INDUSTRIAL AND ENGINEERING *Chemistry*

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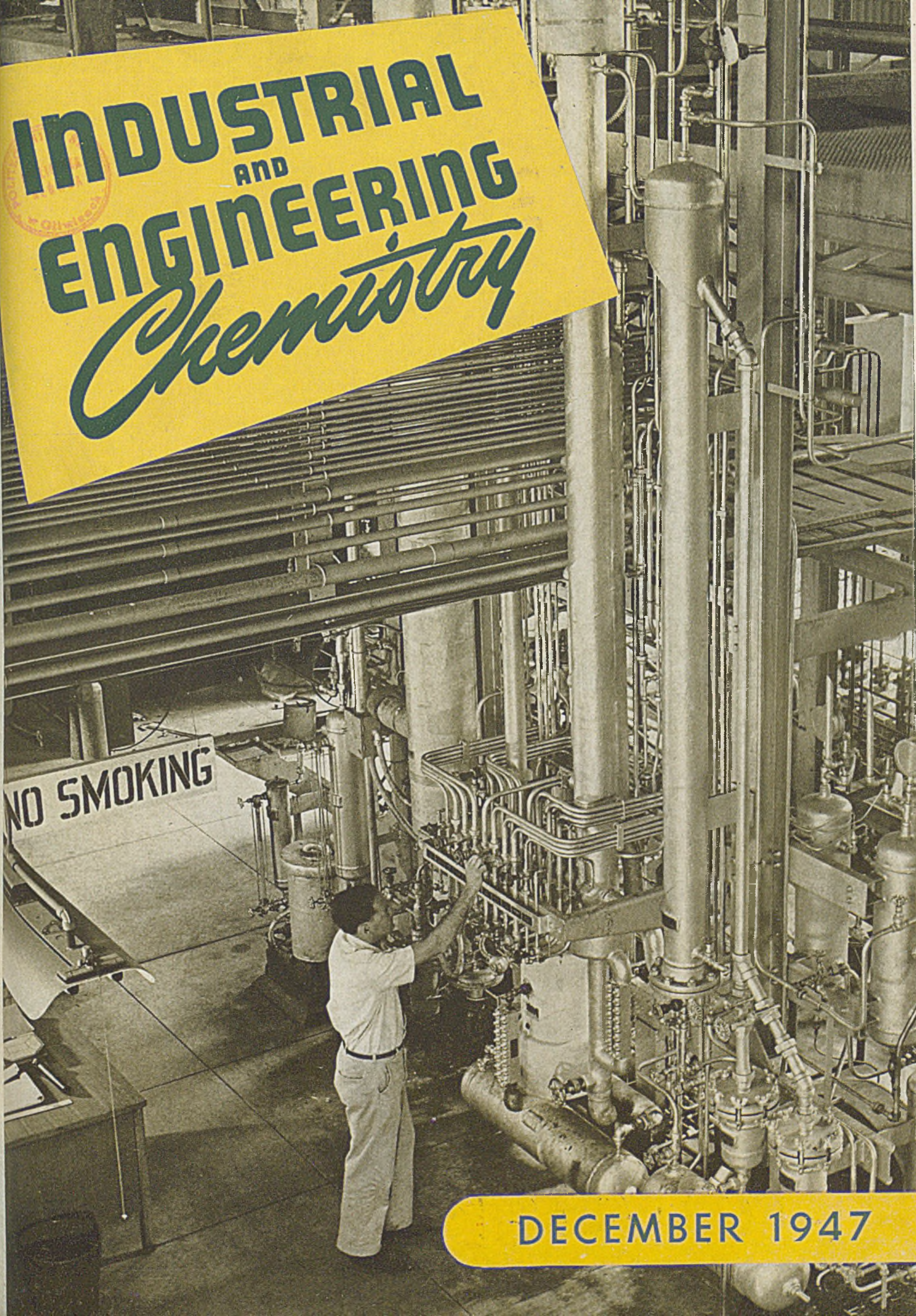

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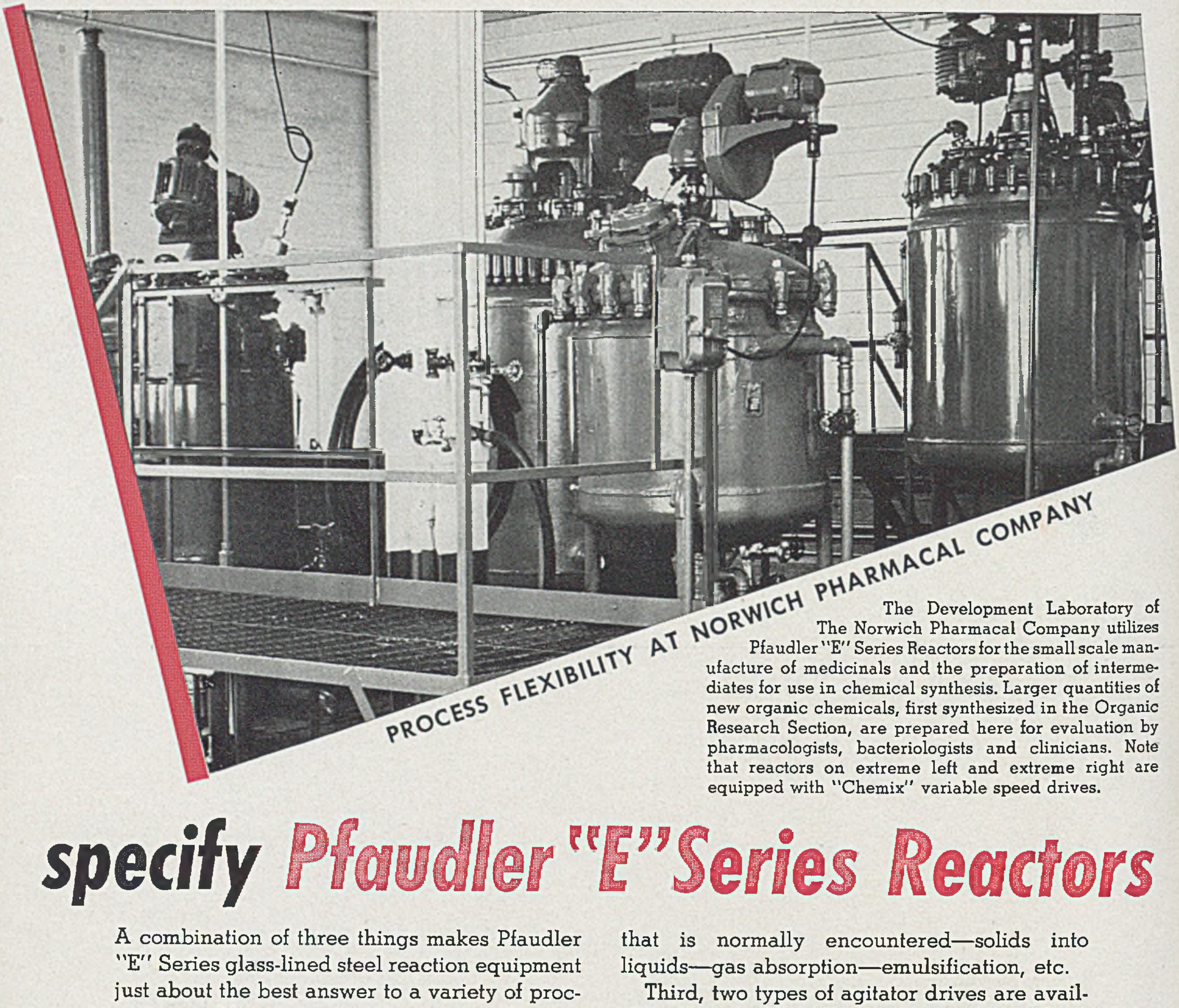

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Cover view is of a catalyst testing pilot plant in a Los Angeles refinery. For another petroleum pilot plant, see page 1685. Photo courtesy Union Oil Company of California, Los Angeles

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INDUSTRIAL and ENGINEERING CHEMISTRY....

Reports

ON THE CHEMICAL WORLD TODAY

REDISCOVERING THE BIG RING

The frequency of reference to benzene derivatives has impressed on those even distantly connected with chemistry the importance of this six-carbon aromatic ring. An entire field—aromatic chemistry—has been built around this one nucleus and its combinations. It is interesting to compare the field of aliphatic chemistry, wherein the discovery of the value of a chain of given length leads to the investigation of its homologs, built up by the addition of units, in this case CH_2 groups. Not so with the aromatic nuclei, the unique character of which is credited to the existence of conjugated, or alternating, double bonds in a carbon ring. The four-carbon ring, next possible aromatic homolog below benzene, has not been made, whereas the next higher or eight-membered ring, synthesized only once until recently, has been a curiosity. Today the picture is changed. Cyclo-octatetraene, the ring of eight carbons with four double bonds, has been made by a method with commercial possibilities and is attracting an interest which has lifted it from the laboratory curiosity class.

It has been found that cyclo-octatetraene (COT) can be made from acetylene. As a result the preparation of research quantities has led to the demonstration of its nonaromatic character and reactivity, and not only contributed an advance in theoretical and classical knowledge but opened the possibility, for the first time, that industrial organic chemistry may get into the field of eight-membered rings on a large scale. Diene addition products from COT may be valuable in lacquers and related products. Caprylic lactam and suberic acid, two compounds of interest in the preparation of polyamides, can be made from it, and conceivable possibilities in synthetic rubbers and other polymers are thought-provoking. Suggestions have been made for the use of diesters as plasticizers. COT could be expected to form the basis for alkaloid synthesis, of value in the field of drugs. Even in considerable dilution COT absorbs ultraviolet rays; thus it is of interest in light-stabilization of plastics and surface materials as well as in protective cosmetics. This and other characteristics suggest dyestuffs.

COT achieved classical status after its synthesis by Willstätter and his observations relative to the classical problem of aromaticity.

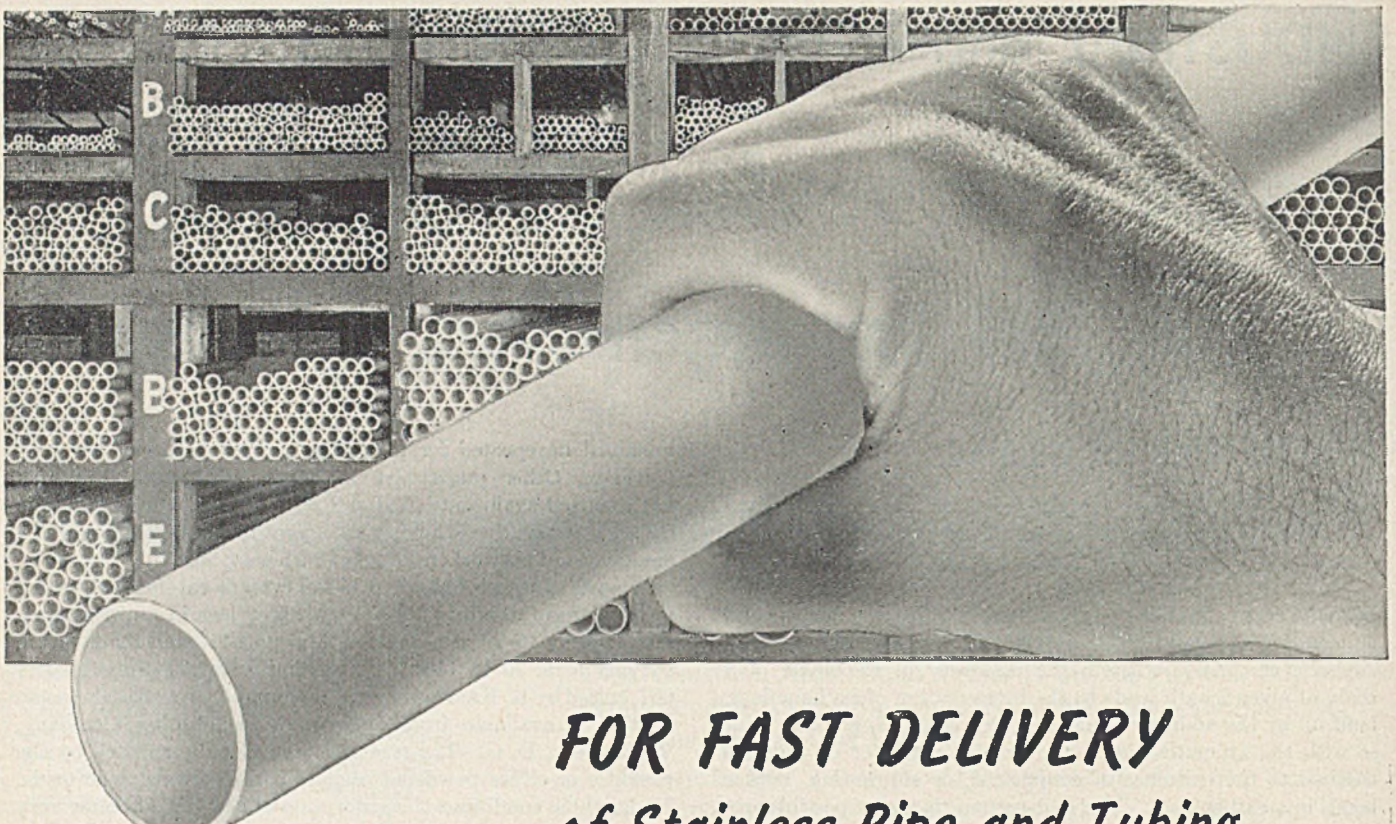
He reported in 1911 that the eight-carbon ring containing four conjugated double bonds did not exhibit the diminished unsaturation characteristic of benzene and its difference in reaction from simple alkenes, but was aliphatic. Much attention was drawn to this work, and some doubts were expressed that Willstätter's compound was of the structure claimed. However, his tedious synthesis, starting with pseudopelletierine, a pomegranate alkaloid—which was converted, through a large number of steps, into COT in yields of 3–4 grams per 100 kg. of pomegranate tree bark—remained unrepeated for thirty-five years in spite of the controversy. Other preparative attempts failed, and COT was not reported again until Walter Reppe of I. G. Farbenindustrie included its synthesis among the many remarkable accomplishments he and his workers wrought with acetylene.

Reppe's synthesis brought a nickel cyanide catalyst suspended in tetrahydrofuran into contact with acetylene in a nitrogen atmosphere at 15–20 atmospheres total pressure and temperature varying from 70 to 150° C., according to FIAT Final Report 967, edited by K. Kammermeyer; a completely translated version of this is available from the Hobart Publishing Company, Washington, D. C. The reaction was markedly speeded by the presence of either powdered calcium carbide or ethylene oxide. Under these conditions the absorption of acetylene became very slow after 50–60 hours. The reaction products consisted of cuprene, benzene, COT, and C_{10} and C_{12} hydrocarbons, which accounted for about 90% of the acetylene added. In general the formation of benzene was 10–15% of the amount of COT, while about an equal amount of resinous material and one third or less that quantity of cuprene were formed. The yields and proportions varied, of course, with conditions. This reaction was carried out in an autoclave. Attempts to develop a continuous process using either a tower with packing wet by the liquid, over which the gas passed, or a flooded catalyst bed through which the gas bubbled, gave reaction, but neither was so satisfactory as the autoclave method. Either the catalyst plugged or very little COT was formed.

The reporting of this work out of Germany revived the interest in COT and also provided a check on the earlier claims. As substantiation of Willstätter's report, Cope and Overberger of M.I.T. have repeated the synthesis, starting with pseudopelletierine prepared by the combination

(Continued on page 8 A)

An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries



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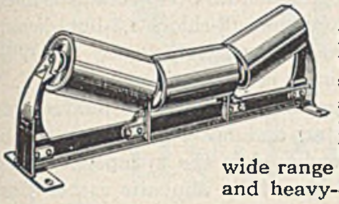

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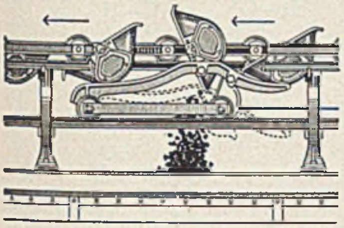

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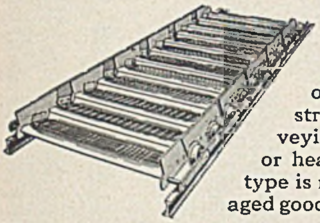

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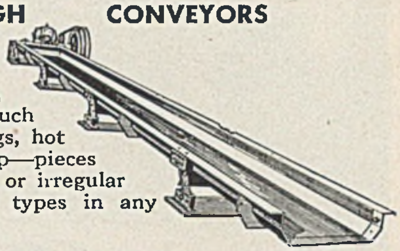

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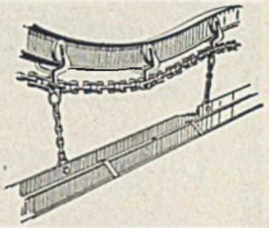

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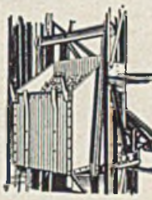

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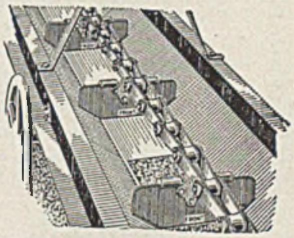

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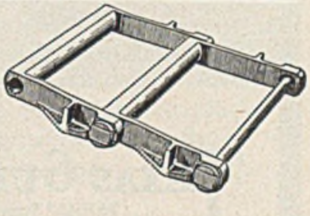

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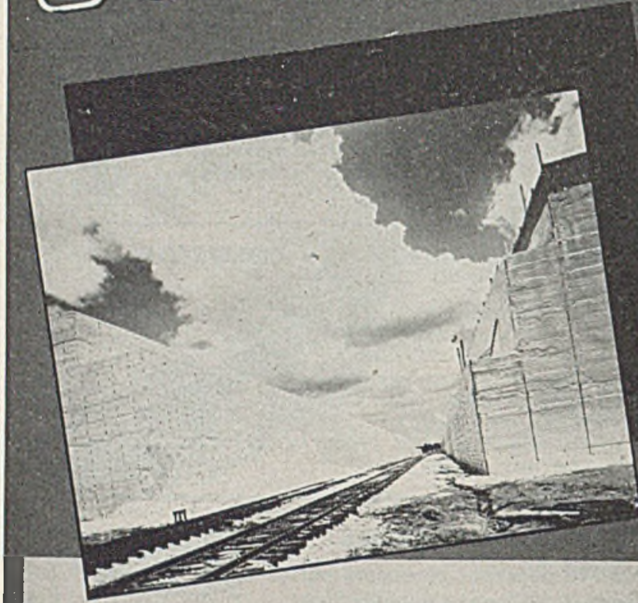

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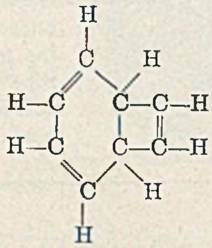
of glutaraldehyde with methylamine hydrochloride and acetone dicarboxylic acid, and proceeding with the original reactions. Ample evidence indicated identity of this product with that from acetylene, and its variation in melting point from that of the original COT was attributed to the fact that the latter was not purified by fractional distillation.

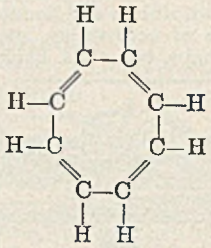
In addition, Cope and Bailey prepared 1,5-cyclo-octadiene more simply from the dimer of chloroprene (2-chloro-1,3-butadiene), dibrominated this, and proceeded from that point by the Willstätter reactions to COT. Work is being continued at M.I.T.

Examination of COT by Reppe indicated that his product was the same as that of Willstätter, and has also produced substantial evidence that the compound is the symmetrical ring 1,3,5,7-cyclo-octatetraene and that it is aliphatic rather than aromatic in nature. However, it was also shown that it can react to yield derivatives of three fundamental structure types:

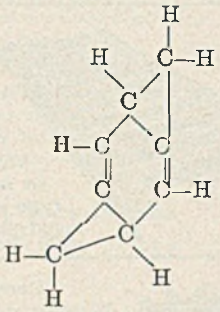
I. 1,3,5,7-Cyclo-octatetraene



II. Bicyclo[0,2,4]-2,4,7-octatriene



III. 1,2,4,5-Dimethylene-2,5-cyclohexadiene

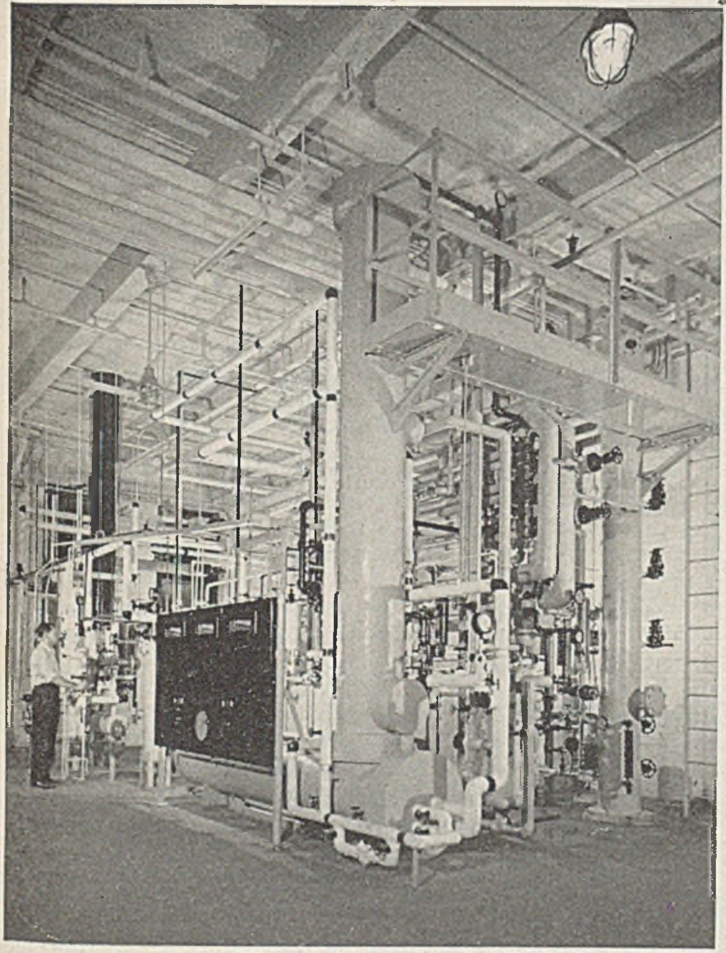


Extensive thermochemical studies are in progress at the National Bureau of Standards under Rossini, Prosen, and Johnson, who have recently reported measurements of heats of formation and combustion and have concluded COT to be less stable than styrene.

