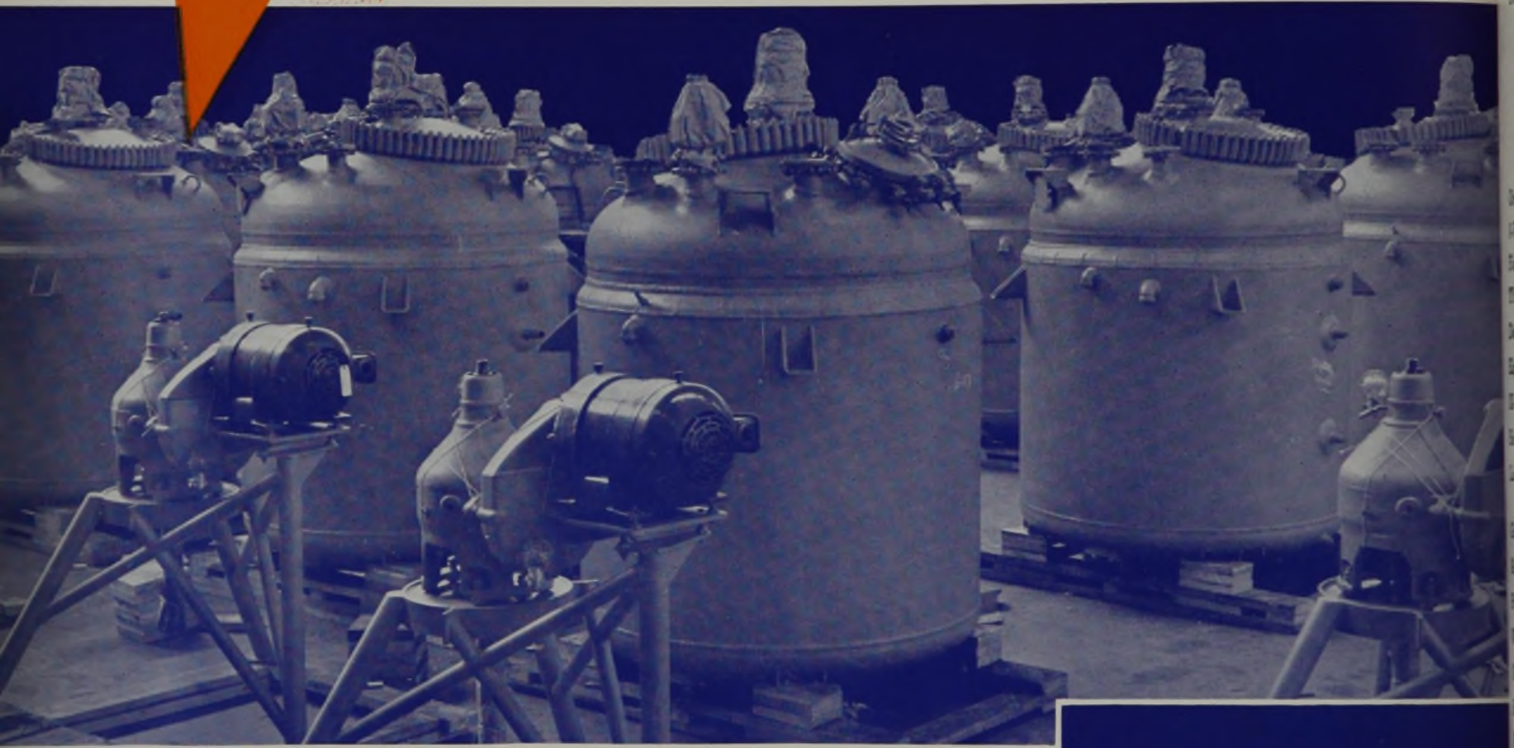
INDUSTRIAL
AND
ENGINEERING CHEMISTRY

B

YOUR PRODUCTION DRIVE STARTS WITH YOUR EQUIPMENT

Increase yield

BY STEPPING UP PRESSURES

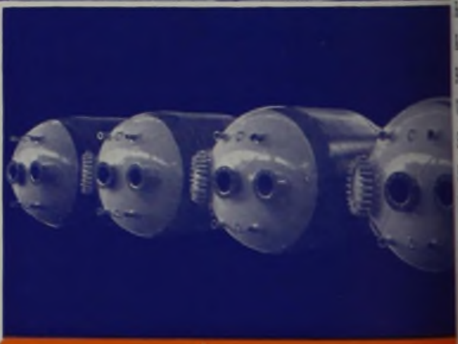


In many processes, such as the manufacture of glutamic acids, increased pressure increases yield. In other cases, higher pressures have meant the difference between satisfactory and unacceptable quality.

Today, Pfaudler glass-lined steel reaction equipment is operating at higher pressure ranges than ever before. The limiting factor is not the glass fused into steel—it is the ability of gaskets to hold pressure. This problem has received constant study and marked improvement has been achieved.

For example, standardized reaction kettles in capacities of 2,000 gallons and larger are built for 125 pounds per square inch internal pressure. Smaller equipment, particularly autoclaves, have been built to withstand 1,000 pounds per square inch internal pressure.

Remarkable diversity of operation can be carried on with standardized Pfaudler equipment. Wherever possible, this should be specified, since better deliveries can be made. However, where special designs are required, we urge you to begin negotiations well in advance. Make sure you have our latest catalog before you make your next move.

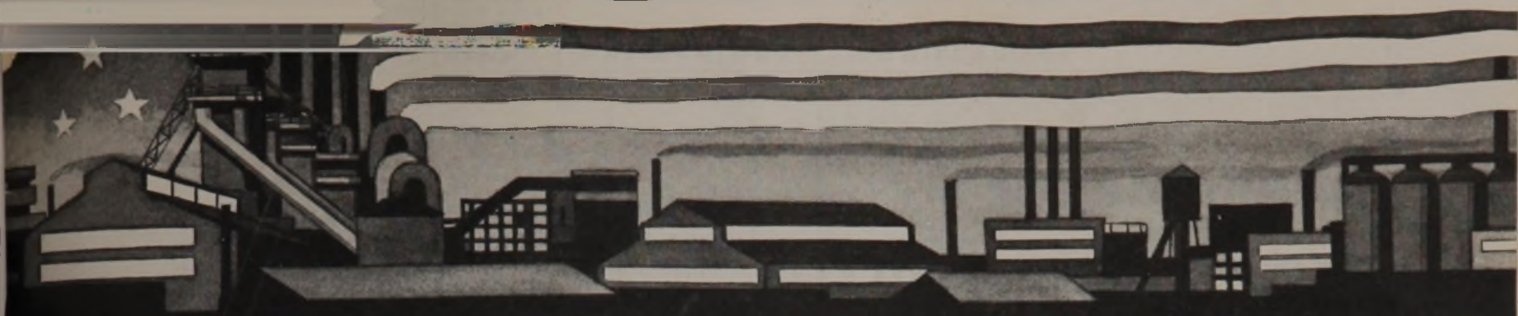


Glass-lined polymerizers used in the manufacture of synthetic rubber. These units are tested at 150 lbs. pressure and operate at 100 lbs. working pressure.

PFAUDLER GLASS-LINED STEEL IS RESISTANT TO ALL ACIDS (EXCEPT HF)

PFAUDLER

The Pfaudler Co., Rochester, N. Y. Branch Offices: 330 West 42nd Street, New York City; 1442 Conway Bldg., Chicago, Ill.; 1325 Howard St., San Francisco, Calif.; 455 Paul Brown Bldg., St. Louis, Mo.; 751 Little Bldg., Boston, Mass.; 7310 Woodward Avenue, Detroit, Mich.; 1318 1st National Bank Bldg., Cincinnati, 1228 Commercial Trs. Bldg., Philadelphia, Pa.



INDUSTRIAL AND ENGINEERING CHEMISTRY • INDUSTRIAL EDITION

WALTER J. MURPHY, EDITOR • ISSUED FEBRUARY 1, 1943 • VOL. 35, NO. 2 • CONSECUTIVE NO. 3

COAL IN INDUSTRY

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for your wartime formulae!

*Amorphous, diatomaceous, opaline silica

Improve quality and cut costs by using Celite inert mineral fillers for your regular and wartime formulae. Available in both standard and recently developed grades.

The Unique Characteristics of these diatomaceous silica fillers make them highly useful in a wide diversity of products. Here are four specific examples where Celite Fillers are being used today with important benefits:

1. In asphalt products, Celite provides a higher melting point, increased toughness, decreased brittleness, greater durability.
2. In household cleansers, it increases bulk and improves absorption.
3. In catalyst carriers, the high porosity and tremendous specific surface of Celite afford maximum exposure of the catalyst.
4. In match heads, Celite helps control the rate of combustion, as well as serving as an absorbent.

Whatever you make—paint, paper, insecticides or battery boxes—chances are Celite Mineral Fillers can help you solve both regular and wartime formulae problems.

Brief Data on a Few of the Standard Grades of Celite Mineral Fillers

GRADE DESIGNATION	COLOR	FINENESS	AVERAGE PARTICLE SIZE (Oden Method)	FREE MOISTURE CONTENT	ABSORPTION* WATER	ABSORPTION* LINSEED OIL	BULKING VALUE** LOOSE	BULKING VALUE** WET	SPECIFIC GRAVITY
Celite FC	Light buff	Maximum 7% on 150 mesh	4-6 microns	About 4%	205	195	8	17	2.00
Celite SSC	Light pink	Maximum 5% on 150 mesh	6-8 microns	Bone dry	210	195	9	17	2.15
Celite HSC	White	Maximum 7% on 150 mesh	7-9 microns	Bone dry	220	190	10.5	17	2.30
Snow Floss	Light buff	Maximum 1% on 325 mesh	1-2 microns	About 4%	210	175	8	24	2.00
Super Floss	White	Maximum 1% on 325 mesh	2-4 microns	Bone dry	150	120	9	28	2.30
Celite 374	Light pink	—30 mesh +60 mesh	———	Bone dry	172	159	23.5	—	2.15

*Gardner-Coleman Method—lbs. of liquid per 100 lbs. of Celite
**Lbs. per cubic ft.

CELITE PROVIDES

HIGH ABSORPTION, LIGHT WEIGHT, LARGE SURFACE AREA, LOW REFRACTIVE INDEX, SUPERIOR SUSPENSION. CELITE IS INERT.

And Celite is low in cost . . . available for prompt shipment. Mail Coupon for details.

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CELITE MINERAL FILLERS

JOHNS-MANVILLE, Dept. I-2
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Please send me my copy of brochure No. FI-500. I am interested in the use of Celite Fillers in:

☐ Absorptive packings
☐ Asphalt Compounds
☐ Battery Boxes
☐ Bituminous Compounds
☐ Catalyst carriers
☐ Cleansers—Household
☐ Enamels
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☐ Molded plastics
☐ Paints
☐ Paper
☐ Polishes
☐ Source of active silica
☐ Textile coatings
☐ Varnishes
☐ Welding-rod coatings

*Other uses*____________________
*Name*____________________
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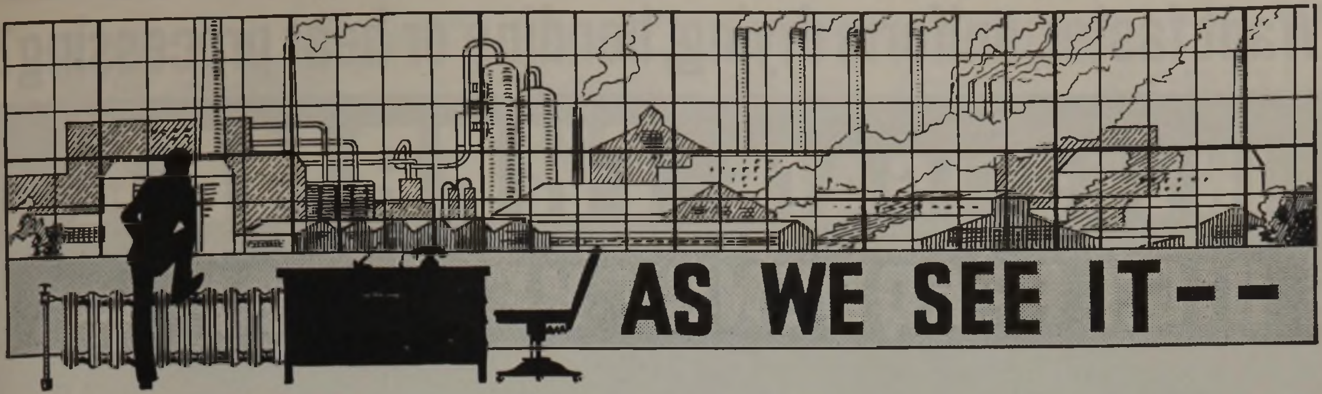


AS WE SEE IT--

▶ Alcohol Shortage and wheat surplus are offsetting each other as demand for the solvent grows in this all-out war. Performance of wheat, alone and in combination with other cereals, as a raw material for alcohol has been investigated by Stark, Kolachov, and Willkie (page 133), who give both laboratory and plant results.

▶ Coal and its products are important to agriculture in many ways and in many forms, according to Guy (page 139). Estimates of quantities consumed are presented together with a survey of applications.

▶ Filter Capacities of several types of plants have been increased from 25 to 100 per cent through the use of Pennsylvania anthracite as a filter medium. Turner (page 145) notes, however, that care must be exercised in the selection and preparation of the coal for this application.

▶ Foundry Coke of satisfactory quality can be made from Alabama coals only by blending several types. Mobley (page 148) describes coals used and results obtained.

▶ Weathering of Coal affects its coking properties, according to Schmidt, Elder, and Davis (page 150), who tested samples after accelerated weathering.

▶ New Products of Coal obtained by direct degradation reactions are reported by Howard (page 156). These possess higher molecular weights and more intricate ring structures than customary coal by-products. Their possibilities are interesting for future development.

▶ Plastic Sheetings are finding widening fields of usefulness, in many of which resistance to flexing is important. Duggan and Fligor (page 172) have determined fatigue resistance of a number of resins with different plasticizers under flexing.

▶ Paint Tests of any kind must be confirmed by actual weathering in the field to be fully useful. The planning and execution of a test fence program are described by McMullen and Ritchie (page 161), and important details of both exposure and interpretation of results are given.

▶ Patents, their value to industry, and calamity likely to result from the success of recent efforts to destroy our patent system are the subjects discussed by Wilson (page 177) in his significant address accepting the thirty-seventh Perkin Medal. This departure from the tradition of previous Perkin Medal addresses provides a penetrating analysis of the situation.

▶ Sugars can be graded by photoelectric measurements of reflected color, using the instrument described by Gillett and Holven (page 210). Previously these investigators had discussed grading by transmitted color.

▶ Ionic Exchange Agents for removing both anions and cations from solution have been developed to the point where their use provides the practical equivalent of distilled water for most purposes. Tiger and Sussman (page 186) give a survey of progress in this field and describe a two-step process for demineralizing solutions capable of important applications.

▶ Cellulose Acetate Solutions have been investigated by Montonna and Winding (page 214) to determine their viscosity-concentration relations.

▶ Rubber Accelerators react with activators during vulcanization, according to x-ray findings of Clark, LeTourneau, and Ball (page 198). Orientation of crystallites on stretching is shown, as well as behavior of reinforcing pigments.

▶ Research Is Defined by Work (page 221), particularly emphasizing the methods and results which characterize it.

▶ Research Accounting is at once important and involved from the administrative viewpoint. Sheehan and Curtis (page 225) discuss this necessary phase of research programs.

▶ Graduate Fellowships, according to Hass (page 223), have become well established aids to industrial research but, because of their unique quasi independence, require special planning.

▶ Dehydration of Vegetables as now practiced on a widening scale carries these materials beyond equilibrium with air of normal humidity. Makower and Dehority (page 193) have determined equilibria of a number of vegetables at various relative humidities, approached from both dry and normal states.

▶ Hydrogen Chloride is of expanding usefulness in reactions involving hydrocarbons. Data on its vapor-liquid equilibria with *n*-butane have been determined by Ottenweller, Holloway, and Weinrich (page 207).

▶ Acid Wastes of industry requiring disposal have increased substantially in volume with accelerated production. Rudolfs (page 227) analyzes this urgent problem and suggests methods for its solution that have been found useful.

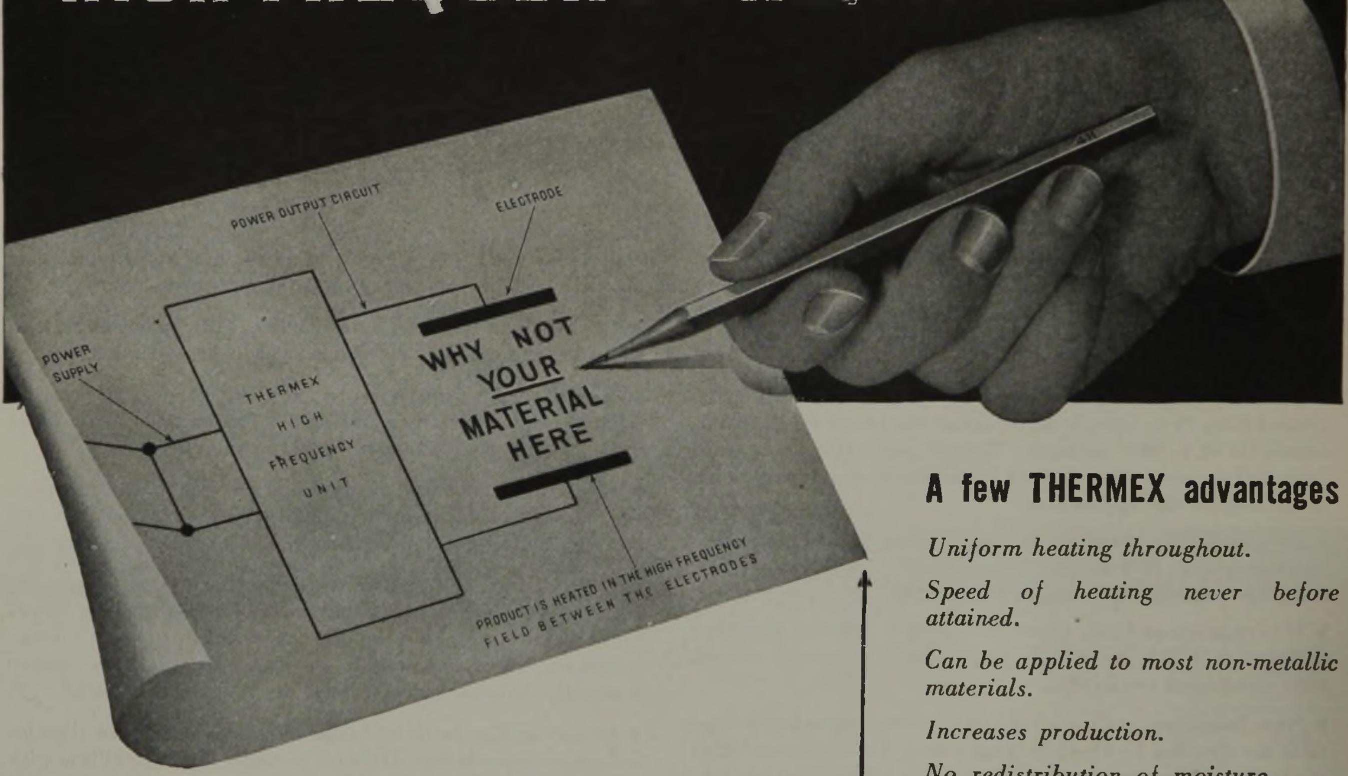
▶ Strength Measurements of Starches as indices of their value are compared by Morgan and Vaughn (page 233) with true viscosity. Significant discrepancies are found which indicate that viscosity is the more useful property as a specification.

▶ Hydrocarbons having boiling points close together vary widely from the ideal during distillation, according to Griswold (page 247), and this requires special consideration in designing fractionating systems to produce pure compounds.

▶ Activated Carbons adsorb certain constituents of raw whisky preferentially, according to Williams and Fallin (page 251).

▶ Zein Dispersions, useful in many important applications, are normally unstable and tend to set to gels in a short time. Evans and Manley (page 230) have found that superheating a dispersion containing a small amount of aldehyde materially enhances stability.

DHKilleffer


POWER OUTPUT CIRCUIT
ELECTRODE
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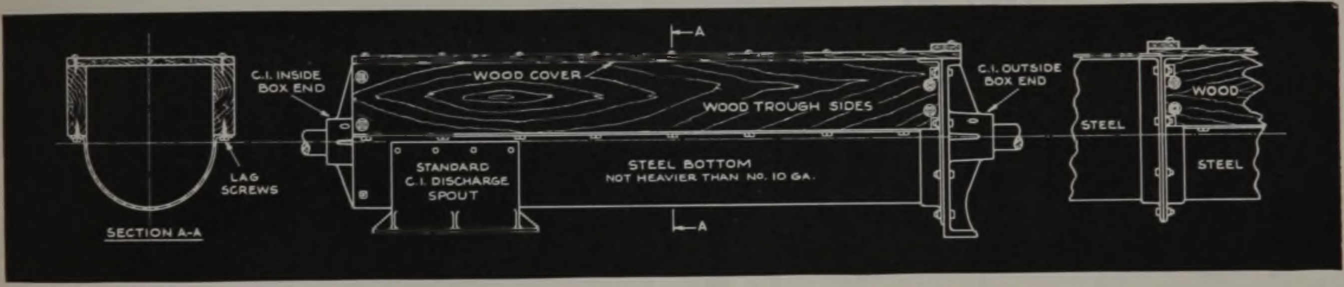
THERMEX HIGH FREQUENCY UNIT
WHY NOT YOUR MATERIAL HERE
PRODUCT IS HEATED IN THE HIGH FREQUENCY FIELD BETWEEN THE ELECTRODES

Now— COMBINATION WOOD AND STEEL SCREW CONVEYOR TROUGHS *TO CONSERVE STEEL*

Our ships, tanks, guns and aircraft are the front line defense of American liberty. Industrial uses of steel must be measured by actual necessity and the tonnage reduced with consideration for safety of life and fire hazard only.

Designs heretofore made popular by conveniences and the ultimate in years of service must be re-engineered as metal savers.



Section thru Combination Wood and Steel Screw Conveyor Trough.

Complete unit showing how standard inside or outside box ends and cast iron discharge spout can be applied.

Illustrating how Combination Wood and Steel Screw Conveyor Troughs can be connected to existing all steel troughs.

The necessity for an uninterrupted flow of food products to sustain our soldiers while operating ships, tanks, aircraft and artillery has taxed existing materials handling equipment. Extensions and replacements thus made necessary can now be accomplished with the Link-Belt Combination Wood and Steel Screw Conveyor Trough.

Adapted to all standard screw conveyor fittings.

Will connect with existing steel troughs without costly alterations. The drop bottom feature facilitates cleaning or replacement and gauges of steel adopted as standard conform to those listed for all steel trough, not exceeding No. 10 gauge.

Link-Belt engineers have a thorough knowledge of limitation orders and are at your service in this vital war effort.

LINK-BELT COMPANY
Engineers and Manufacturers of Materials Handling and Mechanical Power Transmission Machinery Since 1875
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SCREW CONVEYOR

UNIT processes take the March limelight with a group of some dozen papers providing new data and new ideas on a number of these fundamental chemical transformations. Chlorinolysis, by which is designated the splitting up of compounds in the presence of excessive amounts of chlorine, will be further elaborated for us in its many useful applications. Alkylation, increasingly valuable as a method of transforming hydrocarbons into more desirable structures, is applied to phenols and to benzene in a way to give new data on the process and its possible wider applications. Destructive distillation of cellulosic materials and the various processes connected with it receive attention. Polymerization and condensation are considered in this connection, as well as partial pyrolysis of hardwood in high-temperature steam. Sulfonation of aromatic compounds will also be treated and the application of partial-pressure distillation methods to this process. One inorganic reaction, the metathetic preparation of strontium carbonate, will be described with results given on pilot plant operations on strontium ore.

Coal oxidation (in storage, not in the firebox) will receive attention, particularly as it affects the subsequent value of the coal.

Ketones, we shall learn, can be synthesized by condensation of acid anhydrides with olefins. Details of the process will be given as practiced on a pilot plant scale.

Surface-active agents can perform important functions in the dispersion of pigments in nonaqueous media as used in paints, lacquers, inks, and the like. These will be elucidated for us, and their applications to commercial products stressed.

Iron compounds are objectionable in water used for most purposes. Their removal is consequently necessary with many natural waters. The functioning of exchange agents for this purpose will be discussed.

Coloring materials impart to plastics valuable characteristics and often are as important as the plastic itself in many applications. Consequently a study of colors for use with copolymers of vinyl acetate and chloride possesses special interest. Light fastness is emphasized, and methods of compounding for accelerated weathering tests have been devised and results described.

Azotobacter cells form a good source of the several members of the vitamin B complex and hence the growing of these nitrifying bacteria becomes a matter of considerable interest. We shall learn about this process and the results obtained by applying it on a pilot plant scale, as well as methods of utilizing the cells.

Corrosion of the interior of gasoline pipe lines, always a matter of interest, looms large now when pipe lines are overtaxed. Sodium nitrite has value as a preventive of timely interest.

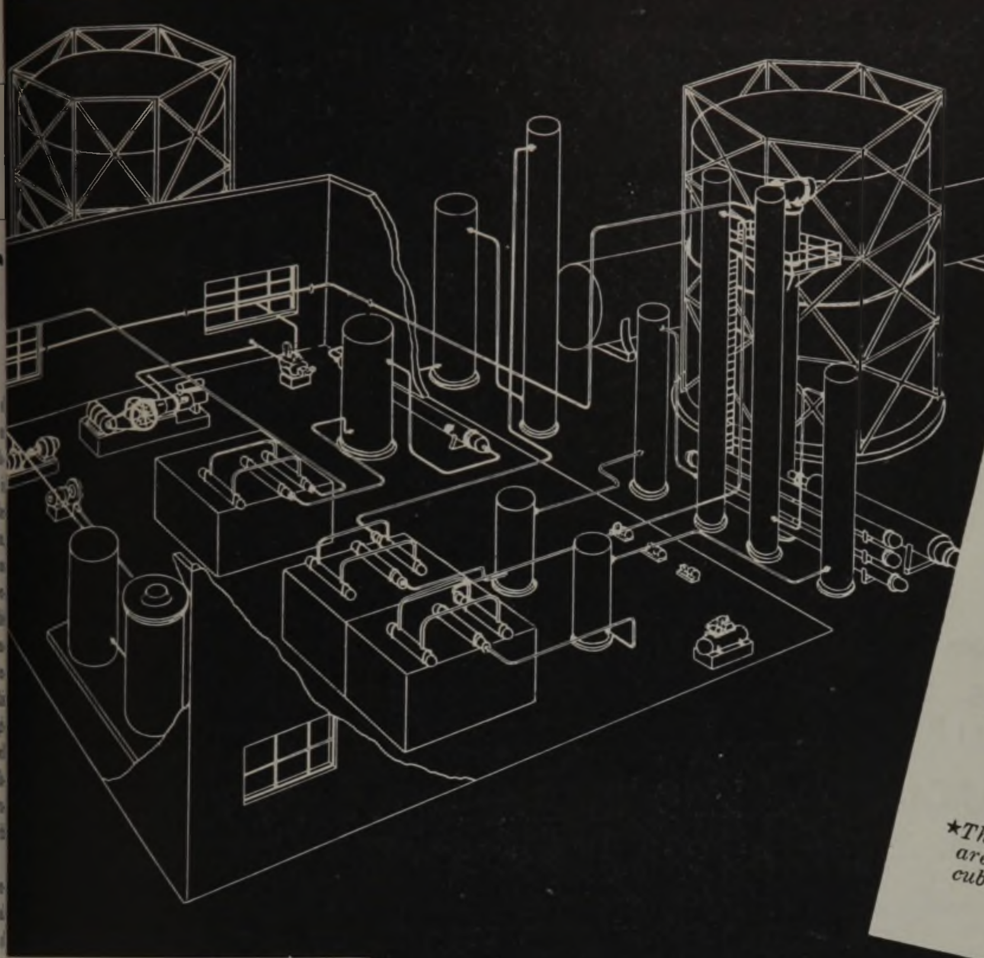
Industrial applications of the esters of starch, interesting materials from many points of view, will be discussed for us.

And of course, there will be much more on other subjects that will be both useful and timely.

YOUR HUMBLE SPY

OCESS MAKES HYDROGEN A

LOWER COST THAN ANY OTHER KNOWN METHOD



PROOF OF ACTUA OPERATING ECONOM

COKE	40-42 lbs.
STEAM	375 lbs. (325 lbs. of t quantity may be 15- gauge exhaust steam)
WATER	1,800 gallons
POWER	1.5 kilowatts
FUEL OIL	0.2 gallons (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. of gas per day. (In larger plants, an additional man would be required on each shift.)

★The above figures are approximate and are based on the production of each 1000 cubic feet of hydrogen.

5 OTHER ADVANTAGES

Coke, steam, air and water only raw materials necessary.

May be operated from 20% to 100% of rated capacity *continuously.*

Practically automatic. Saves labor.

Savings will pay for new piant in short time.

Carbon dioxide is valuable by-product—used for fire protection or many other purposes.

Continuous, practically automatic operation

● Compare any of the many methods for manufacturing hydrogen and you will find the Girdler Process produces raw hydrogen at lower cost than any other process.

The only raw materials necessary are coke, steam, air and water.

The purity of Girdler hydrogen permits its use in most cases without further treatment. However, for those who require super-purity, a Girdler Hydrogen Purification unit can be added. The hydrogen thus produced may be substituted for uses where electrolytic hydrogen heretofore has been required, as there is no measurable difference in behavior. Yet, the cost of producing hydrogen with the Girdler Process is far less than other method

The Girdler Process may be operated from 20 to 100% of rated capacity in a *continuo* manner. This means practically automat operation and a big saving in labor cos Units are available in capacities from o thousand to one million cubic feet *per ho*

If you now use or contemplate using hydrog gas, investigate the many advantages of t Girdler Process. Write today for bullet No. 103.

Specialists in the PRODUCTION, PURIFICATION, SEPARATI REFORMING or DEHYDRATION of Hydrogen Sulfide, Org Sulfur, Carbon Monoxide, Carbon Dioxide, Blue Water Hydrocarbons, Hydrogen, Nitrogen, Oxygen and various mixtu

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Louisville, Kentucky

Please send bulletin No. 103 describing th Girdler Hydrogen Manufacturing Process.

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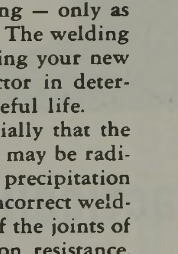


Every engineer that comes across Clark's ad this month will begin to wax enthusiastic (that is, if they can find "enthusiastic" around the plant — chances are he's down in Washington on some board or other). A two-cycle engine has been developed by Clark Brothers, and they show a picture of a six-cylinder, 600-h. p., two-cycle angle compressor proving that it can be done and in a big way.

"Two cycles" means that every down stroke is a power stroke, and that the flywheel's job of carrying the piston for two extra nondividend-paying strokes is finished. This means that for size, double power is obtained. Clark also says "greater simplicity," because there are no intake or exhaust valves but there is greater fuel economy, less wear, smoother operation, lower oil consumption, upkeep, and installation costs. In case you're interested in more efficient power for those new plants, Clark has engineers ready to answer questions and solve problems. Give it a thought, for more efficient engines mean more horsepower per pound of motor, which means that it is a novel way to save metal.

No matter what type of plant or piece of equipment you chemical engineers have to build, Acme Coppersmithing and Machine Co. have the experience and staff to help over the hard spots. In their message this month they show everything from alcohol to exchangers—including evaporators, a complete distillery, drying tanks for smokeless powder, and a clever looking multistage continuous vacuum dryer. Acme will help you with some of those construction-day blues.

This is an excellent time for Johns-Manville to remind you how to get increased efficiency from present filtration equipment. Now that more material must be jammed through the plant—and equipment as scarce as kangaroo feathers—ways and means for getting more for the same effort are well received. They recommend four steps: Select a filter aid which provides the desired clarity and flow rate; estimate correct addition of filter aid; determine proper filter cycle time; and be certain that the optimum pH, temperature, and concentrations exist. It is possible, they say, that by following these suggestions, filter capacities may be increased three or four times.

Using rare and little used minerals to win the battles of this war won't seem strange to the chemical family for they are familiar with strange doings, but the advice of this column is to read the story told this month by the Foote Mineral Company. Well written and interesting, it may strike a responsive chord on some production problem.

Dow Chemical, which started by making only bromides, now has more than five hundred industrial chemicals, all ready to serve you. This well known company truly states that their chemicals are indispensable to industry and victory.

Alorco tabulates the various types of aluminas used in catalytic processes and manufacturers of high-octane, synthetic rubber, plastics, and explosives, are all going to be interested in getting further information.

R. E. Ackshun

HOW TUBE-TURN
WELDING FITTINGS
BENEFIT WAR
INDUSTRY

The FIRST WELDING FITTINGS 1ST AND STILL THE BEST

Two ways that Tube-Turn welding fittings avoid wasting men and hours in war plants!

SPEED-UP PIPING INSTALLATION

2 GREATLY REDUCE MAINTENAN

aster installed, trouble-free piping steps-up production schedules!

TUBE-TURN fittings speed up piping installation four ways: (1) Need only butt-welds, easy for veteran or novice welders. (2) Less lining-up, for ttings have *uniform* walls and true circularity. 3) Sections pre-assembled on the ground save ime. (4) Torch cutting and fabricating are liminated. Tube-Turn fittings are ready to weld -types, sizes and weights for all needs.

You can depend on piping welded with Tube-Turn fittings to be practically maintenance-free, as Tube-Turn welding fittings give the *greatest possible strength* and *long life.* They're *permanently leakproof.* There are no bolts to loosen, no gaskets to replace, no threads to corrode and weaken.

No plant *ever* can afford a break-down or production slow-up, but in war-time it's a disaster! The best insurance in the world against trouble in piping systems is *welding* with *Tube-Turn fittings!*

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

TUBE-TURN *Welding Fittings*
TRADE MARK

★

OTHER WAR-TIME ADVANTAGES

SAVES CRITICAL MATERIAL: Absence of many flanges, bolts, nuts and heavy cast steel construction saves many tons of metal in a single piping system.

FASTER AND EASIER TO INSULATE: Tube-Turn fittings are insulated as easily as the pipe itself, for the welds form one continuous tube.

SAVE SPACE: Pipe systems welded with Tube-Turn fittings permit streamlined, compact lay-outs and sharp angles.

LAST LONGER: Smooth inner walls—with no ridges, waves or scale—means less corrosion and longer life.

LESS PRESSURE LOSS: Because of full effective radius and exact O.D. and I.D. alignment with the pipe, the flow is more efficient and pressure loss is less.

FEWER SUPPORTS NEEDED: Since welded piping weighs less and stands vibration better than flanged systems, few hangers or supports are required.

OIL SAVERS—PQ SILICATES

With greases and oils on the critical list, those processing methods get priority that prevent the waste of even a drop or gob. Many of these conservation methods effectively and economically use PQ Silicates of Soda. Do you know how PQ Silicates can serve you as oil savers? Check the uses below about which you want more details and mail those paragraphs with your letterhead to us in Philadelphia.

☐ *Reclaiming Used Crank Case Oil:* B-W or O Brand agitated with the oil and water wets carbonaceous and other solid impurities, so that they settle into the watery layer, leaving clear oil.

☐ *Greaseproofing Concrete:* Oil storage tanks are protected against oil penetration and oil loss as well, by a treatment with PQ Silicate of Soda. Recommended for either mineral or vegetable oils.

☐ *Lining Wood Barrels:* Coating wooden packages to prevent absorption of vegetable and animal oils is established practice. Silicate is the cooper's most economical lining material.

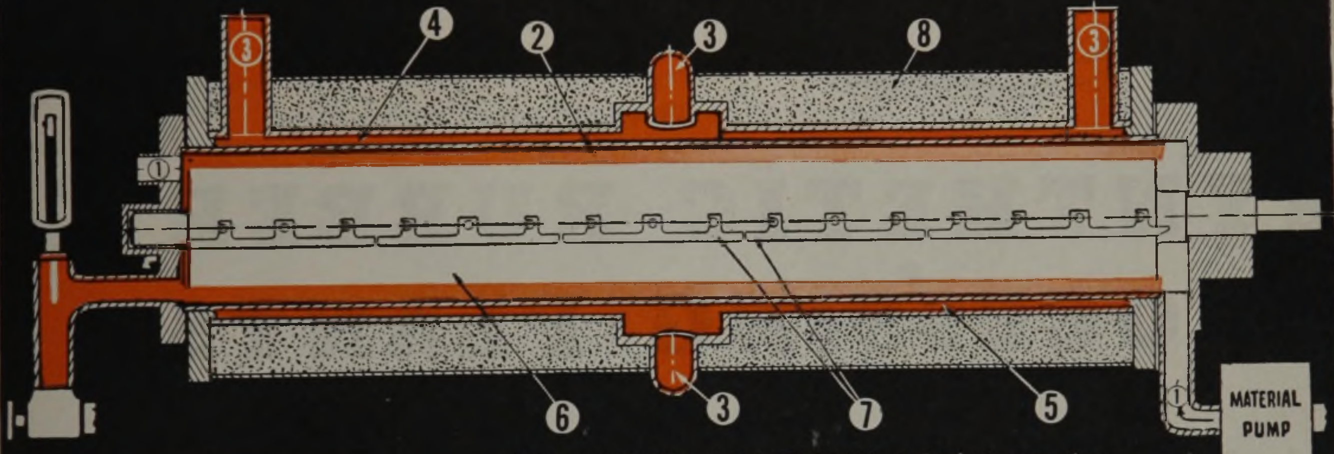
☐ *Greaseproofing Paper:* Paper and paperboard coated with the correct brand of silicate are used for packaging greasy and oily products. The vermin-proof qualities of silicate are important for food products.

PHILADELPHIA QUARTZ CO.

Established 1831 . . . General Offices and Laboratory: 125 S. Third Street, Philadelphia, Pa.
Chicago Sales Office: Engineering Bldg. Sold in Canada by National Silicates Ltd., Toronto, Ont.

VOTATOR is adaptable for many war materials:
Chemicals • Aviation Gasoline
Plastics • Oil Products

REVOLUTIONARY VOTATOR UNIT HEATS OR COOLS LIQUIDS OR VISCOUS MATERIALS IN SECONDS!



KEY TO VOTATOR FLOW DIAGRAM—1. Product connections. 2. Annular space thru which product passes. 3. Heat transfer medium. 4. Heat transfer medium passes thru this annular space. 5. Heat transfer tube. 6. Mutator shaft. 7. Scraper blades. 8. Insulation.

7 VOTATOR ADVANTAGES

- Heat transfer takes place in seconds.
- Continuous, rapid flow of product.
- Fully closed system.
- Uniform temperature, accurately controlled.
- Simultaneous mixing, emulsifying or aerating.
- More economical.
- Saves critical materials and refrigeration load.

Cut-away view of heat transfer tube—heart of the Votator.

Votator Permits Very Accurate, Rapid, Continuous Heat Transfer—with Simultaneous Mixing or Emulsifying!

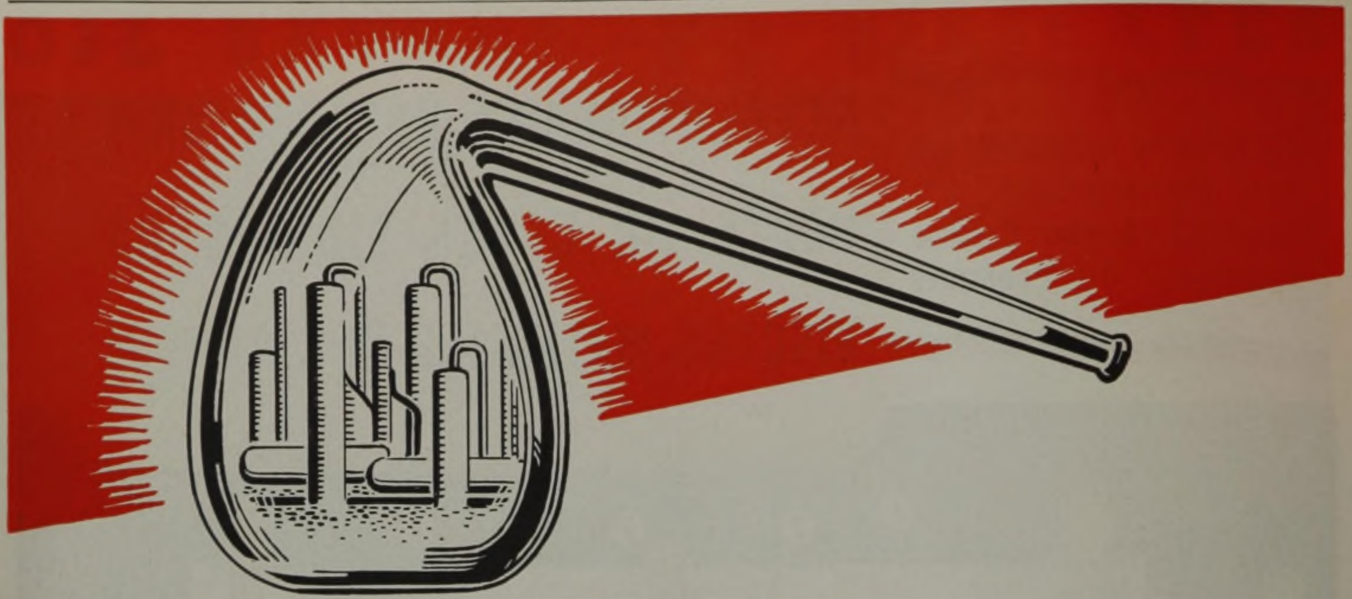
The VOTATOR is a unique, continuous, closed heat transfer unit that heats or cools liquids and viscous materials BETTER AND FASTER than any known system. Its extraordinary efficiency is due to the patented principle of passing a very thin film of product over a relatively large heat transfer surface. Heating or cooling takes place in SECONDS instead of minutes. By treating only a small amount of product at any time, but pumping it through continuously at a high rate, the VOTATOR assures very accuarte uniform temperature.

VOTATOR'S ability to MIX, EMULSIFY OR AERATE the product at the same time it is heated or cooled is an important added advantage to many industries. Numerous pilot tests and studies show VOTATOR'S increased speed and efficiency to be invaluable in processing many vital war materials.

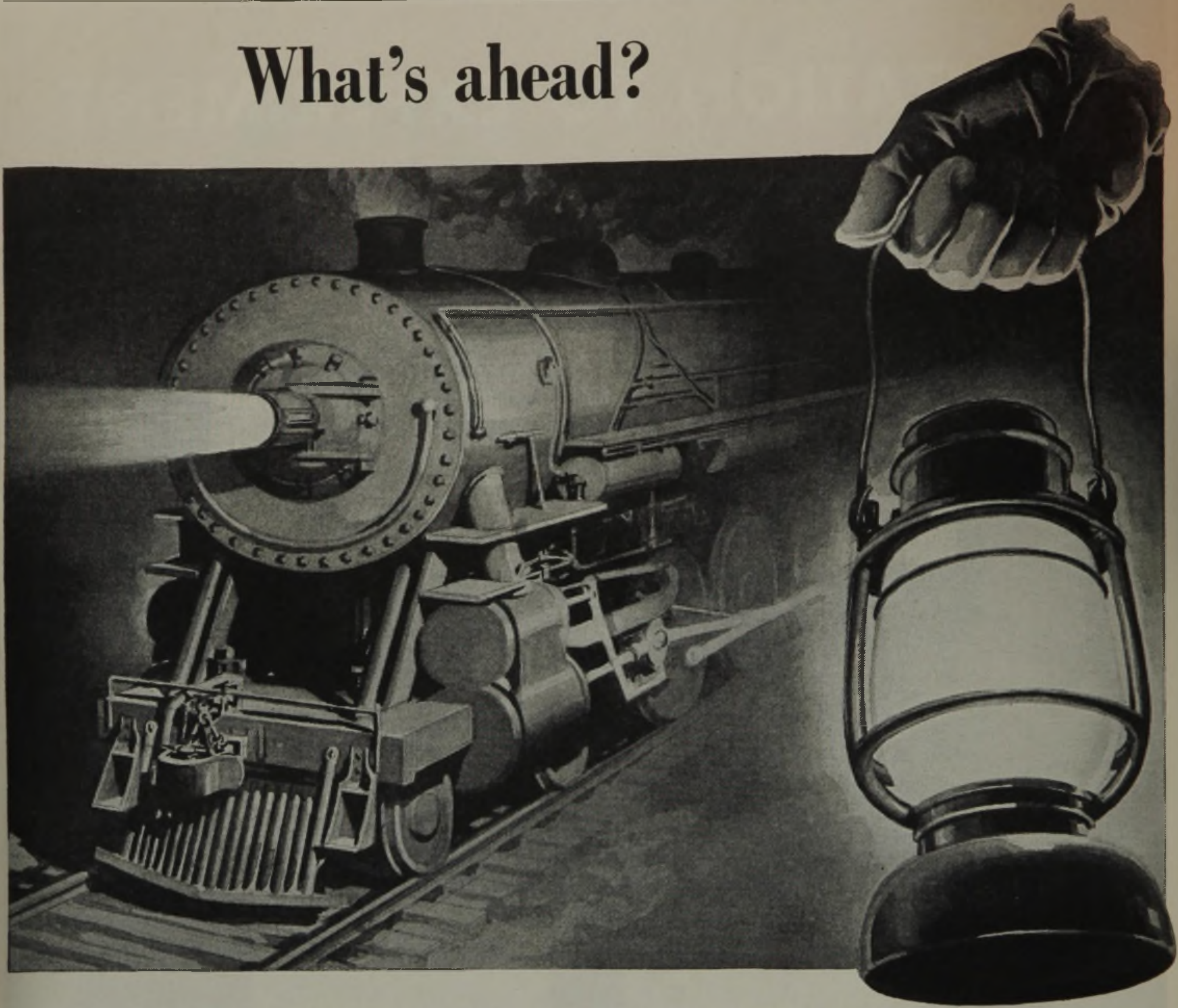
Send now for free descriptive booklet No. 300-B describing this highly efficient, continuous heat transfer unit!

The VOTATOR

THE GIRDLER CORPORATION
VOTATOR DIVISION • LOUISVILLE, KY.



What's ahead?



Like the trains that form her life-line, the America of a new year gathers speed as the first mile is passed. The track is straight, the wheels are strong; and aboard is a treasure—for every signal, every safety device to protect.

Part of it is the oil, the gasoline, the priceless chemicals that comprise America's liquid ammunition. And into the hands of those who produce it is given its guardianship — to protect it as zealously as it was produced.

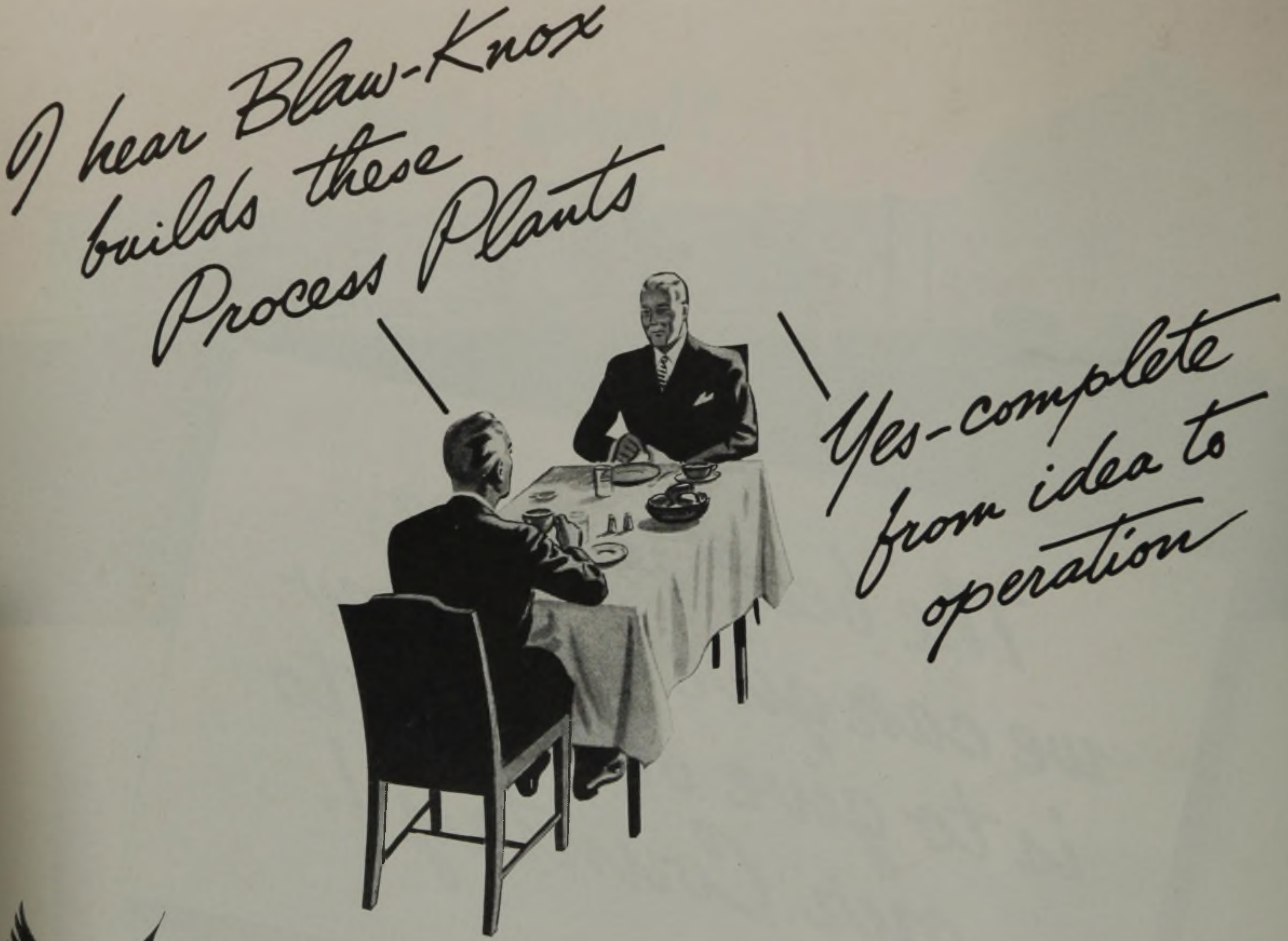
Just as yours is the pride of making this, America's liquid treasure, ours is in helping to safeguard it—with closures that make every drum a fortress, and every questioning "what's ahead?" quickly answered "safety."

Call to mind the hazards a drum can encounter — leakage, waste, pilferage and sabotage — and you sum-up the complete protection of Tri-Sure Closures. These are the closures that give *triple protection* — with a seal, a plug and a flange that keep every hazard out of a drum and every drop of its contents in.

Today, when liquids that are more precious than ever are being transported and stored under conditions more hazardous than ever, Tri-Sure has answered the call for closures that really seal and really protect; for closures that make every shipment a safe shipment; for closures that keep the drums rolling — safely.

Tri-Sure
Reg. U. S. Pat. Off.
CLOSURES

AMERICAN FLANGE & MANUFACTURING CO. INC., 30 ROCKEFELLER PLAZA, NEW YORK
TRI-SURE PRODUCTS LIMITED, ST. CATHARINES, ONTARIO, CANADA



Whatever your Process—depend on Blaw-Knox to do the whole job. Research, engineering, fabrication, erection, initial operation—all under the single guarantee and single responsibility of Blaw-Knox!

BLAW-KNOX DIVISION OF BLAW-KNOX CO.
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Complete plants or equipment for the following processes . . .

- Distillation
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- Heat Transfer
- Furnacing
- Cracking
- Kilning and Calcining
- Polymerizing
- Evaporation
- Crystallization
- Drying
- Mixing and Stirring
- Organic Synthesis
- Emulsification
- High Pressure Processing
- Impregnating
- Gas Cleaning
- and others

BLAW-KNOX builds complete PROCESS PLANTS

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

U.S.I. CHEMICAL NEWS

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

Dibutyl Phthalate Good Softener for Perbunan Rubber

Imparts Excellent Resistance To Cold and Gasoline Immersion

ELIZABETH, N. J. — Dibutyl phthalate is rated among the most satisfactory softening agents for the compounding of Perbunan type synthetic rubber, it is indicated by the reports of research workers here.

The effect of a number of softeners was studied from the standpoint of response of the compounded rubber to subzero temperatures, and also of contact with petroleum oils. As a result of these tests, it was found that dibutyl phthalate is one of a small group of ingredients which are effective in preventing hardening at low temperatures.

Effect of Petroleum

Since Perbunan is largely used for making hose, gaskets, and other parts subjected to contact with petroleum oils, behavior of the softener under these conditions is a matter of extreme importance. Undue extraction of the softener would result in marked shrinkages in volume of the compounded part. From this standpoint also, dibutyl phthalate shows good resistance to immersion in gasoline, as measured by volume change, tensile strength retention, and low increase in hardness.

Drug Trades Section to Hold Dinner on March 4

The 18th Annual Dinner sponsored by the Drug, Chemical, and Allied Trades Section of the New York Board of Trade will be held at the Waldorf-Astoria in New York on Thursday, March 4.

Following the precedent established last year, it has been announced that a substantial donation to a war charity will be made from the proceeds of the dinner. The cooperation of the industry in maintaining a high level of attendance at the dinner will help to make the contribution as large as possible.

Sulfa Drug Films Studied For Burns, Cuts, Surgery

BALTIMORE, Md.—Translucent films containing sulfa drugs are undergoing study here as a surgical dressing for burns and cuts and for the treatment of wounds. Preliminary reports indicate that the films are effective in preventing infection.

The films are prepared by making an emulsion of 3% sulfadiazine or sulfanilamide, 2.5% methyl cellulose, 3% triethanolamine, and 0.5% sorbitol with ethanol or acetone. This emulsion is sprayed on a smooth glass sheet, from which it is stripped off in the form of a film. The film is applied after preliminary cleaning of the affected area.

New Pittsburgh Address

U.S.I.'s Pittsburgh Office is now located in the Fulton Building, 107 Sixth Street.

New Source of Glycerol Opened By Process Developed by U.S.I.

Fermentation Procedure is Key to Vitally Needed Supplies For Manufacture of Explosives and Other Urgent Requirements

In view of the current importance of glycerol as a raw material in the manufacture of nitroglycerine for explosives, the development by U.S.I. of a commercially practicable method for producing this vital material by fermentation of molasses assumes outstanding interest. Pilot plant operations have demonstrated the feasibility of the technique, and commercial production is soon expected to alleviate the critical demand for glycerol.

Glycerol (more commonly known as glycerine), discovered in 1779 by Karl W. Scheele, is one of the oldest and most widely used chemicals. The value of glycerol rests on its physical properties rather than on its chemical constitution although it is employed chemically to make certain very important compounds. Of the physical attributes of glycerol, the most outstanding is its strong affinity for water. This has led to its employment as a humectant and plasticizer, and since it is non-toxic, it can be used in cosmetics and foodstuffs where an agent for the holding of moisture is necessary to keep the products in condition. Glycerol is a remarkably good solvent, comparing in this respect with water and ethanol. Many antiseptics and essential oils are soluble in glycerol, and this solvent property, combined with the fact that it is non-toxic, gives the compound its unique place in the manufacture of pharmaceutical preparations and as an ingredient of food products.

This article lists some outstanding uses of glycerol in military and civilian applications. A much more detailed listing is given in Bulletin GU, which is available without charge from U.S.I.

Manufacture of Resins

In recent years glycerol has taken an important place in the plastic field as a constituent of alkyd resins. These resins (phthalic anhydride and glycerol) are made in a variety of ways. Glycerol and resin are combined to make the well-known ester gums widely used

(*Continued on next page*)

New Method Described for Making Chroman Compounds

MINNEAPOLIS, Minn. — A novel process for making tocopherol-like chroman compounds has been revealed in a patent granted to an inventor here. Since alpha-tocopherol is Vitamin E, these new compounds, apparently of a similar character, are expected to have medical and biological applications.

Key to the new process lies in the preparation of the primary intermediate. A halo-alkyl derivative of a diether of hydroquinone is first prepared. This compound is then used to alkylate a *beta*-keto ester, preferably ethyl sodium acetoacetate, resulting in the formation of the primary intermediate.

Ethyl sodium acetoacetate is produced by U.S.I.

Non-Discoloring Adhesive Made with Aid of Urethan

WESTFIELD, Mass. — Discoloration of the adhesive on envelope flaps can be prevented by means of a novel formulation involving the use of urethan, it is claimed in a patent granted to an envelope maker here.

The discoloration is caused, according to the patent, by chemical reaction between degraded protein in the paper and reducing sugars in the adhesive. It can be prevented, it is claimed, by decreasing the reducing sugar content. The fluidity necessary to apply the adhesive to the envelope, ordinarily obtained by high sugar content, is achieved by addition of a carbamic acid ester, such as urethan.

The manufacture of nitroglycerine for explosives is one of the most important applications of glycerol. Procedure developed by U.S.I. will make additional supplies available for this and other purposes.

February ★ U.S.I. CHEMICAL NEWS ★ 1943

Applications of Glycerol

(Continued from preceding page)

in varnishes. Glycerol is an important ingredient in adhesives, acting as a means of controlling the flexibility of these products so as to give them the maximum of strength under the conditions of use. A similar application is found in certain cements such as the familiar litharge-glycerol combination used as a plumber's cement and a cement for aquaria. Here advantage is taken of the readiness with which glycerol combines with the lead salt used in the cement to form a hard insoluble compound.

Plasticizing Cellophane

One of the outstanding uses of the compound in modern technology is the employment of glycerol in plasticizing cellophane. It is only necessary to consider how widely used this material is to realize the important part that glycerol plays in our everyday affairs. In cellophane the glycerol exists in the form of a solution of approximately 60% strength. About 25% of the weight of the finished product is made up of the plasticizer. Without a suitable softening agent, the cellophane film is brittle and useless.

Lubricating Properties

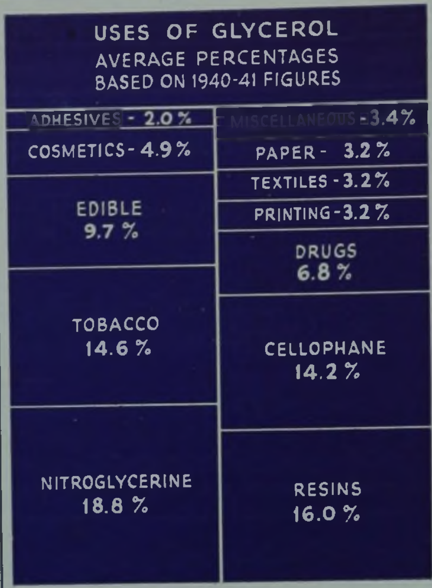
Other widespread uses of glycerol rest on its lubricating properties. Certain machinery used in processing foods must be lubricated with a tasteless and non-toxic lubricant. Glycerol fits these specifications well and has in addition a high degree of stability under the conditions existing in bearings.

In textiles, glycerol has uses which depend largely on its properties as a lubricant. It thus renders fabrics soft and facilitates weaving, and since it is so readily miscible with water, it aids in dyeing and printing operations on cloth.

Another major use of glycerol is in tobacco. Here the hygroscopicity of the material comes into play to keep the tobacco moist and thus to hold it in condition over long periods of time during which the tobacco without such protection would dry out completely. It is difficult to find a substitute for this particular use of glycerol.

Making of Explosives

The most important purely chemical use of glycerol is as a raw material in the manufacture of nitroglycerine for explosives. Modern ammunition requires precisely formulated propellants and nitroglycerine has a place of major importance as an ingredient in these propellants. Since the ballistics of long range guns is based on the propellant, the propellant formula cannot be changed without revising the data on which the aiming of the guns is based. The employment of nitroglycerine in powders overshadows all other uses at the present time.



An approximate breakdown of the amounts of glycerol employed in various fields is shown in the accompanying chart. Four uses, nitroglycerine manufacture, resin manufacture, tobacco conditioning and cellophane plasticizing account for over 60% of all the glycerol produced. The figures in the graph are averaged from 1940 and 1941 statistics.

The use of glycerol showed an increase of approximately 33⅓% from 1940 to 1941, and expanding military use, plus the necessity for adequate stock piling, makes a shortage of this vital chemical a possibility to be reckoned with during the coming months. Substitutions are possible to some extent and certain uses can be curtailed, but the restriction of available glycerol to explosive manufacture and its consequent elimination from all civilian uses poses a very difficult problem due to the widespread use of this versatile chemical.

This brief review of the major applications of glycerol indicates the importance of developing new sources of supply. The fermentation procedure developed by U.S.I. to meet this demand will be discussed in a second article on glycerol, which will appear in the March issue of U.S.I. Chemical News.

TECHNICAL DEVELOPMENTS

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

New adhesives, made from a vegetable base, are said to compare in range and flexibility of action with animal-base adhesives. According to the maker, they can be used undiluted or mixed with water, to give firm adhesion in combinations of paper, cardboard, fabrics, leathers, and imitation leathers. **(No. 660)**

U S I

A sponge rubber substitute can be vulcanized directly to such surfaces as metal and plastics, and has flex-cracking resistance which improves at lower temperatures, it is reported. In many other respects, properties are said to be very similar to those of natural rubber. Material is immediately available for many war applications. **(No. 661)**

U S I

New gaskets made from solution-proof kraft paper are described as suitable for replacements for rubber gaskets in drums, pails, bungs, and spouts. They are said to have been tested for the transportation of all liquids except corrosive acids. **(No. 662)**

U S I

Drying oil substitutes can be produced by fractionation of domestic oils, research work indicates, and commercial production is expected soon. It is reported that the process is adaptable to the making of special fractions for specific purposes. **(No. 663)**

U S I

A suspension agent is reported to aid in preventing the settling or caking of pigments used in luminous paints. It is said that the product can be used in high concentrations to form thick supporting gels. **(No. 664)**

U S I

A lintless filter paper is described as having high retention qualities. Maker says that it is supplied washed with nitric acid, and that it is primarily suitable for the filtering of intravenous and subcutaneous injectibles. **(No. 665)**

U S I

Agitator tanks are now being constructed from wood, including cypress, redwood, pine, fir, oak, and poplar, it has been announced. Storage tanks up to 100,000 gallons capacity are also being produced. The wood tanks are expected to be useful to the processing industries. **(No. 666)**

U S I

Pure nickel foil is now being produced on a small scale in widths up to 16 inches and thicknesses from 0.00025 to 0.0015 inch, it is reported. Possible applications are seen as container linings, diaphragms, and wrappings. **(No. 667)**

U S I

Analytical sets now being supplied include the necessary apparatus and chemicals for the testing of plating solutions. One set is designed for determining total and free sulfuric acid; a second for total and free chromic acid. **(No. 668)**

U S I

Imitation perfume oils developed by one supplier are said to include products that simulate the following natural oils: cassia, bergamot, cinnamon, citronella Java, geranium, lavender, lemongrass, peppermint, and sassafras. **(No. 669)**

U.S.INDUSTRIAL CHEMICALS, INC.

CHEMICALS · INDUSTRIAL · ANTI- · USI · SERVICE TO INDUSTRY · SOLVENTS · ALCOHOLS · FREEZE

60 EAST 42ND STREET, NEW YORK · BRANCHES IN ALL PRINCIPAL CITIES

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

Ethanol (Ethyl Alcohol)
- Specially Denatured—All regular and anhydrous formulas
- Completely Denatured—all regular and anhydrous formulas
- Pure—190 proof, C.P. 96%, Absolute
- U.S.I. Denatured Alcohol Anti-freeze
- *Super Pyro Anti-freeze
- *Solox Proprietory Solvent
- *Solox D-I De-icing Fluid

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

ACETIC ESTERS
- Amyl Acetate
- Butyl Acetate
- Ethyl Acetate

OXALIC ESTERS
- Dibutyl Oxalate
- Diethyl Oxalate

PHTHALIC ESTERS
- Diamyl Phthalate
- Dibutyl Phthalate
- Diethyl Phthalate

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

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

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

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

*Registered Trade Mark

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STEEL SEPARATOR TANKS

Fabricated by

Builders of Anything in Iron and Steel Not Already Produced as a Specialty

if it's made of Iron or Steel, draw a picture of it—we'll build it.

The "Jay-Cee" Steel Separator Tanks illustrated above were fabricated for a large producer of chemicals. Seven (7) air-tight steel tanks, all welded construction, 7'0" in diameter x 15'6" long with flat top and conical bottom, complete with flanged openings and man holes; thickness of material—3/8". These tanks were used by this producer to separate light ash after it had been dried.

The "Jay-Cee" organization of technicians and craftsmen have contributed greatly to War Industry as proved by the fact that "Jay-Cee" production has increased by more than 400% in the last 27 months.

Take advantage of "Jay-Cee" knowledge and experience for the production of "anything in Iron and Steel not already produced as a specialty." Inquiries will receive prompt attention and incur no obligation.

JAY-CEE *PRODUCTS*

ALUMINUM PLANTS
- Hoppers & Chutes
- Stacks & Breechings
- Annealing Baskets
- Special Machinery

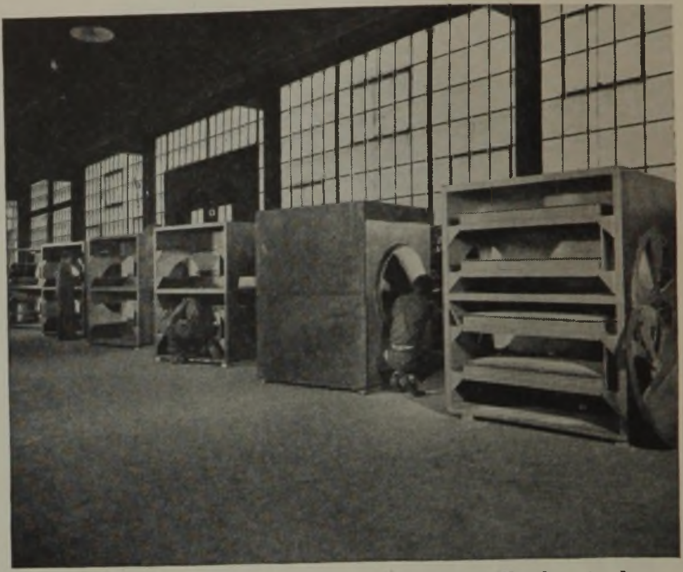
POWDER PLANTS
- Tanks
- Pressure Vessels
- Fabricated Piping
- Special Machinery

OTHER PLANTS
- Structural Steel
- Sheet and Plate Work
- Iron Castings
- Special Machinery

JOHNSON CITY FOUNDRY & MACHINE WORKS
JOHNSON CITY, TENNESSEE EST. 1883
GRAY IRON and ALLOY IRON CASTINGS — STRUCTURAL STEEL — MISCELLANEOUS and ORNAMENTAL IRON WORK — SPECIAL MACHINE WORK

Food Processors

TAKE A TIP FROM THE DRUG INDUSTRY



Service performed by hundreds of Lectrodryers like these in the Drug Industry guide our engineers' recommendations to you.

There are unknowns a'plenty to plague you when you get into food dehydration. Fortunately, the Drug Industry has already solved some of the problems you will encounter.

For years, the pharmaceutical industries have obtained winter dryness in their tray driers on humid summer days by drying the air with Lectrodryers. Thus they have reduced their processing time and held products uniform, regardless of outside weather conditions. Others, needing a greater degree of dryness than is possible with standard methods, have used Lectrodryers to reach moisture contents lower than heretofore possible.

In the food industry, drying operations on which Lectrodryers can certainly help may be grouped as follows: 1. Standardizing drying conditions in your present driers. 2. Giving you a degree of dryness better than the most favorable weather conditions. 3. Conditioning air for processing and packaging operations.

There are hundreds of Lectrodryer installations on comparable work throughout industry. Recommendations on drying given you by our engineers are based on years of experience, not guesswork. If dehumidification is one of your problems, let us help you. Write to PITTSBURGH LECTRODRYER CORPORATION, 305 32nd Street, Pittsburgh, Pa.

LECTRODRYERS DRY WITH ACTIVATED ALUMINAS

PITTSBURGH
LECTRODRYER
CORPORATION

Reg. U.S. Pat. Off.

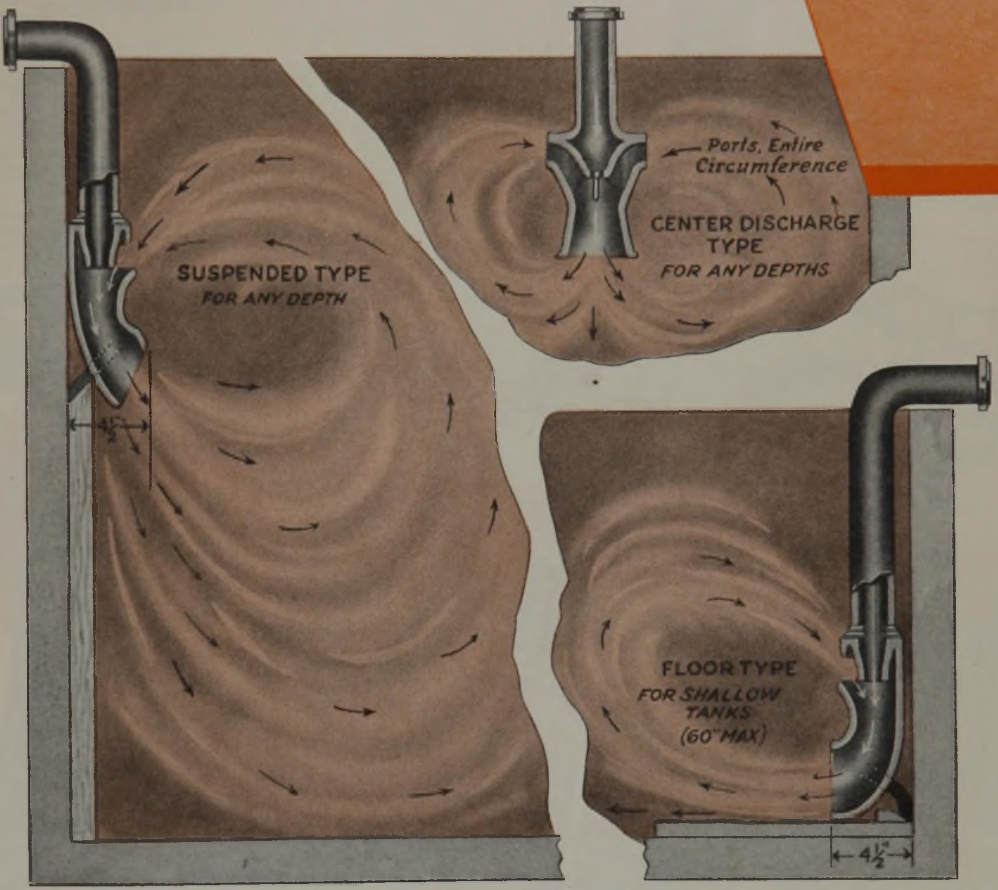
3 NEW CIRCULATING STEAM JETS OF *Duriron and Durimet*

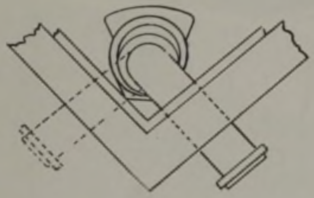
for HEATING and AGITATION; ACID DIGESTION

Duriron Company engineers have designed three new corrosion-resisting steam jets to meet the needs of War Industries. *Note how little space is required in the tank for these jets . . . they "hug" the tank wall, projecting only 4½ inches.*

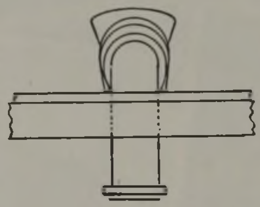
ADVANTAGES

1—Acid and abrasion resisting.
2—Eliminate destructive pounding;
  (a) Practically noiseless in operation.
  (b) Lengthen life of tank or tank lining.
3—Highly efficient circulation of tank contents.

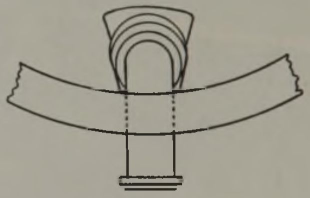




As used in corner of square tank; inlet from either side.



Over or through side of square tank, it fits closely to wall.



Over or through wall of circular tank, it agitates complete area.

SOME SPECIFIC USES

1—Heating acid solutions, such as pickling solutions, wash liquors, numerous acids.
2—Dissolving powder and lump chemicals, such as copper sulphate, alum, salts, sodium chlorate, coagulants, etc.
3—Digestion of ores, such as bauxite, phosphates, Barytes, ilmenite, etc.
4—Sludge acid separation, cooking, etc.

For further details, write

THE DURIRON COMPANY, INC., DAYTON, OHIO
Designers and Manufacturers of Mechanical Equipment for Corrosive Servic

DURIRON · DURICHLOR
CORROSION-RESISTING
DURCO
ALLOYS & EQUIPMENT
THE DURIRON CO. INC.
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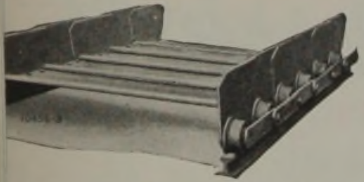
DURIMET · DURCO STAINLESS STEELS

ARMY E NAVY

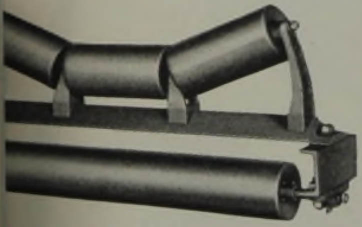
IT'S A PRODUCTION WAR . .

STUDY THIS JEFFREY GUIDE FOR MORE EFFICIEN

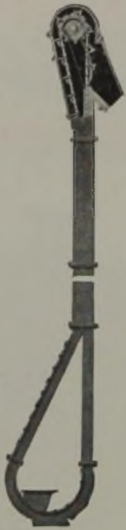


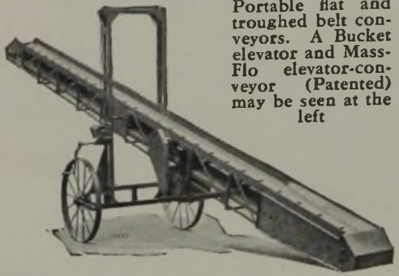
Section of steel apron conveyor

Section of scraper conveyor

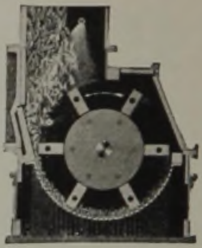


Three-roll belt idler (Patented)



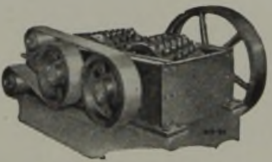


Portable flat and troughed belt conveyors. A Bucket elevator and Mass-Flo elevator-conveyor (Patented) may be seen at the left

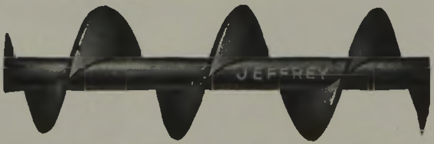


Screenings grinders for chips, sewage and other defibering work

Detachable, Hercules, Re
and Steel Knuckle ch

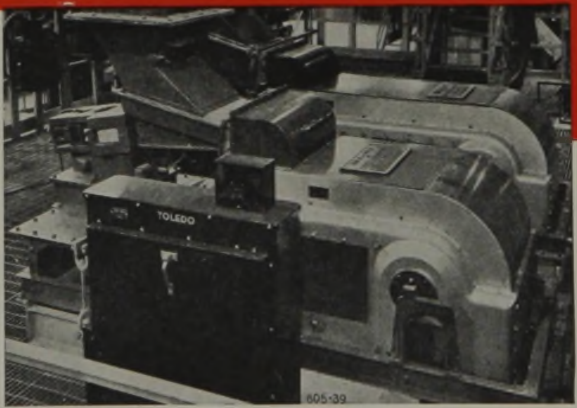


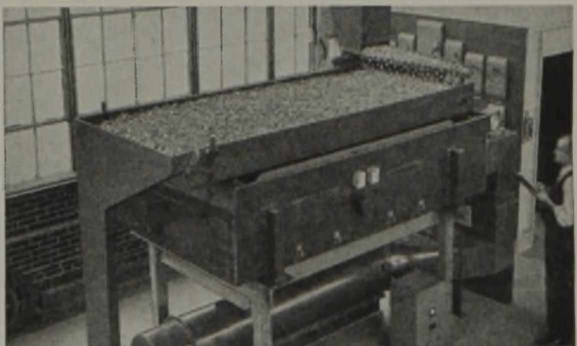
Double roll coke sizer (Patented) — a section of spiral flight is shown below

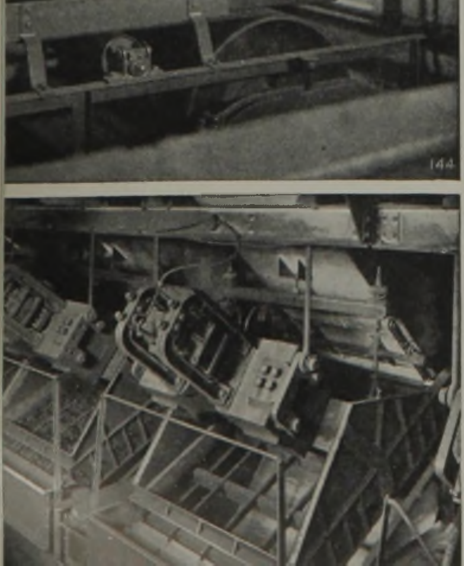


Finished roller chains in single, double or multiple strands — below is the Reliance Drag

The six photographs (left) show some
the applications of Jeffrey-Traylor elect
vibrating feeders, screens, conveyors, d
ers and constant weigh feeders. The
units give a new conception to feed co
trol — are entirely electrical — nothing
wear out or to lubricate.







JEFFREY-TRAYLOR ELECTRIC VIBRATING EQUIPMENT (Patente

COOLERS — Custom built units for pr
essing under closely-controlled con
tions

CONVEYORS — for handling hot, gase
materials without dust lost or degra
tion — tubular or pan types

DRYERS — apply principle of balanced
bration to processing operations — so
or louvered type conveying surface

FEEDERS — special sizes and designs
decks to handle all kinds of feeding pr
lems in chemical plants

PACKERS — high frequency vibration
applied to packing operations —
creases container capacity — decrea
packing time

SCREENS — single or double deck sty
ranging from 2 to 40 sq. ft. of screen
surface

WAYTROLS — used for continuous fe
ing where gravimetric accuracy is
quired. Completely automatic

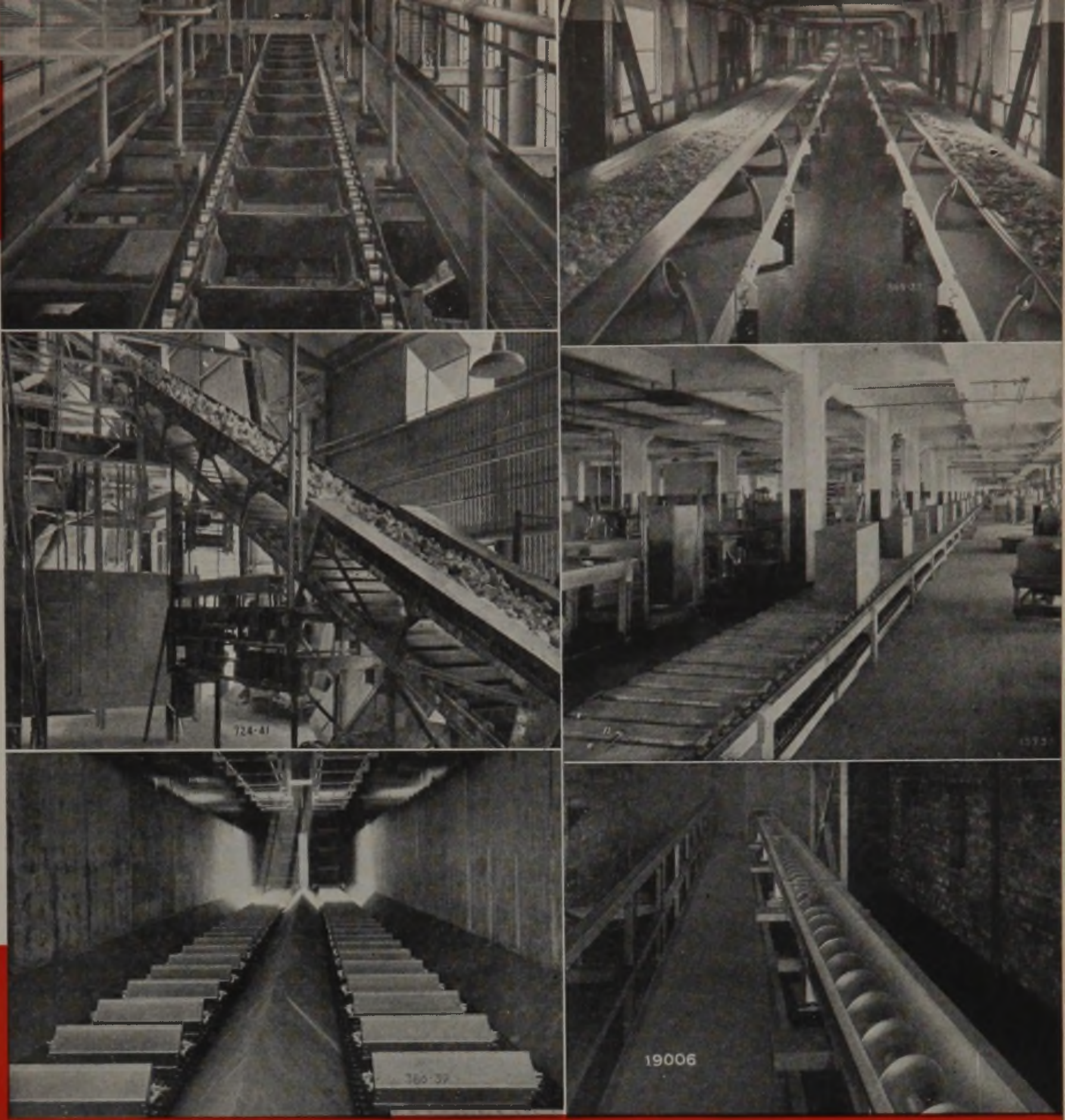
BIN CHECK VALVES — used in con
tion with vibrating feeders — pre
arching and flooding of finely divided
terial

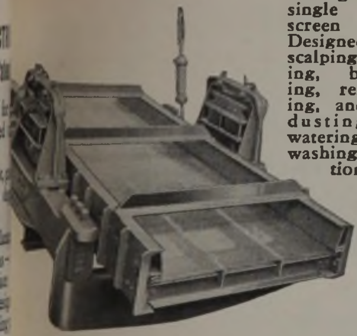
ATERIALS HANDLING

JEFFREY MATERIAL HANDLING AND REDUCTION EQUIPMENT:

- BIN VALVES — Bottom and side discharge types
- CHAINS and SPROCKETS — A complete line for conveying, elevating and driving service
- CONVEYORS — Apron, belt, bucket, portable, scraper, spiral, trolley and V-bucket
- CRUSHERS — Pulverizers and Shredders — single roll, double roll, Flextooth, Rotary ring and swing hammer types
- ELEVATORS — bucket and Mass-flo types
- FEEDERS — Apron, belt and grizzly types
- POWER TRANSMISSION MACHINERY — gears, pillow blocks, take-ups, couplings, clutches, pulleys and shafting
- PORTABLES — Belt, bucket and scraper types for loading and unloading operations — also Stackers for bags, boxes, etc.
- CAR PULLERS — Skip Hoists — Weigh Larries — Mono-veyor systems

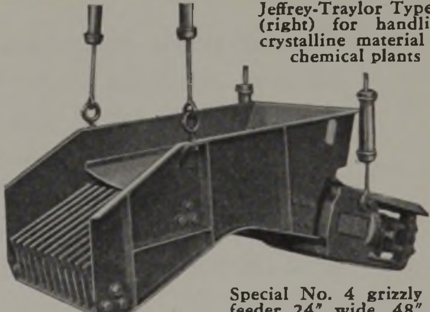
ix Jeffrey material handling installations are shown at the right. Scraper, belt, steel pron, wood apron, spiral and V-bucket onveyors are shown handling various kinds of material in processing and manuacturing operations. If it is to be moved — effrey has the right unit.





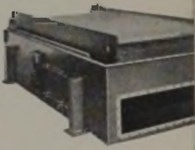
J-T electric vibrating FB-2 single deck screen (left). Designed for scalping, sizing, by-passing, rescreening, and dedusting, dewatering and washing operations

J-T 36" x 72" No. 5 heavy duty electric vibrating feeder

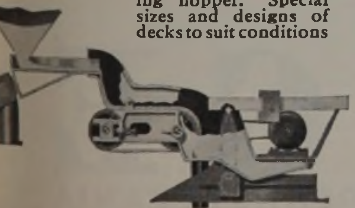


Special No. 4 grizzly feeder 24" wide, 48" long (above). These units come in 7 widths and 6 lengths

Jeffrey-Traylor Type H direct-type Dryer (right) for handling crystalline material in chemical plants



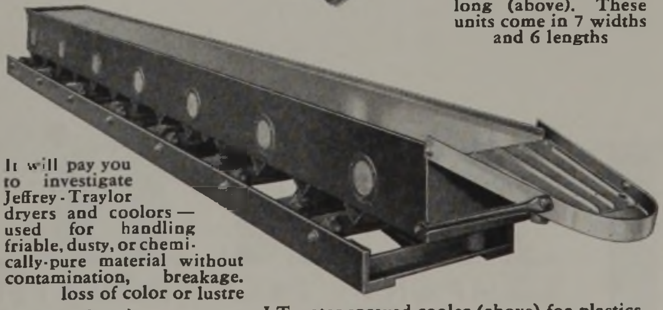
-B small reagent feeder (right) with vibrating hopper. Special sizes and designs of decks to suit conditions



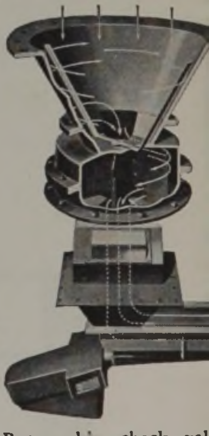
Waytrol (above) used for batching, proportionweighing and feeding

No. 3 special low head barrel packer (above) — set level with floor for easy handling of barrel or container

It will pay you to investigate Jeffrey-Traylor dryers and coolors — used for handling friable, dusty, or chemically-pure material without contamination, breakage, loss of color or lustre



J-T water sprayed cooler (above) for plastics. Has built-in drip pan and equipped with nose screen, for scalping out foreign matter



Rotary bin check val (above) — prevents floo ing and arching of materi

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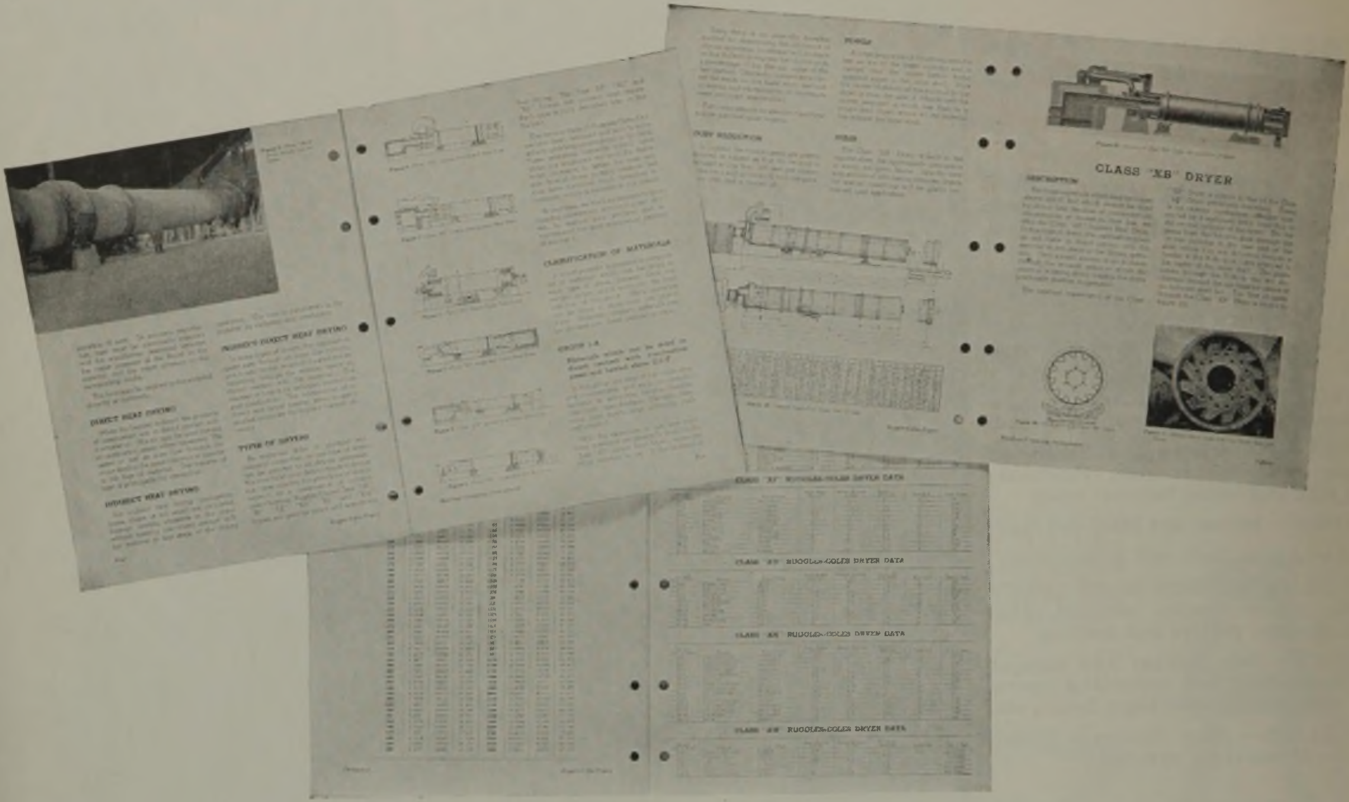
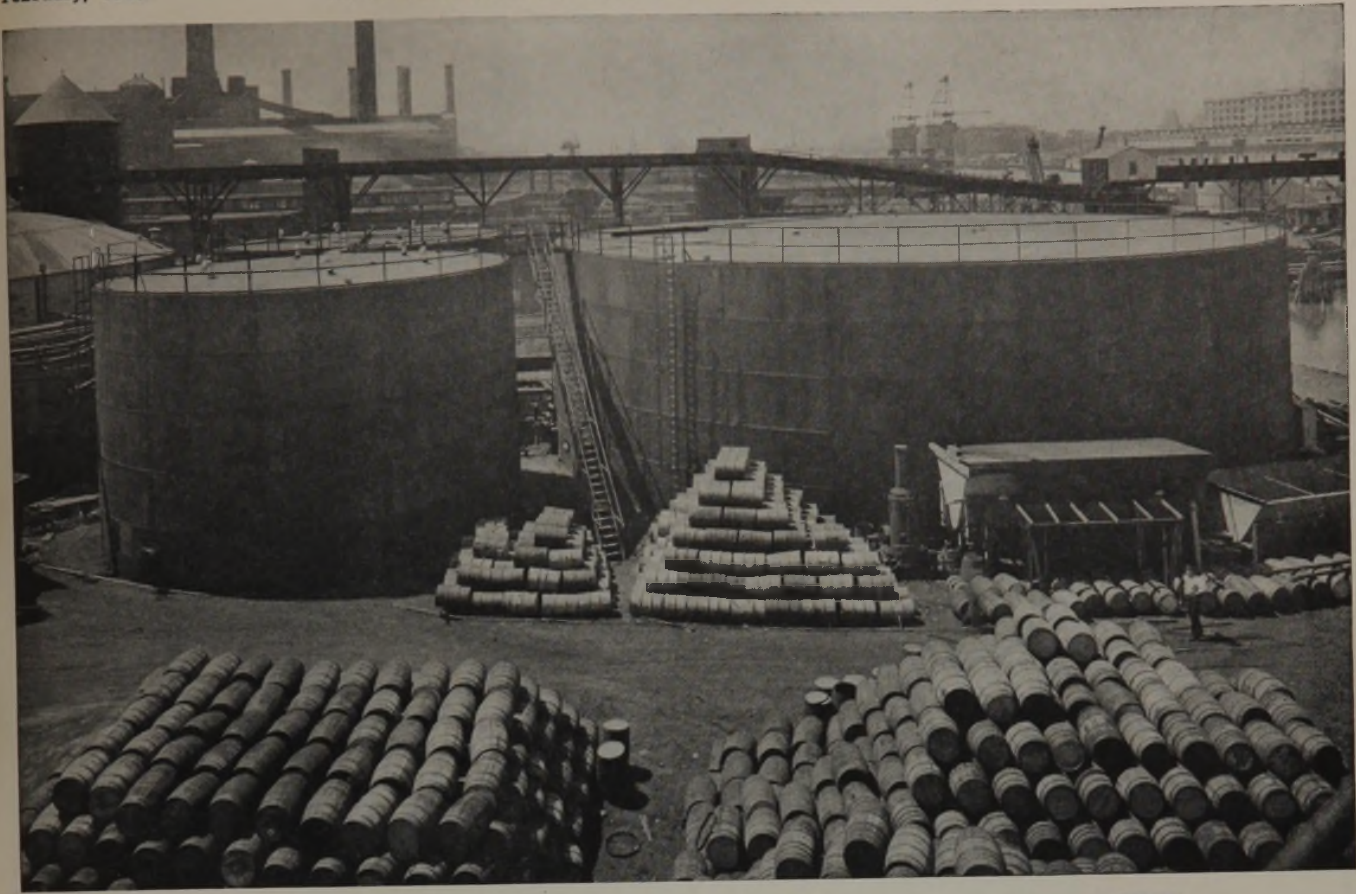
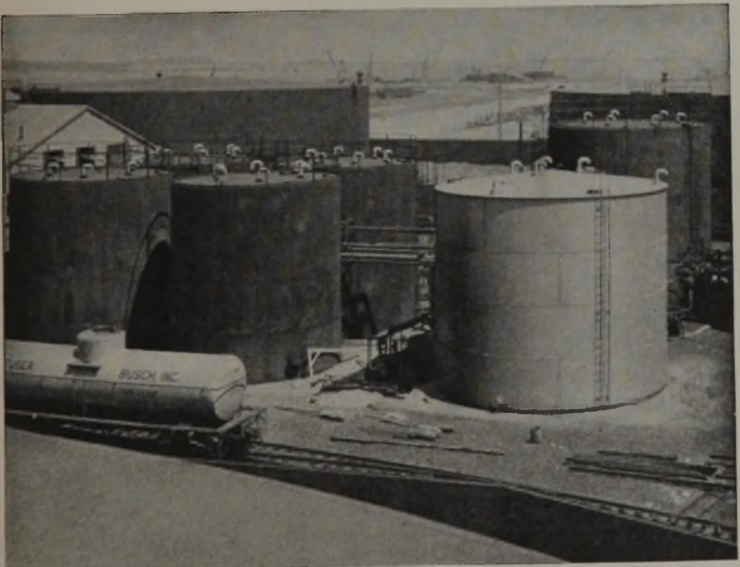




TRAINING CAMP FOR A "*Fighting Food*"



Top: Two 47½ ft. diam. and one 101½ ft. diam. molasses tanks at the Boston Molasses Company Plant.

Directly Above: Four 22¾ ft. diam., one 30 ft. diam. and one 30½ ft. diam. molasses tank at Boston, Mass.

GETTING molasses into condition to help sustain United Nations' fighting forces and civilian workers is made easier with *modern* storage and refining facilities.

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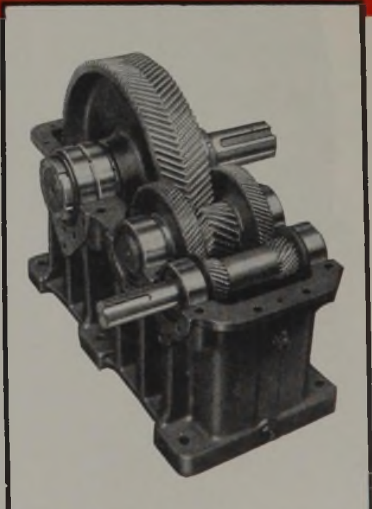

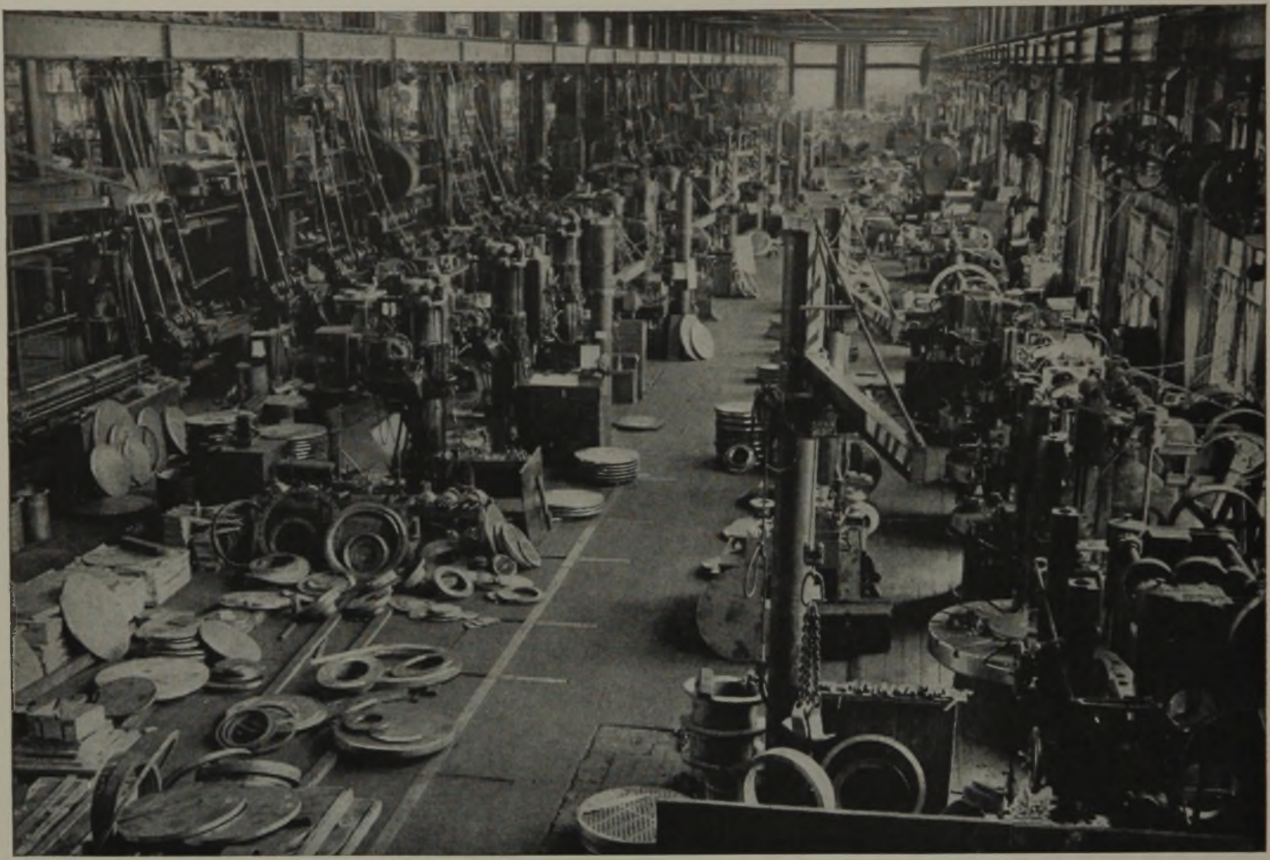

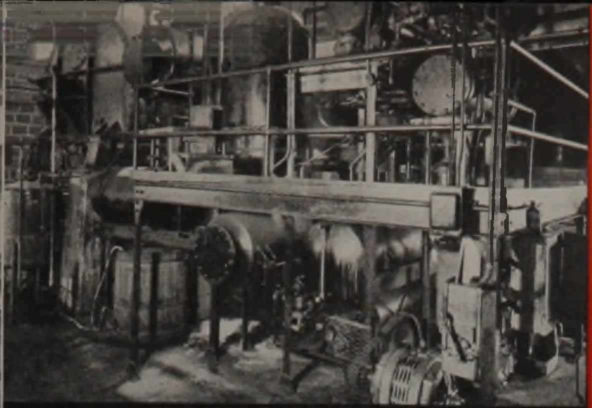

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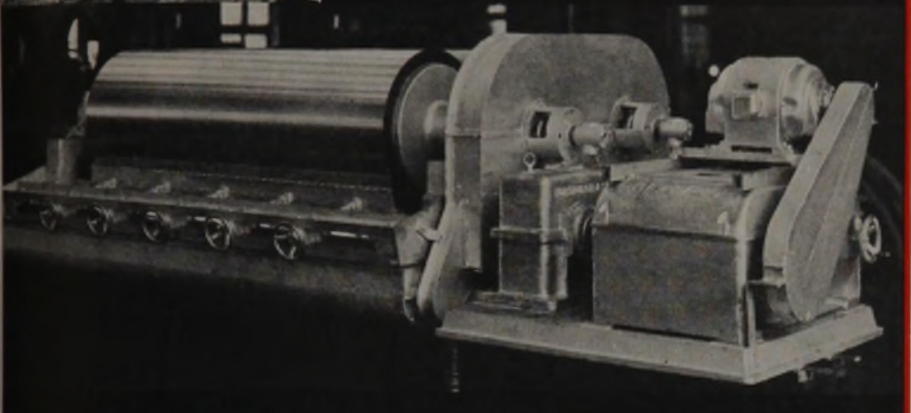
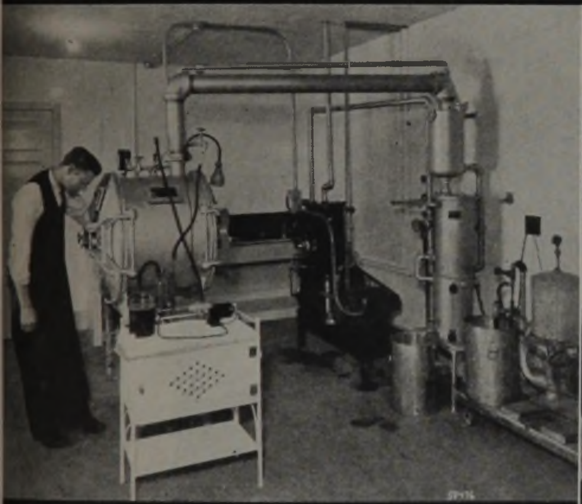


DRYING — Crystal Forming Chemicals



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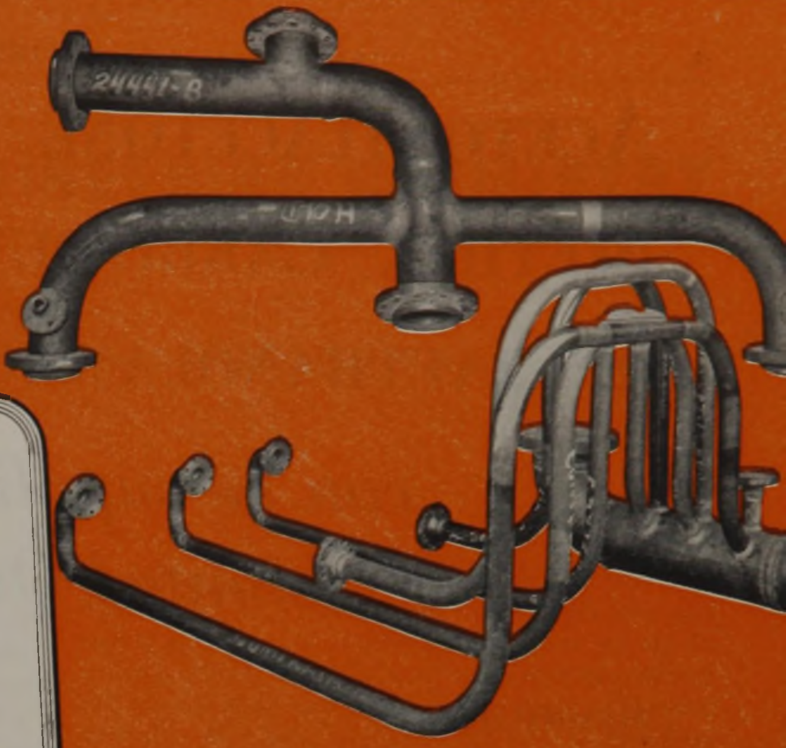

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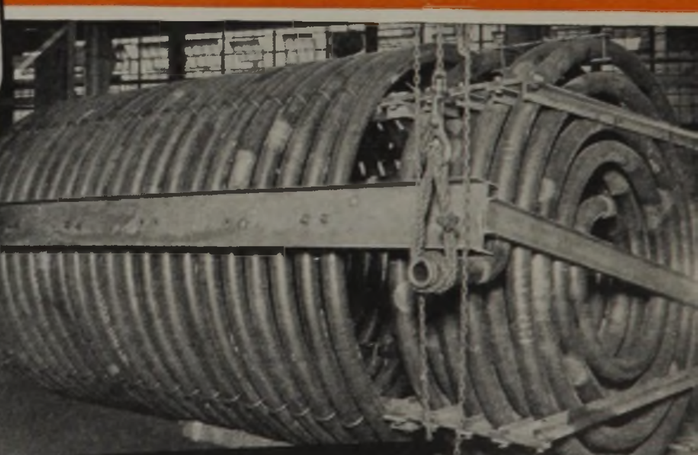

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INDUSTRIAL AND ENGINEERING CHEMISTRY

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

EDITORIALS

Opportunity for Service

THE chemists and chemical engineers of this country constitute a vast reservoir of manpower that can be of very practical assistance to the Office of Production Research and Development headed by Harvey N. Davis, president of Stevens Institute of Technology. The Chemical Industries Branch of the OPRD is under the direction of Donald B. Keyes, and in make-up of personnel it is identical with the Referee Board of the Chemicals Division of WPB created in July of last year. The principal purpose for which the Referee Board was established was to provide a medium to assist individuals and agencies who discover needs for research to contact the many existing competent research organizations. Definitely the plan did not include the creation of any large or complicated organization, in Washington or elsewhere, for either the conduct or the detailed direction of an elaborate research program. Briefly the function of the Referee Board was to act as a sort of clearinghouse, and its successor, the Chemical Industries Branch of the OPRD, is continuing along the same lines.

Local sections of the American Chemical Society can assist in this important work by devoting at least a portion of their program to round-table discussions. Ideas developed at such meetings can be forwarded to Dr. Keyes. Chairmen of local sections will find in the October 10, 1942, issue of *Chemical and Engineering News* (page 1232), the Fifth Provisional Report of the War Production Board on the relative scarcity of certain materials.

Informal round-table discussions by local scientific groups will probably bring to light alternate methods of manufacture of many chemicals vital to the war effort, particularly processes which do not require the use of highly critical and strategic materials and specialized equipment. Practical short cuts in production may be proposed. Many worth-while suggestions and recommendations have been made and others naturally will follow if these problems are but "aired" properly before interested groups well qualified to perform the function of "consultants".

Here is a service in which chemists and chemical engineers can cooperate effectively in the war effort. The Chemical Industries Branch of the Office of Production Research and Development will welcome such assistance, and machinery has been set up to evaluate quickly and effectively all suggestions offered and to centralize, coordinate, and sponsor production research. This plan is a practical way of attacking unsolved problems relating to the war effort.

Research facilities are heavily taxed. A recent nation-wide survey by Dr. Davis discloses that all of the larger industrial research laboratories are carrying heavy loads, and only a few of the smaller laboratories, representing a small percentage of the country's research workers, are available for new war problems. Likewise, in the universities the number of scientists still obtainable for war research represent less than 1 per cent of the total research manpower. On the basis of returns, it is estimated that less than 2 per cent of all the industrial laboratories are completely available for research on war problems, and that more than two thirds have less than a quarter of their capacity available. Under such conditions, it is necessary to employ in the most efficient manner what little technical manpower is at hand.

The Latest—"Synergism"

AN INTERESTING side light of warfare is the stimulating effect that it invariably produces on our vocabulary. Witness the introduction during the present conflict of such expressive phrases as "know-how," "imagineering", and now "synergism". A moment's reflection brings to mind the full significance of each of these new expressions and their closely knit relationship. They truly are descriptive of the proper scientific approach to any technical problem.

One accustomed to thinking in mathematical terms might liken these three words to an equilateral triangle. "Know-how" is both the broad knowledge of scientific fundamentals and the ability properly to utilize such basic knowledge in a practical manner. "Imagineering" is the ingenious capacity for visualizing yet uncharted fields with full regard to established scientific and engineering principles.

"Synergism" has been succinctly described recently by the Atlas Powder Company as the force that can make 2 + 2 = 5. Elaborating on this rather unorthodox mathematical equation, the coiners of this latest expression report that it is derived from two classic Greek words, one meaning "together" and the other "work". Synergism is not really a new word, but has long had its connotations for the chemist, the doctor, and the theologian. Basically, we are told, "it always has meant forces working together to produce a whole greater than the sum of the parts". One word will aptly describe it—cooperation. Thus we have the equilateral triangle—knowledge, imagination, and cooperation, three essential attributes of every good chemist and chemical engineer.

One other attribute is also a prime necessity—intellectual honesty. Carrying on into the realm of solid geometry, we might liken these four essentials to the tetrahedron. Here is a golden opportunity for phrase makers. Their job is not wholly completed.

Men Are Still Necessary

THE War Manpower Commission, operating through its Buffalo-Niagara Area Committee, is using newspaper advertising to appeal for "shock troops of production—men who are not afraid to do a real man's work, a job no woman can do".

Women can and will prove invaluable in maintaining and even increasing the chemical output of the Nation, but as every operating official knows, the "straw boss" and his husky assistants are vital components of the labor force of any chemical plant. Technically trained women will continue in still greater numbers to render highly satisfactory service in our control and research laboratories. A relatively small number have successfully ventured into actual operating duties, and as the pinch in manpower becomes still more acute their numbers will increase. In Great Britain women are employed in chemical plants in many roles, but our friends over there realize that for certain laborious work men are essential.

The printed appeal in the Niagara Frontier area, first of its kind in the Nation, states: "You're needed for the kind of work you wouldn't want your sister or your wife to do—and they couldn't do if they tried."

Simultaneously with the newspaper drive, the War Manpower Commission is soliciting the aid of clergymen in spreading the story of the dire need for capable men in the heavy industries, including the chemical industry. The clergy can extend their contribution to the war effort beyond the primary objective of caring for the spiritual needs of their flocks, for they are usually very close to their congregations and have a thorough understanding of their make-up. We are in a total war..

The fact that three large furnaces located in the Buffalo district, which should have been turning out materials for the production of tanks, bombers, and guns, were down for more than a week in January, solely because there were not enough men to run them, should be the direct concern of every agency in that area maintaining close relationship with labor.

The Fate of the Small Colleges

THAT the seventeen hundred-odd institutions of higher learning in this country are precious assets no one will deny, yet many of the smaller colleges face extinction or will be badly crippled in the next two years. Approximately 575 institutions are publicly controlled, some 700 are under church auspices, and about 425 are privately controlled.

Military and naval authorities have been collaborating with college authorities for months, attempting to evolve a plan whereby boys in the service who do possess extraordinary ability will be permitted to continue their education while they are being prepared for the military services. Such a plan, however, will be operated only in some two or three hundred institutions. The balance do not have much to look forward to during the war if their enrollment has consisted wholly, or to a large extent, of male students.

We are constantly using the terms "total war" and "postwar planning", yet it is difficult at times to believe that we realize or appreciate their full meanings. In total war all men, women, and even youngsters of the upper teen-age are presupposed to be doing those things for which they are best fitted. Intelligent postwar planning should be going on simultaneously with the actual war effort.

It might well be possible, in the light of the more favorable turn in the war, to enlarge the scope of the present plans of the Army and Navy for college training for bright youngsters, always of course with the provision that they are selected along democratic principles and possess outstanding ability. We in the chemical field are generally in agreement that it is a tragic mistake to draft bona fide students of chemistry, physics, engineering, and other scientific subjects. Not only will such men be badly needed next year and the year following to staff our greatly enlarged production facilities, but they will also be necessary in the postwar period to assist in a quick shift from a war to a peace basis. Is it not equally true that in the postwar period we will need young men of superior training in the so-called cultural subjects? Postwar problems will not all be of a technical nature. There will be a serious manpower problem in the reconstruction period if we do not plan properly now.

Wheat as a Raw Material for Alcohol Production

W. H. STARK, PAUL KOLACHOV, AND H. F. WILLKIE
Joseph E. Seagram & Sons, Inc., Louisville, Ky.

Three factors—the molasses shortage, increased requirements for ethanol, and the large surplus of wheat—have forced the alcohol industry to utilize wheat as a raw material. Little work has been done in this country on the production of alcohol from wheat; thus its use has raised several problems, such as the type best suited for alcohol manufacture, methods of processing, and expected yields.

These problems have been investigated, and data from laboratory studies as well as production experience are presented. The utilization of wheat and various combinations of corn and wheat have been investigated. The processing methods employed are presented and the results compared.

These data indicate that wheat may be employed as a partial substitute for barley malt, that under the best conditions determined to date the alcohol yields are slightly lower than those normally obtained from corn, and that the yield varies with the type of wheat processed.

THE majority of the grain distilleries in the United States have had little experience with the production of ethanol from wheat. Prior to the conversion of the industry to an industrial alcohol basis, the three principal grains processed were corn, rye, and barley malt. Owing to a combination of circumstances it has become highly desirable that as much industrial alcohol be produced from wheat as is feasible.

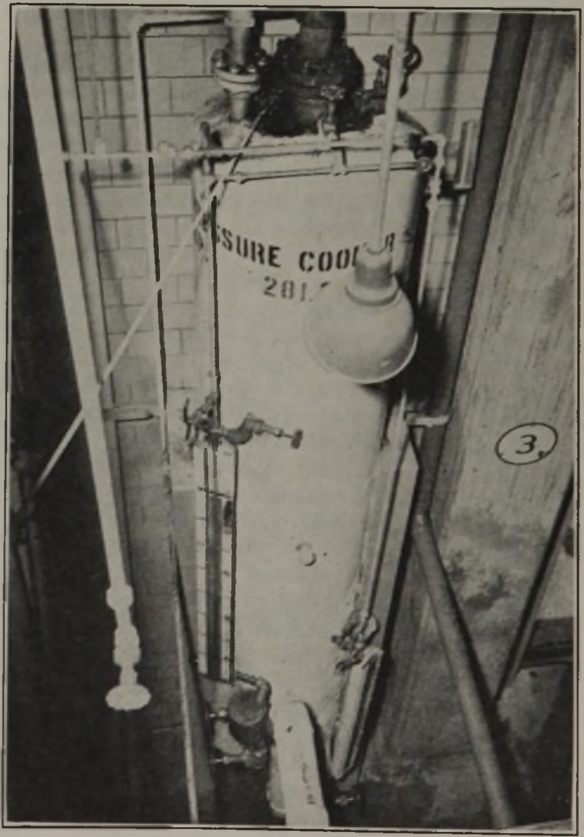
The existing capacity for the production of 190° proof alcohol in this country is 524,000,000 gallons per year, assuming that molasses will be supplied to those plants not yet converted to grain. The requirements of ethanol for 1943 have been estimated by the War Production Board to be 534,500,000 gallons. Conversion of all alcohol producers will provide a total capacity of approximately 657,000,000 gallons. These estimated requirements include no beverage alcohol. The production of 534,500,000 gallons of alcohol from grain (the only assured raw material) requires approximately 220,000,000 bushels of grain based on an average grain alcohol yield of 2.42 gallons of 190° proof alcohol per bushel. A modern distillery should obtain 2.6 to 2.7 gallons. The surplus of wheat has become extremely critical; the carry-over from the 1941 crop is 633,000,000 bushels; the 1942 crop is estimated at 955,000,000 bushels, or a total of approximately 1,500,000,000 bushels of wheat is available. Of this amount, United States consumption is 700,000,000 bushels. Thus a surplus of 800,000,000 bushels remains. The Department of Agriculture considers 250–300 million bushels a safe margin so at least 500,000,000 of wheat are available for increased industrial utilization in spite of crop restrictions.

Obviously, industrial alcohol production from wheat is a partial solution in that a surplus commodity is utilized to alleviate the critical shortage of an essential chemical. With this realization the work reported herewith was undertaken.

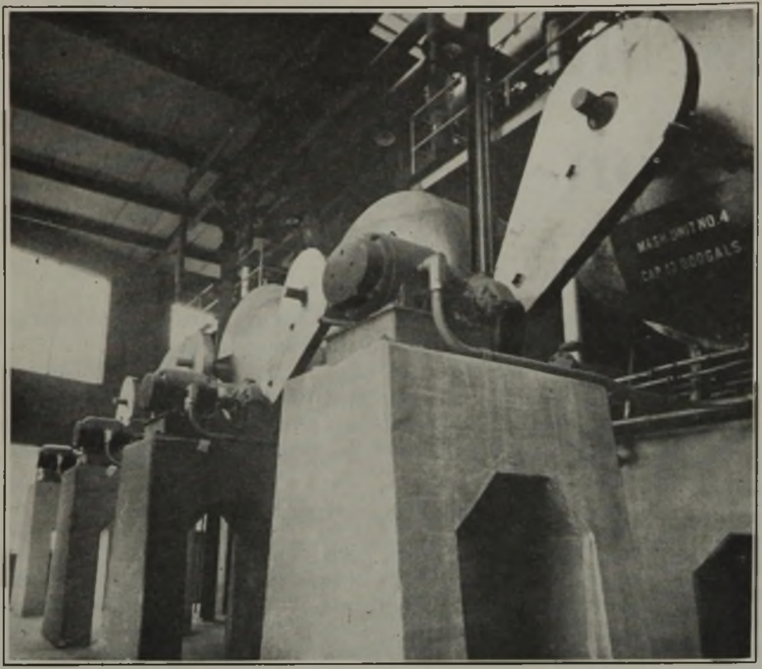
Laboratory Studies

CHEMICAL ANALYSES. The following procedure was used for the laboratory study of several types of wheat for alcohol production. The protein, starch, ash, and moisture contents of each type were determined. A. O. A. C. methods were employed for protein (Kjeldahl-Gunming-Arnold), starch (diastase–hydrochloric acid modification), and ash contents. Moisture was determined by loss of weight on drying for 3 hours at 110° C.

PREPARATION OF GRAIN MASH. Wheat is ground through the medium screen of the Wiley mill (approximately 55 per cent remains on the 20-mesh screen). The barley malt is



281-GALLON CONTINUOUS PRESSURE COOKER WITH A CAPACITY OF 6000 BUSHELS A DAY



13,000-Gallon Pressure Batch Cooker with a Capacity of 2500 Bushels a Day

ground to 40–45 per cent above the 20-mesh screen. Each sample of wheat is cooked, mashed, and fermented in the following manner: 883 cc. of tap water are added to a 2-liter beaker equipped with a laboratory stirrer. The beaker is held in a water bath for accurate temperature control. The temperature of water is raised to 100° F. (37.8° C.), and 2.33 grams of distillers' barley malt are added for premalt. The temperature is then increased to 130° F. (54.4° C.), and 241.2 grams of wheat are added. At this point sufficient 1 N sulfuric acid is added to adjust the pH to 5.7 (acid may be added prior to the grain addition when the required amount has been determined). The temperature is rapidly raised to and held at 185–190° F. (85–87.8° C.) for an hour; the partially cooked mash is then placed in an autoclave at 22 pounds steam pressure (263° F. or 128.3° C.) for an hour to complete cooking. It is then cooled to 152° F. (66.7° C.) in the water bath (with agitation) preparatory to conversion. The barley malt slurry has been prepared meanwhile by adding 20.9 grams of barley malt to 142.5 cc. of tap water at 100° F. The temperature of the slurry is raised to 130° F. in 15 minutes and held for 5 minutes. This slurry is then added to the cooked mash, the temperature of which drops to 145° F. (62.8° C.). The mash is held at this temperature for 1 hour while being vigorously agitated. It is then cooled rapidly to 72° F. (22.2° C.), 300 cc. of sterile stillage are added, the pH is adjusted to 4.8–5.0, and the final volume adjusted to 1500 cc. or a concentration of 37.8 gallons of mash per bushel of grain.

Fermentation. The above mash is quantitatively split into three 250-cc. aliquots and a remaining 450-cc. portion. The first three are each added to a tared, sterile, 500-cc. centrifuge bottle. Each portion is inoculated with 2 per cent by volume (7 cc.) of a 20-hour culture of distiller's yeast grown in 10° Balling barley malt extract medium. Each fermenter is equipped with a simple scrubber and placed in a water bath for incubation. Fermentation temperatures are 72° F. (22.2° C.) for 20 hours, 84° F. (28.9° C.) for 30 hours, and 90° F. (32.2° C.) for the remaining 18-hour period.

