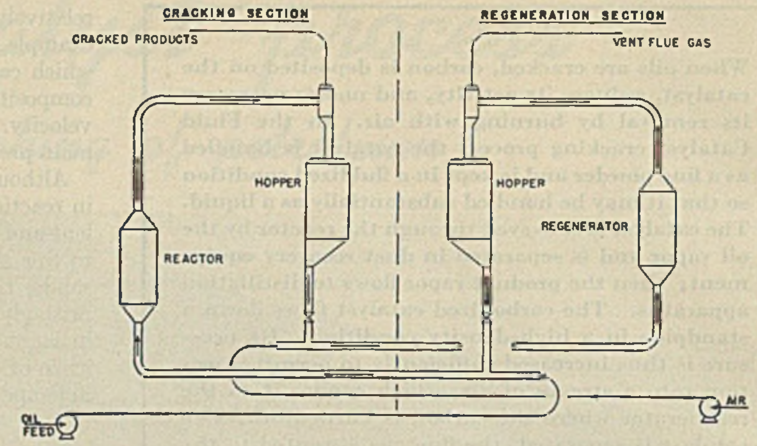


Figure 1. Catalyst Flow in Fluid Cracking Process

Operation of the fluid cracking plant is entirely automatic. The ratio of catalyst flow to oil flow, for example, is controlled by a mechanism actuated by changes in the density of the catalyst-oil mixture. Flow of catalyst to regeneration is ensured by automatic control of the level of the catalyst in the spent catalyst hopper. Similarly, regeneration temperature is governed by automatic regulation of the quantity of catalyst circulated through the heat exchangers.

The flexibility of the Fluid process is demonstrated by the fact that operations can be carried out over a wide range of cracking and regeneration temperatures, as well as depth of cracking. Reaction temperatures can be varied both by amount of heat applied to the oil in the furnaces and of hot catalyst circulated. Normal reactor temperatures lie in the range 800° to 1000° F. The regeneration temperatures can be varied over a relatively wide range and are maintained normally between 1000° and 1200° F. The depth of cracking is governed by both the amount of catalyst in the reaction zone and the ratio of catalyst to oil flow. This flexibility is important in that the character of products is considerably affected by both the temperature and the conversion level employed.

Table I. Motor Gasoline Production and Quality from Fluid Catalytic Cracking of Gas Oils

	East Texas Wide Cut	West Texas Wide Cut	West Texas Heavy	Coastal Wide Cut
Feed properties				
Gravity, ° A. P. I.	31.7	27.3	22.3	22.1
Aniline point, ° F.	180	169	171	180
A. S. T. M. 50% distn., ° F.	680	710	825	781
Sulfur, wt. %	0.48	1.80	2.49	0.63
Product yields				
Motor gasoline[a], vol. %	45.0	43.2	46.0	46.2
Cracked gas oil, vol. %	51.2	51.2	51.2	51.2
Excess butane, vol. %	4.3	3.0	2.0	4.0
Dry gas, wt. %	4.3	6.3	5.6	5.4
Carbon deposit, wt. %	3.1	4.1	3.4	2.6
Motor gasoline[b] properties				
Gravity, ° A. P. I.	60.5	58.2	58.2	57.0
Reid vapor pressure, lb./sq. in.	10.0	10.0	10.0	10.0
A. S. T. M. distillation				
Distillate + loss, %				
At 158° F.	25.5	18.5	18.5	23.0
At 212° F.	47.0	42.0	38.0	43.5
Final B. P., ° F.	406	400	401	406
Recovery, %	97.5	97.5	97.5	97.0
Aniline point, ° F.	85	76	82	71
Sulfur, wt. %	0.03	0.18	0.246	0.044
Acid heat, ° F.	159	162	186	180
Breakdown, hr.	9	14.5	13	10
Octane No.				
CFR-M clear	80.5	79.4	77.9	80.5
CFR-M + 1.5 cc. TEL[c]	84.6	83.0	81.2	84.7
CFR-R ('39) clear	92.0	91.9	91.3	94.3
CFR-R ('39) + 1.5 cc: TEL[c]	97.0	95.9	95.3	98.1
Cracked gas oil[b] properties				
Gravity, ° A. P. I.	30.0	21.7	22.7	22.0
A. S. T. M. 50% distn., ° F.	572	605	605	563
Aniline point, ° F.	144	129	124	96

[a] Reid vapor pressure, 10 lb./sq. in.; end point, 400° F.
[b] Inspections on product as produced without further treatment.
[c] Tetraethyllead.

The pressure level can also be held at any desired point. In most present applications for gas oil cracking, the pressure at the top of the reaction vessel is in the order of 10 pounds per square inch, and the pressure at the top of the regeneration vessel is substantially atmospheric.

MOTOR GASOLINE PRODUCTION

Initial work on the Fluid Catalyst process, begun well before the present war, was directed toward the production of high quality motor gasoline. Exploratory work was carried out in small Fluid Catalyst pilot units having a capacity of approximately 2 barrels of fresh feed per day. Subsequent development work was conducted in a semicommercial pilot unit with a nominal capacity of 100 barrels per day. Typical results on a variety of feed stocks available in the Mid-continent, Gulf, and Eastern Seaboard areas are presented in Table I. The results obtained on the pilot plants have been substantially checked by three large commercial units recently put into operation.

Motor gasoline is normally produced by contacting distillate stocks with catalyst at moderate temperatures in a single-pass operation. The yield data in Table I are based on a conversion of about 49 per cent of feed gas oil (100 minus volume per cent cracked gas oil); at this level high yields of specification motor gasolines ranging from 43 to 46 per cent are obtained from a variety of feed stocks. The conversion of feed gas oil to gasoline and other products can be varied over a wide range, the optimum level being determined by economic considerations.

The high quality of the motor fuel is indicated by octane number ratings (Table I) which range from 91.3 to 94.3 CFR Research ('39) clear. Coastal (more naphthenic) feed stocks are preferable from the standpoint of octane number and gasoline yield. At some sacrifice in yield, gasolines of higher octane number than shown in Table I can be obtained by higher temperature operation. High stability of the gasolines is indicated by the breakdown test. No finishing treatment is normally required aside from a light caustic or soda wash and addition of an inhibitor. The sulfur content of the material obtained from cracking the high sulfur West Texas feed is somewhat above specifications but can be improved by a light acid treatment.

Other desirable products from the motor gasoline operation are (*a*) heating oil which can be cut directly from the gas oil as a finished product, and (*b*) propylene, butylene, and isobutane fractions which are desirable raw materials in the production of high quality aviation components and butadiene.

WAR PRODUCTS OPERATION

Work on the production of motor gasoline as a primary objective was discontinued some time before the United States entered the war, and emphasis was placed on the operation of Fluid Catalyst plants to make war products—in particular, high-octane aviation gasoline, raw materials for synthetic rubber, and synthetic toluene. No major revisions in basic equipment or design were necessary. Through the use of a suitable catalyst and by more severe cracking at higher temperatures, a more desirable product in the aviation gasoline range could be produced, along with increased quantities of the butane fractions used in the synthesis of high quality aviation blending components and synthetic rubber. Only a general discussion of operations and quality of products can be given at this time.

Aviation fuel by Fluid Cracking can be obtained in a number of ways, depending on the local situation and the aviation specifications to be met. The first-pass catalytic cracking conditions can be adjusted, or suitable portions of the first-stage product can be reprocessed by further catalytic treatment or other means. Table II gives typical qualities of the catalytic aviation components which may be derived from such operations.

Table II. Typical Product Quality of Catalytic Aviation Components

	Single-Stage High-Temp. Production		Two-Stage Production		Single-Pass Low-Temp. Production	
	As produced	Hydrogenated light fraction + raw heavy fraction	In feed	Product	Naphthenic feed stock	Paraffinic feed stock
Gravity, ° A. P. I.	60.2	62.7	60.2	56.6	57.6	67.7
Reid vapor pressure, lb./sq. in.	7.0	7.0	7.0	7.0	7.0	7.0
Aniline point, ° F.	66	102	66	64	85	122
Sulfur, wt. %	0.03	0.03	0.03	0.03	0.014	0.01
Bromine No.[a]	63	8	63	13	10	20
Acid heat, ° F	135	13	135	27	24	39
A. S. T. M. distillation, ° F.						
Initial B. P.	121	110	121	108	114	114
10% over	141	139	141	139	140	141
50%	190	189	190	210	203	189
90%	292	288	292	293	273	274
Final B. P.	338	340	338	324	300	316
Octane rating						
A. S. T. M. clear	80.5	79.1	80.5	83.1	81.6	77.9
AFD-1C + 4 cc. TEL	90.6	96.0	90.6	97.0	96.0	93.3

[a] Modified Francis method, centigrams per gram.

Single-Stage High-Temperature Operations. Cracking with a suitable catalyst at elevated temperatures produces, in addition to high yields of olefins and isobutane for alkylation, a gasoline containing fairly large amounts of toluene, xylenes, and the higher aromatics. Typical compositions of fractions in the aviation gasoline range, obtained from a paraffinic gas oil at a conversion level of 65 per cent, are as follows:

Boiling Range, ° F.	Composition, Vol. %			% Total Olefins
	Aromatics	Naphthenes	Acylics	
C_6–200	3	16	81	43
200–225	9	40	51	50
225–250	59	16	25	26
250–335	68	13	19	19
335–350	87	5	8	12

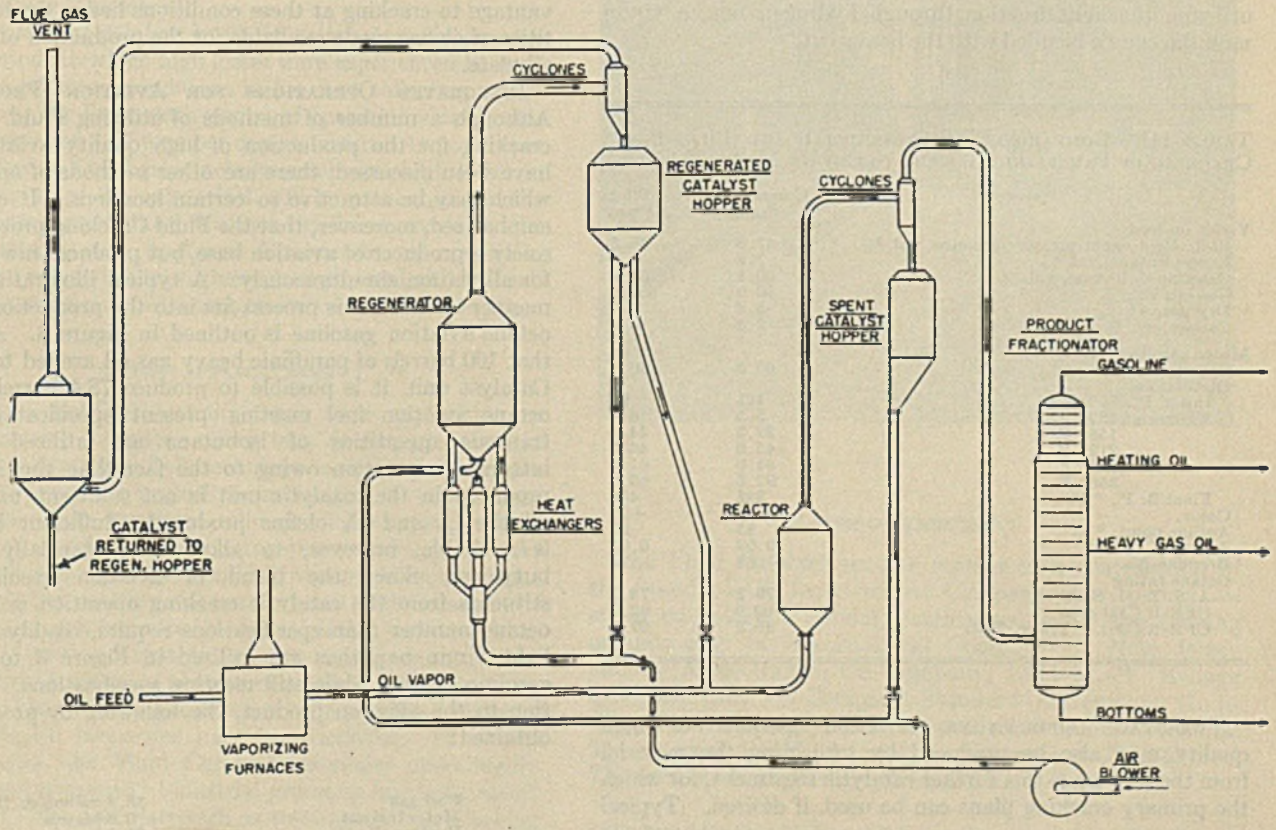


Figure 2. Fluid Catalyst Cracking Plant

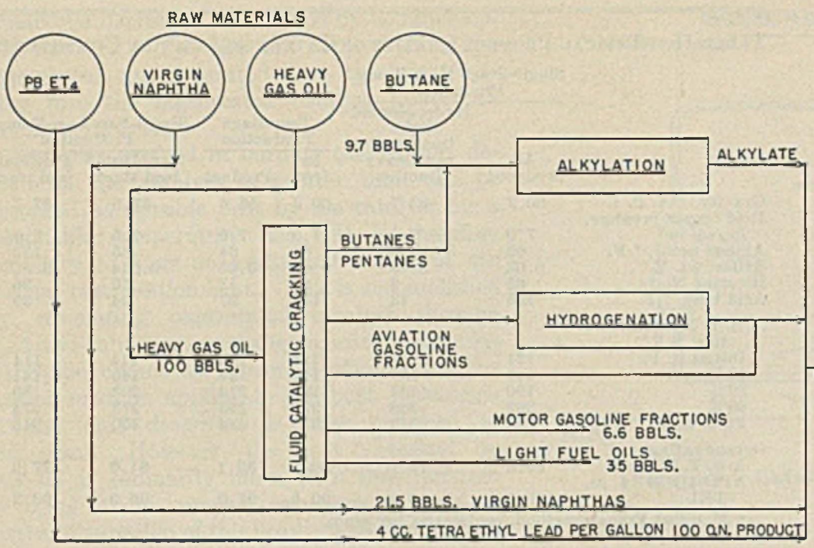


Figure 3. Aviation Gasoline Production by Fluid Catalytic Cracking

Because of their relatively low olefin content, the heavier fractions of the above gasolines are valuable as aviation blending agents, either with or without further treatment. On the other hand, the material boiling below 250° F. is high in olefin content and may be treated further for use in aviation blends. Hydrogenation of this light material results in a quality product which, when blended with the higher boiling aromatic fractions, gives a base rating 96.0 A. S. T. M. aviation[1] with specification lead added. As an alternate, the whole aviation gasoline may be hydrogenated to an A. S. T. M. aviation octane number of 97.0–98.0. This compares with a 90.6 A. S. T. M. aviation quality for the material of similar boiling range as produced (Table II). As an alternate to utilizing the light fraction through hydrogenation, a virgin naphtha can be blended with the heavy cut.

TABLE III. COMPARISON OF COMMERCIAL AND PILOT-PLANT CRACKING OF PARAFFINIC GAS OIL TO OBTAIN MOTOR GASOLINE

	Commercial Scale	Pilot Plant
Yields on feed		
10-lb. Reid-vapor-pressure gasoline, vol. %	42.8	45.6
Excess butane, vol. %	7.3	4.8
Gasoline + butane, vol. %	50.1	50.4
Gas oil, vol. %	50.0	50.0
Dry gas, wt. %	5.8	4.4
Carbon, wt. %	2.5	3.2
Motor gasoline quality		
Gravity, ° A. P. I.	60.3	60.4
Distillation		
Initial B. P., ° F.	101	95
% over at 122° F.	5.5	6.0
158° F.	22.5	24.0
212° F.	45.0	46.0
257° F.	64.0	61.5
356° F.	92.5	90.0
Final B. P., ° F.	385	400
Color	+20	+20
Aniline point, ° F.	85	87
Sulfur, %	0.03	0.04
Bromine No.	66	75
Octane rating		
A. S. T. M. clear	79.2	79.7
CFR-R ('39) clear	92.9	92.0
CFR-R ('39) + 1.5 cc. TEL	97.3	97.0

TWO-STAGE OPERATIONS. Aviation gasoline of high quality may also be produced by subjecting the material from the first stage to a further catalytic treatment, for which the primary cracking plant can be used, if desired. Typical results on the aviation gasoline obtained by such treating are summarized in Table II. The increase in product quality from roughly 90 to 97 octane number is obtained partly through the saturation and elimination of the lower boiling olefins, and partly through the concentration of aromatics in the higher boiling fractions. This operation has particular merit in situations where hydrogenation equipment is not available and where supply of natural light blending naphthas is limited. The aviation gasoline produced is quite aromatic and of high quality.

LOW-TEMPERATURE SINGLE-STAGE OPERATIONS. Cracking operations with this catalyst may also be carried out at relatively low temperatures to produce an aviation gasoline which may be used directly without further processing in aviation blends. The quality of this material when produced from commonly available paraffinic gas oils is inferior in certain aspects to that produced from higher temperature operations. Leaded A. S. T. M. aviation octane numbers of 91–94 are normally obtained with 4 cc. of tetraethyllead per gallon of fuel. However, certain naphthenic gas oils adapt themselves readily to these cracking conditions and result in a specification product high in leaded octane number (96.0 A. S. T. M. aviation). Typical products from this type operation are presented in Table II. An inherent disadvantage to cracking at these conditions lies in the low quantities of olefins made available for the production of aviation alkylate.

INTEGRATED OPERATIONS FOR AVIATION PRODUCTION. Although a number of methods of utilizing Fluid Catalyst cracking for the production of high quality aviation base have been discussed, there are other methods of application which may be attractive to certain locations. It should be emphasized, moreover, that the Fluid Cracking process is not solely a producer of aviation base, but produces raw material for alkylation simultaneously. A typical illustration of the manner in which this process fits into the production of 100-octane aviation gasoline is outlined in Figure 3. Assuming that 100 barrels of paraffinic heavy gas oil are fed to a Fluid Catalyst unit, it is possible to produce 78.4 barrels of 100 octane aviation fuel meeting present specifications. Extraneous quantities of isobutane are utilized in this integrated operation owing to the fact that the isobutane produced in the catalytic unit is not sufficient to alkylate all the C_4 and C_5 olefins produced. Sufficient isobutane is available, however, to alkylate substantially all the butylenes. Since the blend of aviation gasoline constituents from the catalytic cracking operation is higher in octane number than specifications require, readily available light virgin naphthas are utilized in Figure 3 to increase gasoline volume while still meeting specifications. In addition to the aviation product, the following by-products are obtained:

Fuel gas	38.8 million cu. ft.
Motor fuel cut	6.6 barrels
Heating oil cut	23.0 barrels
Fuel oil	12.0 barrels

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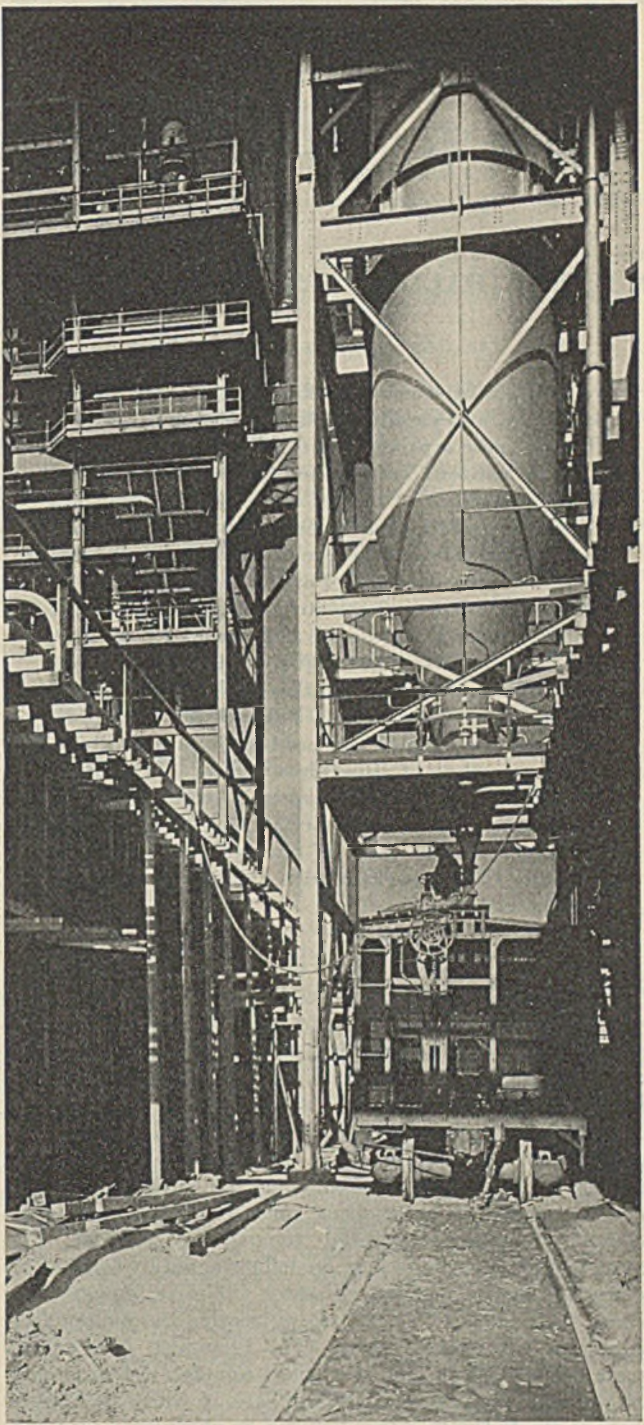
[1] A. S. T. M. Designation DG 14-42T, also referred to as AFD-1C.



Unloading a Finely Powdered Catalyst from Freight Cars into a Hopper, from Which It Is Delivered to the Catalytic Cracking Unit; Here It Circulates with Products Being Manufactured, to Control Intricate Chemical Reactions.

◆

COMMERCIAL OPERATIONS

Three large commercial Fluid Catalyst plants are now in operation; photographs of one of these units are shown on pages 768 and 769. A considerable number of these plants of improved design are being constructed for refiners in the petroleum industry. When this program is completed, the installed capacity of Fluid Catalyst cracking will probably exceed that of any other catalytic cracking process.

The present commerical experience with large Fluid Catalyst plants has been gratifying. The first unit was placed in operation on May 25, 1942, with surprisingly little difficulty. Initial operations were conducted for motor gasoline on heavy wide-cut gas oils since the catalyst required for the war products operation was not available. Smooth performance has been obtained; yields, product quality, and operating conditions were found to be in good agreement with the semicommercial pilot plant, as shown in Table III.

More recently the first commercial plant has operated continuously for five months with a suitable catalyst for aviation gasoline production. Maintenance of catalyst activity was satisfactory; at the end of the run the catalyst was entirely suitable for future operations, and its use in the unit was continued. The plant was in good mechanical condition following this run, and this indicated that maintenance requirements will be low.

The recovery of catalyst has been satisfactory, in general, despite periods in which high losses were experienced because of faulty mechanical conditions in the dust collecting equipment. Over the five-month period of operation actual catalyst loss averaged 2.27 tons per day, or about 0.41 pound per barrel of feed. This figure includes somewhat high losses in the starting up of the unit, which will be preventable in the future. Small mechanical changes are being made in the dust collecting system to ensure dependability of operation, and it is expected that with these changes catalyst loss from a large commercial Fluid Catalyst unit will be nearer 1 ton per day.

OTHER APPLICATIONS

The Fluid Catalyst technique has wide application to many industrial operations which may or may not involve catalyst reactivation. This technique is particularly adaptable as a temperature control means for gas- or vapor-phase reactions since the powdered solid circulates rapidly within a vessel and ensures uniform temperature throughout. At the same time the powdered solid in the vessel imparts heat capacity to the reacting vapors or gases and thus guards against rapid temperature changes. Heat can be either added to or removed from the system by circulation of the powder through suitable heaters or coolers. Application is not confined to catalytic processes, since a powdered material of noncatalytic properties may be employed. In a still broader sense, the Fluid Catalyst technique undoubtedly has application to many industrial processes involving direct handling of solid materials such as treatment of ores, coking of coal, etc.

ACKNOWLEDGMENT

The Fluid Catalyst process represents a contribution of the Standard Oil Development Company to a cooperative study on catalytic refining participated in by the refining organizations of Standard Oil Company of New Jersey and by Anglo-Iranian Oil Company, Ltd., M. W. Kellogg Company, Shell Oil Company, Standard Oil Company (Indiana), Texas Company, and Universal Oil Products Company. The views of the Fluid Catalyst plant on pages 768, 769, and 773 were photographed by Robert Yarnell Richie.

Presented before the Division of Petroleum Chemistry at the 105th Meeting of the American Chemical Society, Detroit, Mich.

Fertilizer by Fusion of ROCK PHOSPHATE WITH OLIVINE

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By fusing a mixture of rock phosphate, magnesia, and silica, and rapidly cooling the melt, it is possible to make a product with a high proportion of its P_2O_5 content soluble in citrated ammonium nitrate solution. Olivine, a mineral magnesium silicate, found in abundance in the Tennessee Valley, is an economical source of magnesia and silica for the fusion process. For example, fusion of 1 pound of rock phosphate and 0.46 pound of olivine yields a product containing 22.8 per cent total P_2O_5 and 21.4 per cent soluble P_2O_5. One fourth to one third of the fluorine in the rock phosphate is volatilized in the process. Pot culture tests indicate that the P_2O_5 of the product is practically as effective as that of superphosphate; the magnesium content should prove advantageous. Because of the inexpensive raw materials and the simplicity of the process, the cost of the product should be favorable in comparison with that of other phosphatic fertilizers.

TO MAKE the P_2O_5 in rock phosphate readily available to plants, it is necessary to break up the structure of fluorapatite, the principal phosphatic component of rock phosphate. [The availability of P_2O_5 in fertilizers to plants is usually estimated by its solubility in solvents such as neutral ammonium citrate solution (*1*) and citrated ammonium nitrate solution (*9*).] The fluorapatite structure may be broken either by removing the fluorine from the rock phosphate or by treating rock phosphate chemically without effecting substantial removal of fluorine. For example, rock phosphate may be defluorinated by calcination with silica in the presence of water vapor at temperatures higher than 1300° C. (*2, 11*) or by treating the molten rock phosphate with water vapor (*3*). Examples of chemical treatment of rock phosphate without complete defluorination are the manufacture of superphosphate, in which rock phosphate is treated with either sulfuric or phosphoric acid and most of the fluorine in the rock phosphate remains in the superphosphate (*7*), and the fusion of rock phosphate with addition agents to make products high in P_2O_5 solubility, but retaining most of the initial fluorine. Both acidulation and fusion with addition agents break up the fluorapatite structure of rock phosphate.

Some information has been published on processes for the fusion of rock phosphate with addition agents to make its P_2O_5 soluble without removal of fluorine. Wolters (*17*) described a process for making a product of high P_2O_5 solubility by the fusion of rock phosphate with alkali and alkaline earth silicates. For example, by fusing a mixture containing 1.00, 0.60, and 0.30 part of rock phosphate, alkaline earth silicates, and alkali silicates, respectively, he obtained a product with an almost completely soluble P_2O_5 content. Also, by fusing a mixture of 1.00, 0.80, and 0.84 part of rock phosphate, calcium carbonate, and silica, respectively, Wolters found that the P_2O_5 was almost completely soluble but that considerable loss of P_2O_5 by volatilization occurred. Giese and Wolters (*4*) obtained a patent on the preparation of soluble phosphates by fusing rock phosphates with silicates, and cooling the melt in a blast of steam and air; they used the proportions (*a*) 1.00 part rock phosphate, 0.45 part sodium bisulfate, 0.28 part limestone, and 0.27 part of silica, or (*b*) 1.00 part rock phosphate and 0.45 part sodium-calcium silicate. Presumably the kinds and proportions of silicates are the same as those stated in the earlier Wolters patent (*17*). Prjanischnikow (*10*) described the preparation of a product of high P_2O_5 solubility by the fusion of 1.00 part of rock phosphate with about 0.5 part of sodium carbonate. Other processes for the fusion of rock phosphate with various addition agents are those of Wiborgh (*16*), Heskett (*5*), and Schleede, Meppen, and Scheel (*13*). The chief disadvantages of these processes are (*a*) the excessively large proportions of inexpensive addition agents required, such as calcium silicate, with resultant high fusion costs and low P_2O_5 concentration in the products, or (*b*) expensive addition agents such as sodium carbonate.

A number of processes (*12, 14, 15*) for the calcination of rock phosphate with addition agents, with or without defluorination, have been used in Europe but have not been adopted in the United States.

PRELIMINARY INVESTIGATIONS

Preliminary investigations indicated that the fusion of rock phosphate with magnesia and silica would yield a product high in P_2O_5 solubility although retaining a large proportion of fluorine. For example, a product was prepared by fusing a mixture of 0.28 pound of magnesia and 0.21 pound of silica per pound of rock phosphate, and quenching the melt in water; the P_2O_5 in this product was completely soluble in citrated ammonium nitrate solution. Other experiments showed that, if such a mixture were either calcined to incipient fusion in a rotary kiln or sintered by mixing with coke and burning, only 15 to 20 per cent of the P_2O_5 in the products was soluble in citrated ammonium nitrate solution.

A process for fusion of rock phosphate with magnesia and silica would have advantages over other rock phosphate fusion processes, if the proportions of magnesia and silica required were not excessive; the raw materials would be inexpensive, and defluorination, which requires special types of furnaces and additional fuel over that required for fusion, would be obviated. Such a process might be practicable in the Tennessee Valley, because large deposits of high grade olivine, a mineral magnesium silicate, are found there. In North Carolina and Georgia, in or adjacent to the Tennessee River watershed, estimates show about a billion tons of dunite containing more than 40 per cent magnesia and 230 million tons of olivine averaging 48 per cent magnesia (*6*). All of the large deposits of olivine are accessible to rail or truck transportation.

A systematic study was therefore made to determine the proportions of magnesia, silica, and olivine required for a product of high or complete P_2O_5 solubility when these materials are fused with rock phosphate. The present paper is limited to a determination of the proportions of constituents required and to pot culture tests as to the effectiveness of the product. Engineering and economic studies of the process will be made later.

MATERIALS, EQUIPMENT, AND PROCEDURE

The chemical compositions of the raw materials are shown in Table I. The rock phosphate was high-grade Tennessee brown rock phosphate sand. Ground magnesite brick was the source of magnesia, and silica pebble the source of silica. The olivine was a commercial product from Spruce Pine, N. C.

Two electric furnaces were used in the course of the investigation. One was a Detroit rocking indirect-arc furnace, lined with silica brick and operated at about 25 kw. The other was a single-electrode direct-arc furnace lined with carbon and operated at about 90 kw. The charges to the indirect-arc furnace weighed about 25 pounds; those to the single-electrode furnace, about 150. The single-electrode furnace was equipped with a quenching system, consisting of a trough through which a high-velocity stream of water was directed.

The fusion procedure consisted in mixing the desired proportions of constituents, ground to −4 mesh or finer, melting the mixture in one of the furnaces, and cooling the melt rapidly by water quenching. When the indirect-arc furnace was used, the melt was poured into a pan of water; when the direct-arc furnace was used, the melt was allowed to flow into the stream of water of the quenching system. About 30 minutes were required to melt a charge in either furnace. The temperature of the melts as they poured from the furnaces was 1450° to 1550° C., determined with an optical pyrometer.

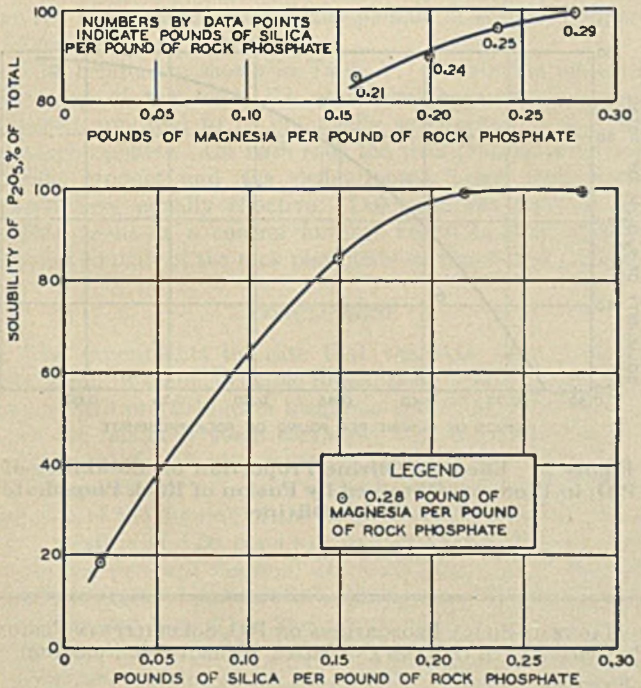

Figure 1. Effect of Magnesia and Silica Proportions on Solubility of P_2O_5 in Products Obtained by Fusion of Rock Phosphate with Magnesia and Silica

Table I. Composition of Raw Materials

Material	Composition, Per Cent P_2O_5	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	F
Rock phosphate A	33.3	47.1	..	6.3	2.8	1.8	3.63
Rock phosphate B	33.2	46.4	..	5.4	2.3	...	3.56
Magnesite brick	..	3.4	86.5	5.7	5.9	...	..
Silica	..	..	..	96	...	...	..
Olivine	..	0.9	45.0	43.9	8.1	...	..

Soluble P_2O_5 in the products was determined by the MacIntire-Shaw-Hardin method (*9*), which employs a citrated ammonium nitrate solution as the solvent. For comparison, a few determinations of citrate-insoluble P_2O_5 were made by the A. O. A. C. method for P_2O_5 remaining "insoluble" in superphosphate and in mixed fertilizers (*1*). The A. O. A. C. method employs a neutral ammonium citrate solution as the solvent for the forms of phosphate, other than undecomposed rock phosphate, that remain after aqueous extractions. The percentage of soluble P_2O_5, determined by subtraction of citrate-insoluble from total P_2O_5, was as much as 1.5 per cent lower than the soluble P_2O_5 indicated by the MacIntire-Shaw-Hardin method.

ROCK PHOSPHATE WITH MAGNESIA AND SILICA

Two series of fusions were made to determine the proportions of magnesia and silica required for complete solubility of P_2O_5. In the first series (Table II-*A* and Figure 1-*A*), from 0.21 to 0.29 pound of silica per pound of rock phosphate was used in each fusion, and the proportion of magnesia was varied from 0.16 to 0.28 pound per pound of rock phosphate. It was found that 96 per cent of the P_2O_5 in the product was soluble when 0.24 pound of magnesia and 0.25 pound of silica per pound of rock phosphate was used, and that essentially complete solubility of P_2O_5 was obtained when 0.28 pound of magnesia and 0.29 pound of silica per pound of rock phosphate was used. The proportion of silica in this series was not constant because the fusions were carried out in a silica-lined furnace, and the amount of silica dissolved from the lining could not be controlled. However, all of the products made in series *A* contained more than the minimum proportion of silica required for complete P_2O_5 solubility, as indicated in the next series.

Table II. Effect of Magnesia and Silica on P_2O_5 Solubility in Fusion of Rock Phosphate with Magnesia and Silica

Fusion No.	Lb. Addition Agent per Lb. Rock Phosphate A MgO	SiO_2	Composition of Product, % P_2O_5	SiO_2	F	Soly. of P_2O_5, % of Total	F Volatilized, % of Initial
A. Magnesia Content Varied (Indirect-Arc Furnace)							
PS66	0.16	0.21[a]	25.4	21.4	1.86	85	33
PS65	0.20	0.24[a]	24.3	22.2	1.10	90	58
PS64	0.24	0.25[a]	23.8	22.6	1.70	96	34
PS57	0.28	0.29[a]	21.6	23.7	1.71	99	30
B. Silica Content Varied (Direct-Arc Furnace)							
PSE5	0.28	0.02	27.2	8.4	2.37	19	20
PSE6	0.28	0.15	23.4	18.3	1.92	85	25
PSE7	0.28	0.22	22.2	21.3	1.72	100	29
PSE8	0.28	0.28	20.9	25.5	1.58	100	31

[a] Calculated from percentage of silica in product.

In the second series (Table II-*B* and Figure 1-*B*), carried out in a carbon-lined furnace, the magnesia was kept constant at 0.28 pound per pound of rock phosphate, and the silica was varied from 0.02 to 0.28 pound per pound of rock phosphate. It was found that 0.22 pound of silica per pound of rock phosphate was required for essentially complete P_2O_5 solubility, when 0.28 pound of magnesia per pound of rock phosphate was used.

In most of these runs the amount of fluorine volatilized from the rock phosphate was between one fourth and one third of that initially present. In Table II-*B*, the fluorine volatilization increased with increasing proportions of silica.

Since magnesium is a desirable plant nutrient, the solubility of the magnesium in one of the rock phosphate–magnesia–silica fusion products was determined. The availability of magnesium in selectively calcined dolomite to plants has been judged by its solubility in neutral ammonium citrate solution (*8*); therefore this solution was used for the present analysis. Ninety per cent of the magnesium in product

Table III. Effect of Olivine Proportion on P_2O_5 Solubility (Direct-Arc Furnace)

Fusion No.	Lb. per Lb. Rock Phosphate B			Composition of Product, %					Soly. of P_2O_5, % of Total	F Volatilized, % of Initial
	Olivine	Olivine constituents								
		MgO	SiO_2	P_2O_5	CaO	MgO	SiO_2	F		
PSE11	0.31	0.14	0.13	23.5	38.3	10.5	18.6	2.12	62	27
PSE14	0.39	0.17	0.17	24.5	35.9	12.1	19.4	1.84	71	33
PSE10	0.46	0.21	0.20	22.8	34.9	14.3	22.0	1.87	94	29
PSE9	0.62	0.28	0.27	21.3	31.5	17.4	23.4	1.71	98	28

PS57 (Table II), which contained 18.5 per cent of magnesium oxide, was soluble in neutral ammonium citrate solution. Thus most of the magnesium in the rock phosphate–magnesia–silica fusion products is readily available to plants.

ROCK PHOSPHATE WITH OLIVINE

Since the foregoing experiments indicated that the proportions of magnesia and silica required for high P_2O_5 solubility were not excessive, and that the ratio of magnesia to silica required was approximately the same as that of magnesia to silica in olivine, it appeared that olivine would be an economical material for fusion with rock phosphate. Results of a series of fusions are shown in Table III and Figure 2. To obtain 94 per cent P_2O_5 solubility of the product, 0.46 pound of olivine per pound of rock phosphate was required; to obtain 98 per cent P_2O_5 solubility, 0.62 pound of olivine was necessary. These results are in good agreement with the fusions of rock phosphate with magnesia and silica (Table II). The amount of fluorine volatilized was about the same as that observed in fusions with magnesia and silica.

The volatilization of P_2O_5 in the fusions of rock phosphate with olivine, as determined by the difference in P_2O_5/CaO ratio of the furnace charge and of the product, was usually about 5 per cent and was as high as 13 per cent in one case. This volatilization was presumably due to reduction by the carbon furnace lining and carbon electrodes. Consequently, a fusion was made in which a mixture that contained 0.60 pound of olivine per pound of rock phosphate was charged continuously into the direct-arc furnace for 8 hours; the furnace was tapped at 30-minute intervals. With this method of operation, the furnace always contained a layer of unfused charge above the molten material; thus any vapors or fumes liberated from the melt rose through the layer of unfused material, whereas in the batch experiments the upper half of the furnace was empty. Analyses of the product from the fusion in which continuous charging was used indicated that the P_2O_5 loss was only 1 per cent; the fluorine volatilization was 11 per cent. This experiment indicates that there would be no appreciable P_2O_5 loss from an electric carbon-lined furnace designed so that the unfused part of the charge could serve as an absorbent for liberated phosphorus or P_2O_5. Also, it is likely that the P_2O_5 losses resulting from fusion of the mixture in a furnace not lined with carbon would be small.

ROCK PHOSPHATE WITH OLIVINE AND SILICA

To determine whether high solubility of P_2O_5 could be obtained with smaller proportions of olivine than those required for high solubility in the above fusions, if larger proportions of silica were used, two series were run in which both olivine and silica were fused with rock phosphate. In the first (Table IV-*A*), 0.31 pound of olivine per pound of rock phosphate was used. The solubility of P_2O_5 could be increased from 62 to 81 per cent by using 0.14 pound of silica per pound of rock phosphate in addition to the olivine, but no further increase in solubility of P_2O_5 was obtained when 0.28 pound of silica per pound of rock phosphate was used in addition. In the second series (Table IV-*B*), 0.39 pound of olivine per pound of rock phosphate was used. The solubility of P_2O_5 could be increased from 71 to 81 per cent when 0.25 pound of silica per pound of rock phosphate was used in addition to the olivine. Because products having P_2O_5 solubility higher than 81 per cent were not obtained, and because the amount of silica needed even for this solubility was relatively large with attendant decrease in the P_2O_5 content of the product, it appears better to use no additional silica for the fusions.

The amount of fluorine volatilized was greater in most cases than when no silica was used.

POT CULTURE TESTS

A sample of product PSE10 (Table III), ground to −100 mesh, was subjected to pot culture tests in the greenhouse. This product had been made by the fusion of a mixture containing 0.46 pound of olivine per pound of rock phosphate and contained 22.8 per cent P_2O_5, 94 per cent of which was soluble in citrated ammonium nitrate solution, as compared with 2.2 per cent for the raw rock phosphate. The test

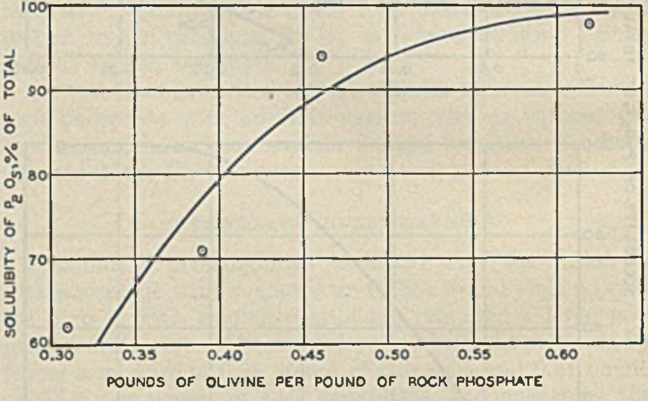

Figure 2. Effect of Olivine Proportion on Solubility of P_2O_5 in Products Obtained by Fusion of Rock Phosphate with Olivine

Table IV. Effect of Magnesia-Silica Proportions on P_2O_5 Solubility in Fusion Products of Rock Phosphate with Olivine and Silica (Direct-Arc Furnace)

Fusion No.	Lb. per Lb. Phosphate Rock B			Composition of Product, %					Soly. of P_2O_5, % of Total	F Volatilized, % of Initial
	Si pebble	Olivine and Si Pebble Constituents								
		MgO	SiO_2	P_2O_5	CaO	MgO	SiO_2	F		
A. 0.31 Lb. Olivine per Lb. of Rock Phosphate B										
PSE11	0.00	0.14	0.13	23.5	38.3	10.5	18.6	2.12	62	27
PSE12	0.14	0.14	0.27	21.9	35.6	9.4	26.7	1.17	81	57
PSE13	0.28	0.14	0.40	18.6	34.2	8.1	32.4	1.37	80	47
B. 0.39 Lb. Olivine per Lb. of Rock Phosphate B										
PSE14	0.00	0.17	0.17	24.5	35.9	12.1	19.4	1.84	71	33
PSE15	0.11	0.17	0.27	22.5	34.5	11.3	24.6	1.80	57	31
PSE16	0.25	0.17	0.40	20.8	31.8	11.0	30.1	1.09	81	55

TABLE V. COMPARISON OF ROCK PHOSPHATE–OLIVINE FUSION PRODUCT WITH OTHER PHOSPHATIC FERTILIZERS IN POT CULTURE TESTS WITH SOILS PRELIMED WITH DOLOMITE[a]

Phosphatic Fertilizer	Composition, %			Lb. P_2O_5 per Acre Surface	Dry Wt. of 2 Crops Sudan Grass, Grams	
	Total P_2O_5	Sol. P_2O_5	Fluorine		Hartsells fine sandy loam	Fullerton silt loam
No phosphate	..	..	..	0	11.2	12.3
Rock phosphate–olivine fusion product	22.8	21.4	1.87	40	22.1	19.7
Defluorinated fused rock phosphate	30.2	27.2	0.02	40	24.3	19.2
Concd. superphosphate	51.2	..	..	40	23.2	21.7
Standard superphosphate	20.0	17.8	1.79	40	21.4	21.0

[a] Tests made under the supervision of W. H. MacIntire of the University of Tennessee in cooperation with the Tennessee Valley Authority.

crop was Sudan grass. Two soils, Hartsells fine sandy loam of 4.9 pH and Fullerton silt loam of 5.3 pH were used. Both soils were limed moderately with dolomite, the Hartsells soil at a rate equivalent to 2000 pounds of calcium carbonate per acre surface, and the Fullerton soil at a rate equivalent to 1000 pounds. After the second harvest the Hartsells and Fullerton soils had pH values of 6.3 and 6.0, respectively. To assure that P_2O_5 would be the limiting factor, 150 pounds of potassium (as potassium sulfate), 25 pounds of manganese sulfate, 25 pounds of copper sulfate, 2 pounds of boron (as boric acid), and 2 pounds of zinc (as zinc sulfate) per acre surface were added in solution to both soils. The incorporations were made only in the upper 3-inch zone. Nitrogen was supplied as ammonium nitrate solution top dressing. Standard and concentrated superphosphate and defluorinated fused rock phosphate were used as controls to supply P_2O_5 at the conventional rate of 250 pounds of standard superphosphate per acre surface.

The results are shown in Table V. Within the limits of accuracy of the tests, the rock phosphate–olivine fusion product appeared to be practically as effective as the two superphosphates. On both soils the rock phosphate–olivine fusion product and the defluorinated fused rock phosphate were equally effective. Dolomite was used as the liming agent as a control for any beneficial effect of magnesium content of the rock phosphate–olivine fusion product.

CONCLUSIONS

The experiments indicate that the P_2O_5 in rock phosphate can be made available to plants by fusion of the phosphate with proportions of magnesia and silica, or of olivine, that are relatively small compared with the proportions of alkaline earth silicates reported as necessary by previous investigators (*4*, *17*), and without removal of the major portion of the fluorine of the rock phosphate. Thus, fusion of a mixture of 1.00 pound of rock phosphate (33 per cent P_2O_5, 3.6 per cent fluorine) and 0.46 pound of olivine (45 per cent MgO, 44 per cent SiO_2) yielded a product containing 22.8 per cent total P_2O_5, 21.4 per cent soluble P_2O_5, and 1.9 per cent fluorine; the products prepared by previous investigators required about 1.6 pounds of alkaline earth compounds or 0.45–1.0 pound of alkali compounds per pound of rock phosphate for products of high P_2O_5 solubility.

PRELIMINARY EVALUATION OF PROCESS AND PRODUCT

A process for making phosphatic fertilizer by fusion of rock phosphate with olivine would have a number of advantages over other processes. In contrast to processes for making superphosphate, expensive acid is not required. Its advantage over processes for making metaphosphates is that expensive elemental phosphorus is not needed. In contrast to processes for making defluorinated fused rock phosphate, it is not necessary to remove substantially all of the fluorine from the rock phosphate, a difficult and expensive task. Its advantages over other fusion processes in which P_2O_5 solubility is obtained by addition agents without defluorination are that the agent required in the present process is inexpensive and the amount required is relatively small. These advantages of the rock phosphate–olivine fusion process should result in lowered costs of production of available P_2O_5.

An advantage of the rock phosphate–olivine fusion product is that it contains soluble magnesium, which should make the product especially adaptable for application to soils that respond to magnesium.

The proposed process would have to be carried out in areas where both rock phosphate and olivine can be obtained cheaply. The olivine deposits in North Carolina and Georgia (*6*) are near both the Tennessee and Florida phosphate deposits. The western phosphate deposits in Utah, Idaho, Montana, and Wyoming are near olivine and serpentine deposits in Oregon and California. Therefore both materials could probably be obtained cheaply enough over a wide area for use in the proposed process. The western phosphate deposits are near magnesite deposits so that it might prove economical to use magnesite and silica as raw materials for the process rather than the mineral magnesium silicates.

Since the product of the rock phosphate–olivine process is not so highly concentrated in P_2O_5 as some other phosphatic fertilizers, it could not be shipped economically over so great a distance. However, the product is somewhat more concentrated than ordinary superphosphate.

ACKNOWLEDGMENT

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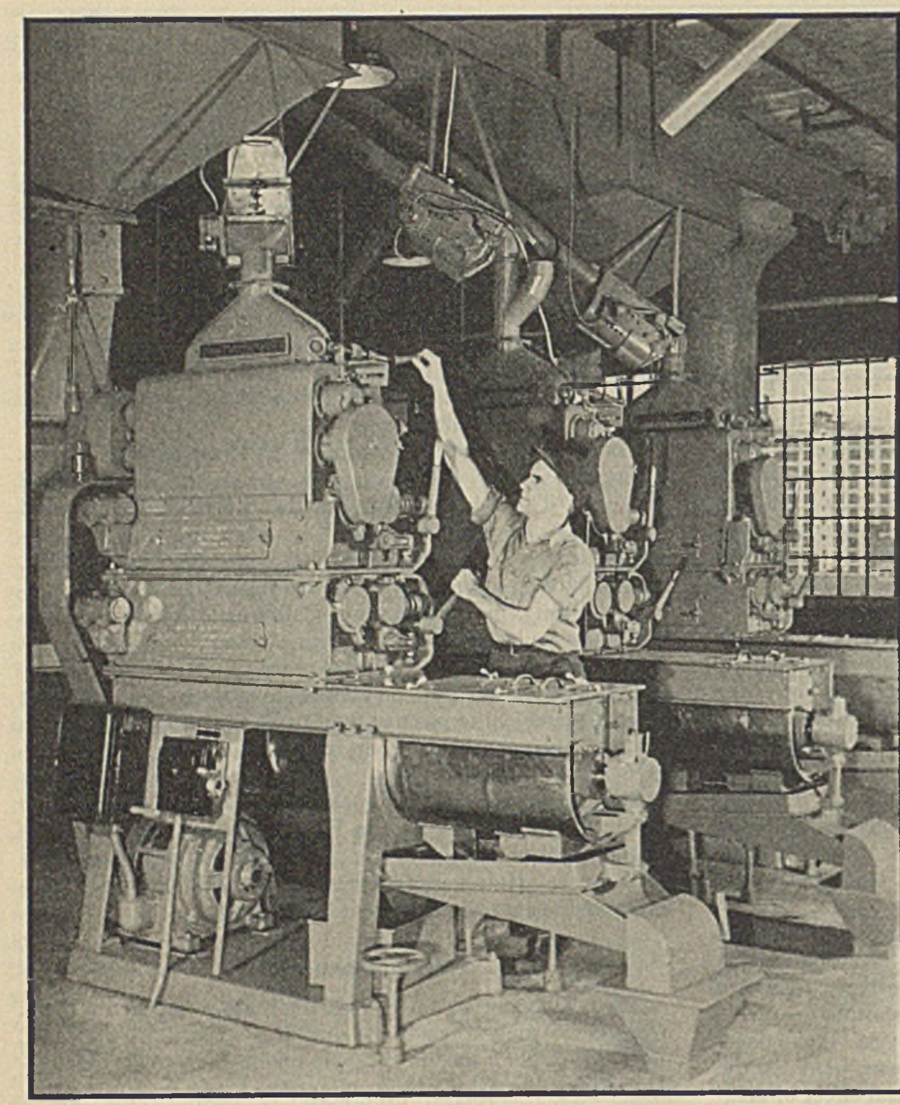

Two-Stage Coffee Granulizer

Roasted whole coffee beans may be viewed through the window at the top of the machine, and ground coffee through the conveyor and chute at the bottom right. Between these points is the mechanism which breaks down the whole beans into suitable grain size. Magnetic separators above the machine provide additional protection.

Staling *vs.* Rancidity in ROASTED COFFEE

Relative Effects of Moisture, Aroma Oxidation, and Aroma Evaporation on Staling

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EARLIER papers in this series (*1*, *2*) showed that staling of roasted coffee cannot be correlated with oxidation of the fatty oil fraction (commonly known as rancidity development), but that the roasting process actually serves to stabilize the fatty oil of green coffee by development of antioxidants in the roasting process, notably pyrrole. Staling has also been associated with the loss of carbon dioxide which occurs spontaneously in ground roasted coffee on storage. Patents have been issued recently, based on the idea of preventing the staling of coffee by preventing the loss of carbon dioxide (*4*, *5*). Nearly every investigator has recognized that oxygen plays an important part in developing stale flavor. Johnston (*3*) also pointed out that moisture can accelerate spoilage of coffee by staling.

This investigation was undertaken to determine the relative importance of the three factors—moisture, aroma oxidation, and aroma evaporation—by a systematic series of tests in which each effect was evaluated singly and in conjunction with the others. The coffee used was a medium-roast regular-grind commercial blend.

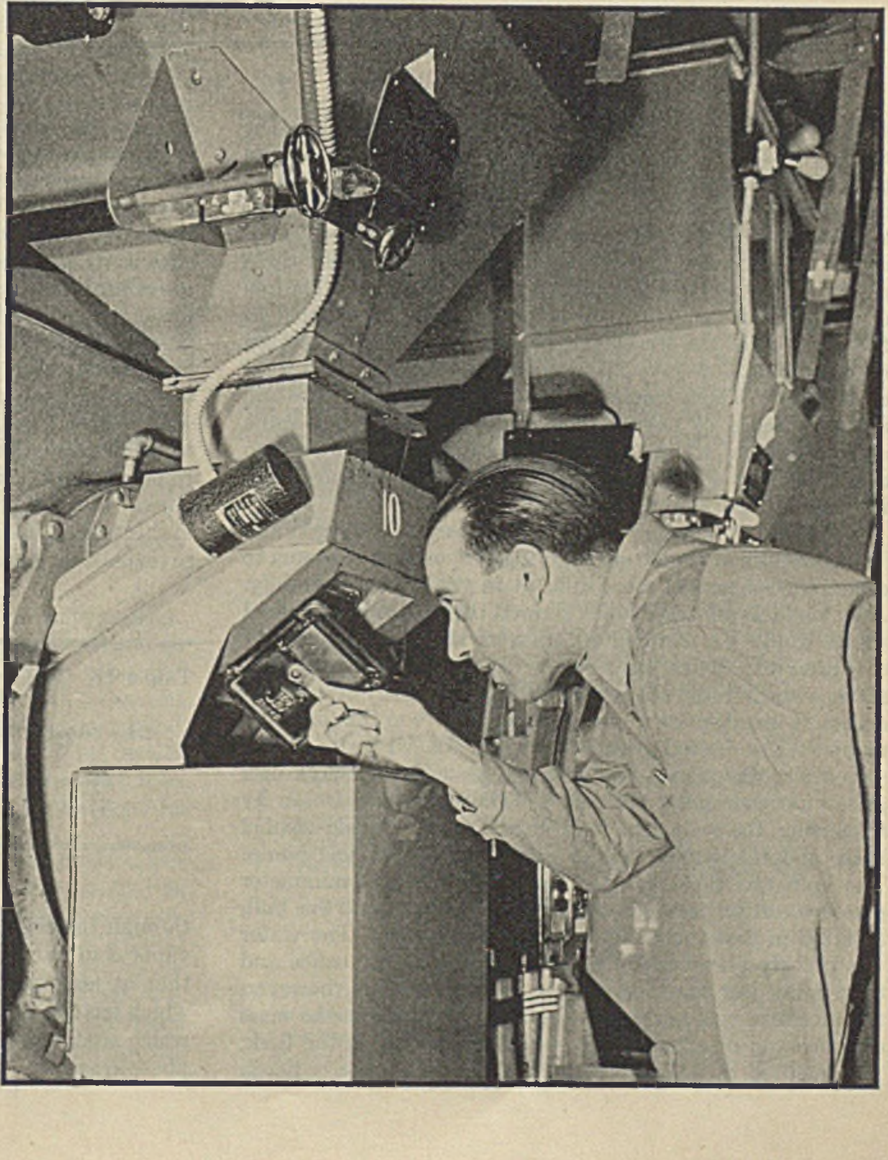
EFFECT OF AROMA EVAPORATION

To study the effect of evaporation independently of oxidation and moisture, half-pound samples of freshly ground roasted coffee were loosely packed in 1-liter aspirating bottles through which dry nitrogen gas was passed, entering at the top of the bottle and passing out through the tubulature at the bottom. The nitrogen gas was scrubbed free of traces of oxygen by passage through Fieser's reagent (an alkaline mixture of sodium hydrosulfite and sodium anthraquinone β-sulfonate), dried over Dehydrite (magnesium perchlorate anhydrous), and then passed through the coffee at the rate of about 1 liter per hour. Duplicate portions of the same coffee used in each test were sealed in glass under the vacuum produced by a Cenco Hyvac pump and held as control samples for evaluating flavor changes produced in the treated samples. At intervals ranging from 5 to 55 days, portions of the vacuum-sealed control samples and of the nitrogen-swept samples were removed for appraisal of cup quality. Cup testing was carried out by professional tasters in a Front Street, New York, coffee buying office. Supplementary tasting tests conducted by members of the laboratory staff were, in general, in agreement with the results reported from the Front Street office. Results of these cup tests appear in

Tests were run to disclose the effect of controlled storage conditions on the cup quality of ground roasted coffee. Samples hermetically sealed in a vacuum remained fresh throughout the test (maximum 48 days). Coffee swept continuously for 55 days with dry nitrogen remained comparatively fresh, showing that there is an abundant supply of aroma in fresh coffee and that evolution of gas has no detectable effect on flavor. The volume of gas into which coffee aroma was allowed to evaporate is approximately 5000 times the volume of the gas space in the vacuumized can. Therefore, coffee cannot suffer a detectable loss of flavor because of evaporation into the container gas space. At least part of the stale flavor produced by exposing coffee to oxygen can be removed by subsequently sweeping the coffee with an inert gas; this suggests that at least part of the stale flavor is due to compounds which are volatile. If oxidation is allowed to proceed far enough, especially in a hermetically sealed container, subsequent sweeping with an inert gas fails to remove stale flavor.

Table I. As was to be expected, all of the vacuum-sealed control samples were judged fresh or comparatively fresh through the entire storage interval of 48 days.

Contrary to what might be expected, on the basis of the earlier publications and patent specifications referred to above, the gases and aroma vapors from coffee can be continuously removed for a period as long as 55 days without impairing the flavor quality as judged by the expert tasters. As shown in Table I-*B*, none of the eleven samples drawn from the beginning of the test until the end of the 55-day period was judged to be more than 7 days old—that is, fresh or comparatively fresh. It is apparent that there is an abundant supply of aroma in coffee, and that as long as oxygen and moisture are excluded, evolution of gas from coffee (such as occurs, for example, in a vacuumized can) can have no detectable effect on the flavor quality. In the 55-day test the volume of gas into which coffee aroma was allowed to evaporate was approximately 5000 times the volume of the gas space in a vacuumized can. By comparison, therefore, the possibility of flavor impairment by evaporation of aroma into the gas space of the commercial container is nonexistent.



One of the World's Largest Coffee Roasters Preparing a Batch of Blended Coffee

Through a small door a skilled operator peers into the radiant depths of the roaster. Inside, in a flash of flame, coffees blended to exacting standards are being roasted according to specifications.

EFFECT OF MOISTURE

The effect of moisture in the coffee on aroma evaporation and subsequent flavor value of the treated coffee was studied by the same technique, except that the nitrogen after being freed from traces of oxygen was passed through a water

TABLE I. RELATION OF CUP QUALITY OF COFFEE TO AGE UNDER VARIOUS STORAGE CONDITIONS

A. Vacuum Sealed		*B.* Swept with Dry Nitrogen		*C.* Swept with Moist Nitrogen	
Days sealed	Cup quality (age in days)	Days swept	Cup quality (age in days)	Days swept	Cup quality (age in days)
5	Fresh	5	Fresh	5	Fresh
5	Fresh	6	Slightly stale (5–7)	12	Fresh (2–3)
5	Comp. fresh (4–5)	6	Comp. fresh (3–5)	14	Slightly stale (5–7)
12	Fresh (2–3)	12	Fresh (2–3)	20	Slightly stale (5–7)
12	Fresh	14	Comp. fresh (3–5)	22	Comp. fresh (2–3)
12	Fresh	19	Comp. fresh (2–4)	48	Slightly stale (7–9)
13	Comp. fresh (3–5)	19	Comp. fresh (3–5)	55	Comp. fresh (3–5)
19	Comp. fresh (2)	20	Comp. fresh (2–3)		
20	Fresh (1–2)	22	Comp. fresh (2–3)		
22	Comp. fresh (2–3)	48	(4–6)		
25	Fresh	55	Comp. fresh (3–5)		
48	(2–3)				

D. Swept with Dry Oxygen		*E.* Swept with Moist Oxygen		*F.* Sealed with Oxygen at Atmospheric Pressure	
Days swept	Cup quality (age in days)	Days swept	Cup quality (age in days)	Days sealed	Cup quality (age in days)
5	Fresh (1–2)	5	Comp. fresh (3–4)	5	Comp. fresh (3–4)
5	Stale	5	Stale	5	Comp. fresh (3–5)
12	Comp. fresh (2–3)	12	Comp. fresh (2–3)	5	Comp. fresh (3–5)
13	Slightly stale (6–8)	13	Slightly stale (6–8)	11	Stale (7–9)
13	Stale (8–10)	19	Stale (7–10)	14	Stale (8–10)
19	Slightly stale (5–7)	20	Slightly stale (6–8)	19	Very stale (20)
19	Slightly stale (5–7)			19	Very stale (30)
19	Slightly stale (6–8)			32	Stale (8+)
20	Slightly stale (5–7)			32	Stale (8+)

saturator instead of a drying tube and sent directly into the coffee container. During the 55-day period, the moisture content of coffee so treated increased from an initial value of approximately 1.4 to about 5 per cent. The results of cup tests on samples treated in this manner appear in Table I-*C* and show that coffee does not remain quite so fresh under these circumstances as when it is swept with dry nitrogen. The loss of flavor value is apparently not uniformly proportional to the duration of the treatment, but the worst value reported (slightly stale, 7–9 days old) was for coffee treated for a total of 48 days. These results indicate that, although moisture in the absence of oxygen does influence the flavor value of coffee from which aroma is continuously allowed to evaporate, the effect of moisture under these circumstances is comparatively slight.