Controversy over the spatial arrangement of the atoms within COT is not yet settled to the satisfaction of all investigators. Two forms, a "tub" and a "crown," are now being supported. It has even been suggested that two forms may exist. Work relative to this question has been reported from England and Norway, as well as from this country.

(*Continued on page 10 A*)

Champion hydrogen plant...



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Reppe has reported reactions effected through each of the three forms. Suberic acid is made from reactions of compound I. Its catalytic treatment with water gas gives cyclo-octyl carbinol, which can be oxidized to the eight-carbon, straight-chain dicarboxylic acid. Easy hydrogenation of I yields cyclo-octene which can be oxidized to suberic acid, or the ring can be converted, by the use of perbenzoic acid, to the oxide, reduced with hydrogen to cyclo-octanol, then oxidized to the acid. On treatment with sulfuric acid, the oxide is aromatized to yield phenylacetaldehyde quantitatively. The latter compound can also be prepared by the treatment of COT with mercuric sulfate and water, the reaction presumably proceeding through form II. The diene synthesis, or addition reaction with compounds such as maleic anhydride or quinone, apparently proceeds through stage II. Examples of reactions in which form III is an intermediate are the oxidations with hypochlorous acid or chromic oxide to yield terephthalic aldehyde or acid, respectively.

From cyclo-octene and glacial acetic acid can be made cyclo-octyl acetate, convertible stepwise to the corresponding octanol, ketone, oxime, and caprylic lactam. Treatment of I with sodium or lithium followed by carbon dioxide effects the addition of two carboxyl groups across one of the pairs of conjugated double bonds. Alcohol treatment yields the diester.

A number of other reactions and supporting evidence for these conclusions are described in the FIAT report.

Another center of extensive research on COT is the Polytechnic Institute of Brooklyn where Mark, Bergmann, Fankuchen, Klotz, and Overberger are studying preparation, dimerization and polymerization, structure, and higher homologs.

The investigation in Germany which began in 1940 and was stopped in 1944 was still in the research stage, and Kammermeyer states that little patent protection exists in this country on the work. Large-scale developments may grow from the improvement of the synthesis described here, which lies in a comparatively new field, into a more economic process. Work on COT is now proceeding in a number of industrial laboratories but few, if any, are willing to talk about their investigations at the present time.

Benzene remains unique in its aromaticity, but its quadruply unsaturated eight-carbon cousin is promising real achievement in its own right. R.L.K.

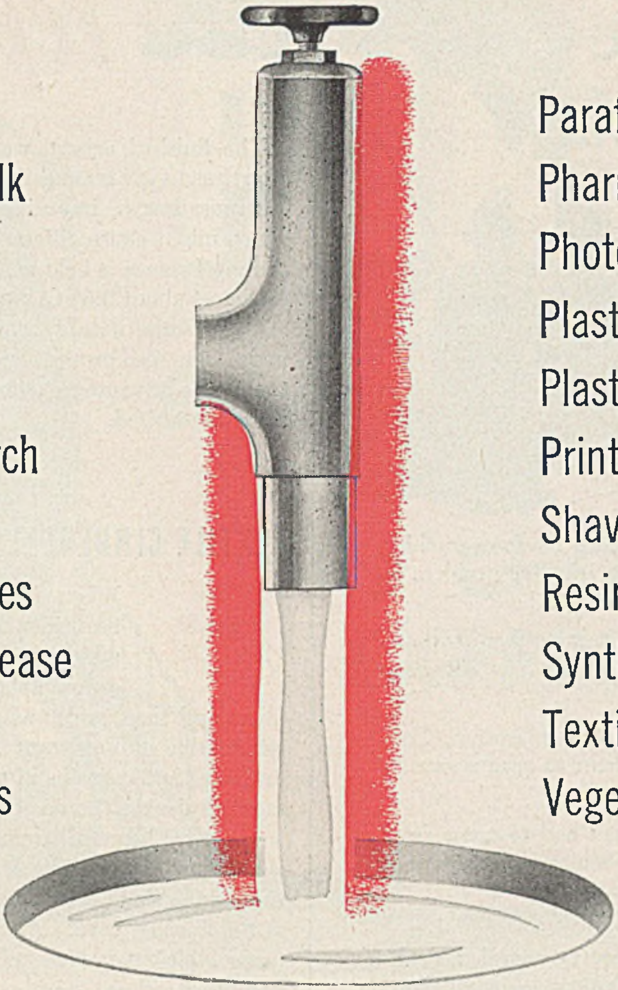
CYLINDER SALT

Crystalline sodium chloride is a common contributor to every meal, but the salt crystals produced at the Oppau-Ludwigshafen plant of I. G. Farbenindustrie during the war were intended for bigger things than increasing the palatability factor of your morning eggs. In fact the 30-cm.-diameter crystals produced by Herr Ingenieur Korber undoubtedly would obliterate the eggs, bacon, breakfast plate, and perhaps the table as well.

The crystals were grown for use in infrared spectrometer optical systems by suspending a cylindrical seed crystal in a sodium chloride melt held at a temperature around 870° C. The seed was held in a water-cooled chuck which rotated once every 2 hours and rose 1 mm. per hour. The diameter of the crystal was limited to about 30 cm. by the size of the melting crucible, but the length was determined only by the volume of the melt and the stroke of chuck.

(*Continued on page 12 A*)

- Chemicals
- Condensed Milk
- Drying Oils
- Dyestuffs
- Fruit Juices
- Industrial Starch
- Lard
- Leather Finishes
- Lubricating Grease
- Margarine
- Paper Coatings



- Paraffin Wax
- Pharmaceuticals
- Photo Emulsions
- Plastic Cream
- Plastics
- Printing Ink
- Shaving Cream
- Resins
- Synthetics
- Textile Sizing
- Vegetable Shortening

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Let it Flow!

PRODUCTION literally flows along for new heights of speed, quality, and economy when you process things in the above category with VOTATOR apparatus.

The material is pumped in at one end, comes out the other a finished product of proper temperature, texture, and consistency.

Incorporating a highly efficient heat transfer mechanism, VOTATOR apparatus heats and/or cools, mixes and plasticizes, as the material flows through. The operation takes seconds. Remarkable volume is achieved in relation to use of floor space, manpower, heat transfer medium.

The continuous nature of the VOTATOR operation cuts cost. And its closed, controlled character makes for uniform quality. Time and temperature cycles, viscosity, aeration, and other factors can be precisely regulated. "Weather" problems are eliminated. Contamination and spoilage are prevented.

Do you process a liquid or viscous material? Tell us what it is. We may be able to tell you how to streamline the job.

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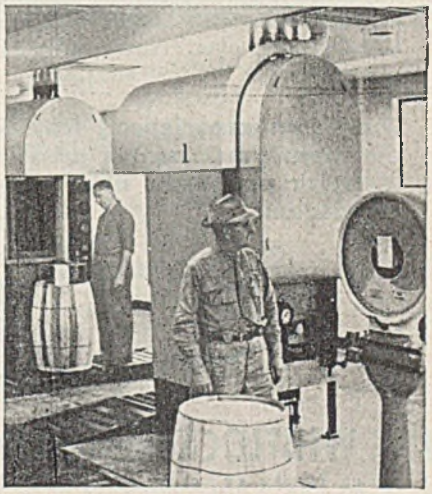

One of many variations of VOTATOR apparatus, for paraffin wax in this case. Four of these units at Continental Oil process more than double the volume formerly achieved with open-type equipment occupying about the same floor space. Liquid enters at 138° F. and in 41 seconds is discharged at 116° F. Precise control assures uniform crystallization.

Votator APPARATUS

For the Continuous Processing of Liquid and Viscous Materials in a Closed, Controlled System

Conference in a Rowboat

JIM: Yes, sir, this is the life! And I left everything under control at the office except just *one* problem — those heat exchangers for the new plant!

BILL: If that's your only worry, relax and enjoy yourself. Whitlock can handle that job for you and do it right.

JIM: So I hear, but they're way off in Hartford, Connecticut. I can hardly expect them to send a man to study our job.

BILL: That's right — *if* their man had to come from Hartford! But don't forget that Whitlock has forty or fifty direct sales offices and representatives all over the country, working on jobs like yours.

JIM: But some of my jobs are pretty complex, probably too difficult for most field engineers — what then?

BILL: Very simple — the field engineer's recommendations are all mailed to Hartford and reviewed by their Thermal and Production Engineering Divisions immediately. If necessary, a specialist from Hartford comes out to look the job over,

JIM: Bill you're the guy who knows *all* the answers! That equipment has had me worried. I hadn't realized there was a *local* Whitlock man who could drop in to talk things over. Now, a phone call should settle my problem.

There's an experienced Whitlock representative near you. Ask his advice on your heat transfer problems and follow his recommendations.

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Bends • Coils • Condensers • Coolers
Heat Exchangers • Heaters • Piping
Pressure Vessels • Receivers • Reboilers

AHEAD OF THE TIMES FOR HALF A CENTURY

The finished crystal was dropped onto a conical pile of quartz sand in an annealing furnace. The sand prevents the incorporation of impurities into the plastic lower portion, which might cause differential cooling contraction. The annealing furnace is held at 600° C. for 8 to 10 days and then cooled at about 0.5° C. per hour.

Other salts, notably potassium chloride and sodium bromide, were also processed in the same equipment but seemed to offer no advantages over inexpensive rock salt for the optical units desired. M.L.K.

TEXTILE CINDERELLAS

When chemists decide that a thing has to be beautified, almost anything can happen. We were startled some years ago when such a commonplace material as glass was spun into fibers and then woven as a soft, silken textile material with remarkable fire-resistant properties. Now you can have draperies and curtains of this noncombustible material in almost any color, thanks to new dyeing techniques.

We never heard of anyone dyeing glass either, but the effect is achieved by applying a thin gelatin type of protein film to the yarn during manufacture. This film is 1 to 2% by weight of the finished yarn. As a result the coating will absorb the fast soluble vat dyes as well as the more brilliant acid, chrome, and direct colors.

There are many other striking results of research shaping up in this ancient business of clothing people and beautifying their homes. The consumer usually does not learn of them, however, until the final result is in the shop window.

It took 20 years of unremitting work and study to apply the art of photography to textiles so that it could be used for printing to replace the century-old screen and roller techniques. There is nothing new about printing photos on silk or cotton immersed in a photosensitized emulsion, but the Photone method, as it is called, goes far beyond that. It introduces various colors in subtle shadings to fabrics in place of just flat dyeings. Ammonia vapor is used to bring out the latent image. The emulsion is an unrevealed trade secret; in essence, the chemistry of the operation is somewhat similar to that used in the Ozalid process.

New fibers are not discovered every day; still there have been several outstanding contributions in this field since the close of the war. Like nylon and Vinyon, they are noncellulosic and processed from chemicals such as Terylene, a synthetic fiber of yet undisclosed composition derived essentially from terephthalic acid and ethylene glycol. Strength and heat resistance are the outstanding characteristics, but like nylon, it does not dye too easily.

The work of Robert B. Woodward in synthesizing such giant molecular proteins as the polypeptide polymers may open a door to an entirely new class of synthetic silks and woolens.

Nonwoven fabrics represent man's third effort on this planet to provide himself with textiles. It could conceivably take the place of weaving machinery much as the latter succeeded the hand weaver's frame, but we

(Continued on page 14 A)

PORTER

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PORTER "Better Built" Equipment Established 1888

PORTER "REFINERS" are used by STANOLIND for stratification elimination in its new natural gasoline storage tanks at Pearland, Tex.

Designed by engineers with a thorough knowledge of mixing requirements in the petroleum industry, the PORTER "Refiner" is a precision-built side-entering mixer of exclusive design embodying advanced features found in no other mixer. Created especially for the rapid blending of light hydrocarbon fractions, the "Refiner" is adaptable to the mixing of any *free* flowing liquid, and is completely protected from the weather by a hinged cowl. For complete specifications write for Catalog 801.

The Trend is to Porter *"Better-Built"* Process Equipment

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Fluidyne
AN ECONOMICAL
GENERAL UTILITY
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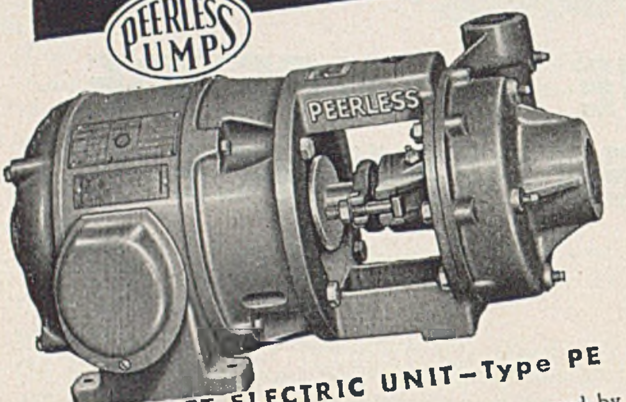
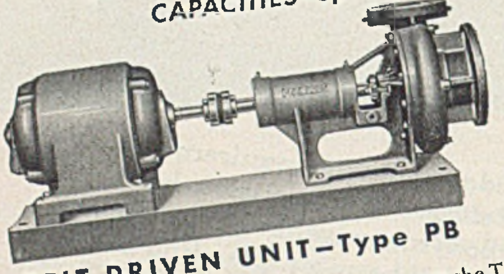


COMPACT ELECTRIC UNIT—Type PE

A close-coupled, end suction, single stage pump powered by standard NEMA electric motor. Compact, highly efficient, versatile, dependable. Easy to install, operate and maintain. Sturdy, rugged construction. Note generous opening for accessibility. Utilizes small space. The ideal pump for liquid transfer.

HEADS—Up to 270 feet.
DRIVES—Fractional to 20 H.P.
CAPACITIES—Up to 1000 g.p.m.



BELT DRIVEN UNIT—Type PB

Integrally cast iron frame and bearing mounts support the Type PB in same manner as Type PE. A precision steel shaft, turning in grease lubricated ball bearings is keyed to either V or flat belt pulley as specified, or can be direct connected to standard stock motor through a flexible coupling, as shown in the view above.

THE FLUIDYNE MOVES WATER AND OTHER LIQUIDS WHERE YOU WANT THEM. Think of all the applications where you can use the Peerless Fluidyne. It not only handles water but also slightly viscous or alkaline fluids. Ideal for scores of domestic and commercial installations and hundreds of light industrial applications. Can be installed in any position, vertical, horizontal or intermediate. FOR FULL DETAILS, REQUEST YOUR COPY OF BULLETIN B-165.

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I&EC reports

prefer to believe that, for the time being, nonwoven textiles will have their own specific uses. Among them are filters, tapes, ribbons, covering for insulation, and containers.

Nonwoven fabrics are fibers which have been bonded together, either through their own adhesive properties such as possessed by Vinyon and cellulose acetate, or with prepared adhesives for nonadhesive fibers such as cotton, wool, and rayon. Heat and pressure are used to lock the fibers in place. Some bonded fabrics introduce dyeing problems, and for these only the pigment-on-fiber coloring method is practical.

Resins are being utilized on an ever-broadening scale to improve the utility and enhance the beauty of textiles. They are the "invisibles" which hold wool shrinkage to less than 3% instead of 30 to 40% by preventing fiber slippage. Resin is also used to impart a built-in crispness and newness to fabrics which withstand repeated launderings by bonding fiber to fiber and imparting semirigidity to the whole fabric without loss in softness. Resin particles as small as 0.1 micron in diameter are flashed onto the fibers at 250° F. and make them adhere permanently.

Visible or invisible, these are all new advances which have endowed us with fibers and fabrics of remarkable usefulness, durability, and appearance. The finery of the little lady with the glass slippers would not have turned back to rags by midnight if modern science, instead of that unimaginative old wench with the wand, had come to her aid. H.S.

CURRENT DEVELOPMENT

It is a fascinating thing to watch a new instrument develop and equally fascinating to see the design of an old one modified; to find out the "whys" of development or modification, which usually include dissatisfaction with the status quo, and then to see the designer dissatisfied with his ideas and to watch the improvements he makes on the work of his own devising. Such a situation we find well exemplified in the development of a new type polarograph by James H. Schulman, H. Bruce Battey, and Demetrius Jealtis at M.I.T., and the addition of further refinements by Schulman and his colleagues at the Naval Research Laboratory. This piece of equipment, described earlier this year in the *Review of Scientific Instruments*, has been subjected to numerous improvements since then, and is now just being advertised on the commercial market as the Polaro-Analyzer. It was in listening to the story of the original design and current modifications that this report came into being.

The whys of the idea behind this modification of existing methods of making polarograms lay in dissatisfaction with speed of operation, with limitations placed on rapidity of voltage changes, with false apparent half-wave potentials, with the presence of personal factors in the estimation of diffusion currents, and with lack of sensitivity. The Heyrovský type, recording galvanometer deflections photographically, and another type involving use of a recording potentiometer and producing an inked chart, have as a common characteristic current measuring systems which are highly damped. The simplest definition of a polarograph seems to be "an instrument which applies a constantly

(*Continued on page 16 A*)

A PRIMARY ALCOHOL *that's Different*

TETRAHYDROFURFURYL ALCOHOL (THFA)

AS A REACTANT:

Tetrahydrofurfuryl alcohol (THFA) differs from many other primary alcohols because of its ring structure and the reactions which it undergoes involving the ring. Typical examples of these are:

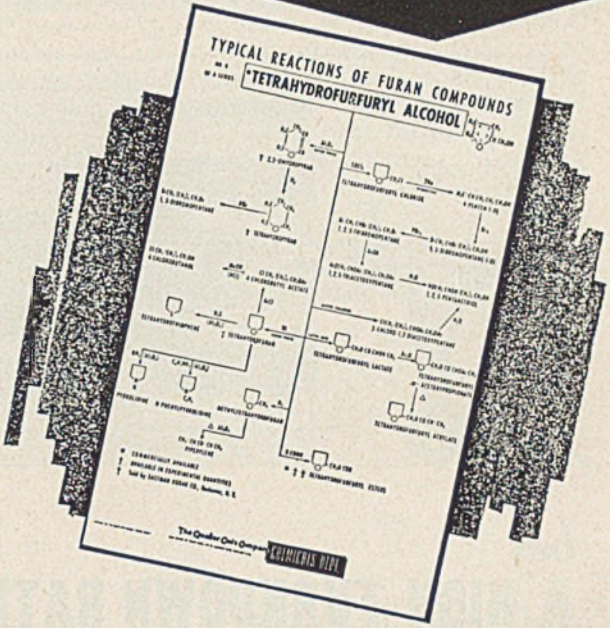
1. Ring expansion with formation of dihydropyran.
2. Substitution of the nuclear oxygen atom with the formation of pyrrolidines and tetrahydrothiophenes.
3. Ring opening with formation of open chain compounds.

In addition THFA undergoes many of the usual reactions of a primary alcohol and is assuming increased importance as a chemical intermediate in the preparation of high boiling esters, ethers and other derivatives.

AS A SOLVENT:

THFA differs from many other primary alcohols in its high boiling point (pure—177.5°C at 743 mm.) combined with complete water miscibility. This characteristic may be of value where reaction with water soluble materials is to be carried out at high temperatures. THFA is a solvent for chlorinated rubber, nitrocellulose, ethylcellulose, cellulose acetate, ester gum, rosin, shellac, many resins and other complex organic materials.

In view of its versatility we suggest that you may be able to use THFA to direct or extend your work with primary alcohols. Our Technical Staff will help on the application of THFA to your requirements.



This reaction chart in wall mounting size (approximately 18" x 24") or file size (8½" x 11") will be sent when requested on your business letterhead. When making request please state size desired. Ask also for Technical Bulletin 87A which gives physical and chemical properties, uses, shipping information and other valuable data.