The 450-cc. portion is utilized for initial analyses. At the end of the fermentation period each fermenter is weighed and the contents split into two portions by weight. Half the water in the scrubber is added to one portion, and the alcohol content determined by distillation and the refractive index of the distillate, as measured by a Zeiss immersion refractometer. The second portion is available for other final analyses.

The alcohol content of the first portion of the mash, representing 0.1168 of the original quantity of grain mashed, is corrected for the inoculum and the yield calculated as proof gallons per bushel. The moisture content of the grain is determined at the time of mashing; thus the yield per dry bushel may be calculated. Over-all fermentation efficiency is calculated from the starch content.

To reduce variation, the same sample of distiller's barley malt was used for conversion throughout.

Results. Thirteen samples of wheat, representing five different classes and eight subclasses, were analyzed as described above. The results are presented in Table I. There is considerable variation in the starch content, and in general the protein varies inversely with the starch content. The moisture content is low, indicating a moisture loss prior to analyses. The wheat as received varies between 11.5 and 12.5 per cent moisture. When evaluating the results of the fermentation tests, it was arbitrarily decided that those wheats yielding over 5.50 proof gallons of alcohol per bushel (dry basis) under the above experimental conditions would be satisfactory for alcohol production. This is in comparison with alcohol yields of 5.9–6.1 proof gallons per bushel dry basis with corn under similar conditions. The bushel weight, starch content, alcohol yield, and over-all efficiency of each type are presented in Table II.

It will be noted that the first six types of wheat are satisfactory, the last seven are unsatisfactory. As would be expected, the starch content varies directly with the alcohol yield; without exception poor yields were obtained with wheat containing 66 per cent starch or less. Similarly, the bushel weight is a fair index of quality. Wheat with a low

Table I. Chemical Analyses of Wheat Samples Subjected to Laboratory Test Fermentations

Type of Wheat	Grade	Weight, Bu.	Moisture, %	Dry Basis, %			Fats, %
				Starch	Protein	Ash	
Winter							
Soft White	2	59.8	10.13	72.1	7.32	1.93	2.10
Soft White	2	59.6	10.65	72.5	8.66	1.65	1.83
Soft Club	2	59.7	10.05	72.3	8.73	1.82	1.65
Soft Red Winter							
Red Winter	1	60.7	10.61	70.9	14.1	1.82	2.32
Red Winter	1	60.2	90.2	68.4	9.5	1.82	1.29
Hard Red Winter							
Hard Winter	1	63.4	9.84	69.1	14.40	1.71	1.59
Hard Winter	1	60.0	9.71	66.0	12.28	2.18	2.12
Hard Winter	2	60.4	9.93	62.3	12.98	1.82	1.85
Dark Hard Winter	3	56.0	9.45	58.0	16.05	2.02	1.47
Red Durum	2	59.6	10.26	62.5	15.7	1.99	1.66
Hard Red Spring							
Dark Northern Spring	3	56.7	9.00	59.2	14.42	1.97	1.82
Northern Spring	2	58.6	10.25	60.9	16.0	1.97	3.03
Dark Northern Spring	3	57.0	9.40	63.4	14.89	2.18	1.25

TABLE II. LABORATORY EVALUATION OF ALCOHOL YIELDS AND EFFICIENCIES OBTAINED WITH SEVERAL TYPES OF WHEAT

Type	Grade	Bushel Wt., Lb.	Starch Content, % by Wt.[a]	Alcohol Yield, Proof Gal./Bu.	Fermentation. Efficiency, %
Winter					
Soft White	2	59.8	72.1	5.80	83.3
Soft White	2	59.6	72.5	5.78	82.5
White Club	2	59.7	72.3	5.75	82.4
Hard Red Winter					
Hard Winter	1	63.4	69.1	5.69	85.2
Soft Red Winter					
Red Winter	1	60.7	70.9	5.67	83.0
Red Winter	1	60.2	68.4	5.60	84.6
Hard Red Winter					
Hard Winter	1	60.0	66.0	5.49	86.0
Hard Winter	2	60.4	62.3	5.46	90.5
Dark Hard Winter	3	56.0	58.0	4.94	88.2
Red Durum	2	59.6	62.5	5.37	89.0
Hard Red Spring					
Dark Northern Spring	3	56.7	59.2	5.29	92.0
Red Spring	2	58.6	60.9	5.27	89.6
Dark Northern Spring	3	57.0	63.4	5.22	85.0

[a] Dry basis.

bushel weight (below 59.5 pounds) is definitely inferior; as can be seen, this index is less reliable. The inverse relation between fermentation efficiency and starch content is of interest since it would indicate that the wheat higher in starch content contains a disproportionate quantity of nonfermentable substances which are analyzed as starch.

It is of considerable importance to note that with certain types of wheat, principally White and Soft Red Winter, alcohol yields only slightly lower (0.2 proof gallon per bushel) may be obtained than with Grade 2 corn. Other types such as Red Durum and Hard Red Spring are not desirable for alcohol production. The Hard Red Winter wheat is intermediate. Of course, exception to above differentiation would be expected with samples abnormal in starch content. It should be stated that factors other than yield also govern the selection of the type of wheat for commercial use. White wheat is less economical for most grain alcohol plants since the point of origin is Oregon and Washington. Thus Soft Red Winter wheat (Red Winter subclass) is economically the most satisfactory for the greater portion of the industry. However the limited supply has necessitated increased use of the Hard Red Winter wheat.

Commercial Production of Alcohol from Wheat

As early as October, 1938, commercial tests of wheat mashing were made. At that time the plant running the tests was equipped only for atmospheric cooking. The test was run with Soft Red Winter (Red Winter subclass) wheat as 91.8 per cent of the grain bill and 8.2 per cent wheat malt. Cooking the wheat to 212° F. resulted in poor yields, however, atmospheric mashing at 155° F. produced yields of 4.75 to 5.02 proof gallons per bushel (wet basis), or approximately 5.4 to 5.75 dry basis (assuming composite moisture of 12 per cent). These yields compare favorably with those obtained in the laboratory tests run in 1942 reported above. This mashing procedure is as follows:

1. Draw water (22 gallons per bushel), heat to 110° F.
2. Add wheat.
3. Heat to 155° F. in 45 minutes.
4. Hold for one hour.
5. Cool to 145–148° F.
6. Add wheat malt.
7. Hold for 30 minutes.
8. Pump to fermenter.
9. Set at normal setting temperature.

With this mashing procedure the wheat should be ground to 55 per cent above the 20-mesh screen.

Early in 1942 further experimental work was conducted in the Louisville plant. Three different grain bills were tested in order to obtain comparisons with different levels of rye malt as contrasted with wheat mashed with 7.05 per cent distiller's barley malt. This was the malt percentage in use for corn mash at the time. Wheat for runs 2, 3, and 4 (Table III) was cooked by the continuous process of Unger (*2*). The Soft Red Winter wheat, Red Winter Grade 1, was ground to 55 per cent above the 20-mesh screen and mixed with water and premalt, precooked 10 minutes at 145° F., passed through the jet heater at 350° F., held 60 seconds, and cooled to 152° F. in a continuous operation. The conversion malt was slurried at 100° F. and added to the cook. The mash was then agitated 10 minutes, and pumped through the coolers and into the fermenters.

Conversion was a batch operation. In the case of run 1, Table III, the cooking conditions were the same, but the fast conversion process described by Gallagher *et al.* (*1*) was used. Run 1 was made approximately 3 weeks after runs 2, 3, and 4.

The results are presented in Table III with alcohol yields reported in proof gallons per bushel (wet basis). It is apparent that 12 per cent rye malt or 7.05 per cent barley malt were equally satisfactory when contrasting the actual yields obtained with runs 2 and 4. A yield of 4.90 proof gallons per bushel (wet basis) is a reasonable comparison with the yields of 5.60 and 5.67 (dry basis) obtained with the same type of wheat in the laboratory. Run 3, with which 9.00 per cent rye malt was used for conversion, yielded slightly poorer results. Run 1, identical with run 2 except for the conversion method, was definitely inferior. However, these data are hardly valid for comparison with the other runs, due to plant operating difficulties at the time of the experiment. There is no reason to expect a lowered yield with the fast conversion process.

Partial Substitution of Wheat for Barley Malt

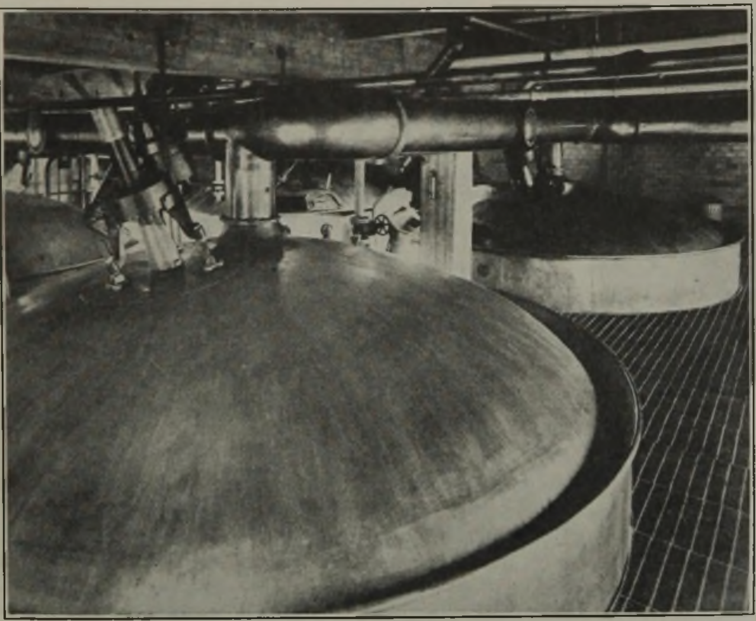
Since wheat has a Lintner value of above 40°, and the starch-converting power is recognized, it was believed that a large part of the conversion malt could be eliminated by the use of wheat. Laboratory studies were undertaken employing the following grain bills:

Corn, %	Wheat, %	Barley Malt (Distiller's) %
80	20	..
70	30	..
60	40	..
60	39	1
60	38	2
60	37	3

The experimental procedure was that outlined for laboratory studies; in each case one third of the wheat was used as premalt for the corn cook, and the remainder was prepared as a conversion slurry according to the procedure outlined for barley malt. When wheat and barley malt were used together, the malt slurry was added first for more rapid lique-

TABLE III. COMMERCIAL PRODUCTION OF ALCOHOL FROM SOFT RED WINTER WHEAT, RED WINTER GRADE 1

Run No.	Grain Processed, Bu.	Grain Bill, %: Wheat	Rye malt	Barley malt	Premalt	Yeast mash	Alcohol Yield, Proof Gal./Bu.: Analytical	Actual
1	34,590	83.25	12.00	..	1.25	3.5	4.72	4.65
2	9,160	83.25	12.00	..	1.25	3.5	4.93	4.90
3	6,120	86.25	9.00	..	1.25	3.5	4.76	4.79
4	6,047	88.13	...	7.05	1.35	3.5	4.78	4.86



Atmospheric-Pressure Batch Cooker, 11,000 Gallons in Size with a Capacity of 1200 Bushels a Day

faction. The amount of water was varied to maintain mash concentration at a constant level. These tests indicated that poor yields were obtained when no barley malt was employed.

The results of tests conducted with 1, 2, or 3 per cent barley malt are shown in Table IV. Good yields were obtained with 2 and 3 per cent barley malt. Earlier work had shown that the minimum malt concentration which could be used with corn mash was 6 per cent. The above mentioned yields compare very well with results obtained with a regular corn mash. One per cent barley malt resulted in a definitely lower yield. It was noted in the course of this work that the maximum yield under these conditions was obtained only when fermentation proceeded for at least 72 hours. Mashes prepared with higher malt concentrations normally ferment to completion in 64 hours.

Since the laboratory results of this test were good, a plant trial was conducted. It was necessary to modify the mashing procedure somewhat to conform with equipment and operating schedules. The revised procedure employed with mashes *C* and *D*, Table IV, is as follows:

1. Draw water.
2. Heat to 125° F.
3. Add prewheat (one third of total wheat).
4. Add corn.
5. Cook to 305° F. (uniformly).
6. Hold at 305° F. for 10 minutes.
7. Blow down to 225° F.
8. Vacuum down to 152° F.
9. Add malt slurry at 90–100° F. (mashing ratio for malt, 35 gallons of water per bushel).
10. Convert for 30 minutes at 145° F.
11. Pump to fermenters.

Table IV. Wheat as a Partial Substitute for Barley Malt

Mash No.	Grain Bill, %			Alcohol Yield, Proof Gal./Bu.	
	Wheat	Corn	Barley malt	Wet basis	Dry basis
			Laboratory Data		
1	39	60	1	5.03	5.65
2	38	60	2	5.23	5.88
3	37	60	3	5.41	6.09
			Plant Data		
					Remarks
A	..	93.8	6.2	5.09	Corn control
B	36.3	57.5	6.2	5.03	Wheat control
C	37.0	60.0	3.0	4.96	Wheat, 72-hr. fermentation
D	37.0	60.0	3.0	4.74	Wheat, 72-hr. fermentation

The wheat for this purpose was to have been ground to 40–45 per cent above the 20-mesh screen. Actually the milling data averaged 63 per cent above the 20-mesh screen. During the same period mash *B* was run. In this case all of the wheat was cooked with the corn as in the above procedure, and barley malt was the sole conversion agent. This procedure is the same as the one normally employed for corn spirits mashes (mash *A*, Table IV) with batch cooking.

Eight fermenters were set with wheat–barley malt converted mash. Four of these (mash *C*) fermented more than 72 hours; four others (mash *D*) fermented less than 72 hours. The average yield is appreciably higher with the extended fermentation period than with the shorter period. The best yield is somewhat lower than the wheat control, and both are lower than the yield obtained with corn spirits mash. However these data indicate that only a slight reduction in yield occurs with wheat substituted for 36.3 per cent of the corn in a normal spirits mash, and that wheat may replace over half of the barley malt required for conversion with reasonable success if fermentation proceeds for at least 72 hours. These are both important points, the latter because of the cost of barley malt and possible shortages due to the conversion of industrial alcohol plants to a grain basis.

Problems Encountered in Processing Wheat

Certain problems arise in connection with the use of all wheat for alcohol production. Foaming during fermentation makes it imperative that fermenters be operated at reduced capacity. This problem is largely reduced by employing not over 40 per cent wheat in the grain bill, the remainder consisting of corn and barley malt. The seriousness of the problem is dependent on the equipment of each plant. Some plants may be so equipped as to be able to maintain maximum capacity on high percentages of wheat (80–90 per cent).

The problem of handling four grains has been eliminated in the Seagram plants by the substitution of wheat for rye in the yeast mash; no data have been presented, but this has proved a satisfactory procedure.

An important phase of distillery operation involves by-product recovery. It has been found that efficient by-product recovery of wheat stillage from high percentage mashes (80–90 per cent) is difficult with conventional equipment. Evaporator tubes foul more readily, and the highest average dryer house yield obtained with wheat was 14.4 pounds dried grain per bushel of grain mashed, as contrasted with 17.0 pounds from corn mash. This problem is greatly reduced when mashing relatively low percentages (35–40 per cent) of wheat mixed with corn. Additional experience will probably tend to solve this problem, at least partially. The problem of by-product recovery obviously does not apply to those plants not equipped for dried grain recovery.

Summary and Conclusions

The types of wheat best suited for alcohol production are White or Soft Red Winter, Red Winter subclass. Durum and Hard Red Spring wheats are generally not suitable for alcohol production, owing to the lower starch content and resultant low yield of alcohol. Hard Red Winter wheat falls between the above two groups. The location of the White wheat and the limited supply of the Soft Red Winter wheat make it imperative that the Hard Red Winter be used.

The starch content of wheat is a reliable index of the anticipated yield of alcohol.

Alcohol yields from wheat are generally lower than yields from corn; the difference is about 0.2 proof gallon per bushel.

Higher yields of alcohol can be obtained from wheat, either by pressure cooking (batch or continuous processes) or by atmospheric mashing at 155° F. Mixed grain bills comprised of over 50 per cent corn, 35–40 per cent wheat, and the remainder distiller's barley malt can be successfully handled in a grain distillery and produce yields only slightly lower than those obtained from corn. The most suitable method of processing for any given plant necessarily depends on the existing equipment.

The minimum concentration of barley malt required for corn mashing may be reduced by 50 per cent through the utilization of wheat–barley malt mixtures as the conversion agent. This is successful if the mash is allowed to ferment for 72 hours. The dried grain yield is 2–3 pounds per bushel lower when recovering spent wheat grains from high percentage (80–90 per cent) wheat mashes.

This and other problems incidental to the utilization of wheat in alcohol production are discussed. These problems vary with the equipment of each individual plant.

Further research must be done to utilize wheat efficiently as a raw material for alcohol production and to minimize the operating problems.

Acknowledgment

The authors gratefully acknowledge the technical assistance of the following members of the Research and Development Department: R. S. Mather, G. A. Snyder, J. S. Hudson, and Luella Shehan.

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Presented before the Division of Agricultural and Food Chemistry at the 104th Meeting of the American Chemical Society, Buffalo, N. Y.

Solubility of Melamine in Water

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The solubility of melamine has been determined at several temperatures over the range 20–100° C. Independent determinations starting from unsaturated and supersaturated solutions yielded values which were in satisfactory agreement. The points thus obtained, when plotted on semilogarithmic paper, coincided closely with a straight line representing the Clausius-Clapeyron relationship. The equation of this line is as follows:

$$\log (\text{solubility}) = -1642 \times 1/T + 5.101$$

By means of the equation reasonably reliable extrapolated values can be obtained down to 0° C.

The purpose of this paper is to present data on the solubility of melamine in water over the range 0–100° C. In his review of the chemistry of melamine, McClellan (*3*) showed that there was a discrepancy between the solubility found by Christmann and Foster (*1*) in this laboratory and that reported by Lemoult (*2*) many years earlier. The Christmann and Foster data were the result of a few rough determinations made for immediate practical use in the crystallization of melamine-dicyandiamide mixtures. Present day interest in melamine and its rapidly growing commercial importance, particularly in the field of amino plastics, made it seem desirable to redetermine in an exact way the solubility-temperature relation of the melamine-water system.

Experimental

Material. Several pounds of the purest melamine available were recrystallized four times from water, air-dried, and micropulverized.

Apparatus. The Walton-Judd apparatus, diagrammed and described in Scott's book (*4*) was adopted with a few additions and modifications; Figure 1 shows the modified apparatus. The outer vessel is a 1000-ml. tall-form beaker without a spout, the inner sampling vessel an ordinary 25 ml. weighing bottle. The small thistle at the lower end of the filter tube is covered with No. 44 Whatman filter paper, reinforced by a piece of strong, white, soluble-free cotton cloth; the filter paper and cloth are tied tightly over the flange of the thistle with thread. The outer vessel, held in a specially designed clamp, is immersed as deeply as possible in an electrically controlled constant-temperature oil bath maintained within 0.1° C. of the equilibrium temperature.

Procedure. Two separate sets of apparatus were used to run simultaneous determinations starting from unsaturation and supersaturation, respectively. Each beaker contained 750 ml. of water and enough melamine to provide a 3–5 gram excess over the necessary amount. Before being placed in position in the bath, one beaker was raised to about 5° C. below the bath temperature, the other 5–10° above the bath temperature, and held there until supersaturated with respect to bath temperature. The two vessels were then lowered into position in the bath and allowed to reach equilibrium.

When the time for sampling arrived, the sampling device (previously raised to bath temperature) was inserted, and the necessary amount of sample allowed to siphon into the sample

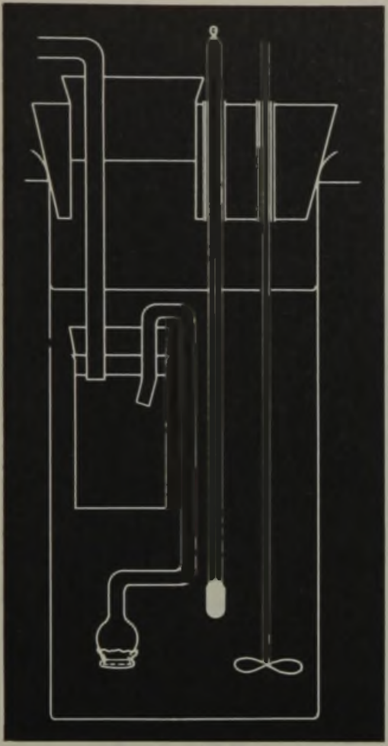

FIGURE 1. MODIFIED WALTON-JUDD SOLUBILITY APPARATUS

bottle. A simple periscope device and a tubular electric light bulb immersed beside the beaker furnished a means of observing when the required amount of solution had passed over. After removal from the solution, the sampling device was rinsed off and dried. The stopper carrying the thistle was replaced by the ground glass stopper, and the sample weighed. The melamine content of the solution was then determined by suitable means. (A direct method developed in this laboratory was used. This method has not yet been published, and its description is outside the scope of this paper. In some instances check determinations were made by evaporating the solution to dryness and weighing the residue. Agreement between the two methods was very good.) The solubility was calculated as follows:

$$100 \times \text{grams melamine}/(\text{grams sample} - \text{grams melamine}) = \text{grams melamine}/100 \text{ grams } H_2O$$

At suitable intervals the sampling was repeated until the unsaturated and supersaturated solutions arrived at the same concentration or were close enough to give satisfactory precision.

Data

At each temperature investigated, at least two runs were made from each side of equilibrium, with the exception of 99° C. where it was practically impossible to get a supersaturated solution. The limiting values obtained from opposite sides of equilibrium were remarkably close, thus boxing in the true equilibrium value within a satisfactory range. The values obtained are plotted in the usual manner in Figure 2 and given in the following table:

Temp., ° C.	Soly., G. Melamine/100 G. H_2O From unsatn.	From supersatn.	Mean
19.9	0.324 0.321	0.324 0.326	0.324
34.9	0.590 0.590	0.591 0.590	0.590
49.8	1.040 1.040	1.048 1.051	1.045
64.1	1.69 1.69	1.75 1.69	1.70
74.5	2.34 2.35	2.43 2.35	2.37
83.5	3.15 3.14	3.17 3.15	3.15
94.8	4.55 4.58 4.53	4.63 4.64 4.60	4.59
99.0	5.03 5.07	.. ..	5.05

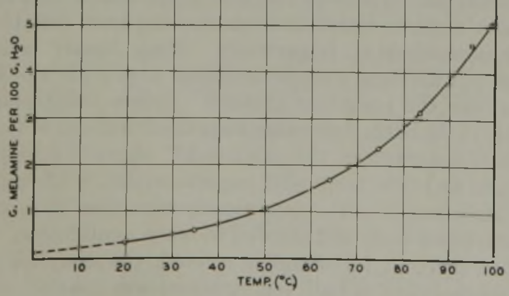

FIGURE 2. SOLUBILITY OF MELAMINE

Since melamine is relatively not very soluble, particularly at lower temperatures, its change of solubility with temperature should obey the Clausius-Clapeyron equation reasonably closely. The integrated equation, assuming constant ΔH over the range studied, was employed here. A plot of log (solubility) against the reciprocal of the absolute temperature should therefore exhibit a straight-line relation. The experimental data, plotted in this manner and shown in Figure 3, were found to be remarkably close to a straight line whose equation, constructed from the two points at 34.9° and 83.5° C., is as follows: $\log(\text{solubility}) = -1642 \times 1/T + 5.101$. Solubility is expressed in the conventional unit, grams per 100 grams of solvent, and T is the absolute temperature.

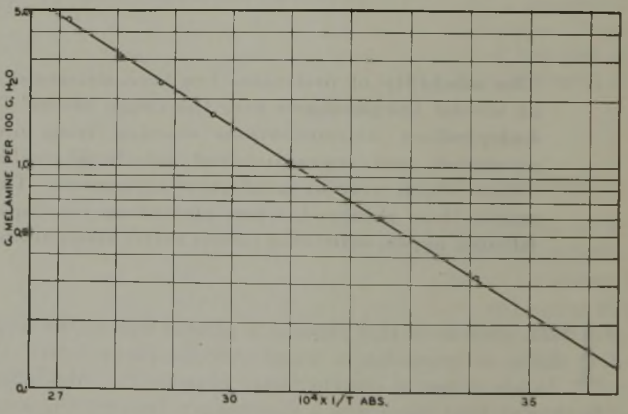

FIGURE 3. PLOT OF LOG SOLUBILITY *vs.* THE RECIPROCAL OF ABSOLUTE TEMPERATURE

The higher values show some tendency to deviate from the straight line. This might possibly be expected from theoretical considerations, since melamine solutions saturated near the boiling point might be classed as fairly concentrated solutions. At lower temperatures the Clausius-Clapeyron equation should be quite valid, so that extrapolation of the curve to 0° C. should be justifiable. The extrapolated value thus calculated is 0.12 gram melamine per 100 grams water at 0° C.

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COAL IN INDUSTRY

Agricultural Uses of Coal and Its Products

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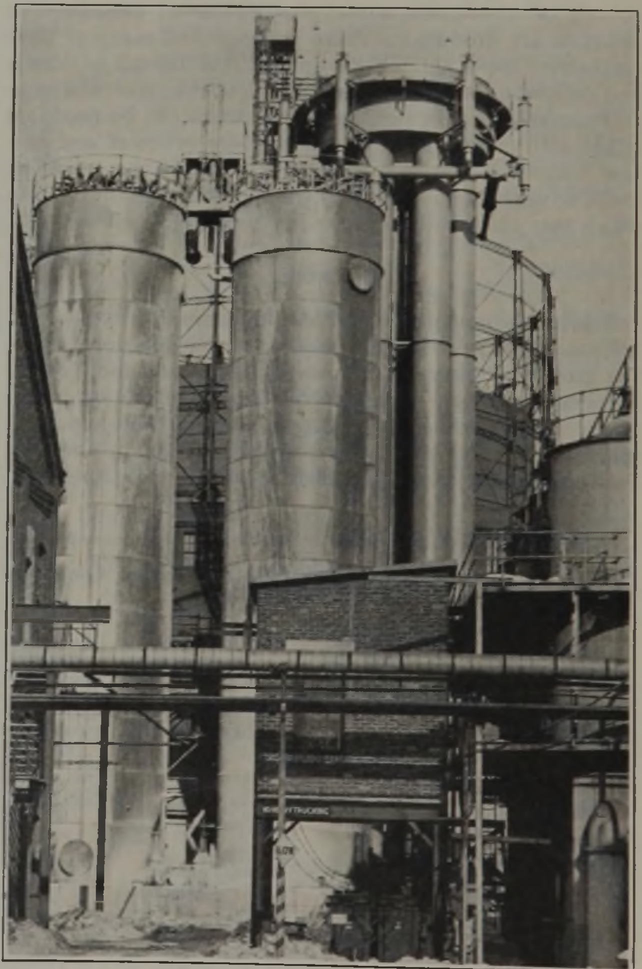
The close relationship of the coal-processing industry to agriculture is discussed. The consumption of products derived from the carbonization of coal, as well as derivatives of these primary products, has been estimated and is presented. The materials derived from coal have been found to be useful in agriculture as fertilizers, insecticides, disinfectants, herbicides, fungicides, fumigants, preservatives, plant-growth regulators, and food dyes.

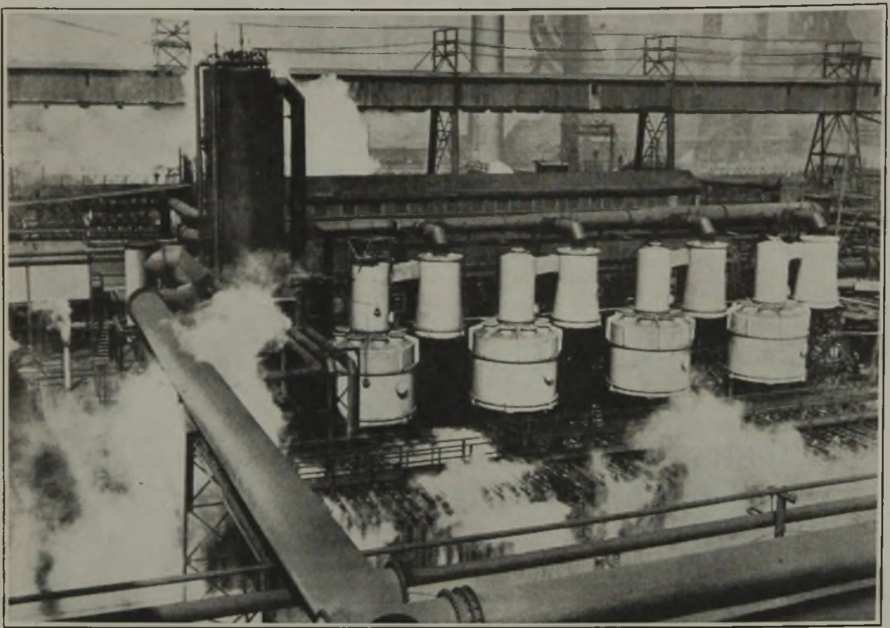
THE close relationship of the coal processing industry to agriculture is not generally realized. Few farmers know that many of the essential chemicals purchased by them for the growing of animals and plants are derived from coal. Conversely, the extent, importance, and complexity of the agricultural industry are not fully understood by those not vitally concerned with agriculture. It seems well to point out certain statistics that will emphasize the complexity of agriculture and the economic importance of this major industry. In 1938 the total farm value of agricultural products was over $14,000,000,000 (Table I). This does not include forest products which many consider a part of agriculture. In addition to livestock, poultry, and other animal products, there are over eighty different crops important enough to be considered separately in the annual statistics prepared by the United States Bureau of Agricultural Economics (*20*).

Coal itself is not directly used in agriculture except as fuel. It is not the intention of the author to include those materials that indirectly influence agricultural production. It has been suggested that coal be added to the soil to absorb heat from the sun, or as a fertilizer and soil amendment. While coal might be valuable for such purposes, no record of any large-scale consumption has been found. The Utah Agricultural Experiment Station has reported that the addition of coal to the soil does not benefit the growth of corn (*11*). Coal has meliorative or catalytic effect when used with ammonia fertilizers but is of no value alone, according to Musierowicz (*14*) who worked with finely ground coal from Upper Silesia. Leached coal ashes are commonly used in greenhouse benches to improve soil drainage and to lighten soil. Ashes do not supply plant foods and must be used in combination with fertilizers (*12*).

More than 82,000,000 net tons of coal were carbonized in by-product ovens during 1941 in the United States. According to Ramsburg (*15*), the modern oven carbonizes 26 tons of pulverized coal per day; in addition to 19 tons of coke, approximately 300,000 cubic feet of gas, 210 gallons of tar, 600



Thylox Gas Purification Plant for Production of Agricultural Sulfur



Four Late Type Saturators for the Production of Ammonium Sulfate

pounds of sulfate of ammonia, 75 gallons of light oil, and 120 pounds of recoverable sulfur plus additional miscellaneous products are produced. These products and many of their derivatives are of agricultural value. It is difficult to draw a line separating such synthetic products into coal and noncoal derivatives. In fact, certain of them can be produced either with or without involving any derivative of coal as a raw material. However, in order to simplify this report, it seems advisable to discuss the various products in the order in which they are usually separated in by-product plants.

Ammonia

The most fundamental problem in agriculture is plant nutrition. Nitrogen is one of the essential elements necessary to the growth of plants and, consequently, to all life. Plants utilize nitrogen only in combined form, including ammonium, nitrite, nitrate, and organic compounds. The most important source of this element for commercial fertilizers is ammonia derived from the destructive distillation of coal or from coke, air, and water. The development of the by-product coke oven followed by the development of synthetic ammonia, has permitted the farmer to purchase for 40 cents today as much inorganic nitrogen as $1.00 would buy 25 years ago. America's capacity to produce by-product and synthetic nitrogen has been increased 1300 per cent in the last 25 years and has made this country entirely independent of foreign sources for this vital plant food (Table II).

The use of inorganic nitrogen as a plant food has developed within the last hundred years Ammonium sulfate and chloride, while early recognized as plant foods, were not generally available until the development of the by-product coke oven. The first by-product coke ovens in this country were built at Syracuse, N. Y., in 1893 for the primary purpose of producing ammonia. Because of its high cost and other disadvantages, ammonium chloride is not commonly used as a fertilizer. Ammonium sulfate, however, remains the standard source of nitrogen for fertilizers in this country because of its low cost per unit of available nitrogen and has replaced Chilean nitrate to a considerable extent.

Table I. Number and Value of Farm Products of Continental United States in 1938

Farm Product[a]	No. of Different Crops and Products	Total Acreage Harvested	Total Farm Value
Fruit crops	22	...	$ 475,829,000
Vegetables and truck crops	21	4,757,240	282,443,000
Field crops	36	394,052,700	4,450,997,000
Other crops	4	...	6,373,000
Animals	8	...	6,366,865,000
Animal products	7	...	2,705,037,000
Total	98		$14,287,544,000
		Production	
Forest Product			
Saw timber[b] (1930)		1,667,803 million ft. board measure	
Lumber		25,997 million ft. board measure	
Pulpwood (consumption)		10,393,800 cords	

[a] Includes only those products having an annual farm value of $150,000 or over.

[b] Acreage of 188,645,000; 54,642 million feet (board measure) cut.

Table II. Wholesale Prices of a Unit (20 Pounds) of Nitrogen in Fertilizer Materials (6)

Year	Sodium Nitrate	Ammonium Sulfate	Calcium Cyanamide
1910	$2.76	$2.64	$3.43
1915	3.04	3.09	2.54
1920	4.44	4.08	3.40
1925	3.28	2.65	2.20
1930	2.49	1.79	1.65
1935	1.47	1.13	1.20
1939	1.68	1.33	1.16

As illustrated in Table III, the consumption of fertilizers, including nitrogen-containing fertilizers, by farmers has increased steadily during the past twenty-five years, and even those in the black soil areas of the corn belt are beginning to find it necessary to add nitrogen to the soil. The consumption of nitrogen in Minnesota (*7*), for example, has increased from 176 tons of available nitrogen in 1933 to 449 in 1940. In the United States 8,310,853 tons of fertilizers were produced in 1940 (*3*).

The standard of living in backward areas, such as India, could undoubtedly be raised if the people could be persuaded to use manufactured fertilizers. As repeatedly demonstrated, the increase in yield from the judicious use of inorganic fertilizers more than offsets the additional cost. The fear that the world would not be able to support the increasing population, expressed in the early nineteenth century, has been overcome by the use of inorganic fertilizers. Although present conditions are causing a tight situation, there is no possibility of future shortage of nitrogen when it is realized that in 1938 synthetic nitrogen plants, on the average, operated at about 53 per cent capacity. Before the present war and consequent increased capacity, it was estimated that the annual world capacity for producing synthetic nitrogen, including cyanamides, was approximately 4,100,000 tons.

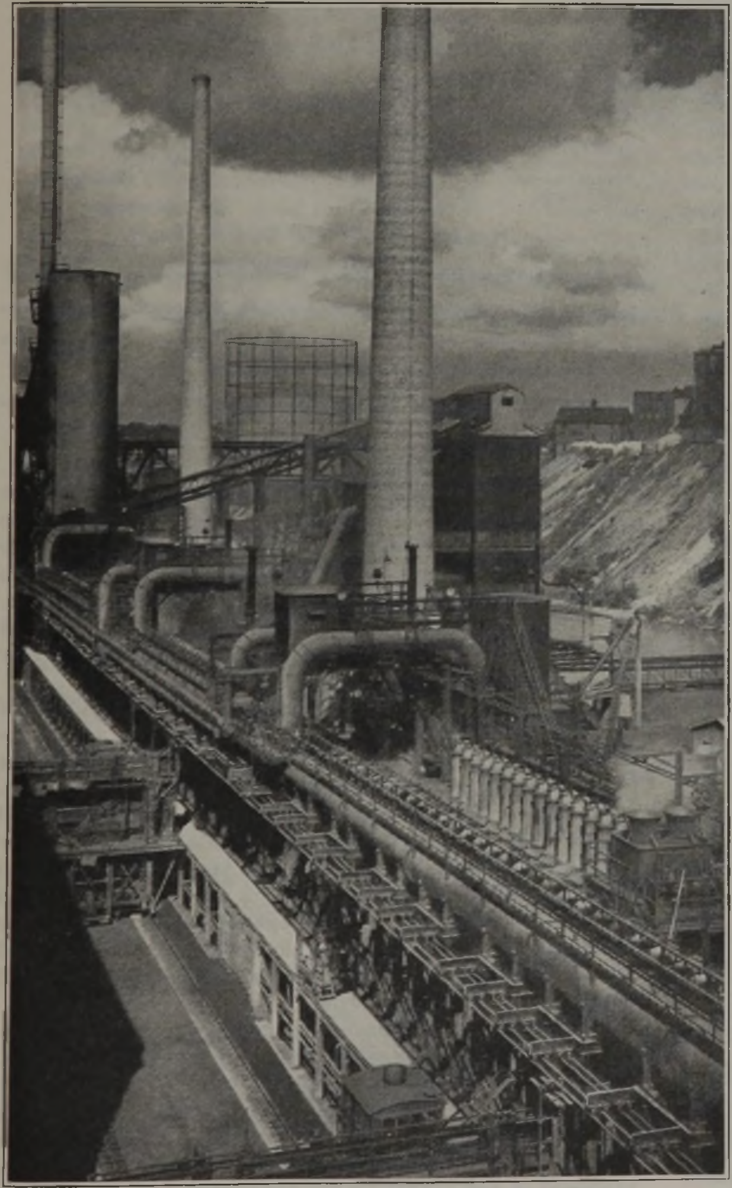
In an effort to save freight and other handling charges, the concentration of available plant food in mixed fertilizers has tended to increase, leading to the development of ammoniated superphosphates and similar materials. It is now estimated that over 70 per cent of the mixed fertilizers produced in this country contain ammoniated superphosphate.

Ammoniated superphosphate is prepared by the treatment of superphosphate with ammonia liquor, anhydrous ammonia, or so-called nitrogen solutions containing ammonium nitrate or urea and ammonia liquor. The quantity of ammonia that can be added without serious formation of citrate-insoluble phosphate amounts to 3 per cent with ordinary superphosphate and 9 per cent with double superphosphate. Aside from the lower cost of the nitrogen, ammoniation greatly improves the mechanical condition of superphosphate and mixed fertilizers containing superphosphate. It reduces the setting action when ammonium sulfate is used with superphosphate. In 1937 the fertilizer industry consumed for this purpose 6000 short tons of anhydrous ammonia, 25,000 tons of 30 per cent ammonia B liquor, and 70,000 tons of ammoniated solutions of the fortified type (*9*).

Table III. World Consumption of Pure Nitrogen (*1*)

Product	1933	1934	1935	1936	1937	1938
	Thousand metric tons					
Ammonium sulfate						
Synthetic	560	535	533	630	688	765
By-product	258	307	321	376	429	411
Cyanamide	168	195	232	269	291	305
Calcium nitrate	118	107	153	156	179	195
Other forms of N_2[a]						
Synthetic	462	516	607	724	851	931
By-product	40	48	45	46	53	49
Chilean nitrate of soda	71	84	179	192	206	224
Total	1677	1792	2070	2393	2697	2880

[a] Includes nitrogen products used for industrial purposes except Chilean nitrate and ammonia in mixed fertilizers.



Modern Battery of By-Product Coke Ovens

It has been known for some time that it is possible to ammoniate superphosphate or to produce ammonium phosphate by direct treatment with coke-oven gas. Certain manufacturing difficulties, however, have prevented the utilization of this procedure. Ammonium phosphate has been imported from Germany as the principal component of Nitrophoska. The total domestic consumption of this product amounted to 6500 short tons in 1937.

Ammonia will combine with humic substances at low temperatures in a form that is available for assimilation by plants. Ammoniated peats and brown coals have been investigated as fertilizers in Europe. These products have also been successfully treated with phosphoric acid. Peat as a soil corrective has been marketed on a small scale in this country (*5*).

Although in the past ammonia liquors have been used only indirectly in this country for the fertilization of plants, promising results have been obtained in certain areas for their direct use. In irrigated areas, ammonia liquor has been added to the irrigation waters with excellent results (*17*). The stimulation of plants from such treatment is very rapid. This new development is being watched with considerable interest by agricultural investigators.

The large-volume low-cost production of urea has made this product available for fertilizer manufacture. This synthetic urea has also been found useful as a means of supplementing proteins in livestock feeds.

Cyanogen

The presence of hydrogen cyanide in coke-oven gas suggests that this valuable product can be utilized. As a step in this direction ammonium thiocyanate is being produced commercially on a large scale in this country from coke-oven gas. This compound has been suggested by agricultural investigators as a weed killer, potato wart eradicator, and seed disinfectant. It has also been mentioned as a means to speed the coloring of apples and to regulate the dormancy of plants. It is not being utilized for these purposes at present. Ammonium thiocyanate also serves as a raw material in the production of complex organic thiocyanates useful as insecticides. These insecticides are utilized for the control of houseflies and other household insects, and are tending to make this country independent of foreign supplies of pyrethrum and rotenone.

It is possible that sodium or calcium cyanide and hydrocyanic acid could be prepared from coke-oven gas. These materials are well known as fumigants to control insects and other pests in warehouses and similar establishments.

Sulfur

The Thylox, Ferrox, and other methods of gas purification have produced finely divided sulfur, as an end product which is being successfully used for the control of insects and diseases in agriculture. Commonly known as flotation sulfur in the agricultural industry, it is sold either as a paste containing approximately 50 per cent water or in the dry form as either a dust or "dry-wettable" product. It has certain advantages over ground elemental sulfur—ultrafine particle size and great adhesiveness to plant foliage.

In the removal of organic sulfurs from gas it is possible to produce dithiocarbamates. Certain salts of dithiocarbamic acid have recently been found promising as fungicides, seed treatments, and also as insect repellents (*19*).

Through the use of the hot activation sulfur recovery process, hydrogen sulfide in coke-oven gas can be removed in a form readily convertible to sulfuric acid. This sulfuric acid can be used in agriculture for the preparation of superphosphates from phosphate rock, etc., and as a weed killer. Sulfuric acid has been used extensively as a selective weed killer for the elimination of weeds in grain and similar crops where cultivation is difficult. The importance of weeds is usually underestimated. In a survey of this problem, the Chamber of Commerce (*2*) estimated that weeds tax the farmers for $3,000,000,000 annually.

Light Oil

The primary product, light oil, and its components are not extensively used in agricultural productions. Benzene, toluene, and xylene have been reported to be more toxic than carbon disulfide as fumigants (*13*), but certain of their characteristics, such as residual odors, have prevented their widespread use for this purpose. The solvent naphthas, mesitylene, styrene, pseudocumene, and indene also have not been developed as agricultural chemicals. The estimated consumption of the primary products from coal carbonization is given in Table IV.

Intermediates produced from light oil and naphthalene are used in agriculture either directly or combined with other intermediates or other chemicals. Such products are particularly useful as pest control agents. Insects, fungi, weeds, and others of the lower forms of life are considered pests. It is estimated that agricultural production is reduced at least 10 per cent by their destructive action. The estimated consumption of these secondary derivatives of coal carbonization is given in Table V.

Table IV. Principal Primary Products Used in Agriculture

Product	Use	Ann. Vol. in U. S.	Year	Reference
Naphthalene	Insecticide (clothes moths, greenhouse insects, cattle lice, etc.)	16,500,000 lb.	1940	(*16*)
Creosote	Wood preservative	174,625,305 gal.	1940	(*8*)
	Rope preservative	500,000 gal.	1940	"
	Weed killer	2,000,000 gal.	1940	"
	Insecticide (chinch bug)	3,500,000 gal.	1934	...
Anthracene oil	Wood preservative	Small	No reports	
Tar acid oil	Disinfectants	Large	No reports	
Cresylic acid, cresols, phenol	Cattle & sheep dips	Listed with industrial disinfectants		
Ammonium sulfate	Fertilizer	753,216 tons	1937	(*20*)
Sulfur (flotation)	Fungicide, insecticide	8,500 tons	1940	*a*

[a] Writer's estimate from discussions with individuals closely associated with the industry.

Table V. Important Secondary Products Used in Agriculture

Product	Use	Ann. Vol. in U. S., Lb.	Year	Reference
p-Dichlorobenzene	Fumigant (insecticide and fungicide)	5,000,000	1936	(*16*)
o-Dichlorobenzene	Soil poison (termites), wood preservative	700,000	1940	*a*
Benzoic acid, benzoates	Food preservatives	281,202	1940	*b*
Organic thiocyanates	Insecticides	800,000	1939	*a*
Chlorophenols	Disinfectants, preservatives (total)	8,150,000	1940	*a*
	Wood	6,000,000		
	Wallboard	850,000		
	Fabrics	400,000		
	Latex	100,000		
	Paints	200,000		
	Proteinaceous	600,000		
Dinitrophenol	Preservative	200,000	1940	*a*
p-Nitrophenol	Preservative	200,000	1940	*a*
Dinitro-*o*-cresol	Insecticide	50,000	1940	*a*
	Weed killer	250,000	1940	*a*
Dinitrocyclohexylphenol (DN)	Insecticide	250,000	1940	*a*
β-Naphthol	Soil poison	140,000	1940	*a*
	Wood preservative	100,000	1940	*c*
	Proteinaceous	300,000	...	*a*
	Insecticide	Traces	...	*c*
Diphenylamine	Insecticide	150,000	1942	*b*
Phenothiazine	Anthelmintic	2,500,000	1942	*b*
α-Naphthalene acetic acid	Plant growth regulator	1,000	1941	*a*
Sulfonates[d]	Wetting agents for sprays and dusts	800,000	1940	*a*

[a] Estimate of the writer and numerous individuals closely associated with the insecticide and fungicide industry, including those in state and federal agencies.

[b] Estimated by the writer from reports of WPB allocations in *Oil, Paint and Drug Reporter*.

[c] No information found on volume; represents an approximation by the writer.

[d] Other than those from phenols and naphthalene.

At this point it seems well to mention coal-tar food dyes. While produced in small quantities, these dyes are the most important food coloring materials. Through the use of these uniform, dependable, and safe dyes, farmers have been able to make their products more attractive to the consumer who frequently makes selections on the basis of appearance alone. The Food and Drug Administration reports that 454,254 pounds of coal-tar food dyes were certified during the year ending June 30, 1939.

It is estimated that approximately 420,000 gallons of benzene were used in 1940 for the production of *o*-dichlorobenzene. *o*-Dichlorobenzene has been widely recommended as a soil poison to control subterranean termites and as a brush-on treatment for wood infested with termites and other wood borers. The production of *p*-dichlorobenzene consumed over 1,000,000 gallons of benzene the same year. This compound has been widely adopted as a control for clothes moths and other household insects, and has replaced naphthalene to some extent for this purpose. *p*-Dichlorobenzene is the standard remedy for peach-tree borers and can also be used to control blue mold in tobacco seedbeds.

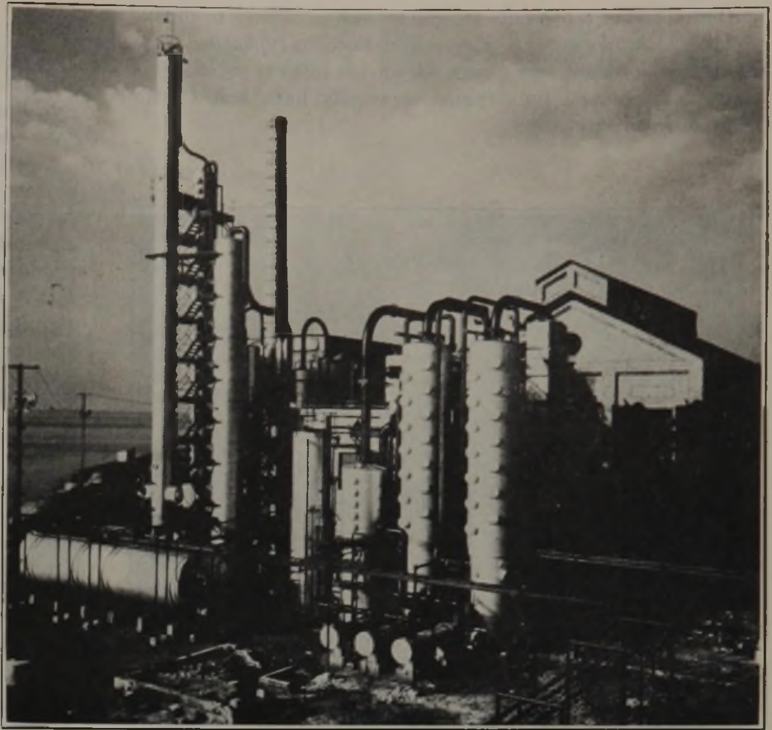
Diphenylamine and phenothiazine have recently been discovered to be extremely useful for certain parasites of animals. Diphenylamine is now the standard remedy recommended by the United States Department of Agriculture for the control of screwworm, a serious pest of cattle in the southern states. Phenothiazine, discovered to be useful by workers of the Department of Agriculture for the removal of internal parasites of animals, is being received enthusiastically by farmers.

According to Jardine (*10*), this new anthelmintic is expected to become one of the farmer's most important chemical aids.

Creosote

In 1940, 265,473,149 cubic feet of wood were treated with wood preservers (*8*). The most important one in volume is coal-tar creosote. The direct relationship of wood preservation to agriculture is not generally realized. Through the use of pressure-treated wood, farmers can reduce their overhead to a considerable extent through longer life of fence posts, farm buildings, etc. Well-built corn cribs, silos, and hay storage sheds effect better curing of farm crops and, by preserving their quality, help reduce feeding expenses. Wood preservers now offer treated lumber, precut and ready for assembly, for the following farm buildings: hog houses, dairy barns, corncribs, granaries, silos, vegetable and fruit bins, and manure pits.

Creosote is also used as a stock dip for the extermination of lice and ticks, and in poultry houses as a general disinfectant. To control poultry mites, attention must be given to the house rather than to the bird, and excellent control may be obtained by treating the roost and interior of the poultry house with creosote. This product, usually diluted with petroleum oil, is an excellent weed killer. Creosote is also used as an insect barrier to prevent the spread of such pests as chinch bug. Chinch bug outbreaks occurred at irregular intervals, but in 1934, 3,500,000 gallons of creosote were used to control this pest.



Modern Light Oil Recovery Plant

Naphthalene

Naphthalene is an important by-product from coal carbonization. Over 16,000,000 pounds are used annually for agricultural purposes. The control of clothes moths is considered an agricultural problem since the products of the farm as well as the household goods of the farmer need to be protected from its ravages. Approximately 10,000,000 pounds of naphthalene are used annually to control clothes moth and carpet beetle. Both naphthalene and *p*-dichlorobenzene will kill these pests when applied to clothing in airtight containers. Many people use these products without taking precautions to make their clothes closets airtight. Neither of these materials will kill the pests unless a sufficient atmospheric concentration is reached, and they do not act as repellents. The Department of Agriculture recommends that 1 pound of naphthalene be used per 10 cubic feet of space. However, Coleman (*4*) found that less than lethal concentrations will greatly retard the feeding of these insects. Applications of naphthalene in open closets will give protection against clothes moths but will not wipe out the infestation present.

Naphthalene is utilized to control greenhouse pests (such as red spiders, thrips, and white flies) by fumigation, as a dry dip for cattle and hogs to control lice, for the preservation of hides in storage, and as a soil treatment to control such pests as carrot rust fly. Back-yard gardeners have found naphthalene moth balls to be useful as repellents for rabbits. The moth balls are scattered around the plants to be protected, but are not allowed to come in direct contact with the plants.

Naphthalene and other coal-tar products serve as raw materials for the production of sulfonates. These sulfonates are used as wetting agents in the preparation of agricultural sprays and as detergents for the washing of agricultural products before marketing.

β-Naphthol is a wood preservative, disinfectant, and soil poison for the control of termites. Cardboard bands, impregnated with β-naphthol, are used in apple orchards for trapping codling moth larvae.

A recent development in agriculture that offers considerable promise is the discovery of synthetic plant hormones. These growth regulators have been found useful in the production of fruit without fertilization, for the development of roots on cuttings, and for the prevention of premature dropping of fruit. The better known of these synthetic hormones are α-naphthalene acetic acid, indole butyric acid, phenyl acetic acid, and β-naphthoxy acetic acid. It is interesting to note that all the effective materials discovered to date have an aromatic nucleus. Farming in the future may become more of a science and less of an art through the development of synthetic plant growth regulators.

Tar Acids

Tar acid oil and cresylic acid, either alone or in combination with petroleum oils to make dormant sprays for the control of overwintering aphids and other insects on fruit trees, have been largely replaced with dinitro-*o*-cresol and dinitrocyclohexylphenol. These nitrated phenols are also used for the control of red spiders in citrus trees and certain greenhouse crops. Dinitro-*o*-cresol is an extremely powerful contact insecticide but must be used with caution due to its tendency to injure foliage. Advantage has been taken of the phytocidal properties of this compound to develop a selective herbicide for the control of weeds in grain and other crops. Its selective action is believed to be due to differential wetting of foliage.

Tar acid oils, cresylic acid, xylenol, cresols, and phenols are well known as disinfectants. Phenol was suggested as a bactericidal agent by Lister in 1865, and is now the standard for all disinfectants. The phenol coefficient of the disinfectants marketed today represents the relative effectiveness to phenol in killing *Staphylococcus aureus* and *Bacillus typhosus*. The volume of disinfectants consumed on the farm is substantial. Dairy farmers and poultrymen especially have learned the value of farm sanitation.

Coke Being Pushed from a By-Product Oven into a Hot Car

The development of chlorinated phenols in the last twenty years as disinfectants, wood and fabric preservatives, sap stain controls, etc., has been phenomenal. Most of these products are prepared from synthetic phenol, and 8,000,000 gallons of benzene were used in 1940 for the production of synthetic phenol.

The development of chlorinated phenols as fungicides and bactericides was initiated by the discovery that the toxicity of phenol increased as the number of chlorine atoms was increased. Suter (*18*) reported that the introduction of a halogen into the nucleus of a phenolic compound increases its bactericidal potency, without exception. As was to be expected, pentachlorophenol is the most toxic to fungi, but certain of its physical properties and industrial requirements have made it necessary to use other products such as 2-chloro-*o*-phenyl phenolate. A wide variety of chloro- and nitrophenolic compounds are now on the market in order to fill the specific requirements of various industrial and agricultural needs.

Tar Bases

The heterocyclic nitrogen compounds obtained from coal tar have been investigated as insecticides and fungicides. Pyridine has considerable insecticidal action, and attempts have been made to produce synthetic nicotine from this product without commercial success. Quinoline has been reported to be an excellent ovicide. Substituted quinolines, such as 8-hydroxy-quinoline, are good fungicides. The agricultural consumption of these tar bases and their substituted products, however, is small. The tendency of farmers to fortify their feeds with vitamins may result in the larger consumption of tar bases for agricultural purposes. A large volume outlet for low-cost vitamins exists in the agricultural field.

Hydrocarbons

Anthracene, phenanthrene, carbazole, methylnaphthalenes, acenaphthene, diphenylene oxide, and fluorene have also been investigated by agricultural workers. These products are known to have insecticidal and fungicidal action, but as yet little effort has been made to utilize them. Anthracene oil has been recommended as a wood preservative but has not been accepted generally in this country for the purpose. These materials will, without doubt, eventually be used for agricultural purposes. Organic chemicals have been found to be very specific in their action as insecticides and fungicides. There are a number of possibilities not yet investigated for these compounds.

The agricultural consumption of organic compounds, particularly as insecticides, fungicides, plant growth stimulants, and preservatives, should increase in future years. There are over 450,000 known species of insects and several hundred thousand species of plants. Each species is more or less separate from all others in structure and metabolism. The usefulness of any given compound can be determined only by actual test; and while considerable knowledge has been accumulated on the relation of chemical structure to toxicity, etc., biological investigations must still be conducted by trial and error methods. An increased consumption of organic chemicals should result in an increased consumption of coal derivatives, since these materials can serve both as final products and raw materials in the manufacture of new agricultural chemicals.

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Pennsylvania Anthracite as a Filter Medium

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Since Pennsylvania anthracite is essentially a carbon and hence more nearly chemically inert than other substances used in filters, it is well suited for many filtration processes. Its conchoidal fracture produces a particle which has the most desirable shape for filter use; its low specific gravity and angular particle shape make possible longer filter runs and more effective filter bed washing at lower backwash rates. Filter capacities have been increased from 25 to 100 per cent through the use of anthracite as a filter medium.

Pennsylvania anthracite is used in municipal filters, power plant filters for the hot process softening of waters and for oil removal from boiler condensates, swimming pool filters, filters for the clarification of chemicals, and sewage filters.

In the preparation of Anthrafilt, care is given to the selection of a low-ash material with the optimum particle shape; the most important single factor involved is the manufacture of the correct particle size to meet the conditions of filter use and design.

◆

RESEARCH on the use of Pennsylvania anthracite as a filter medium was initiated by the Anthracite Institute in 1930. The early experiments were conducted at Lehigh University under the writer's direction; later the laboratory was moved to Pennsylvania State College where the experimental work was continued to its conclusion in 1934. Since that time field studies have been conducted and are still in progress.

The use of Pennsylvania anthracite in filters was originated by James H. Fuertes about 1896 when he built an experimental filter at Harrisburg, Penna., using dredged river coal as a filter medium because no local sand was available. Fuertes later built plants at Dallas, Texas, Cumberland, Md., and Denver, Colo. All these plants used dredged river coal. The Cumberland and Denver plants are still in operation although they have rescreened their original filter medium and added anthracite specially selected and prepared for filter purposes.

The filters in these early plants were designed to fit the coal. Dredged river coal is not the right size nor does it have the proper particle shape. This may explain why thirty-nine years were to elapse before anthracite was again used in filters. Of course, little was known about filter media in general at that time and nothing was known about the proper size, shape, and bed depth of anthracite to use in filters. As against three filtration plants in thirty-nine years we find a total of eleven hundred filtration plants of all kinds using filter anthracite (Anthrafilt) over the past seven years Figure 1 shows how this growth has taken place.

Preparation of Anthracite

The preparation of anthracite for filters requires more care than does the preparation of anthracite for fuel purposes. The first step is the selection of a coal that will yield a particle free from small fracture cracks and possessing the best shape. The particle must be strong enough to withstand years of backwashing without breaking into smaller grains; its shape should be longer than it is wide but should not be extremely thin.

This anthracite must be cleaned to a low ash product, and of course that comes within the province of the coal-breaker engineer. The coal-breaker engineer can also make it to the desired particle size; special knowledge is required, however, to know what size to make. It has been found that three fine sizes fit most cases, but the selection of which size to use in a given filter comes within the province of an engineer thoroughly versed in filter design, treatment methods, and filter operation.

Since all Pennsylvania anthracites are not suited for use in filters and since quality, particle shape, and particle size are critical factors in all anthracites that are suitable, the term "Anthrafilt" has been used to designate Pennsylvania anthracite that meets all requirements for successful use in filters. For the sake of brevity and clarification, therefore, it is proposed to use the term Anthrafilt throughout this paper so the reader will know that a specially selected and prepared anthracite is being described.

Properties of Anthracite and Sand

Since the dawn of filtration, silica sand has been the prevailing filter medium in industrial and municipal water filters. It is composed almost entirely of SiO_2. It is insoluble in most acids but reacts readily with alkalies. The particle shape is usually rounded. It weighs approximately 100 pounds per cubic foot.

Aside from mineral matter associated with it, anthracite is essentially a carbon and hence is neutral in its behavior with acids and alkalies. The mineral matter associated with anthracite is composed of about 60 per cent silica, the remainder being oxides of aluminum with minor amounts of magnesium, calcium, and iron. The particle shape is sharp, angular, and flat. It weighs about 50 pounds per cubic foot.

The particle charge on silica sand is negative and so likewise is the particle charge on crushed anthracite. The charge on silica sand is weak, however, compared to the strong charge on anthracite.

SIGNIFICANCE OF PROPERTIES. Since silica sand is about the only medium other than Anthrafilt to be used extensively in filters, the properties of these two materials will be discussed from the standpoint of their contrasting behavior in filters.

In the removal of solids from liquids by drainage beds, filters act as entrapping agents rather than as strainers. The water or other liquid is usually treated with a coagulant which agglomerates the solid particles, many of which are so small that they would pass through an ordinary filter. Since the degree of entrapment is directly proportional to the surface exposure of the filter medium, the sharp angular particle of Anthrafilt is more efficient than the same size sand having a spherical shape. In practice it has been found that Anthrafilt having an effective size of 0.70 mm. and a uniformity coefficient of less than 1.60 removes the same amount of solids as does a rounded silica sand with an effective size of 0.45 mm. and a uniformity coefficient of 1.60.

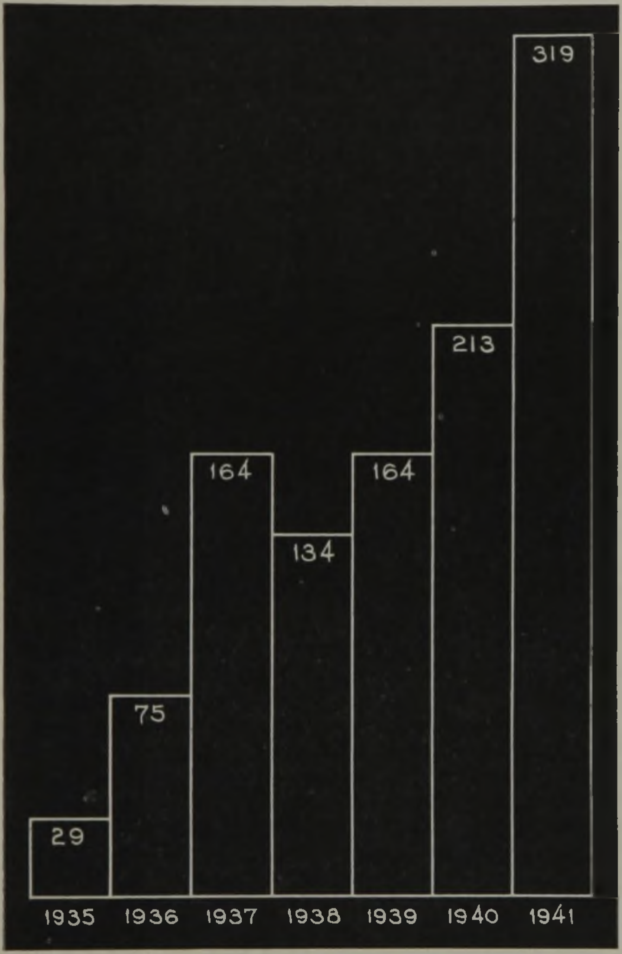

Figure 1. Growth in the Number of Filtration Plants of All Kinds Using Anthrafilt during the Years from 1935 through 1941

For many years the average sand size used in filters has been one with an effective size of 0.45 mm. and a uniformity coefficient of less than 1.60. Recently, however, there has been a trend toward a coarser particle size. One of the limiting factors has been that most filters are not designed with a wash water velocity high enough to produce the necessary degree of bed expansion when the filter is backwashed.

Hulbert (*4*) showed that 50 per cent expansion of a filter bed is desirable for effective washing of a filter. Because of the light weight of Anthrafilt a 50 per cent expansion is possible without increasing backwash velocities, even when the particle is considerably coarser.

As compared with a fine filter medium, a coarse one will give longer runs between backwash periods, will not clog so readily with fibrous turbid matter, will release the dirt on grains with greater ease when backwashed, will have less head loss through the filters, and will permit higher filtration rates.

Since Anthrafilt of coarse size is as efficient in turbid matter removal as finer sand and weighs half as much, it can obviously be substituted for fine sand without sacrificing quality of effluent and without detracting from a high degree of bed expansion under the same backwash velocity as used with fine sand.

Because of the carbon composition of Anthrafilt, it does not react chemically with the turbid matter which envelopes the grains during filtration; hence the filter particles are more readily cleaned under routine backwashing, and with proper filter design the particles will never coat with salts such as those of lime, iron, and manganese. Sand, on the other hand, often coats so badly that it has to be discarded because of filter-bed cementation or because the sand particle becomes so heavy that it can no longer be lifted by the backwash water.

Where water is treated with lime in cold-process softening, silica sand becomes badly coated with layers of lime that cannot be removed by mechanical means because of the chemical reaction between the acid silica and the alkaline lime.

Where hot-soda process softening is used, as in boiler water treatment, the hot alkaline waters dissolve the silica sand and impart a silica scale to boiler tubes which is difficult to remove. A small amount of silica is leached out of Anthrafilt (*8*) under these conditions, but after the first few days of operation the effluent is practically free of silica. This advantage of Anthrafilt is so marked that it is rapidly replacing sand in filters of this kind in all parts of the United States and in many foreign countries. Mercerizing plants have also found Anthrafilt a boon in the filtration of caustic soda. It can be seen also that Anthrafilt is advantageous in the filtration of many chemicals which would react with other filter media.

Case Histories

Many filtration plants have reported longer filter runs, higher rates, and cleaner filters through the use of Anthrafilt in place of sand.

The Passaic Valley Water Commission, Paterson, N. J., reports (*2*) marked increase in plant capacity through the use of Anthrafilt.

The plant capacity of Oklahoma City was increased from 16 million gallons per day to 30 million by substituting Anthrafilt for sand.

Anthrafilt increased the capacity of the New Toronto, Canada, plant 50 per cent.

The filtration plant of Cornell University, Ithaca, N. Y., using Anthrafilt reports (*3*) experimental runs of 300 hours each, which is considerably longer than runs for the usual sand filters.

Swimming pool filters have used Anthrafilt with marked improvement over sand. The turbid matter of swimming pool filters is largely fibrous, being composed chiefly of lint and hair. This kind of turbid matter clogs fine sand in a few hours but does not clog coarse Anthrafilt. Furthermore, swimming pool filters are usually provided with a low washwater velocity which is not very effective with the relatively heavy silica sand.

Lake waters are commonly infested with algae during spring and autumn. At such times Anthrafilt filters still give long runs (*6*), whereas runs through sand are so short as to be serious in the reduction of plant capacity. Buffalo, as well as many other cities along the Great Lakes using Anthrafilt, reports long runs during algae periods.

In the removal of emulsified oil and turbidity from boiler feed condensate, Anthrafilt has been found very effective. Coagulants such as alum, ferric sulfate, or ferrous sulfate are added and produce spongy gelatinous masses which are easily removed without clogging the coarse Anthrafilt filter bed.

In the removal of iron and manganese salts from municipal water supplies, Anthrafilt has been more effective (*2*) than sand in spite of the fact that, it is commonly believed, a sand must be coated with iron or manganese oxides to be effective; Anthrafilt apparently does not coat.

Use in Sewage Filters

One of the earliest significant references to the use of anthracite in sewage work is found in a report (*5*) of the State Board of Health of Massachusetts referring to the Lawrence Experiment Station Report for 1910. In connection with the preliminary treatment of sewage appears the following paragraphs:

"Strainer *E*, containing 12 inches in depth of Buckwheat coal, was put into operation in 1901, and has been operated at a rate of 800,000 gallons per acre daily throughout 1910. Sixty-six per cent of suspended matter was removed as shown by albuminoid ammonia determinations; and the total removal of organic matter was about 39 per cent, as shown by albuminoid ammonia and oxygen consumed determinations.

"The work of this strainer is remarkable and in some respects unexplainable. Year after year it removes large percentages of suspended matter from the sewage, and by some biological process not fully understood appears to destroy this matter with great rapidity. During the entire nine and one half years which this strainer has been receiving sewage at rates from 800,000 to 1,500,000 gallons per acre daily, averaging 1,000,000 gallons per acre daily, sludge has been removed from the surface only twice, and the filtering material has been raked or otherwise disturbed only four times. The two scrapings were made during the first year of operation. Of the other four disturbances of material, three were necessitated by the collapse of the tank, requiring the transfer of the material to a new tank. From September 23, 1905, when the material was last transferred, to January 28, 1910, when the strainer was raked to a depth of three inches, or during a period of four and one third years, no treatment of the surface or removal of sludge was required."

The Borough of State College used Anthrafilt in sewage sludge beds (*1*) and found that the effluent was about the same as that from sand beds; the Anthrafilt beds did not freeze during winter weather and did not pack when walked on by the man lifting the sludge. The companion sand beds froze shut during the same winter weather.

Anthrafilt has been used in rapid mechanical filters employed in the clarification of waters from chemical precipitation of sewage. This installation was in the sewage plant of Oklahoma City. It was reported that three filters were used at the outset, one provided with New Jersey sand, one with Texas sand, and the third with Anthrafilt. The sand filters became clogged within the first three months, but the Anthrafilt did not clog. The one Anthrafilt filter is now doing the job of the three filters. This rather confirms the findings of the Lawrence Experiment Station.

One large canning factory is using Anthrafilt in sludge bed type filters for clarifying canning wastes. They report favorable results.

Anthracite is well suited for trickling filters although, as far as I know, it has not been used for this purpose. It should have several advantages over limestone or traprock which are the materials now in common use.

Combination with Other Filter Media

The first attempt to use Anthrafilt in combination with other filter bed materials (*7*) was reported in 1935 by the city of Raton, N. Mex., in connection with its domestic water supply. Silica gravel was used as a supporting base for a bed of coarse activated carbon on top of which was a bed of fine Anthrafilt. The theory was that Anthrafilt would remove all turbid matter so that the activated carbon could operate with clear water in taste and odor removal for a long time without becoming clogged. This combination filter is said to produce 88 per cent more filtered water than the sand filter, and the effluent is free from turbidity, taste, and odors.

Three municipal filtration plants (Chester and Erie, Penna., and Buffalo, N. Y.) are now using a combination of Anthrafilt and sand. The theory is that a relatively coarse bed of Anthrafilt on top of a fine bed of sand will provide a roughing and finishing filter in one unit. The coarse Anthrafilt will remove practically all the turbid matter, and the fine sand will catch the almost colloidal particles that may escape the Anthrafilt. The advantages of a very fine sand can be obtained without the usual handicap of short runs, low rates, and clogged beds.

Combination Anthrafilt and sand beds are feasible only where the filter is provided with agitation devices to be used during backwashing. It has been found that a layer of the turbid matter forms at the junction of the sand and Anthrafilt, and this can be removed only by agitation during backwashing.

Where sand combinations are used, the total filter bed depth should be made up of 50 to 66 per cent Anthrafilt for best results.

Relative Cost of Filter Sand and Anthrafilt

High-quality silica sand for use in filters is prepared in very few places in the United States. Most of it is prepared at sandbanks in New Jersey. Practically all foreign countries secure their filter sand from the United States. For this reason good sand for filters is not so inexpensive as one might assume.

Anthrafilt is prepared by one of the large anthracite-producing companies in Pennsylvania. In most parts of the United States it costs more per ton than does filter sand, but since it takes half as many tons to fill a given space, it is no more expensive than sand, volume for volume. In distant parts of the country and in foreign countries Anthrafilt has a decided price advantage over sand because in such cases the cost is largely freight. By virtue of its light weight Anthrafilt will require half as many freight cars and half as many ships.

From the standpoint of degradation, Anthrafilt and sand have the same length of life in filters. Where renewals of filter medium are made necessary through incrustations on the filter medium, Anthrafilt will last about twice as long as sand.

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Foundry Coke from Blending of Southern Coals

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A. S. T. M. specifications for foundry coke were set aside in 1941 by Committee D-5 on account of inability to meet the varying demands of the individual cupola operators. In this paper broad standards are set up for foundry coke which will fill the requirements of the average consumer.

No coal in the Alabama field will produce a coke of the desired characteristics when coked alone, and blending is necessary. The experience of one company is related in the selection of coals from available sources, and evaluations are given of the chemical and coking properties of the coals selected for blending. The cleaning and special preparation of the coals before use are discussed. The proportions of the various coals used are then balanced according to the coking characteristics of each to produce a coke designed to meet the average requirements of the foundry trade.

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THE production of coke in modern by-product ovens may be divided under two general heads, blast furnace and foundry coke. Specifications for furnace coke can be well defined, as its purpose is to furnish carbon monoxide for the reduction of the iron ore and heat for melting the metallic iron, the operation of the furnace stack being somewhat standardized. The one purpose of foundry coke in the cupola is to heat the iron charge to the desired tapping temperature; one might logically think that specifications for this grade could be drawn with even closer limits than for the furnace coke, but unfortunately the reverse is true. Cupola practice covers both the malleable and gray iron foundries where operating conditions must vary in accordance with the size of the cupola unit, rate and tapping temperature of melt, as well as the physical and chemical characteristics desired in the cast product. In other words, each cupola is an individual problem, and most operators have definite ideas as to requirements and specifications. A committee of the American Society for Testing Materials was working on foundry coke specifications until recently when it was dismissed because the question was too complex to be covered by one or even more sets of specifications covering the broad nomenclature of foundry coke. The problem of satisfying each cupola operator is now the responsibility of the individual coke producer, and the purpose of this paper is to show how one coke plant approached and handled this rather difficult problem by blending available coals which were not entirely suitable when coked alone.

Although there are no A. S. T. M. specifications to cover foundry coke, broad standards can be set that this grade of coke must meet for satisfactory use in the cupola. It would be impractical to make a special coke for the individual cupola operator, and the alternative is to produce the best coke possible to meet the fundamental requirements of general cupola practice. As the primary purpose of the coke is to furnish heat for melting the charge, the B. t. u. value should be high. Coke is principally fixed carbon and ash; therefore the ash content must be reasonably low (10 per cent or under) to give 90 per cent carbon for burning. The coke should be as free as possible from fingering and cross fracture so that it can support the burden in the cupola without breaking down and blocking the upward passage of the gases by close packing of the fine sizes. This is indicated by the shatter index, which should be 80 or better. The tumbler test and stability factors indicate the degradation of the coke in handling from the ovens to the consumer, which is an important factor as under-size coke is not used. Porosity, or cell space, has two important functions. A dense coke (high apparent gravity) is generally stronger and, at the same time, permits a greater concentration of the coke in a given volume of the cupola as compared with a more open coke of higher porosity. Since combustion is a surface reaction, the combustibility or burning rate will be indicated by the porosity index, the more open coke having more exposed surface for combustion. It is desirable that the ignition temperature of the coke be high in order to shorten the combustion or melting zone in the cupola and conserve fuel by the concentration of the heat at this place. Sulfur content of the coke should be as low as possible to avoid excessive use of desulfurizing agents. Fusion temperature and fluidity of the coke ash must also be taken into consideration. Thus, the foundry coke producer has a difficult problem, especially since the raw material, coal, is available only as nature made it countless ages ago, and no two seams are alike in chemical or physical characteristics. Therefore the evaluation of available coals for their coking characteristics and blending qualities should be the first consideration of the foundry coke producer.

AT THE close of the last war this company found itself with a modern by-product plant built to supply coke for the cyanamide synthetic nitrate plant at Muscle Shoals and with coal mines producing from only one seam, the Black Creek. The coke, although ideal for the carbide furnaces, was not entirely suitable for foundry trade and steps were taken to find other desirable coking coals in the Alabama field. Full-size oven tests were made on every available source; although we now have a large number of tests for indicating coking properties such as box or small oven tests, agglutinating, plasticity, swelling values, etc., which give valuable information, the final and conclusive tests must be made under actual oven operating conditions, followed by tests in cupolas.

Although there are a number of seams of coking coals in Alabama, no one coal was found which yielded on coking all the desirable characteristics discussed above, so blending was the only alternative and it had to be approached from the economic standpoint as well as the needs of the foundryman. Uniformity of the product must be maintained from day to day to satisfy the requirements of the various cupola operations. By this means the foundryman can adapt the coke to his particular needs and obtain good, reproducible results. Strict laboratory control of the coal cleaning plants operated by the company is necessary to obtain this desired uniformity.

Coal from the Black Creek seam was available but not entirely suitable for coking alone. Although the coal is a high-grade coking and steam coal, the mining is exceedingly difficult. The average thickness of the seam is only 22 inches, necessitating the removal of a large amount of rock to give working room and producing an excess of fines when undercutting 6 inches by machines in mechanical mining. The coal in the seam itself is relatively clean for an Alabama coal, the inherent ash (1.40 specific gravity) being only 1.50 per cent. Washing for the removal of the heavy rock is not difficult, plunger-type jigs being used, and the ash in the cleaned coal averages a little less than 3 per cent. Analysis of the coal (dry basis) follows:

Proximate Analysis, %		Ultimate Analysis, %	
Volatile	33.20	Hydrogen	5.1
Fixed carbon	63.80	Carbon	85.0
Ash	3.00	Nitrogen	1.8
Sulfur, total	0.64	Oxygen	4.5
Pyritic	.07	Sulfur	0.6
Organic	.48	Ash	3.0
Sulfate	.09	Total	100.0

Ash softening temp., °F. 2,650
B. t. u. 15,030

Coke made from 100 per cent of this coal has a large amount of sponge and black ends; the porosity is high and the structure somewhat weak with a definite tendency to finger—that is, produce longitudinal shrinkage cracks. The sulfur content, although low, is mostly of the organic type which remains in the coke. The high volatile content of the coal gives a low coke yield, an increase in sulfur content, and a coke ash of 4.50 per cent from the 3 per cent ash coal. Also, due to the high volatile and coking characteristics, the coke is very open with a porosity of 50 or over, and final shrinkage on coking is excessive. The coke is fast burning, and, while giving high heats on a batch cupola operation, on continuous runs the bed soon burns out and cold iron results. Shatter index is low, averaging between 60 and 65.

To offset the disadvantages of the straight Black Creek coke, other local sources were tested; after preliminary analyses over thirty Alabama coals from different seams and mines were given full-size oven tests. The final choice was the Mary Lee seam because of its blending qualities with the Black Creek and the availability of the mines and coal reserves.

For comparison, an analysis of the Mary Lee coal as used today (dry basis) is:

Proximate Analysis, %		Ultimate Analysis, %	
Volatile	29.40	Hydrogen	5.0
Fixed carbon	61.10	Carbon	78.5
Ash	9.50	Nitrogen	1.6
Sulfur, total	1.06	Oxygen	4.3
Pyritic	0.39	Sulfur	1.1
Organic	.65	Ash	9.5
Sulfate	.02	Total	100.0

Ash softening temp , ° F. 2,695
B. t. u. 13,790

The seam is divided into the upper and lower benches, separated by a 20-inch rock parting called the "middle man". The lower bench (22 inches) is relatively clean solid coal with an inherent ash (1.40 specific gravity) in the $-1/_4$-inch size of 6.75 per cent and total sulfur of 0.80 per cent. The upper bench (40 inches) is badly laminated with thin, irregular streaks of bone coal in addition to small rock partings which are included in the raw coal by mechanical mining. The inherent (1.40 specific gravity) ash in the $-1/_4$-inch size of this coal averages 9.30 per cent and sulfur, 1.24 per cent. The raw coal, 20 to 25 per cent ash, as washed in the existing plunger type jigs could be reduced to 10 per cent ash and 1.20 per cent sulfur.

COKE made from 100 per cent of this Mary Lee coal gave little sponge and black end coke. Cross fracture was particularly noticeable in contrast to the fingering fracture of the Black Creek. The lower volatile gave less final shrinkage and a denser harder coke of 42 to 43 porosity. The shatter showed little improvement. A thorough investigation indicated that the excessive cross fracture and resulting low shatter index was largely due to the bone impurities left in the coal cleaned by the jig washing. This material, although not high in ash, had no coking properties and caused breakage in the coke by not fusing to the plastic mass of coal in coking. The larger pieces increased the internal weakness of the coke structure, and the natural shrinkage cracks followed the path of least resistance.

As the bone was closely laminated with the clean coal, crushing to $-1/_4$ inch was necessary to crack it off before washing. The washing problem was most difficult, as the gravity of the coal was 1.37 and the bone 1.45–1.55, allowing little difference to make a clean gravity separation, especially in treating these fine sizes. After pilot-plant tests of different methods, concentrator type coal tables were selected and installed. Good results in cleaning and bone coal elimination were obtained, but the operation was expensive on account of the low tonnage per unit, the middling boiler fuel that must be made, and the amount of refuse handled.

Blending of the Mary Lee coal with the Black Creek produced a much better coke than either coked separately. More of the Mary Lee had to be used to offset the high volatile, shrinkage, and porosity characteristics of the Black Creek. As 9.00 per cent coke ash had been set as the maximum, the amount of 9.50 per cent Mary Lee coal used had definite limits. The coke from such an adjusted mix gave a shatter index of 75–80 and a porosity of 46–70, was of good firm structure, and had normal fingering and cross fracture, some sponge, and little black ends. An increase in the shatter to 80 or better and a decrease in porosity to 45 was desirable, and tests showed this could be done by lowering the volatile in the blended coal mixture. Increasing the percentage of the Mary Lee coal (with higher ash and sulfur) was not desirable for obvious reasons, and Alabama has few coals of lower volatile content with other desirable characteristics.

The low-volatile Pocahontas coals from the eastern fields were then considered. Low volatile, sulfur, and ash contents were absolutely essential for maximum blending effects as freight rates doubled the cost of this coal as compared to the selected Alabama coals. Economics were the determining factor in the maximum amount which could be used. Some ten or more coals of this type were tried in extensive tests before final selection was made. Analysis of this coal used for many years is as follows (dry basis):

Proximate Analysis, %		Ultimate Analysis, %	
Volatile	16.20	Hydrogen	4.0
Fixed carbon	78.70	Carbon	86.8
Ash	5.10	Nitrogen	1.3
Sulfur	0.56	Oxygen	2.2
		Sulfur	0.6
		Ash	5.1
		Total	100.0

Ash softening temp., ° F. 2316

After many different mixtures of these three coals were tried and the various factors balanced, a blend was established with analysis as follows (dry basis):

Proximate Analysis, %		Ultimate Analysis, %	
Volatile	29.28	Hydrogen	4.9
Fixed carbon	63.92	Carbon	81.7
Ash	6.80	Nitrogen	1.6
Sulfur, total	0.86	Oxygen	4.1
Pyritic	.29	Sulfur	0.9
Organic	.53	Ash	6.8
Sulfate	.04	Total	100.0

Ash softening temp., ° F. 2625

The foundry coke produced from the established coal mixture has been maintained with little variation and has found wide acceptance by the foundry trade. While the Pocahontas coal has had an advantage in reaching set standards for foundry coke, its substitution by Mary Lee would yield a coke of good physical standards but slightly higher in ash and sulfur contents. An average analysis of the 3-inch and higher foundry coke as now produced is as follows:

Volatile, %	0.93	Shatter (+ 2 in.)	83
Fixed carbon, %	89.97	Tumbler test, %	
Ash, %	9.10	Stability	36.5
Sulfur, %	0.70	Hardness	62.9
True gravity	1.89		
Apparent gravity	1.04		
Porosity	45		

Ash softening temp., ° F. 2646

ONE point mentioned in the above discussion of blending to produce foundry coke is the economic side which is most essential for continued, successful oven operation. Although the production of good foundry coke is the principal consideration, the other by-products must meet certain requirements for their disposal. The total, as well as the foundry coke yield from the coal charged, should be as high as possible. From this established blending operation, the total coke yield is 75 per cent, with 60 per cent of this amount screening out into the 3-inch and higher foundry size, and the remaining 40 per cent going into the various sizes of domestic grades. This is considered good for a 16-inch width oven and 24-hour coking time. These domestic grades require a coke of high B. t. u., combustibility, and ash fusion. The latter was one point considered in the selection of the coals now used. The yield of by-products is of secondary importance, and the operator must be satisfied if the coke meets the market demands. It may be of interest, however, to state that the yield of by-products from these coals is somewhat higher than the lower volatile coking coals of other sections of this country.

Influence of Storage on Caking and Coking Properties of Coal

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Samples (400 pounds) representative of fifteen different coal beds were oxidized progressively in an accelerated weathering apparatus and then subjected to a series of tests to follow the changes in various aspects of their coking and caking behavior. The length of time each coal could withstand standard oxidizing conditions before losing its coking power (termed "durability of coking power") showed a sixteen fold range among the coals tested.

The durability of coking power of most coals can be predicted with fair accuracy from their analysis by the method developed. Loss in caking tendency (leading to improved performance in underfeed stokers) was followed by several different tests. Comparisons showed: (*a*) Decrease in agglutinating value predicts decreased strength of coke; (*b*) the amount of unfused char remaining in the retort after carbonization can be correlated with strength of coke and also with the agglomerating index that is based upon classification of coke buttons made in the standard volatile matter test.

The caking tendency of coals can be reduced greatly by storage or oxidation long before the true loss in heating value exceeds 1 or 2 per cent.

STORAGE of coal near the point of consumption assures regularity of supply and evens out seasonal demands on railroads and coal mines. An important factor determining the amount and kind of coal to be stored is the extent of deterioration and loss to be expected on storage. Previous work by the Bureau of Mines has shown that if spontaneous heating does not occur, the loss in heating value on storage is so small as to have little commercial importance (*6*).

The loss of coking power is, however, of vital interest in the operation of coke plants where large quantities of coal must be stored to assure absolute dependability of supply. Use of coal that has suffered too much deterioration in storage results in decreased production of usable coke and causes operating difficulties, such as trouble in removing coke from ovens. In severe cases damage to the coke ovens may result. Changes in the properties of coke brought about by use of oxidized coal often result in decreased production of iron in the blast furnace and decreased efficiency of operation.

Experience has shown that some coals can be stored for years without serious loss in coking power, while others should not remain in storage more than a few weeks before being carbonized.

The changes that take place in coal on storage are not always disadvantageous. Some coals show somewhat greater coking power after some time in storage (*9*). Furthermore, complete loss of coking power may even be considered advantageous in special instances, such as that of coal to be used in domestic underfeed stokers.

Accelerated Storage Tests

To investigate the effects of storage on representative coking coals, an accelerated weathering or storage test was developed by the Bureau of Mines. Coal samples (400 pounds) that are representative of the coal bed are stage-crushed to pass a $^1/_4$-inch screen and then exposed to air at 100° C. in a steam-jacketed drum that rotates slowly. Periodically 90-pound samples are taken for carbonization in steel retorts at 800° C. (Bureau of Mines–American Gas

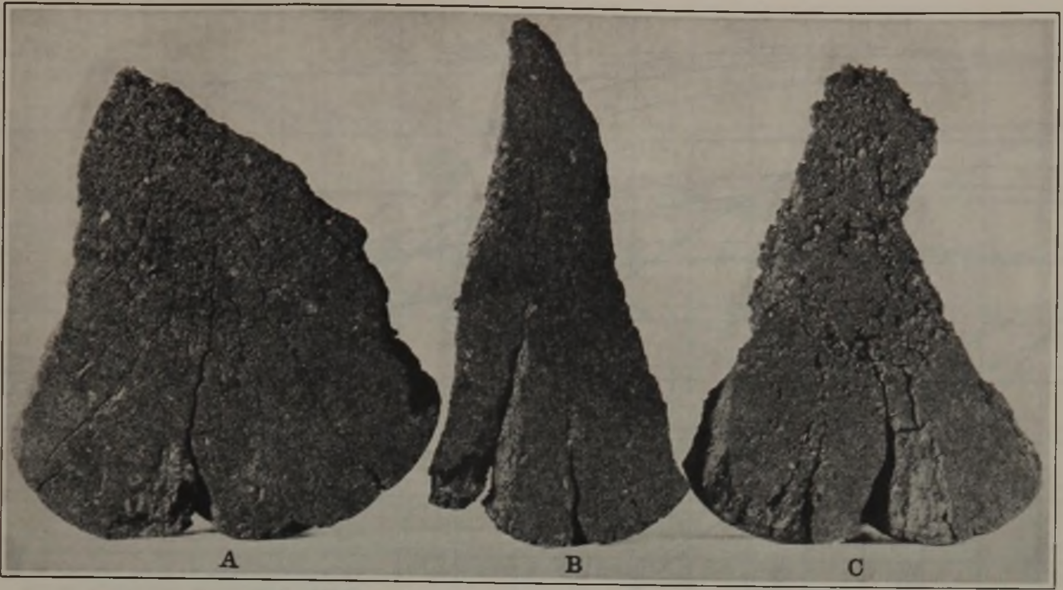

Figure 1. Sections of Coke from Pond Creek Coal Carbonized at 800° C., Showing Effect of Oxidation

Association Carbonization Procedure, *2*). In this way enough coke is made so that standard methods of coke testing can be used to determine the quality of coke.

The rates at which various coals consume oxygen in the accelerated weathering drum (*8*) as well as studies on the effect of various storage conditions on rate of oxidation (*7*) were reported previously.

Previous studies (*10*) showed that major changes in carbonizing properties brought about by oxidation or storage are: decreased strength of coke, decreased yield of tar, increased yield of coke breeze or unfused char, decreased pore size in the coke, in general, increase in the apparent specific gravity of the coke.

Figure 1 illustrates the changes in the appearance of coke produced when Pond Creek coal No. 53 is preoxidized. Coke *A* was made from fresh coal, whereas *B* and *C* were made from coal oxidized 6.4 and 10.3 days, respectively, in air at 100° C., consuming 1.4 and 2.0 per cent of its weight of oxygen, respectively. The cell structure of coke *B* was finer, as can be seen from the photograph, and the strength was somewhat higher than that of coke *A*. Additional oxidation resulted in the poorly fused, weak, pebbly coke seen in coke *C*.

Under a given set of storage conditions, the length of time a coal can be stored without serious impairment of its coking properties depends on several specific properties of the coal, including characteristic rate of oxidation, sensitivity of coking power to oxygen (that is, the amount of oxygen required to give a certain decrease in coke strength), and the friability of the coal (that is, the property that sometimes determines the amount of surface exposed to air). In general, other conditions being equal, a coal of high characteristic rate of oxidation tends to heat spontaneously in storage, and a coal whose coking power is very sensitive to oxygen deteriorates rapidly in storage, even though no serious heating occurs.

Table I. Sources, Rank, Volatile-Matter Content, Oxygen Content, and Durability of Coking Power of Coals Tested

Coal No.	Bed	County and State	Rank[a]	Volatile Matter Content[b], $(V)_0$	Oxygen Content[c], $(O)_0$	Durability of Coking Power: T_{15}, days	Durability of Coking Power: Ratio to Pittsburgh bed coal
57	Pocahontas No. 4	Raleigh, W. Va.	Low-volatile	17.3	2.5	3.4	0.25
56	Pocahontas No. 3	Wyoming, W. Va.	Same	18.3	2.4	6.5	0.48
55	Sewell	Wyoming, W. Va.	Medium-volatile	22.5	2.8	10.4	0.77
64	Bakerstown	Tucker, W. Va.	Same	23.1	3.2	9.7	0.72
58	Lower Banner	Buchanan, Va.	Same	23.1	2.9	11.1	0.82
60	Lower Freeport	Indiana, Penna.	Same	26.4	3.9	>15	>1.1
59	Upper Freeport	Monongalia, W. Va.	High-volatile A	32.0	5.7	12.6	0.93
53	Pond Creek	Pike, Ky.	Same	34.3	6.1	10.9	0.81
67	Taggart	Harlan, Ky.	Same	37.3	6.5	13.5	1
72	Thick Freeport	Allegheny, Penna.	Same	38.3	6.3	12.6	0.93
73	McAlester	Pittsburg, Okla.	Same	39.2	8.6	2.4	0.18
52	Pittsburgh	Allegheny, Penna.	Same	39.3	7.1	13.5	1
54	High Splint	Harlan, Ky.	Same	39.6	8.8	2.4	0.18
71	Bevier	Cherokee, Kans.	Same	42.8	6.5	20.8	1.54
68	Henryetta	Okmulgee, Okla.	High-volatile B	38.0	7.2	1.3	.10

[a] All are bituminous coals, and the samples are representative of the beds at the points taken.
[b] Fresh coal, moisture- and mineral-matter-free basis.
[c] Fresh coal, moisture- and ash-free basis.

Results previously reported (*7*) showed that the effect of oxidation and storage on coking power can be represented very well by the changes in the coke-strength index:

Coke-strength index = 0.225 ($1\frac{1}{2}$-inch shatter) + 0.293 ($\frac{1}{4}$-inch tumbler) + 0.352 (1-inch tumbler) + 0.202 (per cent fusion) + 0.408 (100 − friability)

This index is obtained from the results of the various standard tests on coke by averaging five test values, weighted so as to give approximately equal weight to each value. A coke-strength index of 100 corresponds to the average coke-strength index of nine representative coking coals (*7*).

Figure 2 shows that the coke-strength index of fifteen coking coals (unoxidized) ranges from 68 to 115. The coke-

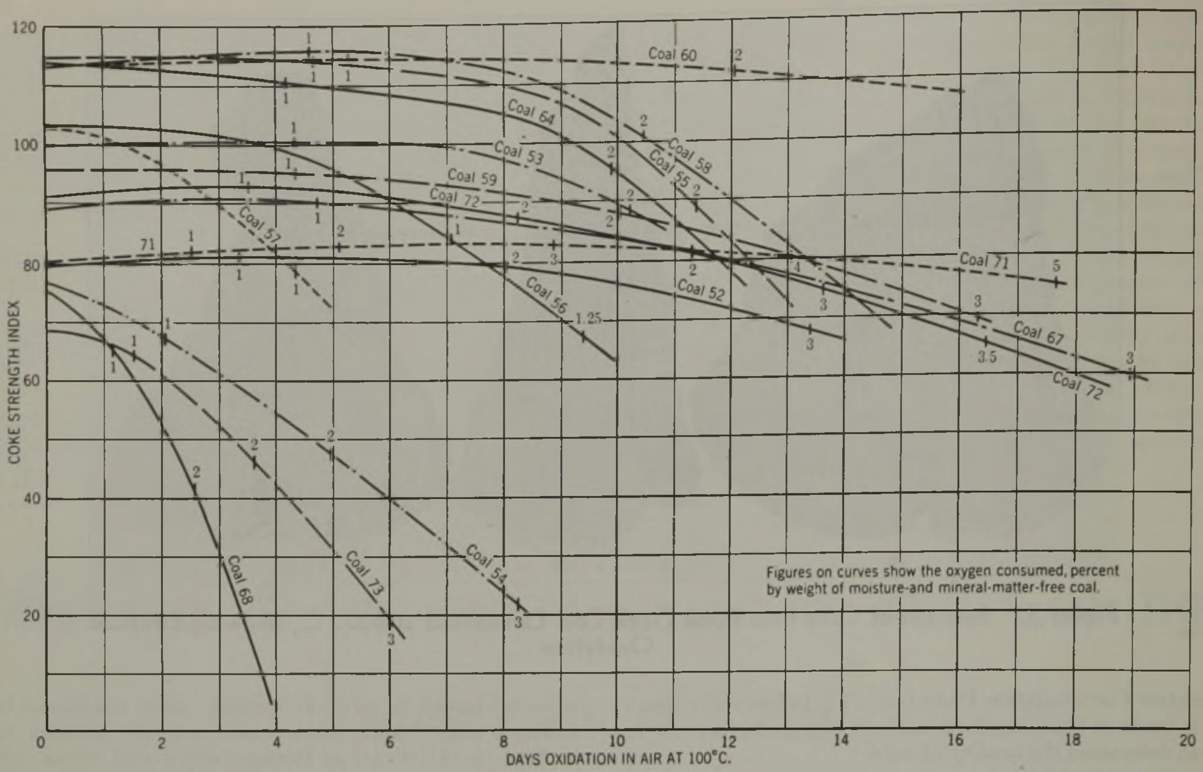

Figure 2. Effects of Storage (Accelerated) of Coal on Strength Index of Coke Produced on Carbonization

strength index is plotted against the time (days) of oxidation of $^1/_4$-inch slack in air (20.93 per cent oxygen) at 100° C. It will be noted that some coals withstand the effect of oxidation much longer than do others. For many coals the coke-strength index even rises somewhat for a time. However, in all instances the end result is the same, loss of coking power.

The figures on each of the curves indicate the quantity of oxygen consumed by the coal, in per cent by weight of moisture and mineral-matter-free coal. The distance between these figures on each curve is a measure of the characteristic rate of oxidation of the coal and, hence, is a measure of its propensity to heat spontaneously in storage.

The sources and partial analysis of the coals tested are given in Table I. In all tables the coals are listed in the order of decreasing rank.

The testing procedure calls for oxidizing each coal sufficiently to reduce its coking power below that required for use in commercial coke ovens. No standards are available, but this result probably was achieved for each coal tested by the time the coke-strength index had been reduced by 15 per cent. Hence, using Figure 1 as a master chart, we find the time of oxidation under standard conditions ($^1/_4$-inch slack in air at 100° C.) required for each coal to reduce its coke-strength index by 15 per cent. The time of oxidation (T_{15}) required to give this standard decrease in coke-strength index will be used as a measure and definition of "durability of coking power". Thus, durability of coking power is a specific property or characteristic of each coal and differs from coal to coal. Table I shows that the values of the durability of coking power for the various coals tested range from 20.8 days for Bevier coal to only 1.3 days for Henryetta coal. This means that if storage conditions, such as screen size, temperature, oxygen concentration, etc., are maintained exactly equal, Bevier coal can be stored sixteen times longer than Henryetta without serious impairment of coking power.

The basis chosen for calculating durability of coking power—that is, the point at which the coke-strength index had decreased by 15 per cent—is entirely arbitrary. The allowable time of storage of any coal, in piles outdoors, is difficult to predict because of the great effect of small variations in storage conditions (*7*). One day in the accelerated weathering drum is, however, roughly equivalent to about 100-day storage outdoors (with no serious spontaneous heating). Regardless of the basis of comparison chosen, the relative durability of coking power (Table I) should remain about the same. In this table the ratios of durability of coking power are based on that of Pittsburgh bed coal taken as unity.

Figure 3 shows an empirical correlation of durability of coking power with the proximate and ultimate analyses of the fresh coals and leads to an equation for predicting durability of coking power from analysis. The accuracy of this prediction for the coals tested is shown in Table II. It indicates that durability of coking power could have been predicted accurately enough for many purposes, for all coals except 60 and 68. The reason for the abnormal behavior of these two coals is not known with certainty.

Figure 4 shows the effects of oxidation on the agglutinating value. The agglutinating value is obtained from a laboratory

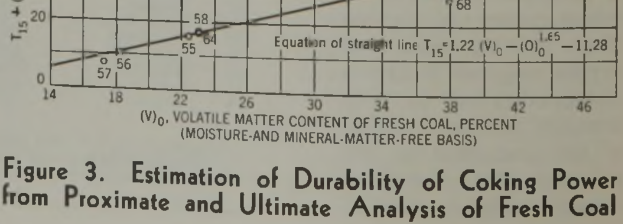

Figure 3. Estimation of Durability of Coking Power from Proximate and Ultimate Analysis of Fresh Coal

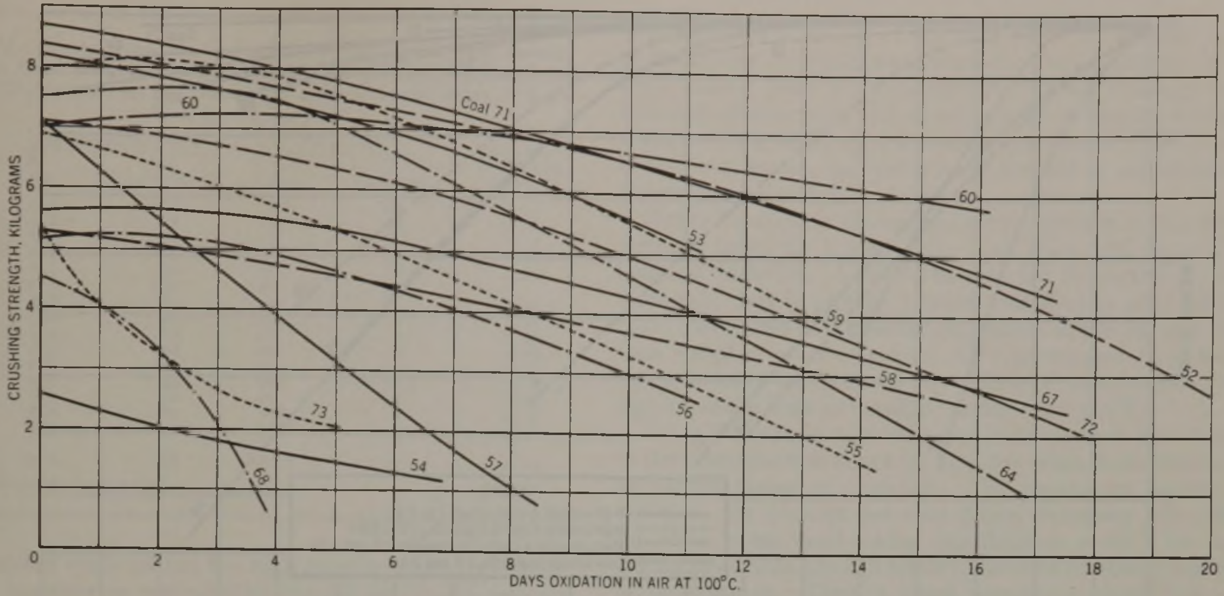

Figure 4. Effect of Storage (Accelerated) of Coal on Agglutinating Value

test and indicates the crushing strength of pellets made by carbonizing a small charge containing 15 parts of sand or silicon carbide to 1 part of powdered coal (*1*).

Table II. Comparison of Observed and Calculated Value of Durability of Coking Power (T_{16})

Coal No.	Durability of Coking Power T_{16}, Days: Observed	Calculated	Deviation
57	3.4	5.3	+1.9
56	6.5	6.8	+0.3
55	10.4	10.7	+0.3
64	9.7	10.1	+0.4
58	11.1	11.1	0
60	>15	10.7	>4.3
59	12.6	9.8	−2.8
53	10.9	10.8	−0.1
67	13.5	12.3	−1.2
72	12.6	14.6	+2.0
73	2.4	1.7	−0.7
52	13.5	11.3	−2.2
54	2.4	0.85	−1.55
71	20.8	19.0	−1.8
68	1.3	9.1	+7.8

Agglutinating value decreases with oxidation of the coals in much the same way that the coke-strength index does. Consequently, agglutinating value can be used as a measure of the extent of oxidation of a stored coal where the agglutinating value of the original fresh coal is known.

So far we have considered only the coking power of coal—that is, the strength of the coke obtained when the charge is carbonized in containers with exclusion of air. The behavior of coking coals while burning in the fuel bed brings up other aspects of the same general phenomenon.

Caking in Fuel Beds

The term "caking" is often associated with the melting and coalescence of coal particles in the fuel bed. The agglomerates so formed have more or less strength, but strength usually has secondary importance; the main feature is increased difficulty of getting combustion air to all points partly because of the decreased surface area of the fuel charge. In domestic underfeed stokers, use of highly caking coals often causes formation of coke trees, especially under light heating load. Ostborg, Limbacher, and Sherman (*5*) reported that "in residential stokers excessive coke formations cause deep fuel beds which give trouble in removal of clinker. They result in a slow rate of pick up which, in extreme cases, results in extinction of the fire." Trouble is also experienced in industrial stokers because of formation of excessive amounts of coke.

Oxidized coking coals give less trouble from excessive coke formation in the fuel bed. For this reason it may often prove advisable to burn stored coals, outcrop coal, or deliberately preoxidized coal. Domestic stokers with special arrangements for preoxidizing the coal have been developed for use with highly coking slacks. In these stokers introduction of a portion of the combustion air into the agitated coal about 7 inches below the active burning zone gives enough preoxidation to eliminate coke-tree formation and to improve operation (*4*).

The coke-strength index, as one measure of caking tendency, has already been discussed in connection with the tests on fifteen representative coking coals at various stages of oxidation. Serving as measures of different aspects of the fusing or caking tendency, several other tests were carried out on these coals:

PER CENT FUSION. A screen analysis was made on each coke as it was removed from the carbonization retorts. The amount of the charge retained upon a 1-inch square-hole screen is termed the "per cent fusion". All the coals tested when fresh showed less than 2.5 per cent of the charge smaller than 1 inch, and the average per cent fusion for these fresh coals was 99.2. Progressive oxidation caused a continued increase in the quantity of unfused particles or loose char that would pass through a 1-inch hole. This corresponds to an increase in the quantity of coke breeze formed in commercial ovens. Figure 5 and Table III (column 4) show the decrease in per cent fusion with oxidation of each coal. If the coals were oxidized long enough, the caking tendency would be destroyed and the per cent fusion would approach zero.

AGGLUTINATING VALUE. Comparison of the agglutinating values of fresh coals (column 5, Table III) with the corresponding coke-strength index (column 3) shows that the agglutinating-value test does not predict directly the strength of coke made from fresh coal in a carbonization retort. For example, coal 54, with an agglutinating value of 2.6 kg., gave almost as strong a coke as coal 52, with an agglutinating

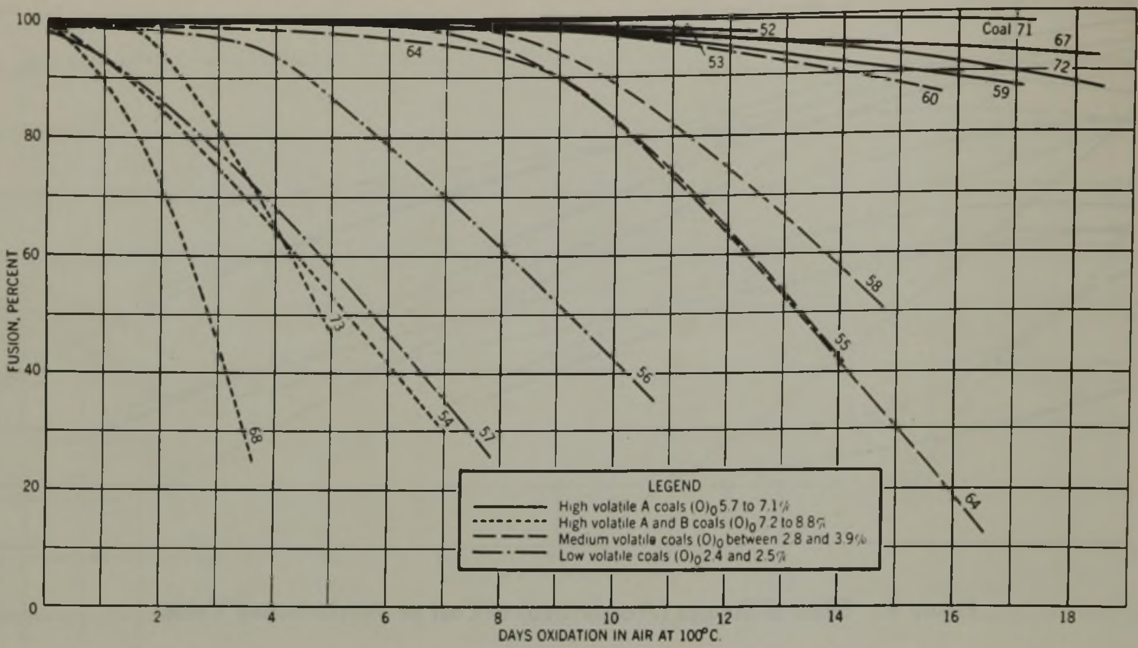

Figure 5. Effect of Storage (Accelerated) of Coal on Fusion

value of 8.4 kg. Nevertheless, as discussed above and shown in Figure 4, the decrease in agglutinating value with oxidation does prove to be a good measure of the decrease (with oxidation) in coke-strength index. This is brought out more clearly in Table IV.

Column 2 shows the agglutinating value after the standard amount of weathering—that is, after each coal has been oxidized sufficiently to reduce its coke-strength index by 15 per cent. The average agglutinating value of all the coals at this point is 3.9 kg., with some variation between coals. This corresponds to an average decrease in agglutinating value of 38 per cent of the value for fresh coal. This large decrease shows that the agglutinating-value test is a valuable laboratory test for measuring the extent of oxidation of a stored coking coal.

Carbonizing conditions in the agglutinating-value test simulate caking in the fuel bed in two respects—that is, in high rate of temperature rise and in essentially free expansion conditions.

Column 4, Table IV, shows for all coals the per cent fusion in the carbonization retort after oxidation has decreased the coke-strength index of each coal by 15 per cent. The average per cent fusion at this point is 87.5; that is, 12.5 per cent of the carbonized charge remained as essentially unfused char. Study of these data shows that, in general, progressive oxidation results in a general decrease in strength of coke for the

Table III. Effect of Storage (Accelerated) of Coal on the Coke-Strength Index, Fusion, Agglutinating Value, and Agglomerating Index

Coal No.	Days of Storage in Air at 100° C.	Coke-Strength Index	Fusion, Per Cent	Agglutinating Value, Kg.	Agglomerating Index
57	0	103.1	97.9	7.1	CG
	4.54	76.5	62.5	3.4	CP
	7.79	...	26.1	1.9	CP
56	0	103.5	98.6	5.1	CG
	3.29	101.5	96.4	5.0	CG
	9.85	64.4	43.7	3.0	CF
55	0	114.9	100.0	6.8	CG
	3.97	114.4	100.0	5.7	CG
	12.95	73.4	53.5	2.0	CF
64	0	114.1	99.5	7.5	CG
	3.95	111.0	98.1	7.6	CG
	8.01	105.0	93.9	5.5	CG
	11.82	79.5	53.4	2.8	CG
	16.11	...	30.4	2.1	CP
58	0	113.4	99.5	5.3	CG
	5.09	115.8	98.9	4.3	CG
	13.68	77.0	60.0	3.2	CF
60	0	113.6	100.0	7.0	CG
	6.65	114.3	99.0	7.0	CG
	15.18	108.2	87.9	5.9	CG
59	0	95.7	99.3	7.9	CG
	9.12	89.6	97.8	5.7	CG
	13.79	77.6	92.2	3.7	CG
53	0	99.9	99.1	8.2	CG
	6.40	100.1	98.6	6.8	CF
	10.33	87.8	97.2	5.4	CF
67	0	89.2	98.6	5.6	CG
	4.61	90.5	98.6	5.4	CG
	8.03	87.6	97.4	4.6	CF
	11.91	76.5	96.0	3.5	CF
	17.40	65.5	93.2	2.6	CF
72	0	91.4	98.7	7.1	CG
	3.26	93.3	99.4	6.7	CG
	7.12	90.0	98.4	4.8	CG
	10.49	79.8	97.9	4.4	CF
	17.23	62.5	89.4	2.8	CP
73	0	68.7	99.4	5.4	CF
	1.41	65.5	98.6	3.7	CF
	2.85	52.7	83.1	2.7	CP
	4.79	34.0	50.4	2.1	CF
52	0	79.6	97.5	8.4	CF+
	7.96	79.3	98.0	6.9	CF+
	11.67	72.3	97.8	6.0	CF
54	0	76.7	99.5	2.6	CF
	4.04	50.5	63.3	1.6	CF
	6.64	38.8	34.2	1.8	CF
71	0	81.2	100.0	8.7	CG
	1.61	76.9	99.1	8.9	CG
	4.06	76.9	99.6	7.7	CG
	8.46	82.8	99.9	6.9	CG
	16.65	76.2	98.6	4.5	CF
68	0	75.4	99.8	4.5	CF
	1.27	63.7	85.2	3.9	CF
	2.57	...	39.8	1.3	CP
	4.18	...	25.6	0.4	CP

Table IV. Comparison of Agglutinating Value, Per Cent Fusion, and Per Cent Decrease in Heating Value of Coals at the Point Where Oxidation Has Decreased the Coke-Strength Index of Each Coal by 15 Per Cent

Coal No.	Agglutinating Value Kg.	Agglutinating Value % decrease	% Fusion Value	% Fusion % decrease	Decrease in Heating Value, %
57	4.4	38	74	24	0.55
56	4.2	18	74	25	0.68
55	3.1	54	79	21	1.54
64	4.8	36	85	15	1.24
58	3.5	34	81	19	1.23
60	<6	>14[a]	<83	>17[a]	...
59	4.2	47	94	5	1.80
53	5.2	37	97	3	1.69
67	3.4	39	95	4	1.80
72	4.0	44	96	3	2.09
73	3.0	44	89	10	1.05
52	5.5	35	98	−0.5	2.46
54	1.9	27	81	19	3.78
71	3.3	62	97	3	4.23
68	3.8	16	85	15	0.72
Av.	3.9	38	87.5	12	1.78

[a] Not included in averages.

high-volatile coals (of not too high oxygen content), but the caking tendency as measured by the per cent fusion remains relatively strong. Conversely, with low-volatile coals the caking tendency decreases rapidly, but the coke produced tends to remain relatively strong.

Column 6 shows the per cent decrease in heating value of the coal at the point where the coke-strength index has been reduced by 15 per cent. At this point, where the coking power has been essentially destroyed as far as use in commercial ovens is concerned, the average decrease in heating value caused by oxidation is only 1.78 per cent. This decrease has no commercial importance, especially when it is realized that the true loss in heat on storage is probably only about one third this apparent loss in heating value. Study of the changes in analysis of these coals on oxidation leads to the rough estimate that, on the average, about two thirds of the observed loss in heating value shown in column 6 is due to the gain in weight of the coal caused by addition of oxygen.

AGGLOMERATING INDEX. The agglomerating index (*3*, *11*) of a coal is obtained by examination and classification of the button remaining in the crucible after the standard volatile-matter determination. The buttons are made under free swelling conditions and at a high rate of heating. Thus, the carbonizing conditions in these tests simulate in these respects the conditions in a fuel bed; consequently, the agglomerating index may serve as a measure of the caking tendency.

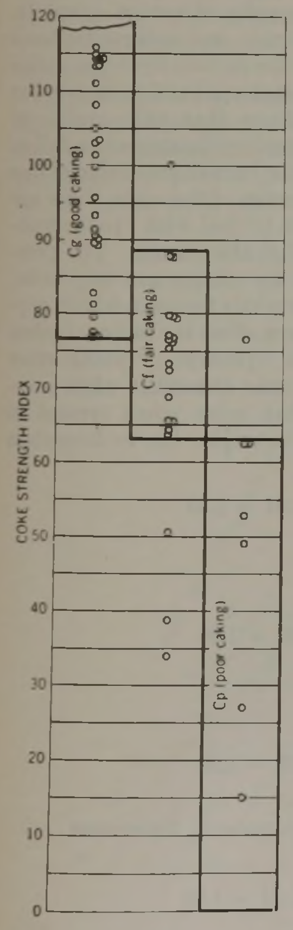

Figure 6. Comparison of Agglomerating Index and Coke-Strength Index of Various Coals

Comparison of columns 2 and 6 in Table III and reference to the system of classification show that with oxidation most coals passed from buttons showing strong swelling, pronounced cell structure, and metallic luster to buttons showing slight swelling, small cells, and slight gray luster. In the case of each coal tested, the swelling and amount of cell structure decreased with oxidation of the coal.

Figure 6 compares the agglomerating index with the coke-strength index for fifteen coals, both fresh and at various stages of oxidation. As would be expected, the points are very scattered; but in general, buttons classified as good caking (CG) correspond to coke-strength indices above 75, and buttons classified as poor caking (CP) correspond to a coke-strength index below about 65. There is considerable overlapping of the buttons classified as fair caking (CF).

Table V compares agglomerating index and per cent fusion in the carbonization retort for fifty-five coals, both fresh and at various stages of oxidation. The results are scattered; however, the average per cent fusion decreases from 96.4 for coals in the good-caking classification to 83.8 for fair-caking coals, with the still lower value of 51 for coals classified as poor caking. Thus, a rough correlation exists between these two different tests of the caking tendency.

Table V. Comparison of Agglomerating Index and Per Cent Fusion in Carbonization Retort

Agglomerating index	CG	CF	CP
Number of tests	27	21	7
Range of per cent fusion	53.4–100	34.2–99.8	25.6–89.4
Average per cent fusion	96.4	83.8	51

Conclusions

In conclusion, the work has shown that there is a wide range (more than sixteen fold) in durability of coking power—that is, in the allowable time of storage (under exactly equal condition as to screen size, temperature, etc.) for coal to be used in coke ovens. Durability of coking power can be predicted for most coals from the standard coal analysis ordinarily available before a coal is selected for storage. The effects of storage can be assayed by either the agglutinating-value test or by examination of coke buttons made in the standard volatile-matter determination.

Acknowledgment

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Possible New Uses for Coal

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The low-boiling fractions in the by-products from coal carbonization have been the great source of aromatic compounds for the chemical industry. Recent demands for benzene, toluene, naphthalene, and phenolic compounds and some of their derived products, such as aliphatic and aromatic dicarboxylic acids, lead to consideration of other possible sources of these compounds.

Direct degradation of bituminous coals can furnish good yields of any desired range of molecular sizes of carbo- and heterocyclic structures. Under certain conditions up to 80 per cent of a bituminous coal can be converted to ash-free "bitumens," condensed cyclic structures of molecular weight ranging from a few hundred up to perhaps 1000. Mild oxidation reactions produce the so-called regenerated humic acids, of similar nuclear structure to the bitumens, but with sufficient peripheral polar groups to give them acid properties.

More drastic degradation of bituminous coals leads to simpler molecular types which are, for the most part, distillable. These are predominantly aromatic hydrocarbons, although significant amounts of naphthenes and paraffins are also present. Under certain conditions an appreciable fraction of the oxygen of the coal may appear as phenolic compounds, and of the nitrogen, as organic bases.

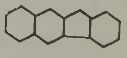
Oxidation at elevated pressures and temperatures results in the production of simple aliphatic acids such as acetic and oxalic, along with aromatic acids of the benzene carboxylic series, from the phthalics to mellitic, and other polycarboxylic acids of more complex nuclei.

Increasing demands of the synthetic chemical industry for aromatic structures may be met by the application of these methods of degradation either directly to bituminous coals or to the complex cyclic structures, the tars and pitches.

OTHER papers in this symposium have dealt with the use of some of the simple degradation products from the carbonization of coal, such as benzene, naphthalene, and phenols, in building up the complex polymeric structures which constitute the synthetic rubbers and the various plastics. In connection with these discussions it is appropriate to consider to what extent coal itself may become a primary material for the chemical industry. Coal is indirectly the raw material for many important synthetic processes—ammonia, methanol, and liquid and solid hydrocarbons through the water gas reaction, and synthetic rubbers and certain plastics through carbide and acetylene. These depend upon conversion of the greater part of the coal by carbonization to the highly condensed carbocyclic structure, coke, followed by reaction of coke to form such simple molecules as carbon monoxide, hydrogen, or acetylene, which in turn are recombined to form the desired more complex forms. Such processes have the enormous advantage of giving good yields of a relatively small number of molecular types, and it may well be that it is along similar indirect paths that the most spectacular advances of the future utilization of coal by the chemical industry will be made. Such processes have, however, so far supplied chiefly either simple linear molecules or their polymers, and coal has remained the great, and until recently, almost exclusive source of cyclic compounds. It appears worth while, therefore, to consider what possibilities may be ahead for products derived from coal by reactions which involve less complete destruction of the original coal structure. To understand what these may be, let us look at coal through the chemist's glasses.

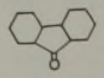
Composition of Coals

Aside from associated inorganic impurities, coals contain carbon, oxygen, hydrogen, nitrogen, and sulfur and, neglecting for the moment the last two which are present usually only in amounts of 1 to 2 per cent, the compositions of all coals fall on a narrow band when plotted on a triangular diagram involving carbon, hydrogen, and oxygen as shown in Figure 1. This band (*14*) includes at one end such compounds as cellulose and lignin and at the other, graphite. The atomic ratios of carbon to hydrogen in the band range from 0.596 for the aliphatic structure, cellulose, to infinity for the completely condensed carbocyclic structure graphite. Lignin, peats, lignite, bituminous coals, and anthracites have values intermediate. Table I lists the carbon:hydrogen ratios of a number of structures from the coal band and various types of hydrocarbons. Comparison shows that only chains of conjugated double-bond or condensed cyclic structures fall in the range of possibilities. Since the former are excluded due to the physical and chemical properties of the coals, there appears to be no doubt that we have to deal with cyclic structures or mixtures of them with aliphatic chains. The presence of oxygen in the coals affects the comparison very little, since a brief consideration of the various forms in which oxygen may occur shows that it does not affect the carbon:hydrogen ratio at all when present as hydroxyl or linear ether structures; that it increases the ratio somewhat when present as cyclic ethers and somewhat more when present in carbonyl groups. Compare, for example, the hydrocarbon



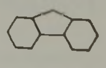
C:H = 1.41

its heterocyclic analog, brazan



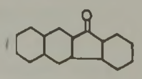
C:H = 1.60

the hydrocarbon, fluorene



C:H = 1.20

and the corresponding carbonyl compound, fluorenone



C:H = 1.62

Naturally the effect depends upon the amount of oxygen present and cannot be great with the amount present in the bituminous coals.

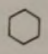
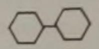
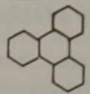
Molecular Structure

Except at temperatures where there is definite evidence for thermal decomposition or where there is strong probability of its occurrence, the coals are not significantly soluble or volatile. The failure to obtain significant amounts of distillable products from coal, even in the molecular still (*8*), at temperatures below which thermal decomposition occurs, sets a probable lower limit to molecular weight of 500 to 1000. Less exact conclusions can be drawn from the failure of coals to dissolve since we know that solubility depends greatly on the type of molecular structure. Very high molecular weights have been ascribed to, and are generally accepted for, the units in solutions of such linear structures as cellulose and rubber, but in the case of large network molecules such as the Glyptal and Bakelite resins, insolubility sets in at relatively low values. Since we have few means of even estimating "molecular weights" in insoluble and nonvolatile structures, we can assume either that such structures have passed suddenly from low to very high molecular weights in passing from soluble to insoluble stages, or that they have intrinsically lower solubilities at the same molecular weight as the linear structures.