The effect of moisture alone, in the absence of oxygen and in the absence of conditions allowing evaporation of aroma to occur, was somewhat more difficult to study experimentally. After preliminary tests which showed that a period of several weeks would be required to transfer the desired quantity of water into coffee samples by distillation under circumstances which would not permit the removal of any evaporated aroma, it was decided to prepare the samples in the following manner: The desired quantity of water (boiled free from dissolved air) was placed in a side arm sealed to the neck of a glass bulb containing the coffee. The water was frozen by immersing the side arm in a solid carbon dioxide–alcohol bath, and the system was evacuated with a Hyvac pump. The bulb was then sealed under a fraction of a millimeter pressure. After sealing, the ice was melted and the bulb inverted so that the water ran onto the coffee. The water was quickly absorbed by a small amount of the coffee and thoroughly wet this portion. After a few hours, however, the moisture was fairly well dispersed throughout the mass of coffee and no signs of wet coffee were visible in the flask. This method of adding moisture is subject to the criticism that a small portion of the coffee is thoroughly wet by the water, which perhaps alters the properties of the coffee. Subject to the qualifications implied by such conditions, the results of cup tests on the treated coffee which appear in Table II show that water alone in the absence of oxygen and in the absence of conditions allowing evaporation of aroma can adversely affect the cup quality of coffee after a certain minimal storage interval. The moisture content of coffee can be raised by 2.6 per cent and the mixture held for as long as 12 days without impairing its flavor, but at the end of 39 days as little as 0.9 per cent added water produces the effect of 7–9 day storage in air. Although this is a noticeably unfavorable effect, it is not so serious as the effect of oxygen.

OXIDATION

The effect of aroma evaporation in the presence of dry oxygen was studied by the procedure used for evaporation in nitrogen, substituting a stream of pure oxygen gas for the purified nitrogen. In this manner an atmosphere of oxygen was maintained at all times in contact with the coffee; at the same time the aroma volatilized from the coffee was continuously swept away, and any possible reaction product between oxygen and coffee aroma in the vapor phase and any volatile oxidation products of the coffee itself were continuously removed. The results of cup tests on samples withdrawn in this series appear in Table I-*D*. The fact that coffee remains comparatively fresh under these circumstances for as long as 12 days was quite unexpected, since coffee exposed to ordinary air in a paper bag or slip-covered can will be definitely stale in about 9 days. For the same reason it was also surprising to find that even after 20 days of sweeping with oxygen gas, during which time the coffee was subjected to a full atmosphere oxygen pressure, the cup quality of the coffee was no worse than that of coffee exposed to air for 5 to 7 days. In spite of the fact that the partial pressure of oxygen in this test was four times as high as that in air, staling was not so extensive when the oxygen was dry and was moving through the coffee in such a way as to remove the volatile vapor continuously, as it would be in still air. This suggests that at least part of the stale flavor developed in coffee which has been exposed to oxygen may be due to compounds which are themselves volatile or which are formed in a vapor-phase reaction. In such a case the major part of the stale

TABLE II. RELATION OF CUP QUALITY OF COFFEE TO AGE WHEN SEALED WITH WATER

Days Sealed	Water Added, %	Cup Quality (Age in Days)
12	2.6	Fresh
39	0.9	Stale (7–9)
39	2.6	Stale (8–10)
39	4.4	Slightly stale (5–7)

flavor could be swept away with the stream of gas and fail to appear in the cup brewed from the coffee so treated.

The combined effects of moisture, oxygen, and aroma evaporation were studied by using oxygen gas saturated with water vapor in the same manner as described above for moist nitrogen. The cup quality of samples drawn during this test are shown in Table I-*E*. The change in flavor value due to ventilation with oxygen, wet or dry, is not uniformly proportional to the duration of the treatment, but a definite trend toward staling, of about the same magnitude in each case, is obvious. No positive acceleration of staling by moisture can be observed in this case. Again, the age of the coffee as indicated by the cup tests is not so great as the actual age of the coffee samples indicated by the number of days of sweeping. This is further evidence for the idea suggested above, that the oxidation products responsible for stale flavor are at least partly volatile and partly removed from the coffee by the oxygen gas stream.

The effect of oxygen and moisture, singly and in combination but in the absence of any opportunity for aroma evaporation, were studied as follows: One series of samples was prepared by placing coffee samples in glass bulbs which, after being pumped down to a fraction of a millimeter pressure with a Cenco Hyvac pump, were filled with cylinder oxygen at atmospheric pressure and sealed off. Samples withdrawn for cup testing at intervals yielded the results shown in Table I-*F;* it appears that under these conditions the age of the coffee, as indicated by the results of the cup test, is nearly parallel to the age of the coffee as indicated by the number of days the bulbs were stored after sealing. Apparently, the higher partial pressure of oxygen employed, as compared to that of air, is partly compensated by the fact that coffee exposed to the air can pick up some moisture, as well as lose some stale flavor by ventilation. The coincidence of the estimated and actual age is therefore partly accidental.

Table III. Relation of Cup Quality of Coffee to Age When Sealed with Oxygen and with Oxygen and Water

A. Sealed 24 Days with Oxygen		*B.* Sealed with Oxygen plus Water			
Cc. O_2 added[a]	Cup quality (age in days)	Days sealed	Cc. O_2 added[a]	% H_2O added[b]	Cup quality (age in days)
2	Fresh (1)	15	20	2.6	Comp. fresh (3–5)
20	Fresh (1)	20	2	0.9	Slightly stale (6–8)
260	Stale (15)	20	20	2.6	Stale (8–10)
		20	260	4.4	Very stale (10+)

[a] Per 250 grams of coffee; 2 cc. corresponds to 29-inch vacuum; 20 cc., to 18-inch vacuum; 260 cc., to atmospheric pressure.
[b] Coffee originally contained 1.4% water.

Another series of samples was sealed in the same manner, except that after evacuation the oxygen was not restored to full atmospheric pressure, but smaller quantities measured in a gas buret were introduced (Table III-*A*). At the end of 24 days, samples sealed with less than 1 atmosphere partial pressure of oxygen were still judged fresh. These results confirm the well known fact that the rate of coffee staling is to a certain extent a function of the partial pressure of oxygen in the container.

For storage intervals as short as 24 days, the relation between initial partial pressure of oxygen and storage stability of coffee was not studied, but it is known that the relation is not linear. For the storage intervals involved in ordinary trade channels, the initial partial pressure of oxygen must be reduced substantially below $^1/_4$ inch mercury (equivalent to a 29-inch initial vacuum) in order to prevent the appearance of detectable stale flavor by the time the coffee reaches the consumer.

A third series of samples was sealed in glass bulbs by evacuation and refilling with measured quantities of oxygen as described above; but the bulbs in this case also carried a side arm containing water which was frozen during evacuation and subsequently mixed with the coffee, as described in a preceding paragraph for the test involving the effect of moisture alone in the absence of oxygen. Results of the cup tests (Table III-*B*) again show that the addition of water increases the rate of staling due to oxygen. Specifically, the sample sealed with 2 cc. of oxygen and 0.9 per cent added moisture was reported 6 to 8 days old after 20-day storage; the corresponding sample in Table III-*A* sealed with 2 cc. of oxygen and no added water was reported fresh at the end of approximately the same interval. Similar comparisons can be made between samples sealed with 20 cc. of oxygen which, when dry, were judged fresh at the end of 24 days, but in the presence of 2.6 per cent added water were judged 8 to 10 days old at the end of 20-day storage.

Table IV. Relation of Cup Quality of Coffee to Age When Swept with Nitrogen 7 Days after Being Sealed with Oxygen

Days Sealed with O_2	Cup Quality (Age in Days)	
	Before N_2 sweeping	After N_2 sweeping
18	Very stale (20)	Slightly stale (6–8)
18	Very stale (20)	Slightly stale (6–8)
19	Very stale (30)	Comp. fresh (3–5)
32	Stale (8+)	Stale (10+)

As an independent check on the hypothesis that compounds responsible for stale flavor in coffee are volatile or are formed in the vapor phase, the following test was carried out: The samples of coffee which had been sealed in glass with 1 atmosphere oxygen for 18, 19, and 32 days, respectively, were swept with dry nitrogen for 7 days in aspirator bottles. Samples were cup-tested before and after sweeping with nitrogen with the results shown in Table IV. The nitrogen washing treatment markedly reduced the staleness of the three samples which had been sealed for 18 and 19 days. Table IV also shows that there is apparently a limit to which coffee can be allowed to accumulate oxidized products and still release them to a stream of nitrogen during 7 days, to a sufficient extent to restore comparatively fresh cup quality. At the end of 32 days, oxidation had proceeded so far that 7-day nitrogen sweeping failed to change the stale flavor score reported.

CONCLUSIONS

The storage conditions in these tests which led to the development of stale flavor in roasted coffee can be listed as follows, arranged in order from conditions protective against staling to conditions producing most rapid staling:

1. Hermetic vacuum pack.
2. Ventilation with moist or dry nitrogen.
3. Hermetic pack with added moisture, no oxygen.
4. Hermetic pack with small amounts of dry oxygen.
5. Ventilation with dry oxygen.
6. Ventilation with moist oxygen.
7. Hermetic pack with small amounts of oxygen and added water.
8. Hermetic pack with oxygen at atmospheric pressure.

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Action of Light on Cellulose

APPLICATION OF COPPER NUMBER DETERMINATIONS TO CELLULOSE ACETATE

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A satisfactory method for determining the copper numbers of cellulose acetates has been developed. The results of determinations on various samples indicate a high degree of degradation in the lower-viscosity cellulose acetates. Light increases the copper number of cellulose acetate, exposed either in the solid phase or in solution. The presence of oxygen is not necessary in the atmosphere surrounding the exposed acetate. Water appears to be necessary to allow this degradation to take place.

COPPER numbers are commonly used for the qualitative determination of the amount of degradation of cellulose and cellulose products, but the merits of this determination are a subject of controversy. It is generally admitted that copper numbers must be regarded as only qualitative in significance and, even so, must all be made according to a rigid empirical method. In spite of its qualitative empirical status, this determination, in the hands of experts, is one of the most successful methods for discovering overbleached or overheated paper or fabrics. Work in this laboratory had shown that it was a convenient tool for following the action of light on cellulose; when additional methods of following changes in cellulose acetate were desired, a consideration of copper number suggested that this determination might be applied to cellulose acetate.

The use of copper number determinations for cellulose acetate was mentioned as a possibility by Rinse (*6*) and Barthelemy (*1*) but neither gave detailed information as to method. The common methods of Schwalbe (*7*), Knecht and Thompson (*4*) and Braidy (*2*), as well as their various modifications, were unsatisfactory for this work because they require unnecessarily large samples. Heyes (*3*) published a method using a 0.25-gram sample, but the amount of solution is so small that it is applicable only up to copper numbers of 5.

The method used here was developed by modifying a combination of the Braidy (*2*) and Heyes (*3*) determinations, employing a microsample of 0.25 gram; it is capable of giving copper numbers up to 50. The permanganate method is used for the cuprous copper determination, but the electrolytic method may be employed by those who favor it without changing the essentials of the procedure.

COPPER NUMBER DETERMINATION

One of the most important parts of a copper number determination is the preparation of the sample. Not only must it be representative, but successive samples should have a uniform particle size and the individual particles should be as small as possible to facilitate the reaction between a solid and a solution. The best method of fulfilling these conditions is a rapid precipitation from solution into a nonaqueous precipitating agent. Approximately 0.6 to 0.7 gram of cellulose acetate is put into a solution in acetone. This amount is sufficient for duplicate determinations as each sample weighs 0.25 gram. Approximately three times the solution volume of isopropyl ether is brought to a boil on the steam bath, and the cellulose acetate solution is added slowly with stirring. The acetone flashes off almost instantly. The remaining suspension is concentrated to a volume of about 50 cc. The last of the isopropyl ether is removed in a slow current of warm air (35° to 40° C.). This procedure gives a finely divided dry sample which is stored in a desiccator over P_2O_5 for 48 hours before analysis. The acetate is left unchanged by this procedure but must be handled carefully during weighing to prevent it from becoming electrically charged and consequently sticking to the walls of the weighing bottle.

The solutions are those recommended by Braidy (*2*):

1. 150 grams sodium carbonate (anhydrous) and 50 grams sodium bicarbonate per liter of water.
2. 100 grams crystalline copper sulfate per liter of solution.
3. 40 grams ferric sulfate and 100 cc. concentrated sulfuric acid per liter of water.
4. 0.04 *N* potassium permanganate.

Approximately 0.25 gram of cellulose acetate is weighed out and placed in a 150-cc. suction flask. Ninety-five cubic centimeters of solution 1 are quickly heated to boiling, and 5 cc. of solution 2 are added. About 65 cc. of this solution are poured over the cellulose acetate, and the flask is put into a boiling water bath. A reflux condenser is attached, and nitrogen is blown slowly through the side arm of the flask during the entire 3 hours of heating. At the end of the first hour the remaining 30 cc. of the reaction mixture are poured down the condenser. This serves to wash down any fine particles that may tend to creep up the sides of the flask. After cooling rapidly, the solution is filtered off from the precipitated cuprous oxide and cellulose acetate by a sintered glass crucible. Care should be taken not to expose the cuprous oxide to the air unnecessarily. The crucible is transferred to a small suction flask, and the Erlenmeyer flask washed out with 15 cc. of solution 3; this solution is poured over the precipitate on the filter without applying suction, allowed to remain for a few minutes, and finally removed by the application of vacuum. The same procedure is repeated using 10 cc. of solution 3, followed by three or four washings with 4-cc. portions of distilled water. The titration with permanganate is carried out without removing the solution from the suction flask.

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The blank determination is very small and can be neglected for the relatively large copper numbers of cellulose acetate.

Table I shows the data obtained by this method. The duplicate results indicate the accuracy to be expected with careful manipulation.

TABLE I. COPPER NUMBERS OF CELLULOSE ACETATES

Material	Copper No.	Acetyl Content, %	[η]
Medium-viscosity acetate (12A)	2.16–2.18–2.37	41.6	1.12
Medium-viscosity acetate (107)	2.60–2.70	41.4	1.23
High-viscosity acetate (101)	1.95–2.15–2.00	39.5	1.35
Low-viscosity acetate (50A)	5.20–5.00–4.96	42.2	0.77
Low-viscosity triacetate	6.00–6.14–5.90	46.1[a]	
High-viscosity triacetate	0.52–0.55	44.8	
Absorbent cotton	0.15–0.15	0	
Paper pulp	0.60–0.65	0	

[a] This value, exceeding the theoretical value for cellulose triacetate, has been carefully checked. In conjunction with the high copper number, it indicates that this sample is an acetylated, partially degraded cellulose. Whether the cellulose was degraded before acetylation or degradation took place during the acetylation process, is not known.

COPPER NUMBERS OF ACETATES

The copper number, as used in the cellulose industry, is defined as the number of grams of copper reduced by 100 grams of cellulose, when an arbitrary procedure is followed exactly. It is necessary to specify a definite method because the oxidation of cellulose is very sensitive to conditions such as concentration, time, temperature, and the subdivision of the sample. The same definition has been used in this work on cellulose acetate. It should be remembered, in comparing these results with those obtained on cellulose, that the weight of the structural unit of the acetate is from 75 to 80 per cent greater than cellulose itself, so that these copper numbers are in reality that much greater than the numerical values indicate.

The strong, hot alkaline solution hydrolyzes off the acetate groups, leaving regenerated cellulose. Blank runs with additions of sodium acetate showed that the acetate group had no effect on this method of determining copper number. An alternative method might involve hydrolyzing off the acetate groups before running the copper number determination, except that the regenerated cellulose obtained by hydrolysis is usually a hard, horny substance that resists attack by copper number solutions. No evidence was noted of any discrepancies in this method because of the use of the cellulose acetate in place of cellulose itself. In addition, further unpublished work performed in this laboratory has shown that mannitol hexa-acetate does not give a copper number. This evidence indicates that primary alcohol groups, even though acetylated, do not enter into this reaction.

The copper number is inversely proportional to the viscosity classification of the various samples, and the large copper numbers of the low-viscosity acetates show a high degree of degradation. The extremely low copper number of carefully prepared triacetates indicates that the acetylation reaction itself does not necessarily cause degradation, but the subsequent hydrolysis to produce commercial or secondary cellulose acetate involves considerable degradation. In several instances the viscosity characteristics of triacetates were accurately predicted before being experimentally determined.

EFFECT OF LIGHT ON COPPER NUMBER

The loss of tensile strength, discoloration, and general deterioration of cellulose and its derivatives by light is well known, but to study and follow this degradation are difficult because of the high molecular weights involved. After the method of determining the copper number of cellulose acetate had been developed, it was decided to study the effect of light on the acetate and to attempt to follow the degradation by means of the copper number determination. Since the copper number should indicate any depolymerization of cellulose, it appeared that this might be an independent method of following the effect of light, because the copper number is indicative of the number of free potential aldehyde "end groups" on the long straight-chain cellulose acetate particles. This relation may not be direct because of the complicated crystalline structure of the solid and the peculiar course of oxidation of carbohydrates in alkaline solutions. The one fact that has been generally accepted is that a free aldehyde group must be present to allow oxidation to occur. How much further the oxidation will proceed is not known, but from independent determinations of the molecular weight it is evident that a greater degree of oxidation occurs than would be predicted by the oxidation of each aldehyde group to the corresponding carboxyl group (*5*). Therefore, if the action of light causes depolymerization without oxidation, the increase in free aldehyde groups should be revealed by an increase in copper number.

All exposures were made in clear quartz flasks. An air-cooled Cooper-Hewitt mercury vapor lamp was surrounded by a double-walled enclosure through which water was circulated for additional cooling. The flasks were inserted in holes cut in this enclosure so that a definite area could be exposed at a distance 12 inches from the lamp. In the case of the exposure of solids, the atmosphere in the flask was controlled as desired. When solutions were exposed, an atmosphere of solvent vapor was maintained above the solution. Table II shows the effect of light on the copper numbers of cellulose acetates and related substances.

TABLE II. EFFECT OF LIGHT ON COPPER NUMBER OF VARIOUS MATERIALS

Material	Exposure, Days	Method of Exposure	Copper No. Before exposure	Copper No. After exposure
Medium-viscosity cellulose acetate	63	Acetone solution	2.0	13.45
	42	Acetone solution	2.7	10.00
	34	Acetic acid solution	2.0	13.40
	30	Films, N_2 atmosphere	2.0	12.10
High-viscosity cellulose acetate	33	Acetone solution	1.7	11.03
Low-viscosity cellulose acetate	94	Acetone solution	5.0	19.4
Pulp	30	Solid, exposed to air	0.60	5.08
Absorbent cotton	30	Solid, N_2 atmosphere	0.15	2.0
Glucose	20	10% water solution	2.27	2.28[a]
Sucrose	10	5% water solution	0.20	[b]
Sucrose[c]	10	Solid, N_2 atmosphere	0.17	0.16

[a] Not a true copper number; relative only.
[b] Reduced all available copper in 5 minutes.
[c] Dried over P_2O_5 for 48 hours.

The cellulose acetates were representative samples of commercial acetate as manufactured by two different companies; the pulp was a high-grade commercial alpha-cellulose.

In view of the modern conception of the structure of cellulose and the fact that a free aldehyde group is necessary to give a copper number, an increase in copper number must indicate that the long straight chains of $C_6H_{10}O_5$ groups have been broken down into shorter chains, or that some of the primary alcohol groups have been oxidized to produce more aldehyde groups. The possibility of the oxidation of primary alcohol groups was eliminated in this work by the use of purified nitrogen atmospheres as well as the fact that glucose shows no increase in copper number upon exposure. Therefore, depolymerization must take place to account for the large increase in copper number. This degradation might also cause the decrease noted in the relative viscosity of the acetate solutions on exposure as well as the loss of tensile strength of cellulose and its derivatives.

Apparently the effect of light is nearly independent of the method of exposure. Similar results are noted whether the acetate is exposed in solution, as films, or powdered. Changing the atmosphere in the flasks also had little effect on the amount of degradation. However, the carbon-oxygen-carbon bonds between $C_6H_{11}O_5$ groups cannot be broken without introducing other atoms. From the results of the sucrose exposures it is obvious that water is necessary for the breaking of the bond between the C_6 groups in the case of this single sugar since no hydrolysis took place when thoroughly dried sucrose was exposed. The cellulose acetates used were dried in desiccators, but the handling and preparation of the solutions and films unavoidably allowed a certain amount of moisture to be picked up from the air as well as the water remaining after desiccation. It is not possible to dry cellulose or cellulose acetate completely in a desiccator. If light does promote the depolymerization of the long straight chains by hydrolysis, the increase in copper number can be readily understood as one new aldehyde end group being formed each time the chain is split. Therefore, these results indicate that light is, in effect, a catalyst promoting the hydrolysis of the cellulose acetate chains in a manner similar to its action on sucrose solutions.

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THE first paper in this series appeared in February, 1943, page 214. Abstracted from the Ph.D. thesis of C. C. Winding, University of Minnesota.

Sorption of Water Vapor by SOAP CURD

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Anhydrous soap, pure or commercial, takes up to 1 or 2 per cent of water according to a sorption mechanism of physical type. Except for sodium oleate, the curd or supercurd then suddenly forms a hemihydrate, which again takes up water more rapidly (up to 10 or 12 per cent) according to a sorption law until another phase forms. At low temperatures these new phases are higher hydrates; that is, they are masses of crystalline fibers containing much larger amounts of water. The higher hydrates readily revert to hemihydrate when the relative humidity falls by 15 per cent or less. The sorption curves, through a high value of $1/n$ exceeding unity, unmistakably show the presence of capillary liquid in pores and interstices of the fibrous mass.

PREVIOUS communications have dealt with those vapor pressure relations of soap systems that are best discussed from the standpoint of the phase rule and of phase diagrams. The present paper discusses the sorption of water vapor by soap systems containing only solids.

At ordinary temperature anhydrous soap curd fibers can exist in several unstable crystalline forms, alpha and other monoclinic forms, as well as in the stable monoclinic γ form. On heating, another form of crystalline curd fiber appears which we have named "supercurd". For example, sodium stearate supercurd exists as a stable crystalline phase between 90° and 117° C. and sodium oleate supercurd between 38° and 65° C. Just above this temperature the first of the three waxy translucent crystalline forms, entitled "subwaxy" soap, is stable (*3, 25, 26*). The curd, supercurd, and subwaxy phases will be discussed with regard to their vapor pressure relations before they have taken up sufficient water to yield any liquid or liquid crystalline phase.

The data are of general interest and significance for all colloidal powders, fibers, and gels; in the solid soap systems, as in many of the systems just mentioned, the following are simultaneously present: typical adsorption, formation of genuine compounds or hydrates, adsorption on the latter, and condensation of the unsaturated water vapor in all capillary pores and interstices of appropriate dimensions.

THE experiments were carried out with the purest single soaps used in previous work (*18, 27, 28*). The McBain-Bakr spiral silica spring with platinum bucket was employed. Owing to the discovery that silica springs can stretch when exposed to heated water vapor, it was obligatory to begin all critical experiments with anhydrous soap, the water being frozen in the lower part of the tube with solid carbon dioxide or liquid air. Furthermore, it is necessary after a series of experiments to return to this point to check for stretching of the spring. Thirty-five extended isotherms were presented in abbreviated form in another publication (*14*); the present paper is confined to a more detailed examination of the initial portion of a few typical isotherms. Those isotherms are plotted in the customary manner as x/m, the number of grams of water sorbed per gram anhydrous soap, against p/p_s, the relative humidity or actual pressure p divided by the vapor pressure of saturated vapor p_s at that temperature. To avoid duplication, reference should be made to those isotherms for further evidence supporting some conclusions drawn in the present communication.

All isotherms begin with a smoothly rising curve representing soap containing steadily increasing but slight amounts of water until, at about 40 to 50 per cent relative humidity, not more than 1 or 2 per cent of water has been taken up by the soap. (Even waxy sodium palmitate at 145° C. behaves similarly.) Then at a definite value between 40 and 70 per cent relative humidity, with curd and supercurd but not with the subwaxy and waxy phases, there is a sudden break and the composition goes over to about 97 per cent soap, corresponding to a crystalline hemihydrate containing 0.5 mole of water to 1 mole of soap. Thereupon the curve continues with increasing slope; water is more and more rapidly taken up until 10 or 15 per cent is incorporated in the soap mass before any phase change occurs.

Throughout the region described, the phenomena may be grouped together as sorption except for the break corresponding to the rather sudden formation of hemihydrate. This is shown by the example chosen for Figure 1 and the further illustrations in Figure 2, where the data are tested by the classical empirical sorption isotherm,

$$x/m = kp^{1/n}$$

where x/m = weight of water taken up by 1 gram soap
p = relative humidity

When plotted as logarithm x/m against logarithm p, this equation gives a straight line. Since the data (represented by circles on Figures 1 and 2) fall on straight lines for the anhydrous curd and then for the hemihydrate, it is a necessary conclusion that they refer to sorption. An example is given of one isotherm for sodium laurate, where the break to hemihydrate did not appear. The Langmuir isotherm is usually less accurately followed.

Most of the data fall on two straight lines—one for sorption of water vapor by otherwise anhydrous curd or supercurd, and the other for sorption of water vapor on the hemihydrate which appears in the higher ranges of relative humidity. The figures include curd, supercurd, and subwaxy crystalline forms of the different soaps; but sodium oleate is distinguished by the fact that even curd and supercurd seem to form no hemihydrate. The isotherm for subwaxy sodium oleate is the same for hydration and dehydration. Where no hemihydrate has been formed for subwaxy and waxy soaps, the isotherms are reversible. Such reversibility must be ascribed to the flexibility of the curd fibers which produce only a semirigid structure.

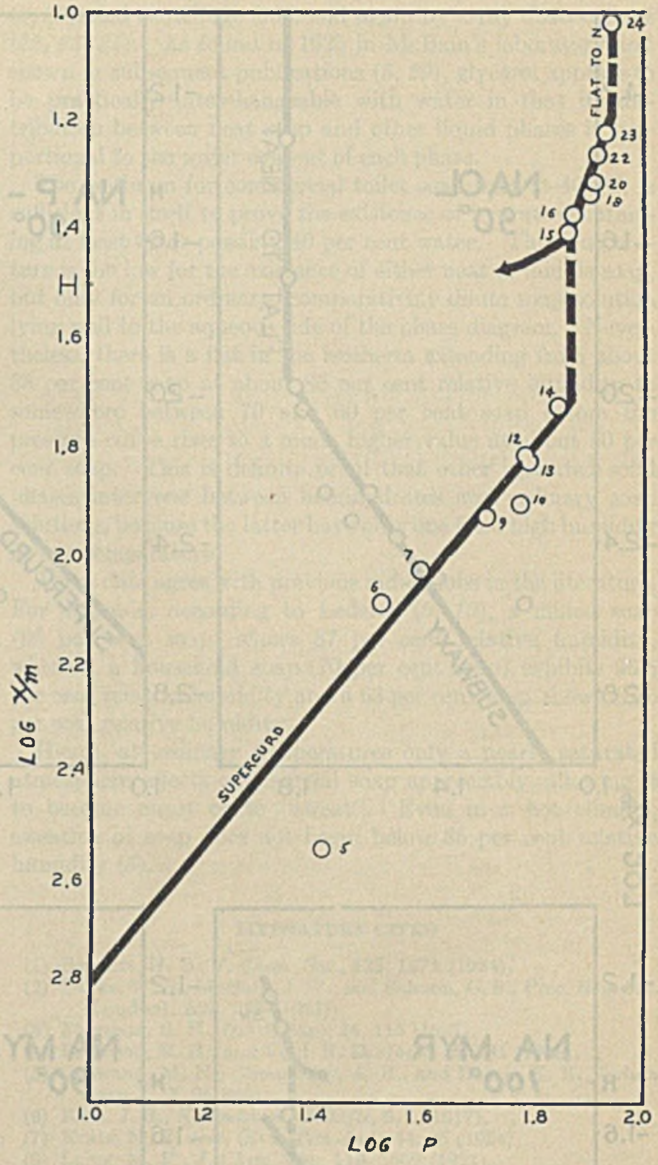

Figure 1. Isotherm Showing Sorption of Water Vapor by White Opaque Crystalline Fibers of Sodium Palmitate as Supercurd and Hemihydrate at 90° C. with Transition to Hemihydrate at 72 Per Cent Relative Humidity

H = hemihydrate (NaP.1/2 H_2O) containing 3.14 per cent H_2O; N = almost clear, liquid crystalline, soap-boilers' neat soap phase.

IN CONTRAST, dehydration of all the other soaps after forming hemihydrates proceeds with retention of almost the exact hemihydrate composition until very low relative humidities are reached. Although the evidence is incomplete, it appears that some hydrate water is progressively lost in accordance with the conclusion that a chemical compound exposed on a surface containing a volatile constituent must form and decompose according to a sorption law (*11*). At very low humidities desorption becomes much greater until complete dehydration occurs. Any subsequent rehydration then follows the original sorption curve for anhydrous soap.

TABLE I. EMPIRICAL CONSTANTS FOR THE SORPTION ISOTHERM

Soap	Supercurd		Hemihydrate		Subwaxy	
	k	$1/n$	k	$1/n$	k	$1/n$
NaP (90° C.) + 50% NaCl on basis of:						
Total solids	0.98×10^{-4}	1.1	4.6×10^{-10}	4.2	....	...
Soap alone	1.9×10^{-4}	1.1	9.2×10^{-10}	4.2	....	...
NaP (90° C.) + 2% NaCl	1.8×10^{-4}	1.0	....	...	....	...
NaP (90° C.)	1.1×10^{-4}	1.2	5.4×10^{-7}	2.6	....	...
NaMyr (90° C.)	0.5×10^{-4}	1.4	1.9×10^{-7}	2.8	....	...
NaMyr (100° C.)	0.89×10^{-4}	1.3	....	...	9.5×10^{-9}	3.6
NaOl (90° C.)	....	...	....	...	0.24×10^{-4}	1.5
NaL (65° C.)[a]	1.0×10^{-4}	1.3				

[a] The values given are for curd.

Our data are in agreement with the findings of Katz (*6*) and Kratz (*7*), who observed a sorption isotherm with anhydrous soap taking up less than 3 per cent water up

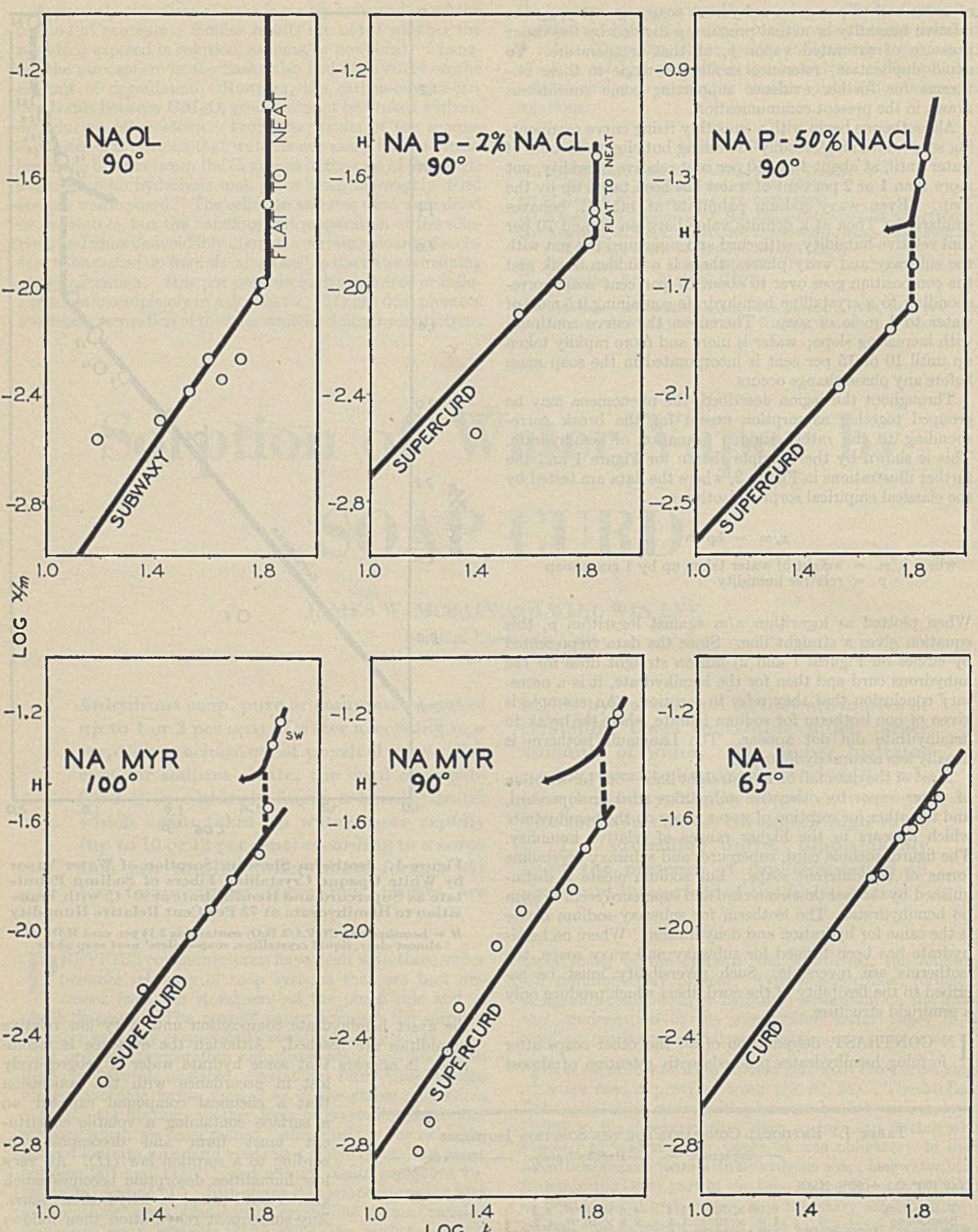

Figure 2. Isotherms for the Taking Up of Water Vapor by Originally Anhydrous Soap Systems

H = composition hemihydrate; SW = subwaxy phase. Straight lines on this logarithmic graph of x/m against p indicate sorption.

to 50 per cent relative humidity. The ensuing sorption was termed "swelling" by Kratz (*7*) and Lederer (*9, 10*). Sorption is always accompanied by swelling—for example, in the case of charcoal taking up carbon dioxide (*21*)—but typical swelling is not mere sorption.

The first sorption line in the lower part of each diagram (except that at 65° C., Figure 2) is followed by a flat vertical portion of constant relative humidity until the next phase is reached, whether hemihydrate, neat soap (as for sodium oleate at 90° C.), or subwaxy (as for sodium myristate at 100° C.). In the last case the subwaxy form intervenes before hemihydrate can form because the subwaxy extends over this field at this temperature. Such phases as subwaxy and neat are readily distinguished from each other and from curd by their visual appearance.

One of the most significant features is that, although the Langmuir sorption formula and the logarithmic formula are approximately obeyed, there are deviations from the usual adsorption relation: The slope is too steep, the exponent $1/n$ exceeds unity instead of being less, and the usual sorption curves have an opposite curvature to that generally found. In other words, sorption increases more rapidly than pressure. This behavior always indicates the presence of free capillary liquid in pores of greater diameter, which possibly increase in size by swelling as sorption increases (*11*).

The important point in porous and fibrous systems is that, with a wettable solid for each value of relative humidity, all pores below a definite size must fill with liquid—that is, capillary water (*11*). This capillary water becomes an essential part of the gross composition of the solid mass. On a phase diagram this gross composition, and not the supposed or actual composition of the fiber or solid structure itself, constitutes the end of the tie line for any heterogeneous equilibrium. The capillary liquid here may take the form of dilute soap solution or liquid crystalline soap solution, depending upon the temperature and the solubility of the particular soap. For partial wetting—that is, for a finite contact angle—larger pores will fill at a given low relative humidity.

Values of the empirical constants k and $1/n$ for the sorption isotherm are given in Table I. Sorption of water by supercurd appears to decrease with increase in molecular weight; that is, at higher relative humidities higher soaps are less hydroscopic than lower soaps. This agrees with the findings of Stiepel and of Godbole but not of Martin Fischer. However, owing to the differing values of the exponent $1/n$, this relation is reversed at low humidities. The same complication applies to the temperature coefficient which is slight, corresponding to a physical type of exothermic sorption.

The empirical isotherm holds also for subwaxy soap. In this respect subwaxy and curd are similar, confirming x-ray data to the effect that both are crystalline and fairly closely related.

THE question of the exact hydration of curd fibers is an incompletely solved problem, partly because a comparatively small reduction of relative humidity suffices to produce a dehydration of all the higher hydrates down to hemihydrate. However, there is no doubt of the reality of hydration, since its existence is demonstrated by many measurements with solutions of inert reference substances. With the significant exception of glycerol, these are rejected by the hydrate water, increasing the concentration of the resulting mother liquor (*1, 8, 12, 15, 17*). A similar conclusion resulted from previous studies of the vapor pressure of water (*4, 12, 16*), dilatometric measurements of freezing curds (*19*), microscopic and ultramicroscopic examination (*2, 20*), and centrifuge (*13*), and again by x-ray observations (*22, 23, 24*). As found in 1925 in McBain's laboratory and shown in subsequent publications (*3, 29*), glycerol appears to be practically interchangeable with water in that its distribution between neat soap and other liquid phases is proportional to the water content of each phase.

The isotherm for commercial toilet soap base at 40° C. is sufficient in itself to prove the existence of hydrates containing at least 30 or possibly 40 per cent water. This temperature is too low for the existence of either neat or middle soap, but only for an ordinary, comparatively dilute soap solution lying well to the aqueous side of the phase diagram. Nevertheless, there is a flat in the isotherm extending from about 88 per cent soap at about 85 per cent relative humidity to somewhere between 70 and 60 per cent soap before the pressure curve rises to a much higher value at about 50 per cent soap. This is definite proof that other hydrated solid phases intervene between hemihydrates and ordinary soap solutions, because the latter have only one fixed high humidity at one temperature.

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Hence, at ordinary temperatures only a nearly saturated atmosphere affects commercial soap appreciably, allowing it to become moist or to "sweat". Even in a hot climate, sweating of soap does not begin below 85 per cent relative humidity (*5*).

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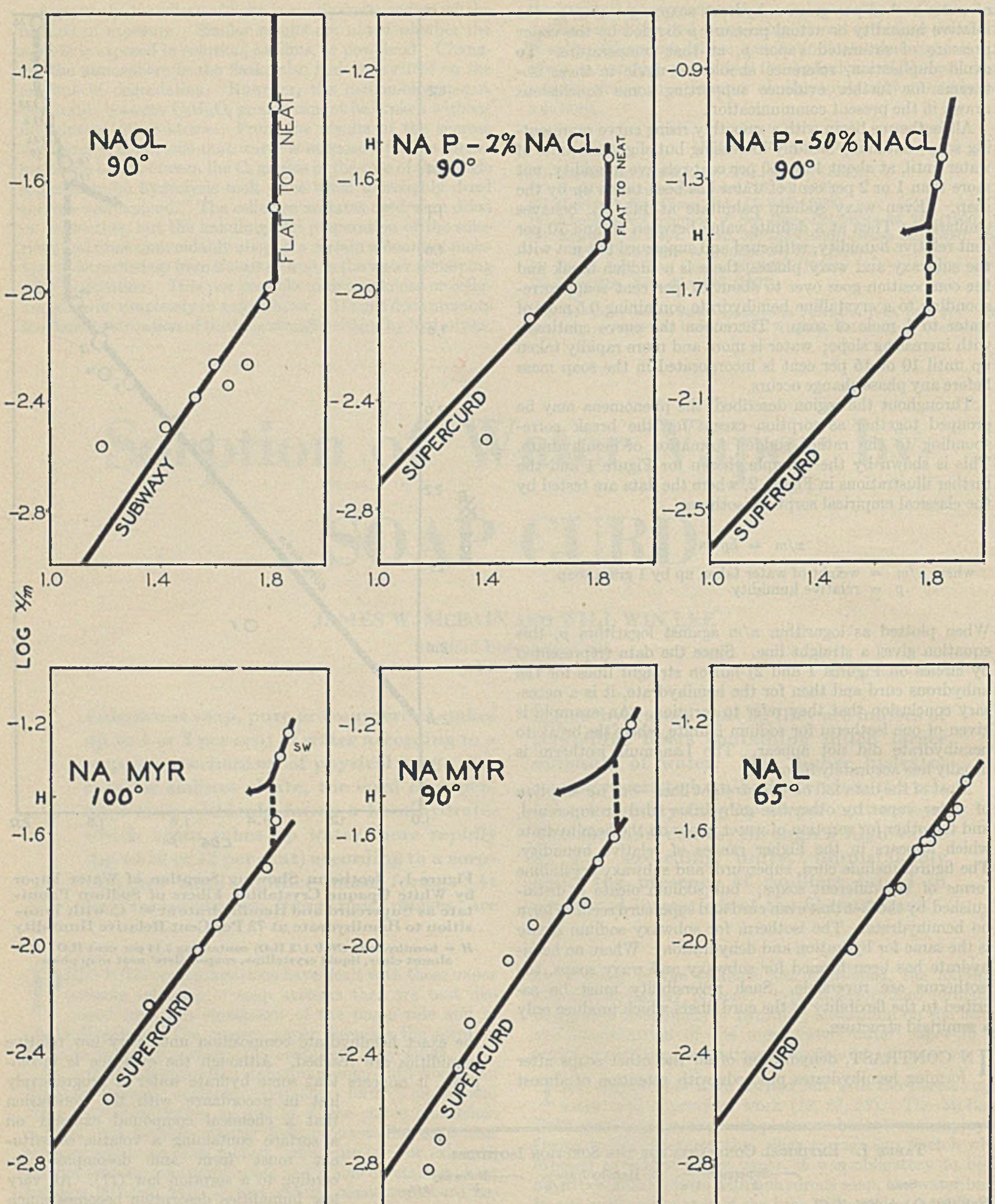

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Aliphatic Hydrocarbon Densities

CORRELATION IN THE CRITICAL REGION

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A simplified correlation of densities of paraffin (and to some extent olefin) hydrocarbons is presented. Based on reduced temperatures and reduced pressures, it gives densities directly without the use of intermediate reduced volumes. Calculated data agree with experimental data within 2 to 5 per cent deviation.

CALCULATION of the density of hydrocarbons under a variety of pressure and temperature conditions is necessary in almost all phases of petroleum engineering. Among these is the calculation of the equivalent cracking time in furnace coils. This involves the calculation of the density of the oil in the liquid phase, through the critical region, and into the vapor phase. The part of these calculations for which the least reliable engineering data have been available has been that phase of the liquid-vapor regions immediately adjoining the critical temperature. It is hoped that the curves presented here will correlate available data in that region and at the same time simplify this type of calculation.

TABLE I. CRITICAL CONSTANTS FOR HYDROCARBONS

Hydrocarbon	Critical Temp., ° Rankine	Critical Pressure, Lb./Sq. In. Abs.	Citation
Methane	344	673	(*5*)
Ethylene	508	745	(*5*)
Ethane	549	717	(*5*)
Propylene	656	661	(*5*)
Propane	665	617	(*5*)
Isobutane	732	544	(*5*)
n-Butane	766	529	(*5*)
Isopentane	829	483.4	(*5*)
n-Pentane	846	485	(*5*)
2,3-Dimethylbutane	901	449.5	(*7*)
n-Hexane	915	441	(*8*)
2-Methylpentane	902	472	(*8*)
n-Heptane	972	393.7	(*5*)
Diisobutyl	989	360.0	(*5*)
n-Octane	1024	361.4	(*5*)

The present data correlate density of paraffin hydrocarbons and are applicable to some extent to olefin hydrocarbons. Any further extension of the curves, such as to include aromatics or make the general curves applicable to mixtures by means of a characterization factor, aniline point, or similar method, will require further experimental data than are here available.

A previous unpublished correlation by the authors indicated that for liquids a satisfactory plot could be made of reduced temperature, reduced pressure, and reduced volume. A further observation that the critical volumes of paraffin hydrocarbons was approximately constant led to the conclusion that the specific volume could be plotted instead of the reduced volume; or for more direct use, the reciprocal of specific volume or density could be plotted as one of the coordinates. On this assumption Figure 1 was prepared. To use this chart it is necessary to know the reduced temperature and reduced pressure of the material in question. Read directly from the chart its required value of density in pounds per cubic foot.

Critical constants of the lower hydrocarbons as published by Edmister (*5*) and Kelso and Felsing (*7*, *8*) are given in Table I.

ACCURACY OF CORRELATION

The correlation is believed to reproduce the experimental data with an accuracy of 2 to 5 per cent deviation for the most part in the range of reduced temperatures from 0.700 to 1.500. Above a reduced temperature of 1.500 there are insufficient experimental data to achieve a correlation of this accuracy. The dotted lines are tentative curves based on meager data from methane and on estimates from generalized compressibility data. For temperatures well below the critical it has been customary to apply temperature corrections and to ignore the effect of pressure. This procedure is probably still satisfactory for the range below the reduced temperature of 0.700.

TABLE II. ACCURACY OF METHOD

Hydrocarbon	Citation	Max. % Deviation from This Correlation
Methane	(*9*)	35
Ethane	(*3*)	6.7
	(*13*)	13.0
Propane	(*1*)	7.0
	(*4*)	17.0
	(*11*)	7.4
Propylene	(*16*)	6.8
n-Butane	(*2*)	4.2
	(*14*)	2.7
Isobutane	(*10*)	2.8
n-Pentane	(*12*)	2.9
Isopentane	(*17*)	1.0
2,3-Dimethylbutane	(*7*)	2.7
n-Hexane	(*8*)	3.7
2-Methylpentane	(*8*)	9.4

Table II indicates maximum deviations of densities read from Figure 1 compared with experimental data from the literature. In general, the average is far better than the maxi-

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mum figure shown. The maximum figure appears usually at a point in the curves where the slope is such that relatively small deviations in the reduced pressure will produce disproportionate errors in the density. Extreme discretion must be exercised when the curves are used in this range. The data of Kay for butane (*6*) and of Smith, Beattie, and Kay for heptane (*15*) show large deviations from the correlated curves. Superficial examination of the data and calculations have not revealed any reason for this discrepancy; no explanation will be attempted here.

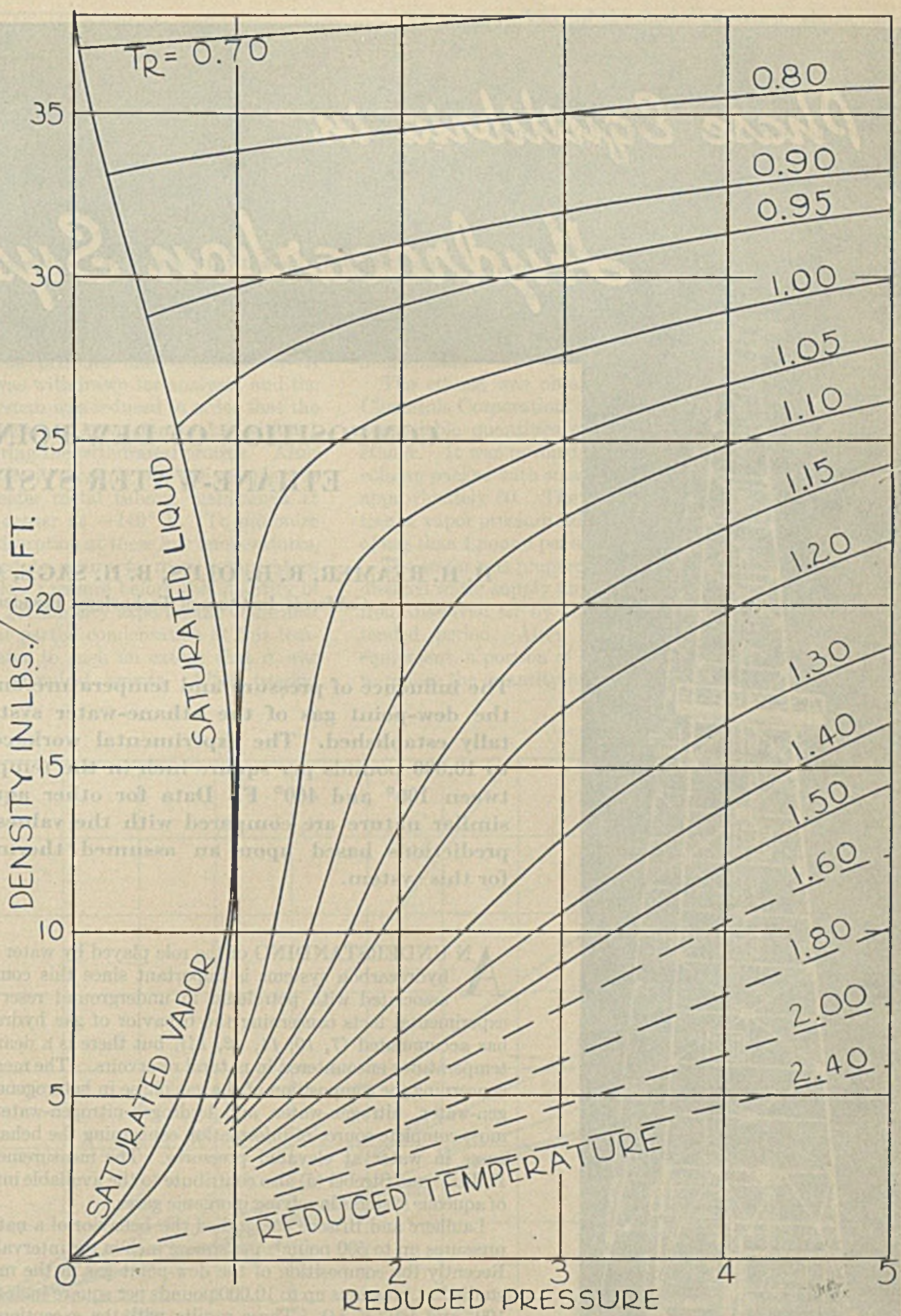

Figure 1. Correlation of Densities of Aliphatic Hydrocarbons in the Critical Region

ACKNOWLEDGMENT

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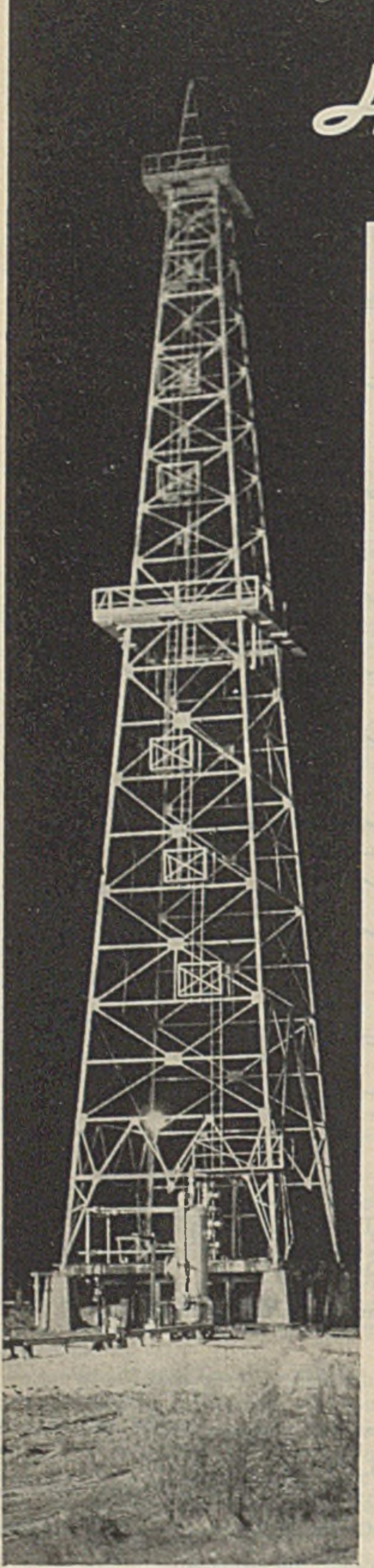
Phase Equilibria in Hydrocarbon Systems



COMPOSITION OF DEW-POINT GAS IN ETHANE-WATER SYSTEM

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The influence of pressure and temperature on the composition of the dew-point gas of the ethane-water system was experimentally established. The experimental work covered pressures up to 10,000 pounds per square inch in the temperature interval between 100° and 460° F. Data for other aqueous systems of a similar nature are compared with the values obtained and with predictions based upon an assumed thermodynamic behavior for this system.

AN UNDERSTANDING of the role played by water in the phase behavior of hydrocarbon systems is important since this component is nearly always associated with petroleum in underground reservoirs. A background of experimental facts concerning the behavior of gas hydrates at low temperatures has accumulated (*7, 10, 11, 12, 14*), but there is a dearth of information at the temperatures encountered in natural reservoirs. The measurements of Bartlett (*1*) concerning the composition of the gas phase in heterogeneous regions of the hydrogen-water, nitrogen-water, and hydrogen-nitrogen-water systems constitute the most complete source of information concerning the behavior of difficultly soluble gases in water at elevated pressures. The measurements of McHaffie (*3*) and Pollitzer and Strebel (*5*) also contribute to the available information on the behavior of aqueous systems involving inorganic gases.

Laulhere and Briscoe (*2*) studied the behavior of a natural gas-water system at pressures up to 500 pounds per square inch in the interval between 60° and 100° F. Recently the composition of the dew-point gas in the methane-water system was studied at pressures up to 10,000 pounds per square inch for temperatures between 100° and 460° F. (*4*). These results, with the exception of the measurement for the hydrogen-water system, indicate higher concentrations of water in the gas phase than would be predicted on the basis of the assumption underlying the Poynting equation (*6*). To extend the data on the behavior of water-hydrocarbon systems involving organic components of intermediate molecular weight, a study of the ethane-water system was undertaken.

METHODS AND MATERIALS

The composition of the dew-point gas was established by the withdrawal of a portion of the gas phase of a heterogeneous system under isobaric isothermal conditions. This procedure is in contrast to the essentially dynamic approach employed by Bartlett (*1*). A mixture of ethane and water was

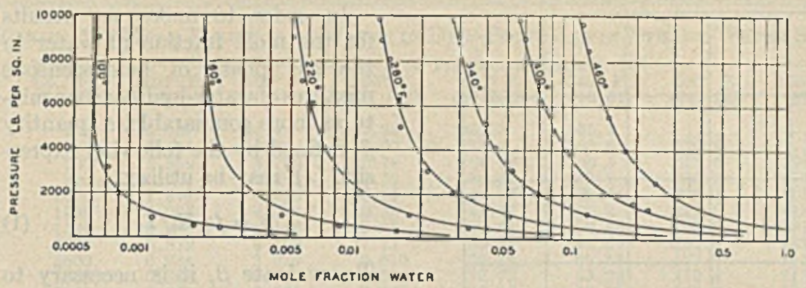

Figure 1. Pressure-Composition Diagram in Ethane-Water System

confined over mercury and was brought to thermodynamic equilibrium at the desired pressure and temperature. A sample of the gas phase was withdrawn for analysis, and the effective volume of the system was reduced in order that the pressure might be maintained at a constant value within 1 pound per square inch during the withdrawal process. After being throttled to atmospheric pressure, the gas sample was transferred in small-diameter metal tubing, maintained at 140° F., to a partial condenser at −140° F. To minimize solution of ethane or its adsorption at these low temperatures, the condenser was allowed to return to room temperature and then recooled under low pressure before the quantity of ethane was ascertained. Preliminary experiments confirmed earlier indications (*4*) that partial condensation at this temperature removed the water to such an extent that it was unnecessary to employ chemical agents. After passing through the low-temperature partial condenser, the residual ethane was collected in an isochoric glass chamber kept at a constant temperature by means of an agitated air bath. The quantity of ethane was determined from the change in pressure of the gas within this vessel as established from the indications of a mercury-in-glass manometer. The details of the experimental program were similar to those employed in an earlier study of the methane-water system (*4*); the equilibrium apparatus has also been described (*9*). The determination of the primary variables was believed to be such that the mole fraction of water was within 3 per cent of the value reported, except perhaps at the lower temperatures where the small concentration of water made its estimation more difficult. Available volumetric data for pure ethane were utilized (*10*) in connection with the determination of the mole fraction of ethane from the volumetric measurements made.

The ethane was obtained from the Carbide and Carbon Chemicals Corporation. The material as received contained appreciable quantities of gaseous hydrocarbons other than ethane. It was purified by repeated fractionation in a glass column packed with small glass helices, using a reflux ratio of approximately 50. The purified material exhibited a variation in vapor pressure from dew point to bubble point at 70° F. of less than 1 pound per square inch.

The water was prepared by the redistillation of the regular distilled water supply furnished the laboratory. It was freed from dissolved air by boiling at reduced pressure for an extended period. After introduction into the equilibrium equipment, a portion of the gas phase was removed in order to reduce the quantity of extraneous material still further.

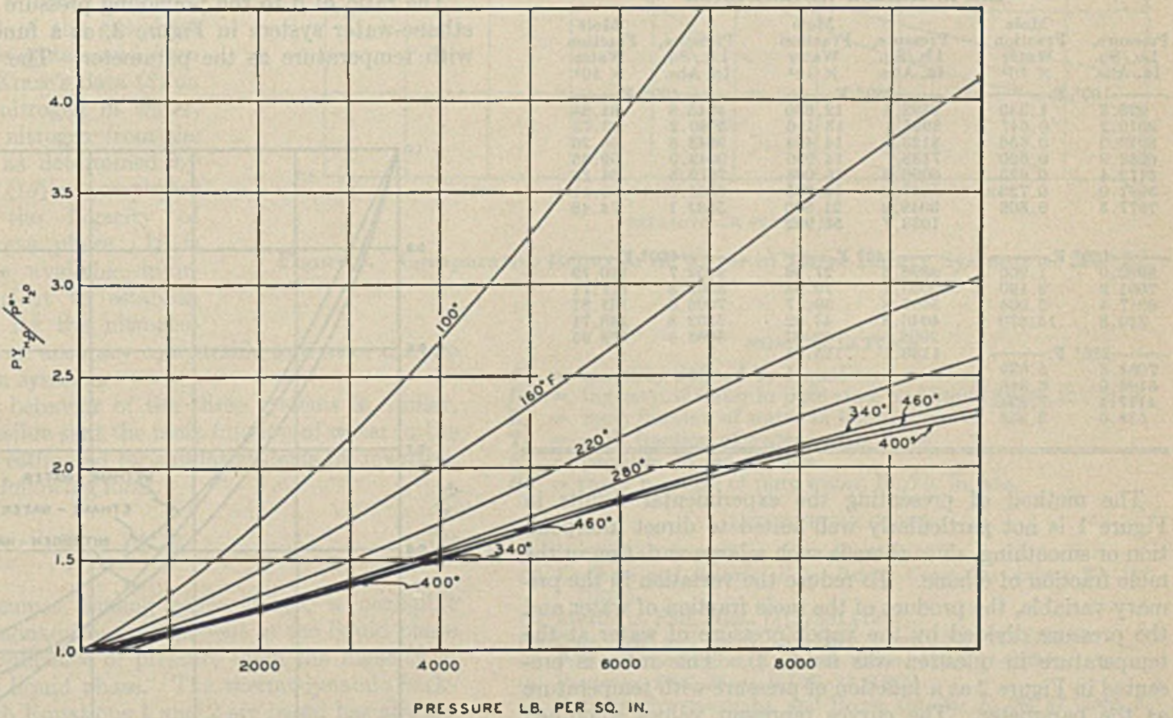

Figure 2. Influence of Pressure upon Dew-Point Gas Composition of Ethane-Water System

COMPOSITION OF GAS PHASE

The composition of the gas phase in the ethane-water system as determined experimentally is given in Table I and Figure 1. The full curves represent smoothed values obtained in the graphical interpolation of the results.