TETRAHYDROFURFURYL ALCOHOL (THFA)

$C_4H_7O\text{-}CH_2OH$

A limpid liquid with a mild odor

Molecular Weight	102.13
Boiling Point (pure) °C (743mm)	177.5
Specific Gravity (20/20°C)	1.064
Flash Point (open cup) °C	75-80
Refractive Index (n 20/D)	1.4505
Surface Tension 25°C (Dynes/cm)	36.5 ± 0.5
Viscosity at 25°C (Centipoises)	5.49

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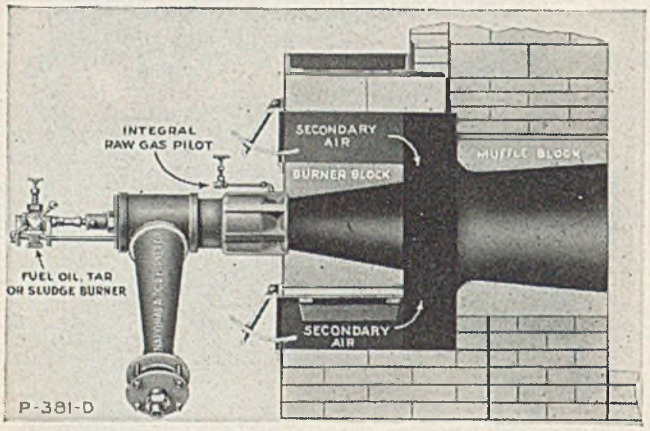
NATIONAL AIROIL FUEL OIL · GAS BURNERS

TANDEM COMBUSTION UNIT



has

A HIGH TURNDOWN RATIO WITH A STEADY FLAME...

It maintains a high flame temperature with either fuel oil or gas; can be brought quickly to full capacity with a clean flame; and flame can be regulated and directed to uniformly radiate heat to the absorbing surfaces without flame impingement. The Tandem Combustion Unit is also designed for firing vertically upward and for forced draft preheated air, when necessary. It may be applied to all types of boilers and process furnaces. For details about the Tandem Combustion Unit and the various types available, write for supplement 6 to Bulletin 50.

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increasing potential across a solution and at the same time measures the intensity of current through the solution." Because in a highly damped system only average current values are measured and only slow rates of voltage change are possible without falsification of half-wave potentials, Schulman and his co-workers determined to design an instrument of their own, which would eliminate the undesirable factors and add some new elements of design. To get to the end of our story first, there emerged a piece of equipment using negligible damping, in which the voltage change rate had no appreciable effect on the value of the half-wave potential, and which eliminated the personal factor in measuring currents.

With the original model the recorder was a separate piece of equipment, external to the cabinet that housed the polarizing unit and the amplifier. The cabinet of the improved instrument has a built-in recorder. The original voltage range went up to 4 volts; since in no application of polarography up to now has anyone gone beyond 3 volts, the spread in the new design was reduced to that as a maximum figure.

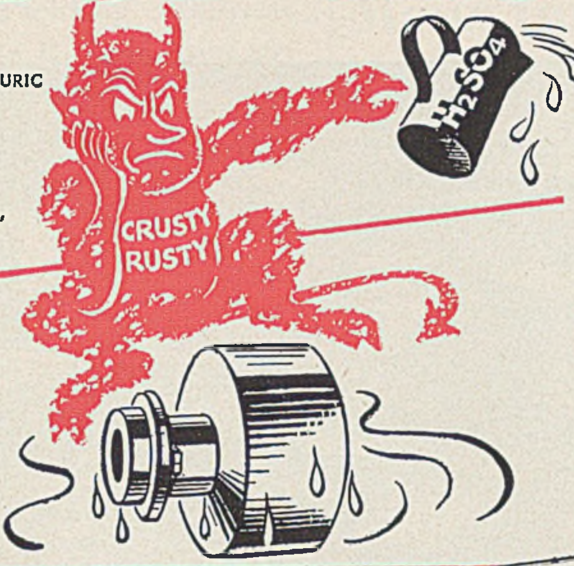
Six polarizing ranges—0-1, 0-2, 0-3, 1-2, 1-3, and 2-3 volts—are made available by means of a single control, and three other special ranges are added by throwing an auxiliary switch. Five hundred microamperes was the first figure used as the upper limit of the amplifier range. This corresponds to relatively high concentrations of impurities—in the order of 0.05 molar. Since, in general, polarography is not used for determining impurities in this concentration, or if it is done, the solution can be diluted to bring it into a range of smaller diffusion currents, the amplifier maximum has been reduced to 200 microamperes, with a new lower limit of 0.5 microampere added for increased sensitivity.

Operation of the Polaro-Analyzer is simple enough. With the working voltage at 3 volts on the polarizing unit voltmeter, the voltage range is selected, the amplifier is warmed up, current range is chosen, and zero adjustments are made. In the original design the operator had to have split-second reflexes—the recorder chart was started, and then, just when the pointer crossed one of the time markings, the motor switch had to be closed. They soon did away with that. Now the operator manually rolls the chart to a point where the pen coincides with a time marking on the chart; when he starts the actual run the chart automatically begins to roll, and when the run ends the chart drive stops.

As regards the personal factor, the damped operation gives a wavy or oscillating line, particularly at the top of the wave. In addition to a smaller net current recorded by this method, there is also the human element in choosing an average value for the current. In the new instrument the current value is clear-cut, the polarogram being the envelope of all the current peaks. The originators of the Polaro-Analyzer believe that the manufacturers of other commercial instruments, in realizing the disadvantages present in the "damped" machines and trying to control these disadvantages by increasing the damping still further, have only compounded the evils associated with damped operation.

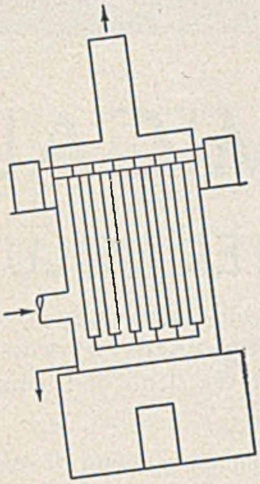
Schulman considers the instrument an excellent piece of apparatus for both research and rapid routine work. In accuracy it compares favorably with the best of the other methods, while in speed an analysis takes a maximum of 5 minutes as compared to 10 to 30 minutes in other designs. W.H.S.

STOP H_2SO_4 COLD!

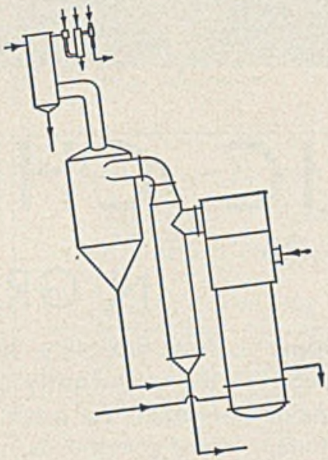


with Carbon . . . Graphite . . . and "KARBATE" Impervious Graphite!

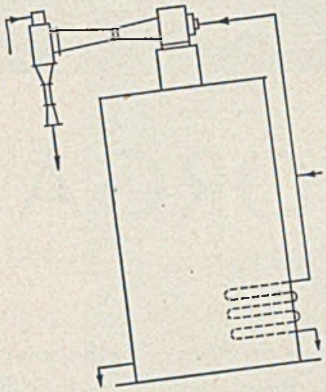
● "National" Carbon, Graphite, and "Karbate" Impervious Graphite are the most efficient materials for handling sulphuric acid. Equipment made of these materials is resistant to chemical attack by sulphuric acid up to 96% concentration. Moreover, it is light in weight, machinable, and mechanically strong. It is resistant to thermal and mechanical shock. There is no metallic contamination of the product. Both Graphite and "Karbate" Impervious Graphite have the highest heat-transfer rate of any practical material used in handling corrosive substances.



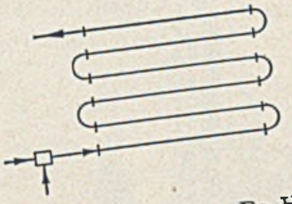
Electrostatic Precipitators for Acid Mists—All corrosion eliminated with **carbon** housing, stack, tubes, beams, and grillage.



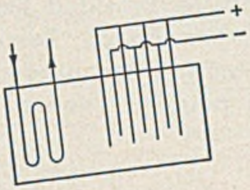
Spin-Bath Evaporators—Improved heat-transfer rates and no metallic contamination with **"Karbate" Impervious Graphite** heating elements and auxiliary parts.



Acid Concentrators—Spalling problems solved with carbon-lined bodies. Vapor piping, steam ejectors, and barometric condensers protected from erosion and corrosion by **carbon or graphite** linings.



Acid-Dilution Equipment—66 deg. Be. H_2SO_4 "cut" to any lower concentration quickly and economically with **"Karbate" Impervious Graphite** mixers, coolers, pumps, pipe, fittings, and valves.



Plating-Solution Heat Exchangers—No metallic contamination with high-heat-transfer, corrosion-resistant **"Karbate" Impervious Graphite** exchangers.

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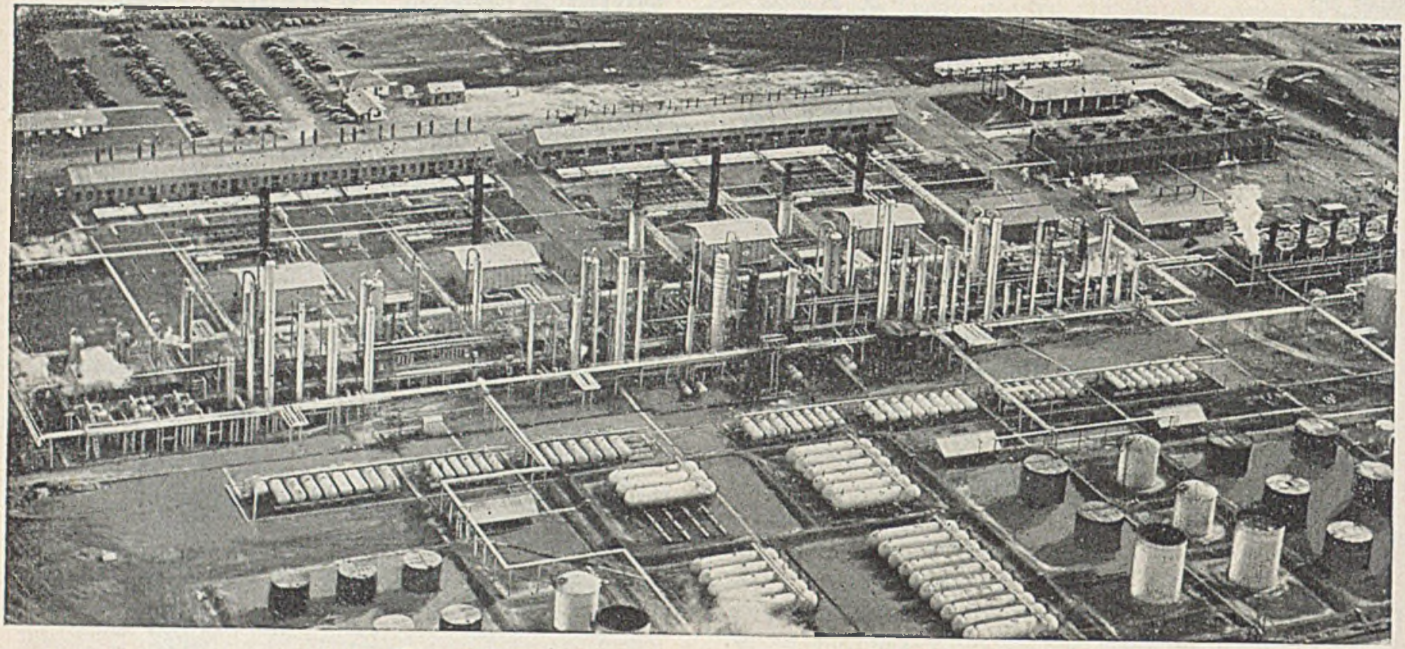

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Look to Celanese as a dependable source of supply for your chemical requirements. A leading producer of Formaldehyde, Acetaldehyde and Acetic Acid, Celanese is also producing Methanol, Acetone, n-Propyl and iso-Propyl Alcohols in addition to other related organic compounds.

Fifteen years of Celanese research in the field of petroleum chemistry have provided the large Celanese Chemcel plant, at Bishop, Texas, with a high degree of flexibility in the production of organic chemicals from petroleum natural gases.

This flexibility has enabled Celanese to meet the constantly changing needs of chemical markets for basic organic chemicals and important new compounds.

New chemicals are continuously being developed in the extensive Celanese laboratories. Specifications on new products as well as data on a regular list of Celanese* organic chemicals are available on request. CELANESE CORPORATION OF AMERICA, Chemical Division, 180 Madison Ave., New York 16, N. Y.

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U.S.I. CHEMICAL NEWS

December ★ A Monthly Series for Chemists and Executives of the Solvents and Chemical Consuming Industries ★ 1947

Claims Pickling Solutions Can Be Regenerated by Means of Ethyl Alcohol

Process Said to Be Efficient, Economical – Regains All Acid

An efficient and economical method of removing the bulk, or practically all, of the iron contents of pickling solutions and regaining all of the acid solution for further pickling treatment is based on the addition of ethyl alcohol to the spent pickling liquor. A complete description of the process is contained in a government report issued recently.

The alcohol is not added in a concentrated form but is diluted with three times its own volume of distilled water. One gallon of this mixture is added to every ten gallons of pickling solution and cooled down to room temperature. The solution is stirred thoroughly, all the iron precipitating in the form of iron sulfate. The alcohol can be removed by fractional distillation, while the liquor is reacidified to full strength.

Complete Regeneration

The liquor regenerated in this fashion is said to possess all the characteristics of a freshly made solution. Mixtures of surfuric and hydrochloric acids can also be regenerated by this process, the sulfates crystallizing out, while the harmless chlorides remain in solution.

The ethyl alcohol process is claimed to be of special importance for the regeneration of electrolytic pickling baths in which the articles after de-scaling are covered with a thin protective film of lead, zinc, copper, tin or cadmium.

NEW PACKAGE DESIGN

Solox, U.S.I.'s popular proprietary alcohol-type solvent for general use, is now packaged in

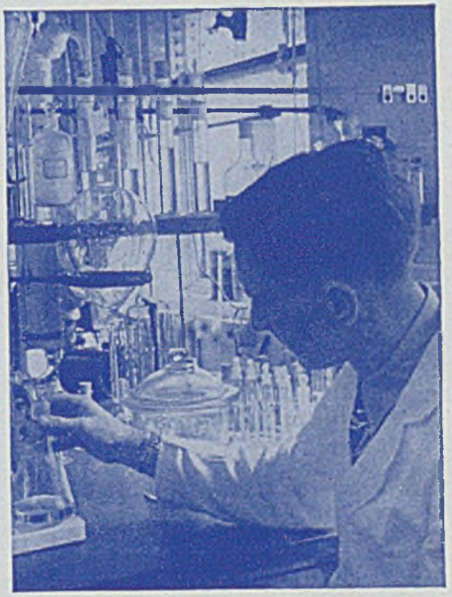
Many Important New Commercial Alcohols To Be Made Available From Fischer-Tropsch Process

Large Quantities Will Help Alleviate Continued Material Shortages —Products Will Include 2-Methyl-1-Pentanol, 2-Ethyl-1-Hexanol

Shortage of important alcohols currently experienced in the chemical industry will be greatly alleviated by new supplies to be made available by U.S.I. These products, basic to the industry, will be among the wide range of chemicals which U.S.I. will market from the American version of the Fischer-Tropsch process.

Increased Supplies of Ethanol, Butanol

Wartime shortages of ethanol and butanol did not stop with the end of hostilities. Demand for these versatile solvents exceeded expectations, and users continue to experience difficulty in meeting their total needs. The new Fischer-Tropsch source for these two alcohols has received enthusiastic response from members of the chemical and related industries.



New *Alcohols* in large quantities will be made available by U.S.I. from the output of the first Fischer-Tropsch plants. Constant research in U.S.I. laboratories accelerates the development of these new compounds.

Makes n-Amyl Alcohol Commercially Available

In addition to ethanol and butanol, U.S.I. will also offer n-propyl and n-amyl alcohol. Normal amyl alcohol has not been available commercially before, and the commercial availability of n-propyl alcohol has been comparatively recent. The production of n-amyl alcohol will offer new opportunities for research and development on this basic chemical. The paint, varnish, and lacquer, and the pharmaceutical industries, in particular, are expected to make wide use of both these compounds.

MORE

New Cancer Treatment Shows Promising Results

The use of urethan as a treatment for prostatic cancer has shown promising results, according to a report emanating from a midwestern university. Urethan is said to reduce the size of the cancer and to bring about beneficial results even when other therapies have failed. Other experimenters have reported favorable results with the use of urethans on experimental animal tumors, and in the treatment of leukemia (cancer of the blood).

Nylon Hair Brush Broken? Here's How to Repair It

While many hair brushes today have nylon bristles, the handles and backs are usually made of some other plastic. If it's transparent, it's probably polymethyl methacrylate—and there's no trick at all sticking pieces of this together. The best adhesive is a solution of the plastic itself in acetone. Household cements are a second choice, but do a good job too.

Titanium Found to Keep Metals from 'Tiring'

When a piece of iron, like a wire paper clip, is bent many times, it gets "tired" and finally breaks with about half the stress required when the metal is fresh. However, by alloying the iron with certain other metals, of which titanium is most effective, it tires much less easily, according to a paper read recently before an American scientific society. The study showed that, after titanium, most effective in improving fatigue strength of iron are molybdenum, silicon, manganese, nickel, cobalt, and chromium.

8500 Rare Chemicals Listed

Need parachlorobenzotrifluoride? muconic acid? beta-isopropoxypropionitrile? potassium tertiary-butoxide? or any other rare chemicals? One way to locate them is to contact the National Registry of Rare-Chemicals. Their files, which list the supply sources of more than 8.500 rare chemicals, are the most complete of their kind in this nation.

ADVERTISEMENT—*This entire page is a paid advertisement*

December — **U.S.I. CHEMICAL NEWS** — ★ 1947

CONTINUED NEW COMMERCIAL ALCOHOLS

Variety of New Alcohols

U.S.I. will also market 2-methyl-1-pentanol and 2-ethyl-1-hexanol, new alcohols derived from Fischer-Tropsch aldehydes. The large quantity of aldehydes made from the Fischer-Tropsch process are of primary interest because they are raw materials for long-chain, high-molecular-weight alcohols. Included as possible products from synthesis beginning with aldehydes are: 2-methyl-1-butanol, 2-ethylbutanol, n-hexanol, 2-ethyl-1-pentanol, and 2-methyl-1-hexanol.

Wide Range of Applications

Interest is focused on these alcohols to a large extent because their chemical combinations with monobasic and dibasic acids yield products of a wide range of applications. The acetates of the lower alcohols are widely known as lacquer solvents. Higher boiling esters resulting from the reaction of aliphatic acids and longer chain alcohols offer solutions of problems when higher boiling solvents are required. Of even greater interest, however, are the higher alcohol esters of the dibasic acids such as phthalic and sebacic. These esters are well known as plasticizers for a wide range of resinous materials.

Will Stimulate Development

The more certain raw material supply made possible by the Fischer-Tropsch process will undoubtedly stimulate development and increase the application of these materials. The accelerating use of all resins, with its correspondingly increased need for plasticizers, makes the provision of a new supply of alcohols especially significant.

Plant construction and marketing plans required by this new source of materials are being actively pursued, and it is anticipated that these new materials will be available within a two-year period. Prior to that time, U.S.I. will offer sample quantities of these new alcohols. The date of availability will be announced in these columns.

FIRST PACIFIC COAST CHEMICAL EXPOSITION ATTRACTS 15,000

Ninety-three exhibitors, representing leading manufacturers of chemicals and solvents on the Pacific coast and many national concerns with west coast offices, played host to approximately 15,000 visitors at the first Pacific Coast Chemical Exposition in San Francisco. The U.S.I. exhibit, featuring a wide range of U.S.I. chemicals, proved a popular meeting place. Here, left to right, seated, are R. C. Curtis of the Dow Chemical Co., San Francisco; S. L. Schwartz of the L. H. Butcher Co., Los Angeles; D. E. Eichelberger of the American Marietta Co., Seattle; L. A. Keane, U.S.I., New York; Ronald Benson, of the Carl F. Miller Co., Seattle; and Norman MacBeth of the MacBeth Corporation, New York. Standing, in the same order are G. C. Dohm, Clyde West, and R. E. Alexander of U.S.I., Los Angeles, and Wells Newell, U.S.I., New York.