The preceding discussion has been based on the assumption of an average composition, and just how heterogeneous coal is from a molecular viewpoint cannot be definitely stated. Obviously "islands" of highly condensed structure such as is exemplified by coronene, combined with considerable amounts of aliphatic chains, will lead to the same average carbon: hydrogen ratios as though the structure were predominantly of a linear condensed type with fewer aliphatic chains present. In either case the structure with which we have to deal is predominantly cyclic and, for the most part, carbocyclic in character.

Coals in their original unmodified form are brittle and have little tensile strength; they are readily attacked by air and oxidizing reagents, and, while thermoplastic at elevated temperatures, the process is not reversible and the product is a porous brittle solid, coke. Thus, the problem for the chemist is to modify or degrade the structure so that it may have useful applications either directly or in combination with other molecular building units.

Table I. Carbon:Hydrogen Ratios

Coal Series	Atomic C:H	Hydrocarbons	Atomic C:H
Cellulose	0.59		
Lignin	0.90	Paraffins	0.25–0.50
Peat	0.96		
Brown coal	1.08	Olefins and naphthenes	0.50
Lignite	1.14	Conjugated double-bond chains	0.66–1.00
Bituminous coals			
Illinois 6	1.27		
Pittsburgh	1.29		1.00–2.00
Pocahontas 3	1.54		
Anthracite	3.2		
Graphite	∞		
			1.20–1.50
			1.50
			3.0

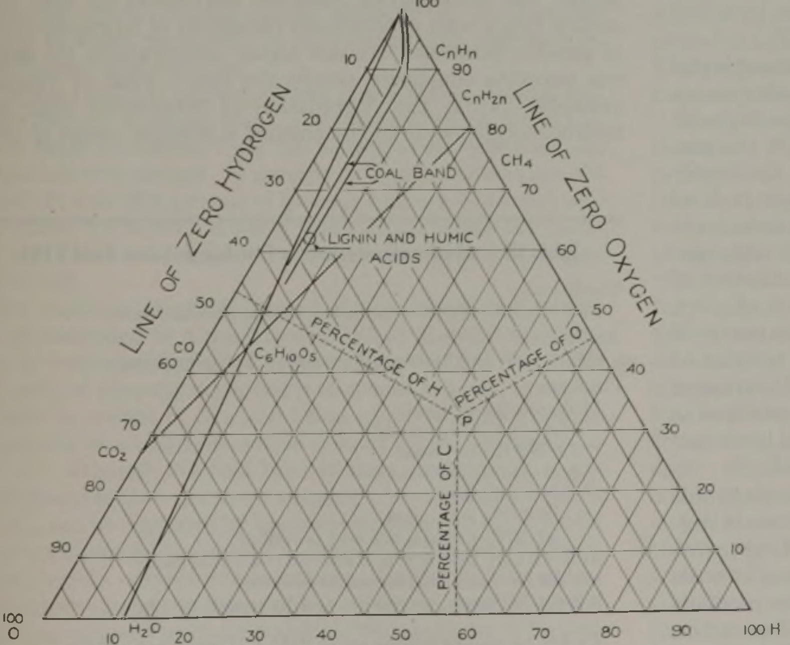


Figure 1. The Coal Band

Methods of Degradation

A cheap and effective means of degrading complex molecules to those of useful size, which has found enormous application in the petroleum industry, is pyrolysis. Unfortunately simple pyrolysis, when applied to coals, leads to only relatively small yields of molecules of small and intermediate sizes, and the greater part of the carbon appears as the completely condensed carbocyclic structure, coke. For, as Brooks (*4*) pointed out, "in the aromatic series, in which the remarkably stable six-carbon ring structure is present, the result of heating is chemical condensation, carbon to carbon combination, to larger and larger molecules and eventually to coke, with the liberation of hydrogen and other simple split products such as methane, ethylene, and so forth".

As would be expected, this undesired series of reactions can be avoided to a certain degree by controlling the conditions of pyrolysis. Increased heating rate leads to increased yield of volatile products, but there are definite limitations to the effects. It has been shown (*21*) that a twenty fold change in heating rate from 1° to 20° C. per minute resulted, in the case of a Pittsburgh seam coal, in a 2–3 per cent increase in yield of liquid products and a corresponding decrease in the yield of coke. The effect of high heating rates obtained by blowing finely divided coal against heated metal or refractory surfaces does not appear to have been investigated.

Other methods of controlling the course of the reaction consist in thermal degradations under such conditions that the reactions which are responsible for the splitting of simple gaseous molecules and consequent condensation of the bulk of the carbon cycles to still more complex structures are hindered either by conducting the decomposition in the presence of a liquid or by the use of high hydrogen pressures.

Table II. Degradation of Pittsburgh Seam Coal by Solvents *(1)*

	Coal	Aniline	Tetralin				Phenol
Temp., ° C.	..	225	250	300	350	400	250, 300
Total ext., % of coal	..	47	33.8	17.0	30.8	3.9	66.7
Compn. of ext., %							
Acids	..	0.07	1.2	0.9	0.6	0.3	0.2
Bases	..	1.3	0.5	0.4	0.6	1.1	0.2
Phenols	..	0.5	0.9	1.0	1.8	2.0	1.0
Neutral							
Ether-sol.[a]	..	2.73	38.2	25.5	31.3	69.2	12.2
Ether-insol.	..	95.40	59.2	72.3	65.7	27.4	86.4
Ratio C:H	1.29	1.48	0.93	0.95	1.02	...	1.31 (250° C.)

[a] By difference.

Degradation by Solvents

When bituminous coal is heated to elevated temperatures in the presence of a liquid phase, the thermal decomposition takes a different course than is the case in a simple pyrolysis. The extent of the decomposition depends both on the temperature and on the nature of the solvent used. Solvents of low internal pressure such as the aliphatic hydrocarbons are least effective and those of high internal pressure, especially the aromatics with polar groups such as phenol and aniline, are very effective (*1*, *11*). The temperatures which can be employed naturally depend upon the stability of the solvent. Phenolic compounds and the higher aromatic hydrocarbons and their partially hydrogenated derivatives are especially useful.

Typical data, showing the action of phenol and of Tetralin on a Pittsburgh seam coal, are given in Table II. The products recovered after removal of the solvent vary from viscous oils through pitches to powdery bitumens of relatively high melting point. They are very low in ash, indicating that they have been molecularly dispersed in the solvent and are not peptized coal particles. That they are the product of a definite degradation of the coal is also proved by their ready solubility in benzene or mixtures of benzene and ethanol. They are almost exclusively neutral in character, as judged by the conventional tests of alkali or acid solubility, and are obviously a mixture of molecules of condensed cyclic nuclei of similar chemical structure but widely varying molecular weight. Fractionation by distillation is not possible, but they respond to the same methods of fractionation by mixed solvents as do linear polymer homologous series (*2*).

The mechanism by which these products are formed is still obscure. When phenol is used, the material balances are always over 100 per cent and it is possible that the degradation is due to cleavage of certain weak linkages in the coal structure by phenolysis or by hydrolysis due to the loosely bound water always present to a certain extent even in dried coal. It obviously requires reaction at only a few linkages to give greatly reduced molecular weights in a high molecular weight system. That the process involves only rupture of weak bonds is also indicated by its temperature coefficient, calculations from which lead to values of activation energy of not more than 10,000 calories (*5*). The high yields obtained with Tetralin undoubtedly involve reaction of hydrogen since a part of the hydrogenated solvent is always recovered as naphthalene. This is also indicated by the much lower carbon:hydrogen ratio of the extracts with this solvent.

No commercial attempt appears to have been made in this country to make use of this method of obtaining primary degradation products from coal. Abroad Potte and Broche (*13*) patented a process involving solvent decomposition of coals by Tetralin and certain tar acid fractions, and the products so obtained have been carbonized to obtain ash-free carbon for aluminum manufacture (*15*), to furnish an ash-free powdered fuel for internal combustion engines (*22*), and to prepare an ash-free raw material for further hydrogenation to motor fuels (*15*). Chemical uses, which would appear to be worth further investigation, are reactions with maleic anhydride, as units in copolymerization reactions, as fillers and plasticizers, and as raw materials for further hydrogenolysis and oxidation reactions. The former would furnish aromatic and hydroaromatic hydrocarbons of any desired range of molecular sizes and the latter, polycarboxylic aromatic acids. While it is true that the extent of molecular degradation obtained by this procedure is more definitely restricted than is the case with reactions involving hydrogenolysis or oxidation, the procedure is simple and operates at lower temperatures and pressures than hydrogenolysis. Impure solvents obtained from by-product carbonization plants appear to be satisfactory and the loss of these, together with some hydrogen, appear to be the only expensive features. That the products of the process are proposed as competitors for coal tar pitches and for the residues from petroleum stills, in the manufacture of ash-free electrodes, indicates that these costs are not high.

Degradation by Hydrogenolysis

The decomposition of coals at elevated temperatures in the presence of high hydrogen pressures has only been used commercially to prepare hydrocarbons of a suitable range of molecular size for use in the internal combustion engine, but it is possible to recover a large fraction of the coal as cyclic compounds of any desired degree of complexity, depending upon the temperature, the hydrogen pressure, and the type of catalyst employed. At 350° C. with a Pittsburgh seam coal, the process results in high yields of condensed cyclic structures, some of which contain oxygen as hydroxyls and which range in complexity from two to seven or more cycles, together with small amounts of gaseous hydrocarbons of the paraffin series (*3*). As the temperature is increased, the average molecular size of the products is reduced until temperatures of around 450° C. are reached. Above this temperature, unless greatly increased hydrogen pressures are employed, the condensation reactions responsible for coke formation begin with concomitant formation of larger amounts of gaseous paraffins. At still higher temperatures the gaseous paraffins constitute nearly the entire yield of volatile products. Thus, the degradation of bituminous coals by hydrogenolysis offers to the chemist a possible means of pre-

Table III. Hydrogenolysis of a Pittsburgh Seam Coal *(19)*

Conditions
  440° C., 200–300 atm. pressure, 2.75 hr. contact time
Reactants
  100 lb. ash- and moisture-free coal + 7.5 lb. hydrogen
Products
  71 lb. oils made up of:
    10.6–12.8 lb. tar acids[a]
    2.1–3.5 lb. tar bases
    55.2–54.6 lb. neutral oils
      6–8% olefins
      67–70% aromatics
      22–27% naphthenes and paraffins
  21.5–29.4 lb. hydrocarbon and carbon oxide gases
  6.4–8.6 lb. insol. carbonaceous material
  3.2–6.4 lb. water, ammonia, and hydrogen sulfide

[a] 7.5% by weight boiling up to 235° C. (composed of 50% xylenols, 30% cresols, and 20% phenol), and 3.7% by weight boiling from 235–300° C.

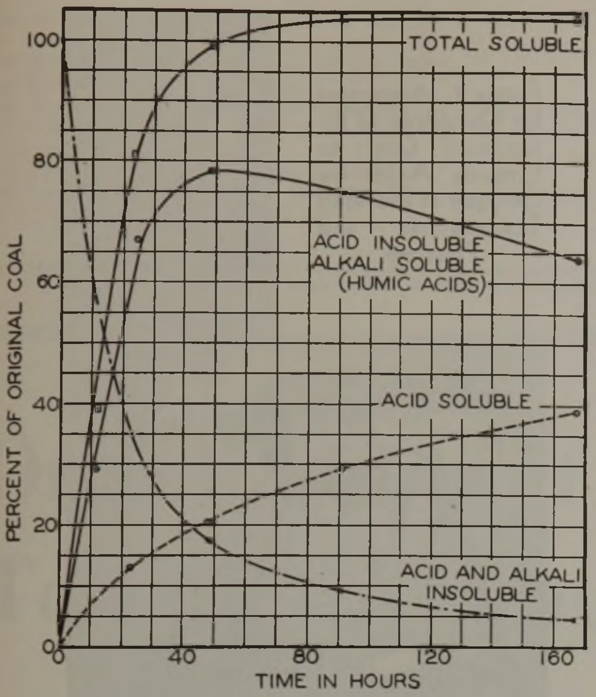


Figure 2. Rates of Formation of Organic Acids from Pittsburgh Coal with 1 *N* Nitric Acid

paring in unlimited amounts many types and sizes of carbocyclic structure. These are chiefly hydrocarbons, but with certain coals a significant fraction of the oxygen in the coal appears as phenolic compounds and, of the nitrogen, as organic bases. The neutral material is predominantly aromatic, but with significant amounts of naphthenes, paraffins, and olefins. The latter have been reported to be cyclic. If the degradation is carried out in the 425–450° C. range, a large fraction of the fragments is sufficiently volatile and stable to permit fractionation by distillation in standard columns. Degradations at 350° C. result in more complex structures which require special methods of fractionation similar to those mentioned in connection with degradations in the presence of solvents.

Typical results of hydrogenolysis of a Pittsburgh seam coal in the Bureau of Mines assay plant are shown in Table III. Under these conditions, from 100 pounds of ash-free coal plus 7.5 pounds of hydrogen, 71 pounds of liquid products are obtained, 21.5 to 29.4 pounds of gaseous hydrocarbons and carbon oxides, 6.4 to 8.6 pounds of insoluble carbonaceous material, and 3.2 to 6.4 pounds of water, ammonia, and hydrogen sulfide (*19*).

The contents of aromatic and hydroaromatic structures can be controlled to a considerable extent through temperature, hydrogen pressure, and type of catalyst employed. The high yield of phenolic materials is of special interest, some 7.5 per cent by weight of this coal being converted into phenolic compounds of a useful molecular weight range, boiling up to 235° C.; although the field has not been investigated, it appears probable that the more complex phenols, boiling above 235° C., can be degraded by hydrogenolysis to simple phenolic compounds plus hydrocarbons. Because of the great interest of the phenolic compounds to industry, further studies of hydrogenolysis of coals to determine the optimum conditions for maximum yields of phenolic materials would appear to be well worth while.

Oxygen balances on the hydrogenolysis of this coal show a large fraction (42.4 to 59.4 per cent) of the oxygen of the coal appearing as water (*18*). Further study would show whether this is a necessary evil or merely a result of the particular operating conditions. The actual amount of oxygen recovered as phenolic compounds, boiling up to 235° C., is 16.1 per cent of that in the coal; thus, if this fraction could be increased to, say, 50 per cent, the weight of phenols in this boiling range would amount to 23 per cent of the weight of the coal employed. It is of interest to note in this connection that high-temperature aqueous alkaline hydrolysis of bituminous coal also yields phenolic compounds (*10*).

The products obtained from coal either by decomposition in solvents or by hydrogenolysis are similar in chemical structure to those obtained in carbonization processes, and the cost of their production would probably be of the same order, so that the question arises as to their economic position. In answer to this it can be stated that coal tars and pitches are only cheaply available near by-product ovens and that, in general, the amounts of aromatic compounds available from carbonization are strictly related to steel production. Even with present high production rates we have had to turn elsewhere for the required amounts of toluene, and benzene has been restricted entirely to chemical and aviation uses. With decreased steel production after the war and increased requirements of benzene and other aromatics for the synthetic chemical industry and for aviation, it appears possible that we may have to develop independent sources for these compounds. There are several possible answers: greatly expanded use of coke for smokeless domestic fuel, direct degradation of coal, or cyclization of petroleum fractions (*20*). Rapid strides have already been made by the petroleum industry in connection with the last.

Degradation by Oxidation

A third possible method by which coal can be converted to compounds of interest to the chemical industry is by controlled oxidation. It has been known for many years that the oxidation of coals at moderate temperatures results in the formation of organic acids (*7*). Just as in the case of the other degradations which have been discussed, the products cover a wide range of molecular sizes, depending upon the conditions of the oxidation. Carbonic acid is always formed and, along with it, varying amounts of acetic, oxalic, and succinic acids, the members of the benzene carboxylic series, from the phthalics to mellitic, and acids of complex cyclic nuclei (*7, 9*). The proportions of each can be controlled to a considerable degree by the oxidation conditions.

Low temperatures and low concentrations of oxidant—for example, 1 *N* nitric acid at 100° C.—result in reaction as shown in Figure 2. Under these conditions approximately 80 per cent by weight of the coal can be recovered as the dark-colored so-called regenerated humic acids. These are acids of complex condensed cyclic nuclei of varying molecular size which owe their acid properties chiefly to the presence of carboxyl groups. They are readily soluble in alkali but reprecipitate on acidification. Ultimate analysis shows a significant fraction of the total oxygen (in some cases 40 per cent) unaccounted for in functional groups, and this is probably in heterocyclics. Decarboxylation leads not to aromatic hydrocarbons, but to black, nonvolatile, insoluble coal-like residues. Similar acids can also be prepared by the action of air or oxygen on bituminous coals at temperatures from room temperature up to the ignition point of the coal (*12*). Acids of this type can obviously be prepared cheaply. No systematic investigation appears to have been made of possible applications, but the ammonium salts have been suggested as fertilizers (*6*). The equivalent weights of these acids range from 200 to 300 so that the ammonium salt would contain as a maximum 7.9 per cent available nitrogen as compared with 21 per cent for ammonium sulfate. Thus, such compounds

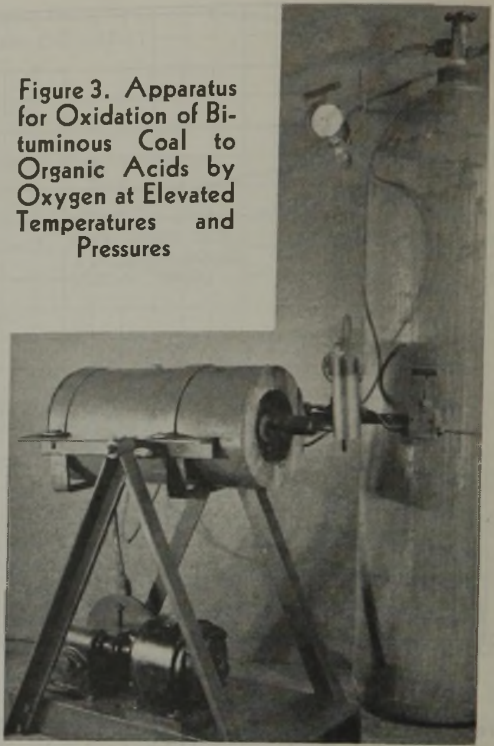


Figure 3. Apparatus for Oxidation of Bituminous Coal to Organic Acids by Oxygen at Elevated Temperatures and Pressures

would be at a disadvantage from the standpoint of shipment, but in view of the wide distribution of coal and the simplicity of the process for the preparation of these acids, this does not appear to be a decisive factor. The strongest argument in favor of the agricultural use of such materials lies in the fact that they would leave desirable organic residues in the soil as contrasted with the undesirable sulfate. Such acids have also been suggested as base-exchange materials, as peptizing agents in clay slip casting, and as desirable fillers in increasing the active area in storage battery plates (*16*).

The soluble acids produced by such an oxidation procedure are made up of varying amounts of acetic, oxalic, and benzenoid acids of differing degrees of complexity. The more complex acids are highly colored and the resulting mixture varies from deep orange to pale yellow, depending upon the extent of the degradation. That these acids are secondary products resulting from the further oxidation of the "humic acids" is indicated by the curves of Figure 2 and also by the fact that with more drastic oxidation procedures no humic acids are recovered and only these soluble types are produced. Their simpler structure is also shown by their solubility in acid as well as alkaline aqueous solutions, and also in such organic solvents as acetone, ether, and alcohol. On decarboxylation they yield simple aromatic hydrocarbons, benzene, and higher homologs, simple phenols and bases, and small amounts of diphenyl and pitches (*9*). These soluble acids can also be prepared by the action of oxygen at elevated temperatures and pressures on aqueous alkaline suspensions of bituminous coals (*17*). The apparatus used is shown in Figure 3 and typical data in Tables IV and V.

Table IV. Pressure Oxidation of Carbonaceous Materials (*17*)

(24 hours at 250° C. in aqueous potassium hydroxide, total pressure 600 pounds per square inch)

	Type of Carbon, %			
	Carbonate	Oxalate	Aromatic	Insol.
Illinois No. 6	58.1	9.3	32.8	..
Pittsburgh	49.7	12.9	36.2	..
High-splint	57.7	8.0	36.5	..
Pocahontas	57.0	4.5	39.1	..
Anthracite	59.3	3.4	37.8	..
500° C. coke	61.3	5.2	33.0	..
700° C. coke	59.8	4.1	21.5	14.5
High-temp. coke (Fairmont)	63.1	2.9	6.7	27.3
Graphite, natural	57.9	1.9	2.3	37.9
Pitch from high-temp. carbonization	44.0	6.4	30.0	19.5

Table V. Properties of Aromatic Acids Formed by Pressure Oxidation of Pittsburgh Seam Coal (*17*)

Yield, per cent	30–40
Composition[a], per cent	
Carbon	51.91
Hydrogen	2.87
Nitrogen	0.45
Sulfur	1.03
Equivalent weight	73.1
Molecular weight	230
Acids isolated	Terephthalic, trimellitic, prehnitic, pentacarboxylic

[a] The trimellitic acid predominated in the mixed acids and the average composition, except, of course, for nitrogen and sulfur, was close to that of a benzene tricarboxylic acid, C, 51.41; H, 2.85; molecular weight, 210; equivalent weight, 70.

Of the mixture of acids produced, oxalic and the members of the simple benzene carboxylic series are of the most immediate interest to the chemical industry. It is possible to isolate the oxalic acid as the sodium salt, from oxidation products of bituminous coal in aqueous alkali, in yields as high as 50 per cent of the coal. Separation and purification of the benzene carboxylic series presents greater difficulties, but it is possible that mixtures of these could be employed in producing Glyptal type resins by reaction with glycols and, after esterification with methanol or butanol, as plasticizers in the various synthetic rubber-like products. Because of their polyfunctional character, satisfactory resins can be made with glycols and even the methyl esters of mixtures of the more complex acids are resinous solids.

No figures on cost of manufacture of organic acids by oxidation of coal are available. The more complex types could probably be made cheaply enough to be considered in connection with fertilizers. The simple types cannot be produced in good yields by atmospheric oxidation and would require oxygen or air at elevated temperatures and pressures, or more expensive types of chemical oxidants such as nitric acid. In producing such soluble types of acids, some 50 per cent of the carbon of the coal appears as carbon dioxide; therefore it is obvious that only cheap oxidants can be considered.

Degradation of Pitches

The methods of degradation which have been discussed as applicable to bituminous coals can also be used to a certain degree with pitches. In some cases, however, in spite of lower molecular weight, the pitches have been found more difficult to react. Whether, in any given case, bituminous coals or pitches are used will no doubt depend upon the special economic factors.

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Organization of a Systematic Test Fence Program

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Many of the details to be considered in planning a test fence exposure program of house paints are discussed. The use of triangular coordinate graphs to select the essential pigment compositions needed to study all practical variations in a single three-component pigment system has been expanded to correlate a large number of systems. The method may be modified to handle as many as five components.

Emphasis is laid on the necessity of complete records and a critical interpretation of results. It is expected that the performance of new paint formulations can be forecast from a continuation of this type of work.

THE exposure testing of exterior paints, such as house paints, has been plant and laboratory routine for many years, and practically everyone connected with the paint industry has had experience with such tests. Exposure tests range in size from comparisons made on a pair of paints to studies involving hundreds of paints.

The literature of house paint technology contains many excellent papers in which the methods and results of exposure testing are discussed. These papers deal with such problems as the effects of the kind of wood being painted (*2, 6, 11, 13, 21, 26*), of variations in the consistency of the paint (*15, 29*), of pigment concentration (*12, 13, 15, 29*), of various thinners (*5, 6, 25*), of various pigmentations and vehicles (*8, 14*), and other variables such as climate and the weathering conditions at the time of exposure (*2, 21, 26*). Other papers have considered such topics as special primers (*6, 21, 27*), the properties of paint systems of two coats (*9, 13, 20, 24*), and many have been written dealing with the special properties of certain specific pigments or pigmentations.

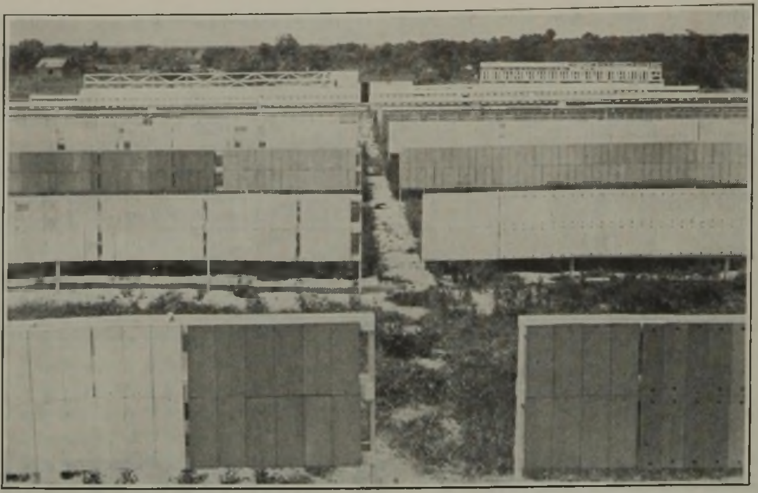
Many of the data concerning the durability of house paints are in the nature of an accumulation of ideas and facts gathered from many separate and unrelated tests. Although useful and valuable, such information does not form a satisfactorily correlated basis for either the formulation of paints to meet specific requirements, or to predict the properties of new and untested formulations. In the fall of 1937 the Eagle-Picher Research Laboratory undertook the job of organizing an exposure study to furnish a body of well-correlated facts.

Many single-pigment paints were made, using as many types of each pigment as were available. These single-pigment tests were preliminary to the systematic study of mixed pigment house paints. Many interesting comparisons were made which were of value in selecting the rather limited number of pigments to receive thorough testing in the mixed pigment part of the testing program.

Exposure Testing Details

In the planning of a comparative study of a small group of paints, the conditions of test and exposure are usually so well defined by the properties of the paints and the purpose for which they were manufactured that many of the possible variables need not be considered. When the object of the test is to obtain basic information on the properties of the individual components that enter into a paint, all the known variables must be considered and, if possible, controlled. The careful control of all details of exposure testing is of particular importance in large studies in which the paint compositions fall into many small and related groups (*1*).

The organization of a test fence program includes the study and planning of the preparation of the paints, their application, and the place and nature of the exposure tests to be made, as well as the selection of the compositions for test. Many of the details involved have been discussed by Ashman (*2*) and others. A few comments on the general methods followed in the preparation of the large panel study described will be in order.



Eagle-Picher Test Fence

Paint preparation was expedited by making up single pigment pastes in oil and mixing these stock pastes in the proper proportions with whatever additional oil was necessary to give the desired pigment vehicle–solids ratio. This ratio is usually abbreviated to PVR. Each single pigment paste was prepared as stiff as could easily be managed on the mill, and the number of passes required was determined by the dispersion of the pigment. The abrasive materials such as the siliceous extenders were dispersed on a laboratory-size stone mill but all other pastes were dispersed on a laboratory-size, three-roller mill.

Only the nonvolatile constituents of the paint were predetermined in this study, with the amount of volatile required being determined by the amount needed to reduce the paint to satisfactory working consistency. Complete viscosity data were recorded and have been found very useful.

It was observed that some paints when made ready for application by the addition of volatile and drier to the paint solids show marked consistency changes in a period of a week or two. These changes are sometimes so large as to make it necessary to add additional thinner before painting at that time. To avoid this difficulty and to maintain as nearly uniform conditions with respect to the age of the paint at the time of use as possible, only fresh stock single-pigment pastes were used, the mixed pastes were not thinned by the addition of turpentine and drier until the day before painting, and the attempt was made to have all paints less than two months old at the time of application.

Paints for the study of tint retention were made by tinting a portion of the white base paint with lampblack in oil. A wet color standard was used, and it was found that some deviation in hue resulted from the effect of the base paint.

The panels were painted in the laboratory under reasonably uniform conditions. The panels were also dried in the laboratory a week between coats and a week more after the last coat before being placed on exposure. The lumber showed a moisture content of 12 to 14 per cent at the time of painting. The painting was done by a well-qualified professional painter.

The film thickness of the applied film has been shown (*9*, *28*, *30*) to have an important bearing on durability. It is satisfactory for the requirements of some tests to make sure that the paint is of the proper consistency for satisfactory brushing and have the paint applied under uniform conditions by a skilled operator, and then to measure the amount of paint applied. It is preferable in most cases, however, to apply a definite amount of the paint to result in a film of the desired thickness. The method of making the necessary calculations has been reported by Browne (*9*).

All the paints of this series were exposed on edge-grained western red cedar boards. These boards were selected after consideration of the fact that this test was primarily intended to study pigment compositions, and hence a kind of wood was desired that would have as little effect as possible on the paint system. These boards were exposed at 45° to the south and vertically facing both north and south. Accelerated weathering panels were also made and tested.

The size of the panels found satisfactory for the different tests are:

	Cm.	*Inches*
Accelerated	7 × 23 × 0.9	$2^3/_4$ × 9 × $^3/_8$
45°	14.3 × 38.1 × 1.9	$5^5/_8$ × 15 × $^3/_4$
Vertical	14.3 × 61 × 1.9	$5^5/_8$ × 24 × $^3/_4$

Panels of 19.4 and 24.4 cm. width ($7^5/_8$ and $9^5/_8$ inches) have also been used, with no particular advantage for the wider boards. To reduce the possibility of erratic results due to differences in boards, duplicate panels were used on all exposures.

The entire surface of all panels was carefully painted, but only the amount of paint on the face of the panel was measured. Although the back and edges of the panels were not given further protection, our experience with this type of rack construction to date is quite satisfactory. The blistering type of failure is almost entirely absent on our fence. Since it has been shown (*18*, *19*) that blistering is in most cases due to moisture that accumulates back of the panel or siding of a house, due to improper structural design or faulty construction, and since special test equipment can be made to give information on blistering (*27*), it was believed that the lack of this type of failure is unimportant.

In a study of pigment combinations it is desirable to keep the vehicle portion constant and to use vehicles known to be satisfactory. The vehicle selected for this study was a mixture of 90 per cent alkali-refined linseed oil to which 10 per cent of a Q-body heat-bodied oil was added. The volatile portion was turpentine. Soluble lead-cobalt naphthenate driers were used at concentrations of 0.3 per cent metallic lead and 0.03 per cent metallic cobalt on the basis of the oil content of the paint. The pigment concentration for each coat of each paint was determined in accordance with a plan to be explained in detail.

An almost infinite number of house paints may be formulated from the four general types of materials: pigments, drying oils, volatile thinners, and driers. Fortunately it is unnecessary to test each possible formulation in order to obtain a clear picture of the paint properties of any particular group of components.

The pigment composition of a base paint may be varied by substituting one or more of the components by either the same weight or volume of some other pigment. If the simple substitution of other pigments does not produce the desired results and it is necessary to investigate the possibilities more thoroughly, it is helpful to the formulator to have some well-defined scheme by which the relations involved in the possible variations may be visualized.

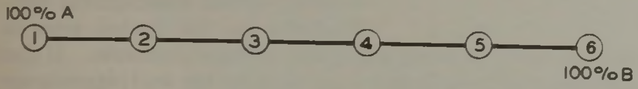
A test program covering the field of mixed pigment paints must be laid out so that all types of pigment compositions will be included. If properly done, the scheme for planning such a program will also be applicable to the evaluation of any possible combination of the pigments by interpolation. The development of such a scheme using graphical methods was attempted.

Advantages of Graphical Methods

Graphical methods have been applied to multicomponent systems in the fields of ceramics and mineralogy for many years. Paint technicians, in general, have been rather slow to utilize them for showing paint compositions, due probably to the large number of components frequently involved. Graphical methods involving triangular coordinates have been used for some time in studying mixtures of solvents and their use in the formulation of lacquers was a logical development (*16*, *17*). Similar graphs have been used in presenting the formulations tested in the exposure study (*3*) and also in showing the relations between large groups of commercial paints (*10*). It is probable that some use has been made of graphical methods by several paint technicians for many years. Reference to three-component pigment mixtures as "ternary mixtures" could imply that graphical methods were actually visualized in this connection as early as 1911 (*23*).

Graphical methods of selecting pigment compositions for test have many advantages when compared with the more frequently used tabular methods. The limitations inherent in the graphical representation of many multicomponent systems may be greatly reduced by certain modifications to be described. In order to approach the subject logically, tabular and graphical methods of representation are compared for two- and three-component systems.

TWO-COMPONENT SYSTEMS. When a systematic study is to be made of the effect of varying the proportions of the components of a two-component system, there is no particular advantage in using graphical methods. However, both graphical and tabular treatments are shown since it is important to understand this simple case before progressing to more complicated formulations. In such a system relatively few mixtures are sufficient to explore the field. As component *A* increases from 0 to 100 per cent, component *B* decreases from 100 to 0 per cent (Figure 1).



TABULAR TREATMENT

FORMULA	%A	%B	TOTAL
1	100	0	100
2	80	20	100
3	60	40	100
4	40	60	100
5	20	80	100
6	0	100	100

FIGURE 1. SYSTEMATIC STUDY OF A TWO-COMPONENT SYSTEM

THREE-COMPONENT SYSTEMS. The graphical method shows to best advantage when the systematic variation of three variables is considered. Figure 2 shows that the base line is identical with the two-component system *AB* of Figure 1, and that two other two-component systems, *AC* and *BC*, have been introduced. Obviously, any point falling within the boundaries will represent a definite formulation and will have a composition determined by the perpendicular distances to the three sides of the triangle. Each corner of the triangle represents a one-component system consisting of 100 per cent *A*, 100 per cent *B*, and 100 per cent *C*, respectively.

It is impossible to construct a table that will show the same data as the graph and maintain the simple relations that are easily apparent in the graph. The data of Figure 2 are shown in Table I.

TABLE I. SYSTEMATIC STUDY OF A THREE-COMPONENT SYSTEM

Compn. No.	% *A*	% *B*	% *C*	Compn. No.	% *A*	% *B*	% *C*
1	100	0	0	12	60	0	40
2	80	20	0	13	40	20	40
3	60	40	0	14	20	40	40
4	40	60	0	15	0	60	40
5	20	80	0	16	40	0	60
6	0	100	0	17	20	20	60
				18	0	40	60
7	80	0	20				
8	60	20	20				
9	40	40	20	19	20	0	80
10	20	60	20	20	0	20	80
11	0	80	20	21	0	0	100

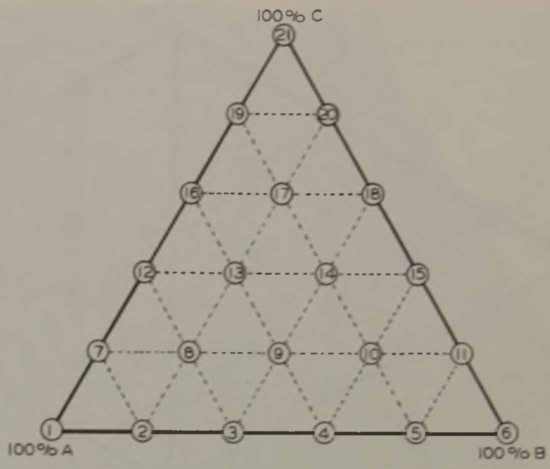


FIGURE 2. SYSTEMATIC STUDY OF A THREE-COMPONENT SYSTEM

TWO RELATED THREE-COMPONENT SYSTEMS. If two three-component systems have two components common to both systems, the two graphs can be united along their common boundary and the points or compositions to be studied in the two systems can readily be compared. This comparison is much simpler than any comparison of tabulated percentage figures. In Figure 3 the system *ABC*, as shown in Figure 2, is compared to the new system *ABD*. A tabular arrangement for the system *ABD* is not given since it involves nothing new.

Two simple patterns for the arrangement of the test compositions are illustrated in the two systems *ABC* and *ABD*. In system *ABC* the points are located in an over-all pattern in which the spacing is uniform in all parts of the diagram and in all directions. In system *ABD* the points are arranged along lines radiating from one of the points, *D* in this case. In *ABD* the components *A* and *B* maintain a constant ratio along each line, and component *D* is added in uniform steps.

As the radiating lines of system *ABD* approach *D*, the points selected come closer together. The graphical presentation shows much better than any tabular arrangement this crowding of points and also shows that the systems could be satisfactorily surveyed by omitting several of the points between 19 and 24.

Both types of patterns are useful. As an example, the over-all pattern would be useful in studying mixtures of sulfate white lead, carbonate white lead, and zinc oxide in which no two components were to be held at a constant ratio. The radiating pattern is used, for example, in studying the effect of the addition of varying quantities of inert to several leaded zinc oxides in which the lead-zinc ratio remains constant for each leaded zinc oxide.

Figure 3 shows that system *ABC* is covered in 20 per cent steps, whereas in system *ABD* component *D* is added in 25 per cent steps. Any desired combination can be used.

To relate this diagram to pigment compositions, substitute zinc oxide for *A*, basic sulfate white lead for *B*, asbestine for *C*, and titanium dioxide for *D*. The indicated points on line *AB* then would represent leaded zinc oxides. The points within the system *ABC* would represent the addition of asbestine to leaded zincs, and points within *ABD* would represent the addition of titanium dioxide. Within the triangle *ABC*, representing the addition of asbestine to leaded zinc oxide, the ratio of basic lead sulfate to zinc oxide will vary for each concentration of asbestine (except for points 9 and 17, which have the same ratio of basic lead

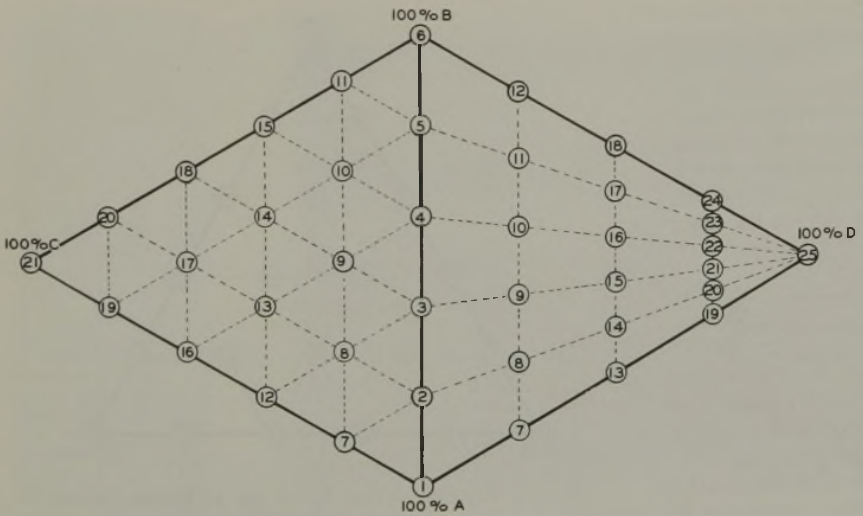


Figure 3. Comparison of Two Related Three-Component Systems

sulfate to zinc oxide). In the triangle ABD the white lead–zinc oxide ratio remains the same as in the six original mixtures shown on line AB, as the concentration of titanium dioxide, D, is increased.

Six Related Three-Component Systems. If in a group of six three-component systems one component is common to all, and if each of the other components is common to two systems, the diagrams may be joined to yield the arrangement shown in Figure 4.

If it is desired to study some combination more extensively than would be possible with the seven different components of Figure 4*A*, the desired component can be repeated on the opposite side of the diagram to give the pattern as shown in *B*. In this diagram, which actually was used in this way, it is evident that the central point of interest was in this case basic sulfate white lead and its combinations with zinc oxide. To these zinc oxide–basic sulfate white lead combinations were added inert, titanium dioxide, basic carbonate white lead, and an experimental pigment as shown in the various systems.

In a set of systems as shown in Figure 4*B*, it is plain that some of the systems will have to be completely covered if a full picture of the possible pigment combinations in the practical range is to be obtained. Other systems need be explored only up to the useful limit of addition of that component. Thus, there is little need to study pigment combinations containing more than 50 per cent inerts or 20 per cent titanium dioxide. A few points in some systems will be satisfactory while many may be required in adjoining systems.

Applications of Diagrams to Selection of Pigment Compositions

Before the graphical method can be applied, it is necessary to decide on the pigment components that are to be used as standard pigments throughout the systematic study and the range of values to be applied to each. It is also necessary to decide upon the size of the steps to be used in varying the components and upon the pattern for their variation.

By standard pigments are meant those pigments used throughout the entire study. At carefully selected compositions these standard pigments may be replaced (one at a time) by other pigments, here termed "alternate" pigments.

The standard pigments used in this study, the ranges studied, and the size of the steps are shown in Table II. A good example of an alternate pigment would be the replacement of the 35 per cent blend of zinc oxide and basic sulfate white lead with a co-fumed 35 per cent leaded zinc oxide.

It is immediately apparent that triangular coordinates will show only three-component systems in detail. Since many practical pigment compositions contain up to six components, it is necessary to consider certain two-pigment combinations (as the leaded zincs or the extended titanium pigments) as single pigments. If that does not provide sufficient simplification, the lead pigments are combined (carbonate and sulfate) with the zinc oxide as a "mixed" leaded zinc Also the total inert portion of the formula can be combined, whether or not the inert is part of an extended titanium pigment or lithopone, or has been added as an inert. By these operations any formula can be reduced to a mixed leaded-zinc-oxide, high-hiding pigment and an inert. Con-

Table II. Pigments Selected as Standard

Pigment	Range of Values, %	Size of Steps
Basic sulfate white lead E-P "Super Sublimed"	0–100	Various, and used in 10, 35, 50, and, 75% leaded ZnO
Zinc oxide, E-P No. 41 AAA lead-free (of acicular type)	0–100	
Inert, asbestine XXX	0–50	15%
High-hiding, "nonchalking" TiO_2	0–20	10%
Basic carbonate white lead, E-P AAA	0–100	Used in a manner analogous to "standard" BSWL
Experimental pigments	0–100	

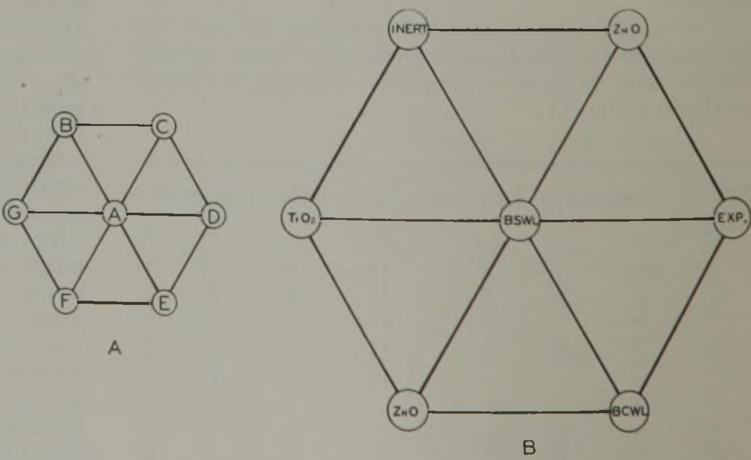


Figure 4. Possible Arrangements of Related Three-Component Systems

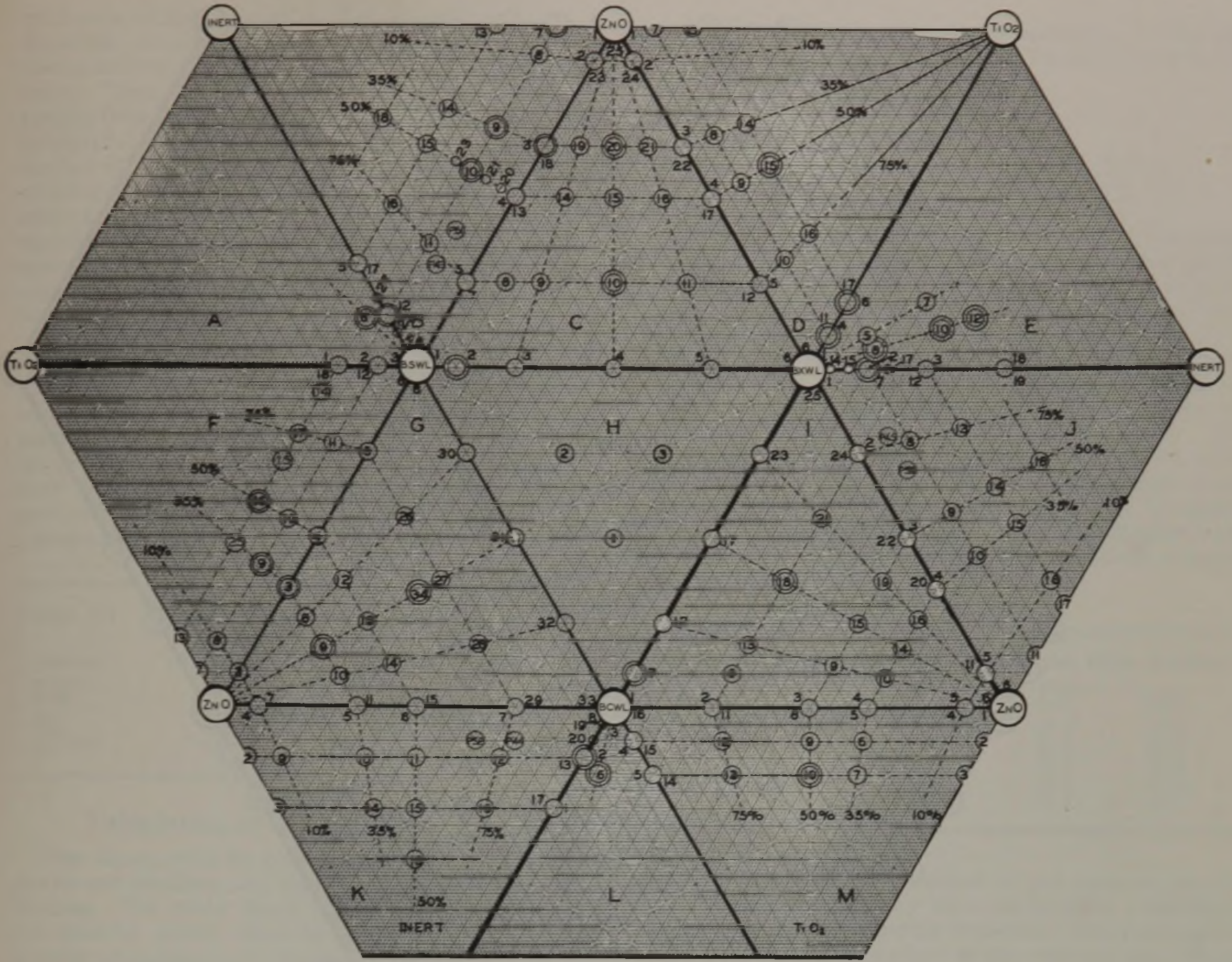


Figure 5. Pigment Compositions on Weight Percentage Basis

clusions drawn from the comparisons made possible by such a procedure are satisfactory in most cases.

Diagram of an Actual Study

Figure 5 shows the thirteen interrelated three-component systems that were studied as a basis for a number of four- and five-component studies. The formulations actually made are shown as circles. The large circles represent single-pigment compositions; the abbreviations are all self-explanatory except BXWL which was used to represent a group of experimental lead pigments. Compositions at which alternate pigments were also tried are represented by double circles. Each system is lettered and each circle is numbered. The letter and number locate the combination whose composition is represented by its position on the diagram. Figure 5 represents a weight basis and Figure 6 gives the same data on a volume basis.

Figure 5 or 6 represents a composite of three hexagonal systems analogous to Figure 4*B*. The central point of interest in each hexagonal system is a white lead—that is, either basic sulfate white lead, basic carbonate white lead, or some member of a group of experimental pigments being studied against the commercial white leads.

Since there are three main points of interest, the diagram contains three complete sets of studies. The four separate systems in each of these studies may be enumerated as follows:

White lead–zinc oxide–inert
White lead–zinc oxide–titanium dioxide
White lead–zinc oxide–second-type white lead
White lead–inert–titanium dioxide

Selection of the type of pattern to be used in locating the compositions to be tested was influenced by the fact that leaded zinc oxides are used in large quantities to furnish the lead and zinc portion of mixed paints. It was therefore logical that the white lead–zinc oxide ratios be kept constant at values including the most commonly used (35 and 50 per cent) commercial leaded zincs. Ratios representing 10, 35, 50, and 75 per cent leaded zinc oxides were used in all systems where both lead and zinc appear, in order to cover the range of values.

The size of the steps to be used in making the variations was determined by several factors which included consideration of the maximum amount of each component that probably would be used in a mixed paint, and the largest step that would permit future interpolation from the data obtained. The goal was to cover thoroughly as much ground as possible with the minimum number of compositions. In case the limits selected are exceeded or the size of our variation step is shown to be too large, it is possible at any time to

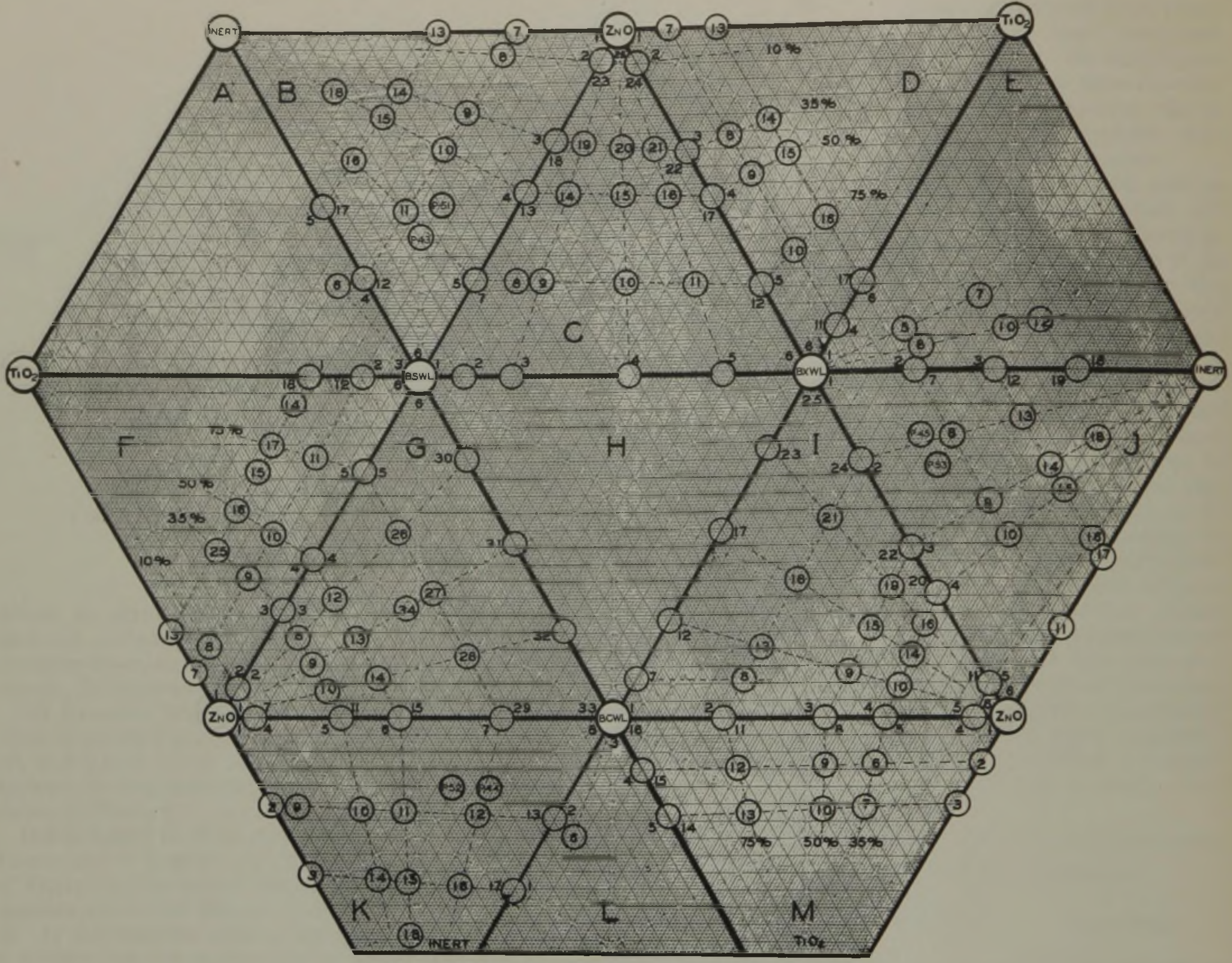


FIGURE 6. PIGMENT COMPOSITIONS ON VOLUME PERCENTAGE BASIS

make additional tests. Such tests will require sufficient control tests to make sure that the new data form one coherent body of facts with the original.

Such a system of ternary diagrams makes possible a large number of actual comparisons. For example, a study of the formulations, composed of 90 per cent of a 50 per cent leaded zinc oxide and 10 per cent of titanium dioxide in which the composition of the white lead is the variable, can be had by comparing the basic sulfate white lead at F-10, the basic carbonate white lead at M-9, and the experimental pigments at D-9. Similar comparisons exist for practically all of the compositions that fall outside of the center ternary diagram, *H*.

Some idea of the amount of work done in one systematic mixed-pigment study may be obtained from the fact that 325 pigment compositions were made and tested in both whites and tints. Since practically all the paint systems of this part of the study were three-coat jobs, 975 paints were actually prepared and tested for weight per gallon, cryptometer hiding power, and viscosity. This study required over 3600 panels.

The actual laboratory handling of a study of this size requires much careful planning if the panels are all to be made ready for exposure within a reasonable period. With four to six men available, this program was placed on the fence in three groups of about 1200 panels each. Each group was exposed after an interval of about 30 days from the previous group; thus only 60 days elapsed from the first to third group-exposure date.

Selection of Pigment-Vehicle-Ratio for Each Coat

Paint applied directly to a new wood surface will lose part of its oil to the wood (*9*). The pigment-oil film left on the surface of the wood will thus have a considerably higher pigment concentration than the paint had originally. Only the nonvolatile portion of the paint is considered, since the volatile part is lost on drying. In order to maintain the proper binder in the first coat of paint, it is customary to add oil so that the binder of the dry film may be high enough for good life (*12*).

The second and third coats are usually thinner with a small amount of additional volatile or are applied "as made". Adding volatile to the paint will give a surface of lower gloss and is therefore generally used for the second or body coat. The top coat is usually applied as manufactured to yield a glossy surface.

The effect of varying the pigment concentration in each coat was first studied with respect to a number of single-pigment paints. As an example, our most extensive study was made on basic sulfate white lead systems. Four paints were made with pigment concentrations ranging from what we considered the lowest to the highest useful value (25, 28, 31, and 34 per cent of nonvolatile by volume). Each paint was successively made the primer while the top coats were varied. Thus, sixty-four systems were actually made, ranging from 25-25-25 to 34-34-34 and including all possible permutations of the four paints taken three at a time. A number of other pigments were tested in several systems covering the practical types. Out of this work considerable information is being obtained on the type of failure to be expected from the various systems. Although many pigments are not used as single pigments in practice, a knowledge of their properties is useful when developing formulations.

This preliminary work extending over several years showed that single-pigment paints of fairly satisfactory working properties could be obtained without excessive reduction with volatile. The pigment concentrations for these single-pigment paints varied with the kind of pigment, but the concentrations were maintained constant at such values that some thinning was desirable for all paints. The values for each coat of a three-coat system selected from the single-pigment studies are shown in Table III.

Table III. PVR Values Assigned to Standard Single-Pigment Paints

Pigment	Primer Coat	Body Coat	Top Coat
BSWL	28	34	31
BCWL	28	34	31
ZnO	18	24	22
TiO_2	25	31	28
Asbestine	25	31	28

Calculation of PVR for Mixed Paints

These figures could be lowered somewhat for the titanium dioxide and asbestine, and the final paints would require less thinning. The actual figure for these two pigments does not, however, greatly affect the results when they are used in minor proportions in mixed-pigment paints.

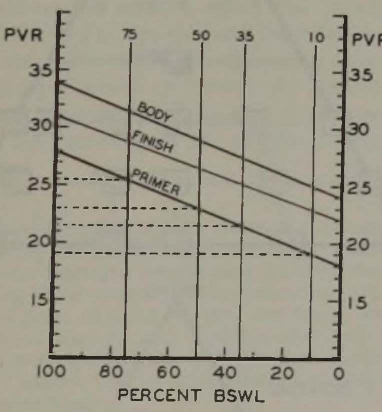


Figure 7. Determination of PVR

In formulating a series of test paints it is necessary to answer the question: If the first coats of basic sulfate white lead and zinc oxide, when used as single-pigment paints, are to be applied at 28 and 18 PVR, respectively, at what PVR should the first coat of a 35 per cent leaded zinc oxide be applied? In other words, how can the PVR of all these compositions be varied in a systematic and uniform manner, so that there will be no sudden breaks or jumps and all tests will be as nearly interrelated as possible?

The answer may be obtained easily by a simple calculation based on the percentage composition of the pigment mixture and PVR values assigned to the components. In the case of the 35 per cent leaded zinc oxide mentioned before, the calculation is as follows:

Component	Compn.		First-Coat PVR		
BSWL	0.35	×	28	=	9.8
ZnO	0.65	×	18	=	11.7
First coat PVR for 35% leaded ZnO					21.5

If the PVR values for several leaded zinc oxides, calculated as shown, are plotted against their composition, they all fall on a straight line connecting the respective values assigned to the first coats of 100 per cent basic sulfate white lead and zinc oxide paints. From this line the corresponding PVR for any mixture of the two may be read directly. Figure 7 shows such a graph for all three coats of all mixtures of zinc oxide and basic sulfate white lead. The PVR values for all the paints of this study were obtained in this way. The three-component systems may require a preliminary operation to determine the PVR values to be used as the limiting values for each group of pigments in the interior of a triangular diagram. Table IV gives the PVR values for all three coats of the series of basic sulfate white lead–zinc oxide mixtures as read from Figure 7.

Table IV. PVR Values as Determined from Figure 7

Compn., %		PVR		
BSWL	ZnO	Primer	Body	Finish
100	0	28.0	34.0	31.0
75	25	25.5	31.5	28.7
50	50	23.0	29.0	26.5
35	65	21.5	27.5	25.0
10	90	19.0	25.0	22.8
0	100	18.0	24.0	22.0

The PVR value to be assigned to any pigment may be determined by preliminary tests studying its consistency characteristics and weathering properties. The values given in this paper were determined in this way and may not be applicable for all purposes. The method of calculating PVR values for mixed paints, as given, may be used regardless of the pigments or the exact values assigned to each component.

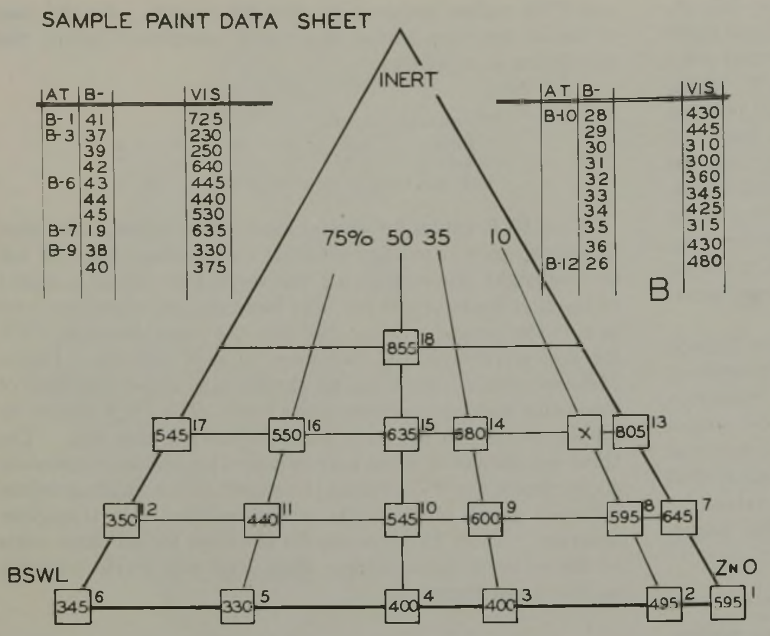
Application of Diagrams to Analysis of Exposure Data

The advantages of organizing a paint study on a graphical rather than tabular basis do not stop with the selection of the pigment compositions for test. By making use of special charts for recording paint and exposure data, it is possible to use the same method throughout the study. As examples, data sheets are shown in Figures 8 and 9.

The A. S. T. M. Stormer viscosities for the unreduced paints of system B, third coats, are shown in Figure 8. This is typical of the paint data records made of the various properties such as weight per gallon, hiding power, Ford cup viscosity, weight and volume percentage thinning required for brushing consistency.

As an example of the reporting of durability data, Figure 9 shows the rating for chalking by the same set of panels after 12 and 17 months. The numerical rating of a perfect panel is 10 and decreases to 0 as failure becomes worse. On some paints the rating for chalking may decrease and later rise again due to the removal of some of the chalk.

When exhibited in this manner it is possible to pick out inconsistent results more easily than if the data were tabulated in the usual form. It is also possible from data arranged in this way to observe trends in behavior as the composition of the pigmentation varies. As an example of how this method of organization operates with a paint formu-



AT	B-	VIS
B-1	41	725
B-3	37	230
	39	250
	42	640
B-6	43	445
	44	440
	45	530
B-7	19	635
B-9	38	330
	40	375

AT	B-	VIS
B-10	28	430
	29	445
	30	310
	31	300
	32	360
	33	345
	34	425
	35	315
	36	430
B-12	26	480

Figure 8. A. S. T. M. Stormer Viscosities for Unreduced Paints of System B, Third Coats

lation whose proportion is not exactly duplicated in the study, the new army cantonment paint, 8000E, whose formulation was published after our study was under way, may be taken: zinc oxide 30 per cent, basic sulfate white lead 15, basic carbonate white lead 15, nonchalking titanium dioxide 14, asbestine 26. This formulation of five components can be reduced to three if the two white leads and the zinc oxide are combined as a 50 per cent mixed-leaded zinc oxide. The formulation then becomes: 50 per cent mixed-leaded zinc oxide 60, nonchalking titanium dioxide 14, asbestine 26.

By comparing this formulation with our 50 per cent leaded zinc, inert, high-hiding system (Figure 10), this composition can be located and is found to lie near to and between the formulations P-16, P-17, and P-18. It is true that the diagram is based on basic sulfate white lead instead of a 50-50 mixture, but little difference could be expected from this cause for two reasons: (*a*) The actual properties of sulfate white lead and carbonate white lead are similar, especially when used in mixed pigment paints; and (*b*) together the two leads represent only 30 per cent, or a minor portion, of the pigment. From the diagram the army cantonment paint would be expected to have a little less hiding than P-18 and a little more than P-17. Its other properties could not be far from the average of the two.

Importance of Records

The selection and calculation of the desired paint formulations, and the preparation and application of the paints, although entailing a large amount of work, represent only the beginning of an exposure program. Complete weathering data on each series of panels involves the inspection of panels at regular intervals for all of the factors which are important in the failure of a paint film. From complete weathering data it should be possible to tell within close limits the time required for the total loss of the initial gloss, the first noticeable appearance of chalking, the appearance of the first checks or cracks, as well as the relative rating of the panels with respect to color (and tint retention), dirt retention, chalking, checking, peeling or scaling, cracking, and blistering. For a large number of panels, the recorded life histories become voluminous.

These life histories, consisting in most cases of numerical ratings on the several types of failure and taken at intervals ranging from a few days to several months, ordinarily do not of themselves afford a categorical answer to the questions: "Which paint is the better?" "Which paint is the longer-lived?" In other words, each paint will have its own peculiar manner of failure, and in some respects it may rate higher than a control formulation while in other respects it rates lower. In addition, a group of panels made from paints of rather similar characteristics will, during their life, frequently show several reversals of order with respect to one or more of the points upon which they are graded. These changes in relative order of rating may occur within short periods and are frequently large.

Different paints will also show marked differences in rate of failure. Some formulations may fail slowly but maintain a constant rate: other paints may fail more rapidly up to a certain state and retain that condition for a long time. Paints fail in many ways, and several schools of thought exist on the question of the relative importance of each type of failure.

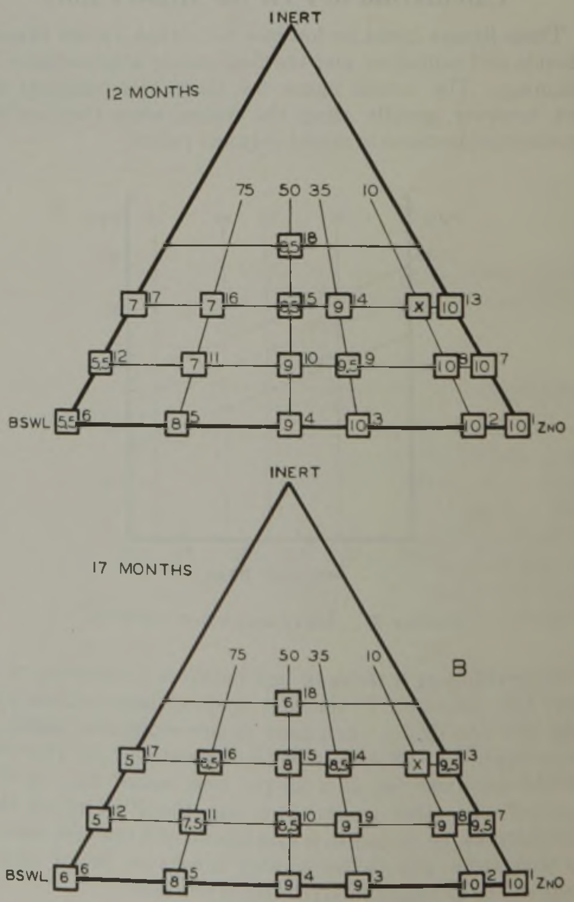


Figure 9. Chalking of a Gray Paint, Exposed Vertically South after 12 and 17 Months

Interpretation of Results

After the paints have been formulated and applied and their life histories have been compiled, the most important part of the exposure work can be started—that is, the analysis and study of the manner and rate of failure of each formulation. Before conclusions can be drawn, the relative importance of the various factors affecting the ultimate failure must be weighed (*2*, *4*, *7*, *8*). The several factors of failure must be weighed in strict accord with all the facts, as they apply to the appearance and protection of the painted surface and the type of failure at the time of repainting, as well as the actual life of the film before repainting is necessary.

A satisfactory paint formulation will yield paint films having long life and good appearance, which may be satisfactorily repainted when it no longer gives protection to the surface. The paint industry is divided into two schools of thought as to the type of formulation that will yield films having the most desirable combination of weathering properties.

Straight white lead and high-lead mixed paints show superficial checking fairly early in life. These checks, however, are barely visible without magnification and will change very little over a period of several years. Paints containing large quantities of inerts seldom check but tend to chalk rapidly. Towards the end of life the film may suddenly be subject to severe erosion and thus offer only a short period for repainting after failure has become noticeable.

Both types of failure may be modified within limits by the proper use of zinc oxide. Formulations of high-quality mixed paints vary with the experience of the formulator and his interpretation of the most suitable compositions for slow chalking, slight checking, and a long period during which repainting is practical without too much film loss from erosion.

It is not the purpose of this paper to go into the merits of each type of paint. Formulations with high inert content are too recent compared to the long time experience with high lead paints to form definite conclusions. One of the major purposes of this comprehensive study is to assemble a mass of data on the subject which will justify a final set of opinions at the end of this test and the repainting to follow.

The analytical study of the life histories is slow and tedious, and is frequently slighted or given only cursory treatment. Several reasons combine to bring this about and since they should affect the planning of the program they are worthy of mention here.

1. Most test-fence studies are exposed to answer a definite question, and only the positive results are given thorough attention, whereas the negative results may be even more important and far-reaching if the reasons for the failures are studied.
2. The complete analysis of the test-fence data is almost entirely statistical, and as such is rather slow and uninteresting to the average paint technician. Statistical methods were used to advantage by Calbeck (*12*) in establishing the desirable range of pigment concentrations.
3. Test-fence studies are frequently started to answer an immediate question, although all concerned know that the panel failure may require several years. When failure has been reached, the question may no longer exist in active form, and the results of the test are never studied. Frequently such studies are simply a waste of time. No exposure test should ever be started unless sufficient personnel exists for its regular inspection and a thorough study of the obtained data. The work leading up to the placing of panels on exposure is only the beginning of the job.

Although the conditions under which paints are formulated and exposed have been rather well standardized, the methods of attacking a large mass of exposure data are still undeveloped. Instead of putting out more and more panels and gathering more and more exposure data, our attention should be focused more on the analysis of the data obtained from a smaller number of more scientifically selected samples.

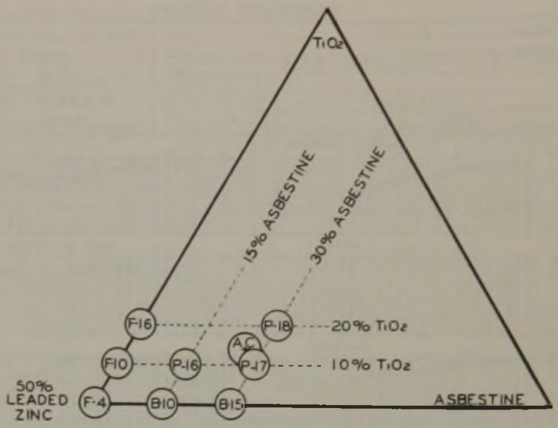


Figure 10. Location of an Army Cantonment Paint Pigment Composition

Results Expressed Graphically

Exposure data are taken and recorded directly on the form adopted by the Federation of Paint and Varnish Production Clubs (*22*). These are excellent for the study of the various properties of one formulation during its entire life. They are not, however, easily handled in making comparisons of a large number of paints and must be used as a source of data which can be tabulated or treated graphically to make the desired comparisons. The exposure data for a group of paints must be considered as having several dimensions. Thus, it is impossible to show the whole story, with respect to all paints for all types of film failure at all the intermediate states of the exposure, on a simple table or graph. Any comparison will represent some section of all this data, and since there are three variables, three types of comparisons exist in each of which one is kept constant:

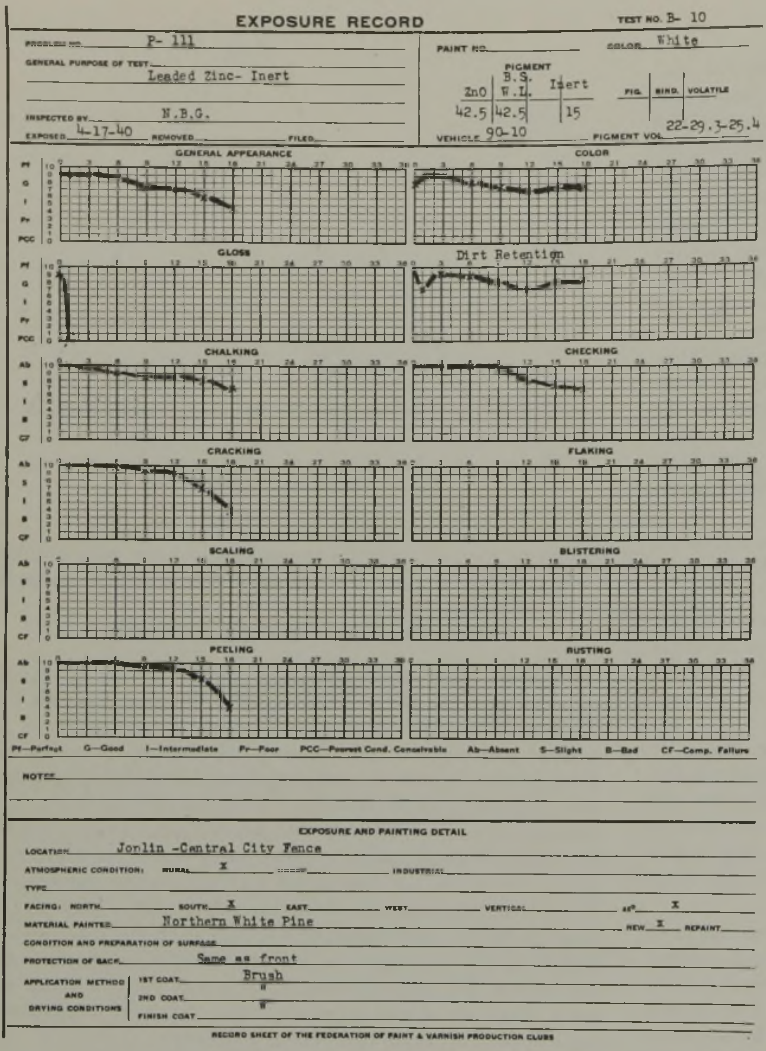
1. The Federation exposure records show the aging of the film by all modes of failure, at all the intermediate times, for one paint. Such a record is shown in Figure 11.
2. For a group of paints, their progressive failure over a period of time may be compared for a single type of failure. Data of this type is shown in Table V for a group of paints with respect to chalking.
3. At one definite period a group of paints may be compared with respect to their ratings for several types of failure. This type of comparison is shown in Table VI for a group of paints with their ratings compared after 12 months.

Table V. Rating for Chalking after Exposure for Various Periods

Time, Months	Chalking for Paint:		
	B-10	B-15	B-18
1	10	10	10
3	9.5	9.5	9.5
6	9	9.5	8
9	8.5	9	8
12	8.5	8.5	6
15	8	8	5.5
18	7	8	5.5

Table VI. Rating for Various Factors after 12-Month Exposure

Paint No.	B-10	B-15	B-18
General appearance	7	4	5.5
Chalking	8.5	8.5	6
Checking	8	6	5.5
Cracking	9	4	6



EXPOSURE RECORD

TEST NO. B- 10

PROBLEM NO. P- 111

GENERAL PURPOSE OF TEST Leaded Zinc- Inert

INSPECTED BY N.B.G.

EXPOSED 4-17-40 REMOVED FILED

PAINT NO.

COLOR White

PIGMENT					
ZnO	B.S. W.L.	Inert	PIG.	BIND.	VOLATILE
42.5	42.5	15			

VEHICLE 90-10

PIGMENT VOL. 22-29.3-25.4

Pf—Perfect G—Good I—Intermediate Pr—Poor PCC—Poorest Cond. Conceivable Ab—Absent S—Slight B—Bad CF—Comp. Failure

NOTES

EXPOSURE AND PAINTING DETAIL

LOCATION Jonlin -Central City Fence

ATMOSPHERIC CONDITION: RURAL X URBAN INDUSTRIAL

TYPE

FACING: NORTH SOUTH X EAST WEST VERTICAL 45° X

MATERIAL PAINTED Northern White Pine NEW X REPAINT

CONDITION AND PREPARATION OF SURFACE

PROTECTION OF BACK Same as front

APPLICATION METHOD AND DRYING CONDITIONS
1ST COAT Brush
2ND COAT "
FINISH COAT "

RECORD SHEET OF THE FEDERATION OF PAINT & VARNISH PRODUCTION CLUBS

Figure 11. Sample of Federation Exposure Record

being conducted cover the entire range of formulations, it soon becomes apparent that each pigment has its proper and improper uses. The fact that each pigment tested is probably showing both to advantage and disadvantage at the same time, but in different formulations or under different conditions, certainly discourages the drawing of hasty conclusions or sweeping generalizations. A biased attitude toward pigments or paint properties, as on many other topics, is largely due to the error of making generalizations that are much too broad for the supporting data.

Until this systematic study was projected, our company, like all other manufacturers interested in paint life, exposed numbers of panels to illustrate points in which they were interested at the time. These panels were not properly correlated nor were the variations in composition made in suitable steps to cover the entire field.

Old pigments are constantly being studied, and new pigments are being developed to meet the changing requirements of the house paint industry. As these new products appear, they must be tested by comparison with the present accepted products they are expected to replace. All the pigment products at present used in house paints fit into the scheme just discussed, and it is probable that any new pigments will also fit. If a new pigment product logically cannot be classified as either of the white lead, zinc oxide, inert, or high-hiding types, some modification of our scheme would be required to enable it to be tested systematically in relation to the pigment systems already tested.

This type of data lends itself nicely to bar chart construction. In Figure 12*A* the separate types of failure are treated separately. If each of the four types of failure is considered as having equal weight, the several ratings may be added and the paints may then be compared by the total height of the bars as shown in Figure 12*B*. Obviously, any agreed-upon weighting other than unity could be applied with the result that the heights of the bars would be altered from those shown in the example.

In each of these three types of comparisons it has been necessary to keep one of the factors constant in order to obtain a two-dimensional layout; thus we must decide whether our studies shall deal with only one paint, one type of failure, or one exposure period. In a few cases it is possible to approach a three-dimensional study by the use of varicolored inks or crayons, but this is not generally useful and may easily become confusing if more than a few lines are drawn on the same graph or chart.

An additional advantage to be obtained by a systematic selection and treatment of test-fence exposures lies in the fact that it creates an unbiased attitude in the minds of the actual operators of the test fence. An open-minded point of view is difficult to keep when only a small group of formulations are being tested in the hope that they will prove a point in which the operator is interested. When the tests

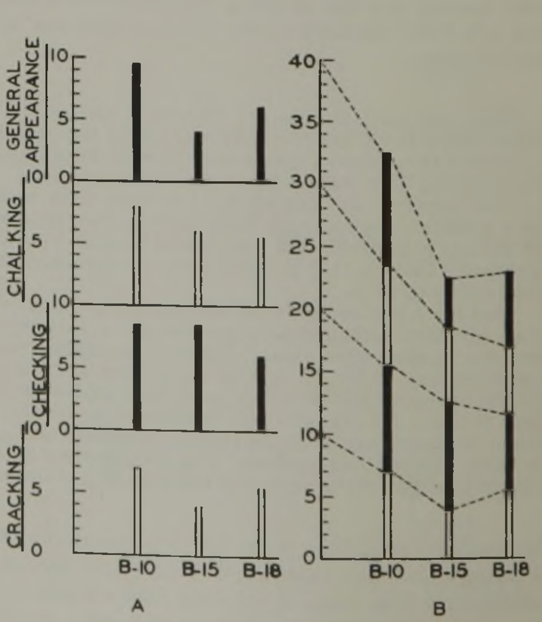


Figure 12. Film Ratings after 12 Months

Tests made at any future time may be linked with the original group of tests by the repetition of the proper formulations as controls. In this way the large exposure study made at the start of this program is not to be considered as separate and distinct from later tests. The use of a definite plan for exposure studies makes it possible to correlate the exposure work over a period of years. Similar schemes can be devised to study systematically the vehicle components of paints. To do so would demand that the components not being studied at that particular time be kept constant.

It is believed that general recognition of the fact that paint compositions for exposure study can be selected according to a systematic plan will benefit the paint industry.

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l-Pimaric Acid Content of Longleaf and Slash Pine Oleoresins

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The oleoresin obtained from slash pine contained 7 to 10 per cent less *l*-pimaric acid than was found in longleaf pine oleoresin. Scrape contained at least as much *l*-pimaric acid as ordinary pine oleoresin. Oleoresin obtained from streaks treated with 10 per cent sulfuric acid did not differ greatly from oleoresin obtained in the normal manner.

Oleoresin from either longleaf (*Pinus palustris*) or slash (*Pinus caribaea*) pine serves as the starting material for the isolation of *l*-pimaric acid and may also be used directly for the production of the addition product of maleic anhydride and *l*-pimaric acid. Therefore, it is desirable to know the *l*-pimaric acid content of the oleoresins obtained from various species of pine and to what extent, if any, the content varies with the season. In the case of longleaf oleoresin, preliminary data indicated a gradual decrease of *l*-pimaric acid with the progress of the season (*1*).

In the present work the *l*-pimaric acid content of the oleoresin obtained from slash and longleaf pine collected during the 1941 season near Olustee, Fla., was determined by the gravimetric method described previously (*1*). The formation of the addition product of *l*-pimaric acid proceeded as well, if not better, from slash oleoresin as from longleaf oleoresin. The results in Table I show that the oleoresin from slash pine contained from 7 to 10 per cent less *l*-pimaric acid than the oleoresin from longleaf pine.

A comparison of the *l*-pimaric acid content of the longleaf oleoresin, collected near Olustee for the 1940 (*1*) and 1941 seasons shows about the same average content. The seasonal variation of the *l*-pimaric acid content was much less in 1941 than in 1940 and did not follow similar trends. For 1940 the highest content of *l*-pimaric acid occurred in April and decreased steadily through the entire season. For 1941 the high point was reached in midseason and was lower at both the start and finish of the season.

The seasonal variation of *l*-pimaric acid content of slash oleoresin was remarkably small; the *l*-pimaric acid content reaches a minimum during midseason instead of a maximum as was found for longleaf oleoresin. These results indicate strongly that the season of the year is not a governing factor in the variation of *l*-pimaric acid content of pine oleoresin.

Samples of both slash and longleaf "scrape" were taken in June and November, 1941, at the same time the oleoresin was collected. (Scrape constitutes a hardened form of the oleoresin obtained by scraping the face of the tree.) Table I gives the surprisingly high results of these determinations. They undoubtedly indicate a somewhat higher *l*-pimaric acid content than is actually present because the *l*-pimaric acid addition product with maleic anhydride isolated from these determinations had melting points of 10–15° C. lower than those obtained with pine oleoresin itself. The impurity pres-

Table I. *l*-Pimaric Acid Present in Resin Acid Fractions of Pine Oleoresin and Scrape

	—% *l*-Pimaric Acid—	
Month of 1941	Longleaf	Slash
Pine Oleoresin		
April	31.2	24.5
	31.3	24.3
June	33.5	23.1
	33.4	23.3
August	33.6	23.7
	33.7	23.3
November	32.1	24.5
	32.5	24.1
Pine Scrape		
June	39.5	32.2
	39.9	32.2
November	38.0	29.4
	38.0	29.7

ent is undoubtedly due to oxidized resin acids not eliminated by the *n*-pentane when the scrape samples were put into solution for analysis.

Considerable work has been done on the stimulation of pine oleoresin flow by treating a newly cut streak on the pine tree with acids (*2*). Inasmuch as the mineral acids used are known to isomerize *l*-pimaric acid rapidly into *l*-abietic acid, determinations of *l*-pimaric acid content of oleoresin obtained in this manner were made to determine to what extent, if any, isomerization has taken place. Analysis of pine oleoresin obtained from streaks treated with 10 per cent sulfuric acid showed the presence of 22.6 per cent *l*-pimaric acid from slash pine and 31.9 per cent from longleaf pine.

These results are in contrast to those of Sandermann (*3*) who found no *l*-pimaric acid in the oleoresin from European *Pinus sylvestris* when the streaks were treated with 25 per cent hydrochloric acid. From untreated streaks of this same specie of pine, 40 to 48 per cent of *l*-pimaric acid was found.

The reason for this difference is not clear, but it seems safe to conclude that as far as the 10 per cent sulfuric acid treatment is concerned, little or no change has been effected on the composition of the oleoresin obtained.

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Fatigue Resistance of Flexible Plastic Sheetings

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In many of the uses to which flexible plastic sheetings are being applied, the fatigue resistance of a sheeting is an important factor in the serviceability of the material. Because of its importance, the study and control of this characteristic were desirable, and for this purpose a flex-fatigue test procedure was developed.

The type of test employed in this laboratory involves simple flexing of a flat or folded sheeting. For some uses the machine is adjusted to provide alternate tension and flexing. At the flexing end of the cycle the test sheeting is bent upon itself rather sharply to a controlled radius at the crease. This feature, the sharp creasing of the sheeting at each cycle, provides a severe test, the severity being controlled by the tightness of creasing. Some of the flexible elastomeric sheetings included in this study possess a high degree of fatigue resistance, and a particularly severe test was required in order that fatigue failures would be obtained within a reasonable period. This test has provided useful information regarding the effects of various factors on the fatigue resistance of certain flexible vinyl resin sheetings.

Method of Test

The fatigue test machine incorporates the essential features of the A. S. T. M. De Mattia flexing machine used on rubber (D430-35T). A stationary head holds one end of the test specimen and a reciprocating head holds the other end. The heads are adjustable for the clearance between them at the closed end of the cycle and for the stroke or total displacement during the cycle. The clearance setting controls the radius of crease during flexing, while the stroke setting controls the degree of stretch imposed.

The standard fatigue test in this laboratory is carried out on a 0.040 × 2.5 × 5 inch sample of press-polished sheeting, folded longitudinally before insertion in the grips. The motion of the reciprocating head bends the folded sample transversely during flexing. The head clearance at the closed end of the cycle is set at 0.090 inch plus the total thickness of sheeting. In the bent position there are four thicknesses of sheeting between the heads so that the clearance $= 0.090 + (4)\ (0.040) = 0.250$ inch. This provides a radius of 0.045 inch at the crease. The stroke is adjusted to draw the specimen taut at the open position but not to apply any stretch. This standard test setup is known as the fold flex at 0.045-inch radius. Tests ordinarily are run at 25° and 0° C.; 0° is particularly useful for accelerated testing. Figures 1, 2, and 3 show the details of the test setup.

The machine tests twenty specimens at a time and operates at 115 cycles per minute. This speed was chosen because much of the early work on the machine was for evaluating flexible sheetings for shoes, and 115 cycles per minute simulates the flexing which occurs when walking at a brisk rate. This relatively low rate of flexing is desirable also because it minimizes the heating of the test piece due to the internal friction of flexing.

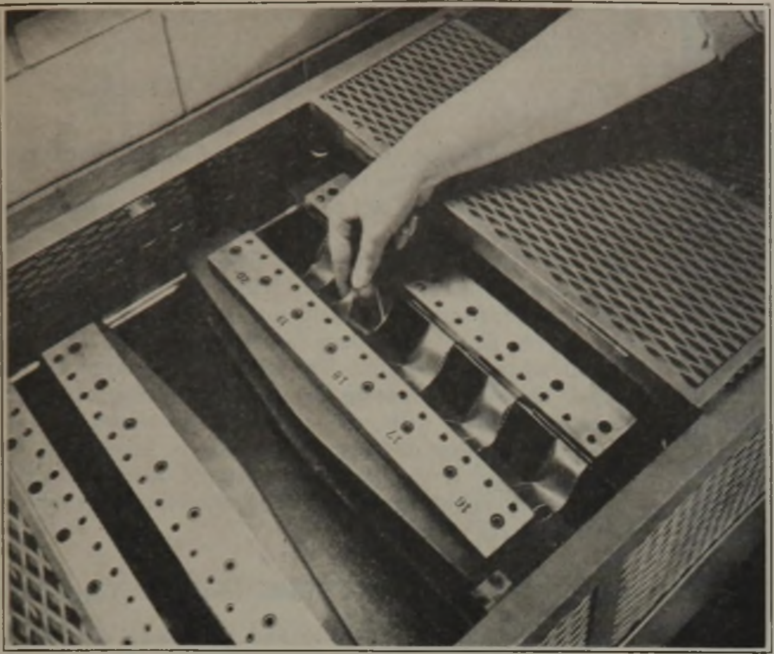


Figure 1. Samples Mounted for Twist-Flex Test

Correlations of laboratory fatigue data with shoe wear tests show that from 5000 to 15,000 cycles in the 25° C. laboratory test approximate one day's wear in shoes. This correlation proved useful in the commercial development of flexible sheetings for use in shoe uppers.

Effect of Physical Factors on Fatigue Values

A number of physical factors (test conditions and machine adjustments) have important influences on the fatigue values obtained for various sheetings. Those factors which are important should either be fixed (as test constants) or specified when the test data are reported. The various factors are discussed below in the approximate order of their importance.

Of the resins used in the tests, S and W were vinyl chloride-acetate type; X was a vinyl butyral resin. The plasticizers employed are designated by the following letters: D, dioctyl phthalate; G, triglycol dioctoate; K, butoxyglycol phthalate; S, dibutyl sebacate.

The fatigue life of flexible vinyl sheetings is shorter at lower temperatures. As the temperature is lowered, the percentage decrease in fatigue life is greatest for those sheetings which stiffen most at low temperature. The extent of decrease in fatigue life, for some of the vinyl resin compounds, is shown in the following table:

Resin	Plasticizer, %	Fatigue Life, Cycles 25° C.	Fatigue Life, Cycles 0° C.
W	D, 35	4,000,000	90,000
S	D, 32	100,000	1,500
X	G, 28	50,000	180

Thus, when compared in equal flexibilities at room temperature, sheeting from resin X has the lowest fatigue life. If these same sheetings are cooled to 0° C., the resin X material will be the stiffest of the three, and as the table shows, its percentage decrease in fatigue life is greatest.

Tightness of Bending. Bending a sheeting more tightly upon itself at the "closed" end of the flexing cycle (thus decreasing the radius at the crease) reduces the fatigue life of the material. The following data on resin W (from Figure 4) illustrate the important effect of changing the radius of bending from 0.020 to 0.085 inch:

Plasticizer D, %	Fold-Flex at 0° C. 0.020-in. radius	0.045-in. radius (standard)	0.085-in. radius
20	30	150	300
25	300	1,300	2,700
30	2,500	11,000	20,000
35	20,000	90,000	170,000

Degree of Stretch. A sheeting which is alternately flexed and stretched will have a lower fatigue life than the same sheeting under flexing only. The decrease in fatigue life is roughly proportional to the degree of stretch imposed, by the following data on Resin W:

Plasticizer D, %	Fold-Flex No stretch (standard)	10% stretch	25% stretch
	At 0° C.		
30	10,000	1,400	200
35	90,000	23,000	6,000
	At 25° C.		
25	80,000	....	12,000
30	550,000	....	150,000

As Figure 5 shows, the percentage decrease in fatigue life with stretching is greatest in the case of the stiff sheetings (low plasticizer concentrations).

Flexing of Flat or Folded Sheetings. If a 0.045-inch or greater radius at the bend is maintained, the manner of mounting samples of sheeting in the machine apparently does not affect fatigue results. The following variations were investigated: simple flexing of flat sheeting (flat-flex), transverse flexing of sheeting folded longitudinally (fold-flex), and transverse flexing of sheeting folded and twisted longitudinally. In this series of tests the machine settings were adjusted to provide 0.045-inch radius at the bend, and practically identical fatigue values were obtained with all three mountings.

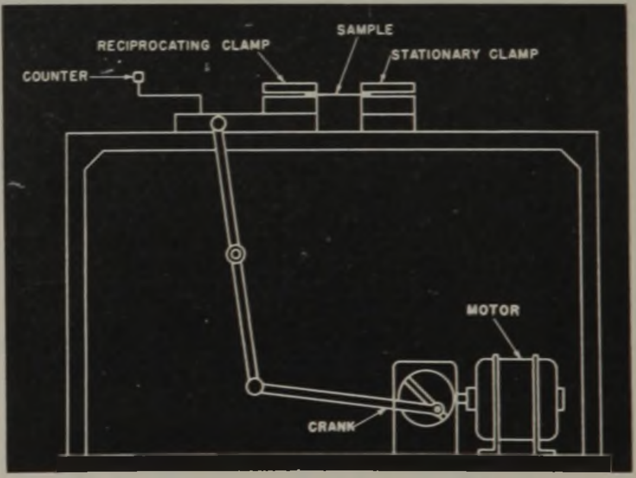


Figure 2. Fatigue Test Machine

However, when the radius at the bend was reduced to 0.020 inch, the folded sheetings were found to have shorter fatigue life than that of the samples flexed flat. These relations follow as determined at 0° C. on resin W:

Plasticizer D, %	Fatigue Cycles at 0° C. 0.020-in. radius at bend Folded	Flat	Standard value at 0.045-in. radius
20	30	75	150
25	300	800	1,300
30	2,500	9,000	11,000

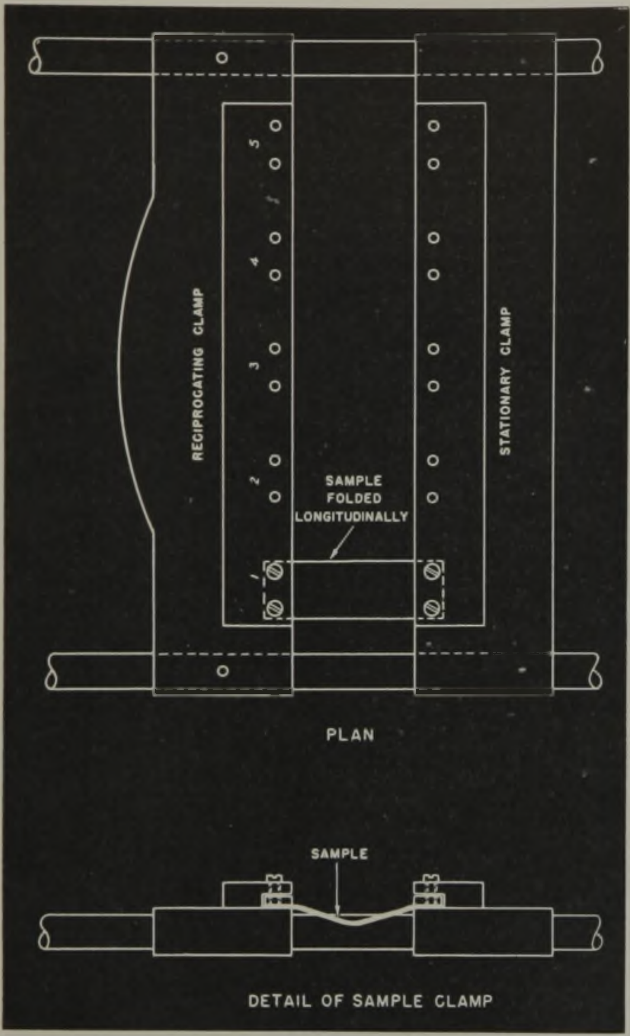


FIGURE 3. MOUNTING OF SAMPLES FOR STANDARD FOLD-FLEX TEST

At 25° C. the same trend in relations was obtained. Reducing the radius at the bend from 0.045 to 0.020 inch reduced the fatigue life of the flat samples slightly and reduced the life of the folded samples considerably.

SHEETING SURFACE. Sharp irregularities in the surface of a flexible sheeting reduce the fatigue life of the material. This is illustrated by the following data on sheeting prepared from resin W with 35 per cent plasticizer D, compared in the press-polished and matte-finished forms:

	Fatigue Life at 25° C.	
Surface	Unstretched	25% stretch
Press-polished	4,000,000	1,500,000
Matte-finished	1,700,000	500,000

Thus, perfection of surface is a factor even when no stretching is applied, and flexible sheetings fall in line with fatigue trends on rigid materials in this respect.

It should be pointed out that the data in this report were obtained on sheetings which had been annealed under pressure and fairly high temperature (150° C.) and thus contained very little residual strain. However, it is possible, by improper adjustment of calendering or forming conditions, to produce flexible sheetings which contain an excessive amount of residual strain. The effect of such strain on the fatigue life of the sheeting has not been investigated, but from correlations with other physical properties, an appreciable reduction in fatigue life would be expected. For that reason the levels of fatigue resistance described in this report should not be expected unless the sheetings are properly fabricated.

Effect of Compound Formulation on Fatigue Life

By combining various resins and plasticizers in suitable proportions, it is possible to prepare a large number of flexible plastic sheetings which are alike in flexibility and outward appearance. However, these various combinations may differ greatly in fatigue life. The following discussion brings out the effects of various components on the fatigue life of a compound.

TYPE OF RESIN. Of the various vinyl resins studied, resin W had the greatest resistance to fatigue, as shown in the first table which compared different resin types in compounds which had been adjusted to the same flexibility at room temperature.

The fatigue life of the various compounds appears to be a function of their elasticity or rate of elastic recovery from strain. It was noticed that fatigue failures most often occurred on the inside of the bend, as if a compound which

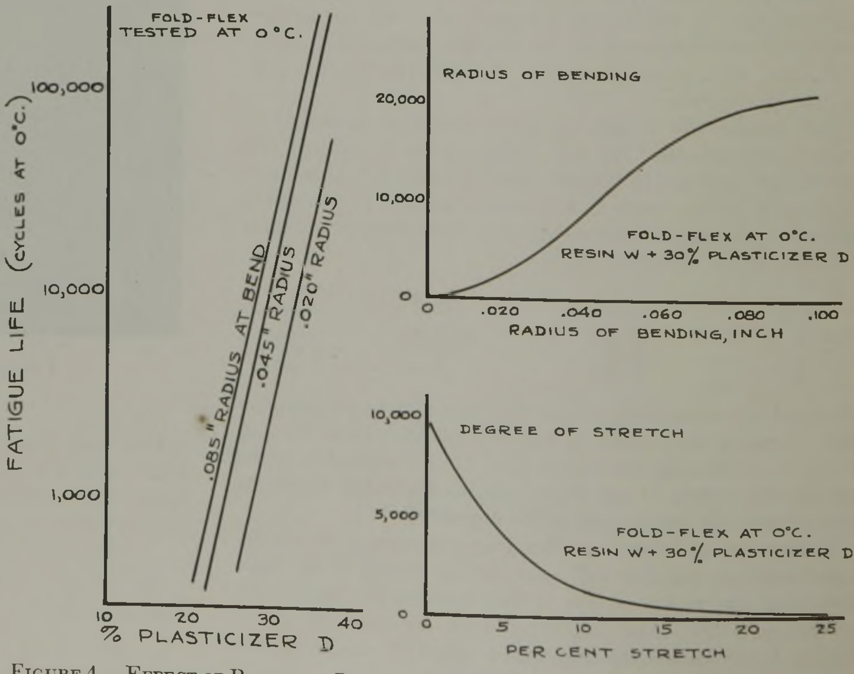


FIGURE 4. EFFECT OF RADIUS AT BEND ON FATIGUE LIFE OF SHEETINGS FROM RESIN W

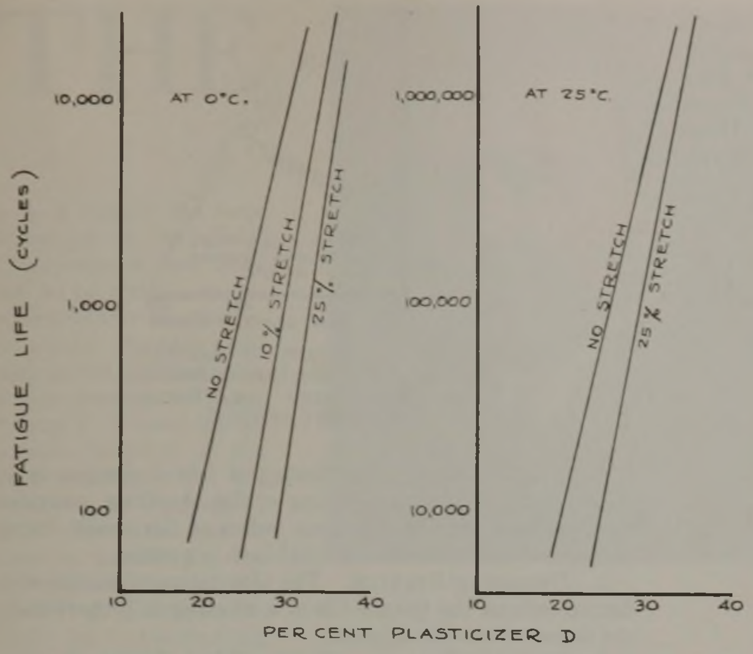


Figure 5. Effect of Stretching on Fatigue Life of Sheetings from Resin W

was slow to recover from bending stress would be torn by tensile stress as the flexing cycle progressed.

Concentration and Type of Plasticizer. In a series of flexible sheetings prepared from a given base resin, the fatigue life increases rapidly with increase in plasticizer concentration. Figure 6, with log of fatigue life plotted against plasticizer concentration, shows this trend. The following typical data, on effect of plasticizer concentration on fatigue life (of resin W), were taken from Figure 6 (left):

Plasticizer D, %	Fatigue Life 25° C.	Fatigue Life 0° C.
20	10,000	.....
25	70,000	1,200
30	500,000	10,000
35	4,000,000	90,000
40	......	800,000

If different plasticizers are compared at concentrations which provide equal flexibilities, the type of plasticizer has no appreciable effect on fatigue life. This comparison was made on commonly used plasticizers which are readily compatible in the resin. Typical data (taken from the right-hand graph of Figure 6 and other sources) are shown in the following table on resin W:

Plasticizer, %	Fatigue Life 25° C.	Fatigue Life 0° C.
D, 35	4,000,000	90,000
K, 33	4,000,000	60,000
S, 29	4,000,000	150,000

The three sheetings have equal flexibilities and equal fatigue strengths at room temperature (25° C.). There is a difference in fatigue life at the lower temperature, but this may be explained by the fact that the three sheetings do not have equal flexibility at 0° C. The different plasticizers impart different low-temperature stiffening characteristics. The sheeting containing plasticizer S remains most flexible, and that containing plasticizer K, least flexible of the three at 0° C. As the table shows, fatigue life at 0° C. parallels these flexibility differences.

Fillers. The effect of fillers on fatigue life depends on the type of base resin used in the compound. In vinyl chloride–vinyl acetate copolymers (resins W, S, etc.), fillers reduce the fatigue life of the sheeting to an extent depending on the proportion of filler present. In polyvinyl butyral resin (resin X), certain fillers appear to have reinforcing action.

The degrading effect of fillers in copolymer vinyl chloride-acetate resins is shown by the following data (from Figure 7) on different fillers. All the compounds were plasticized to equal flexibility at room temperature:

Resin	Filler, %	Fatigue Life 25° C.	Fatigue Life 0° C.
W	None	4,000,000	90,000
W	Calcene, 40	50,000	12,000
W	York Whiting, 40	170,000	15,000
W	Raven Black, 40	.....	23,000
S	None	100,000	2,000
S	Calcene, 40	.....	400

The reinforcing action of certain fillers in polyvinyl butyral resin (X) is still under investigation, but the following data (from Figure 8) illustrate the trend:

% Calcene	Fatigue Life at 0° C.
None	180
20	280
40	450

Coloring Agents. Limited data on plastic compounds containing coloring agents show that these materials, in the

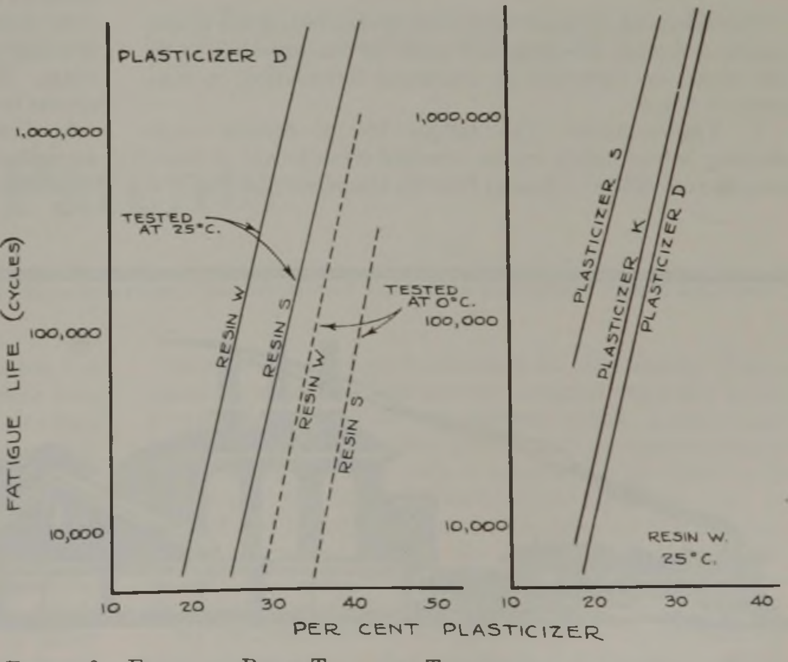


Figure 6. Effect of Resin Type and Temperature and of Plasticizer Type and Concentration on Fatigue Life at 0.045-Inch Radius of Bend

concentrations normally used, have no appreciable effect on the fatigue life of the compound. Among the coloring agents checked and found essentially neutral in effect were the following: 1 per cent Excello 2X Black, 1 Genoa Toner X-1180, 1 Blue Toner B-3, 1 Opaline Green G-1, 2 c. p. Deep Orange A-4337, 2 Cadmium Red 4333, 2 Titanox A, 2 Osaka Yellow Lake X-1630, and 1 per cent Hoover Brown 7764.

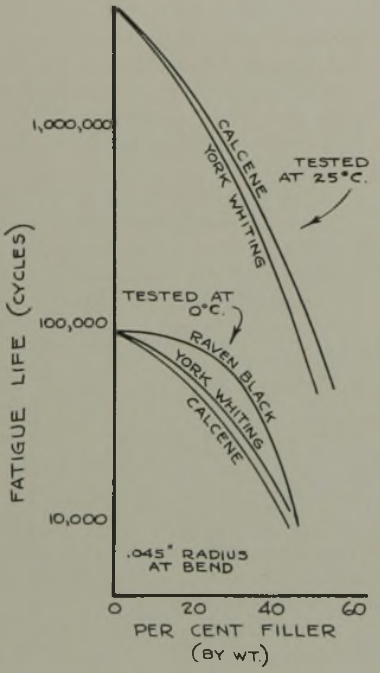


Figure 7. Effect of Filler and Temperature on Fatigue Life of Sheetings from Resin W, Plasticized to Equal Flexibility at 25° C.

Conclusions

The effects of physical test factors on the fatigue life of the resulting flexible sheetings are given in conclusions 1 to 4; the effects on variations in compound formulation, in conclusions 5 to 9.

1. Temperature. The fatigue life of flexible vinyl sheeting is from thirty to two hundred times longer at room temperature (25° C.) than at freezing temperature (0° C.).

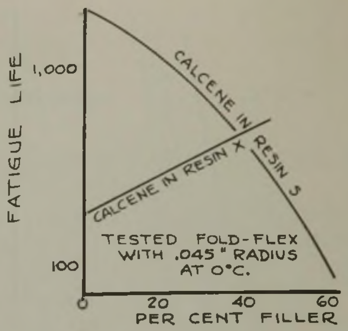


Figure 8. Effect of Calcene Filler on Fatigue Life of Sheetings, Plasticized to Equal Flexibility at 25° C.

2. Type of Fold. The flexing of folded samples is no more severe than simple flexing of flat sheetings, provided they are both bent to the same radius at the crease during flexing and that this radius is 0.045 inch or greater.

3. Degree of Stretch. The alternating of tension with flexing reduces the fatigue life of a sheeting in proportion to the degree of stretch imposed.

4. Sheeting Surface. Press-polished sheeting has two or three times the fatigue life of sheeting with a matte finish (sharp irregularities in the surface).

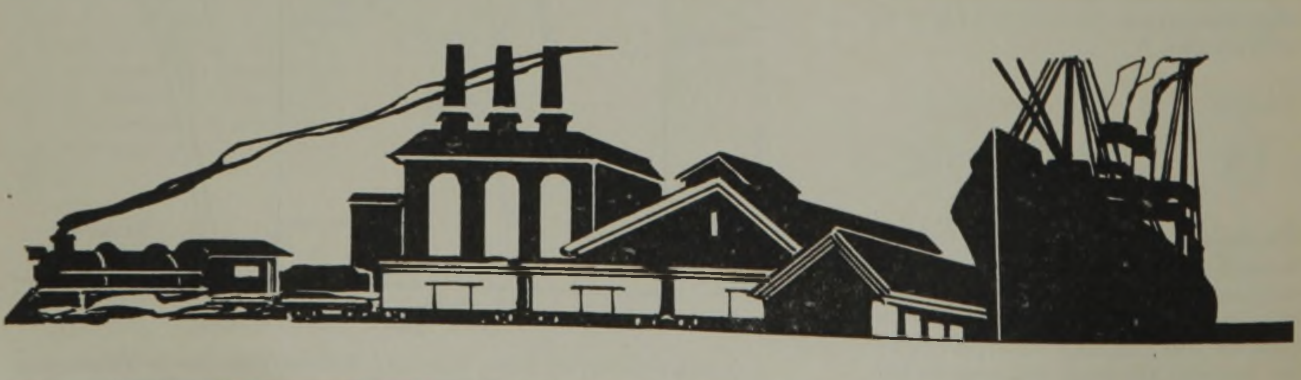
5. Type of Resin used in a sheeting is an important determinant of its fatigue life. Of the vinyl resins studied, W (a high-molecular-weight copolymer of vinyl chloride and vinyl acetate) provided sheetings with the greatest resistance to fatigue.

6. Concentration of Plasticizer. In a series of flexible vinyl sheetings prepared from a given base resin, the fatigue life increases rapidly with increase in plasticizer concentration. A compound containing 40 per cent plasticizer will have from two to twenty thousand times the fatigue life of a compound containing 20 per cent plasticizer.

7. Type of Plasticizer. If we consider only those plasticizers which are readily compatible with the resins involved, and if we make comparisons on compounds of equal flexibility, the type of plasticizer used in a sheeting has little effect on fatigue life.

8. Fillers greatly reduce the fatigue life of flexible sheetings prepared from copolymer vinyl chloride-acetate resins. However, sheetings prepared from polyvinyl butyral appear to be reinforced by the inclusion of certain fillers.

9. Coloring Agents, in the 1 or 2 per cent concentrations normally used, have no appreciable effect on the fatigue life of flexible plastic sheetings.



THE PERKIN MEDAL


Robert E. Wilson

▸ ▸ ▸ One of the large ballrooms of the Hotel Commodore in New York had to be secured to accommodate nearly five hundred chemists and their guests, gathered at a dinner meeting to honor Robert E. Wilson, thirty-seventh recipient of the Perkin Medal, on the evening of January 8, 1943. The medal may be awarded annually by the American Section of the Society of Chemical Industry for outstanding work in applied chemistry. Wilson, now president of the Pan American Petroleum and Transport Company, is honored for his research studies on such varied subjects as flow of fluids, oiliness, corrosion, motor fuel volatility, plasticity, and humidity, and for his industrial contributions in the use of tetraethyllead, petroleum hydrocarbon cracking, and adaptation of chemical engineering principles to the oil industry.

Foster D. Snell presided over the meeting immediately following the dinner, and introduced the speakers. Thomas Midgley, Chairman of the Board of Directors and President-Elect of the AMERICAN CHEMICAL SOCIETY, told with evident relish of the personal and human side of the medalist, a friend of long years' standing. Walter G. Whitman, of the Chemical Branch, War Production Board, paid tribute to the importance of Robert Wilson's work in both science and war service. Marston T. Bogert added several interesting anecdotes about the medalist before actually presenting him with the medal. The address then made by Wilson is given below.

The Perkin Medal was founded in 1906 in commemoration of the fiftieth anniversary of the coal-tar color industry, the first medal being awarded to Sir William H. Perkin, discoverer of aniline dyes. The award may be made to any chemist residing in the United States of America for work which he has done at any time during his career, whether this work proved successful at the time of execution or publication, or whether it became valuable in subsequent development of the industry. The medalist is chosen by a committee representing the Society of Chemical Industry, the AMERICAN CHEMICAL SOCIETY, the Electrochemical Society, the American Institute of Chemical Engineers, and the Société de Chimie Industrielle.

The list of medalists from the date of founding to the present is as follows:

1906	Sir William H. Perkin
1908	J. B. F. Herreshoff
1909	Arno Behr
1910	E. G. Acheson
1911	Charles M. Hall
1912	Herman Frasch
1913	James Gayley
1914	John W. Hyatt
1915	Edward Weston
1916	Leo H. Baekeland
1917	Ernst Twitchell
1918	Auguste J. Rossi
1919	F. G. Cottrell
1920	Charles F. Chandler
1921	Willis R. Whitney
1922	William M. Burton
1923	Milton C. Whitaker
1924	Frederick M. Becket
1925	Hugh K. Moore
1926	R. B. Moore
1927	John E. Teeple
1928	Irving Langmuir
1929	E. C. Sullivan
1930	Herbert H. Dow
1931	Arthur D. Little
1932	Charles F. Burgess
1933	George Oenslager
1934	Colin G. Fink
1935	George O. Curme, Jr.
1936	Warren K. Lewis
1937	Thomas Midgley, Jr.
1938	Frank J. Tone
1939	Walter S. Landis
1940	Charles M. A. Stine
1941	John V. N. Dorr
1942	Martin H. Ittner
1943	Robert E. Wilson

(For list of achievements of each medalist up to 1934, see IND. ENG. CHEM., February, 1933, page 229.)

Research and Patents

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THE time-honored custom of most Perkin medalists has been to discuss either the broad outlines of their own scientific work or the details of some recent developments with which they have been particularly concerned. To depart from that custom of my predecessors demands some explanation. First is my enforced separation from frequent direct contact with research activities; second, only three years ago, before much the same audience, I covered the field in which I had been most recently active—namely, the chemical utilization of cracked refinery gases; third, secrecy orders now ban detailed public discussion of many of the more interesting recent technical developments in my own industry.

However, no apology is necessary for devoting my time to discussing a matter which gravely threatens the whole future of industrial research and our national welfare. I refer to the recent widespread and unfair attacks upon our patent system. Unless we, as scientists, help to educate the lay public as to the facts of the situation, ill-considered legislation may be adopted which would prevent the prompt and free exchange of new information, destroy the market of the independent inventor, and discourage the continuance of American industrial research of which we are so justly proud.

My own experience in the field of patents has afforded unusual opportunity to view the practical workings of our patent system from all aspects. Briefly, this includes four years as an independent inventor, with numerous patents sold or licensed; two years as an inventor in government service; seven years as a so-called "kept inventor", directing research for a large oil company; and six years as the head of the development and patent department of that company. For the past eight years I have been directing the activities of an oil company of moderate size, which has been on the royalty-paying and not the royalty-collecting side of the fence. Our policy in developing and expanding our refinery has always been to install the best processes in sight, whether or not this necessitated royalty payments which, in our experience, comprise only a small part of the prospective savings. My recent service as a director of a corporation taken over by the Alien Property Custodian has also brought me in contact with many of the problems involved in handling foreign-owned patents. In view of this background, I believe I can justly claim the right to discuss the practical workings of our patent system.

Critics of our patent system generally say that they recognize the necessity of giving some reward to inventors, although they are vague as to the form which that reward should take, and they usually object to giving him even a limited monopoly on what he discovers. The alternative of trying to determine the fair cash value of an invention is, however, about the most impossible task a government could undertake; it involves, first, appraising the degree of novelty and value of the inventor's contribution before one knows what other inventors may have been doing in the same field, and, second, appraising industrial trends many years in advance and deciding whether or not, and how soon, some other and better invention will supersede the one in question. Such a task would give pause to a combination of judge, seer, and prophet—and such a man would be too wise to undertake the job.

Thomas Jefferson Recommended and Helped Administer the First Patent Law, as Provided in the Constitution

Whoever first conceived the notion of granting an inventor a limited monopoly in return for public disclosure of his invention had a brilliant idea, because it takes advantage of the fact that every inventor tends to overvalue his own invention; and no reasonable cash sum would encourage him as much as the thought of being able to control his own invention for a period of seventeen years. Furthermore, it is difficult to think of a fairer method of reward, because its magnitude is largely dependent on how important his invention turns out to be and on his intelligence in handling his patent. If he tries to charge too much, his invention will be little used and competitive research will be stimulated. In any case the public, at very small average cost, gets three advantages: prompt knowledge of the invention to add to the scientific background on which further research can be based, reasonable assurance that the worth-while inventions will be commercialized, and free use of the invention after the patent expires.

MISUNDERSTANDING OF THE PATENT MONOPOLY

▶ **Prevalence of Misrepresentations.** In my opinion the greatest danger to our patent system lies in the lack of clear understanding of the nature of the patent monopoly and the compelling reasons for granting one to the discoverer of a really new product or process. Some of this misunderstanding arises naturally out of the complexity of the situation, but much of it is due to a studied misrepresentation of the essential facts by a small group who have apparently undertaken to destroy or nullify our patent system. One of their outstanding methods of confusing the public has been the old-fashioned one of name calling. Thus the right to the exclusive use of one's own invention for a limited period as provided for in our constitution and enacted into law on the recommendation of that great antimonopolist, Thomas Jefferson, is supposed to be damned by calling it a "monopoly". The public traditionally dislikes a monopoly, regarding it as something carved out of the public domain and acquired by an individual. A patent right, however, covers something discovered or created by the individual and is a natural monopoly as long as he can keep it secret. The patent law simply offers him a legally protected monopoly, limited in time, in return for prompt disclosure, so that the information is immediately, and all rights are eventually, *added to* the public domain. As another example, a mere exchange of free cross-licenses and technical information between a group of companies engaged in research in a given field is condemned as a "patent pool" or a "monopoly of monopolies". Even the magazine *Fortune*, evidently under the spell of recent Washington releases, went so far in a recent issue as to picture a patent pool as a jail with laboratory research workers as the prisoners in striped suits and armed guards shooting escaping prisoners.

If an American company, in order to get the right to manufacture under an important patent, granted by our Government to a foreign owner, had to agree to confine its operations under the patent to the United States, it is charged with participating in a cartel; and if war develops ten years later, the company is publicly accused of having conspired with our present enemy to deprive our present allies of needed products. A small inventor is publicly accused before the Senate Patent Committee of blocking the manufacture of an essential item in airplane equipment by refusing to grant licenses, whereas it shortly developed that the device was not essential but merely one of several alternative devices, and that the only reason he had not been able to supply his entire demand was that government officials had refused to permit him to buy the necessary equipment to enlarge his plant.

I do not mean to say that patents cannot be or have not been abused, as rights of every kind can be misused, but I do believe that a deliberate attempt has been made to discredit our patent system in much of the publicity which has emanated from Washington during the past year or two.

As another example of these unfair attacks on patents and inventions, consider the public remarks before this same Senate committee of Thurman Arnold regarding tetraethyllead. This audience appreciates the tremendous economic value of this invention and knows the story of the long and brilliant series of researches by Midgley; they led to the discovery of this antiknock agent which increased the total available horsepower of the automobile engines made in 1941 by an amount equal to seventy-five Boulder Dams. It was also one of two inventions which made 100 octane gasoline possible and has contributed so much to the air superiority of the United Nations. This discovery was the primary basis for the award to him of the Perkin medal a few years ago. Mr. Arnold, however, airily dismissed it all with the remark: "Now whether these (ethyl) patents were good, I do not know. It struck me at the time, what else could you do with tetraethyllead but put it in gasoline? You can't put it in coffee."

Such statements by government officials in key positions are particularly dangerous in complex scientific matters which the lay public cannot appraise. The statement would have been much less dangerous, though no less unsound, if it had been: "Now whether these telephone patents were good, I do not know. It struck me at the time, what else could you do with a telephone but talk over it. You can't play tennis with it."

I hope these examples are adequate evidence that we as scientists must do our part to educate the public and the lawmakers as to the essential facts about our patent system. As the first step in this educational process we must escape from what Justice Cardozo called "the tyranny of words" and try to get at fundamental meanings.

▶ **Real Nature of the Patent Monopoly.** Our patent system was not created to enrich inventors but to benefit the public by encouraging the invention and the development of new and useful processes or products. To secure these benefits, Congress, on behalf of the public, has solemnly offered a monopoly, limited in time to anyone who will make prompt and full disclosure to the public of a new and useful invention, instead of keeping it secret. If he does not make such full disclosure, the patent is *ipso facto* void. A patent represents an addition to and not a subtraction from the public wealth. Under our present laws and decisions a patent cannot be used to fix resale prices, to control unpatented articles used in connection with the invention, or otherwise to extend improperly the patent monopoly beyond its limited purview. Judicial decisions are steadily narrowing the field of what it is permissible to do under a patent. Nevertheless, a patent is a monopoly, is supposed to be a monopoly, and should not be considered damned by being called a "monopoly".

As a matter of fact, a monopoly is not the inherent evil many would have us believe. Indeed, one of the greatest factors in the early development of America was the fact that our settlers could acquire the ownership of land "in fee simple"and thus monopolize forever their land, its products, its minerals, and the improvements which they made thereon. No greater incentive to hard work and self-sacrifice has ever been found than this right of a man to own and control the fruits of his labors. No one today questions the social value and fairness of this monopoly incentive which did so much to extend our geographical frontiers and bring new lands under cultivation. The monopoly granted to the discoverer of a mining claim was likewise largely responsible for the rapid development of our mineral resources. Is it not equally important and valuable to extend our only remaining frontiers, those of science and invention, when, to do so, we need only offer a monopoly for a short span of years?

Probably the first clear perception of the need for and justice of a patent monopoly was in the Statute of Monopoly which the English Parliament forced through in 1623 during the reign of James I, to stop the Crown from granting monopolies to court favorites on everyday commodities of life, such as salt, spices, playing cards, etc. This statute prohibited all monopolies except those for new inventions and new importations into the realm. This was the first express recognition of the fact that a man should be entitled to some form of property right in and protection of his new ideas and developments. The patent laws of the entire world have sprung from this statute and the gradual recognition of the great incentive thus created has had much to do with the scientific and industrial progress of the past two centuries.

Seventy-Five Boulder Dams Would Represent the Increase in Available Automotive Horsepower in 1941 Cars Due to Tetraethyllead

▶ **Success of American Patent System.** In an early review of the results of our first patent law, Thomas Jefferson said:

> An act of Congress authorizing the issue of patents for new discoveries has given a spring to invention beyond my conception.... In the arts, and especially in the mechanical arts, many ingenious improvements are made in consequence of the patent right giving exclusive use of them for 14 years. Certainly an inventor ought to be allowed a right to the benefit of his invention for some certain time. Nobody wishes more than I do that ingenuity should receive liberal encouragement.