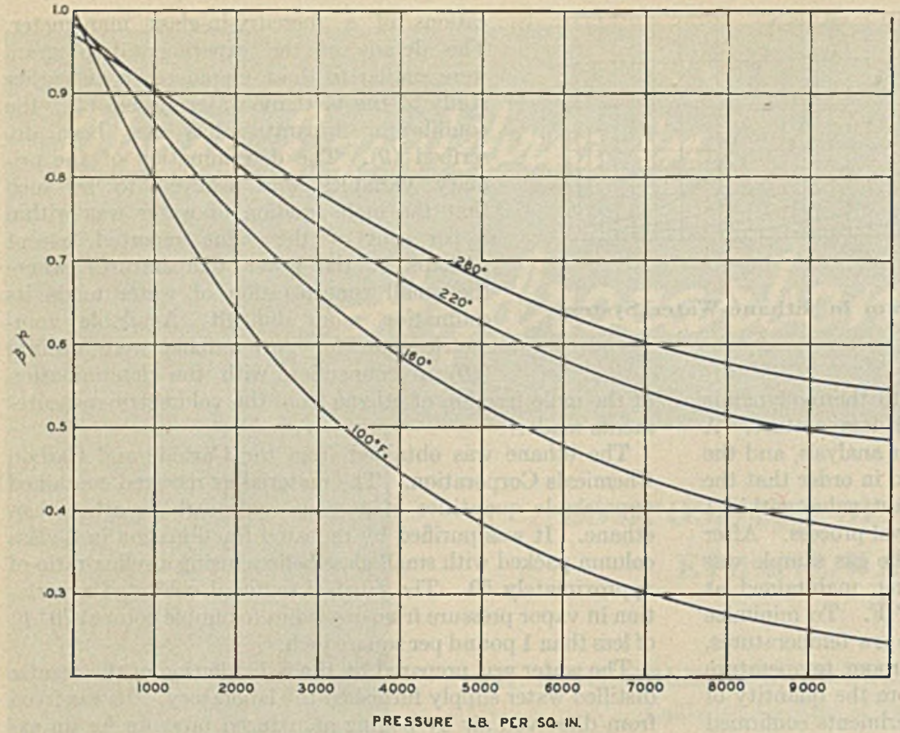

Figure 3. Influence of Pressure upon $f^{\circ}_{11} X_1/Y_1$

TABLE I. EXPERIMENTAL DATA ON COMPOSITION OF DEW-POINT GAS IN ETHANE-WATER SYSTEM

Pressure, Lb./Sq. In. Abs.	Mole Fraction Water × 10^3	Pressure, Lb./Sq. In. Abs.	Mole Fraction Water × 10^3	Pressure, Lb./Sq. In. Abs.	Mole Fraction Water × 10^3
100° F.		280° F.		400° F.	
926.3	1.330	9892.1	12.680	4945.8	81.84
9010.2	0.647	8985.1	13.196	3989.2	93.73
8010.0	0.656	8123.6	14.404	9843.6	56.26
6982.9	0.620	7138.7	14.990	9042.9	59.85
5172.4	0.623	6096.8	16.006	7979.5	64.26
3091.0	0.723	5047.0	16.235	6855.6	69.11
1977.3	0.802	3049.8	21.800	5982.1	74.48
		1033.7	51.982		
160° F.		340° F.		460° F.	
8992.0	1.960	9896.3	27.96	9652.7	110.79
7001.2	2.190	9003.1	29.63	8503.8	117.71
6017.4	2.034	5097.8	39.17	7006.8	131.81
320.8	15.570	4046.8	43.62	5502.8	148.71
		2998.5	52.81	3983.6	179.95
220° F.		1150.1	115.76		
7084.8	5.639				
6106.6	6.346				
4117.4	7.224				
536.6	3.362				

The method of presenting the experimental results in Figure 1 is not particularly well suited to direct interpolation or smoothing, since there is such a large variation in the mole fraction of ethane. To reduce the variation in the primary variable, the product of the mole fraction of water and the pressure divided by the vapor pressure of water at the temperature in question was used (*4*). This ratio is presented in Figure 2 as a function of pressure with temperature as the parameter. The curves represent values smoothed with respect to both pressure and temperature. The rather complex behavior indicated at temperatures above 280° F. is similar to that found for the methane-water system. Smoothed values of the mole fraction of water in the gas phase of heterogeneous mixtures of ethane and water at even values of pressure and temperature are given in Table II. It is believed that the methods utilized in obtaining these results did not add uncertainty beyond that of the experimental values in Table I.

In order to make the results for the mole fraction of water in the gas phase of heterogeneous mixtures of water-hydrocarbon mixtures more comparable, a quantity β, defined by the following expression (*4*), may be utilized:

$$\beta = f^{\circ}_{11} X_1/Y_1 \qquad (1)$$

To evaluate β, it is necessary to establish the composition of the liquid phase as a function of pressure and temperature. Some values of ethane solubility in water at relatively low temperatures and pressures are available and have been used in conjunction with Henry's law to predict the mole fractions of ethane in the liquid phase as a function of pressure. A 50 per cent uncertainty in the mole fraction of ethane as predicted by these methods would modify the value of β in Equation 1 only by approximately 1.0 per cent. For this reason it is believed that the assumption of Henry's law and the use of a rather meager experimental basis for the solubility of ethane in water do not introduce large uncertainties in the values of β obtained from Equation 1.

The ratio of β to the prevailing pressure is shown for the ethane-water system in Figure 3, as a function of pressure with temperature as the parameter. The curves were not

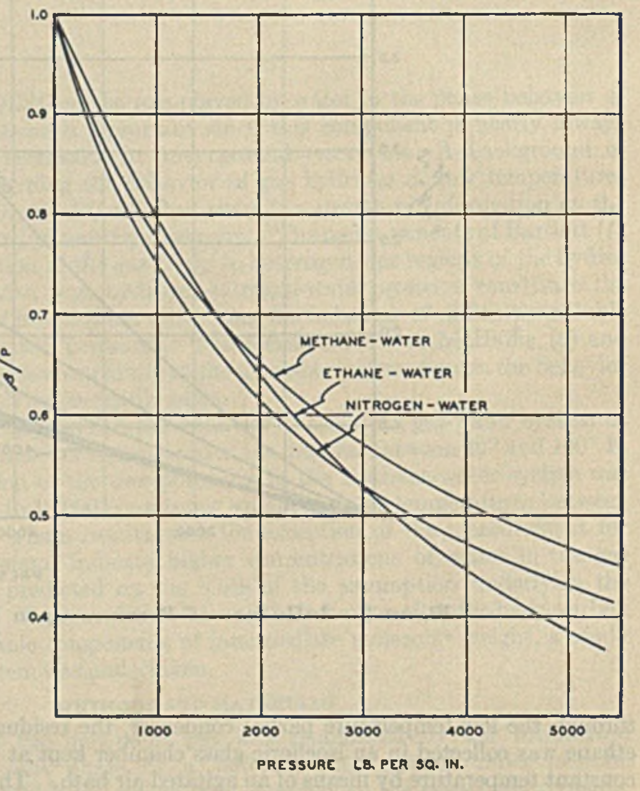

Figure 4. Comparative Behavior of Water in Three Binary Systems at 100° F.

Table II. Mole Fraction of Water in Dew-Point Gas in Ethane-Water System

Pressure, Lb./Sq. In. Abs.	Mole Fraction of Water × 10^2						
	100° F. (0.9492)[a]	160° F. (4.741)	220° F. (17.186)	280° F. (49.203)	340° F. (118.01)	400° F. (247.31)	460° F. (466.9)
200	5.007[a]	24.49	87.82	250.7	595.4	....	...
400	2.641	12.69	45.07	127.9	303.6	629.4	...
600	1.859	8.779	30.79	86.93	206.5	429.5	793.7
800	1.474	6.833	23.72	66.61	158.1	330.2	613.4
1000	1.244	5.675	19.51	54.47	129.1	270.1	505.2
1250	1.065	4.752	16.16	44.87	106.2	222.6	418.3
1500	0.949	4.147	13.96	38.41	90.47	190.9	361.1
2000	0.812	3.409	11.21	30.51	71.69	151.4	289.0
2500	0.734	2.979	9.610	25.78	60.42	127.9	245.2
3000	0.688	2.709	8.553	22.72	53.22	112.4	215.6
3500	0.658	2.521	7.827	20.53	48.05	101.6	194.8
4000	0.640	2.390	7.300	19.05	44.25	93.42	178.8
4500	0.626	2.292	6.905	17.91	41.38	87.11	166.8
5000	0.620	2.218	6.603	17.01	39.06	82.01	157.0
6000	0.617	2.118	6.173	15.70	35.60	74.19	142.3
7000	0.619	2.068	5.890	14.75	33.18	68.61	131.3
8000	0.623	2.030	5.650	13.96	31.17	63.90	122.5
9000	0.626	1.993	5.431	13.32	29.44	59.90	114.7
10,000	0.629	1.952	5.207	12.74	27.95	56.49	107.9

[a] Figures in parentheses are vapor pressures of water in pounds per square inch absolute.

extended to all the temperatures because of uncertainties regarding the mole fraction of ethane in the liquid phase.

Figures 4 and 5 present the comparative behavior of water in the methane-water, ethane-water, and nitrogen-water systems at 100° and 220° F. The data for the methane-water system were obtained from earlier measurements (*4*); the behavior of the nitrogen-water system was ascertained from Bartlett's measurements (*1*) of the gas-phase composition of this system and from Saddington and Krase's data (*8*) on the solubility of nitrogen in water. The deviation of nitrogen from the perfect gas laws as determined by Wiebe and Gaddy (*13*) was employed in establishing the fugacity of nitrogen in the gas phase. It is believed that the available information was sufficient to establish the values of β for the nitrogen-water system with an accuracy comparable to that of the two water-hydrocarbon systems.

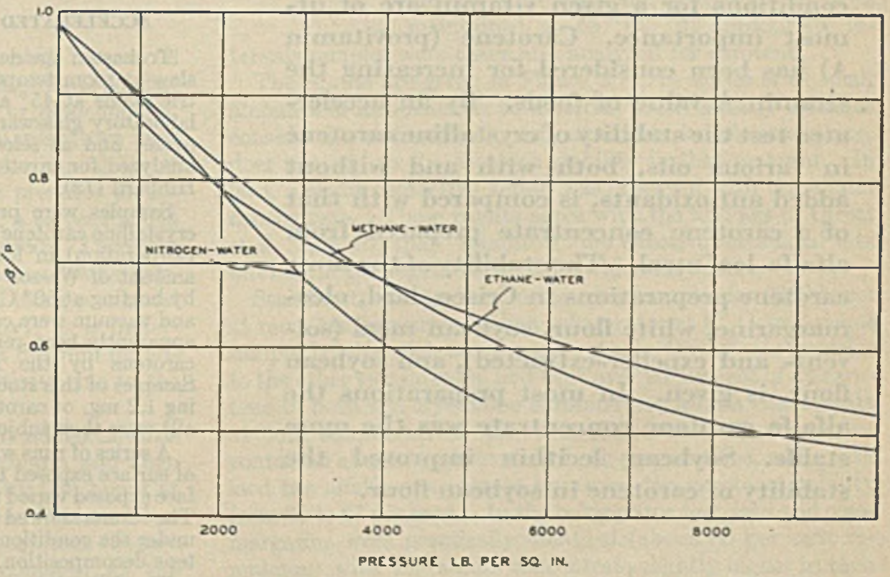

Figure 5. Comparative Behavior of Water in Three Binary Systems at 220° F.

In general, the behavior of the three systems is similar. Therefore it is possible that the mole fraction of water in the gas phase may be estimated for similar systems by rewriting Equation 1 in the following form:

$$Y_1 \approx P_1^{\circ\prime\prime}/\beta \qquad (2)$$

Equation 2 assumes, among other things, a negligible solubility for the nonaqueous component in the liquid phase and neglects the influence of pressure upon the fugacity of pure water in the liquid phase. The thermodynamic background upon which Equations 1 and 2 are based has already been described (*4*).

The results shown in Figures 4 and 5 at the higher pressures and lower temperatures indicate approximately five times the mole fraction of water in the gas phase that would be predicted from simple vapor pressure considerations. These effects are of sufficient magnitude to be of industrial importance when gases at high pressures are in contact with water in the liquid phase. Such situations are often encountered in petroleum reservoirs and may become of especial significance during cycling operations in high-pressure fields. As found for the methane-water system (*10*), the critical pressure of the ethane-water system is markedly in excess of 10,000 pounds per square inch at all the temperatures investigated.

ACKNOWLEDGMENT

The measurements reported constitute a part of the activities of Research Project No. 37 of the American Petroleum Institute. The interest and financial support of the institute are acknowledged. Louise M. Reaney assisted with the calculations and preparation of the figures.

NOMENCLATURE

β = quantity defined by Equation 1
$f_1^{\circ\prime}$ = fugacity of water in pure state and liquid phase, lb./sq. in.
X_1 = mole fraction of water in liquid phase
Y_1 = mole fraction of water in gas phase
P = pressure, lb./sq. in. abs.
$P_1^{\circ\prime\prime}$ = vapor pressure of pure water, lb./sq. in. abs.

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Fortification of Oil, Fat, and Flour

STABILITY OF ADDED CAROTENE AND EFFECT OF ANTIOXIDANTS

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The fortification of foods with vitamins serves as a nutritional benefit only in so far as the vitamins have not decomposed before the food is consumed. Therefore stability tests to determine the most stable conditions for a given vitamin are of utmost importance. Carotene (provitamin A) has been considered for increasing the vitamin A value of foods. By an accelerated test the stability of crystalline carotene in various oils, both with and without added antioxidants, is compared with that of a carotene concentrate prepared from alfalfa-leaf meal. The stability of the same carotene preparations in Crisco, lard, oleomargarine, white flour, soybean meal (solvent- and expeller-extracted), and soybean flour, is given. In most preparations the alfalfa carotene concentrate was the more stable. Soybean lecithin improved the stability of carotene in soybean flour.

RECENT trends in nutrition have been toward the addition of vitamins to the common foods (*1*). Milk has been fortified with vitamin D and margarine with vitamin A. In 1941 enriched flour and bread were produced which contain, in addition to the usual ingredients, proper amounts of thiamine, nicotinic acid, and iron as specified by the Food and Drug Administration.

Considerable interest has been shown in the possibilities of fortifying various foods, such as margarine, soybean flour, etc., with carotene as a source of vitamin A. Carotene (provitamin A) is found widely distributed in nature and in some instances, notably carrots and dehydrated alfalfa-leaf meal, in sufficient concentration and availability to warrant the development of processes for its commercial isolation (*2, 7, 11*). With our imports of fish liver oils containing vitamin A practically cut off as a result of the war, we may be forced to obtain much of our vitamin A supply from domestic sources. Since vitamin A and carotene, as well as most of the other vitamins, are subject to destruction under various conditions, it is essential that they should not be added to foods in which they are not relatively stable.

Many leafy-green plants contain vitamin E and other antioxidants (*9*) which are concentrated along with the carotene and sterols in the unsaponifiable concentrate. Therefore, to compare the stability of these preparations when incorporated in foods with an oil solution of crystalline carotene (*13*), accelerated carotene decomposition tests were made with both crystalline carotene-in-oil and dehydrated alfalfa-leaf unsaponifiable concentrate (*7, 11*). Various antioxidants were added to some of the preparations to determine their effectiveness.

ACCELERATED DECOMPOSITION TEST FOR CAROTENE

To hasten the decomposition of carotene, which may be very slow at room temperature, two thermostatically controlled electric ovens at 45° and 60° C. were used. Weighed samples, in laboratory glassware and exposed to the air, were placed in the ovens, and at selected intervals duplicates were removed and analyzed for carotene by the method of Petering, Wolman, and Hibbard (*12*).

Samples were prepared by dissolving a weighed amount of crystalline carotene (90 per cent beta, 10 per cent alpha, S. M. A. Corporation) in low-boiling petroleum ether, adding a definite amount of Wesson oil, and evaporating off the petroleum ether by heating at 50° C. under nitrogen and reduced pressure. Heat and vacuum were continued for 20 minutes after the solvent had apparently been removed. The solution was then analyzed for carotene by the Petering, Wolman, Hibbard method (*12*). Samples of this stock solution of carotene in Wesson oil (containing 1.2 mg. of carotene, or 2000 I. U. of vitamin A, per gram of oil) were then subjected to the accelerated decomposition test.

A series of runs was made to determine the effect of the amount of surface exposed to the air on the carotene stability. The surface exposed varied from 31 to 630 sq. mm. per 0.1 gram of sample. The results showed that the amount of surface exposed to the air under the conditions of our test was not a critical factor in carotene decomposition.

The following procedure was used in the subsequent stability tests: A 0.2-gram sample of carotene in oil was weighed into glass vials 12 mm. in diameter and 25 mm. high. Larger samples and vials were used for the fat and flour preparations. For convenience the vials were placed into holes in hardwood blocks.

STABILITY IN OILS

Crystalline carotene in both Mazola and Wesson oil showed approximately the same stability as an alfalfa carotene concentrate in the same two oils. Figure 1 presents the stability of crystalline carotene in Wesson oil. Since alfalfa-leaf meal is known to contain vitamin E which has antioxidant activity, and possibly other antioxidants also, it might be expected that alfalfa carotene concentrate would be more stable than crystalline carotene in the same solvent. To clarify this point, antioxidants were added to a solution of crystalline carotene in Wesson oil to determine their effect on the carotene stability.

A solution of crystalline carotene in Wesson oil was prepared as previously described except for the addition of the antioxidant before the solvent was removed. The antioxidants were hydroquinone, phenyl-α-naphthylamine, phenyl-β-naphthylamine (*14, 15*), and α-tocopherol added at 0.01 per cent level based on the weight of oil. The hydroquinone and α-tocopherol were also used at the 0.1 per cent level.

The data (Figure 1) show that only hydroquinone was effective in retarding carotene decomposition; other antioxidants were ineffective. The same result was obtained with alfalfa

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[1] Present address, Purdue University, Lafayette, Ind.

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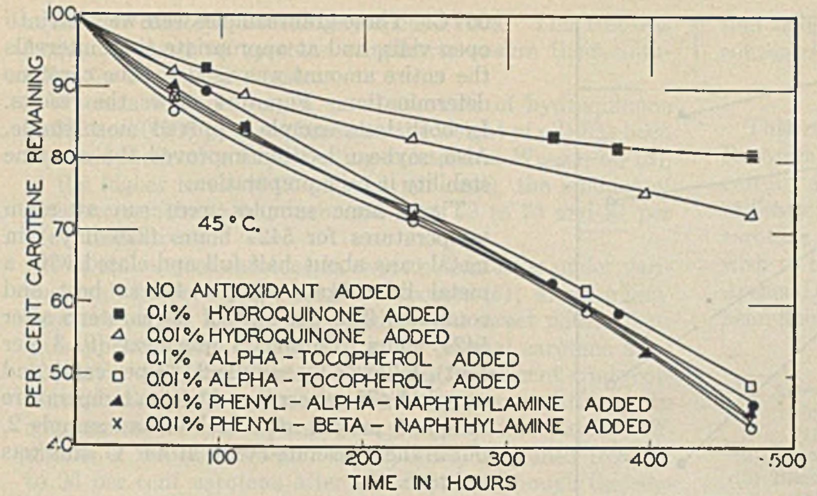

Figure 1. Effect of Added Antioxidants on Stability of Crystalline Carotene in Wesson Oil

carotene concentrate in Wesson oil. Presumably Wesson oil contains a sufficient quantity of natural antioxidants so that the addition of the phenylnaphthylamines, or α-tocopherol, or the natural antioxidants in alfalfa, in the quantities used have practically no effect in retarding the decomposition of carotene dissolved in it. To determine the presence or absence of antioxidants in a given preparation, a solvent which was free of antioxidants would have to be used. Therefore to show that the alfalfa carotene concentrate contains antioxidants, a similar series of runs were made using a mineral oil solvent (Petrofol, United Drug Company); it is understood that mineral oil is not satisfactory as a medium for administering carotene for its provitamin A activity due to the poor absorption attendant upon its use (*4*).

Crystalline carotene in mineral oil without added antioxidant remained quite stable for about 230 hours and then underwent almost complete decomposition by 280 hours at 45° C. By comparison, crystalline carotene in Wesson oil at 280 hours contained about 65 per cent of its carotene (Figure 1). The phenylnaphthylamines and α-tocopherol at the 0.01 per cent level and the α-tocopherol and hydroquinone at the 0.1 per cent level effectively protected the carotene in mineral oil so that about 88 per cent remained in each case after 476 hours. The 0.001 per cent α-tocopherol had dropped to 39 per cent in the same time, while the 0.01 per cent hydroquinone was only slightly better than the unprotected carotene. The 0.1 per cent hydroquinone sample protected the carotene very well and, when analyzed after 838 hours, was found still to contain 81.8 per cent of its original carotene. The alfalfa carotene concentrate contained 89 per cent of its carotene after 865 hours, which is even better than the protection afforded by 0.1 per cent hydroquinone, the best antioxidant used.

It thus appears evident that the alfalfa carotene concentrate does contain naturally occurring antioxidants which undoubtedly protect the carotene from decomposition during its extraction and concentration. Although these antioxidants do not add to the carotene stability when in Wesson oil, because of the antioxidants already present in that solvent, they do become effective stabilizers in solvents which are naturally deficient in antioxidants. Therefore, when added to foods relatively poor in antioxidants, the alfalfa carotene concentrate should also show greater carotene stability than crystalline carotene.

STABILITY IN EDIBLE FATS

Accordingly, alfalfa carotene concentrate and crystalline carotene were added to certain food products to compare the stability. Commercial samples of Crisco, lard (Armour's Star pure lard), and oleomargarine (not fortified with vitamin A, John F. Jelke Company) were obtained and prepared for the test as follows: Wesson oil stock solutions of both crystalline carotene and alfalfa carotene concentrate were prepared as before. To 200 grams each of Crisco, lard, and oleomargarine, sufficient Wesson oil stock solution was added to bring the fat to the equivalent of 10,000 units of vitamin A per pound. After thorough mixing at 34° C., 2.2-gram samples were weighed directly into vials and placed in an oven maintained at 45° C. At appropriate intervals samples were taken and analyzed for carotene.

The results are given in Figure 2. The addition of small amounts of antioxidants to material which already contains considerable antioxidants, such as Crisco and oleomargarine, does not add to the carotene stability in that material. In lard, a slight protective action was observed with the alfalfa concentrate. These results agree with the findings of Olcott *et al.* (*8*, *9*, *10*) that "inhibitols" are effective for animal fats but not for the vegetable oils from which they come.

Stability tests were run on the same samples for 6060 hours at room temperature and in a refrigerator at 8° C. in 2-ounce sample bottles with screw tops. Again Crisco was superior to the other two samples, and kept over 90 per cent of its carotene in both the crystalline carotene and alfalfa concentrate at both temperatures. At room temperature oleomargarine contained about 50 per cent for both preparations, while with lard the alfalfa concentrate improved the carotene stability from 30 to 67 per cent. In the refrigerator test, lard and oleomargarine were practically identical (about 80 per cent remaining) with the alfalfa concentrate slightly higher in each case.

STABILITY IN FLOUR AND MEAL

A white, bleached flour (Gold Medal brand, enriched), and two soybean meals, one solvent-extracted and the other expeller-extracted, were obtained. Stock solutions of crystal-

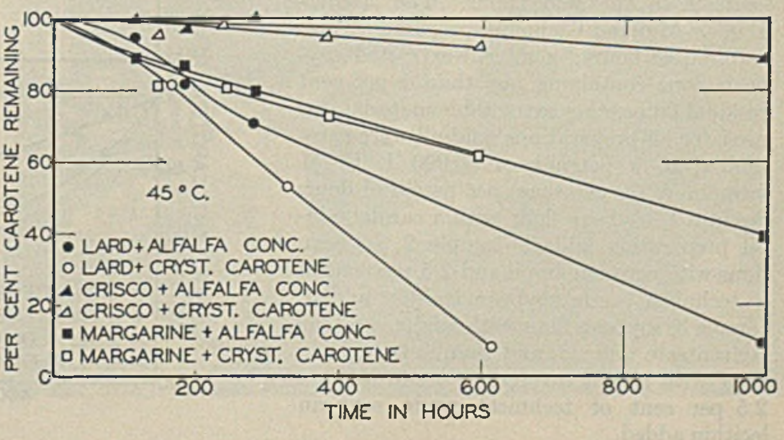

Figure 2. Stability of Crystalline Carotene and Alfalfa Carotene Concentrate in Lard, Crisco, and Margarine

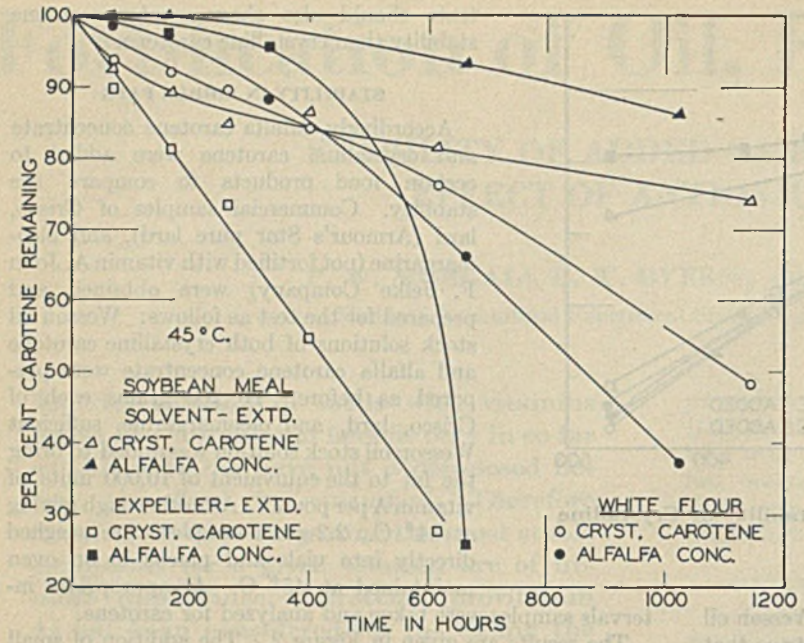

Figure 3. Stability of Crystalline Carotene and Alfalfa Carotene Concentrate in White Flour and Soybean Meals

line carotene and alfalfa carotene concentrate were added to 150-gram portions each of the white flour, solvent-extracted soybean meal, and expeller-extracted soybean meal to give a potency of 60,000 I. U. of vitamin A per pound of flour or meal. Petroleum ether was added, the mixture was stirred thoroughly, and the petroleum ether was removed as before. After thorough mixing, a carotene determination was run in duplicate, and each preparation was divided into equal portions and placed in open beakers. One sample was stored at room temperature in a dark closet, and the other was placed in an oven at 45° C. Three-gram samples were taken for analysis. The results are shown in Figure 3. Stability tests were run at room temperature for those samples containing the alfalfa concentrate. The order of stability was the same as at 45° C.; solvent-extracted soybean meal was best (90 per cent), then the white flour (77 per cent), and last the expeller-extracted soybean meal (34 per cent), at the end of 6060 hours.

Carotenized soybean flour was available commercially, and a comparison was made of the stability of the carotene in this product with the stability of our alfalfa carotene concentrate in the same flour. The Archer-Daniels-Midland Company prepared several carotenized flours; a solvent-extracted soybean flour containing less than 1 per cent residual fat or ether extractable material was used for all preparations, and all were carotenized to a potency of 60,000 I. U. of vitamin A (as carotene) per pound of flour: Sample 1, soybean flour with a carotene-in-oil preparation added; sample 2, soybean flour with carotene-in-oil and 2.5 per cent of a technical grade soybean lecithin added; sample 3, soybean flour with alfalfa carotene concentrate added; and sample 4, soybean flour with alfalfa carotene concentrate and 2.5 per cent of technical grade soybean lecithin added.

All four products were subjected to the same decomposition tests at both 45° and 60° C. Three-gram samples were weighed into open vials, and at appropriate time intervals the entire amount was used for the carotene determination. Figure 4 shows the results. In both tests sample 4 proved most stable. Also, soybean lecithin improved the carotene stability in each preparation.

These same samples were run at room temperatures for 5424 hours (226 days) in metal cans about half full and closed with a metal lid. Again sample 4 was best and contained 94.5 per cent of its carotene after 5424 hours. Sample 3 was next (91.3 per cent), followed by sample 2 (83 per cent) and sample 1 (75 per cent). At room temperature sample 3 proved more stable than sample 2, but in the accelerated tests at 45° C. this was not true.

The alfalfa carotene concentrate used in these tests contained some xanthophyll, and since the xanthophyll content was readily obtainable during the progress of the tests (*7*), the xanthophyll stability was determined under the same conditions as the carotene. The original xanthophyll content of samples 3 and 4 of Figure 4 was 15 mg. per pound of flour. At both 45° and 60° C. the addition of soybean lecithin improved the stability of xanthophyll approximately as much as it did that of the carotene. The sample containing lecithin in the 45° C. test still contained 51.5 per cent of its xanthophyll after 1895 hours.

DISCUSSION

Crystalline carotene, to be suitable for stability tests, must not have been exposed to air for any appreciable time before it is used in a test, as it oxidizes rapidly (*5*). Partially decomposed carotene accelerates carotene decomposition in oils; although this is not so pronounced in vegetable oils, such as Wesson, it is striking in an oil free of antioxidants. A crystalline carotene sample which had been exposed to air for some time was completely decomposed in less than 24 hours at 45° C. in mineral oil, whereas 300 hours were required with

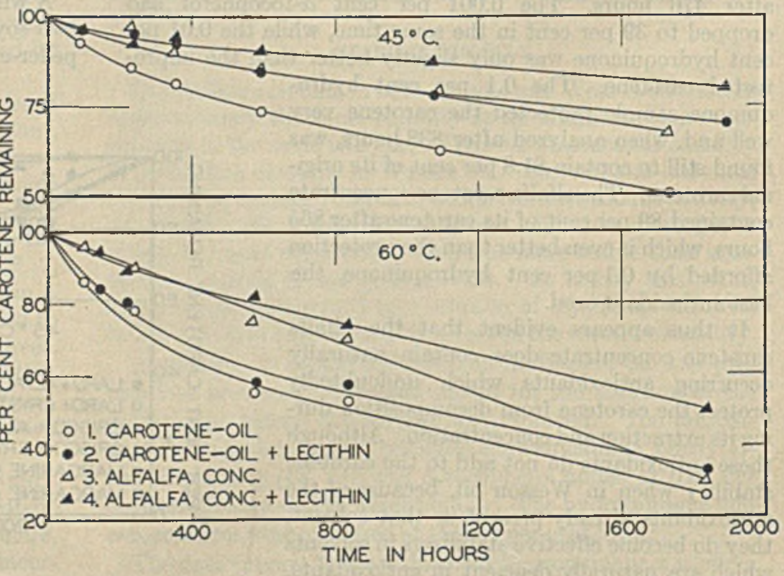

Figure 4. Stability of Crystalline Carotene and Alfalfa Carotene Concentrate in Soybean Flour, with and without Added Lecithin

crystalline carotene from freshly opened vials. This test was frequently used on carotene samples to ensure their suitability for the stability tests.

Whereas the addition of small amounts of hydroquinone (0.002 and 0.005 per cent based on the weight of oil) has been reported ineffective in protecting carotene in Wesson oil (*3*), at the higher levels (0.01 and 0.1 per cent), the amount of carotene remaining was increased from 43 to 73 and 81 per cent, respectively.

The stability of carotene in sweet potato flour under various conditions of storage has been reported (*6*); at room temperature and in loosely stoppered bottles sweet potato flour had approximately 25 per cent of its original carotene after 120 days, while sweet potato flour plus 10 per cent crude cottonseed oil had 61 per cent under the same conditions. In comparison, the four soybean flour samples, under similar conditions of temperature and air exposure, contained from 81 to 96 per cent carotene after 169 days. Although the soybean flour samples contained only 60,000 I. U. of vitamin A (as carotene) per pound and the sweet potato flour contained almost twice that amount, it appears that carotene is more stable in soybean flour than in sweet potato flour.

CONCLUSIONS

The stability of carotene is greatly influenced by the presence or absence of antioxidants contained in the solvent. In solvents free of antioxidants, the addition of antioxidants has a strong stabilizing effect; in solvents like Wesson oil, which contain naturally occurring antioxidants, little additional effect is observed.

Carotene is much more stable in solvent-extracted than in expeller-extracted soybean meal.

Soybean lecithin improves the stability of carotene in soybean flour.

Alfalfa carotene concentrate showed better stability in many of these products than crystalline carotene, an indication that the naturally occurring antioxidants present in the concentrate are effective in these food products.

ACKNOWLEDGMENT

This research was supported by the Horace H. Rackham Research Endowment of the Michigan State College of Agriculture and Applied Science for studies on the industrial utilization of agricultural products. In connection with the carotene stability tests on the soybean flour preparations, we wish to thank the Department of Biological Research of the Archer-Daniels-Midland Company for supplying the soybean flour and incorporating the carotene concentrate in it.

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ALCHEMIST

By David Teniers

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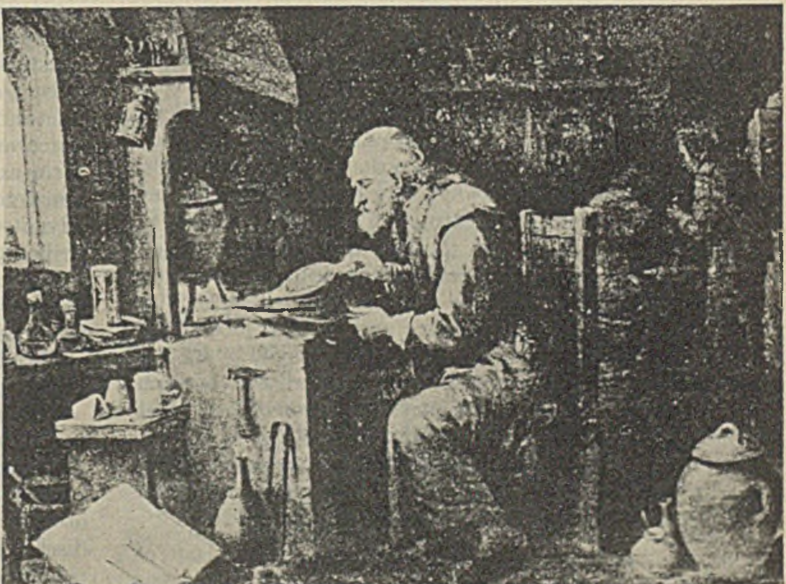

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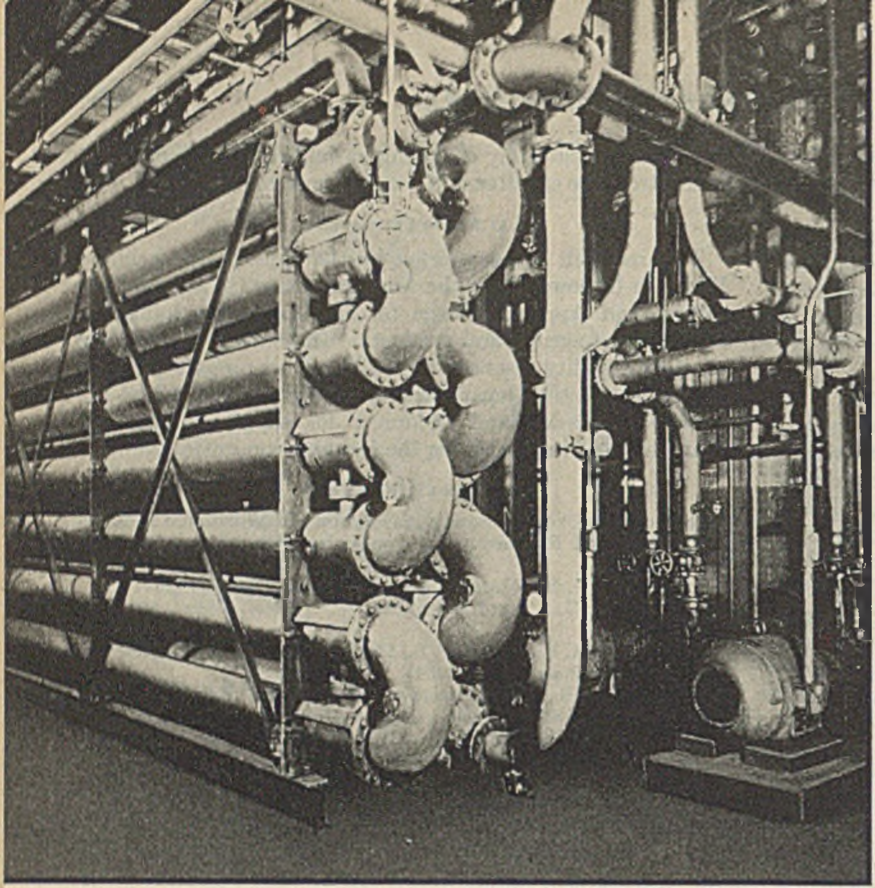


Heat Exchange Equipment for a Continuous, High-Pressure Distillation Unit Built by Vulcan Copper and Supply Company

Organic liquids, such as alcohol and acetone, have been separated by solvent extraction from dilute aqueous solutions and subsequent distillation of the extract layer to give the organic liquid overhead (*2*). This method of recovery of low-boiling alcohols, ketones, aldehydes, etc., has been found experimentally to require less heat than usual methods. Dilute solutions may be recovered more economically by extraction with a suitable solvent prior to distillation. The distillation equipment is smaller, and the total

Alcohol and Acetone by

DONALD F. OTHMER AND
ROBERT L. RATCLIFFE, JR.
Polytechnic Institute, Brooklyn, N. Y.

THE simple rectification of dilute aqueous solutions of alcohol or acetone has been possible only by use of considerable heat and large columns. Liquids have heretofore been separated by extraction only where it has been impossible to use rectification. Even the two pairs of liquids, acetone-water and ethanol-water, may be separated in some cases more economically by extraction (*2*). Two classes of solvents were suggested: (*a*) those immiscible with water, such as chlorobenzene (monochlorobenzene), benzene, and toluene, and (*b*) those partially miscible with water, such as methyl isobutyl ketone for acetone and isoamyl alcohol for ethanol. Calculations showed that the heat saved by extraction and then distillation of the "extract layer" was as much as 75 per cent compared to ordinary distillation of 2 per cent acetone solutions, and even greater for more dilute solutions.

The object of the present work was to measure experimentally the heat requirements of the usual distillation and of the combined extraction and distillation process.

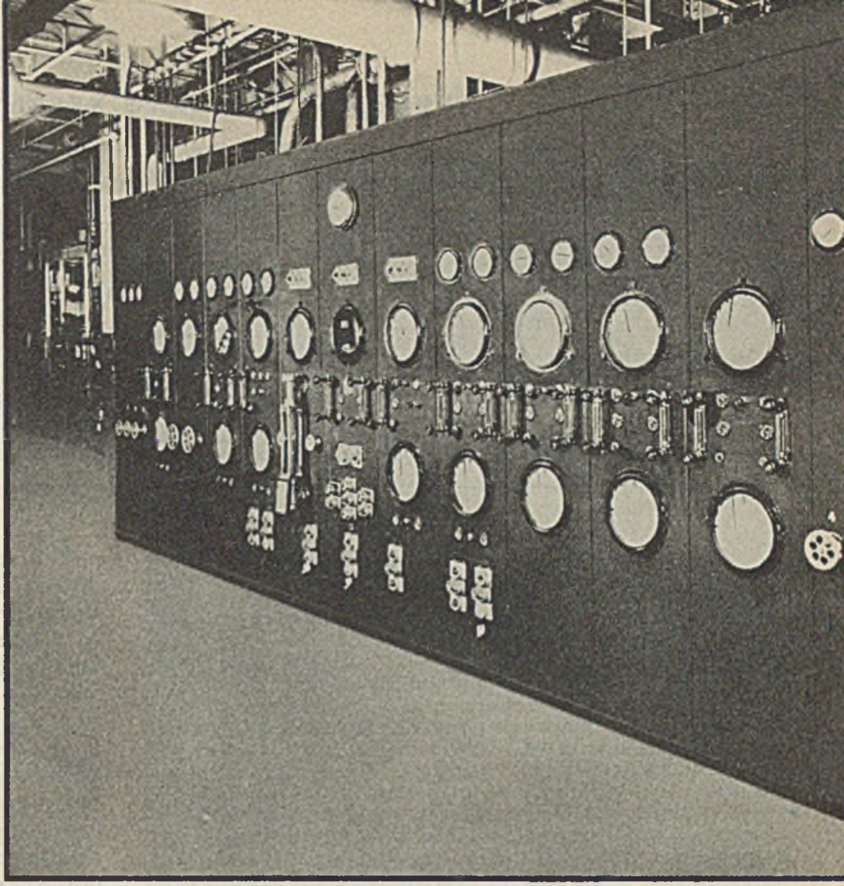
EXTRACTION AND RECTIFICATION

Figure 1 (left) shows the proposed continuous process using an immiscible solvent of lower density than water. (For solvents heavier than water, the flows to and from the extractor will be reversed.)

Letters indicate the various liquids flowing in each part of the system: *A* represents the organic solute to be recovered; *W*, water; and *S*, the immiscible solvent. A countercurrent extractor is fed the dilute aqueous solution, and the fresh solvent charged into the extractor at the opposite end exhausts the aqueous feed of solute (acetone, for example). The solvent or extract layer, discharged from the top of the extractor, is saturated with solute and an unavoidable trace of water, and is fed to the still for separation. From the bottom of the extractor the water layer is discharged to waste, almost completely exhausted of acetone and containing a trace of solvent (0.1 per cent). This may be recovered by a simple stripping operation if the solvent loss balances in value the cost of this distillation (not indicated in Figure 1). The immiscibility of the solvent with water is of critical importance; and a minimum of solvent dissolved in waste water is essential to the economic operation of the extraction process if there is no additional water-stripping operation.

The extract layer enters the rectifying column and the acetone passes overhead, using suitable reflux. The solvent, exhausted of solute, flows from the bottom in substantially pure form, ready for re-use in the extractor. The small amount of water unavoidably introduced in the extract layer cannot discharge with low-boiling acetone at the top of the distilling column or with high-boiling solvent at the bottom. It collects at a mid-point in the column as an insoluble layer and must be drawn off by a gravity separator or decanter, *D*, which separates water and solvent. The latter, dissolving a small amount of solute, is returned to the column at a lower

equipment, including the extractor, is less expensive. The process is economical, particularly for handling aqueous solutions of less than 5 per cent strength, and allows the recovery of many liquids, of which alcohol and acetone are only examples, from solutions too dilute to be handled by previous methods. These are obtained, for example, in solvent recovery operations or after the fermentation of waste liquors obtained from wood processing, such as wood hydrolysis or sulfite pulp manufacture.



Courtesy, Vulcan Copper and Supply Company

Centralized Control Station for Continuous, Pressure Distillation Unit

SOLVENT EXTRACTION

point; the aqueous layer passes to a mid-point of the extractor for the recovery of the small amount of acetone which it contains. The small amount of acetone which may be brought into the decanter does not interfere with the separation unless enough is present to make the two layers completely miscible. Proper location of the drawoff and proper operation of the column prevents this. If the mixture of water and solvent is completely exhausted of solute, which may be the case, it can be discharged from the column base directly to the bottom of the extractor.

The extraction process using partially miscible solvents is similar in principle. Figure 1 (right) illustrates the case for a solvent lighter than water. The extractor discharges the solvent saturated with solute and water at the top and the exhausted water layer saturated with solvent at the bottom. The water layer is sent to the stripping still for recovering the small amount of dissolved solvent, which in this case is sufficient to warrant recovery.

The extract layer is fed to the distilling column, and the solute is separated from water in the upper part and passes overhead. Solvent and water are exhausted of solute in a two-phase distillation in the middle of the column. The more volatile solute and some water pass upward; most of the solvent passes into the decanter in a two-layer aqueous mixture, containing substantially no solute. The solvent layer on top is recycled to the bottom of the extractor for re-use; the aqueous layer on the bottom is combined with the discharged water layer from the extractor and passed to the stripping section of the column for recovery of the dissolved solvent. Either open or closed steam may be used; and the water is entirely exhausted of solvent before being discharged at the base. Heat-interchanging equipment and other necessary accessories are not shown in Figure 1.

APPARATUS FOR DETERMINING HEAT REQUIREMENTS

STILL POT. A 3-liter, 3-neck, Pyrex flask was provided with an outlet and stopcock for withdrawal of bottoms continuously (Figure 2). A heating coil of Nichrome wire to supply 572 watts at 110 volts was connected with a pressure switch, *B*, to maintain a constant boil-up. This was a mercury manometer so connected that, when a predetermined pressure was reached, a relay broke the electrical circuit to the reboiler heater.

DISTILLATION COLUMN. The 1-inch column was packed with single-turn glass helices, about $^{5}/_{32}$ inch in diameter, to a total height of about 7.5 feet for the two sections and wrapped with Nichrome resistance wire over small vertical strips of insulation material. This heating element was connected with a variable resistance so that the heat input could be controlled. A 2-inch Pyrex tube was placed as a jacket around this heater to compensate for radiation losses of the column.

There were two branches in the upper section. The lower one was the feed inlet, and a thermometer was placed in the upper one. The temperature on this thermometer was useful in securing uniform operation.

STILL HEAD. The overhead vapors passed to the pencil type condenser with the tilting-funnel reflux controls (supplied by Ace Glass Company). The reflux was controlled by an electrical timer having a cycle of 20 seconds which energized a solenoid coil. This attracted an iron core attached to a tilting funnel and thereby diverted the condensate out of the system as product. The timer could be adjusted for any desired ratio of time of energizing of magnet to time not energized, and this determined the reflux ratio.

TABLE I. SUMMARY OF COLUMN PERFORMANCE DATA

Test Mixture	Reflux Ratio	Compn.[a], of More Volatile Liquid, Mole %			No. Theoretical Plates[c]			Superficial Vapor Velocity, Ft. per Sec.	Theoretical Plates per Foot	H. E. T. P., Inches
		Top	Side[b]	Bottom	Total	Fractionating	Strip			
$CCl_4 + C_6H_6$[d]	Total	45.0	6.0	3.0	15.5	11.9	2.5	0.81	2.07	5.7
Acetone-water[e]	2.06	99.2	...	0.3	14.7[g]	12.5	2.2	1.96	1.96	6.1
n-Heptane + methylcyclohexane[f]	Total	..	...	...	..	..	...	0.55–1.65	..	2.9–5.5

[a] Refractive indices were used to determine the composition
[b] The side stream sample was taken from the decanter.
[c] Determined graphically by the McCabe-Thiele method.
[d] Experimental determination, packed section of column; stripper 1.5 ft., fractionating 6.0 ft.; and total 7.5 ft. Packing, $^3/_{32}$-inch single-turn glass helices.
[e] Continuous experimental distillation in column; data from 5% acetone in water-feed composition.
[f] Data from Robinson and Gilliland (*4*, page 221); packing, $^5/_{32}$-inch single-turn nickel helices.
[g] Allowance was made for the use of a cold feed to the column, using the method described by Robinson and Gilliland (*4*).

DECANTER AND SIDE-STREAM DRAWOFF. Decanter *H* (Figure 2) separated the two-phase mixture leaving the upper column. The water layer was removed as a side-stream drawoff if an immiscible solvent was being used; and the solvent layer was removed if a partially miscible solvent was being used. Since the distillation column operated under a slight positive pressure, a liquid trap, *I*, allowed a nearly constant flow for the side-stream drawoff even though the pressure in the column varied.

FEED TO COLUMN. A 5-gallon can, *K*, was used as a feed reservoir. As liquid flowed out, air was drawn in through the left tube and was therefore under a pressure less than atmospheric by a head equal to that above the bottom of this tube. As the level fell, this supernatant pressure increased at the same rate as the hydrostatic pressure fell, so that the net pressure was always the same—i. e., that below the bottom of this air inlet tube. The feed rate was therefore constant and was measured by withdrawing the stream into a graduate for a given number of seconds.

COLUMN PERFORMANCE

The rectifying efficiency of the column was evaluated on (*a*) a carbon tetrachloride–benzene mixture with total reflux and (*b*) a dilute solution of acetone in water with continuous distillation and partial reflux. The data obtained (Table I) indicated a total of about fifteen theoretical plates in the entire column. The H. E. T. P. agrees favorably with published values for a mixture of *n*-heptane and methylcyclohexane when the packing was $^5/_{32}$-inch single-turn nickel helices (*4*).

RADIATION LOSSES. It was desirable to correct for any radiant heat losses which existed, notwithstanding the thermally jacketed column. Several pure liquids were used to determine losses at the temperatures of their different boiling points—chlorobenzene, water, isopropyl alcohol, and acetone. At a definite measured heat input during distillation of a pure material, all of which was withdrawn as overhead product, the radiant heat loss was determined as the difference between the heat input to the still pot and the output recovered as condensed distillate. These radiant heat losses were recorded for different air jacket temperatures maintained during the runs. Smooth curves were obtained of the heat loss in B. t. u. per hour plotted against the difference between the top vapor temperature in the column and the top air jacket temperature. A family of curves resulted with the normal boiling point of the substance being vaporized as the parameter. Graphical methods were used to determine the average temperature difference between the inside vapor temperature and the outside air jacket temperature of the column from the observed data, so that this correction could be made.

In operating a column with a heated jacket, it is possible to control the heat input to the jacket so that the temperatures in it are either higher or lower than the corresponding temperatures of the vapor stream. When these are higher, heat will be flowing into the column; when lower, heat will be flowing out from the column. Since the second condition is easier to consider, the jacket temperatures were always maintained somewhat below the vapor temperatures. Thus, in the heat balances the correction for heat loss was always positive and was made as indicated above.

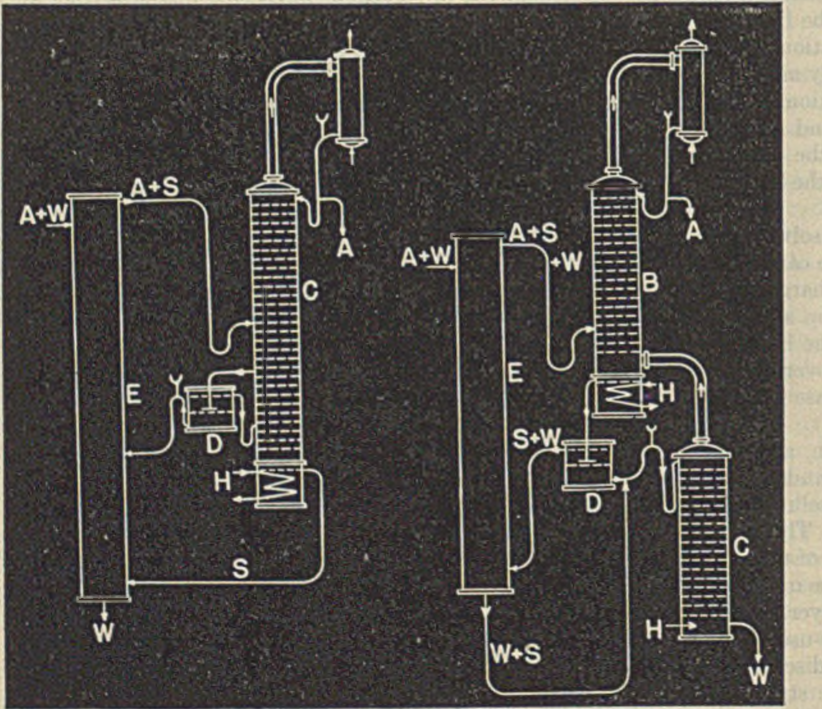


Figure 1. Flow Diagrams of Extraction and Rectification with Immiscible Solvent (*left*) and Partially Miscible Solvents (*right*)

A. Solute (acetone, alcohol, etc.)
W. Water
S. Solvent
E. Extractor
B. Distilling column
C. Stripping column
D. Decanter
H. Heating steam

Courtesy, American Institute of Chemical Engineers

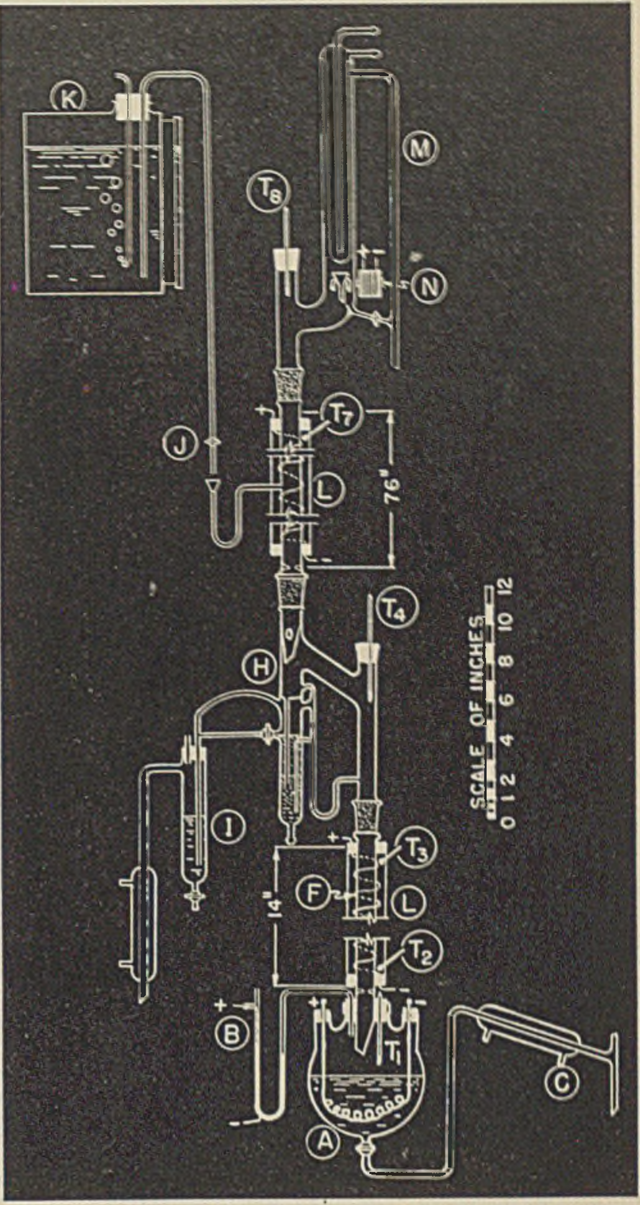


Figure 2. Distillation Column and Accessories

A. Still pot
B. Pressure controller
C. Bottoms drawoff
F. Heater element for air jacket
H. Decanter
I. Trap for side-stream drawoff
J. Feed control valve
K. Feed container
L. Distillation column
M. Still head and reflux controller
N. Magnet for tilting reflux splitter, electrically connected to reflux cycle timer for automatic reflux control

Thermometers
T_1 Still pot
T_2 Bottom of lower jacket
T_3 Top of lower jacket
T_4 Top of lower column
T_5 Mid-point of upper column (46 inches down from top, not shown)
T_6 Mid-point of upper jacket (37 inches down from top, not shown)
T_7 Top of upper jacket
T_8 Top of upper column

●

HEAT REQUIREMENTS

Several different methods of conducting the distillation steps were necessary:

1. Ordinary distillation of dilute aqueous acetone solutions.
2. Distillation of acetone-chlorobenzene mixtures with a trace of water, which would come as an extract layer from an extractor. Chlorobenzene is practically immiscible with water, and the small quantity of water was removed from the decanter.
3. Rectification of mixtures (such as would come from an extractor) of acetone, water, and a solvent partially miscible with water such as methyl isobutyl ketone. The solvent was removed as a side stream.
4. Ordinary distillation of dilute aqueous solutions of ethanol.
5. Rectification of mixtures (such as would come from an extractor) of ethanol, water, and the partially miscible solvent, isoamyl alcohol. The solvent was removed as a side stream.

Dilute Acetone-Water Solutions. A series of continuous distillations with feed concentration of 2, 5, 10, and 20 per cent acetone were carried out at different reflux ratios (Table II). The cycle timer was first set for a certain reflux ratio. The heat input to the still pot was regulated to give a vapor rate somewhat below the flood point of the column under the reflux conditions. The temperature in the air jacket was also adjusted slightly below the vapor temperature. The feed rate was then adjusted to correspond with the rate of product withdrawal. A material balance was maintained for about one hour, while the top vapor temperature remained constant at the boiling point of pure acetone. (It was found advisable to wet the packing well before a distillation run was started.)

The control of the column for aqueous acetone solutions was relatively simple, except for the dilute solutions such as the 2 per cent mixture, since it was somewhat difficult to get accurate material balances with such a small throughput of overhead product. If any condition changed, this temperature just above the feed point (at T_5, Figure 2) would change correspondingly; then adjustments could be made without upsetting the entire system.

For each concentration of acetone in the feed, three different reflux ratios were used in separate runs with the rates of feed, bottom, and overhead products carefully measured. Several attempts were made to find experimentally for the particular distillation the theoretical minimum reflux ratio

Table II. Acetone-Water Separations by Distillation (Feed Temperature 80° F.)

	Per Cent Acetone in Feed											
	2.0			5.0			10.0			20.0		
Reflux ratio	7.08	8.0	10.5	2.06	2.65	4.5	1.55	2.0	3.50	1.55	2.0	3.50
Rate, grams/min.												
Feed	49.0	45.0	40.7	52.0	48.2	43.5	33.2	30.0	27.0	25.3	23.5	20.0
Bottom	51.0	43.2	39.0	48.0	45.0	42.6	29.0	28.0	24.5	20.0	18.3	17.
Product	0.87	0.88	0.77	2.5	2.35	2.02	3.3	3.1	2.7	5.1	4.8	3
Temperature, ° F.												
Vapor												
Top fractionating	132.2	132.4	132.2	132.2	132.2	132.3	132.2	132.0	132.5	132.8	132.5	132.6
Mid-fractionating	202	200	201	193	193	199	193	196	200	192	193	195
Top stripping	211	211	211	211	211	211	212	212	212	212	212	212
Liquid, still pot	213	213	213	214	213	213	214	214	214	214	213	214

Table III. Acetone-Chlorobenzene Separation by Distillation with Immiscible Solvents (Feed Temperature 75° F.)

	Per Cent Acetone in Feed											
	1.33			3.33			6.67			13.3		
Reflux ratio	4.7	6.00	8.70	1.93	2.25	3.82	1.18	1.70	3.56	0.84	1.65	3.55
Rate, grams/min.												
Feed	57.5	50.0	42.0	56.3	53.0	46.0	47.0	40.0	33.2	32.5	26.5	20.4
Bottom	55.0	49.3	44.0	54.5	53.0	45.0	42.5	37.0	28.0	29.0	23.0	17.0
Product	0.79	0.66	0.50	1.80	1.75	1.65	3.2	2.7	2.2	4.2	3.5	2.7
Temperature ° F.												
Vapor												
Top fractionating	132.5	132.5	132.4	132.5	132.4	132.7	132.5	133	132.6	132.7	132.7	132.8
Mid-fractionating	215	215	210	208	208	210	207	206	209	206	205	210
Top stripping	233	237	235	222	222	225	248	247	255	262	265	266
Liquid, still pot	269	268	268	269	268	268	268	270	269	269	270	270

which was obtained graphically by the McCabe-Thiele method. The reflux cycle timer was set for a reflux ratio very near this point, but it was found impossible to control the column for minimum reflux conditions and still obtain a pure overhead product. This was considered proof that the actual minimum reflux ratio was very close to that determined graphically.

Mixtures of Acetone in Chlorobenzene. After the extraction of a 5 per cent aqueous acetone solution with 150 per cent of the theoretical minimum of chlorobenzene (assumed as an industrially operable ratio), there is an extract layer composed of 3.33 per cent acetone, 96.3 per cent chlorobenzene, and 0.3 per cent water (*3*). The separation of acetone from this extract layer can thus be treated as a binary distillation from chlorobenzene because of the small amount of water. During extended continuous distillation, the small amount of water entering the feed of extract layer was collected in decanter *H* (Figure 2).

Table IV. Acetone-Water Separation by Distillation with a Partially Miscible Solvent, Methyl Isobutyl Ketone (Feed Temperature 75° F.)

Acetone in feed, %	2.66[a]		6.67[a]	
Water in feed, %	2.10		2.51	
Methyl isobutyl ketone, %	95.2		90.8	
Reflux ratio	1.7	3.35	1.97	3.4
Rate, grams/min.				
Feed	47.5	44.5	38.0	33.0
Side	47.1	46.0	37.0	30.0
Product	1.25	1.18	2.7	2.2
Temperature, ° F:				
Vapor				
Top fractionating	132.5	132.5	132.2	132.5
Mid-fractionating	180	180	178	178
Top stripping	210	210	210	209
Liquid, still pot	214	213	213	213

[a] Based on the concentrations of extract layers which would result from an original concentration of acetone in the aqueous feed before extraction of 2 and 5 per cent, respectively, and when 1.5 times as much solvent is used for extraction as is required theoretically.

The data for the acetone-chlorobenzene runs were taken by the method used for the acetone-water series (Table III). The concentrations of the ternary mixture of acetone, chlorobenzene, and water were obtained by extracting 2, 5, 10, and 20 per cent aqueous acetone solutions with the required amount (50 per cent excess over the theoretical minimum) of chlorobenzene.

Mixtures of Acetone, Water, and Methyl Isobutyl Ketone. Methyl isobutyl ketone is a good solvent for acetone, is partially miscible with water, and has a much better distribution coefficient (*3*) than the immiscible solvents of which chlorobenzene is representative. In this case a much larger amount of water was present; the water was placed in the still pot and its vapor was used to supply the heat for the vaporization and rectification of the feed. The feed mixtures supplied to the column had the same concentrations that would result if an extraction were made on a 2 and 5 per cent aqueous acetone solution, respectively, with the partially miscible solvent, methyl isobutyl ketone, using a 50 per cent excess of solvent over that theoretically required.