TECHNICAL DEVELOPMENTS

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

To cut tinting time in oil paints and enamels, a new compound has been marketed which is said to eliminate all types of silking, flooding, and floating. **(No. 265)**

USI

A new rubber, claimed to have excellent dry heat resistance and to maintain its rubbery characteristics even at 300 deg. F. for 700 hours, is alleged to be easier to manufacture than butadiene rubbers. **(No. 266)**

USI

To improve the surface qualities of polystyrene plastics, a new treatment is offered which is said to increase mar resistance, repolishability, light transmission, and resistance to solvents. The process does not require special equipment and is completed in 20 minutes, the makers state. **(No. 267)**

USI

For use in dispersions and emulsions, a low-cost industrial product is now available in tank car quantities. This by-product is rich in gums and pentosans. **(No. 268)**

USI

A new fungicide, stated to provide permanent protection against dry rot, fungi, and most insects, is claimed to be easily-applied, non-toxic, non-injurious to wood or fabric and to maintain its strength indefinitely even after washings. **(No. 269)**

USI

To help prevent eye injuries from acids, an eye washing fountain is now on the market. It is ready for instant action on the scene of the accident, and is operated by the forehead, leaving hands free to open eyelids and wash both eyes, according to the manufacturer's description. **(No. 270)**

USI

To extend phenolic resin and protein adhesives, a new plywood glue constituent has been developed which is claimed to provide uniform spreading over protracted periods, and to decrease glue-line costs. **(No. 271)**

USI

An improved slide rule is now being produced. According to the manufacturer, the scales on the front of the rule are so arranged that only one setting of the hairline gives with each result its square, cube root, and logarithm. The log scale on the back gives five readings with each setting of the hairline. **(No. 272)**

USI

A new adhesive for carpets, described as a self-curing liquid, is said to be strong enough to butt-join sections of carpet padding without reinforcement. It can also be used to repair areas of dry rot, the makers claim. **(No. 273)**

USI

To prevent pre-cured rubbers from sticking, a new pre-cure wax finish is offered which is said to be applicable to molded, extruded, or calendered products and to serve as a mold release as well. **(No. 274)**

U.S. INDUSTRIAL CHEMICALS, INC.

60 EAST 42ND ST., NEW YORK 17, N. Y. BRANCHES IN ALL PRINCIPAL CITIES

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- Amyl Alcohol
- Butanol (Normal Butyl Alcohol)
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Ethanol (Ethyl Alcohol)
- Specially Denatured—all regular and anhydrous formulas
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- Pure—190 proof, C.P. 96% Absolute
- *Super Pyro Anti-freeze
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- Ansol M
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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
- Alpha-acetylbutyrolactone
- 5-Chloro-2-pentanone
- 5-Diethylamino-2-pentanone
- Ethyl Acetoacetate
- Ethyl Benzoylacetate
- Ethyl Alpha-Oxalpropionate
- Ethyl Sodium-Oxalacetate
- Methyl Cyclopropyl Ketone

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

FEED CONCENTRATES
- Riboflavin Concentrates
- *Vacatone 40
- *Curbay B-G
- *Curbay Special Liquid

ACETONE
- Chemically Pure

RESINS
- Ester Gums—all types
- Congo Gums—raw, fused & esterified
- *Aroplaz—alkyds and allied materials
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- *Arochem—modified types
- Natural Resins—all standard grades

OTHER PRODUCTS
- Collodions
- Ethylene Glycol
- Nitrocellulose Solutions
- Ethylene
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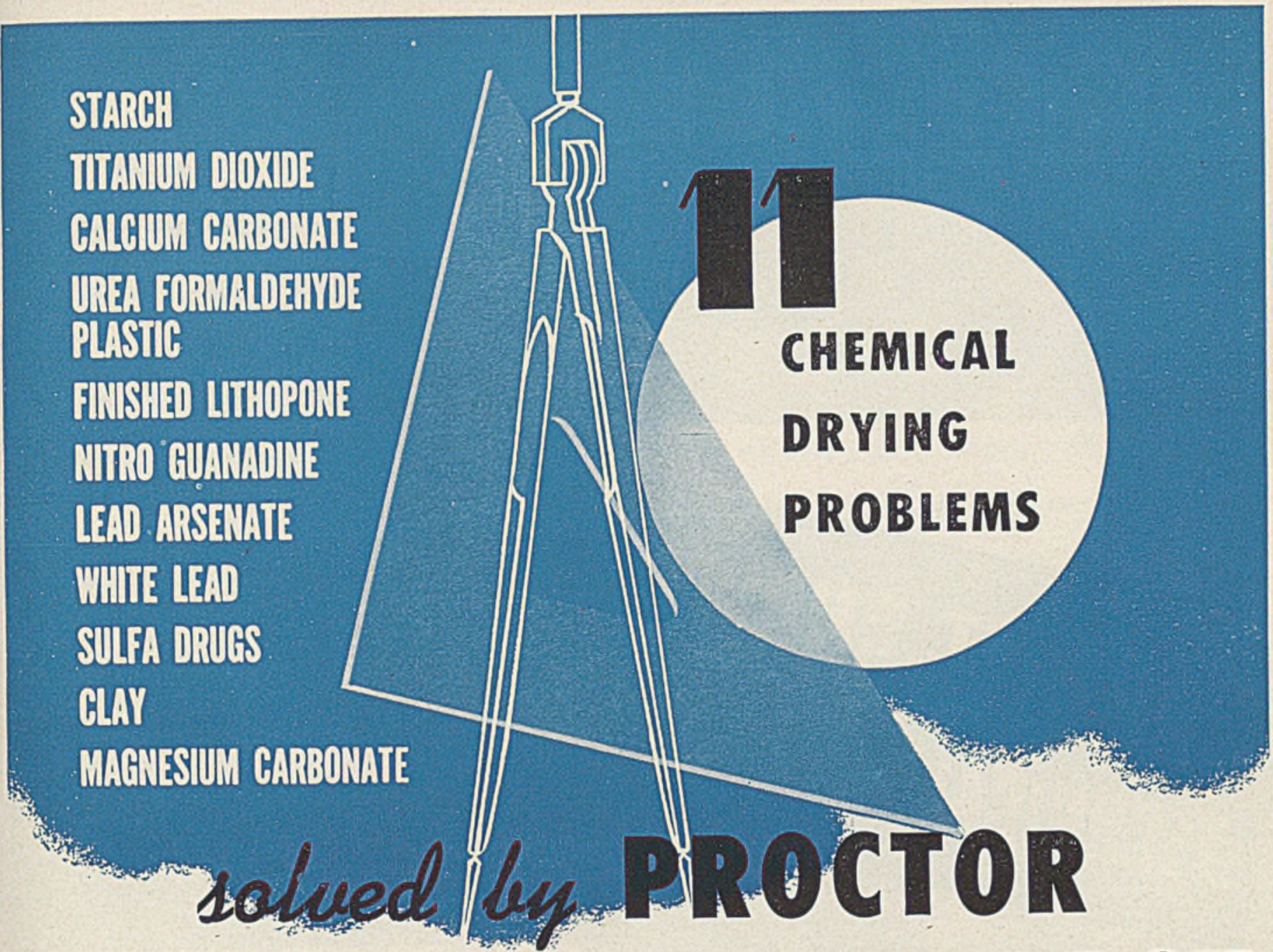


STARCH
TITANIUM DIOXIDE
CALCIUM CARBONATE
UREA FORMALDEHYDE PLASTIC
FINISHED LITHOPONE
NITRO GUANADINE
LEAD ARSENATE
WHITE LEAD
SULFA DRUGS
CLAY
MAGNESIUM CARBONATE

11 CHEMICAL DRYING PROBLEMS

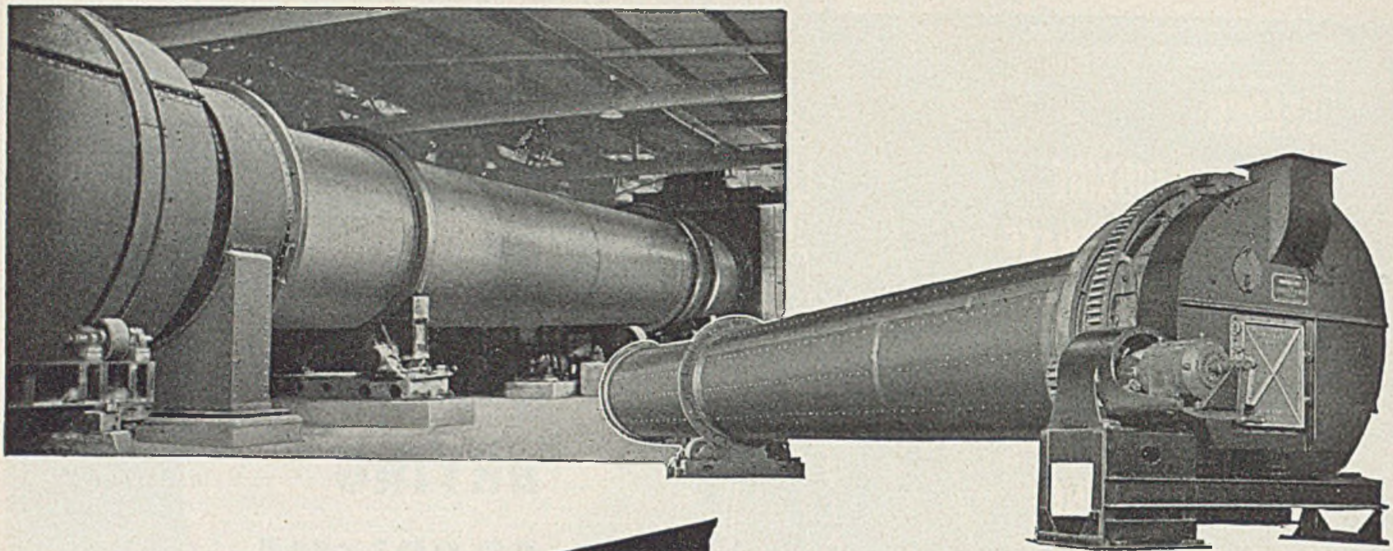
solved by PROCTOR RESEARCH

Each of the 11 products listed above represents a distinct and different drying problem. Magnesium carbonate, for example, must be dried from an initial moisture content of 565% (bone dry weight basis) to a moisture content of 0.1% at the rate of 500 pounds per hour (commercial dry weight), while starch is dried from 78.5% initial moisture content to 13.6% at the rate of 4,800 pounds per hour. Each of these products (and the list could be expanded many times) was studied by Proctor engineers, and the performance of the Proctor equipment finally installed was guaranteed in writing in the sales contract. In some cases the basic designs of the equipment was similar—but in each case modifications were made to suit the individual product or plant requirements. While all of these products are being dried in huge continuous systems equipped with preforming feeds—many problems brought to Proctor engineers have called for small tray or truck dryers. You may be sure that any problem — large or small—that you bring to Proctor & Schwartz, Inc. will receive the full benefit of all of the ingenuity and means at our disposal that were applied to solving the problems covered by these case histories.

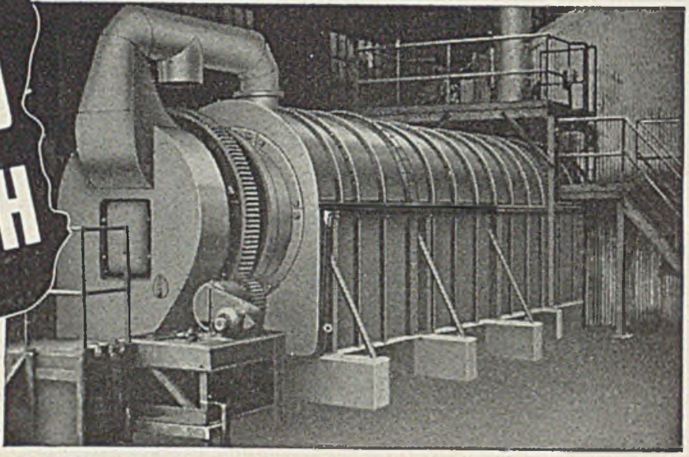
Write for your copy of this New Proctor Booklet

If you have not already received this latest booklet—which gives complete information on these 11 chemical drying problems—write for your copy today. Ask for Bulletin #309.

PROCTOR & SCHWARTZ, INC. • PHILADELPHIA 20, PA.



BARTLETT-SNOW'S TECHNICAL APPROACH



can *Help Solve* your drying problems, too

● Ten years ago it was an adventure, this matter of rotary dryer design. Recommendations were made almost blindly, based largely on experience with other—and frequently dissimilar materials. Guess-work bulked large in making decisions . . . But the Bartlett-Snow heat engineers have changed all this.

Today "Technical Approach",—the advantage of mathematical formulas developed, tested and proved by our heat processing engineers has replaced guess-work—and luck—in Bartlett-Snow design. All factors—including those of surface evaporation and diffusion, corrosion, abrasion, tendency to cake in cooling, the dust condition, and possible galvanic action are disassembled from each other, studied, checked. Findings are verified when necessary, by running samples of the material through an ingeniously arranged rotary test dryer. Thus all requirements of the problem become known,—and full allowance for all conditions can be made in the design of the equipment to be built.

The advantage of this highly technical, highly accurate, mathematical solution of dryer problems is reflected only in Bartlett-Snow equipment. It's your assurance that the size and type, method of firing, pitch, rate of feed and all other specifications of the equipment recommended will be exactly suited to the requirements of the service. Let us help you with your next heat engineering problem.

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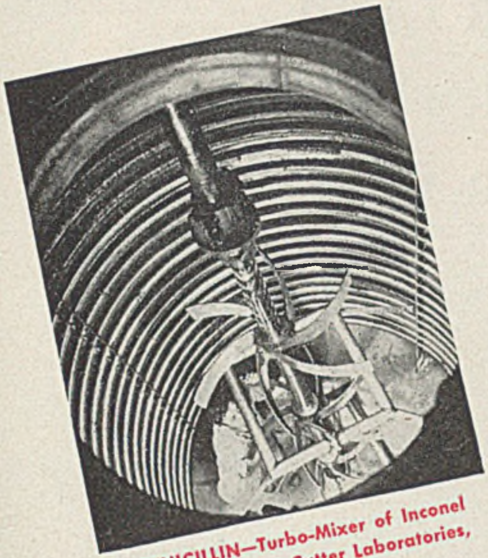
Turbo-Topics

SOLVING DIFFICULT MIXING PROBLEMS IN INDUSTRY HAS BEEN OUR BUSINESS FOR YEARS

The three illustrations shown are typical of the variety of difficult problems of mixing liquids with liquids, solids and/or gases successfully solved by the Turbo-Mixer technique.



PENICILLIN—Turbo-Mixer of Inconel in fermenter at Cutter Laboratories, Berkeley, California.

PHOSPHORIC ACID — Lead covered Turbo-Mixers in strong acid leach tanks with Atlas Mineral Products' "Rewbon" brick lining.

SYNTHETIC LEATHER — Battery of Turbo Nitro-Cotton Dissolvers preparing the synthetic leather base.

The fact that each mixing problem is treated individually, and approached from the chemical engineering viewpoint by men specially trained in interpreting and applying data, gathered from many unrelated industries, accounts to a large extent for the unusually high percentage of repeat orders received.

Once you submit your mixing problem to Turbo-Mixer you can depend upon a solution that will improve your operation. This thorough painstaking approach has substantially reduced operating and maintenance costs.

The benefit of these years of experience devoted to solving mixing problems is available to you.

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- Tanks
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- Evaporators
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GATX GENERAL AMERICAN

Check us first . . .

FOR LAND

FOR PLANTS

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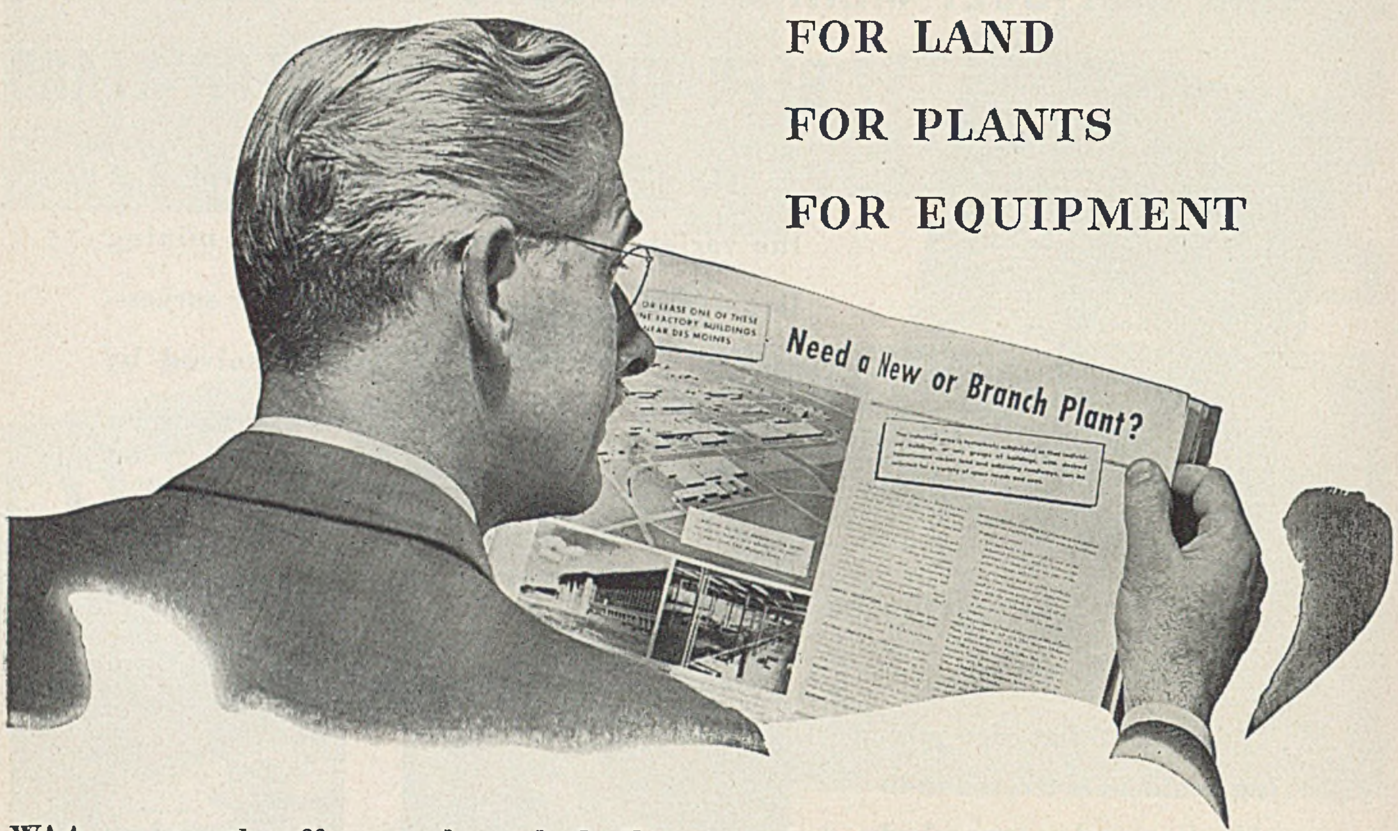

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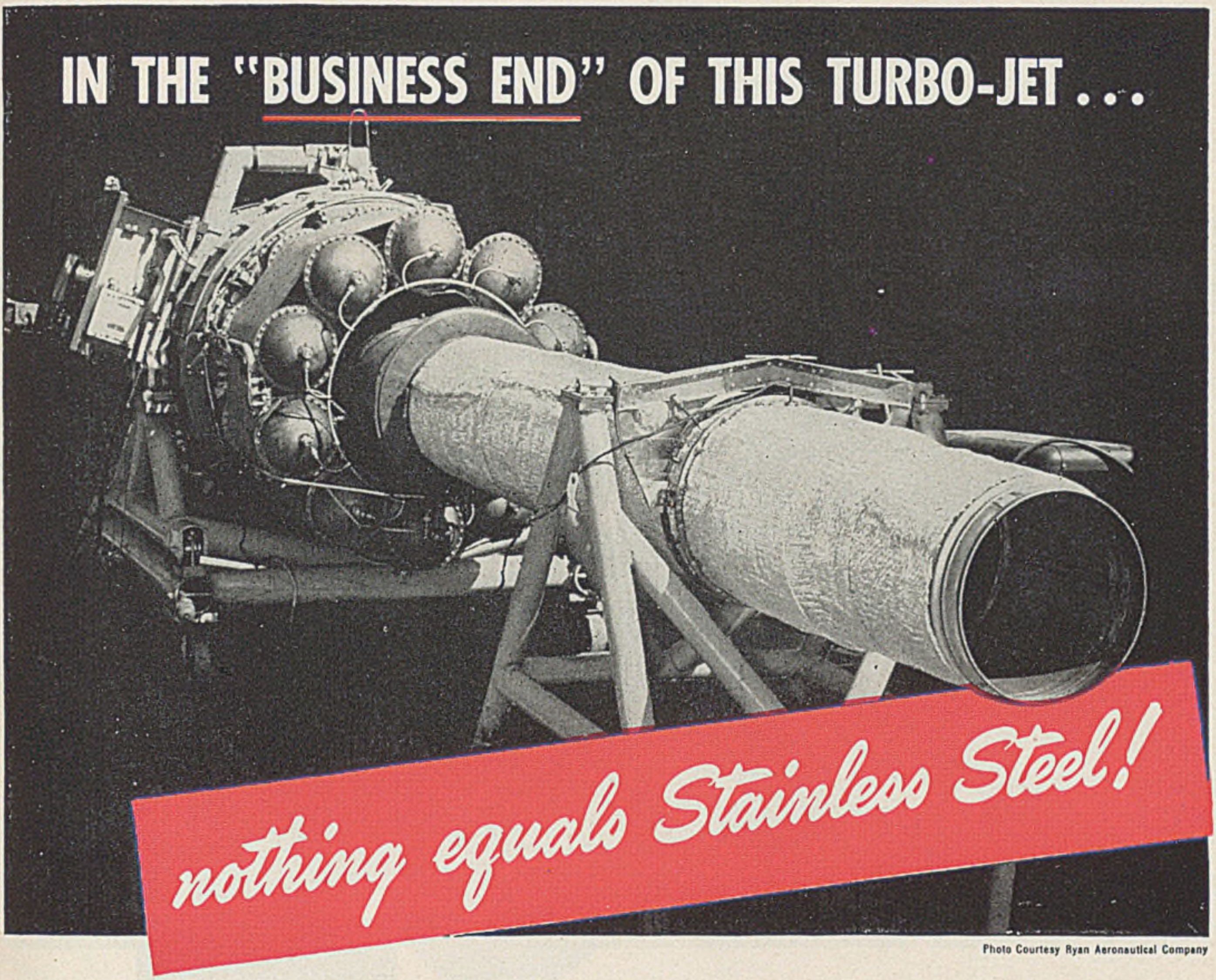

Photo Courtesy Ryan Aeronautical Company

Fabricated of U·S·S Stainless Steel, this jet tail-pipe of one of the Navy's newest fighters blasts a 1000 m.p.h. tailwind at a temperature of 1000°F. This hurricane of searing exhaust gas, which would destroy the airframe structure if unleashed, is channeled safely within walls of heat-resisting Stainless Steel. The combustion chambers, too, which rim the engine are made of Stainless to resist high temperatures and the corrosive attack of the combustion products.