Lincoln well summarized the whole situation in his laconic statement that "the patent system added the fuel of interest to the fire of genius".

Regardless of theory, the experience of this country during the past 150 years has demonstrated that the American patent system has been an outstanding success. It was based on a sound understanding of human nature, and its principles have no more been outmoded than has human nature been outmoded. It has stimulated and supported the natural inventive genius of our people, and has resulted in technical and industrial developments which have made us the envy of all other nations. I can speak from close personal knowledge of the stimulation afforded by the outstanding success of the Burton process and the related patent situation. It was unquestionably the major factor in stimulating research in our industry, first on competitive methods of cracking, and then on the myriad of new processes which have transformed the whole industry in recent years. Dr. Burton in 1912 was one of probably not more than a dozen scientists in this country engaged in petroleum research. In 1922 when I entered the industry there were about 250, and in 1942 there were more than 7000 such research workers in our field.

It might be argued that other nations also have patent systems without getting such outstanding results, but the American patent system has real advantages over most of the foreign systems in several respects. For example, it provides that the first inventor, and not the first one who files his application in the Patent Office, is entitled to the patent. This encourages a man to take adequate time to appraise his invention, work out the details, and even discuss it with others, without jeopardizing his position as the first inventor provided he keeps adequate records.

In the second place, American patents are not subjected to heavy taxes or compulsory licensing provisions which greatly decrease their practical value, especially to an ordinary independent inventor during the early years when his financial resources are likely to be inadequate.

Furthermore, the fact that sound patents are generally respected by the responsible business interests of this country increases the market for, and the value of, a patent in contradistinction to the practices in many foreign countries. As John Anderson, an independent inventor of note, has well said:

> People seldom plant gardens where thieves abound and police protection is inadequate. Pirates are everywhere and inventors will not continue to invent, nor will small investors support their inventions, if patent rights are not sympathetically protected.

▶ **Value of Cross-Licensing Agreements.** Another object of misinformed criticism is the simple cross-licensing agreement between parties actively engaged in similar lines of research. Such research generally results in many Patent Office interferences and overlapping patents which would prevent any party from using the best process in sight. Under such circumstances there has been an increasing tendency to avoid the expense and delay attendant upon interference and infringement litigation by arbitrating the interferences and exchanging cross licenses as to both past and future developments in a given field, usually on a royalty-free basis. Such an agreement generally involves provisions for the licensing of others upon reasonable terms and a division of royalties based upon the best estimate of the parties as to the relative value of their respective positions. Usually each party also agrees to conduct further research in the field in question and is left free to license his own patents on such terms as he sees fit.

In spite of recent attempts to arouse opposition to such arrangements labeling them all "patent pools" without analyzing their provisions, it seems clear that the ordinary cross-licensing arrangement between companies actively engaged in research is very much in the public interest, since it facilitates and stimulates research, prevents unnecessary duplication, removes obstacles to prompt commercial development, and avoids wasteful litigation. The free and prompt exchange of ideas and information between rival laboratories is a tremendous accelerator of new developments. Such cross-licensing arrangements also make available to an outside licensee all the necessary patents and, what is frequently more important, the combined experience of several companies so that he can select and operate the process best suited to his needs without having to acquire licenses and information from several different sources. The only party who could reasonably complain against such an arrangement is the individual or company which hopes to use with impunity the new process while the owners of the patents fritter away the life of their patents in lengthy and often suicidal litigation with one another.

Since cross-licensing agreements of this type tend to promote not only research and invention, but the prompt commercial application of the inventions, the question might be raised as to why free cross-licensing agreements covering entire industries would not be still better in this respect. The main difficulty of such arrangements is that they run up against human nature; when some individuals or companies realize that their competitors will have the same rights they have to anything new which they may develop, they frequently decide to leave most of the expense of research and development to the other fellow and hope for a free ride for themselves. Other companies which, as a matter of principle, continue their research, sooner or later become irritated when the fruits of their research are appropriated by others who have contributed nothing. Such industry-wide pools also remove the main incentive of any company to pioneer radical new developments; they have everything to lose and little to gain by such action which will quickly be copied by everyone if it proves popular.

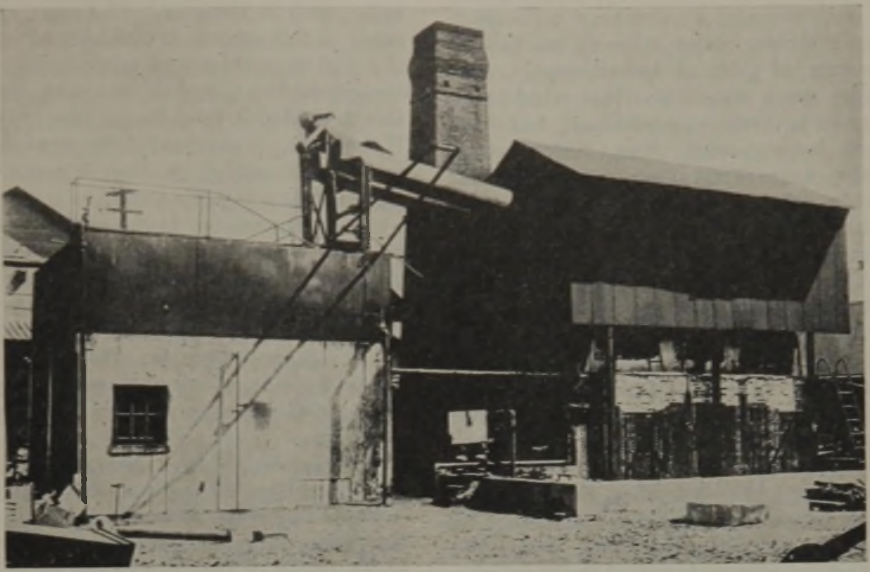
While it is true that cross-licensing agreements have occasionally been used as a screen for an attempt to divide the market or to control unpatented devices, such arrangements are clearly under the prohibition of the antitrust laws and are practically obsolete today, thanks in part to the vigorous activity of the antitrust division. Accordingly there seems to be no reason to legislate against the ordinary and desirable type of cross-licensing agreement which I have described. If a few of the larger companies in a major industry made a cross-licensing arrangement covering every branch of their business without regard to their respective patent and research positions and excluded others from such an arrangement, it might be open to criticism; but where, as in the petroleum industry, each new important field of development generally becomes the basis for one or more cross-licensing arrangements with different participants, depending upon who has pioneered in the new field, and with the arrangement open to newcomers who can contribute substantial patent assets, it is an altogether healthy thing. Certainly it is an efficient method of getting new developments into prompt production without awaiting the result of lengthy patent litigation.

SUGGESTED CHANGES IN PATENT LAWS

While I do feel that our patent system is basically sound and vital to the future of research, this does not mean that patent laws do not from time to time need revision to meet changing conditions and avoid possible abuses.

The Commissioner of Patents not long ago suggested a number of administrative changes in the patent law which had general approval of those most concerned with patents; most of these have already been adopted. Others have vigorously urged more drastic suggestions which have not received such general support; it is to these that I would particularly call your attention.

▶ **Compulsory Licensing.** At the head of the list of proposed drastic changes in the patent system are various types of provisions for compulsory licensing. The argument generally used in favor of such provisions is that many patents are used to suppress inventions. If that were actually the case, there would admittedly be argument for some form of compulsory licensing but, to the best of my knowledge, none of the extensive hearings on patent matters has dug up a single authentic case of this kind. In all my work in dealing with patents and inventors or trying to get licenses, I have never found a patent owner who took that attitude. Frank Jewett whose experience in this field is unexcelled recently wrote:


One of the Original Burton Stills (No Longer in Use)

> Despite the fact that I have made diligent inquiry over the years, I have never been able to locate a suppressed patent nor have I ever found any one who could cite an authentic case of suppression. . . . The plain truth of the matter is that a large part of unused patents are worthless things which the inventors insisted on patenting and on which the Patent Office had to issue patents because the ideas presented were technically new and novel—the Patent Office does not pass judgment on the utility of the patents it grants. They are not and never were anything anybody would use, in the face of better things, even if you gave the patents to him.
>
> Then there is the great group of unused patents which, although they may have had original merit, were rendered obsolete by subsequent inventions. Except for patents on really fundamental new ideas every new patent tends to kill the value of those which preceded it. . . . The only possible way for a business at all dependent on live patents to avoid extermination in the competitive struggle is to keep eternally at the process of replacing its dead and dying patents by new and better ones and that mainly by its own creative effort.

Recent headlines about the suppression of patents on devices needed for war are nothing more than imagination, because legislation has been in effect since the last war providing in effect for compulsory licensing of any patent needed by the Government in time of war. Accordingly the whole matter should be dissociated from the war and be viewed more calmly from a long-range point of view.

The greatest objection to compulsory licensing in normal times is that it largely cancels the very reward the inventor was supposed to receive. It also interferes with the incentive of the patent owner or licensee to make a large investment in a new development if he is faced with the possibility that he may at any time be forced to give a competitor a license on terms which are unpredictable. If there were some way in which one could properly determine a fair royalty and other reasonable terms in the event of compulsory licensing, it would overcome much of the objection to such licensing, but inventions are so widely different in character and in the investment required to develop them that it is impossible to set up any general standards as to the proper terms for a license. The old American art of horse trading between the patent owner and the man who wants a license is often time consuming and annoying, but it is probably the best way to arrive at the fair value of a license, and it has the further advantage of generally being open to readjustment from time to time as conditions change.

It is sometimes proposed that the value of the compulsory license be arbitrated. While the principle of arbitration appeals to everyone as reasonable, the intangible factors make arbitration peculiarly difficult in the case of granting a patent license, because both the terms and the royalty rate are open to so much trading back and forth, with back licenses under other patents often constituting part of the consideration, that it is even harder than the case I previously mentioned of determining the value of a single patent. Furthermore, the patent owner is at a peculiar disadvantage in such an arbitration in that he would be compelled to grant a license on the terms set by the arbitration, whereas if the prospective licensee who requested the arbitration did not like the terms, he could always find some reason for not going ahead with substantial use of the patent; therefore arbitration in such a case is really a one-sided proceeding, binding only on the patent owner.

Compulsory licensing would militate most seriously against individuals and smaller companies who would have to go outside to secure financing to develop and exploit their patented development. Venture capital cannot be attracted into new and hazardous fields without the prospect of unusual returns, which compulsory licensing would prevent.

▶ Proposed Prohibition of Restrictions in Licenses. While the granting of a patent monopoly seems virtually essential to afford an adequate incentive for research and invention which is every year becoming more expensive and difficult, it is nevertheless equally true that once the invention has been disclosed and the patent granted, it is thereafter in the public interest, and usually in the inventor's interest, to have licenses granted to as many people as can make effective use of the invention. Any license, however restricted, is in essence a voluntary concession of part of the owner's rights under his original patent monopoly. In disposing of part of his monopoly, the patent owner naturally must make clear just what he is giving away and what he is retaining for himself, but such limitations in licenses have recently been under heavy attack as though they were fundamentally undesirable, and legislation forbidding almost any such limitations has been proposed. Actually, the net effect of drastic provisions against restrictions in licenses is likely to be the opposite of that intended. The practical aspect of this can possibly be best illustrated by again referring to the analogy of the ownership of land. Suppose a man owning a tract of land is asked to grant a right-of-way for a road across his land. He would probably be quite willing to grant such a right-of-way provided he received reasonable compensation and could protect his own rights in the remainder of the land by providing that the man who acquired the right-of-way must keep a certain distance from his house, construct and maintain fences and agree not to trespass on the remainder of the land. These provisions are restrictive as to the rights and duties of the man who acquires the right-of-way, but the important thing is that he does not lose any rights he ever had; he simply agrees to definite limitations on the new rights which he acquires. Now if we pass a law saying that all grants of right-of-way must be unrestricted and without limitation, it is certain that the land owner will be much less willing to grant rights-of-way; or if he does, he will charge much more for them. Exactly these considerations apply in the case of many of the proposed prohibitions against restrictions in licenses. It should be made as easy as possible for a man to chip away his monopoly gradually, however small the individual pieces.

One set of proposals put forward last spring in Senate Bill 2491 would specifically outlaw any restrictions in licenses as to (1) price, (2) quantity permitted to be manufactured, (3) geographical limitations, and (4) limitations as to the use to be made of patents.

As to the restrictions on the price or quantity of patented articles to be produced under a license, the modern trend in licensing, at least in the industries with which I am most familiar, is away from all such restrictions, and I cannot argue strongly against the prohibition of such restrictions. However, even such prohibitions would tend to discourage licensing or force up royalty rates in certain cases where a patent owner feels that such restrictions on first sale are necessary for his self-preservation.

The matter of prohibiting geographical restrictions is much more serious. For example, take a man who is manufacturing an article in the East or Middle West on which the freight to the Pacific Coast is large. He might be approached by a Pacific Coast manufacturer who wanted a license, and since the patent owner could not readily fill this market himself, he would be glad to grant a license if it could be limited to manufacturing on the Pacific Coast. If, on the other hand, geographical restrictions were prohibited so that he could not grant a license without throwing open the whole world to his licensee, he would probably decide to give no license at all, and the Pacific Coast would continue to suffer from the lack of a convenient source of supply.

Even more unfortunate would be the practical effect of the proposed prohibition of any limitations as to the use to which a licensee might make of a patented process or apparatus. This entirely overlooks the way most licenses are desired and granted by most companies operating in the process industries. Suppose *X* oil company owns a patent on a process capable of being used to make products of high value, such as 100 octane gasoline, as well as products of relatively low value, such as kerosene. If *Y* company wanted to take a license on this process to make kerosene, it would undoubtedly say that it could afford to pay only a small royalty under these conditions, and *X* company would probably agree to this, provided it used the process only for making kerosene. If, however, *Y* company later wanted to use the process for making 100 octane gasoline or some other product of high value, such a royalty would be unreasonably low. Since it would be impossible to determine in advance a fair royalty for every possible use to which the user might want to put the process, it would best suit the needs of both *X* and *Y* companies to set a royalty rate for the use or uses definitely contemplated and limit the license to such uses. If *X* company were permitted to give only an unlimited license for unknown future uses, it might well decide not to grant any license at the low rates appropriate for making kerosene.

Furthermore, while *Y* company would be primarily interested in getting a license on only one or two specific patents, it would undoubtedly want, and expect to get, drawings and designs for complete equipment to carry out this process and in the design of that equipment there might be half a dozen minor patented devices which neither *X* nor *Y* might have in mind. If *Y* were well advised, it would insist that it have the right to use any of *X*'s patents in carrying out the specific process, and *X* might well agree to this "throwing in" of all incidental patents, provided such uses were limited to the process under discussion; but it would certainly not throw in all of his patents for use in any process which might come along merely for the payment of a small royalty based on a kerosene operation. The great bulk of the process licenses granted in our industry do not attempt to enumerate all the patents and applications which might be useful in a given process but give a blanket license under any of the patent owner's present or future patents for the defined process. Such broad licensing of all the licensor's patents for the desired use is certainly in the public interest but would be made impossible by the proposed type of restriction.

► **Shortening of the Patent's Life.** One abuse which has been clearly evident in a few cases is the practice of deliberately and excessively prolonging the period of argument back and forth in the Patent Office so that a patent is not issued until many years after the application, in order to get the benefit of a later effective period of life. For this reason one of the suggested reforms which would keep the life of the patent at not more than seventeen years but also limit the expiration date to not more than twenty years after the application was filed seems to have real merit. Even the seventeen-year life is open to question in view of the accelerated industrial tempo which, in general, makes it possible to get a new invention into operation much more promptly than was the case when the seventeen-year term was originally set. On the other hand, it is getting more and more expensive and difficult to make and develop new inventions as the frontiers of science are pushed farther and farther afield, and there should be some offsetting increase in incentive. Seventeen years seems a long period when we are in the midst of a new development, but it is a short time in the life of a nation or an industry. Certainly no one today begrudges James Watt his monopoly on the steam engine from 1769 to 1794, or Bell his telephone from 1876 to 1893.

▶ **Greater Care in Granting Patents.** It must be conceded that a large number of patents issued by our Patent Office relate to minor or petty details of routine improvement and do not cover true inventions. While these weak patents are being consistently knocked down by the courts, they are often a source of harassment, confusion, and expense. There appears to be too low a standard of patentability in the Patent Office, and in recent times too awesomely high a standard of patentability in the courts. Although the Patent Office is required to resolve its doubts in favor of the inventor, it seems that the Patent Office has in general been too liberal. The Patent Office is not alone at fault in this connection. It is subjected by attorneys and applicants to strong and relentless pressure to issue some kind of a patent even though the applicant or attorney realizes that it may be of doubtful validity. This type of patent is sometimes called an "insurance" patent because its main purpose is to prevent someone else from being granted a patent later on the same thing.

The character of patents probably would also be improved simply by raising the salary standards in the Patent Office. The present salary situation is such that there is little incentive for the patent examiner to regard service in the Patent Office as a lifetime career, with the result that the Patent Office functions to a considerable degree as a training school for patent attorneys.

There is also room for improvement in the information available to examiners in making searches for patentable novelty. Much practical knowledge and information from the industry should be but is not available in the Patent Office. One constructive move to help remedy this situation would be to establish a procedure whereby the examiners, at least those of senior rank, would have frequent personal contact with development and manufacturing activities in the particular fields which they are examining.

EFFECT ON RESEARCH OF DRASTIC WEAKENING OF OUR PATENT SYSTEM

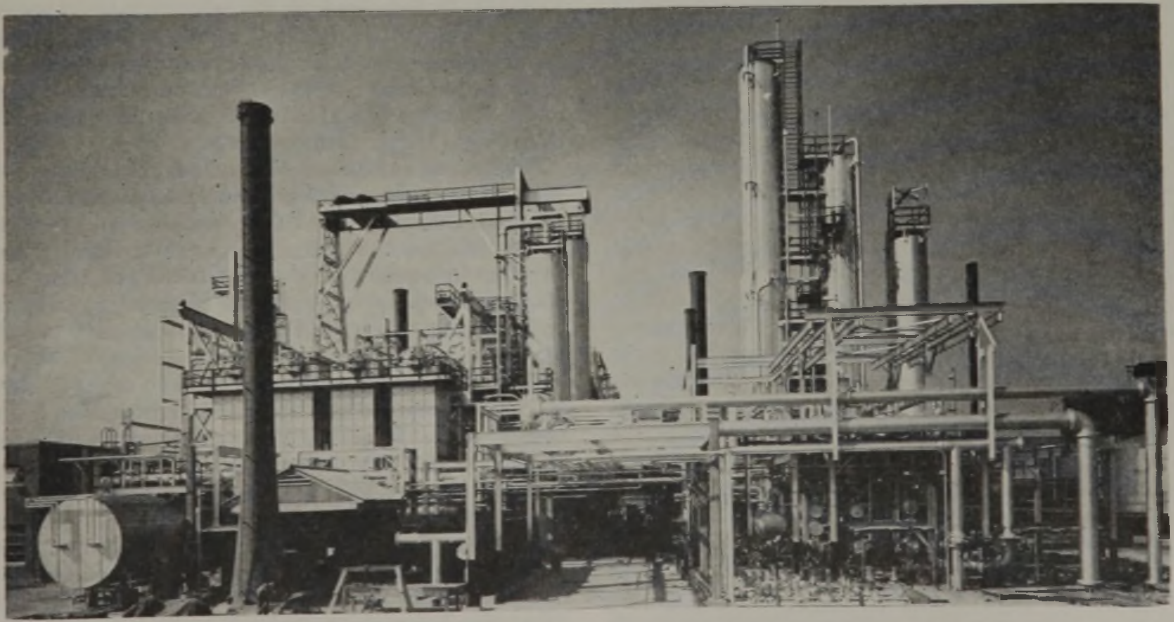
For an authoritive and considered statement as to the relation of patents to research, one would logically go to the National Research Council. In their December, 1940, report to the National Resources Planning Board they have said:

> It is generally recognized, however, that patents play an important part in the motivation of research, and no changes in the patent system should be made without most careful consideration of possible effects on the welfare of industrial research.

Emasculation of our patent system is bound to discourage much industrial research which has grown so amazingly in recent years until it employed about 70,000 research workers in 1940. However, the effect on the amount of research done will vary greatly with the industry and particularly with the size of the company, and in a direction which would seem to be socially undesirable as it would in the long run weaken the competitive position of the smaller companies. Let us consider the relative effect on companies of various sizes.

▶ **Little Effect on Large Companies.** A drastic weakening of our patent system will least affect the research policies of the large companies. Such companies can readily afford to carry on research programs covering their principal fields of activity solely for the purpose of maintaining their competitive position and keeping down their manufacturing costs. They regard royalties mainly as incidental by-products of their research, and their main interest in patents is to help them secure maximum operating freedom by virtue of exchanges of licenses. Obviously, if they find it expedient not to depend on patents, such companies will not stop their research but will tend to keep their "know how" largely to themselves.

▶ **Major Effect on Medium and Small Companies.** The effect of emasculation of our patent system on the research activities of medium and small companies will be much more severe. Such companies must have some research organization if they are to keep anywhere near abreast of competition, but their laboratories cannot possibly do original research in all their fields of activity. In general they concentrate mainly on operating problems and the application of various patented processes to their own needs. In either type of work they frequently run across some new



Fractionating Equipment in a Catalytic Cracking Unit idea which seems to have merit; and even though their own activities would not justify the cost of a thorough investigation, as long as they have the prospect of patent protection and substantial royalty income, they can and do exploit such ideas, at least through the phase of laboratory development. Many small laboratories have more than financed all their research activities by one or two important inventions. Also, when they come to the point of needing to undertake large-scale development, which in our industry frequently costs several hundred thousand or even a few million dollars, such companies can usually, by virtue of patent protection, interest other companies in joining with them and sharing such development costs. Several small companies in our industry have attained a position of preeminence in certain fields by just such methods, but without the incentive and protection of a sound patent system the ideas would probably never have been developed. As Patent Commissioner Coe has said: "Speculative capital will not back new inventions without patent protection."

Another factor which would tend to reduce research in such companies would be that, without our patent and licensing system, the companies which develop major new processes would not be giving out information and trying to sell licenses, and hence the smaller companies would not be able to study promptly the application of these new processes to their own needs, so the whole process of development in industry would be retarded.

▶ **Elimination of Research and Licensing Companies.** In addition to the research conducted by operating companies, in many industries one or more nonoperating companies have maintained research and development programs which have resulted in important processes. Outstanding among these in the petroleum industry is the Universal Oil Products Company which first developed the Dubbs cracking process. This company has for over twenty years maintained a large research staff and has made many other outstanding contributions to the refining of petroleum and to the chemical field as well. In the past twenty years it has spent approximately $25,000,000 for research and process development, more recently at the rate of about $2,000,000 annually. The income of this company is derived entirely from the licensing of its patented processes, and the major portion of its royalty income has been used for continuing research and development. The income derived from royalties on thermal cracking was largely used to study and develop some of the present catalytic processes which are so vital in the war effort, including catalytic cracking, alkylation, isomerization and dehydrogenation for aviation gasoline, and other processes for the production of components of synthetic rubber, etc. Universal Oil Products also maintains a group of skilled technicians who for years have advised and assisted its smaller refiner licensees to maintain operations on the most efficient basis. The weakening of our patent system will automatically result in the disappearance of these research, development, and licensing companies which have proved so important, particularly to the smaller operating companies.

▶ **Effect on University and Foundation Laboratories.** A generation ago most research workers in the medical field and many of those in our universities felt that it was not quite ethical to patent their discoveries, particularly in matters relating to public health. During the past twenty years, however, there has been a growing recognition of three facts: (1) Failure to patent is more likely to delay than to encourage the development and marketing of new products, especially if any substantial investment or advertising is required to get them started. (2) Failure to patent leaves new remedies open to widespread abuse by unethical manufacturers and promoters, whereas patenting permits a control of quality and marketing practices which is highly desirable in the case of many new drugs. (3) Failure to patent simply throws away a large potential income from those who benefit from new discoveries, which income might better be collected and used to promote further research in related fields. Growing appreciation of these three facts has largely changed the attitude toward patents of the workers in these fields, so that patenting is now the usual practice. Partly due to the outstanding example of the Wisconsin Alumni Research Foundation, millions of dollars a year are today being devoted to pure research in medical and other lines from royalties obtained from the inventions of earlier workers, generally in the same organization. This is a sound and socially desirable method of financing research work which would be lost if the value of patents were to be greatly reduced.

▶ **Back to Dark Ages of Secret Processes.** Probably the most serious effect that emasculation of our patent system would have on the future of research would be to encourage the use of secret processes. This would be highly unfortunate, since one of the principal factors in the rapid advance of science and technology in the past thirty years has been the practical elimination of the secret process in favor of full disclosure and patenting as the preferable method of protecting one's rights and interests in his invention. If we take away a large part of the reward for disclosure, the tendency to revert to the dark ages of secret processes will be inescapable. The loss to our country would not be merely that due to the absence of competitive use of new processes, but even more in the slowing down of the exchange of basic information and new ideas. Intercompany research conferences and reports on new lines of development would practically cease, and early publication of industrial research work would seldom be permitted. Industrial espionage would rear its ugly head, and efforts to prevent it would force the elimination of the open-door policy of most of our industrial laboratories. As Kettering has said, "when you lock the research laboratory door you always lock out a great deal more than you lock in", but serious weakening of our patent system would inevitably result in just such a situation. Modern industry based on applied science is a great cooperative affair which cannot thrive in a world ruled by secrecy.

Another unfortunate result of secret processes would be that a small company would no longer be able, as a prospective licensee, to get full information and detailed plans on competitive new processes. Even though the owners of the secret processes were willing to sell the know-how, they could not make prior disclosure of their processes for comparison with others, and the small company would either have to buy a "pig in a poke" or do without.

Even the workers in pure science who might discover some new principle would probably hesitate to publish it until they could work out some of the practical applications for sale on a secret process basis, because once a new discovery was published it would largely lose its value. Even though the attempt at secrecy might usually fail within a few years, the cumulative effect of the loss of time between successive improvements would tremendously retard our progress. Under present conditions new discoveries are frequently published long before the patent is actually issued, and the effect on the whole tempo of industrial progress is very large because so little time elapses between the discovery and the general availability of the information to stimulate other re-

Official Photo, U S. Army Air Forces

100-Octane Gasoline Contributes to United Nations Air Superiority

searches in a variety of fields not even dreamed of by the original discoverer.

▶ **Loss of Information from Abroad.** We must also not overlook the effect of a drastic weakening of our patent system on our future ability to get information from abroad. Foreign manufacturing conditions are usually better adapted to protecting the secrecy of processes than those in this country, and it is only the liberality of our patent system and the existence of a real market for worth while patents that have led most foreign patentees to make early application for a patent in this country. No country has, or can expect to have, anything like a monopoly on brains, and anything which will discourage our receiving prompt information regarding new foreign developments will be another serious bar to industrial and scientific progress. Even though some foreign inventors might still apply for patents in their own countries so that some information would eventually become available, it would not be possible for us to secure the detailed plans, specifications, and know-how which can usually be obtained when it is possible to negotiate for a patent or a license. This know-how is particularly necessary on foreign patents because their background of language and industrial technique is frequently not well understood in this country.

To indicate a little of the extent to which our ability to meet war demands has arisen out of information obtained from our principal enemy, Germany, thanks to the enterprise of American companies and the existence of our patent system, I might cite the following brief summary of a few important items in this category from an article by Lawrence Langner in a recent *Atlantic Monthly*. In quoting this list I do not mean to imply that similar or alternative processes were not being, or would not have been, developed in this country under the stress of war needs. The important thing is that we obtained early information which permitted prewar industrial development of the processes and products which have proved so important to the war effort. Langner's list is as follows:

> Tetracene, a percussion explosive. Information obtained from Germany by Remington Arms Company, a subsidiary of the Du Pont Company.
>
> Optical glass and instruments. Information obtained from Germany by Bausch & Lomb Company.
>
> Plexiglas, a plastic glass used for airplanes. Information obtained from Germany by Röhm & Haas Company.
>
> Carboloy, a tungsten steel alloy important for cutting tools. Information obtained from Germany by General Electric Company.
>
> Buna rubber. Information obtained from Germany by Standard Oil Company of New Jersey.
>
> Magnesium. Information about new processes obtained from Germany by Aluminum Company of America and others.
>
> Atabrine, a vitally needed substitute for quinine. Information obtained from Germany by Winthrop Chemical Company.
>
> 100-octane aviation gasoline. Information on which the principal American process is based obtained from Germany by Standard Oil Company of New Jersey.
>
> Synthetic toluene for TNT. Information on which the principal American process is based obtained from Germany by Standard Oil Company of New Jersey.

This impressive list of American weapons forged from German research certainly belies frequent loose statements that our leading industrialists were serving as blind tools for Hitler when they acquired their patent licenses.

CONCLUSION

In conclusion I hope that what I have said will convince both this audience and later readers that our patent system is in real jeopardy, and that this jeopardy is due to public misunderstanding which, in turn, is largely due to deliberate misrepresentations as to the nature of the patent monopoly and the part which patents play in encouraging inventions and their prompt disclosure to the public. The inevitable alternative of secrecy would tremendously retard the progress of both science and industry in this country. Under these circumstances it is surely incumbent upon every scientist to take his share of the job of educating the public and our legislators as to the truth about our patent system.

In many ways the most encouraging aspect of the Washington outlook was the appointment by the President of a Patents Planning Commission under the chairmanship of Charles F. Kettering. This committee has been expressly directed by the President to conduct a comprehensive survey and study of the American patent system and to make suggestions for its permanent improvement. Rather than being stampeded into making drastic patchwork changes as urged by some of our theorists and nonresearch industrialists, we should certainly await with confidence the completion of the studies of this committee. I think we can reasonably anticipate a report as sound and important to our industrial picture as the recent Baruch report on the rubber problem. If such a report is given the weight it deserves, I believe we can look forward with confidence to the future of research and invention in this country, which is our greatest hope for prompt postwar readjustment of our economy.

Were it my job as supersaboteur to destroy America's future greatness, I can think of no more effective way than to destroy our patent system. The tragedy is that if we permit impractical theorists and faddists to distort the facts and hypnotize our nation into this act of *hara-kiri* all of us will suffer and yet no adequate punishment can be meted out to those really responsible. Let us not by our inaction have any share in such a terrible responsibility.

Demineralizing Solutions by a Two-Step Ion Exchange Process

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With the advent of the acid-regenerated organic cation exchangers (so-called hydrogen zeolites), it became possible to replace all metallic cations with hydrogen ions, leaving only the corresponding acids in solution. The operating principles of these hydrogen cation exchangers in the field of water treatment have been discussed in previous papers. Various classes of organic cation exchangers have been developed: coal derivatives, lignite derivatives, materials made from paper waste and acid sludge, and resins such as tannin-formaldehyde and other polyhydric phenol-formaldehyde derivatives.

After it became practical to replace the metallic cations in solution by hydrogen ion, it was clear that, if the resultant free acids could be absorbed by some insoluble substance which could be regenerated and operated indefinitely in repeated cycles like the cation exchangers, it would be possible to remove both cations and anions by a practical process. Various materials for absorbing these acids appeared in rapid succession and the principles of operation are discussed. Anion exchangers have been developed that eliminate troubles experienced with earlier materials and, in some respects, excel the well-established cation exchangers, especially in capacity and regenerating efficiency. The principles of operation with respect to electrolyte contents of waters that can be economically treated by this process are discussed, as well as the influence of type of anion and operating cost. The method of operation to be followed to obtain a properly demineralized final effluent is described.

FOR almost a hundred years, it has been known that salts like calcium and magnesium bicarbonate, which are frequently present in water supplies, can be removed to a substantial extent by precipitation with lime. By this means their concentration can be reduced to about 15–50 p. p. m., depending upon the temperature and excess of reagents.

With the advent of the acid-regenerated organic cation exchangers (so-called hydrogen zeolites), it became possible to replace all metallic cations with hydrogen ion, leaving only the corresponding acids in solution. It was clear that if only the resultant acids could be removed, it would be possible for the first time to reduce the total dissolved solids chemically rather than by distillation in waters containing chlorides, sulfates, or sodium bicarbonate.

The first actual attainment of this objective occurred with waters containing sodium carbonate or bicarbonate. The volatile carbonic acid formed by reaction of these salts with the acid-regenerated cation exchanger was readily removed by degasification (*3*).

Removal of the nonvolatile acids and production of an effluent comparable in quality to distilled water depended upon the development of an insoluble material that would absorb acids and that could be regenerated and operated indefinitely in repeated cycles, like the cation exchangers. Various acid absorption materials soon appeared in rapid succession, and the ion-exchange process of removing salts from solutions (commonly called "demineralizing") was launched commercially.

Principles of Two-Step Demineralizing

In principle the process is a two-step series operation as illustrated in Figure 1. The reactions involved in these steps may be represented as follows, using calcium chloride as a typical salt:

$$CaCl_2 + H_2Z \rightleftharpoons CaZ + 2HCl \qquad (1)$$

$$HCl + R_3N \rightleftharpoons R_3N.HCl \qquad (2)$$

where Z = cation exchanger
R_3N = anion exchanger

Any chlorides and sulfates present in the original solution will be transformed by this treatment into the corresponding hydrochloric and sulfuric acids. Bicarbonates are transformed into carbonic acid.

In step 2, the anion exchanger (called "De-Acidite" in the Permutit process) absorbs the strong acids but does not take up the weaker carbonic acid, which is readily decomposed into water and carbon dioxide in the degasifier that follows the two ion exchange units in series.

Thus, a final effluent which approaches distilled water in quality is obtained. The precise composition of this demineralized effluent depends to some extent upon the quality of the raw water, but in general the following average analysis represents its composition:

Expressed as p. p. m. of $CaCO_3$	
Total hardness	0–2
Alkalinity to methyl orange	1–6
Chlorides	0–4
Sulfates	0–3
Free CO_2, p. p. m.	5–10
Color (A. P. H. A.)	Below 5

The demineralizing process does not remove silica from water. If the influent contains a sufficiently high silica concentration to be harmful in the particular application under consideration, as is frequently the case in the treatment of high-pressure boiler feed water, then silica removal treatment must precede the demineralizing treatment. Practical processes and equipment for effective silica removal are now available (*17*), and several large-scale installations are in operation.

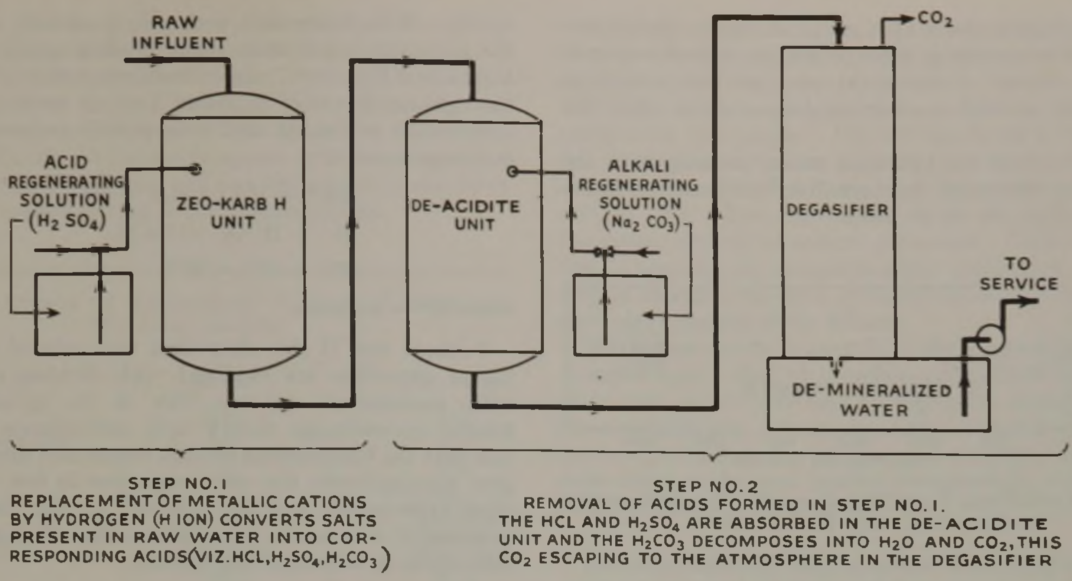

Figure 1. Two-Step Process for Demineralizing Water

In the acid regeneration, the cation exchanger is reconverted to its original condition as follows:

$$CaZ + H_2SO_4 \rightleftharpoons H_2Z + CaSO_4 \qquad (3)$$

Although De-Acidite and similar materials are usually called "anion exchangers", the indications are that they may take up all the free acid molecules in much the same way that ammonia reacts with hydrochloric acid (*14*). In the case of these anion exchangers, the acid absorption is accomplished by amino groups which form a part of large insoluble organic molecules.

When the capacity for absorbing acids has been exhausted, the material is regenerated with an alkali, such as sodium carbonate, according to the following reactions:

$$2R_3N.HCl + Na_2CO_3 \rightleftharpoons 2R_3N + 2NaCl + H_2O + CO_2 \qquad (4)$$

The sodium chloride, sodium sulfate, and carbon dioxide formed in this regeneration pass to waste in the rinse.

Of the many factors influencing the demineralizing of a particular water supply, the most obvious are the nature and performance of the cation exchanger and acid absorber used.

Cation Exchangers

Various classes of organic cation exchangers have been developed: sulfonated coal derivatives, caustic-treated lignite derivatives, materials from paper waste and acid sludge, tannin-formaldehyde and other polyhydric phenol-formaldehyde resins, and modifications of these produced by supplementary treatments.

The coal derivatives, such as Zeo-Karb, were the earliest materials developed and have been most extensively applied in practice. Zeo-Karb installations have been operating for a number of years and for thousands of cycles without deteriorating physically, dropping in capacity, or developing colored effluents. It appears that although some resins are slightly higher in capacity, a good sulfonated coal is more resistant and has greater stability.

Figure 2 presents typical results on organic cation exchangers which indicate their long-term stability. These results were obtained under identical experimental conditions and are expressed in milliequivalents (meq.) per liter of original bed volume. They can be conveniently converted to the usual form of expression, "kilograins per cubic foot expressed as $CaCO_3$" by dividing by 45.8.

With certain ion exchangers there is a gradual loss of material as the result of solution or attrition. Since the total capacity of the installation may be dropping while the materials show an apparently constant capacity per unit volume of ion exchanger when measured at the same time the capacity of the installation is measured, data in Figures 3 and 4 are given in terms of the initial bed volume of ion exchanger. This is done since, in commercial installations, knowledge of the capacity of the entire installation is of greater value than the capacity per unit volume of exchanger.

These capacity data were obtained by a tube testing method which provides a means for simulating large-scale operation in the laboratory (*15*). A water or solution of known composition flows through a laboratory tube containing a definite volume of the granular ion exchanger until the predetermined end point is reached. The capacity is calculated from the volume of water treated, the amounts of cations or anions removed from solution, and the volume of ion exchanger employed. Except when a series of compara-

Table I. Effect of Type of Anions on Cation Exchanger Capacity (Tube Tests)

(Influent solution concentration, 8 meq. per liter; flow rate, 50 ml. per minute in a 2.3-cm. diameter tube; regenerated by 605 meg. of 0.4 *N* H_2SO_4 per liter of bed.)

Salt	Capacity (Meq./L. of Cation Exchanger)	
	Sulfonated coal	Polyhydric phenol-formaldehyde resin
NaCl	198	268
$CaCl_2$	224 (318[a], 342[b])	266
$MgCl_2$	323 (332[b])	303
$NaHCO_3$	492	496
$Ca(HCO_3)_2$	296 (505[a])	296
$Mg(HCO_3)_2$	444	...

[a] Initial run on calcium influent.
[b] Regenerant = 605 meq. of 0.4 *N* HCl per liter of bed.

tive tests is made under a fixed set of identical experimental conditions, it is necessary when presenting capacity data to specify the amount of regenerant used per unit volume of ion exchanger, as well as other conditions which affect the capacity.

The operation of the hydrogen cation exchangers in the field of water treatment has been fully discussed in earlier papers (*1–6*, *8*, *9*, *10*, *12*, *16*, *19*).

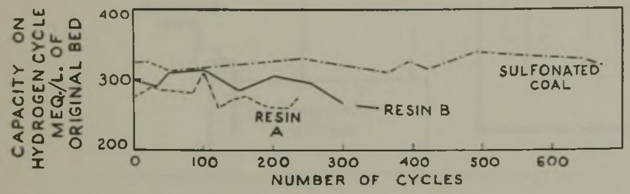

FIGURE 2. LONG-TERM TUBE TEST CAPACITY DETERMINATIONS ON ORGANIC CATION EXCHANGERS

The quantity of cation exchanger necessary for demineralizing a particular water has been found to depend partly upon the nature of the anions present. Experiments performed in this laboratory indicate that the capacity of a cation exchanger operating on the hydrogen cycle is profoundly affected by the type of anions present.

Table I illustrates this phenomenon with data obtained by tube testing; the results are the averages of three to six runs.

Table II presents similar data obtained by a simplified capacity test. This test is carried out by shaking solutions of at least two known concentrations with weighed amounts of the ion exchanger until equilibrium is reached. The residual concentrations of ions in solution are determined, and the quantities of the ions removed from solution per unit weight of exchanger are then calculated. The logarithms of amount of a given ion absorbed per unit weight of exchanger are plotted against the logarithms of the concentrations of the corresponding ions in the final solution. The resulting Freundlich isotherms are extrapolated to any desired concentration. As a rule, extrapolation to final concentrations of 1 meq. per liter under certain conditions gives results that are comparable to those obtained by the tube testing method. This method is useful for the rapid estimation of ion exchanger capacities on very small samples of material.

TABLE II. EFFECT OF TYPE OF ANIONS ON CATION EXCHANGER CAPACITY (EQUILIBRIUM DETERMINATIONS)

	Capacity (Meq./L. of Cation Exchanger)	
Salt	Sulfonated coal	Polyhydric phenol-formaldehyde resin
$NaCl$	53	73
$CaCl_2$	209	167
$MgCl_2$	209	185
Na_2SO_4	53	73
$MgSO_4$	209	185
$NaHCO_3$	281	270
$Mg(HCO_3)_2$	316	324

The general improvement in cation exchanger capacity observed when the influent water contains appreciable concentrations of anions of weak acids is caused by a shift to the right in the cation exchanger–salt equilibrium (Equation 5 below) as a result of the removal of hydrogen ions from the solution by the formation of the weakly ionized carbonic acid (Equation 6). With strong acids, such as hydrochloric, sulfuric, etc., the ionization equilibrium shifts predominantly to the left-hand side of Equation 7, and introduces a common ion effect on the right-hand side of Equation 5 which tends to drive this equilibrium to the left and consequently reduces the cation exchange capacity:

$$2M^+ + H_2Z \rightleftharpoons M_2Z + 2H^+ \quad (5)$$

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \quad (6)$$

$$H^+ + Cl^- = HCl \quad (7)$$

where M^+ = metal ion

Tables I and II also show that with salts of strong acids higher capacities are obtained with divalent cations than with monovalent cations. This is in agreement with known ion-exchange theory and performance (*18*). The fact that the bicarbonates of both mono- and divalent metals give approximately the same capacities in flow and equilibrium experiments may be ascribed to the fact that the presence of this anion overshadows the effect produced by differences in valence of the cations.

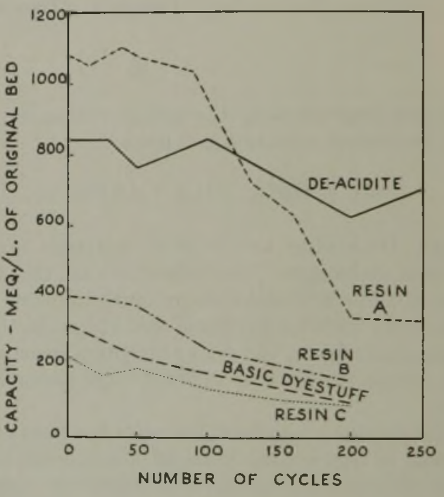

FIGURE 3. LONG-TERM TUBE TEST CAPACITY DETERMINATIONS ON ANION EXCHANGERS

The differences between the capacities obtained with calcium salts and those with magnesium salts were apparently caused by the deposition of insoluble calcium sulfate on the cation exchanger during regeneration. This precipitated material apparently blocked access to a part of the cation exchanger surface, thereby reducing the capacity. Confirmation of this hypothesis was obtained by determining capacities on fresh cation exchanger beds and on beds regenerated by hydrochloric acid. In runs on fresh cation exchanger beds (results marked [a] in Table I), the capacities agreed with those obtained when using the corresponding magnesium salts. Subsequent runs on relatively high calcium influents with the same cation exchangers resulted in reduced capacities. Runs made when using hydrochloric acid as regenerant (results marked [b] in Table I) gave calcium capacities in agreement with magnesium capacities obtained when using either regenerant.

In practice, this calcium sulfate deposition occurs only rarely, and in these cases, in view of the higher cost of hydrochloric acid and the difficult corrosion problem introduced by its use, it is cheaper and more expedient to use a larger volume of cation exchanger than to attempt to obtain maximum cation-exchange capacity by regenerating with this acid.

For use in demineralizing, it is essential that the cation exchanger replace, with hydrogen ions, all of the metallic cations in the influent water. Since the anion exchanger functions solely as an acid absorber and will not remove metallic cations, any of these which appear in the cation-exchanger effluent will inevitably appear in the demineralized water. Of course, the latter will also contain a concentration of anions equivalent to that of the cations present.

Table III. Effect of Regenerant Dosage on Effluent Metallic Cations

Influent Water	P. P. M. as $CaCO_3$[a]	Meq./Liter
Total hardness	428	8.55
Sodium salts	25	0.50
Methyl orange alkalinity	107	2.14
Chlorides	336	6.71
Sulfates	10	0.20

Regenerant[b] Dosage, Meq./Liter	Zeo-Karb[c] Capacity, Meq./Liter	Av. Metallic Cations in Effluent, Meq./Liter
303	248	0.58
605	342	0.12
1210	404	0.06

[a] 50 p. p. m. as $CaCO_3$ = 1 meq./liter.
[b] Regenerant = 0.4 N H_2SO_4.
[c] Flow rate = 50 ml./minute.

The use of a larger cation exchanger regenerant dosage is a satisfactory precaution to ensure maximum displacement of metallic cations, especially when treating waters with high chloride and sulfate content. The cost of the additional acid is not entirely chargeable to improved effluent quality, since increased cation exchanger capacity is obtained at the same time. Table III summarizes experimental results obtained when treating a water of high electrolyte content with a sulfonated coal cation exchanger regenerated with varied amounts of sulfuric acid.

Anion Exchangers

For some time after 1937 when the first commercial demineralizing unit was installed, the adoption of this two-step demineralizing process was slow, mainly because of the poor anion exchangers available. As might be expected, the earlier anion exchangers, such as the *m*-phenylenediamine–formaldehyde resins and the insoluble basic dyestuffs, left much to be desired. Their capacities were limited and dropped substantially after a relatively small number of cycles. Also, they decomposed with resultant loss and contamination of the effluent by colored materials. Worst of all, the chemical quality of the effluent deteriorated with repeated operation and caused a steady rise in the electrolyte content of the demineralized water.

These shortcomings were quickly realized, and during the few intervening years, as a result of intensive research activity, products have been developed that not only eliminate the troubles encountered with the earlier materials but, in some respects, excel the well-established cation exchangers, especially in capacity and regenerating efficiency.

Figure 3 summarizes the results on various materials on the market at the present or in use during the past few years. The data were obtained under identical experimental conditions, using the tube testing method previously described. These long-term studies bring out the substantial differences in the stability and capacity of various materials. The data also show that the more recent high-capacity materials give promise of good stability over a long period of operation.

Typical of these new anion exchangers is the aliphatic amine resin, De-Acidite. Figure 3 shows the performance of this kind of material on an influent water containing 1.5 meq. per liter of hydrochloric acid and 2.5 meq. per liter of sulfuric acid, when regenerated with only 1.25 times the theoretical amount of sodium carbonate. This material has been in operation for several hundred cycles with only a small drop in capacity, no color contamination, and no rise in the electrolyte content of the effluent.

It is still too early to state that the life of these anion exchangers equals that of the resistant sulfonated-coal cation exchangers, which have been operating day in and day out for years without any drop in capacity. But the experience to date indicates that the present acid absorber, coupled with these cation exchangers, renders commercially practicable the two-step demineralizing process.

Demineralizing Equipment and Applications

Good ion exchangers alone are no guarantee of good demineralizing performance. Proper equipment design and operation are essential for satisfactory results at economical operating costs. As stated above, a properly designed and operated demineralizing installation delivers a final effluent that approaches distilled water in quality. This water can be used in almost any application for which distilled water has been used or for which its use would be desirable, if costs were sufficiently low. Some idea of the variety of uses to which demineralized water has been applied may be obtained from Table IV. Among recent applications are alcohol deproofing, brewing, and photographic film preparation.

Certain reports have been made as to the suitability of such a process for removing salt from sea water; as might be expected, this sensational reference has been picked up and published in confused and exaggerated form by popular scientific magazines and newspapers all over the world. There is no factual basis for assuming that this process can compete with distillation when the concentration of salts is anywhere near as high as in sea water. The reasons are obvious. For the regeneration of the cation exchanger, an amount of acid is required substantially higher than the theoretical equivalent of the cations removed in the hydrogen exchange. Similarly, the regeneration in step 2 requires an amount of alkali slightly greater than the theoretical equivalent of the acid absorbed. Assuming that it would be possible to carry out the reactions on sea water, about 150 pounds of sulfuric acid and 100 pounds of sodium carbonate

Table IV. Partial List of Demineralizing Installations

Company	Application	Date of Installation	Flow Rate, Gal./Min.	Meq./Liter of Influent Water: Total cations	Meq./Liter of Influent Water: Chlorides + sulfates
A	Mirror silvering	1937	2.5	0.94	0.48
A-2[a]	Mirror silvering	1941	9–23	5.70	2.58
B	Cellulose acetate mfg.	1938	100	13.98	0.18
B-2	Plastics mfg.	1940	10	0.84	0.36
C	Chemicals mfg.	1938	1	2.80	1.92
C-2	Chemicals mfg.	1940	8	5.84	3.76
C-3	Chemicals mfg.	1940	8	5.84	3.76
D	Drug mfg.	1939	3	2.00	0.90
E	Drug mfg.	1939	10	7.54	1.54
E-2	Drug mfg.	1940	10	7.54	1.54
F	Cosmetics mfg.	1941	10	2.90	0.74
G	Plastics mfg.	1941	150	3.38	2.18
H	Process	1941	5	3.00	0.92
I	Synthetic rubber mfg.	1941	55	5.22	1.40
J	Boiler feed	1942	10	11.65	6.16
K	Boiler feed	1942	4.5	9.43	5.62

[a] Numbers indicate repeat installations for the same company.

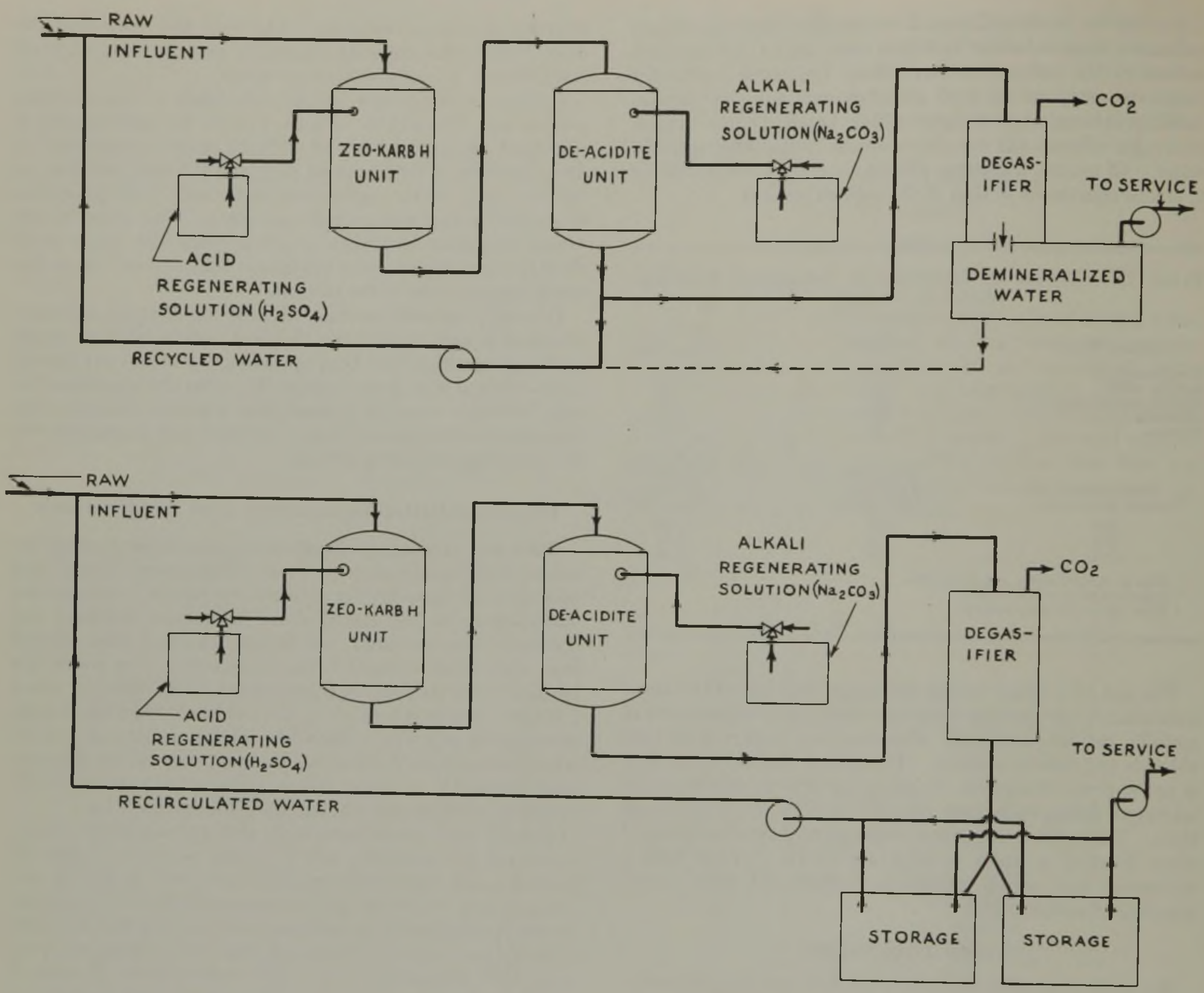

Figure 4. Demineralizing with Partial Recirculation (*above*) and Multiple Demineralizing (*below*)

would be required per 1000 gallons of water passed through these units for the regeneration of the respective units. Obviously, the cost of these huge amounts of chemicals would be far greater than the cost of distillation. Furthermore, with such high salt concentrations, the large volume of rinse water required to remove the excess regenerant and the salts displaced by regeneration, compared with the volume of useful effluent, makes the process impractical for the treatment of sea water.

However, demineralizing may prove useful for reducing the high salt content of brackish waters, which periodically trouble industrial plants in certain sections of the country. For example, in the highly industrialized area along the Delaware River from Philadelphia to Wilmington, the river water becomes brackish during periods of drought or low water. Even when large-capacity storage basins are provided so that the total water requirements may be drawn only at ebb tide when the salt content of the water is at a minimum, the dissolved solids are sufficiently high to reduce substantially steam-plant capacities and, in some instances, to force a boiler plant shutdown. The composition of Delaware River water during normal periods and at high tide and low tide during drought periods is given in Table V.

In order to demineralize waters of such high electrolyte content economically, special operating procedures must often be employed. Several of them are described in the following sections.

Figure 1 illustrates the usual demineralizing installation. This is suitable for the large majority of cases. However, with waters of very high electrolyte content, such as those described above, particularly where high-quality effluent is desired, it may be advisable to modify the method of operation to obtain the desired effluent quality at economical operating costs.

One method is to use two pairs of cation exchanger and anion exchanger units in series. However, this usually increases the initial cost and the space requirements, and it is therefore not practical.

Partial Recycling. Another method of obtaining economical operation on a water of high electrolyte content may be described as partial recycling. In this procedure a portion of the demineralized water (taken either from the outlet of the anion exchange unit or the outlet of the degasifier) is mixed with the raw influent to reduce the salt concentration. Figure 4 illustrates such an arrangement.

When partial recycling was used to convert a raw water containing 650–700 p. p. m. of dissolved salts to a demineralized water containing 6 p. p. m. of dissolved salts, a pilot plant installation gave an average run of 800 gallons of good water. Using the same equipment and raw water, but operating by the normal single-pass method, the yield of good water per run was only 525 gallons.

Table V. Delaware River Water at Marcus Hook, Penna.

	Typical Analysis during Normal Period	Typical Drought-Period Analysis	
		At high tide	At low tide
P. P. M. as $CaCO_3$			
Total Hardness	91	629	300
Sodium Salts	54	3871	1346
Alkalinity to methyl orange	50	50	50
Chlorides	25	4200	1440
Sulfates	70	250	156
Iron, p. p. m. as Fe	1.8	2.0	4.5

Multiple Demineralizing. Under certain conditions a total recycling process may be applied. The equipment for this procedure is also shown in Figure 4. This procedure requires a minimum of chemical control while producing a maximum yield of good-quality effluent. A volume of water, chosen on the basis of the water composition and capacity of the demineralizing installation, is passed through both units. When the prearranged volume of water has entered the first storage tank, a float switch shuts off the raw water influent and starts circulation of the water from the storage tank, through the ion exchangers, and into a second storage tank. If this second pass has not sufficiently reduced the electrolyte content, the operation may be repeated until the effluent quality is acceptable or until the total electrolyte content, as measured by a conductivity instrument, is not appreciably reduced by further recycling. If acceptable, the water is pumped to service. When no further reduction in electrolyte content is obtained on repeated passes, both ion exchangers are regenerated, and the partially demineralized water is further recycled until it is of satisfactory quality.

It is important to note that this scheme does not require regeneration of the ion exchangers after each successive pass of the same portion of influent water. Regeneration is required only when no further reduction in electrolyte content is produced on successive passes through the exchangers.

Comparative experiments were made on a water similar in composition to an average brackish Delaware River water, using ordinary single-pass operation, partial recycling, and multiple demineralizing. The experimental conditions and results of these runs are given in Table VI.

Under the conditions used, it was impossible to obtain a good-quality effluent by single-pass operation. Partial recycling resulted in the formation of only a limited amount of good-quality water, and this was increased but slightly by increasing the ratio of recycled volume to effluent volume from 3 to 5. Multiple demineralizing, however, produced an excellent yield of good-quality effluent. It required only three passes of the liquid through the ion exchangers to obtain this result. Since a single influent was treated by the same ion exchangers regenerated in the same manner, these experiments provide a clear picture of the wide variations in performance which may be brought about by altering the operating procedure.

Rinse Recycling. After regeneration, the anion exchanger is normally rinsed with cation exchanger effluent until the final effluent has a low methyl orange alkalinity. Further economies may be obtained in any of the foregoing procedures by recycling rinse effluent from the anion exchanger to the cation exchanger after the total electrolytes of the rinse effluent fall below those of the raw water (*13*). A twofold saving is achieved by this procedure. In the first place, the quantity of raw water wasted in the rinse operation is reduced. In the second place, a smaller proportion of the cation exchanger and anion exchanger capacities are needed to treat the rinse water, thereby leaving additional capacity available for the useful run.

In one test on a raw water containing 8.55 meq. per liter electrolytes (6.15 chlorides plus sulfates and 2.40 bicarbonates), the usual rinse procedure required 100 gallons of raw water to reach an anion exchanger effluent quality of 5 p. p. m. methyl orange alkalinity, 2 p. p. m. chlorides, and 2 p. p. m. sulfates. By recycling the rinse after 30 gallons (at which point the total electrolytes had fallen to 6.4 meq. per liter), the useful cation and anion exchanger capacity was increased by more than 15 per cent, while the wasted raw water required for rinsing was reduced by more than 50 per cent.

Initial and Operating Costs

Demineralizing costs depend upon the quantity and nature of the salts present in the raw water. For example, a water high in bicarbonates but low in sulfates and chlorides will require smaller cation exchanger and anion exchanger installations than a water of equal electrolyte concentration but low in bicarbonates. In addition to the smaller initial investment, the high-bicarbonate water will require a smaller chemical cost for regenerants since the carbonic acid is not absorbed by the anion exchanger in step 2 but is removed without further cost in the degasifier. A rough estimate of demineralizing operating costs for a raw water of known composition may be made from Figure 5.

These calculations are based on a cost of 2 cents per pound for 66° Bé. sulfuric acid and 2 cents for soda ash. These costs would be much lower in the case of large installations or in the case of plants that use these chemicals for other processes so that purchasing is done in carload lots. Methyl orange alkalinity is removed by step 1 and aeration, and hence consumes only acid. The chlorides plus sulfates (theoretical mineral acidity) require acid for step 1 regeneration and alkali for step 2 regeneration, and the chemicals consumed for these two steps must therefore be added to arrive at the cost of removing this theoretical mineral acidity.

Table VI. Comparison of Demineralizing Procedures

Influent

Cations, P. P. M. as $CaCO_3$		Anions, P. P. M. as $CaCO_3$	
Ca^{++}	102	Alkalinity (methyl orange)	110
Mg^{++}	312	Cl^-	2457
Na^+	2368	SO_4^{--}	215
Total	2782	Total	2782

Ion Exchangers[a]

Type	Name	Volume, Ml.	Tube Diam., Cm.	Regenerant	Concn., Normality	Volume, Ml.
Cation	Zeo-Karb	400	3.5	H_2SO_4	0.403	1200
Anion	De-Acidite	200	2.3	Na_2CO_3	0.75	280

Results

Procedure	Best Effluent Produced, P. P. M. as $CaCO_3$				
	Total hardness	Methyl orange alkalinity	Cl^-	SO_4^{--}	Yield of this quality, ml.
Single pass	28	29	1	0	500
Partial recycling					
3 recycle, 1 effluent	1	4	0	0	500
5 recycle, 1 effluent	1.5	8	1	0	800
Multiple demineralizing	1–2	3	1	0	2250

[a] Flow rate, 100 ml. per minute; regenerant contact time, 30 minutes.

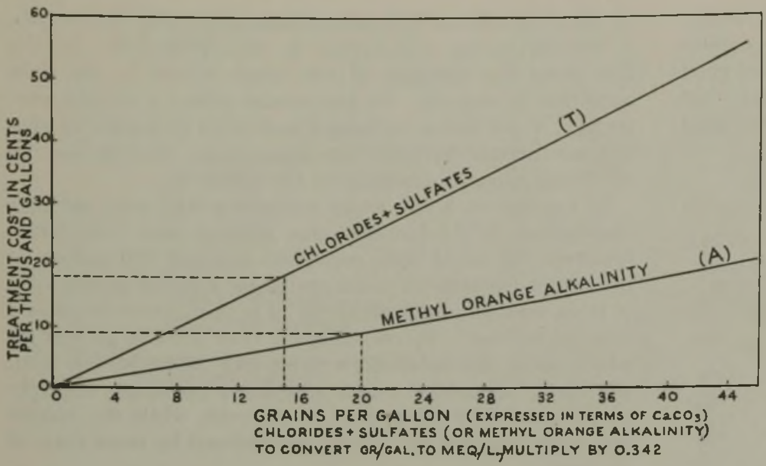

FIGURE 5. DEMINERALIZING REGENERATION COST

Costs can be read directly from these curves as shown by the following example: Raw water contains 20 grains methyl orange alkalinity per gallon and 15 grains theoretical mineral acidity. From 20 grains on abscissa (Figure 5), follow dotted line to curve *A* and then follow horizontally to ordinate, arriving at cost of 9 cents per 1000 gallons for alkalinity removal. From 15 grains on abscissa, follow dotted line to curve *T* and then follow horizontally to ordinate, arriving at cost of 18 cents per 1000 gallons for theoretical mineral acidity removal. Thus the total cost of demineralizing this water is $9 + 18 = 27$ cents per 1000 gallons, based on the chemical costs stated above.

Other Applications

Two-step demineralizing by ion exchange has also been applied to the removal of electrolytes from solutions of neutral organic materials. For some years numerous investigations have been carried on in this laboratory and in actual plants in various parts of the country in demineralizing sugar solutions at various stages of beet sugar manufacture and cane sugar refining. As is well known, these refining processes consist essentially of successive vacuum evaporations, followed by sugar crystallizations for the separation of the pure sugar from the mother liquor carrying the dissolved mineral impurities. The actual removal of a substantial portion of these dissolved impurities by two-step demineralizing, at certain steps in the process, makes it possible to crystallize a larger proportion of the sugar from these solutions, and actual experiments have also shown lower ash content in the sugar thus produced. Demineralizing experiments carried out in a beet sugar factory showed a reduction in ash content of the sugar sirup from 0.87–0.89 to 0.08–0.15 per cent in single-pass operation.

The value of this increased yield and improved quality must be balanced against the operating costs and fixed charges involved in the demineralizing process. Such costs also include required replacement of ion exchange material, which loses capacity at a somewhat greater rate when used with these more contaminated solutions. Experiments with the earlier ion exchange materials available in past years were successful in producing increased yields and improved quality of product. However, the economic balance of more and better yield *vs.* operating and depreciation costs was not very favorable. But with the better ion exchange materials now available and with improved methods of using these materials, recent experiments show a more favorable trend. Several of the special operating methods described in the preceding sections are specially applicable to demineralizing solutions of high electrolyte content, such as impure sugar solutions containing high concentrations of electrolytes. Other experiments on purification of sugar solutions by ion exchange were reported recently (*11*).

Gelatin solutions may also be demineralized (*7*). Using single-pass operation, the ash content of one gelatin sample was reduced from 2.6 to 0.09 per cent. This process was carried out at 40° C., using a 5 per cent gelatin solution.

Demineralizing has also been suggested for the removal of salts from enzymes, glycerol solutions, and other solutions of organic materials. Further investigations in these and various other fields are in progress in this laboratory.

Acknowledgment

The cooperation of C. Calmon, P. C. Goetz, F. C. Nachod, R. Riley, and other associates in making this development a reality is hereby acknowledged.

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PRESENTED before the Division of Water, Sewage, and Sanitation Chemistry at the 104th Meeting of the AMERICAN CHEMICAL SOCIETY, Buffalo, N. Y.

Specific Heat and Viscosity Nomographs for Calcium Chloride Brines—Correction

In the explanatory text accompanying these nomographs on page 1532 of the December, 1942, issue, the equation at the top of the second column should read as follows:

$$\log \mu = a + b[t - (10)^{0.154\,t\,-\,6.075}]$$

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Equilibrium Moisture Content of Dehydrated Vegetables

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The equilibrium moisture content of some dehydrated vegetables was determined by allowing them to attain equilibrium in air-free desiccators containing sulfuric acid solutions to control the relative humidity. Fresh vegetables were used for desorption measurements and dried vegetables for adsorption. Experiments were carried out on carrots, cabbage, yams, spinach, and white potatoes. The sorption isotherms for all the vegetables are S-shaped and are characterized by an inflection point in the neighborhood of 5 per cent moisture content.

Measurements were also made on blanched white potatoes. Blanching causes a decrease in the equilibrium moisture content. The decrease is ascribed to a change in the physical state of the starch granules in the potato.

Application of the sorption data to dehydration and packaging of vegetables is briefly discussed.

IN THE course of a pilot plant investigation of the dehydration of vegetables, it was found necessary to determine the moisture retained by dehydrated vegetables after they had been allowed to reach equilibrium in an atmosphere of known humidity and temperature. The information was needed to define the limits for the dehydration of fresh vegetables and for the moisture uptake of dehydrated vegetables under any given conditions of temperature and humidity.

The moisture uptake or loss in dehydrated vegetables is a sorption phenomenon and depends on temperature and humidity. As in the case of cotton, paper, and other materials investigated by Wilson and Fuwa (*11*), it is found that the rate of change of the moisture content with temperature is small when the moisture is represented as a function of relative humidity rather than absolute humidity.

In the present work, measurements of adsorption and of desorption were made on five vegetables at various relative humidities and at two temperatures. Most of the measurements were made on unblanched vegetables, with the exception of a few on potatoes, where blanched material was also used.

Measurements of sorption by vegetable materials present difficulties not ordinarily encountered with other substances. It is probably not safe to assign a value for the moisture retention of a definite species of vegetable—for example, carrots—because it may differ in properties as a result of differences in variety, chemical composition, maturity, source, and other factors. Within any one carrot there may be differences between the part near the root and that near the top, and also between the outside and the inside portion. In addition, changes in the sample may occur during the course of the measurement as a result of metabolic processes and alterations in the physical structure. In this investigation no exhaustive studies were attempted to determine the effect of these various factors. The measurements were made only on those materials that were used for the pilot-plant dehydration experiments.

Experimental Method

Samples of vegetables were placed in vacuum desiccators, each of which served as a constant-humidity chamber. The vapor pressure of water in a desiccator was controlled by an aqueous sulfuric acid solution of known concentration, and the desiccator was kept at constant temperature so that the relative humidity within the desiccator was fixed. The water content of the samples placed in the desiccators changed with time until equilibrium was reached. The samples were removed from the desiccators at various intervals and weighed. When no further change in weight occurred, as indicated by two successive weighings, a sample was considered to have reached equilibrium. The moisture content of the sample was obtained from the difference between the weight at equilibrium and the weight of the sample after the complete removal of water.

This method was first employed by van Bemmelen (*2*) to determine the water absorption by silicic acid gels. Later Zsigmondy showed (*12*) that the time of approach to equilibrium can be greatly reduced by evacuating the air from the desiccators. This effect was confirmed in the present investigation. At the highest relative humidity studied (77 per cent), less than 2 days were required to reach desorption equilibrium in the absence of air and about 4 days in the presence of air.

To reduce further the time of approach to equilibrium, it is important that the samples be as thin and have as large a surface as possible to facilitate the exchange of water vapor between the interior of the sample and the surrounding atmosphere. Whenever possible—for example, with carrots, yams, and white potatoes—the practice was to prepare the samples in the form of thin sections cut on a microtome. The thickness was 320 microns. Thinner sections proved too difficult to handle. With leafy vegetables such as spinach, parts of the leaf were used directly without any sectioning. The thin sections were mounted on special sample holders made of glass and designed in the shape of a spike mounted on a circular base. Each holder was about 25 mm. high with a base approximately 18 mm. in diameter and was marked with an identifying number. The sections of vegetable were impaled on the spike of the previously weighed holder, and the unit could thus be moved about conveniently without disturbance of the fragile sample. The holders weighed about 0.5 gram each and were designed to fit snugly in weighing bottles which were 30 mm. high with a diameter of 20 mm. Sufficient material was used on each holder to make a sample weighing between 0.5 and 1.0 gram.

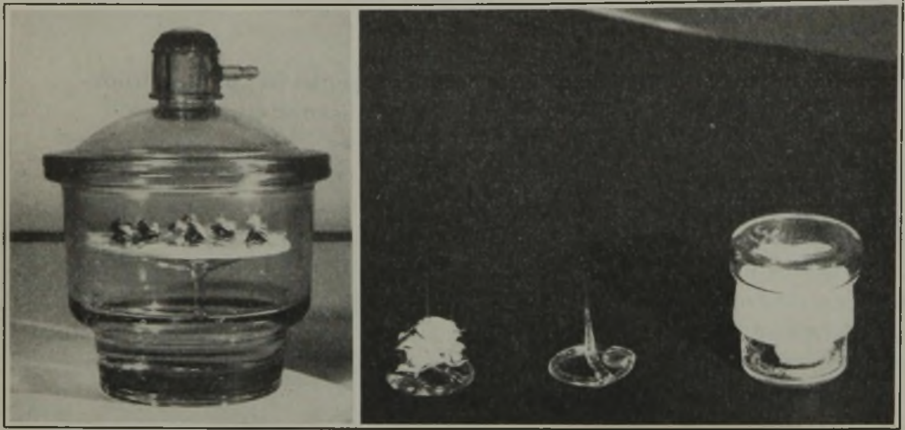

Figure 1. *Left:* Desiccator Filled with Samples for Sorption Determination. *Right:* Loaded and Unloaded Sample Holder, and a Holder in a Weighing Bottle

The desiccators were the all-glass vacuum type, about 150 mm. in diameter. Each one was filled with approximately 250 cc. of sulfuric acid solution of known concentration. The volume of the acid was large enough so that any exchange of water vapor between the solution and the samples, during the approach to equilibrium, was not sufficient to change the concentration of the acid appreciably. Another factor which was effective in minimizing changes in concentration of the acid resulted from the fact that each desiccator was usually filled with two types of samples, one undergoing adsorption and the other desorption. In order to lessen the chance of accidentally splashing the acid over the samples, the perforated porcelain plate which supported the samples was placed high above the level of the solution on specially constructed glass supports. The arrangement is shown in Figure 1. The top of the plate was divided radially into six sections by means of glass rods cemented to the surface of the plate, in order to keep the sample holders from sliding or turning over on the slippery surface of the plate. Each desiccator was capable of holding about twenty-four samples. Five desiccators were used, each one containing a different acid concentration to cover a range of relative humidities from about 10 to 75 per cent.

The experimental method has the advantage of permitting simultaneous measurements to be made on a great many samples at different humidities with very simple equipment. A disadvantage is the necessity for interrupting the experiment to make weighings. The interruptions can be obviated by the use of a McBain-Bakr (*6*) quartz spiral balance. Such a balance is now being set up in this laboratory.

Sampling. The fresh vegetables were sampled as follows: The carrots, yams, and potatoes were first trimmed and scraped. Representative samples were made up by combining on each sample holder the microtome slices taken from four different parts of the vegetable at approximately equidistant points along its length. The intention was to approximate in the sample the composition of the whole vegetable in case there should be any difference in the sorptive properties among the various parts of the vegetable. In the case of spinach, whole leaves were cut up into smaller pieces and mounted on the holders. Cabbage presented somewhat greater difficulties because of the possibility that the inside leaves might differ from the outside ones. The procedure finally adopted was to remove the inside core of the cabbage, divide the head into four quarters, and chop one of the quarters into small particles with the aid of a vegetable salad chopper. If subdivision is carried too far, a marked loss of plant juices occurs, and care had to be taken not to go beyond this point. Samples were made up by placing small amounts of the chopped material in the weighing bottles ordinarily used in conjunction with the sample holders. The use of the spiked holders was not practicable in this case. Blanched potatoes which were ground in a food chopper also had to be handled directly in the weighing bottles.

Treatment of Samples. After all the samples for an experiment had been prepared, they were divided into two groups. One group was used for adsorption and the other for desorption experiments. The desorption samples were immediately distributed among the desiccators corresponding to the different relative humidities and were allowed to stand at room temperature. Before the adsorption samples were placed in the desiccators, they were dried by heating in a vacuum oven at 70° C. for 3 to 4 hours. No attempt was made to remove all the water from the samples; it was considered sufficient to lower the water content below the value which obtains at the lowest relative humidity. While it is conceivable that drying at an elevated temperature might change the adsorptive properties of the material, this method has been used because it is relatively rapid and practicable. In a few experiments on carrots, preliminary drying was at room temperature in evacuated desiccators containing Anhydrone (anhydrous magnesium perchlorate), and the samples were compared with those dried at 70° C. The adsorption values obtained in the two cases did not differ by more than the experimental error of the measurements. Furthermore, the agreement found in most cases between adsorption and desorption values would seem to indicate that any changes that may occur at the higher temperature are not significant.

The desiccators were evacuated at room temperature to a pressure of about 5 mm. of mercury and were transferred to a constant-temperature oven maintained to within ±1° C. After 2 days the samples were quickly transferred to the small weighing bottles and weighed. They were returned to the sulfuric acid desiccators, and another weighing was made 2 or 3 days later. The last weight checked the preceding one within less than 0.3 mg., which was considered evidence that equilibrium had been attained.

After the weights at equilibrium were determined, the dry weight of the samples was obtained by heating in a vacuum oven at 70° C. for 6 hours. This procedure is the same as the official method adopted by the Association of Official Agricultural Chemists for moisture in dried fruits (*1*), and gave results in agreement with a slower method of drying in vacuum at room temperature over phosphorus pentoxide.

At the end of each experiment the concentration of sulfuric acid in each desiccator was determined from measurements of the specific gravity by a Westphal balance. The humidity in the desiccators was obtained from tables given by Wilson (*10*) for the relation between vapor pressure of water and concentration of sulfuric acid.

Results

The results of the measurements were calculated as follows:

$$\text{Moisture content (\% of dry weight)} = \frac{(A - B)}{B} \times 100$$

where A = weight of sample at equilibrium
B = weight of completely dehydrated sample

It should be noted that $(A - B)$ is numerically a very small quantity and is, therefore, subject to a large percentage error resulting from the relatively small percentage errors in the individual values of A and B.

Measurements were made on Savoy cabbage, Prickly Winter spinach, Puerto Rico yams, Russet white potatoes, and Chantenay and Imperator varieties of carrots.

The experimental data in Table I were used to draw the isotherms in Figure 2. Each value for moisture content in Table I is an arithmetical mean of the results obtained for two or three samples measured simultaneously under the same conditions. Deviations from the mean value for the individual samples were not greater than ±0.5 for the lowest relative humidity (10 per cent), and ±1.0 for the highest relative humidity (77 per cent).

The results obtained for adsorption are in agreement with those obtained for desorption. If any hysteresis effect exists, it is probably small, and the precision of the experimental data is not sufficient to detect it. The isotherms for adsorption and desorption were therefore represented in Figure 2 by single curves. It is important to note that, while sorption measurements are ordinarily made on the same sample of material over the entire range of the isotherm, in the present case different samples were used for desorption and adsorption measurements and for different humidities. There was also a slight difference in the history of the adsorption and desorption samples as explained previously. In view of these factors, it can be said that the agreement between the adsorption and desorption measurements is satisfactory.

TABLE I. EXPERIMENTAL DATA FOR WATER SORPTION OF VEGETABLES

Relative Humidity, %	Moisture, % of Dry Wt.	
	Desorption	Adsorption
CABBAGE, SAVOY, UNBLANCHED Temperature, 37° C.		
10.9	2.5	2.3
29.8	4.9	5.5
49.0	10.1	9.8
64.7	17.8	18.4
77.1	30.8	29.8
Temperature, 70° C.		
15.8	2.3	1.9
53.2	6.8	8.7
YAMS, PUERTO RICO, UNBLANCHED Temperature, 37° C.		
11.5	3.1	3.5
30.5	5.2	6.1
49.0	8.4	9.8
64.7	12.9	13.3
77.3	20.5	20.3
Temperature, 70° C.		
15.8	2.7	3.1
53.2	7.4	7.0
SPINACH, PRICKLY WINTER, UNBLANCHED Temperature, 37° C.		
12.0	3.9	3.4
31.5	6.1	5.3
48.8	9.7	8.5
64.7	15.1	14.1
76.7	27.2	21.6
Temperature, 70° C.		
13.9	1.3	1.0
52.2	5.2	3.1
WHITE POTATOES, RUSSET Unblanched, 37° C.		
11.4	4.6	4.4
30.9	7.4	7.4
49.1	10.8	11.0
64.4	14.5	14.0
76.9	19.4	18.5
Blanched, Not Dehydrated, 37° C.		
12.3	1.7	4.5
49.8	6.4	9.8
Blanched, Not Dehydrated, 70° C.		
15.8	1.0	3.4
53.2	5.3	7.7
Blanched, Dehydrated, 37° C.		
9.2	3.0	2.2
31.1	6.7	6.0
49.6	8.7	8.4
CARROTS, CHANTENAY, UNBLANCHED Temperature, 37° C.		
6.0	1.9	0.7
10.2	2.5	1.3
29.3	5.2	4.6
48.4	11.5	10.9
77.1	32.9	32.4
Temperature, 70° C.		
33.4	6.1	5.5
67.4	18.0	16.7
CARROTS, IMPERATOR, UNBLANCHED Temperature, 37° C.		
12.3	2.0	1.9
49.8	9.7	11.1

That previous treatment can markedly affect the sorptive properties of vegetables is illustrated by the results obtained on potatoes. Measurements were made on blanched and unblanched (fresh) potatoes. The blanching process consisted, in effect, of cooking in live steam for 30 minutes. After blanching, the potatoes were mashed and then dehydrated. While the adsorption and desorption results for the unblanched potatoes were in satisfactory agreement, those on the blanched potatoes prior to dehydration (Table I) show an anomaly in having the adsorption values much higher than the desorption values. For example, at a relative humidity of 50 per cent, the moisture content at 37° C. for adsorption was 9.8 per cent, while that for desorption was 6.5 per cent. At 70° C. the values were 7.3 and 4.7 per cent, respectively.

An explanation for this behavior may be made by taking into account the changes which occurred in the physical characteristics of the desorption and adsorption samples during the approach to equilibrium. The adsorption samples had first been subjected to rapid vacuum drying and had assumed a puffed-up, porous structure. The desorption samples, on the other hand, had dried slowly and formed a shrunken, hard, solid mass in which the partially gelatinized starch grains had probably coagulated into larger particles of smaller total surface and thus were not capable of holding much water.

The change that occurred in the desorption samples is apparently irreversible, as shown by the results on a set of blanched dehydrated potatoes. The treatment in this case was as follows: The blanched potatoes were first dried slowly (to about 5 per cent moisture content) to form the shrunken, coagulated product. Part of this material was used for adsorption and another part for desorption experiments. The desorption samples were first allowed to readsorb a large amount of water at high humidity (nearly 100 per cent) and were then brought to equilibrium at a lower humidity. The adsorption samples received the usual preliminary drying treatment in vacuum at 70° C. The moisture content for the adsorption and desorption samples was nearly identical, showing that no further change in the samples had occurred after the initial slow drying.

The isotherms in Figure 2 are similar to those referred to by Emmett (*4*) as the S-shaped isotherms which he found in the study of nitrogen adsorption on the surface of inorganic materials. They are characterized by an inflection point which is considered by Emmett (*4*) and other investigators (*5, 7, 9*) to represent the approximate limit of ordinary surface adsorption occurring at low humidities, and the beginning of "multilayer adsorption" or "capillary condensation" occurring at high humidities. It is interesting to note that, for all the vegetables studied in this investigation, the inflection point at 37° C. occurs in the neighborhood of 20 per cent relative humidity, corresponding to a moisture content of about 4 to 6 per cent. This similarity in behavior would seem to indicate that the plant tissue in all these vegetables is probably sufficiently similar in its adsorptive properties and in the extent of its adsorptive surface so that

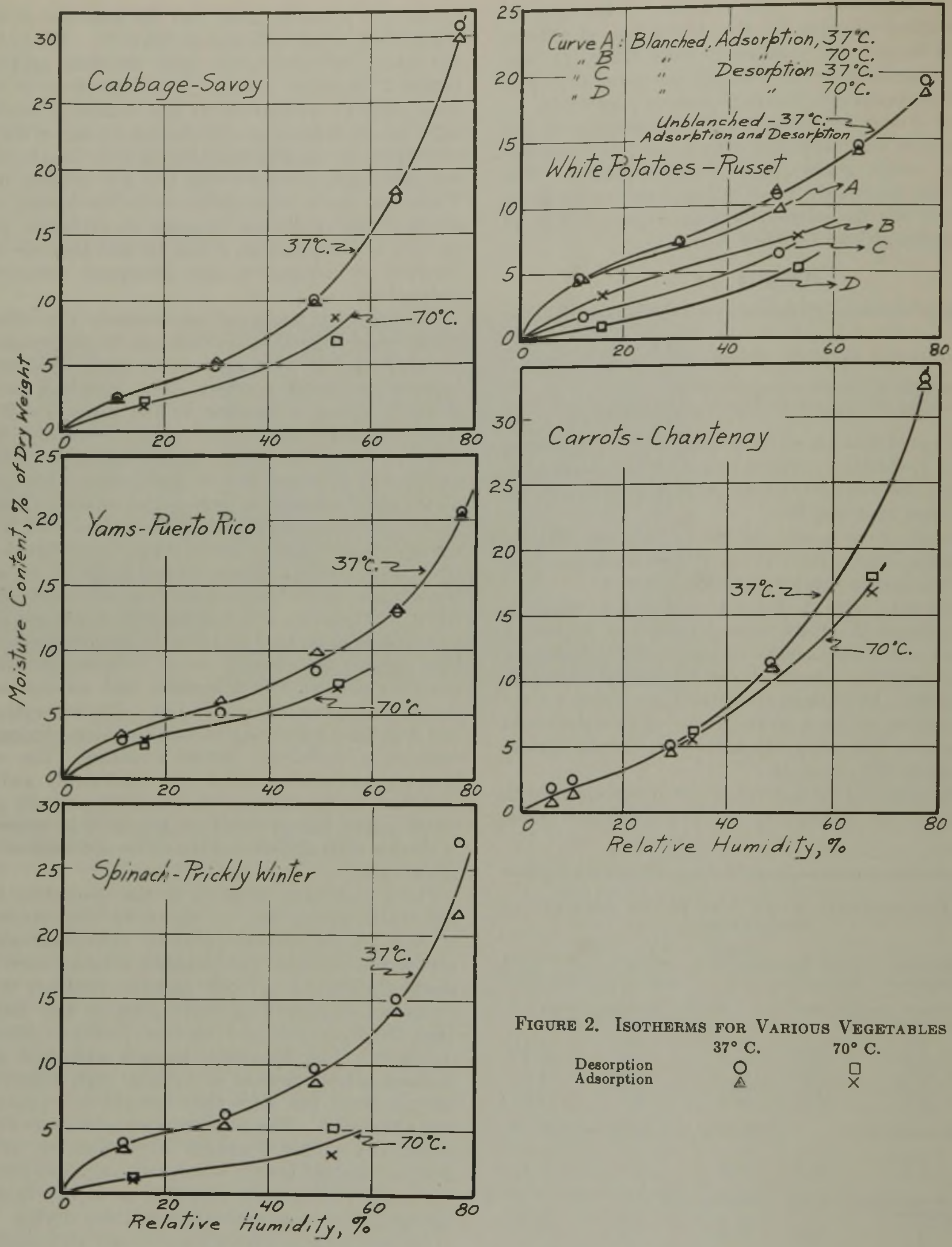

FIGURE 2. ISOTHERMS FOR VARIOUS VEGETABLES

	37° C.	70° C.
Desorption	○	□
Adsorption	△	×

the ordinary physical or surface adsorption is of the same order of magnitude in all cases.

At higher humidities, where capillary condensation occurs, differences may be expected to occur as a result of differences in the sizes of capillaries and in chemical composition. This is shown in Table II where the values of the moisture content taken from Figure 2 are arranged to permit a comparison of results for different vegetables at the same relative humidity. The differences become most apparent at high humidities. At 37° C. and a relative humidity of 70 per cent the moisture content varies from the lowest value of 15.3 per cent for yams to the highest of 24.2 per cent for carrots.

At constant relative humidity the moisture content decreases with increasing temperature. The magnitude of the effect for a temperature rise from 37° to 70° C. is apparent from Figure 2 or Table II. While the experimental measurements at 70° C. are not sufficiently detailed to define the isotherms accurately, an attempt was made to indicate them as shown in Figure 2. The temperature effect varies with the different vegetables. For carrots the isotherms at 37° and 70° C. are nearly identical at low humidities and begin to diverge at a relative humidity of 30 per cent. For spinach, the two corresponding isotherms differ greatly even at very low humidities. At 30 per cent relative humidity the moisture content for spinach at 37° C. is 5.6 per cent,

Table II. Equilibrium Moisture Data from Isotherms for Vegetables

	Moisture Content, Per Cent of Dry Weight													
									Potatoes, Russet					
										Blanched				
	Cabbage, Savoy, Unblanched		Yams, Puerto Rico, Unblanched		Spinach, Prickly Winter, Unblanched		Carrots, Chantenay, Unblanched		Unblanched	Desorption		Adsorption		
Relative Humidity, %	37° C.	70° C.	37° C.	70° C.	37° C.	70° C.	37° C.	70° C.	37° C.	37° C.	70° C.	37° C.	70° C.
10	2.3	1.4	3.2	2.1	3.4	0.9	1.8	1.8	4.2	1.7	0.6	4.0	2.3
20	3.8	2.5	4.6	3.4	4.6	1.6	3.1	3.1	6.0	2.6	1.3	5.6	3.9
30	5.2	3.6	5.8	4.3	5.6	2.1	4.9	4.9	7.4	3.7	2.1	6.8	5.2
40	7.3	5.0	7.2	5.2	7.3	2.8	8.0	7.4	8.9	4.8	3.2	8.0	6.2
50	10.3	6.9	9.2	6.6	9.5	3.8	11.9	10.4	10.9	6.5	4.7	9.8	7.3
60	15.1	...	11.6	...	12.4	...	17.1	14.0	13.2	...	...	...	...
70	22.2	...	15.3	...	17.9	...	24.2	..	16.1	...	...	...	...

which is more than double the 2.1 per cent value obtained at 70° C. It is difficult to say now whether this high temperature coefficient is wholly accountable by the variation of sorption with temperature, or whether it is partly due to the change in sorption resulting from physical or chemical changes which might occur in the material at the higher temperature.

The sorption of water by more than one variety of a vegetable was determined only in the case of carrots. The data on the Imperator variety (Table I) are incomplete, but they are sufficient to indicate that the moisture content, at least up to 50 per cent relative humidity, was nearly the same as that for the Chantenay carrots.

Application of Results to Dehydration of Vegetables

In the dehydration of vegetables it is necessary to lower the moisture content far enough to ensure that the product will not undergo appreciable decomposition and spoilage on subsequent storage. The upper limit of permissible water content was determined empirically (*8*) for a number of vegetables; and while it varies somewhat for the different vegetables, it lies in the neighborhood of 5 per cent. It is worthy of note that the 5 per cent value corresponds approximately to the value found at the inflection point of the isotherms for all the vegetables studied here. From this observation it might be inferred that the deterioration of vegetables will not be sufficiently reduced until the moisture content is lowered at least below the region of capillary condensation (below the inflection point).

If further investigations bear out this hypothesis, the experiments to determine the permissible water content of other dehydrated vegetables would need to be confined only to the region below the inflection point, as defined by the isotherms.

The isotherms also provide information for the limiting conditions of the dehydration process. This information is important in designing dehydrating equipment. Regardless of whether vacuum drying or air drying is used, the isotherms make it possible to specify the maximum permissible pressure (for vacuum drying) or the maximum permissible humidity (for air drying) to reduce the moisture content to a desired value. If the moisture content of cabbage, for example, is to be 5 per cent, the relative humidity of the drying air would have to be less than 28 per cent at 37° C. or less than 40 per cent at 70° C. (Figure 2).

Knowledge of the equilibrium moisture content is also important in the study of packaging of dehydrated vegetables. The equilibrium values yield information concerning the vapor pressure of water within the package and are thus helpful in estimating, from known permeability data (*3*), the effectiveness of the packaging membrane in protecting the dried material against moisture uptake.

In conclusion it may be said that the results obtained so far are valid only for certain varieties of vegetables and are not sufficient to permit generalizations concerning any one species. This investigation is being continued to include other vegetables and their varieties, and to determine whether moisture content can be correlated with chemical composition and maturity and how it is affected by physical treatments encountered in blanching processes.

Acknowledgment

The authors are grateful for assistance in this work to various staff members of the Western Regional Research Laboratory, and particularly to W. B. Van Arsdel and A. L. Pitman.

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» » » X-Ray Study of Reactions

Orientation of Crystalline Phases on

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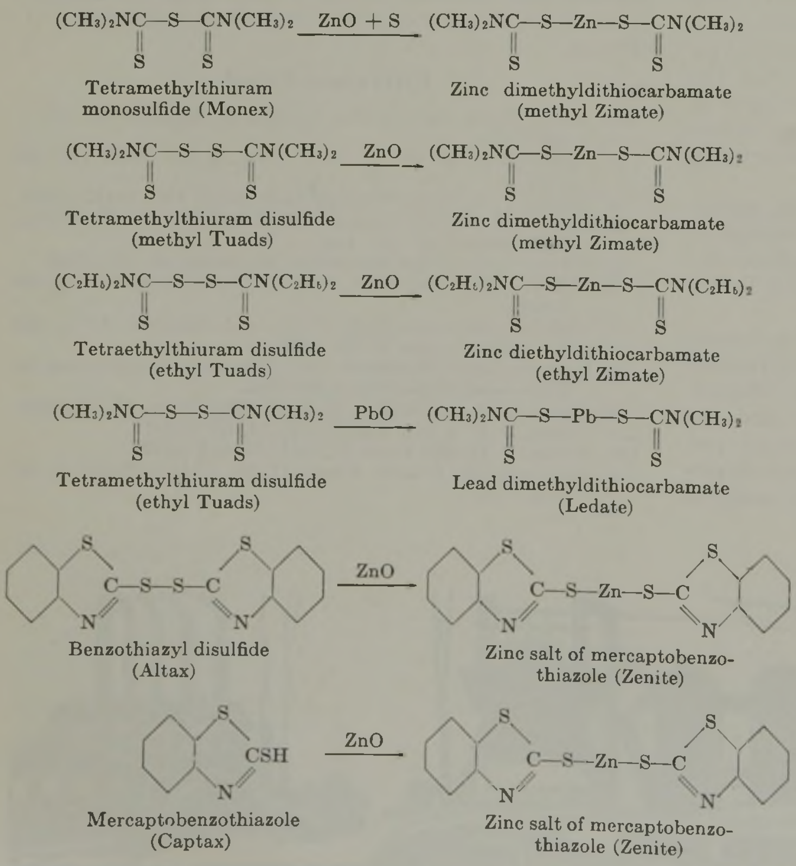
Chemical reactions between accelerator and accelerator activator are shown by the x-ray method to take place in rubber stocks at the curing temperature; e. g., tetramethylthiuram disulfide reacts with zinc oxide to form zinc dimethyldithiocarbamate.

These crystalline accelerator salts are highly oriented in the rubber matrix on stretching. This signifies a strong bond between the rubber crystallites and the grains of accelerator salt. Perhaps this explains some of the desirable physical

ABOUT a year ago, in the course of a systematic survey of the x-ray diffraction patterns of a number of routine rubber samples with different accelerators present, certain similarities were noted in the diffraction effects from the accelerators in these stocks. Close examination of these effects showed that they were identical. The stocks contained the accelerators Tuads, Monex, and Zimate which are chemically similar (Table I); the first is the disulfide, the second, the monosulfide, and the third, the zinc salt. Thus, the diffraction patterns indicate that, on curing, the disulfide and the monosulfide in the presence of sulfur react with zinc oxide to form the zinc salt. This is not a new concept. The zinc salts have been extracted with solvents from stocks similar to the above, and it has been supposed that such reactions occur. However, the extraction method leaves some doubt as to whether the salt was originally present in the rubber matrix or whether it was formed in the solvent on extraction.

TABLE I. REACTIONS BETWEEN ACCELERATOR AND ACTIVATOR



$$(\mathrm{CH_3})_2\mathrm{N}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}-\mathrm{S}-\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{N}(\mathrm{CH_3})_2 \xrightarrow{\mathrm{ZnO + S}} (\mathrm{CH_3})_2\mathrm{N}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}-\mathrm{S}-\mathrm{Zn}-\mathrm{S}-\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{N}(\mathrm{CH_3})_2$$

Tetramethylthiuram monosulfide (Monex) — Zinc dimethyldithiocarbamate (methyl Zimate)

$$(\mathrm{CH_3})_2\mathrm{N}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}-\mathrm{S}-\mathrm{S}-\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{N}(\mathrm{CH_3})_2 \xrightarrow{\mathrm{ZnO}} (\mathrm{CH_3})_2\mathrm{N}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}-\mathrm{S}-\mathrm{Zn}-\mathrm{S}-\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{N}(\mathrm{CH_3})_2$$

Tetramethylthiuram disulfide (methyl Tuads) — Zinc dimethyldithiocarbamate (methyl Zimate)

$$(\mathrm{C_2H_5})_2\mathrm{N}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}-\mathrm{S}-\mathrm{S}-\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{N}(\mathrm{C_2H_5})_2 \xrightarrow{\mathrm{ZnO}} (\mathrm{C_2H_5})_2\mathrm{N}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}-\mathrm{S}-\mathrm{Zn}-\mathrm{S}-\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{N}(\mathrm{C_2H_5})_2$$

Tetraethylthiuram disulfide (ethyl Tuads) — Zinc diethyldithiocarbamate (ethyl Zimate)

$$(\mathrm{CH_3})_2\mathrm{N}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}-\mathrm{S}-\mathrm{S}-\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{N}(\mathrm{CH_3})_2 \xrightarrow{\mathrm{PbO}} (\mathrm{CH_3})_2\mathrm{N}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}-\mathrm{S}-\mathrm{Pb}-\mathrm{S}-\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{N}(\mathrm{CH_3})_2$$

Tetramethylthiuram disulfide (ethyl Tuads) — Lead dimethyldithiocarbamate (Ledate)

Benzothiazyl disulfide (Altax) $\xrightarrow{\mathrm{ZnO}}$ Zinc salt of mercaptobenzothiazole (Zenite)

Mercaptobenzothiazole (Captax) $\xrightarrow{\mathrm{ZnO}}$ Zinc salt of mercaptobenzothiazole (Zenite)

Every crystalline material has its own characteristic x-ray diffraction pattern which is different from that of every other crystalline material, just as the fingerprints of each person are different from that of every other person. Thus, with x-ray "fingerprint" patterns it is possible to identify positively the presence of these salts in the rubber matrix and show that they must have been formed in the rubber mix on curing. Further, it was noted that this crystalline salt is strongly oriented in the rubber matrix on stretching. It seemed advisable, then, to investigate other similar reactions by the x-ray method and to investigate the significance of the strong orientation of these reaction products in the rubber matrix.

Experimental Procedure

The rubber stocks listed in Table I were prepared (in the Vanderbilt laboratory) and tested by the x-ray method (at the University of Illinois). Series A consists of stocks made up according to standard compounding practice. Series B is prepared with larger quantities of accelerator than are usually employed so that the reaction products will be larger in amount and thus more easily detected in the rubber matrix

Involving Accelerators « « «

Stretching of Rubber Stocks

properties imparted when these accelerators are used in higher loadings.

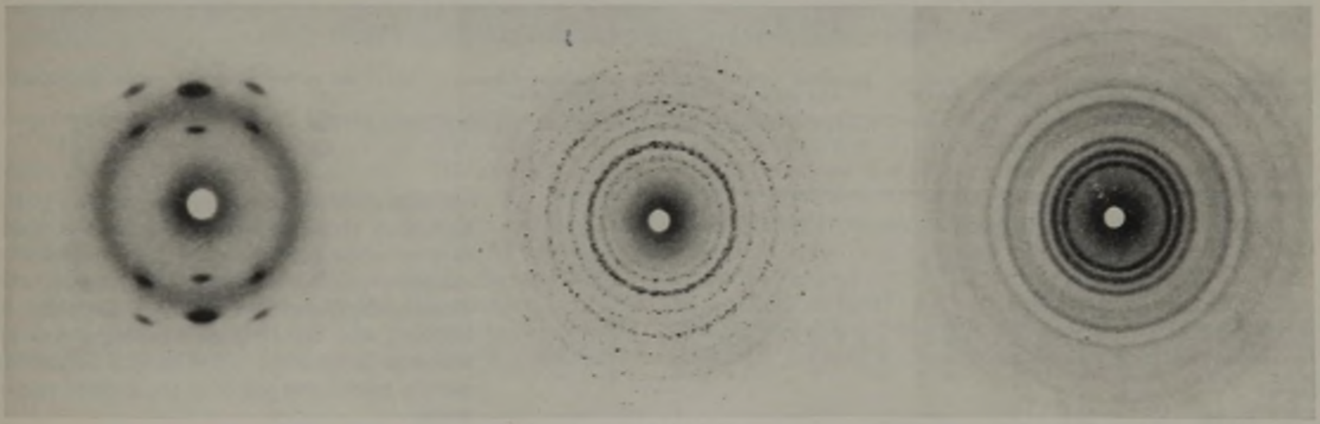
Reinforcing pigments, such as small-particle-size whiting and zinc oxide orient themselves in the rubber matrix on stretching, whereas coarse nonreinforcing pigments do not orient. The orientation of crystal grains in the rubber matrix is correlated with the particle size and shape of the crystal grains as observed under the electron microscope.

by the x-ray method. Series C is the same as series B except that it contains no stearic acid. It was prepared to observe the effect of stearic acid on the chemical reactions between accelerator and activator.

The x-ray diffraction apparatus consisted of a Philips Metalix copper-target tube mounted in a Hayes multiple diffraction unit. The tube was operated at 28 kilovolts potential and 20 milliamperes. The radiation was filtered through one-mil nickel foil to remove the beta radiation. Agfa nonscreen x-ray film was used and developed in Eastman developer.

The rubber samples in most cases were cut from rubber slabs with scissors along the grain of the rubber to give a small sliver. This sliver was simply stretched over the pinhole of the collimating system, and a flat cassette exposure of 2 hours made at a sample film distance of 5 cm. In some cases dumbbell test specimens were used, and the elongation was noted in the usual manner.

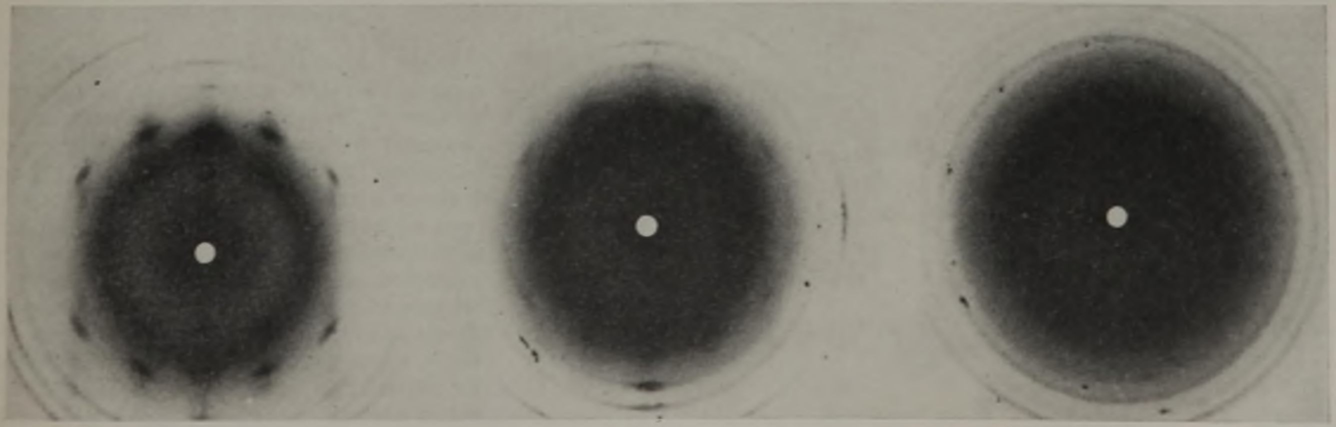
The RCA electron microscope at the University of Illinois was employed to determine the particle shape of some of the materials which showed themselves by the x-ray method to be strongly oriented in the rubber matrix on stretching. The sample screens of the electron microscope were prepared in the usual manner, with a film formed by dropping a dilute



Pure stretched rubber

Powdered ethyl Tuads

Powdered ethyl Zimate

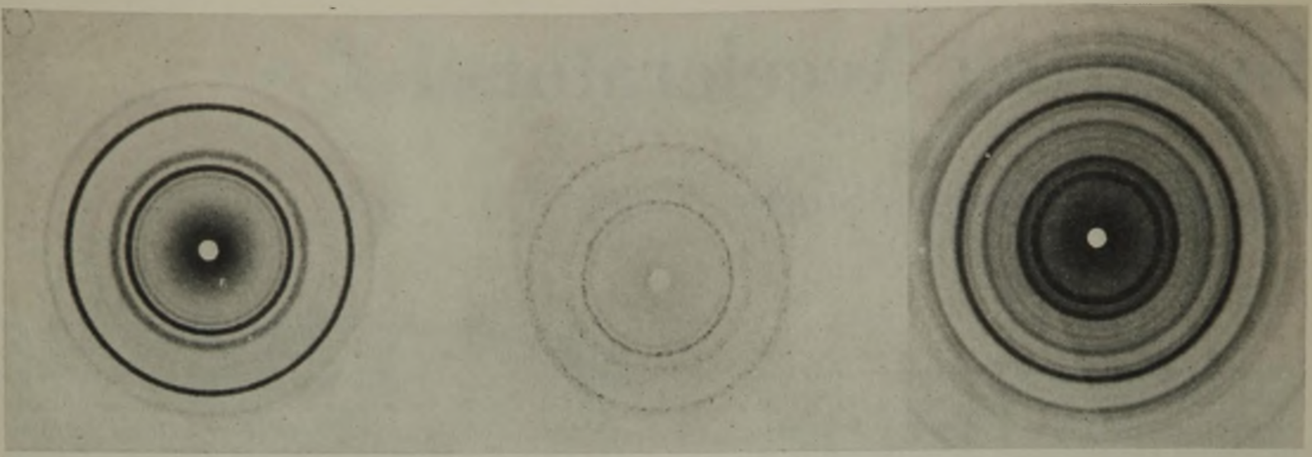


Stretched rubber stock A_4 containing nominal amount of accelerator ethyl Tuads and zinc oxide, showing evidences of ethyl Zimate

Stretched rubber stock B_4, containing 3 per cent ethyl Tuads, showing presence of ethyl Zimate

Stretched rubber stock B_2, with ethyl Zimate added originally

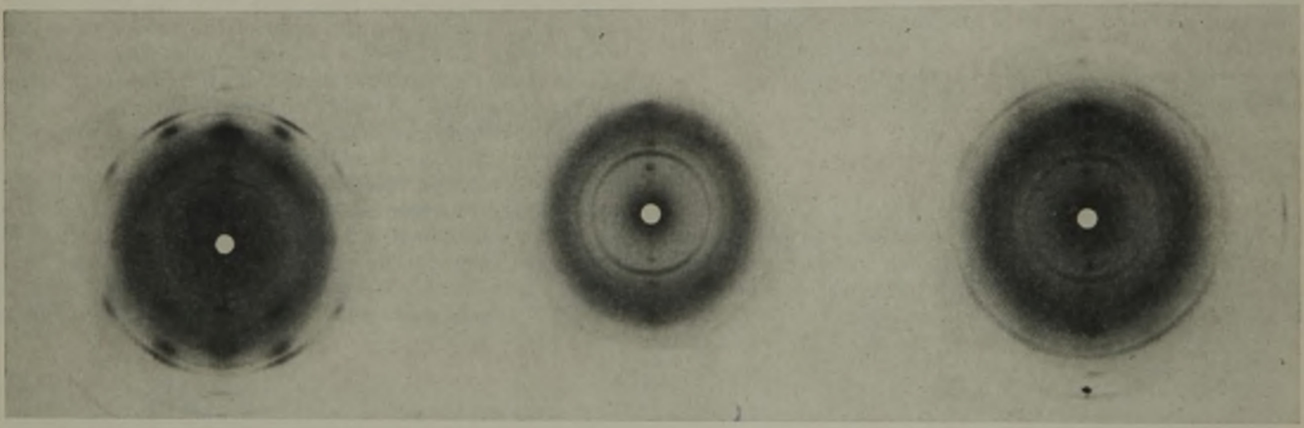
FIGURE 1. X-RAY DIFFRACTION PATTERNS OF ETHYL DERIVATIVES



Powdered methyl Tuads

Powdered Monex

Powdered methyl Zimate



Stretched rubber stock B_3, containing methyl Tuads and showing presence of methyl Zimate

Stretched rubber stock C_6, containing Monex and showing presence of methyl Zimate

Stretched rubber stock C_1, with methyl Zimate originally added

FIGURE 2. X-RAY DIFFRACTION PATTERNS OF METHYL DERIVATIVES

TABLE II. RUBBER STOCKS[a] CURED 30 MINUTES AT 274° F.

SERIES A

Material	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}
Smoked sheet	100	100	100	100	100	100	100	100	100	100
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	1
Zinc oxide	3	3	3	3	3	..	..	..	3	3
Sulfur	2	2	2	2	2	2	2	2	3	3
Methyl Zimate	0.5	...	...	...	...	...	...	...	..	..
Ethyl Zimate	...	0.5	...	...	...	...	...	...	..	..
Methyl Tuads	...	...	0.5	...	...	0.5	0.5	0.5	..	..
Ethyl Tuads	...	...	...	0.5	...	...	...	...	..	..
Monex	...	...	...	...	0.5	...	...	...	..	..
Captax	...	...	...	...	...	...	...	...	1	..
Zenite	...	...	...	...	...	...	...	...	..	1
Litharge	...	...	...	...	...	3	...	...	..	..
Iron oxide	...	...	...	...	...	...	3	...	..	..
Light calcined magnesia	...	...	...	...	...	...	...	3	..	..

SERIES B

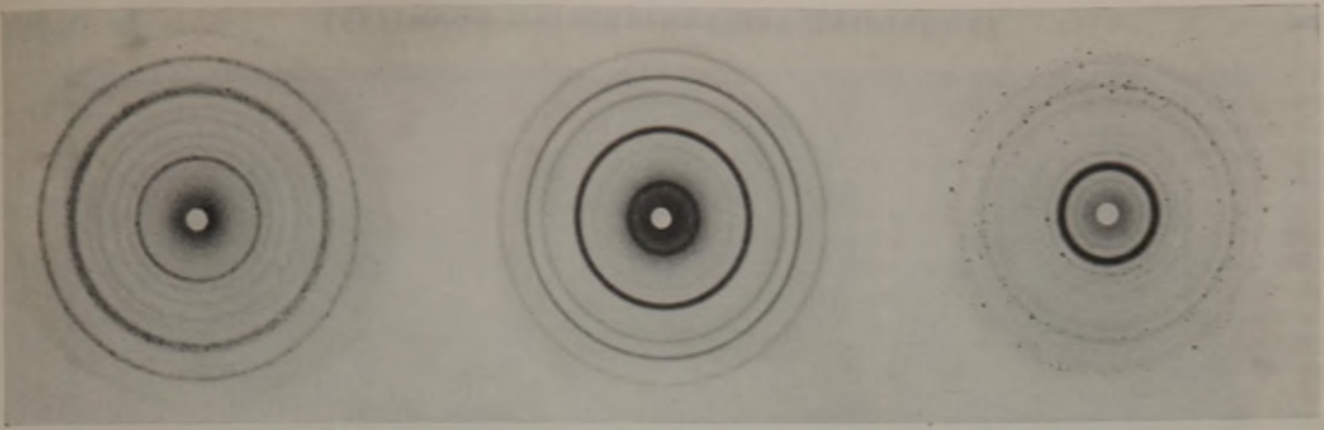
Material	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8	B_9	B_{10}	B_{11}
Smoked sheet	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	3	3	3	3	3	..	..	..	3	3	3
Sulfur	2	2	2	2	2	2	2	2	3	3	3
Stearic acid	1	1	1	1	1	1	1	1	1	1	1
Methyl Zimate	3	..	..	..	..	..	..	..	..	..	..
Ethyl Zimate	..	3	..	..	..	..	..	..	..	..	..
Methyl Tuads	..	..	3	..	..	3	3	3	..	..	..
Ethyl Tuads	..	..	..	3	..	..	..	..	..	..	..
Monex	..	..	..	..	3	..	..	..	..	..	..
Captax	..	..	..	..	..	..	..	..	5	..	..
Zenite	..	..	..	..	..	..	..	..	..	5	..
Altax	..	..	..	..	..	..	..	..	..	..	5
Litharge	..	..	..	..	..	3	..	..	..	..	..
Red oxide	..	..	..	..	..	..	3	..	..	..	..
Light calcined magnesia	..	..	..	..	..	..	..	3	..	..	..

[a] The C series stocks are the same, respectively, as the B series except that no stearic acid is used in them.

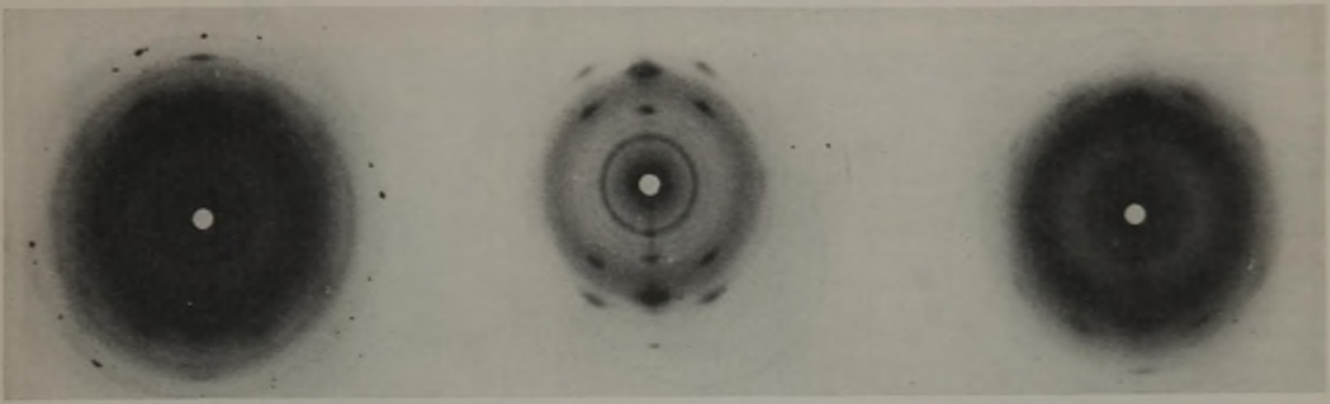
solution of collodion in amyl acetate on water and then stripping the film from the water surface. The materials to be studied—for example, calcium carbonate, zinc oxide, lead dimethyldithiocarbamate—were dispersed in butanol, and the butanol dispersion was allowed to dry on the collodion film before the sample holder was placed in the electron microscope.

Chemical Reactions

Table I gives the chemical reactions which occur in the rubber matrix at the curing temperature. The evidence for these reactions is presented in the form of x-ray diffraction patterns of the various stocks involved. Figure 1 shows a pattern of pure crepe rubber (free from all fillers and compounding agents); it is stretched nearly to break and taken with a monochromatized beam (pentaerythritol crystal monochromator). The patterns of ethyl Tuads and ethyl Zimate are "fingerprints" of these compounds. The relative intensities for the different interferences are very different in the two. Each has intense long-spacing rings (near the center of the pattern) by which these materials may be identified in the rubber matrix. Compound A_4 (Table II) contained a very small amount of ethyl Tuads,



Powdered Captax — Powdered Altax — Powdered Zenite

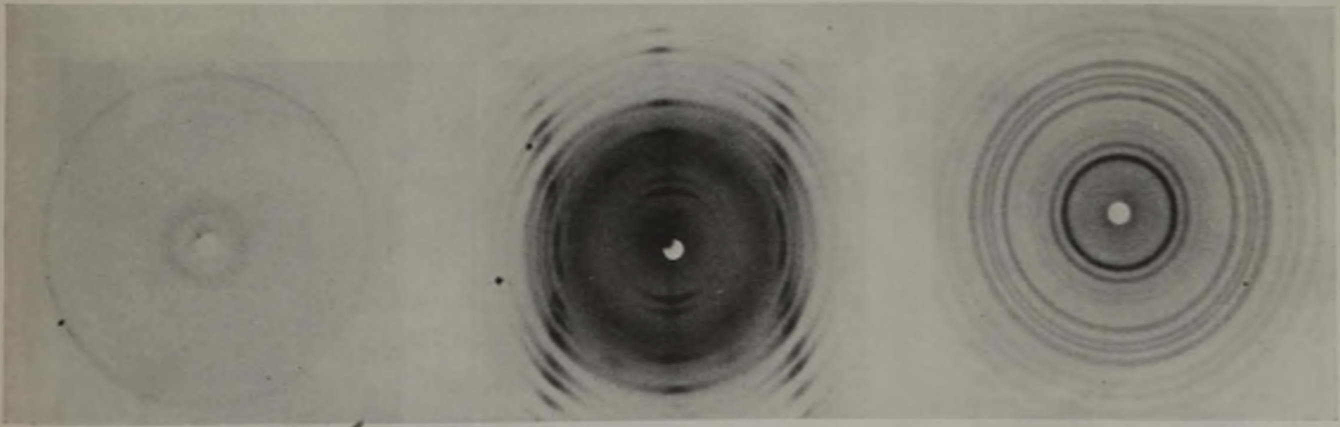


Stretched rubber stock C_9, containing Captax and showing presence of Zenite — Stretched rubber stock C_{11}, containing Altax and showing presence of Zenite — Stretched rubber stock C_{10} with Zenite originally added

FIGURE 3. X-RAY DIFFRACTION PATTERNS OF CAPTAX FAMILY

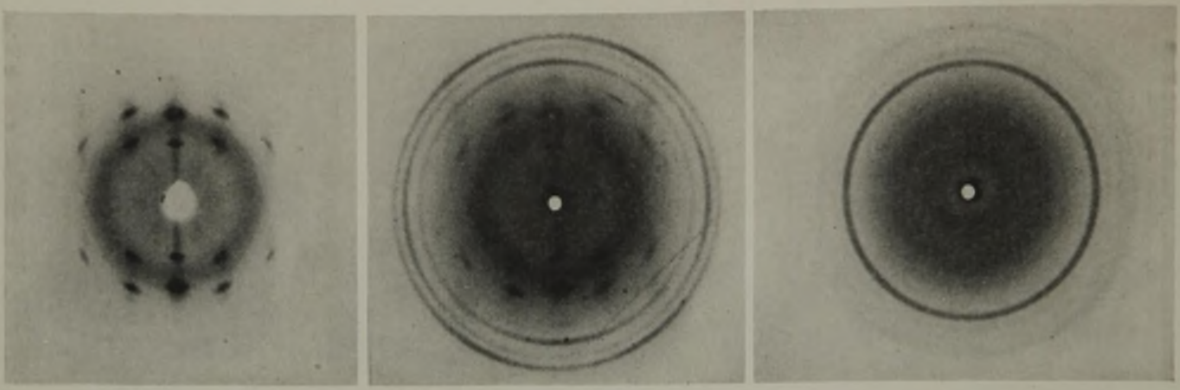
corresponding to its use as an accelerator in ordinary practice. The three diffraction rings at the outer edge of the pattern are due to the zinc oxide present. The characteristic lines of ethyl Zimate show up rather faintly in the central part of the pattern. Compound B_4 contains a much higher percentage of ethyl Tuads than would ordinarily be used. Here the ethyl Zimate lines show up strongly. B_2 was originally compounded with ethyl Zimate as accelerator and is shown for comparison with B_4. The patterns are identical except that the intensity of the zinc oxide lines is somewhat less in B_4, showing that much of it has been used up in the reaction to form the zinc salt of Tuads.

Figure 2 shows the patterns for the methyl derivatives. Monex is also converted to the dithiocarbamate salt as shown in C_5. Figure 3 tells a similar story for the Captax family. The acid (Captax) and the disulfide (Altax) both react in the rubber matrix to give the zinc salt (Zenite). For C_9, C_{10}, and C_{11} patterns, all three accelerators show the same product in the final vulcanizate, which corresponds to the Zenite. The fingerprint patterns of Captax and Zenite show that they are



Powdered litharge — Stretched rubber stock B_6, containing methyl Tuads and lead oxide and showing presence of Ledate — Powdered Ledate

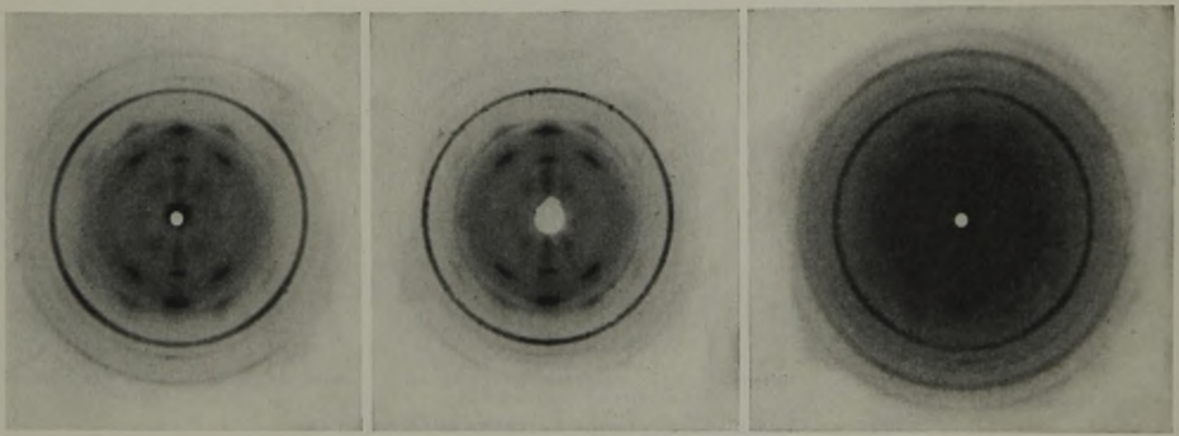
FIGURE 4. X-RAY DIFFRACTION PATTERNS OF LEAD DERIVATIVES



a. Pure stretched rubber

b. Stretched rubber containing zinc oxide, showing fibering of zinc oxide as well as rubber

c. Rubber stock containing Kalvan stretched 200 per cent



d. Rubber stock containing Kalvan stretched 550 per cent and showing fibering of Kalvan filler as well as rubber

e. Stretched rubber stock containing whiting

f. Stretched rubber stock containing Kalvan and iron oxide

FIGURE 5. DIFFRACTION PATTERNS SHOWING ORIENTATION

put into the rubber in rather large grains (specked diffraction rings). The vulcanizate patterns show uniformly small grain size, indicating that even in the case of the Zenite the accelerator has melted or dissolved in the rubber matrix at the curing temperature and reprecipitated in colloidal form. Figure 4 tells the story for lead dimethyldithiocarbamate accelerator. When litharge is used with methyl Tuads instead of zinc oxide as an activating agent, the lead dimethyldithiocarbamate is found to be the reaction product in the cured sample.