The acetone (the low boiler) was taken overhead at the boiling point of the pure material. A two-phase azeotropic mixture collected in the column below the feed point at a point where the acetone had been exhausted completely. The constant-boiling temperature of the methyl isobutyl ketone–water azeotrope is 189° F., and the vapor temperature (T_5, Figure 2) above the feed point, designated as vapor, mid-fractionating, in Table IV, shows a temperature around 180° F. Therefore, the true azeotrope temperature of 189° F. is below this point and probably just below the feed point. The two-phase mixture flowed down the column and collected in two layers in the decanter. The decanter interface level was adjusted to give smooth flow for the top layer as a side stream. Thus, the solvent was withdrawn as fast as it was fed into the system. This side-stream drawoff of methyl isobutyl ketone (saturated with water, but stripped entirely of acetone) would be recycled to the extraction column to pick up again its equilibrium concentration of acetone, and then be returned to the distillation column feed to start the cycle again.

Since some methyl isobutyl ketone was dissolved in the water layer of the decanter, this layer was sent to the top of the stripper section which exhausted it completely to give pure water discharging at the base.

After the column had reached a steady state during each run, the rates of feed, side-stream drawoff, and overhead product were measured; these data are also recorded in Table IV.

Dilute Aqueous Solutions of Alcohol. These distillations were run in the same manner as those for the acetone-water distillations, while maintaining a top vapor

Table V. Ethanol-Water Separation by Ordinary Distillation and with Isoamyl Alcohol

	Ethanol and Water		Ethanol–Water[a]–Isoamyl Alcohol	
Ethanol in feed, %	2.0	5.0	1.81	4.53
Water in feed, %	98.0	95.0	10.3	11.3
Solvent in feed, %	0	0	87.9	84.2
Reflux ratio	14.2	6.18	6.18	6.18
Rates, grams/min.				
Feed	24.8	19.2	18.5	12.0
Bottom	25.0	18.5	0	0
Side	0	0	18.4	11.8
Product	0.50	0.98	0.28	0.55
Temperature, ° F.				
Vapor				
Top fractionating	172	172	172.5	172.5
Mid-fractionating	206	204	199	197
Top stripping	211	211	210	210
Liquid, still pot	214	213	214	214

[a] These concentrations are based on those of an extract layer which would result from an original concentration of acetone in the aqueous feed before extraction of 2 and 5%, respectively; and when 1.5 times as much solvent is used for extraction as is required theoretically.

TABLE VI. MATERIAL AND HEAT BALANCES AROUND THE COLUMN IN ACETONE-WATER SEPARATION BY DISTILLATION

	Per Cent Acetone in Feed											
	2.0			5.0			10.0			20.0		
Reflux ratio	7.08	8.0	10.5	2.06	2.65	4.5	1.55	2.0	3.56	1.55	2.0	3.56
Rate, grams/min.												
Feed	49.0	45.0	40.7	52.0	48.2	43.5	33.2	30.0	27.0	25.3	23.5	20.0
Bottoms	51.0	43.2	39.0	48.0	45.0	42.6	29.0	28.0	24.5	20.0	18.5	17.0
Product	0.87	0.88	0.77	2.5	2.35	2.02	3.3	3.1	2.7	5.1	4.8	3.9
Material balance, grams/min.												
Acetone in feed	0.98	...	0.81	2.6	2.4	2.17	3.3	3.0	2.7	5.06	4.7	4.0
Bottoms + overhead product	51.9	...	39.8	50.5	47.4	44.6	32.3	31.1	27.2	25.1	23.3	20.9
B. t. u. required per lb. acetone recovered	1800	...	2590	688	823	1239	575	675	1025	575	675	1028

TABLE VII. MATERIAL AND HEAT BALANCES AROUND THE COLUMN IN ACETONE-CHLOROBENZENE SEPARATION BY DISTILLATION

	Per Cent Acetone in Feed											
	1.33			3.33			6.67			13.3		
Reflux ratio	4.7	6.00	8.70	1.93	2.25	3.82	1.18	1.70	3.56	0.84	1.65	3.55
Rate, grams/min.												
Feed	57.5	50.0	42.0	56.3	53.0	46.0	47.0	40.0	33.2	32.5	26.5	20.4
Bottoms	55.0	49.3	44.0	54.5	53.0	45.0	42.5	37.0	28.0	29.0	23.0	17.0
Product	0.79	0.66	0.50	1.80	1.75	1.65	3.2	2.7	2.2	4.2	3.5	2.7
Material balance, grams/min.												
Acetone in feed	0.765	0.665	0.560	1.87	1.77	1.56	3.15	2.67	2.22	4.32	3.52	2.72
Bottoms + overhead product	55.8	49.9	44.5	56.3	54.8	46.7	45.7	39.7	30.2	33.2	26.5	19.7
B. t. u. required per lb. acetone recovered	1285	1575	2180	660	737	1088	473	608	1028	415	598	1030

temperature of 172° F., the boiling point of 95 per cent alcohol. The distillation data for 2 and 5 per cent concentrations of alcohol in water were obtained at reflux ratios 150 per cent greater than the minimum reflux ratio determined graphically; the data are shown in Table V.

MIXTURES OF ALCOHOL, WATER, AND ISOAMYL ALCOHOL. The same distillation method was used for these mixtures representing extract layers from an extractor, as were those of acetone, water, and the partially miscible solvent methyl isobutyl ketone; the data are shown in Table V.

HEAT SAVINGS IN RECOVERY OF ACETONE WITH CHLOROBENZENE

Ordinary distillation of dilute aqueous acetone solutions is standard industrial practice and will be used for comparison with extraction using an immiscible solvent such as chlorobenzene. The overhead product of the distilling column is acetone in both cases; and the total heat cost may be assumed to be that of vaporizing the acetone product and the necessary reflux. This is true if it is assumed that the sensible heats are disregarded as being (*a*) less important, (*b*) comparable in magnitude for both cases, and (*c*) recoverable to a large extent by heat exchangers. These assumptions appear to be reasonably close to the truth.

Material and heat balances were calculated for the experimental data (Tables VI and VII). The material balances check quite well because the column was adjusted to operate at a steady state for at least 30 to 60 minutes. For the feeds representing 1.33 and 2.0 per cent acetone for both chlorobenzene and water mixtures, the greater difficulty of operating with such a small amount of acetone shows in less exact balances.

A heat balance was first computed around the column, and the difference between the heat input and heat output was taken as the radiation loss. These radiation losses were also estimated by the graphical method. There was a good check between the estimated radiation losses and those obtained by difference; and only two runs had unaccounted-for heat losses above 3 per cent. These two were off by about 10 per cent.

The heat requirements, based on the amount of vaporized acetone required, are also listed in Tables VI and VII. For each concentration of acetone in the feed to the distilling column, the most economical reflux ratio was arbitrarily taken as 50 per cent above the theoretical minimum reflux ratio which

TABLE VIII. HEAT REQUIREMENTS FOR SEPARATION OF DILUTE MIXTURES OF ACETONE AND WATER

	Straight Aqueous Distillation		Extn. with Chlorobenzene + Distn. of Solvent and Acetone			Heat Savings over Straight Distn.	
% Acetone in Feed	Reflux ratio	B. t. u./lb. acetone recovered	% acetone in feed[a]	Reflux ratio	B. t. u./lb. acetone recovered	B. t. u./lb. acetone recovered	Decrease, %
2.0	9.56	2370	1.33	6.03	1575	795	33.5
5.0	3.05	810	3.33	2.25	720	190	20.9
10.0	1.71	600	6.67	1.18	470	130	21.7
20.0	1.71	600	13.3	0.84	415	185	30.8

[a] Feed to distillation column is extract layer from extractor.

TABLE IX. MATERIAL AND HEAT BALANCES AROUND THE COLUMN IN ACETONE-WATER SEPARATION BY DISTILLATION WITH METHYL ISOBUTYL KETONE

Acetone in feed, %	2.66[a]		6.67[a]	
Water in feed, %	2.10		2.51	
M. I. K. in feed, %	95.2		90.8	
Reflux ratio	1.7	3.35	1.97	3.4
Rate, grams/min.				
Feed	47.5	44.5	38.0	33.0
Side	47.1	46.0	37.0	30.0
Product	1.25	1.18	2.7	2.2
Material balance, grams/min.				
Acetone in feed	1.26	1.18	2.54	2.2
Side + overhead product	48.4	47.2	39.7	32.2
B. t. u. required per lb. acetone recovered	605	980	670	990

[a] Based on the concentrations of extract layers which would result from an original concentration of acetone in the aqueous feed before extraction of 2 and 5 per cent, respectively, and when 1.5 times as much solvent is used for extraction as is required theoretically.

Table X. Heat Requirements for Recovery of Acetone by Straight Distillation and with Methyl Isobutyl Ketone

Acetone in Feed, %	Straight Distn.		Solvent Extn. and Distn.					
	Reflux ratio	B. t. u./lb. acetone recovered	Feed[a] analysis, %			Reflux ratio	B. t. u./lb. acetone recovered	Heat Saving, %
			Acetone	Water	M. I. K.			
2.0	9.56	2370	2.66	2.10	95.2	1.71	605	74.5
5.0	2.05	910	6.67	2.51	90.8	1.71	605	33.5

[a] This feed to the distillation column is the extract layer from the extractor.

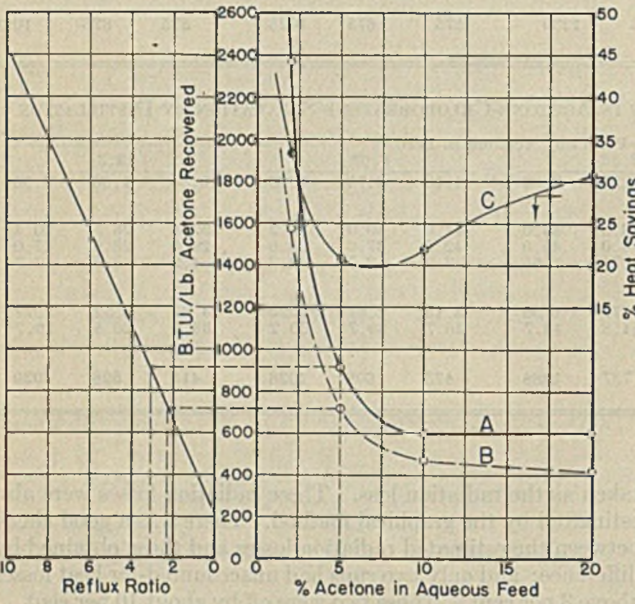


Figure 3. Heat Requirements

A. Distillation of acetone from aqueous solutions of different concentrations

B. Preliminary extraction of aqueous solutions with chlorobenzene and distillation of extract layer

C. Per cent heat savings of *B* (extraction and distillation) over *A* (straight distillation)

was calculated from data previously reported (*1*); 150 per cent of theoretical minimum is used in all calculations hereafter. (This depends on the balance of the cost of equipment against the cost of steam. An investigation of this factor was beyond the present scope, especially since substantially the same conditions would hold both for the usual distillation and for the distillation of the extract layer.) Table VIII and Figure 3 present the heat requirements for distilling both the aqueous acetone solutions and the corresponding extract layers after chlorobenzene extraction.

The "per cent decrease" curve of Figure 3 indicates that the greatest heat savings (34 per cent and more) occur when very dilute aqueous solutions of acetone (2 per cent and less) are to be recovered, and the curve goes through a minimum point at aqueous feed concentrations of about 7 per cent acetone. The heat savings curve approaches a constant value of about 32 per cent as the feed concentration of acetone increases.

Othmer and Trueger (*2*) were able to make predictions for these heat savings based on reflux requirements. Their values, recalculated to the more logical basis of total overhead vapor, check the experimental values.

For convenience in determining the reflux ratio to be used when recovering dilute aqueous acetone solutions, by either straight distillation or the combination process of extraction and distillation, another curve was plotted in the left-hand graph of Figure 3. An example shows that, if a 5 per cent aqueous acetone is to be recovered, about 910 B. t. u. per pound of acetone will be required to make a straight distillation with a reflux ratio of 3.05. But if the combination process is used, the same 5 per cent aqueous acetone feed will require 710 B. t. u. per pound of acetone recovered and a reflux ratio of 2.25 in order to make the separation between the extracting solvent, chlorobenzene, and acetone.

CRITICAL CONCENTRATIONS

Othmer and Trueger (*2*) mention so-called critical concentrations existing for mixtures of acetone-water and acetone-chlorobenzene. Thus, aqueous mixtures containing more than 10 per cent acetone require the same reflux ratio for the recovery of substantially pure acetone, owing to the upward concavity of the vapor composition curve for acetone and water, since the minimum reflux ratio is determined by the same tangent to the vapor composition curve. The experimental data also indicate the existence of the critical concentration, especially for acetone-water separations by distillation. Figure 3 indicates a constant minimum reflux for mixtures above 10 per cent acetone.

The critical concentration in chlorobenzene-acetone mixtures is not definitely shown, although it is indicated by the experimental data since no feed concentrations greater than 20 per cent by weight acetone were studied. Othmer and Trueger show that the critical concentration for the acetone-chlorobenzene mixture is 20 per cent by weight acetone.

Table XI. Material and Heat Balances around the Column in Ethanol-Water Separation by Distillation

	Ethanol and Water		Ethanol–Water–Isoamyl Alcohol	
Ethanol in feed, %	2.0	5.0	1.81[a]	4.53[a]
Water in feed, %	98.0	95.0	10.3	11.3
Solvent in feed, %	0	0	87.9	84.2
Reflux ratio	14.2	6.18	6.18	6.18
Rate, grams/min.				
Feed	24.8	19.2	18.5	12.0
Bottoms	25.0	18.5	0	0
Side	0	0	18.4	11.8
Product	0.50	0.98	0.28	0.55
Material balance, grams/min.				
Ethanol in feed	0.495	0.96	0.33	0.54
Bottoms or side + overhead product	25.5	19.5	18.7	12.4
B. t. u. required per lb. ethanol recovered	5430	2560	2570	2570

[a] Based on the concentrations of extract layers which would result from an original concentration of ethanol in the aqueous feed before extraction of 2 and 5 per cent respectively, and when 1.5 times as much solvent is used for extraction as is required theoretically.

Table XII. Heat Requirements for Recovery of Ethanol (95 Per Cent)

Ethanol in Feed, %	Straight Aqueous Distillation		Extn. with Isoamyl Alcohol and Distn. of Extract Layer					Heat Saving, %
	Reflux ratio	B. t. u./lb. ethanol recovered	Feed[a] analysis, %			Reflux ratio	B. t. u./lb. ethanol recovered	
			Ethanol	Water	Isoamyl alcohol			
2.0	14.2	5430	1.81	10.3	87.9	6.18	2570	52.6
5.0	6.18	2560	4.53	11.3	84.2	6.18	2570	0

[a] This feed to the distillation column is the extract layer from the extractor

HEAT SAVINGS IN ACETONE RECOVERY WITH METHYL ISOBUTYL KETONE

Material and heat balances were made for the experimental distillations carried out to investigate this system (Table IX). The heat balance checks very well for the extract layer for a 5 per cent aqueous acetone solution; but the radiation losses during distillation of the 2 per cent aqueous acetone solution could not be accounted for entirely. However, the experimental data (Table X) for the combination process using partially miscible solvents show heat savings of 74.5 and 33.5 per cent for 2.0 and 5 per cent by weight acetone in the aqueous feed, respectively, in comparison to a straight distillation recovery.

HEAT SAVINGS IN ETHANOL RECOVERY WITH ISOAMYL ALCOHOL

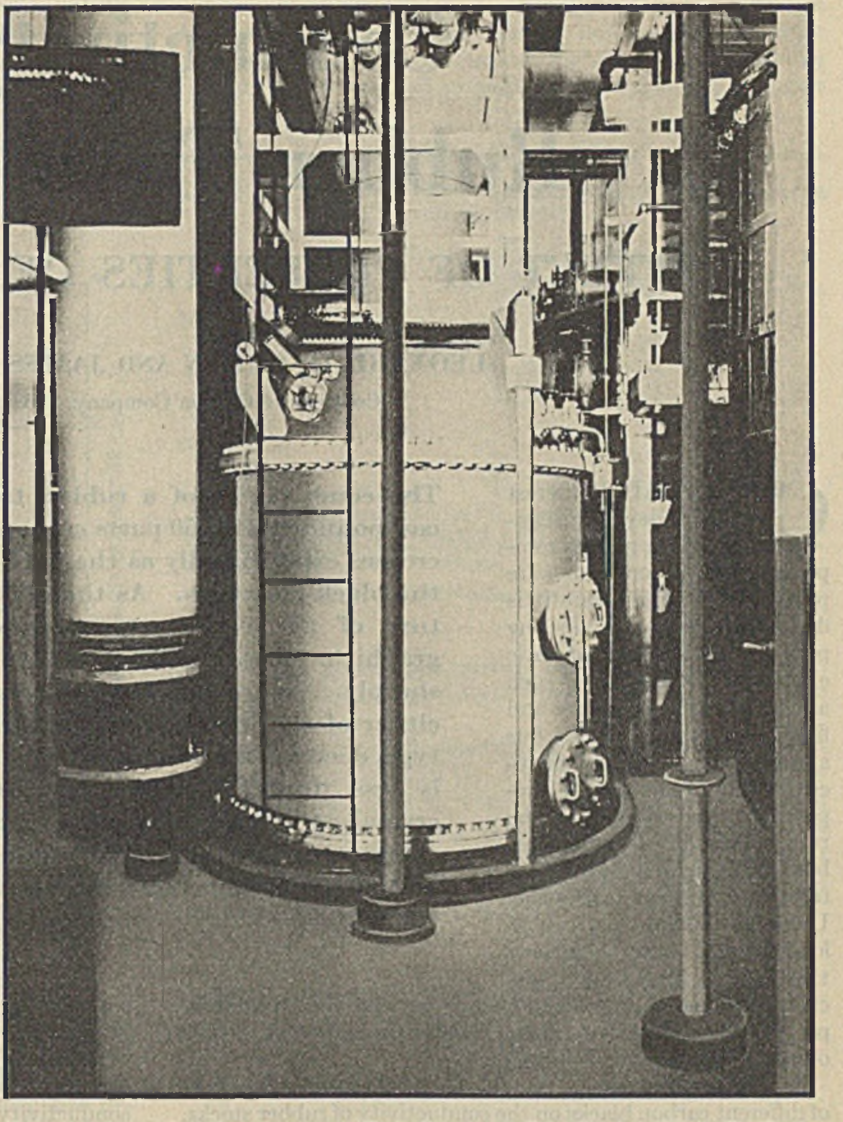
Table XI summarizes the material and heat balances for the ethanol-water and ethanol–water–isoamyl alcohol distillations. These material balances check satisfactorily for ethanol-water distillations, but the sum of the overhead product and side stream was greater than the amount of feed in both cases for the ethanol–water–isoamyl alcohol separation. This discrepancy can probably be attributed to the fact that solvent on leaving the column by the side-stream drawoff at the decanter carried some droplets of the aqueous layer with it as a result of incomplete decantation. This condition was also noticed in the acetone–water–methyl isobutyl ketone experiments (Table IX). The operation of the distilling column or extractor in a commercial process would not be affected by this condition. All of the heat losses could be accounted for within a few per cent.

Table XII shows that considerable heat savings (52.6 per cent) can be realized by using the combination extraction and distillation process to recover 95 per cent ethanol (constant-boiling mixture) from a 2 per cent aqueous feed. There are no heat savings if aqueous alcohol solutions of 5 per cent and greater are to be recovered; however, larger heat economies will be realized when less than 2 per cent aqueous alcohol solutions are to be recovered by the combination process (*2*). These very dilute alcohol solutions would probably be encountered in recovery systems for alcohol in the fermentation of liquors from the hydrolysis of cellulose, from sulfite waste liquors, and other marginal sources of this material.

CONCLUSION

Dilute aqueous solutions of acetone and alcohol may be recovered with a substantial saving in operating costs by a combination of extraction and rectification, using solvents which are substantially immiscible or partially miscible with water. This conclusion was reached previously (*2*) from careful calculations rather than experimental results as obtained here, and the method of calculation is thus substantiated. As a direct result of the considerable reduction in the amount of heat required, there is a comparable saving in the required amount of cooling water. Furthermore, the size of the distillation equipment may be reduced proportionally to the reduction in heat required. This will result in a large saving in copper or other construction material.

While the experimental work was only with acetone and alcohol, other low-boiling water-soluble organic materials may be recovered by the same methods. Patent coverage on the commercial applications is being secured.



Top Section of a Continuous, High-Vacuum Distillation Unit Built by Vulcan Copper and Supply Company

ACKNOWLEDGMENT

The help and suggestions of Edward Trueger in this work are gratefully acknowledged.

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Conductivity of Rubber Tread Stocks

EFFECT OF PROPERTIES OF CARBON BLACK

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The conductivity of a rubber tread stock compounded with 50 parts carbon black increases exponentially as the particle size of the black decreases. As the crystal structure of the carbon approaches a more graphitic form, the conductivity increases sharply. Noncarbon surface constituents, either of the hydrocarbon or carbon oxide type, decrease the conductivity. This effect is less important than particle size or crystal structure. However, increases in conductivity of more than tenfold can be brought about by removal of surface constituents.

CONSIDERABLE interest has been shown in semiconducting rubber compounds. These compounds are particularly useful where it is desirable to have a conducting path for the dissipation of static electricity. Examples of such application are: shoe soles and flooring in certain plants, bus and automobile tires, etc. Semiconducting rubber can be prepared by the addition to the rubber formula of certain carbon blacks manufactured both from natural gas and acetylene. Unloaded rubber or rubber loaded with other pigments than carbon blacks has a specific resistance of 10^{12} to 10^{16} ohm-cm. By the addition of proper types of carbon black, resistances as low as 30–500 ohm-cm. can be readily obtained.

Several publications (*6, 7, 8, 10, 11*) have reported the effect of different carbon blacks on the conductivity of rubber stocks. In the present work an effort has been made to determine the influence of various fundamental properties of carbon black on the conductivity of a typical rubber tread stock test formula. The properties considered are ultimate particle size, crystal form, and surface structure.

PROCEDURE AND APPARATUS

The blacks were milled into the following standard tread formula:

Smoked sheet	100	Sulfur	2.81
Zinc oxide	7.85	Captax (mercapto-benzothiazole)	0.743
Pine tar	3.00		
Stearic acid	3.30	Carbon black	50.5

Tensile sheets were cured at 280° F.; a soap solution was used for mold lubrication, and reasonable care was exerted in curing and handling to prevent defacing the surface of the sheets. Resistance measurements were made before tensile strips were cut and broken. The specific resistance, R_s, listed for each black was taken on a tensile sheet cured at or near the cure giving the maximum tensile value. Resistance was determined by placing the tensile sheet between brass electrodes and measuring the current I and voltage E. All measurements were made at about 15 volts. Specific resistance R_s was calculated from the formula:

$$R_s = \frac{E}{I} \times \frac{31.6}{t}$$

where t = thickness of the rubber sheet, cm.
31.6 = area of the electrode, sq. cm.

A previously described apparatus (*3*), equipped with a device for applying sustained pressure, was used. The measurements were made under pressure in order to duplicate as far as possible the conditions under which a tire tread actually operates. Within the range of pressures used, a limiting value was reached beyond which increasing the pressure decreased the resistance very little; a constant pressure of 36 pounds per square inch was used which was well above this limiting value. The average deviation of measured resistance for a given black run in the standard formula under standard conditions was found to be 25 per cent.

Degree of dispersion of the carbon black in the rubber compound has been shown by other investigators to effect conductivity (*4, 11*). However, rubber tests such as aged and unaged tensile, hardness, resilience, and abrasion resistance indicated that for the stocks reported here, the degree of dispersion was very similar and could therefore have only a negligible influence on the general trends.

EFFECT OF PARTICLE SIZE

Table I gives the effect of particle size of the carbon black on the conductivity of the rubber stock. Since the color of a rub-up of carbon black in oil varies principally with particle size, the color index as given in Table I is taken as a rough measure of surface area per unit weight. Also included in the table are estimates of actual particle diameters made from published electron microscope (*16*) and adsorption (*14*) measurements on similar blacks. In Figure 1 the logarithm of R_s is plotted against color index and estimated particle size.

TABLE I. EFFECT OF PARTICLE SIZE OF CHANNEL BLACK ON RESISTIVITY

Black	Estd. Particle Diam., mμ	Color	Volatile Matter, %	R_s, Ohm-Cm.
Continental AA	33	60	5.5	7×10^6
Continental E	25	80	5.7	5×10^5
Continental G	20	98	5.4	3×10^4
Low-color	17	127	6.0	6×10^3
High-color (Continex)	10	222	4.7	2×10^2

As Table I shows, the specific resistance of a rubber stock varies exponentially with the diameter of the ultimate particles of carbon black used; these are channel blacks prepared from almost identical gases and permit the reasonable assumption that their crystal structure is very similar. The volatile content is a measure of the amount of volatilizable surface constituents of the black and is sufficiently constant to have little influence on conductivity.

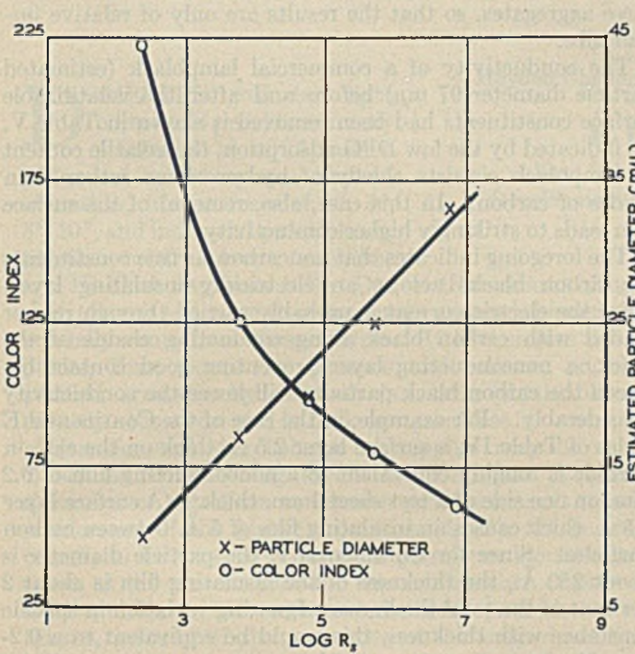

Figure 1. Effect of Particle Size and Color Index on Specific Resistance

Kemp and Hermann (*11*) and Habgood and Waring (*6*) stated that the conductivity of rubber loaded with carbon probably occurs through chains of carbon particles which act as leakage paths for the current. As the particle size decreases, the number of particles in a given weight increases and the probability of the formation of carbon chains increases enormously. The results of Table I are in full agreement with these considerations.

EFFECT OF CRYSTAL STRUCTURE

Blacks listed in series 1, Table II, have similar particle size and fairly similar volatile content but different crystal structures. Continental AA is a commercial channel black prepared from natural gas. Materials of this type give an x-ray pattern with diffuse bands. Graphon is prepared by heating channel black for several hours at about 2000° C. (*12*). As a result of this treatment the x-ray pattern becomes much sharper and more nearly approximates that of graphite (*2*); the conductivity as indicated in Table II is markedly increased. Shawinigan black is made by the thermal decomposition of acetylene gas, and the higher temperature prevailing during formation of this black makes it probable that a greater extent of crystal growth should occur. The results of heat of combustion determinations indicate that acetylene black is closer to graphite than channel black (*13*). Likewise, x-ray photographs indicate a more nearly graphitic structure for acetylene black than for ordinary channel black (*2*, *5*). However, Biscoe and Warren (*2*) indicated that channel black heated at high temperature, as in the case of Graphon, increases in crystal dimensions and becomes similar to acetylene black.

The position of acetylene black in Table II is in qualitative agreement with these considerations; however, in comparison with Graphon, acetylene black is slightly better conducting than might be expected considering the x-ray data of Biscoe and Warren (*2*) and the particle size estimates of Table II. Statex is prepared by partial combustion at rather high temperatures.

Table II. Effect of Crystal Structure of Carbon Blacks on Resistivity

Black	Estd. Particle Diam., mμ	Volatile Matter, %	R_s, Ohm-Cm.
Series 1			
Continental AA (devolatilized)	33	1.0	8×10^5
Statex	34 (*16*)	0.8	2×10^3
Graphon	33 (*14*)	0.4	5×10^2
Shawinigan acetylene black	43 (*16*)	0.9	1×10^2
Series 2			
P-33	74[a]	0.5	2×10^{10}
Gastex	81[a]	0.2	2×10^8
Lampblack devolatilized	97[a]	0.6	7×10^4

[a] Values were determined with the electron microscope by Wiegand and Ladd (*16*). Smith, Thornhill, and Bray (*14*) give the following particle diameters as calculated from adsorption measurements: Gastex = 75 mμ, lampblack = 107 mμ, P-33 = 200 mμ.

A second series of blacks of similar particle size and volatile content appears in Table II. Owing to the different production conditions (P-33 by thermal decomposition of natural gas diluted with hydrogen, Gastex by partial combustion of natural gas and lampblack by partial combustion of higher hydrocarbons), we would again expect differences in crystal structure among the products.

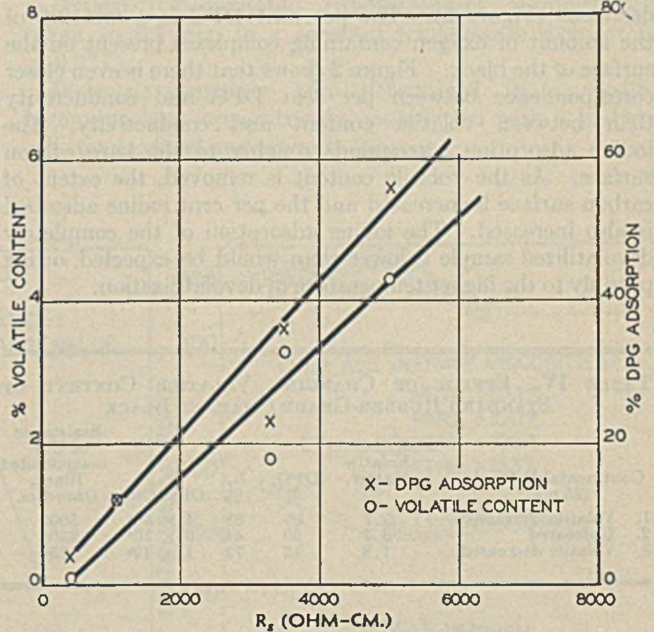

Figure 2. Relation of Specific Resistance to DPG Adsorption and Volatile Content

Both lampblack and acetylene black were reported to differ from other blacks in their appearance under the electron microscope (*15*). Ultimate particles of lampblack and acetylene black group together as irregular networks in the specimens prepared for examination with the electron microscope, whereas other blacks, such as ordinary channel black, Statex, Gastex, and P-33, appear either as individual particles or flocs. These tendencies are probably due to crystal structure factors which distinguish acetylene black and lampblack from the other blacks. The conductivity values in series 2, Table II, show that, like acetylene black, lampblack has a higher conductivity than other carbons of similar diameter and volatile content.

EFFECT OF SURFACE STRUCTURE

The samples listed in Table III were prepared by partially removing the volatilizable surface constituents from a moderately small particle size (17 mμ) channel black (Continental C-15).

Table III. Effect of Surface Structure of Carbon Blacks on Resistivity

Medium-Color Black	% Volatile Matter (9)	% DPG (1)	% I_2*	R_s, Ohm-Cm.
Original	4.3	56	62	5000
Partly devolatilized	3.3	36	65	3500
Partly devolatilized	1.8	23	70	3300
Partly devolatilized	1.2	12	75	1100
Completely devolatilized	< 0.15	4	73	400

* Adsorbed by 1 gram black (to which 10 cc. 10% H_2SO_4 has been added) from 100 cc. of I_2 solution in KI containing 2.7 grams I_2 and 4.05 grams KI per liter of solution.

The volatile matter was reduced by heating the black for various periods in a nonoxidizing atmosphere. Since the temperature in all cases was kept below 800° C., no significant change in either particle size or crystal structure could have occurred. Thus the differences in conductivity can be attributed solely to the surface structure of the blacks. The conductivity increases appreciably as the volatile content decreases (Figure 2). The per cent DPG is a measure of the amount of oxygen containing complexes present on the surface of the black. Figure 2 shows that there is even closer correspondence between per cent DPG and conductivity than between volatile content and conductivity. The iodine adsorption corresponds roughly to the bare carbon surface. As the volatile content is removed, the extent of carbon surface is increased and the per cent iodine adsorbed is also increased. The iodine adsorption of the completely devolatilized sample is lower than would be expected, owing possibly to the higher temperature of devolatilization.

Table IV. Effect of Changing Volatile Content of Standard Rubber-Grade Channel Black

Continental E Black (25 mμ)	Volatile Matter, %	DPG, %	I_2, %	R_s, Ohm-Cm.	Resistance of Uncompounded Black, Ohm-Cm.
1. Volatile increased	9.7	86	28	4×10^6	5000
2. Untreated	5.7	50	44	5×10^5	2500
3. Volatile decreased	1.8	12	72	1×10^5	750

The influence of volatile matter content is further illustrated in Table IV. Sample 2 was the untreated black, 3 was the same black with the volatile partially removed, and 1 was prepared by treating 2 in an oxidizing atmosphere to increase the oxides present on the surface. The results are in complete agreement with those of Table III. Also shown in Table IV is the effect of changes in volatile content on the conductivity of the uncompounded carbon black. This type of measurement depends on physical factors such as the size of pellets or aggregates present in the black and the degree of packing of these aggregates, so that the results are only of relative importance.

Table V. Results on Lampblack

Lampblack	Volatile Matter, %	DPG, %	I_2, %	R_s, Ohm-Cm.
Original	4.5	21	16	1×10^7
Devolatilized	0.6	5	28	7×10^4

The conductivity of a commercial lampblack (estimated particle diameter 97 mμ) before and after the volatilizable surface constituents had been removed is shown in Table V. As indicated by the low DPG adsorption, the volatile content of lampblack consists chiefly of hydrocarbons rather than oxides of carbon. In this case, also, removal of the surface film leads to strikingly higher conductivity.

The foregoing indicates that noncarbon surface constituents on carbon blacks act as an electrically insulating layer. Since the electric current is probably carried through rubber loaded with carbon black along conducting chains of the black, a nonconducting layer preventing good contact between the carbon black particles will lower the conductivity considerably. For example, in the case of the Continental E series of Table IV, a surface layer 2.5 Å. thick on the carbon particle is roughly equivalent to a nonconducting film of 0.2 mm. on one side of a test sheet 1 cm. thick. (A surface layer 2.5 Å. thick causes an insulating film of 5 Å. between carbon particles. Since for Continental E the particle diameter is about 250 Å., the thickness of the insulating film is about 2 per cent of the total thickness. Ignoring variation in specific resistance with thickness, this would be equivalent to a 0.2-mm. film on a sheet 1 cm. thick.)

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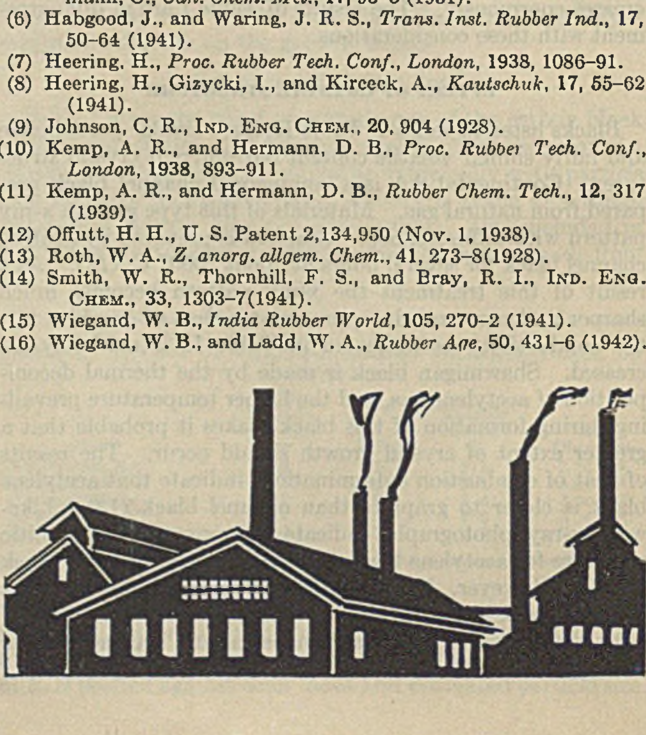

SOLVENT PROPERTIES OF C_8 Aromatic Hydrocarbons

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DOMESTIC coal tar light oil sources provide annually a total of 10 to 15 million gallons of mixed xylenes and C_9 aromatics, in the form of 1°, 3°, 5°, 10°, and industrial pure xylenes, together with solvent naphthas and Hi-Flash naphthas (*13*). Double this amount of nearly pure toluene and more than ten times as much benzene have annually come from these sources. It is therefore not surprising that, except for benzene and toluene, no highly purified aromatic hydrocarbon has been obtainable until recently at low cost and in tank car quantities.

Henceforward this balance of supplies may be shifted. While industrial coking favors the formation of benzene, a number of petroleum conversion processes result in a preponderance of the higher aromatics (*3, 12*). It is not, of course, to be expected that such petroleum stocks may be taken at the present time for the manufacture of pure aromatics, either for solvent use or chemical synthesis. Nevertheless, a study of the properties of the individual higher-boiling aromatics may be of interest to both the chemical manufacturers and the purchasers of solvents. Isoparaffins have been shown (*8*) to differ so markedly in solvent properties from the isomeric normal paraffins that one might suspect commercially significant differences to exist within groups of isomeric or homologous aromatics. A brief study of the four C_8 aromatics has therefore been made.

The *p*-xylene used was recrystallized from commercial 1° xylene. The *o*-xylene was recrystallized from a commercial *o*-xylene. The *m*-xylene was obtained by the reduction of *m*-xylidine diazonium chloride. The *m*-xylidine used for diazotization was purified from commercial *m*-xylidine by crystallization of the acetate salt. A sample of the *m*-xylidine in dilute hydrochloric acid gave no turbidity when boiled with formaldehyde solution; this indicated the absence of other xylidines.

DEGREES OF PURITY

Cross reference between the values given in Table I and those obtained by previous authoritative investigators reveals that the present samples of *o*- and *p*-xylenes (both finally purified by crystallization) probably contain less than 1 per cent impurities and possibly less than 0.5 per cent. Density and optical data indicate the impurities to be aromatic. The *p*-xylene appears to be less pure than that of Boord and Henne (*4*); the *o*-xylene is somewhat purer and equal to that characterized by the Bureau of Standards "best values" (*14*). Purity of the ethylbenzene and *m*-xylene may be estimated at about 99 per cent, again with impurities largely aromatic.

Freezing points were taken in a Bureau of Standards type apparatus (*5*), made from two coaxially mounted Dewar tubes. The inner tube, of 75 ml. capacity, was fitted with a controlled-speed motor-driven stirrer. Temperatures were taken with a Bureau of Standards standardized platinum resistance thermometer. Cottrell boiling points were read with a Bureau of Standards standardized Anschutz type thermometer, ranging from 125° to 150° C. and graduated in 0.2° C. Correction was made for barometric pressure.

Surface tension was obtained with a du Noüy tensiometer. The ring was mounted on the left-hand side of an analytical (Chainomatic) balance, check readings being taken to 0.1 mg. in a constant temperature room at 25° ± 0.2° C.

Dielectric constants were determined in a modified heterodynebeat apparatus, in conjunction with a platinum cell standardized against pure benzene.

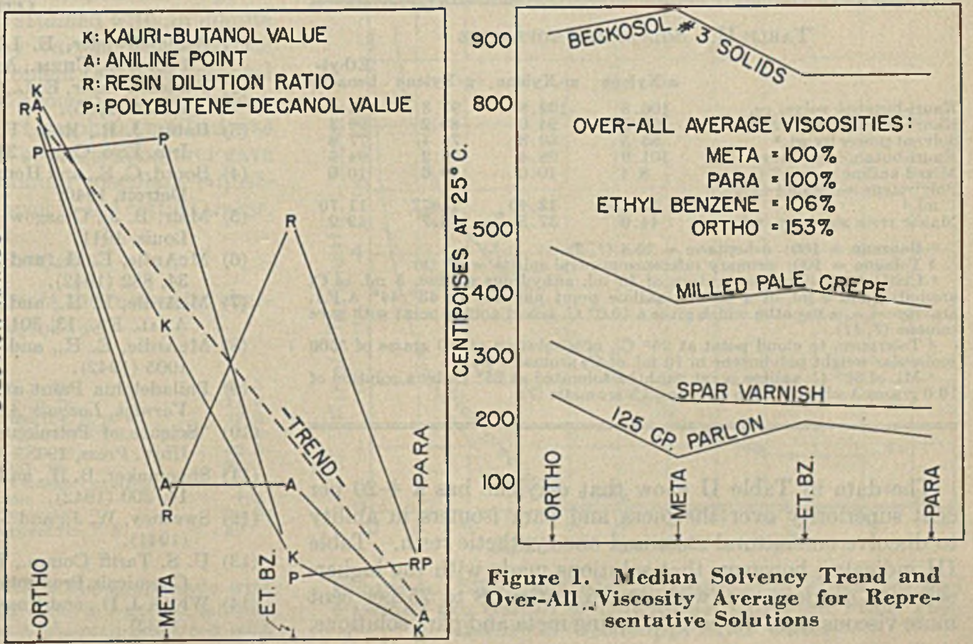

Figure 1. Median Solvency Trend and Over-All Viscosity Average for Representative Solutions

TABLE I. COMPARISON OF PHYSICAL PROPERTIES OF MATERIALS USED WITH PREVIOUS VALUES

	o-Xylene	m-Xylene	p-Xylene	Ethylbenzene
	Present Materials			
Freezing point, ° C.	−25.30	−48.56	+13.00	−95.30
Plateau time, min.	21.5	8	7.5	11
Bath composition	CO_2 + isopropyl alcohol	Commercial nitrogen	CO_2 + isopropyl alcohol	Commercial nitrogen
Gradient at F. P., ° C.	55	144	93	97
Cottrell spread, initial B. P. to 50% distd., ° C.	144.4 to 144.4	139.1 to 139.1	138.5 to 138.6	136.3 to 136.5
d_4^{25}[a]	0.8759	0.8600	0.8576	0.8624
d_4^{20}[b]	0.8809	0.8650	0.8626	0.8674
Gravity[b], ° A.P.I.	28.3	31.2	31.6	30.7
Lb./gal. at 60° F.	7.39	7.26	7.24	7.28
n_D^{20}	1.5053	1.4970	1.4959	1.4958
Dispersion at 20° C.	158.2	155.8	156.5	151.3
Sp. dispersion at 20° C.	179.6	180.1	181.4	174.4
Du Noüy surface tension at 25° C., dynes/cm.	31.56	30.46	29.95	30.50
Dielectric constant at 30.05° C.	2.571	2.351	2.264	2.382
	Bureau of Standards Values (*14*)			
Freezing point, ° C.	−25.30	−47.55	+13.35	...
Boiling point, ° C.	144.4	139.3	138.4	...
d_4^{20}	0.88040	0.86401	0.86100	...
	Boord and Henne Values (*4*)			
Freezing point, ° C.	−25.5	−48.9	+13.19	−94.96
Boiling point, ° C.	144.5	139.2	138.5	136.5
n_D^{20}	1.5054	1.4971	1.4958	1.4959
d_4^{20}	0.8799	0.8639	0.8609	0.8661
Estd. impurities, mole fraction	0.010 ± 0.003	0.026 ± 0.009	0.0010 ± 0.0005	0.006 ± 0.002

[a] 10-cc. pycnometer at 25° ± 0.002° C.

[b] Coefficient of cubical expansion of all four C_8 aromatics taken as 0.0010 (*10*).

DILUTION RATIO VALUES

Solvent properties, such as kauri-butanol solvency, aniline point, and other dilution ratio values, have been characterized (*8*) as estimates of affinity or relative structural similarity between solute and solvent, and may thus be regarded as measuring the ability of a solvent to dissolve a certain solute, or an intrarelated class of solutes. That such values do not necessarily predict viscosity effects has been demonstrated in the case of certain isomeric paraffins (*8*); this behavior is strikingly evident among the C_8 aromatics.

TABLE II. SOLVENCY PROPERTIES

	o-Xylene	m-Xylene	p-Xylene	Ethylbenzene
Kauri-butanol value, cc.	106.8	102.8	97.3	98.6
Kauri-butanol solvent power[a]	97.7	94.0	89.2	90.3
Solvent power by wt.[a]	85.5	80.8	76.4	77.8
Kauri-butanol solvency[b]	101.9	98.4	93.2	94.5
Mixed aniline point, ° C.[c]	8.4	10.0	10.6	10.0
Polybutene n-decanol value, ml.[d]	12.38	12.40	11.72	11.70
Maleic resin solvency, ml.[e]	44.0	37.5	36.7	42.2

[a] Benzene = 100; n-heptane = 25.4 (*1, 2*).

[b] Toluene = 100; primary reference mineral spirits = 40 (*9*).

[c] Critical solution temperature of 10 ml. anhydrous aniline, 5 ml. of C_8 aromatic, and 5 ml. of a 60° C. aniline point naphtha of 43°/44° A.P.I. gravity—i. e., a naphtha which gives a 10.0° C. mixed aniline point with pure toluene (*7, 11*).

[d] Tolerance, to cloud point at 25° C., of a solution of 2.0 grams of 5500 molecular weight polybutene in 10 ml. of C_8 aromatic (*8*).

[e] Ml. of 60° C. aniline point naphtha tolerated at 25° C. by a solution of 10.0 grams Amberol 801 in 40 grams C_8 aromatic (*7*).

The data in Table II show that *o*-xylene has a 4–20 per cent superiority over the meta and para isomers in ability to dissolve one natural resin and one synthetic resin. Table III indicates, however, that solutions made with the higher-solvency *o*-xylene are, with one exception, 8 to 75 per cent more viscous than the corresponding meta and para solutions. Thus *o*-xylene suggests itself as a doubly desirable solvent. Not only may it answer a demand for critically high solvency, but it appears able to serve with representative solutes where a higher viscosity is needed at a stipulated solids content, or a lower solids content is desirable at a fixed viscosity—e. g., in the mechanical application of adhesives or saturants.

Ethylbenzene, which may or may not eventually become available at a price competitive with commercial xylenes, appears to offer little advantage as a solvent over a meta-para mixture, the bulk component of present-day narrow-cut fractions.

Figure 1 illustrates a median solvency trend and an overall viscosity average for representative series of solutions. Divergencies are regarded as effects of structural relations since past experience (*1, 2, 6–9*) has shown that the experimental errors involved in running dilution ratios and determining viscosities (under carefully controlled conditions) are of the order of 1–3 per cent. In the present instance weighings and volume readings were made to 0.1 per cent, and all operations were carried out in a constant temperature room at 25° ± 0.2° C.

TABLE III. SOLUTION VISCOSITIES AT 25° C.

	Gardner-Holdt/Centipoises[a]			
	o-Xylene	m-Xylene	p-Xylene	Ethylbenzene
50% wt. cut of Beckosol No. 3 solids[b]	V + 1/3 907	V + 1/3 945	V − 1/4 840	V − 1/4 840
50% wt. cut of 25-gal. tung oil–Beckacite No. 3000 varnish solids	M 320	I 225	H/I 210	I − 1/3 218
20% wt. soln. of 125-centipoise Parlon (chlorinated rubber)	I/J 237	F − 1/4 136	G 165	H − 1/4 191
100 grams/liter soln. of milled pale crepe rubber	R 470	O + 2/3 382	O 370	P 400

[a] Solutions made at 25° C., by tumbling at 15 r. p. m.; corked bottles back-tared.

[b] Phenol-modified alkyd resin.

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Silica Sol as Auxiliary Coagulant with Copperas

GRAPHICAL DETERMINATION OF OPTIMUM PROPORTIONS OF DUAL COAGULANTS IN WATER TREATMENT

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BAYLIS discovered the importance of colloidal silica in turbidity removal by coagulants (*1–4, 6*); and techniques were developed by Baylis (*1, 5*) and by Graf and Schworm (*8, 11*) for the preparation and application of activated silica solutions as an adjunct to alum and some of the other coagulants. Following their work, a number of investigators have reported successful experiences in the use of silica sol with chemical treatments, usually with alum. Only one investigation (*10*) failed to note generally beneficial effects. Activated silica has also given favorable results in the chemical treatment of sewage (*7, 9*). Nevertheless when first announced, universal benefits were disclaimed for this reagent, and its limitations in practical use have been indicated. Applicability of activated sodium silicate to the treatment of a given water is a matter of individuality as regards character of water, process, and plant.

This paper relates some laboratory studies with activated silica sol on the Lower Mississippi River water, at the Carrollton plant of the New Orleans Sewerage and Water Board, to determine its advantages as an auxiliary coagulant in treating a slightly alkaline, fairly hard, colorless, moderately turbid, but readily flocculated raw water. Plant treatment consists in preliminary grit removal, lime softening to bicarbonate neutralization, intervening primary sedimentation, coagulation by copperas, and final sedimentation. Using the pair copperas–activated silica sol, it is evident that a given clarity in the settled water might be attained with an infinite number of combinations simply by varying the amounts and ratios of the chemicals. The problem therefore resolved itself into the selection of the most economical proportions of coagulants based on cost. A direct graphical method was employed that involved a minimum of calculation and gave immediately a program for the optimum coagulant adjustment to yield any desired turbidity level in the settled water.

EXPERIMENTAL CONDITIONS

During the period of these experiments the raw water characteristics and plant feed data were as follows:

Color, p. p. m.	10	Ca, p. p. m.	40.3
Turbidity, p. p. m. SiO_2	62	Mg, p. p. m.	11.0
Free CO_2, p. p. m.	0	Na (calcd.), p. p. m.	22.3
Alkalinity, p. p. m. $CaCO_3$	106	SiO_2 (gravimetric), p. p. m.	5.4
pH	8.2	SO_4, p. p. m.	42.3
Incrustants, p. p. m. $CaCO_3$	41	Cl, p. p. m.	32
Total hardness, p. p. m. $CaCO_3$	147	Plant dosage, grains/gal.	
Total hardness (calcd.)	145	Lime	4.3
Total dissolved solids (105° C.), p. p. m.	249	Copperas	0.34
		Temperature, ° F.	49

The stirring machine used for this work was shop-made with a belt-driven arrangement for treating twelve 1-gallon samples simultaneously. The stirring arm was a $^3/_{16}$-inch brass rod with the bottom carefully bent at the experimentally determined best angle—namely, 42°; over this deflection was slipped sufficient rubber tubing to reach almost to the side of the vessel. After a flash mix and about 10 minutes of stirring at 175 r. p. m., the next chemical was added without removing the sample from the machine; the same rate continued for 10 minutes more. The speed was then lowered progressively to about 10 r. p. m., allowing 0.6–2 hour total slow speed stirring according to the needs of each particular series for good flocculation. Quiescent settling ranged from 16 to 24 hours before pipetting off a 400-ml. portion of the supernatant for reading on a Hellige turbidimeter. Identical procedure was followed throughout a given run.

Silica sol was prepared from 41.1° Bé. sodium silicate (containing 8.85 per cent Na_2O and 28.7 per cent SiO_2; ratio of Na_2O to SiO_2, 1 to 3.22) after dilution to 1.5 per cent SiO_2, almost complete neutralization down to 1200 p. p. m. calcium carbonate alkalinity using 12.6 per cent of the sodium silicate weight of 66° Bé. sulfuric acid, 2-hour aging, and final dilution to 0.56 per cent SiO_2 (or 1.95 per cent sodium silicate content). This same batch of Baylis sol was used throughout all experiments; its age at the time of dosing varied from 6 to 12 days. By applying coagulant doses in geometric series, a wide range of experimental results was obtained.

RESULTS OF JAR TESTS

RAW WATER WITH SILICA SOL. Silica sol alone does not coagulate turbid natural waters (*1*). Silica sol failed utterly to flocculate 60 p. p. m. turbidity in raw Mississippi River water

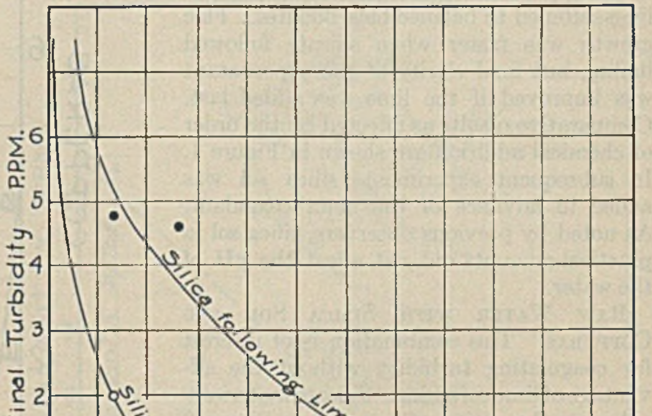

Figure 1. Effect of Order of Addition of Silica Sol and 4 Grains per Gallon of Quicklime Slurry on Final Turbidity of Mississippi River Water

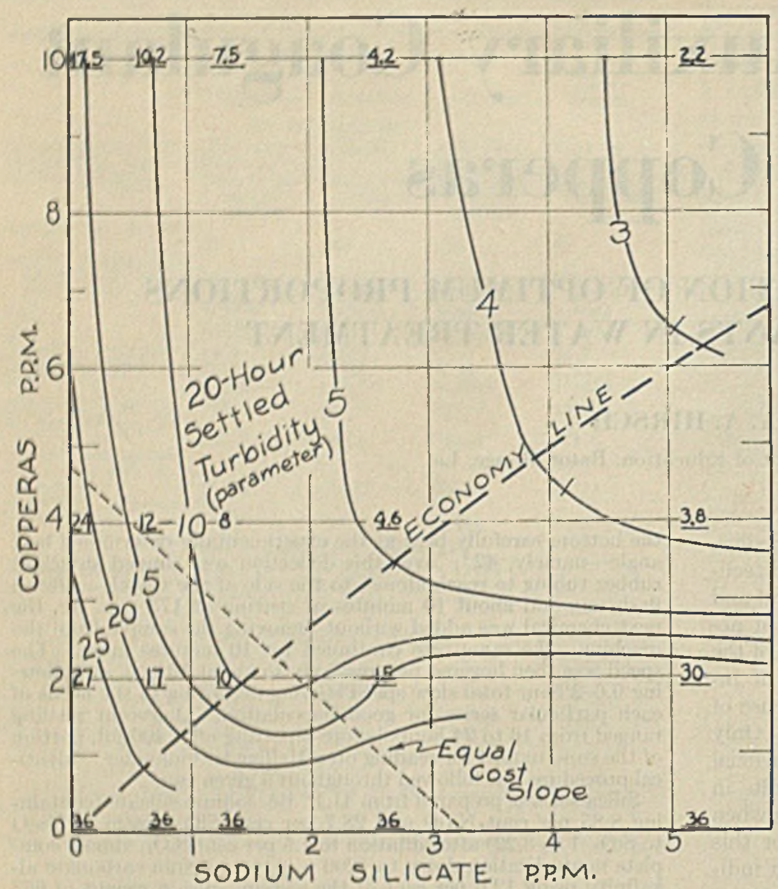

Figure 2. Copperas–Silica Sol Coagulation of Raw Mississippi River Water

Figures underlined represent 20-hour settled turbidities.

and even, with ascending dosage, caused a small increase in final turbidity of the settled water by its action as a dispersion agent.

Limed Water with Silica Sol. Activated silica effectively coagulates Lower Mississippi River water that has first been lime-softened to balance bicarbonates. Floc growth was faster when silicate followed liming, but final clarity of the supernatant was improved if the lime was added last. Comparative results as affected by the order of chemical addition are shown in Figure 1. In subsequent experiments silica sol was added in advance of the main coagulant. As noted by previous observers, silica sol in practical amounts did not affect the pH of the water.

Raw Water with Silica Sol and Copperas. This combination is of interest for coagulating turbidity without the advantage of lime softening. Silicate materially enhances the action of copperas as Figure 2 shows. The two coagulant doses are plotted along the coordinate axes with final turbidities smoothed in parametrically. The figures underlined are the experimentally observed turbidity readings used to interpolate the contours. In this way the plot shows all combinations of coagulants possible to produce a desired settled water turbidity. Reference to the dashed lines will be made later.

Addition of activated silicate to a given copperas dose, except for the uncertain dip zone with low dosages of both materials, will improve final clarities down to a residual value where the curves flatten out parallel to the silicate axis. A limit in benefits possible from silicate is thus indicated. Increase in copperas lowers final turbidities, without exception. Iron alone can produce fairly low turbidities, particularly if the dosage is high enough; silicate alone is valueless. However, their combination is most effective, as the decided vertex in the curves shows. Floc break with sufficient iron present was aided by a very small silica addition.

Lime-Softened Water with Silica Sol and Copperas. This combination is of particular interest, as the silicate meshes into the lime-iron process used locally. Starting with lime-softened primary settled water from the plant, various combined doses of silica sol and copperas were added to explore their composite flocculating value. Results of the trial coagulations (Figure 3) show maximum curvature in the turbidity lines somewhat near the silicate axis. The curves run out at lower silicate than iron doses, an indication of the superiority of silicate if either is to be used alone. Curves for

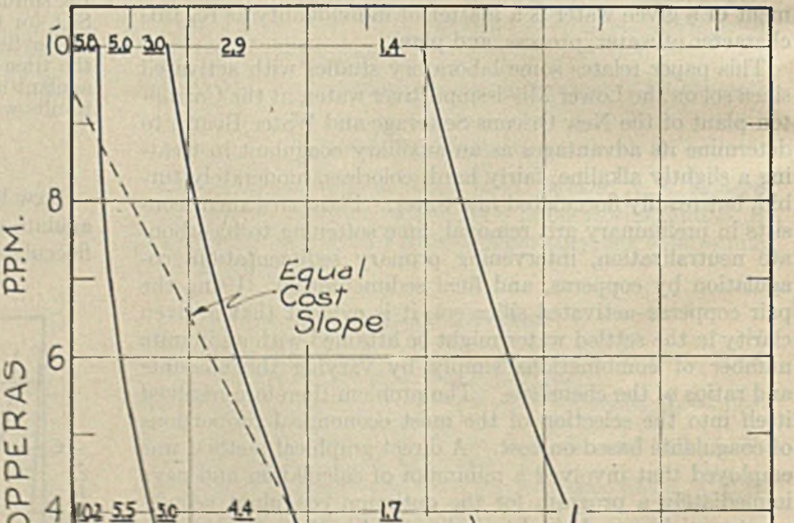

Figure 3. Copperas–Silica Sol Coagulation of Limed, Settled Water

Plant quicklime dose, 4.39 grains per gallon. Figures underlined give 18-hour settled turbidities.

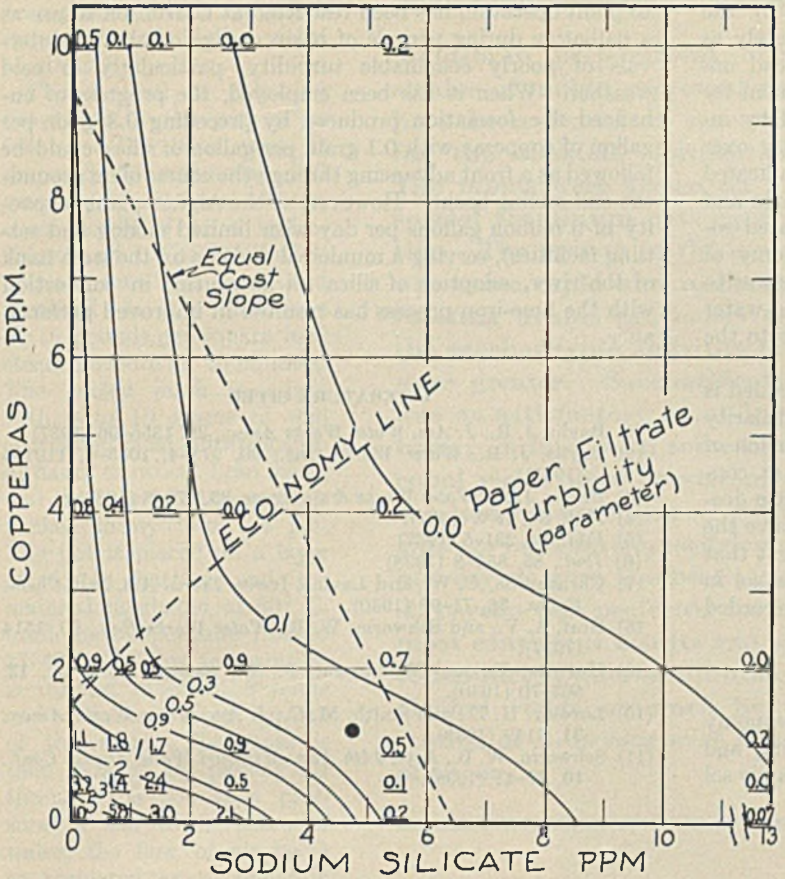

Figure 4. Filtrate Turbidities (through Whatman No. 41 Paper) Following the Copperas–Silica Sol Coagulations in Figure 3

Figures underlined are turbidimeter readings.

very clear water are asymptotic to the iron axis and demonstrate the inapplicability of copperas alone in this region. From the pronounced convex inward type of curvature, it is apparent that mixed coagulation surpasses a single coagulant in flocculating value and enables lower residual turbidities.

Floc containing silicate was larger, especially when first formed, than when it contained copperas alone; mechanical envelopment of soil particles was thus promoted. But on aging, the silicated floc shrank to a smaller volume and showed greater resistance to breaking on agitation. Tough compact floc is not only ideal for filtering, but may also retard scouring of reservoirs and lengthen cycles between cleaning. Iron up to 4 p. p. m. also aided bottom floc consolidation at a given silicate level. With either iron or silicate alone as coagulants, the silicate showed the greater degree of final floc compaction.