Because it so ideally combines light weight, corrosion resistance, and strength under heat, Stainless Steel is the best material for countless other applications where these qualities are important . . . especially in chemical engineering equipment where new processes involving high temperatures and pressures, increase the severity of corrosive conditions. To resist their effects, Stainless Steel is today being used in ever increasing tonnages by the chemical and allied industries.

But in using Stainless Steel it is well to remember that "Stainless" covers a wide field of superior steels that vary considerably in their properties. They differ in their resistance to corrosion. Their strength under high temperatures is not the same. They have different hot and cold working properties. They are not alike in their machining characteristics. They also vary in cost.

That is why it is advisable to talk your problems over with our metallurgists. They know what Stainless Steel has done and what it will do in almost any kind of service. Their cooperation can be extremely helpful in the proper selection of the right Stainless for your needs—and in its efficient fabrication as well.

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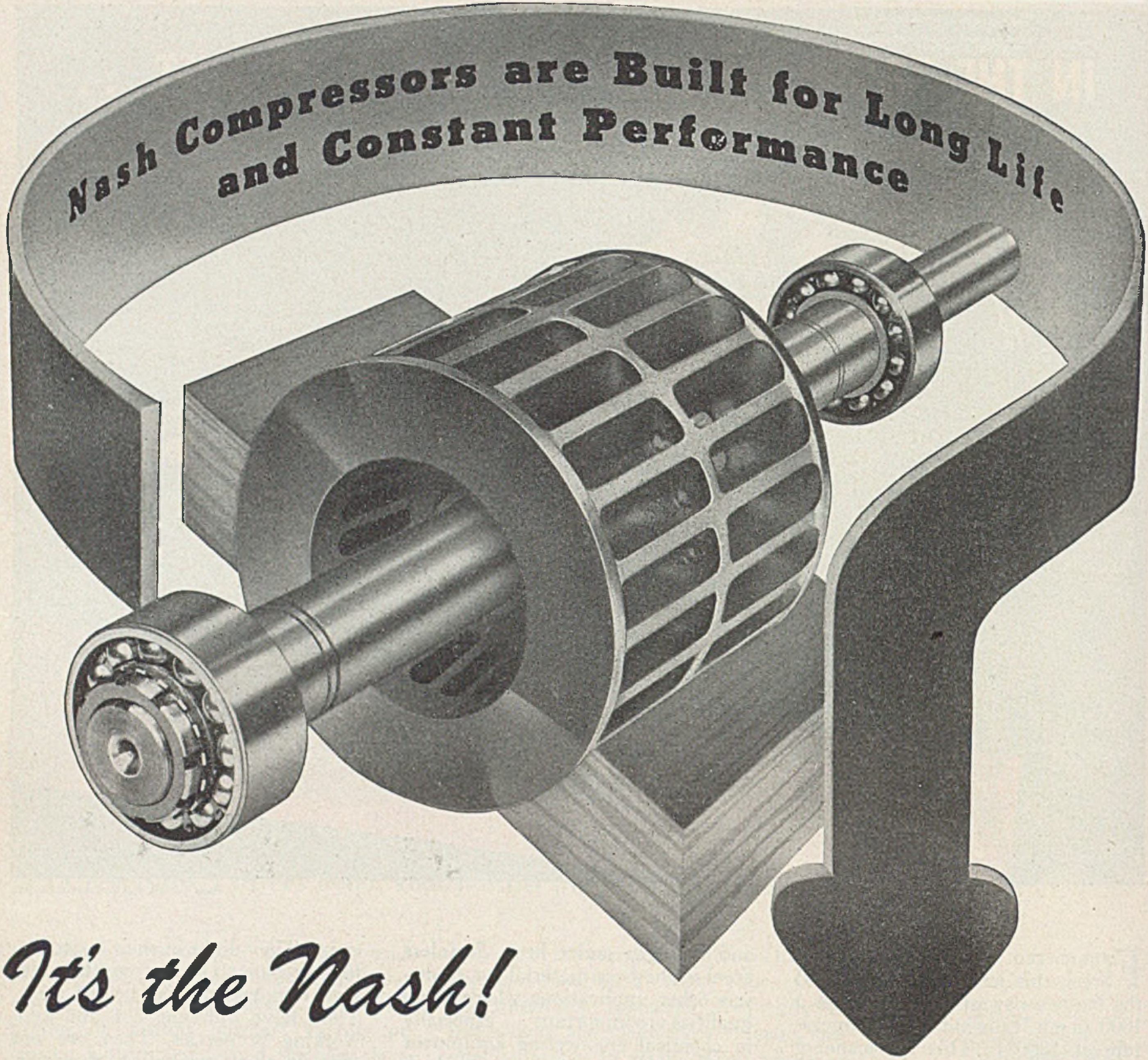

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The ability of Nash Compressors to maintain original performance over long periods is no accident. Nash Compressors have but a single moving element, the Nash Rotor. This rotor is precision balanced for long bearing life, and it revolves in the pump casing without metallic contact. Internal lubrication, frequent cause of gas contamination, is not employed in a Nash. Yet, these simple pumps maintain 75 lbs. pressure in a single stage, and afford capacities to 6 million cu. ft. per day in a single compact structure.

Nash Compressors have no valves, gears, pistons, sliding vanes or other enemies of long life. Compression is secured by an entirely different principle of operation, which offers important advantages often the answer to gas handling problems difficult with ordinary equipment.

Nash Compressors are compact and save space. They run without vibration, and compression is without pulsation. Because there are no internal wearing parts, maintenance is low. Service is assured by a nation-wide network of Engineering Service offices. Write for bulletins now.

No internal wearing parts.

No valves, pistons, or vanes.

No internal lubrication.

Low maintenance cost.

Saves floor space.

Desired delivery temperature
Automatically maintained.

Slugs of liquid entering pump
will do no harm.

75 pounds in a single stage.

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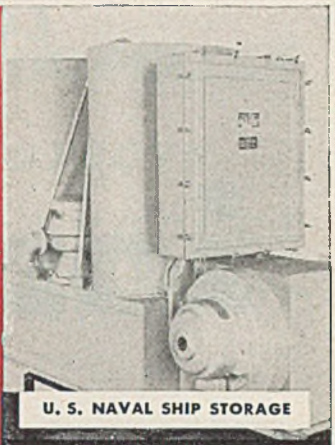
MOISTURE - - - -

going, going, gone



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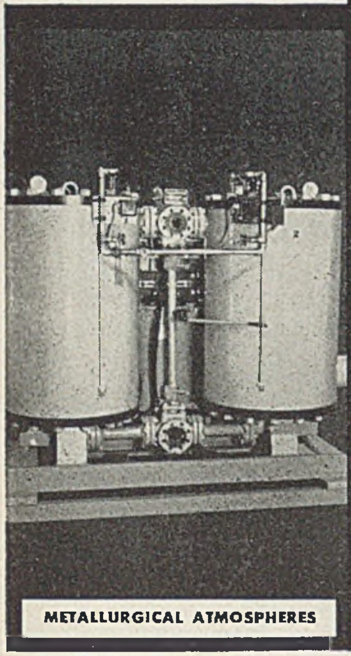
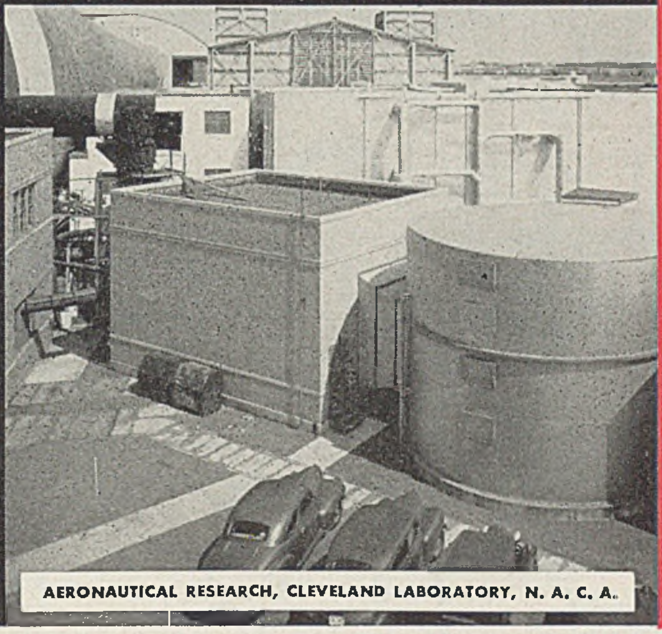
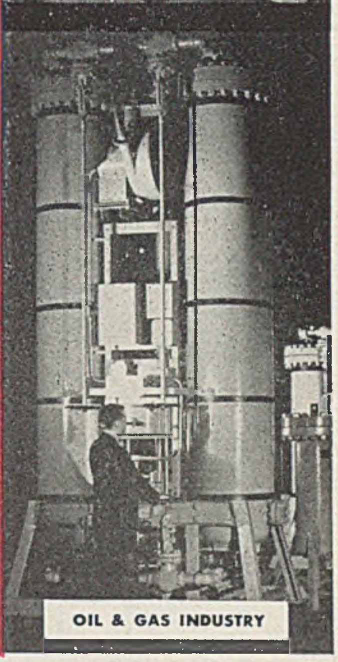


METALLURGICAL ATMOSPHERES



AERONAUTICAL RESEARCH, CLEVELAND LABORATORY, N. A. C. A.



OIL & GAS INDUSTRY

Thousands of Lectrodryers*—charged with Alcoa Activated† Alumina—are solving dehumidification and dehydration problems all over the world. From small portable dryers using but a few handfuls of Activated Alumina, to wind-tunnel air dryers containing carloads, these machines operate under all kinds of conditions—serve all kinds of industries.

Yet one desiccant—Alcoa Activated Alumina—functions with high efficiency in *all* of these wide-spread and varied applications.

The Pittsburgh Lectrodryer Corporation chose Activated Alumina because it is among the very few drying agents that can hold appreciable quantities of moisture without objectionable changes in form or properties . . . because with Activated Alumina, Lectrodryer provides Industry with a practical, efficient and economical system capable of removing substantially 100 per cent of the moisture from vapors, gases and liquids.

If MOISTURE is a problem with you, why not write or call your nearest Alcoa sales office *today*. ALUMINUM COMPANY OF AMERICA, CHEMICALS DIVISION, 1911 Gulf Building, Pittsburgh 19, Pa.

*Lectrodryer Equipment, manufactured by Pittsburgh Lectrodryer Corporation.

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ALUMINAS AND FLUORIDES

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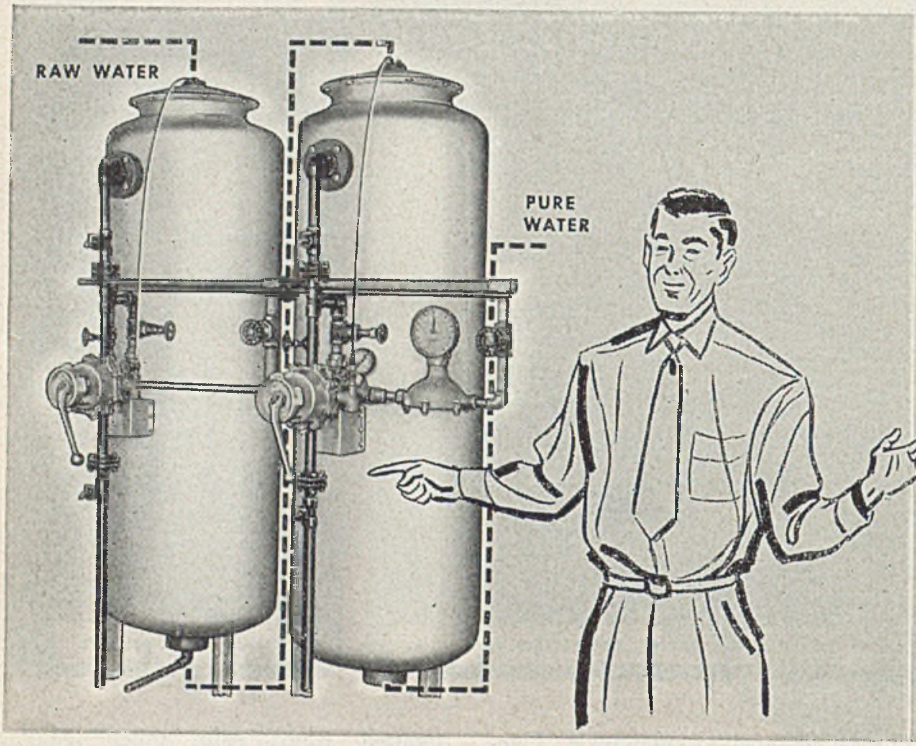
LOW-COST PROCESS WATER IN YOUR PLANT BY

ionXchange



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The ionXchange process as developed by ILLCO-WAY gives modern plants chemically pure process water *at a fraction of the cost of distilled water*—10,000 gallons for less than a dollar. The equivalent of distilled water, De-ionized water meets exacting standards in pharmaceutical, chemical, cosmetic, and other industrial plants. No fuel is required, no cooling water; no periodic dismantling for cleaning. ILLCO-WAY De-ionizing units, simple and compact, are available for practically any industrial water treatment problem—and in *many other fields outside of water conditioning* (sugar refining, etc.). Write for basic facts of ILLCO-WAY ionXchange today—indicate your manufacturing problem so we can send specific literature.

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OPERATING PRINCIPLE—Raw water passes in series through two reactor tanks containing high-speed, high-capacity ion-exchange resins. These resins have the property of adsorbing and exchanging all the cations and anions in the water supply, giving an effluent water that is equal in purity to distilled water. No heat, no fuel, no cooling water involved in the process. Units are compact, requiring small floor space and little attention. There are only a few simple valves and minimum piping. The range of flow rates is practically limitless. Water is used here as an example, but the same operating principle applies to the De-ionization of any liquid.

ILLCO-WAY

ENGINEERING AND EQUIPMENT DE-IONIZERS for process water treatment and treatment of liquids and solutions other than water; waste treatment; reclamation of specific constituents. DE-ALKALIZERS: Boiler feed (external); bottling water. SOFTENERS: Industrial, domestic. FILTERS, etc.

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NON-ELECTRIC MAGNETIC PULLEY

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YOUR PRODUCT
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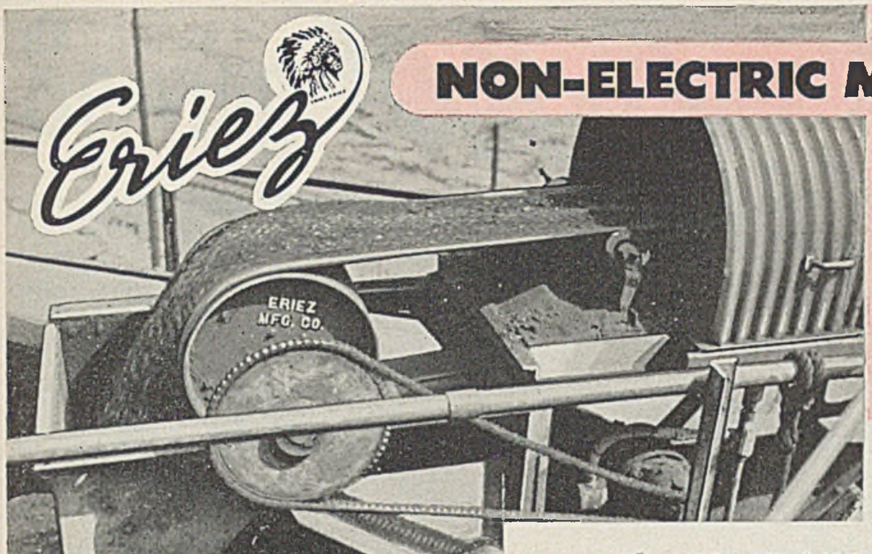
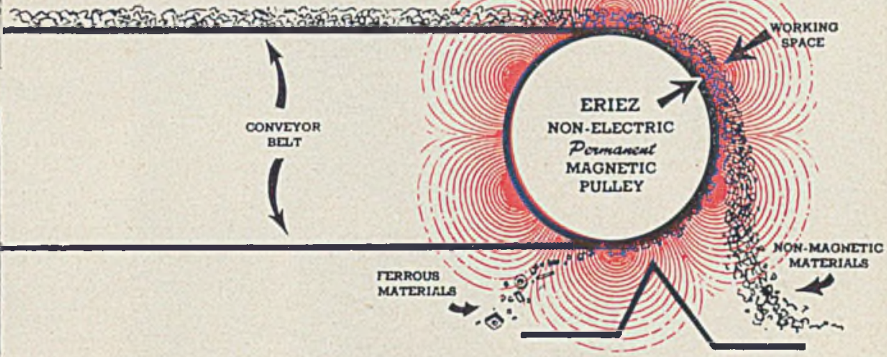
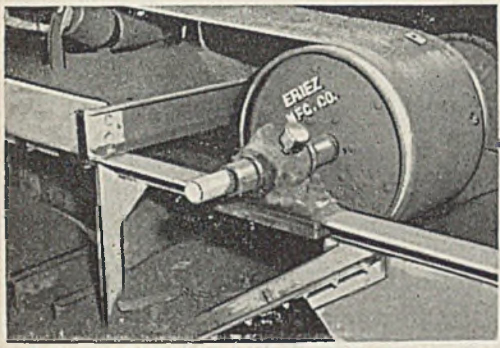
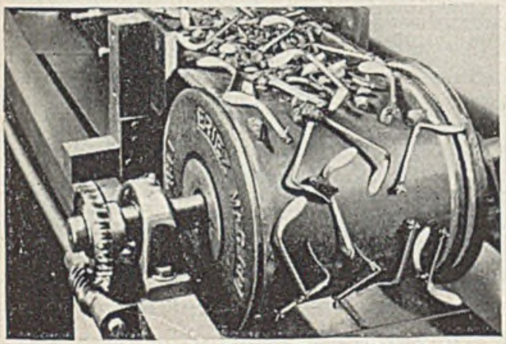






General Aniline and Film Corp.
(Power House Coal)



L. C. Smith and Corona Typewriters, Inc.
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The Englander Co., (Cotton Waste)

Here is Magnetic Protection
in a wide diversity of industries

THESE three outstanding users in their respective fields are assured of positive separation of magnetic from non-magnetic materials by using Eriez Permanently Magnetized Pulleys . . . Completely self-cleaning, Eriez units provide automatic separation . . . They are your insurance against contaminated products, explosions and damage to processing machinery . . . Spark-proof and non-electric, they easily meet all requirements for installation in hazardous areas . . . No rectifiers, transformers or other attendant electrical equipment needed. Eriez Pulleys are self-energized. Operating and maintenance costs are eliminated by the use of Permanently Powerful Alnico Magnets. Since moisture, heat or cold does not affect their operating efficiency, Eriez pulleys can be installed out-of-doors, deep in a mine or at any point where electric current is not available . . . Leading industrial plants specify Eriez because they want tried and proven permanent magnetic protection.

CLIP AND MAIL TODAY
Please send bulletin No. 501A. We are interested in removing tramp iron or ferrous particles from the following materials:..............
We would like to know more about installation of ERIEZ on: IEC 12
☐ Gravity Conveyors ☐ Mechanical Conveyors ☐ Pneumatic Conveyors
☐ Liquid Pipelines Magnetic Trap ☐ Equipment or Processing Machines
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● *When It's Magnetic Protection . . . See Eriez First*

Eriez Magnets Are Engineered to Fit Your Equipment.