Accelerator activators are always used with accelerators to make them work properly. Tuads will not vulcanize if zinc oxide is not present. It is suggested that one of the steps in activation is the chemical reaction between accelerator and accelerator activator which takes place in the rubber matrix at the curing temperature.

Examination of the C series stocks showed that the presence or absence of stearic acid had no apparent effect on these reactions.

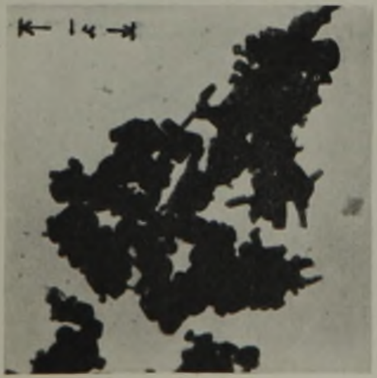


FIGURE 6. ELECTRON PHOTOMICROGRAPH OF ZINC OXIDE USED IN FIGURE 5*b*

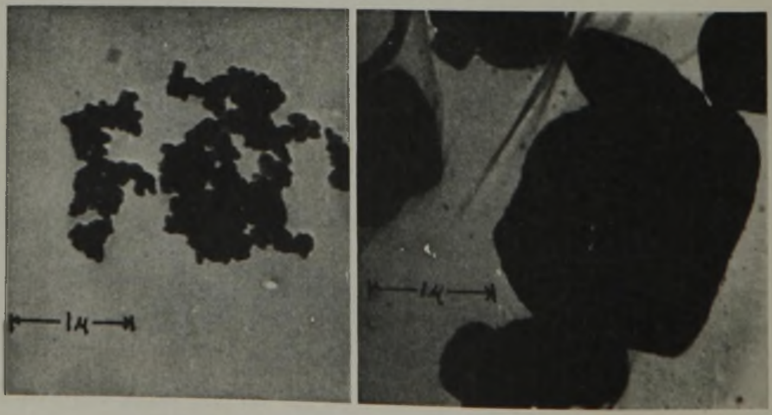


FIGURE 7. ELECTRON PHOTOMICROGRAPHS OF KALVAN (INDICATING PRIMARY PARTICLE SIZE OF ABOUT 300 Å.) AND OF WHITING (*right*)

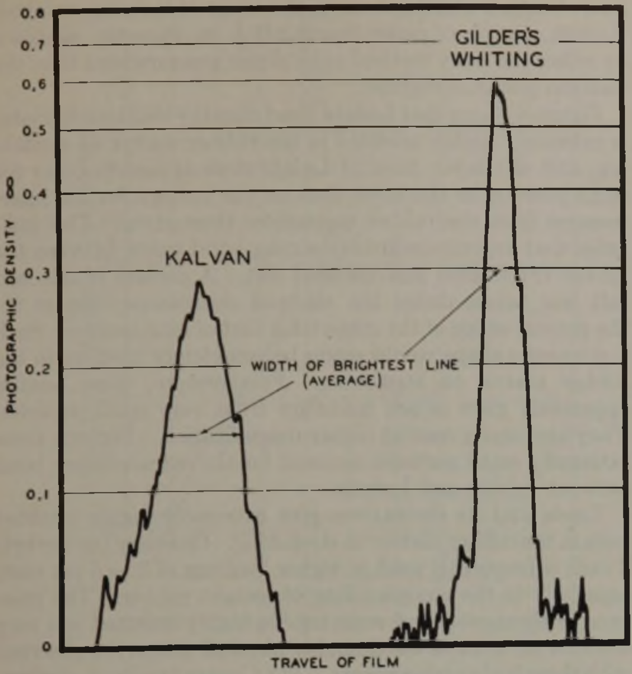


Figure 8. Microphotometer Tracings of Same Calcium Carbonate Diffraction Line in Kalvan and Gilder's Whiting for Use in Particle Size Determinations

Orientation of Various Materials

Zinc dimethyldithiocarbamate is strongly oriented in the rubber matrix on stretching. This shows in the x-ray diffraction pattern by nonuniform intensity of the diffraction rings. The degree of orientation may be judged by the sharpness of the arcs into which the rings are broken. Rubber crystallites are an example of a completely oriented material. The arcs are so sharp that they appear as spots. Figure 5 shows the orientation of some of the inorganic fillers in rubber. A discussion of the orientation of these fillers is necessary to an understanding of the importance of the orientation of accelerator salts in the rubber matrix.

A dry film from latex, stretched 550 per cent (Figure 5*a*), is shown as the pattern for rubber free from all fillers. This pattern was taken at a sample film distance of 3 cm.; therefore the rubber diffraction spots appear closer to the central portion of the film than in Figures 1, 2, 3, and 4.

The sample shown in Figure 5*b* is stretched 550 per cent. Here all the rings, in addition to the rubber interferences, are due to zinc oxide. The amount of accelerator used is so small that it does not show up. These rings are not uniformly intense, as they are for the zinc oxide in a fingerprint pattern, but appear with localized intensity maxima. This means that during stretching of the rubber, the embedded zinc oxide grains are rotated and lined up in a preferred direction with respect to the direction of stretching. It is possible to calculate from the positions of the maxima on the rings the actual arrangement, with the normal to the (001) planes parallel to the fiber or stretching axis. This means, in turn, that such a powerful bond exists between the zinc oxide grains and the rubber that the rubber does not tear away from the oxide surfaces during stretching but instead tends to pull all the grains into parallel alignment. This is a distinct property of the zinc oxide and, to some extent, of the compounding; for in the course of years of investigation many specimens containing 5 parts of zinc oxide showed no such fibering[1] of these crystal grains at 550 per cent elongation.

An electron microscope picture of the zinc oxide compounded into this stock is shown in Figure 6. The individual particles are much longer in one direction than in the other two, and it may easily be understood how they would be oriented in the rubber matrix on stretching.

The stock shown in Figure 5*c* contains 25 parts of Kalvan, a finely divided calcium carbonate. Stretched only 200 per cent, the central rubber halo shows no evidence at this elongation of crystalline spots. The intense ring is characteristic of calcite, and all others may be identified by comparison with fingerprint patterns as belonging either to calcite or zinc oxide. The rings are continuously uniform, indicating random arrangements of all crystal grains.

Figure 5*d* represents the same stock stretched 550 per cent. Now the crystal fiber pattern for rubber has appeared; in addition the calcite lines, especially the faint line just outside the rubber interferences and the very intense ring, show definite evidence of fibering. Again this means a remarkably powerful bond between Kalvan and rubber, and a sufficiently small size so that the grains rotate and align themselves with respect to the direction of stretch. The reverse is true as the rubber itself crystallizes; for on release of tension, the specimen again reverts to an entirely random arrangement of rubber molecules and filler crystals. Fibering of the filler appears just when fiber spots appear for the rubber.

In Figure 5*e* the stock containing 25 parts of gilder's whiting, a coarse calcium carbonate, is stretched 550 per cent. Under these identical conditions the contrast with the preceding pattern is remarkable. The rubber crystallizes at this elongation, but the whiting crystal grains are entirely unaffected by the stretching operation and remain in the original random arrangement. The grains are too large and the bond

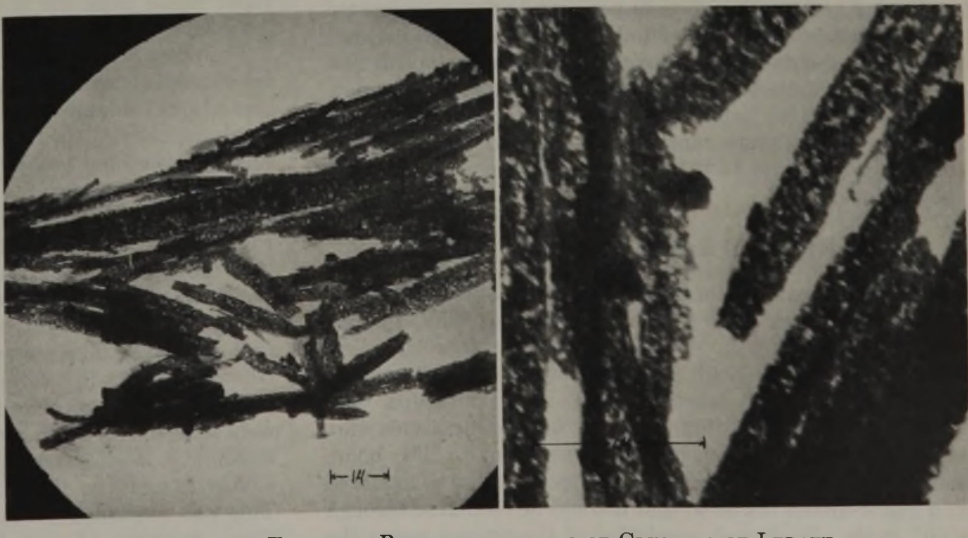


Figure 9 Electron Photomicrographs of Crystals of Ledate

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[1] Katz, J. R., and Bing, K., *Z. angew. Chem.*, 38, 439 (1925).

is too weak to permit a response to stretching deformation; the rubber must tear loose and, in a sense, flow around and past these particles like water in a stream around a fixed boulder; an exaggerated case is the same effect seen when rubber contains grains of sand. Stretching to break at about 700 per cent has no greater effect on the whiting grains.

Figure 5*f* shows a specimen containing 25 parts Kalvan and 5 parts red oxide, stretched 675 per cent. It again demonstrates the marked fibering of the Kalvan grains. Exactly the same phenomenon is shown for any specimen containing Kalvan, from 5 to 75 parts. With 75 parts of Kalvan as a common commercial proportion, the fibering is prominent; but on account of the preponderance of the mineral crystals which absorb much of the x-ray energy, it is difficult to reproduce clearly the rubber interferences. Especially noteworthy is the enormous increase in tear resistance in increasing the Kalvan content from 25 to 75 parts. This is but another indication of the great capacity of the rubber to bond itself to Kalvan particles. In the stretched condition it might be expected that the resistance to tear across the fibers will be greater than parallel to them, just as it is easier to split asbestos fibers apart parallel to their length than to break a bundle across the fibers.

The differences between Kalvan and gilder's whiting have already been noted in rubber. The differences in particle size and shape of these materials accounts for the difference in behavior. Figure 7 shows electron photomicrographs of these two materials; Figure 8 is a microphotometer tracing of the principal interference of calcite taken from x-ray patterns of these two materials for the purpose of computing particle size. Gilder's whiting is out of the range of the x-ray method. Kalvan consists of plates about 300 Å. in diameter, as shown by either the x-ray method or by direct measurement from the electron photomicrograph.

Figure 4 shows that Ledate (lead dimethyldithiocarbamate) is extremely highly oriented in the rubber matrix on stretching, and the layer lines of Ledate even appear to be in the same position as the layer lines on the pattern for the interferences from the rubber crystallites themselves. This indicates that an extraordinarily strong bond exists between the rubber crystallites and the lead salt. A picture of this lead salt was taken under the electron microscope (Figure 9); the general shape of the material is that of long needles. Such a geometric shape would easily be completely lined up in the rubber matrix on stretching. Furthermore, these needles apparently grow or are made up from very small particles. They are clearly seen at higher magnification. Perhaps these extremely small particles account for the extraordinary bond between rubber and Ledate.

Tuads and its derivatives give extremely highly oriented salts in the rubber matrix on stretching. Ordinary (or methyl) Tuads is frequently used in higher loadings of 3 to 5 per cent, especially in the compounding of reclaim rubber. The presence in these stocks of considerable highly oriented salt may account for some of the desirable physical properties observed with these higher percentages. The Captax family of accelerators is not so highly oriented in the rubber matrix as the Tuads family.

PRESENTED before the Division of Rubber Chemistry at the 104th Meeting of the AMERICAN CHEMICAL SOCIETY, Buffalo, N. Y.

Solubility of Hydrogen in *n*-Butane

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IN THE course of an investigation of the solubility of hydrogen in *n*-butane, it was noted that the bubble-point portion of the pressure-temperature curves for mixtures of 3 to 4 mole per cent hydrogen contained minima; likewise, the paths of the bubble-point curves of mixtures containing greater than 4 mole per cent hydrogen suggested that minima would have been obtained for these mixtures if the measurements had been extended to higher temperatures. These results are reported because they exemplify an interesting type of phase behavior which may be a characteristic property of a mixture consisting of a liquid and a slightly soluble gas, and because they will be useful in engineering calculations.

Experimental Apparatus and Procedure

The apparatus used for obtaining the solubility data was a stainless steel bomb with a capacity of 400 cc. The sampling line was a $^{3}/_{8}$ inch o. d. × $^{1}/_{16}$ inch i. d. steel tube which extended to a point $^{1}/_{4}$ inch from the bottom of the bomb. A thermowell of similar length was provided. Pressures were read from a calibrated Bourdon gage, and temperatures were measured by an iron-constantan thermocouple. The bomb was incased in an electrically heated jacket and was mounted in a motor-driven cradle so that it could be oscillated through a 60° angle. With each revolution of the driving motor the longitudinal axis of the bomb passed through the horizontal, and thus it was possible to sample either the liquid or the vapor phase from the same sampling line by stopping the bomb motion at either the bottom or the top of the arc.

The procedure followed in making a series of solubility determinations was to charge the bomb with hydrocarbon to give a liquid volume of approximately 50 per cent of the total bomb capacity. After the bomb had been placed in the insulated jacket and heated to the desired temperature, hydrogen was charged from a high-pressure cylinder. Samples were not taken until the bomb temperature had remained within 0.5° C. of the desired value for at least 10 minutes; then the bomb motion was stopped in either the high or low position, depending upon which phase was to be sampled, and the sample line was purged by venting to ensure representative sampling. The pressure and temperature were recorded before and after the sample was taken. Gas samples of approximately 500 cc. were taken by displacement of brine and were analyzed for hydrogen by being passed over copper oxide at 300° C. At this temperature the hydrogen was completely oxidized, and the *n*-butane was not appreciably affected. This was confirmed by the preparation and analysis of synthetic mixtures of pure hydrogen in pure *n*-butane. The

The solubility of hydrogen in *n*-butane was determined at 23.9°, 82.2°, and 115.6° C., and at pressures up to 100 atmospheres. At pressures below 30 atmospheres, solubility decreases with increase in temperature, from 30 to 40 atmospheres temperature has little effect on solubility, and above 40 atmospheres solubility increases with increase in temperature over the temperature range investigated. At concentrations of hydrogen above 3 mole per cent, the shapes of the *P-T* bubble-point curves derived from the solubility data suggest the existence of a region of isobaric retrograde condensation at temperatures far below the critical region of the mixtures.

Data reported by Kay (*2*) for the system hydrogen-naphtha show a similar phase behavior, and it is believed that the measurements on hydrogen–*n*-butane constitute additional evidence in support of Kay's suggestion that this may be a characteristic property of a general class of mixtures consisting of a liquid and a slightly soluble gas.

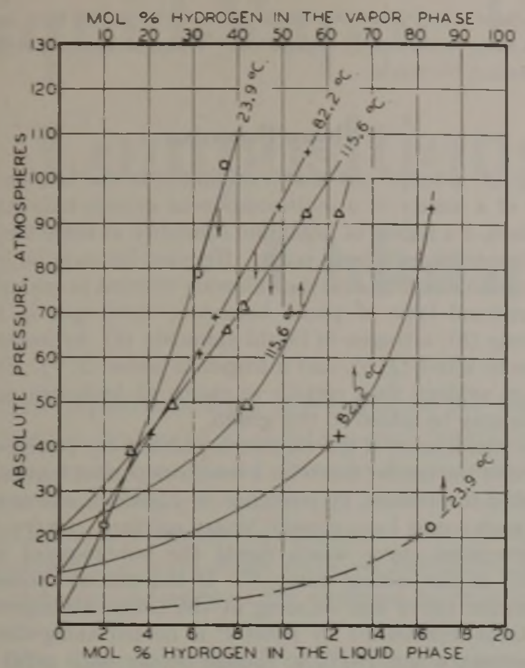

Figure 1. Solubility of Hydrogen in *n*-Butane

water vapor formed in the oxidation of the hydrogen was condensed in a small water layer present in the analytical apparatus; hence the humidity of the sample was not changed by any appreciable amount during analysis, and the decrease in volume represented the volume per cent hydrogen. Portions from each sample were analyzed until the results of successive analyses agreed within 0.2 per cent. The volume percentages of hydrogen determined by the oxidation analyses were corrected to mole percentages by compressibility factors for hydrogen and *n*-butane, and a correction was applied for the amount of water vapor present during analysis.

Experimental Data

The experimental results obtained at 23.9°, 82.2°, and 115.6° C. are summarized in Table I, and the data are plotted in convenient form in Figures 1 and 2. The relation between total pressure and solubility at constant temperature is given by the curves of Figure 1, which also includes some data on vapor composition. The vapor phase samples were taken primarily to determine whether a single- or two-phase condition existed within the bomb; although these vapor phase data are incomplete, they have been included since they will be useful in estimating phase equilibria. Figure 1 shows that the constant-temperature lines intersect in the range of 3 to 4 mole per cent hydrogen. Below about 3 mole per cent, solubility decreases with increase in temperature for a given pressure. For mixtures containing 3 to 4 mole per cent hydrogen, composition is substantially independent of temperature over the range investigated, and for mixtures containing more than 4 mole per cent, solubility increases with an increase in temperature.

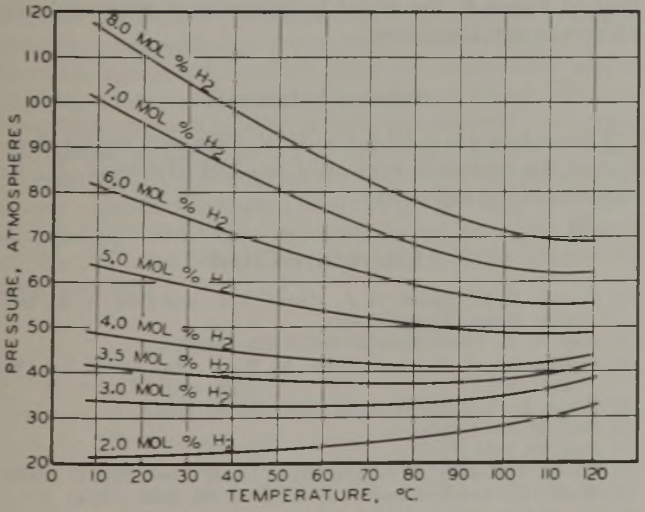

Figure 2. Bubble-Point Curves for Mixtures of Hydrogen and *n*-Butane

Table I. Solubility Data for Hydrogen in *n*-Butane

Temperature, ° C. (° F.)	Pressure, Atm. Abs.	Mole % H_2 in: Liquid phase	Mole % H_2 in: Vapor phase
23.9 (75)	22.2	2.0	83.2
	78.6	6.2	...
	103.0	7.4	...
82.2 (180)	42.6	4.0	62.7
	60.8	6.3	...
	69.0	7.0	...
	93.6	9.9	83.3
	105.8	11.1	...
115.6 (240)	38.6	3.2	...
	48.9	5.1	42.0
	65.9	7.5	...
	71.0	8.3	...
	91.8	11.1	62.4

When the liquid phase data of Figure 1 were replotted as bubble-point pressure against temperature, the curves of Figure 2 were obtained. The accuracy of these curves is questionable since only three points were available for drawing each curve; however, it is clear that a minimum occurs in the bubble-point curve for mixtures containing 3 to 4 mole per cent hydrogen, and the curvature of the bubble-point curves of mixtures containing greater than 4 mole per cent is such that a minimum would probably have been obtained if the measurements had been extended to higher temperatures.

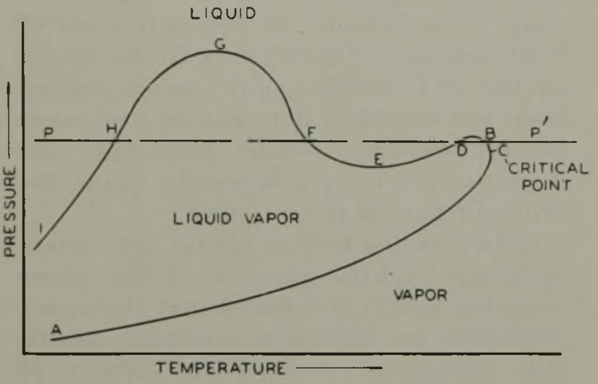

Figure 3. *P-T* Border Curve for a Mixture Having a Minimum Point in Its Bubble-Point Curve

The solubility data reported here are not to be considered as derived from precision measurements; however, the data are sufficiently accurate for engineering purposes. The method of analysis was checked by preparing synthetic mixtures of pure hydrogen in pure *n*-butane. Analyses of these mixtures indicated that the degree of accuracy to be expected from the method of analysis was ±0.2 mole per cent hydrogen; thus the possible percentage error in solubility caused by inaccuracy in analysis would be relatively high at low concentrations, but would be as low as 2 per cent for a mixture containing 10 mole per cent hydrogen.

The hydrogen used for the solubility measurements was commercially pure, cylinder hydrogen. Analysis of synthetic samples of this hydrogen in nitrogen showed a purity greater than 99.5 per cent. Fractionation of the *n*-butane in a microcolumn indicated a purity of over 99 per cent.

The pressure change accompanying the withdrawal of a liquid phase sample from the bomb was never over 2 per cent of the total bomb pressure, and it is believed that the total probable error in the liquid phase data is in the neighborhood of 5 per cent. The vapor phase data should be used with discretion because so few points were obtained, and because the volume of the solubility bomb was such that the total pressure on the bomb dropped by about 7 per cent when a vapor phase sample was taken. This error was tolerated since the vapor phase samples were not taken to secure equilibria data but merely to ascertain whether a single- or two-phase condition existed within the bomb.

The only previous data found on the solubility of hydrogen in *n*-butane were those reported by Frolich, Tauch, Hogan, and Peer (*1*) who determined three experimental points at 25° C. These results show an appreciably higher solubility at room temperature than was obtained by us; however, the solubilities reported by Frolich *et al.* are expressed as volume of hydrogen at standard temperature and pressure per volume of liquid hydrocarbon, and it is not clear whether the hydrocarbon volume refers to volume at the normal boiling point or volume at dry ice temperature at which the two components were presumably separated. Thus, a rigorous comparison cannot be made.

Phase Behavior

Kay (*2*) pointed out that a minimum in the bubble-point curve of a binary or a multicomponent system indicates the existence of a region of minimum solubility at some temperature below the minimum point. He cited his data on hydrogen-naphtha and data on the following systems as examples of this unusual type of phase behavior: hydrogen in liquid ammonia (*8*), nitrogen in liquid ammonia (*6*), hydrogen and helium in water (*4*, *5*), and nitrogen in water (*3*, *7*). It now appears evident that certain mixtures of hydrogen and *n*-butane may be added to this group.

The significance of the minimum point in the bubble-point portion of the border curve for a multicomponent system may be better understood by reference to Figure 3, which represents such a case for a specific binary mixture. Curve *AC* is the dew-point curve which meets the bubble-point curve, *IGEBC*, at the critical point, *C*. If the mixture possessing this border curve and existing at the pressure-temperature conditions represented by point *P* is heated along the constant-pressure line, *P-P'*, no change occurs until point *H* is reached and a bubble of vapor appears. As the temperature is increased between *H* and *F*, the relative proportion of vapor to liquid phase reaches a maximum and then decreases (retrograde condensation) until point *F* is reached and all vapor has been condensed. Further heating above *F* produces no second phase until the border curve is reached at point *D*, and a bubble of vapor again appears; between *D* and *B* the amount of vapor reaches a maximum and then decreases (retrograde condensation) until only liquid exists when point *B* is reached. Thus there are two regions of isobaric retrograde condensation for mixtures which contain a minimum in the bubble-point curve, the region associated with the critical state and the region associated with the temperature of minimum solubility.

The temperature range covered by the hydrogen–*n*-butane data is such that the bubble-point curves of Figure 2 correspond to that region of the hypothetical border curve of Figure 3 included between points *F* and *D*. Unfortunately the apparatus employed for these measurements was not suitable for measurements outside the range of temperature covered; and although the *P-T* border curve for mixtures containing 3 to 4 mole per cent hydrogen must of necessity be similar to that of Figure 3, the actual temperature of minimum solubility was not determined.

Acknowledgment

The authors are indebted to R. P. Gilmartin for his direction of the analytical work, and to Clark Holloway, Jr., for criticism of the manuscript.

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Presented before the Division of Petroleum Chemistry at the 104th Meeting of the American Chemical Society, Buffalo, N. Y.

Liquid-Vapor Equilibrium Compositions in Hydrogen Chloride–*n*-Butane System

Phase equilibria data are required for the efficient design of absorption and fractionating equipment, and since hydrogen chloride is assuming a constantly greater role in petroleum refinery operations, it appears desirable to have such data on mixtures of hydrogen chloride with various hydrocarbons.

The compositions of equilibrium vapor-liquid mixtures in the hydrogen chloride–*n*-butane system have been determined at temperatures of 70°, 120°, and 180° F. for pressures below 550 pounds per square inch, using a constant volume type apparatus. The data, which are presented in both tabular and graphical form as pressure-composition and equilibrium constant-pressure diagrams, indicate general agreement with Raoult's law.

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HYDROGEN chloride is used as a promoter for the aluminum chloride isomerization of *n*-butane to isobutane. In a continuous isomerization unit it is necessary to introduce the hydrogen chloride with the *n*-butane charge in controlled amounts and also to recover it from the reactor effluent for recycling, since the hydrogen chloride consumption must be low if the process is to be economically feasible. Phase equilibria data for the hydrogen chloride–*n*-butane system are required if absorption and fractionating equipment handling these two components are to be designed with confidence. A literature search revealed some data on the solubility of hydrogen chloride in propane (*2*), hexane (*5*), benzene (*1*), octane (*1*), dodecane (*1*), and cyclohexane (*7*), but nothing was found for the system hydrogen chloride–*n*-butane. This paper presents the equilibrium liquid and vapor compositions for the latter system at 70°, 120°, and 180° F. and at pressures up to 550 pounds per square inch.

Apparatus and Materials

The equilibrium chamber was a cylindrical one-gallon bomb constructed from a section of 6-inch, extra heavy, S. A. E. 1015 seamless steel tubing, and was provided with a thermowell and with both liquid and vapor sampling lines made of $^1/_8$-inch steel tubing. To avoid excessive liquid holdup, the transverse area of the liquid sampling line was reduced about 75 per cent by the insertion of a steel rod. The stainless-steel Bourdon-tube pressure gage was attached to the vapor-sampling line of the bomb.

The constant-temperature bath was equipped with immersion heaters and a cooling coil, and the fluid of the bath was constantly recirculated by a centrifugal pump. The temperature was controlled with a bimetallic expansion thermoregulator, and the actual temperature reading was taken with a calibrated A. S. T. M. thermometer. Water was used in the bath for the 70° and 120° F. determinations, and oil was employed for the 180° F. determinations. The equilibrium chamber was supported vertically in the constant-temperature bath by side arms so that it could be rocked through an angle of about 90° and so that the sampling valves were below the level of the fluid in the bath.

One-gallon bottles and 700-cc. burets, respectively, were used for sampling the liquid and vapor phases. A Cenco high-vacuum pump was available for evacuation of the sample containers, and mercury manometers were employed in sampling for pressure control and measurement.

The C. P. *n*-butane used in this work was obtained from the Phillips Petroleum Company and was 99.6 per cent pure. The impurities were hydrocarbons boiling in the same range as *n*-butane, and since the solubility of hydrogen chloride in hydrocarbons of similar boiling points should not vary a great deal, no attempt was made to remove the 0.4 per cent impurity. The butane was passed through an activated alumina dryer to remove any traces of moisture.

The hydrogen chloride for the experimental work at 70° F. was obtained in the dry anhydrous form from the Harshaw Chemical Company and was from 97 to 98 per cent pure. The hydrogen chloride used for the 120° and 180° F. determinations had a purity of over 99 per cent and was produced by the reaction of concentrated sulfuric acid with rock salt. A flanged steel bomb was used, and the generation was allowed to continue until a hydrogen chloride pressure in excess of that desired in the equilibrium chamber had developed.

Method of Operation

Before charging *n*-butane to the equilibrium chamber for each series of determinations, it was washed with acetone, dried, and flushed out several times with butane. Sufficient

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n-butane was then added for the series of isothermal determinations, and air was swept from the line leading to the hydrogen chloride supply with a stream of butane. The equilibrium chamber was rocked steadily while hydrogen chloride was being admitted, and the admission was continued until hydrogen chloride solution into the liquid phase became negligible at about the desired pressure. The pressure and temperature usually assumed constant values within an hour after the hydrogen chloride addition was stopped, but samples were never taken earlier than 8 hours after the last addition of hydrogen chloride.

In sampling, precautions were taken to remove stagnant materials from the internal lines and air or other foreign gases from the external lines. Gas samples from the liquid phase were taken into clean, dry, evacuated one-gallon bottles. They were flushed with three or four times their volume of sample in a slow continuous flow under slightly superatmospheric pressure, and no pressure drop on the system was noticeable during the sampling operation. For analysis, gas was allowed to flow from the bottle into 700-ml. evacuated (2 mm. mercury) gas burets which were constructed with a one-way glass stopcock at one end and a three-way stopcock at the other end. This three-way cock permitted evacuation and flushing of the connection between the buret and the one-gallon bottle before the sample was withdrawn from the bottle. The buret samples were taken at a pressure of 150–200 mm. mercury, and the exact pressure together with the temperature and buret volume determined the weight of sample. The hydrogen chloride in the sample was neutralized with an excess of measured standard sodium hydroxide solution which was added through the three-way stopcock. This mixture was diluted with distilled water to provide adequate solution for absorbing the hydrogen chloride, and the buret was shaken vigorously. The excess sodium hydroxide was back-titrated with standard acid to the phenolphthalein end point.

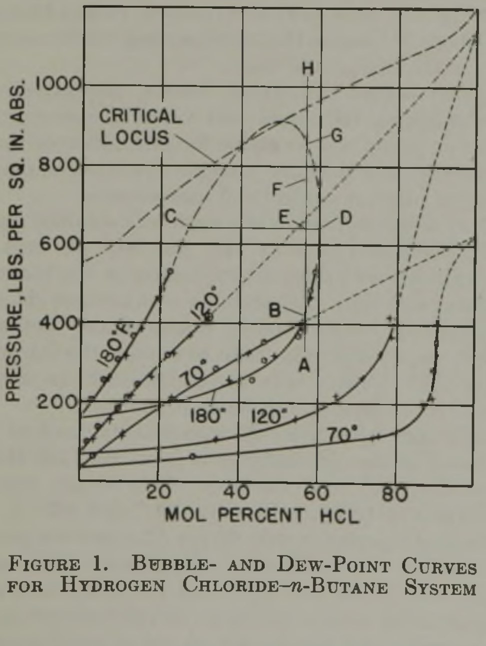

FIGURE 1. BUBBLE- AND DEW-POINT CURVES FOR HYDROGEN CHLORIDE–*n*-BUTANE SYSTEM

Gas samples of the vapor phase were taken and analyzed by the same procedure as for the liquid phase samples, except that the sample was passed directly into the buret from the equilibrium chamber in order to keep the amount withdrawn at a minimum. When taking a vapor phase sample, the total pressure on the system did not drop more than 1 or 2 pounds per square inch.

TABLE I. COMPOSITIONS OF BUBBLE-POINT LIQUID AND DEW-POINT VAPOR FOR HYDROGEN CHLORIDE–*n*-BUTANE SYSTEM

Pressure, Lb./Sq. In. Abs.	Mole % HCl	
	Liquid	Vapor
	At 70° F.	
66	3.3	38.8
114^a	10.8	74.5
119^a	10.8	75.7
200^a	22.6	87.0
211^a	23.1	89.3
283	34.1	89.4
323^a	42.6	90.2
351	46.5	90.4
403	56.4	90.5
	At 120° F.	
100	2.0	..
106^a	3.5	34.5
137	4.6	..
154^a	7.6	54.7
186	9.5	..
213	11.9	..
215^a	12.9	64.8
242	14.5	..
261^a	18.1	71.5
319	22.3	..
321^a	23.6	76.3
366^a	27.8	79.0
415^a	32.3	78.5
417	32.4	..
	At 180° F	
199^a	3.5	24.5
205	2.8	23.8
254	5.8	43.7
257^a	7.3	38.7
306	9.5	46.7
317	11.4	49.4
366	13.3	55.3
385^a	15.4	56.3
466^a	19.4	58.2
484	20.1	58.5
531	22.4	59.4

[a] Points in a decreasing series.

Experimental Data

The equilibrium pressures in the system hydrogen chloride–*n*-butane were determined for 70°, 120°, and 180° F. at concentrations up to 56 mole per cent hydrogen chloride in the liquid phase, and they varied from 50 to 500 pounds per square inch absolute. The observed pressures, together with the corresponding liquid and vapor compositions for each of the three temperatures are presented in Table I and shown graphically in Figure 1. Distinction is made between points taken as the pressure was increased between successive analyses and points taken as the pressure was decreased. Deviations in the liquid phase data between series of determinations made with increasing and with decreasing pressure were consistent; that is, in a series made by successively increasing the pressure, the concentration of hydrogen chloride would tend to be low, whereas in a decreasing series the concentration would tend to be high. This indicates either some holdup in the liquid sampling tube or a considerable lag in reaching complete equilibrium. Smooth curves for the liquid phase compositions were drawn through the mean of the two sets of data, and since the departure of individual points from the curve was never more than one mole per cent hydrogen chloride, errors due to holdup and lack of equilibrium should be nullified.

Individual points in the vapor phase data failed to lie on a smooth curve in some cases by as much as 2 mole per cent hydrogen chloride. This scattering of points from the curve exhibits no definite trend, although it is probably due to changes in the vapor samples caused by disruption of the equilibrium as the vapor was being withdrawn.

The over-all accuracy of the data is considered to be within the following limits:

Pressure, lb./sq. in.	±2
Temperature, ° F.	±0.4
HCl in liquid, mole %	±0.4
HCl in vapor, mole %	±3

The equilibrium chamber was designed with a capacity of one gallon so that the amount of material withdrawn for sampling purposes would be a small percentage of the total contents, and the amount actually withdrawn in sampling either phase amounted to less than one weight per cent of the phase. Sampling tubes were of small cross-sectional area, and care was taken to prevent sample contamination by adequate purging of the sampling lines. The analytical procedure as previously described is considered to involve less uncertainty than other details of the work, and as a further precaution, the hydrogen chloride content as determined by the acid ion equivalent was checked by a chloride ion analysis. The unit of graduation on the Bourdon tube gage was 5 pounds per square inch, and the pressure could be read accurately to 2 pounds per square inch. The gage is thought to be accurate within this limit, since it was calibrated with a dead weight tester at frequent intervals as the work proceeded. All temperatures were taken with a calibrated mercury-in-glass thermometer which could be read accurately to 0.2° F. Bath temperature varied by not more than ±0.2° for the 70° and 120° F. determinations, and by not more than ±0.4° for the 180° F. determination.

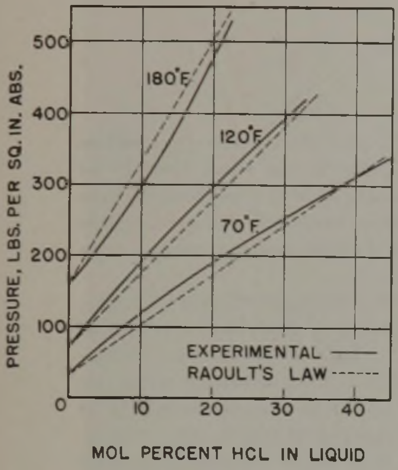

Figure 2. Comparison of Experimental Data with Raoult's Law

Phase Behavior

In a binary hydrocarbon system the critical locus for mixtures of the constituents is often in excess and may be far in excess of the critical pressure of either pure constituent. This phenomenon does not exist in the hydrogen chloride–propane system and, assuming an analogy between the systems hydrogen chloride–n-butane and hydrogen chloride–propane, the critical locus for mixtures of hydrogen chloride and n-butane was drawn on Figure 1 similar in shape to the critical locus of mixtures of hydrogen chloride and propane (*2*). The data at 70° and 120° F. were extended to the respective vapor pressures of hydrogen chloride, and little opportunity is seen for errors of greater than 5 mole per cent hydrogen chloride at a given pressure in either the bubble-point or the dew-point curves. In order to present qualitatively the shape of a border curve for a temperature above the critical temperature of hydrogen chloride, the data at 180° F. were extrapolated to the critical locus. Retrograde effects, as defined by Katz and Kurata (*3*), can occur at this temperature. For example, if a gaseous mixture at 180° F. and the pressure and composition defined by point A is compressed isothermally along line AEH, at point B a drop of liquid will form. As compression is continued, the amount of liquid will increase until a maximum is reached at some point, F. Under further compression, the amount of liquid will decrease (retrograde vaporization) until at point G the system consists of a single phase. It is perhaps not generally realized that this and other retrograde conditions can be easily demonstrated by actual calculation of the relative amount of liquid and vapor present at various points within the border curve. Thus, at point E where the total system in question contains 57 mole per cent hydrogen chloride and where the equilibrium liquid and vapor as represented by points C and D contain 26.3 and 60.2 mole per cent hydrogen chloride, respectively, the mole per cent of the system in the liquid phase is represented by the unknown term in the equation:

$$0.263x + 0.602\,(100 - x) = 0.57\,(100)$$

Similar calculations based on the pressure-temperature type of diagram are possible, provided sufficient constant composition envelopes are available.

The nearly linear relation of the composition to the pressure for the bubble-point curves in Figure 1 indicates approximate agreement with Raoult's law. This is illustrated to better advantage in Figure 2, where the experimental data are compared directly with the calculated predictions. The fugacities of hydrogen chloride were obtained by graphical integration of P-V-T data according to the method of Lewis and Randall (*4*), and the fugacities of n-butane were taken from the data of Sage, Webster, and Lacey (*6*).

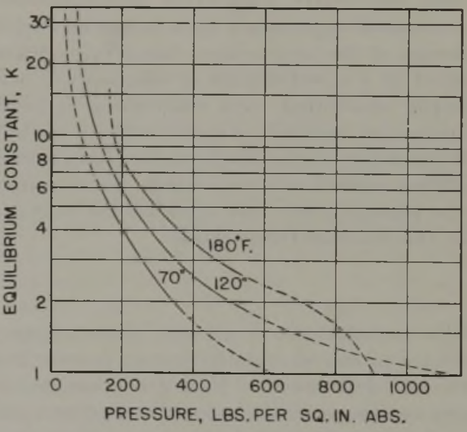

Figure 3. Equilibrium Constant Curves for Hydrogen Chloride in n-Butane

Equilibrium constants, or the mole ratio of the hydrogen chloride concentration in the vapor phase to the concentration in the liquid phase, were calculated from the smooth curves in Figure 1 and are presented in Figure 3 for the three temperatures investigated. At the vapor pressure of n-butane the value of K will approach infinity. For temperatures below the critical temperature of hydrogen chloride, the curves terminate at the vapor pressure of hydrogen chloride and a K value of unity. For temperatures above the critical temperature of hydrogen chloride, the curves terminate at a K value of unity and the maximum pressure attained by the dew point–bubble point border curve on a pressure-composition type diagram. On this type of diagram the maximum pressure point is coincident with the critical point.

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Grading of Soft Sugars

PHOTOELECTRIC REFLECTANCE MEASUREMENTS

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In a previous publication a photoelectric instrument was described for measuring the transmitted color of raw sugar solutions and other dark colored liquids. The basic principles of this instrument have since been applied to the development of a photoreflectometer for measuring the reflected color of brown sugars and other such products.

The basic type of circuit employed is similar to that previously used—two photogenerative cells connected opposingly in a balanced circuit. The design of the instrument, however, is different and involves a novel means of eliminating errors normally associated with reflectance measurements. Instead of incident or direct reflection which introduces errors due to glare, surface irregularities, etc., diffuse reflection is measured. To accomplish this, the photoelectric cell surfaces are located parallel to the illuminated surface.

A particular feature is the absolute nature of the measurements, all results being read directly in absolute absorption units relative to magnesium carbonate. As a working basis of reference, white tile which has been calibrated against magnesium carbonate is used.

In measuring the reflected color of brown sugars, it was necessary to develop a standard method of preparing the sample. In operating the instrument, an initial balance is first obtained with the standard tiles in place. The comparison tile is then replaced by the sample of sugar, the instrument rebalanced, and the color read directly on the slide-wire in absolute absorption units.

In addition to the several instruments which have been constructed for brown sugar color measurement, a modified reflectometer for measuring the color of dry white sugars is described.

IN THE manufacture of soft or brown sugars, various grades are produced, usually ranging in color from a pale yellow to a dark brown. Each grade has its own selling price based on the particular color that has been established for that grade. As it is desirable to maintain the color of these different grades within rather narrow limits, it is essential that accurate means of color measurement be available.

Color measurement frequently involves both quantitative and qualitative characteristics. However, most refined sugar products vary little in quality of color, and therefore means for measuring the quantity of color is usually sufficient in the sugar industry. These characteristics of color in sugar products are described in considerable detail by Peters and Phelps (*13*) and by Honig and Bogtstra (*4*), with considerable discussion being given on suitable nomenclature for use in color measurement.

Because of the importance of soft sugar color measurement in the sugar industry, considerable investigation has been done on the subject. Meade and Harris (*9*) pioneered in this work on soft sugar, using the Hess-Ives photometer. Rice (*14*) later adapted the Meade-Harris scale to a $-\log T$ basis. Knowles (*7*) and Wills (*15*) described the preparation of artificial color standards for visually estimating the color of soft sugar. Wills also described a method employed by Schlegel with the Hess-Ives photometer. However, these and other visual methods of comparison have been subject to the inaccuracies of vision and personal judgment of the observer. Such errors inevitably result from the inability of the human eye to distinguish small quantitative or qualitative differences in the color of the sugar. Therefore it has generally been found that readings of different observers frequently varied widely, and even individual observers could not be depended upon to reproduce their results.

Although these various difficulties with visual methods have been recognized, artificial or synthetic color standards were used in this laboratory for many years for lack of a more satisfactory method of soft sugar color measurement. However, with the development of improved types of photoelectric cells in comparatively recent years, it appeared that errors in visual methods might be avoided by substituting photoelectric cells for the human eye. When the subject was first considered, few photoelectric colorimeters were available and the majority of these were not particularly applicable to this type of measurement. An investigation was made which has resulted in the development of a photoelectric reflectometer (*3*) which gives a quantitative reading directly indicative of the amount of color in soft sugar and which has entirely replaced our former visual method of comparison. This new photoelectric reflectometer has operated satisfactorily for the past few years and has eliminated the principal personal errors which have always been associated with the visual methods of color determination previously employed. Since the development of this instrument, other photoelectric means of measuring the transmittancy or reflectance of sugar products have been described—i. e., Keane and Brice (*6*), Nees (*12*), and Morse and McGinnis (*10*), although these have been mainly for use on white refined sugars, primarily in solution.

Development of Photoelectric Reflectometer

In the early stages of this investigation, much of the preliminary work usually associated with the development of an electrical instrument of this type was avoided by use of a circuit which was basically similar to that employed in the photoelectric colorimeter previously developed by the authors (*2*). While a number of different photoelectric circuits have

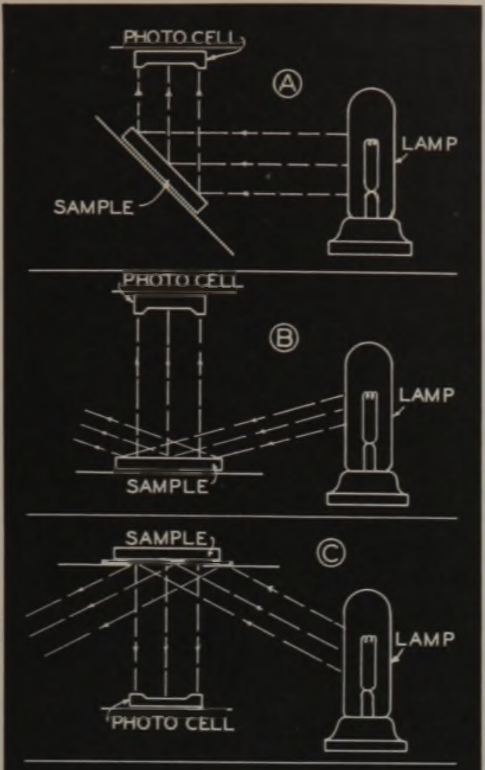

FIGURE I
VARIOUS ARRANGEMENTS FOR MEASURING LIGHT REFLECTION

been described in the literature (*1*, *8*, *11*), the former circuit had proved extremely sensitive and accurate, and appeared to be most suitable for the purpose. The particular circuit as modified for the photoelectric reflectometer consists of two photogenerative cells connected in an opposing type circuit. Photogenerative cells are preferable to emissive type cells as they develop their own output and thus avoid the use of complicated amplifiers. Furthermore, their current response upon illumination gives practically a straight line relationship within the light intensity range normally encountered in color work. This is of great advantage as it permits the color intensity to be measured directly in accordance with fundamental physical laws of light transmission and reflection. In measurements of this type the use of two photoelectric cells is preferable to one, as compensation can be automatically obtained for fluctuations in light intensity, voltage variation, and other such factors. Also, by the use of two photoelectric cells, measurements which are relative to a selected reference standard are obtained. By using a basic standard, the shades of color may thus be expressed in fundamental units of reflection.

The principle employed in the photoreflectometer developed in this investigation was that of photoelectric measurement of the diffused light reflected by the test sample. A number of different arrangements were tried, including 45° viewing as illustrated in diagram *A* of Figure 1, and normal or 90° viewing as indicated in diagram *B*. Of these two, the latter gave greater accuracy, as errors due to irregularities in the reflecting surface were minimized. This principle, modified as shown in diagram *C*, was therefore adopted. While some consideration was given to reflecting spheres, these did not appear particularly suitable for routine use by inexperienced observers because of their elaborate construction and complicated method of operation.

Another phase of this investigation which required considerable experimental work was the establishment of a suitable method of preparing the soft sugar sample. Obviously, it was necessary to provide a smooth surface which could be easily duplicated, and this did not appear practical without compressing the sugar on a level plate. In forming such a surface it was found that insufficient compression caused a very irregular surface while excessive compression resulted in separation of the sirup from the crystals. Also, it developed that compression of the sample directly on the glass plate in the instrument caused formation of a sirup film on the glass which interfered with the reflectance measurement. These various sources of error were overcome by use of the modified arrangement shown in diagram *C* of Figure 1 and by a standardized method of preparing the sample. This latter procedure involved use of a large metal ring approximately 4 inches in diameter and $^5/_8$ inch thick which is placed on a separate glass plate. The ring is filled with sugar and the top scraped off evenly to provide a uniform, loosely packed volume of sugar for each sample. The sugar is then compressed uniformly by means of a plunger with a $^5/_{32}$-inch shoulder, and the prepared sample is moved from the plate on which it was prepared onto the glass plate on the instrument. This procedure resulted in good reproducibility of samples.

Description of Instrument

Figure 2 shows the general arrangement finally adopted for the photoelectric reflectometer. Light from the illuminating source is directed through the apertures onto the reflecting surfaces, which are located on the glass plates shown. Large light apertures (approximately 3.25 inches in diameter) are used in order to reduce the effect of irregularities in the surface of the sugar. Immediately below and parallel to the reflecting surfaces are located the photoelectric cells. These cells are protected from extraneous light by the use of cylindrically shaped shields. The light source employed is a 200-watt projection type lamp which operates on 110 volts a. c. In order to protect the cells from excessive heat, an insulating chamber is situated between the lamps and the photoelectric cells. This consists of an air space between two glass plates. Ventilation of this air space as well as the light housing thus avoids high operating temperatures which might adversely influence the accuracy of response of the photoelectric cells.

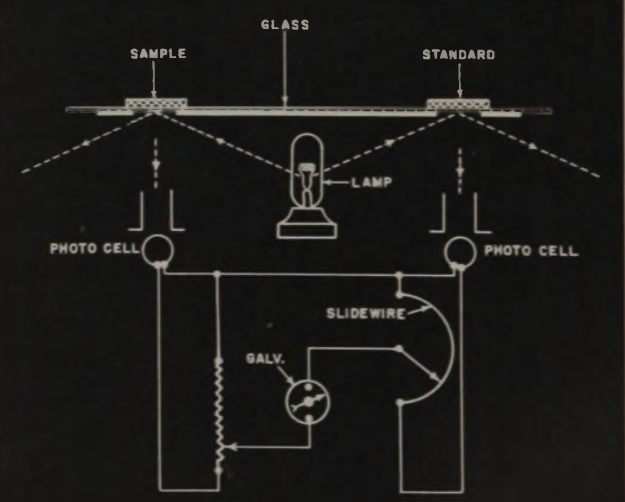

FIGURE 2
SCHEMATIC DIAGRAM OF PHOTO-REFLECTOMETER

As Figure 2 shows, the two photoelectric cells are connected opposingly in a balanced electrical circuit of a potentiometric type. Each cell is shunted by a fixed resistance, the resistances being substantially equal in value. One of the shunting resistances is a precision wire wound type. The other shunt is a uniformly wound slide-wire resistance accurate to approximately 0.1 per cent. This slide-wire is uniformly calibrated in equal divisions from 0 to 100. The relation between potentials developed across these two shunts is determined by adjustment of the contact on the slide-wire, using a lamp and scale galvanometer as a null-point indicator.

The lamp is originally positioned so that both photoelectric cells are illuminated equally. Any slight inequalities in the circuit are initially compensated for by adjustment of the contact on the precision resistance mentioned above. Tests indicated that this electrical method of balancing was extremely simple, and did not affect the accuracy or calibration of the instrument. The adjustable contact on the slide-wire resistance is used to obtain a measure of the reflectance. When all of this resistance is in circuit, the slide-wire reads zero, and when all of the resistance is out of circuit it reads 100. This will be described in more detail in a later section.

The particular reference standard normally employed in reflection measurements is magnesium carbonate, which is the closest approach to pure white and has a reflective power of 98 per cent according to International Critical Tables (*5*). However, this material is not particularly suitable for industrial measurements due to its fragile nature, and a more durable standard was therefore used. The standard selected is a glazed white tile which had an apparent reflection of 88.9 per cent compared to magnesium carbonate or 87 per cent against pure white—i. e., 98 per cent of 88.9 per cent. Two of these tiles are used, one over each photoelectric cell, to provide the reflecting surfaces for initial balancing of the instrument. In subsequent reflectance measurements, the sample is substituted for one of the tiles. A number of these white tiles having substantially the same reflectance are being held in reserve.

In order to provide light of a suitable spectral character, a color filter such as Corning No. 590 Daylite may be utilized. Such a filter transmits light, the spectral quality of which is similar to that of daylight. However, as the total spectral response of the photoelectric cell used does not differ greatly from that of the human eye, and only a measure of the total reflectance is desired, monochromatic color filters need not be used unless a spectral color analysis is required. In such an event, primary color filters or, if desired, monochromatic color filters may easily be inserted in the light path and a measurement obtained of the qualitative color characteristics of the sample.

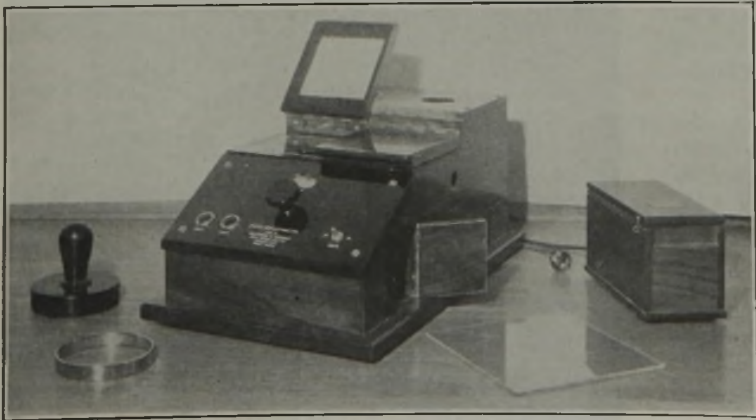

FIGURE 3. PHOTOELECTRIC PHOTOMETER

The photoelectric reflectometer constructed on the above principles is shown in Figure 3. The illumination is housed in the rear of the cabinet. The glass plate, which is located over the apertures and on which the sample or tiles are placed, is apparent near the center of the instrument. The two tiles are mounted in hinged frames so that they can be readily raised or lowered over the photoelectric cells. The electrical equipment is mounted on the panel at the front of the cabinet and in the interior. Other details of construction are obvious.

Calibration of Photoelectric Reflectometer

In expressing the reflectance of opaque substances, any one of a number of different systems of units might be used. However, some of these are empirical in nature and have no fundamental basis. In order to avoid the use of such arbitrary units, the photoelectric reflectometer was purposely designed so that measurements based on the apparent reflection of the sample relative to pure white could be obtained. To secure readings which increased with increasing concentrations of coloring matter, the percentage light absorption, which is merely 100 minus per cent reflection, was adopted. These units have been termed "apparent absorption" units.

As will be recalled, the slide-wire is calibrated uniformly from 0 to 100. Therefore, if a pure white reflecting surface of 100 per cent were obtainable, the instrument would read directly in per cent; that is, a pure white would read 0 per cent light absorption and a pure black 100 per cent light absorption. As previously mentioned, this was an impractical condition and white tiles having an apparent absorption of 13 per cent had been used instead. If the slide-wire was balanced at zero with these tiles, obviously per cent absorption would not be read directly. However, it appeared that if the instrument was initially balanced with the slide-wire set at the predetermined apparent absorption of the tile—i. e., 13 per cent—then all subsequent readings would be directly in per cent. To prove this, three different sets of measurements were made on the same group of samples. The first of these were readings made with magnesium carbonate as a standard and the slide-wire set at zero, the results being corrected from 98 to 100 per cent basis as follows:

$$100 - (\% R \times 0.98)$$

$\% R$ = per cent apparent reflection

The second set was obtained with the white tile as a standard and the slide-wire set at zero, the results being calculated to a percentage basis by means of the formula:

$$100 - (\% R \times 0.87)$$

The third set was obtained by the method described above in which the instrument is balanced with the white tile, the slide-wire being set at 13. The results of these three sets of determinations are shown in Table I. As will be noted, the data agree closely and indicate that the photoelectric reflectometer operated in this manner can be depended upon to give an accurate measure of per cent absorption in terms of any accepted standard of whiteness. As a means of assuring that this calibration remains unchanged, a series of colored tile have been standardized and are used on a routine check basis. In conjunction with this calibration work, some observations were made on the general character of the measurements. One of these points involved the effect a mixture of light and dark brown sugar in a sample would have on the reading.

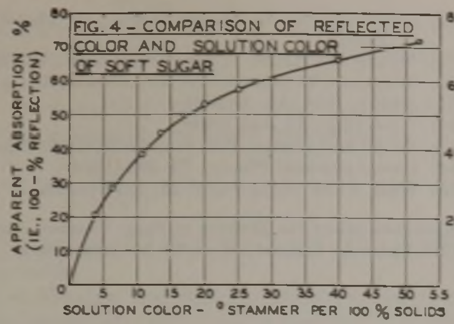

FIG. 4 – COMPARISON OF REFLECTED COLOR AND SOLUTION COLOR OF SOFT SUGAR

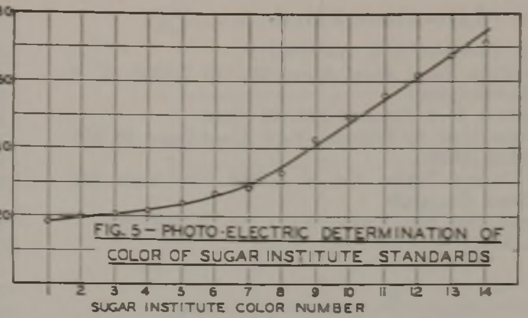

FIG. 5 – PHOTO-ELECTRIC DETERMINATION OF COLOR OF SUGAR INSTITUTE STANDARDS

Observations along this line indicated that, within the small color variations encountered, the photoelectric reflectometer integrated the color of the sample and gave a value representative of its average reflectance.

Table I. Photoelectric Comparison of Reflectance of Soft Sugars against Various Standards

Sample No.	Apparent Absorption Measured against: MgCO₃, slide-wire balanced at 0.0 [100 − (% R × 0.98)]	White tile, balanced at 0.0 [100 − (% R × 0.87)]	White tile, balanced at 13.0
1	13.5	13.5	14.0
2	15.0	14.2	14.5
3	17.6	17.1	16.8
4	20.5	19.7	19.7
5	28.0	27.4	28.4
6	36.5	36.4	36.3
7	45.0	44.1	44.9
8	56.7	56.5	56.9
9	60.0	60.2	60.6
10	65.5	66.0	66.4

Results

Before this new instrument was officially adopted, the calibration was checked against available standards, and many comparisons were made against other methods. These comparisons indicated that photoelectric reflectance measurements were considerably more accurate and reproducible by this means. Table II shows one such typical comparison between visual readings obtained by comparison against color standards and photoelectric reflectance determinations obtained with the photoelectric reflectometer by five observers. The maximum deviation with the visual method for this group was 7 units as compared to only 0.8 unit for the photoelectric method. The average deviation was 1.0 unit for the visual method and only 0.1 unit for the photoelectric method. These data indicate that substitution of the photoelectric reflectometer for methods based on visual comparison with standards has eliminated about 90 per cent of the personal error involved in such determinations. Tests have also been made on the reproducibility of the readings and the reproducibility of sample preparation, and they also indicate good precision.

Another group of data gathered over a considerable period of time compared the reflectance of soft sugars as determined on the photoelectric reflectometer with the transmittancy of solutions of the same samples as measured on the photoelectric colorimeter. These results are plotted on Figure 4 and indicate, as might be expected, that the ratio between reflectance and transmittancy decreases as the total amount of color increases.

In order to ascertain the relation between the calibration of the photoelectric reflectometer in terms of apparent absorption and a system used elsewhere in the sugar industry, the reflectance of each sample in a complete set of ground glass standards prepared by the Sugar Institute was determined. These results (Figure 5) are included as a matter of general interest.

It has been our experience that use of these photoelectric reflectometers in the refinery and laboratory has not only simplified our soft sugar color control, but also has greatly increased its accuracy. As a further step in eliminating inaccurate visual methods, two additional instruments have since been developed. One of these is a modified reflectometer for dry white sugars; the other is for determining the color index and turbidity index of white sugar solutions. With the development and adoption of these various instruments our transition from comparatively unreliable visual methods to a precise photoelectric basis for the grading of sugars has been completed. Although the use of these photoelectric devices has largely been confined to sugar products, their application is now being gradually extended to other materials.

Table II. Comparison of the Color of Soft Sugar Determined Visually and Photoelectrically by Various Observers

Sample No.	Visual Method								Photoelectric Method								Deviation of Av. Visual Color from Av. Photoelectric Reflectance
	Observer					Max. deviation	Av. deviation	Av.	Observer					Max. deviation	Av. deviation	Av.	
	A	B	C	D	E				A	B	C	D	E				
1	56.2	57.0	55.0	55.5	54.3	2.7	0.8	55.6	55.8	56.2	56.1	56.3	56.2	0.5	0.1	56.1	−0.5
2	56.7	55.5	56.5	55.0	53.5	3.2	0.8	55.5	55.6	55.8	55.5	56.1	56.0	0.6	0.2	55.8	−0.3
3	57.0	56.7	56.5	56.0	55.0	2.0	0.6	56.2	55.5	55.3	55.5	55.2	55.5	0.3	0.1	55.4	+0.8
4	53.5	54.0	52.5	52.0	52.0	2.0	0.8	52.8	53.0	53.2	52.8	52.9	52.6	0.6	0.2	52.9	−0.1
5	58.0	57.0	57.0	55.0	54.0	4.0	1.4	56.2	57.3	57.3	57.3	57.4	57.2	0.2	0.0	57.3	−1.1
6	57.3	57.3	57.0	55.0	56.0	2.3	0.8	56.5	57.1	57.3	57.0	56.7	57.2	0.6	0.2	57.0	−0.5
7	56.0	56.5	57.5	55.0	55.5	2.5	0.7	56.1	57.3	57.0	57.1	57.4	57.1	0.4	0.1	57.1	−1.0
8	56.5	57.5	56.5	55.0	54.7	2.8	1.0	56.0	56.2	56.5	56.0	56.4	56.1	0.5	0.2	56.2	−0.2
9	55.3	55.7	55.5	56.0	53.0	3.0	0.8	55.1	55.4	55.1	54.9	55.1	54.8	0.6	0.2	55.1	0.0
10	54.6	55.0	53.0	55.0	52.5	2.5	1.0	54.0	53.0	53.5	53.3	53.6	53.8	0.8	0.2	53.4	+0.6
11	34.0	37.5	36.0	37.0	40.0	6.0	1.5	36.9	37.2	37.2	..	..	..	0.0	0.0	37.2	−0.3
12	33.0	35.5	34.5	40 0	35.0	7.0	1.7	35.6	34.4	34.8	..	..	..	0.4	0.2	34.6	+1.0
13	67.0	66.0	67.7	68.0	..	2.0	0.6	67.2	67.6	67.4	..	..	..	0.2	0.1	67.5	−0.3
14	66.0	66.0	67.5	67.5	..	1.5	0.8	66.7	67.8	67.6	..	..	..	0.2	0.1	67.7	−1.0
						Average	1.0								0.1		−0.2

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Action of Light on Cellulose

Viscosity-Concentration Relations of Cellulose Acetate Solutions

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The equation

$$\eta_r = 1 + kc + k^1c^2$$

which is analogous to the expanded form of the expressions derived by Einstein and by Kunitz, describes the viscosity behavior of dilute solutions of cellulose acetate. An easy and rapid method for obtaining the limiting specific viscosity, $[\eta]$, defined by the equation

$$[\eta] = \frac{\lim}{c \longrightarrow 0} \left(\frac{\eta_r - 1}{c}\right)$$

is described.

SEVERAL authors have derived mathematical expressions for the viscosity of colloidal dispersions, either based on experimental evidence or obtained from theoretical considerations. These equations all attempt to relate the relative viscosity, η_r, with the volume of the dispersed phase, ϕ, and it is generally accepted that the relative viscosity should be definitely determined by the volume of the dispersed phase alone, provided the particles are spherical in shape.

Among the expressions frequently used are those of Einstein (*2*),

$$\eta_r = 1 + 2.5\phi \qquad (1)$$

and Hatschek (*4*)

$$\eta_r = 1 + 4.5\phi \qquad (2)$$

Equation 1 is the expanded form to the first approximation of

$$\eta_r = \frac{1 + 0.5\phi}{(1 - \phi)^2}$$

and Equation 2 is the expanded form of

$$\eta_r = \frac{1 + 0.5\phi}{(1 - \phi)^4}$$

which is the relation proposed by Kunitz (*6*).

These mathematical relations have either been developed on the assumption that the dispersed particles are approximately spherical without interference between particles, or they are empirical equations that have been determined under conditions where the above assumption was not greatly in error. However, in studying the viscosity of dispersions of cellulose acetate, we encounter conditions where the individual particles do not even approximate spherical shapes. This statement must be true whether we concede the existence of long straight-chain macromolecules as proposed by Staudinger (*11*) or micelles composed of bundles of these linear molecules as suggested by McBain (*7*).

Smoluchowski (*10*) and Sakurada (*9*) pointed out that the coefficient 2.5 of the Einstein equation includes a shape factor which is a minimum for spheres.

Onsager (*8*) calculated the case for a suspension of rotation ellipsoids and found that the shape factor of Einstein's equation increases with the square of the ratio of major to minor axes.

Eisenschitz (*3*), by a less rigorous analysis, reached the conclusion that, as a first approximation, the shape factor would increase linearly with this ratio.

It appears obvious, and in agreement with the various theoretical concepts, that coefficients for these equations derived on the assumption of the existence of spherical particles should not be applied to cases where other shapes are known to exist. Since the difficulty of determining particle shape is so great, and the hydrodynamical calculations of shapes other than spherical have not generally been worked out, it seems logical to turn to experimental data in order to determine the true coefficients. In order to do this, such dilute solutions must be used that the assumption of noninterference of particles is valid. A search of the literature reveals the fact that most of the work on the viscosity of dispersions of cellulose derivatives has exceeded the limit imposed by this condition since the results of this work

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indicate that, even for the relatively low viscosity cellulose acetates used, this limit is in the neighborhood of 0.5 gram per 100 cc. of solution.

The value of characterizing the viscosity properties of solutions by the limiting specific viscosity, $[\eta]$, defined by

$$[\eta] = \lim_{c \longrightarrow 0} \left(\frac{\eta_r - 1}{c} \right) \tag{3}$$

was discussed by Kraemer (*5*) and Dobry (*1*), and is substantiated by this work.

The equations of Einstein and Kunitz can be expanded to include a term involving ϕ^2; and since ϕ is equal to $cv/100$ where v is the partial specific volume and c is the concentration in grams per 100 cc., a general equation

$$\eta_r = 1 + kc + k^1c^2 \tag{4}$$

may be written. In this equation k and k^1 are constants containing a shape factor and a specific volume term, both of which are constant for any given material. Rearranging,

$$\frac{\eta_r - 1}{c} = k + k^1c \tag{5}$$

If the value $(\eta_r - 1)/c$ is plotted against concentration c, a straight line of slope k^1 and intercept k should result. In addition, the intercept k is the value of $(\eta_r - 1)/c$ at infinite dilution and is equal to the previously defined "limiting specific viscosity" $[\eta]$.

Experimental

The cellulose acetate used in this work consisted of ten samples of commercial material manufactured and furnished by the Eastman Kodak Company, E. I. du Pont de Nemours and Company, Inc., and the American-British Chemical Supplies, Inc. Grateful acknowledgment is made for their use.

The acetyl contents of the various types were as follows:

Sample No.	Manufacturer's Type Designation	Acetyl Content, %
21	High viscosity	40.6
12	Medium viscosity	41.6
50	Medium viscosity	42.2
101	High viscosity	39.5
102	Medium viscosity	39.1
107	Medium viscosity	41.4
108	Low viscosity	40.0
15	Medium viscosity	38.4
10	Medium viscosity	38.7
5	Low viscosity	38.6

To purify the acetone used as a solvent, it was stored over calcium chloride for at least 48 hours; potassium permanganate was then added, and the mixture was allowed to stand and was finally distilled through a 90-cm. column, packed with glass tubing, in 2-liter batches. The first 500 cc. coming over were arbitrarily discarded, and the distillation was stopped after 1.5 liters had distilled over. The intermediate fraction of 1 liter was saved and used. This fraction distilled at a constant temperature.

The cellulose acetate was dried in a desiccator over P_2O_5 for 48 hours and dispersed in the proper solvent; the solution was analyzed for the cellulose acetate content and placed in calibrated 50-cc. volumetric flasks. Pipets, calibrated to hold either 10 or 25 cc., were used to remove samples for viscosity determinations. By this means a definite volume was removed for each determination after temperature adjustments had been made. At least 24 hours were allowed between determinations after the addition of solvent to permit complete dispersion.

Viscosities were determined by Ostwald pipets of approximately the proper dimensions, at 30° ± 0.1° C. Various pipets were used so that in no case was the time of flow less than 100 seconds. The volume of flow varied from approximately 4 to 8 cc., depending on the pipet used. In any one case check runs were made with different pipets. The concentration was varied from 1.6 down to 0.02 gram per 100 cc. The resulting viscosity-concentration data were first plotted on large graph paper so that curves for η_r against c were obtained; 25 to 50 points were taken for each type of acetate, and the best curve was drawn through them. The values of η_r and c in Figure 1 were obtained by reading from this curve. This method tended to smooth out slight inaccuracies in the viscosity determinations and gave good average values for the viscosity at any one concentration.

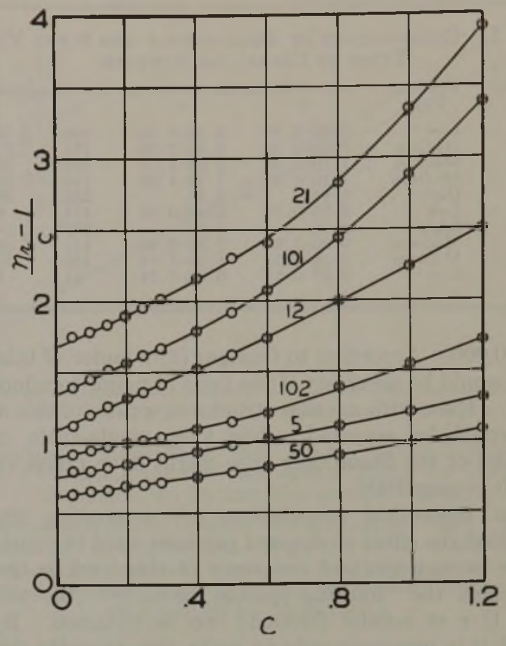

Figure 1

Figure 1 shows typical curves obtained by plotting c *vs.* $(\eta_r - 1)/c$ for dispersions of various types of cellulose acetate in acetone. In all cases a straight-line relation is obtained up to a concentration of approximately 0.5 gram. At this point the higher viscosity cellulose acetates give a curve which begins to deviate from a straight line. Table I gives the values for the intercept, k, and the slope, k^1, for dispersions of various types of cellulose acetate in acetone. The duplicate values are the results of check runs.

Discussion of Results

Although this method of presenting viscosity-concentration relations is admittedly approximate and applies only to very dilute solutions, it does illustrate the fact that the theoretical equations developed can be correlated with experimental data, provided the fundamental assumptions are modified to apply to the particular system under consideration. Table I presents the values of the coefficients a and b in the equation:

$$\eta_r = 1 + a\phi + b\phi^2 \tag{6}$$

These values were obtained, using a partial specific volume of 0.66 for cellulose acetate. Since $\phi = cv/100$,

$$a = \frac{k \times 100}{v} \text{ and } b = \frac{k^1 \times 10{,}000}{v^2}$$

At first glance these values appear to be surprisingly large, but if a shape factor of 100 were substituted in place of unity in the original equations, a would be 250 in Equation 1 or 450 in Equation 2. Corresponding values of b would be 30.000

TABLE I. COEFFICIENTS OF EQUATIONS 4 AND 6 FOR VARIOUS TYPES OF CELLULOSE ACETATE

Sample No.	Viscosity Type	Equation 4		Equation 6	
		k	k^1	a	b
5	Low	0.86–0.90	0.64–0.50	136	13,100
10	Medium	1.10–1.16	0.99–0.98	171	21,500
12	Medium	1.10–1.12	1.04–1.02	168	23,700
15	Medium	1.19–1.20	1.18–1.06	182	25,300
21	High	1.66	1.25	252	28,700
50	Low	0.76–0.77	0.46–0.31	115	9,000
101	High	1.30	1.08	197	24,800
102	Medium	0.96–1.06	0.94–0.80	151	20,000
107	Medium	1.18–1.23	1.24–1.13	182	27,200
108	Low	0.57–0.62	0.38–0.34	91	8,300

and 100,000. According to Onsager (*8*) a factor of this magnitude would be necessary if the ratio of major to minor axes was 10. Even with micellar structures, a ratio of this magnitude would be expected, while long, single-chain macromolecules of the Staudinger type might have ratios varying from 10 to over 1000.

These theoretical speculations are interesting and indicate that the effect of shape of particles must be considered, but the most important discovery of this work is the ease with which the "limiting specific viscosity" [the value of $(\eta_r - 1)/c$ at infinite dilution] can be obtained. By this method it is necessary only to make two viscosity determinations at two different concentrations below 0.5 gram per 100 cc., and $[\eta]$ can be obtained assuming only the validity of the linear relation between $(\eta_r - 1)/c$ and c in this concentration range. No available experimental data invalidate this assumption. This value is slowly coming into general use as a means of characterizing the properties of this type of colloidal solution. Staudinger and Kraemer have both correlated $[\eta]$ with molecular weight determinations, and unpublished work in this laboratory has indicated that it is the best means of following the degradation of cellulose derivatives. Its chief advantage is the fact that thixotropic effects seem to be eliminated as infinite dilution is approached. The very satisfactory check runs in different pipets are an indication of this fact. The constancy of this value, coupled with its ease of determination, should ultimately lead to its use to designate viscosity types of cellulose acetate in place of the falling-ball viscometer.

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ABSTRACTED from a thesis submitted by C. C. Winding to the faculty of the Graduate School of the University of Minnesota, in partial fulfillment of the requirements for the degree of doctor of philosophy.

Properties of Rubber Solutions and Gels

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The writer's theory of the thermodynamic properties of solutions of long-chain molecules is shown to be applicable to rubber solutions. Each rubber-solvent system is characterized by a constant which determines the dependence of the activity (and, therefore, of various properties derived from the activity) on concentration. The theoretical equations hold over the whole range of composition, for the rubber-benzene system at least. Theoretically sound equations for the determination of molecular weights from osmotic pressure and cryoscopic data are presented; the errors inherent in the use of other equations are pointed out.

RUBBER solutions, like other solutions of long-chain molecules in small-molecule solvents, show large deviations from Raoult's law even when the heat of mixing is small. As Meyer (*17*, *18*) pointed out, this can be attributed to a large entropy-of-mixing effect, a result of a randomness of orientation of each segment of the solute molecule chain relative to the adjacent segments. This conception has been put on a quantitative basis by the writer (*9*, *10*, *11*) and, independently, by Flory (*3*).

Combining his theoretical equation for the entropy of mixing with an approximate expression, due to van Laar (*15*), Scatchard (*23*), and Hildebrand (*8*), for the heat of mixing, the writer deduced the following equation for the thermodynamic activity of the small-molecule component:

$$\ln a_1 = \ln \not{V}_1 + \left(1 - \frac{\bar{\bar{V}}_1}{\bar{\bar{V}}_2}\right) \not{V}_2 + \mu_1 \not{V}_2^2 \qquad (1)$$

where a_1 = thermodynamic activity
$\not{V}_1, \not{V}_2$ = volume fractions
$\bar{V}_1, \bar{V}_2$ = partial molal volumes of components (for present purpose assumed equal to actual molal volumes, V_1 and V_2 of pure components)
μ_1 = a constant (approximately), characteristic of a given solute-solvent system at a given temperature

The corresponding equation for $\ln a_2$ is like Equation 1, except for the interchange of all subscripts.

Such properties as vapor pressures, osmotic pressures, freezing-point depressions, and solubilities are related by

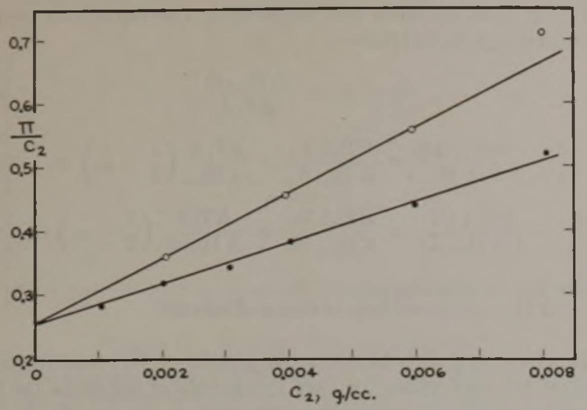

FIGURE 1. DEPENDENCE OF OSMOTIC PRESSURE ON CONCENTRATION, FOR GUTTA-PERCHA SOLUTIONS IN TOLUENE (BLACK CIRCLES) AND IN CARBON TETRACHLORIDE (OPEN CIRCLES)

Data from Staudinger and Fischer (*25*). The inclusion of a term ($-RTC_2^2/3V_1d_2^3$) would lower the two right-hand points (at $C_2 \approx 0.008$) about 0.005.

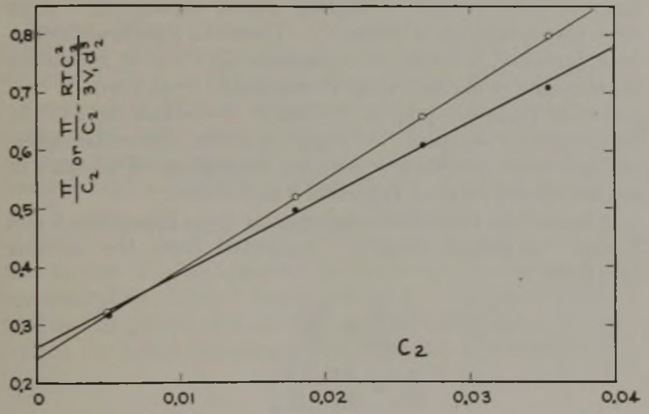

FIGURE 2. EFFECT OF THE TERM $-RTC_2^2/3V_1d_2^3$ ON EXTRAPOLATION OF OSMOTIC PRESSURE DATA TO INFINITE DILUTION, TO OBTAIN MOLECULAR WEIGHTS

The intercepts give M_2 = 94,000 with this term and "M_2" = 102,000 without it. Data of Caspari (*1*) on solutions of "fresh" rubber in light petroleum.

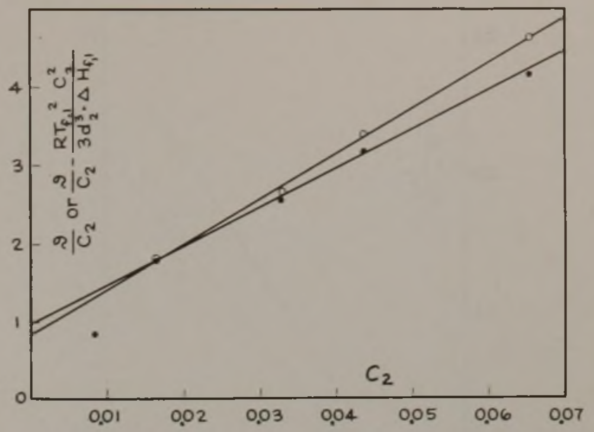

FIGURE 3. EFFECT OF THE TERM $-RT_{f,1}^2C_2^2/3d_2^3\,\Delta H_{f,1}$ ON EXTRAPOLATION OF CRYOSCOPIC DATA TO INFINITE DILUTION, TO OBTAIN MOLECULAR WEIGHTS

The intercepts give M_2 = 27,000 with this term and "M_2" = 23,000 without it. Data of Kemp and Peters (*12*) on solutions of rubber (preparation 2, fraction 2) in cyclohexane. (They give "cryoscopic molecular weights", obtained without extrapolation, ranging from 6050 to 30,870 for this material.)

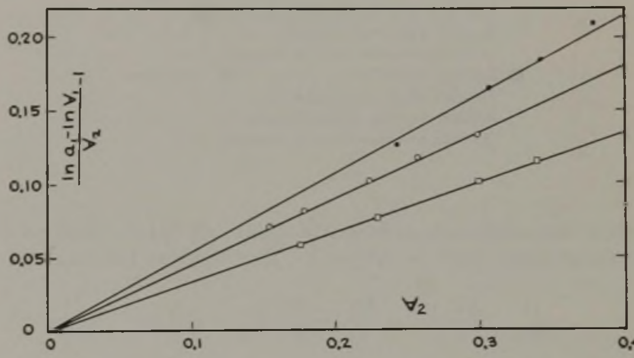

FIGURE 4. DETERMINATION OF μ_1 FROM SWELLING PRESSURE DATA OF POSNJAK (*20*), ACCORDING TO EQUATION 2

● Rubber-ether, μ_1 = 0.55
○ Rubber-thiophene, μ_1 = 0.45
□ Rubber-cymeme, μ_1 = 0.33

simple thermodynamic equations to the activities of the solution components. There are thus ample data on a wide variety of systems, available for testing Equation 1. These tests have yielded such uniformly satisfactory results (*9, 11*) that this equation must represent a close approximation to the truth.

In this paper Equation 1 will be applied to solutions of rubber.

The "Constant" μ_1

The quantity μ_1 depends in part on the heat of mixing and in part on the departure from perfect randomness of mixing of the molecules in the solution. Crudely speaking, it is a measure of the preference of each molecule (or submolecule) to have other like molecules (or submolecules) rather than units of the other kind, for immediate neighbors.

Rearranging Equation 1,

$$\frac{\ln a_1 - \ln V_1}{V_2} - 1 = -\frac{\bar{V}_1}{\bar{V}_2} + \mu_1 V_2 \qquad (2)$$

A plot of the left-hand member of this equation against V_2 should therefore give a straight line (if μ_1 is constant) having a slope equal to μ_1 and an intercept at $V_2 = 0$ (i. e., at infinite dilution) equal to $-\ \bar{V}_1/\bar{V}_2$ (hence, for a given solvent, inversely proportional to the molecular weight of the solute). Any accurate method for determining a_1 as a function of concentration (V_2) will thus serve to give the molecular volume (and so the molecular weight) of the solute particles and also the value of μ_1.

If data are available on osmotic pressure (Π), for example, substitution may be made into Equation 2:

$$\ln a_1 = -\frac{\Pi \bar{V}_1}{RT} \approx -\frac{\Pi V_1}{RT} \qquad (3)$$

where R = molal gas law constant
T = absolute temperature

The value of R depends, of course, on the units in which Π and V_1 are expressed. Also, $\ln V_1$ may be expanded:

$$\ln V_1 = \ln(1 - V_2) = -V_2 - \frac{V_2^2}{2} - \frac{V_2^3}{3} - \ldots \qquad (4)$$

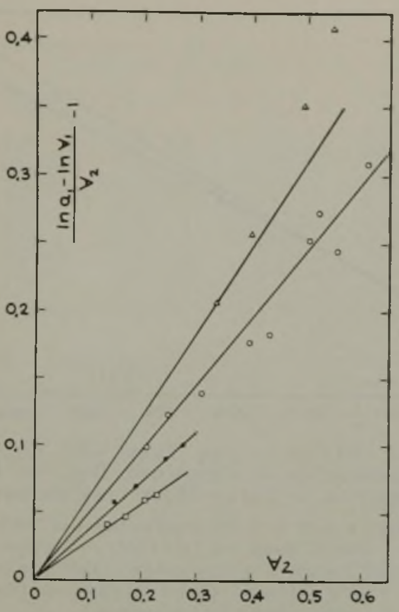

FIGURE 5. DETERMINATION OF μ_1

○ Rubber–carbon disulfide, $\mu_1 = 0.49$; vapor pressure data of Stamberger (*24*)
△ Rubber–ethylene chloride, $\mu_1 = 0.62$(?); swelling pressure data of Posnjak (*20*)
● Rubber–chloroform, $\mu_1 = 0.37$; swelling pressure data of Posnjak (*20*)
□ Rubber–carbon tetrachloride, $\mu_1 = 0.28$; swelling pressure data of Posnjak (*20*)

and if the solution is sufficiently dilute, all but the first two or three terms may be dropped. This leads to the relation,

$$\frac{\Pi}{V_2} - \frac{RT\,V_2^2}{3\,\mathrm{V}_1} = \frac{RT}{\mathrm{V}_2} + \frac{RT}{\mathrm{V}_1}\left(\frac{1}{2} - \mu_1\right) V_2 \qquad (5)$$

the second term on the left-hand side usually being negligible. Similar equations involving concentrations in other units are readily deduced. If the concentrations are in grams of solute per cc. of solution (C_2), for example,

$$\frac{\Pi}{C_2} - \frac{RTC_2^2}{3\,\mathrm{V}_1 d_2^3} = \frac{RT}{\mathrm{M}_2} + \frac{RT}{\mathrm{V}_1 d_2^2}\left(\frac{1}{2} - \mu_1\right) C_2 \qquad (6)$$

where d_2 = density of pure solute
M_2 = molecular weight of pure solute

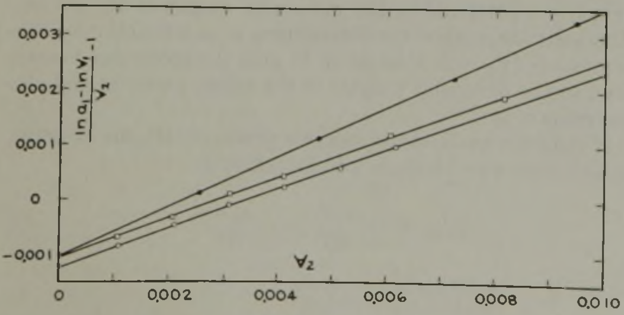

FIGURE 6. DETERMINATION OF μ_1 AND M_2 FROM OSMOTIC PRESSURE DATA OF STAUDINGER AND FISCHER (*25*) ON SOLUTIONS IN TOLUENE

● Hydrorubber (less soluble fraction), $\mu_1 = 0.45$, $\mathrm{M}_2 = 90{,}000$
□ Gutta-percha (preparation II), $\mu_1 = 0.36$, $\mathrm{M}_2 = 98{,}000$
○ Balata (preparation I), $\mu_1 = 0.36$, $\mathrm{M}_2 = 84{,}000$

If the data at hand are cryoscopic, the equations corresponding to 3, 5, and 6 are

$$\ln a_1 = -\frac{\Delta \mathrm{H}_{f,1}\,\vartheta_f}{RT_{f,1}^2} \qquad (7)$$

$$\frac{\vartheta_f}{V_2} - \frac{RT_{f,1}^2\,V_2^2}{3\,\Delta \mathrm{H}_{f,1}} = \frac{RT_{f,1}^2\,\mathrm{V}_1}{\Delta \mathrm{H}_{f,1}\,\mathrm{V}_2} + \frac{RT_{f,1}^2}{\Delta \mathrm{H}_{f,1}}\left(\frac{1}{2} - \mu_1\right) V_2 \qquad (8)$$

$$\frac{\vartheta_f}{C_2} - \frac{RT_{f,1}^2\,C_2^2}{3\,\Delta \mathrm{H}_{f,1}\,d_2^3} = \frac{RT_{f,1}^2\,\mathrm{V}_1}{\Delta \mathrm{H}_{f,1}\,\mathrm{M}_2} + \frac{RT_{f,1}^2}{\Delta \mathrm{H}_{f,1} d_2^2}\left(\frac{1}{2} - \mu_1\right) C_2 \qquad (9)$$

where $T_{f,1}$ = freezing point, ° K.
$\Delta \mathrm{H}_{f,1}$ = molal heat of fusion of solvent

In agreement with Equation 6, graphs of Π/concentration against concentration, for very dilute rubber solutions (as for solutions of other long-chain compounds, *9, 10, 11, 16*) show a rectilinear relation (*4, 19*). A typical example is shown in Figure 1.

In this case, the omission of the second term on the left-hand side of Equation 6 makes little difference. This is not true, however, if the data are for somewhat higher concentrations, as illustrated by Figure 2. Over the concentration range shown, the agreement with a straight-line relation is not much altered. (In this case the inclusion of the second term actually results in slightly poorer agreement; more often the agreement is bettered.) There is a significant difference, however, between the intercepts (at $C_2 = 0$) and hence between the molecular weights calculated from them.

Similar remarks apply to the use of cryoscopic data to obtain molecular weights. As Figure 3 shows, somewhat different molecular weights are deduced, depending on whether or not the second term of Equation 9 is included.

It is obvious from these figures and from Equations 6 and 9 that "molecular weights" computed from the limiting equations,

$$\frac{\Pi}{C_2} = \frac{RT}{\mathrm{M}_2} \qquad (10)$$

$$\frac{\vartheta_f}{C_2} = \frac{RT_{f,1}^2\,\mathrm{V}_1}{\mathrm{M}_2\,\Delta \mathrm{H}_{f,1}} \qquad (11)$$

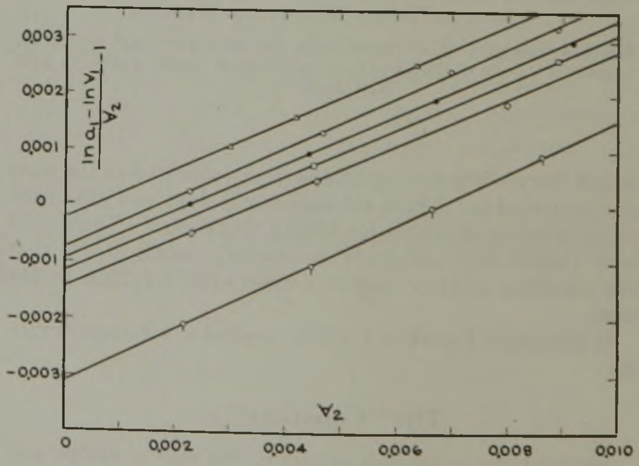

FIGURE 7. DETERMINATION OF μ_1 AND M_2 FROM OSMOTIC PRESSURE DATA BY STAUDINGER AND FISCHER (*25*) ON SOLUTIONS IN TOLUENE

△ Rubber treated with Al_2O_3, $\mu_1 = 0.44$, $\mathrm{M}_2 = 395{,}000$
○ Masticated rubber (technical; less soluble fraction), $\mu_1 = 0.45$, $\mathrm{M}_2 = 130{,}000$
● Crepe rubber I, oxidized with $KMnO_4$, $\mu_1 = 0.43$, $\mathrm{M}_2 = 102{,}000$
□ Masticated rubber (technical; more soluble fraction), $\mu_1 = 0.43$, $\mathrm{M}_2 = 83{,}000$
◇ Masticated rubber (more soluble fraction), $\mu_1 = 0.42$, $\mathrm{M}_2 = 68{,}000$
ϙ Cyclic rubber made with $SnCl_4$, $\mu_1 = 0.46$, $\mathrm{M}_2 = 32{,}000$

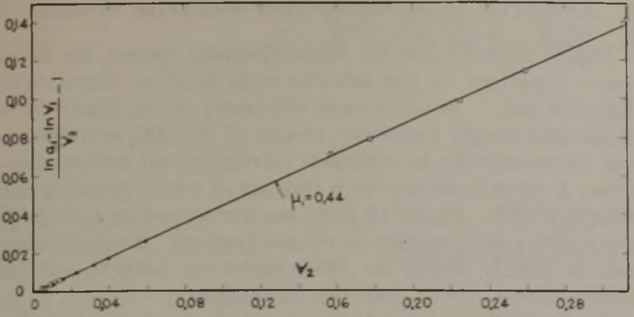

FIGURE 8. RUBBER-BENZENE SYSTEM

○ Osmotic pressure data (40° C.) of Kroepelin and Brumshagen (*14*)
● Osmotic pressure data (25° C.) of Caspari (*1*)
□ Swelling pressure data (15–20° C.) of Posnjak (*20*)

or other equations equivalent to them, are true molecular weights only if the concentration is not significantly different from zero or if μ_1 for the particular combination of solvent and solute is close to $^1/_2$. Otherwise the so-called molecular weights are erroneous, and their use is likely to lead to false conclusions (*12*, *13*, *21*, *22*), as pointed out by Gee (*6*).

Values of the constants μ_1 for different systems can be computed from the slopes of the straight lines obtained when the quantity $(\Pi/C_2) - (RTC_2^2/3V_1d_2^2)$ is plotted against C_2 or from corresponding plots of cryoscopic data. If the data to be used are for more concentrated solutions, however—for example, Posnjak's data (*20*) on swelling pressures and Stamberger's (*24*) and Gee and Treloar's (*7*) on vapor pressure—it is more convenient to compute $\frac{\ln (a_1/V_1)}{V_2} - 1$ and plot this against V_2, as suggested by Equation 2; Figures 4 to 9 are examples. Table I lists values of μ_1, obtained from these and similar graphs, for various systems containing rubber, as well as for a few containing gutta-percha, hydrorubber, etc.

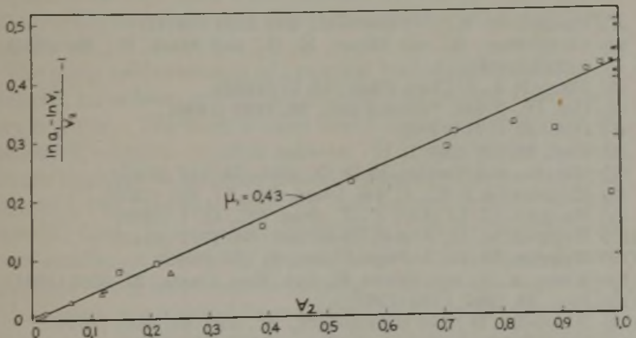

FIGURE 9. RUBBER-BENZENE SYSTEM (25° C.), FROM DATA OF GEE AND TRELOAR (*7*)

○ Osmotic pressure
△ Equilibrium against triolein
□ Direct manometric method
● McLeod gage method

The value of μ_1 is apparently independent of molecular weight, as it is for other high-polymer systems studied. The slight differences in slope shown in Figure 7 are probably due in part to experimental error; on the other hand, minor differences in the chemical nature of the molecules (and so in their attractions for one another and for the solvent, resulting in differences in μ_1) would be expected from the differences in the chemical treatment undergone by the various samples studied.

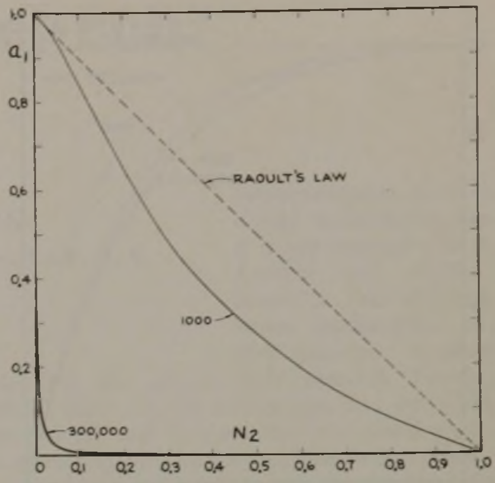

FIGURE 10. ACTIVITY AS A FUNCTION OF MOLE FRACTION FOR RUBBER-BENZENE SYSTEM (μ_1 = 0.43)

Heavy curve: molecular weight = 300,000
Light curve: molecular weight = 1,000

As Figure 9 shows, a constant value of μ_1, represented by the straight line, agrees with the experimental observations on the rubber-benzene system over the whole range of composition, within or nearly within the probable experimental error. (The scattering of the experimental points at high values of V_2 is due partly to the impossibility of reading the coordinates of the points on the published graphs accurately; the numerical data were not published. One might expect slightly low values at high rubber concentrations, however, as a result of failure to obtain equilibrium.)

The value of μ_1 would be expected to vary somewhat with the temperature. In the case of the rubber-benzene system, this variation is very slight, as indicated by the fact that experimental results obtained at three different temperatures agree reasonably well with the same straight line (Figure 8). From Gee and Treloar's measurements of osmotic pressure at 30.6° and at 8.8–9.95° C., one can compute an average

TABLE I. VALUES OF μ_1 FOR VARIOUS SYSTEMS

System	μ_1	Temp., ° C.	Citation
Rubber–			
Benzene + 10% C_2H_5OH	0.26	25	(*5*)
Carbon tetrachloride	0.28	15–20	(*20*)
Camphor	0.29	180	(*6*)
Cymene	0.33	15–20	(*20*)
Cyclohexane	0.33	6.5	(*12*)
Tetrachloroethane	0.36	15–20	(*20*)
Chloroform	0.37	15–20	(*20*)
Cumene	0.38	15–20	(*20*)
Light petroleum	0.43	25	(*1*)
Acetylene dichloride	0.43	15–20	(*20*)
Toluene	0.43–0.44	27	(*25*)
Benzene	0.43–0.44	7–40	(*1*, *2*, *7*, *14*, *20*)
Chlorobenzene	0.44	7	(*2*)
Thiophene	0.45	15–20	(*20*)
Carbon disulfide	0.49	25	(*24*)
Amyl acetate	0.49	25	(*5*)
Benzene + 15% CH_3OH	0.50	25	(*5*)
Ether	0.55	15–20	(*20*)
Ethylene chloride	0.62?	15–20	(*20*)
Gutta-percha–			
Carbon tetrachloride	0.28	27	(*25*)
Toluene	0.36	27	(*25*)
Benzene	0.52	25	(*1*)
Balata-toluene	0.36	27	(*25*)
Hydrorubber-toluene	0.45	27	(*25*)

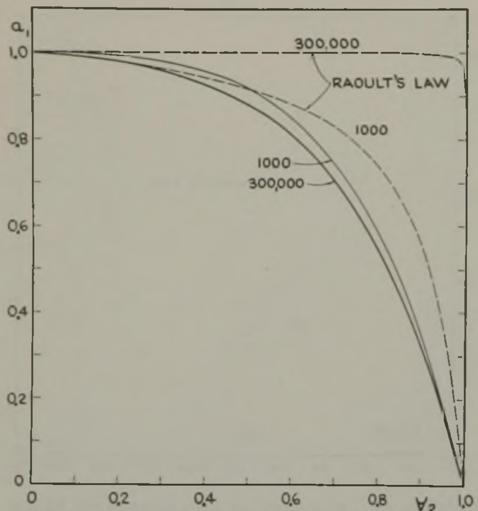

FIGURE 11. ACTIVITY AS A FUNCTION OF VOLUME FRACTION FOR RUBBER-BENZENE SYSTEM ($\mu_1 = 0.43$)

Heavy curve: molecular weight = 300,000
Light curve: molecular weight = 1,000

value of $d\mu_1/dT$ of about -0.0002. The higher the temperature, the smaller the value of μ_1. Considerably larger values of the temperature coefficient would be expected for many other systems.

The swelling pressure data on rubber gels containing ethylene chloride indicate an increasing value of μ_1 with increasing concentration (Figure 5). This may perhaps be real; it seems more likely, however, that the experimental data are in error. The swelling pressure is over 5 atmospheres at the highest concentration.

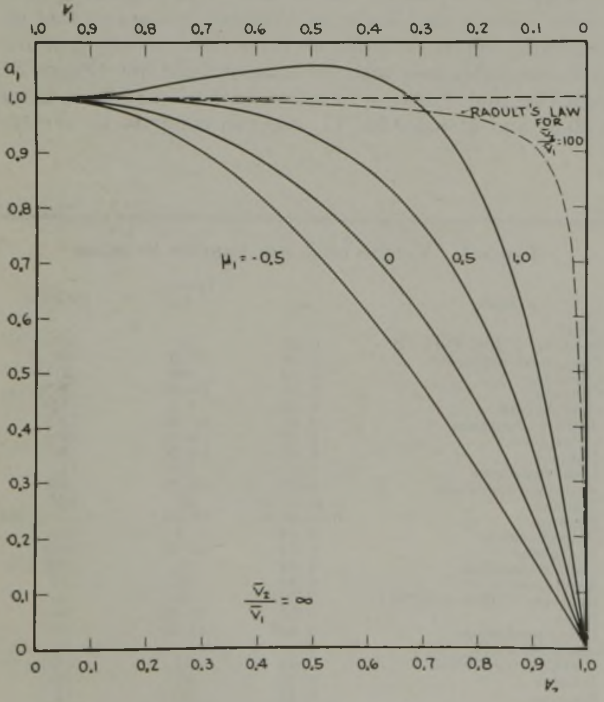

FIGURE 12. ACTIVITY AS A FUNCTION OF VOLUME FRACTION FOR A "SOLUTE" (E. G., RUBBER) OF INFINITE MOLECULAR WEIGHT (A GEL), FOR DIFFERENT VALUES OF μ_1

Activity Curves for Rubber-Benzene System

Figure 10 shows, for the rubber-benzene system, the enormous departure of the activity–mole fraction curve from Raoult's law. In addition to the heavy curve, drawn for a (number-average) molecular weight of 300,000, corresponding approximately to ordinary unfractionated rubber solutions, a curve is shown for a fraction of very low molecular weight (1000). Figure 11 gives the corresponding curves for the activity as a function of volume fraction. Similar curves can be readily drawn for other molecular weights and for other systems, once μ_1 has been determined.

Figure 12 shows the activity *vs.* volume fraction curves for certain arbitrary values of μ_1, with the size of the "solute" molecules (component 2) assumed to be infinitely large relative to the size of the solvent molecules. (This state of affairs may be assumed to exist in any gel.) As previously pointed out (*3*, *10*) the curves corresponding to values of μ_1 greater than 0.5 have a double inflection, indicating a separation of phases. Except when μ_1 is very close to the limiting value, one phase is practically pure solvent; the other consists of the high-molecular-weight component (rubber) containing an amount of the low-molecular component determined by the concentration at which its activity equals unity.

Conclusion

Although the data presented suffice to show the general applicability of our theoretical equations to rubber systems, large gaps in our knowledge obviously remain. In particular, it would be desirable to have more data on systems having large μ_1 values.

Acknowledgment

The writer takes pleasure in acknowledging the assistance of Dorothy Davis and Kuan Han Sun with the calculations involved in the preparation of this paper.

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What Is Research?

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SOME time ago I enlisted the help of George Curme to cooperate in planning a session on research. There were a number of aspects of current importance worthy of an evening's discussion; but it seemed that the treatment of each was contingent upon a definition. As a consequence, the subject became, "What Is Research?" My part was merely to propound the question. George Curme, vice president of Carbide and Carbon Chemicals Corporation, discussed it from the viewpoint of an industrialist; John P. Hubbell, of Singmaster and Breyer, from that of a consultant; and L. W. Bass, then of Mellon Institute, from that of an institutional director. Having had the benefit of their erudition, I am supposed to answer the question.

The dictionary would appear to make our problem simple. Broadly, research is "a studious inquiry"; specifically, it is "a scientific experimental investigation". Beside the dictionary others have described it variously as "finding out what you want to know" and "an inquiring state of mind". Could it be that research is nothing more than the process of becoming educated; or, might we better say that it connotes creative thinking? Since we can view this word "research" from so many angles, it acquires a magic value unattainable by a more precise word.

In the field of chemistry, scientific experimental investigation has brought to light ever increasing data, and interpretation has proceeded apace. Research in this sense has been the basis for the tremendous growth of science, and through its service industry has found the way to meet our expanding standards of living and the needs of rapidly changing times. Though man may long have thought creatively, research in the scientific sense and on a substantial scale is but about three decades old.

The great achievements of chemical industry, attributed to research, have been so highly publicized as to make the word very popular. The term is used freely and is not restricted to chemistry, physics, or other science. It is used in the motion picture business to indicate studious inquiry into the clothing worn and the furniture used by the ancient folk to be portrayed in film. It is used in advertising and merchandising to cover studies of consumer appeal, seasonal trends, and store locations. It is employed in banking, psychology, sociology, and in many unexpected ways. It is also a popular word with the press. On my arrival in Buffalo, I noticed a newspaper headline: "Sister's Long Research Cuts Convict's Term".

Apparently the word cannot be ours alone, for it has attained a meaning, broad but indefinite, through common usage. During the interval while chemical research was expanding so greatly and while the word "research" was gaining in popularity, little was done in our field toward finding a new term or in making an exact definition of this one. Rapid changes were in progress, and the purpose of research leaders was to make the creative thinking and experimental investigations effective. These were problems dominating consideration of the definition.

RECOGNIZING that the word, apart from its context and not otherwise modified, is not isolated in the public mind as a chemist's word, let us attempt to limit it. One form of modification is to draw the distinction between experimental and nonexperimental research; but, though occasionally employed, it is not restrictive as to field. Another with similar limitation is the difference between fundamental and applied research. In passing we may note that one of our early research directors has aptly defined this: In the former you find out what happens, then use it; and in the latter you direct your effort toward a specific application to find how to do it best. Further, that word "fundamental" is just about as popular, and hence just as loosely definable, as "research". We may, of course, modify the word with respect to a field of science or technology. Terms such as chemical or chemical engineering research do make the scope more definite. We did not feel that we should abandon the word "research" in favor of terms like "technical" and "experimental". In fact, our first limitation was to call it "industrial chemical research"; and we considered this in the light of practices in our industrial organizations and in the related consulting and institutional agencies.

This still did not furnish the answer. You need but examine a few industrial organizations from your own experience to find how divergent are their views and practices. These same things which gave indefiniteness to the term "research" still exist. One would hardly expect or desire that all organizations would follow the same path from their beginnings and attain the same final form, since circumstances and personalities are so important that they often dominate an organization chart. When a company was small and there was but one outstanding chemical technologist, with perhaps a few helpers, he could serve all parts of the company. He could improve the production processes and even substitute new processes to make other or better products. He could help the sales department, so that it did not make rash commitments that could not be fulfilled; and he could help that department to find new markets. He could test raw materials and finished products to see that the quality of goods was maintained. The great measure of success of these technical men led to the employment of still more. When one man could no longer handle this, the growth in different companies led to different types of structures.

In one type they grew within a department which might be called the technical department; and all chemical knowledge was confined there. This possesses some merit because the men could work together and keep the technical information well correlated. There was also some objection because the efforts were not so well correlated with the department to which each was assigned to work. Often it became very cumbersome, as when a technical department would be controlling inspection at plants located far apart, or when men on research projects would have to break away to solve a customer's complaint. Perhaps in their enthusiasm for research they would neglect the call of production or sales—at least offer too little and be too late. This is still the type of structure with some companies, usually those in nontechnical lines.

There was another type of growth. The success of a limited technologic program revealed to sales and to manufacturing departments the merit of the scientific method to replace rule-of-thumb methods. These departments added technical men and equipped them with the tools for experimentation. In such cases there may be several laboratories within the company devoted to specific types of experimental work. These often overlap; and then there is a problem of correlating the experiences of the technical groups.

The two types of growth cited above have resulted in many variations in the technical structure within a company. Obviously some designation must be applied to this technical scope and to the divisional functions within it. Let me quote George Curme in that connection:

> It is of interest to examine the various functions of industrial operations where the application of scientific methods, resulting from experimentation, has created new values. In all cases an exploration into the unknown has been involved; in all cases benefits have resulted; in most cases there is very little difference in the academic training and qualifications of the technical workers employed. However, if they are all to be considered as "industrial chemical research", then that term is just a synonym of "experimentation", and we are going to need a new word.

SUPPOSE we do examine the types of activities very briefly. There is, of course, the pioneer investigation needed to open new fields of business expeditiously. Chemical processes are subject to rapid obsolescence and one must consider anew not only the processes upon which his organization depends for subsistence but must be alert to the major ramifications growing therefrom. Such an experimental group is, under wise management, set aside for the function of studying the future well-being of the company. It is not concerned with the day-by-day problems, and its subjects may take a long period of uninterrupted effort before coming to fruition. In the sense that this work is intended to assist in solution of a problem of company policy, it may become a department called "research". In fact, as distinguished from subsequent groupings, there may be some reason to call it "industrial chemical research".

There is another division closely associated with this one which often bears the name "development". This word speaks for itself, and implies a carrying forward of an investigation which has been started. Nevertheless, the physical distinction may be at many points, depending on how far the one who initiates the project carries it before giving it over to development. In some cases the pilot plant, often associated with development, is the stage in which the initial study must be carried out.

Another experimental activity is the service to manufacturing. Testing and evaluation of raw materials with the possible result of securing cheaper ones, investigation of losses and by-products within the process, and improvement in the quality of the product—all come within this scope. Still another is the service to sales. Many a customer can be persuaded to purchase a commodity on the basis of technical evaluation. This service may also partake of inspection of the product which the company intends to sell, and there may be further the question of adaptation to new uses. Other phases may include experimental investigation in engineering, patent and legal work, and advertising. All these may come within the scope of the technical service developed according to the first pattern, but if developed according to the second, they may be parts of several company departments. Somewhere in the group the term "research" is used, sometimes to cover all and sometimes to cover only the pioneering ventures. Depending upon what the term "research" is applied to in the industrial structure, there are a number of questions which must be settled in the light of that definition. I mention two of these and offer some discussion of them:

WHERE should research be done in an industrial organization?

Within the organization it is essential to know who should carry out the research and how it should be coordinated with other agencies to attain production and sales. Where no real research department exists, some companies have prided themselves upon the fact that every production man is a research man, and in such cases, there is neither best production nor effective research. On the other hand, there is a question as to whether a selected group of men should be expected to discover all of the new ideas needed to sustain and expand an industrial organization while they themselves are apart from that organization.

There have been many schools of thought as to the location of the research organization, whether it should be directly in connection with the plant to give research men viewpoint and possibly to permit them to devote some part of their time to trouble shooting; whether the laboratory should be located near the main office to make it possible for the sales and production executives to keep in close touch with the work that is being done; or whether it is better to place the laboratory in extreme isolation or in institutional environment where the processes of creative thinking can be indulged in without serious interference. The fact that many answers to this problem exist undoubtedly lies in the emphasis being placed by different people upon the thing they call "research" probably without analyzing it fully.

HOW should research be budgeted?

In the publicity which has made "research" the popular word it now is, there has developed the concept that some proportionate allocation of the gross volume of the business of the company should be made. C. M. A. Stine in his Perkin Medal address before the Society of Chemical Industry a few years ago[1], gave certain figures ranging from a fraction of a cent to several cents on every dollar of sales as the ratio between research budgets and the volume of business. There is a group which has steadily popularized "2 per cent for research", which is a rough average related to figures cited by Stine. The question arises as to just what this 2 per cent should cover—the fundamental aspects of developing new processes, the pilot plant, the trouble shooting in the plant, the service to sales?

This question logically arises as a result of the different types of organization we have noted—the one with all technical effort concentrated in a department which has only a portion of its efforts devoted to pioneer investigation, the other with the technical effort assigned to function within the several departments of the company and with one of these groups assigned to creative experimental investigation—or shall we say research?

This discussion reveals the present state of indefiniteness in the use of the term "research" as it is applied to chemical industry. It arrives at no arbitrary answer, because we make no brief to possess a favored word. In our experience in science we have seen rigorous methods applied to nomenclature, as the labeling of organic compounds or the symbols in heat and thermodynamics, and we have seen differences of opinion reconciled by debate or through committee correspondence. The strength of our science lies in this very exactness, and the progress which it has made has been made because we understood one another. Clarity in the use of the term "research" in connection with a department of an industrial organization will do much toward simplifying questions about research.

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Graduate Fellowship System

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THE principal functions of a university are the creation, preservation, and dissemination of knowledge. The first of these is fulfilled largely by research, which is one of the creative arts. As such, it reflects the personality of the researcher and does not lend itself readily to complete rational analysis. There are, however, various organizations which have been devised for the purpose of facilitating scientific investigation; this article deals with one of them, the Purdue Research Foundation, with the underlying thought that the demonstrated success of the policies here described may make them of general interest.

History of Purdue Research Foundation

In December, 1930, a group of courageous men under the leadership of David E. Ross, president of the Board of Trustees of Purdue University, and J. K. Lilly, chairman of the Board of Directors of Eli Lilly & Company, established the Purdue Research Foundation, the purpose of which is to promote closer relations between industry and the university. The wisdom of this objective has been argued elsewhere (*2*); for present purposes it is sufficient to point out that Purdue is a land-grant institution and was created specifically for the purpose of aiding "agriculture and the mechanic arts". Since the university charter did not clearly give it the right to own patents and perform certain other functions necessary to a close research partnership with industry, the foundation was organized with this in view.

The foundation discovered at once an eager and active ally in the Department of Chemistry where a mutuality of interests led to continuous, close cooperation. In the decade since 1932 the research funds in this department obtained from the foundation have increased fairly steadily from five thousand dollars a year to twenty times that figure.

Policies and Practices of the Foundation

In order to understand the operation of the foundation, let us see how a project originates. Frequently independent thinking on the part of a faculty member, supported by preliminary experimentation, results in a research problem of sufficient promise to attract the interest of an industrial group. The contract is negotiated by Director G. S. Meikle, one or more fellows are assigned to the problem, and laboratory work is begun. When the pilot-plant stage is reached, it is preferred to allow the industry to take over the problem although on more than one occasion the Purdue group has assumed this responsibility also.

In recent years industry has brought its projects to the foundation to an increasing extent. Before attempting the solution of a problem originating from a source external to the university, the foundation assures itself that it is of vital interest to one or more staff members, is of genuine scientific importance, and has a reasonable chance of success. The reason for the first of these requirements is that cooperation between the foundation and faculty members is on a purely voluntary basis, and there is no means of compelling a professor to attack a problem distasteful to him. In general, the best research is done by persons so excited about their experiments that they think of them during most of their waking hours. Anything substantially less than this represents a poor bargain for the industry.

While considerable postdoctoral research has been done on foundation fellowships, in most cases the results become incorporated in a doctoral thesis. This is one reason for accepting only scientifically important problems and for insisting upon ultimate publication. It also accounts for the fact that research can be done more economically in the university than in an industrial laboratory. The stipend received by the fellow is carefully calculated to enable him to live healthfully and decently but leaves little for outside activities. The fellow's principal reward is the training represented by the doctoral degree. In case the project reaches commercial success, the fellow also receives a share of the royalty payments. The knowledge of this fact is a stimulus to earnest endeavor.

The professor directing the research receives no extra income except from royalties. If there was a "flash of genius" in the establishment of the foundation, it came at this point. The effects of this policy are far-reaching. There is no temptation for a professor to assume the direction of a problem in order to augment his income and then give the matter relatively little thought and attention. An unsuccessful problem brings no remuneration. The man who is ignorant of the requirements of industry has a strong incentive to correct his deficiencies and to cooperate with the scientists who must ultimately decide whether the new process or product will be adopted or discarded. Finally, the professor with an aversion to the practical is not tempted to waste his own time and the company's money.

Patents resulting from the researches are assigned to the Purdue Research Foundation. This provision sometimes seems inequitable, at first glance, to industrial executives who feel that their company is paying for the creation of an intangible asset which then becomes the property of the foundation. It should be recalled, however, that the skilled direction of the research is not paid for, and the fellow is receiving most of his reward from the university (in the form of training) rather than from the industrial sponsor. Since the university has such a large stake in the projects, it is equitable for the foundation to profit if (and only if) the industry profits. The exact royalty to be paid varies from one case to another and is best left to negotiation and, if necessary, to arbitration, after the laboratory work is complete and the value of the new discoveries can be more nearly appraised.

The question of whether the license under a foundation patent should be exclusive or not is difficult. The foundation believes that it is obviously inequitable to expect any company to furnish the funds for a research project, assume the risk that perhaps no valuable results will be obtained, and then, in case commercial success is achieved, to allow another corporation to enter the field merely by matching the financial contribution of the first group. Such a policy would act as a deterrent against assuming the financial hazard involved in the support of research and would thus defeat the principal objectives of the foundation. On the other hand, it sometimes happens that a process or product of little or no value to the company sponsoring the research which created it may be worth adopting by some other corporation, which is more favorably situated with respect to raw materials, markets, or other dovetailing processes. It would be contrary to public policy for such a situation to result in an artificial dormancy for the life of the patent, and it will be recalled that Purdue University is a state and federal institution. If the question of general public policy controlling tax-supported institutions did not dominate the situation, one solution would be a minimum license agreement which would serve to force the industry either to use the results of the research, allow their rights to revert to the foundation, or suffer an economic penalty. We find industry, very understandably, reluctant to accept minimum royalties. The commonest arrangement on this point is a contract providing for the licensing of another company unless due diligence is shown by the sponsor in applying the results of the research. If this seems to require a great deal of confidence in the ethics of the Board of Directors of the foundation, it should be remembered that this group is composed of first-rank scientists and business men who may not profit financially by this connection.

The foundation is a nonprofit organization and royalties received are used for two purposes: furtherance of fundamental research, and rewarding the faculty member and fellow responsible for the discoveries and/or inventions resulting in the patents upon which royalty payments are based. The decision as to the distribution of royalties between these two objectives rests with the Board of Directors of the foundation. Before beginning work on a project, all patent rights are assigned to the foundation by fellow and professor. It will be recalled that cooperation with the foundation upon the part of any faculty member is not compulsory, and this serves as a substantial guarantee of fair treatment. In this department a uniform policy has been adopted of sharing royalty payments equally between fellow and professor.

Such a system obviously requires very careful records. A United States patent is invalid if it can be proved that the wrong names or too many or too few appear on it as inventors. Duplicate bound notebooks are kept with the aid of carbon paper, and the usual precautions are observed: entries direct, entries dated, no blank spaces, all entries in ink, and experiments described with sufficient care that they can be repeated with the notebook as the only source of information. In addition to the notebook, monthly reports are required of all fellows. Copies of these are sent to whomever is designated by the industrial group to receive them and the fellow has full responsibility for correctness of content and form. The writer reads all reports and is fairly unmerciful in criticism of both English and chemistry. Unofficial nomenclature as well as split infinitives, confusion between yields and conversions, and occasionally, mistakes in the interpretation of results are called to the fellow's attention, usually by written memorandum. Each report begins with a one-page abstract supplied for persons unable to spend the time required to read the entire copy. It is our belief that the monthly summing up of results is of great value in training the fellow for writing similar reports later in connection with industrial research work. It is of obvious assistance to those following and directing the work and to the patent attorneys, and often the recapitulation of data suggest new experiments to be tried. Graduate students seriously deficient in written English are uncommon, but a few are discovered each year and remedial measures are taken while sufficient time is available to make them effective.

Foundation System as a Teaching Mechanism

Almost without exception, foundation fellows from this department have entered and are now occupying positions in industrial research organizations. Our belief that this system prepares men unusually well for such responsibilities seems to be widely shared by their employers. In many instances the graduates have gone with sponsoring companies where their fellowship experience has been directly applicable. In most cases, however, the enhanced value of the training has been indirect and is probably attributable, at least in part, to the following factors: close contact with leading industrial chemists who usually make frequent visits to Purdue during the course of the work; experience in the use of expensive equipment provided by industry and beyond the reach of most university budgets; familiarity with the industrial viewpoint, the habit of including dollars and cents in his chemical thinking; and the additional motivation provided by a problem of obvious social importance.

The Foundation and Fundamental Research

The question has frequently been raised as to the effect of all this upon fundamental research. Let us define our terms. "Fundamental" means "of or pertaining to the foundation". A foundation is something that can be built upon, and a fundamental scientific discovery is one that forms the basis for other scientific advances. Let us remember that, in general, fundamental discoveries are usually a source of benefit to the public sooner or later. The classification of a given phenomenon as belonging in the category of "pure" or "applied" science has meaning only as of a given date. What begins as pure science frequently is applied subsequently.

It has become fashionable among some scientific groups to feel that the worker in pure science is, in some esoteric way, "a little closer to heaven" than his confrere who is attempting to use scientific discoveries to benefit humanity. The fallacy of this is exposed when the same worker in pure science is asked to justify public support of his researches; he invariably does so by pointing to the numerous instances in which investigations in pure science have created new industries, improved the general health, or in some other way ameliorated the condition of humanity. He is tacitly assuming a truism—namely, the only valid argument for public support of research is that benefits to the public flow from it—which demolishes the logical foundations of his feeling of superiority over the scientist or engineer who is trying to create exactly these human values. If pure science is important because of its impact upon humanity, then the conscious effort to use science for the welfare of people should be a part of the thinking of every serious scientist.

The only distinction between pure and applied science that will bear logical analysis is to designate a given problem as long-range or short-range and the results as potential or active. Research on the mechanism of photosynthesis would be an example of the former. The solution to this important problem might revolutionize the production of food and the utilization of solar energy, but such results could be expected only after decades of intensive research. An example of a short-range, immediately applicable, research problem is the improvement in the yield from a chemical reaction capable of being used for the manufacture of valuable products, by a systematic study of temperature, pressure, reaction time, catalysts, and concentration of reagents. The results could yield financial returns almost immediately.

It is true that industrial support is more easily obtained for short-range than for long-range problems. And yet the more forward-looking companies are keenly aware of the necessity of having in the literature a vast stockpile of potentially useful knowledge from which industry may select ideas that some new development has for the first time made practicable. A well known instance is Cavendish's experiment in which he used an electric spark to produce combination between the oxygen and nitrogen of the air. Approximately a century later, when electrical energy became cheap, this process was developed by Birkeland and Eyde into a commercial source of nitric acid.

It is to assist in replenishing the store of potential knowledge that du Pont, Allied Chemical & Dye, Abbott Laboratories, and J. T. Baker Chemical Company have established fellowships in pure chemistry at Purdue. It is of interest to note, however, that these fellowships came to us only after research on projects leading to rapid commercial success had attracted attention to this department as a research agency.

The generosity of certain philanthropists, particularly J. K. Lilly, David Ross, and H. N. McCoy, have contributed tremendously to the achievements of this department in both pure and applied science. Fellowships established by these men, and administered by the Purdue Research Foundation, have enabled various members of this department to make fundamental contributions to chemistry without thought of immediate applications. A considerable proportion of the preliminary experimentation, which later resulted in industrial research fellowships, was made possible by these funds. The new methods for the resolution of enantiomorphs (*1*, *7*), the Lecky-Ewell spiral gauze rectifying column (*6*), and the work leading to the establishment of the fundamental rules of aliphatic chlorinations (*3*, *4*, *5*) were done under these circumstances.