Supernatant samples were also filtered through Whatman No. 41 paper in a 4-inch funnel and filtrate turbidities were determined. Results are plotted in Figure 4. Again the vertex in the turbidity lines is very distinct, an indication of the advantages of bicoagulants. As before, some curves which follow along the copperas axis bend downward and outward at the silicate axis; therefore, if a single coagulant is to be selected, activated silica sol is superior to copperas on a paper filter performance basis. The reversed curvature, near the silicate axis, is probably due to experimental uncertainties in measuring very low turbidities.

LOCATION OF OPTIMA

Obviously, the higher the cost of a coagulant per ton, the greater will be the relative amount of its associate in the dual system. In Figure 5 the price in dollars per ton of coagulant X is laid off along the coagulant Y in any arbitrary units. Inversely, the cost per ton of coagulant Y is marked off along the coagulant X axis in the same units, after this figure is adjusted for the difference in p. p. m. scale factors, as indicated in the diagram. Along the "equal cost slope" connecting these two points the total coagulant cost is a constant. By drawing lines parallel to the equal cost slope, tangent to all of the residual turbidity curves, the locus of the most economical coagulant adjustment is obtained through the points of tangency. Any other equal cost slope would cut a given turbidity curve as a secant and, from the direction of curvature, involve a higher cost. Locating an economy line by this method obviates the necessity for replotting the data directly on a cost basis. Correctness in establishing the slope of a constant cost line may be checked by multiplying its intercept dosage on any axis by the corresponding cost for the same coagulant; the products so found should be equal along either axis.

ECONOMICS OF SILICATE-COPPERAS PAIR

Equal cost slopes and the loci of most economic pairing are indicated in Figures 2, 3, and 4 by the dashed lines. For purposes of calculation, prices per ton f. o. b. plant are taken as follows: sodium silicate \$20, 66° Bé. sulfuric acid \$15, and copperas \$15. The cost of sulfuric acid for partially neutralizing the silicate amounts to \$1.89 per ton of sodium silicate, or slightly less than 10 per cent of the sodium silicate cost.

For silicate-copperas clarification of raw river water (Figure 2) greatest economy is gained, particularly for the clearer settled samples, when the sodium silicate dose is roughly three fourths of the copperas dose.

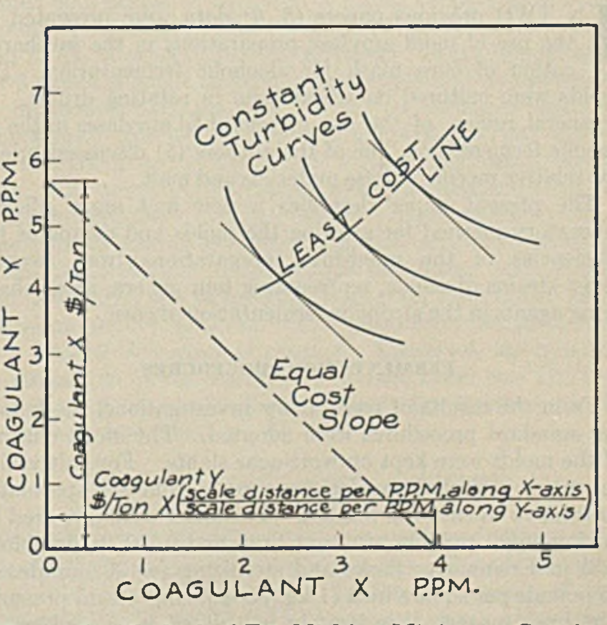

Figure 5. Method of Establishing Minimum Cost in a Bicoagulant System

When coagulating lime-softened water (Figure 3) the economy line indicates the value of using approximately as much silicate as copperas beyond a very small iron lead until a dosage of 3 p. p. m. copperas is reached; treatment for lower turbidities can be more economically selected by increasing only the silica sol and still retaining slightly over 3 p. p. m. copperas as a constant feed. The high indicated relative amount of silica here reverses the roles of main and auxiliary coagulants and gives more value to activated sodium silicate than do previous studies. The economy of high silica proportions can be appreciated from its power to produce very clear water. However, if high settled-water turbidities are tolerable, the limiting condition points to the economy of copperas alone.

For inferior filtrate quality (Figure 4) copperas unaided is the economical choice up to 2 p. p. m., but for improved clarity activated sodium silicate is best added in the proportion of 2 p. p. m. for every 1 p. p. m. copperas above a 2 p. p. m. copperas level. Figure 4 indicates that economical silicate dosage approximately equals the copperas dose at and above the 4 p. p. m. level. From these observations it is evident that considerably more emphasis is due to activated silica sol in its joint performance with copperas than has been accorded heretofore.

APPLICATION TO PLANT PRACTICE

Although these curves definitely demonstrate the economy of sodium silicate in conjunction with lime softening and final coagulation with copperas, application of the Baylis sol to plant operation has been restricted at Carrollton to use as a palliative during periods of basin outage or obscure intervals of poorly coagulable turbidity, particularly in cold weather. When it has been employed, the progress of enhanced floc formation produced by preceding 0.3 grain per gallon of copperas with 0.1 grain per gallon of silica could be followed as a front advancing through the course of an around-the-end mixing basin. However, at the Algiers plant (capacity of 6 million gallons per day with limited mixing and settling facilities), serving a municipal division on the west bank of the river, adoption of silica sol as routine in connection with the lime-iron process has resulted in improved performance.

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FUNGAL AMYLASES AS SACCHARIFYING AGENTS IN THE

Alcoholic Fermentation of Corn

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IN TWO previous papers (*3*, *6*) data were presented on the use of mold amylase preparations in the saccharification of corn mash for alcoholic fermentation. The molds were cultured on wheat bran in rotating drums. In a general review of the use of microbial amylases in the alcoholic fermentation, one of the authors (*5*) discussed briefly the relative merits of these materials and malt.

The present paper describes a new and more efficient laboratory method for growing the molds and compares the efficiencies of the mold-bran preparations from twenty-seven strains of molds, representing four genera, as saccharifying agents in the alcoholic fermentation of corn.

FERMENTATION PROCEDURES

From the results of preliminary investigations, the following standard procedures were adopted. The stock cultures of the molds were kept on wort-agar slants. For cultivating the molds in flasks, transfers were made from well sporulated cultures to wheat bran mashes. The latter were prepared by mixing equal weights of wheat bran and 0.3 *N* hydrochloric acid in Erlenmeyer flasks and sterilizing for 30 minutes at 15 pounds per square inch (1 kg. per sq. cm.) steam pressure. The bran mashes were heavily inoculated from well sporulated stock cultures and the flasks, lying on their sides, were incubated at 30° C. For most of the work here reported, 500-ml. Erlenmeyer flasks containing 25 grams of bran were employed, but it was found later that more rapid growth and sporulation are secured if 10 grams of bran are used in 250-ml. flasks. After abundant sporulation had taken place, the cultures were used as inoculum for larger batches of bran mash. The well sporulated mold cultures on the bran may be allowed to dry undisturbed in the flasks and kept at incubator or room temperature for many months without loss of potency as inoculum.

The mold amylase preparations were produced by growing the molds on the wheat bran mash in special 3-quart aluminum pots equipped for aeration. The apparatus is simply constructed (Figure 1); it is a modification of that employed by Beresford and Christensen (*2*), and has several advantages over the drum method previously employed in these laboratories (*3*, *6*). It takes less space and requires no special mechanical devices. There is no disturbance of the mold mycelium during growth and more uniform aeration is obtained. The growth of the molds is more rapid, and the pot preparations lead to more consistent and higher yields of ethanol.

Mold-bran preparations of twenty-seven strains of molds, representing four genera, have been tested as saccharifying agents for the alcoholic fermentation of corn. The molds were grown on wheat bran in special aluminum pots equipped for aeration. The growth of the molds in the pots was more rapid and uniform than in the rotating drums previously employed, and the saccharifying activities of the products were greater. Saccharification at 30° C. was as satisfactory as at higher temperatures; in fact, with some molds higher alcohol yields were consistently obtained at the lower temperature. Strains of *Aspergillus oryzae*, *Rhizopus delemar*, and *Rhizopus oryzae* gave the best yields. However, *A. oryzae* was preferred for it showed the most consistent results and was the easiest to handle. Under optimum conditions the alcohol yields obtained by using certain strains of *A. oryzae* were about 95 per cent of theory.

The method of culturing the molds in the pots is as follows: The bran mash is prepared by moistening 750 grams of wheat bran with an equal weight of 0.3 *N* hydrochloric acid. The wet bran is packed into the pot and sterilized in the autoclave at 15 pounds per square inch steam pressure for 30 minutes. The cooled mash is mixed with 5 to 10 grams of well sporulated mold culture grown in flasks on wheat bran mash, and the inoculated material is packed firmly into the pot. The pot is placed on a layer of cotton batting and the material incubated at 30° C. until the temperature rises to 37–40° C. This temperature is reached in about 8 hours and indicates rapid growth of the mold. The mass is then aerated by passing air through the pot at a pressure of 0.3 to 3 inches of water, the flow of air being so regulated as to maintain a temperature below 45° C. After aeration for 12 to 24 hours the contents are removed, spread on paper, and dried at room temperature. The dried material is ground in a Wiley mill and is used as the saccharifying agent in the fermentation tests. Such material is designated "mold-bran".

Yields of ethanol from fermentations of 20 per cent corn mash, saccharified with the various mold-bran preparations, were employed as the index of their amylolytic effectiveness. The authors believe (*6*) that the final yields of ethanol furnish the only reliable means for comparing the usefulness of the saccharifying agents; Lintner numbers are wholly unreliable in such comparisons. The data represent the averages of duplicate fermentations, and all were confirmed by repeated experiments.

The corn meal used in these investigations was prepared by grinding whole yellow corn, obtained in several lots at different times; moisture and starch analyses were carried out on each lot. The starch analyses were made by the official A. O. A. C. diastase method with subsequent acid hydrolysis (*1*); the reducing sugars formed were determined by the modified Shaffer-Somogyi method developed in these laboratories (*7*). The average moisture content ranged from 11 to 14 per cent, and the starch content from 56 to 60 per cent. The wheat bran was purchased from a local grain elevator. Blue Ribbon malt extract (Premier-Pabst Corporation) was employed in the preparation of the wort for yeast culture.

The method employed in the comparison of the different mold-bran preparations follows: 60.0 grams of corn meal are mixed with 300 ml. of 0.04 *N* hydrochloric acid in a 500-ml. Erlenmeyer flask, and the starch is gelatinized by heating the mash on a hot plate or over a small flame with occasional stirring to produce a uniform paste. The mash is then cooked in the autoclave at 20 pounds per square inch (1.4 kg. per sq. cm.) steam pressure for 30 minutes. Upon removal from the autoclave the pH is adjusted to 4.5–5.0 using sodium hydroxide, sodium carbonate, or calcium carbonate; for most of the work here reported sodium hydroxide was employed. The mash (at 30° C.) is transferred to a Whiz mixer or similar equipment, and the mold-bran added in the form of a slurry in water. The mixture is agitated for one minute, returned to the flask, and allowed to stand in the incubator at 30° C. for about an hour. The mash is then inoculated by adding 20 ml. of a 24-hour yeast culture (*Saccharomyces cerevisiae* No. 43) grown on a 10 per cent malt extract medium. After fermentation for 3 or 4 days, the fermented medium is transferred to a Kjeldahl flask, and about 0.5 gram of solid sodium carbonate or a little solid calcium carbonate is added to neutralize the acids. The mixture is then distilled, and exactly 100 ml. of the distillate are collected in a volumetric flask. The specific gravity of the distillate (25°/25° C.) is determined by means of a Chainomatic Westphal balance, and the alcohol content read from an appropriate table.

Corrections were made for the ethanol from the inoculum and from the mold-bran. That is, the activities of the various mold-bran preparations were compared on the basis of the alcohol yields from the starch of the corn alone. The theoretical yield of ethanol was calculated from the well known equations for the conversion of starch to sugar and the latter to ethanol by alcoholic fermentation.

In a typical experiment the fermentation mash contained 60.0 grams of corn with a starch content of 57.9 and a moisture content of 12.5 per cent, 3.6 grams of mold-bran, and 20 ml. of yeast culture as inoculum. After fermentation for 3 days the entire fermented mash (365 ml.) was subjected to distillation and the first 100 ml. of distillate collected. The specific gravity (25°/25°) of the distillate was 0.9686, corresponding to 19.77 grams of ethanol produced from the corn, mold-bran, and inoculum, which represents 5.41 grams of ethanol per 100 ml. of final beer or 6.87 per cent by volume. The ethanol derived from inoculum and mold-bran, as determined from control fermentations containing malt extract and mold-bran, was as follows: 0.68 gram from the 20 ml. of inoculum and $3.6 \times 0.045 = 0.16$ gram from the mold-bran, or a total of 0.84 gram of ethanol. Therefore, the quantity of ethanol from the starch of the corn alone was $19.77 - 0.84 = 18.93$ grams of ethanol. From the equation for the alcoholic fermentation,

$$C_6H_{10}O_5 + H_2O \longrightarrow 2CO_2 + 2C_2H_5OH$$

it is evident that the complete fermentation of 162 grams of starch yields 92 grams of ethanol; i. e., 1 gram of starch yields 0.568 gram of ethanol. In the 60.0 grams of corn there were $60.0 \times 0.579 = 34.74$ grams of starch which would give a theoretical yield of $34.74 \times 0.568 = 19.72$ grams of

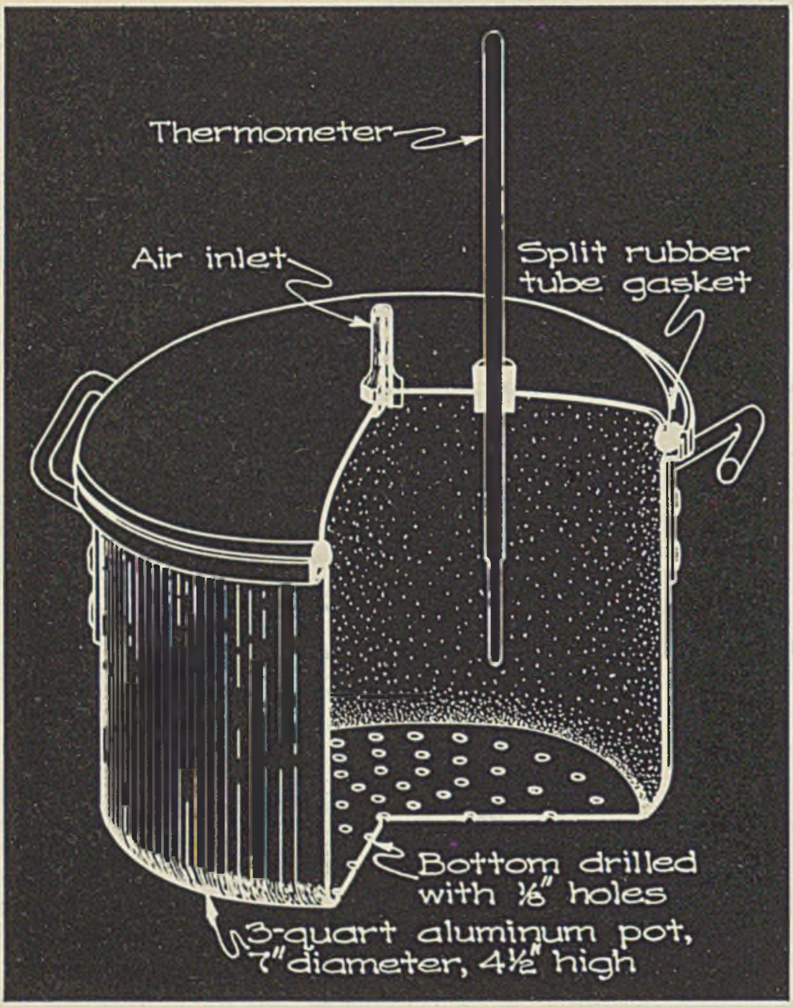

Figure 1. Apparatus for Growing Mold

ethanol. The yield from the above fermentation was, therefore, 100 × (18.93/19.72) = 96.0 per cent of theory.

It is evident from the above example that the activities of the various mold-bran preparations were compared on the basis of the alcohol yields from the starch of the corn alone, in terms of the percentage of theoretical yield of alcohol obtained. However, in order to make possible a more ready comparison of the results obtained in this study with industrial plant practice, the data of the above typical experiment may be used to calculate the results as commonly done in the distilling industry. Since 18.93 grams of ethanol were obtained from 60.0 grams of corn, this would represent 18.93 pounds of ethanol from 60.0 pounds of corn or 56 × (18.93/60.0) = 17.67 pounds of ethanol or 5.34 proof gallons of alcohol per bushel of corn as used. Since the corn as used contained 12.5 per cent moisture, 60.0 pounds would be equivalent to 60.0 × 0.875 = 52.5 pounds of moisture-free corn. The yield on the dry basis, therefore, was 100 × (18.93/52.5) = 36.06 pounds of ethanol or 10.9 proof gallons of alcohol per 100 pounds of dry corn, or was 36.06 × (56/100) = 20.19 pounds of ethanol or 6.10 proof gallons of alcohol per 56 pounds of dry corn.

The standard procedures were based upon many preliminary experiments. For example, Table I gives data on the effect of saccharification temperature and time upon alcohol yields. It is evident that the alcohol yields are just as good, or better, when the conversion takes place at 30° C. for 1 hour as at 55° for 1, 2, or 3 hours. In commercial practice it may be advantageous to add the mold-bran at 55° C. to lower the mash viscosity and then pump immediately through the mash coolers into the fermenters.

Table II shows the effect upon alcohol yields of cooking the corn mash with various concentrations of hydrochloric acid for 30 minutes at 20 pounds per square inch steam pressure. There is a definite optimum at 0.04 *N* acid. There was a distinct difference in the consistency of the mash cooked with 0.02 *N* and with 0.04 *N* acid; the former was quite thick, the latter was very thin. The mashes cooked with concentrations of acid higher than 0.04 *N* were brown in color, and the extent of caramelization increased with increasing acid concentration. The decrease in viscosity of the mash markedly increases the ease of handling and simplifies the procedure of saccharification. The mash can also be thinned by the preliminary addition of mold-bran or of malt, but the use of acid gave much more uniform results.

AMYLASE PREPARATIONS FROM DIFFERENT MOLDS

Twenty-seven representative strains of molds were chosen for detailed studies; four genera were included, *Aspergillus*, *Mucor*, *Penicillium*, and *Rhizopus*. The strains are listed in Table III. With the exception of two unidentified black molds (probably species of *Rhizopus*) which were isolated in these laboratories, all cultures were obtained from carefully kept collections and are designated by the names under which they were received.

Data on the alcohol yields from corn mash saccharified with representative mold-bran preparations are given in Table IV. All the strains of *Aspergillus* were very active; cultures of *Aspergillus oryzae* Nos. 2, 38, and 40 were es-

Table I. Effect of Saccharification Temperature and Time on Alcohol Yields from Corn Mash Saccharified by Several Mold-Bran Preparations

Preparation	Temp., ° C.	Time, Hours	Mold-Bran, % of Corn	Alcohol Yield, % of Theory
Aspergillus oryzae 2	30	1	4	88.6
	30	1	6	91.5
	30	1	8	91.3
	55	1	4	87.0
	55	1	6	88.4
	55	1	8	89.5
	55	2	4	86.1
	55	2	6	88.0
	55	2	8	89.5
Aspergillus oryzae 38	30	1	6	94.5
	30	1	8	94.8
	55	3	6	93.5
	55	3	8	93.7
Rhizopus oryzae 15	30	1	6	92.0
	30	1	8	93.5
	55	3	6	93.0
	55	3	8	94.0
Rhizopus delemar 34	30	1	6	92.5
	55	3	6	91.0

pecially potent. *Mucor rouxii* and *Mucor circinelloides* proved to be as effective as the Aspergilli; *M. javanicus* was inferior to the other preparations. The two species of *Penicillium* were inferior to the Aspergilli, the *P. chrysogenum* being particularly poor. With the exception of one strain of *R. oryzae*, all of the strains of *Rhizopus* gave very active mold-bran preparations.

TABLE II. EFFECT OF HYDROCHLORIC ACID CONCENTRATION USED IN COOKING CORN MASH ON ALCOHOL YIELDS

(Cooked for 30 minutes at 20 pounds per square inch steam pressure; 8 per cent mold-bran prepared from *Rhizopus delemar* No. 12)

Normality of HCl	Alcohol Yield, % of Theory
0.005	86.5
0.01	86.7
0.02	87.5
0.04	93.5
0.08	90.0
0.16	88.8
0.32	85.8

EFFECT OF STORAGE. Studies were made of the effect of several variants in the handling of the mold-bran. Mold-bran preparations from *Aspergillus oryzae* No. 38, added to the mash in the form of wet lumps, dry lumps, dry powder, and wet powder, showed no significant differences in alcohol yields. The effect of storage upon the activity of the dry powdered preparations is shown in Table V. It is evident that there is no significant deterioration during storage. In order to avoid deterioration, however, it is advisable that the moisture content be not above 12 per cent; in a few cases where the moisture content was from 15 to 17 per cent, spoilage occurred.

TABLE III. MOLDS TESTED FOR AMYLASE PRODUCTION

Lab. No.	Name	Source
1	Aspergillus niger	Botany Dept., Iowa State College
2	Aspergillus oryzae	A. T. C. C.[a], No. 4814
3	Aspergillus niger	N. R. R. L.[b], No. 3
4	Mucor rouxii	A. T. C. C., No. 4855
7	Penicillium chrysogenum	Thom[c], No. 5034.11
8	Penicillium purpurogenum	Thom, No. 413.2670
11	Rhizopus nigricans	A. T. C. C., No. 1210
12	Rhizopus delemar	A. T. C. C., No. 4859
13	Rhizopus delemar	A. T. C. C., No. 4858
14	Rhizopus oryzae	Lockwood[d], No. 649
15	Rhizopus oryzae	Lockwood, No. 660
16	Rhizopus oryzae	Lockwood, No. 664
17	Rhizopus oryzae	Lockwood, No. 704
18	Rhizopus peka I	Lockwood, No. 839
19	Rhizopus tritici	Lockwood, No. 654
20	Mucor circinelloides	Lockwood, No. 840
21	Mucor javanicus	Lockwood, No. 718
32	Rhizopus oryzae	N. R. R. L., No. 395
33	Rhizopus oryzae	N. R. R. L., No. 1034
34	Rhizopus delemar	N. R. R. L., No. 1472
35	Rhizopus shanghaiensis	N. R. R. L., No. 1518
38	Aspergillus oryzae	Rohm and Haas[e], No. 38
40	Aspergillus oryzae	Rohm and Haas, No. 40
42	Aspergillus oryzae	Rohm and Haas, No. 42
67	Aspergillus niger	N. R. R. L., No. 67
K_1	Unidentified black mold	Isolated in lab.
K_2	Unidentified black mold	Isolated in lab.

[a] American Type Culture Collection, Georgetown Univ. Medical School, Washington, D. C.

[b] Northern Regional Research Laboratory, U. S. Dept. Agr., Peoria, Ill.

[c] Charles Thom, Bur. of Agr. Chem. and Eng., U. S. Dept. Agr., Washington, D. C.

[d] L. B. Lockwood, Bur. of Agr. Chem. and Eng., U. S. Dept. Agr., Washington, D. C.

[e] Rohm and Haas Co., Bristol, Penna.

TABLE IV. ALCOHOL YIELDS FROM CORN MASH SACCHARIFIED WITH AMYLASE PREPARATIONS FROM STRAINS OF FOUR GENERA

Mold and Culture No.	Mold-Bran, % of Corn	Alcohol Yield, % of Theory
	ASPERGILLUS	
A. niger 1	4	86.4
	6	91.4
	8	91.3
A. niger 3	6	90.0
	8	91.6
A. niger 63	6	84.1
	8	89.5
A. oryzae 2	4	88.6
	6	91.5
	8	93.2
A. oryzae 2	4	90.5
	6	92.8
	8	92.5
A. oryzae 38	4	93.2
	6	93.8
	8	93.5
A. oryzae 40	4	92.5
	6	93.5
	8	93.0
A. oryzae 42	4	89.4
	6	91.1
	8	91.6
	MUCOR	
M. rouxii 4	6	87.5
	8	92.7
M. circinelloides 20	6	91.0
	8	92.8
M. javanicus 21	6	72.8
	8	82.8
	PENICILLIUM	
P. chrysogenum 7	6	64.7
	8	73.4
P. purpurogenum 8	6	86.1
	8	90.5
	RHIZOPUS	
R. delemar 12	6	92.5
	8	93.9
R. delemar 13	6	92.5
	8	93.7
R. delemar 34	4	93.8
	6	93.8
	8	93.4
R. oryzae 14	6	90.5
	8	90.9
R. oryzae 15	6	92.0
	8	93.5
R. oryzae 16	6	85.2
	8	90.5
R. oryzae 17	6	71.6
	8	84.0
R. oryzae 32	4	85.0
	6	90.6
	8	93.0
R. oryzae 33	4	92.8
	6	93.5
	8	94.0
R. nigricans 11	6	81.0
	8	89.5
R. shanghaiensis 35	6	86.9
	8	91.0
R. tritici 19	6	90.8
	8	89.6
Unidentified, K_1	8	88.5
Unidentified, K_2	6	90.3
	8	90.3

EFFECT OF SECONDARY ADDITION OF MOLD-BRAN. If the amylase preparation were added at intervals, in amounts which might maintain the concentration of the enzymes at a level where possible synthesis of fermentable into nonfermentable sugars would not take place, it was thought that the alcohol yield would be improved. Data on this secondary addition of mold-bran are given in Table VI. Preliminary tests had shown that 2 per cent mold-bran was an adequate amount for the secondary addition and that the best time for its addition was between the twentieth and twenty-fourth hour of fermentation. The data show that the secondary addition leads to small but consistent increases in alcohol yields. The advantage decreases with increase of alcohol yield. It is probable that secondary addition is of

TABLE V. EFFECT OF STORAGE ON AMYLOLYTIC ACTIVITY OF MOLD-BRAN PREPARATIONS

Mold and Culture No.	Pot Run No.	Time of Storage, Months	Mold-Bran, % of Corn	Alcohol Yield, % of Theory	
				Stored	Fresh
A. oryzae 2	17	1	6	92.5	92.8
A. oryzae 2	15	3	6	94.2	94.0
A. oryzae 2	13	3.5	8	93.3	93.2
A. oryzae 2	8	6	8	90.6	90.2
A. oryzae 2	8	10	8	91.0	90.2
A. oryzae 2	3	7.5	8	92.2	90.5
A. oryzae 2	1	9	8	90.6	91.0
A. oryzae 2	1	13	8	91.0	91.0
A. oryzae 2	Drum	24	6	91.5	92.0
A. oryzae 38	00	4.5	6	93.5	93.8
R. oryzae 33	33	3	8	93.0	93.5

TABLE VI. ALCOHOL YIELDS FROM CORN MASH SACCHARIFIED WITH AMYLASE PREPARATIONS, WITH AND WITHOUT SECONDARY ADDITION

Mold and Culture No.	Mold-bran, % of Corn		Alcohol Yield, % of Theory
	1st addition	2nd addition	
A. oryzae 38	4	0	92.0
	2	2	92.5
	6	0	93.5
	4	2	94.3
	8	0	94.8
	6	2	95.0
R. oryzae 33	4	0	92.8
	2	2	93.0
	6	0	93.5
	4	2	94.2
	8	0	93.1
	6	2	93.5

little or no value when the alcohol yields, without secondary addition, are already close to maximum. Tertiary addition of mold-bran was also tried—i. e., dividing the amount of mold-bran into three portions, and adding one portion before the fermentation starts and the other two portions at 20-24 hour intervals; a secondary addition of 10 ml. of active yeast culture was also made. . Neither of these modifications nor a combination of them further improved alcohol yields.

The effect of mixtures of various mold-bran preparations, representing different genera, was also studied. None of them, with or without secondary addition, gave higher alcohol yields than those obtained by using the corresponding amount of the better strain alone.

EFFECT OF MINERAL SALTS. It is well known that traces of mineral salts stimulate the growth of molds. The salts recommended by Steinberg (4) were added to the acid used in preparing the bran mash for the growth of the molds. To each liter of the dilute acid were added 0.000625 gram each of ferrous sulfate and zinc sulfate. The alcohol yields obtained from fermentations of mashes saccharified with these preparations are given in Table VII. The addition of the salts increases somewhat the amylolytic activity of the strains of *Aspergillus oryzae* but is disadvantageous with the representatives of *Rhizopus*. It is possible, however, that the latter might be stimulated by different concentrations of the salts.

COMPARISON OF STRAINS. On the basis of the above data and other repeated experiments, certain strains of *Aspergillus oryzae* proved to be the most satisfactory molds. Although some of the species of *Rhizopus* gave excellent results, the cultures of *Aspergillus* are much easier to handle. The Aspergilli produce more abundant sporulation, which facilitates growth of the inoculum, makes possible a heavier inoculation of the mash, and thus minimizes danger of contamination. Moreover, the mycelium formed by the Aspergilli is more dense and makes the mold-bran easier to handle.

The three best strains of *Aspergillus oryzae* were selected, and two mold-bran preparations of each were compared in the same fermentation series (Table VIII). The preparations all give yields of about 95 per cent of theory, and the results are remarkably uniform. It is unlikely that much better alcohol yields than those shown above may be expected under laboratory conditions since some of the carbohydrate must be utilized in building up the protoplasm of the yeast, some alcohol is lost by evaporation, and small amounts of by-products, such as glycerol, are always produced in the normal fermentation.

TABLE VII. ALCOHOL YIELDS FROM CORN MASH SACCHARIFIED WITH AMYLASE PREPARATIONS FROM MOLDS GROWN ON BRAN, WITH AND WITHOUT MINERAL SALTS

Mold and Culture No.	Mold-Bran, % of Corn	Alcohol Yield, % of Theory	
		With salts	Without salts
A. oryzae 2	4	91.0	90.5
	6	94.2	92.8
	8	95.5	93.2
A. oryzae 38	4	94.0	93.2
	6	94.5	93.8
	8	95.0	93.5
A. oryzae 40	4	92.5	92.5
	6	94.4	93.5
	8	92.0	93.0
R. delemar 12	4	91.0	..
	6	93.0	92.5
	8	92.0	93.9
R. delemar 13	4	88.4	..
	6	90.2	92.5
	8	90.6	93.7
R. delemar 34	4	92.5	93.8
	6	91.9	93.8
	8	90.3	93.4
R. oryzae 32	4	90.4	85.0
	6	90.2	90.6
	8	90.0	93.0
R. oryzae 33	4	89.3	92.8
	6	89.1	93.5
	8	88.9	94.0

TABLE VIII. ALCOHOL YIELDS FROM CORN MASH SACCHARIFIED WITH DIFFERENT AMYLASE PREPARATIONS FROM STRAINS OF *Aspergillus oryzae*

Culture No.	Pot Run No.	Mold-Bran, % of Corn	Alcohol Yield, % of Theory
2	15	6	95.7
		8	96.0
2	38	6	94.3
		8	95.0
38	00	6	95.5
		8	96.0
38	44	6	95.0
		8	96.0
40	18	6	94.5
		8	95.5
40	41	6	95.3
		8	95.5

ACKNOWLEDGMENT

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Nitric Acid Pulping of Whole Cotton

PROPERTIES OF CELLULOSES OBTAINED

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Whole cotton and its components have been pulped separately with 5 per cent nitric acid at atmospheric pressure. There was no undue degradation of cellulose. Examined for alpha- and beta-cellulose and pentosan content and for copper number and cuprammonium viscosity, the pulps compared favorably with those from commercial woods. No practical reason appeared for separating the components for the production of pulp.

INTEREST in cellulose pulps prepared by the action of nitric acid on various raw materials is steadily increasing. Macormac and Cameron (*12*) cited data on such substances as bagasse and cotton stalks; a further study of the latter was reported by Korzheniovskiĭ and Raskina (*11*) and Shikata and Akagi (*23*). Simoda and Yosino (*25*) pulped rice straw. Aronovsky and Lynch (*2*) pulped woods with alcoholic nitric acid; Aronovsky and Dryden (*1*), Reid and Lynch (*16*), and Whittemore, Reid, and Lynch (*26*) studied pulps from woods and cotton linters. Routala and Sevón (*19*) pulped fir. Benson and Walton (*4*) studied the use of nitric acid for pulping Douglas fir; they reported that the acid has been used in Germany to produce 40 tons per day of high grade cellulose from beechwood, and at least one American producer has used it.

Macormac and Cameron (*12*) pulped whole cotton with a 2.1 per cent aqueous solution of nitric acid, after removing oil and wax from the pulverized mass of stems, cusps, and seed cotton. A more concentrated solution is desirable. For the present study a 5 per cent solution was used. The procedure of Chen and Cameron (*6*), who investigated the distribution of cellulose in the several components of the cotton plant, was followed. This paper records some of the properties found for pulps made from whole cotton and from its several components. Because there is no lignin in seed cotton and not enough in stems and cusps to affect the pulp from whole cotton significantly, determinations were not made. Nor were the physical properties of the pulps studied quantitatively.

MATERIALS AND PULPING PROCEDURE

The whole cotton was grown in 1940 and has been stored in an open shed. This same cotton was used in the studies reported by Chen and Cameron (*6*) and by Powell and Cameron (*14*). It was harvested 25 weeks after planting and contained some immature seeds, but a fair proportion of the seeds was shown to be viable by a planting experiment. Zakoshchikov and colleagues (*27*) reported that the lint of immature plants has the same value commercially as that from mature plants.

About 400 pounds, taken at random, were sent to the laboratory where the mass was quartered and several 25-pound samples were prepared. The content of stems was 20.5 per cent; of cusps, 19.5 per cent; and of seed cotton, 60.0 per cent. Seed was delinted with sulfuric acid. All samples prepared for pulping were ground in a hammer mill; a 3/32-inch screen was used for whole cotton, and a 3/50-inch screen to shorten the pulping period for stems and cusps.

Before pulping, whole cotton was washed with aqueous sodium sulfide, as suggested by Powell and Cameron (*14*) to remove coloring agents and then extracted with a low-boiling petroleum ether. The delinted seeds were likewise extracted with petroleum ether, leaving for pulping a residue of hulls and degreased seed meats.

The pulping was carried out in a 5-liter flask. In it were placed 250 grams of air-dried sample with 2500 ml. of a 5 per cent solution of nitric acid. The flask was then placed on a steam bath and heated for 4 hours. During the digestion, the temperature in the fluid mass was between 80° and 90° C. The pulp was then washed free of acid and heated on the steam bath with 2500 ml. of a 2 per cent solution of sodium hydroxide. Filtered on a copper screen, the pulp was washed until the washings were neutral to litmus. It was then washed with 500 ml. of a 10 per cent solution of acetic acid. Washed free of this acid the pulp was bleached with 2 liters of a 0.5 per cent solution of commercial bleaching powder.

The appearance of the pulps was satisfactory. A few brown spots or specks were found in a wet pulp from cusps, and close inspection showed a few in a pulp from whole cotton. Raitt (*15*) and Heim de Balsac and co-workers (*8*) noted such spots in their work on cotton stalks. In making pulps from whole cotton which had been harvested several years before, Macormac noted such spots, but they disappeared when the pulps were beaten. Many pulps without specks have been made from the cotton used here. However, the cotton had been in storage 18 months when our pulps were made. It is a reasonable conclusion that the specks are due to aging of the cotton.

The scanty occurrence of the specks and their disappearance on beating make it improbable that they can affect any practical use of the pulps. It seemed desirable, nevertheless, to determine their origin. Raitt suggested that they come from the cuticle or outside skin of the stems. We found large pieces of stems pulped completely without specks. When whole cusps were pulped separately, little nodules near the base of some of the cusps were found to have resisted the action of the pulping liquid. Some nodules were gathered and treated separately and proved to be very resistant. Even when broken into small fragments in the grinding of a sample for a regular pulping, an occasional fragment may not be completely disintegrated in the pulping and becomes a speck in the resulting relatively large mass of cellulose.

PROPERTIES OF THE PULPS

ALPHA-, BETA- AND GAMMA-CELLULOSE. Alpha-cellulose is defined as that part of the total pulp which is not dispersed when the pulp is digested in a 17.5 per cent solution of sodium hydroxide; beta-cellulose is defined as the precipitate when an excess of acetic acid is added to the dispersion. The unregenerated material in the dispersion is estimated by difference as gamma-cellulose. The alpha-cellulose of all these pulps compares favorably with those usually reported for commercial bleached wood pulps.

This is true for the figures for whole cotton, although the latter is not quite so high as might be expected, assuming the lint to be practically pure cellulose. In a pulp from another sample of this same crop, Chen and Cameron (*6*) found 97.34 per cent alpha-cellulose; Macormac and Cameron (*12*) found 86.7 to 94 per cent in five pulps from the crops they investigated.

The beta-cellulose content of the pulps from stems, cusps, and seeds are in accord with the 1.2 and 2.5 per cent for whole cotton, as reported by Macormac and Cameron. The figure for whole cotton in Table I is comparable with that commonly reported for commercial pulps but must be regarded as high and an indication of degradation in the preparation of this particular pulp.

TABLE I. CHARACTERISTICS OF CELLULOSE FROM WHOLE COTTON PULPED WITH NITRIC ACID

Source	Stems	Cusps	Seeds	Whole Cotton
Alpha-cellulose, %	82.10	82.15	83.00	84.11
Beta-cellulose, %	1.09	2.89	3.24	10.58
Pentosans, %	8.78	9.30	14.61	4.44
Copper number	1.89	2.07	2.03	1.17
Cuprammonium viscosity, centipoises	14.3	17.4	21.2	7.42
Ash, %	0.93	0.23	0.18	0.26

COPPER NUMBER. The standard method of the Technical Association of the Pulp and Paper Industry (*22*) is the Braidy modification (*5*) of the original Schwalbe method (*20*) and was studied critically by Clibbens and Geake (*7*). With it, we obtained good duplicate determinations. The values obtained for stems, cusps, and seeds are somewhat low as compared with those for commercial wood pulps, while the value for whole cotton is that characteristic of highly purified wood cellulose. Two possible explanations of these low copper numbers have been published. Korzheniovskiĭ and Raskina (*11*) suggest that the cellulose fibers are protected from attack by nitric acid by a buffer action of impurities in the crude plant material. Simoda (*24*) boiled purified cellulose with dilute solutions of nitric acid and found that in solutions of 10 per cent or less little oxycellulose was formed. He did find some hydrocellulose, but it had little effect on copper number.

PENTOSANS. Although considered impurities in a pulp, the presence of pentosans is sometimes desirable or even necessary for certain kinds of paper. They are thought to interfere with esterification and must be removed from pulps so destined. The method employed for their determination is that of the Association of Official Agricultural Chemists (*3*), based on the fact that pentosans yield furfural, whereas cellulose yields glucose.

The high value found for the seed is probably due to content of hulls. Ivanova and Kurennova (*9*) reported 15 per cent furfural from hulls and predict much higher results from delinted hulls. The low value for whole cotton is due to the high content of lint, which itself contains less than 1 per cent of pentosans. The pentosan content found for whole cotton is about that in a bleached coniferous wood pulp; that for stems and cusps, for a bleached hard wood or aspen pulp (*18*).

VISCOSITY OF DISPERSIONS IN CUPRAMMONIUM SOLUTIONS. Although Rich (*17*), Richter (*18*), and others reported results by methods requiring less than 30 minutes, the standard method of the Technical Association of the Pulp and Paper Industry requires 20 hours, special equipment, and rigid control. Essentially, the standard method was used to obtain the results here recorded, following the specifications of Mease (*13*) and Scott (*21*), and satisfactory duplicates were obtained without difficulty. Korzheniovskiĭ (*10*) found that purified cellulose, after treatment with nitric acid, gave higher viscosities when dispersed in cuprammonium solutions. Moreover, high temperatures in pulping tend to lower this viscosity. The moderate temperature and short pulping period when nitric acid is the reagent would be expected to be followed by relatively high viscosities.

ASH AND COLOR. The ash contents of the pulps are as low as generally found for commercial wood pulps; but since they were due largely to adhering soil, they could have been materially lowered by mechanical manipulation in the preparation of the pulps. These pulps were not "purified". In all cases the color was a good clear white, and bleaching was easily accomplished.

SUMMARY

Cotton stalks and cusps are essentially wood and, it is to be expected, would react as do woods generally towards pulping agents. The degreased seeds, a mixture of meat residue and hulls, might be suspected of showing a different response. The present study confirms previous work in this laboratory and shows that all the components of the cotton plant, treated either separately or as a whole, are pulped readily by a 5 per cent solution of nitric acid, at atmospheric pressure and a moderate temperature, within a short time interval, and without undue degradation of cellulose. It is not suggested as having general application, since Chen and Cameron (*6*) showed that some woods were pulped with difficulty and with a decomposition of nitric acid which implied a considerable chemical change in the cellulose content.

The pulp obtained from whole cotton compares favorably with the pulps from tree woods, commonly used as raw materials. The composition and properties of the components, including seeds (see meats and hulls), have been found to be fairly close, and the data obtained suggest that each can be retained with advantage in whole cotton which is to be processed for its cellulose content.

It has been found that the dark colored specks occasionally observed in pulps made from relatively old cotton plants are undigested or partially pulped fragments of a concretion sometimes (but not always) to be found at the base of a cusp. They have been observed only as a few widely scattered spots in any one pulp.

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THE USEFUL LIFE OF
Pyro-, Meta-, and Tetraphosphates

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The rate of hydration of meta- and pyrophosphates in 1 *N* acid and of metaphosphate in 1 *N* alkaline solution is too rapid to permit their commercial use under these conditions unless an almost instantaneous reaction occurs. The pyrophosphate hydrates very slowly in 1 *N* alkaline solution. The "useful life" of all materials tried is at least 24 hours at 85° C. in waters whose pH is between 7.0 and 9.0. Daily dosage therefore will maintain the desired conditions without danger of loss of effectiveness under similar operating conditions. At 56° C. the useful life of all materials tried is much greater. Maintaining the pH of the solutions between 7.0 and 9.0 increases the useful life appreciably. Commercial fused tetraphosphate does not hydrate in solution in the same manner as a comparable physical mixture of meta- and pyrophosphates.

The development and uses of phosphates produced by removal of water from within an orthophosphate molecule ("molecularly dehydrated phosphates") have been thoroughly discussed in recent articles (*3*, *8*). Work in this laboratory on the corrosion-inhibiting properties of some of these materials revealed no quantitative data on the rate of reversion to the orthophosphate form. Since all of the unique properties of the molecularly dehydrated phosphates are lost when hydration to the orthophosphate form occurs, a quantitative determination of the useful life of the materials is of value. "Useful life" is defined here as that time when 50 per cent by weight of the original P_2O_5 content of the molecularly dehydrated material has reverted to the orthophosphate form. It must be borne in mind that under certain conditions these materials perform their "useful" function rapidly and remain valuable as complex ions for a longer period than indicated. The rate of inversion of the complex ions was not studied.

The materials tested were those commercially available phosphates that the chemical engineer might use for corrosion resistance purposes. No attempt was made to determine the properties of specially purified reagent chemicals. It is not the intention of this paper to enter into a discussion of the structure of the materials but to point out that the different materials behave differently in aqueous solution under conditions which might be met in practice.

There has been some discussion (*2*) as to whether the hexametaphosphate hydrates directly to the orthophosphate according to the following equation:

$$NaPO_3 + H_2O \longrightarrow NaH_2PO_4 \qquad (1)$$

and whether the pyrophosphate hydrates to the orthophosphate:

$$Na_4P_2O_7 + H_2O \longrightarrow 2Na_2HPO_4 \qquad (2)$$

Work in this laboratory seemed to indicate that the metaphosphate, at least in part, formed some pyrophosphate as an intermediate in the hydration:

$$2NaPO_3 + H_2O \longrightarrow Na_2H_2P_2O_7 \qquad (3)$$

This subject was also investigated.

There is also uncertainty in the literature (*3*, *7*) regarding the physical state of tetraphosphate ($Na_6P_4O_{13}$). Since these materials are glasses, they may all be classed as supercooled solutions of the system Na_2O–P_2O_5. In this work it was desired to determine how the commercial $Na_6P_4O_{13}$ mixture acted, in so far as reversion to the orthophosphate form is concerned. The results shed some light on the behavior of commercially available materials in this respect. Whether $Na_6P_4O_{13}$ is a solid solution containing tripolyphos-

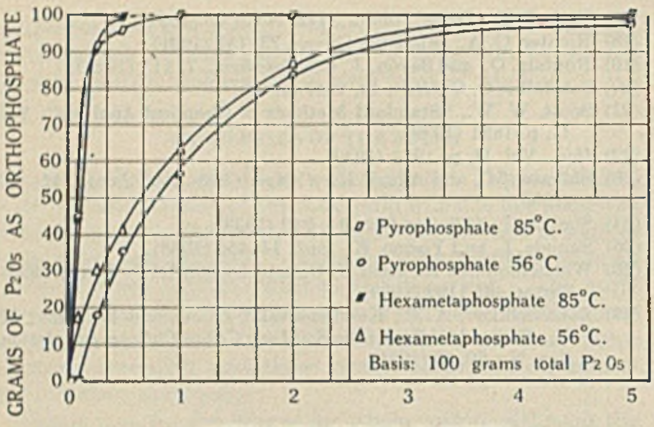

Figure 1. Hydrolysis of Commercial Sodium Hexametaphosphate and Tetrasodium Pyrophosphate to Orthophosphate in 1 *N* Acid

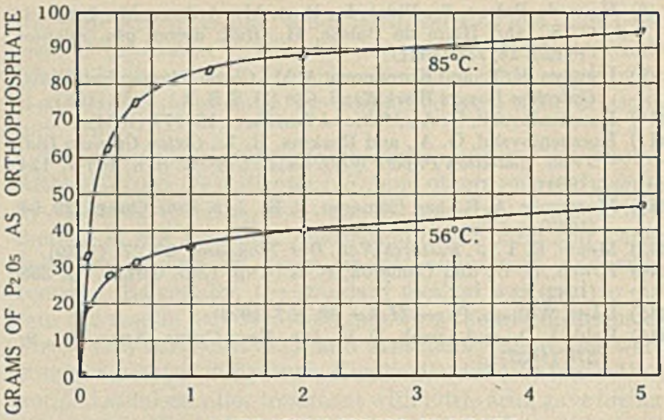

Figure 2. Hydrolysis of Commercial Sodium Hexametaphosphate to Orthophosphate in 1 *N* Alkali

phate dissolved in metaphosphate or a glass of the system Na_2O–P_2O_5 of composition $3Na_2O.2P_2O_5$ is immaterial to this discussion.

HYDRATION

Materials. The sodium hexametaphosphate used was the commercial unadjusted glass obtained from Calgon, Inc. This sample was found by analysis to consist of 76.2 per cent sodium hexametaphosphate ($NaPO_3$) and 23.8 per cent tetrasodium pyrophosphate ($Na_4P_2O_7$), based on the P_2O_5 content. This material is referred to throughout as metaphosphate.

The tetrasodium pyrophosphate, anhydrous, c. p. was obtained from the J. T. Baker Chemical Company. This material is referred to as pyrophosphate.

The sodium tetraphosphate pellets ($Na_6P_4O_{13}$) were obtained from the Rumford Chemical Works. This material is referred to as tetraphosphate. Both the monosodium orthophosphate crystals, c. p. ($NaH_2PO_4.H_2O$), and disodium orthophosphate crystals, c. p. ($Na_2HPO_4.12H_2O$), were obtained from J. T. Baker Chemical Company.

The disodium pyrophosphate ($Na_2H_2P_2O_7$) was the commercial U. S. P. product obtained from Monsanto Chemical Company.

Table I. Composition of Hydration Products (in Grams P_2O_5) Obtained by Gravimetric Procedure (Basis, 100 Grams Total P_2O_5)

	0.2% Soln. Pyrophosphate, 1 *N* HNO_3				0.2% Soln. Commercial Metaphosphate				0.2% Soln. Pyrophosphate, 1 *N* NaOH, 85° C.
	56° C.		85° C.		Orthophosphate with 1 *N* HNO_3		Orthophosphate with 1 *N* NaOH		
Time	Pyro	Ortho	Pyro	Ortho	56° C.	85° C.	56° C.	85° C.	
0	100	0	100	0	0	0	0	0	0
5 min.	100	0	54.8	45.2	16.4	44.7	20.0	33.6	..
15	81.5	18.5	7.6	92.4	30.2	91.1	27.8	62.1	..
30	64.0	36.0	4.1	95.9	40.7	100.0	31.6	75.0	0
1 hr.	43.4	56.6	0.5	99.5	63.4	...	35.5	84.2	..
2	15.6	84.4	0.25	99.75	87.6	...	39.7	88.0	..
5	1.3	98.7	0.5	100.5	99.4	...	46.3	94.3	0[a]

[a] No orthophosphate; crystals of $Na_4P_2O_7$ settle on the bottom of the container after 5, 168, and 1000 hours.

Procedure. Solutions were held at the desired temperature (±0.5° C.) in glass-stoppered Erlenmeyer flasks in a Freas electric oven. Samples were pipetted out at suitable intervals and analyzed by one of two methods.

Data for Table I and Figures 1 and 2 were obtained in this laboratory (*1*, *9*) by gravimetric precipitation of orthophosphate with ammonium molybdate as described by Griffin (*5*).

The other data (Table II) were obtained by the colorimetric pH method of Gerber and Miles (*4*). A 50-cc. aliquot of a sample with a known P_2O_5 content of 0.4 gram per 100 cc. was adjusted to pH 4.4, using 1 *N* nitric acid and 0.1 *N* carbonate-free standard sodium hydroxide with bromocresol green indicator. The meta-, pyro-, and orthophosphates are then in the forms $NaPO_3$, $Na_2H_2P_2O_7$, and NaH_2PO_4, respectively.

When an excess of silver nitrate is added, the precipitation of normal silver phosphates occurs and the H^+ formed from the hydrogen ions of the $Na_2H_2P_2O_7$ and NaH_2PO_4 is titrated with standard sodium hydroxide, using methyl red indicator. Each mole of pyro- or orthophosphate requires 2 moles of sodium hydroxide.

Ten grams ±0.5 gram of sodium nitrate were added to another 50-cc. aliquot which was then adjusted to pH 8.8, using thymol blue indicator. The phosphates then exist as $NaPO_3$, $Na_4P_2O_7$, and Na_2HPO_7, respectively.

An excess of silver nitrate was added, and the mixture titrated with sodium hydroxide and methyl red as before. In this titration each mole of sodium hydroxide is equivalent to one mole of orthophosphate. Knowing the moles of orthophosphate, moles of orthophosphate plus pyrophosphate, and total P_2O_5 content, the amounts of pyrophosphate and of metaphosphate may be calculated.

Actually, volumes of standard sodium hydroxide are recorded at pH 4.2, 4.4, and 4.6 in the bromocresol green titration because at this point the pH of dihydrogen orthophosphate is 4.6 while that of dihydrogen pyrophosphate is 4.2. Likewise, in the thymol blue titration, sodium hydroxide volumes are recorded at pH 8.4, 8.6, 8.8, 9.0, and 9.2 because under these conditions the pH of monohydrogen orthophosphate is 8.5 and that of tetrasodium pyrophosphate is 9.1. Using the provisional pH values of 4.4 and 8.8, the approximate ratio of ortho-P_2O_5 to pyro-P_2O_5 is calculated. This ratio is then used to interpolate the correct bromocresol green end point pH between the values of 4.2 for pyro- and 4.6 for orthophosphate, and to interpolate the correct thymol blue end point pH between 9.1 for pyro- and 8.5 for orthophosphate. A detailed discussion of this method is given by Gerber and Miles (*4*), and Jones (*6*). pH values were determined with a W. A. Taylor and Company slide comparator.

USEFUL LIFE DATA

Since the hydration of most of the molecularly dehydrated phosphates is known to proceed at a rapid rate in strong acid or alkaline solutions, the first series of experiments were run in 1 *N* nitric acid and 1 *N* sodium hydroxide solutions. Two temperatures, 56° and 85° C., were chosen as typical of conditions that might be expected in heat exchangers or similar equipment.

Hydration data for pyro- and metaphosphates are shown in Table I. At 85° C. the useful life of both materials in 1 *N* nitric acid is less than 10 minutes (Figure 1) while complete hydration occurs in less than 1 hour. At 56° C. the useful life is prolonged to 45 minutes and complete hydration takes 5 hours.

In 1 *N* sodium hydroxide solution the useful life (Figure 2) of the hexametaphosphate is still only 10 minutes at 85° C. At 56° C. the useful life is increased to somewhat more than 5 hours. A probable explanation for this phenomenon is that the metaphosphate tends to hydrate in two ways as shown by Equations 1 and 3. The pyrophosphate hydrates at a much slower rate in alkaline solution, and therefore this becomes the controlling reaction.

Attempts to obtain the rate of hydration of the pyrophosphate in 1 *N* sodium hydroxide solution at 85° C. indicate that less than 1 per cent hydrates in 60 days. When the concentration of $Na_4P_2O_7$ is as low as 7.5 grams per liter of 1 *N* sodium hydroxide solution, crystals of $Na_4P_2O_7.10H_2O$ precipitate after about 10 days at 85° C. The slow rate of hydration can be ascribed, in part at least, to the fact that only a small amount of pyrophosphate is present in the strongly alkaline solutions at any one time. That some hydration of the pyrophosphate occurs is demonstrated by the fact that the metaphosphate hydration always shows some intermediate pyrophosphate which disappears in complete hydration.

The next series of runs were made in distilled water, and the pH of the solution was allowed to vary as hydration proceeded. Typical data from these runs are summarized in Table II. As noted in the hydration of hexametaphosphate, the pyrophosphate content actually increases during the early stages of hydration (Figure 3). As long as the solution contains sufficient salt to buffer the pH above 6.5, little hydration of pyrophosphate occurs. When the pH of the solution drops to 6.5, the pyrophosphate content drops rapidly and approaches zero within 80 hours. The over-all rate of hydration of metaphosphate appears to slow down when the pH becomes less than 6.2. During this stage the controlling factor is either the direct hydration of metaphosphate to orthophosphate or to pyrophosphate, or the rate of depolymerization of hexametaphosphate to metaphosphate:

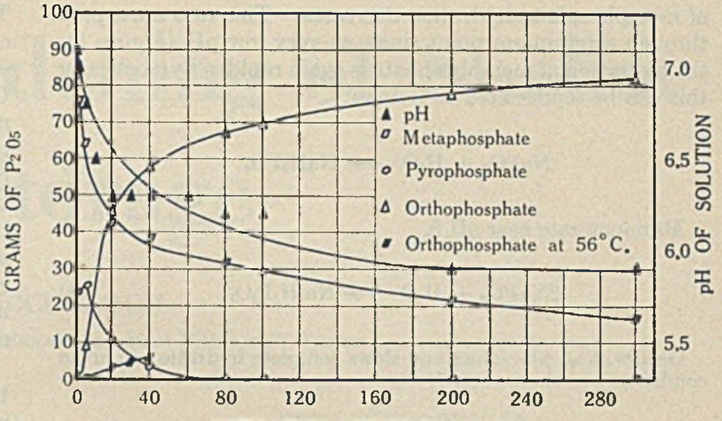

Figure 3. Rate of Hydrolysis of Commercial Sodium Hexametaphosphate at 85° C. (Note Initial Increase in Pyrophosphate Content)

$$(NaPO_3)_6 \rightleftharpoons 6NaPO_3 \qquad (4)$$

Figure 4 and Table II compare at 85° C. the total orthophosphate formation against time for each of the materials used, hexametaphosphate, pyrophosphate, tetraphosphate, and a physical mixture of 2 moles of metaphosphate and 1 mole of pyrophosphate, which is the analytical equivalent of the tetraphosphate.

The curve for the hexametaphosphate is about as expected, except that only 83 per cent hydration has occurred at the end of 300 hours. In the early stages the pH is above 7, and Table II shows that the pyrophosphate content increases and the metaphosphate decreases. As the pH decreases, the speed of pyrophosphate hydration increases and

Table II. Composition of Hydration Products (in Grams P_2O_5) Obtained by Volumetric Analysis (Basis, 100 Grams Total P_2O_5)

	0.62% Soln. Commercial Metaphosphate							0.75% Soln. Pyrophosphate, 85° C.				Mixt. of 2 Moles Metaphosphate per Mole Pyrophosphate[a], 85° C.				0.66% Soln. Tetraphosphate			
	56° C.			85° C.												85° C.		56° C.	
Time	Meta	Pyro	Ortho	Meta	Pyro	Ortho	pH	Meta	Pyro	Ortho	pH	Meta	Pyro	Ortho	pH	Ortho	pH	Ortho	pH
0	76.2	23.8	0	76.2	23.8	0	7.1	0	100	0	10.3	50	50	0	8.7	0	8.3	0	8.3
5 min.	..	..	...	..	..	..	...	..	...	..	..	..	..	..	...	..	...	..	...
15	..	..	...	..	..	..	...	..	...	..	..	..	..	..	...	..	...	..	...
30	..	..	...	..	..	..	...	..	...	..	..	..	..	..	...	..	...	..	...
1 hr.	74.5	25.5	0	..	..	..	7.0	..	...	..	10.3	..	..	..	8.7	..	8.3	..	...
2	..	..	...	..	..	..	...	..	...	..	..	..	..	..	...	..	...	..	...
5	71.8	27.6	0.6	64.4	26.3	9.3	6.8	..	...	..	10.1	..	..	...	8.4	..	7.5	..	...
10	..	..	...	..	..	..	6.5	..	..	..	9.7	..	..	..	7.8	..	7.0	..	...
20	70.5	26.5	3.0	43.0	11.0	46.0	6.3	0	100	0	9.7	38.1	52.9	9.0	7.3	43.6	6.8	0	8.3
30	66.8	28.8	4.4	..	..	..	6.3	..	...	..	9.6	32.6	45.5	21.9	7.0	..	6.8		
40	65.1	29.0	5.9	38.4	3.4	58.3	6.3	0	100	0	9.6	29.0	14.7	56.3	6.9	68.5	6.8		
60	..	..	...	..	..	..	6.3	..	...	..	9.5	26.2	4.8	69.0	...	..	6.8		
80	..	..	...	32.1	0.5	67.4	6.2	..	...	..	9.5	24.8	3.0	72.1	6.8	92.2	6.7		
100	..	..	..	29.9	0.5	69.6	6.2	0	97.6	2.4	9.4	15.9	5.4	78.7	6.5	96.9	6.7		
200	..	..	...	22.2	0.0	77.8	5.9	0	69.0	31.0	9.2	..	..	..	6.5	..	6.4		
300	..	..	...	17.5	0.0	82.5	5.9	0	48.2	51.8	9.0	..	..	..	6.5	..	6.3		
400	..	..	...	..	..	..	5.9	0	33.6	66.4	8.9	..	..	..	6.4	..	6.3		
500	..	..	...	..	..	..	...	0	21.8	78.2	8.9	..	..	..	6.4	..	6.3		
600	..	..	...	..	..	..	5.8	0	11.7	88.3	8.8	..	..	..	6.4	..	6.3		
700	..	..	...	..	..	..	5.8	0	3.5	96.5	8.7	..	..	..	...	..	6.3		
800	..	..	...	..	..	..	...	0	2.0	98.0	8.6	..	..	..	...	..	...		
900	..	..	...	..	..	..	5.8	0	1.7	98.3	8.5	..	..	..	...	..	6.2		

[a] As in empirical formula for tetraphosphate.

of metaphosphate hydration decreases. This rate must pass through a minimum point since, at very low pH (Figure 1), the hydration of metaphosphate is again rapid. Symbolically this can be represented as follows:

$$NaPO_3 + H_2O \longrightarrow NaH_2PO_4 \qquad (5)$$

Minimum rate near pH 5.

$$2NaPO_3 + H_2O \longrightarrow Na_2H_2P_2O_7 \qquad (6)$$

Occurs at all pH values and slows complete hydration to ortho condition due to reaction 7.

$$Na_4P_2O_7 + H_2O \longrightarrow 2Na_2HPO_4 \qquad (7)$$

Slower rate, becoming infinitely slow at high pH, helped by salting-out effect of buffer salts.

The pyrophosphate curve (Figure 4) shows an induction period during which little detectable orthophosphate is formed. However, the initial pH of the solution is 10.1 (Table II), probably due to some impurity. As the pH drops to 9.5, orthophosphate is detected, and by the time pH 9.2 (70 hours) is reached, the rate of hydration becomes appreciable. At the end of 700 hours the hydration is 96.5 per cent complete. During the next 200 hours the hydration continues at a much reduced rate so that at the end of 900 hours the hydration is only 98.3 per cent complete.

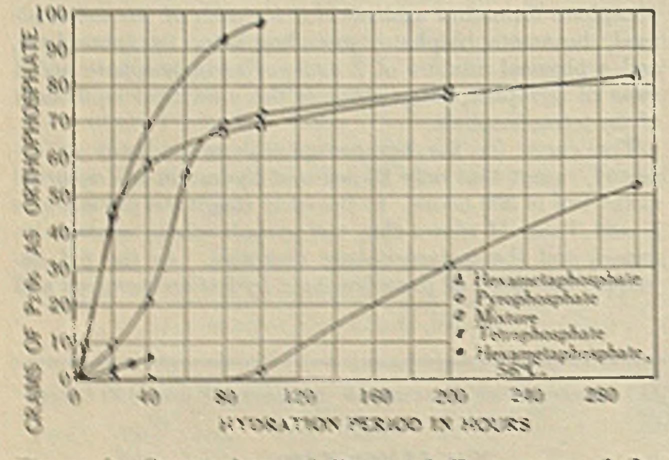

Figure 4. Comparison of Rates of Formation of Orthophosphate from Different "Molecularly Dehydrated" Phosphates in Unbuffered Water at 85° C.