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ERIEZ MANUFACTURING CO.
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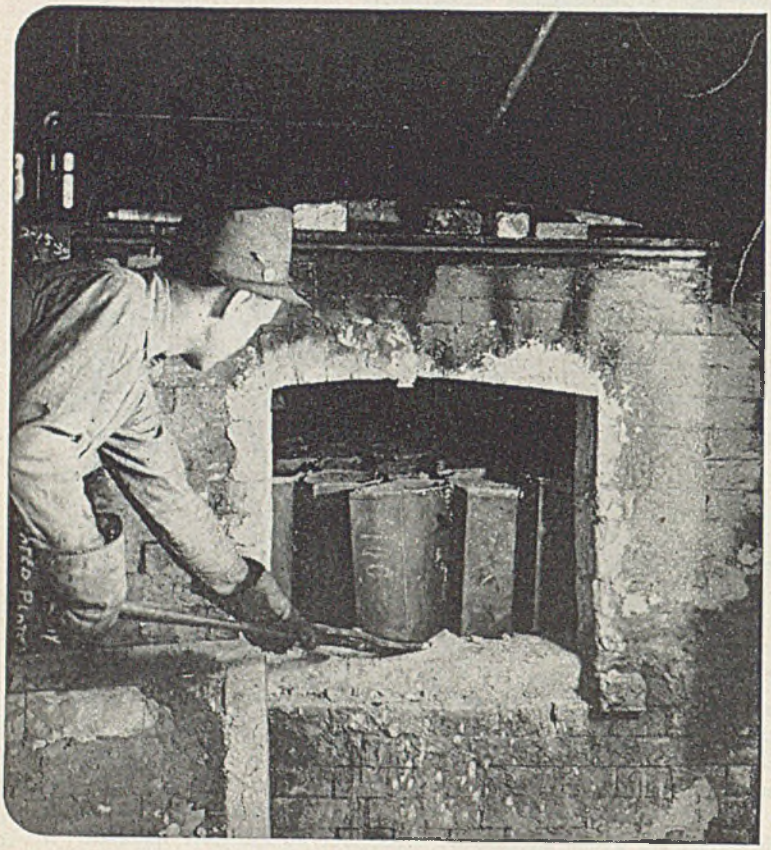
REPUBLIC *Enduro* STAINLESS STEEL



These ENDURO Stainless Steel baking boxes for carbon brushes are heated to 1100°-1800°F. for periods of 8 to 300 hours. Installed more than seven years ago, they still are giving satisfactory performance—show no signs of fatigue—in severe service where ordinary steels failed completely in 16 to 120 hours.

Resists Heat, too!

● Because it is resistant to scaling as well as corrosion at high temperature—and because it is high in creep strength—Republic ENDURO Stainless Steel is the ideal material for extreme temperature applications.

Countless examples similar to that described at the left illustrate ENDURO'S high resistance to the weakening effects of sustained severe temperatures . . . illustrate, too, how the use of this versatile metal has saved thousands of dollars in maintenance and replacement expense.

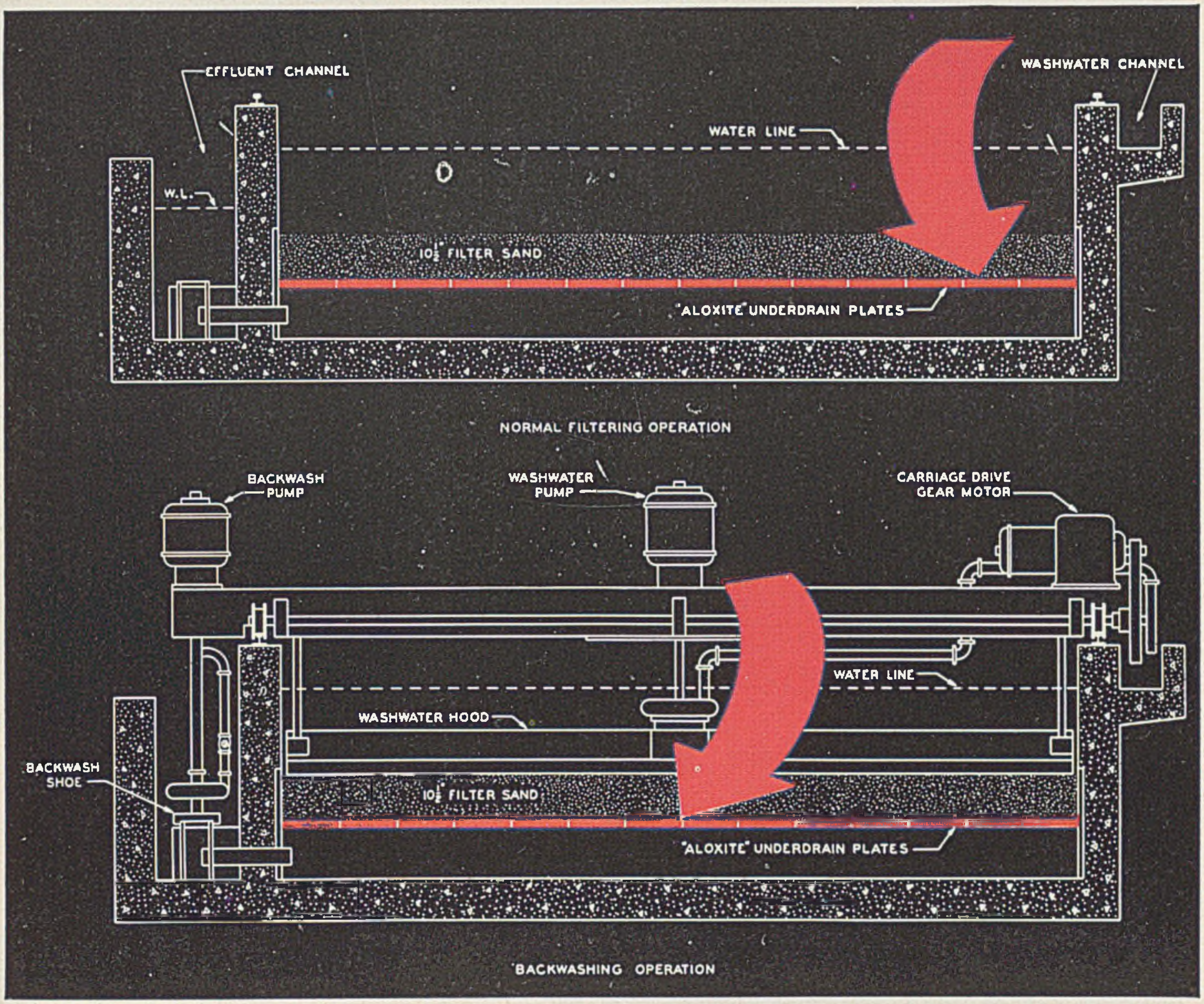
Included in ENDURO'S broad range of analyses are stainless and heat-resisting steels to solve your high temperature and corrosion problems. For more detailed information—interesting facts and figures—or for metallurgical assistance, just write:

REPUBLIC STEEL CORPORATION
Alloy Steel Division • Massillon, Ohio
GENERAL OFFICES • CLEVELAND 1, OHIO
Export Department: Chrysler Building, New York 17, New York

Republic REPUBLIC STEEL REG. U. S. PAT. OFF.
ENDURO STAINLESS STEEL
REG. U. S. PAT. OFF.

Other Republic Products include Carbon and Alloy Steels—Pipe, Sheets, Bolts and Nuts, Tin Plate, Tubing, Stevens Barrels and Drums

Serving Large Paper Mill and Town



Hardinge Automatic Back Wash Rapid Sand Filter Using ALOXITE Porous Plates

Operated steadily for more than a year, this 1100 sq. ft. Hardinge filter, equipped with ALOXITE aluminum oxide underdrain plates, has proved eminently satisfactory. Installed by the paper mill, it supplies water to both mill and town.

Using a 10½" deep sand bed, solids removal of over 97% is accomplished. The effluent averages less than 1 ppm. of suspended solids. And this is achieved without chemical treatment of the raw reservoir water.

With ALOXITE porous plates on the job, there is no need for graded gravel. Eliminated, therefore, are the difficulties encountered so frequently with gravel-sand combinations. Backwash water is distributed uniformly. Affording full use of the automatic backwashing principle as applied to this unit, continuous operation and lower maintenance expense are assured.

Adaptable to new or old, large or small gravity and pressure units, the ALOXITE underdrain system provides highly worth while savings. Check its possibilities for your filters. Complete details will be furnished by our engineers. Write Dept. E127, The Carborundum Company, Refractories Division, Perth Amboy, New Jersey.

Underdrain Plates

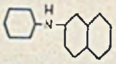
BY CARBORUNDUM

TRADE MARK

"Carborundum" and "Aloxite" are registered trademarks which indicate manufacture by The Carborundum Company

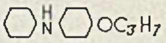
Secondary Aromatic Amines

Good-rite
CHEMICALS

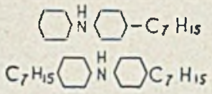


Phenyl B-Naphthylamine

p-Hydroxy Diphenylamine



p-Isopropoxy Diphenylamine

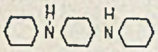


Mixed Mono and Diheptyl Diphenylamines

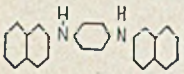
These amines are suggested for use as stabilizers, antioxidants, polymerization inhibitors, and for organic synthesis. It is believed that they will find wide usage in the following industries: Dyes, explosives, plastics, petroleum, photographic, drug, medicinal, and soap.

Other organic Chemicals

Di-secondary Aromatic Amines

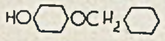


Diphenyl p-Phenylenediamine

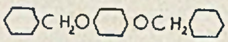


Di B-Naphthyl p-Phenylenediamine

Ethers of Hydroquinone

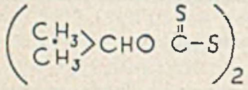


Monobenzyl Ether of Hydroquinone



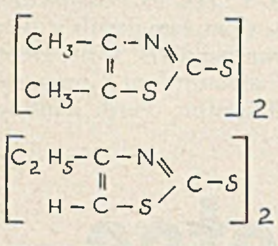
Dibenzyl Ether of Hydroquinone

Miscellaneous

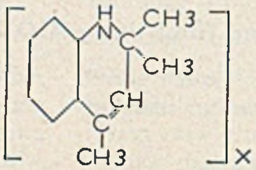


$\left(\begin{matrix}CH_3\\CH_3\end{matrix}>CHO\overset{S}{\overset{\|}{C}}-S\right)_2$

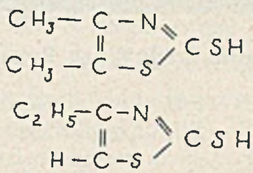
Di-Isopropyl Dixanthogen



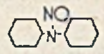
Mixed Aliphatic Thiazyl Disulfides



Trimethyl Dihydro Quinoline Polymer



Mixed Ethyl and Dimethyl Mercaptothiazoles



N-Nitroso Diphenylamine

All materials listed here are available in commercial quantities. Prices and technical information are available on request. Please write Dept. CC-12, B. F. Goodrich Chemical Company, Rose Building, Cleveland 15, Ohio.

B. F. Goodrich Chemical Company

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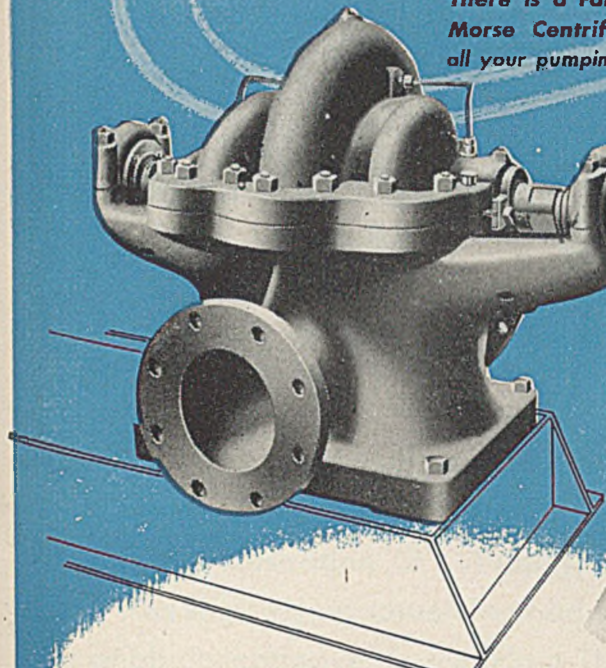
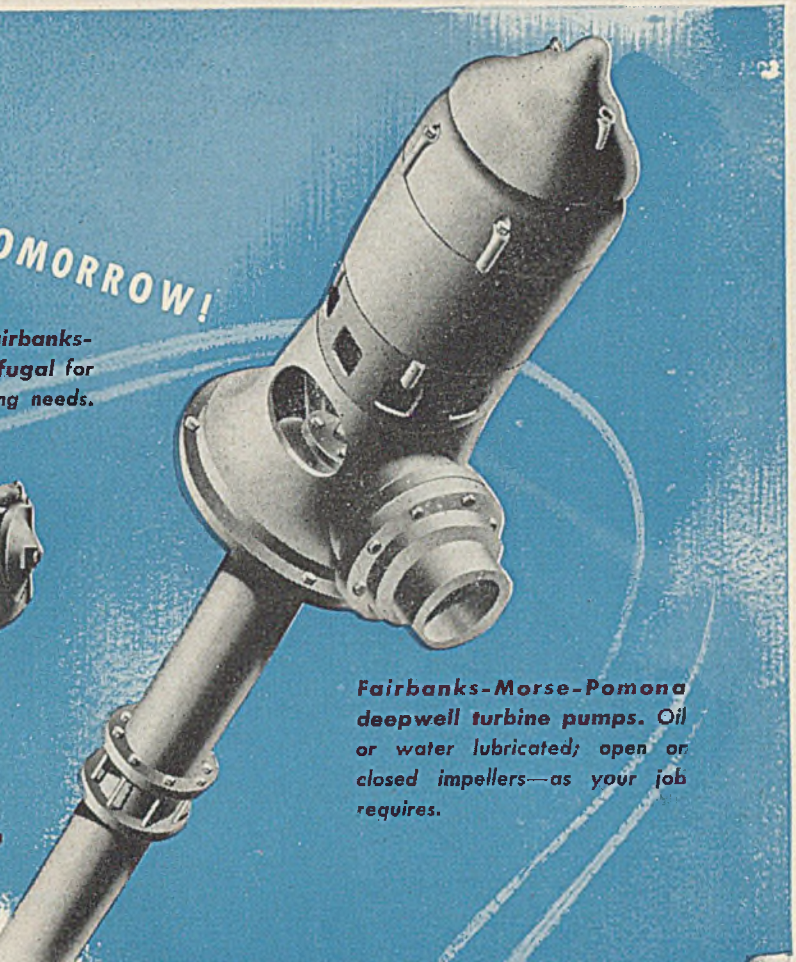
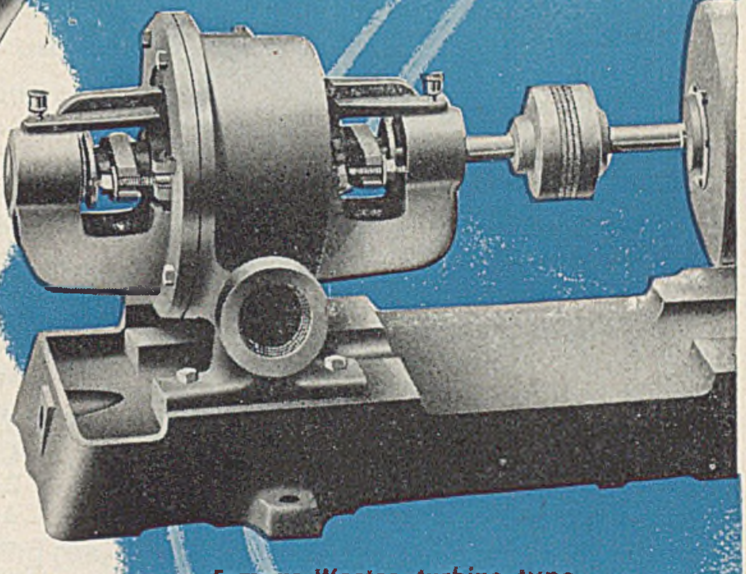


There is a Fairbanks-Morse Centrifugal for all your pumping needs.



***Fairbanks-Morse-Pomona deepwell turbine pumps.** Oil or water lubricated; open or closed impellers—as your job requires.*



***Famous Westco turbine-type pumps** have exclusive advantages for service involving small capacities, high heads and low speeds.*

The values in doing business with one of the hundreds of well-established, progressive Fairbanks-Morse pump dealers are many:

First, of course, you gain immediate advantages from the intensive research, skilled productive techniques and well-developed service organization that have long been identified with the Fairbanks-Morse name.

Too, you gain the long-term advantages of continued aid in keeping your pumps on the job—continued benefits from the widespread, quickly available Fairbanks-Morse dealer organization.

For a pump that's to give high efficiency year after year, buy from the dealer who will stand by you, year after year. See your Fairbanks-Morse pump dealer for all your pumping requirements.

FAIRBANKS-MORSE

A name worth remembering

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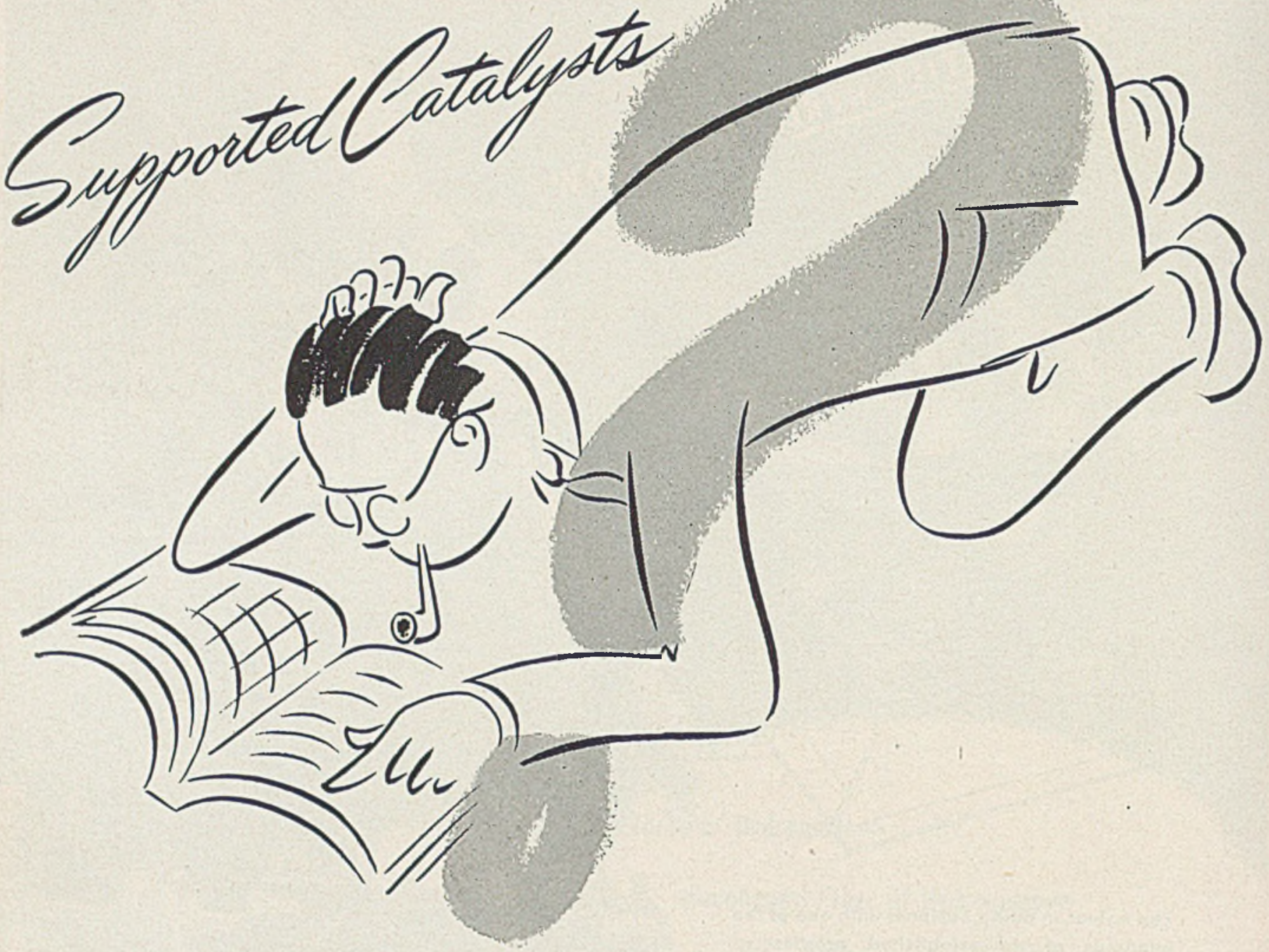
Want the answer to Low Cost



THE answer is, let Porocel Corporation put your catalyst on activated bauxite.