The royalty system of the foundation constitutes a further guarantee that research on long-range problems will continue to receive substantial financial support. Industrial profits derived from the application of discoveries made in this department are thus utilized for the direct furtherance of the type of research upon which the foundation might be presumed by some persons to have an inimical effect.

Another aspect of this problem deserves mention. The rate at which potential knowledge is accumulated is largely a matter of the magnitude of the total research effort being put forth. The most important scientific discoveries usually involve a considerable element of the fortuitous. The instance of the chemist who succeeded in his efforts to oxidize naphthalene to phthalic acid by means of sulfuric acid only after he broke his thermometer and introduced catalytic quantities of mercury is not too far from the typical. In the development of a science that is partly empirical, researchers working for immediately useful results will inevitably create potential knowledge as a by-product if they have learned to keep their eyes and minds open.

The fact that every recently published textbook of organic chemistry has devoted space to a discussion of the results of the nitroparaffin researches carried on by the Purdue Research Foundation is strong evidence that there is no essential conflict between the creation of fundamental knowledge and the foundation procedures.

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Research Accounting

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BECAUSE of the considerable amount invested in research programs by many of the larger companies, it has been found necessary to exercise careful control over expenditures for this purpose. Such control is not intended as a restriction upon the initiative or resourcefulness of the director of research, but is for the purpose of ascertaining that the proper amount is expended on each project in the program commensurate with its importance in relation to all other projects. One of the most important and effective tools which may be used in exercising this control is accounting. It supplies both the management and the research director with valuable information which should be of material assistance in the planning of this work. I believe it a fair statement to say that all other factors being equal, the company having the most effective accounting control of research expenditures will obtain the best results from this work at the lowest cost.

The accounting for research is usually divided into two phases—the projection or budgeting of research expenses, and the determination of the actual cost. Effective supervision and control of such expenditures makes it necessary not only to budget and accumulate research cost by classes of expense, such as salaries, wages, materials, supplies, etc., but also by classes of research and by individual projects.

There are undoubtedly many research classifications in use but our company has found it desirable to segregate these expenditures into: production research, research on new processes for present products, research on related new products, research on unrelated new products, application research, pilot-plant research, engineering research, purchased processes, and outside research. With the exception of production research, application research, and engineering research, the titles of the various classes are self-explanatory.

Production research represents work on processes currently used in the manufacture of the company's products. Such service is usually performed at the request of production departments.

Application research is performed with a view to finding new uses for present products. This work is done usually in collaboration with the sales department.

The work done by mechanical engineers in the designing of equipment for pilot plants and other research uses is considered engineering research.

A research director who receives monthly reports of the expenses of his department, showing a breakdown of cost by expense classification, by class of research, and by each individual project, all of which are compared with budgeted amounts, is in a better position to direct the activities for which he is responsible than he would be without such information. Many of the large companies have several research departments, each with a separate director. In such cases monthly research reports are prepared for each department.

It is obvious that the research budget should be prepared in accordance with the classifications used in the determination of actual costs in order that the desired comparisons between budgeted and actual amounts can be made.

It should be the responsibility of the research director to prepare the budget, as he is in the best position to know the work in progress and what will be undertaken. In doing this, he is guided by the wishes of the management as to research policies and is assisted in the projecting of research costs by members of the research staff and by the comptroller's office. On the other hand, it is the responsibility of the comptroller's office to devise adequate records for accounting for actual research costs and to prepare monthly informative research reports.

THE first step in setting up a research budget is to prepare a list of the projects expected to be worked on during the coming year. Estimates should then be made of the amount to be spent on each project during that period. This is accomplished by first estimating the amount of salaries, wages, and materials required for each project. Next, estimates of other direct laboratory costs, such as supplies, power, repairs, etc., as well as indirect expenses, such as depreciation, insurance, and taxes, are made for the department as a whole. Likewise, administrative expenses of the department are estimated for the year. The estimated direct costs (except salaries and materials) and indirect laboratory expenses, together with the research department administrative expense, are then allocated to the various projects, thus obtaining the budget of the department for the year by each project and in total. After the budget by projects has been completed, it is merely a matter of summarizing to obtain a budget by classes of research. A helpful guide in the preparation of the budget is the research reports of previous years.

It is desirable in most cases to maintain the original over-all budget throughout the year, but such practice need not necessarily be followed with respect to individual projects. It has been our experience that many projects in the original budget are never carried through, while the work in connection with other projects is greatly expanded, and new fields are explored. As the work progresses during the year, the research director may consider it desirable to change the amounts budgeted as between projects and provide for additional items, maintaining at the same time, as nearly as possible, the total amount forecast at the beginning of the year.

The preparation of a research budget entails a considerable amount of work. It should be kept in mind, however, that the budget is of value, not only to the research department, but also to the management in the formulation of financial and other policies, as it is an important factor in estimating a company's net income and cash position.

THE second phase of research accounting, the determination of actual cost, requires adequate accounting records for the accumulation of such costs. Provision should be made for accumulating costs both by classification of expenses and by projects. In order to obtain the project cost, it is desirable to give each research job a number, which is used in the distribution of all direct costs and expenses. Amounts expended for salaries, wages, materials, power, and other direct costs can be charged directly to each project. For example, salaries of chemists can be distributed to the various projects based upon reports of the time spent on the jobs. Likewise, all requisitions for materials should carry a project number so that the costs of materials can be charged to the proper job. Other direct items of cost can be determined in a similar manner. We have found that the most satisfactory method of allocating indirect costs to the various projects is on the basis of the total of materials and labor.

It may be of interest to mention briefly the method of accounting for materials produced in the research laboratory and in pilot plants. Our experience is that only a small amount of salable material is produced in the laboratory. When it is disposed of, research expense is credited with the sales value of the material. At times considerable quantities of salable materials are produced in pilot plants. It is our practice to credit research expense with the actual manufacturing cost of these materials. Losses from the sale of such materials are charged to operations.

To obtain reliable and accurate costs, there must be close cooperation between the research and accounting departments. The research directors of our company take great interest in the costs of their departments, and consequently our accounting department has received their complete cooperation.

Each month a research report is prepared by the accounting department, showing the actual cost of each project for the month and year to date, along with the accumulated cost since its inception. In the early stages of a problem, the comparison of actual cost with the amount budgeted may not be important; nevertheless, the budgeted amounts should be shown in the monthly report as such information becomes more important as the work progresses. In addition, this monthly research report should include a statement showing the expense by classes of research, setting forth the actual expense for the month and year to date as compared with the amounts budgeted. We also have found it advisable to include in the research report an analysis of the administrative research expense allocated to the various projects.

THE preceding paragraphs cover in a general way the accounting for research expenses. There is a difference of opinion as to whether certain research expenditures should be deferred or immediately written off to expense, and what accounts should be charged with that written off. Some companies charge all research expenses to cost of production, others charge only a portion, while some do not include any part of them in cost. It would not seem improper to charge certain types of research expenses to cost of production—for example, those we describe as production research. However, it is a conservative practice to consider all research expense as general rather than manufacturing expense, for by so doing no portion of it is included in the inventory valuation of goods produced.

One other point is the classification of research expense on the income statement. If research expense is considered an element of cost, it should be included under the cost of goods-sold caption. If not, it should be included among the general and administrative expenses. In any event, if the research expense is of consequence, the amount should be disclosed on the income statement.

Experience has proved the value of careful control of research expenditures both from the viewpoint of the management and the director of research. In the manner which has been described, accounting serves in a definite and helpful way this important activity of modern business.

PRESENTED as part of a Symposium on Research Management before the Division of Industrial and Engineering Chemistry at the 104th Meeting of the AMERICAN CHEMICAL SOCIETY, Buffalo, N. Y.

Acid Waste Treatment with Lime

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Expansion of chemical industries on account of war work has made the problem of acid waste disposal more acute. The wastes studied caused sewer corrosion, interference with biological sewage treatment processes, and stream pollution, and affected aquatic life. The wastes consisted primarily of mixtures of sulfuric, nitric, and hydrochloric acids, with some alkalies, solvents, and poisons present. The character and volumes fluctuated materially.

Methods of treatment were developed, and depended upon the type of acids, volume of flow, materials in the waste, and purpose of treatment. Neutralizing agents used for experimental purposes were calcium and magnesium hydrates, quick limes, limestones, soda ash, caustic soda, and their combinations.

During experimentation with nitrocellulose waste it was found that neutralization with calcium hydrate proceeded gradually until about 90 per cent of the total acids was destroyed, followed by a sharp break. The contact time required and amounts of sludge formed varied with the type and concentration of lime used. A combination of dolomitic hydrate with soda ash was preferable over lime, soda ash, or caustic soda alone. The dry weight of sludge decreased with increasing quantities of soda ash, but the volume of sludge increased and the ease of dewatering decreased. The reaction time required for complete neutralization increased with increasing quantities of soda ash.

THE treatment and disposal of relatively dilute acid wastes produced by chemical industries has been, in many instances, a considerable problem for a number of years. Expansion of these industries on account of war work has made the problem more acute. Although the wastes produced vary in composition and strength, they consist mainly of mixtures of acids or mixtures of acids and alkalies discharged intermittently with or without some salts, solvents, and poisons present.

The problems created by the discharge of these wastes pertain mainly to corrosion in sewers and equipment at sewage treatment plants, severe effects on biological sewage treatment processes, interference with fish life and self-purification of receiving waters.

This paper is primarily confined to a discussion of the characteristics of the wastes, their variations in strength and fluctuations in flow, and the presentation of laboratory results pertaining to treatment of the wastes to prevent difficulties.

The wastes studied were produced by:

1. A large chemical laboratory and pilot plant causing sewer corrosion.
2. Plant waste causing sewer corrosion and interference with sewage treatment processes.
3. Plant waste causing pollution and interference with aquatic life.
4. Plant waste causing stream pollution.
5. Plant waste causing sewer corrosion.

The character of the wastes from different sources varied materially, both within each plant and among the different plants, as shown in Table I. The variations given were obtained by frequent sampling during 8–24 hour periods on several days. In some cases pH variations were within rather narrow limits, whereas in others intermittent discharges of alkalies caused material fluctuations. The wastes consisted primarily of sulfuric acid mixed with nitric and/or hydrochloric acid. Cooling water and wash water were present in all cases, while wastes 2, 4, and 5 contained relatively small amounts of domestic sewage.

The flow of the various wastes fluctuated in most cases materially.

Methods of Treatment

The neutralization agents used for experimentation were calcium and magnesium hydrate, soda ash, caustic soda, and combinations of the various neutralization agents. After considerable experimentation the most effective and most economical methods of treatment for the various wastes were as follows:

Waste 1. Neutralization of the mineral acidity by filtering through a bed of calcium limestone with a contact time of 5 minutes.

Waste 2. Equalization and neutralization to pH 6.0 with high calcium hydrate.

Waste 3. Neutralization with high magnesium hydrate and soda ash to any desired pH value.

Waste 4. Equalization and neutralization of mineral acidity with high magnesium hydrate.

Waste 5. Neutralization with dolomitic limestone and aeration.

It is evident that the method of neutralization to be used depends not only on the type of acid and volume of flow, but also upon other ingredients in the wastes and the purpose to be served by the treatment. A more detailed discussion of one of the wastes and a description of the treatment plant constructed will be published in the future.

Table I. Variation in Character of Wastes and Flows

Waste No.	Principal Ingredients	pH	Acidity[a], P. P. M.	Alkalinity[a], P. P. M.	Type of Acids	Flow, Gal./Day Minimum	Flow, Gal./Day Maximum
1	Acids, alkalies	2.0– 8.6	0–910	0–85	H_2SO_4, HCl, HNO_3	14,400	35,000
2	Acids, alkalies, solvents, poisons, salts	1.7–10.5	0–1180	0–1140	H_2SO_4, HCl	865,000	1,800,000
3	Acids, solvents	0.9– 1.4	9000–11,800	0	H_2SO_4, HNO_3	3,400,000	7,800,000
4	Acids, alkalies, solvents	1.0– 3.2	250–4000		H_2SO_4, HCl	325,000	365,000
5	Acids, alkalies	1.8– 4.3	0–3000	0–5600	H_2SO_4, HCl	90,000	160,000

[a] As $CaCO_3$.

During the course of experimentation a number of questions were raised pertaining to the behavior of the various neutralization agents. Results on part of the work[1] are presented to illustrate the action of the neutralization agents and indicate some of the more important factors involved. The particular waste used for illustration, discharged from a nitrocellulose process, consisted essentially of a mixture of sulfuric and nitric acids, some solvents, and a very small amount of nitrocellulose floc. The total acidity of the waste, expressed as $CaCO_3$, was 11,810 p. p. m., with 3660 p. p. m. nitric and 8150 p. p. m. sulfuric acid.

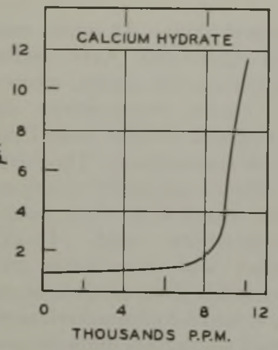

Figure 1. Effect of Lime Concentration on pH of Acid

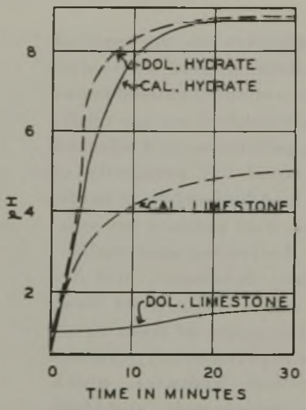

Figure 2. Effect of Contact Time

The procedure of the general method employed for neutralization consisted of placing 100-cc. samples in beakers equipped with a stirring device and the electrodes of a pH apparatus placed stationary in the liquid. Various types of lime used were added dry while the waste was rapidly stirred. When the dosage necessary to complete neutralization was found, the sludge produced was dewatered, dried, and weighed. Observations were made regarding the character of the sludge formed, its rate of formation, the rate and completeness of settling, ease of dewatering, and amounts of cake produced.

Effect of Lime

Type of Lime. Keeping the contact time between the various types of lime and acid waste constant at 30 minutes, the quantities of neutralizing agent were determined. The theoretical amounts of lime, actual quantities, and resulting pH values are summarized in Table II. Calcium and dolomitic quick lime were unsuitable, because the lime balled in the waste on account of a coating of calcium sulfate formed before complete hydration could take place. The dolomitic limestone was unsatisfactory, because with this material, even when dosages far in excess of the theoretical amounts were employed, neutralization could not be completed in 30 minutes. Calcium limestone liberates considerable carbon dioxide. Most of this is removable by aeration for 15 minutes and by paddle mixing for an appreciably longer time. When paddle mixing is employed, only part of the carbon dioxide is removed after 30 minutes, giving a final pH value of 4.7. Removal of carbon dioxide with air produces considerable foaming. Calcium hydrate addition required larger quantities and produced more sludge than dolomitic hydrate.

Concentration. Series of experiments were made with a wide range of hydrate lime dosages to determine the effect of lime concentration on the resulting pH values. The contact time was kept constant at 20 minutes, with vigorous stirring to remove the carbon dioxide formed as much as possible. A typical example, using calcium hydrate, is illustrated in Figure 1. Neutralization proceeded gradually until about 90 per cent of the total acids was destroyed. There was then a sharp break in the curve, giving evidence of the unbuffered character of the waste. Acid wastes containing appreciable quantities of salts in solution may behave differently.

Table II. Quantities of Lime Required to Raise pH Values in 30-Minute Contact Time

Type of Lime	Theoretical, P. P. M.	Actual, P. P. M.	Final pH
High-calcium hydrate	9,200	9,250	8.6
Dolomitic hydrate	7,020	7,750	8.5
High-calcium limestone	12,240	13,000	4.7
Dolomitic limestone	10,930	15,000	1.4
High-calcium quick lime	6,900	9,000	3.4
Dolomitic quick lime	6,000	8,000	3.3

Contact Time. The effect of contact time varies with the type and concentration of lime used. Employing quantities of lime sufficient to raise the pH values to 8.6, the rate of neutralization with increasing time is illustrated in Figure 2, for high calcium and magnesium hydrate and limestones. In all cases the mixtures were vigorously stirred. The dolomitic hydrate reacts most rapidly, followed by calcium hydrate, the reactions being completed in 20 minutes. With calcium limestone the pH was raised rapidly during the first 5 minutes and gradually tapered off, while the dolomitic limestone required several hours to raise the pH to 5.5.

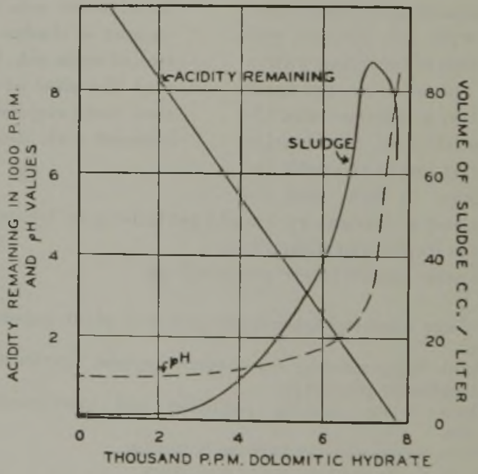

Figure 3. Sludge Formation with Varying Degrees of Neutralization

Sludge Formation. The quantities of sludge formed by the different types of lime varied materially. This is indicated by the following figures, showing the amounts of lime added and quantities of sludge formed per 1000 gallons of waste:

Type	Pounds Added	Pounds Dry Sludge	Type of Sludge
Calcium hydrate	76.8	55	Plastic
Dolomitic hydrate	64.0	21	Plastic
Calcium limestone	108.0	67	Granular

All sludges dewatered well and could be readily vacuum-filtered. The rate of sludge formation, employing increasing

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[1] Part of the laboratory work was performed under the fellowship grant from the National Lime Association.

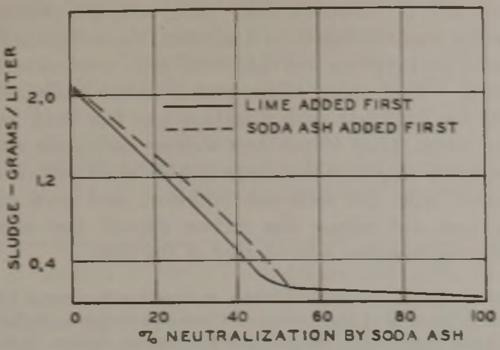

Figure 4. Weight of Sludge Production with Varying Percentages of Magnesium Hydrate and Soda Ash

quantities of dolomitic hydrate, increases rapidly with a decrease of acidity remaining until about 90 per cent of the acidity is neutralized. With further neutralization the volume of sludge decreases, although the total dry weight increases slightly. The maximum amount of sludge formation varied between 8 and 9 per cent of the total volume of waste. The relation between sludge volume, the degree of neutralization, and the resulting pH values is graphically shown in Figure 3. The greatest volumes of sludge were produced when the liquor had pH values between 2.5 and 5.7 with a maximum at about pH 3.5. The decrease in sludge volume with higher pH values appears to be related to the physical character of the sludge. In this connection, it is of interest that completely neutralized waste does not contain water of hydration.

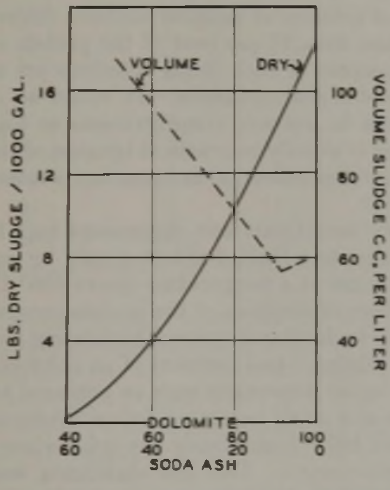

Figure 5. Volume of Sludge Produced after 2-Hour Settling Compared with Dry Weight

Of the various limes used for treatment of this acid waste, dolomitic hydrate was found best for neutralization, but it produced considerable quantities of sludge.

Soda Ash and Caustic Soda

Considerable experimentation with soda ash and caustic soda for neutralization showed that soda ash was preferable because of the tendency of intense color formation with caustic soda. Aside from the question of availability and cost, the intense foam formation with soda ash alone made it undesirable for this purpose.

Combination of Lime and Soda Ash

To complete neutralization of the waste with lime alone 7750 p. p. m. of dolomitic hydrate were necessary, but large volumes of sludge were formed.

Experiments were performed particularly to determine whether the quantities of sludge could be reduced without interference with dewatering. Amounts of lime and soda ash were calculated to give the neutralization effect of lime alone. The technique used was to add the materials dry, stir vigorously for 6 minutes, and then add the other material. The sludge formed was dewatered and the dry weight determined.

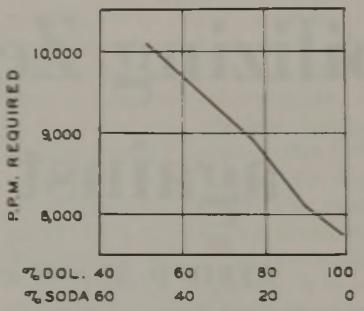

Figure 6. Relation between Neutralization Agent Required and Ratio of Lime and Soda Ash

Addition of lime first appeared to give slightly better results than partial neutralization with soda ash followed by lime. When soda ash is added first, large amounts of carbon dioxide are liberated. Most of this is immediately expelled as long as the pH is below 4.5. The carbon dioxide remaining, however, may cause carbonization of the lime when added later.

Table III. Change in pH Values on Addition of Chemicals to Acid Waste

Dolomitic Hydrate, %	Na_2CO_3, %	Total Neutralizing Agent, P. P. M.	pH after Minutes:					
			3	6	9	12	15	18
51.5	48.5	10,050	1.3	1.3	4.7	6.3	6.9	7.0
64.5	35.5	9,430	1.5	1.5	5.5	6.7	7.1	...
77.5	22.5	8,820	1.7	1.7	5.7	7.2	...	...
90.3	9.7	8,180	2.2	2.6	7.5	...	...	...
100	0	7,750	3.1	5.6	6.2	6.7	7.1	7.3

The weight of sludge produced when varying percentages of magnesium hydrate and soda ash are added is illustrated in Figure 4. With less than 50 per cent dolomitic hydrate added to complete neutralization, the weight of dry sludge is very small, increasing rapidly with the percentage increase of lime. It is possible, therefore, to balance the cost of sludge treatment against the cost of two-stage treatment. With increasing quantities of soda ash, however, the sludge becomes increasingly lighter, more voluminous, and more difficult to dewater. The fluffiness of the sludge produced with the larger percentages of soda ash increases with time of settling, so that after 18 to 24 hours the sludge volume is three to four times larger than sludge produced with dolomitic hydrate alone. The volume of sludge formed after 2-hour settling is illustrated in Figure 5. Neutralization with 90 per cent dolomitic hydrate and 10 per cent soda ash produced about the same amount of sludge as neutralization with magnesium hydrate alone. The smallest volume and lowest dry weight were obtained when the acids were neutralized with about 80 per cent lime and 20 per cent soda ash. This sludge, however, did not settle so well as that produced by dolomitic lime alone.

The moisture content of the filter cakes produced with different treatments varied, but the filter yields decreased with increasing quantities of soda ash.

Complete neutralization with lime and soda ash required a larger quantity of chemical than lime alone. As an example, some results obtained are illustrated in Figure 6. In this respect the rate of neutralization in a given time is of particular interest. When soda ash is added following the addition of lime, the higher the sodium carbonate percentage, the longer it takes before neutralization is accomplished. Some results given in Table III illustrate this. After addition of lime vigorous stirring was continued for 6 minutes, the sodium carbonate was added, and stirring was continued until neutralization was completed. With about 10 per cent soda ash added, the time required for complete neutralization was less than half that required when about 50 per cent sodium carbonate was used. The probable reason is that large quantities of carbon dioxide are formed with the soda ash addition, and even vigorous stirring does not release the carbon dioxide fast enough to prevent carbonization and coating of the lime.

PRESENTED before the Division of Water, Sewage, and Sanitation Chemistry at the 104th Meeting of the AMERICAN CHEMICAL SOCIETY, Buffalo, N. Y. Journal Series Paper, N. J. Agricultural Experiment Station, Rutgers University, Department of Water and Sewage Research.

Stabilizing Zein Dispersions against Gelation[1]

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ZEIN disperses readily in a large number of single and mixed solvents such as diethylene glycol, the lower mono ethers and esters of the glycols, the lower mono and diesters and ethers of glycerol, aqueous mixtures of methyl, ethyl, and isopropyl alcohols, aqueous acetone, and numerous organic acids, amides, and amines, as shown by Swallen (*4*), Evans and Manley (*1, 3*), and others. In all of these solvents zein tends to set spontaneously with time to a solid gel which is useless for most commercial purposes. The stability of such zein sols may be increased by storage at low temperatures, by the use of substantially anhydrous solvents, by the addition of certain reagents, or by keeping the concentration of zein at a practical minimum. Effective control of temperature is usually not practical, as summer room temperatures are frequently high enough to cause commercially usable concentrations of zein to gel in a few days. Thus, a dispersion of 20 grams of dry commercial zein dissolved in 100 ml. of 85 per cent aqueous ethyl or isopropyl alcohol may be expected to set to a useless gel in 4 or 5 days if stored at 38° to 40° C.

Swallen (*4*) pointed out that alcoholic zein dispersions containing a low concentration of water are, in general, more resistant to gelation than are those in the more highly aqueous alcoholic solvents. This is illustrated by the observation that 20 grams of dry zein dissolved in 100 ml. of aqueous 90 per cent ethyl alcohol will not set to a gel in 2 weeks at 40° C., whereas 20 grams of dry zein in 100 ml. of aqueous 70 per cent ethyl alcohol will usually gel in less than 1 day at the same temperature.

The stabilization of zein dispersions by the simple addition of small amounts of gelation retarders at room temperature has thus far proved unsatisfactory. Addition of 20 grams or more of acetaldehyde to alcoholic solutions of zein containing 20 grams of protein in 100 ml. of 85 per cent ethyl alcohol may, however, postpone gelation as long as several months. Amounts in the range of 2 to 5 grams of the aldehyde added to 100 ml. of similar dispersion have little stabilizing effect. Benzene, morpholine, the nitroparaffins, and the chloronitroparaffins also stabilize zein dispersions under proper conditions but to a lesser extent than the aldehydes.

The rate of gelation of aqueous alcoholic dispersions of zein containing less than 10 per cent of the protein is very slow, but the viscosities of such dilute solutions are so low as to limit their industrial usefulness. It would be desirable for some purposes to use zein concentrations as high as 40 per cent, but this is usually impractical because of the rapid rate at which such dispersions gel at room temperatures.

IT HAS been found that zein dispersions may be stabilized against gelation to a limited extent simply by heating for 15 minutes or longer at a temperature above 100° C. and below the point where destruction of the protein occurs; that their stability may be further improved by heating the dispersion, followed by adding 1 to 5 per cent of an aldehyde; and that much more stable dispersions may be prepared by heating in the presence of a small percentage of an aldehyde at a temperature above 100° C. and below the point where destruction of the protein occurs. This last stabilizing treatment also improves materially the color and flexibility of films formed from such dispersions. Heat treatment of aqueous alcoholic zein dispersions containing as little as 1 or 2 per cent of an aldehyde and as much as 50 per cent of water increases their resistance to gelation many fold as shown in Table I. Simple addition of such small amounts of aldehyde without heat treatment has little stabilizing effect.

Films and coatings produced from the aldehyde heat-treated zein dispersions are made insoluble in the ordinary zein solvents by baking, and are also made strongly resistant to the discoloring and softening action of water to which untreated zein films are so sensitive (*2*). For example, 20 grams or more of commercial zein may be dispersed in 90 ml. of 85 per cent ethyl alcohol and 10 ml. of 37 per cent formaldehyde and the dispersion then heated in a sealed container at ap-

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[1] A patent application covering the results of this work has been filed in the U. S. Patent Office and assigned to the Secretary of Agriculture.

proximately 120° C. for 15 minutes. The resulting dispersion will be stable towards gelation for 4 months or longer when stored at 40° C. Films formed from this dispersion, when air-dried at room temperature and then baked at 100° to 140° C. for 5 to 20 minutes, will not lose their transparency when immersed in water for several months at room temperature and will absorb approximately 10 per cent of water on 24-hour immersion. By comparison, a dispersion made simply by dissolving a similar amount of commercial zein in 100 ml. of 85 per cent ethyl alcohol may be expected to gel in 4 days or less when stored at 40° C. Both baked and unbaked films made from this latter dispersion will turn white after immersion for 2 or 3 minutes in cold water, and will absorb approximately their own weight of water on 24-hour immersion.

TABLE I. EFFECT OF HEAT TREATMENT ON RATE OF GELATION OF ZEIN DISPERSIONS

(20 grams zein/100 cc. solvent, heated 15 minutes at 120° C.)

Compn. of Solvent, Parts by Wt.			Stability, Days at 40° C.	
Ethanol	Water	Formaldehyde	Not heated	Heated
47.0	44.7	2.05	2	54+
63.8	24.4	2.05	5	54+
44.5	43.2	4.11	2	54+
60.5	21.8	4.11	5	54+
42.0	41.9	6.16	5	54+
57.2	19.4	6.16	2	54+
57.2	30.8	0.0	4	4
73.6	8.2	0.0	30+	30+
Ethanol	Water	Acetaldehyde		
66.4	16.7	1.2	2	31
56.5	30.4	1.2	2	28
65.6	16.4	2.4	1	67+
40.5	49.5	2.4	1	50
65.2	16.3	3.9	1	73+
39.6	48.4	3.9	1	73+
Ethanol	Water	Propionaldehyde		
66.7	16.9	0.0	5	11
66.9	16.7	0.8	2	11
64.2	16.0	4.0	2	20
Ethanol	Water	Butyraldehyde		
65.6	16.4	2.5	2	48+
64.2	16.1	4.1	2	48+
51.2	34.2	2.5	4	41
50.2	33.5	4.1	3	48+
Ethanol	Water	Furfuraldehyde		
67.6	16.9	0.0	5	17
66.9	16.7	1.1	2	17
64.2	16.0	5.7	3	15
Ethanol	Water	Benzaldehyde		
67.6	16.9	0.0	5	..
66.9	16.7	1.0	4	19
64.2	16.0	5.2	3	16
Dioxane	Water	Formaldehyde		
71.4	30.6	0.0	2	6
70.0	31.4	0.82	3	40+
67.9	32.5	2.05	6	40+
Acetone	Water	Formaldehyde		
60.9	26.1	0.0	1	Gels on autoclaving
60.3	26.5	0.41	9	40+
57.8	28.2	2.05	40+	40+

AQUEOUS acetone and aqueous dioxane dispersions of zein are likewise stabilized by an autoclave-aldehyde treatment. In aqueous acetone the reaction appears to go forward more easily than in aqueous alcohol, inasmuch as smaller amounts of aldehyde are required, and the minimum effective temperature to form a stable zein solution in aqueous acetone is lower than that required to obtain a stable zein dispersion in aqueous ethyl alcohol containing the same concentration of aldehyde.

As Table II shows, the viscosities of zein solutions in both aqueous ethyl alcohol and aqueous acetone containing aldehydes are essentially the same before and after heating. It has been further observed that the length of the heat treatment within the range of 15 to 60 minutes has little effect upon the viscosities of the dispersions. Thus it would seem that the stabilizing effect of the autoclave treatment is not due to partial hydrolysis of the protein, as has been suggested. If this were the case, then polymerization or denaturation would presumably have to be taking place simultaneously with hydrolysis at such a rate that the summation of the two effects would be equal. The resultant of the two reactions would be expected to effect substantial changes in the solubility of the zein and in the strength and flexibility of its films. Neither of these changes has been observed, except that films formed from the autoclaved solutions were found to be smoother and more homogeneous and to have better spreading and covering properties than those of unautoclaved samples. Upon storage, as indicated in Table III, the viscosity of the stabilized as well as the unstabilized solutions slowly increased, the rate and the amount depending upon the treatment and the amount of aldehyde present.

THE critical peptization temperatures of a large number of zein samples in aqueous ethyl and isopropyl alcohol and aqueous acetone solutions were determined before and after stabilization by the aldehyde-heat treatment. In all instances where the concentration of alcohol was in the range 45 to 55 per cent, the heat treatment at 120° C. for periods ranging from 15 to 60 minutes had no effect upon the critical peptization temperature of the dispersions. However, as the concentration of alcohol was raised, the critical peptization temperature of the autoclaved samples was found to drop progressively below that of unautoclaved dispersions. Thus, an unautoclaved dispersion in 65 per cent ethyl alcohol containing 5 per cent acetaldehyde precipitated from solution at −12° C., while an autoclaved sample of the same material precipitated at −16° C. Likewise, an unautoclaved dispersion in 80 per cent ethyl alcohol containing 5 per cent acetaldehyde showed a critical peptization temperature of −17° C., while an autoclaved portion of the same material precipitated at −28° C.

TABLE II. VISCOSITIES OF ALDEHYDE-HEAT STABILIZED ZEIN DISPERSIONS AT 30° C.

(20 grams zein/100 cc. solvent, heated 15 minutes at 120° C.)

% Solvent by Wt.		85% Ethyl Alcohol		70% Acetone	
		Un-heated	Heated	Un-heated	Heated
		Centipoises			
Formalin	12.5	52.3	65.9	23.4	32.2
Formalin	2.6	47.3	55.6	22.7	27.3
Acetaldehyde	14.0	70.4	70.4	23.8	27.1
Acetaldehyde	4.6	43.4	55.9	19.1	21.1
Butyraldehyde	14.5	63.6	62.5	16.8	19.7
Butyraldehyde	4.8	46.1	54.0	19.5	22.8

TABLE III. CHANGE IN VISCOSITY OF ALDEHYDE-HEAT STABILIZED ZEIN DISPERSIONS UNDER STORAGE AT 25° C.

(20 grams zein/100 cc. solvent, made up of 85% ethyl alcohol + aldehyde)

% Solvent by Wt.		Viscosity at 30° C., Centipoises				
		1 day	4 days	9 days	16 days	23 days
Formalin	12.7	65.9	72.8	75.2	82.1	91.3
Acetaldehyde	14.0	70.4	78.4	77.7	81.1	87.0
Butyraldehyde	14.5	62.5	65.8	70.8	76.4	80.5

Stabilization against gelation by heating in the presence of an aldehyde is effected with equal readiness throughout the pH range of 5.5 to 10. However, blush-proof water-resistant films are produced only in neutral or acidic dispersions, and the speed of the reaction is greatly increased by the addition of small amounts of mineral acids, acid salts, or salts of strong acids and weak bases.

The extent of floc formation during and subsequent to the aldehyde-heat treatment also varied with the quality of the original zein. In no case was the floc sufficiently heavy to interfere with the formation of clear and transparent films.

When desired, the floc could be removed either by settling or in the centrifuge.

In stabilizing zein dispersions by the aldehyde-heat treatment, it has been found that the stabilizing effect is improved as the concentration of aldehyde is increased, and that if too low concentrations of aldehyde are used, prolonged heat treatment causes the dispersion to gel despite the presence of the aldehyde.

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Vapor Pressure Nomograph for Isomeric Octanols

D. S. DAVIS

Michigan Alkali Co., Wyandotte, Mich.

RECENT vapor pressure data[1] covering twenty-two isomeric octanols appeared as a table of boiling points for pressures of 20, 100, 300, and 760 mm. mercury, supplemented by pressure-temperature curves for twelve of the series. The accompanying line coordinate chart enables convenient estimation of boiling points at other pressures or vapor pressures at any temperature in the range of the data. It is based upon the expression

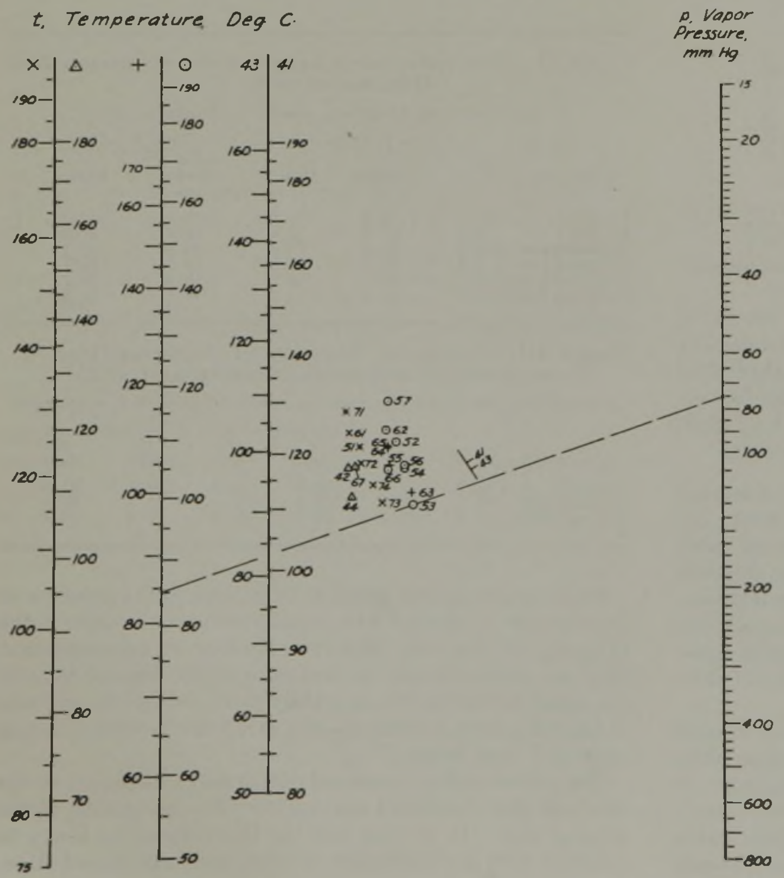
$$\log p = A/(t + \alpha) + B$$

where p = vapor pressure, mm. mercury
t = temperature, ° C.

and A, B, and α have values, depending upon the compound, as follow:

Key No.	A	B	α	Key No.	A	B	α
41	−2340	8.040	[a]	61	−1144	6.599	120
42	−1155	6.586	140	62	−1802	7.726	200
43	−2258	8.190	270	63	−1126	6.417	160
44	−1130	6.638	140	64	−1341	6.990	160
51	−1074	6.383	120	65	−1335	6.961	160
52	−1678	7.393	200	66	−1782	7.885	200
53	−1483	7.078	200	67	−1105	6.385	140
54	−1580	7.214	200	71	−1170	6.596	120
55	−1326	7.032	160	72	−1066	6.434	120
56	−1580	7.197	200	73	−940	6.089	120
57	−1782	7.500	200	74	−992	6.229	120

[a] $\alpha = 270 - 10^{5.934 - 0.05947t}$



With respect to the key numbers which appear on the chart and in the table, the original investigators stated, "The first digit locates the methyl group and the second the hydroxyl group: thus 72 is 7-methyl-2-heptanol, i. e., 2-octanol, and 53 is 5-methyl-3-heptanol. Sometimes the key numbers depart, for convenience, from official nomenclature."

The temperature scales on the chart bear symbols or numbers which must correspond with those of the gage points for the various compounds. The circled points, for instance, are employed with the temperature scale headed by a circle.

The use of the chart is illustrated as follows: What is the vapor pressure of 5-methyl-3-heptanol at 85° C.? The key number for this compound is 53 which appears as a circled point on the chart. Connect this point with 85 on the t scale topped by a circle and produce the line to the p scale where the vapor pressure is read as 75 mm. mercury. Vapor pressures read from the chart deviate from the original data by an average of about 0.8 per cent.

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[1] Dorough, G. L., Glass, H. B., Gresham, T. L., Malone, G. B., and Reid, E. E., *J. Am. Chem. Soc.*, 63, 3100 (1941).

Starch Viscosity or Strength

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The fluidity funnel commonly employed throughout the starch producing industry and the experimental factors affecting its use are examined.

The strength funnel is not a true viscometer, and the strength scale varies in its relation to viscosity. A single unit of strength change from 0 to 20 represents an enormous change in true viscosity, whereas a unit change in the 80 to 100 strength range is only a slight change in viscosity. Apparent viscosity of starch pastes varies widely with the rate of shear used in the measuring viscometer. Apparent viscosity of starch pastes changes rapidly with concentration which indicates that the effect is largely mechanical. Graphs based on strength figures are often misleading. Plots of apparent viscosity figures during progressive modification by dextrinization, oxidation, and acid thin-boiling treatment result in simple type curves which clarify the nature of such changes.

The commercial variation in starches permit extremely large ranges of viscosity and solids combinations.

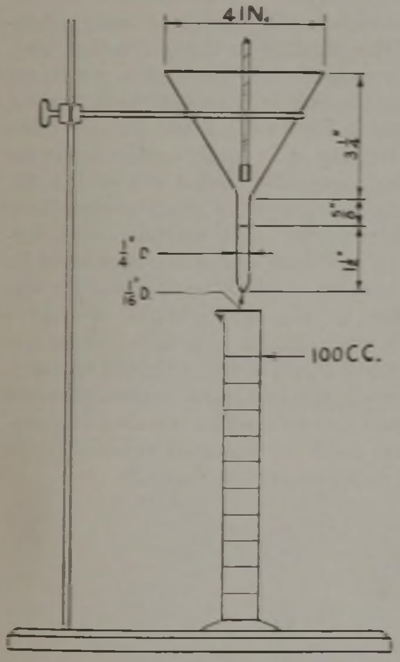

FIGURE 1. STARCH FUNNEL

Strength = cc. flow in 45 sec. (feed, 100 cc.); calibration = 100 cc.; water flows out in 45 sec. (feed, 115 cc.).

IN THE great majority of their uses the viscosity of starches is a main controlling factor in determining their utility. The preparation of starch dextrins and other modified starches is also generally followed and controlled by observing the progressive shifts in viscosity of starch pastes which are suspensions of the swollen material. For this purpose the various starch producers generally use a simple funnel with a restricted tip of the type shown by Figure 1. The use of such a funnel appears to have begun with the Corn Products Refining Company, the funnel and some of the factors involved in its use being described by Buel (*2*) in 1912. While such funnels are in common use, the tips, calibration method, and other constructional details have been varied in some plants during the intervening years.

One modification attempting to maintain relatively constant head conditions appears in Figure 2. The adoption and use of these funnels arise from the attempt to make a single instrument cover the extreme ranges in viscosity found in the numerous materials sold as starches. The funnels also provide easy cleaning which is a distinct necessity with these gelatinous and pasty materials.

To those familiar with the nature of viscous flow, it is apparent that such a funnel can hardly be expected to measure true viscosity, as most of the flow measured will be hydraulic. The flow of ordinary liquids from such a funnel occurs in general accord with Equation 1, and the energy lost in hydraulic flow given by the second term is generally large instead of

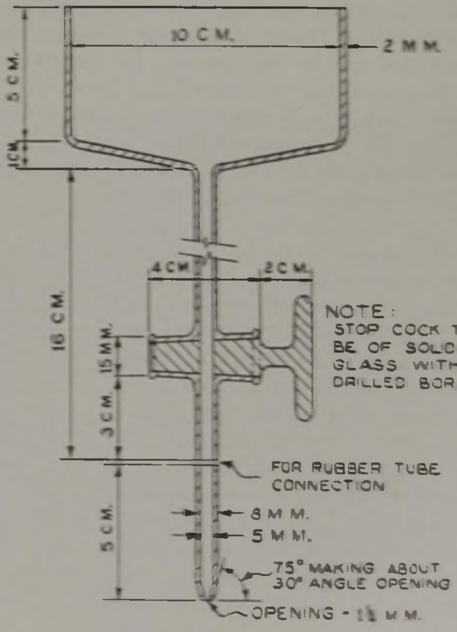

FIGURE 2. MODIFICATION OF STARCH FUNNEL

Strength = cc. flow in 58 sec. (feed, 300 cc.): calibration = 200 cc.; water flows out in 58 sec. (feed, 300 cc.).

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[1] Present address, Prolamine Products, Inc., Columbus, Ohio.

[2] Present address, Hercules Powder Company, Hopewell, Va.

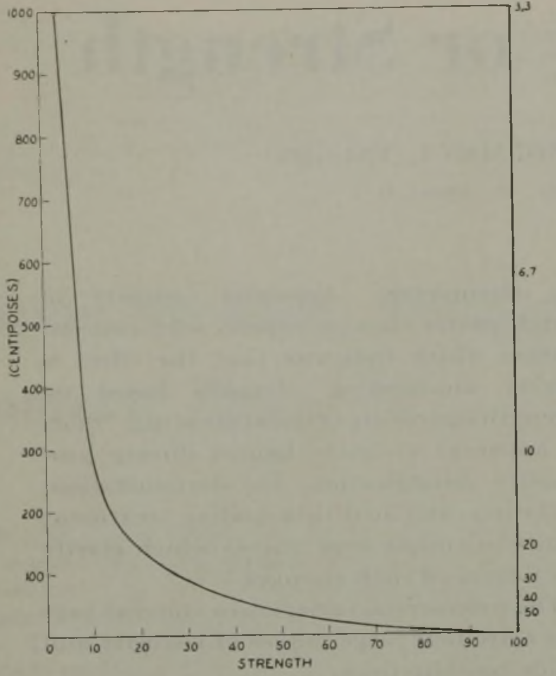

Figure 3. Centipoises *vs.* Starch Funnel Strengths

negligible, as is desirable in a good viscometer (*1*). The Poiseuille equation corrected for kinetic energy loss is:

$$\eta = \frac{\pi g r^4 PT}{8Vl} - \frac{1.14\, dV}{8\pi lT} \qquad (1)$$

where η = apparent viscosity measured
g = gravity constant
P = averaged pressure head
r = effective capillary radius
l = capillary length
d = density of liquid
V = volume flow
T = time of flow

The funnel shown in Figure 1 follows Equation 1 only approximately, depending upon the tip. In use it is made with a tip such that when 115 cc. of water are placed in the funnel, 100 cc. will flow out in 45 seconds. In use 100 cc. of the starch paste are put into the funnel, and the number of cubic centimeters which flow through in this time is referred to as the strength. It is apparent that the greater the thickening effect, the lower is the strength; strength is, then, a fluidity factor.

If instead of starch pastes we run through this funnel ordinary liquids, such as glycerol, sulfuric acid, castor oil, etc., of known viscosity (as determined by a true viscometer such as a suitable set of capillaries) and plot the strength figures thus secured against the known true viscosities for these liquids, Figure 3 results. This shows that only in a small range at the left of the curve does the instrument measure viscous flow. It also shows that there is a large difference in viscosity per strength unit in this range, while at the higher strengths a unit change in strength corresponds to only slight changes in viscosity. Thus the scale or the yardstick on which the strength scale is laid out is a highly distorted one as shown at the right-hand side of Figure 3. Attempts to follow any progressive alteration of a starch using the starch strength scale results in irregular-appearing data which make true understanding difficult. The mere intercomparison of starch data as at present reported (Table I) giving a single strength figure at some ratio of solids to water is often so difficult that one cannot determine the relative thickening order without further experimental work.

Table I. Single Point Data

Type of Starch	Concentration Ratio	Concentration %	Strength	Apparent Relative Viscosity Units	Relative Thickening Order
Raw corn	10:250	3.85	16	190	*b*
Raw tapioca	10:400	2.44	27	100	*a*
Roasted tapioca	10:150	6.25	8	335	*c*
White corn dextrin	20:120	14.28	88	5	*d*
Yellow corn dextrin	50:50	50.0	52	38	*e*

Apparent Viscosity Unit

The conversion of the cubic centimeters of flow or strength of starches into apparent viscosity units is of real help in the systematic study of starchy materials. In suggesting such a scale we wish to point out that, in order to avoid later misunderstandings, the figures secured should not be referred to as so many centipoises but might more properly be termed "relative" or "apparent" viscosity units. The starch pastes are suspensions and not true liquids. Starches show anomalous viscosity, the apparent viscosity indicated being dependent upon the rate of shear existing in the instrument used. Thus, no two differently constructed viscometers can be expected to show the same apparent viscosity with a given starch paste as illustrated in Figure 4. While a starch paste may show an apparent vicosity of so many centipoises in the funnel described, it is to be expected that it will show a different apparent viscosity in centipoises when measured on any of the standard instruments; such variation with capillaries of different radius and head are amply illustrated by Hixon (*7*). What we wish to indicate by the relative viscosity unit readings, then, is only that a starch of a given value flows through the given funnel in a time comparable with the time of flow of a true liquid of the indicated viscosity. Despite the wide difference in the two starch funnels shown in Figures 1 and 2, it appears that the second one used at a relatively constant head was made to duplicate reasonably the earlier type instrument, as is apparent in Figure 5.

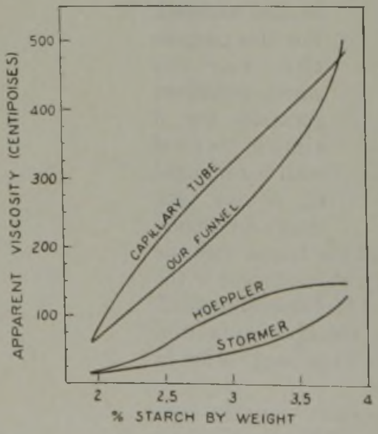

Figure 4. Viscosity Curves for Raw Corn Starch

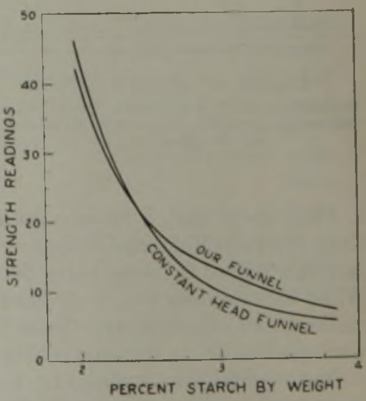

Figure 5. Funnel Comparison for Raw Corn Starch

The variation of apparent viscosity with rate of shear makes intercomparison of data on other instruments which are in general use in the starch consuming industry difficult. For very heavy pastes, such as are utilized in the textile printing trade, Glarum (*6*) showed that the Stormer viscometer is particularly adaptable, provided slippage is avoided. The food and paper trades frequently use the MacMichael instrument which, like the Stormer, offers easy study under varied rate-of-shear conditions. Capillaries and the Hoeppler viscometer can be used only on very thin solutions, and a little gelation upsets the readings and causes cleaning to be difficult.

Hixon (*7, 8*), Porst and Moskowitz (*10*), and Farrow and Lowe (*4*) have given considerable data showing the variation in apparent viscosity of starches when measured in capillaries at various rates of shear secured by varying the pressure head or capillary size. Gallay and Bell (*5*) made a thorough study of the similar variation in apparent viscosity of starches with varying rate of shear in the MacMichael torsional type of apparatus. Like Farrow and Lowe, they find that the phenomena in the main fit the empirical equation

$$F = KP^n$$

where F = rate of flow, dv/dt
P = pressure
n, K = constants depending on starch and instrument, respectively.

Thus with a MacMichael viscometer the data for the logarithm of the deflection *vs.* the logarithm of the r. p. m. applied plots over a considerable range as a straight line, but at the lower shearing rates this type of equation is not followed:

$$\log v/t = n \log P + \log K$$

It would appear that through the Williamson formulas (*12*) intercomparison of data on the various viscometers could be carried out once several apparent viscosities have been determined at several different rates of shear. Thus, for the complete characterization of a starch flow picture the MacMichael instrument appears best.

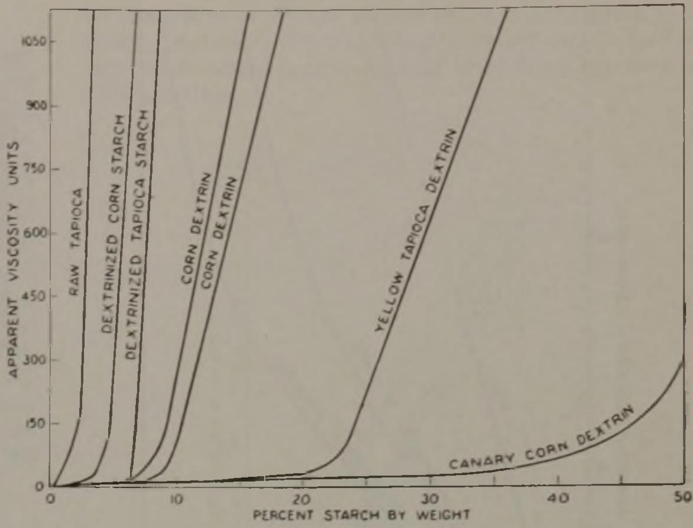

FIGURE 6. APPARENT VISCOSITY RANGE OF COMMERCIAL STARCHES

However, for plant control and investigations involving large numbers of determinations, the simple funnel appears to offer advantages, provided care is taken to use it in the best ways; namely, an attempt should be made to secure values in the 10–25 range. Below 10 it is difficult to get duplicable data and certainly above 80 the differences indicated by the strength scale are mainly without actual significance. In an actual determination the preparation of the cooked starch dispersion or paste is just as important a source of variation as is the instrument. Starches variously swell, burst, or disintegrate during cooking; and, depending on the time and temperature, the degree to which this is carried out varies with a wide variation in the resultant thickness or apparent viscosity. Temperature effects were previously reported by one of the writers (*9*). Mechanical agitation is necessary to prevent sticking and to ensure the full action of the heat, but mechanical agitation also causes rupture of the swollen grains with consequent large decreases in apparent viscosity. This effect is well illustrated by the work of Caesar (*3*) whose consistometer curves also clearly show the rather rapidly occurring increases in apparent viscosity which take place when the pastes are cooled and gelation starts to set in.

Consequently, an arbitrary procedure for preparing starch pastes must be followed closely in systematic comparison work. The following method which reduces variation from

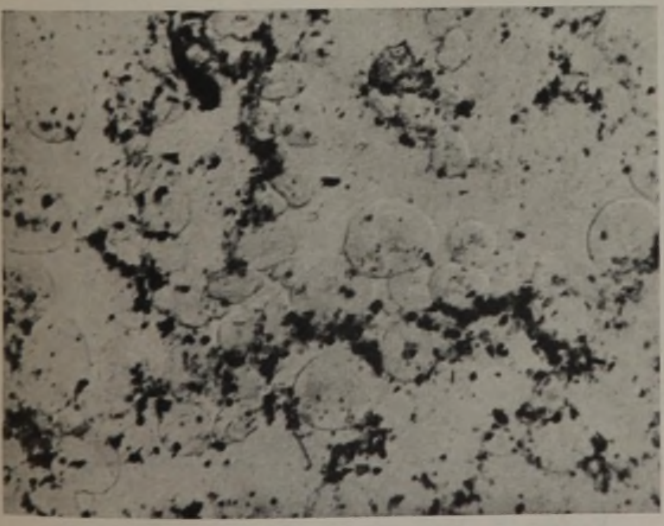

FIGURE 7. PHOTOMICROGRAPH OF THICK RAW STARCH (× 260)

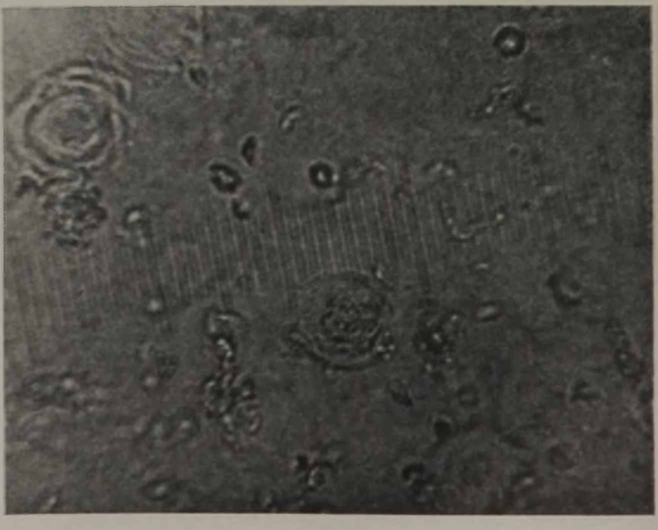

FIGURE 8. PHOTOMICROGRAPH OF CORN DEXTRIN DISPERSED IN ALKALI (× 550)

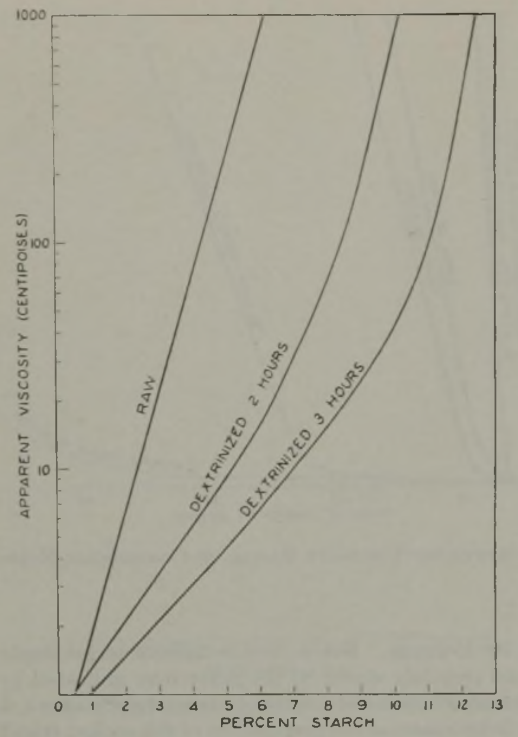

Figure 9. Relation of Log Viscosity to Concentration for Mixture of Half Corn and Half Tapioca Starch

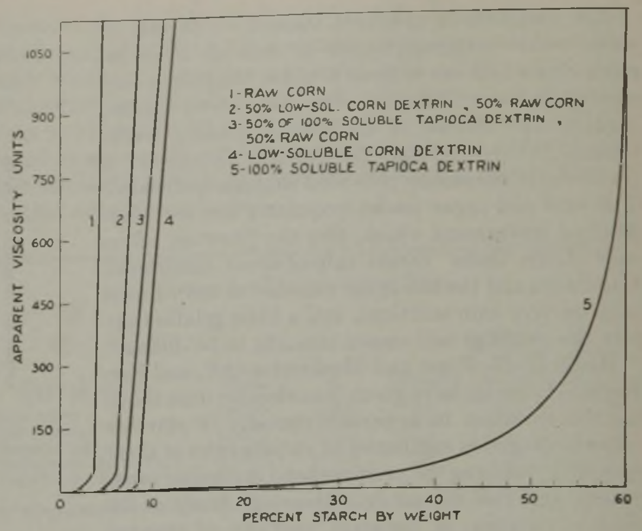

Figure 10. Viscosities of Mixtures

the operator to a minimum was used to secure the data of this study:

To the weighed starch sample, water was stirred in slowly to prevent lumping, the final volume being 200 cc. The starch mixture in a 250-cc. beaker was heated to boiling in 15 minutes by an electric hot plate while being constantly stirred by a three-bladed Lightning mixer running at 400 r. p. m. During cooking each batch lost 3 grams of water, and as viscosity changes in these pastes corrected for their loss in moisture could not be observed, no adjustments were made. As soon as the 15-minute cooking was completed, the pastes were placed in flasks, stoppered, and cooled to 25° C., at which temperature they were run immediately. The average of three strength readings was taken. The consistency of the strength readings of two operators is illustrated by the following data:

Starch	Concn. Ratio	Strength Reading	
		Operator 1	Operator 2
Raw	10:300	6 5 7	5 6 6
Dextrinized	20:120	88 92 93	87 91 92

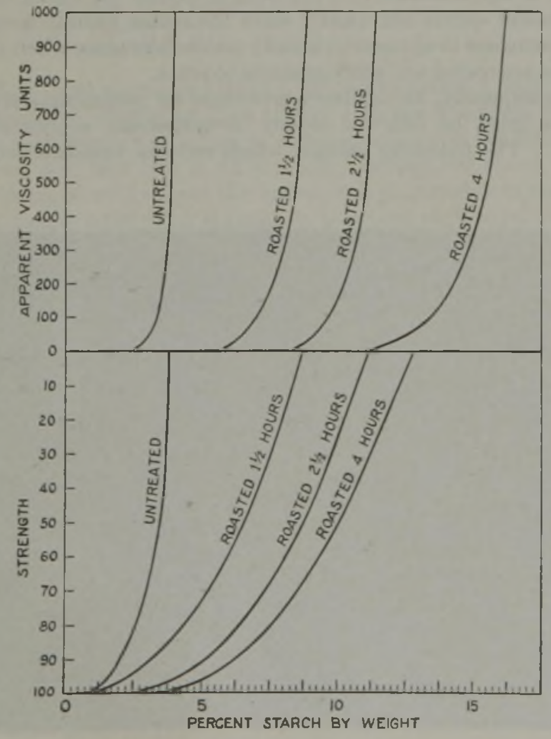

Figure 11. Progressive Dextrinization Curves of a Mixture of Tapioca and Corn

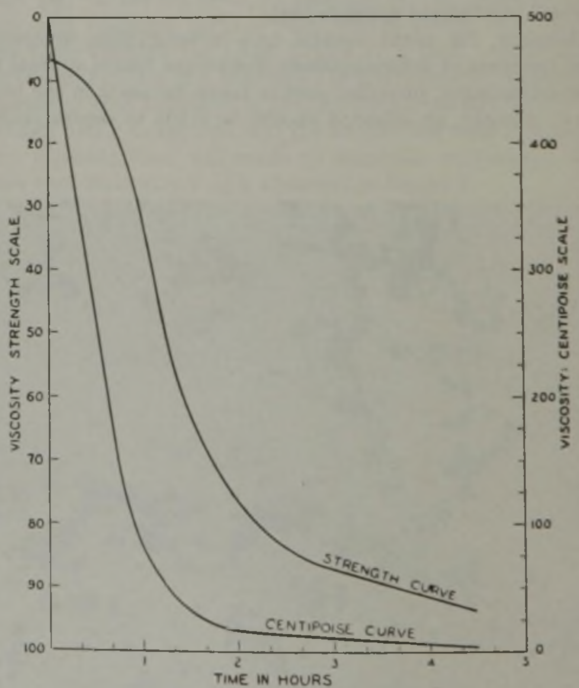

Figure 12. Viscosity Change during Conversion for a Mixed Corn and Tapioca Dextrin of 6 Per Cent Concentration

Viscosity *vs.* Concentration

The viscosity of starch solutions varies rapidly with changes in concentration, and in the practical use of the starch funnels the practice in industry is to select a starch concentration suitable to the various starches such that strength measurements can be secured on the funnel. However, the comparison of starches for apparent viscosity with the data at varied solids percentages is difficult. Consequently, apparent viscosities at several different solids contents are frequently desirable. Figure 6 shows several curves for starches (not corrected for density of solution) of widely different natures; this is the only means of bringing out the seldom realized extreme variation in apparent viscosity that can be secured with the wide range of materials offered industrially under the name of starches. By running along a constant apparent viscosity unit figure of, say, 300, approximately forty times as much of the canary corn dextrin starch is needed per 100 cc. of water as of the raw tapioca starch to give the same viscosity; conversely, the thin starch can obviously be used at a high solids concentration without trouble arising from too thick solutions.

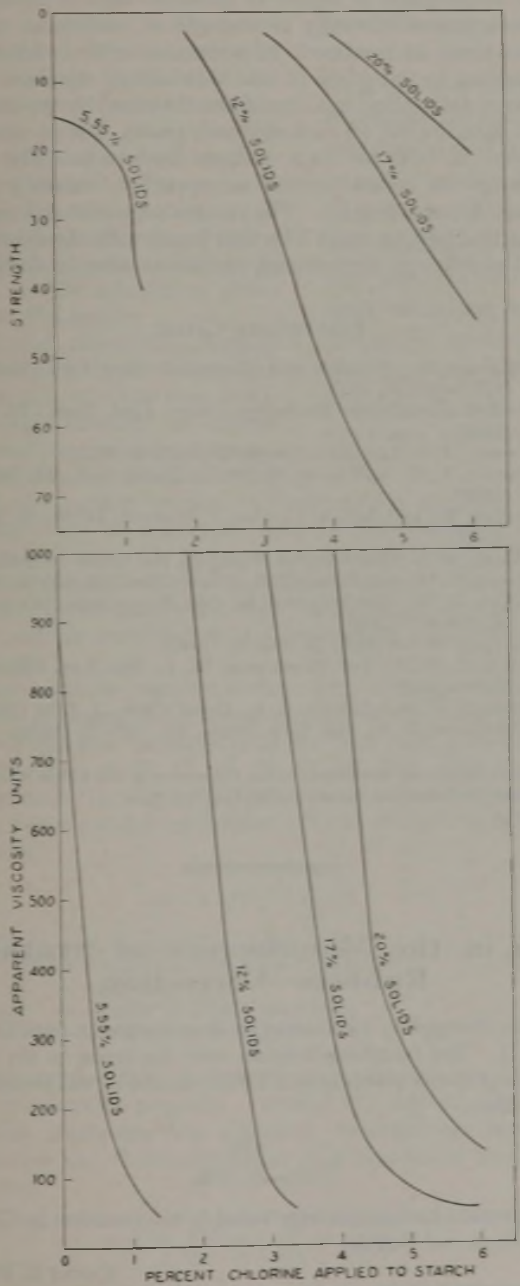

FIGURE 13. DATA ON OXIDIZED CORN STARCHES

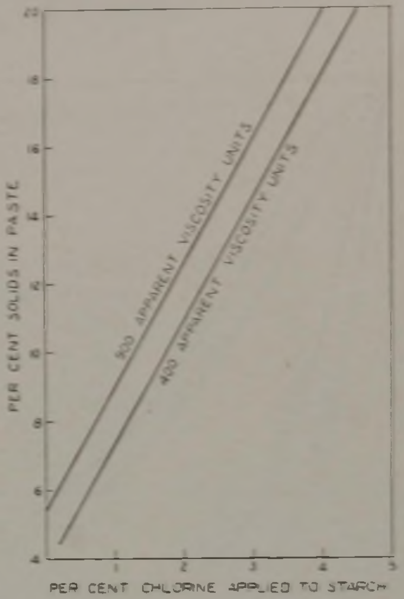

FIGURE 14. CONSTANT VISCOSITY CONDITIONS FOR OXIDIZED CORN STARCHES

Each curve shows an almost linear increase in apparent viscosity at first, followed by a rapid increase with further increases in concentration; still further slight increases of solids concentration result in enormous increases in viscosity. In the latter range it appears that the swollen particles occupy most of the volume and are rubbing on one another and intermeshing. Figure 7, shows the swollen, largely unbroken sacs common to the very thick, essentially raw starches; Figure 8 shows the broken and swollen pieces found in a heavy paste of a highly soluble dextrinized starch. A plot of the rate of increase of viscosity with successive units of concentration gives three separate slopes indicating free suspensions at low solids; a second range apparently corresponds to some intermeshing; and there is a final range where apparently the mass of swollen particles all rub on one another. Figure 9 shows that the logarithm of the viscosity is a straight-line function of the concentration only over very short ranges of viscosity, and that the Rask and Alsberg relation (*11*) cannot be generally used (*7*).

The apparent viscosities of mixtures of starches are interesting; Figure 10 covers such experiments and shows that at least the mechanical and physical phenomena determining the apparent viscosities are additive and sum up as expected from the data for the individual starches when the raw or slightly modified starches alone are considered. In these cases the volume of the swollen grains is probably the main determining factor as indicated by Hixon (*7*). As the data also show, viscosities for mixtures with highly soluble starches are not additive, and other factors besides the actual volumes of the grains become important.

Viscosity *vs.* Modification

Figure 11 compares the graphs secured on a mixture of corn and tapioca starches where the strength figures and the apparent viscosity units are plotted against per cent solids. The distortion caused by the strength scale is apparent. The data in Figures 9 and 11 cover samples taken progressively during dextrinization, and the shift to thinner starches is noted. The progress of dextrinization is better followed, however, by a curve drawn from these data for cases where the cooked pastes all contain a constant amount of starch, such as in Figure 12.

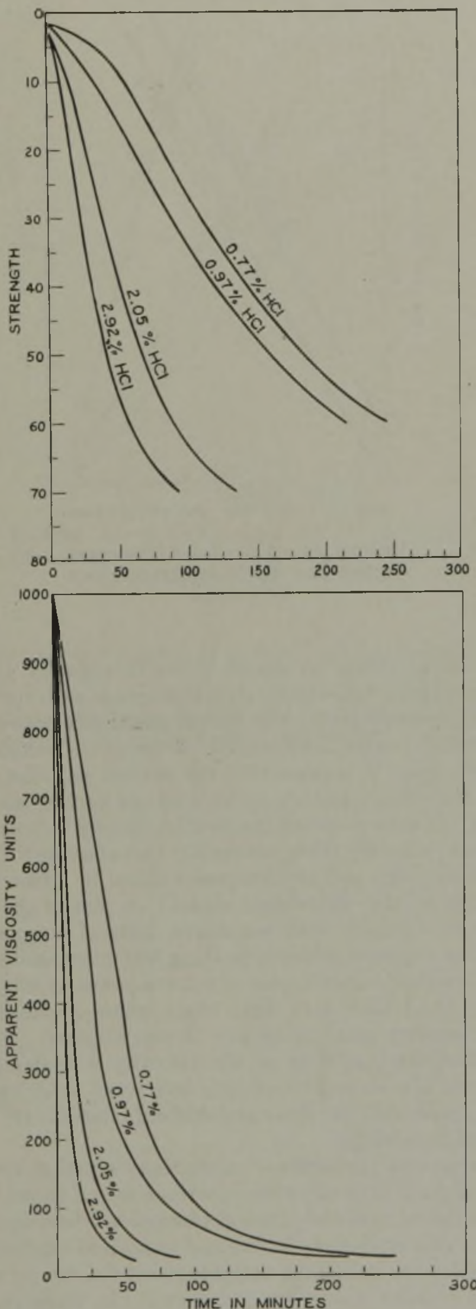

Figure 15. Preparation of Acid Thin-Boiling Corn Starches (Constant Temperature, 122° F.)

Here, where the strength plot indicates relatively little change in the first hour which might readily be misinterpreted as a heating-up or induction period, it is clear from the plot using the apparent viscosity units that no such period occurs; the apparent period comes from the distortion existing in the strength scale or yardstick. In line with the known sensitivity of starches to acids even at room temperature, the dextrinization starts off immediately the heat is applied and appears through most of the early part of its course to proceed at a linear rate.

A series of corn starches oxidized in aqueous suspension at 110° F. with various amounts of free chlorine, based on the starch and supplied as sodium hypochlorite, gave the peculiar set of curves in the upper graph of Figure 13; the picture simplifies when the data are plotted against apparent viscosity units, as in the lower graph. Since the variation in viscosity in this series of starches is large, curves at several constant solids contents are shown. In Figure 14 this difficulty is overcome, since the curves read for constant viscosity conditions. The two sets of curves taken together would indicate that successive units of chlorine applied to the starch have approximately the same apparent viscosity-lowering effect, or that the viscosity lowering is directly proportional to the percentage of chlorine applied to the starch.

The upper graph of Figure 15 gives the data of Gallay (*5*) on the apparent viscosity or strength of cornstarch during various times of treatment in suspension with hydrochloric acid leading to formation of acid thin-boiling starches. The data were determined in a funnel like that used by the writers.

The data are not on cooked starch pastes, but on starches dissolved in one per cent sodium hydroxide. The data straighten out when plotted as apparent viscosity units (Figure 15, lower graph). The process proceeds with respect to time in a fashion much like that found with the closely related but different dextrinizing conditions already described.

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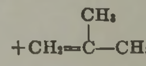
Presented before the Division of Sugar Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J

Coal in the Manufacture of Synthetic Rubbers—Correction

In the November, 1942, issue an error occurs on page 1384 in Figure 1. The butadiene formula over the arrow in the lower right-hand corner pointing to BUTYL should be the formula for isobutylene:



$$+CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3$$

I appreciate having this error called to my attention by Charles F. Smith, Jr., of Buffalo.

Harry L. Fisher

U. S. Industrial Chemicals, Inc.
Stamford, Conn.

Surface Tensions of Methane-Propane Mixtures

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University of Michigan, Ann Arbor, Mich.

The surface tensions of the liquids in equilibrium with vapor have been determined for the methane-propane system over the range 5° to 194° F. and 40 to 1500 pounds per square inch. The capillary-rise and drop-volume methods were used in a glass-windowed equilibrium cell. Differences in results between these methods are explained by the high rates of drop formation in the drop volume method.

A formula is developed which reproduces the methane-propane data within 0.1 dyne per cm. This formula may be applied to any mixture when the molecular weight, density, and composition of each phase are known. The research indicated that liquids in the entire critical region have very low surface tensions.

SURFACE tension is becoming an important property describing the behavior of the petroleum hydrocarbons in the producing and refining industry. Capillary action may become the controlling property in oil recovery (*1, 12, 15*). Entrainment in fractionating equipment is closely related to the surface tension of liquid hydrocarbons (*3, 13*). The engineer needs the surface tension of hydrocarbon mixtures, containing dissolved gases at high pressures, for the solution of problems of this nature.

Although the surface tensions of most pure hydrocarbons are known (*13*), no data were available for mixtures of known compositions under pressure. To develop a correlation by which the surface tension of hydrocarbon mixtures under pressure may be predicted, data on the methane-propane system (*22*) over the temperature range 5° to 194° F. and pressure range 40 to 1500 pounds per square inch were obtained. These data were used to establish a pattern by which surface tension data on hydrocarbon mixtures may be correlated.

The literature contains surface tension data measured at various pressures for a great number of pure compounds. Several relations for correlating the data have been brought forward (*2, 6, 7, 10, 13, 17, 19, 25, 26, 28*). The equation of Macleod (*17*), which was suggested on an entirely empirical basis, was expanded by Sugden (*25*) to obtain the following equation:

$$\gamma^{1/4} = [P]\,\frac{d_L - d_V}{M} \qquad (1)$$

where γ = surface tension, dynes/cm.
$[P]$ = a constant called the "parachor"
M = molecular weight
d_L = density of liquid, grams/cc.
d_V = density of vapor, grams/cc.

Sugden showed that the parachor is primarily an additive and constitutive property. Fowler (*7*) derived Macleod's equation, including the parachor, by applying statistical mechanics and thermodynamics to a reasonable model and obtained

$$\gamma^{1/4} = \frac{BN^4}{4A^2\,T_c}\left(\frac{d_L}{M_L} - \frac{d_V}{M_V}\right) \qquad (2)$$

where A, B = constants
T_c = critical temperature
N = Avogadro's number
M_L = molecular weight of liquid
M_V = molecular weight of vapor

Equation 2 will easily reduce to Equation 1 for pure compounds.

Hammick and Andrew (*8*) found that the surface tension of mixtures at low pressure could be calculated by Equation 1, provided the parachor used was the molal average of the parachors and M was the average molecular weight of the liquid. This method is unsatisfactory at elevated pressures or when the mixtures are either associated, dissociated, or polar.

Swartz presented data on crude oils containing dissolved gases (*27*) but did not report compositions of phases.

Equilibrium Cell

A double glass equilibrium cell was used to permit visual observation of the capillary-rise and drop-volumes of the mixtures. The cell was mounted in a constant-temperature air bath, supported by two spindles and bearings. This arrangement permitted the air bath and cell to be rocked in order to facilitate the attainment of equilibrium between the gas and liquid phases. The general arrangement of the equipment is shown in Figures 1 and 2. The shield shown in Figure 2 was for protection in case the glass windows ruptured.

To obtain positive circulation of the air in the bath, a partition was placed in the center of the bath and a high-speed stirrer on one side of the partition. This fan directed the air first along the heaters and then around the equilibrium cell. Until this arrangement was tried, continuous boiling of the liquid occurred from some point in the cell because of an unequal temperature distribution. The temperature of the air in the bath was controlled between ±0.1° C. of the temperature desired. Since the system being considered was in the equilibrium cell which is essentially a steel container weighing about 50 pounds, it is believed that the temperature of the system was within ±0.05° C. of the reported value.

Since the gaskets used to seal the glass windows of the equilibrium cell came into contact with the liquid under observation, each gasket was carefully covered with alumi-

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[1] Present address, Phillips Petroleum Co., Bartlesville, Okla.

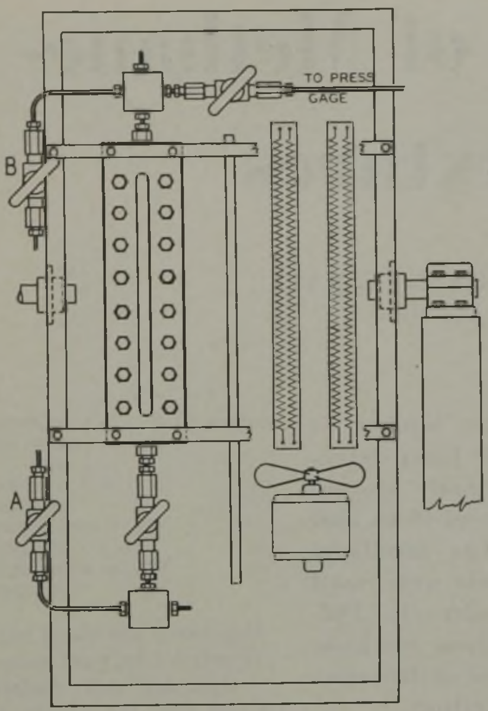

Figure 1. Diagram of Pressure Apparatus

num foil. This precaution prevented any foreign material from being dissolved out of the gasket by the mixtures. Oxides of mercury, which formed from the confining fluid, and solid particles were filtered out by a closely packed asbestos plug in the feed line. This detail also was a necessary improvement for satisfactory operation.

A mercury fluorescent light was placed behind the cell to supply illumination. To obtain equilibrium, a driving mechanism consisting of a motor, gear reducer, and eccentric arms rotated the constant-temperature bath and its contents through angles of ±30° from the horizontal at a rate of approximately 15 cycles per minute. Bourdon-tube pressure gages were used after calibration by a dead weight tester. The thermometers were graduated to 0.1° C. and calibrated against National Bureau of Standards thermometers.

In charging the hydrocarbons to the apparatus, the cell and supply lines were always evacuated, purged with propane, and re-evacuated and purged again at least three times. Then a predetermined amount of propane was allowed to flow into the gage from a cylinder attached to feed line *A* (Figure 1). The temperature of the air in the bath was brought to the desired value and held there for at least an hour before any surface tension measurements on pure propane were made. After these measurements had been obtained, methane was injected into the equilibrium cell through the bottom feed lines. After the cell was rocked 15 minutes, the surface tension of this mixture was determined and then more methane was added to the system. This procedure was repeated at constant temperature until the surface tension became so small that accurate results could no longer be obtained. Another series of measurements was made by bleeding off gas to reduce the pressure.

To prove that the system had not become contaminated by heavier constituents during the run, the 45° C. isotherm was determined by both the bleeding-off and injection processes. If any foreign material had become dissolved in the liquid during the injection process, it would not only have remained during the bleeding-off operations, but have been concentrated and thus have changed the surface tension measurements.

Capillary Rise Method

Since the mixtures used were not viscous and little, if any, absorption of one of the constituents on the surface was expected, the capillary rise method (*5*, *20*, *21*) was chosen as one means of determining surface tension. A glass capillary tube of less than 0.5 mm. inside diameter was mounted in the equilibrium cell by two small springs. This tube was calibrated in place with c. p. benzene in order to include the correction for the rise of the liquid outside the tube in the computed radius of the capillary. The radius determined by this method is not the true one but a pseudo radius containing a correction factor. The height of the capillary rise measured at five different positions averaged 3.030 cm., the greatest deviation being less than 1 per cent. This rise, the density of benzene at the temperature of the calibration (25.5° C.), and the surface tension of benzene (28.30 dynes per cm.) gave a pseudo radius of 0.02177 cm. for the capillary.

The usual formula, corrected for the liquid in the meniscus and the density of the vapors, was used to compute the surface tension from the rise of the liquid in the capillary above that in the gage:

$$\gamma = \frac{1}{2} rg \left(h + \frac{r}{3}\right)(d_L - d_V) \tag{3}$$

where r = pseudo inside radius of tube, cm.
g = gravitational constant, 980.6
h = height of rise, cm.

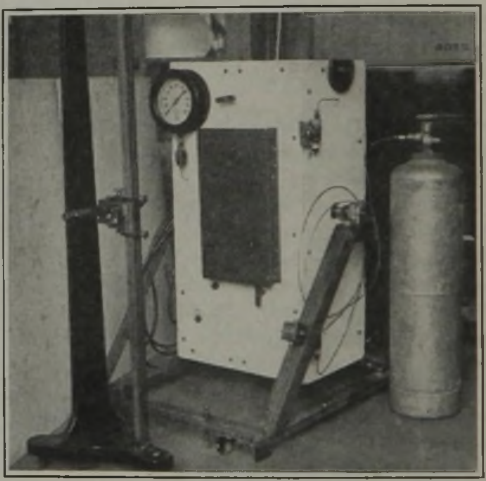

Figure 2. Front View of Pressure Apparatus

The use of a pseudo radius for r when correcting for the liquid in the meniscus involves an error not exceeding 0.001 cm. in the corrected height. Height h was measured with a cathetometer, reading direct to 0.001 cm.

Drop Volume Method

In order to establish more closely the absolute value of the surface tension, another method was used to determine a few check points. The drop volume method was tried because it has been rather completely studied by Harkins and Brown (*9*) and does not depend on the contact angle being zero as does the capillary rise method. The usual drop volume equipment could not be used because, once it was placed inside the equilibrium cell, no adjustments or manipulations could be made. A glass measuring bulb with a brass tip (Figure 3) was designed to measure the volume of the liquid. The difficulty of reading the etched marks was surmounted by etching them quite deep and placing a fine chromel wire in each groove.

The brass dropping tip was constructed with a taper on one end that corresponded to the taper of the standard ground-glass joint. Since the liquids considered showed a tendency to crawl up the sides of the tip, the portion directly above the dropping surface was machined back to form a sharp edge over which the liquid had to crawl. The rate at which the drops were formed was controlled by soldering shut the top end of the hole in the tip and then making a small hole in this plug with a needle. The assembled glass bulb and brass tip were mounted inside and at the top of the equilibrium cell so that the flattened part of the offset funnel was against the back window of the cell. The method for filling the glass bulb was to tip the cell so that the front window was up and most of the liquid was in the top of the cell. Then the cell was quickly swung to its vertical position and the liquid running along the back window was caught by the offset funnel filling the glass measuring bulb. Immediately the drops began falling and the number of drops were counted for a volume measured between the two etched stems. The data were interpreted by the following equation, proposed by Harkins and Brown (9):

$$\gamma = \frac{(W - w)g}{2\pi r g\, f\left(\frac{r}{a}\right)} \tag{4}$$

where W = weight of a drop
w = weight of a volume of vapor equal to volume of a drop
π = 3.1416
$f\left(\frac{r}{a}\right)$ = correction factor which is a function of $\left(\frac{r}{a}\right)$
r = radius of dropping tip, cm.
a = square root of capillary constant

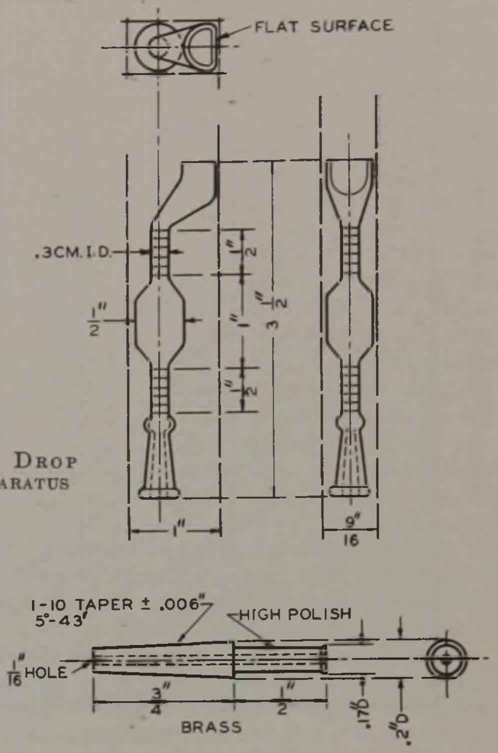

Figure 3. Drop Volume Apparatus

Table I. Surface Tension Data for Methane-Propane Mixtures by Capillary Rise

Temperature, ° F.	Temperature, ° C.	Abs. Pressure, Lb./Sq. In.	Mole Fraction Methane, Liquid x_1	Mole Fraction Methane, Vapor y_1	Densities, Grams/Cc., d_L	Densities, Grams/Cc., d_V	Densities, Grams/Cc., $d_L - d_V$	Reading h, Cm.	γ, Dynes/Cm.
5.0	−15.0	1094	0.479	0.887	0.4340	0.1059	0.3281	0.345	1.23
		1037	0.457	0.889	0.4467	0.0986	0.3481	0.400	1.51
		887	0.372	0.887	0.4748	0.0803	0.3945	0.678	2.88
		600	0.250	0.865	0.5142	0.0503	0.4639	1.116	5.56
		314	0.123	0.803	0.5380	0.0255	0.5125	1.573	8.64
		42	0	0	0.5511	0.0063	0.5448	2.083	12.13
50.0	+10	1210	0.450	0.783	0.3661	0.1290	0.2371	0.190	0.50
		1109	0.418	0.788	0.3931	0.1120	0.2811	0.308	0.98
		916	0.327	0.787	0.4340	0.0871	0.3469	0.542	2.04
		773	0.266	0.776	0.4562	0.0719	0.3843	0.715	2.97
		575	0.183	0.736	0.4807	0.0518	0.4289	0.966	4.46
		375	0.122	0.654	0.4993	0.0339	0.4654	1.238	6.19
		201	0.057	0.469	0.5113	0.0210	0.4903	1.472	7.74
		94	0	0	0.5175	0.0139	0.5036	1.578	8.52
86.0	30	1230	0.452	0.684	0.3273	0.1243	0.2030	0.081	0.19
		1039	0.355	0.688	0.3786	0.1089	0.2697	0.284	0.82
		982	0.336	0.687	0.3903	0.1011	0.2892	0.351	1.11
		948	0.314	0.684	0.3972	0.0864	0.3008	0.398	1.30
		858	0.279	0.678	0.4125	0.0861	0.3264	0.489	1.73
		808	0.255	0.672	0.4200	0.0807	0.3393	0.549	2.14
		744	0.229	0.661	0.4290	0.0734	0.3556	0.609	2.34
		583	0.166	0.616	0.4489	0.0575	0.3914	0.800	3.37
		510	0.136	0.582	0.4569	0.0508	0.4061	0.886	3.83
		419	0.100	0.520	0.4660	0.0426	0.4234	0.974	4.43
		311	0.059	0.418	0.4755	0.0336	0.4419	1.104	5.25
		220	0.024	0.233	0.4831	0.0265	0.4566	1.205	5.91
		163	0	0	0.4877	0.0235	0.4642	1.286	6.39
113.0	45	982	0.297	0.584	0.3646	0.1109	0.2537	0.230	0.64
		893	0.258	0.577	0.3808	0.0982	0.2826	0.315	0.97
		872	0.250	0.575	0.3840	0.0954	0.2886	0.336	1.06
		821	0.230	0.568	0.3922	0.0889	0.3033	0.395	1.30
		733	0.194	0.548	0.4051	0.0787	0.3264	0.474	1.68
		728	0.192	0.547	0.4059	0.0781	0.3278	0.479	1.70
		692	0.178	0.536	0.4108	0.0743	0.3365	0.512	1.87
		623	0.151	0.509	0.4200	0.0671	0.3529	0.586	2.23
		619	0.149	0.507	0.4205	0.0668	0.3537	0.601	2.30
		518	0.110	0.454	0.4326	0.0571	0.3755	0.688	2.79
		348	0.046	0.295	0.4499	0.0423	0.4076	0.861	3.78
		222	0	0	0.4610	0.0327	0.4283	0.998	4.58
149.0	65	935	0.233	0.438	0.3228	0.1243	0.1985	0.097	0.22
		830	0.184	0.420	0.3468	0.1048	0.2420	0.203	0.54
		718	0.136	0.380	0.3686	0.0890	0.2796	0.285	0.87
		615	0.096	0.323	0.3867	0.0771	0.3096	0.380	1.28
		480	0.047	0.211	0.4053	0.0637	0.3416	0.506	1.87
		435	0.032	0.158	0.4108	0.0593	0.3515	0.539	2.05
		340	0	0	0.4215	0.0507	0.3707	0.642	2.57
194.0	90	547	0	0	0.3434	0.1180	0.2254	0.138	0.35

The correction factors were obtained from Harkins and Brown's plot of $f(r/a)$ against (r/a). The term $(W - w)$ is calculated by means of

$$(W - w) = V(d_L - d_V) \tag{5}$$

where V = volume of a drop

The volume of the glass bulb and etched stems were calibrated with distilled water and checked with mercury. The radius was measured with a standardized micrometer caliper and found to be 0.2140 cm.

The methane used in this investigation was obtained from the Buttonwillow Field, Calif., and has an analysis of 99.7 mole per cent methane, 0.3 carbon dioxide, and less than 0.02 ethane or heavier hydrocarbons. Propane having a purity of 99.9 mole per cent was furnished through the courtesy of the Phillips Petroleum Company.

Presentation of Data

A total of forty-seven different conditions of temperature and pressure for equilibrium liquids in the methane-propane system

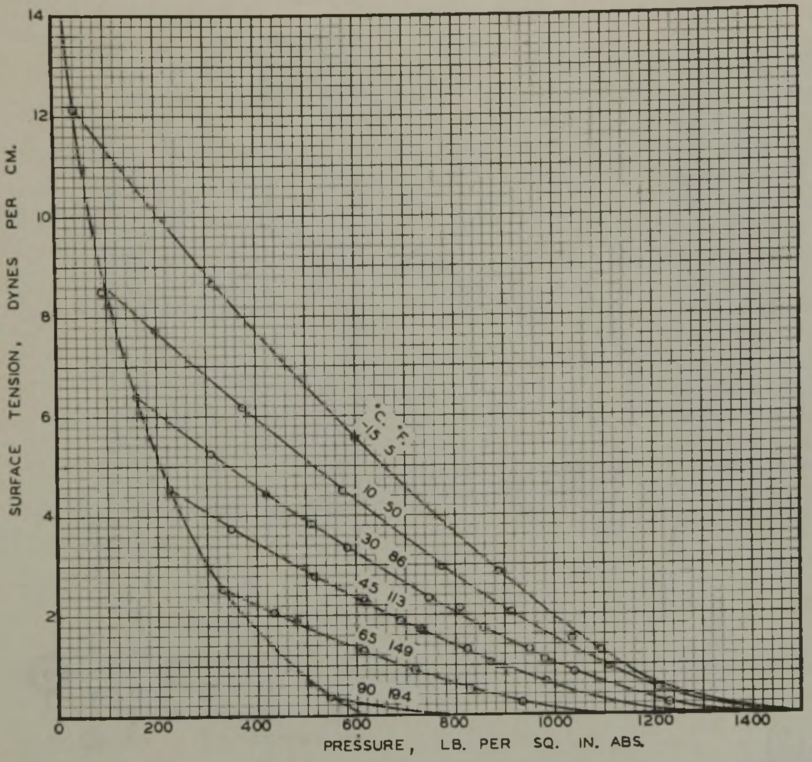

Figure 4. Surface Tension *vs.* Pressure for Methane-Propane System

was investigated. The six isotherms at which the surface tensions were measured are 5°, 50°, 86°, 113°, 149°, and 194° F. The capillary rise data for these isotherms are presented in Table I, using Equation 3 for the surface tension calculations. The composition and density data given in this table were interpolated and extrapolated from the data of Sage, Lacey, and Schaafsma (*22*). The surface tensions are plotted in Figure 4 as isotherms. The boundary curve for the isotherms is the surface tension curve of pure propane. The pressure at which the surface tension becomes equal to zero on this plot is the critical pressure of a methane-propane mixture whose critical temperature is the temperature of the isotherm.

Figure 4 is cross-plotted as isobars in Figure 5, with pure propane values as the boundary curve. Using Figures 4 and 5, lines of constant surface tension have been superimposed on a pressure-temperature plot of the phase diagrams of various mixtures of the methane-propane system, Figure 6. From these three graphs, the surface tension can be read if any two of temperature, pressure, composition of liquid, or composition of vapor are given. The surface tensions below 5° F. on Figures 5 and 6 were extrapolated, using values of methane obtained from Katz and Saltman's correlation (*13*) as a guide.

To establish more closely the absolute value of the surface tension, the drop volume data on the methane-propane mixtures presented in Table II were taken. The calculations follow Equation 4.

A comparison of the interfacial tensions measured by the drop volume and the capillary rise methods showed considerable differences. Therefore the drop volume method was studied further. The rate of formation of a drop seemed to be the cause of the difference. Harkins and Brown (*9*) called attention to this but did not investigate the effect of rate, since their data were obtained at such small rates of flow that the effect was negligible. The experimental conditions of this investigation required complete disassembly of the equipment to control the rate of flow. Therefore the effect of rate of drop formation on the value of the surface tension of several materials was studied at room conditions, yielding the data in Table III.

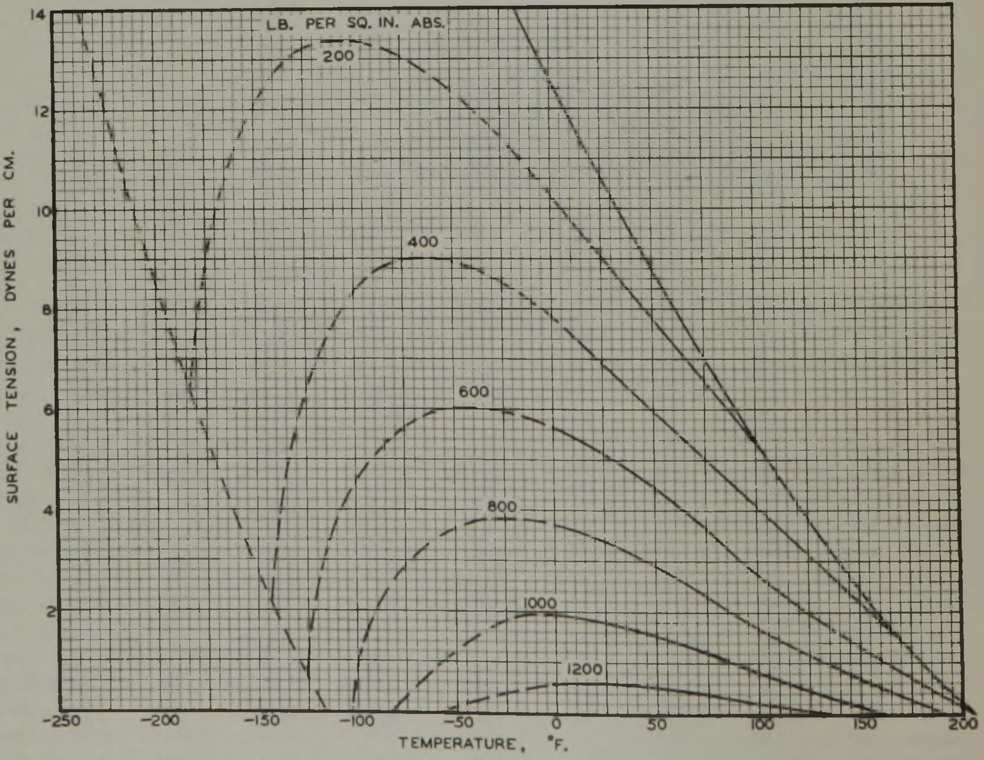

Figure 5. Surface Tension *vs.* Temperature for Methane–Propane System

Table II. Drop Volume Data on Methane-Propane Mixtures

Temp., ° F.	Abs. Pressure, Lb./Sq. In.	Vol. of Liquid in Drops Cc.	No. of Drops, n	Time, Min.	a	$f(r/a)$	$d_L - d_V$, G./Cc.	t/n, Min./Drop	γ, Dynes/Cm.
50	94	1.621	107	3.266	0.1859	0.5993	0.5040	0.03055	9.29
	94	1.627	110	14.333	0.1859	0.5993	0.5040	0.13020	9.08
	201	1.621	119	9.833	0.1794	0.6002	0.4903	0.08260	8.09
	375	1.610	136	3.856	0.1646	0.6049	0.4654	0.02835	6.64
	375	1.621	137	4.280	0.1646	0.6049	0.4654	0.03120	6.64
	575	1.610	167	3.729	0.1451	0.6177	0.4288	0.02235	4.76
	575	1.616	168	3.880	0.1451	0.6177	0.4288	0.02310	4.75
	773	1.610	218	6.390	0.1248	0.6380	0.3843	0.02930	3.25
	773	1.610	219	8.290	0.1248	0.6380	0.3843	0.03785	3.23
	916	1.616	277	5.938	0.1094	0.6550	0.3469	0.02140	2.25
	916	1.609	280	6.636	0.1094	0.6550	0.3469	0.02365	2.22
86	163	1.627	139	58.000	0.1677	0.6027	0.4642	0.4170	6.57
	311	1.623	159	61.150	0.1556	0.6100	0.4419	0.3845	5.40
	419	1.629	177	66.750	0.1461	0.6210	0.4234	0.3770	4.57
	583	1.629	215	59.816	0.1325	0.6294	0.3914	0.2785	3.44
	808	1.652	310	94.983	0.1100	0.6550	0.3593	0.2115	2.13
113	222	1.621	165	3.883	0.1477	0.6164	0.4283	0.02355	4.97
	348	1.610	186	4.866	0.1375	0.6247	0.4076	0.02620	4.12
	518	1.603	218	3.033	0.1230	0.6403	0.3755	0.01391	3.14

The time to form a drop was plotted against the percentage deviation of the surface tension obtained by this method from the accepted values (Figure 7). This graph shows that the rate data for each compound fall very close to a smooth curve. All of these curves seem to have the same form and can be extrapolated to zero per cent deviation, as would be expected. The anticipated biaxial asymtotic property of the curves described for benzene (*9*) is verified in Figure 7. Since all the rate curves seemed to exhibit similar characteristics, a short study was made of the variables which could be introduced to make one general curve. This study was unsuccessful with regard to variables which could be evaluated for the methane-propane mixtures.

Those drop volume measurements on the methane-propane system which were made at low rates of drop formation agreed with the values found by the capillary rise. Figure 7 appears to explain satisfactorily the discrepancies at higher rates, although complete proof is lacking. Only the surface tensions by capillary rise method will be considered in the correlations.

Correlations

The correlation found satisfactory for pure paraffinic hydrocarbons (*13*) was tested for mixtures by plotting the surface tensions against both true reduced temperature and pseudo reduced temperature of the liquid phases and then against the true and pseudo reduced pressures of the liquid phases (*14*). Figure 8 shows the scattering of the data for the reduced temperature relation, and the reduced pressure function was even more unreliable. These data indicate that surface tension data cannot be correlated on any simple reduced basis, but there were insufficient data to test the relation of surface tension *vs.* reduced temperature for lines of constant reduced pressure.

This method of correlation takes into account only the liquid phase, which is probably one reason for the failure of the data to correlate. But when one starts to take into account the effect of the vapor phase, the problem arises of determining the basis upon which the critical data are to be computed. This problem is mainly concerned with determining what the total system is, since the composition of the system can be considered as being any value between the compositions of the liquid and vapor. This is true because any amount of liquid or vapor phase can be added or taken away without changing the surface tension and gives rise to the same difficulties which arise in vapor-liquid equilibria.

Since the critical locus is also the locus of zero surface tension, the empirical method of Mayfield (*18*) for completing critical loci for binary systems was used to try to predict loci of constant surface tension. Figure 6 shows that the shape of the constant surface tension lines departs more and more from that of the critical locus as the surface tension increases, and hence such a method could apply only in the critical region.

Table III. Drop Volume Rate Data

Temp., ° F.	Vol. of Liquid in Drops, Cc.	No. of Drops, n	Time, Min.	a	$f(r/a)$	$d_L - d_V$, G./Cc.	t/n, Min./Drop	γ, Dynes/Cm.
				Benzene				
76	1.629	60	15.960	0.259	0.6080	0.8740	0.2660	28.45
	1.672	61	7.000	0.259	0.6080	0.8740	0.1167	28.75
	1.618	59	7.000	0.259	0.6080	0.8740	0.1167	28.75
	1.649	58	1.267	0.259	0.6080	0.8740	0.00218	29.30
	1.699	60	1.425	0.259	0.6080	0.8740	0.00238	29.70
	1.629	59	7.157	0.259	0.6080	0.8740	0.1212	28.75
	1.640	60	7.766	0.259	0.6080	0.8740	0.1293	28.70
	1.623	60	18.216	0.259	0.6080	0.8740	0.3045	28.35
	1.649	59	2.097	0.259	0.6080	0.8740	0.03555	29.25
	1.637	59	2.829	0.259	0.6080	0.8740	0.04800	29.05
	1.619	59	8.420	0.259	0.6080	0.8740	0.1402	28.75
	1.637	60	12.520	0.259	0.6080	0.8740	0.209	28.55
	1.650	60	4.945	0.259	0.6080	0.8740	0.0825	28.90
				Water				
76	1.713	27	13.433	0.386	0.6408	0.9970	0.498	75.00
	1.707	26	1.375	0.386	0.6408	0.9970	0.0529	77.55
	1.650	26	14.550	0.386	0.6408	0.9970	0.5600	75.10
	1.692	26	1.625	0.386	0.6408	0.9970	0.0625	76.95
				Carbon Tetrachloride				
76	1.620	118	27.480	0.184	0.5995	1.587	0.2330	26.40
78	1.620	117	13.193	0.184	0.5995	1.586	0.1128	26.60
78	1.612	116	10.604	0.184	0.5995	1.586	0.0915	26.75
76	1.637	117	10.092	0.184	0.5995	1.587	0.0863	26.92
76	1.628	118	25.756	0.184	0.5995	1.587	0.2180	26.62
74	1.620	118	50.273	0.184	0.5995	1.588	0.4260	26.42
78	1.629	118	17.197	0.184	0.5595	1.586	0.1458	26.55
				Pentane				
78	1.630	77	7.790	0.2223	0.6009	0.6209	0.1011	15.90
	1.627	77	6.568	0.2223	0.6009	0.6209	0.0852	15.87
	1.619	77	6.974	0.2223	0.6009	0.6209	0.0906	15.78
	1.629	77	5.443	0.2223	0.6009	0.6209	0.0576	15.89
	1.640	77	6.929	0.2223	0.6009	0.6209	0.1133	15.80
				Heptane				
78	1.608	66	15.568	0.2435	0.6048	0.6788	0.2355	19.88
	1.628	66	5.708	0.2435	0.6048	0.6788	0.0865	21.00
	1.650	67	5.875	0.2435	0.6048	0.6788	0.0877	21.00

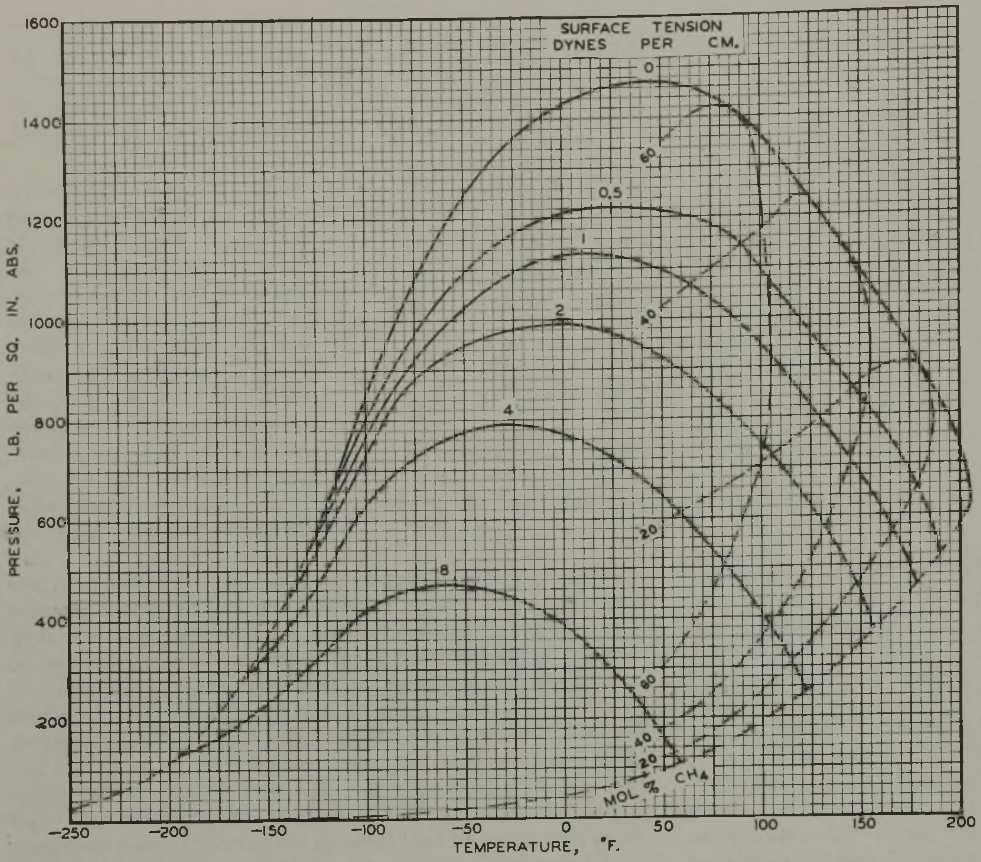

Figure 6. Surface Tension Diagram for Methane-Propane System

Macleod's equation was tried and found to be of no value in the initial form or in the form proposed by Sugden in Equation 1. The method of Hammich and Andrew, using a parachor based on the molal average of the parachors of the compounds in the liquid phase, was found to give a good correlation at low pressures but became unsatisfactory at higher pressures.

Theoretical Equation 2, derived by Fowler to establish Macleod's equation, was then carefully considered. Since terms d_L/M_L and d_V/M_V are the molal volumes of the liquid and vapor phases, respectively, a method of applying the mole fraction of each constituent in its respective phase to these terms was conceived, and the following equation resulted:

$$\gamma^{1/4} = [P]_1\left(\frac{d_L}{M_L}x_1 - \frac{d_V}{M_V}y_1\right) + [P]_2\left(\frac{d_L}{M_L}x_2 - \frac{d_V}{M_V}y_2\right) + \ldots \qquad (6)$$

where M_V = molecular weight of vapor phase
x = mole fraction of constituent in liquid phase
y = mole fraction of constituent in vapor phase
Subscripts on P, x, and y = individual components

Equation 6 was used to compute the surface tensions at the conditions of the experimental points for the methane-propane system. The experimental data and smoothed points read from Figure 4 were compared with those computed by Equation 6 in Table IV; there was excellent agreement in most cases. The greatest deviations occur at 5° and 50° F., probably because the density and composition data used in these computations are extrapolated 65° and 20° F., respectively, from the original data (*22*). When these two temperatures are not considered, the arithmetic average deviation of the computed from the observed and smoothed values are 0.05 and 0.04 dyne per cm., respectively. These deviations are well within the experimental error. The algebraic average deviation is only +0.03 dyne per cm. These small deviations are even more remarkable when the form of Equation 6 is considered, for a small error in the right-hand side of the equation appears in the final answer raised to the fourth power and thus is increased approximately fourfold.

Equation 6 is an expansion of Fowler's, which shows that the surface tension of a pure compound is proportional to the fourth power of the difference between the number of moles per cc. in the liquid and vapor, given by the terms d_L/M_L and d_V/M_V. Equation 6 considers each component of the mixture as if all the others were absent and uses the apparent molal volumes of each constituent $(d_L/M_L)x$ and $(d_V/M_V)y$. The differences of these terms for each component is multiplied by the parachor for that compound, and the sum of these products is raised to the fourth power giving the surface tension desired.

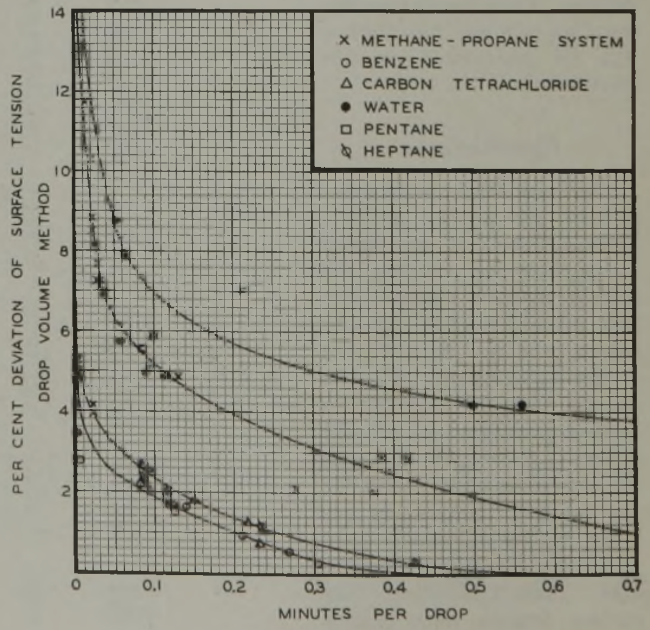

Figure 7. Drop Volume Rate Curves

Table IV. Comparison of Observed, Smoothed, and Calculated Surface Tensions

Temp., ° F.	Abs. Pressure, Lb./Sq. In.	γ, Dynes per Cm.: Obsvd.	Smoothed	Calcd.	Obsvd. − Calcd.	Smoothed − Calcd.
5.0	1094	1.23	1.23	1.14	+0.09	+0.09
	1037	1.51	1.65	1.26	+0.25	+0.29
	887	2.88	2.87	2.63	+0.25	+0.24
	600	5.56	5.56	3.30	+0.26	+0.26
	314	8.64	8.64	8.71	−0.07	−0.07
	42	12.13	12.13	12.00	+0.13	+0.13
50.0	1210	0.50	0.50	0.45	+0.05	+0.05
	1109	0.98	0.94	0.93	+0.05	+0.01
	916	2.04	2.04	2.11	−0.07	−0.07
	773	2.97	3.02	3.17	−0.20	−0.15
	575	4.46	4.57	4.75	−0.29	−0.18
	375	6.19	6.19	6.41	−0.22	−0.22
	201	7.74	7.74	8.09	−0.35	−0.35
	94	8.52	8.68	8.77	−0.25	−0.09
86.0	1230	0.19	0.25	0.27	−0.08	−0.02
	1039	0.82	0.86	0.77	+0.05	+0.09
	982	1.11	1.11	1.05	+0.06	+0.06
	948	1.30	1.26	1.22	+0.08	+0.04
	858	1.73	1.73	1.66	+0.07	+0.07
	808	2.14	1.99	1.95	+0.19	+0.04
	744	2.34	2.36	2.39	−0.05	−0.03
	583	3.37	3.37	3.29	+0.08	+0.08
	510	3.83	3.85	3.83	0.00	+0.02
	419	4.43	4.46	4.50	−0.07	−0.04
	311	5.25	5.25	5.28	−0.03	−0.03
	220	5.91	5.91	5.85	+0.06	+0.06
	163	6.39	6.39	6.36	+0.03	+0.03
113.0	982	0.64	0.64	0.60	+0.004	+0.04
	893	0.97	0.97	0.89	+0.08	+0.08
	872	1.06	1.06	1.00	+0.06	+0.06
	821	1.30	1.27	1.23	+0.07	+0.04
	733	1.68	1.68	1.55	+0.03	+0.03
	728	1.70	1.70	1.63	+0.07	+0.07
	692	1.87	1.88	1.84	+0.03	+0.04
	623	2.23	2.23	2.20	+0.03	+0.03
	619	2.30	2.25	2.25	+0.05	0.00
	518	2.79	2.81	2.78	+0.01	+0.03
	348	3.78	3.81	3.75	+0.03	+0.06
	222	4.58	4.58	4.58	0.00	0.00
149.0	935	0.22	0.26	0.22	0.00	+0.04
	830	0.54	0.54	0.49	+0.06	+0.06
	718	0.87	0.85	0.85	+0.02	0.00
	615	1.28	1.26	1.27	+0.01	−0.01
	480	1.87	1.84	1.86	+0.01	−0.02
	435	2.05	2.05	2.09	−0.04	−0.04
	340	2.57	2.57	2.58	−0.01	−0.01
194.0	547	0.35	0.35	0.35	0.00	0.00
			Arithmetic average (all values)		0.09	0.07
			Arithmetic average (above 50° F.)		0.05	0.04
			Algebraic average (all values)		+0.02	+0.02
			Algebraic average (above 50° F.)		+0.03	+0.03

Hammick and Andrew (*8*) developed and tested the following equation at atmospheric pressure for binary mixtures:

$$\gamma^{1/4} = \{[P]_1 x_1 + [P]_2 (1 - X_1)\} \frac{d_L}{M_L} \quad (7)$$

This is Equation 6 simplified for a binary mixture at low pressures at which the density of the vapor is small. The successful use of Equation 7 to several binary mixtures at low pressure and the ability of general Equation 6 to reproduce the methane-propane data under pressure indicate that Equation 6 would be likely to apply to binary mixtures under pressure, provided they were neither associated, dissociated, nor polar.

While only two-component mixtures have been considered so far, there is no reason to believe that other

$$[P]_n \times \left(\frac{d_L}{M_L} x_n - \frac{d_V}{M_V} y_n\right)$$

terms cannot be added, thus producing a completely general equation for multicomponent systems.

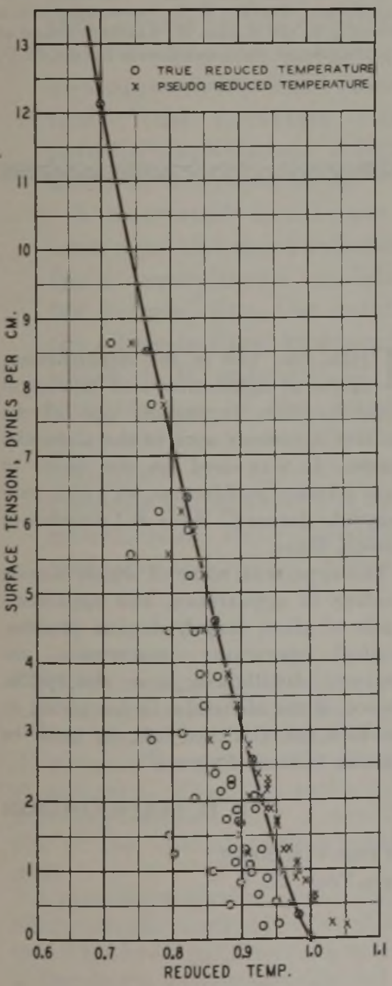

Figure 8. Surface Tension *vs.* Reduced Temperature

To facilitate the use of Equation 6 in computing the surface tension of mixtures under commercial conditions, the parachor values for a few common compounds are as follows:

Methane	77.0	*n*-Hexane	271.0
Ethane	108.0	*n*-Heptane	312.5
Propane	150.3	*n*-Octane	351.5
Isobutane	181.5	Ethylene	100.1
n-Butane	189.9	Acetylene	88.6
Isopentane	225.0	Propylene	139.9
n-Pentane	231.5	Hydrogen	34 (approx.)

These parachors were computed from surface tension data (*4, 11, 13, 16*), equilibrium densities, and molecular weights by Equation 1, and may be used in the general Equation 6. The density of the liquid and vapor must be known or computed (*23, 24*) in the absence of reliable data. An example calculation of the surface tension of the liquid on the top plate of a stabilizer follows. The negative effect of methane indicates that it has a greater concentration in the vapor phase than in the liquid, and therefore the methane tends to form a surface from the vapor side of the system.

Computation of Surface Tension of a Stabilizer Plate Liquid. The composition of the equilibrium liquid and vapor at 232 pounds per square inch absolute and 120° F. is:

	Mole Fraction: Vapor, *y*	Liquid, *x*
Methane	0.231	0.015
Ethane	0.220	0.071
Propane	0.289	0.275
Isobutane	0.131	0.268
n-Butane	0.128	0.367
Isopentane	0.001	0.004
Calcd. mol. wt.	38.2	51.7
Calcd. density (*23, 24*), gram/cc.	0.0268	0.505

Then $\frac{d_V}{M_V} = \frac{0.0268}{38.2} = 0.000701$ mole/cc.

$$\frac{d_L}{M_L} = \frac{0.505}{51.7} = 0.00977 \text{ mole/cc.}$$

The solution of Equation 6 follows:

	$\frac{d_L}{M_L}x$	$\frac{d_V}{M_V}y$	$\frac{d_L}{M_L}x - \frac{d_V}{M_V}$	Parachor	$[P]\left(\frac{d_L}{M_L}x - \frac{d_V}{M_V}y\right)$
Methane	0.0001465	0.000162	−0.0000155	77	−0.0012
Ethane	0.0006940	0.000154	+0.0005398	108	+0.0577
Propane	0.002684	0.0002025	0.002482	130.3	0.3581
Isobutane	0.002618	0.0000919	0.002526	181.5	0.3295
n-Butane	0.003582	0.0000897	0.003502	189.9	0.6650
Isopentane	0.000039	0.0000007	0.000038	232.0	0.0088
					1.4179

Surface tension $\gamma = 1.4179^4 = 4.05$ dynes/cm.

In commercial practice the compositions of the heavier petroleum fractions are not determined as pure compounds but only as cuts. Measurements of surface tensions, liquid densities, and molecular weights on these cuts at atmospheric pressure permit computation of their parachors. Terms in Equation 6 may apply for close-boiling fractions or cuts as well as for compounds. This enlargement provides a mechanism for computing the surface tension for any hydrocarbon mixture for which the compositions of the equilibrium phases are known.

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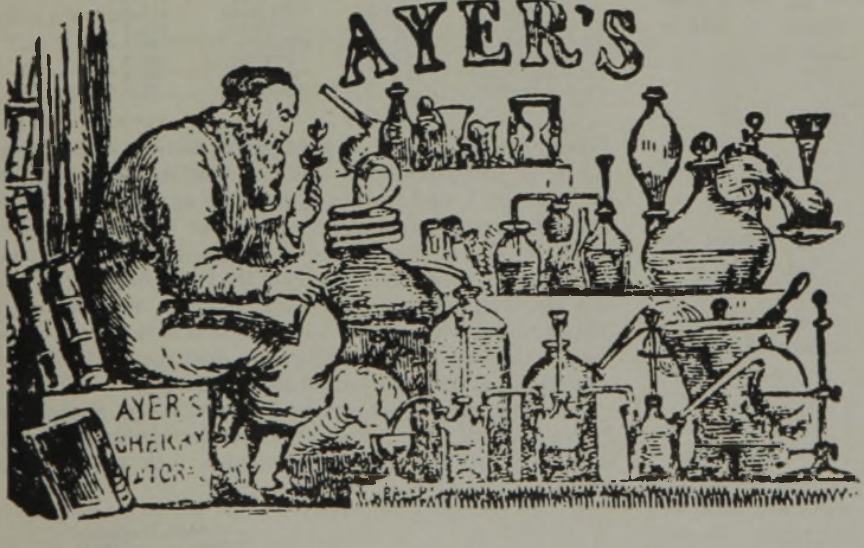
AYER'S ALCHEMIST

By W. R. Baker



THIS, No. 146 in the Berolzheimer series of Alchemical and Historical Reproductions, represents one of the earliest American uses of the alchemist theme. It was used on the cover of Ayer's American Almanac for 1853, published by James C. Ayer & Company of Lowell, Mass.

The apparatus, some of which is quite modern in appearance, and apparently made of glass, largely depicts pharmaceutical operations — maceration, extraction, distillation, and absorption. Hence, if the alchemist is not trying to produce the elixir of life, he must be making "Cherry Pectoral".

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Pure Hydrocarbons from Petroleum

Vapor-Liquid Equilibria of Close-Boiling Hydrocarbons[1]

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The University of Texas, Austin, Texas

Close-boiling hydrocarbon mixtures deviate from ideality in both vapor and liquid phases to the extent that the relative volatility ($\alpha = P_A/P_B$) calculated as the ratio of vapor pressures, may not be relied upon. Deviations from the ideal gas law and from Raoult's law usually oppose each other in their effects on the relative volatility. The system *n*-heptane–methylcyclohexane deviates appreciably from ideality of the solution; this indicates that close-boiling paraffin-naphthene mixtures may not safely be assumed ideal.

A fractional distillation method is presented as the most reliable means of verifying vapor-liquid equilibrium data, and for determining the relative volatility of the close-boiling hydrocarbon systems in which α is substantially constant. Reexamination of the vapor-liquid equilibrium and fractional distillation data on the *n*-heptane–methylcyclohexane system both gave the same value: $\alpha = 1.083$. A determination on the *n*-heptane–isooctane system gave the value: $\alpha = 1.023$.

THE problem of separating pure hydrocarbons from petroleum fractions requires an accurate knowledge of their behavior on distillation. The previous paper (*8*) discussed the complicating effects caused by the presence of aromatics. These aromatics may be removed from a petroleum fraction by any of several processes; then resolution of the residual paraffin-naphthene mixture is much easier.