The hydration of the physical mixture of 2 moles of metaphosphate and 1 mole of pyrophosphate follows the hydration curve of the metaphosphate very closely. The pH of this mixture starts at 8.7, in the region where the pyrophosphate hydrates rather readily. The induction period is much less than that of pure pyrophosphate, which can also be explained on the basis of the lower pH value and Equation 7. After 80 hours the curve has reached that of the commercial metaphosphate and then continues to parallel that curve.

On the other hand, the hydration of the fused tetraphosphate sample follows an entirely different curve (Figure 4). The rate of hydration closely follows the metaphosphate curve for the first 36 hours, but does not slow down and is substantially hydrated to the orthophosphate in 100 hours. Using the method of Gerber and Miles (*4*), separate determinations of meta- and pyrophosphate could not be obtained. These results indicate that the fused tetraphosphate remains in a different condition from that of the same analytical mixture of pyro- and metaphosphates even in solution. Whether this different form is tripolyphosphate in solution was not determined. As far as useful life is concerned, the 50 per cent hydration point of the tetraphosphate under these conditions is about the same as that of the metaphosphate.

To show the effect of temperature on rate, a portion of the curve for hydration of the metaphosphate at 56° C. is included. This shows about 5 per cent hydration to orthophosphate in 40 hours. Samples in distilled water at room temperature averaged less than 10 per cent hydration to the orthophosphate in 30 days. The pyrophosphate under the same conditions showed no measurable hydration at 85° C. after 80 hours and no measurable hydration at room temperature at the end of 30 days.

The data in Table II indicate that the pH of the solutions has a considerable effect on the relative rates of hydration of metaphosphate to orthophosphate, metaphosphate to pyrophosphate, pyrophosphate to orthophosphate, and tetraphosphate to orthophosphate. Attempts were made to buffer the solutions at known pH values and then follow the hydration. However, the buffer solutions interfered with the titrations to such an extent that the results were inconclusive. The above discussion indicates that pH values, in the vicinity of 8–9, slow the rate of hydration of all the molecularly dehydrated phosphates to an appreciable extent and hence increase the useful life. When these materials are used for scale control or corrosion control in heat exchangers or condensers, it is relatively easy to maintain the pH between 8 and 9 and thus increase the useful life.

No attempt has been made in this study to evaluate the relative values of the different molecularly dehydrated phosphates from an efficiency standpoint in scale control, corrosion control, or emulsion formation. That is planned for future study. In addition, no attempt was made to study the life of the complex ions formed with Ca^{++} and Mg^{++}. The purpose of this work was to find out how long the unreacted phosphates would remain available for use to form complexes or to exercise some function.

ACKNOWLEDGMENT

Acknowledgment is made for the contribution of Wallace Armstrong, now with the Ethyl Corporation, and Alfred Smith, now at the Louisiana State University, for some of the earlier measurements. Thanks are due to Calgon, Inc., and the Rumford Chemical Works for the contribution of materials.

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Reversible Hardening of Shellac in Storage

L. McCULLOCH

Westinghouse Research Laboratories, East Pittsburgh, Penna.

SHELLAC is one of those useful natural products which have many substitutes but no duplicates. It is the basis of molded products in which it exhibits such a combination of useful properties that it has not been entirely displaced by the synthetic resins. Shellac was the first thermal-setting resin known, with the property of conversion by heat into an infusible, insoluble form. It has been of great aid to the electrical industry on account of its adhesive properties, and because at carbonizing temperatures it vaporizes without leaving an electrically conducting residue.

At temperatures below 100° C. shellac is relatively nonvolatile and stable, not subject to change by oxidation. Its thermal hardening property is attributed to the presence of carboxyl and hydroxyl groups which react into cross linkages of several types, and cause the resin to harden and yield water. The purpose of this paper is to show that the reactions which lead to hardening are modified by the presence of water and may be reversed by it. Shellac is hydrophilic in nature; it is somewhat permeable to water, which it absorbs to the extent of 5 per cent at saturation (*2*).

The hardening of shellac takes place in two definite stages, and proceeds at a rate dependent upon the temperature and upon the water content. During the first or fluid stage there is a progressive increase in viscosity and in the so-called melting point up to the point of gelation, which is the beginning of the second stage. In the gelled state the resin acquires a fixed shape which cannot be deformed beyond an elastic limit without fracture. Gelled shellac cannot be made fluid by heat below the decomposition temperature, and its structure is not broken down or dissolved by alcohol at ordinary temperatures. After reaching gelation, the process of hardening may continue until the maximum strength is attained. The change proceeds by a "drying out" process, and the ultimate strength is not attained if the resin is confined (as in a mold) so that vapors cannot escape. The degree of hardness in the gelled resin is judged by a suitable test of mechanical strength—for example, by the shearing resistance. Thoroughly cured and hardened shellac remains slightly thermoplastic within its elastic limit, accommodating itself to the thermal contraction of the surfaces to which it is adhering. This is one of the reasons for the adhesive strength of shellac.

The reversible hardening of shellac by water has been demonstrated by treating the thoroughly hardened resin with water in an autoclave at 150° to 210° C. (*1*). This treatment renders the resin again fusible and soluble. This soft resin can be rehardened by heat with drying substantially as before. These reversals can be carried through repeatedly. It is probable, however, that the resin recovered by the autoclave is not identical with the original shellac in all respects. Rangaswami and Aldis (*1*) reported: "Depolymerized shellac slowly repolymerizes. This effect is somewhat more rapid than with a normal shellac." Information is lacking as to the utility of such recovered resin.

STORAGE IN AMPOULES

To study the autoclave process of recovering shellac that had hardened in storage, a series of experiments was made with shellac and water in ampoules of Pyrex at various temperatures. The ampoules were 1 inch in diameter and 6 inches in length, and contained 20 grams each of new orange shellac and water. They were enclosed in capped iron pipes for safety and were heated in controlled electric ovens.

An unexpected difficulty had appeared while the writer was treating a pound of shellac in the autoclave. The center of the mass after cooling was found to be gelled and infusible, whereas all of it should have liquefied. The previous workers (*1*) also encountered this difficulty, remarking that "shellac can repolymerize within the autoclave on cooling". At first the writer attributed the gelation at the center to evaporation of water from the hot center to the cooler walls of the autoclave. The experiments with the ampoules led, however, to another explanation; namely, gelation is reversed by changes in temperature alone, and the gel structure is stable at lower temperature and unstable at the temperature of the autoclave.

The behavior of the shellac samples within the ampoules was as follows:

Temp., ° C.	Shellac Behavior
70	Gelled in about 30 days
90	10 days
100	7 days
110	6 days
125	6 days
150	6 days
160	Did not gel in 8 days
200	3 days

Shellac that had been liquefied at 165° and at 200° C. gelled in less than one day at 90°, although from the above table new shellac required 10 days to gel. After having gelled at 90° it liquefied in a few hours at 165° and 200° C. The temperature of reversal lies between 150° and 165° C. Above this temperature there is liquefaction and below there is gelation. The samples were said to have gelled when no flow was seen within the ampoules after they had been inverted in the ovens for a few hours.

EFFECT OF MOISTURE

In another experiment in a flask of water boiling with reflux, some new shellac gelled after 7 days. It is well known, however, that shellac, baked in air at 100° C., gels or has a "life under heat" of about one day. Thus the effect of saturation with water is to retard gelation by at least seven times.

In an experiment in a flask at room temperature, shellac under water for 600 days is not yet infusible, although the fluidity is only a fraction of its former value.

Unfortunately, shellac proceeds to harden slowly even at the storage temperatures and results in loss of usefulness from infusibility and insolubility. The following experimental findings lead to the conclusion that spoilage in storage can be lessened by keeping the shellac dry. Two samples of orange shellac were kept in glass jars at room temperature for months; one was stored over calcium chloride, the other over wet sodium chloride which gives 75 per cent humidity. After 1000 days the condition of the shellacs was as follows:

Orange Shellac	Over Dry $CaCl_2$	Over Wet NaCl
High-flow	Still fusible	Hardened
Low-flow	Still fusible	Infusible

An experiment was commenced with orange shellac in two friction-top tin cans, covered with cloth to permit passage of moisture; one contained a small jar of calcium chloride, the other of wet sodium chloride. The two cans were kept in an oven at 40° C. until the shellacs became infusible. Over dry calcium chloride the shellac was infusible after 400 days; over wet sodium chloride, after 175 days.

CONCLUSIONS

Shellac can best be preserved by storage in a dry atmosphere. Since, however, the fluidity and other molding properties vary with moisture content (*2*), the dry resin can be restored to the desired condition by adding a measured amount of water shortly before it is to be used.

Shellac at temperatures below 150° C. approaches the gelled state whether dry, moist, or wet.

Shellac in storage should be kept dry to retard the reactions of hardening.

At higher temperatures gelation is greatly retarded by water and does not occur in water above 150° C. Gelation under water is reversible between about 150° and 165° C.

Since the effect of water at room temperature is to hasten gelation and at higher temperatures to retard it, there must be an intermediate range where water is without effect upon the rate; this temperature seems to be between 40° and 70° C.

ACKNOWLEDGMENT

For criticisms of the manuscript, the writer expresses thanks to A. T. Krogh and L. R. Hill of this company, and to Paul F. Bruins of the Polytechnic Institute of Brooklyn.

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CORRESPONDENCE

Calculation of Relative Volatility

SIR: A recent paper by John Griswold [Ind. Eng. Chem., 35, 247 (1943)] shows convincingly the need for accurate relative volatility values in distillation calculations. There is, however, a slight error in his reference to my equation for the relative volatility of normal liquids at atmospheric pressure [*J. Inst. Petroleum Tech.*, 25, 558 (1939)]. The constant of 11.5 was not derived from the Clausius-Clapeyron equation and Trouton's rule, but was a mean value obtained from consideration of a large number of hydrocarbon mixtures, mostly wide boiling. The constant obtained in the theoretical derivation was 11.1. Converting natural to common logarithms, this is nearly the same as the modified constant proposed in Griswold's Equation 4A. Thus it appears that the "constant" varies from 11.1 for close-boiling to 11.5 or more for wide-boiling mixtures.

If the approximate Clausius-Clapeyron equation is combined with Kistiakowsky's equation instead of with Trouton's rule, the following is obtained:

$$\log \alpha = \frac{T - T_A}{T} \log T_A + \frac{T_B - T}{T} \log T_B + \frac{T_B - T_A}{T} \log R$$

where R = gas constant, (cc.) (atm.) (° C.)$^{-1}$ (mole)$^{-1}$ = 82.048
P_A P_B = vapor pressures of components at abs. temp. T
T_A T_B = atm. boiling points of components, abs. scale
α = relative volatility at abs. temp. T

This equation applies only to nonpolar liquids at atmospheric pressure when the gas law and Raoult's law deviations are such that the relation $\alpha = P_A/P_B$ can be assumed. It contains no empirical constant and is likely to be more accurate than my earlier equation. Checked against the experimental results of Griswold and a few others, it gives values of $(\alpha - 1)$ from 4 to 15 per cent low.

R. Edgeworth-Johnstone

Trinidad Leaseholds, Ltd.
Pointe-a-Pierre, Trinidad, B. W. I.

SIR: The new formula by Johnstone for calculating α_{ideal} ($= P_A/P_B$) is a real contribution. It is probably as accurate as can be developed from theoretical considerations only without becoming complicated.

For accuracy in wide-boiling hydrocarbon systems, both this formula and my Equation 6 leave something to be desired. When the vapor pressure curve of each component fits the type form equation:

$$\log P = a - b/T$$

as is usually the case, then:

$$\log (\alpha_{\text{ideal}}) = \log (P_A/P_B) = \beta/T - \gamma$$

β and γ are constants applicable over fairly wide ranges. Two vapor pressures for each component are needed to evaluate β and γ, one of which may be the normal boiling point. When a vapor pressure curve has not been determined, a synthetic curve may be drawn through the boiling point on a suitable hydrocarbon vapor pressure chart, of which several are available.

This procedure is recommended as the best at the present time for calculation of α_{ideal} of wide-boiling hydrocarbon systems, and it is applicable to pressures other than atmospheric.

John Griswold

The University of Texas
Austin, Texas

• • •

SIR: I am obliged to Griswold for his remarks on my formula for α, and agree that with wide-boiling components for which vapor pressure curves are available or can be approximated, his method is probably better than any theoretical formula. With very close-boiling components it is possible that the formula might be more satisfactory, since atmospheric boiling points are often known with greater accuracy than vapor pressures at other temperatures.

R. Edgeworth-Johnstone

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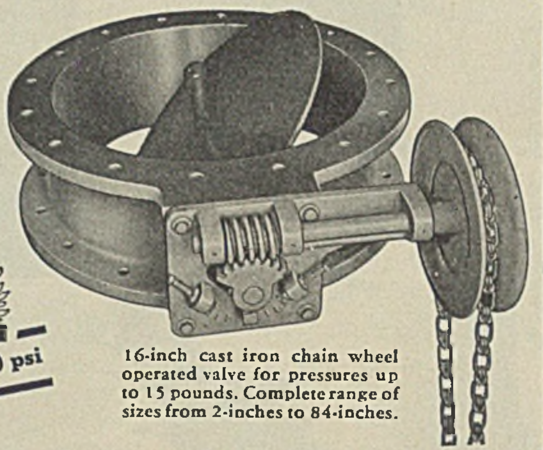

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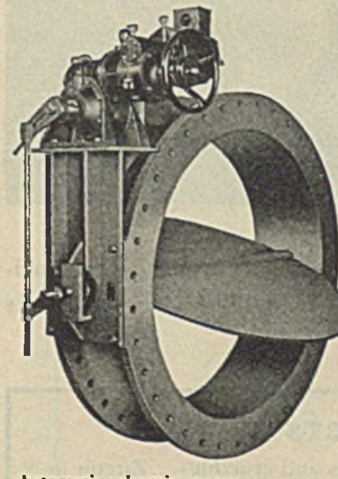

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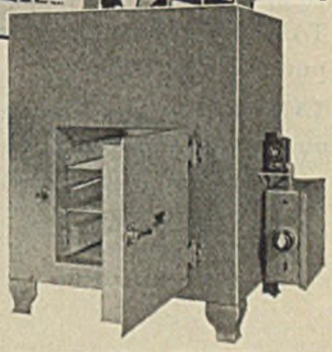


Despatch V-15 Oven; 13"x13"x13" inside. Electric. Max. heat 500°F. Control accuracy ± 1°C.

ASK YOUR CHEMICAL JOBBER
or write to Despatch Oven Co.

DESPATCH OVEN COMPANY MINNEAPOLIS

Perhaps REVERE can help you with your NON-FERROUS

Heat Exchanger tubes and shells

Intercoolers

Receivers

Strainers

Evaporators

Water treating equipment

Revere is trying in every way to help iron out kinks in war production problems for old and new users of copper and copper alloys. In addition to supplying condenser and heat exchanger tubes and tube plates, Revere may be able to give first aid to you in one or more of four ways:

1 **Revere copper and copper-base alloys** . . . sound, superior metals produced in a range of compositions and forms meeting the special requirements of war processes.

2 **Revere Bimetal** . . . where war requirements and service conditions demand, Revere can supply bonded Bimetal sheets and plate of S.A.E. 1010 carbon steel clad on one or both sides with copper as well as with certain other metals and alloys.

3 **Welding technique** . . . *practical* assistance in welding these products, which will aid in the completion of equipment *when* needed and insure uninterrupted service.

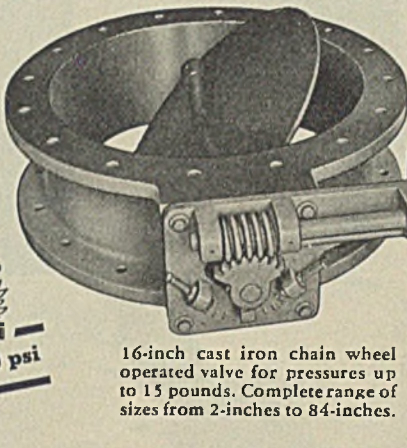
4 **Revere Engineering Service** . . . to help Revere customers in the selection of metals and in methods of fabrication so as to save time, increase output and reduce costs wherever possible.

If you have special problems, send us specifications and full details of your requirements. We will endeavor to supply an answer promptly. Get in touch with Revere today.

REVERE
COPPER AND BRASS INCORPORATED
Founded by Paul Revere in 1801
Executive Offices: 230 Park Avenue, New York
Sales Offices and Distributors in Most of America's Major Cities

Easy to Operate...

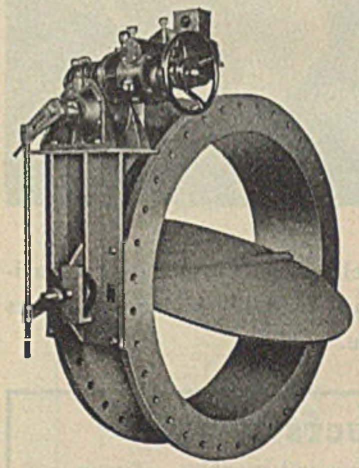
Streamlined for Self-Cleaning



R-S QUALITY PRODUCTS SINCE 1908

15 to 900 psi

16-inch cast iron chain wheel operated valve for pressures up to 15 pounds. Complete range of sizes from 2-inches to 84-inches.



Automatic electric-motor operated American Standard Valve with hand wheel for manual operation in case of current failure. Available in 125 lb iron, 150 to 900 lb steel.

THE ACTION of an R-S Butterfly Valve is rapid and smooth. Four to six revolutions of the hand wheel or chain wheel fully open or close the valve vane. The compact, inherently narrow face-to-face dimensions, and the fact that there is no long stem or gate well, reduce clearance requirements to the minimum.

There is free passage for direct flow with no restrictions other than the streamlined vane. Sediment cannot collect since there are no right angle bends or reverse turns. Hence, the R-S Valve is ideal for the control and shut-off of dirty gas, dirty water, pulverized fuel or similar flowing solids.

The beveled vane wedges tight against the valve body for shut-off duty.

Write for catalog and detailed information about the use of R-S metals for resistance against heat, abrasion and corrosion.

VALVE DIVISION
R-S PRODUCTS CORPORATION
Germantown Ave. & Berkley Sts., Phila., Pa.

R-S Streamlined BUTTERFLY VALVES

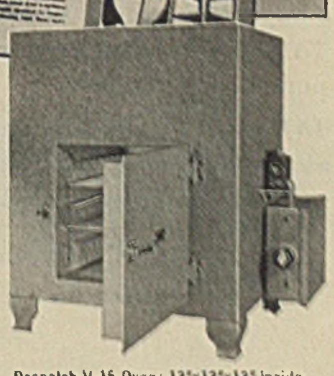
THE LABORATORY OVEN YOU'VE BEEN LOOKING FOR!

SAVES TIME!
FAST HEAT RECOVERY and rapid heat transfer in *Despatch* Ovens increases the number of test-runs per day.

ACCURACY GUARANTEED!
POSITIVE TEMPERATURE CONTROL and heat uniformity in the work chamber guarantees accuracy.

100% DEPENDABLE!
FOR OVER 41 YEARS *Despatch* Ovens have proven dependable for the exacting requirements of Laboratory Technicians.

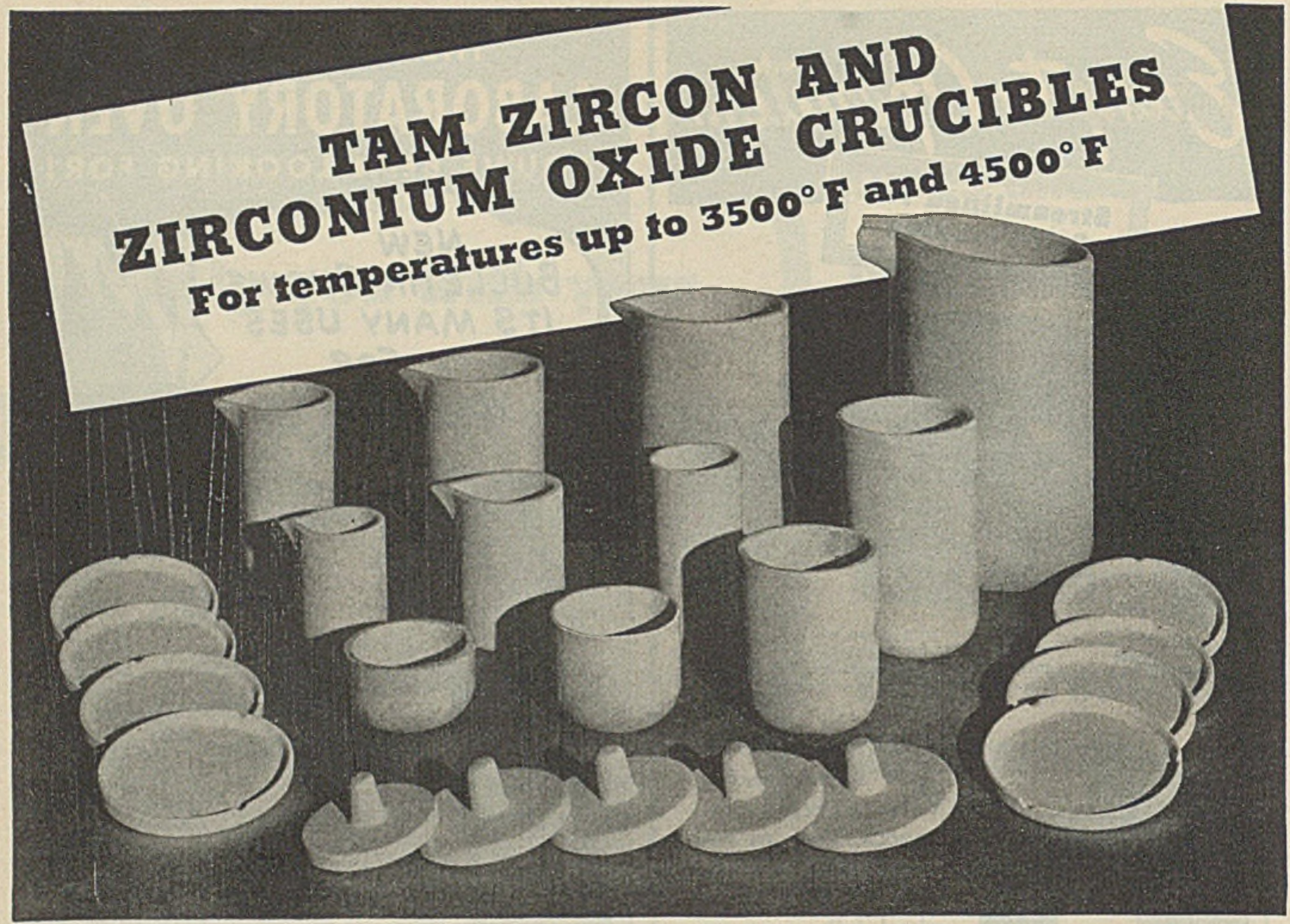
Send for Your Copy of Bulletin 105-N Today!



Despatch V-15 Oven; 13"x13"x13" inside. Electric. Max. heat 500°F. Control accuracy ± 1°C.

ASK YOUR CHEMICAL JOBBER
or write to Despatch Oven Co.

DESPATCH
OVEN COMPANY MINNEAPOLIS



TAM Zircon crucibles are finding wide application for various high temperature applications up to 3500° in non-ferrous melting such as aluminum, platinum, etc. These Zircon crucibles not only resist various acid and alloy reactions, but due to the straight line expansion coefficient of Zircon, exhibit exceptionally good heat shock properties. Refractory bonds consisting of other compounds are not necessary in the manufacture of TAM Zircon crucibles thereby assuring the user of a pure Zircon product.

TAM small crucibles and shapes of semi-vitreous Zirconium oxide are manufactured for use in quartz fusions and high temperature applications up to 4500° F.

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

FOR VICTORY
Buy
U. S. War
Bonds and
Stamps

GENERAL OFFICES AND WORKS: NIAGARA FALLS, N. Y., U. S. A.
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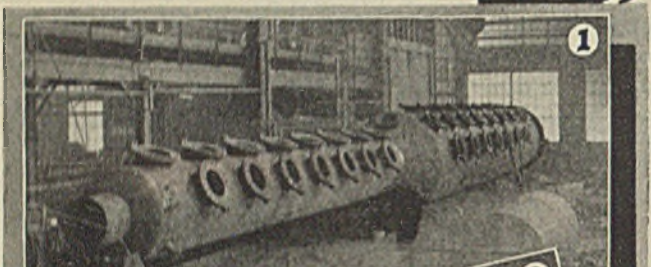
LUBRICANT
IMPREGNATING MEDIUM
ELECTRICAL CONDUCTOR
HIGH TEMPERATURE LUBRICANT
OPAQUE FILM
PARTING COMPOUND


dag
colloidal graphite

A.P.I.—A.S.M.E. and A.S.M.E. CODES • CARBON STEEL AND SPECIAL STEEL

WELDED PRODUCTS *by* Vogt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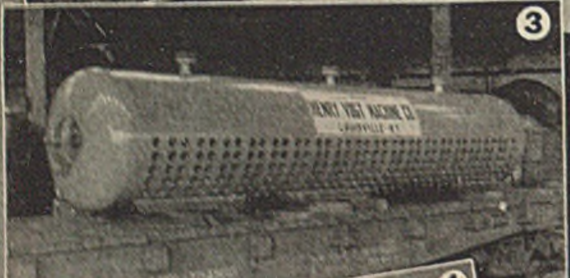
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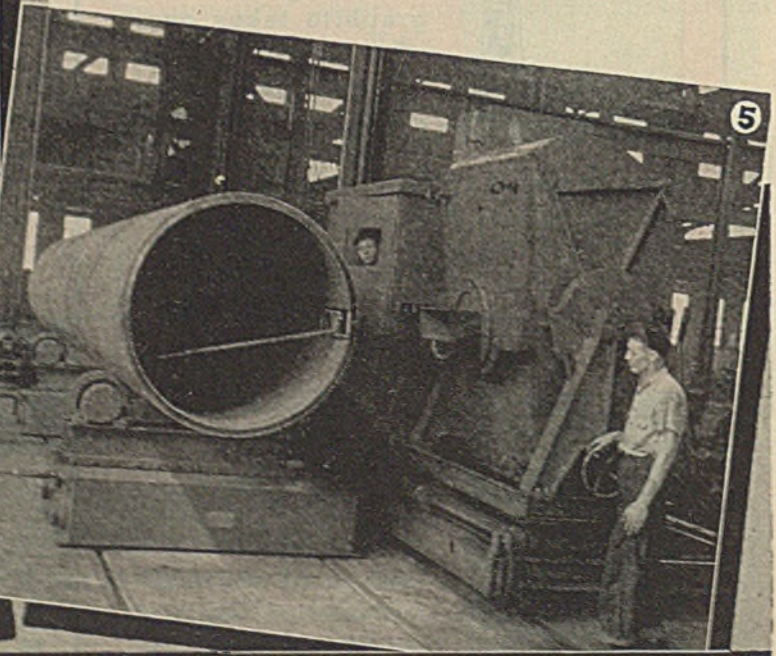

⑤

1 - 4′—0″ dia. x 7′—6″ dia. x 82′—5″ high Stabilizer Tower for a Texas Refinery. Fabricated to A.P.I.-A.S.M.E. Code, stress relieved and X-rayed. 250# working pressure.

2 - Heat Exchangers, for an Eastern Refinery, on the testing floor. Units have fusion welded Monel Metal shells and were built to customer's specifications.

3 - 48″ dia. x 22′—6″ long mud drum for a Vogt Water Tube Boiler designed to operate at 450# S.W.P. Fusion welded to A.S.M.E. Boiler Code.

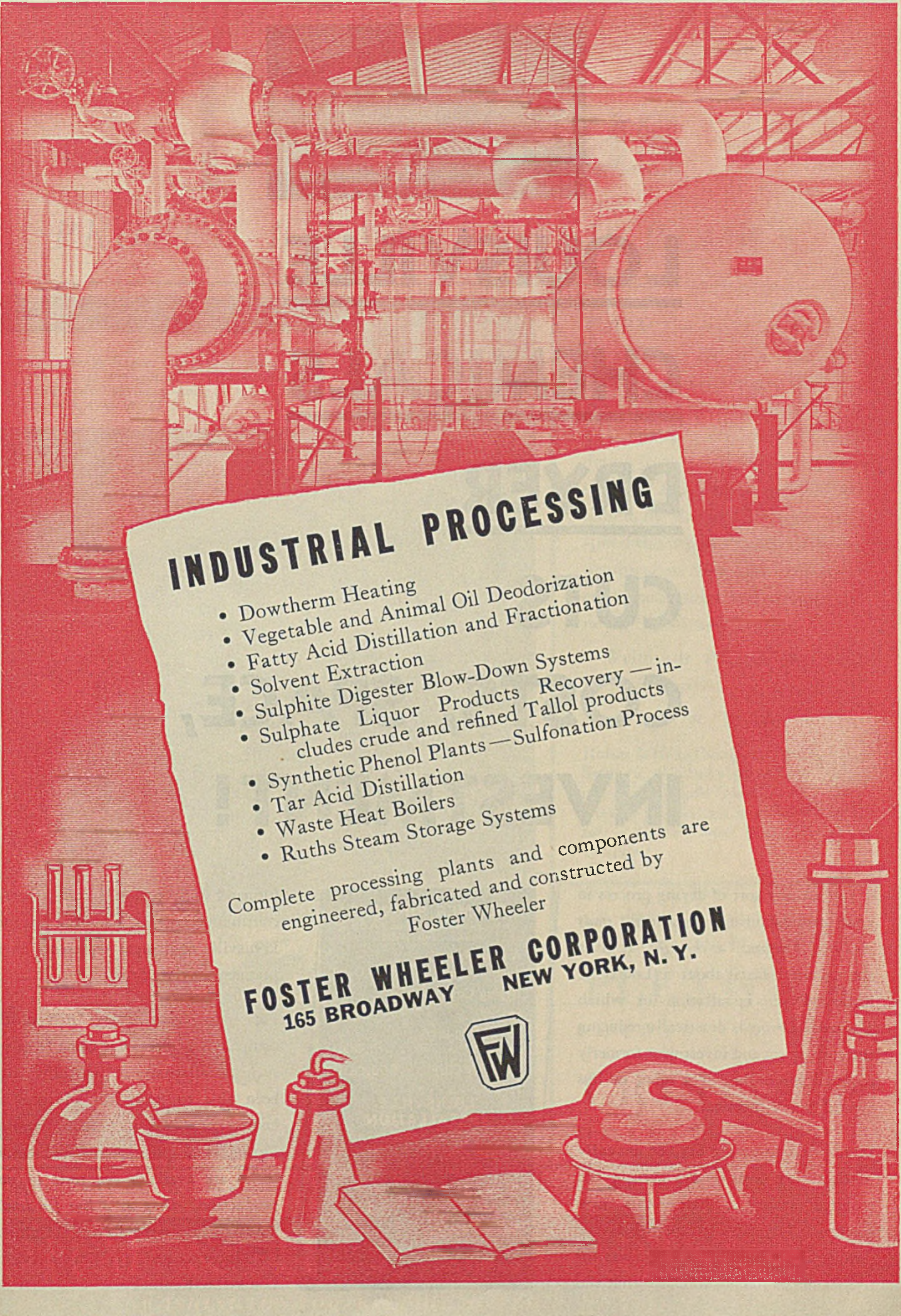
4 - Battery of Absorption Columns in a Western Refinery. Units are 33″ dia. x 41′—0″ high and were stress relieved after welding.

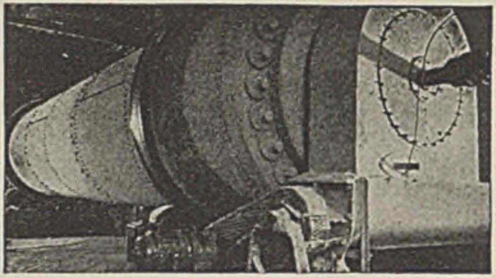
5 - 400 KV Industrial X-ray unit in our plate welding department. Exographs of welded seams can be quickly made because of the special motor operated rolls and traveling carriages which are adjustable to vessels of any size.

Vogt FOR BETTER PRODUCTS


VIEW OF 18 ACRE VOGT PLANT

HENRY VOGT MACHINE CO.
Incorporated
LOUISVILLE, KENTUCKY
BRANCH OFFICES: NEW YORK - PHILADELPHIA - CLEVELAND - CHICAGO - DALLAS





LOUISVILLE CHEMICALS DRYER CUTS COSTS, SPACE, INVESTMENT!

If you use any sort of drying process in your manufacturing operations, *study the little "blueprint" at the right*. It gives the essential facts about a Louisville Rotary Dryer installation in which *Engineered Drying* is drastically reducing the cost, space and investment formerly required for drying of a more or less typical heavy chemical. . . .

In addition to saving $13,680 annually in operating costs — and cutting the required space in half — this new Louisville Dryer is also solving a very serious dust problem which was in itself a major item. Note also that the former batch process is now a rotary, continuous process, and that the new Louisville equipment represents an investment of only $7,000!

FORMER PROCESS

(Steam-jacketed filter presses with hot air introduced under pressure)

Annual Production, tons	18,000
Drying Cost, per ton	$1.30
Space Required, sq. ft.	1,000
Installed Cost	$55,000

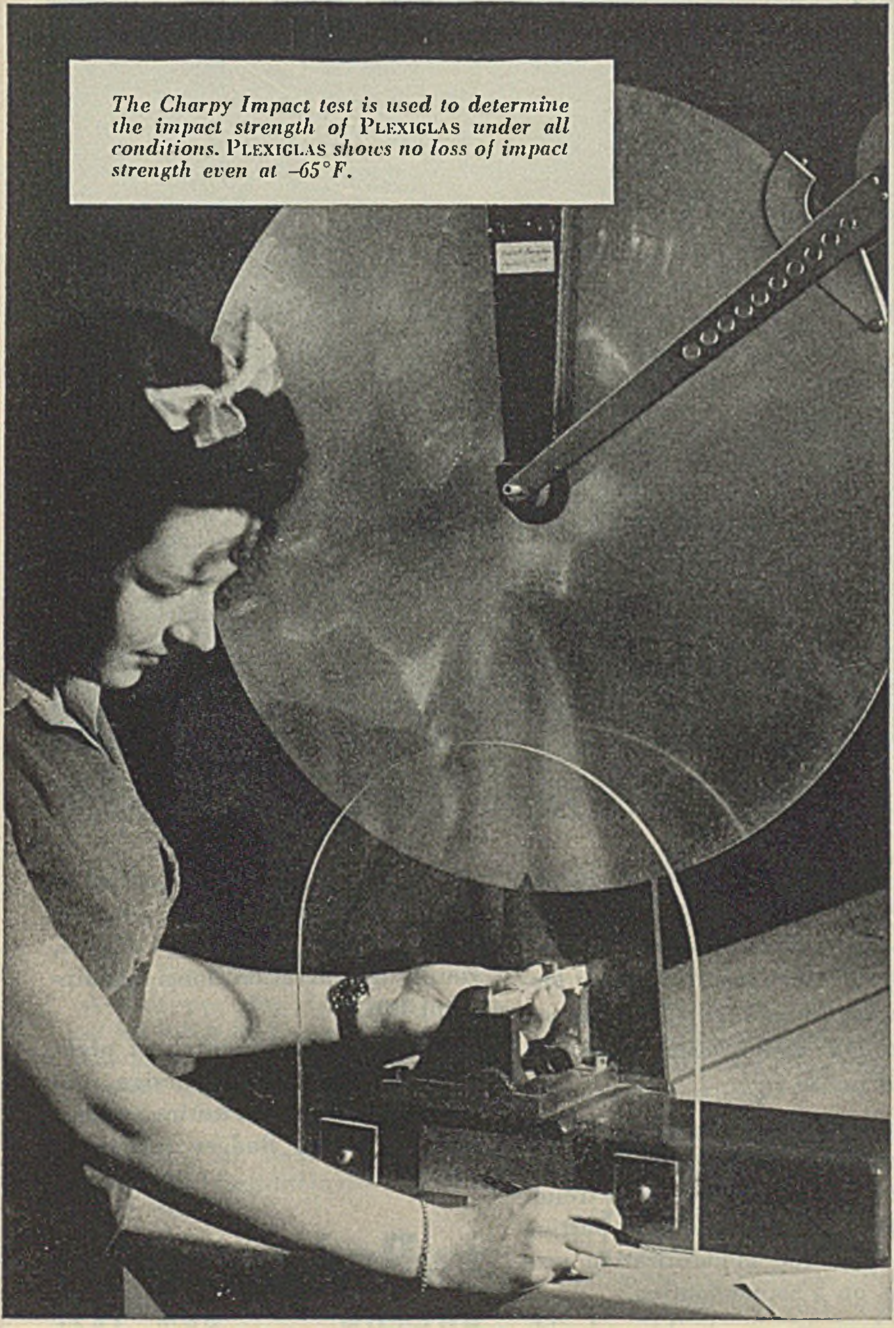
LOUISVILLE INSTALLATION

(Louisville Rotary Steam Tube-Dryer)

Annual Production, tons	18.000
Drying Cost, per ton	$0.54
Space Required, sq. ft.	450
Installed Cost	$7,000

For many years a large part of this company's business has come from just such installations, in which we have been able to prove, in advance, the lasting economies of real *Engineered Drying*. Our pilot plants and laboratories are available for tests of your production. *Drop us a line for details. Address:* Louisville Drying Machinery Co., Incorporated, 433 Baxter Avenue, Louisville, Kentucky.

IMPACT STRENGTH OF
Plexiglas
PROVED BY MEASURED BLOWS



The Charpy Impact test is used to determine the impact strength of PLEXIGLAS *under all conditions.* PLEXIGLAS *shows no loss of impact strength even at –65°F.*

IMPACT strength, tensile, compressive, flexural, and shear strength, hardness and cold flow are a few of the important PLEXIGLAS properties described in detail in the new PLEXIGLAS *Mechanical Properties* Manual. Published by Rohm & Haas to help speed the use of PLEXIGLAS in war production, this new handbook contains graphs and photographs never published before.

Write our Philadelphia office for your copy.

★ ★ ★

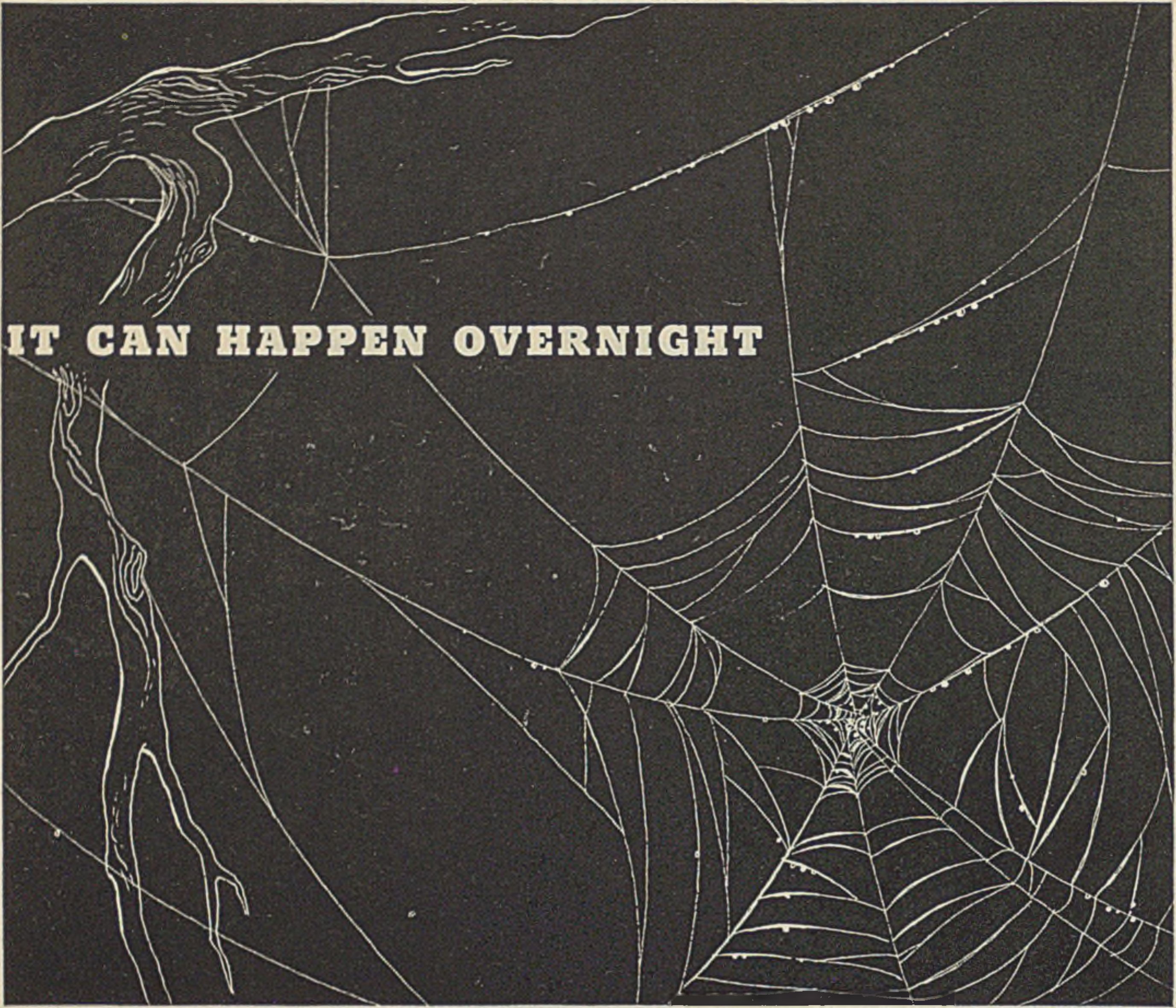
Rohm & Haas Company, Washington Square, Philadelphia, Pa. *Other offices in:* South Gate, Los Angeles—Detroit—Chicago. *Canadian Distributor* — Hobbs-Glass Ltd., Montreal, Canada.

THE CRYSTAL-CLEAR
ACRYLIC PLASTICS
PLEXIGLAS
SHEETS AND RODS
★
CRYSTALITE
MOLDING POWDER

PLEXIGLAS *and* CRYSTALITE *are the trade-marks, Reg. U. S. Pat. Off., for the acrylic resin thermoplastics manufactured by the Rohm & Haas Company.*

ROHM & HAAS COMPANY
WASHINGTON SQUARE, PHILADELPHIA, PA.

Manufacturers of Chemicals including Plastics . . . Synthetic Insecticides . . . Fungicides . . . Enzymes . . . Chemicals for the Leather, Textile and other Industries


IT CAN HAPPEN OVERNIGHT

"I like the way they engineer 'em"

HE DESIGNS PIPING . . . One of the most important parts of his job is making dead sure that the strength of every part of the system is equal to the strain imposed on it.

WeldELLS and other Taylor Forge Welding fittings* are in key with this:

—They have extra reinforcement of the inner wall where stress is greatest.

—They have full pipe thickness at the outer wall.

—They have tangents that keep the weld away from the zone of greatest stress.

—They meet every condition; are made in a wider range of sizes, materials and thicknesses than any other welding fittings.

In short, they are the fitting that gives the engineer *everything* he wants—at no extra cost.

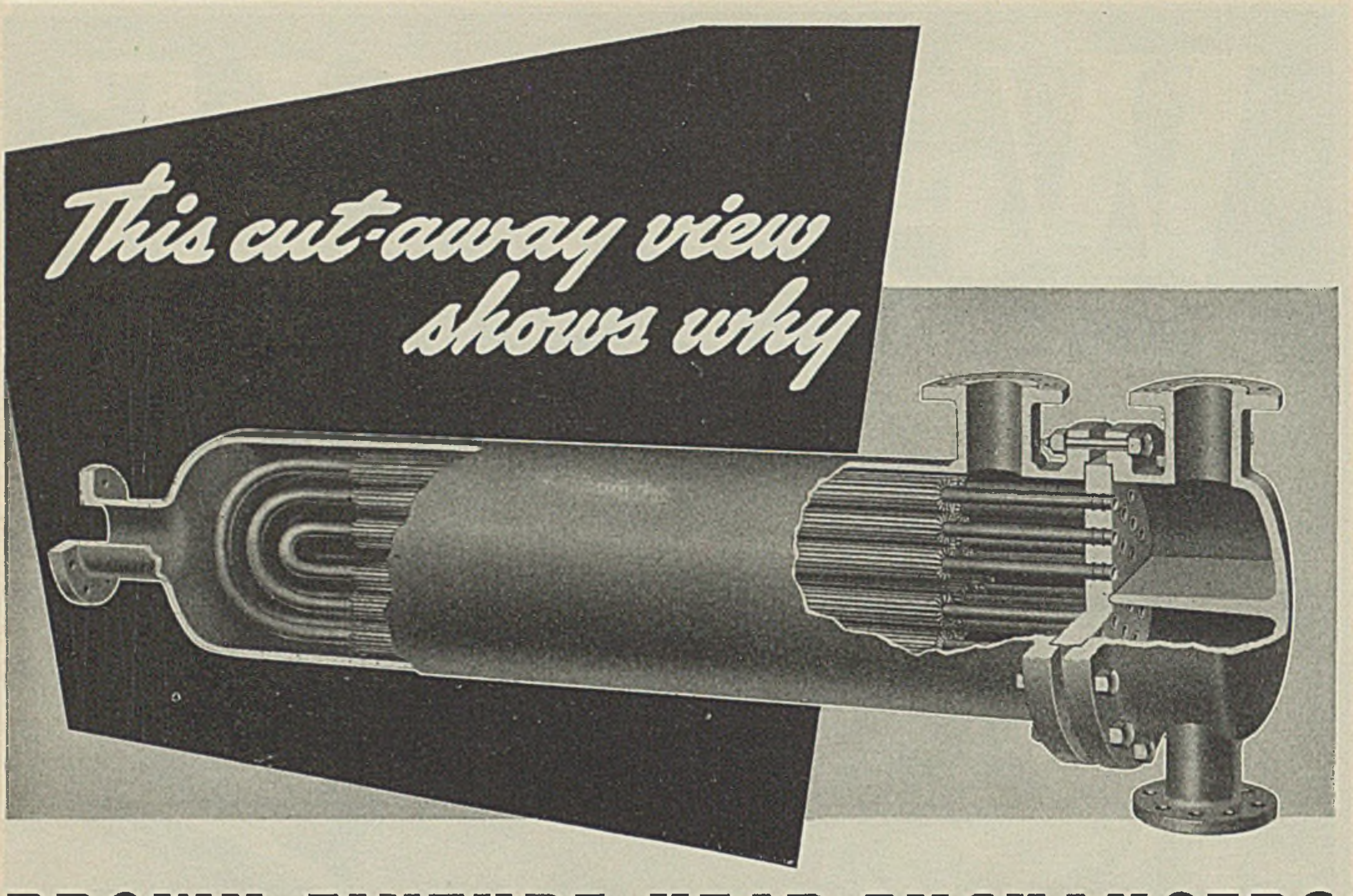
TAYLOR FORGE & PIPE WORKS
General Offices & Works:
Chicago, P. O. Box 485
New York Office: 50 Church St.
Philadelphia Office: Broad St. Station Bldg.

* WeldELLS and many other Taylor Forge products are produced in Byers Genuine Wrought Iron.

★ WeldELLS have every feature found in any welding fitting; some features found in no other fittings:

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

• The list of Taylor Forge's contributions to the war effort only begins with WeldELLS. Every Taylor Forge product is playing a vital part. One of many examples is Forged Steel Welding Nozzles, essential to hundreds of transports and fighting ships.



BROWN FINTUBE HEAT EXCHANGERS

Give extra capacity for any exchange between liquids and gases... or other materials having unequal heat transfer co-efficients

● Because Brown integrally bonded Fintubes, having the desired number and depth of fins, are used in effecting the heat transfer,—the primary and secondary tube surfaces of Brown Fintube Heat Exchangers can be proportioned to the transfer co-efficients of the materials being heated or cooled, thereby compensating for any deficiency in the heat transfer rate of one or another of the commodities.

This avoids the necessity of using hundreds, sometimes thousands of feet of bare tubing to satisfy the requirement of the commodity having lower heat transfer co-efficient. It permits a fewer number, or shorter, Brown Fintubes to be used for a given heat transfer service than if plain bare tubes were used . . . and results in smaller shells, less back pressure, less pressure drop, and many other important savings in manufacturing, shipping, installation and maintenance costs.

Six standard and many special types of Brown Fintube Heat Exchangers meet every requirement for effecting transfers between liquids and gases, or other commodities having unequal transfer co-efficients,—and provide the high thermal efficiency and trouble-free operation that only Brown resistance-welded integrally bonded Fintubes can give you.

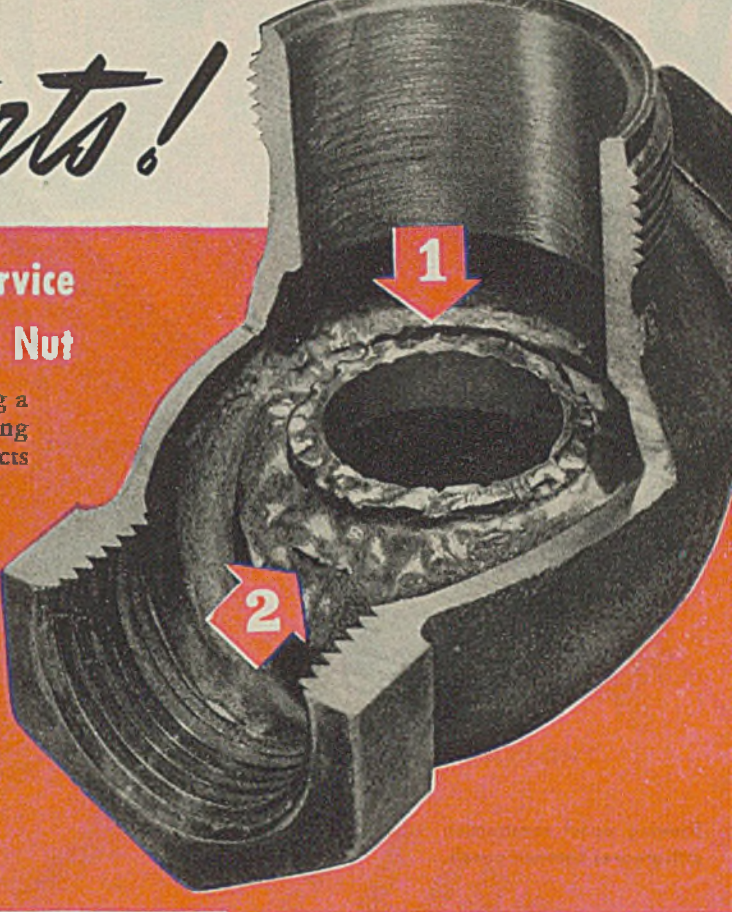
More complete details, engineering assistance, estimates, and descriptive literature furnished gladly on request. Let us quote on your heat exchanger requirements.

Brown Integrally Bonded Fintubes are used in all Brown Fintube Heat Exchangers—in exchangers made by most other manufacturers—and are available in a wide variety of sizes, and in mild carbon or special steels, for practically any heating or cooling requirement.

THE BROWN FINTUBE CO.

120 FILBERT STREET • ELYRIA, OHIO

MANUFACTURERS OF INTEGRALLY BONDED FINTUBES AND FINTUBE HEAT EXCHANGERS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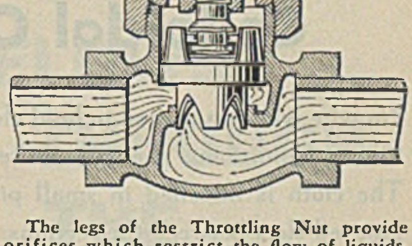
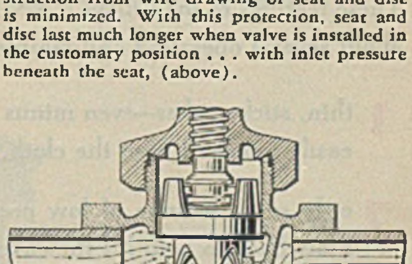
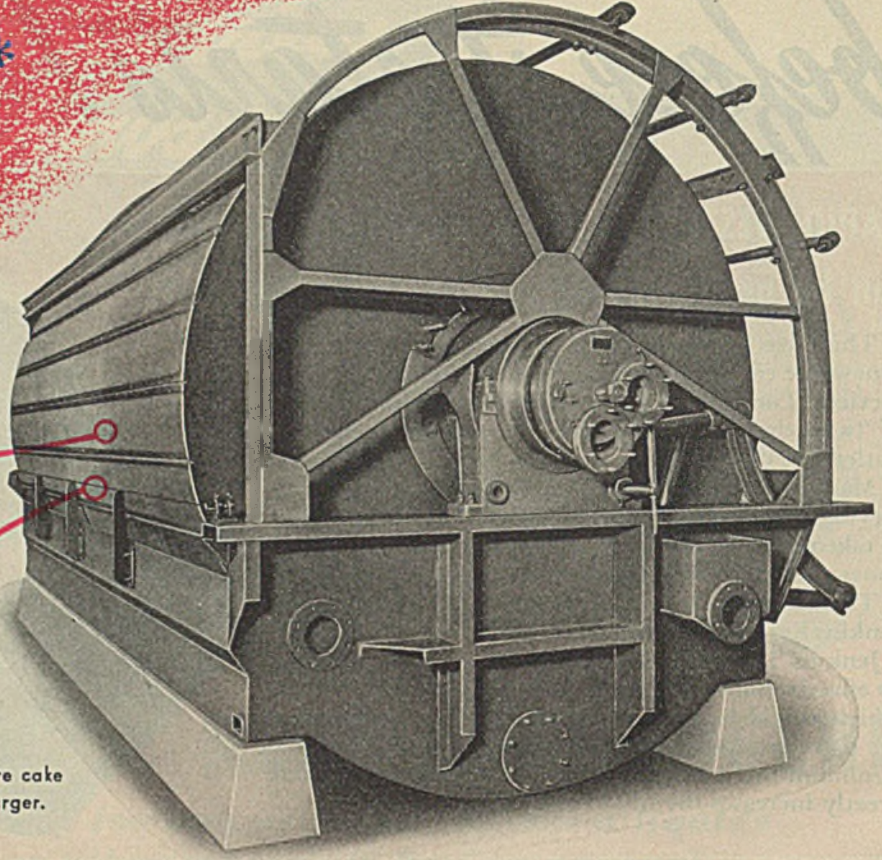




OLIVER PANEL TYPE FILTER*



Showing panel construction with grooves between panels.

Tight-wire cake discharger.

Best for Pulps Forming Thin, Sticky, Colloidal Cakes That Must Be Recovered

No wire winding is used to hold cloth on the drum of this Oliver Continuous Vacuum Filter except on the ends. The cloth is installed in small pieces and caulked into grooved slots between the sections. Cake is discharged by an ingenious cross-wire device.

These features of the Oliver PANEL TYPE Filter* bring about several operating and maintenance advantages:

1. thin, sticky cakes—even minus 1/16th of an inch—are easily removed from the cloth.
2. only small volume of low pressure air is needed for blow back to help lift the cake from the drum.
3. worn cloths are replaced in small sections; or holes can be readily patched.

Commercial sizes of Oliver PANEL TYPE Filter,* now being used on many different products, have already proved their operating effectiveness and low maintenance cost. If you are handling a product which you believe would be suitable for this filter, tell us about it. If you have *any other* filtration or clarification problem, consult us about that, too. Our experience in installing more than 16,000 filters of various types should be helpful.

When the cake is sticky or colloidal but is to be discarded, we recommend investigation of the Oliver Continuous Precoat Filter.

*PATENTED

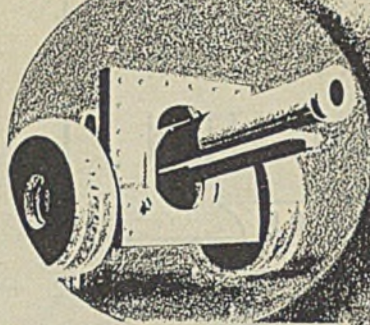
OLIVER UNITED FILTERS INC.

New York, N. Y.
33 West 42nd Street

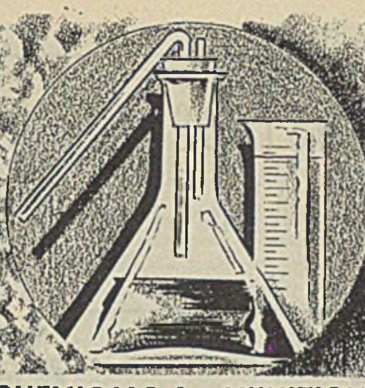
San Francisco,
California

Chicago, Ill.
221 N. LaSalle Street

Western Sales Division
Oakland, Calif.

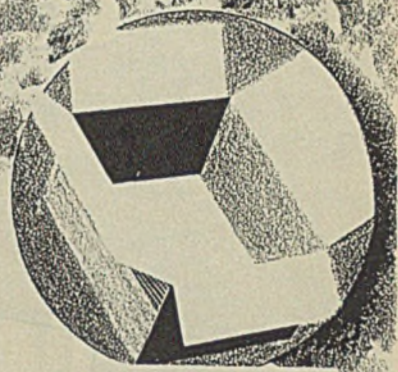


STEEL for ARMAMENT



CHEMICALS for MUNITIONS and SANITATION

LEATHER for SHOES



BOXBOARD for SUPPLY CARTONS

MARBLEHEAD

HIGH-CALCIUM CHEMICAL LIME

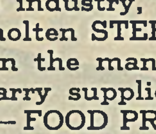
THE extent of Marblehead's participation in the production of war needs in industry, is amazing. It is extensively used to purify molten STEEL in open hearth furnaces, for armament — in the manufacture of BOXBOARD for cartons that carry supplies — in LEATHER for the service man's shoes — FOOD PRODUCTS for their mess — CHEMICALS for munitions and sanitation — WIRE for fences in field and camp — PAPER for Government records — PAINTS and VARNISHES, WHITEWASH and BRICKS for camp buildings and war plants — TEXTILES for uniforms and blankets — GREASES for lubricating machines — WATER TREATMENT for camps, factories, war-busy railroads and municipalities — and scores of other uses too numerous to mention.

In all of these applications, Marblehead Chemical Lime offers unusual chemical and physical qualities to do the job quickly, thoroughly, dependably, and at lowest cost. It has been outstanding in the field for over 70 years.

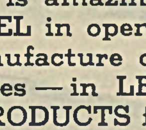
FLOWS ALL THROUGH THE WAR EFFORT

★ **FOUR FORMS** ★

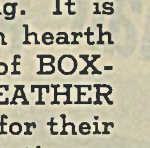
TRY A CAR NOW IN YOUR OWN PLANT



POWDERED QUICK LIME



PEBBLE LIME

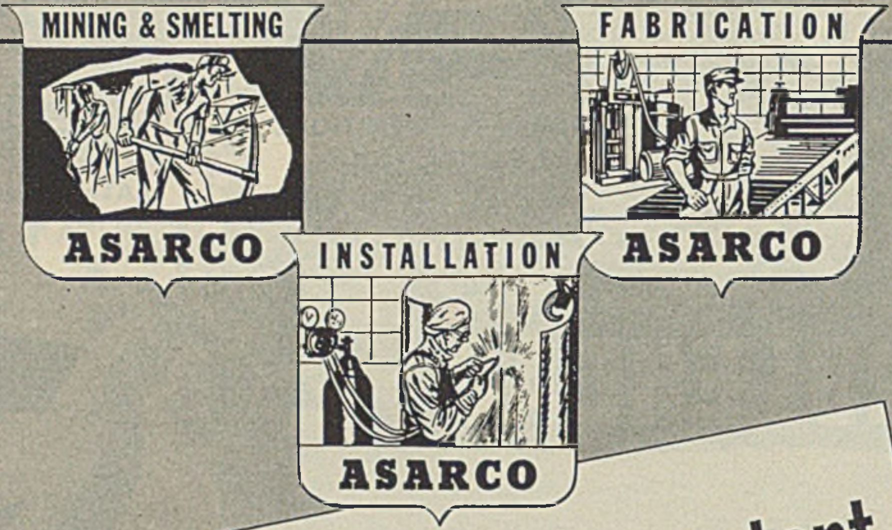


HYDRATED LIME

LUMP LIME

MARBLEHEAD LIME CO.