Our carrier—Porocel—with a price range of 2½ to 4½ cents per pound, costs much less than other supports (frequently high-priced synthetic materials). Its rugged, granular character eliminates the need for costly forming steps—permits direct impregnation by simple, inexpensive techniques. The result is savings of 20-50% in initial cost of the ready-to-use catalyst.

Porocel is inert in the great majority of cases. The degree of purity in low-iron, low-silica Porocel means almost complete freedom from unwanted side reactions. Hence, Porocel catalysts exhibit clean-cut reactions and long life. Result? Low unit operating costs.

With a surface area of about 225 square meters per gram and porosity averaging 55% of its total volume, Porocel is capable of adsorbing large quantities of many inorganic salts or other compounds. Impregnation of the active ingredient is uniform and widely dispersed over areas easily reached by gaseous and liquid reactants—most important in surface catalysis.

Catalysts are made in mesh sizes ranging from 2/4 to 20/60 or in special grades when desired. And these tough, uniform particles withstand wide ranges of temperature, pressure and flow—stand up under severe handling.

As pioneer developers of bauxite-supported catalysts, we have produced efficient materials for others. Now, let us show you how economically it can be done for you. Outline the details to: Attapulgus Clay Company (Exclusive Sales Agent), Dept. C, 210 West Washington Square, Philadelphia 5, Penna.

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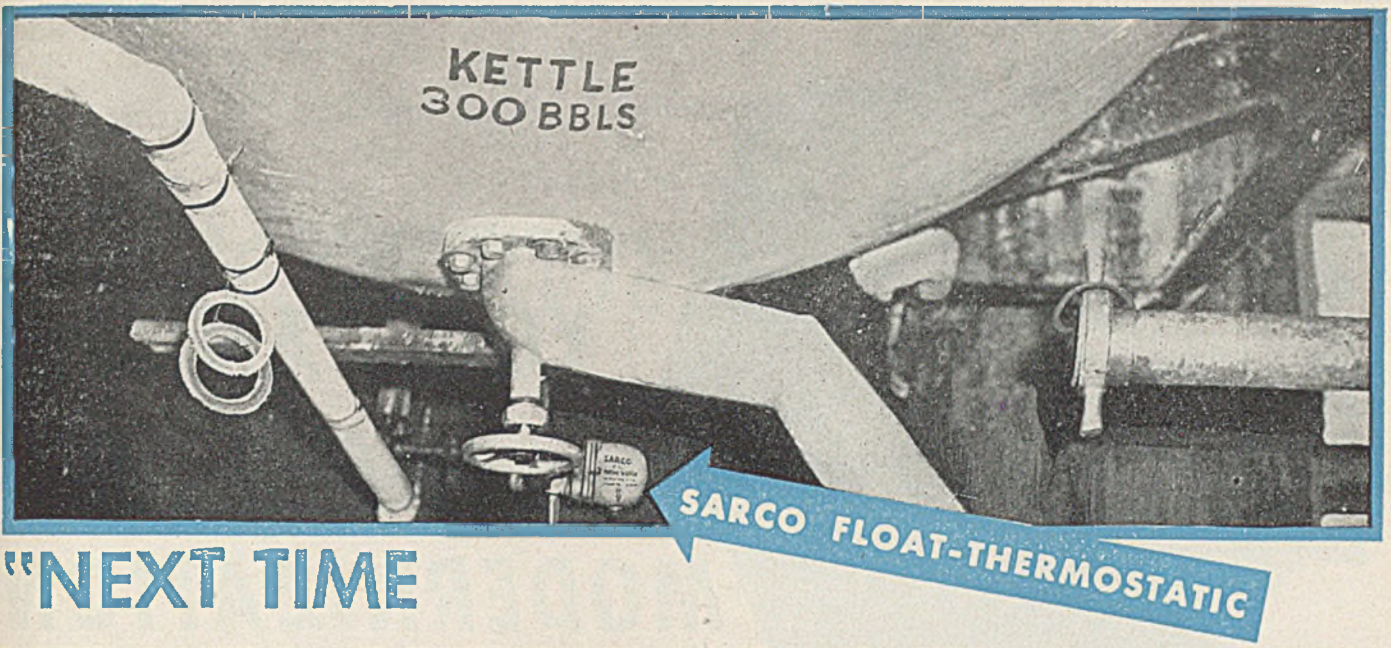
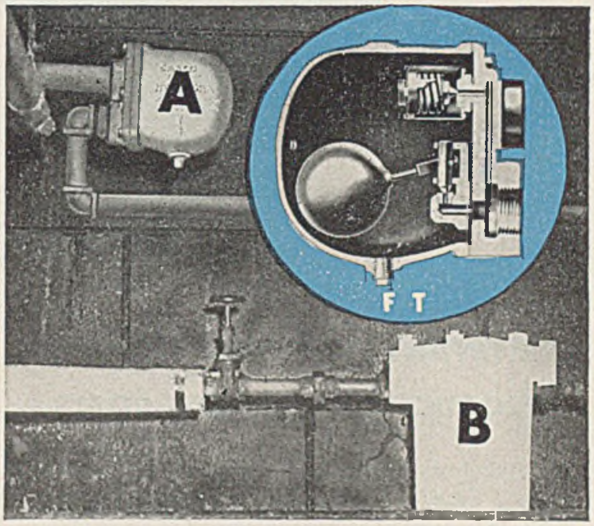


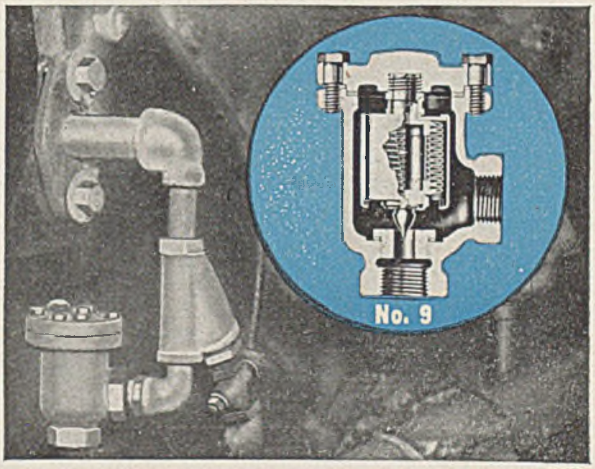
"NEXT TIME WE WILL GET THE RIGHT TRAP—FIRST"

This 300 barrel brew kettle never did work right with the large old fashioned steam traps originally installed (see illustration "B" at right). When plant output was stepped up something had to be done. The small inexpensive Sarco Float-Thermostatic Trap (A) now drains the largest coil in the kettle and everything is OK.

On the large bottle washing machines, two other types of traps were tried without success, and then all troubles were ended with the new Sarco No. 9 Thermostatic Steam Trap shown at the right. The Brewmaster has decided that hereafter he will see Sarco first.

It costs no more—actually much less in the long run, to get the right combination of steam traps and temperature control. Sarco makes all types—a family of products that works together on any specific job. The Sarco Representative can show you how.





153

SARCO SAVES STEAM

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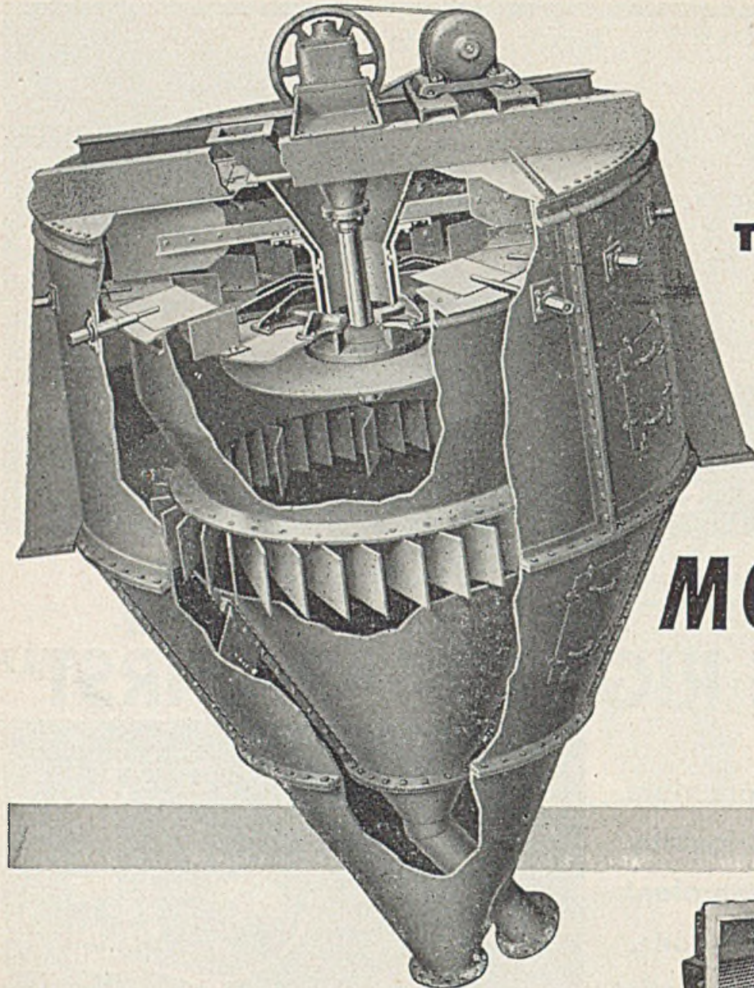

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Sturtevant Equipment is your answer to today's high labor and production costs.

For instance, take the Sturtevant air separator . . . this versatile machine increases output from 25% to 300% . . . lowers power costs by as much as 50%, too. In addition, it assures accurate fines to 325 mesh and finer. No wonder you'll find hundreds of Sturtevant Separators in all types of industry.

Look into the profit-making advantages of other Sturtevant equipment . . . blenders, grinders, crushers, screens, pulverizers and elevators. All are designed to increase production and cut costs. Write for complete information and catalog, today.

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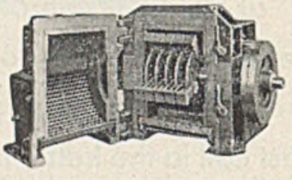
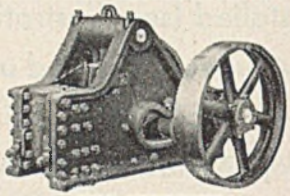


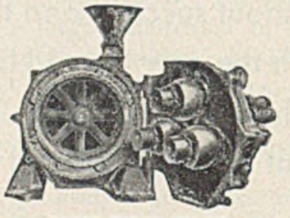
SWING-SLEDGE MILLS

for coarse and medium reduction (1" to 20 mesh). Open door accessibility. Soft, moderately hard, tough or fibrous substances. Built in several types and many sizes.



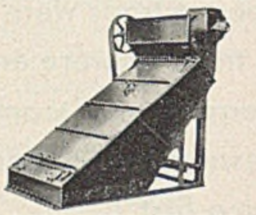
JAW CRUSHERS

for coarse, intermediate and fine reduction of hard or soft substances. Heavy or light duty. Cam and Roller action. Special crushers for Ferro-alloys. Several types, many sizes.



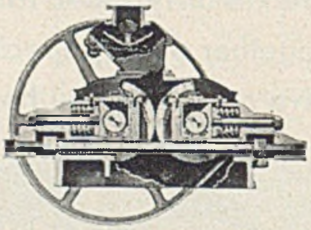
RING-ROLL MILLS

for medium and fine reduction (10 to 200 mesh), hard or soft materials. Very durable, small power. Operate in closed circuit with Screen or Air Separator. Open door accessibility. Many sizes. No scrapers, plows, pushers, or shields.



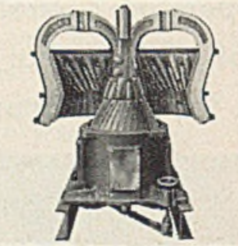
MOTO-VIBRO SCREENS

screen anything screenable. Classified vibrations. Unit construction — any capacity. Open door accessibility. Open and closed models with or without feeders. Many types and sizes — range of work ½ inch to 60 mesh.



CRUSHING ROLLS

for granulation, coarse or fine, hard or soft materials. Automatic adjustments. Crushing shocks balanced. For dry or wet reduction. Sizes 8x5 to 38x20. The standard for abrasives.



ROTARY FINE CRUSHERS

for intermediate and fine reduction (1" to ¼"). Open door accessibility. Soft or moderately hard materials. Efficient granulators. Excellent preliminary Crushers preceding Pulverizers.

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or engineers this handbook provides a wealth of arefully integrated new technical data to simplify nd speed up solutions to complex piping system esign and operating problems.

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PROPERTIES OF PIPE TABLES—comprehensive data on physical characteristics of pipe assist in calculating stress, heat loss, insulation, support and anchorage problems.

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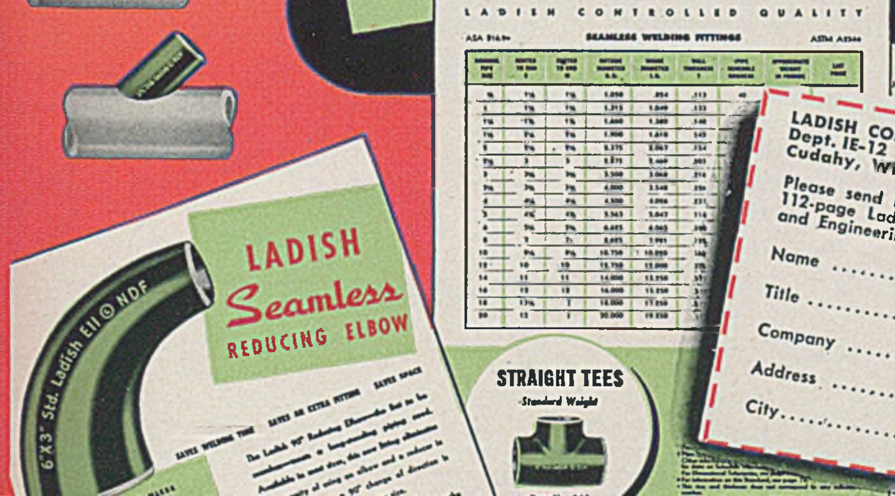
112 Pages of Listings Charts Diagrams

82 PAGES OF SPECIFICATIONS AND LISTINGS ASSIST IN SELECTING FITTINGS

For buyers and specifiers this catalog provides in convenient form the detailed information they require on types, sizes, weights, dimensions to assist in selecting the proper fitting for any piping application.

Included are data on American Standards, Stainless Steel and Alloy Fittings as well as details about new Ladish developments such as Seamless Reducing Elbows and Tapered Tee Design.



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Please send me without cost or obligation the new 112-page Ladish Seamless Welding Fittings Catalog and Engineering Handbook.

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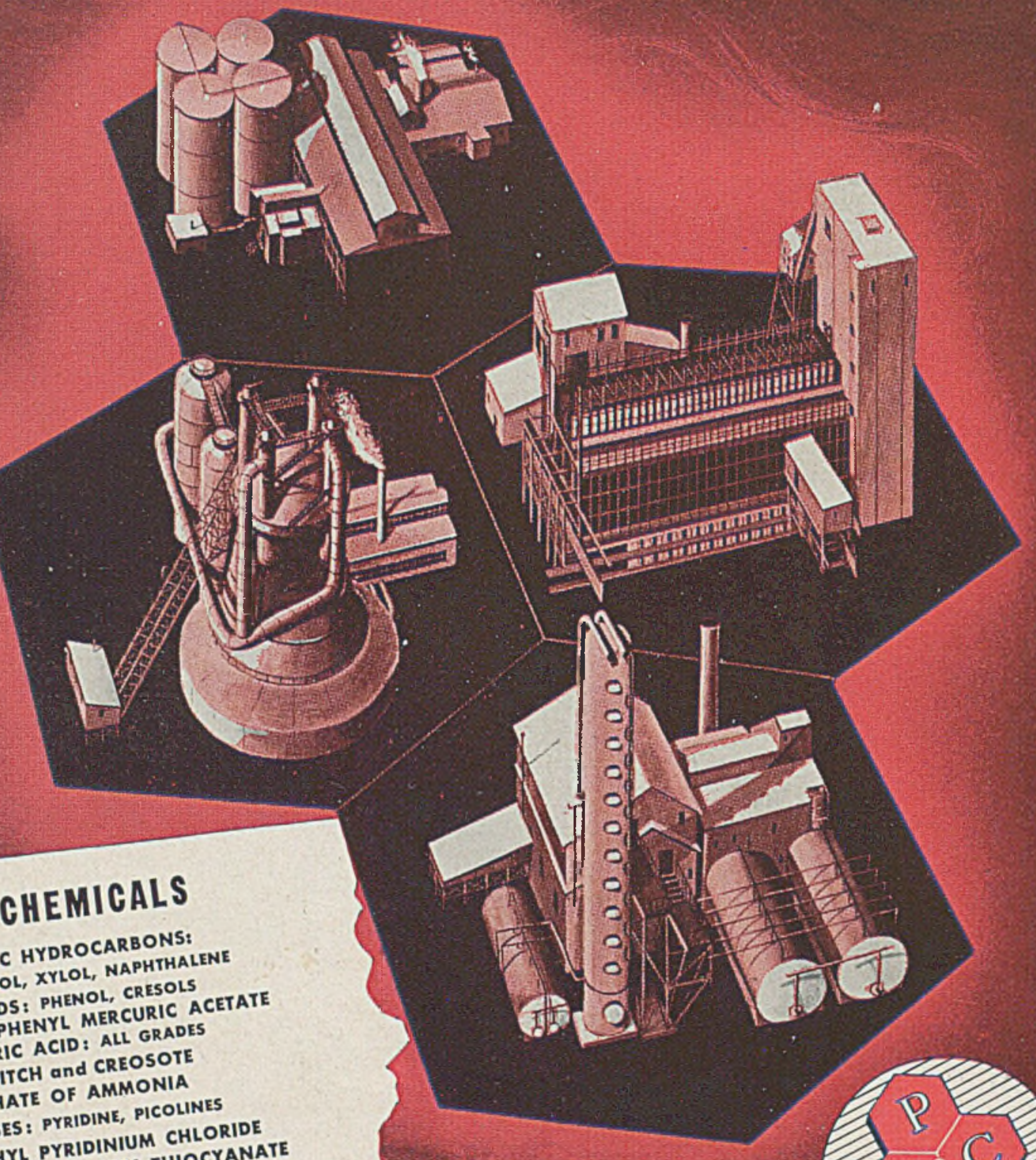

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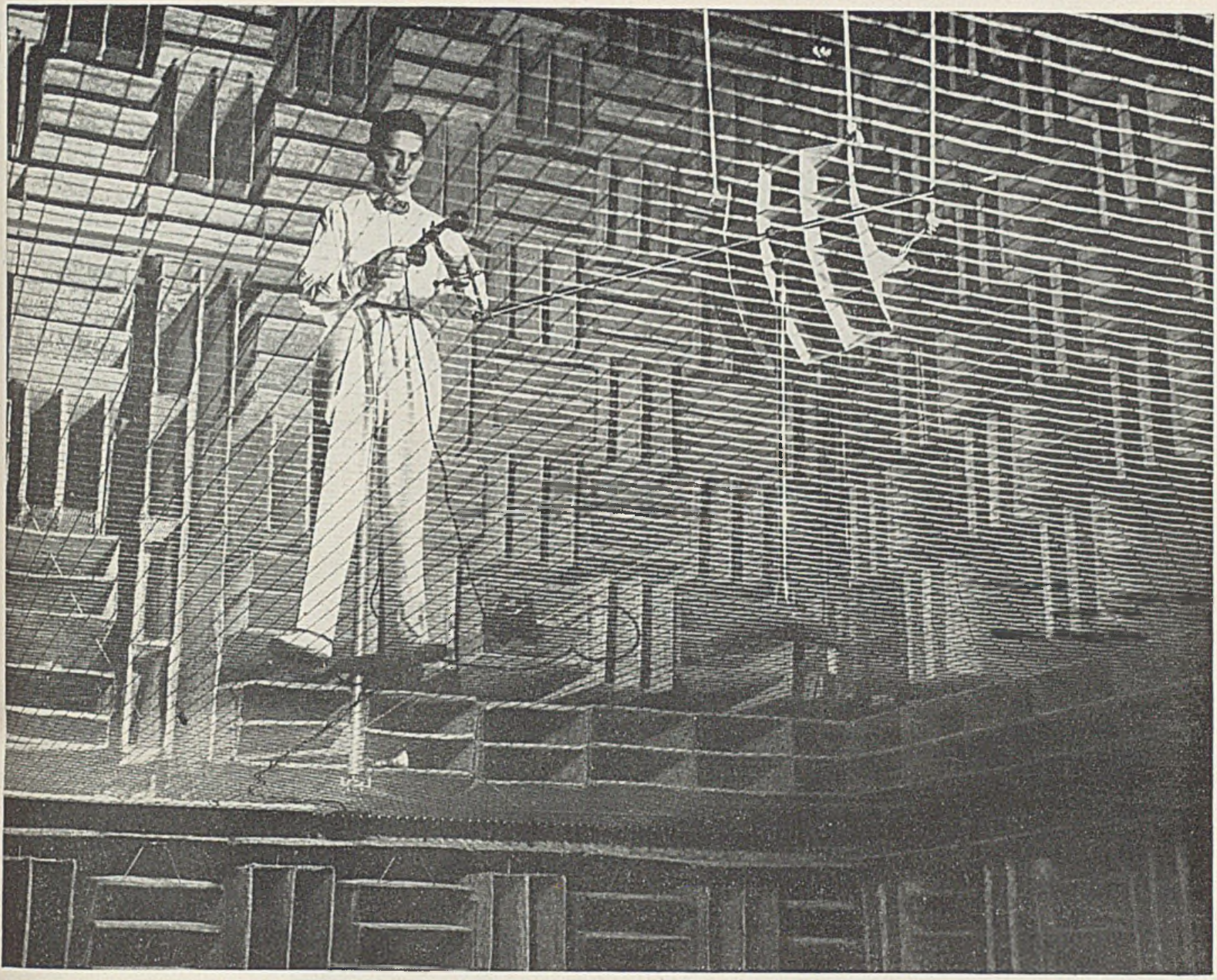

A telephone listens to a loud speaker in the new "free field" acoustic test room at Bell Telephone Laboratories. The sound-transparent "floor" is built of steel cables.