A valuable property of close-boiling paraffin and naphthene mixtures is the constancy of the relative volatility, α, between two of the hydrocarbons over a wide range of concentrations, as long as the temperature does not change more than a few degrees. When α is constant or changes but slightly so that an average value may be used, the number of theoretical plates required to effect a given separation may be calculated by the equation of Smoker (*13*), which for total reflux reduces to the simpler equation derived by Fenske (*6*):

$$\frac{X_{N,A}}{X_{N,B}} = (\alpha^N)\frac{X_{1,A}}{X_{1,B}} \tag{1}$$

where X_1 = mole fraction of a component at plate 1
X_N = mole fraction of the component at plate N
α = relative volatility

When the still-pot composition is used as X_1, the exponent of α becomes $N + 1$.

As an illustration of the importance of knowing exact values of α for close-boiling mixtures, suppose it is desired to fractionate a 50 mole per cent mixture of *n*-heptane and isooctane (2,2,4-trimethylpentane) to obtain 99 per cent pure *n*-heptane. Using relative volatility values of 1.052 and 1.023, the calculated numbers of theoretical plates are 91 and 202.5, respectively. Since, in practice, 2 to 10 actual plates at partial reflux are required for each theoretical plate at total reflux, seemingly small differences become significant when α is close to unity.

Calculation of α for Ideal Systems

The relative volatility of component A to component B in a mixture (*16*) is, by definition,

$$\alpha_{AB} = \frac{Y_A X_B}{Y_B X_A} \tag{2}$$

where Y and X are mole fractions or mole percentages in equilibrium vapor and in liquid phases, respectively.

When the ideal gas and solution laws apply, Equation 2 simplifies to

$$\alpha_{\text{ideal}} = P_A/P_B \tag{3}$$

where P_A and P_B are the vapor pressures of the pure liquid components. When the system is ideal, α may be calculated directly from vapor pressures. However, accurate vapor pressure data have not been obtained for all hydrocarbons which one may wish to separate from petroleum, and an equation relating normal boiling temperature to relative volatility will be a real convenience.

Edgeworth-Johnstone (*5*) derived the relation for hydrocarbons at atmospheric pressure:

$$\log_e \alpha = 11.5\,\frac{(T_B - T_A)}{T} \tag{4}$$

The temperatures are the atmospheric boiling points expressed in an absolute temperature scale. The Clausius-Clapeyron equation and Trouton's rule with a constant of 22.0 were assumed. The constant should be modified to obtain best accuracy for close-boiling hydrocarbons, giving

$$\log_{10} \alpha = 4.85\,\frac{(T_B - T_A)}{T} \tag{4A}$$

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[1] The first paper in this series appeared on pages 117 to 119, January, 1943, issue.

A formula which gives somewhat better accuracy for hydrocarbons boiling within 5° C. of one another is:

$$\alpha_c = 1 + \frac{T_B - T_A}{10.56 + 0.0633\,T} \tag{5}$$

Equation 5 was derived by fitting an empirical linear temperature equation to the values of dt/dp for pure hydrocarbons given by Brooks (*3*). For wider boiling compounds, the formula is proposed:

$$\alpha_w = 1 + \alpha_e\,(4.4 + 2.3 \log T)\,\frac{(T_B - T_A)}{T} \tag{6}$$

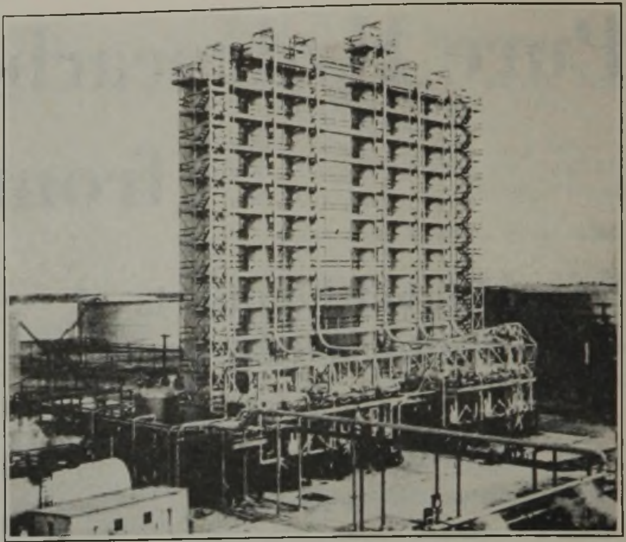
in which the temperatures are expressed in ° K. Additional approximate relations incorporated into Equation 6 are the Kistiakowsky equation for latent heat of vaporization and the Clapeyron equation. For wide-boiling compounds, Equation 5 predicts relative volatilities somewhat low, while Equation 6 gives values slightly high.

Deviations from Ideal Gas and Solution Laws

The relative volatility is strictly equal to P_A/P_B only when the laws of Amagat, Boyle, Charles, Dalton, and Raoult all apply rigorously. This is almost never the true case, yet the relation $\alpha = P_A/P_B$ is sometimes a satisfactory approximation.

Deviations from Ideal Gas Law. Inspection of vapor density and *P-V-T* data for pure six-carbon to eight-carbon hydrocarbons (*9, 14*) near their normal boiling points shows gas law deviations ranging from 4 to 10 per cent ($\mu = PV/RT = 0.96$ to 0.90). These deviations result in vapor concentrations higher than those given by the gas law, and α is affected unless the deviations happen to be equal, or $\mu_A = \mu_B$. The effect of gas law deviations on α may be eliminated by the substitution of fugacities for vapor pressures (*10*), and this procedure works well at high pressures. When fugacities are used at atmospheric pressure, the result is a calculated α which is usually lower than both P_A/P_B and the experimental vapor-liquid equilibrium value.

This anomaly is explainable on the hypothesis that "ideal" hydrocarbon solutions are rare. In general, the gas law deviation of hydrocarbons is negative, and that of the more volatile component of a binary mixture (component *A*) is somewhat greater in magnitude than that of component *B*. Likewise, Raoult's law deviations (activities) of hydrocarbons are most frequently positive, and the activity of component *A* is often somewhat greater than that of component *B*. Negative gas law deviations and positive activities oppose each other in their effects on α; and in some cases, although neither effect is negligible, the net effect is so slight that the system appears to be ideal with respect to the relation $\alpha = P_A/P_B$. This situation may be detected by comparison of observed total pressures of mixtures with the sum of calculated partial pressures, as was done by Beatty and Calingaert (*1*). It does not follow that $\alpha = P_A/P_B$ whenever observed total pressures approximate ideal values.



Plant for Separation of Pure Hydrocarbons from Natural Gasoline Fractions

Table I. Relative HETP Values[a]

Citation No.	Systems with Accordant Values	Citation No.	Systems with Discordant Values
(*7*)	A. Carbon tetrachloride–benzene	(*15*)	A. Carbon tetrachloride–benzene
	B. Benzene-toluene		B. Heptane-methylcyclohexane
(*4, 7*)	A. Carbon tetrachloride–benzene	(*7, 15*)	A. Carbon tetrachloride–benzene
	B. Heptane-toluene		B. Heptane-toluene
(*7*)	A. Benzene-toluene	(*7*)	A. Heptane-toluene
	B. Heptane-toluene		B. Heptane-methylcyclohexane
(*15*)	A. Carbon tetrachloride–benzene	(*15*)	A. Methylcyclohexane-toluene
	B. Methylcyclohexane-toluene		B. Heptane-methylcyclohexane

[a] Comparative data for two systems obtained on the same fractionating column at total reflux over the same range of boiling rates.

Verification of Binary Equilibrium Data

The Duhem-Margules equation may be used to detect incongruities in vapor-liquid equilibrium data. Beatty and Calingaert (*1*) used it to develop a number of criteria for testing such data. By relations so developed and close scrutiny of experimental data, they found certain inconsistencies and experimental errors in most of the systems investigated, and concluded that such data were unreliable. They also developed a method of calculating vapor-liquid equilibria of nearly-ideal solutions by constructing synthetic partial pressure curves from total pressure measurements by assuming the ideal gas law and "that the deviations of these pressures from the ideal lines vary with *X* in a more or less uniform manner". This procedure gave values of α which are constant or independent of concentration. Of the relative volatilities so calculated by the same authors, the benzene-cyclohexane azeotrope was undetected and this article will show that the values reported for the *n*-heptane–methylcyclohexane and the *n*-heptane–isooctane (2,2,4-trimethylpentane) systems are in serious disagreement with experimental vapor-liquid equilibria and rectification data. Hence, although the method may detect deviations from ideality of the solution, its merit for predicting relative volatilities of close-boiling hydrocarbons has never been established.

Since the use of equilibrium data is to compute separations obtainable by fractional distillation, direct data may not be dispensed with until another method is available which shows positive agreement with fractional distillation data. An obvious method of verifying vapor-liquid equilibrium data is to compare it with the results of fractional distillation.

Verification of Vapor-Liquid Equilibria by Fractional Distillation Data

If it is granted that the diffusional theory of fractionation is correct, the rate at which vapor-liquid interaction proceeds in a packed or bubble-tray column (operated at total reflux) will be nearly the same for systems of approximately equal viscosities and normal boiling ranges at equivalent vapor rates. This condition is manifested in packed columns by equal and constant values of the height equivalent of a theoretical plate (HETP) or height of a transfer unit (HTU) for different systems run in the same column, and by equal plate efficiencies for different systems in the same bubble-tray tower.

Modern data suitable for comparison are reported in several articles (*4*, *7*, *15*). Equivalent HETP values were obtained in a number of the tests, as well as a number of divergent values. All systems on which comparisons could be made are listed in Table I under "Accordant" or "Discordant" columns or both, as the case may be. There are five binary systems in the "Discordant" column. Of these, the carbon tetrachloride–benzene system has been subjected to a great deal of experimental study over a period of years, and there is scarcely room for doubt about the essential accuracy of its vapor-liquid equilibrium. It is further verified by its frequent presence in the "Accordant" column. On the basis that the vapor-liquid equilibrium of this system and the fractionation data are correct, vapor-liquid equilibrium of the system *n*-heptane–toluene and the relative volatility value of 1.07 for *n*-heptane–methylcyclohexane are open to question.

The *n*-heptane–toluene and carbon tetrachloride–benzene pair appears in both "Accordant" and "Discordant" columns of Table I. Of the data suitable for comparison, there was a total of thirty-five experiments on *n*-heptane–toluene in four fractionating columns. Vapor-liquid equilibrium data used in all cases were those determined by Bromiley and Quiggle (*2*). Inspection of the thirty-five experiments revealed twenty giving accordant HETP values and fifteen giving discordant values. In every case the distillate composition in the accordant runs was below 80 mole per cent *n*-heptane whereas the distillate composition of the discordant tests was above 80 mole per cent *n*-heptane. It must, therefore, be concluded that the vapor-liquid equilibrium data are essentially correct below 80 mole per cent *n*-heptane but appreciably in error at concentrations above that figure. Since the system is nonideal, the relative volatility may not be assumed constant and independent of X. The discordant HETP values are low; this indicates that y/x above 80 per cent heptane is too low, or that the system deviates from ideality in this zone less than the vapor-liquid equilibria indicate.

The methylcyclohexane-toluene results are slightly out of line in the same direction as those of *n*-heptane–toluene. The distillate composition was above 90 mole per cent methylcyclohexane in each of the four experiments on this system, which indicates that the vapor-liquid equilibrium are also in error, possibly at high heptane concentrations only.

The error in both systems is explainable by the hypothesis that the charge to the equilibrium still contained quite small amounts of benzene as an impurity, which would exert a greater and greater analytical effect on the equilibrium as the concentration of heptane or methylcyclohexane increased. As the previous paper (*8*) showed, benzene forms azeotropes with six-carbon hydrocarbons and is likely to behave abnormally with seven-carbon hydrocarbons other than toluene.

Vapor-Liquid Equilibrium of *n*-Heptane–Methylcyclohexane

Table I indicates an appreciable error in the vapor-liquid equilibrium of *n*-heptane–methylcyclohexane. This system is of particular interest, since it is widely used for testing laboratory columns. The only vapor-liquid equilibrium data are those of Bromiley and Quiggle (*2*). Beatty and Calingaert (*1*) found errors of various magnitudes in these data and criticized them as inaccurate, inconsistent, and unreliable. The latter authors recommended the relative volatility of 1.07 derived from their total pressure measurements, and this figure was then accepted with no supporting experimental verification. In order to arrive at the most dependable relative volatility, values will be calculated from both equilibrium and fractional distillation data.

Ideal-System Value. The vapor pressure curve for *n*-heptane has been accurately determined by Smith (*12*). The vapor pressure ratio of *n*-heptane to methylcyclohexane at the accepted boiling point of the latter (100.8° C.) is 1.0694. Equation 5 indicates an increase of 0.0003 at the boiling point of *n*-heptane (98.42° C.).

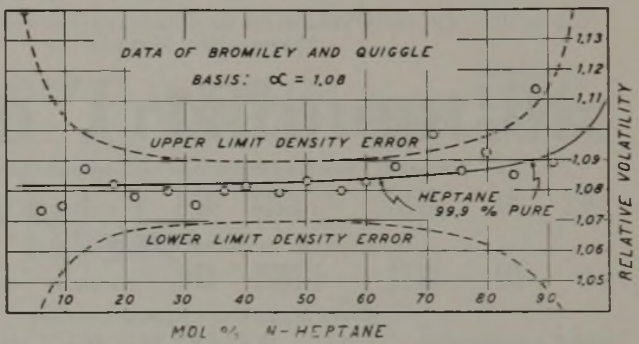


Figure 1. Relative Volatility of *n*-Heptane–Methylcyclohexane

Re-examination of Equilibrium Data. The relative volatility was calculated for each experiment of Bromiley and Quiggle's tabulation. The determinations in which the heptane concentration was less than 5 or greater than 85 mole per cent were rejected in order to minimize the effect of analytical error. (This will be discussed later.) The average of the eighteen determinations of intermediate concentration was 1.083, with an uncertainty of 0.002. The authors made an unfortunate choice in the use of density rather than refractive index for analysis, since use of the refractive index would have greatly reduced analytical error. The experimental values of α are plotted on Figure 1. Except for the ends of the curve (at which errors of analysis are greatly magnified) the data are remarkably consistent. The hypothetical effect of a density error of ±0.0001 on a relative volatility of 1.08 is shown by the dashed curves, and indicates that a precision of about ±0.00005 in the density determination was realized in the great majority of the analyses. The data show a slight trend of α, increasing with *n*-heptane concentration. This would result if the heptane contained a trace of low-density, volatile impurity. As an illustration, suppose the true α is 1.08 and independent of concentration. If the heptane was 99.9 mole per cent pure and contained 0.1 mole per cent *n*-hexane, α observed from exact density analyses would form the solid curve shown on Figure 1.

The physical constants of the materials used in these experiments were within analytical agreement of more recent values. These constants with the purification history of both hydrocarbons indicate that the materials were as pure as any likely to be used for purposes of fractional distillation.

Table II. Relative Volatility of *n*-Heptane–Methylcyclohexane from Fractional Distillation Data

Run No.	Velocity of Liquid at Top, L./Hr.	Mole % *n*-Heptane: Distillate	Mole % *n*-Heptane: Still	Relative Volatility α from Equation 1
A. U-Type Packing, 32.4 Theoretical Plates				
1	1.8	80.5	25.5	1.080
2	2.0	84.0	24.0	1.090
3	2.1	90.0	24.0	1.108
4	2.2	81.0	22.8	1.086
5	2.3	82.0	26.6	1.081
6	4.6	76.0	20.5	1.081
7	4.8	75.0	25.6	1.069
8	5.0	80.0	28.0	1.075
			Average	1.084
B. One-Turn Helices, 18.0 Theoretical Plates				
1	5.2	51.0	20.7	1.080
2	5.5	47.0	19.3	1.076
3	5.6	48.0	18.0	1.083
4	5.8	45.8	17.5	1.080
			Average	1.080

Table III. Relative Volatility of *n*-Heptane–Isooctane by Fractional Distillation Method

Time of Run, Hours	Liquid Rate at Top of Column, Cc./Hr.	No. of Theoretical Plates	Distillate n^{20}_D	Distillate Mole % *n*-hydrocarbon	Still Pot n^{20}_D	Still Pot Mole % *n*-hydrocarbon	No. of Theoretical Plates α = 1.07	No. of Theoretical Plates α = 1.083
A. Equivalent Theoretical Plates from *n*-Heptane–Methylcyclohexane								
8.5	321	63 (*11*)	1.39068	90.4	[a]	[a]	63.7	54.1
27.0	273	73 (*11*)	1.38962	93.8	1.41868	11.2	70.7	60.1
B. *n*-Heptane–Isooctane								
4	312	55.2[b]	1.38898	69.8	[a]	[a]	1.0228[c]	
8	312	55.2[b]	1.38898	69.8	1.39014	40.0	1.0228[c]	

Known Mixtures of *n*-Heptane–Isooctane

Mole % *n*-hydrocarbon	0	12.1	17.6	24.3	35.3	36.2	51.9
n^{20}_D	1.39150	1.39110	1.39092	1.39071	1.39032	1.39023	1.38967
Mole % *n*-hydrocarbon	53.5	54.6	57.1	60.3	65.8	67.7	74.8
n^{20}_D	1.38962	1.38953	1.38947	1.38943	1.38913	1.38907	1.38883
Mole % *n*-hydrocarbon	77.3	80.3	82.0	82.3	89.8	100	
n^{20}_D	1.38868	1.38858	1.38845	1.38852	1.38818	1.38870	

[a] Still pot not sampled until end of runs; final analyses used; less than 0.5 cc. distillate withdrawn.
[b] Using same column as in A, and α = 1.083 for *n*-heptane–methylcyclohexane.
[c] Relative volatility α calculated by Equation 1.

Fractionation Data. The equivalence of experimental HETP values obtained on a given column with different liquid mixtures is sufficient evidence that such data may be used to calculate α for a system, once the number of equivalent theoretical plates in the column has been established by data on some other system of known behavior. Two sets of data by which α for *n*-heptane–methylcyclohexane may be calculated are given in Table II (*14*). The fractionating column was 32 mm. i. d. and had 2.74 meters of packing. The second system was carbon tetrachloride–benzene, which was more extensively used and gave more consistent results in these experiments than any other system.

For the data of Table IIA, a U-type packing was employed. The results show no consistent trend with vapor velocity and so are directly comparable. Rejecting runs 5 and 8 as deviating too greatly from the other six, the average number of equivalent theoretical plates in the column from the carbon tetrachloride–benzene runs is (33.4 − 1) = 32.4.

In Table IIB the same column packed with one-turn helices, was used, and a trend of HETP with boiling rate is apparent. Experiments at comparable rates are runs 1–4 on *n*-heptane–methylcyclohexane and runs 3–5 on carbon tetrachloride–benzene, since in all of these the "liquid velocity" was between 5.2 and 5.8 liters per hour. The number of equivalent theoretical plates in the column averaged (19.0 − 1) = 18.0 from carbon tetrachloride–benzene runs 3–5. From Table IIA (eight observations), $\alpha_{av.}$ = 1.084, while Table IIB (four observations) gave $\alpha_{av.}$ = 1.080.

Relative Volatility of *n*-Heptane–Isooctane

The system *n*-heptane–isooctane (2,2,4-trimethylpentane) should be nearly ideal, since it consists of two paraffins of nearly the same boiling point. Smith (*12*) determined accurate vapor pressure curves on highly purified samples of each hydrocarbon. From his data $\alpha = P_A/P_B = 1.0237$ at atmospheric pressure.

Samples of pure materials (tested at the National Bureau of Standards) were obtained from the California Chemical Company (*n*-heptane) and Röhm & Haas Company (2,2,4-trimethylpentane). Since the relative volatility of these hydrocarbons is close to unity and their gravities and refractive indices also lie close together, the analytical precision of density or refractive index determinations obtainable with instruments of the conventional types would render vapor-liquid equilibrium determinations futile.

The relative volatility was determined by the fractional distillation method, using a high-temperature Podbielniak apparatus equipped with an 11-mm. distilling tube containing 36 inches of Heli-Grid packing (*11*). Analysis was by refractive index, using a Bausch & Lomb precision-type oil refractometer, accurate to 0.00003 unit. The data are given in Table III. The experimental value of α was 1.0228. An error of one theoretical plate would affect this value by ±0.0004.

Summary

The data and observations on close-boiling binary hydrocarbon systems are summarized in Table IV. The recommended relative volatilities of *n*-heptane–methylcyclohexane and *n*-heptane–isooctane (2,2,4-trimethylpentane) systems

Table IV. Relative Volatilities of Close-Boiling Hydrocarbon Systems

System	Method of Determining α: Total pressure[a]	Ideal formula[b]	Ideal system (P_A/P_B)	Ideal solution[c]	Vapor-liquid equilibrium	Fractional distn.	Recommended Value of α
Benzene-cyclohexane	1.021	...	...	...	Azeotrope	...	...
n-Heptane–methylcyclohexane	1.07	1.0693	1.0694	1.0650	1.083	1.084 1.080	1.083
n-Heptane–isooctane	1.052	1.0237	1.0237	1.0222	...	1.0228	1.023

[a] Beatty and Calingaert (*1*, Table I).
[b] From Equation 5.
[c] Fugacity calculation (*10*).

for use in fractional distillation are 1.083[2] and 1.023, respectively. The former system was found to deviate appreciably from an ideal solution. From the information now available, systems of sufficient ideality to permit valid use of the relation $\alpha = P_A/P_B$ are limited to close-boiling mixtures of the same hydrocarbon class—i. e. paraffin-paraffin, naphthene-naphthene, and aromatic-aromatic compounds.

Analytical error in vapor-liquid equilibrium determinations becomes pronounced at extremes of concentration, and consistent errors which may be due to slight impurities are most pronounced at the low-boiling end of the curve. Such errors do not of themselves justify rejection of data on intermediate concentrations.

The fractional distillation method is proposed as the most reliable to date for verification of vapor-liquid equilibrium data and determination of α for close-boiling hydrocarbon systems in which it is essentially constant.

Acknowledgment

The Bureau of Industrial Chemistry of the University of Texas loaned the fractionation equipment. The relative volatility of *n*-heptane–isooctane was determined by E. E. Ludwig.

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[2] The multiplier to convert theoretical plates from the basis of α = 1.07 is 0.85, and the corresponding HETP multiplier is 1.176.

Activated Carbon Treatment of Raw Whisky

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The chemical changes and changes in taste characteristics that take place when a distillate from an alcohol fermentation process is treated with each of several activated carbons are reported. The effect of one carbon was investigated over a temperature range from 20° to 80° C.

Tables of results are included, and figures illustrate the percentage change effected by the treatment.

At room temperature it was noted that the change in acids, esters, aldehydes, and fusel oil was slight but not consistently in one direction. Permanganate time was increased in all treatments and to approximately the same extent. However, the treatment at elevated temperatures definitely produced an increase in acids and permanganate time, while it indicated decreases in ester, aldehydes, and fusel oil.

IN DISTILLATION industries, adsorption methods are often used to remove impurities, particularly those present at relatively low concentrations. These methods are used although very little is known of the actual chemical changes effected by the treatment. In a liquid mixture or solution, some constituents are preferentially attracted to the surface of different adsorbents to the almost complete exclusion of others.

The program described in this paper was to determine some of the more important chemical changes brought about in the raw whisky by different kinds of activated carbons, and to determine the effect of temperature on one of the carbon treatments. Taste preference was utilized to show a correlation with the extent of these chemical changes. Such a relation would substantiate the effects of the various treatments.

The chemical changes involved are many and complex. Different amplitudes are affected by the kinds of material used as containers during storage, as shown by laboratory investigations of Valaer and Frazier of the Bureau of Internal Revenue (*6*). They found upon storing raw whisky for four years in charred white oak barrels that the most rapid changes of acids, esters, solids, and color took place in the first six months. During the four years acids increased from 24.9 to 56 mg. per 100 ml. while esters increased from 7.4 to 21.3 mg. per 100 ml. Fusel oil content, however, dropped from 69 to 58.4 mg. per 100 ml.

It was also found that raw whisky changes while standing

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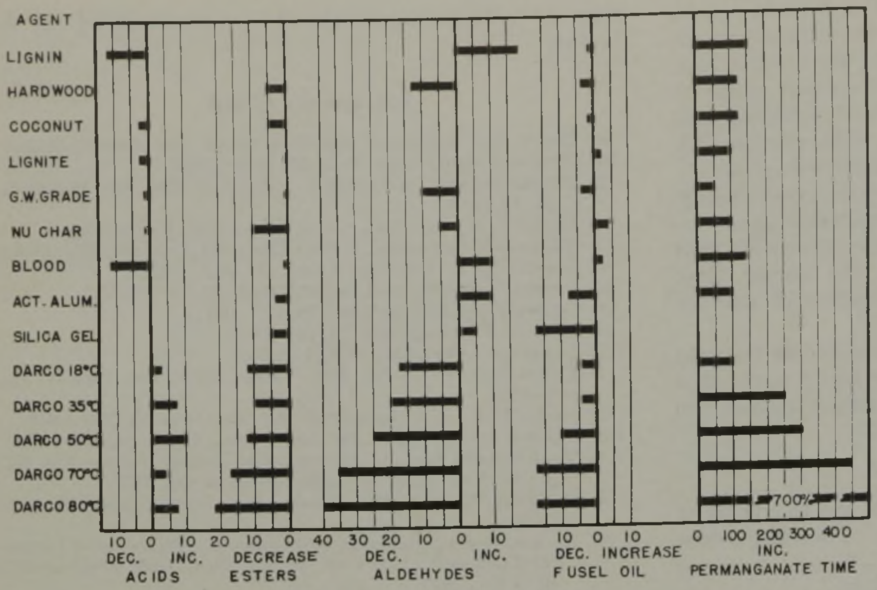

Figure 1. Effect of Various Types of Activated Carbon on Raw Rye Whisky

in glass. The acids, aldehydes, and furfural contents decrease while the esters and color increase. It was nearly four years before the whisky had lost the major portion of its green or slop taste and odor.

The practice of some distilleries has been to treat raw whisky with charcoal to remove undesirable green characteristics. In 1908 Dudley (*3*) found that fatty oils and other insolubles could be removed from raw whisky distillates by filtration through a sugar maple wood charcoal. He also asserted that soluble constituents are removed partly by adsorption but principally by diffusion into the charcoal, where particles of higher molecular weight are held longer while the lighter materials pass more rapidly.

Thomas and Hochwalt (*5*) patented a process for making an improved beverage substantially free of usual green characteristics by subjecting the liquor to a hydrogenation treatment in the presence of a catalyst of finely divided platinum, nickel, and cobalt. By this method, it is maintained, the odor and taste characteristics are permanently improved.

Chabot (*1*) found that beer worts treated by activated carbon were greatly improved in taste and foam retention properties, and that protein turbidity was removed.

Fritzweiler and Dietrich (*4*) purified absolute alcohol by percolation through carbon. Wuoorinen and Lawren (*7*) reported that birchwood charcoal removes a large number of aldehydes from alcoholic solutions, formaldehyde being an exception. In some cases they found that the removal was more easily accomplished in lower proof alcohols.

Chaney (*2*) stated, from a study of the properties of activated carbon in industrial application, that the adsorption power for particles of colloidial dimensions is a mathematical function of the ratio of its activity to its apparent density, fineness being constant. The adsorption is most effective if the carbon carries an opposite electric charge.

Zaharız, Angelescu, and Motoc (*8*) stated that animal charcoal removes, in varying amounts, the different impurities in commercial alcohols when the adsorption is performed under conditions precluding oxidation.

As a general review on effects that may be expected from treating an alcohol solution with activated carbon, it is worthwhile to consider many different viewpoints.

The treatment of a solution with an adsorbent such as activated carbon results in the phenomenon of the adhesion of molecules of a gas or dissolved substances to the surfaces of the solid bodies. This results in a relatively high concentration of the gas or solution at the place of contact, while the carrier solution is freed of these substances.

Activated carbon has a large surface area per unit volume which is increased with a reduction in particle size. Some kinds of activated carbons, too, are more porous than others and have a larger surface area per unit volume. This surface area is capable of holding the adherent molecules. The amount adsorbed increases with the length of time allowed for the treatment until equilibrium is reached. Agitation of the solution will accelerate the contact with the adsorbent and thus reduce the time required for reaching this equilibrium.

An increased temperature will decrease the viscosity of the alcoholic solution. This results in an increasing number of *usable* pores of the activated carbon and an increase in the *usable* surface area, and thus varies the amount adsorbed. A temperature change will also alter the rate of circulation and diffusion.

The removal of the adsorbed substances from the solution will disturb the chemical equilibrium, and additional chemical changes will take place. Any variation in temperature or pressure will affect both the rate of chemical change and the solubility factors. The chemical and mechanical changes will be accelerated as the temperature and pressure are increased.

The presence of air in the pores of an adsorbent will oxidize some solutions. The raw whiskies treated in the following experiments contain alcohol, acids, esters, and aldehydes which may be oxidized by the air present, but these substances will also be adsorbed by the carbon. Either oxidation or adsorption may predominate according to the kind of activated carbon used and the temperature and pressure maintained during the treatment.

Whiskies and Carbons Used

The distillate from an alcohol fermentation process of 51 per cent rye, 39 per cent corn, and 10 per cent small grain mash was stored in one-gallon glass bottles. This whisky was clear, 100-proof alcohol and had no visible colloidal suspended materials. A 100-proof, raw bourbon whisky from a grain mash of 51 per cent corn and 49 per cent small grain was also used. This, too, was clear and had no colloidal suspension perceptible to the naked eye.

For treating raw whiskies, several different kinds of activated carbon of various particle sizes were used, as well as activated alumina and silica gel as adsorptive agents.

All the samples were tested for proof before and after treating. A special test was used as an indication of the amount of reducing compounds present in the alcohol, which was considered to give an indication of various impurities. This test was called "permanganate time", as it consists in bringing a 50-ml. sample to 18° C. in a Nessler tube and adding 1 ml. of standard potassium permanganate solution. The time which elapses from the adding of the permanganate until the solution turns from pink to yellow is the permanganate time.

The alcohol solutions were treated with various carbons. For each test 0.4 gram of activated carbon was made into a thin paste and gradually diluted with a portion of the one-liter sample of alcohol to be treated. The remaining part of the liter was quickly added and the solution placed in a one-gallon, glass-stoppered bottle. The bottle was shaken for 30 minutes, and the carbon filtered out through ashless double-acid-washed filter paper. It was filtered the second time to make certain that all traces of carbon were removed. This procedure was carried out on each treatment with the several different kinds of activated carbons, activated alumina, and silica gel. Only Darco carbon was used for further experiments at elevated temperatures.

At the higher temperatures the entire shaking mechanism was placed inside an oven where the treatments were carried out at constant temperatures of 35°, 50°, 70°, and 80° C. Chemical analyses were run for acids, esters, fusel oil, aldehydes, and permanganate time. These tests were made on the samples both before and after treatment with the various adsorptive agents (Table I).

Since it was desired to determine the effects of activated carbon on the residual nitrogen content of whisky, a one-liter sample of bourbon was treated in the usual manner and an analysis made for residual nitrogen, before and after treatment:

Bourbon Whisky	Untreated, Mg./Liter	Treated with Darco, Mg./Liter	Per Cent Change
I	0.464	0.3712	20.0
II	0.476	0.2784	20.5

Samples of treated and untreated bourbon and rye whiskies were submitted to a taste-preference laboratory with the following results:

Whisky Sample	% Preference	Probable Error
Untreated bourbon	35.0	1.35
Bourbon, Darco-treated at 18° C.	65.0	
Untreated rye	21.6	1.25
Rye, Darco-treated at 35° C.	34.2	2.5
Rye, Darco-treated at 80° C.	44.2	

The various chemical analyses were carried out principally by A. O. A. C. methods. Aldehydes were calculated as acetaldehyde from the colorimetric determination. Acids were determined by titration of 0.05 N sodium hydroxide and calculated as acetic acid. Esters were calculated as ethyl acetate. The esters were determined by back-titrating with sulfuric acid the sample used for the acid determination, which had been made alkaline and allowed to stand overnight. This is in accord with standard procedure.

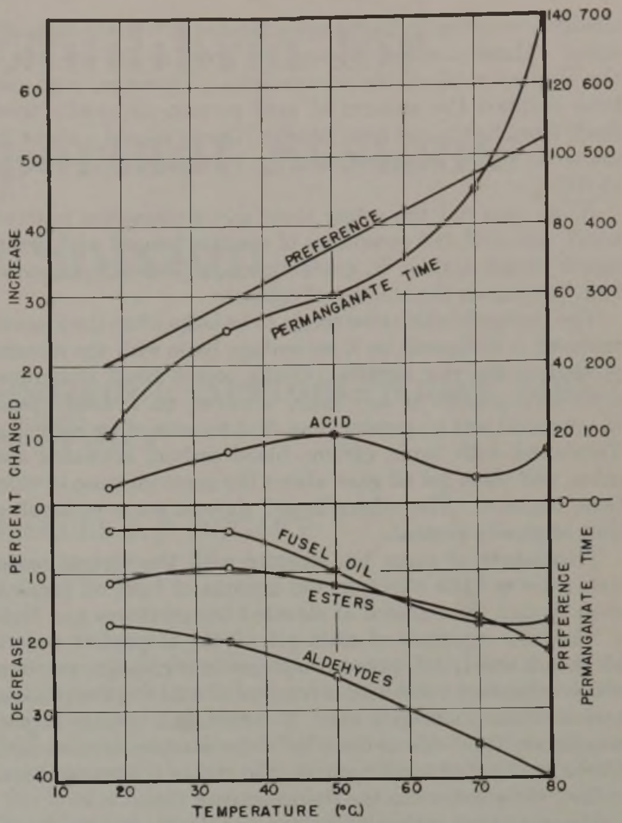

Figure 2. Action of Darco G-60 Activated Carbon at Elevated Temperatures on Raw Rye Whisky

Chemical Changes Due to Carbons

The data show that the amounts of various impurities present in the ethyl alcohol of raw rye whisky are materially changed by treatment with activated carbon, silica gel, or activated alumina. A much greater change is shown, however, in the treatments conducted at elevated temperatures.

Figure 1 gives the percentage of chemical changes that take place during treatment. Figure 2 indicates the chemical

Table I. Effect of Various Carbons on Whisky Samples

Sample No.	Adsorptive Agent	Chemical Analysis, Mg./100 Ml.				Permanganate Time, Sec.	Proof	Per Cent Change by Carbon Treatment				
		Acids	Esters	Aldehydes	Fusel oil			Acid	Esters	Aldehyde	Fusel oil	Permanganate time
R-1	None	3.9	10.50	1.15	270	30	100.4					
R-2	None	4.0	10.50	1.15	270	30	99.1					
R-3	None	3.9	10.50	1.10	260	..	100.0					
R-4	None	4.0	10.50	1.00	260	30	99.7					
R-5	None	...	...	1.00	255	..	99.5					
R-1	Lignin carbon	3.45	10.50	1.35	265	75	99.2	11.50	0	17.40	− 1.85	150
R-2	Hardwood carbon	4.00	9.95	1.00	260	65	98.8	0	− 5.25	−13.05	− 3.70	117
R-2	Coconut carbon	3.90	10.05	1.15	265	65	99.1	−2.50	− 4.28	0	− 1.85	117
R-2	Lignite carbon	3.90	10.40	1.15	275	60	99.8	−2.50	− 0.95	0	1.85	100
R-3	G.W. grade carbon	3.85	10.40	1.00	250	45	99.5	−1.30	− 0.95	− 9.10	− 3.85	50
R-3	NuChar	3.85	9.45	1.05	270	60	99.2	−1.30	−10.00	− 4.55	3.85	100
R-4	Blood carbon	3.55	10.40	1.10	265	70	97.9	11.25	− 0.95	10.00	1.93	133
R-4	Activated alumina	4.00	10.15	1.10	240	60	99.6	0	− 3.33	10.00	− 7.70	100
R-4	Silica gel	4.00	10.05	1.05	215	30	98.9	0	− 4.28	5.00	−17.30	0
R-1	Darco[a], 18° C.	4.00	9.30	0.95	260	60	99.0	2.50	−11.42	−17.40	− 3.70	100
R-5	Darco[a], 35° C.	4.30	9.55	0.80	245	105	97.2	7.50	− 9.05	−20.00	− 3.92	250
R-5	Darco[a], 50° C.	4.40	9.25	0.75	230	120	96.6	10.00	−11.90	−25.00	− 9.80	300
R-5	Darco[a], 70° C.	4.15	8.75	0.65	210	165	96.7	3.75	−16.65	−35.00	−17.60	450
R-5	Darco[a], 80° C.	4.30	8.25	0.60	215	240	96.6	7.50	−21.42	−40.00	−17.30	700

[a] Grade G-60.

changes occurring in the samples treated at various temperatures. These chemical changes are given as the per cent of the original value of the raw samples. However, most carbons reduced the amount of acid present, especially those made from lignin and from blood. Darco caused a slight increase at higher temperatures, the maximum being reached at 50° C.

In no case did the esters show any increase due to treatment, and, with the exceptions of samples treated with lignin, lignite, blood, and G. W. grade carbon, all showed a considerable decrease in the amount of esters.

The change in aldehydes seems to be large when the amount removed is compared on a percentage basis with the amount present in the raw sample. Owing to the small amount of aldehydes present at any time, however, on a weight basis the removal was no greater than that for any other impurity. Treatment with lignin carbon, blood carbon, activated alumina, and silica gel all gave about the same increase in aldehyde content. The others tested showed some removal of that originally present.

Treatments at room temperature with the various materials showed little effect on the amount of fusel oil present, even though the removal at elevated temperatures was high.

With the exception of silica gel, all the absorptive materials caused nearly 100 per cent increase in permanganate time, which indicates a considerable removal of reducing compounds, such as sulfur, nitrogen, etc. A tremendous change in permanganate time was noticed for those samples treated with Darco at elevated temperatures; the higher the temperature, in fact, the greater was the permanganate time.

The activated carbons NuChar and Darco are similar in effect. The change Darco produced was magnified at higher temperatures. The activated carbons from lignin and blood also resemble each other in the effect produced but are different from NuChar and Darco in that they increase the aldehydes and lower the acids. This latter reaction may be attributed to the presence of alkalies in these carbons.

The residual nitrogen determinations show that the untreated raw bourbon samples contained an average of 0.470 mg. per liter. The treatment of the sample with Darco at room temperature removed 20 per cent of the nitrogen in the sample.

The taste preference indicates strongly that the treatments remove undesirable taste characteristics. As far as the treatment of the bourbon is concerned, the difference is statistically significant, as indicated by the probable error of 1.35. This means that in approximately 85 chances out of 100, the trend toward improvement is duplicable.

In a similar manner the various samples of rye whisky are well differentiated from one another in terms of preference. The 30° C. treatment is significantly superior to the control, while the 80° C. treatment is reproducible to the extent of 100 per cent with respect to the control.

The adsorptive powers of the various activated carbons at room temperature, regardless of particle size, were only slightly different in effect on whiskies in comparison to those at elevated temperatures.

It appears that certain of the adsorptive agents were effective in causing oxidation of the ethyl alcohol to acids and aldehydes in excess of the amount adsorbed by the carbon itself. Other agents either failed to cause oxidation or, if oxidation did take place, were sufficiently adsorptive to remove the new substances thus produced as well as a portion of those impurities already present, so that to all appearances oxidation might never have occurred.

It is probable that only a small amount of oxidation did occur during these treatments, since small quantities of carbon were first made into a thin paste, diluted several times, and then added to the whisky sample. As Figures 1 and 2 show, considerable activity took place at elevated temperatures. Acids were increased but only at 70° C. However, there was a decided and uniform decrease of aldehydes and esters as the temperature was increased.

An even more outstanding change is noticeable in the permanganate time. A 700 per cent increase was obtained for treatment at 80° C., which would indicate a high removal of reducing compounds such as those made up of sulfur, nitrogen, etc., that were carried over in the distillation from the fermentation process. The determination showing a removal of 20 per cent residual nitrogen also supported this conclusion.

The tests for taste preference showed that treatment with activated carbons removed from the raw whisky impurities that are undesirable to human taste.

Conclusions

These tests gave definite evidence that the treatments carried on at elevated temperatures were superior to those at room temperature for removing the impurities from the distillate of an alcohol fermentation process.

Taste preferences and the desirable effects of aging on whiskies are not completely understood. Some theories hold for low fusel oil, aldehyde, and acid values; some consider a high ester value necessary; and a third group considers the relative amounts of all materials more important than the absolute values of each. On this basis it may be of interest to consider the action of activated carbon as a substitute for some aging time in the whisky industry, as well as a possible procedure for the reduction of impurities in the manufacture of industrial alcohol.

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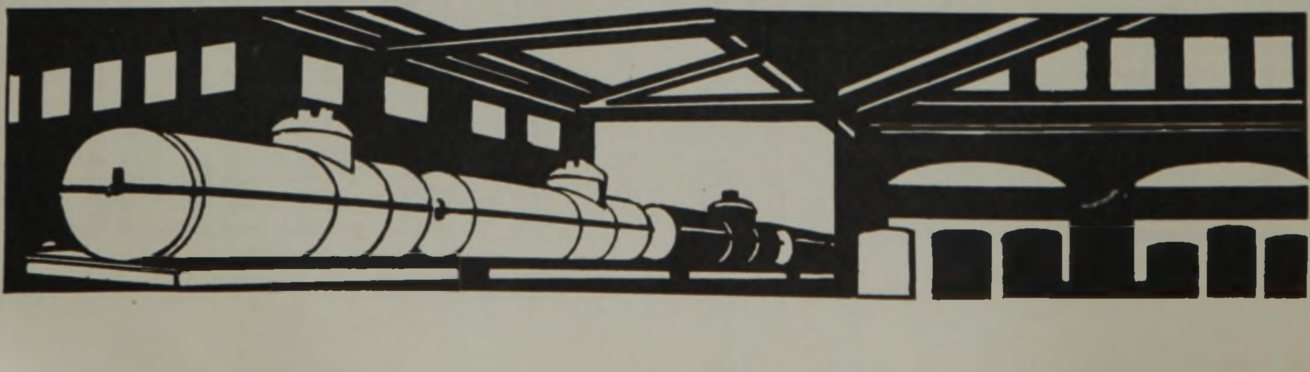

Vapor-Liquid Equilibria for Commercially Important Systems of Organic Solvents

The Binary Systems Ethanol-*n*-Butanol, Acetone-Water and Isopropanol-Water

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Vapor-liquid equilibrium data are presented for the three binary systems ethanol-*n*-butanol, acetone-water, and isopropanol-water. Activity coefficients for the acetone-water and isopropanol-water systems are also given. These data, together with observations on the operation of commercial distillation equipment, show that the original published values for these two aqueous systems were not sufficiently accurate for engineering purposes.

DATA are available on the vapor-liquid equilibria for most of the binary systems involved in the distillation of the solvents obtained from the acetone-butanol fermentation of molasses or grain. Of the six possible binary systems which comprise the quaternary system *n*-butanol–acetone–ethanol–water, all of the equilibrium data have been published in the literature except those for mixtures of ethanol and *n*-butanol. While it might be expected that mixtures of the two monohydric alcohols would closely follow the ideal solution laws, it was considered desirable actually to determine the experimental data for comparison with theoretically calculated values.

In the production of high-purity acetone from aqueous mixtures by distillation, it has been found that fractionating column performance is at variance with that predicted from existing vapor-liquid equilibrium data. This was also noted by Luaces (*12*), who cited large discrepancies in equipment sizes for acetone-water distillation units by various designers, although he was not able to ascribe these differences to their true source. Hence the original data of Bergström (*2*) were carefully redetermined, the region of the high acetone concentration receiving particular attention. Data on this system were also recently determined by York and Holmes (*23*).

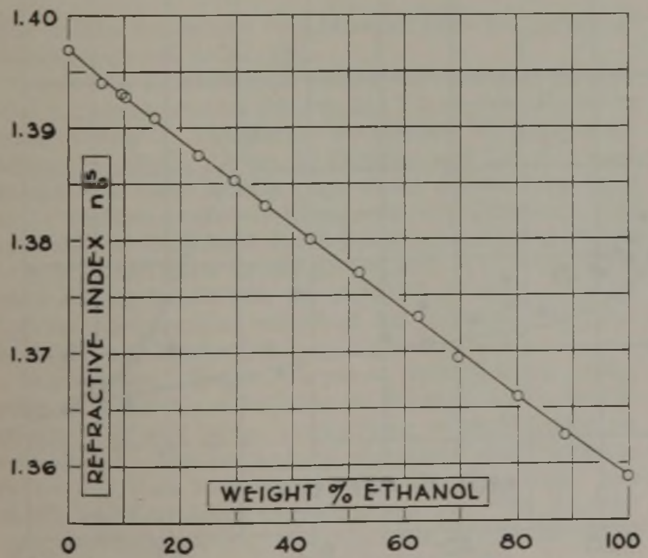

FIGURE 1. REFRACTIVE INDEX OF MIXTURES OF ETHANOL AND *n*-BUTANOL AT 25° C.

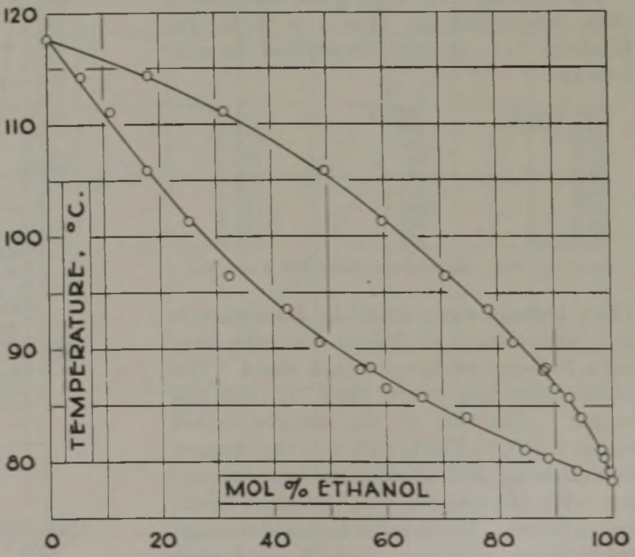

FIGURE 2. TEMPERATURE-COMPOSITION DIAGRAM FOR SYSTEM ETHANOL–*n*-BUTANOL AT 1 ATMOSPHERE

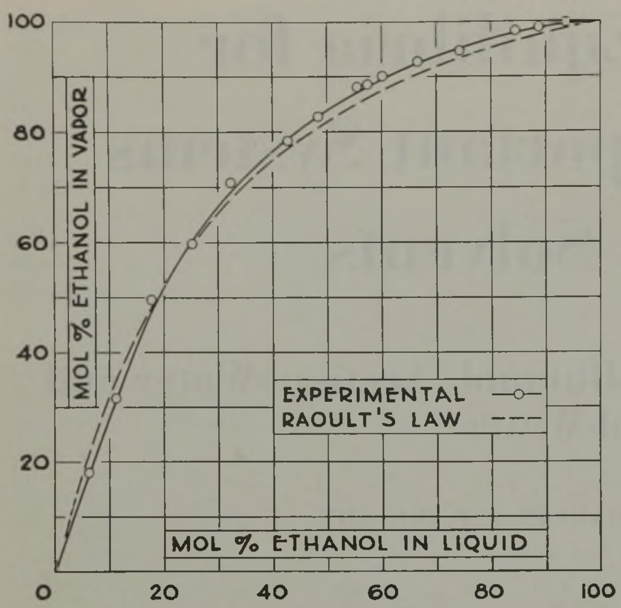

Figure 3. Vapor-Liquid Equilibria for System Ethanol-*n*-Butanol at 1 Atmosphere

Table I. Vapor-Liquid Equilibrium Data for the System Ethanol-*n*-Butanol

Run No.	Cor. Temp. at 760 Mm. Hg ° C.	° F.	Ethanol in Liquid Wt. %	Mole %	Ethanol in Vapor Wt. %	Mole %
1	79.1	174.4	90.3	93.8	99.6	99.7
13	80.3	176.5	83.0	88.7	98.0	98.7
2	81.0	177.8	77.2	84.5	96.9	98.2
3	83.3	181.0	63.8	73.8	96.0	97.6
14	83.9	183.0	64.3	74.3	91.4	94.6
16	85.7	186.1	55.5	66.6	88.6	92.7
4	86.4	187.5	48.4	60.1	84.9	90.0
15	88.3	190.9	45.7	57.4	82.7	88.5
5	88.1	190.5	43.7	55.5	82.1	88.1
6	90.6	195.0	36.9	48.8	75.0	82.8
7	93.5	200.3	31.7	42.7	69.3	78.4
8	96.4	205.6	22.9	32.3	60.3	70.8
9	101.3	215.3	17.3	25.2	48.1	59.7
10	105.9	222.5	12.0	17.8	38.0	49.6
11	111.1	232.0	7.3	11.3	22.3	31.6
12	114.3	237.9	4.0	6.2	12.2	18.1

The original vapor-liquid equilibrium data on the system isopropanol-water were determined by Lebo (*10*) who used simple batch distillation with an averaged liquid composition. Equipment designed from these data again did not operate at the reflux ratio and the overhead composition predicted from Lebo's data. It was thus decided to redetermine these data according to more recent technique. Miller and Bliss (*13*) determined a few points for this system while studying isopropanol-isopropyl ether mixtures. Schumacher and Hunt (*18*) also recently determined points for this system.

Purification of Materials

n-Butanol. The c. p. grade was used in these determinations. The A. S. T. M. distillation (*1*) of the unpurified sample follows:

First drop C.	238° F.	114.4°
10% over	239	115.0
20%	240	115.5
30%	241	116.1
40%	241.8	116.5
50%	242	116.6
90%	242	116.6
95%	242	116.6
End point	242	116.6

Recovery, 97%; corrected pressure, 760.4 mm. Hg.

The *n*-butanol was purified by fractionation in a glass column of 2.5-cm. diameter, having a 73.7-cm. packing of jack chain. The portion distilling below 116.7° C. was discarded. The rest of the sample boiled within 0.5° C. The sample was then shaken with Drierite and allowed to stand in contact with the reagent with frequent shaking for 3 days. It was refractionated through the column equipped with a calibrated Anschutz thermometer. The entire fraction distilled off at 117.8° C. under a corrected pressure of 759.4 mm. of mercury. Density and refractive index determinations of two samples gave the following results:

d_{25}^{25}	0.8081_5	0.8081_5
d_4^{25}	0.8056_7	0.8056_7
n_D^{25}	1.3970	1.3970

These values are in good agreement with those of Brunell, Crenshaw, and Tobin (*4*); Clarke, Robinson, and Smith (*7*).

Ethanol. The raw material used was 190-proof ethanol. This was dried by refluxing for 4 hours each with two batches

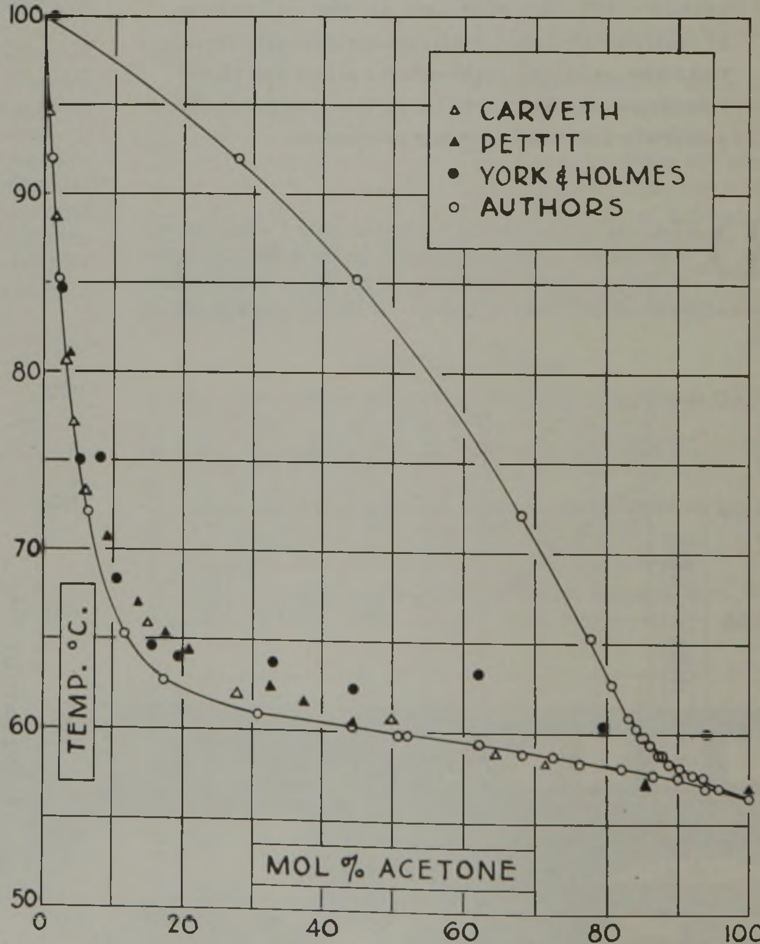

Figure 4. Temperature-Composition Diagram for System Acetone-Water at 1 Atmosphere

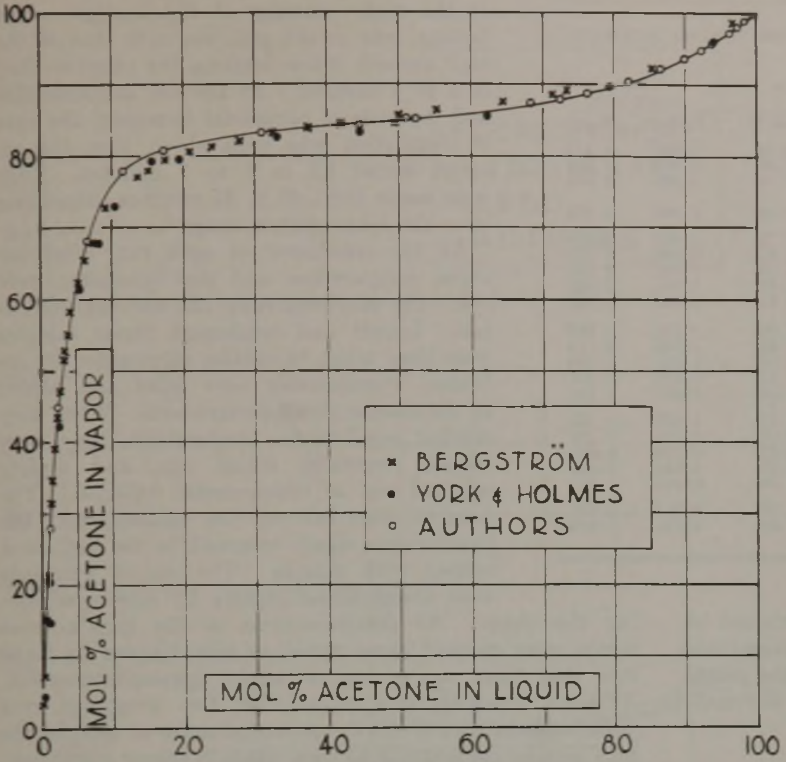

Figure 5. Vapor-Liquid Equilibria for System Acetone-Water at 1 Atmosphere

of quicklime, according to Fisher (*9*). The alcohol was distilled off from the lime into a previously dried receiver and was found to contain 0.37 per cent water by weight. Severe humidity conditions prevailing at the time prevented further dehydration. This alcohol was considered satisfactory for the purpose of this experiment and was stored in bottles equipped with tin-foil covered stoppers. The density and refractive index of the alcohol are tabulated below:

d_{25}^{25}	0.7886_3
d_4^{25}	0.7862_3
n_D^{25}	1.3589

The density conversions were obtained from the Bureau of Standards alcohol tables (*22*).

Acetone. Reagent-grade acetone was repeatedly agitated with anhydrous calcium chloride, and the mixture allowed to stand overnight. The acetone was decanted off and distilled through a column 2.5 cm. in diameter and 137 cm. long, packed with glass Raschig rings, under a reflux ratio of 2 to 1; the first portion distilling over was discarded. The remainder of the sample distilled at a constant temperature of 56.6° C. and had a specific gravity (d_{25}^{25}) of 0.7862_3. This value is in agreement with the experimental value of Perkin (*16*) and the computed value from the equation of Timmermans (*21*) and Squibb (*19*).

Isopropanol. The C. P. grade as received had a boiling point of 81.72° C. at 760 mm. of mercury, and a specific gravity (d_{15}^{20}) of 0.7888_8, corresponding to 98.86 weight per cent alcohol. This checked the analysis furnished with the sample and, since the remainder was reported as water this sample was not further purified before use. The gravities were determined at 20/15° C. in order to use the tables furnished by the Standard Alcohol Company (*20*).

Water. The water used in the equilibrium and analytical runs was double-distilled and freshly boiled.

Experimental Procedure

The well established method of Othmer (*14, 15*) was used for the determination of the equilibrium data in each of the systems studied. The original apparatus was modified to permit the use of external gas heating, and an auxiliary vent condenser was permanently sealed onto the vent. When running the ethanol-butanol system, a large drying tube filled with soda lime and anhydrous calcium chloride was attached to the vent line beyond the condenser. When running the acetone-water system, an additional long jacketed condenser was attached directly to the end of the small vent condenser on the still.

Refractive indices were determined on a Bausch & Lomb Abbe-type refractometer equipped with a microvernier and held at constant temperature by circulating water from the thermostat. Sodium flame illumination was provided by a shielded Bunsen burner and a mixture of sodium carbonate and borax. A metal shield covered the top and three sides of the instrument, and excluded stray white light from the room.

Specific gravities were determined by 25-ml. pycnometers equipped with thermometers and caps having no vent holes at the extremities. They were immersed in the constant-temperature bath for a sufficient time before each weighing to come to equilibrium temperature.

The System Ethanol-*n*-Butanol

A series of mixtures of the two alcohols were weighed out on the basis of an approximately 10-gram total sample and

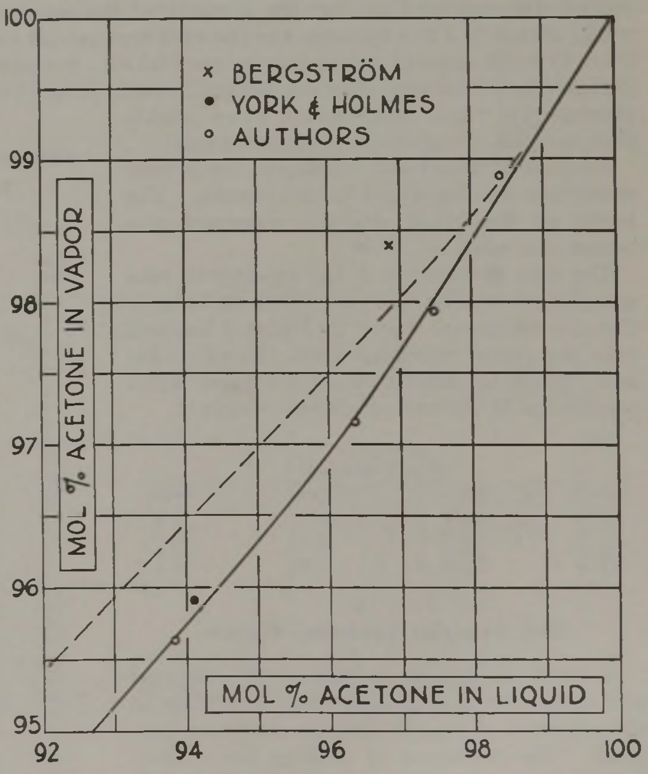

Figure 6. Magnified Section of Vapor-Liquid Equilibria for High Acetone Concentrations

TABLE II. VAPOR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM ACETONE-WATER

Run No.	Cor. Temp. at 760 Mm. Hg		Acetone in Liquid		Acetone in Vapor		Activity Coefficient	
	° C.	° F.	Wt. %	Mole %	Wt. %	Mole %	Acetone	Water
19	56.5	133.7	99.50	98.40	99.65	98.44	0.996	4.212
20	56.6	133.9	99.20	97.47	99.35	97.93	0.992	4.900
21	56.8	134.2	98.85	96.38	99.10	97.15	0.989	4.665
1	Determination lost							
22	57.0	134.6	98.00	93.83	98.60	95.62	0.990	4.278
10	57.7	135.9	97.50	92.37	98.30	94.72	0.973	4.034
2	57.6	135.7	96.70	90.04	97.90	93.53	0.988	3.777
3	57.7	135.9	95.40	86.55	97.40	92.08	1.011	3.349
4	58.1	136.7	93.65	82.08	96.80	90.37	1.031	2.998
5	58.3_5	136.9	91.20	76.29	96.20	88.71	1.083	2.632
6	58.7_5	137.8	89.50	72.57	95.90	87.90	1.110	2.393
7	58.8	137.9	87.40	68.29	98.65	87.23	1.168	2.174
8	59.4	138.9	84.20	62.32	95.20	86.03	1.237	1.946
9	59.8	139.8	78.60	52.28	94.85	85.12	1.434	1.607
11	59.8	139.8	77.00	50.96	94.90	85.24	1.477	1.551
12	60.3	140.5	72.00	44.39	94.50	84.21	1.653	1.429
13	60.9	141.6	58.20	30.85	94.00	83.09	2.297	1.197
14	62.7	144.9	40.20	17.27	93.10	80.73	3.744	1.050
15	65.3	149.4	29.75	11.64	91.85	77.77	4.930	1.008
16	72.1	161.8	18.00	6.38	87.30	68.09	6.362	1.014
17	85.2	185.3	6.80	2.21	72.40	44.88	8.253	0.981
18	92.0	197.6	3.60	1.15	55.50	27.91	8.216	0.978

the refractive indices of the mixtures were determined at 25° C. When a sufficient number of mixtures had been made to define the refractive index–composition curve, the points were plotted and a smooth curve drawn through the data. Figure 1 is a plot of the following data:

Weight % Ethanol	n_D^{25}	Weight % Ethanol	n_D^{25}	Weight % Ethanol	n_D^{25}
0.00	1.3970	23.19	1.3875	62.45	1.3731
5.96	1.3940	29.57	1.3853	69.61	1.3694
9.60	1.3930	35.06	1.3830	80.29	1.3660
10.14	1.3929	43.06	1.3800	88.78	1.3626
15.51	1.3909	51.91	1.3770	100.00	1.3589

Four hundred milliliters of a mixture of ethanol and butanol were introduced into the equilibrium still; the rate of boiling was regulated so that the contents of the receiver would change in 3 to 4 minutes, and the runs were carried on from 45 to 60 minutes before samples were taken. Samples of high ethanol concentration reached equilibrium, judged by constancy of vapor temperature, more quickly than samples of high butanol concentration.

Samples of liquid and condensed vapor were withdrawn simultaneously in small bottles. The bottle on the liquid side was immersed in a beaker of crushed ice.

The data obtained from the equilibrium runs are plotted in Figure 2 and listed in Table I. The x-y values are shown in Figure 3 together with the values computed from Raoult's ideal law. These theoretical values for vapor-liquid equilibrium at 760 mm. of mercury follow:

Mole % Ethanol			
Liquid	Vapor	Liquid	Vapor
94.7	98.8	25.2	59.6
71.2	92.2	15.1	43.0
52.8	83.9	6.7	22.7
37.9	73.3	2.84	10.5

The System Acetone-Water

A curve of specific gravities was computed and drawn on a large-scale plot according to the equation of Squibb (*19*) for analytical purposes. The technique of making the equilibrium runs and handling the samples was modified from the standard procedure because of the high volatility of the acetone. The boiling rate in the still was such that at the high acetone concentrations the receiver filled in 3 to 4 minutes. At the low concentration end, because of occasional bumping, the rate of distillation was reduced so that the receiver would fill in 6 to 7 minutes. Runs were made from 40 to 75 minutes, depending upon the concentration range.

At the conclusion of each run, after the vapor temperature and the barometer were read, the still was shut off and allowed to cool. Liquid and condensed vapor samples were then taken in bottles surrounded by ice baths. Pycnometers were filled and placed in the constant-temperature bath. When they reached equilibrium temperature, they were capped, carefully wiped dry, and rapidly weighed on a Chainomatic balance. The weights were left on the balance, and the pycnometers again returned to the bath and refilled with sample. The second weighings were accomplished rapidly by merely adjusting the chain. All determinations in the high acetone region were checked three times in this manner to make sure that there was no loss of weight due to evaporation. At lower concentrations of acetone, two weighings were found sufficient for a check. A second series of runs on the high acetone concentrations were made to ensure a sufficient number of points to define clearly the equilibrium curve in the region where previous data have been questionable.

The data for the system are reported in Table II. The boiling point–composition curves are plotted in Figure 4 together with the data of Carveth (*6*), Pettit (*17*), and the recent data of York and Holmes (*23*) for comparison. Figure 5 is a plot of the equilibrium data showing a comparison with the data of Bergström (*2*) and those of York and Holmes. Figure 6 is an enlarged section of the upper portion of the equilibrium diagram, the dotted line showing the previously accepted curve of Bergström and the solid line, the data of this paper. This difference in the position of the curve accounts for the discrepancy between the older data and

TABLE III. VAPOR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM ISOPROPANOL-WATER

Run No.	Cor. Temp. at 760 Mm. Hg		Isopropanol in Liquid		Isopropanol in Vapor		Activity Coefficient	
	° C.	° F.	Wt. %	Mole %	Wt. %	Mole %	Alcohol	Water
1	81.21	178.2	97.85	93.19	96.82	90.11	1.012	2.963
2	81.01	177.8	97.29	91.53	96.07	88.01	1.014	2.912
3	80.75	177.4	96.33	88.72	94.97	85.00	1.022	2.741
4	80.51	176.9	95.05	85.20	93.54	81.26	1.027	2.657
5	80.30	176.5	93.42	81.00	91.77	76.98	1.032	2.564
6	80.14	176.3	91.77	77.02	90.47	74.01	1.050	2.409
7	80.07	176.1	90.15	73.33	89.28	71.42	1.067	2.289
8	80.05	176.1	88.48	69.71	88.27	69.31	1.123	2.166
9	80.03	176.0	88.15	69.05	88.02	68.79	1.093	2.157
27	80.04	176.0	87.90	68.57	87.74	68.24	1.091	2.163
10	80.05	176.1	87.82	68.38	87.86	68.46	1.098	2.132
28	80.16	176.3	87.70	68.13	87.70	68.13	1.093	2.134
11	80.04	176.1	86.08	64.96	86.91	66.59	1.122	2.041
12	80.14	176.3	82.39	58.38	85.34	63.58	1.190	1.864
13	80.44	176.7	73.95	45.97	82.98	59.39	1.395	1.582
14	80.77	177.4	62.30	33.14	81.27	56.54	1.820	1.350
15	Determination lost							
26	81.11	178.0	51.15	23.87	80.67	55.59	2.448	1.195
25	81.19	178.2	45.24	19.86	79.93	54.44	2.873	1.160
24	81.39	178.4	39.35	16.29	78.99	52.98	3.380	1.137
22	81.41	178.5	31.90	12.32	79.50	53.78	4.531	1.067
21	82.63	180.9	23.50	8.43	77.10	50.24	5.873	1.049
20	83.80	182.8	14.59	4.88	74.42	46.60	8.926	1.033
18	89.04	192.3	8.01	2.54	63.18	33.99	10.12	1.018
19	90.80	195.4	6.50	2.04	57.96	23.08	8.000	1.102
23	93.19	199.7	4.38	1.36	49.00	22.44	10.54	1.008
17	95.30	203.5	2.72	0.83	36.55	14.73	10.54	1.020
16	98.87	210.0	0.52	0.16	11.16	3.64	11.68	1.007

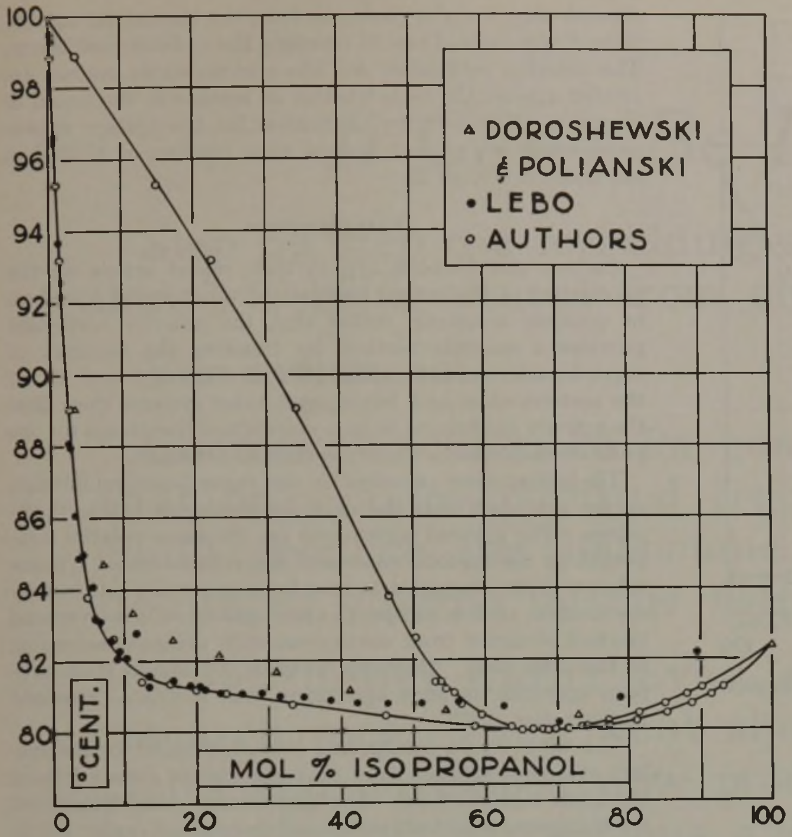

Figure 7. Temperature-Composition Diagram for System Isopropanol-Water at 1 Atmosphere

actual distillation column performance at high acetone product compositions.

The System Isopropanol-Water

Equilibrium runs for this system were made in the same manner as for the ethanol-butanol system, starting with alcohol-rich mixtures. Gravities of the vapor and liquid samples were measured in pycnometers at 20/15° C., and the percentage composition interpolated from the isopropyl alcohol–water gravity tables published by the Standard Alcohol Company (*20*). Small pieces of copper wire were introduced into the still during the runs to destroy any peroxides that might be formed from the presence of minute amounts of isopropyl ether. No tarnishing effects on the wires were noted during the entire series of runs. The data are tabulated in Table III.

Still residues were fractionated through a 100-plate Bragg column (*3*) at nearly total reflux. The distillate was collected at a constant temperature of 80.3° C. under 760 mm. absolute pressure. This fraction was again run through the column at nearly total reflux, and the distillate collected until a sufficient sample was obtained to make a run in the equilibrium still. The temperature remained constant at 80.16° C. under 760 mm. absolute pressure. The equilibrium run gave a liquid and vapor at the above temperature and pressure, both having a composition of 87.7 weight per cent alcohol. Various values reported in the literature are:

Author	Boiling Point, ° C.	Wt. % Alcohol	Mole % Alcohol
Lecat (*11*)	80.37	87.85	68.54
Young (*24*)	80.4	87.90	68.56
Lebo (*10*)	80.4	87.7	68.13
Miller and Bliss (*13*)	80.1	87.9	68.60
Schumacher and Hunt (*18*)	80.3	87.4	67.8
Authors	80.16	87.7	68.13

The temperature-composition plot of the data are shown in Figure 7 and compared with the data of Doroshewski and Polianski (*8*) and Lebo. The vapor-liquid equilibrium curve is plotted in Figure 8. The points of Miller and Bliss, Lebo, and Schumacher and Hunt were added for comparison.

Activity Coefficients

The activity coefficients, γ, were computed from the equation

$$\gamma = Py/P_0x$$

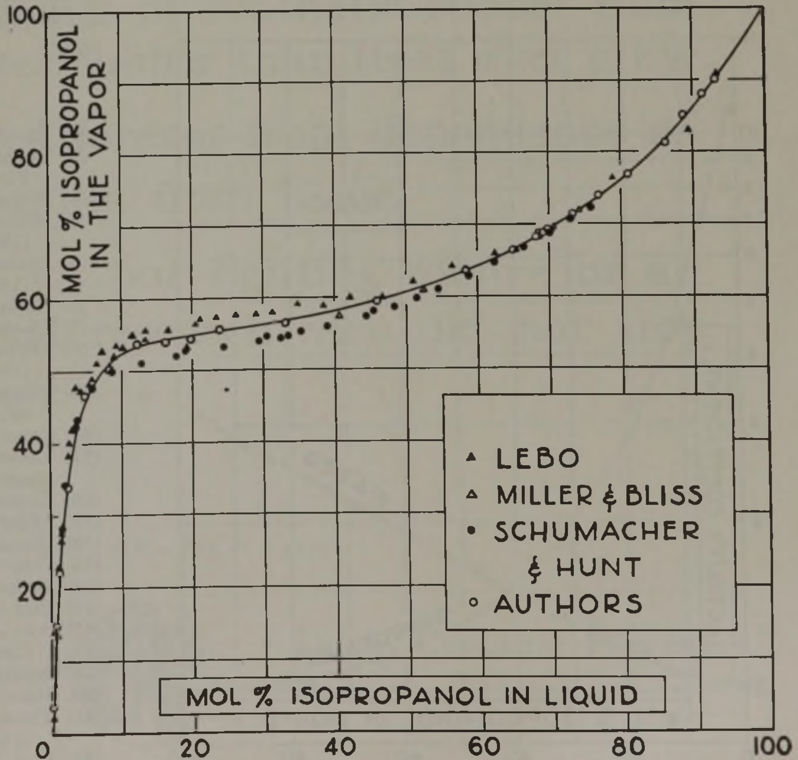

Figure 8. Vapor-Liquid Equilibria for System Isopropanol-Water at 1 Atmosphere

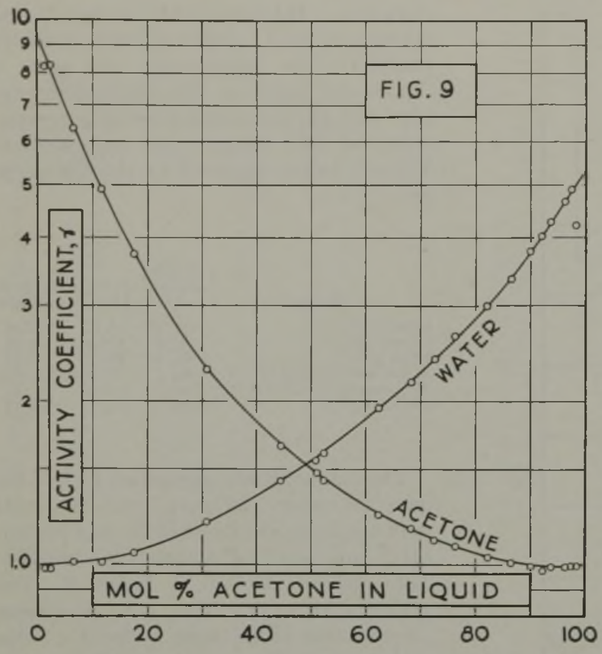

Figure 9. Activity Coefficients for Binary System Acetone-Water at 1 Atmosphere

where P = total pressure on system
P_0 = vapor pressure of given component
y = mole fraction of component in vapor
x = mole fraction of component in liquid

for the acetone-water and the isopropanol-water systems, and are listed in Tables II and III, respectively. The vapor pressures for the pure components were taken from International Critical Tables. Since the ethanol-butanol system showed only a slight deviation from the theoretical equilibrium, it was decided not to compute the activity coefficients. The activity coefficients for the acetone-water system are plotted against the mole fraction of acetone in the liquid in Figure 9. The activity coefficients for the system isopropanol-water are plotted against mole fraction of alcohol in the liquid in Figure 10.

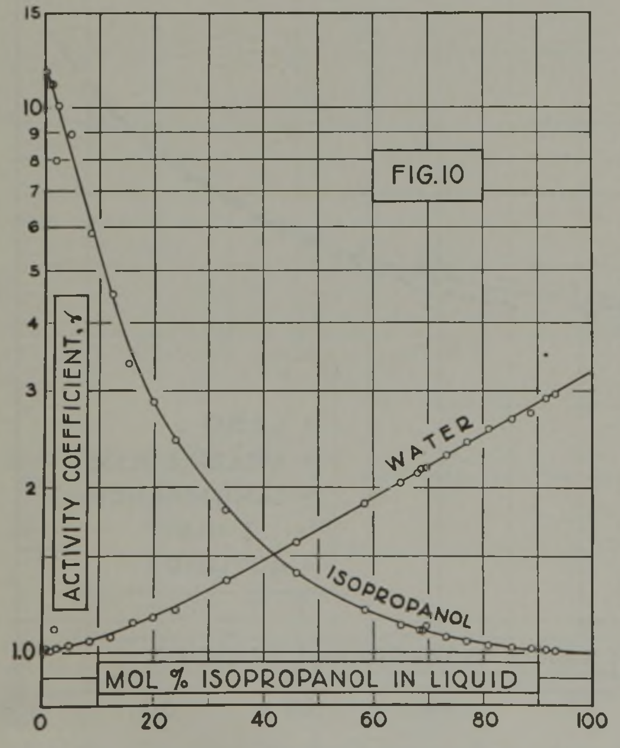

Figure 10. Activity Coefficients for Binary System Isopropanol-Water at 1 Atmosphere

Conclusions

Carlson and Colburn (*5*), in their recent article on the application of theoretical methods to vapor-liquid equilibria in nonideal solutions, stated that the activity coefficient provides a sensitive method for checking the accuracy of vapor-liquid equilibria. The plots in Figures 9 and 10 for the acetone-water and isopropanol-water systems show that the activity coefficients lie on a well defined line except for one point on each system which is a marked deviation.

The boiling point-composition and vapor-liquid equilibrium curves also show that the data are consistent within themselves. The lowered enrichment for the more volatile component in the acetone-water and isopropanol-water systems relative to the original data may be considered a satisfactory explanation of the subspecification quality of the overhead product obtained from continuous stills designed according to the older data. Recently designed continuous stills have been operating in good agreement with the data presented in this paper.

The vapor-liquid equilibrium data determined for the system ethanol–*n*-butanol show that this system closely follows the ideal solution laws. The equilibrium data determined for the systems acetone-water and isopropanol-water are in good agreement with those of recent investigators and indicate that the original data on these two systems did not represent the true values.

Acknowledgment

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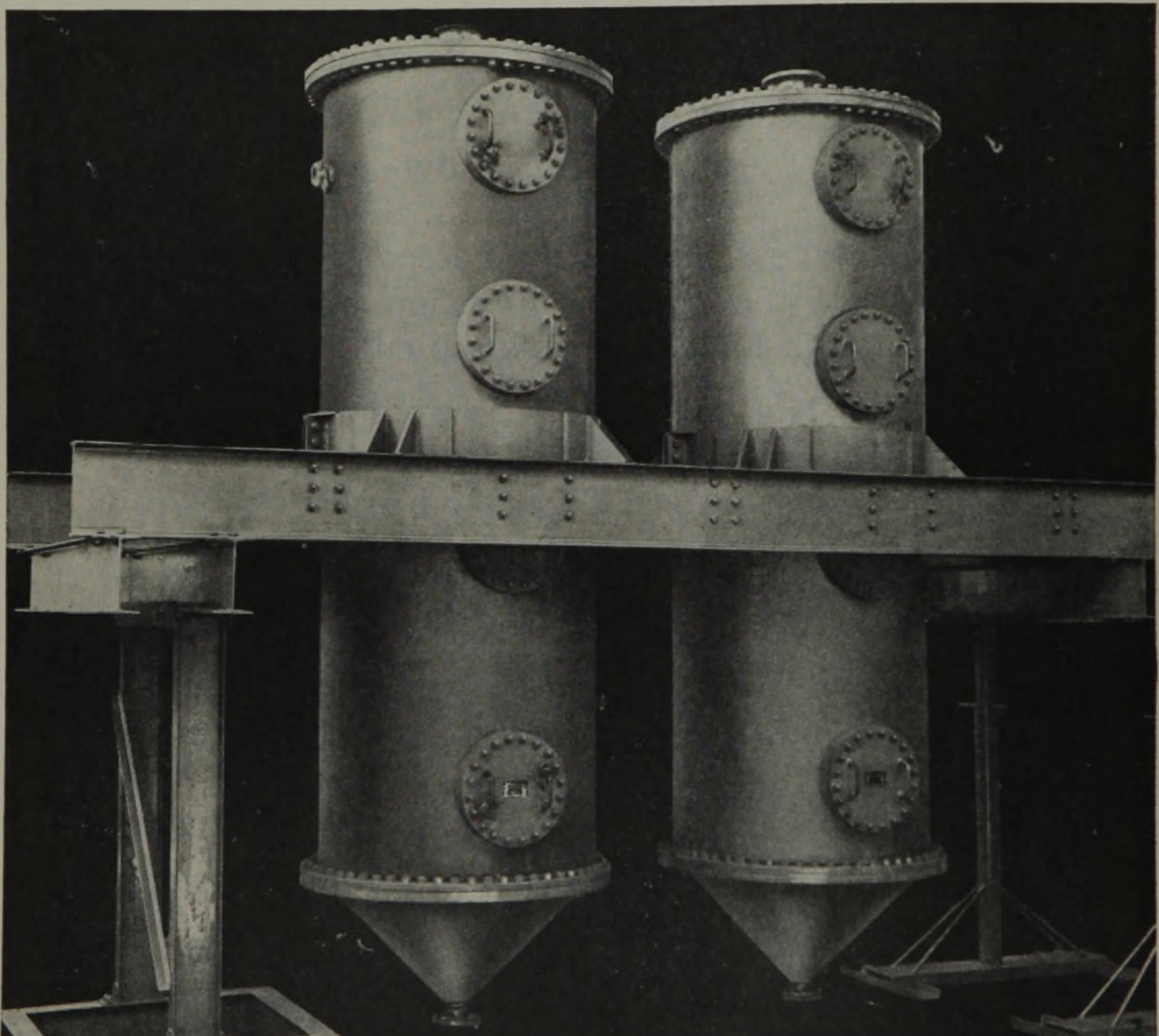
AT THE FRONT..



..AT HOME

TOUGH COPPER ALLOYS

are serving dependably, economically

At the front . . . and in innumerable industrial applications . . . equipment made of Everdur* Metal and other Anaconda Copper Alloys is measuring up to the performance standards demanded by 24-hour-a-day schedules. To give the best possible assistance to those engaged in the war effort, we offer a three-fold service:

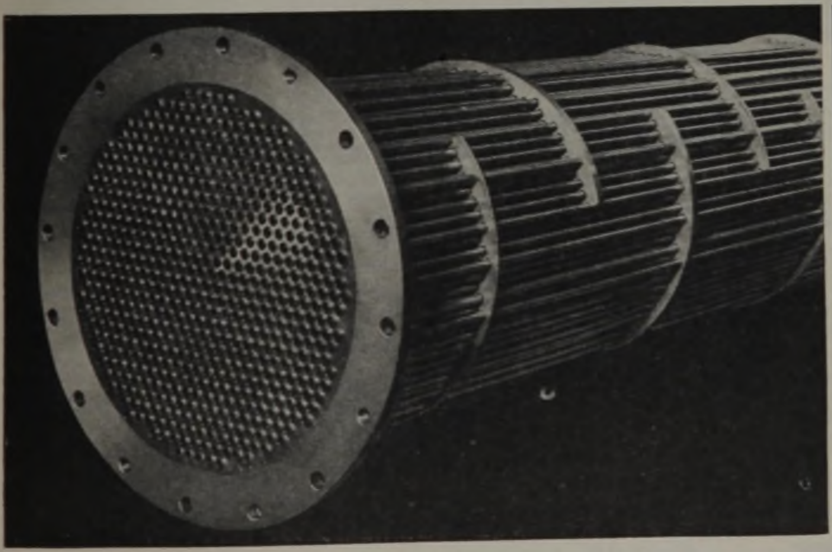
1. Special Engineering Counsel—Our metallurgists and engineers are prepared to cooperate in finding the correct solution to special metal problems involving copper, brass and Everdur.

2. A Laboratory You Can Call Your Own—The technical information acquired through long years of metallurgical experience—and the laboratories responsible for it—are at your service in fitting the right metal to your need.

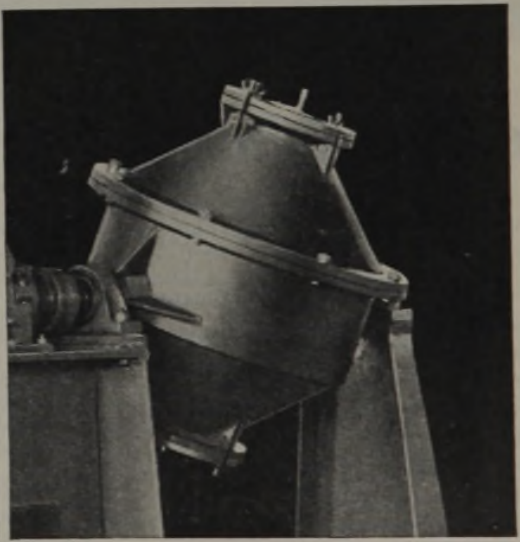
3. Publications From Our Technical Department to Yours—Available to you without cost are a number of up-to-the-minute publications on copper and copper alloys packed with useful technical information which your engineers will find extremely helpful at this critical time. 42116

*Reg. U.S. Pat. Off.

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



Ross BCP bundle with shell pipe (not shown) of Anaconda Seamless Copper Tube. Construction includes tubes and tube sheets of copper-nickel alloy, baffle and support plates of brass. Made by Ross Heater & Mfg. Co., Inc.



Everdur cone blender for mixing tracer bullet powder—made by the H. K. Porter Company, Inc. Everdur is a high strength, corrosion-resistant metal—ideally suited to many process equipment applications.

Copper & Copper Alloys

MADE BY THE AMERICAN BRASS COMPANY

Slow downs may mean . . . "Bare Hands vs. Bayonets"

IT TAKES MORE than courage alone or soldiers to win battles today.

It takes specialized fighting equipment . . as much as our vast industries can pro-luce, working every last hour on the clock. or we are sending millions of men against mechanized foe, and our men must have ighting tools to stand a fighting chance. Nowadays, a *poorly* equipped soldier would tand little more chance than a man with are hands against bayonets.

And so time . . . production time . . . has ecome the most vital element in the war ight now. We simply cannot afford to sab-tage war effort by allowing a slow down here that slow down can be prevented.

There is one type of industrial slow down hat *can* be prevented . . . the interruption caused by failure of the valves that control vital power and production fluids in your plant. The way to prevent this type of slow down is to *avoid valve trouble before it starts!*

Keep your valves operating efficiently, *continuously*, by inspecting them *regularly*. Renew worn parts before they cause destruction of the whole valve. And when valves must be replaced, have the new valves selected by experts, installed by experienced men. Above all, train *new* workers to operate and maintain valves properly.

Jenkins Engineers are ready to assist any management in developing a practical program of valve conservation.

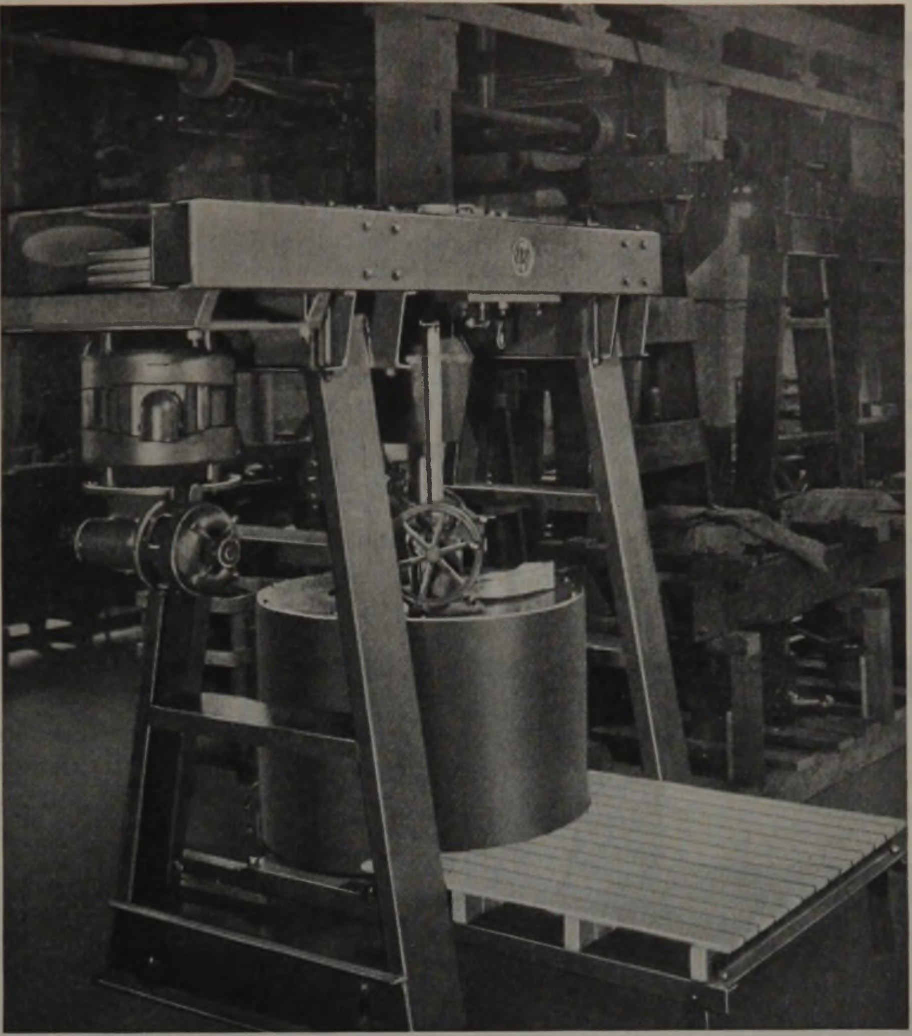
Army-Navy "E" Pennant, awarded to Jenkins Bros. for high achievement in the production of war equipment.

Jenkins Bros., 80 White Street, New York, Bridgeport, Atlanta, Boston, Philadelphia, Chicago. Jenkins Bros., Limited, Montreal, Canada; London, England.

Reprints of this advertisement are available for use in morale-building work.

JENKINS VALVES

For every industrial, engineering, marine and power plant service . . . in Bronze, Iron, Cast Steel and Corrosion-Resisting Alloys . . . 125 to 600 lbs. pressure.



More Lebensraum for Jones & Co., U. S. A.

More *lebensraum* . . . the "living space" which the Germans sought to take away from the world by brute force . . . will be available for your industry after the war is won — through the intelligent application of centrifugal force to extraction, filtration, dehydration, precipitation, impregnation or coating processes.

If you are now using unwieldly drying equipment, space-consuming tanks, or slow, costly squeeze rolls, vacuum boxes or ovens . . . A T & M may be able to help you cut down the amount of space required, lower your production costs, speed your processing, increase your sales, in the peacetime future.

For instance, one manufacturer converting for war, found that limited headroom prevented centrifugals larger than 36″. There was no additional floor space available, yet expansion was imperative. A T & M engineers, studying plant layout, installed five 36″ machines which, by quicker acceleration of motor drive, *doubled production!*

Other firms have even found that new markets can be tapped by replacing a slower, more costly method with AT&M-engineered centrifugal force.

Just as you can centrifuge anything that can be extracted by a filter . . . and many substances too fine for a filter to handle . . . *faster, in less space* by standard A T & M machines — so also in solving exceptional process problems, A T & M engineers can devise special machines to simplify your operations, combine them, often eliminate certain of them altogether.

A T & M centrifugals are furnished in all machinable metals and coatings, link-suspended, suspended or base-bearing. And A T & M engineers stand ready today to help you plan tomorrow's more profitable operations, as national needs permit. Write us. We keep strict confidence. American Tool and Machine Company, 1421 Hyde Park Avenue, Boston, — or 30C Church Street, New York, N. Y.

ONLY EFFICIENT INDUSTRIES CAN "WIN THE PEACE"

Plan now to improve your extraction, dehydration, filtration, precipitation, impregnation or coating processes . . . with A T & M engineered centrifugals.

A T *and* M

A T & M CENTRIFUGALS SAVE TIME AND SPACE

Slow downs may mean . . . "Bare Hands vs. Bayonets"

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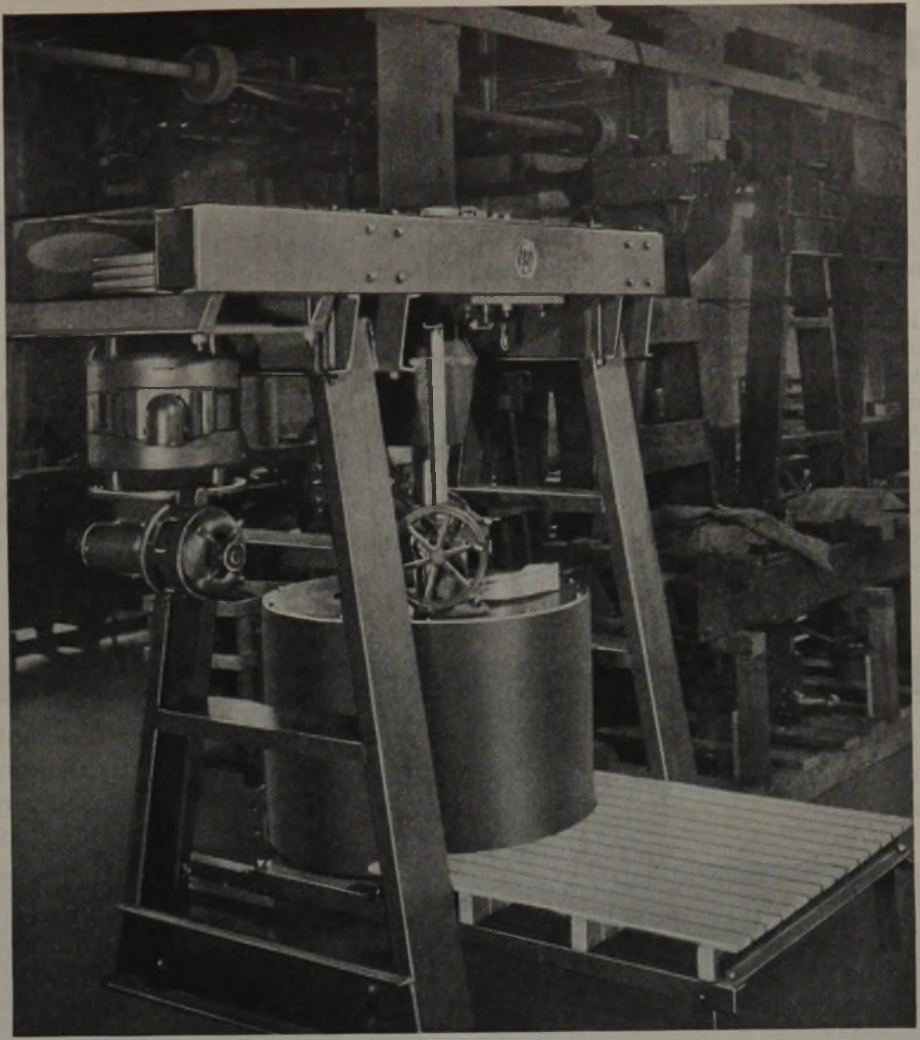

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ONLY EFFICIENT INDUSTRIES CAN "WIN THE PEACE"

Plan now to improve your extraction, dehydration, filtration, precipitation, impregnation or coating processes . . . with A T & M engineered centrifugals.

A T and M

A T & M CENTRIFUGALS SAVE TIME AND SPACE

How Calgon helps speed America's war effort:

5. IN THE WOOLEN MILL

HARD water is the cause of production slow-downs in a variety of industries too numerous to mention. If you have a water problem, you may get a "liftable" idea from how Calgon-treated water speeds up processes in the woolen mills.

The necessity for clothing millions of fighting men has placed a tremendous burden on the woolen mills. For years they have been troubled with lime salts, in the wool or in the water, causing insoluble, sticky soaps which resist good dyeing and finishing. This meant rehandling of faulty goods and a general slow-up of production.

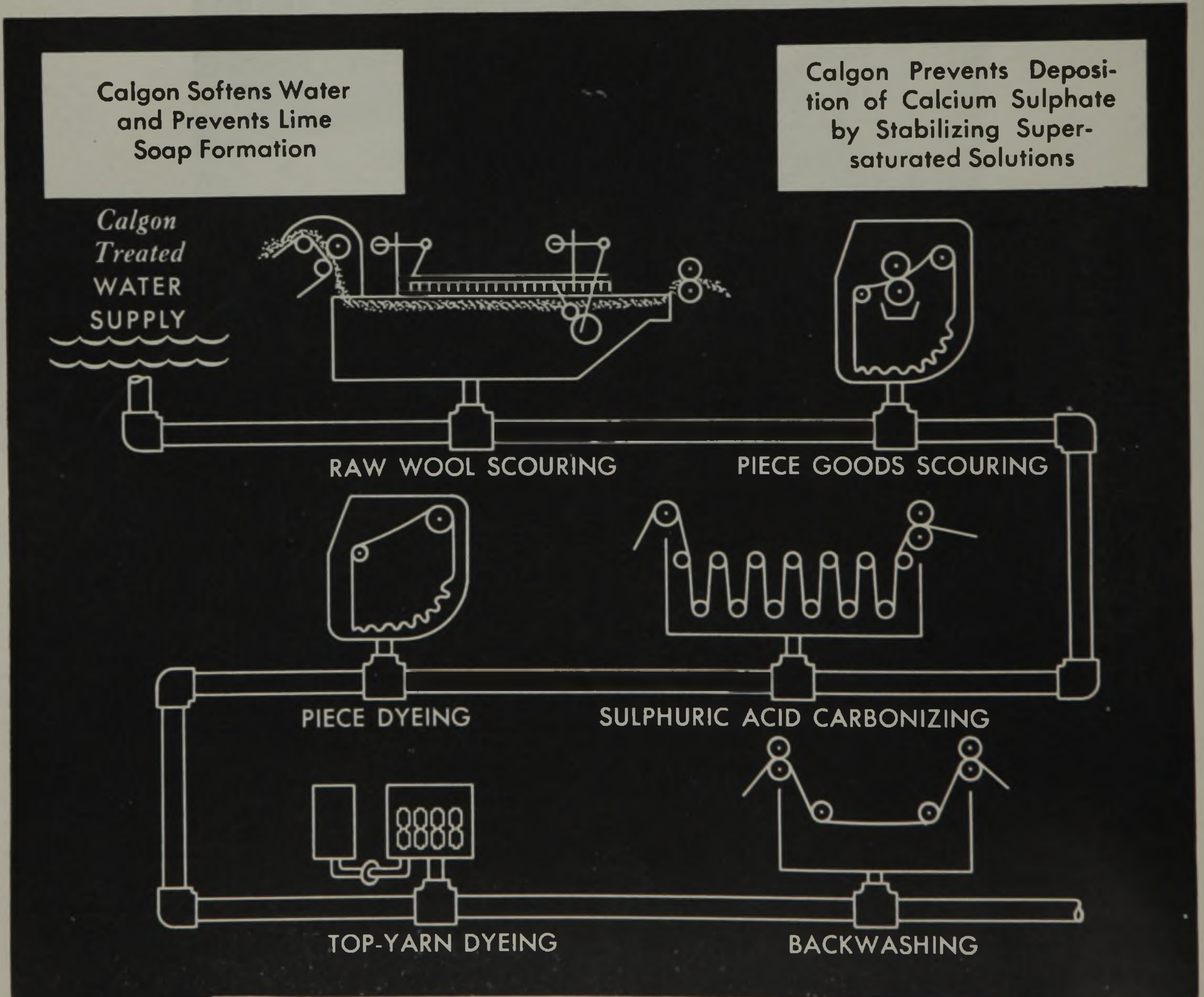
Today, woolen mills use Calgon to obtain water of zero hardness which stops the formation of lime-soap film. Raw wool and fabrics are washed free from soap deposits with the result that dyeing and finishing are greatly improved. Rejects are few.

Calgon has other advantages, too. Used in very small quantities in the carbonizing bath, it prevents the precipitation of calcium sulphate, permitting great savings in sulphuric acid.

Calgon also reduces corrosion in iron pipe lines to such an extent that iron stains from this cause are practically eliminated. What's more, colors come out brighter and less bleach chemicals are needed. Only 2-10 ppm. of Calgon are needed for this job.

No doubt you have a process where Calgon can improve operations by improving water. Tell us your problem and we'll 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.*


Calgon Softens Water and Prevents Lime Soap Formation

Calgon Prevents Deposition of Calcium Sulphate by Stabilizing Supersaturated Solutions

HAGAN
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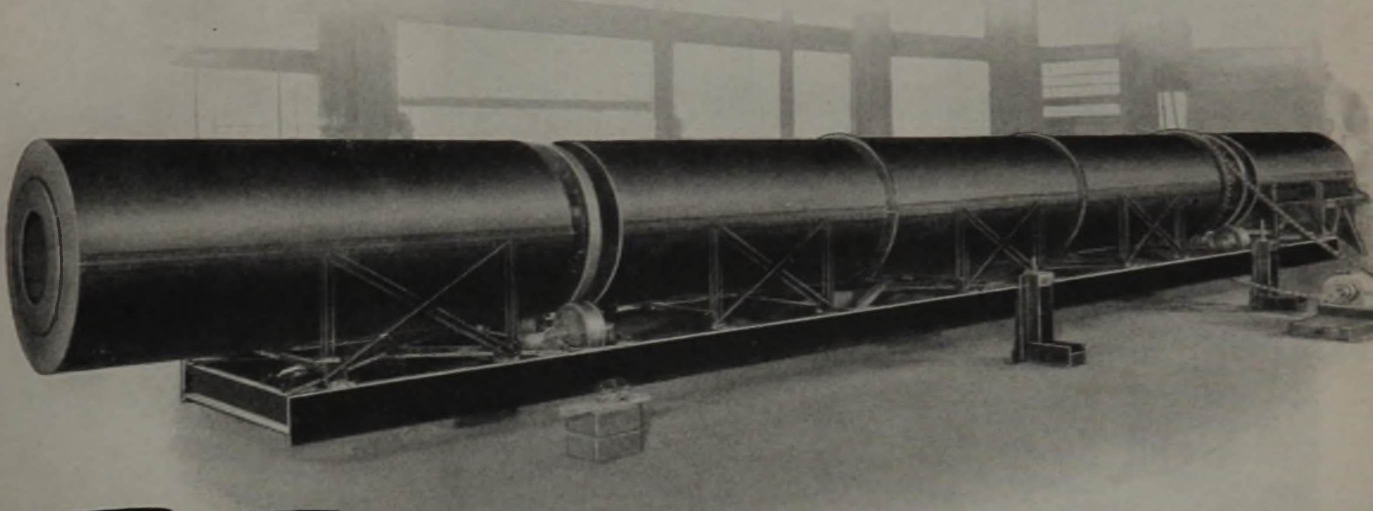
calgon, inc.

A SUBSIDIARY OF
HAGAN CORPORATION

HAGAN BUILDING
PITTSBURGH PA.

ROTARY COOLERS



Two Types for different requirements

● One type of Bartlett-Snow Rotary Cooler is used in lowering the temperature of glass pellets, and other hot materials, from 1800° F. to 200° F. The material is fed in one end, and rolled gently in the continuous tube pitched slightly to the horizontal. It works its way slowly from one water jacketed cooling section to another, and is finally discharged, cooled, polished, and unmarred to command highest market prices. These coolers—see illustration above—are moderately priced, highly efficient and require little power.

The other type processes crystalline salts such as $(NH_4)_2SO_4$; — NH_4NO_3; — NH_4CL; — $NaNO_3$; — $MgSO_4$—and other materials that tend to cake and lump in cooling—keeps them free-flowing, because they lose their tendency to cake, when they are cooled while being agitated. These coolers are fitted with flights tha lift the material up and cascade it downward throug a cooling air stream in a most efficient manner—an imparts extra drying too, since an appreciable amoun of the heat loss is absorbed as latent heat of evaporatio

Our recently issued Bulletin No. 89 describes Bar lett-Snow coolers, and dryers, kilns, calciners, aut claves and other heat engineering equipment in deta —discusses the fundamental principles involved—an contains much technical data of interest to every e gineer and operating man . . . Send for a copy toda

THE C. O. BARTLETT & SNOW COMPAN

6207 Harvard Avenue Cleveland, Ohi

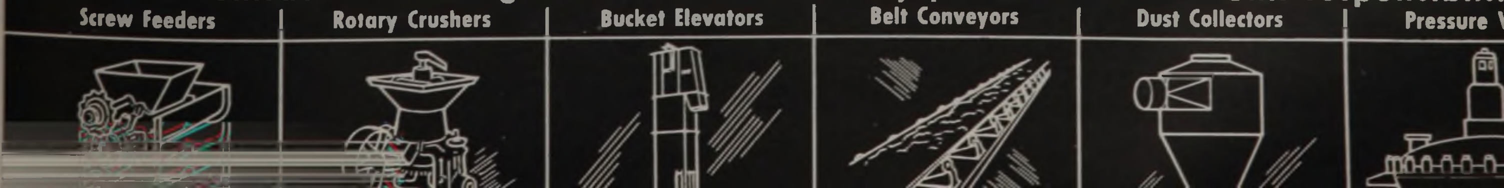
Engineering and Sales Representatives in the Principal Cities

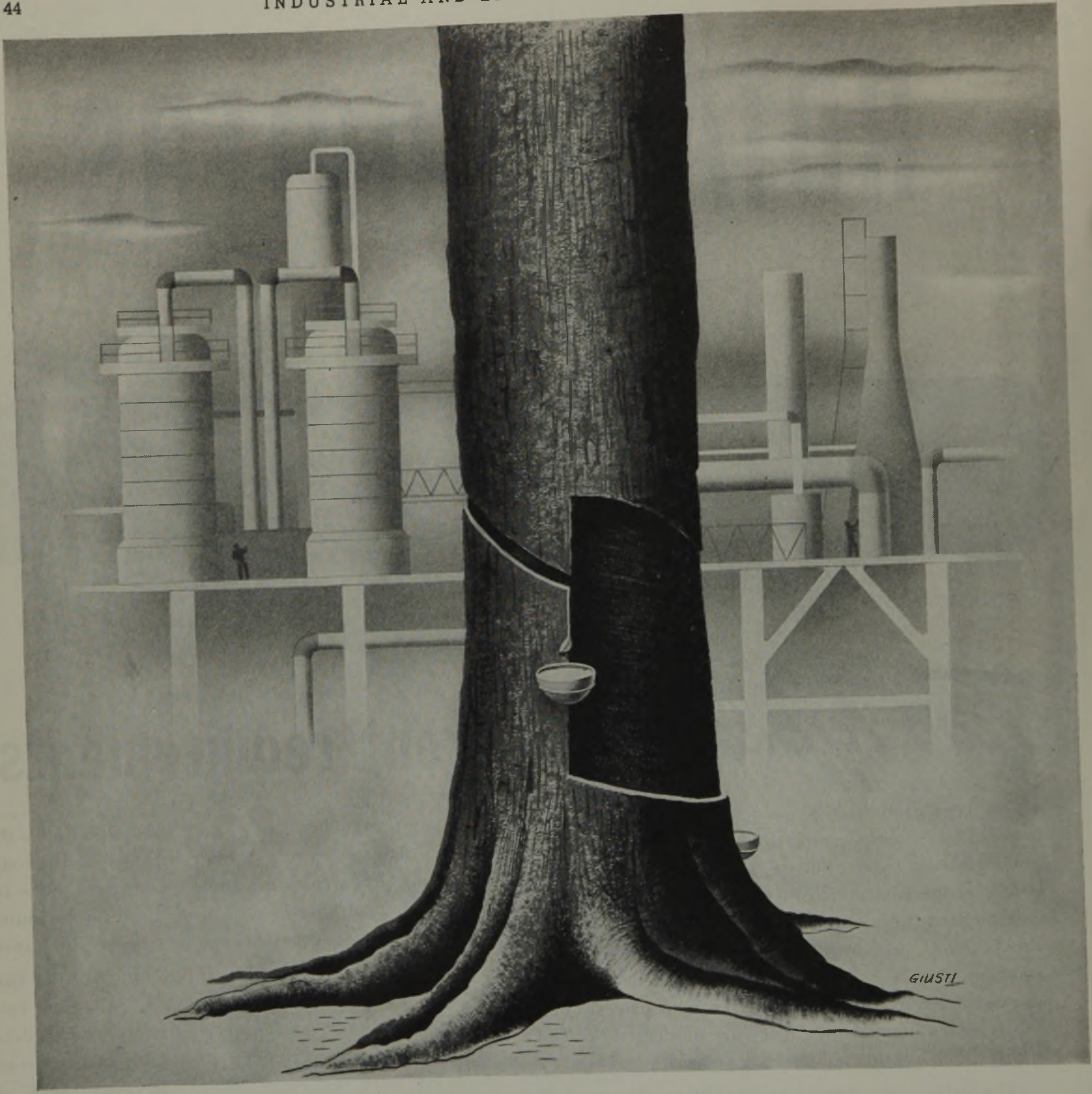
BARTLETT-SNOW

DRYERS • CALCINERS • COOLERS • KILNS

Also complete materials handling facilities to meet any requirement

One contract • One guarantee of satisfactory performance • Unit responsibilit

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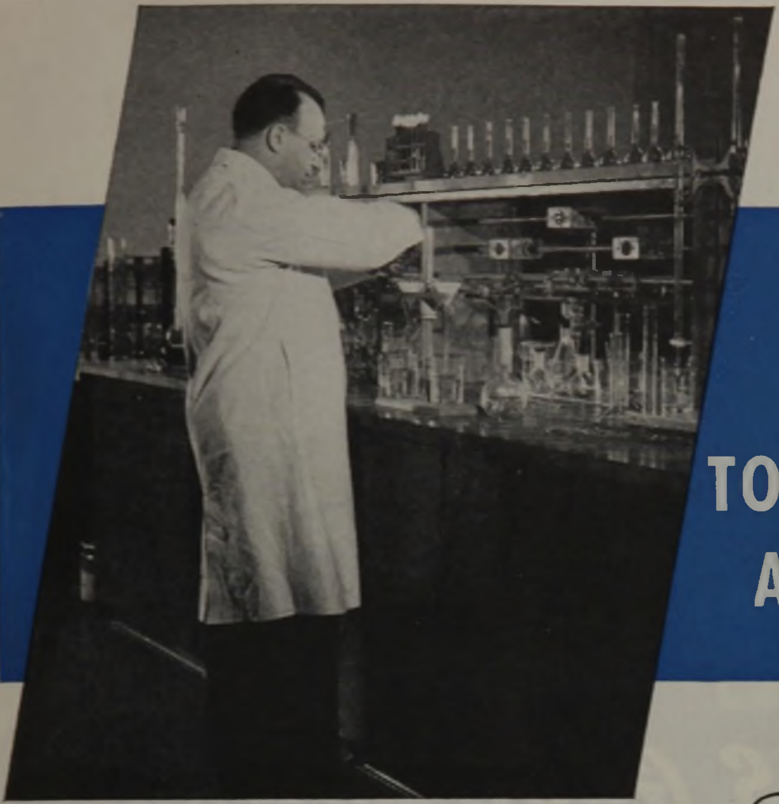
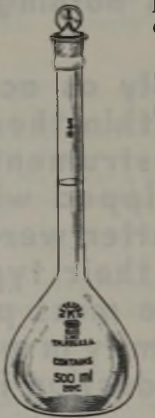
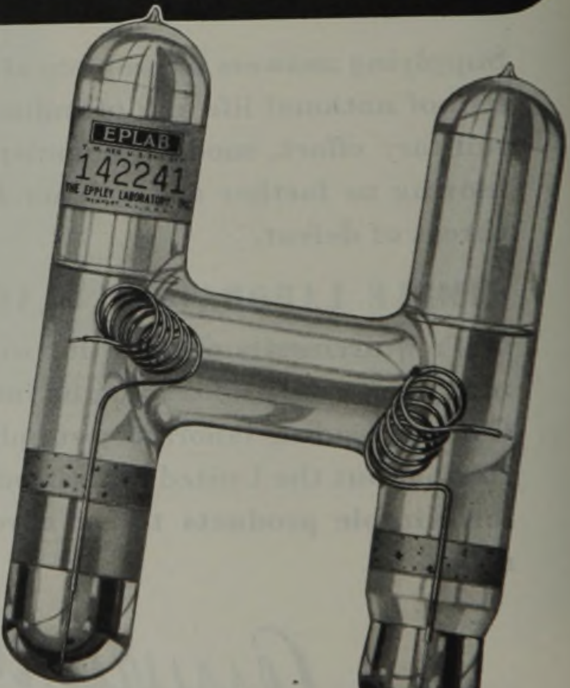





EPLAB
142241
THE EPPLEY LABORATORY, INC.

2-CYCLE *DOUBLES* NUMBER OF POWER STROKES

CLARK 6-Cylinder 600
H.P. "Super-2-Cycle"
Angle Compressor

Every Down Stroke a Power Stroke

The 2-cycle engine was developed to eliminate what was known as the "waste" stroke in 4-cycle operation. In the 2-cycle engine, instead of only half of the piston's down-strokes being power strokes, every down-stroke is a power stroke!

In the perfected CLARK Super-2-Cycle Engine this has resulted in power output also being actually doubled, as compared with the 4-cycle engine of equivalent size and displacement.

In addition to doubled power, the 2-cycle principle as perfected in CLARK "Angle" Compressors, offers these basic advantages:

1. GREATER SIMPLICITY — No intake or exhaust valves.
2. GREATER FUEL ECONOMY—due to Clark patented Fuel Injection.
3. LESS WEAR—as the power is produced with half the number of power cylinders.
4. SMOOTHER OPERATION.
5. FEWER MAN HOURS — due to simple design, few parts, and ease of servicing vertical cylinders.
6. LOWER OIL CONSUMPTION.
7. LOWER INSTALLATION COST—due to shipment assembled, small foundations, small buildings.

These points, explaining the leadership of the CLARK "Angle", merit your thorough investigation. Our engineers are at your service.

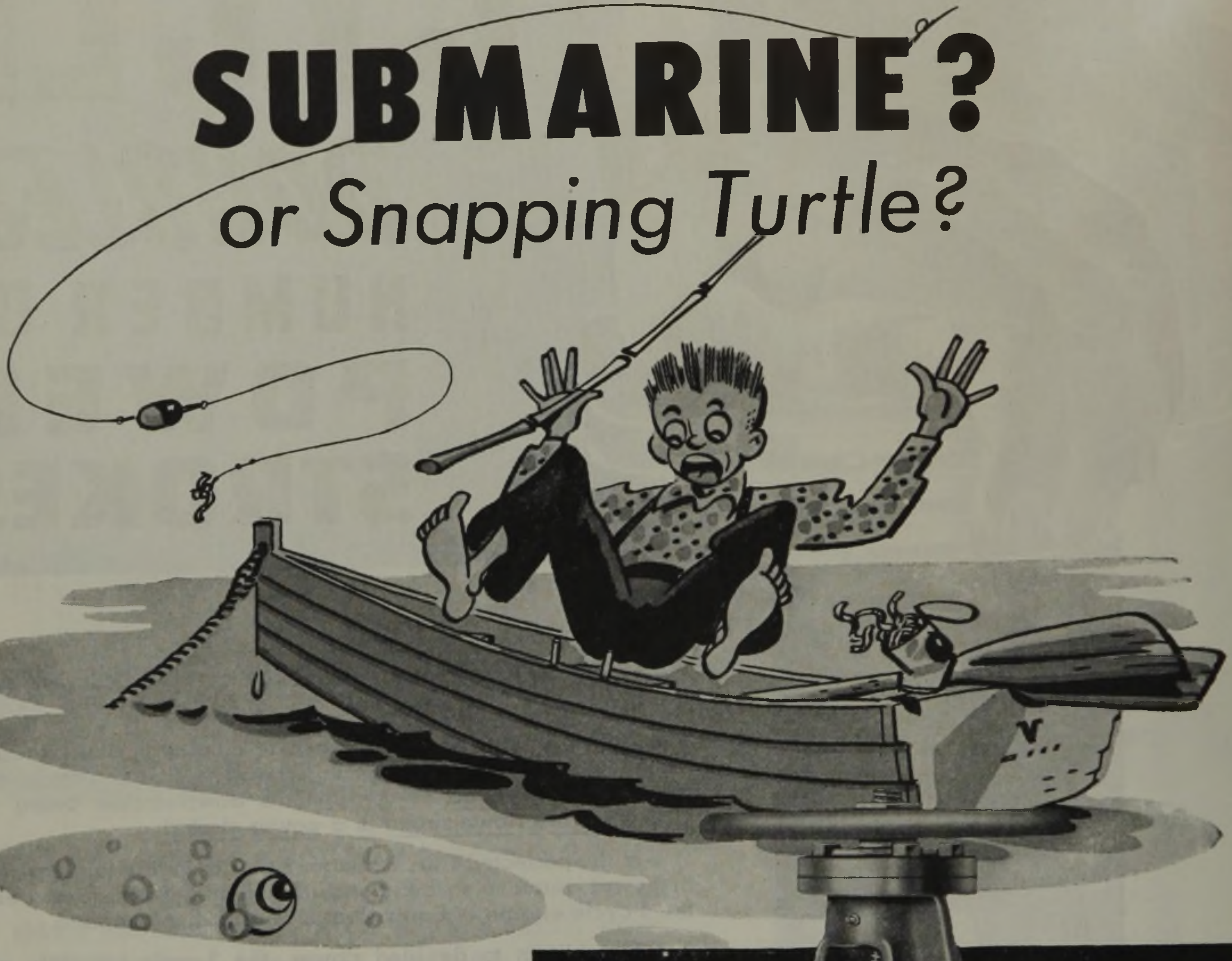
CLARK BROS. CO., INC. . . . . .OLEAN, NEW YORK, U. S. A.

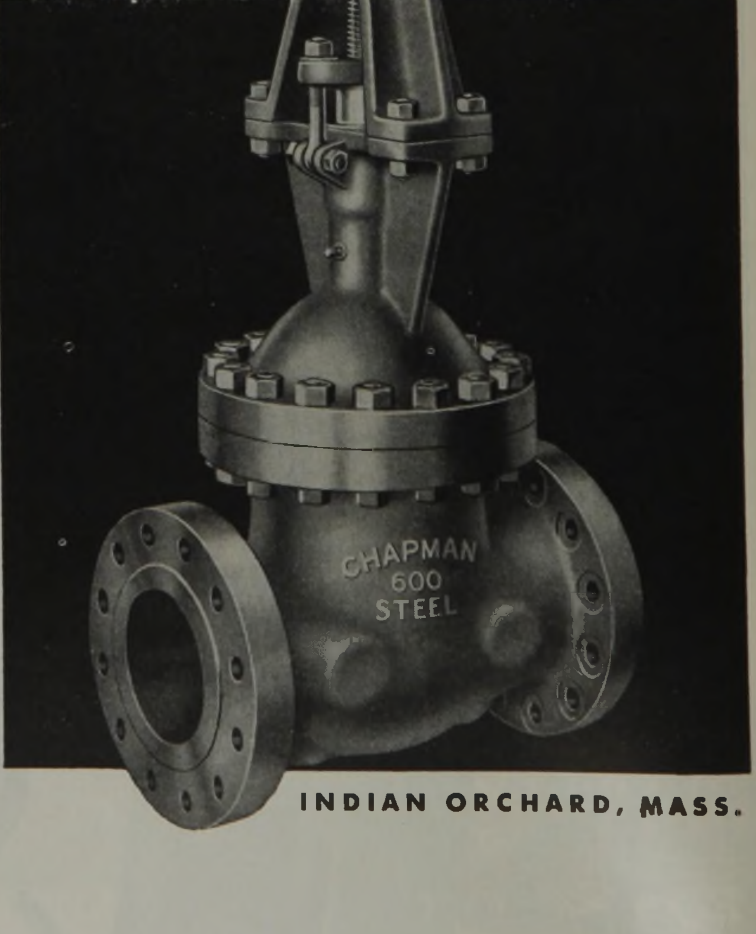
Export Offices: 30 Rockefeller Plaza, New York. Domestic Sales Offices and Warehouses: Tulsa, Okla.; Houston, Texas; Chicago, Ill. (122 S. Michigan Ave.); Boston, Mass. (131 Clarendon St.); Huntington Park, Calif. (5715 Bicket St.) Foreign Offices: 72 Turnmill St., E. C. 1, London; Avda Roque Saenz Pena 832, Buenos Aires.

Affiliated Companies: Dresser Mfg. Co., Bradford Pa.; Pacific Pump Works, Huntington Park, Calif.; Bryant Heater Co., Cleveland, Ohio.

CLARK

Super-2-Cycl

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STEEL


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Thanks A Million!
ARMY
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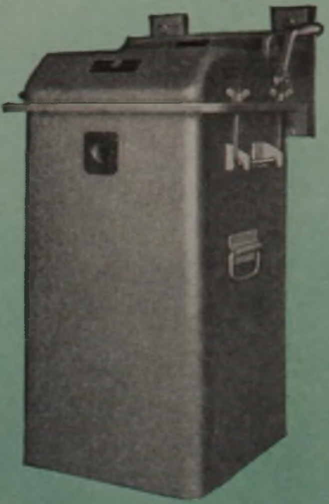
NAVY


How to Repair Valves

Don't
WASTE MAN-HOURS
ND CRITICAL MATERIAL
uilding Special Enclosures

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



CORROSION-RESISTANT

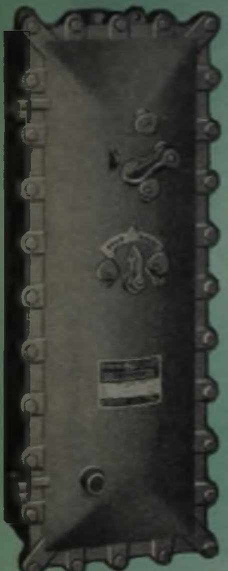
These starters (Type 8) are made in two forms—one for corrosive atmospheres and one for hazardous locations. All their arcing parts and terminals (for use in hazardous locations) are at least six inches under oil.