160 N. LaSalle St.
Chicago, Ill.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ASARCO
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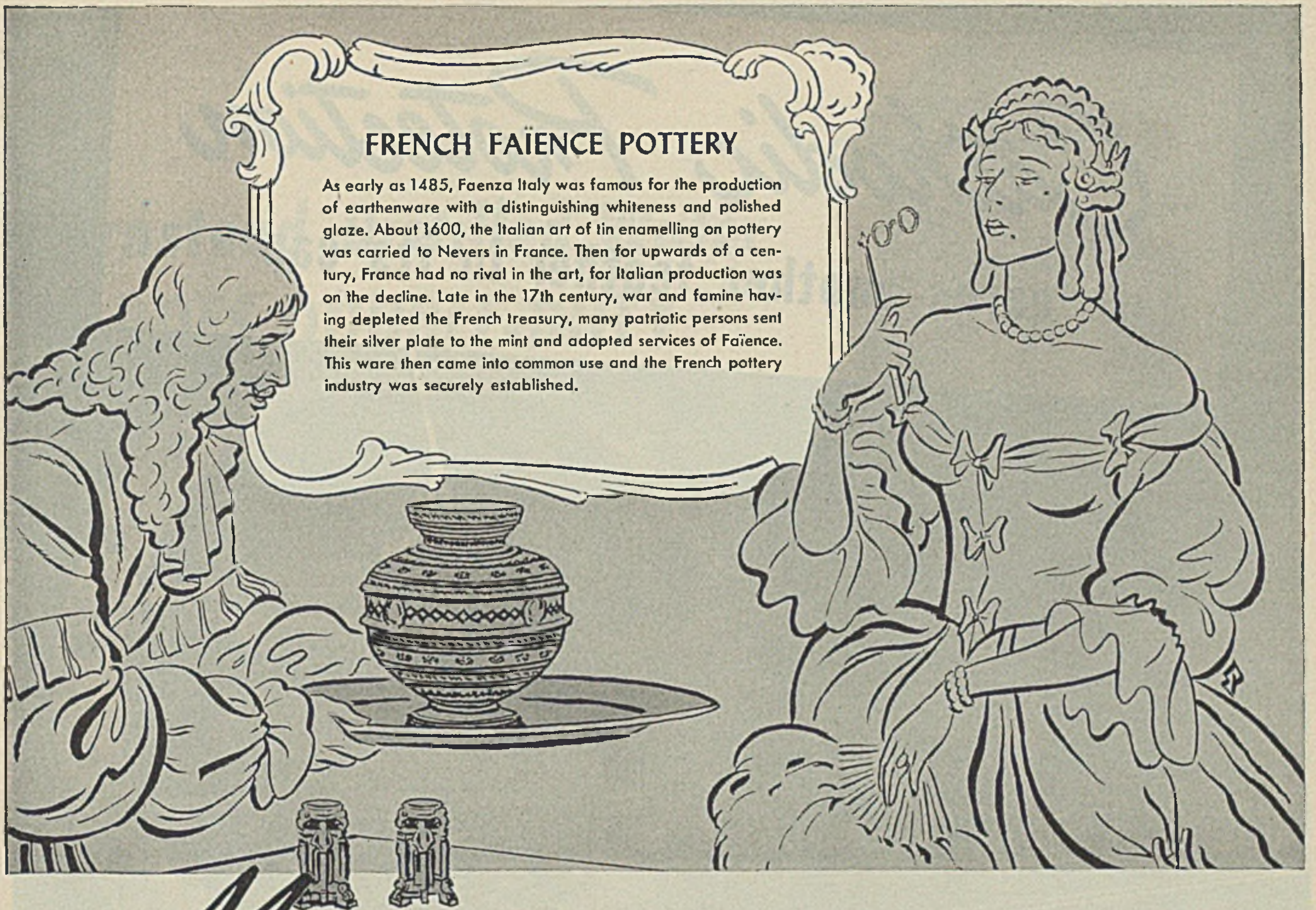
ASARCO



FRENCH FAÏENCE POTTERY

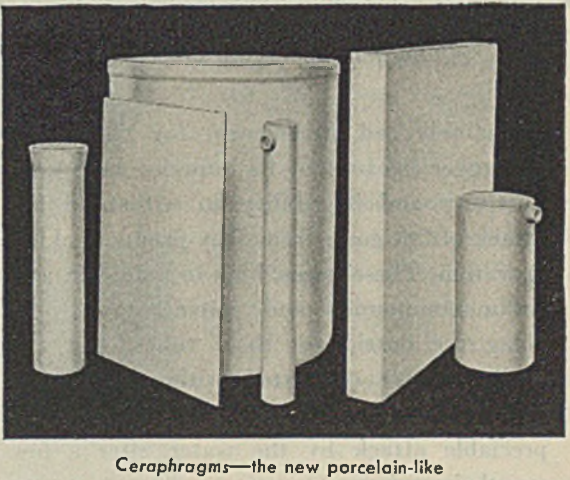
As early as 1485, Faenza Italy was famous for the production of earthenware with a distinguishing whiteness and polished glaze. About 1600, the Italian art of tin enamelling on pottery was carried to Nevers in France. Then for upwards of a century, France had no rival in the art, for Italian production was on the decline. Late in the 17th century, war and famine having depleted the French treasury, many patriotic persons sent their silver plate to the mint and adopted services of Faïence. This ware then came into common use and the French pottery industry was securely established.

Masterpieces **OF POTTERY**

IN THE 17TH CENTURY, pottery came into common use by the French people because of famine and depression. The birth of Chemical Stoneware, on the other hand, grew out of an advancing civilization. Its development was brought about through the stimulus of chemical advancement—the handling, in great quantities, of strong chemicals and corrosive liquids, requiring equipment that was non-corroding.

General Ceramics Chemical Stoneware, in addition to being acid-proof throughout, is built to withstand the roughest handling. Its glazed surface is easy to keep clean, thus eliminating product contamination.

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



Ceraphragms—the new porcelain-like porous diaphragms for electrolysis

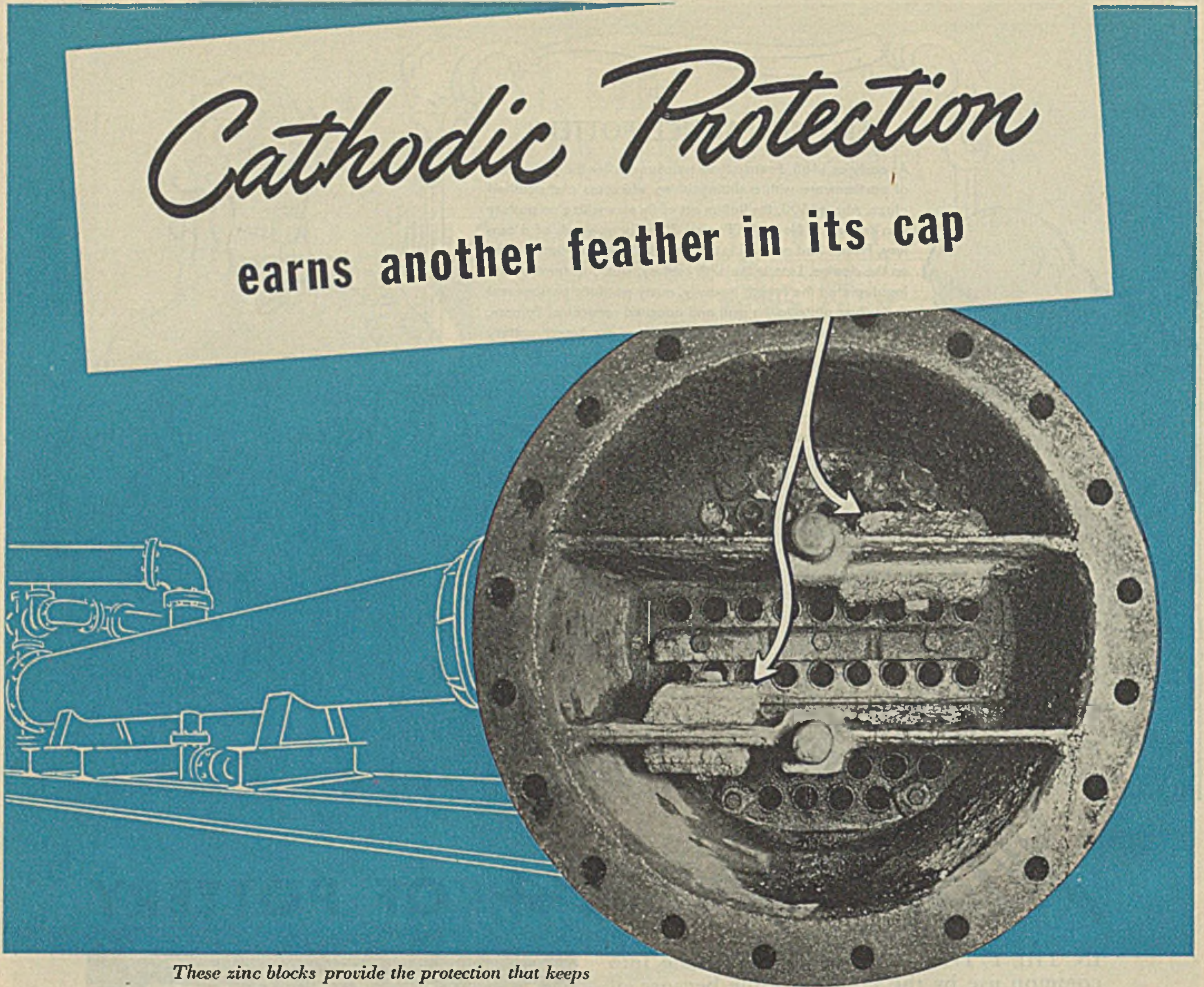
Other products include Steatite Insulators made by General Ceramics & Steatite Corp., Keasbey, N. J.

General Ceramics Co.

GENERAL CERAMICS COMPANY
CHEMICAL STONEWARE

CHEMICAL STONEWARE DIV.
KEASBEY • NEW JERSEY

3949



These zinc blocks provide the protection that keeps this aluminum alloy heat exchanger on the job.

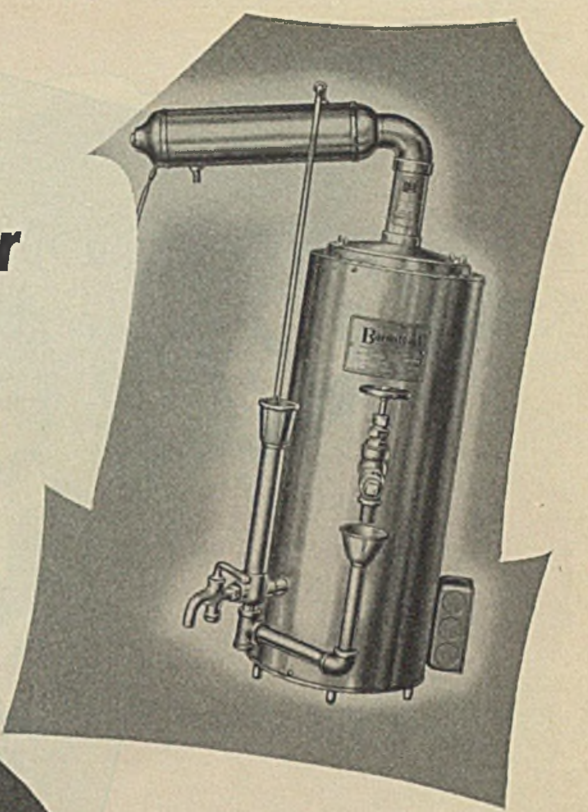
They selected aluminum for this heat exchanger because of its superior heat conductivity and its ability to withstand the attack of hot gases from a by-product coking operation. These gases, high in ammonia and sulfur compounds and water vapor, pass along the outside of these tubes. But the cooling water circulated within the tubes proved corrosive, and the tubes showed appreciable attack by the water after a few months' service.

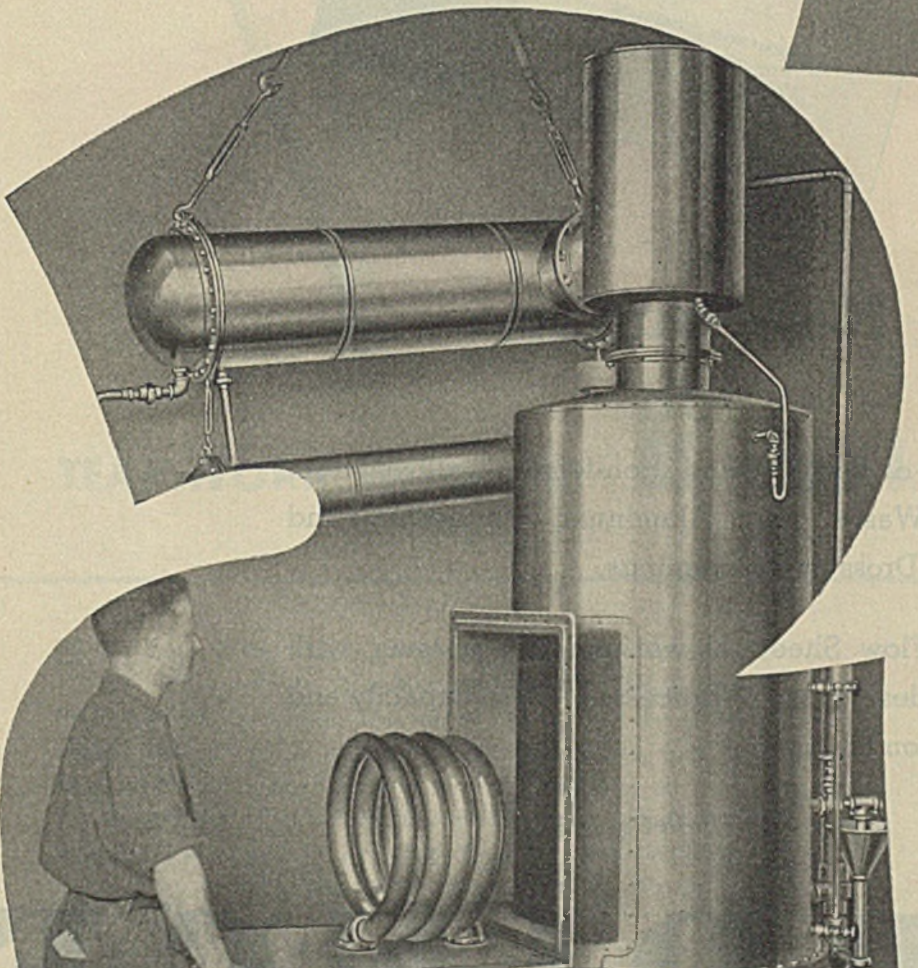
Samples of this water were submitted to Aluminum Research Laboratories for examination. Solution-potential measurements indicated that cathodic protection of the aluminum should be effective in this water, even at elevated temperatures. So the zinc blocks seen in the picture were installed.

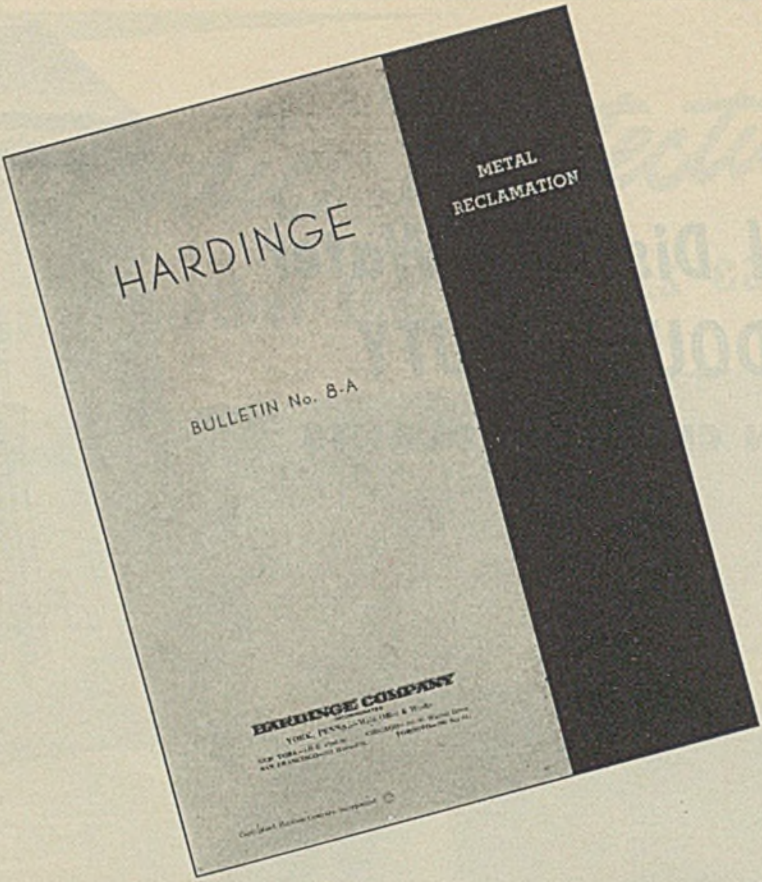
The heat exchanger has since been operated continuously for over a year. No leaks have developed. Examination of the tubes, by opening the ends of the cylinder, indicates that cathodic protection has been very effective in slowing down the attack. Analysis of the scale deposited in the equipment confirms this.

Have you the problem of making irreplaceable aluminum alloy processing equipment last longer? Alcoa engineers have been working on such problems for years. They may be able to aid you. ALUMINUM COMPANY OF AMERICA, 2154 Gulf Building, Pittsburgh, Pa.

ALCOA ALUMINUM





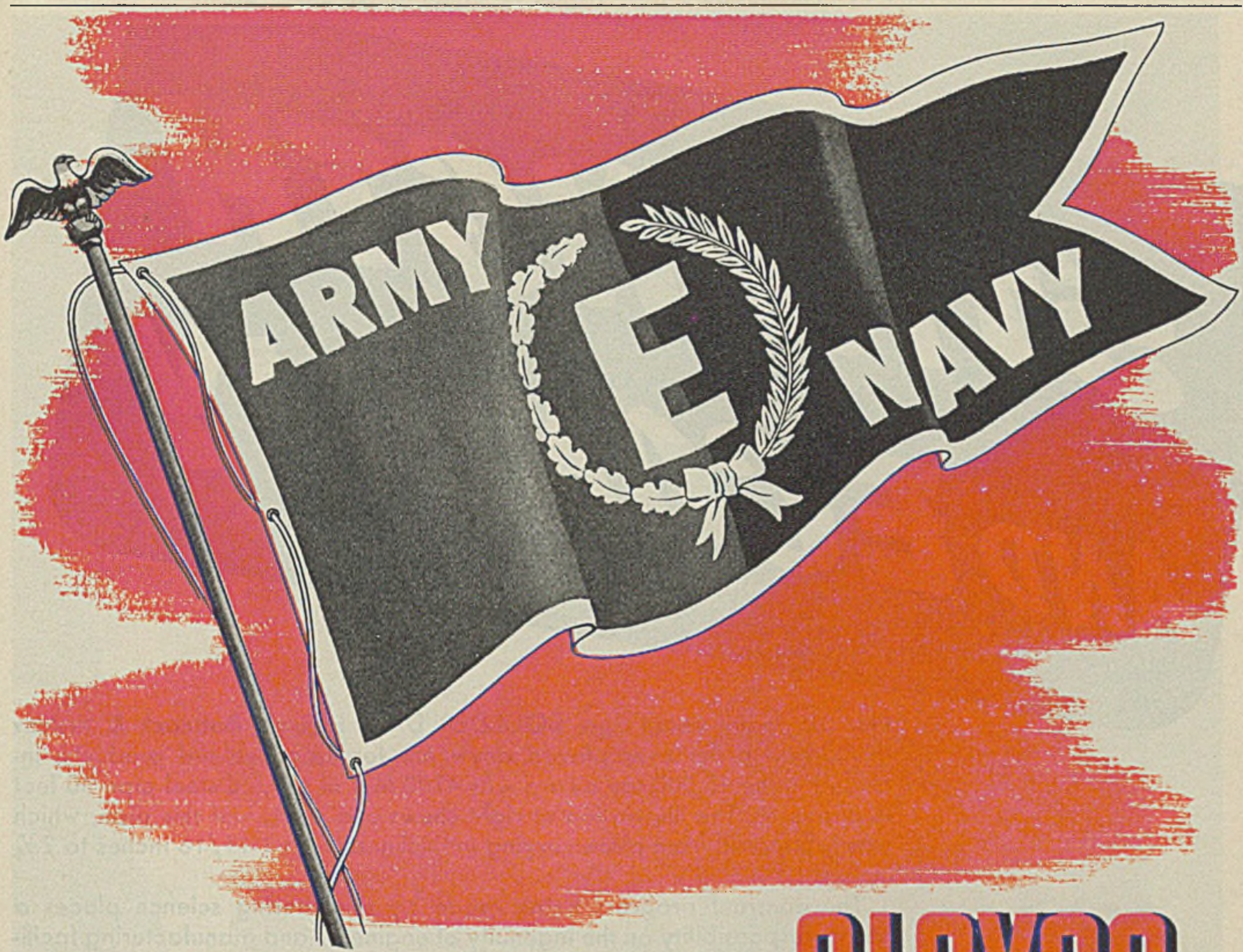


HARDINGE

METAL RECLAMATION

BULLETIN No. 8-A

HARDINGE COMPANY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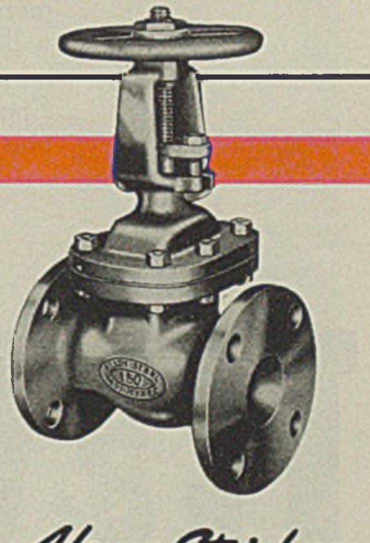


STRENGTH AND ECONOMY

Not too many years ago, BOULDER DAM brought Babcock & Wilcox the largest order ever placed anywhere for fusion-welded products. Included in the 45,000 ton award was 4700 feet of welded steel pipe 30 feet in diameter. The illustration at right shows one section of this pipe, which was fabricated from plate varying in thickness from 1-11/16 inches to 2¾ inches.

The constant progress being made by engineering science places a heavy responsibility on the ingenuity of engineers and manufacturing facilities. The successful fabrication of the Boulder Dam penstocks is only one of many examples of the way we have always gladly accepted our share of this responsibility, and have developed designs and fabricating processes which insure strength and uniformity of material structure in process equipment and economy in its application.

B&W Process Equipment includes vessels, drums, castings, forgings and tubular products for Oil Refinery apparatus, Gasoline Towers, Expansion Chambers and Alloy Castings. These are fabricated from carbon steel and the usual alloy steels, with welded seams, and in sizes limited only by railroad shipping clearances.

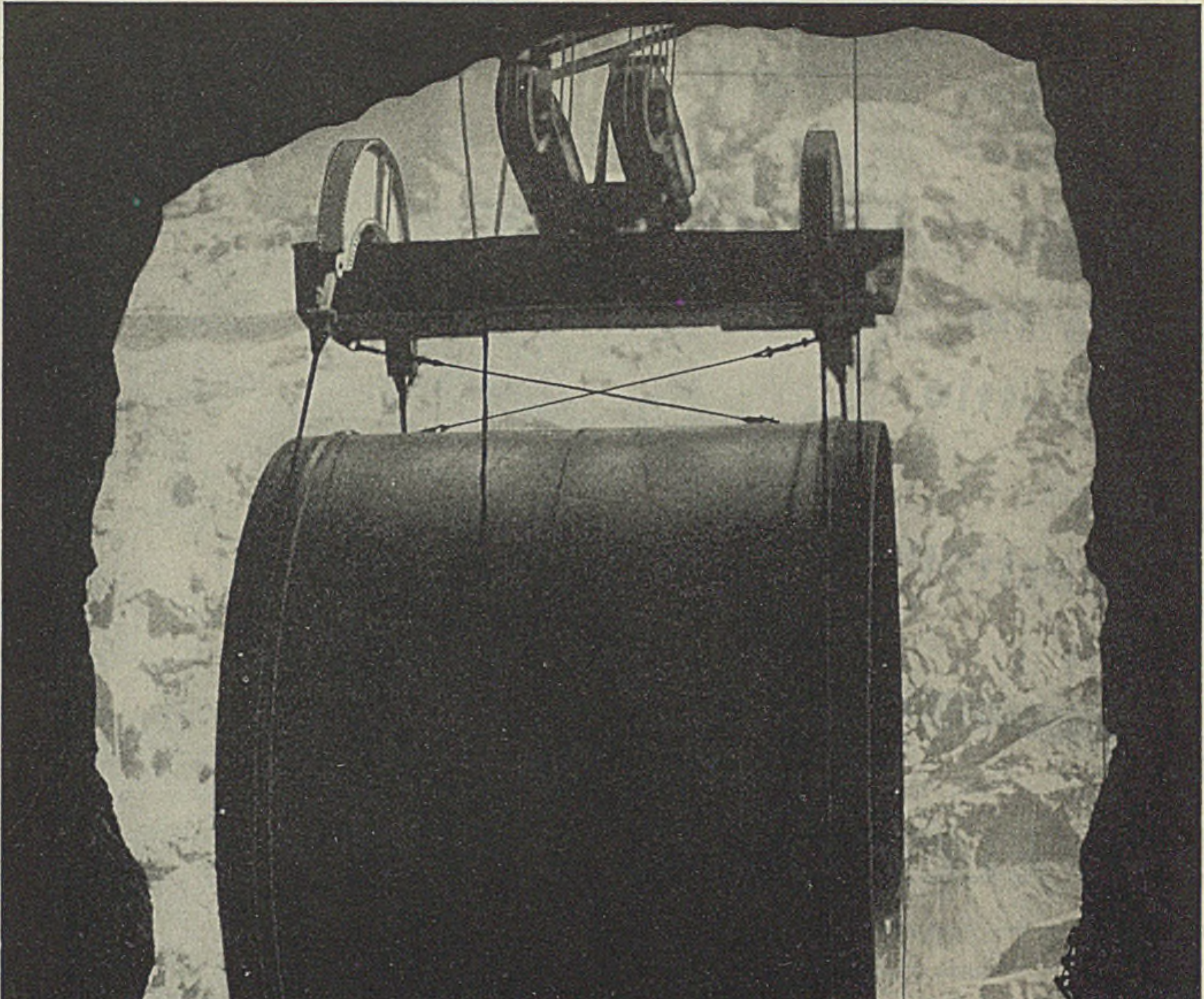
THE BABCOCK & WILCOX COMPANY
85 LIBERTY STREET, NEW YORK, N. Y.

IN

B&W PROCESS EQUIPMENT

for

high pressure and high temperature



EVERY ELLIOTT BLOWER

destined for use in the production of explosives (like all Elliott blowers) must first undergo a course of testing quite as severe in its way as that of an Air Force pilot or Commando soldier. These blowers must show that they have what it takes to fit into the high powered production schedule maintained in ordnance plants. Bearings must run cool at rated speed, and impellers must prove that they are properly balanced to the nicety required by this speed, and machined to the necessary precision needed in developing rated capacity.

A constant stream of Elliott blowers is moving into action to put smashing force into the loads that bombers carry, and to drive projectiles aimed at Axis annihilation.

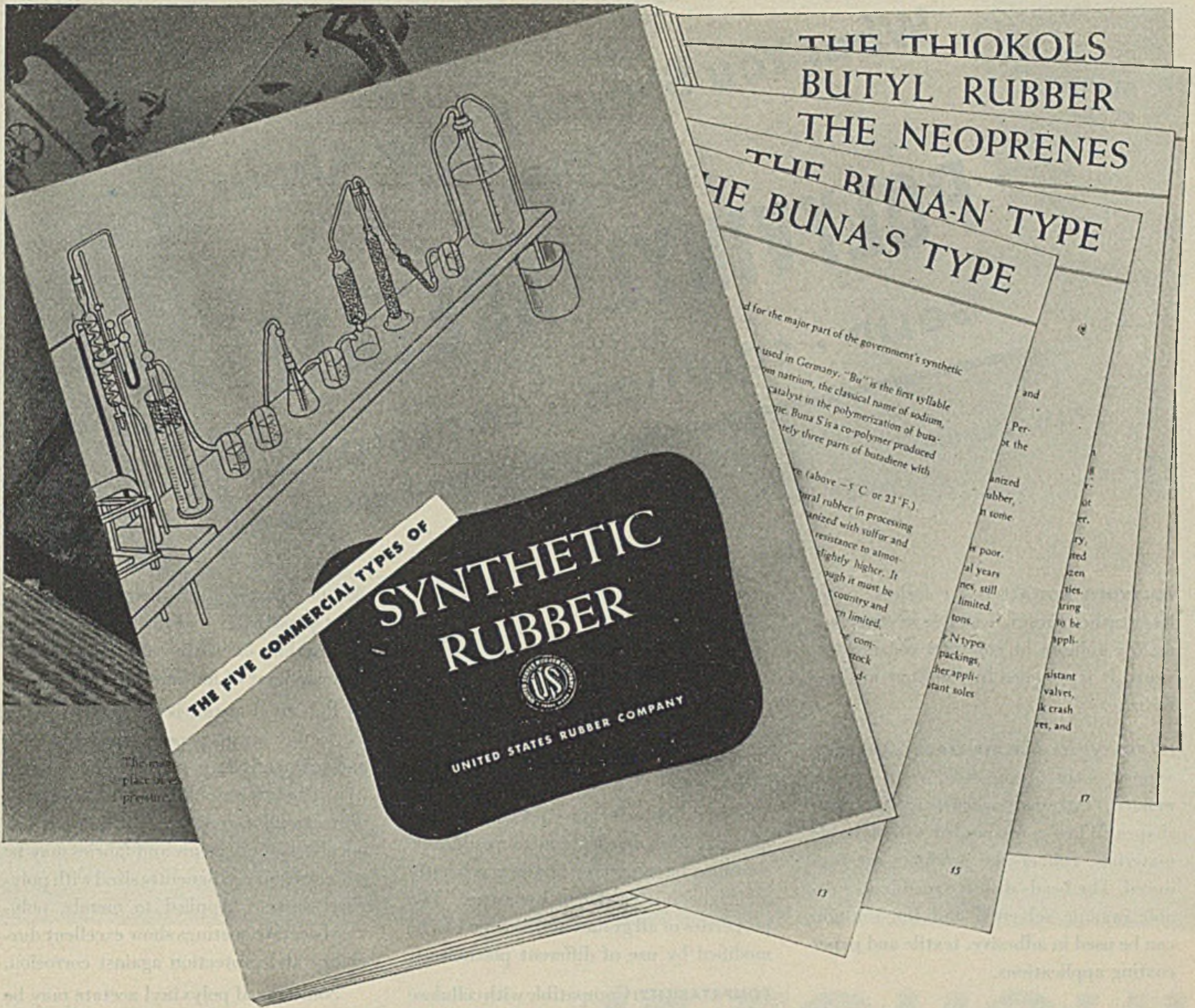
Supplied with drive by Elliott—turbine or motor.

ELLIOTT COMPANY
Centrifugal Blower Department, JEANNETTE, PA.
DISTRICT OFFICES IN PRINCIPAL CITIES

The Army-Navy E has been awarded to both the Jeannette and the Ridgway plants of Elliott Company.

ELLIOTT BLOWERS

helping to put the pow into powder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THE BUNA-N TYPE
THE BUNA-S TYPE

GLASS-CLEAR

THERMOPLASTIC

What You Should Know About

DU PONT
REG. U. S. PAT. OFF.

POLYVINYL ACETATE

RESIN

SOLID • SOLUTION • EMULSION

STABLE

ADHESIVE

FILM-FORMING

COMPATIBLE

POLYVINYL ACETATE is a colorless, tasteless synthetic resin, insoluble in water but readily soluble in common organic solvents. It is supplied by Du Pont in three forms:

(1) POLYVINYL ACETATE BEADS—This convenient form of the solid resin can be molded, extruded or cast into various shapes. When compounded with suitable materials, rubber-like products are produced. The beads dissolve readily in suitable organic solvents, and the solution can be used in adhesive, textile and paper coating applications.

(2) POLYVINYL ACETATE SOLUTION (50% solids in methanol)—This is a convenient form for using the resin whenever suitable facilities for dissolving the solid are not available.

(3) POLYVINYL ACETATE EMULSION (55% solids in water suspension)—This product is an excellent replacement and modifier for rubber latex in many applications. It can be used without toxic or flammable solvents; only water is required for dilution. The emulsion is used for making adhesives which are unusually strong and permanent under many conditions.

GRADES:

Solid Beads—High, medium and low viscosity.

Solution—Low viscosity.

Water Emulsion—High and low viscosity.

The high viscosity products are higher melting, form harder and more durable coatings, have greater bonding strength, and higher heat-sealing temperatures. The properties of all grades of this resin can be modified by use of different plasticizers.

COMPATABILITY: Compatible with cellulose derivatives, chlorinated rubber, terpene resins, rosin, esters of abietic acid, and small amounts of coumarone and indene resins. Some natural resins such as damar, elemi, kauri, copal, sandarac, etc., are not completely compatible, but may be combined with polyvinyl acetate for use in applications where clarity of the mixture is not required.

APPLICATIONS: Polyvinyl acetate is an effective adhesive for a wide variety of materials, including leather, paper, cork, textiles, wood, ceramics, and even highly polished surfaces of glass, metals, and most plastics. It may be employed as a heat-sealing or wet bond adhesive or as an ingredient of hot melts.

Polyvinyl acetate is an effective binder for leather scrap, paper pulp, wood flour and pigments. It is of particular interest as a vehicle for metallic pigments because of its stability and freedom from tarnishing effects. Felt, straw and fabrics may be stiffened and permanently sized with polyvinyl acetate. Applied to metals, polyvinyl acetate coatings show excellent durability and protection against corrosion.

Solutions of polyvinyl acetate may be applied to paper to form glossy coatings which can be heat-sealed at any desired point, as in the fabrication of containers. Paper treated with polyvinyl acetate also shows improved strength and oil resistance. Coated paper foils or unsupported polyvinyl acetate films may be used as dry mounting foils for application by hot pressing.

AVAILABILITY: Commercial quantities are now being shipped on WPB allocation (Allocation Order M-10) for manufacture of essential wartime products.

FOR MORE INFORMATION, SEND FOR BULLETIN 4-243

DU PONT
REG. U. S. PAT. OFF.

POLYVINYL ACETATE

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. . . THROUGH CHEMISTRY

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Electrochemicals Dept., Wilmington, Delaware
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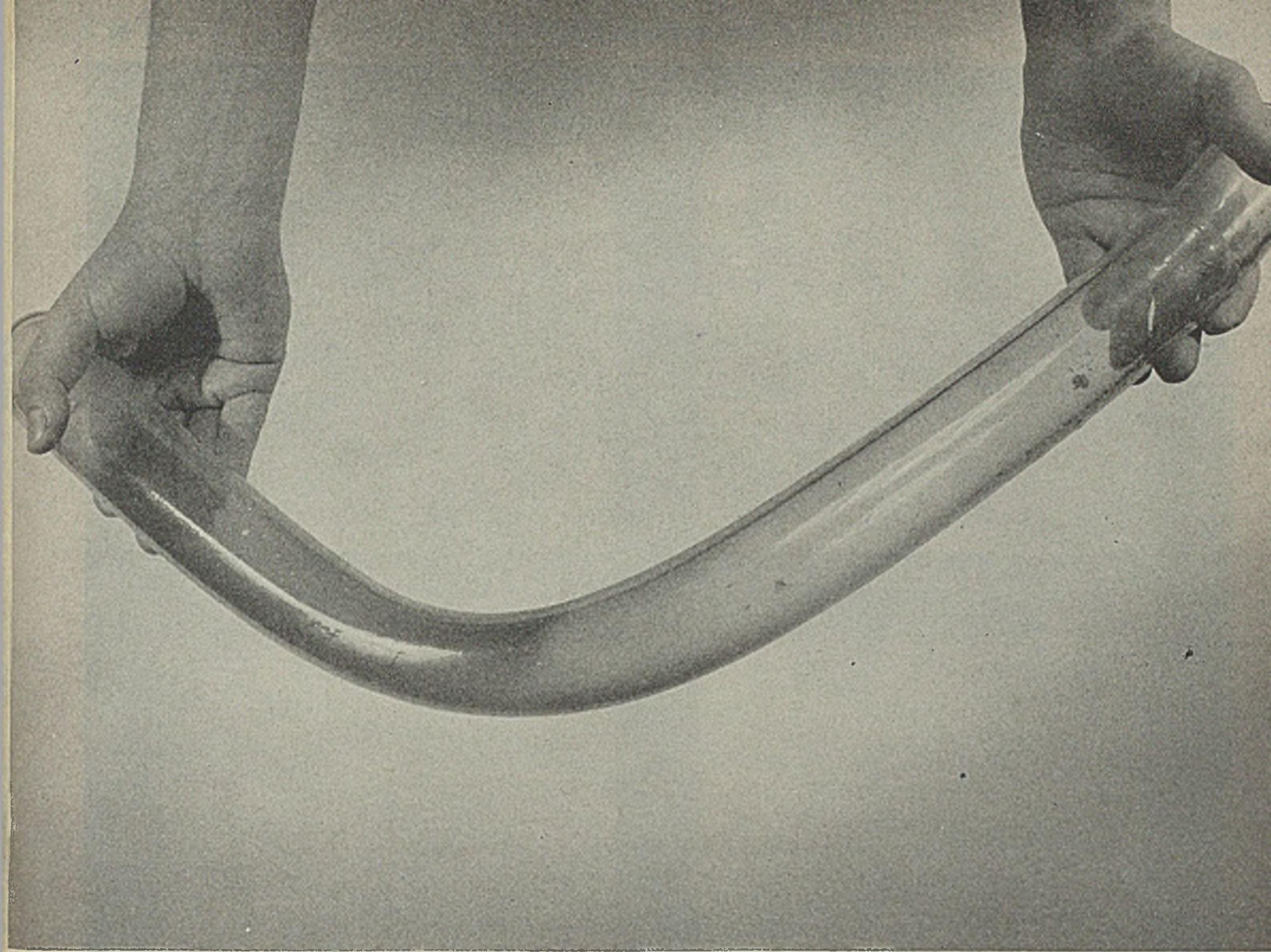
IEC-7



PYREX PIPING *IS TOUGH!*

Part of a well-known wine cellar was razed by fire recently. Almost everything in the burned buildings was destroyed beyond salvage or recognition. But shown above is a section of PYREX brand glass piping picked out of the ruins. It was bent by the heat. One end was chipped when it crashed. It is of no earthly use today, yet it is still clearly a piece of Pyrex piping! By contrast, the tiny flecks visible on its surface are splashes of molten aluminum.

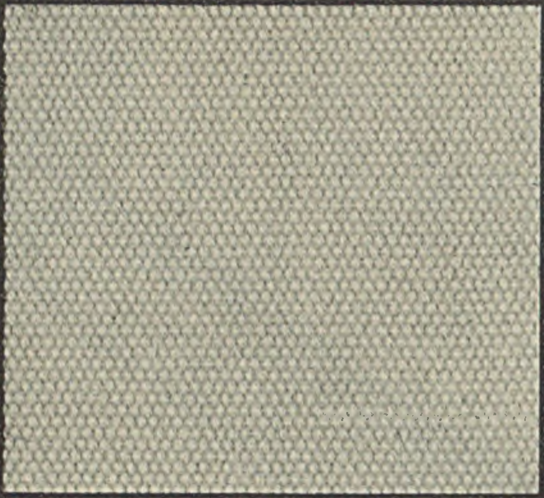
Engineers everywhere know that PYREX piping is chemically stable and highly resistant to thermal shock. They know that it is easy to clean and that its transparency facilitates and even assures the success of many operations. The one objection to its use—and it is raised *only* by those who have had no experience with it—is that glass is fragile. Engineers, however, with large installations of PYREX piping say that even under rough and ready conditions breakage is not a serious problem.

The above survivor of a devastating fire shows that PYREX piping can "take it"—that PYREX brand Industrial Glass has strength and stability far in excess of the demands of most industrial services. If you could benefit by the characteristics obtainable only in PYREX piping, write to the Industrial Division, Corning Glass Works, Corning, N. Y. And remember, PYREX Piping is available *today*.

"PYREX" is a registered trade-mark and indicates manufacture by Corning Glass Works, Corning, N. Y.

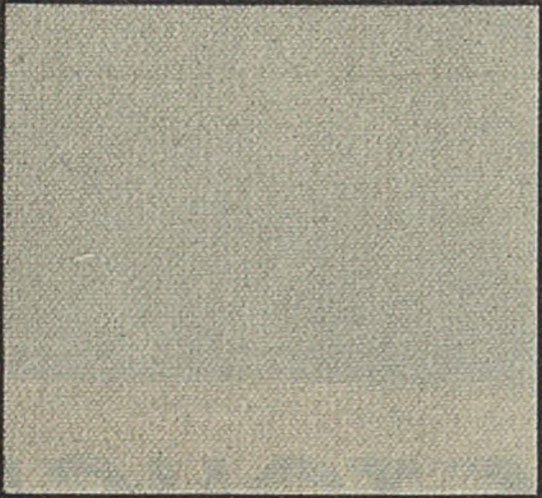
CORNING
Glass Works

Pyrex Industrial Glass

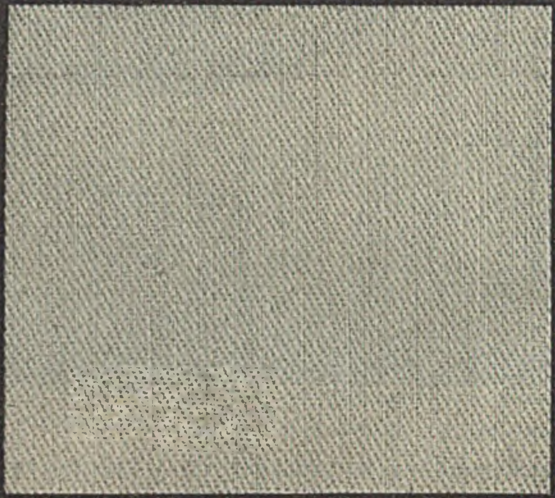


1/0 DUCK

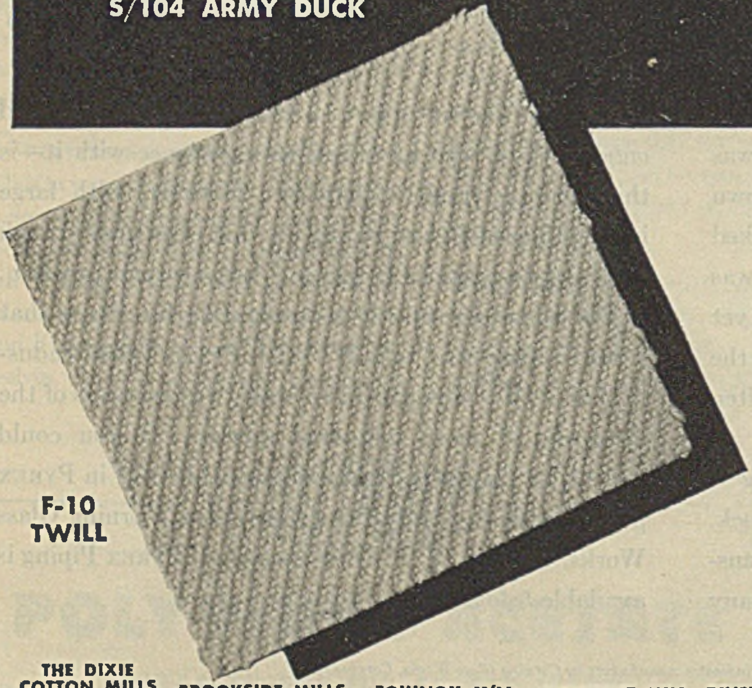
S/770 AIRPLANE FABRIC



S/104 ARMY DUCK



S/455 DRILL



F-10 TWILL

Fig. 1911—Stainless Steel O. S. & Y. Gate Valve. Has flanged ends, outside screw rising stem, bolted yoke bonnet, threaded-through bronze yoke bushing and nested gasket. Body and yoke bonnet are cast the same alloy or metal.

Beginning of a long life in the POWELL Line

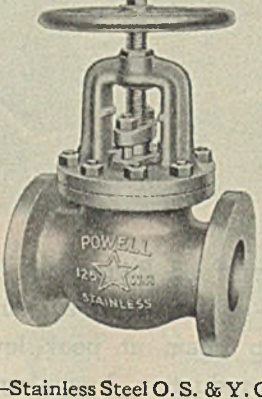


Fig. 2457—Stainless Steel O. S. & Y. Globe Valve. Has flanged ends, outside screw rising stem, bolted flanged yoke and plug type disc. Vulcanized composition disc can be furnished. Made in sizes 4″ to 12″, inclusive.

Powell Valves, available in a wide variety of pure metals and special alloys to meet the exacting requirements of every kind of corrosive service, offer positive protection of end product against contamination.

Before a Powell Valve earns the right to bear this time-honored name, it is called upon to prove its acceptability into an illustrious family. In blunt words, it must fill a need—actual or anticipated—before it is permitted the responsibilities of the family name.

From the moment of its conception by Powell engineers and consultants, that valve is engineered to its purpose. It must meet every requirement of "Standard of Control", which is the family motto.

This goes for *all* Powell Valves . . . of every type . . . of every proved-in-service material . . . for every need. Powell takes this special care because its near-century-old name rests upon the *pre-determined performance of every Powell Valve.*

The Wm. Powell Co.

Dependable Valves Since 1846

Cincinnati, Ohio

POWELL VALVES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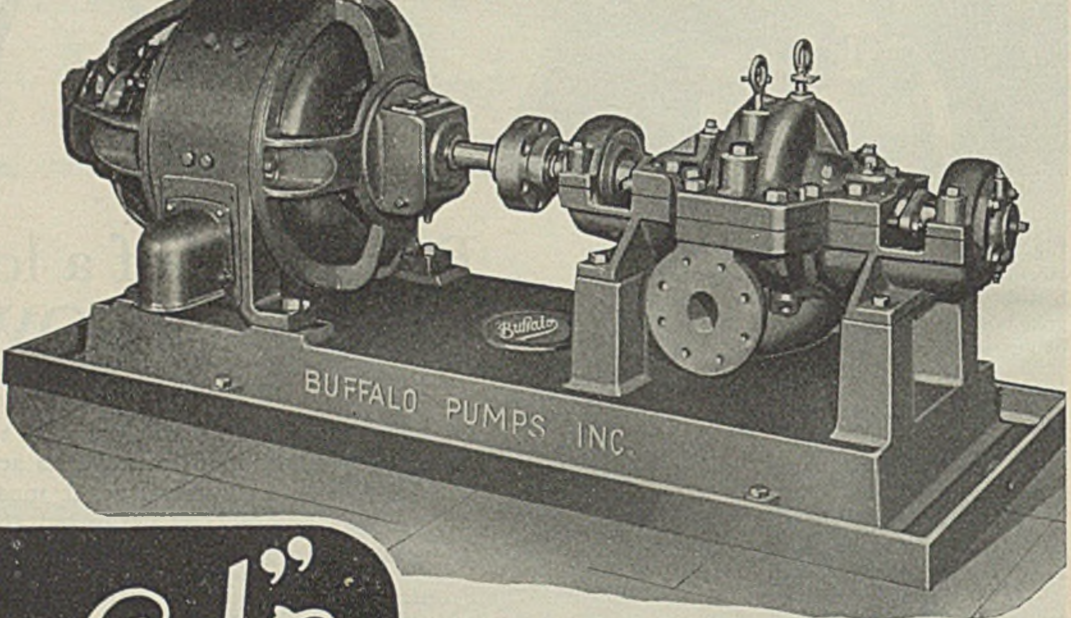
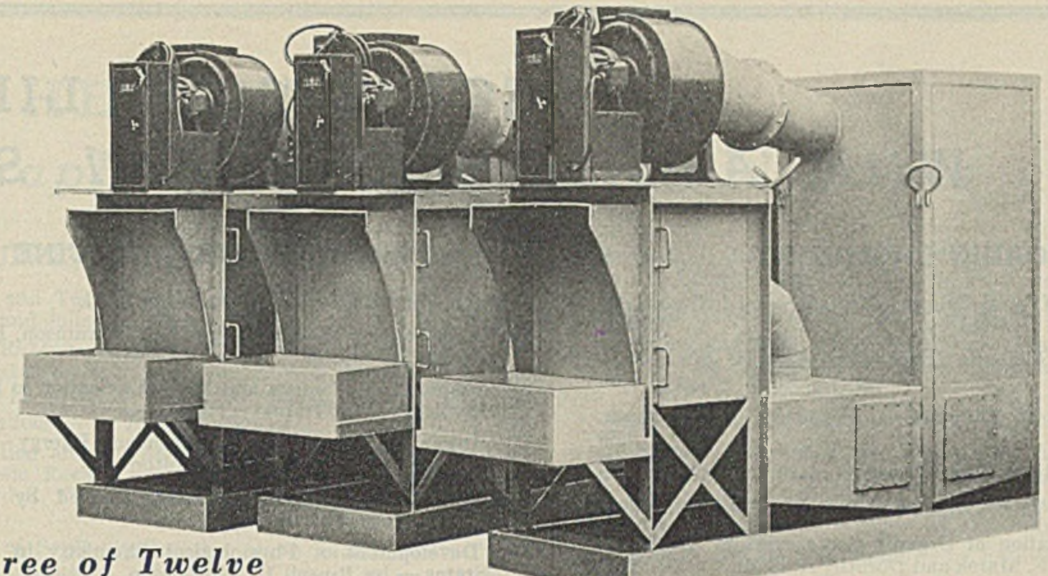
NAVY


Buffalo
BUFFALO PUMPS INC.



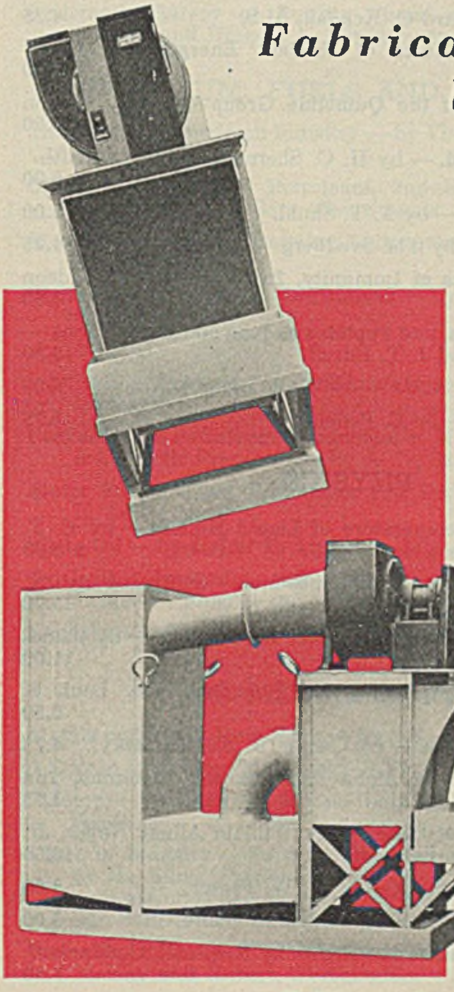
Three of Twelve

FUME ELIMINATORS

Fabricated by

JAY-CEE

In JOHNSON CITY TENN. Since 1883



Builders of Anything in Iron and Steel Not Already Produced as a Specialty

Fabricated from steel plates, sheets and shapes, the compact exhaust units shown above were designed to remove the inflammable ingredients from oil and grease fumes, by pulling the gasses through a liquid bath. Twelve of these units were manufactured by "Jay-Cee" in Johnson City, Tennessee, and assembled completely with the motors, fans and controls for use in large aluminum tube mills.

Produced by JAY-CEE-TENNESSEE

ALUMINUM PLANTS	POWDER PLANTS	OTHER PLANTS
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Gray Iron Foundry—Capacity 15 to 20 tons per day. Also alloy iron castings.

Structural and Plate Shop—All kinds of structural and plate fabricating up to and including 2" plate.

Light Iron Shop—Fabricating sheet steel, and aluminum. Also miscellaneous metal work 16 gauge and heavier in metal work and light structural work.

Machine Shop—Having a wide variety of machinery we are capable of handling highly diversified work.

Our Engineers and Mechanics are familiar with tough problems in fabrication and manufacture. Ask us to help out on the "mean" jobs.

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

JOHNSON CITY FOUNDRY & MACHINE WORKS

JOHNSON CITY, TENNESSEE EST. 1883

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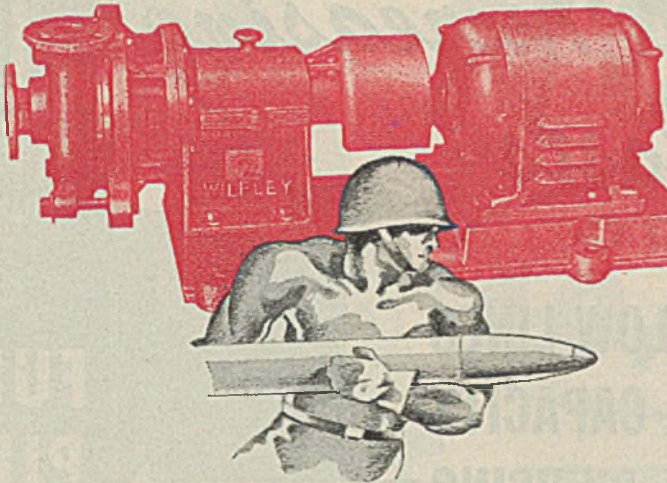

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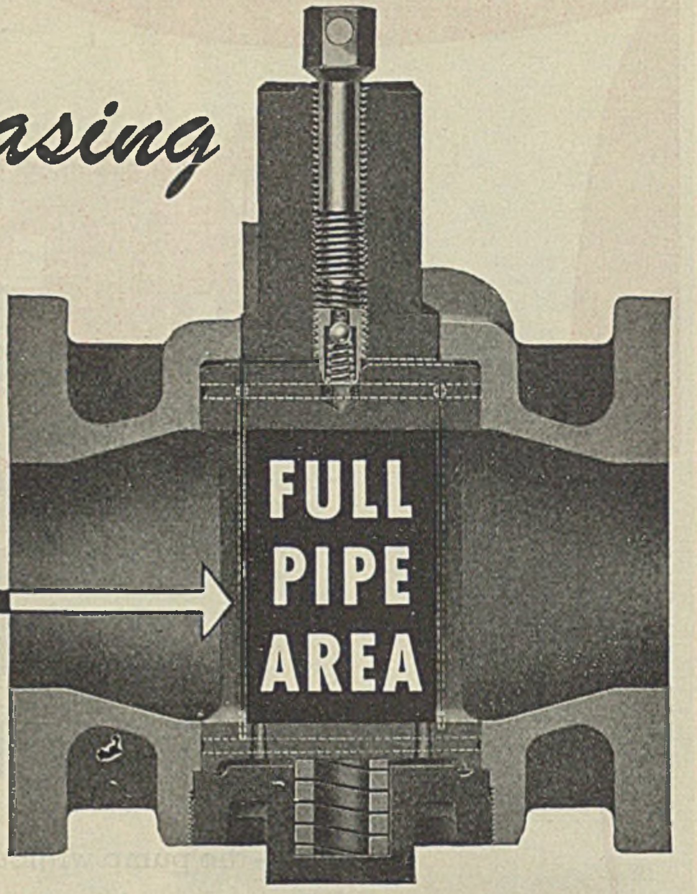
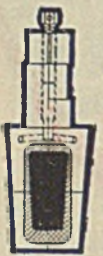


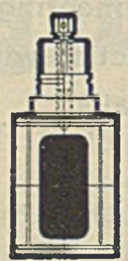
a.c.f.

LUBRICATED PLUG VALVES

Because Processing and Chemical plants are so dependent upon pipe lines for handling of all their ladings, it is extremely important that these lines be permitted to function to the limit of their capacity. a.c.f. Lubricated Plug Valves have ports offering full, unrestricted area to the flow of all fluids, with the further much desired feature of quick operation.



4" Tapered Plug: Area 7.00 sq. in., restricts passage by as much as 42% of area of the pipe.



4" Cylindrical Plug of a.c.f. Valve: Area 12.73 sq. in., full pipe area port opening!

The sketches show the difference in port area of standard tapered plug valves as compared with a.c.f. cylindrical plug valves.

On new pipe lines you can obtain this efficiency by specifying a.c.f. Lubricated Plug Valves — they cost no more.

On old pipe lines you can reduce pumping and other power costs by changing to a.c.f.— reduced operating costs and increased production will pay for the change-over.

Standard 125 lb. patterns have gate valve face-to-face dimensions to facilitate the change without disturbing pipe lines.

Can also be furnished in special alloys, and with full round port openings, having port diameters equal to inside diameter of iron pipe.

SIMPLE TO SERVICE

There is no packing gland and no auxiliary gaskets to be watched and replaced. Lubricant is introduced in sticks, and is forced into the valve by turning the lubricant screw. A bottom base-plate permits dropping out the plug without breaking the pipe connection.

a.c.f. Lubricated Plug Valves are furnished in all standard sizes, screwed or flanged type. Ask about special alloys for corrosive service.

Representatives in principal cities carry adequate warehouse stock available for quick delivery. Send for our Catalog #3-A.

AMERICAN CAR AND FOUNDRY COMPANY
Valve Department
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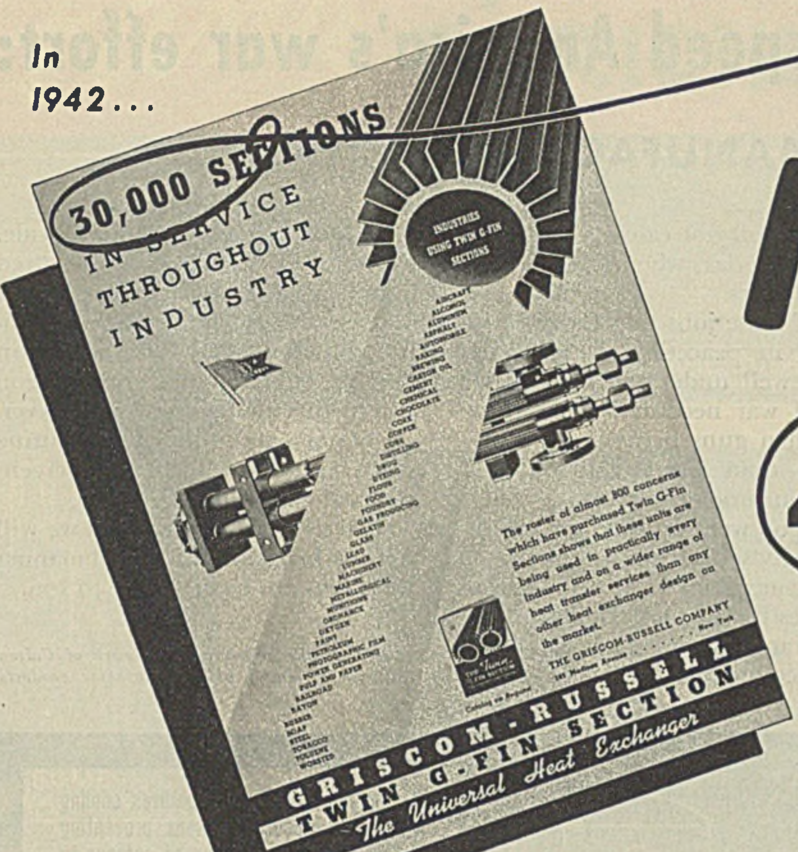
In 1942 . . .



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The roster of almost 800 concerns which have purchased Twin G-Fin Sections shows that these units are being used in practically every industry and on a wider range of heat transfer services than any other heat exchanger design on the market.

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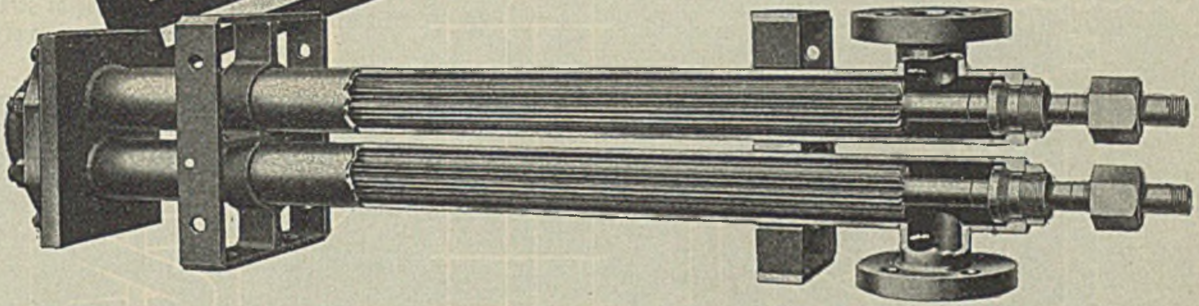

There are important reasons why Twin G-Fin Section sales increase so steadily . . . and so rapidly.

- *The design of these units is backed by 76 years of experience in building heat transfer apparatus.*
- *Their details of construction have been proved by 10 years of service.*
- *More than 800 users have found that these "universal heat exchangers" can be applied to a greater variety of heat transfer processes than any other type of apparatus on the market.*

Write for Bulletin 1613 which explains the wide preference for these units.

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The Universal Heat Exchanger

How Calgon helps speed America's war effort:

10. IN THE MANUFACTURE OF TNT

PREVENTING scale deposition from cooling water passing through process heat-exchangers was a familiar job for Calgon in all sorts of process industries years before the war. Only a few pounds of Calgon* fed to a million pounds of cooling water sufficed to keep calcium carbonate from impeding heat transfer in power-plant, oil-refinery, distillery condensers and similar equipment in many specialized operations.

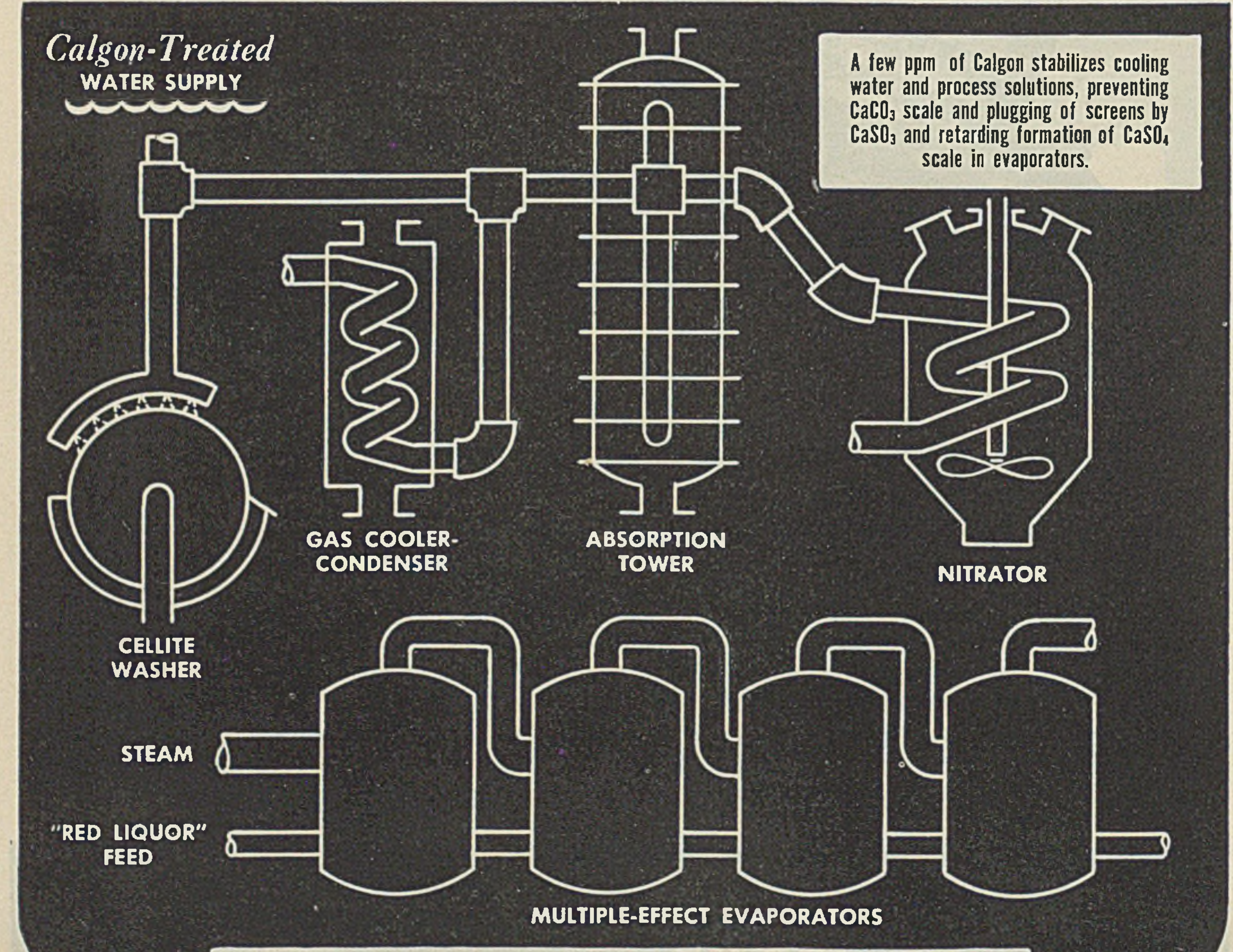
The same "threshold treatment" helped the operators of beet-sugar plants to complete a campaign without having to shut down their evaporators to boil out calcium sulphate scale, saving days when every second meant dollars.

All of these jobs that Calgon did so well in peacetime it is doing equally well under the imperative drive of war necessity. More than that, when guns became more important than butter, and TNT plants mushroomed across the country, Calgon went quickly to work in this deadly serious environment.

A "tremendous trifle" of Calgon now does for gas coolers, absorbers, and nitrators what it had long done for peacetime heat exchangers by inhibiting calcium carbonate scale. Evaporators handling waste "red liquor" now stay on the line longer because Calgon holds back deposition of calcium sulphate here as in the beet-sugar plants. And Calgon still further has demonstrated its versatility as a stabilizer by preventing plugging of the cellite washer screens with calcium sulphite.

Tell us your problem and we will tell you in a straightforward manner if Calgon can be of service to you.

*Calgon is the registered trade-mark of Calgon, Inc., for its glassy sodium phosphate products.



A few ppm of Calgon stabilizes cooling water and process solutions, preventing $CaCO_3$ scale and plugging of screens by $CaSO_3$ and retarding formation of $CaSO_4$ scale in evaporators.

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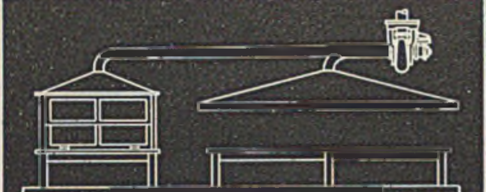
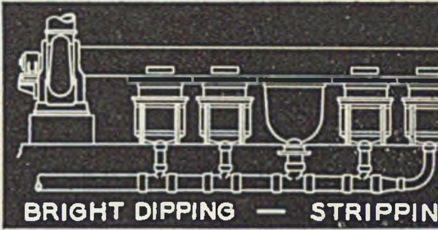
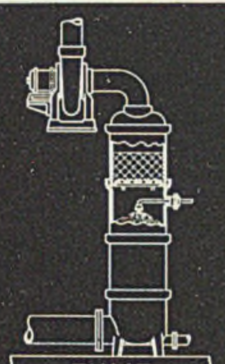
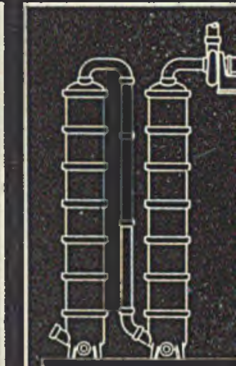
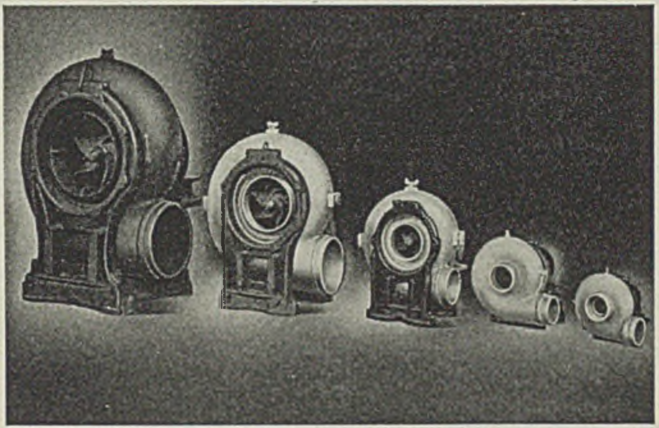

LABORATORY HOODS


KJELDAHL TUBE


BRIGHT DIPPING — STRIPPIN


FUME WASHER


ABSORPTION O
DRYING TOWEF



UNEXCELLED for HANDLING CORROSIVE GASES, because

1—All parts in contact with corrosive are heavy castings.

2—All bearings are external.

3—Each fan casing equipped with opening for drainage of condensate.

4—Impeller shaft equipped with stuffing box to prevent escape of fumes.

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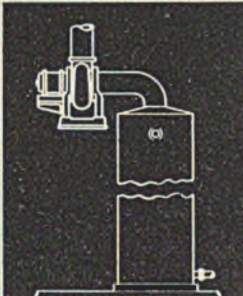
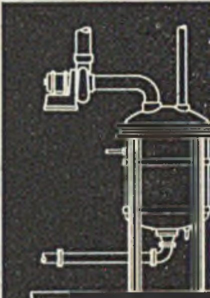
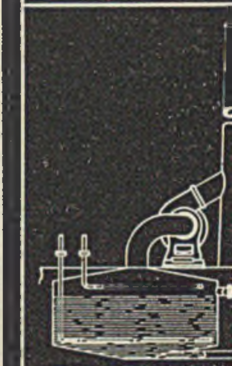
There are thousands of Durco corrosion-resistant fans serving dozens of different industries. Some of the principal applications are shown in these sketches. It is not unusual to find Durco fans that have given uninterrupted service for more than 15 years.

Write for Bulletin giving complete data and specifications.


SULPHURIC ACID CHAMBER PROCESS


REACTION KETTLE


ABSORPTION OR DRYING TOWERS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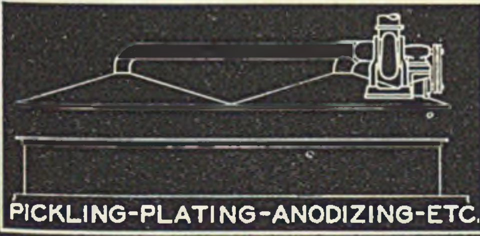
NEUTRALIZIN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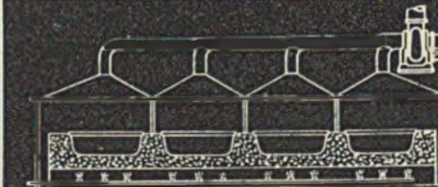
KJELDAHL AND ABSORPTION TOWER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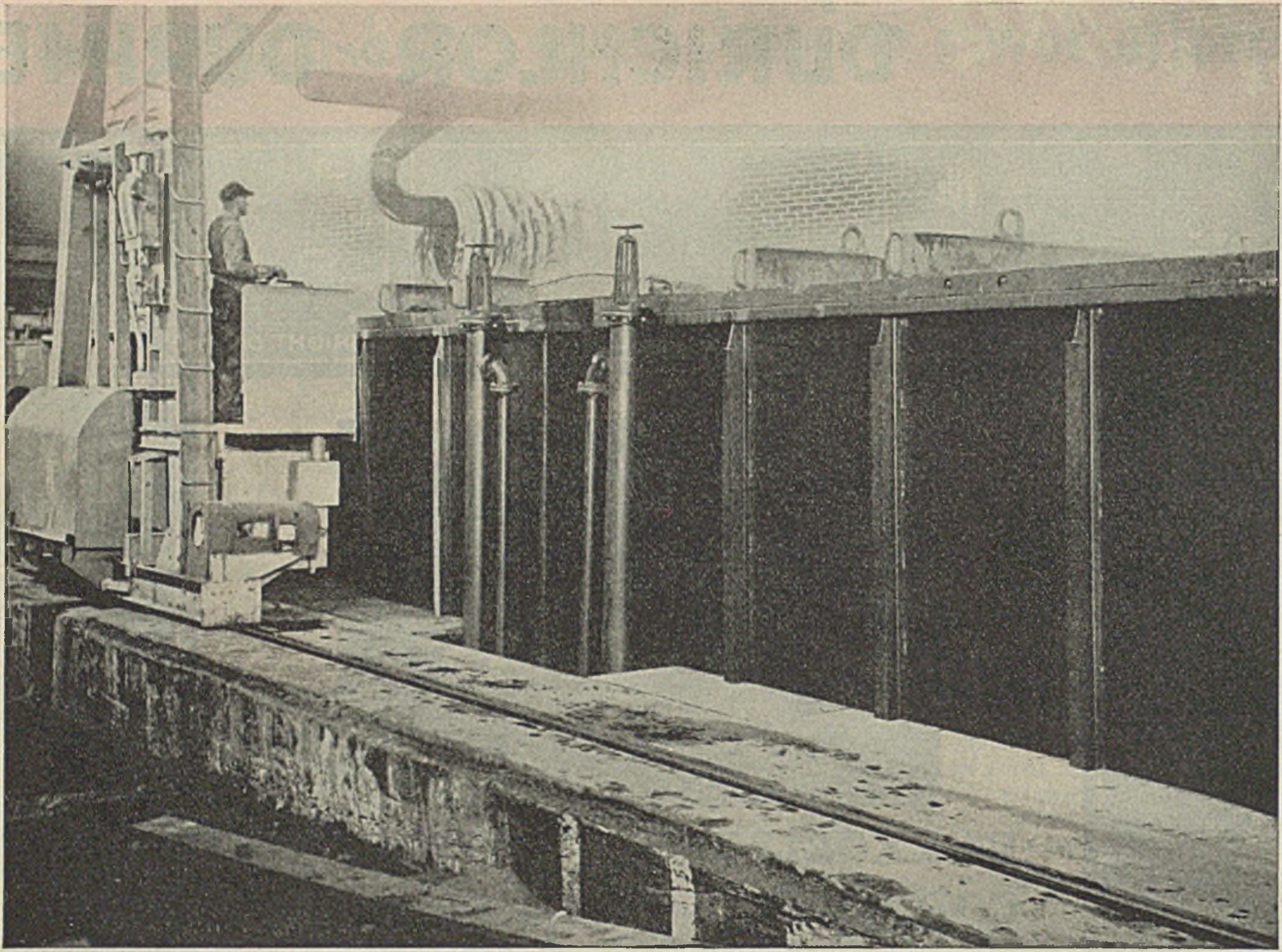
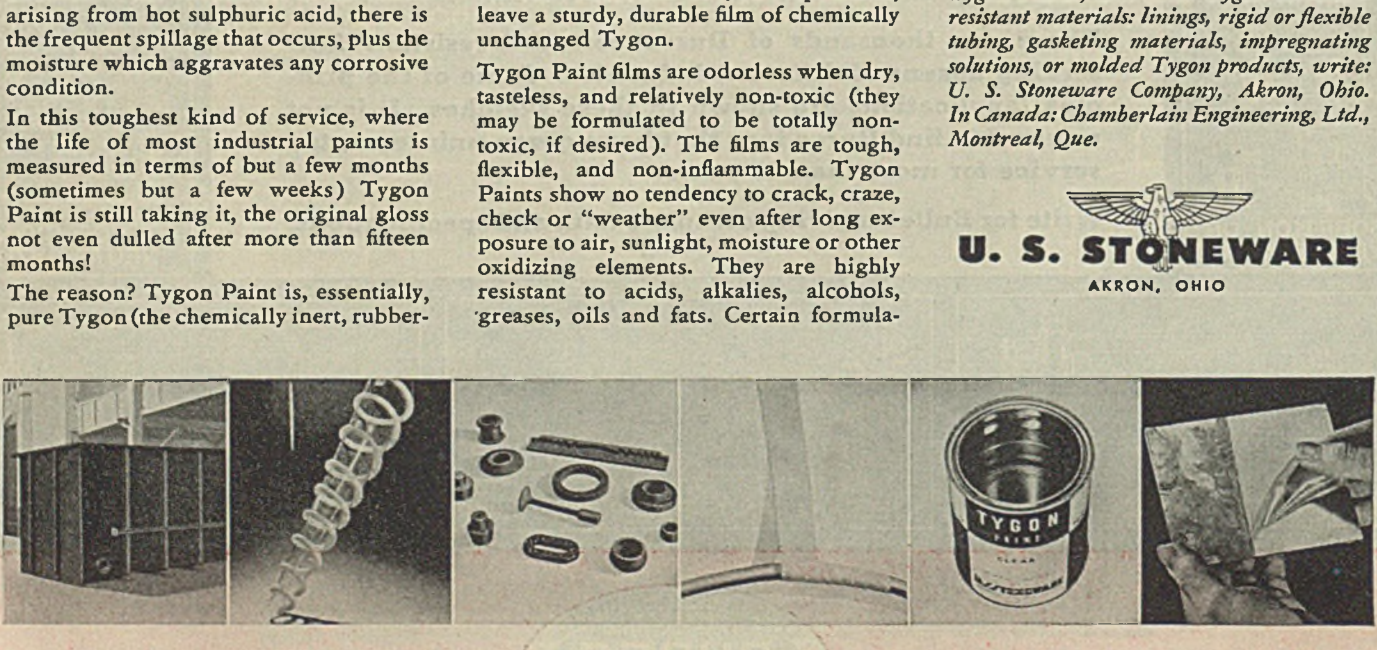
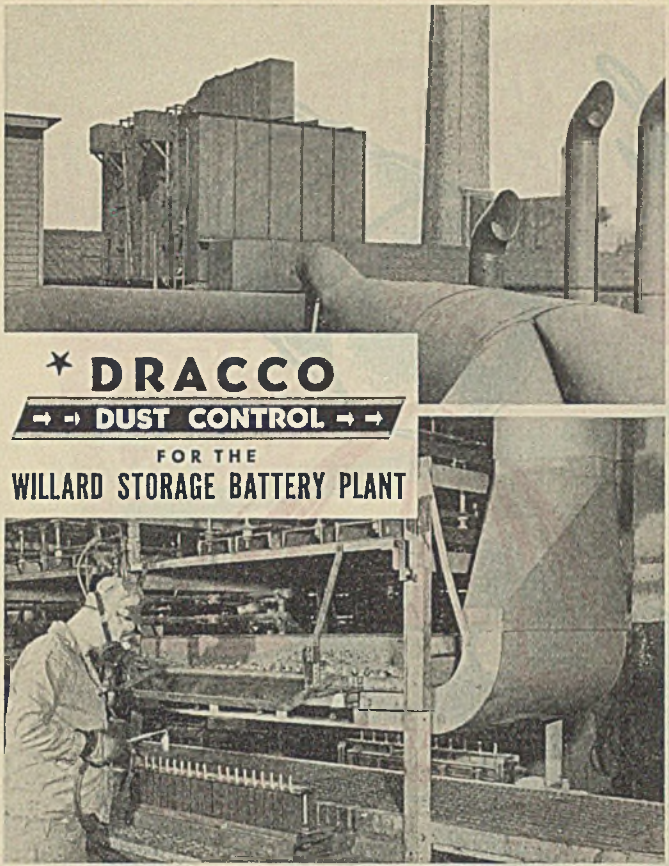



TYGON
PAINT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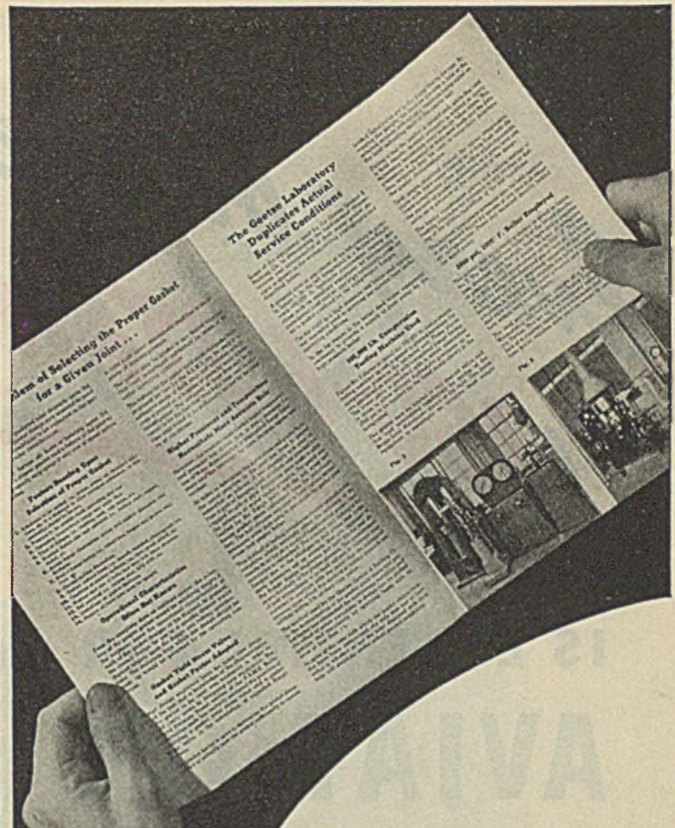
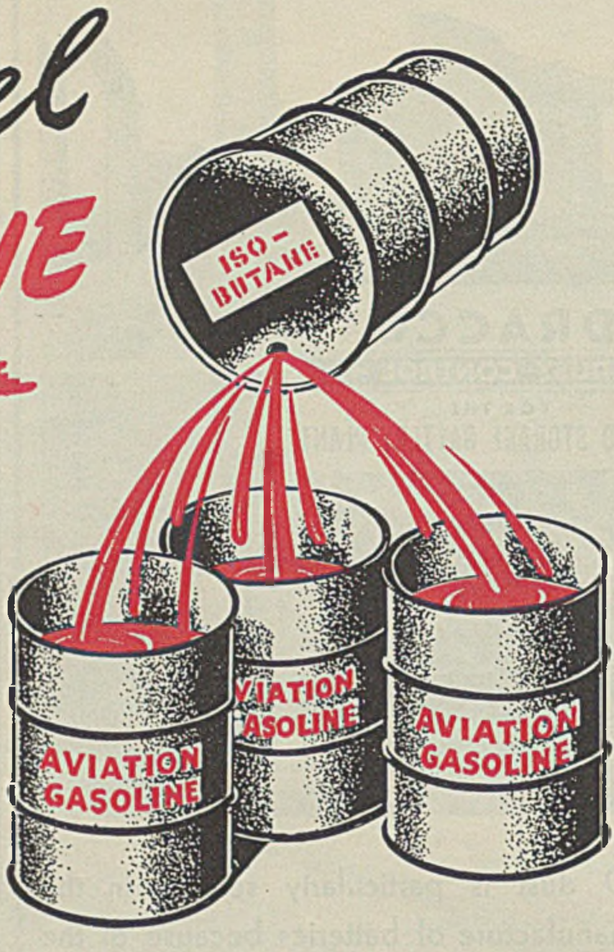

...blem of Selecting the Proper Gasket for a Given Joint . . .
The Goetze Laboratory Duplicates Actual Service Conditions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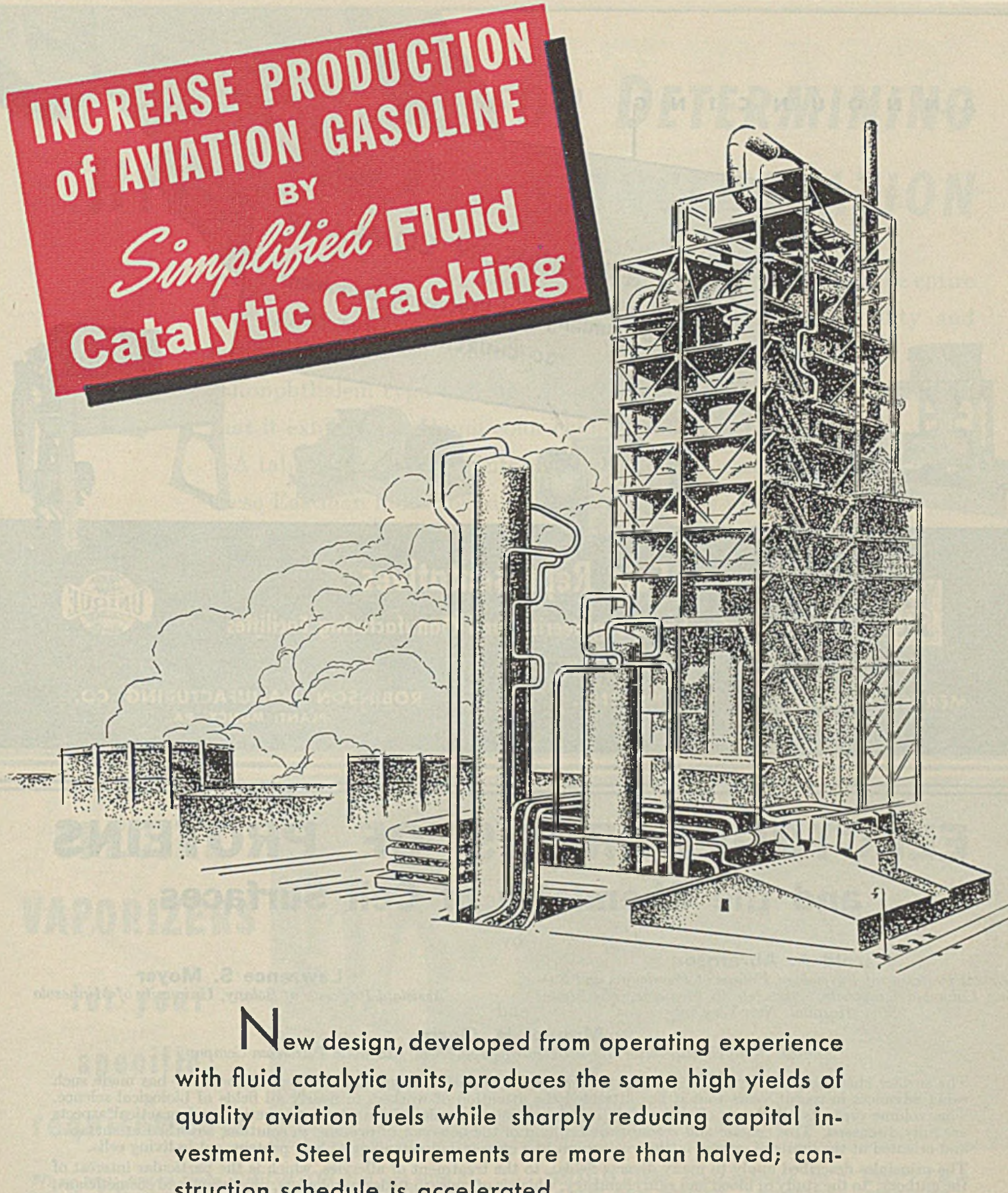
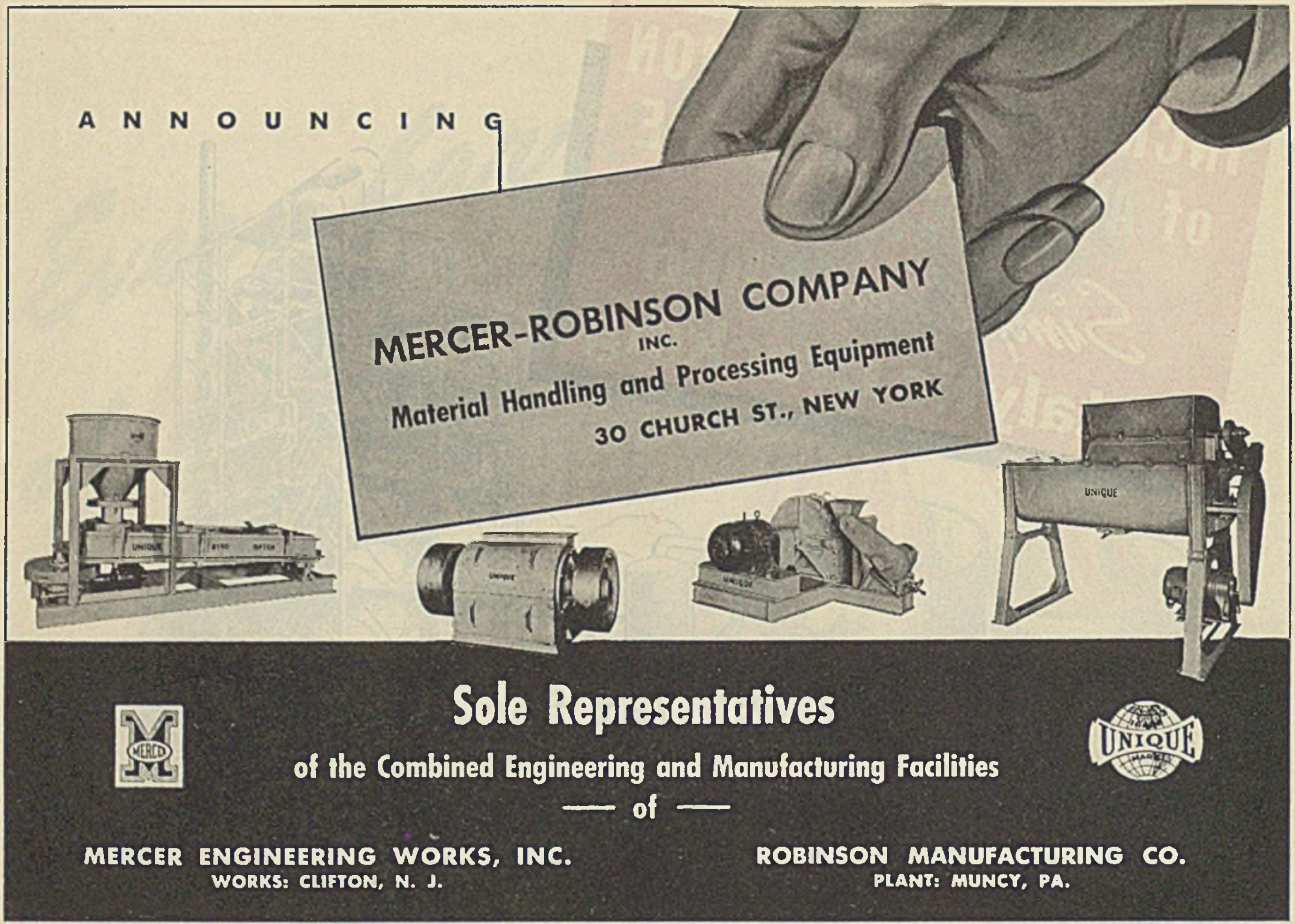
AVIATION GASOLINE
AVIATION GASOLINE
AVIATION GASOLINE


INCREASE PRODUCTION
of AVIATION GASOLINE
BY
Simplified Fluid
Catalytic Cracking



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and the Chemistry of Cell Surfaces

by

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Assistant Professor of Physiology, College of Physicians and Surgeons, Columbia University; Associate in Medicine, The Mount Sinai Hospital, New York City

Lawrence S. Moyer
Assistant Professor of Botany, University of Minnesota

and

Manuel H. Gorin
Chemical Research Supervisor, Field Research Department, Magnolia Petroleum Company

The surface chemistry of living cells — in particular the investigation of proteins by electrophoresis — has made such rapid advances in recent years that it has attracted the attention of workers in nearly all fields of biological science. This volume presents all phases of the subject in substantially complete form; both theoretical and practical aspects are fully discussed. This concise and readable description of the behavior of proteins in solution, adsorbed at surfaces, and oriented at the limits of crystal lattices will result in a clearer understanding of how proteins act in living cells.

The principles described apply to many diverse fields: to the treatment of allergies, which is the particular interest of the authors; to the study of blood and skin chemistry, which is of concern to dermatologists, physicians and cosmeticians; as well as to such industrially practical substances as wool, rubber latex, and other complex molecules in which proteins are involved. A glance at the table of contents will show the variety of subjects touched upon in this able study of protein behavior.

CONTENTS

General Principles of Electric Migration in Liquids
Experiments in the Nineteenth Century
Methods
Dissolved and Adsorbed Proteins and Related Surfaces
Electrokinetic Theory and Migration of Charged Particles
Electric Mobility and the Calculation of the Net Charge
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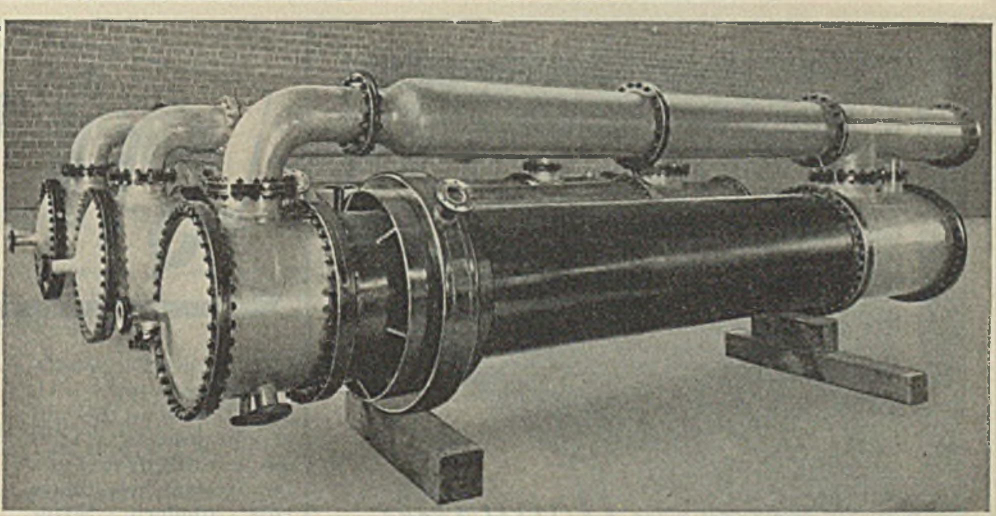

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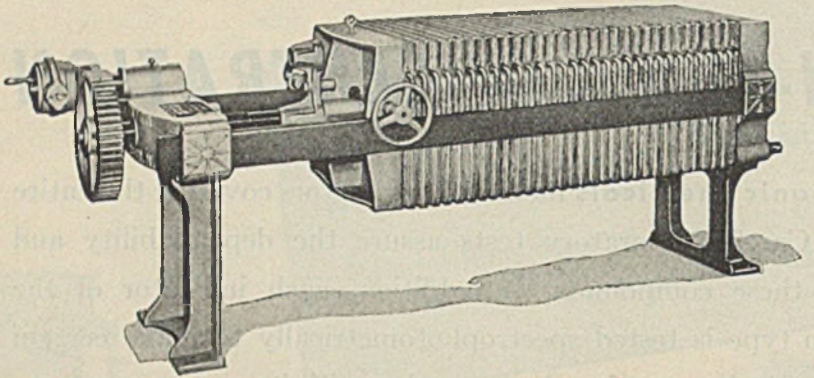

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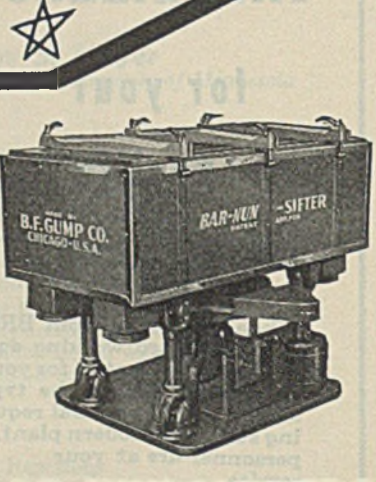

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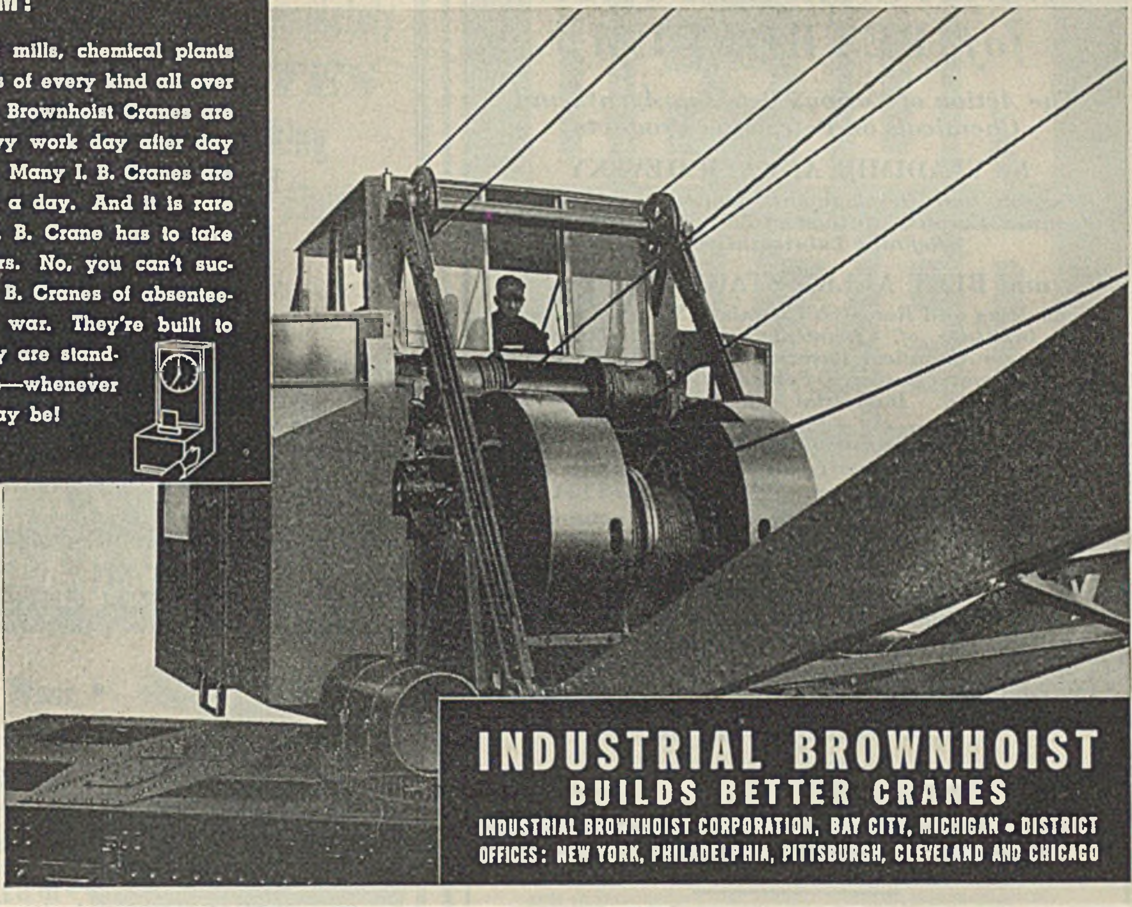

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and **BERT ALLEN STAGNER, Ph.D.**

Consulting and Research Chemist; Member, American Institute of Chemical Engineers; Formerly: Supervisor Chemical Research, Union Oil Company of California; Research Fellow, Mellon Institute of Industrial Research

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A.C.S. Monograph No. 88

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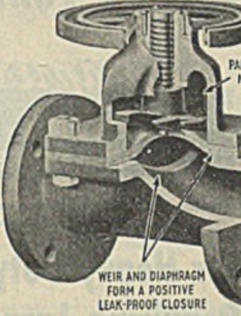
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★ CARBON DETERMINATION

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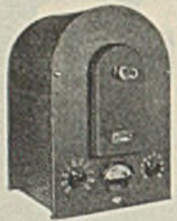

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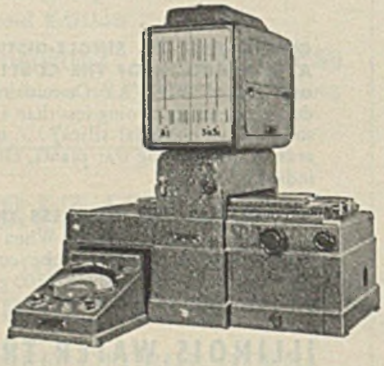
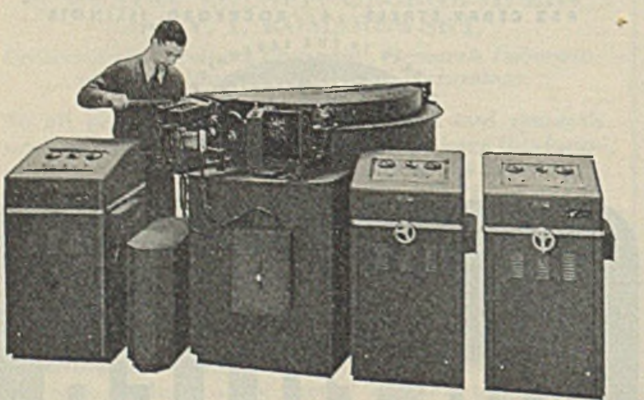


Comparator - Densitometer identifies spectral lines by comparison with a projected Master Plate. A densitometer for reading the transmission of the spectral lines is an integral part of the unit.



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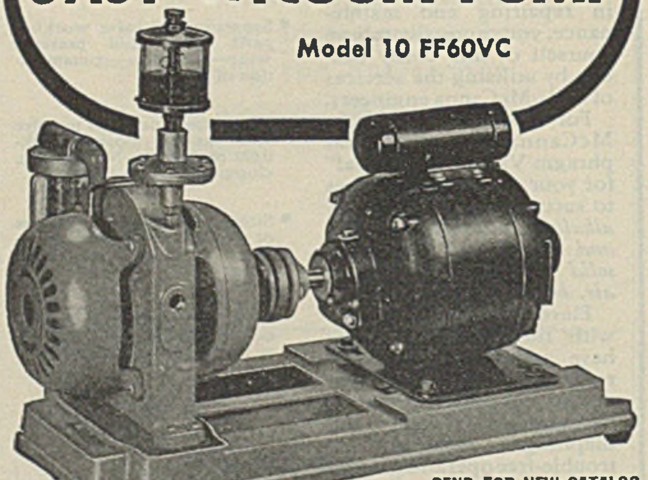

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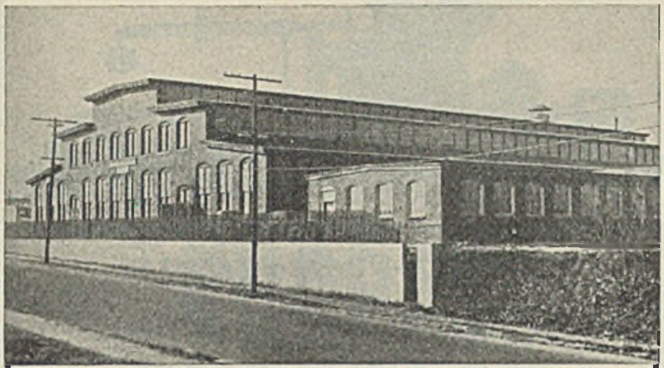

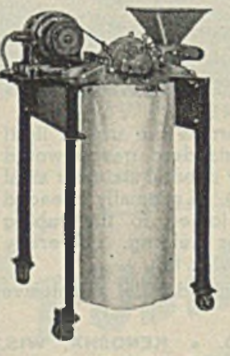

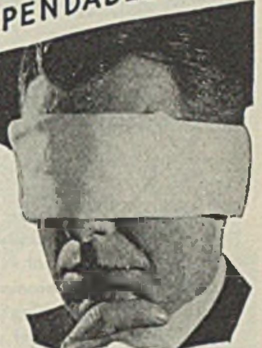


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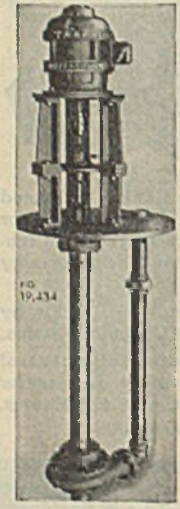

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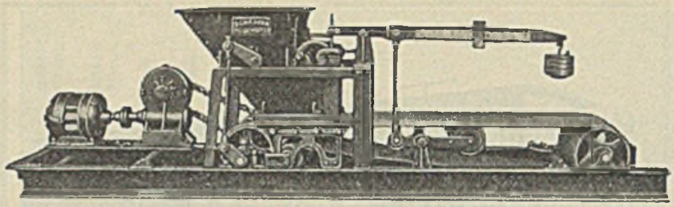

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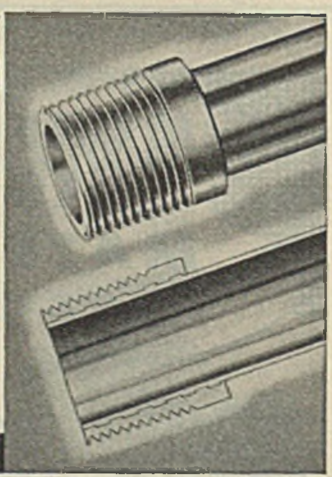

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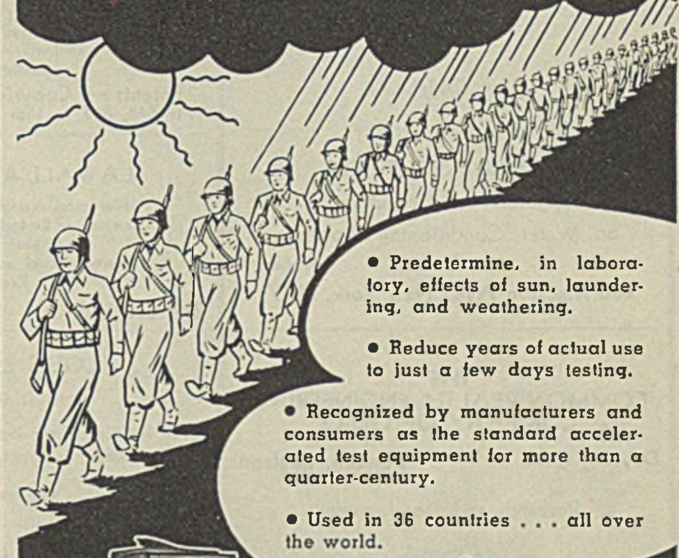

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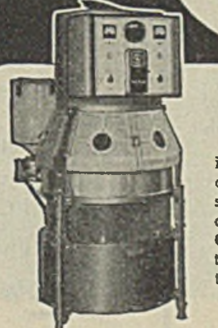

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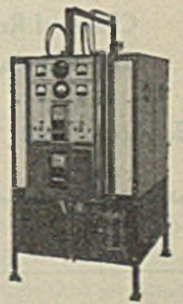

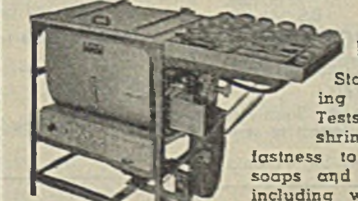

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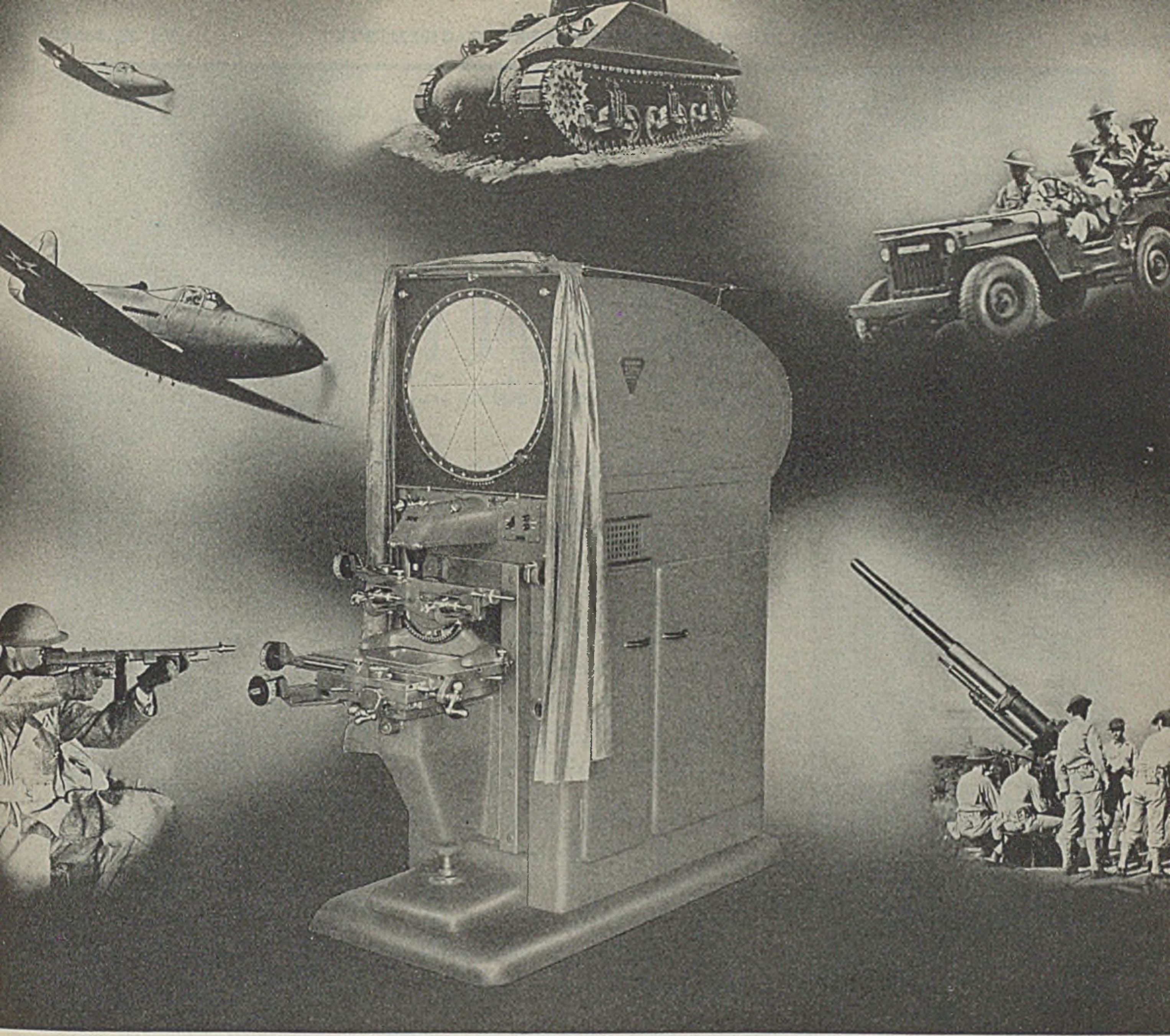

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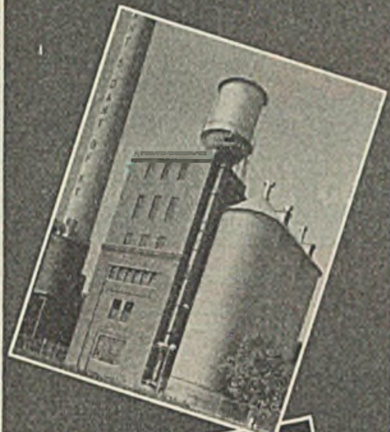

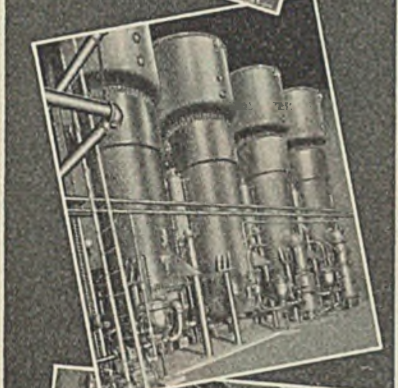

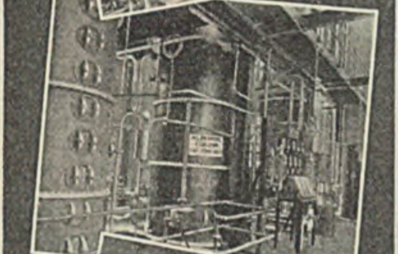

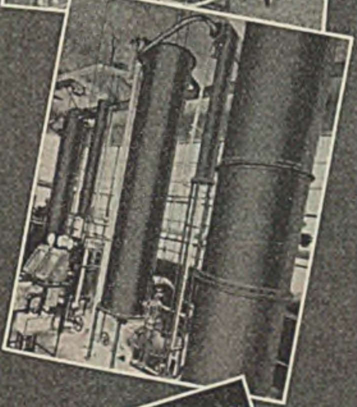

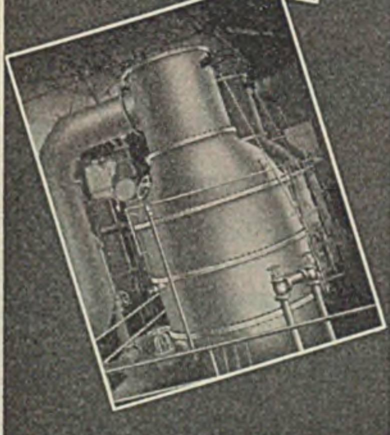

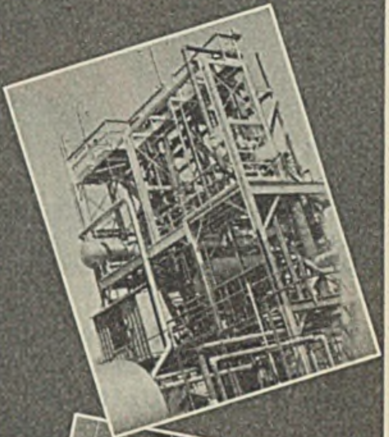

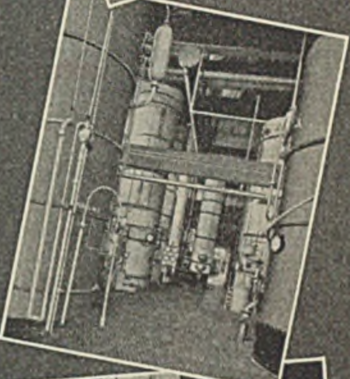

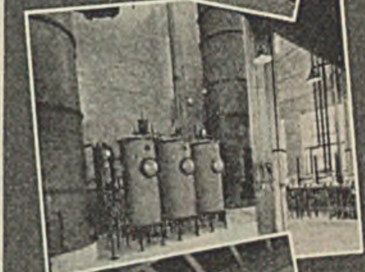

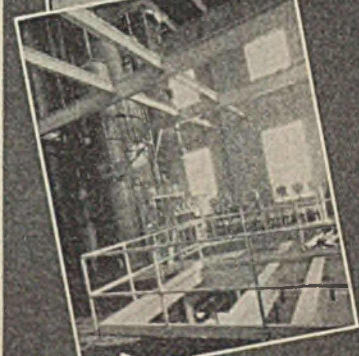

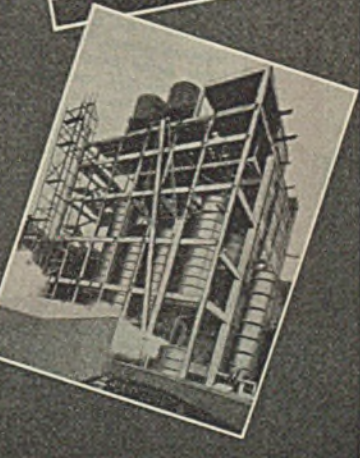

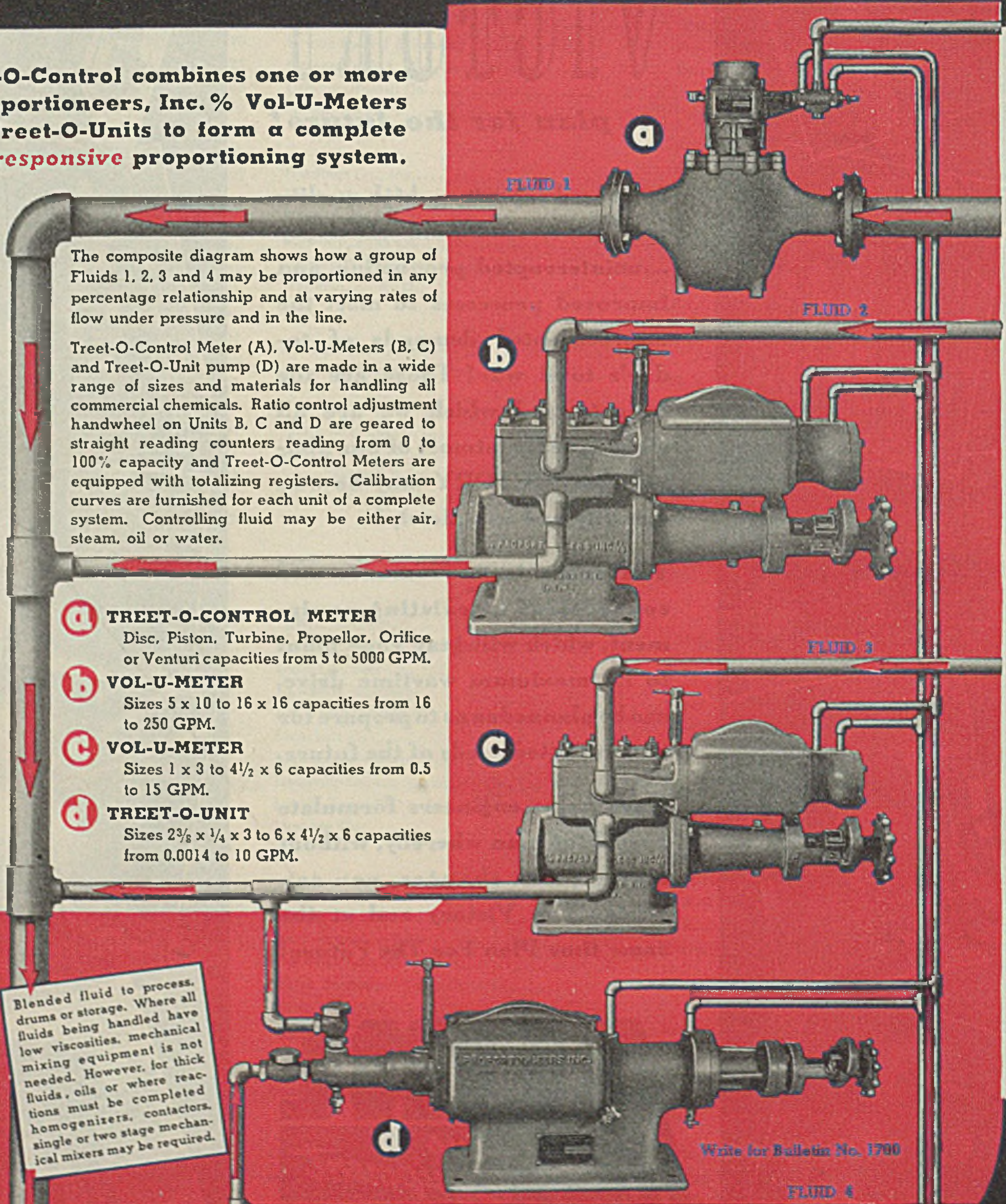
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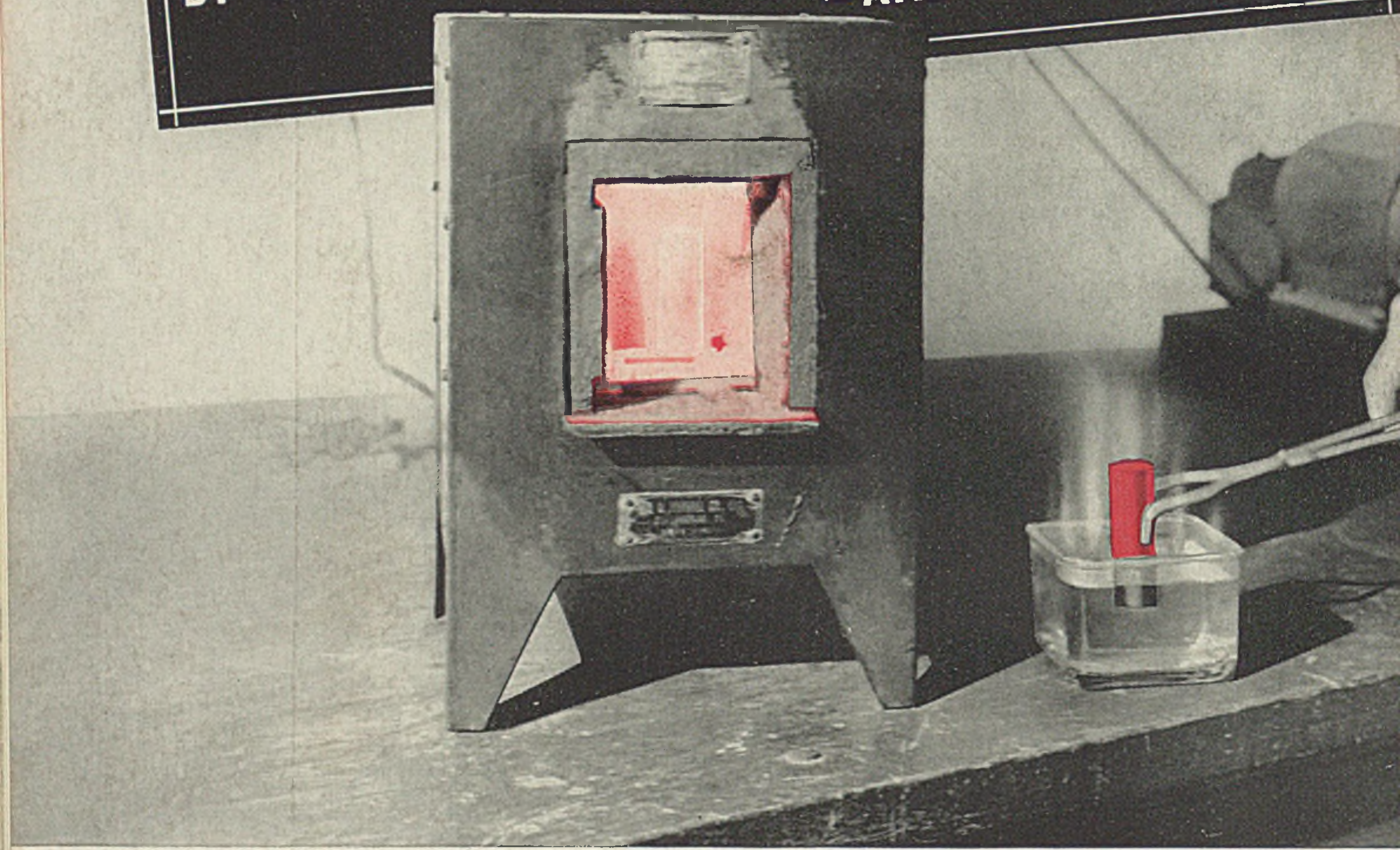

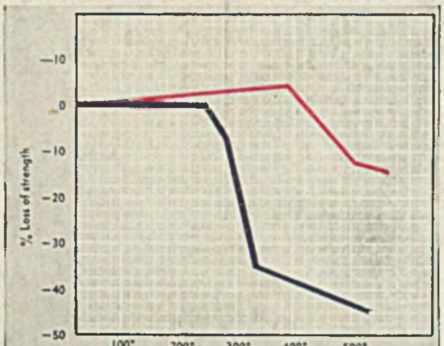

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