GENERAL-PURPOSE

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

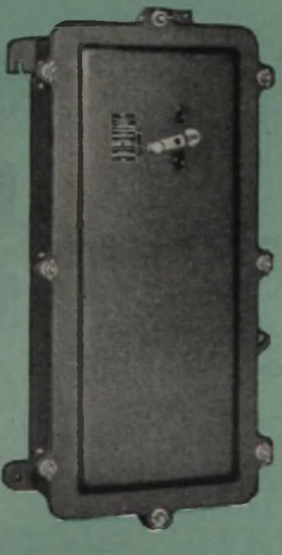
DUST-TIGHT

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



FOR HAZARDOUS LOCATIONS

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



WATERTIGHT

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

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

Order STANDARDS
to save time and material

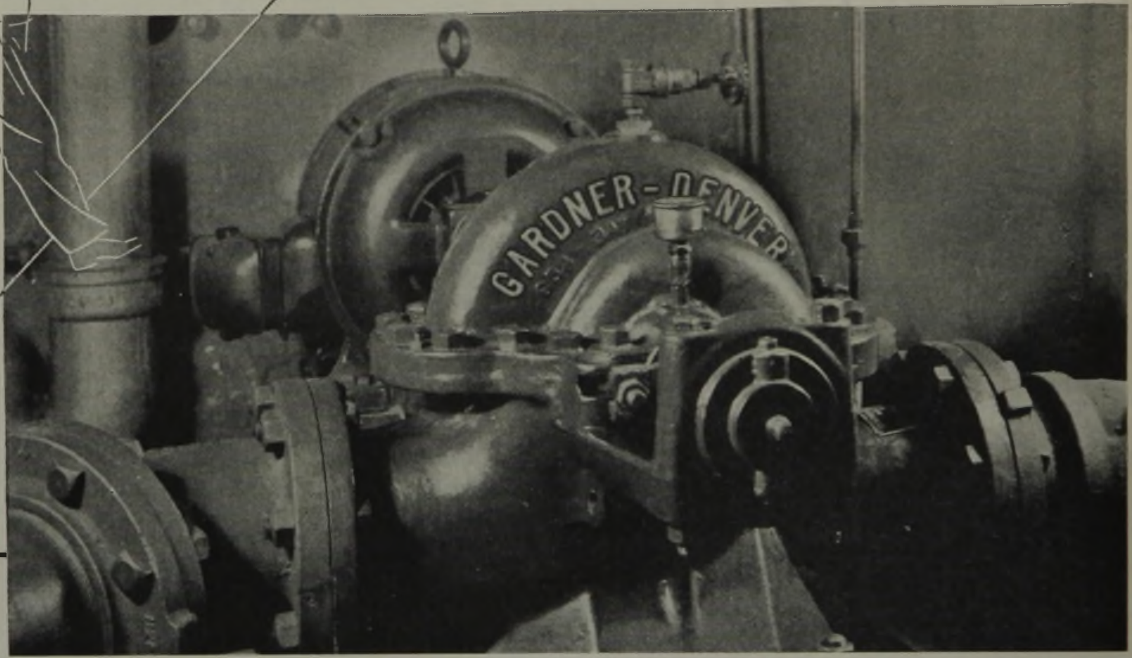
NEVER ENOUGH production time—scarce material urgently needed! Both far too valuable to be spent in building unnecessary control rooms and special enclosures.

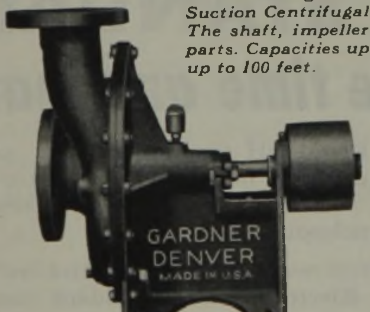
But delivered-ready-to-install control isn't all that the General Electric line of standard combination starters offers you.

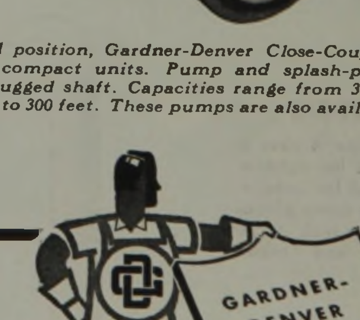
These starters combine two devices—a fused motor-circuit switch and a magnetic starter—in one compact unit. This saves you one complete mounting job. They come to you completely wired and ready to install—saving all the time and material needed to wire up two individually mounted controls.

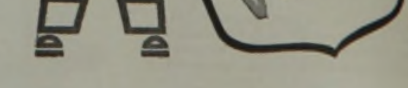
If you wish, our local sales engineers will help you select the proper starter for your job from this standard line of G-E combinations—for a-c motors up to 200 hp. *General Electric, Schenectady, N. Y.*

GENERAL ELECTRIC


GARDNER-DENVER


GARDNER
DENVER
MADE IN U.S.A.




GARDNER-DENVER PRODUCTS HELP SPEED VICTORY

SKILLED ME
BEHIND TH
PRINTED PAG

As you look through Bristol's Bulletins, and then investigate Bristol's application engineering in all aspects of automatic control, you will find yourself moving toward a practical solution of many primary wartime difficulties:

1. Lack of skilled men
2. Shortage of raw materials
3. Need to increase output without increasing space or equipment
4. Unnecessary spoilage and rejects
5. Errors in putting new products into production

Bristol's Bulletins — Clear, Concise, Complete — Sum Up Latest Advances of Wartime Instrument-Engineering

For instance, the Free-Vane system of control, originally developed by the Bristol Company in 1932, is now available in a convertible design, enabling you to adapt your instruments to changing processes by following simple instructions in your own plant. This feature is added to the exceptionally prompt undistorted response of Free-Vane Controllers, arising from the patented, free-floating action of the control mechanism.

Bulletin A 112 describes in 8 concise pages the new convenience and flexibility of Free-Vane Controllers. Write for it, together with other bulletins for your industry, addressing the Bristol Company, 110 Bristol Road, Waterbury, Connecticut.

Acid Plant Meets Problem of Continuous Checking—Uses Bristol's Metavane Transmission of Remote Data, Plus Free-Vane Control

Checking temperature, liquid level and flow i
various parts of the plant is made easy b
Metavane transmitters, which pneumaticall
record the facts at central control panel. Ther
the Free Vane Controllers maintain rigid un
formity. Remote, unvarying control of heater
azeotropic columns and refining columns ha
solved a difficult manpower problem for th
wartime plant.

FREE Bulletins From Bristol's Library of Engineering Data — for Every Executive Responsible for Wartime Production

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Please send me Bulletin A 112.

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automatic control, the type of operatio
controlled, and several installations in mode
processing plants.

☐ Bulletin 103 — Automatic control of sy
thetic rubber processes with Bristol instr
ments describes work done from pilot plan
to completed installations, complete wi
diagrams showing controls applied to vario
processes.

☐ Bulletin 513 — Bristol's Metavane Syste
of transmitting remote data by pneuma
telemetering is described in this folder. F
every executive interested in distant measu
ment of temperature, flow, pressure a
liquid level.

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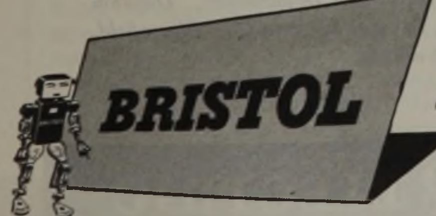


Engineers Process Control for Better Products and Profits

AUTOMATIC CONTROLLING
AND RECORDING INSTRUMENTS

THE BRISTOL COMPANY, Waterbury, Connecticut

[illegible] of Canada, Ltd.

Bristol's Instrument Co., Ltd.
London, N. W. 10, England

The familiar Miracle

Look twice. You think you see a negative of two soldiers clashing in bayonet practice. Actually you are looking at sunlight and silver bromide.

The mysterious action of light on certain silver salts is just as much a miracle today as it was a hundred years ago when the first photographs were made.

Hardly less amazing is the remarkable sensitivity of present-day photographic emulsions.

These new films and papers could not be manufactured without exacting control of temperature, control of humidity and protection against dust. *Air conditioning* makes them possible.

Air conditioning and refrigeration play a part in many photographic processes. They are being used to speed up military photography . . . improve all photography.

Today, air conditioning equipment . . . developed by General Electric . . . has been made more compact, more flexible to meet unusual wartime requirements.

After the war, these improvements will result in better air conditioning for offices, stores, theatres, hotels and many other civilian purposes. When the war is won, General Electric will provide this better air conditioning—for a better world.

Air Conditioning and Commercial Refrigeration Department, Division 432, General Electric Co., Bloomfield, New Jersey.

Air Conditioning by GENERAL GE ELECTRIC

What every plant operator should know about GLASS PIPING!

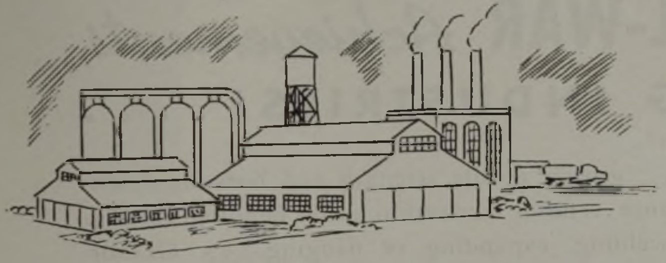
Q: Is GLASS PIPING available now?
A: Yes!

Glass-making materials are still fairly plentiful. And many plant operators are discovering that PYREX Brand Piping not only solves piping shortage problems but also, in many cases, does a better job than the piping they formerly used.

We do need priority ratings that enable us to get accessories (flanges, gaskets), to assign necessary labor, and to establish the position of your order in our production line. With such priorities we have been making 6 to 8-week deliveries.

Available sizes and lengths: 1", 1½", 2", 3", and 4" diameters—and any length from 6 inches to 10 feet (longer lengths on special request). There are corresponding ells, tees, return bends, and reducers.

Accessories: Joints are compression type—with conical pipe ends compressed to a self-centering gasket by metal flanges and clamping bolts. We supply gaskets of materials suited to the liquid or gas you want to convey.



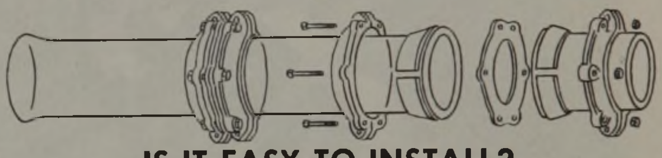
WHERE DOES IT GIVE BEST SERVICE?

Wherever hot or corrosive liquids or gases must be conveyed . . . wherever products must be protected from contamination . . . wherever it is important to know what is happening *inside* a line . . . there PYREX Piping gives you its most profitable service.

Chemical plants use it to eliminate their corrosion problems, because it resists all hot or cold acids (except HF). Food and beverage manufacturers like it because it's easy to keep clean, either by simple flushing or with steam or strong hot cleaning solutions. It helps to produce a purer product.

WATCH FOR CORNING ADVERTISEMENTS!

Watch this magazine for more information in Corning's advertisements headed "What every plant operator should know about Glass Piping." And write for PYREX Piping Bulletin No. 814. Industrial Division, Corning Glass Works, Corning, N. Y. Branch Offices: New York, 718 Fifth Ave.; Chicago, Merchandise Mart.



IS IT EASY TO INSTALL?

Plant workmen have found it easy to make installations themselves. In fact, green plant mechanics have recently done first-rate installations with PYREX Piping.

You may install from one piece to a whole system—for PYREX Piping may be joined to existing metal lines and equipment. And it is hung and supported much like other types of piping. (See photo at top of page.) We do recommend that hangers and supports be padded, to minimize scratching.

WILL IT STAND UP MECHANICALLY?

Yes. PYREX Piping is recommended for working pressures up to 100 p.s.i. But glass in this form is *not* as strong as metal. So, care must be taken to avoid installation strains or sharp impact. Nearly 20 years of service under all kinds of plant conditions have proved that only simple common sense and reasonable care are required to handle PYREX Piping without trouble. The glass itself, incidentally, is very hard—about twice as resistant to abrasion as ordinary plate glass. Thus, the piping is particularly suitable for abrasive, corrosive slurries. You can install and use PYREX Piping with confidence.

WHAT DOES IT COST?

The initial cost of PYREX Piping (accessories included) is about the same or less than the cost of full-weight copper or brass piping, in comparable sizes, and is considerably less than the cost of stainless steel.

And because PYREX Piping does not wear out under acid attack, it gives long trouble-free service, with resultant low long-time cost.

The left-hand photograph at the top of the page is an example. That PYREX Piping has carried a slurry of crushed quartz and sulphuric acid for over eight years—without one cent of maintenance.

"PYREX" is a registered trade-mark and indicates manufacture by Corning Glass Works, Corning, N. Y.

CORNING
Glass Works

Pyrex Industrial Glass


Chemical and physical laboratories manned by graduate metallurgists, are basic to the exact control of production of Globe Stainless Tubes.
GLOBE Stainless STEEL TUBES

DOW INDUSTRIAL CHEMICALS

SERVING AMERICAN INDUSTRY FOR HALF A CENTURY

Numbered among more than 500 Dow chemical products is an important group of industrial or heavy chemicals. Bromine and bromides were Dow's first contribution to the advancement of domestic chemical production. The bromine processes were soon adapted to the manufacture of chlorine. Shortly after 1889, a new field, that of producing chlorinated products such as sulphur chloride, carbon tetrachloride, etc., was added. In turn, the manufacture of Caustic Soda led to new processes for producing aniline, phenol, indigo and other organic compounds.

Thus from a meager beginning, has come a tremendous production capacity for chemical products of quality and dependability.

THE DOW CHEMICAL COMPANY, MIDLAND, MICHIGAN
New York · Chicago · St. Louis · Houston · San Francisco · Los Angeles · Seattle

Dow

CHEMICALS INDISPENSABLE
TO INDUSTRY AND VICTORY

Hersey reviews its *first war year* ★ ★ ★

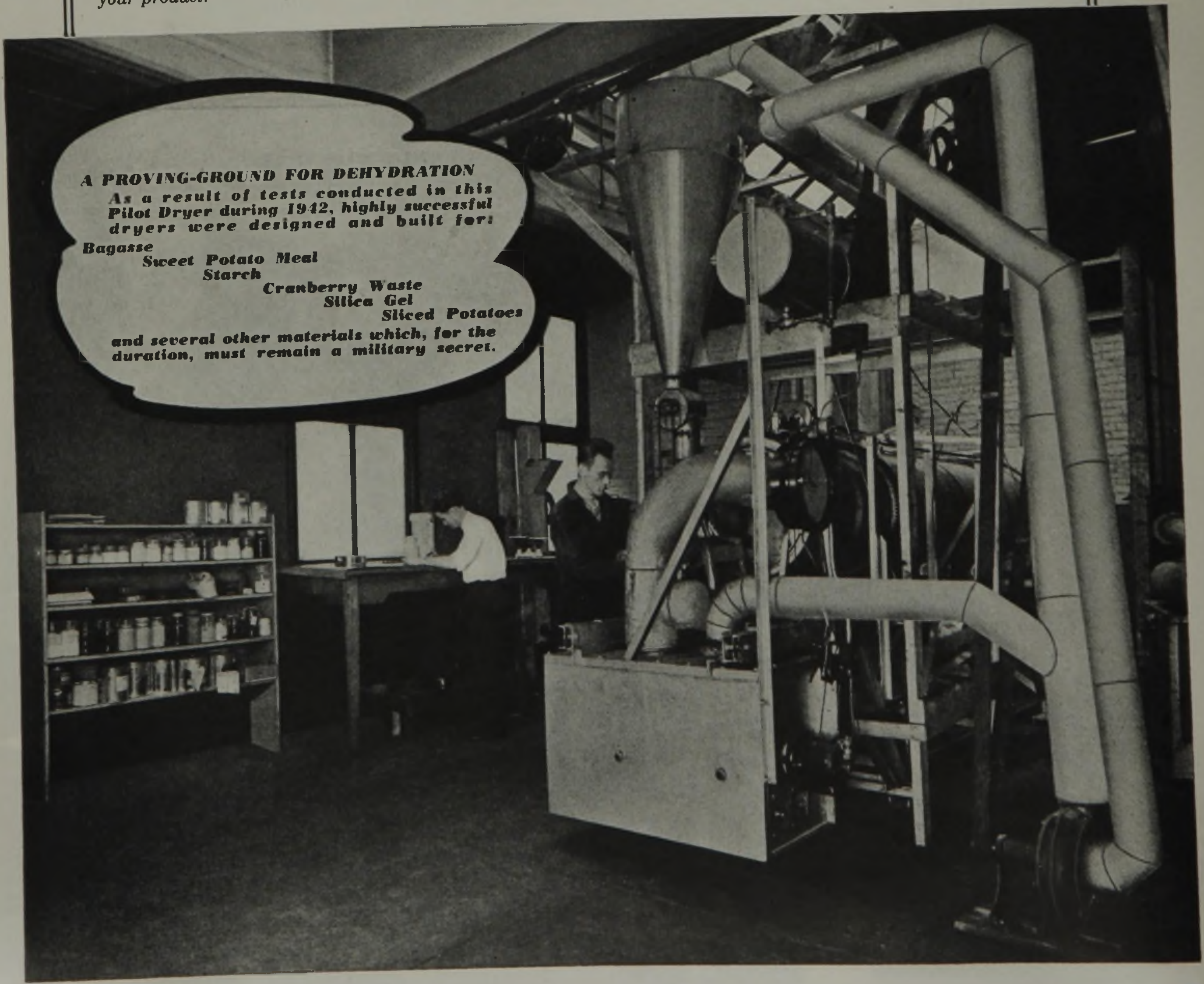
IN step with the rest of American Industry, we at Hersey feel that we have taken tremendous strides during 1942 . . . Strides that are just beginning to suggest the possibilities in the future development of dehydration.

During the past year we have built *twenty-five* different Dryers for *thirteen* varied products — products whose drying temperature requirements range from 140° F. to 1500° F. These Dryers operate with Con-Current, Counter-Current, Cross-Current and Intermediate Flow of both gases and material.

In 1943, a growing expansion in the processing and use of dried products will undoubtedly bring us demands for faster production of Dryers with new and exacting requirements. But an appraisal of the future, based on our 1942 performance, fills us with confidence and enthusiasm. . . . The Hersey organization — our engineers and the rest of the staff — our complete facilities — are "*on the alert*" and ready to attack each new problem with assurance and competence.

The Hersey Pilot Plant operates as a service to customers. *Send for information sheets on which to outline the requirements of your product.*

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

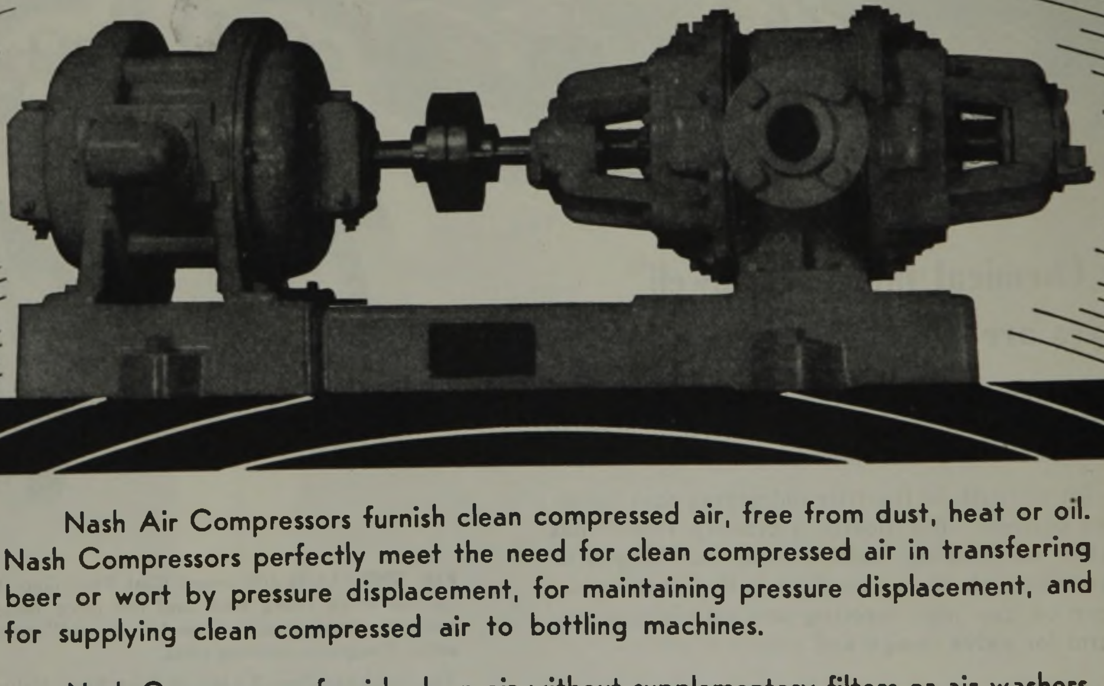


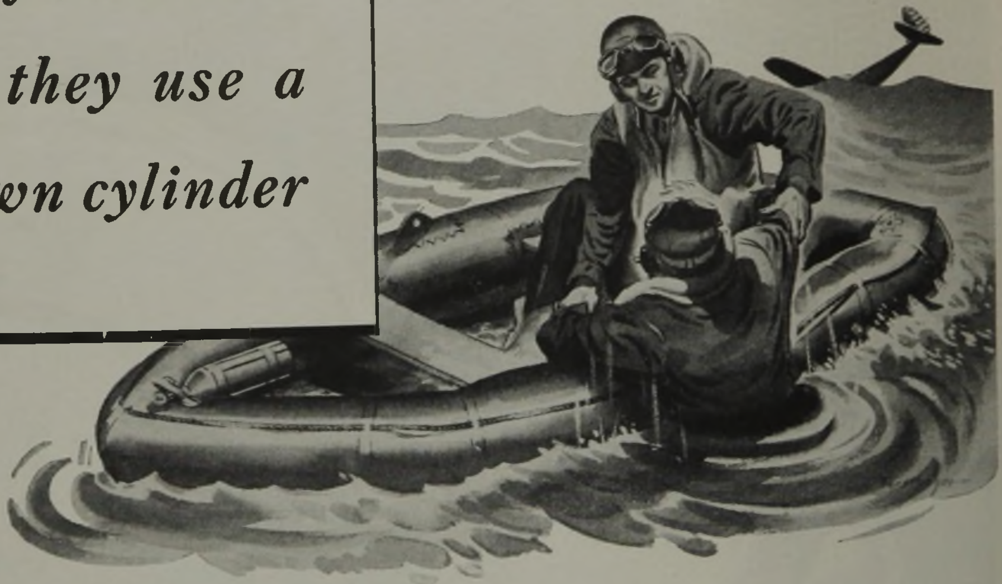
A PROVING-GROUND FOR DEHYDRATION

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

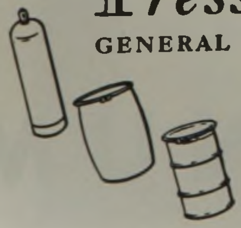
Bagasse
Sweet Potato Meal
Starch
Cranberry Waste
Silica Gel
Sliced Potatoes

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



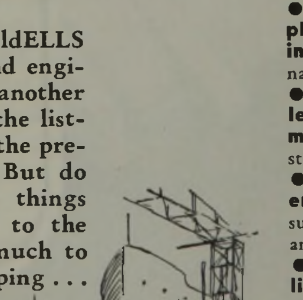



Hackney
MILWAUKEE




Hackney
MILWAUKEE


WeldELLS
have everything ★
Only WeldELLS Have Precision Quarter Markings
6" STD. TAYLOR FORGE WELDELL PAT. 1936805
★

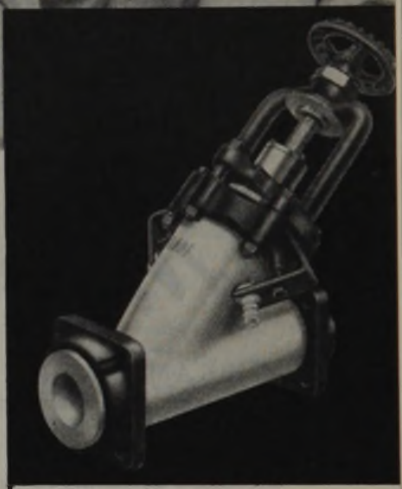


Here's How:

Raschig Rings of Lapp Porcelain

Facilitate

Gas Absorption Processes



• *Pipe and valves of Lapp Chemical Porcelain are still available for industrial installation. For the handling of corrosive liquids they offer highest purity, mechanical ruggedness, and long life.*

☞☞☞☞☞ Raschig Rings of Lapp Chemical Porcelain are standard tower packing in many American plants today because, at low cost, they offer long life and a high purity standard. These are properties of Lapp Chemical Porcelain as a material. A thoroughly vitrified ceramic, completely iron-free, it offers high mechanical strength. Its absolute non-porosity guards against contamination of subsequent batches, means exposure to corrosion is limited to the surface, avoids crumbling.

☞☞☞☞☞ Reasonable quantities of Lapp rings in most sizes are available for shipment from stock. Large orders can be accommodated on a delivery schedule satisfactory to you. For specifications and trial samples, write Lapp Insulator Co., Inc., Chemical Porcelain Division, LeRoy, N. Y.

ARMY E NAVY

Lapp

Chemical Porcelain

Valves · Pipe · Raschig Ring

EGYPT—3000 B. C.

The potter's art was a noble calling in the days of Egypt's glory. The potter and his art were important enough to have a recognized God called Num, the great guiding spirit of the universe. According to Egyptian legends, it was he who first worked in clay to fashion man—his greatest creation.

Masterpieces OF POTTERY

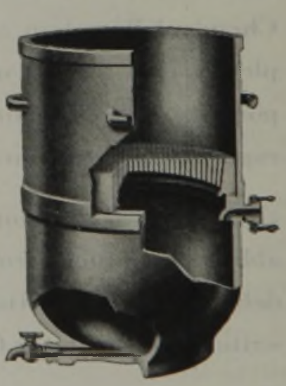
CERAMIC MANUFACTURING today is fundamentally the same as it was in 3000 B.C. — craftsmanship, material, molding and baking, but the increased demands of an advanced civilization have brought modern methods of mass production into play.

With the advent of the great industrial revolution, following the dark ages, ceramics branched out from a purely domestic luxury to find vast uses in industry.

Today, in the handling of large quantities of strong chemicals and corrosive liquids, chemical stoneware equipment plays an ever increasing role. Chemical stoneware, as produced by General Ceramics, is built, with the closest supervision and care, to withstand the ravages of time and hard use. It is acid proof through and through to last indefinitely and assure safety from hazardous leaking. Its glazed surface is easy to keep clean, thus eliminating product contamination.

Included in General Ceramics Chemical Stoneware for industrial use are acid-proof pipe, valves, fittings, kettles, jars, pots, pumps, exhausters, coolers, condensers, acid elevators, towers, filtering equipment, and tourills.

Other products include Steatite Insulators made by General Ceramics & Steatite Corp., Keasbey, N. J.



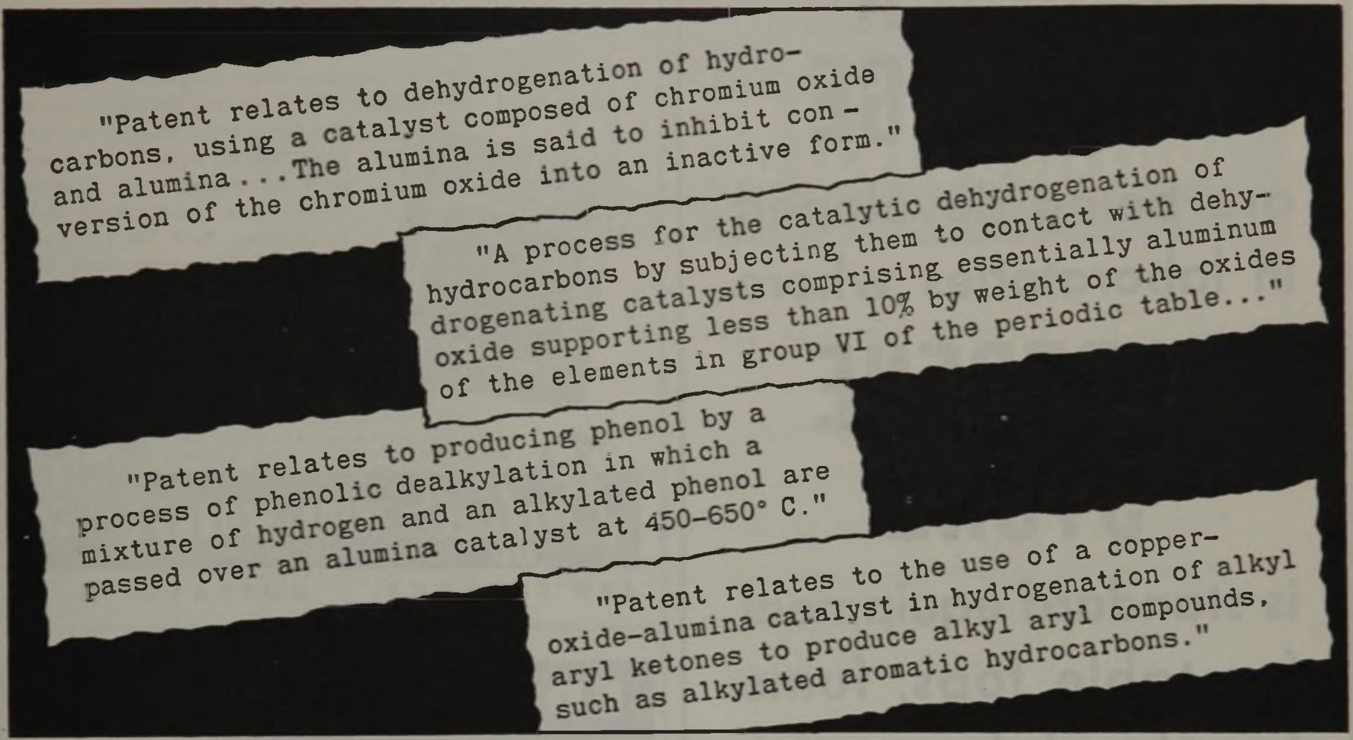
VACUUM FILTER
Three-Piece
with Removable Plate

General Ceramics Co.

GENERAL
CERAMICS COMPANY
CHEMICAL STONEWARE

CHEMICAL STONEWARE DIV.
KEASBEY NEW JERSEY

HERE'S WHAT THEY REPORT ON CATALYTIC PROCESSES USING ALUMINAS



"Patent relates to dehydrogenation of hydrocarbons, using a catalyst composed of chromium oxide and alumina . . . The alumina is said to inhibit conversion of the chromium oxide into an inactive form."

"A process for the catalytic dehydrogenation of hydrocarbons by subjecting them to contact with dehydrogenating catalysts comprising essentially aluminum oxide supporting less than 10% by weight of the oxides of the elements in group VI of the periodic table..."

"Patent relates to producing phenol by a process of phenolic dealkylation in which a mixture of hydrogen and an alkylated phenol are passed over an alumina catalyst at 450–650° C."

"Patent relates to the use of a copper-oxide-alumina catalyst in hydrogenation of alkyl aryl ketones to produce alkyl aryl compounds, such as alkylated aromatic hydrocarbons."

Technical and patent literature contains dozens of references to the use of Aluminas in catalytic processes; as catalysts, carriers and auxiliary catalysts. The few typical excerpts shown above give you an idea of how other chemists include Aluminas in their how-to-do-it thinking.

These Aluminas are suitable for catalytic purposes:

ACTIVATED ALUMINA

This is a catalytically active material when used alone or as a catalyst support. The pores of this granular Alumina occupy 50% of the particle volume.

HYDRATED ALUMINA C-730

This powder Alumina is active after an original heating to 500°F. It has finer particles and greater surface area than are obtainable with ground natural materials.

TABULAR ALUMINA

This high-strength Alumina is a porous form of granular corundum produced from pure aluminum oxide. It is a substantially inactive catalyst carrier. Close mesh sizes are obtainable.

MONOHYDRATED ALUMINA D-50

This is a substantially inactive powder Alumina having crystal structure different from the usual Aluminum Trihydrate. The average particles are 1 micron in diameter.

Aluminas enter into the production of such materials as high octane gasoline, synthetic rubber, plastics, and explosives. They may give your catalytic reactions a boost. You may have samples for trial in your processes, if you are making war materials. ALUMINUM COMPANY OF AMERICA (*Sales Agent for* ALUMINUM ORE COMPANY) 1911 Gulf Building, Pittsburgh, Pennsylvania.

ALORCO

ALUMINUM ORE COMPANY

ALUMINUM AND FLUORINE COMPOUNDS

The Materials
that will overcome the

RUBBER SHORTAGE

are being developed
in laboratories where

ALBERENE STONE

is standard equipment
for table tops, fume
hoods, sinks, tanks,
and shelving.
Prompt deliveries
can still be made.

**ALBERENE STONE CORPORATION
OF VIRGINIA**
419 FOURTH AVENUE, NEW YORK

RUSH SEND YOUR CATALOG TO

Company..........

Address..........

Attention of..........

Play Safe WITH "BUFFALO WIRE" WINDOW GUARDS

. . . . *The Recognized Standard of Highest Quality*

. . . . *The Widely Accepted Leader for 73 Years*

Regardless of your window sizes, shapes or types--all can be fitted with "Buffalo Wire" window guards. Superior and economical square diamond mesh fabric, square mesh wire cloth or conventional diamond mesh on rod, angle iron or channel frames. Built for stationary or swing-open installations. Also, fabrics in rolls for manufacture of guards.

Complete Information in New Window Guard Folder No. 592-AG. Write for your FREE COPY.

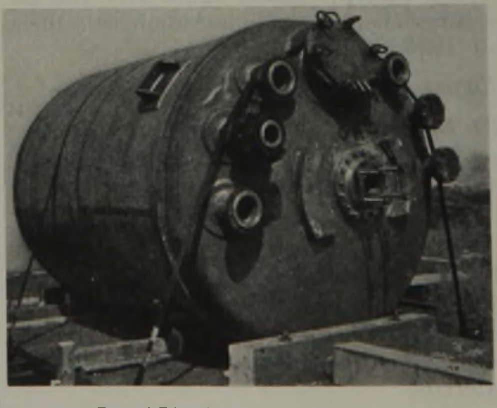
MADE BY THE MANUFACTURERS OF INDUSTRY'S FINEST WIRE CLOTH

Buffalo WIRE WORKS CO., INC.
ESTABLISHED 1869 AS SCHEELER'S SONS

489 TERRACE BUFFALO, N. Y.

EDGE MOOR SINCE 1868

Welding Engineers, in the service of the Process Industries, we work all commercial metals, meet all codes: X-Ray, Stress-Relieve, Pull-Test and Anneal.



PRESSURE TANKS
KETTLES
STILLS
TOWERS
COLUMNS
HEAT EXCHANGERS
MIXERS
BLENDERS
DIGESTORS
PROCESS UNITS

● *A Typical Edge Moor Fabricated Class 1 Pressure Vessel*

We build to your specifications. Our extra margin of ruggedness pays. May we send you complete information covering our large shop facilities.

Write for Bulletin 116C

EDGE MOOR IRON WORKS, INC.
EDGE MOOR, DELAWARE
30 ROCKEFELLER PLAZA, NEW YORK, N. Y.

THROUGH THE MIRACLE OF

ELECTRONICS

FLOATLESS LEVEL CONTROL

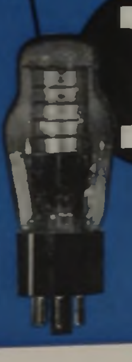
On the industrial front . . . as on the battle front . . . the electron tube, miracle of modern science, is today accomplishing the impossible — with precision, speed, efficiency. It has eliminated from the field of level control the need for complicated mechanical devices. It has made available to industry 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.
- Provide high and low level safeguards.
- Maintain interface between two liquids.
- Control liquids in mixture, for desired concentration or specific gravity.
- Govern pump programming operations.
- Detect water accumulation in gasoline storage tanks and in transformers.
- Provide complete boiler feedwater control.

Affected by manpower shortages . . . mechanical breakdowns? Let us put the science of electronics to work for you — show you how to achieve greater operating efficiencies — freedom from wartime replacement problems. For recommendations on photoelectric smoke density indication, liquid turbidity control, counting, timing, automatic inspection, conveyor control, machinery safeguards, and similar applications . . . consult Photoswitch Incorporated, specialists in photoelectric and electronic controls for industry.

There is a Photoswitch Level Control to meet ***every*** need . . . for use with ***all*** types of liquids and powders. ***Write for complete catalogue information.***



P

PHOTOSWITCH INCORPORATED

PHOTO-ELECTRIC & ELECTRONIC CONTROLS FOR EVERY INDUSTRIAL PURPOSE

CAMBRIDGE, MASS. • *District Offices* IN ALL PRINCIPAL CITIES

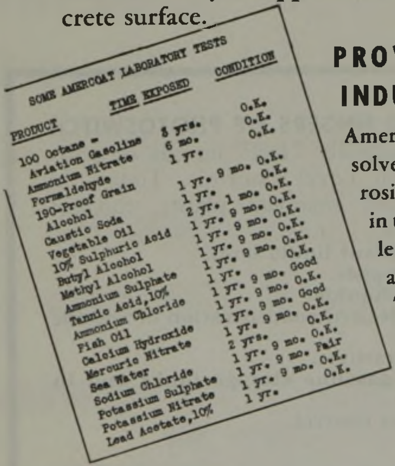
A NAME EVERY ENGINEER SHOULD KNOW

Amercoat

protects vital chemicals in shipment and storage

AMERCOAT...the cold-applied plastic coating ...solves the problem of handling chemicals in available tanks and equipment which, otherwise, would not be suitable for this purpose.

Amercoat protects tanks and equipment from corrosion and the contents from contamination by providing an inert plastic surface which is odorless, tasteless and dielectric to a high degree. Amercoat may be applied to any metal or concrete surface.



SOME AMERCOAT LABORATORY TESTS

PRODUCT	TIME EXPOSED	CONDITION
100 Octane - Aviation Gasoline	3 yrs.	O.K.
Ammonium Nitrate	6 mo.	O.K.
Formaldehyde	1 yr.	O.K.
190-Proof Grain Alochol	1 yr. 9 mo.	O.K.
Caustic Soda	1 yr.	O.K.
Vegetable Oil	2 yr. 1 mo.	O.K.
10% Sulphuric Acid	1 yr. 9 mo.	O.K.
Butyl Alcohol	1 yr. 9 mo.	O.K.
Methyl Alcohol	1 yr. 9 mo.	O.K.
Ammonium Sulphate	1 yr.	O.K.
Tannic Acid,10%	1 yr.	O.K.
Ammonium Chloride	1 yr. 9 mo.	Good
Fish Oil	1 yr. 9 mo.	O.K.
Calcium Hydroxide	1 yr. 9 mo.	Good
Mercuric Nitrate	1 yr. 9 mo.	O.K.
Sea Water	2 yrs.	O.K.
Sodium Chloride	1 yr. 9 mo.	O.K.
Potassium Sulphate	1 yr. 9 mo.	Fair
Potassium Nitrate	1 yr. 9 mo.	O.K.
Lead Acetate,10%	1 yr.	O.K.

PROVED IN MANY INDUSTRIES...

Amercoat has successfully solved problems of corrosion or contamination in the Chemical, Petroleum, Food, Maritime and other industries. Typical examples of the effectiveness of Amercoat are shown in the chart on the left.

All Amercoat products are compounded and pigmented to best meet stipulated problems. Tell us your problem and we'll answer it with Amercoat to meet your specific needs... or we'll tell you Amercoat is not the answer.

Amercoat is fully described and some of its many uses are illustrated in an interesting, informative booklet. Write for your copy today.

Amercoat DIVISION
AMERICAN PIPE
AND CONSTRUCTION CO.
P. O. BOX 3428, TERMINAL ANNEX • LOS ANGELES • CALIFORNIA

Put your SEALING PROBLEMS UP TO FEL-PRO

Industries of every type are calling on Fel-Pro for help in solving war-intensified problems on Gaskets, Mechanical Packing and Stripping.

Most insistent has been the demand for a material to replace rubber and other critical materials. After thorough research and testing, Fel-Pro engineers developed entirely new gasket materials — such as Syntoflex and Lignoflex. More than substitutes, for certain requirements, these are actually *better* gasket materials, with superior characteristics — more resistant to strong chemicals — not affected by petroleum products — better able to withstand increased pressures.

SEND FOR FREE MATERIAL SAMPLE FOLDER

Contains actual samples of 36 Fel-Pro materials, each designed for specific types of sealing requirements. Full descriptions, data, many application suggestions. If none of these materials solve your sealing problems, Fel-Pro's Special Development Staff is at your service.

Helping "KEEP THE POWDER DRY"

One of Fel-Pro's new sealing materials is meeting military needs for an ammunition box sealing material with rubber-like characteristics, but which, in addition, is resistant to poison gas seepage.

★ ★ ★ ★ ★ ★ ★

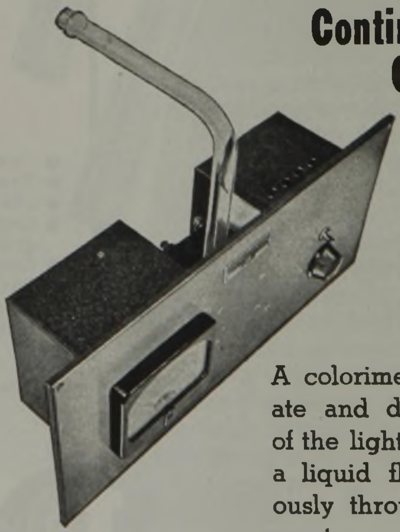
Put It Up to FEL-PRO for solutions to problems involving GASKETS, MOULDING, STRIPPING, MECHANICAL PACKING and other types of Sealing Materials.

Put it up to FEL-PRO

FELT PRODUCTS MFG. CO.
1519 CARROLL AVE., CHICAGO, ILL.

LUMETRON

Continuous-Flow Colorimeter



Mod. 400-S

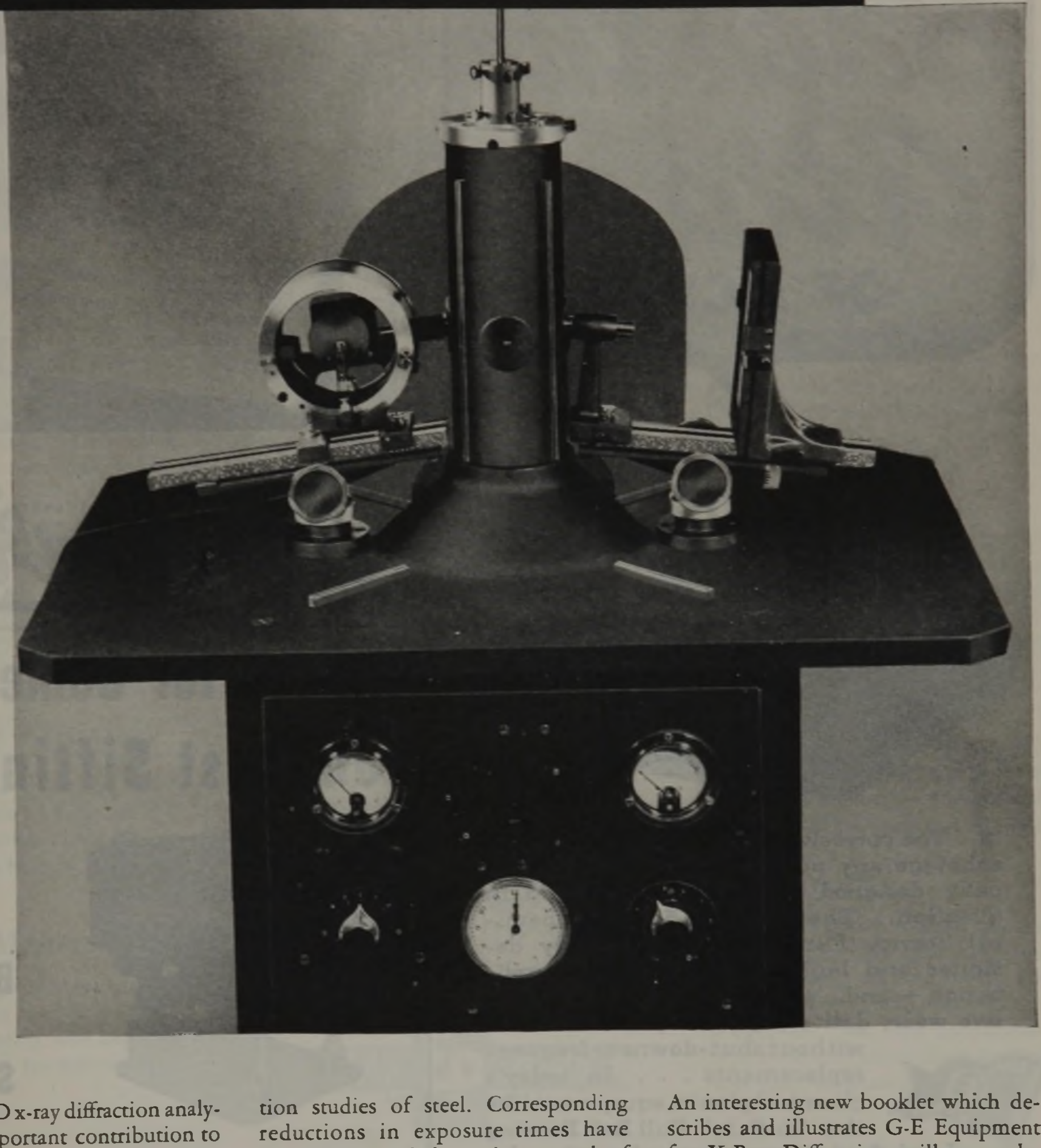
A colorimeter for immediate and direct indication of the light transmission of a liquid flowing continuously through the instrument.

Suited for continuous registration of concentration, color or turbidity of solutions in chemical processes.

Write for Literature.

PHOTOVOLT CORP.
95 Madison Ave. New York City

G-E PROVIDES NEW HIGH-SPEED X-RAY DIFFRACTION EQUIPMENT



HIGH-SPEED x-ray diffraction analysis—an important contribution to war industry—is now available. The development of the G-E Model CA-6 beryllium window x-ray tube for use in the G-E Models XRD-1 and XRD-2 Units permits registration of patterns with exposure times which are from three to twenty times faster than was possible previously.

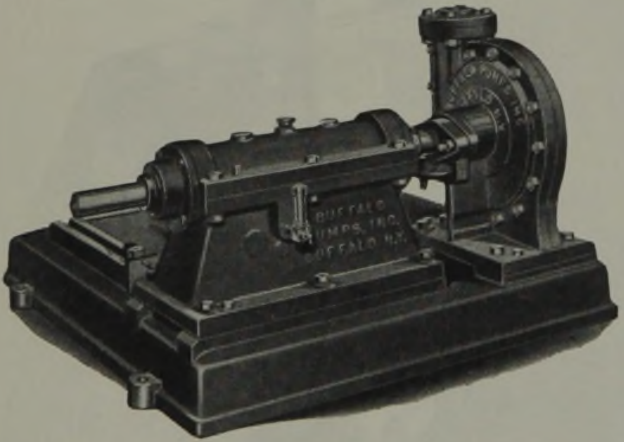
Today, with G-E X-Ray Diffraction Units, 15 to 30 minute exposures have replaced the four to eight hour tests which were formerly routine in diffraction studies of steel. Corresponding reductions in exposure times have materially speeded up the control of aluminum and magnesium refinement. Modern, progressive analytical laboratories have found in the G-E X-Ray Diffraction Units an exceedingly satisfactory method of quantitative and qualitative analysis. The diffraction method is ideal for the analysis of solid compounds, for example, because it provides information not obtainable by conventional analysis which generally identifies elements present rather than compounds.

An interesting new booklet which describes and illustrates G-E Equipment for X-Ray Diffraction will soon be available. To make sure that you receive your copy, address your request to Department N42.

GENERAL ELECTRIC
X-RAY CORPORATION
2012 JACKSON BLVD. CHICAGO, ILL., U. S. A.

Today's Best Buy – U. S. War Bonds

Hurling Back the Attack OF ACIDS



★ The corrosive attack of acids can soon sabotage any pump—unless it is specifically designed to handle the liquid in question. That is why Buffalo Chemical Service Pumps are so carefully designed and built for each special application—and why they resist destructive wear, delivering extra years of service without shut-downs or frequent replacements . . . In today's chemical plants, equipment like the "Buffalo" Full Ball Bearing Lead Acid Pump shown above, is a dependable ally in the all-out war program.

ARMY E NAVY

BUFFALO PUMPS, INC.
153 Mortimer St. Buffalo, N. Y.
Branch Engineering Offices in Principal Cities
Canada Pumps, Ltd., Kitchener, Ont.

"Buffalo" PUMPS FOR CHEMICAL SERVICE

The Proven, basic, precision Cartridge, from which all other Fenwal Thermoswitches are derived.

Let us quote you on a standard Thermoswitch design that fits the needs of your defense contract. (If your job is an unusual one we will design a "special" for you!)

Ratings: —100 to 600°F., 10 amperes or 25 amperes, 115 Volts A. C., sensitivity ±.1°F.

Fenwal INCORPORATED
203 MAIN STREET
ASHLAND, MASSACHUSETTS

Chosen for Some of the Toughest Sifting Jobs

★

BAR-NUN *Rotary* SIFTER

Operating on continuous 24-hour duty, Bar-Nun Rotary Sifters have proved their ability to produce uniform complete separations month after month with minimum attention, power and maintenance costs. First installations in many plants have resulted in orders for additional units. Made in 9 sizes, 4 to 60 square feet of cloth surface. Write today for complete information.

B. F. Gump Co.
ENGINEERS AND MANUFACTURERS SINCE 1872
415 SOUTH CLINTON STREET, CHICAGO, ILLINOIS

EAGLE-PICHER

Industrial Pigments

Red Lead

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

Litharge

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

Sublimed Litharge

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

Orange Mineral

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

White Lead Carbonate

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

Sublimed White Lead

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

Zinc Oxide

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

EAGLE
1843 EP 1943
PICHER

Leaded Zinc Oxides

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

Lithopone

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

Titanated Lithopone

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

Lead Silicate

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

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

THE EAGLE-PICHER LEAD COMPANY

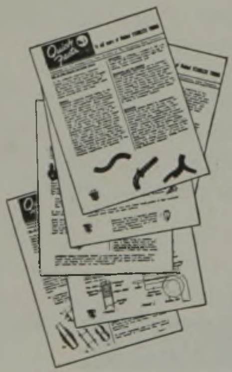
General Offices • Cincinnati, Ohio

IF IT'S **HEAT RESISTANCE** YOU WANT

Thermometer wells, pipe lines and other vital processing equipment withstands corrosion and high heat, and has a *longer service life*—thanks to Carpenter Welded Stainless Tubing.

The *uniform wall thickness* of this tubing means that there are no thin spots to "burn out" first. And it is ductile, easy to fabricate — thus helping to speed the production of vital wartime equipment that must win battles against excessive heat. Then too, tubes are *natural design units.* Parts can often be finish-formed by merely swaging, tapering, expanding, etc. If you have a wartime heat resistance problem that must be solved right now, take advantage of Carpenter's diversified experience in many plants where similar problems have been met and solved.

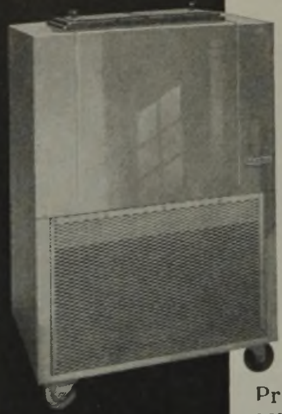
FOR HELP in applying Welded Stainless Tubing, ask for our series of "Quick Facts" bulletins. They contain practical working information to help you with new design or fabricating problems. A note on your company letterhead will start a set of "Quick Facts" bulletins on the way to your desk.



CARPENTER WELDED STAINLESS TUBING
resists corrosion, heat and wear; is 100% hydrostatically tested.

THE CARPENTER STEEL COMPANY
Welded Alloy Tube Division • Kenilworth, N. J.

Carpenter
WELDED
STAINLESS TUBING



KOLD-HOLD

Industrial Sub-Zero Machines . . . *for controlled temperature storage and processing*

Used in:
- Process Plants
- Laboratories
- Hospitals
- Research Institutions
- Pharmaceutical Firms

Preserve and store chemicals, serum, blood, mother's milk, etc., over long periods of time at required sub-zero temperatures with KOLD-HOLD.

Standard 2 cu. ft. machine is shown . . . other capacities up to 11 cu. ft. available. Close, accurate temperature control is provided. Send now for complete details.

NEW YORK — 254 W. 31st St. — Pennsylvania 6-1161
CHICAGO — 201 N. Wells — Randolph 3986
LOS ANGELES — 1015 W. Second — Michigan 4989

KOLD-HOLD MANUFACTURING CO.
447 N. Grand Ave., LANSING, MICH., U. S. A.

LaMotte Phosphate Comparator For Boiler Feed Water

The method for determining phosphates in treated feed water, developed in our research laboratory, affords accuracy and simplicity in procedure that was previously impossible. It is based upon the development of color in the water sample, and this color development is directly proportional to the amount of phosphates present. One important factor to be noted is that the LaMotte method is not affected by the presence of silicates up to concentrations of 800 p.p.m. The results are read off directly from prepared color standards of known phosphate values. For phosphate concentrations up to 100 p.p.m., this method is accurate to ±5 p.p.m. The time required for the test is about five minutes.

Price, complete with instruction booklet, $22.50, f.o.b., Towson, Baltimore, Md.

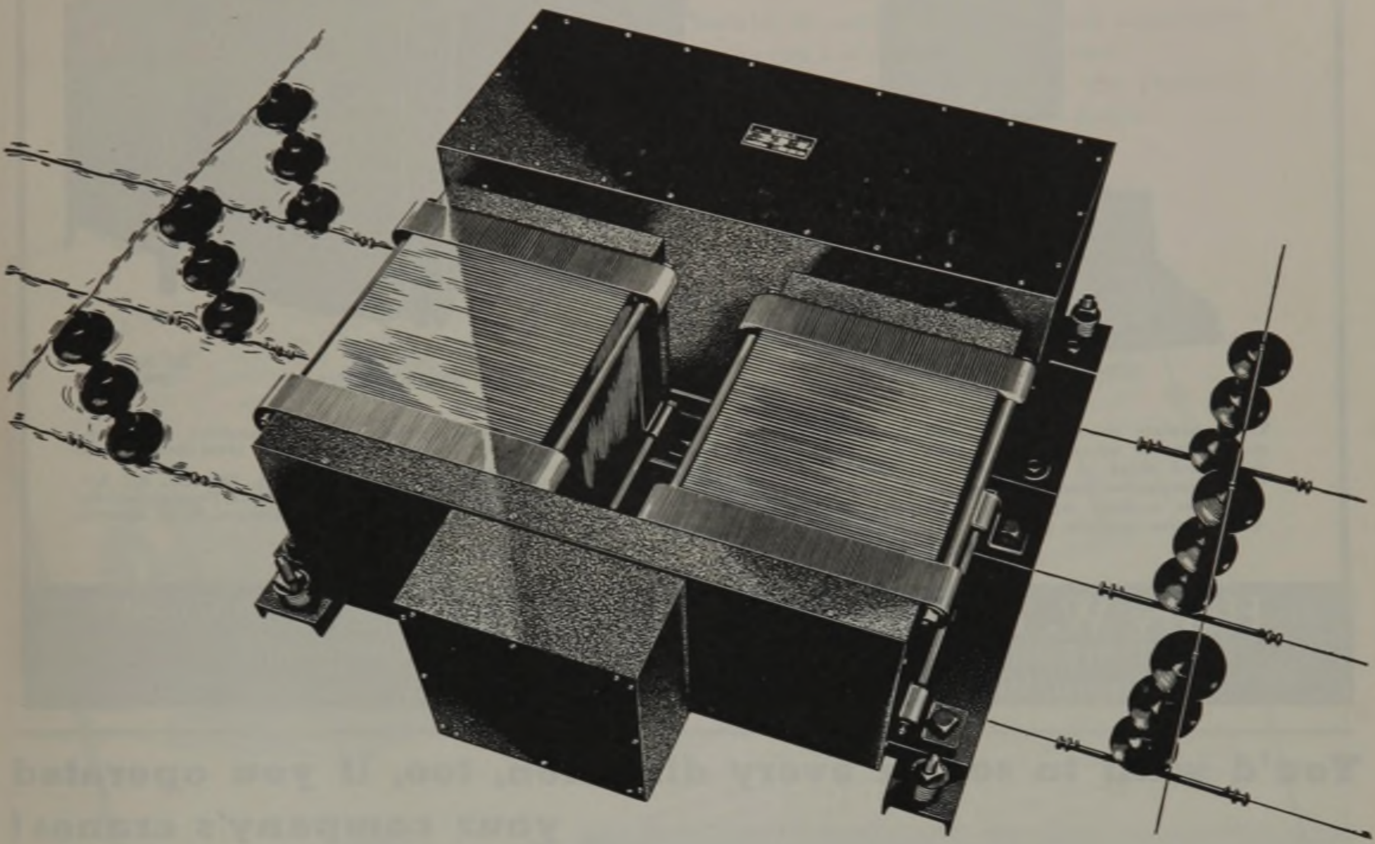
LAMOTTE UNIVERSAL pH OUTFIT

This compact LaMotte outfit is readily portable, yet it covers a wide pH range. Can be supplied with any 3, 4, 5, 6, 7 or 8 sets of LaMotte Permanent Color Standards and will therefore cover any desired part of pH range 0.2–13.6. Applicable to all types of research and industrial pH work. Accurate to 0.1 pH. Excellent for use with highly colored or turbid solutions.

Price $35.00 to $60.00 f.o.b. Baltimore, Md.

LaMotte Chemical Products Company
Dept. F. Towson, Baltimore, Md.

Industry steadies its "nerves"



FACED with production schedules that have no precedent in history, American industry finds the fluctuating voltages of its over-loaded power lines wholly inadequate to meet the "deadly" precision demanded for total war.

Vital "nerve centers" of production lines are geared for precise performance when operated at specific line voltages. Any variation from these rated values, and there are many these days, may well mean lagging production schedules and a noticeable lack of uniformity in products.

Fluctuating line voltages are no problem in plants where Sola "CV's" have taken over. Even though the peaks and valleys of power consumption may cause a voltage variation of as much as 30%—the vital "nerve centers" of their production lines continue to operate smoothly and with unerring precision.

Day and night, without care or supervision, Sola Constant Voltage transformers maintain positive control over electrically operated instruments and machines that are indispensable to the nation's war effort. These transformers are available in standard units with capacities ranging from 15 KVA, which might be used for an entire communications system for instance, to the small 10 VA units for vacuum tubes. Special units can be built to specifications.

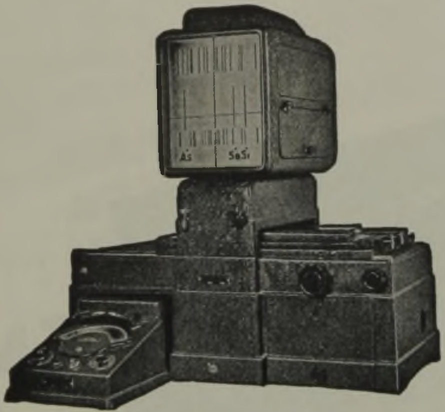
Note to Industrial Executives: *The problems solved by Sola "CV" transformers in other plants may have an exact counterpart in yours. Find out. Ask for bulletin SCV-74*

SOLA

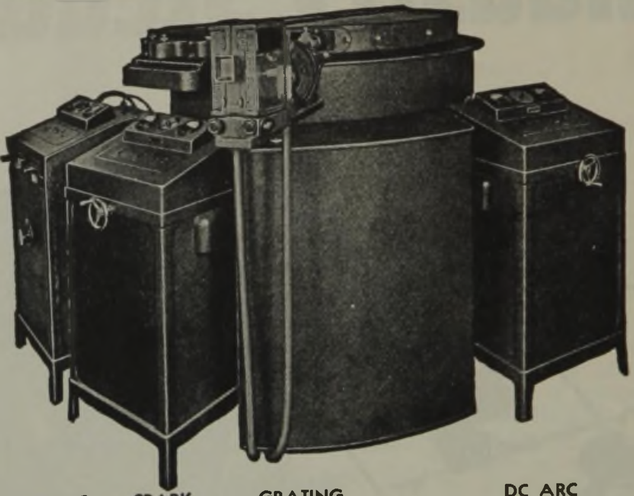
Constant Voltage Transformers

Transformers for: Constant Voltage • Cold Cathode Lighting • Mercury Lamps • Series Lighting • Fluorescent Lighting • X-ray Equipment • Luminous Tube Signs Oil Burner Ignition • Radio • Power • Controls • Signal Systems • Door Bells and Chimes • etc. **SOLA ELECTRIC CO., 2525 Clybourn Ave., Chicago, Ill.**

SPECTROGRAPHIC EQUIPMENT



COMPARATOR DENSITOMETER



The complete mated line of ARL-DIETERT spectrographic equipment increases accuracy, speed and scope of spectro-chemical analysis. The Comparator-Densitometer as illustrated serves as a dual unit for qualitative and quantitative analysis of films or plates.

The ARL-DIETERT Grating Spectrograph, with its constant dispersion, exceptionally high resolution, and long camera, makes an ideal spectrograph for the analysis of all materials.

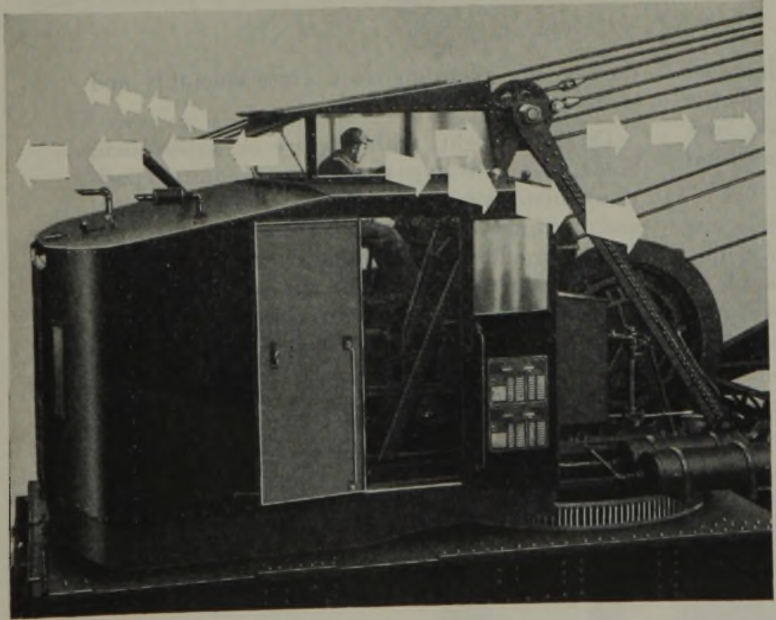
The ARL-DIETERT spectrographic accessories, such as, DC Arc, AC Arc, AC Spark, Controlled Multisource Unit, Developing Machine, Dryers, Calculating Board, and sample preparation accessories, are essential to all spectrochemical laboratories.

EAST Write to *WEST*

Harry W. Dietert Co.
9330B Roselawn Ave.
Detroit, Michigan

APPLIED RESEARCH LABORATORIES
4336 San Fernando Rd.
Glendale, California

You'd want to see in every direction, too, if you operated your company's cranes!



When you're swinging up to 40 tons of heavy material on the end of a fifty-foot crane-boom you want to see what you're doing. That's why the Monitor-type cab on I.B. Cranes is such an important factor in speeding up material handling. For the operator can see clearly in every direction. No blind spots cut off even a segment of his 360° range of vision. Besides visibility, the I.B. Monitor-type cab provides better ventilation, less noise, and less heat. Controls are conveniently placed for handy operation.

From undercarriage to boom-tip Industrial Brownhoist Cranes are designed and built to increase production in material handling whether with magnet, hook or bucket. — Industrial Brownhoist Corp., Bay City, Mich. District Offices: New York, Philadelphia, Pittsburgh, Cleveland and Chicago.

INDUSTRIAL BROWNHOIST BUILDS BETTER CRANES

SMALL SIZE MACHINES WITH FULL SIZE FEATURES

Sturtevant Laboratory Machines are large machines in miniature — capable of running 24 hours a day with the strength of full size equipment and with an even wider range of adjustment.

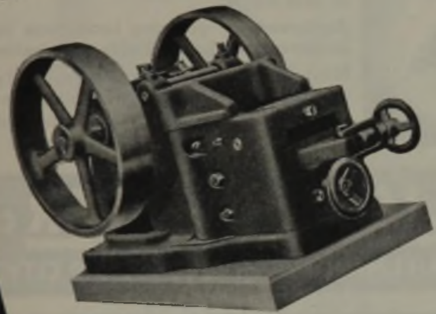
These great little machines are superior in design, construction and accessibility. They have an excellent reputation for the size and quality of their output.

Besides those illustrated below, the line also includes: Screens, Air Separators, Vibrating Test Sieves and Coal Crushers and Sampler. Write for full details.

LABORATORY CRUSHERS

Special Roll Jaw action simplifies close regulation of the product with capacities varying from 300 or 400 lbs. per hour at finest settings, to 1000 or 2000 lbs. when opened for coarser work. Each part of the crusher is accessible for quick and easy cleaning.

These crushers weigh from 900 to 1000 lbs. and are fitted with Manganese Steel jaw plates, reversible shields, and steel pitman. The driving shaft is equipped with anti-friction bearings. The bronze toggles work in tool-steel seats, and all shafts, bearings, and working parts are of ample proportions.



LABORATORY CRUSHING ROLLS

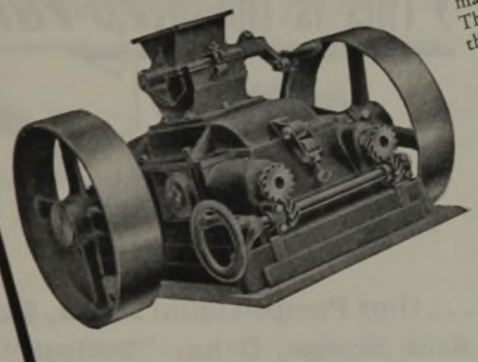
First designed especially for laboratory sampling work, Sturtevant Crushing Rolls are used regularly in many plants where there are limited out-puts.

Adjustments are positive, accurate and automatic. Tires are generally high carbon forgings—very hard and tough. Two sizes are built in practically identical design. Range of output for the 8 × 5 size is from $^1/_2$ in. to 20 mesh — and for the 12 × 12 size from $^3/_4$ in. to 20 mesh. Two stages are necessary for reductions greater than 4 to 1.

LABORATORY SWING-SLEDGE MILLS

Capable of reducing soft, moderately hard and tough or fibrous materials to any degree of fineness between 1 in. and 20 mesh — The Laboratory Swing Sledge Mill is strong, rugged and built on the same principles as full size Swing Sledge Mills.

The full feed opening of 5 × 6 in. may be utilized for soft substances. On harder materials the machine should be fed with pieces not larger than 2 to 3 in. The patented "Open Door" feature permits ready accessibility for cleaning.



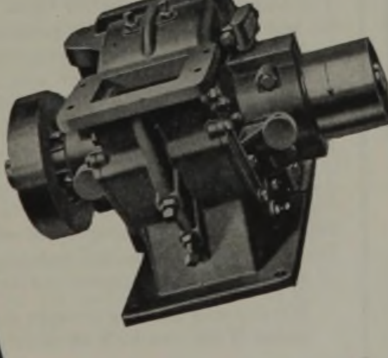
LABORATORY SAMPLE GRINDER

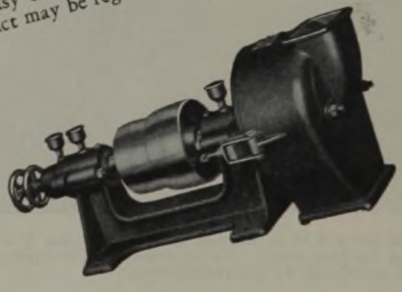
Laboratory Sample Grinders are of the "Open-Door" disc type and are capable of very fine work, producing products as fine as 100 mesh (coarser if desired) when working on dry, friable, soft or moderately hard materials. On many hard rocks and ores, they will operate with somewhat reduced capacities.

Feed may be $^1/_4$" and finer material. Every part is accessible for quick and easy cleaning and by the simple turning of a hand wheel the product may be regulated from 10 to 100 mesh.

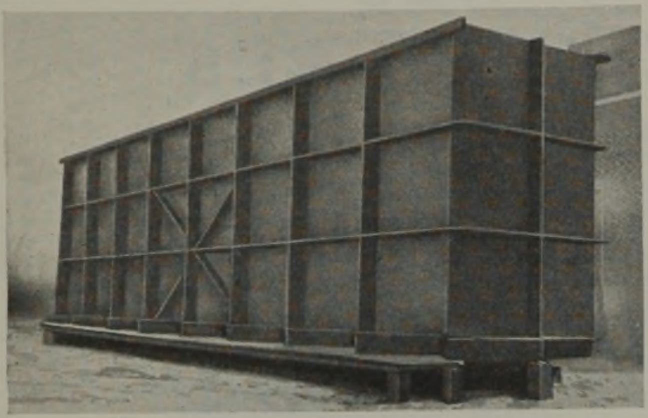
for:

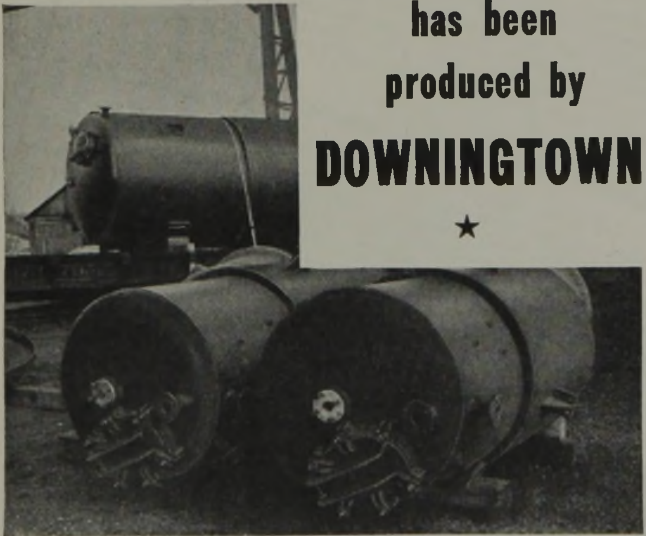
CRUSHING
GRINDING
MILLING
SAMPLING

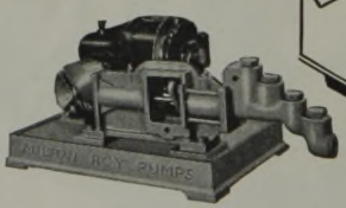


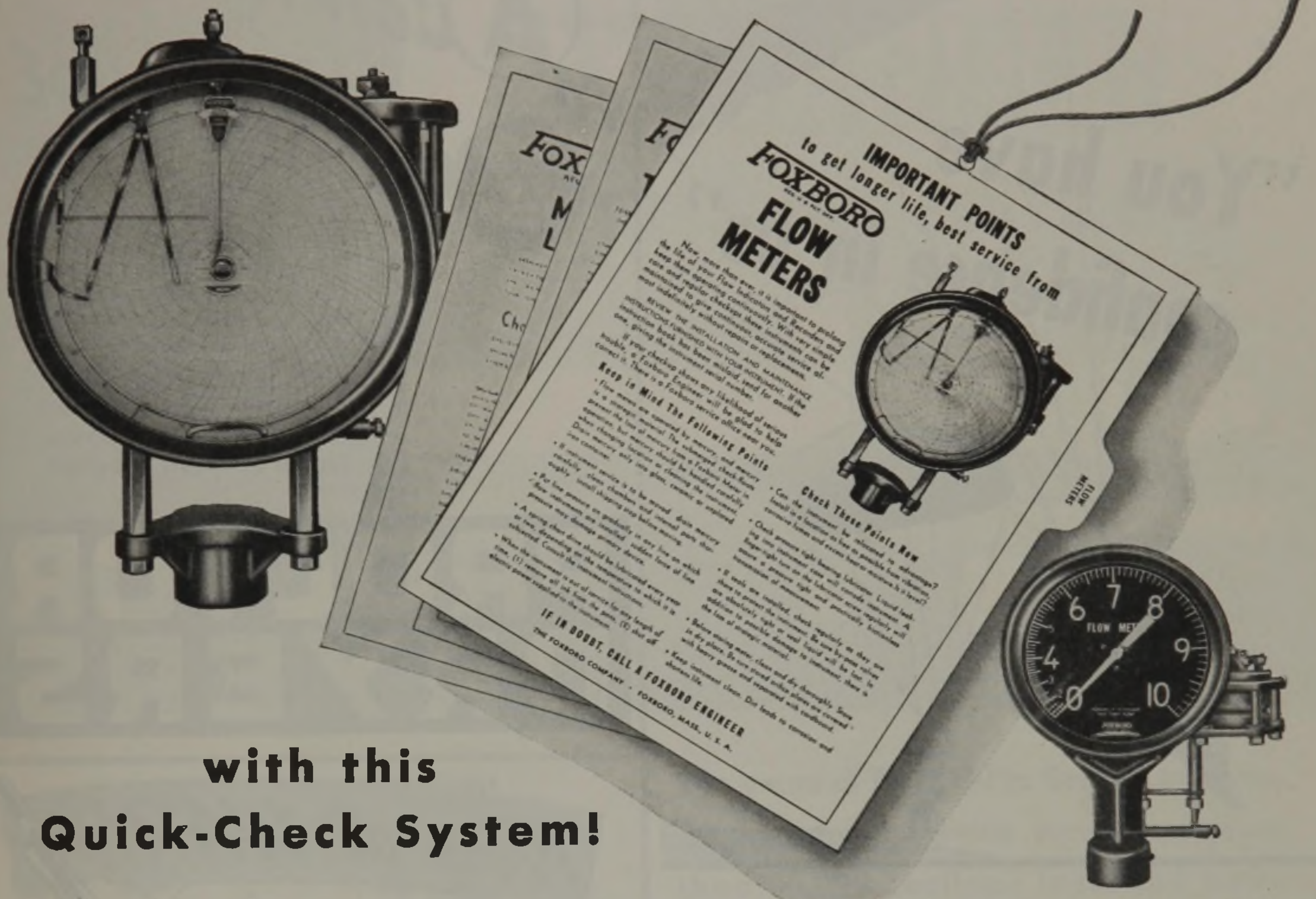


STURTEVANT MILL CO. 2 HARRISON SQUARE **BOSTON, MASS.**






MILTON ROY PUMPS


FOXBORO
IMPORTANT POINTS
to get longer life, best service from
FOXBORO
FLOW METERS
Keep in Mind The Following Points
Check These Points Now
IF IN DOUBT, CALL A FOXBORO ENGINEER
THE FOXBORO COMPANY · FOXBORO, MASS., U. S. A.
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FLOW METER
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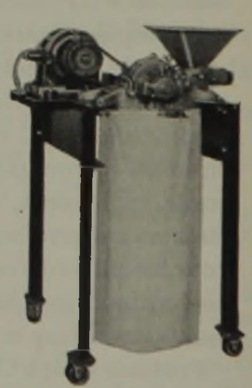
"You have confidence in us"

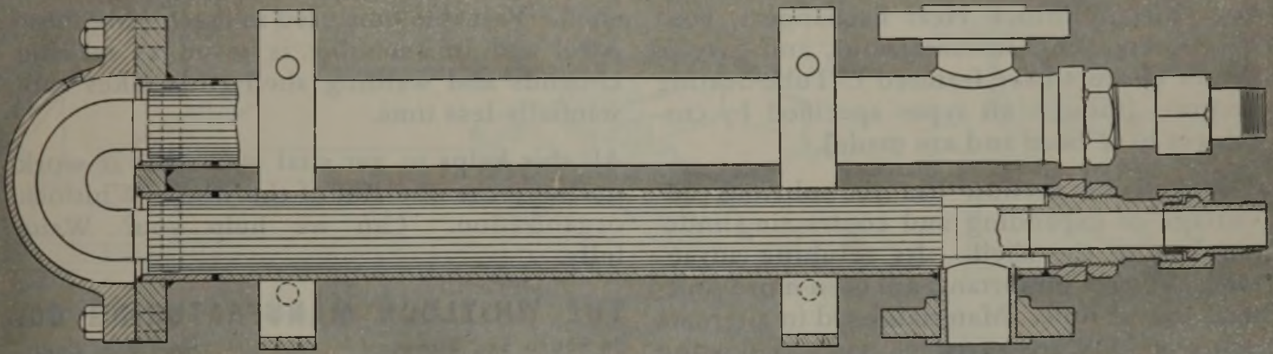

We're at WAR!

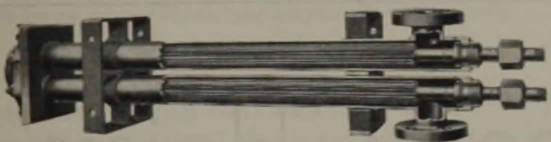



MIKRO-
REG. U. S. PAT. OFF.
PULVERIZER

A UNIVERSAL HEAT EXCHANGER

FOR ALL HEAT TRANSFER SERVICES





THE TWIN G-FIN SECTION . . .

can be used on a greater variety of heat transfer services than any other design . . . can be easily handled without heavy rigging . . . can be applied to changes in service without changing design . . . can be supplied for pressures up to 2000 lb. in shells and 5000 lb in elements, for temperatures up to 900 deg., for dirty liquids and fluids of low heat conductivity . . . can be furnished with elements of standard non-ferrous or ferrous materials . . . has no packed or rolled joints.

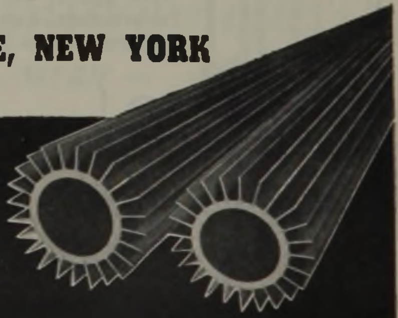
Ten years of Twin G-Fin Section performance and the service records of more than 30,000 sections installed have PROVED the adaptability . . . dependability . . . durability . . . of this design. These standard, interchangeable units are built in a range of types and sizes for any heat transfer requirements, and our expanded manufacturing facilities permit speedy shipments.

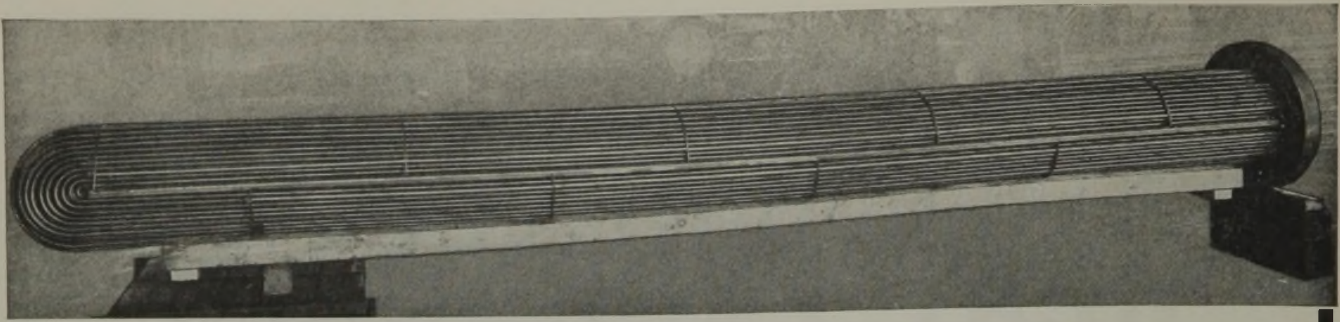
Write for descriptive Bulletin No. 1613.

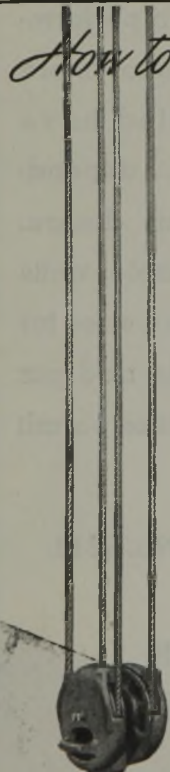
THE GRISCOM-RUSSELL CO. · 285 MADISON AVENUE, NEW YORK

GRISCOM-RUSSELL

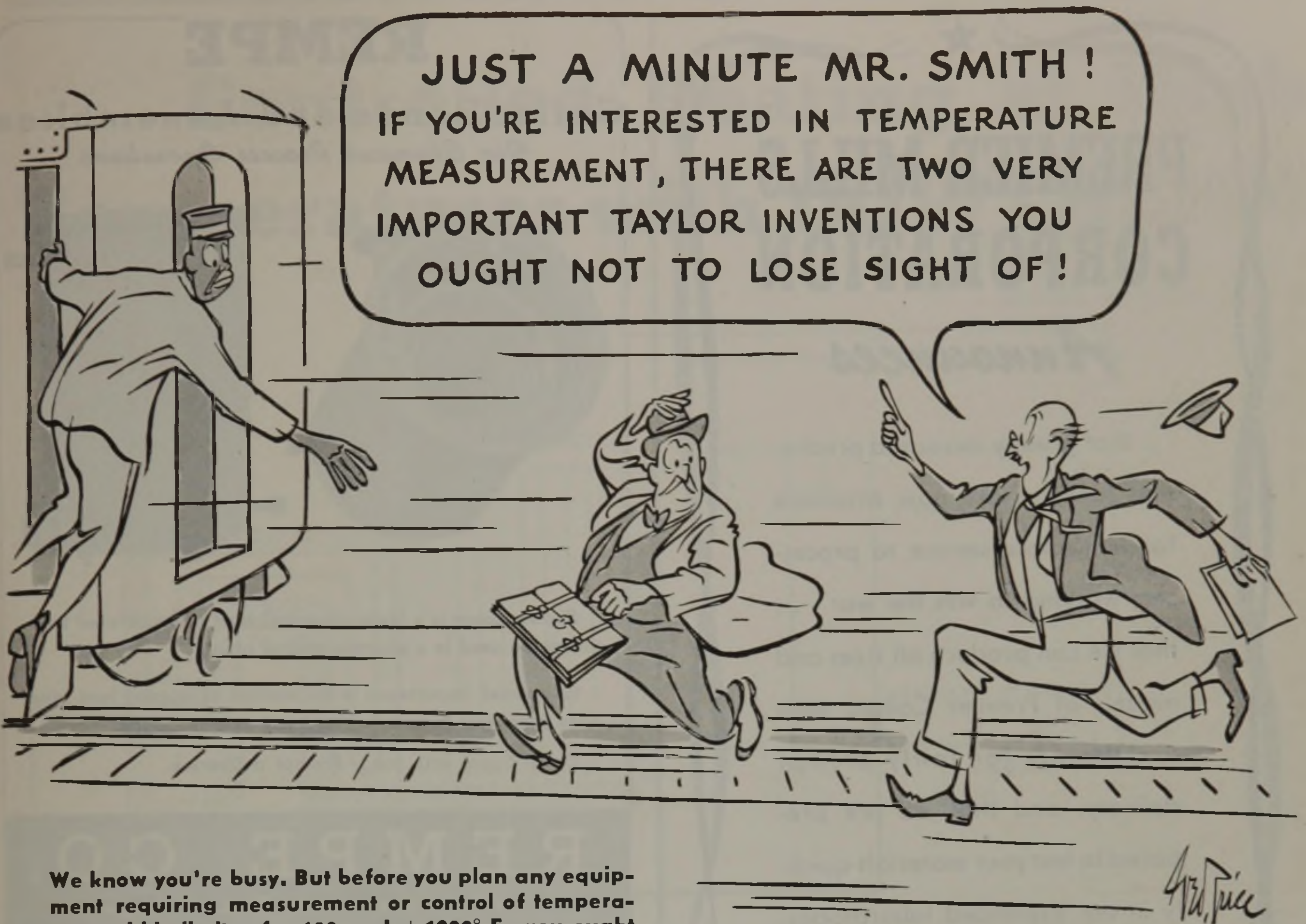
TWIN G-FIN SECTION







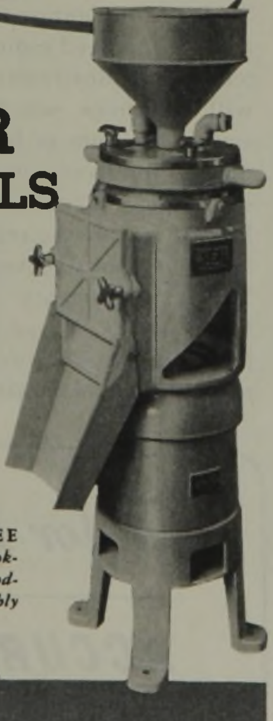

MAINTENANCE & OPERATION OF
SHEPARD NILES
Electric
CRANES & HOISTS


JUST A MINUTE MR. SMITH! IF YOU'RE INTERESTED IN TEMPERATURE MEASUREMENT, THERE ARE TWO VERY IMPORTANT TAYLOR INVENTIONS YOU OUGHT NOT TO LOSE SIGHT OF!

PREMIER MILLS CORPORATION

Announces

. . . that greatly increased production facilities are now available for immediate service to processers working to win the war . . . that we can produce all sizes and models of Premier Colloid Mills and Mixers for fairly prompt delivery, and that we are prepared to test your materials quickly in our expanded laboratories.



PREMIER COLLOID MILLS

For continuous operation without breakdown • Simplest rotor and stator in the world • Adjustments of clearance from .001" to .025" • Economical . . . large output with low power consumption, lower labor cost . . . easy to clean.

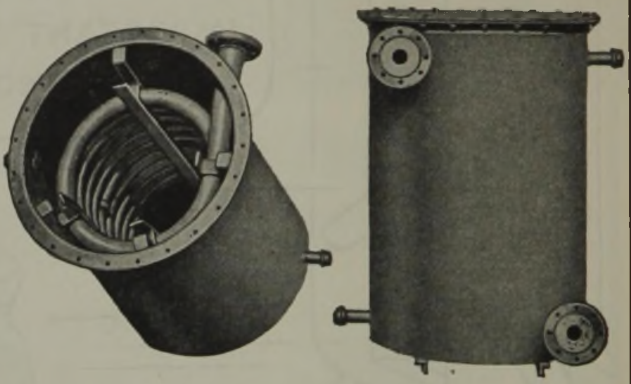
Send for your FREE copy of our new booklet C-2, "Better Products More Profitably Processed".

PREMIER MILL CORP.
218 Genesee Street • Geneva, New York
New York Sales Office: 110 East 42nd Street, New York

REMPE

Coils, Bends and Assemblies

For Chemical Process Operations



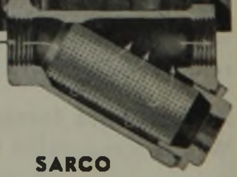
Shown above is a large chemical lead coil and steel tank enclosure used in a pharmaceutical plant.

Of special importance is the method of lapping lead pipe ends over steel flanges to avoid any contamination.

Let us figure with you. Prompt deliveries.

REMPE CO.
342 No. Sacramento Blvd., Chicago

FOR EXPENSIVE EQUIPMENT



SARCO STRAINER

Clean liquids never clogged a pipe line, or caused delicate control and valve mechanisms to slow up.

Put a Sarco strainer in your lines ahead of every trap, valve, pump, burner or lubricator. This insurance costs nothing once installed.

Sizes range from ¼" up to 8" for all commercial pressures with screens for steam, water, oil, brine, ammonia and other fluids.

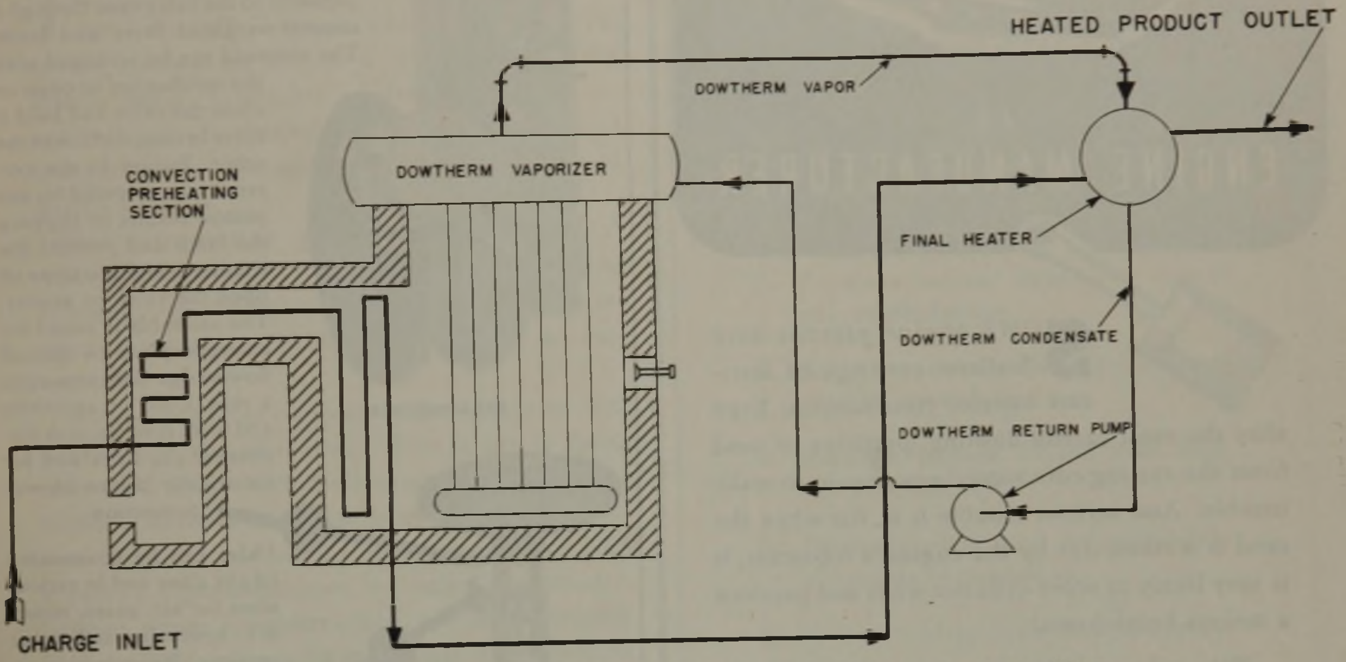
Order an assortment and put them in the line at the points where dirt, scale or other impurities cause shutdowns. They cost little, are easy to install and cleaned in a jiffy by blowing through. Ask for Catalog No. 1200.

161

SARCO SAVES STEAM

SARCO COMPANY, INC.
475 Fifth Avenue, New York, N. Y.
Sarco Canada Ltd., Federal Bldg., Toronto, Ont.

Controlled Heating at High Temperatures with DOWTHERM



Combination process heating featuring Dowtherm sensitive temperature control to 700° F.

An exceptional method for securing high heating efficiency with precise temperature regulation — between 500° and 700° F. — is provided by a system in which heat is furnished from condensation of Dowtherm Vapor. The temperature of the Vapor depends upon its pressure and the rapid release of latent heat provides heating without reduction in temperature. The combination gives that precision control so necessary in many of the new petroleum and synthetic processes.

In a typical commercial application of this type, two phases of heating are employed: Dowtherm Vapor is generated in one cycle, while in another the incoming charge, flowing counter-current to the furnace gases, is preheated on its way to the "final heater." Completion of heating is effected in this "final heater" wherein the charge is raised to processing temperature — flow of Vapor is closely controlled both as to pressure and quantity to insure a constant final temperature of the product. Such a unit affords the most efficient and economic means of effecting the heating functions required.

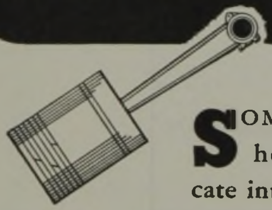
Dowtherm units built by Foster Wheeler, having a total capacity of 480,000,000 Btu per hour, have been contracted for during the past eighteen months. This fact is conclusive of performance satisfaction.

FOSTER WHEELER CORPORATION • 165 BROADWAY, NEW YORK, N. Y.

FOSTER FW WHEELER

How Optics Served

AN ENGINE MANUFACTURER



SOME engine pistons have hollow castings of intricate interior construction. Even after the most careful flushing, particles of sand from the casting core sometimes remain to make trouble. And serious trouble it is, for when the sand is washed out by the engine's lubricant, it is very likely to score cylinder walls and produce a serious breakdown.

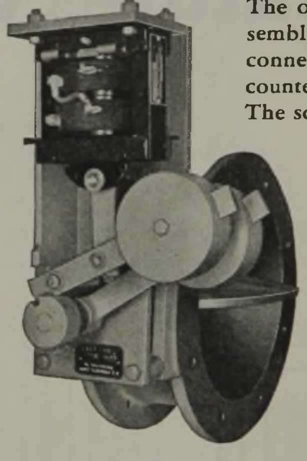
When this problem was presented to Perkin-Elmer engineers, it took just twelve days to design and produce a device which, according to the engine manufacturer, has completely overcome this danger. It is a relatively simple optical instrument, similar to a physician's bronchoscope, enabling inspectors to explore every piston web and pocket. Stray particles of sand are quickly located and removed.

The ways in which the Science of Optics can serve Industry are innumerable. When you have a production problem in which optics might supply a solution, we should be pleased to have you write us. Today our engineering and manufacturing facilities are devoted entirely to the war effort, but if we could help you now, or later on, we should welcome the opportunity.

THE PERKIN-ELMER CORPORATION
GLENBROOK, CONNECTICUT

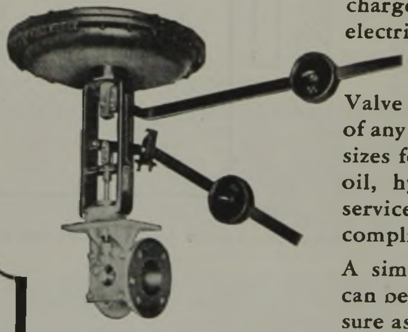
MANUFACTURERS OF PRECISION LENSES • PRISMS and MIRRORS
OPTICAL DESIGN AND CONSULTATION

Emergency FIRE FIGHTERS



PAT. APPLIED FOR

The operating solenoid in this assembly of an R-S Butterfly Valve connects to the valve vane through a counter-weighted lever and latch. The solenoid can be arranged with the mechanism to open or close the valve and hold it there in one position or the other. Failure in the current to the solenoid for any reason results in tripping the latch and permits the counter weight to close or open the valve by gravity. The assembly is suited for emergency use to shut-off flow wedge-tight or to open a vent. Used on sprinkler and foam systems, tank discharge, gas lines and for electrically driven blower protection.

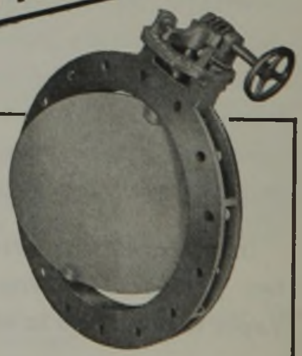


Valve can be constructed of any alloy and in various sizes for air, gases, steam, oil, hydraulic and other services. Resetting is accomplished by hand.

A similar type trip valve can be controlled by pressure as illustrated.

Depend on R-S Butterfly Valves for low-cost, manual or automatic control and wedge-tight shut-off of volume and pressure. Sizes range from 2 to 84 inches.

15 to 900 P. S. I.



R-S QUALITY PRODUCTS SINCE 1908

Wafer (narrow face to face) valves are suitable for pressures up to fifteen pounds. They are light in weight yet high in regulating efficiency.

Write for Catalog No. 10-B.

BUTTERFLY VALVE DIVISION
R-S PRODUCTS CORPORATION
Germantown Ave. & Berkley St. • Philadelphia, Pa.

R-S *Streamlined* BUTTERFLY VALVES

How Industry Will Save $50,000,000 Worth of Solvents Annually

THOUSANDS of pounds of vaporized solvents are lost daily because adequate solvent recovery systems are not used. A solvent recovery system using "Columbia" Activated Carbon can not only prevent this solvent waste, but can speed manufacturing operations and decrease fire and health hazards.

Plants recovering solvents with "Columbia" Activated Carbon . . . those now built and those to be completed shortly . . . have the capacity to recover more than $50,000,000 worth of solvents annually.

Solvent vapor in concentrations as low as 0.25 pounds per thousand cubic feet of air is being recovered, often with efficiencies of 99 per cent or better*. Recovery expense is often less than 0.2 cents a pound and almost never exceeds one cent a pound. Operations can be entirely automatic. Solvent vapor concentrations are automatically kept far below the explosive range—an important safety feature. Solvent recovery plants built sixteen years ago are still operating efficiently and economically.

The solvent recovery system employing "Columbia" Activated Carbon benefits from the research done in America's leading laboratory devoted exclusively to carbon products, and from the experience accumulated by Carbide and Carbon Chemicals Corporation in the manufacture and use of industrial solvents.

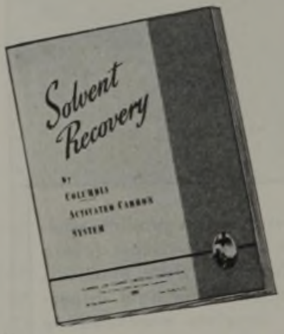
---

*Less than one per cent of the collected solvent vapor is lost. Over-all recoveries of all solvent used vary with the vaporizing operation and the type of vapor-collecting system, but have exceeded 95 per cent.

Seven Advantages of The Solvent Recovery System Using "Columbia" Activated Carbon

1. Recovers all types of volatile solvents
2. Recovers solvent vapors in almost any concentration
3. Recovers solvents efficiently in presence of water vapor
4. Recovers solvent vapors with high overall efficiency
5. Recovery plant may be completely automatic in operation
6. Recovery plant investment moderate
7. Recovery expense low

Send For This Book!



This 32-page book tells more about the solvent recovery system using "Columbia" activated carbon and its profitable applications. When you write for a copy, tell us the names and quantities of solvents you vaporize and how you collect the vapors, so that we can help you determine what you can save. No obligation, of course.

The word "Columbia" is a registered trade-mark of Carbide and Carbon Chemicals Corporation.

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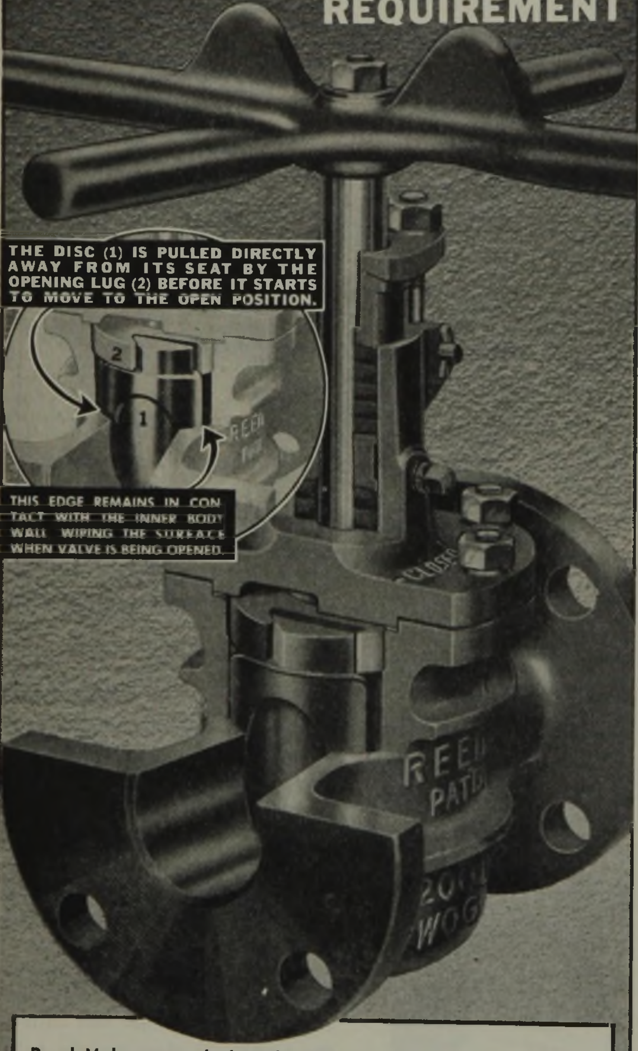
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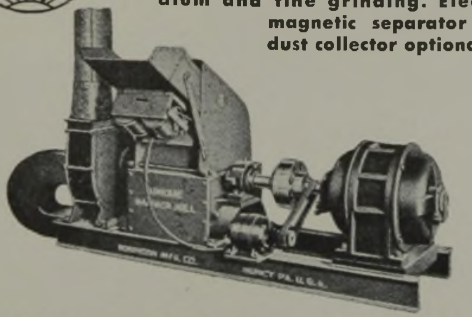

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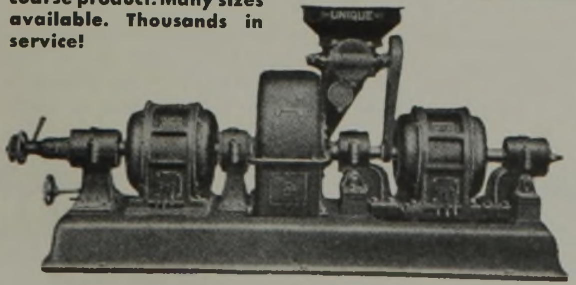

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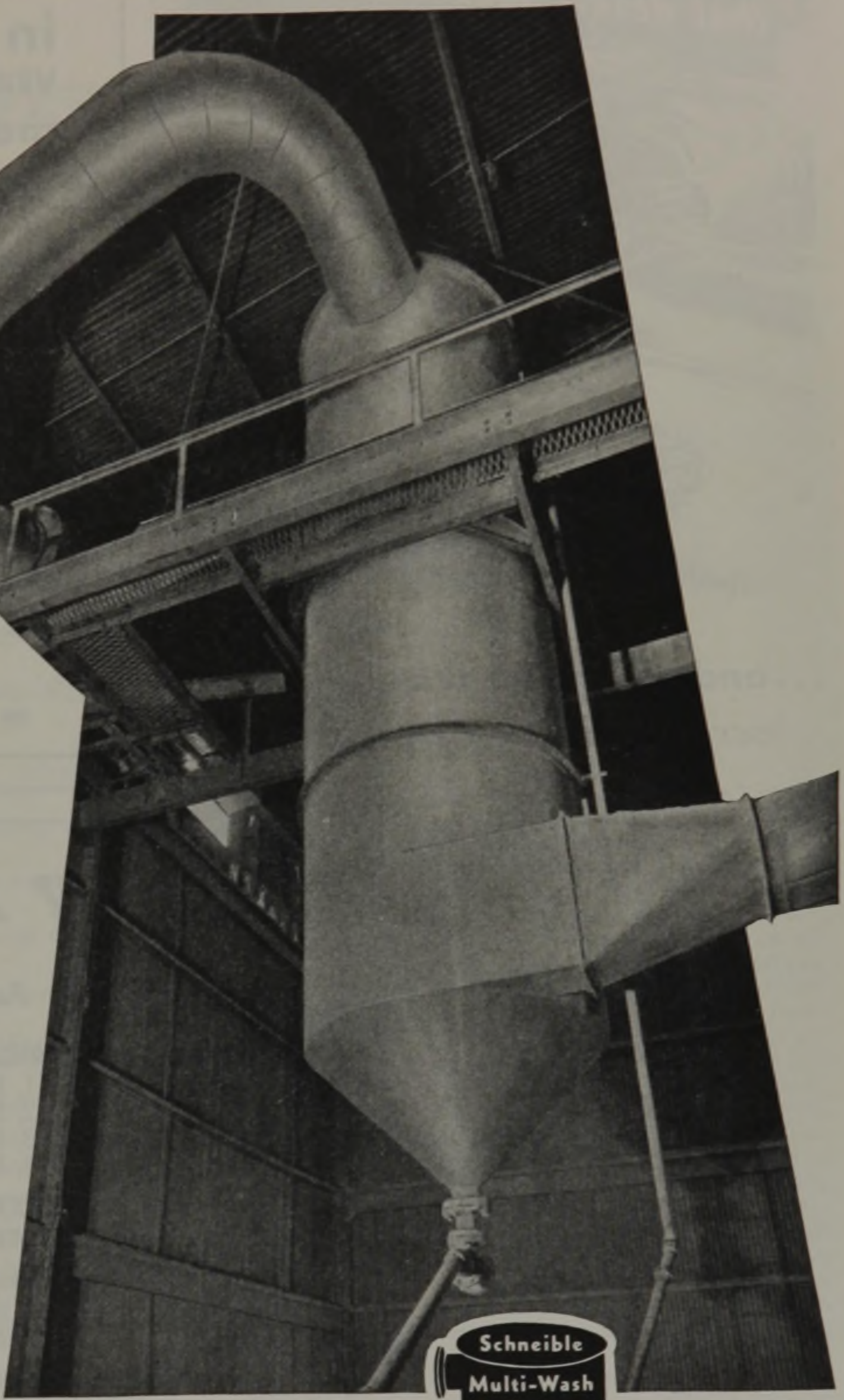

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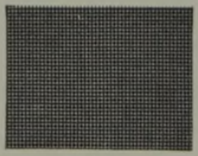

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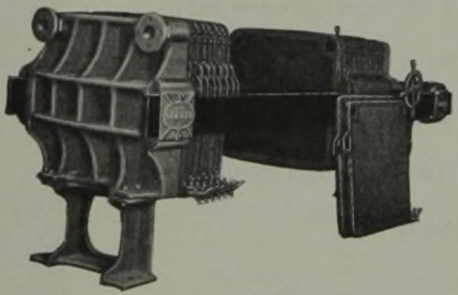

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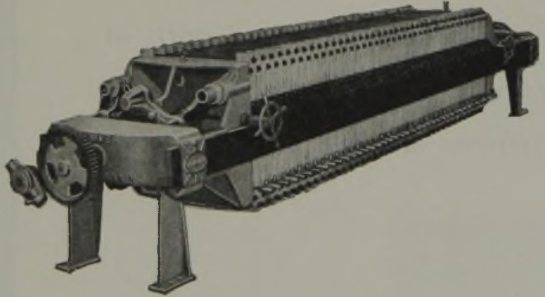

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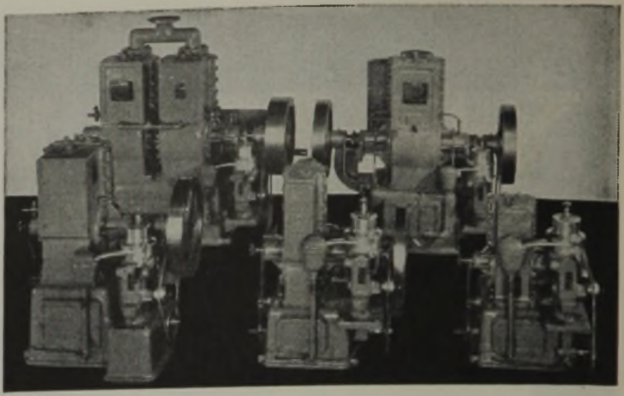

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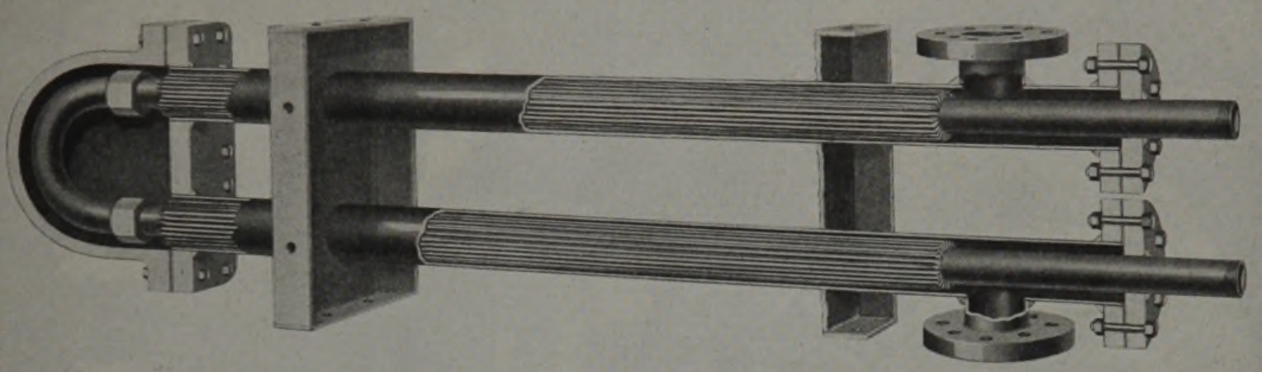

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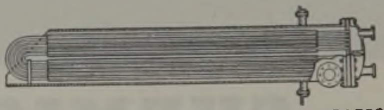

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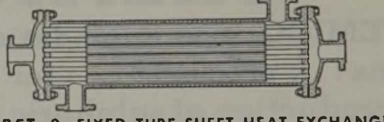

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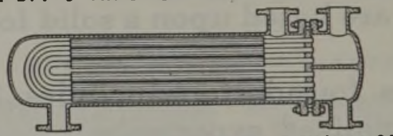

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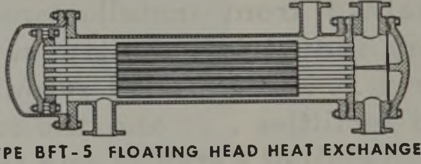

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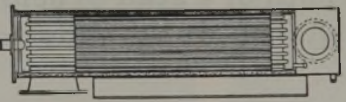

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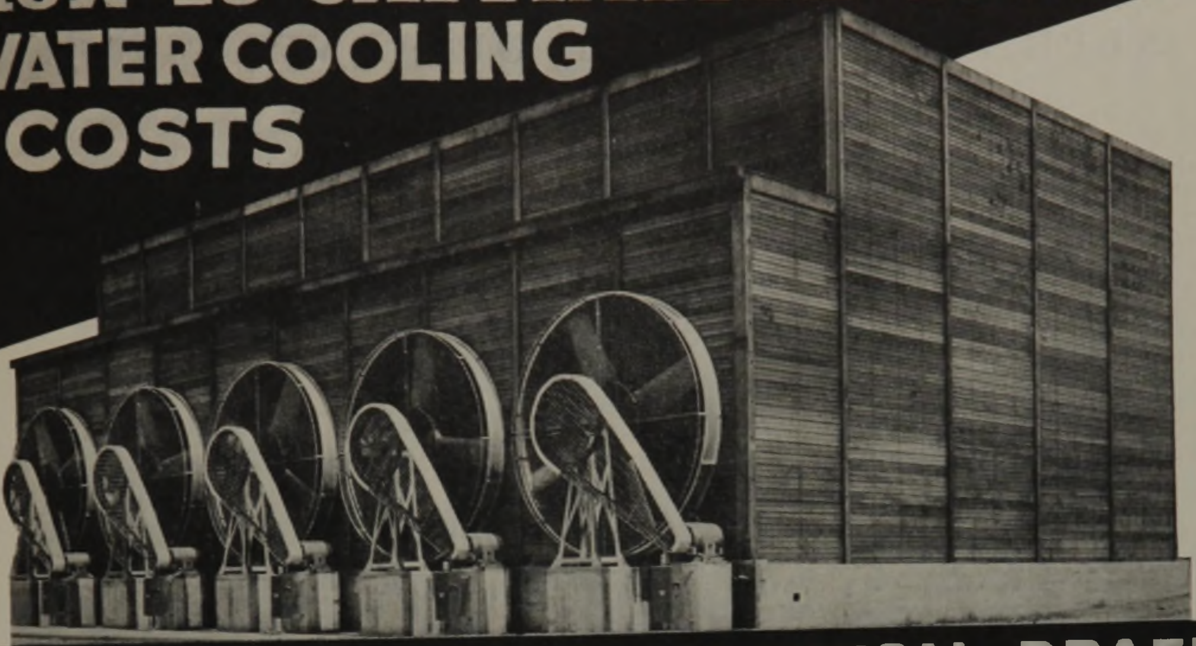
How To CAPITALIZE Your WATER COOLING COSTS



AND KNOW WHOSE MECHANICAL DRAFT EQUIPMENT WILL SAVE YOU MOST . . .

Why Pritchard Towers Save You Money

1. Low Pumping Head. Closed pipe water distribution through gravity sprinklers cuts down frictional resistance; saves pump power for lifting; sometimes even permits building higher towers without waste.

2. Liberal Size and Rating. Any "skimping" on capacity must be made up by an extra load on fans or tower efficiency will suffer. Pritchard towers are sized and rated to permit low air velocities and consequent lighter fan loads.

3. High Efficiency, Light Weight, Non-Corrosive Monel Fans. Pritchard fans are the heart of Pritchard tower efficiency and economy. Their superior design and construction saves tremendous amounts of horse power over a period of years. Blades have a special twist and taper that gives a steady, uniform air flow through the entire fan opening.

The use of non-corrosive sheet monel over a light, strong framework cuts weight to half that of cast alloy—ends corrosion and pitting troubles. Larger blades, and often fewer of them, move the required volume of air with less fan speed and less fan power. Pritchard fan drive design and fan housing design, particularly in induced draft towers, contribute further to fan efficiency and horsepower economy.

Further details on request. Write for them.

On the basis of 1¢ per kilowat hour, 24 hours per day, 250 days per year, the cost of operating a mechanical draft tower for 5 years is $300 per horsepower. Add to this the cost of your tower and you have your total 5-year cost, exclusive of upkeep.

Pritchard welcomes and urges this method of purchase because almost invariably Pritchard towers capitalize out at lower cost.

There are several reasons why—the most important of which are described in the column to the left. Read these reasons carefully. File them for future reference if you will. And be sure to get definite cost capitalization figures from Pritchard—and from any others you may choose—on the next mechanical draft tower you buy.

J. F. PRITCHARD and COMPANY
FIDELITY BUILDING KANSAS CITY, MO.
Branch Offices in Tulsa, Okla.; Houston, Texas; Atlanta, Ga.
Chicago, Ill.; Pittsburgh, Pa.; New York City

PRITCHARD

Atmospheric and Mechanical Draft

WATER COOLING TOWERS

ALPHABETICAL LIST OF ADVERTISERS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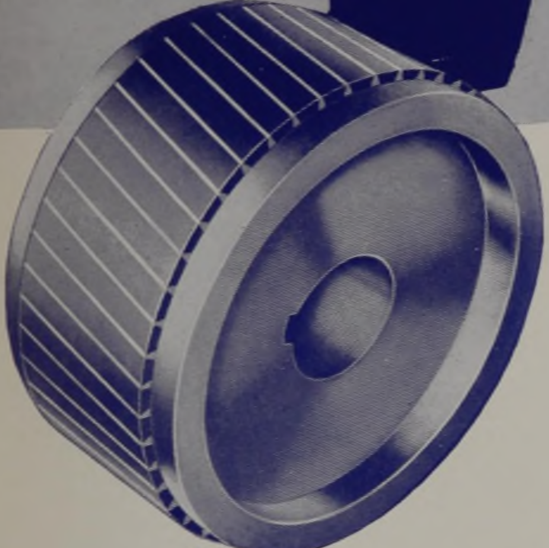
When You Can't Buy 'em *BIG*—Buy 'em *GOOD!*



REALLY, it's no hardship when you have to buy smaller motors. *You save money.* But remember, when you can't buy 'em big—buy 'em good.

Now that you cannot depend on oversize to take your motors through tough service—you must depend on quality.

That is why you should investigate Fairbanks-Morse Motors with *Copperspun* Rotors.

The winding of the *Copperspun* Rotor is centrifugally cast of COPPER in one piece. It provides electrical and thermal characteristics that give this motor the stamina to stand up under the most severe service without mechanical failure. You can operate a Fairbanks-Morse Motor with *Copperspun* Rotor at its full rated capacity continuously and indefinitely without fear of damage from overloading.

Fairbanks, Morse & Co., 600 S. Michigan Ave., Chicago, Ill.

Copperspun

FAIRBANKS-MORSE

Motors

DIESEL ENGINES
PUMPS
ELECTRICAL MACHINERY
SCALES
MOTORS

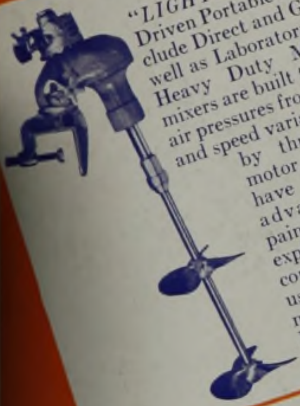
WATER SYSTEMS
FARM EQUIPMENT
STOKERS
AIR CONDITIONERS
RAILROAD EQUIPMENT

NEW APPLICATIONS AND DEV

LIGHTNIN AGITATORS

PLAY AN IMPORTANT PART IN THESE WAR INDUSTRIES

Heat Treating (Shells and Armor Plate)
Synthetic Rubber
Aviation Gasoline
Gas Absorption and Dispersion
Detinning
Magnesium
Alcohol Conversion
Chemical Plant Expansion
Explosives
Moulding Plastic Impregnated Plywood Parts



AIR DRIVEN MIXERS

"*LIGHTNIN*" line of Air Driven Portable Mixers now include Direct and Gear Drive as well as Laboratory models and Heavy Duty Mixers. These mixers are built to operate with air pressures from 60 to 120 lbs. and speed variation is obtained by throttling the air motor. Air driven mixers have a decided safety advantage in mixing paints, chemicals, high explosives and alcoholic compounds. Even when used in heavy liquids air motors will not stall. Models up to 1 H.P. are available.

TURBINE TYPE VERTICAL MIXERS

A new line of heavy-duty, slow speed Turbine Type Vertical Mixers permit the use of a longer shaft. Available in all speeds below 200 R.P.M. Installation is extremely simple. Ready to install on standard I.P.S. nozzles or special drilling. Furnished with many special types of impellers, laboratory and field-proven for superiority in liquid displacement, gas absorption and heat exchange and general agitation.

V-BELT DRIVE

V-Belt drive for top-entering propeller-type mixers for use over open tanks, closed tanks, pressure or vacuum vessels, or for attachment to standard size nozzles. Speed of a unit can be changed by changing the sheave and pulleys or a variable speed pulley can be provided on the motor. Drive can be furnished with electrically conducting belts to do away with danger from static, or with oil resisting belts, where necessary. The motor for the drive can be standard, semi-enclosed, drip-proof, or totally enclosed, air jacketed or explosion proof. Available in sizes from 1 t
25 H. P.

SPECIAL DRIVES

"*LIGHTNIN'S*" Right Angle Drive is designed to save critical materials, cut down manufacturing man-hours and speed up deliveries. It permits the mounting of motors at sufficient distances from the agitator when close proximity would create a hazard. Head room requirements are reduced to a minimum. Complete range of sizes from 1 to 50 H.P. are available. Information on other special drives available on request.

MIXER DRIVE WITH FAN

"*LIGHTNIN'S*" New Mixer Drive with fan is especially designed for mixing hot gases or circulating air or gases over coils for increasing rate of heat exchange or for use in maintaining uniform temperature. This new Mixer Drive further increases the range of application of "*LIGHTNIN'S*" Equipment.

CHAIN DRIVE SIDE-ENTERING MIXERS

Here is another new
"*LIGHTNIN*"
Mixer design—the
chain drive applied to side entering mixers
Construction permits use out-of-doors. Par
of the guard has been removed in this illu
tration to show the chain drive which eli
nates static hazards present in V belt dri
Complete range of sizes from 1 to 25 I
are available.

"*LIGHTNIN*" Mixers are constantly being improved and redesigned to meet your specific requirements under present war production conditions. They proved in actual service that they cut power consumption, conserve vital materials, increase product uniformity and speed up production.

Each product here illustrated is a new development. You can rest assured that 1943 will reveal the same consistent effort to help you solve your mixing problems.

MIXING EQUIPMENT CO., Inc.

1062 GARSON AVENUE, ROCHESTER, N. Y.

MIXING EQUIPMENT COMPANY, INC.
1062 Garson Ave., Rochester, N. Y.

Please send me:

- ....Catalog B-68—Top Entering Mixers
- ....Catalog B-69—Air Driven Mixers
- ....Catalog B-65—Portable (Clamp-on) M
- ....Catalog B-66—Side Entering Mixers
- ....Catalog B-67—Laboratory Mixers
- ....Mi-11—MIXING OPERATIONS I SHEET: The basis for a time-s recommendation
- ....Complete Catalog Binder for Executive Engineers in Authority

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