Test-tube for Sound

This giant "test-tube" is actually an echoless sound room at Bell Telephone Laboratories. Here engineers seek new facts about sound which will help them make telephone service still better and more dependable.

Bell scientists know a great deal about what happens to sound in electrical systems. This new room will give them a powerful tool to find out more about what happens to sound in the air.

In an ordinary living room, most of the sound addressed to you comes by way of reflections. At 10 feet less than 10% reaches you directly.

Sound that *bounces* at you from walls, ceilings, furniture, and your body is all right for hearing—but it poses questions for scientists who would study it uncontaminated by reflections.

The Bell Laboratories "test-tube" gives telephone people the chance to produce pure sound and analyze it reliably with respect to intensity, pitch, and direction. The entire room is lined with glass wool, contained in wire-mesh cases, wedge-shaped to give maximum absorbing area. Sound bounces along the sloping surfaces, sifts into the soft glass wool, and is gradually stifled.

This is one more example of Bell Laboratories' constant work to learn more about everything which can extend and improve telephone service.

BELL TELEPHONE LABORATORIES

Exploring and inventing, devising and perfecting for continued improvements and economies in telephone service.

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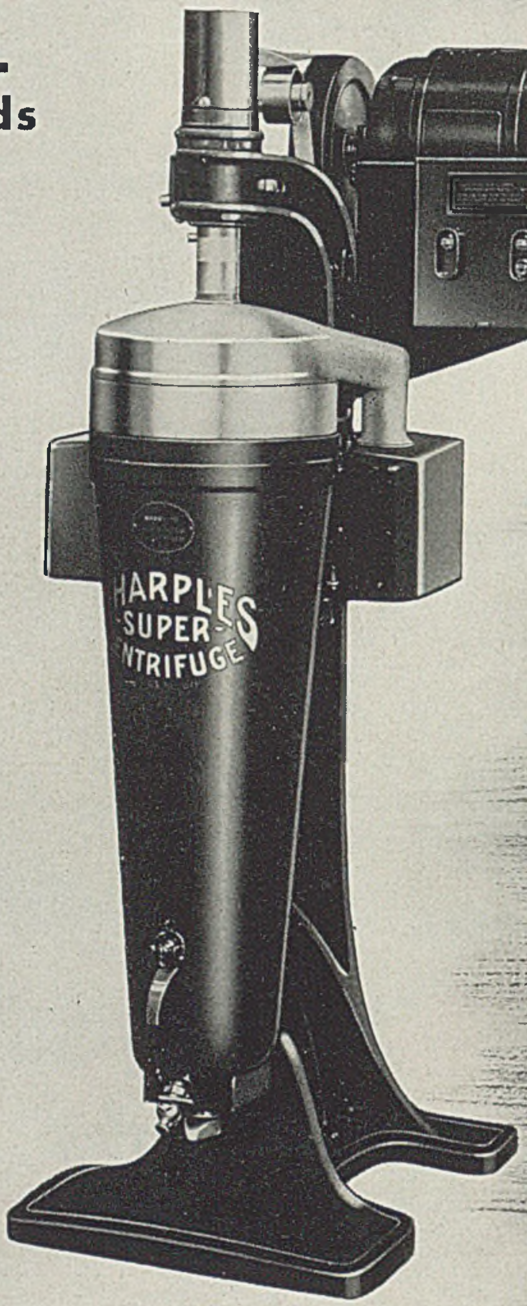
Most problems involving the separation of two immiscible liquids or of removing small quantities of solids from a liquid are readily and efficiently solved by employment of the Sharples Super Centrifuge. This unit develops the highest centrifugal force commercially available; yet is outstanding in simplicity and economy of operation.

The Super Centrifuge is widely employed in various mineral and vegetable oil refining processes, as well as for maintaining the purity of oils during use or reclaiming them after use. It is employed in the processing of countless chemical products and for clarifying such products as lacquers and enamels. To the solution of all such problems the Super Centrifuge brings the advantages of instantaneous, continuous and uniformly complete separation.

For the unusual problem, Sharples also manufactures a complete line of centrifuges designed to perform one or more special services.



The SHARPLES CORPORATION

NEW YORK 17, N. Y. 501 Fifth Avenue
CHICAGO 4, ILL. 80 E. Jackson Boulevard
BOSTON 16, MASS. 230 Congress Street
SAN FRANCISCO 5, CALIF. 686 Howard Street
CLEVELAND 15, OHIO 453 Hippodrome Annex Bldg.
EXECUTIVE OFFICES AND FACTORY, 2300 WESTMORELAND STREET, PHILADELPHIA 40, PENNA.

ADAMS
RUBBER LINED (CFR)
AND LEAD LINED (CFL)
FILTERS

For High-Degree, Crystal-Clear Filtering of Corrosive-Chemicals

- Clarification of industrial acids and corrosive liquids.
- Continuous Flow or batch operation.
- Removal of solids from liquids where the reclamation of the cake is not essential.

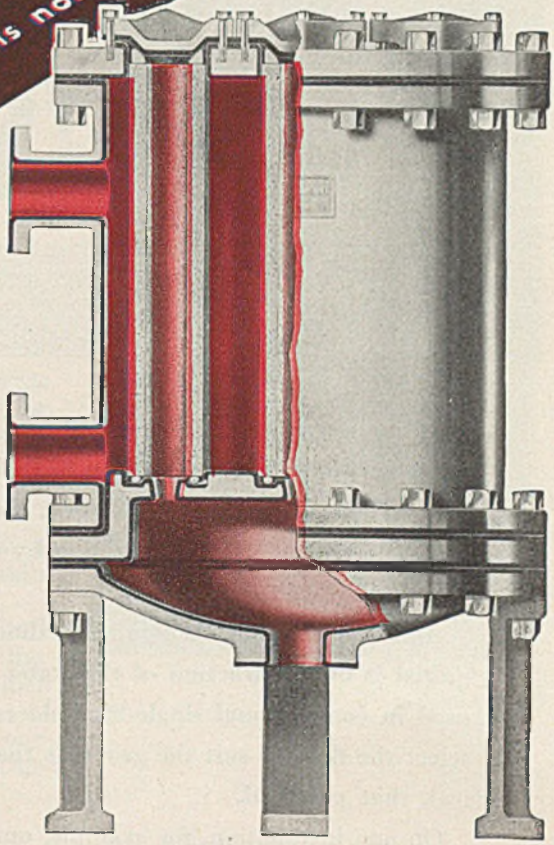
WITH
POROSTONE
AND
PORO-CARBON
FILTER MEDIUM

INERT... Resists action of acids and alkalies.

PERMANENT... Eliminates filter medium replacement.

RIGID... Permits pressure filtering and backwashing.

HIGH DEGREE FILTRATION... Obtainable in various porosities.



TYPE CFL and CFR

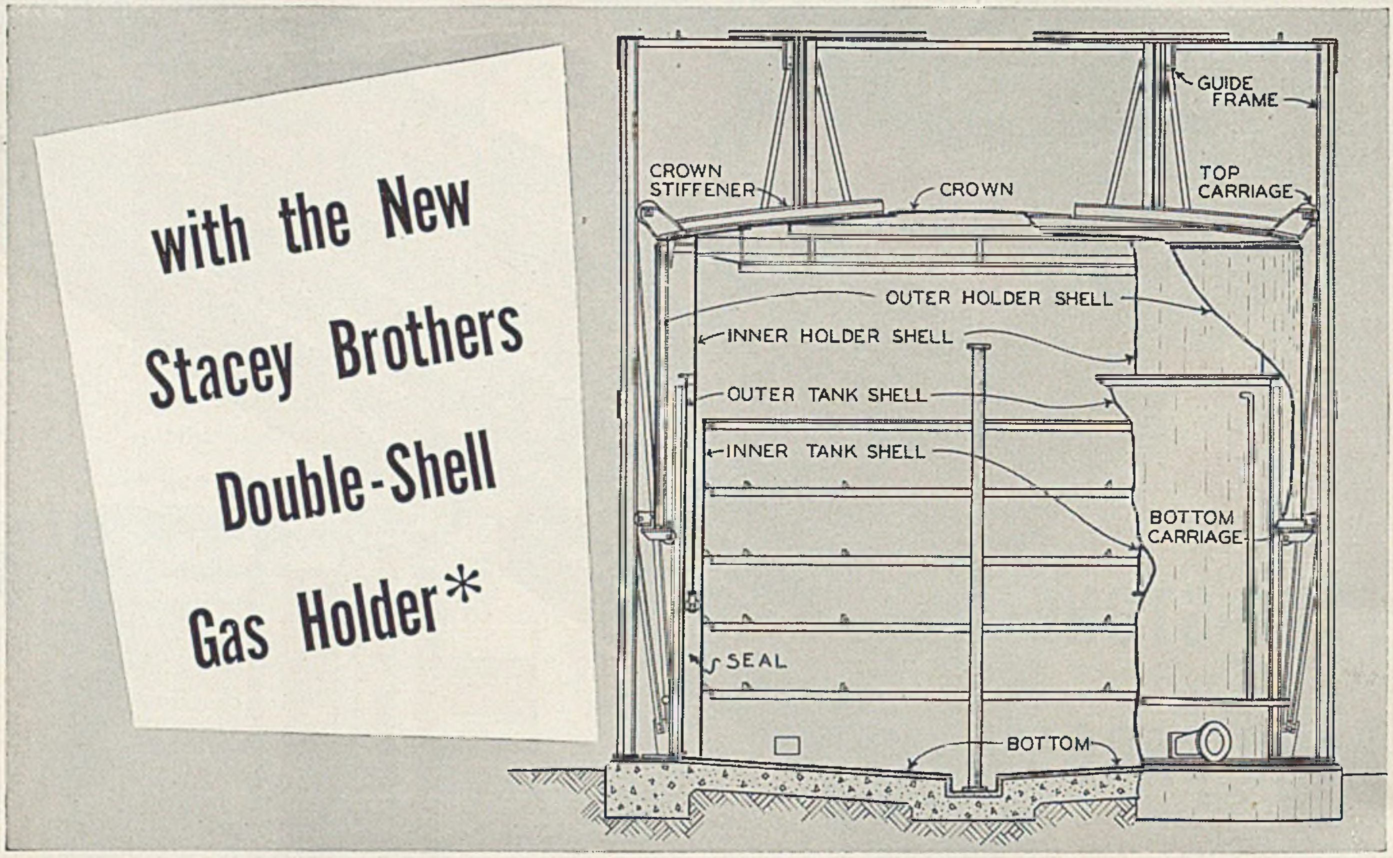
1. **Totally enclosed.** Especially safe for handling hazardous liquids, as dismantling for cleaning is not necessary.
2. **Cleaned by Backwashing...** the Adams *surge tank* method. Filtered liquid under pressure is forced through the filter in reverse flow, thoroughly cleaning the pores in a few seconds.
3. **Complete Liquid Recovery.** Valuable liquids filtered completely and withdrawn before backwashing.
4. **All contact surfaces lined** to resist action of corrosive liquid.

WRITE FOR BULLETIN
for full information on construction and operation of CFL and CFR Type Filters.

R. P. ADAMS CO., INC.
217 EAST PARK DRIVE
BUFFALO 17, NEW YORK
REPRESENTATIVES IN PRINCIPAL CITIES OF UNITED STATES AND CANADA

ELIMINATE CONTAMINATION

IN THE STORAGE OF WATER-SOLUBLE PROCESS GASES



Here's a single-lift gas holder that's an outstanding development for the storage of process gases. Regardless of the sealing fluid used, there's absolutely no chance of contamination by rain water—the design takes care of that.

And because the volume of sealing fluid required is only a fraction of the water ordinarily used in conventional single-lift holders, you can select the fluid to suit the gas—it's that economical, that practical.

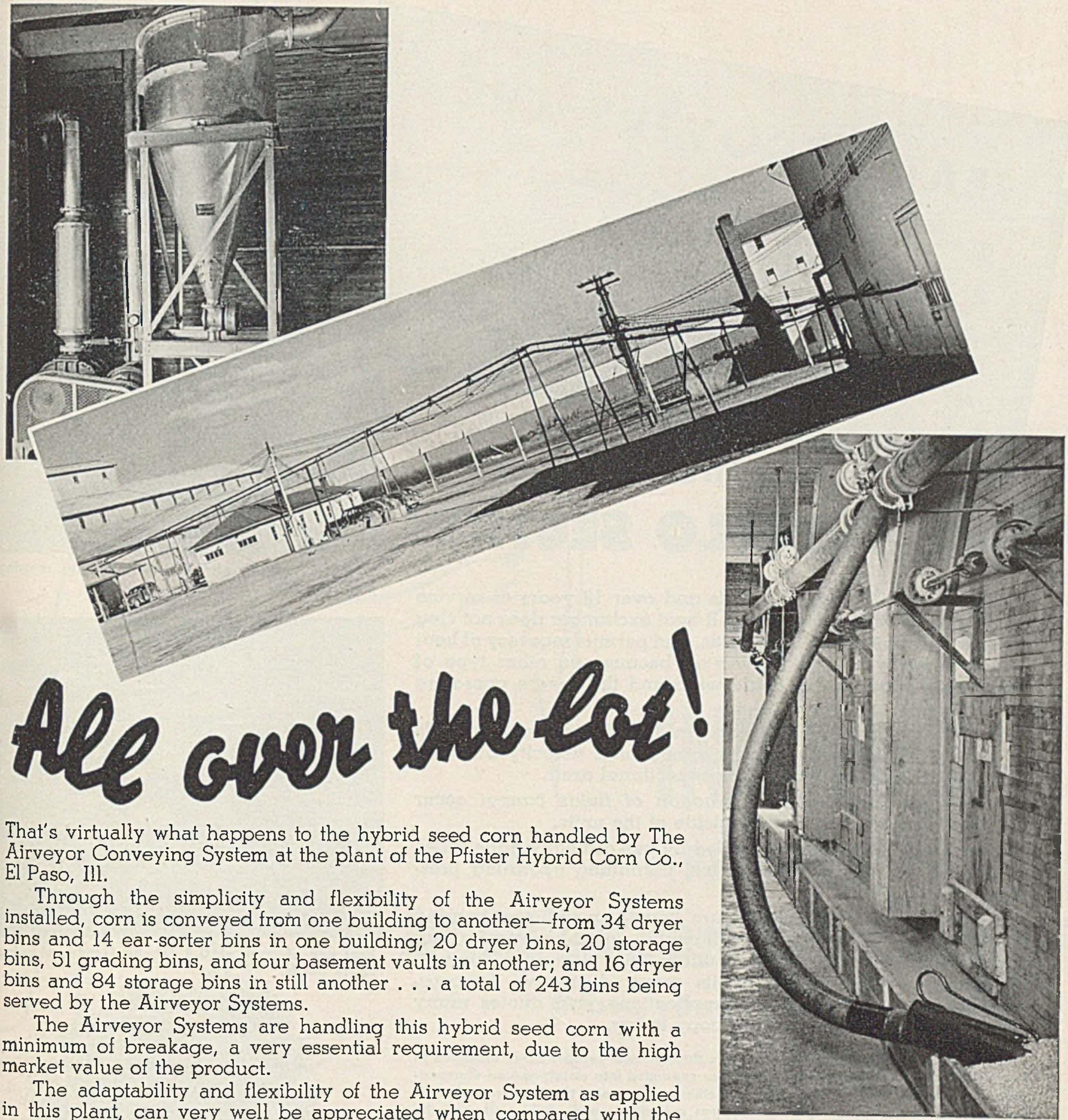
On one installation, for example, our customer is storing N_2, saturated with water-soluble organic compounds—and using octyl alcohol as the sealing compound. The installation even provides for the recovery and re-use of the condensables.

The new Double-Shell Gas Holder is one more proof of Stacey Brothers' continuing leadership in providing storage capacity for gases. No matter what the limitations or how exacting the restrictions, we're ready to design, build and erect the gas holder exactly suited to your requirements. Let us know your needs—we'll carry on from there. No obligation, of course. May we hear from you?

*Patents applied for

STACEY BROTHERS GAS CONSTRUCTION CO.
One of the Dresser Industries
5535 VINE STREET · CINCINNATI 16, OHIO

Stacey Brothers
ALL-WELDED GAS HOLDERS



All over the lot!

That's virtually what happens to the hybrid seed corn handled by The Airveyor Conveying System at the plant of the Pfister Hybrid Corn Co., El Paso, Ill.

Through the simplicity and flexibility of the Airveyor Systems installed, corn is conveyed from one building to another—from 34 dryer bins and 14 ear-sorter bins in one building; 20 dryer bins, 20 storage bins, 51 grading bins, and four basement vaults in another; and 16 dryer bins and 84 storage bins in still another . . . a total of 243 bins being served by the Airveyor Systems.

The Airveyor Systems are handling this hybrid seed corn with a minimum of breakage, a very essential requirement, due to the high market value of the product.

The adaptability and flexibility of the Airveyor System as applied in this plant, can very well be appreciated when compared with the many difficulties to be encountered through the use of mechanical equipment to accomplish the same results.

If you have a conveying problem, consult us. Conveying is our business . . . what we have done for others, we can do for you. Our engineering department is at your service.

FULLER COMPANY, CATASAUQUA, PA.

Chicago 3 · 120 So. LaSalle St.
San Francisco 4 · 420 Chancery Bldg.

FULLER-KINYON, FULLER-FLUXO AND THE AIRVEYOR CONVEYING SYSTEMS . . . ROTARY FEEDERS AND DISCHARGE GATES . . . ROTARY AIR COMPRESSORS AND VACUUM PUMPS . . . AIR-QUENCHING INCLINED-GRATE COOLERS . . . DRY PULVERIZED-MATERIAL COOLER . . . AERATION UNITS . . . MATERIAL-LEVEL INDICATORS . . . SLURRY VALVES . . . SAMPLERS.

FULLER

A-76

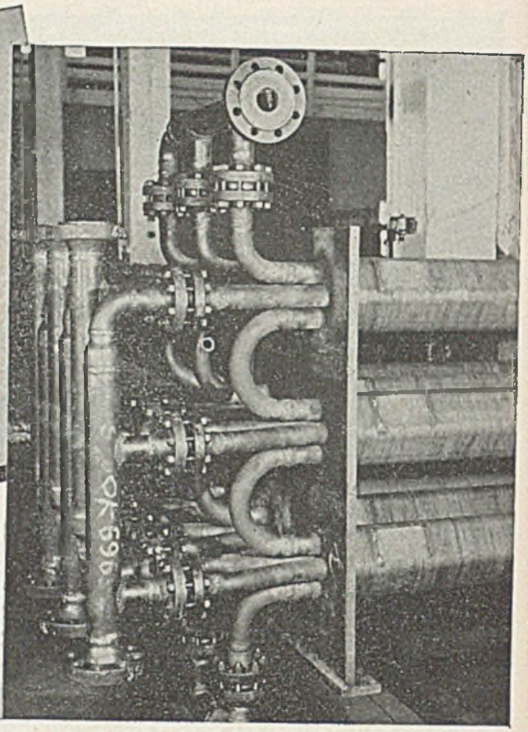
HEAT RECOVERY FROM

- Residuum
- Cracking Coil Tar
- Gas Oil
- Tar Bottoms
- Asphalt
- Clay-Bearing Oil

with maintained rated capacity

in the

G-R TUBEFLO SECTION



Front end of bank of G-R Tubeflo Sections showing pipe connections.

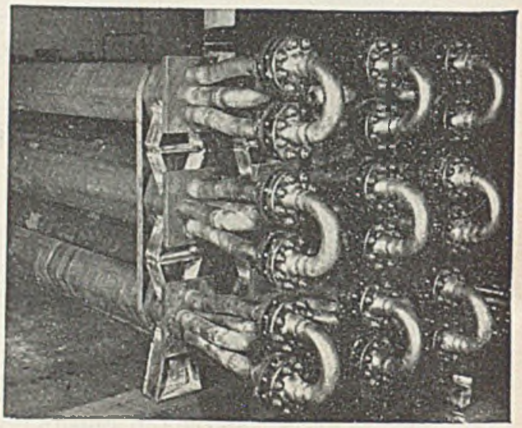
More than 3500 installed units and over 18 years of service records have proven that this G-R heat exchanger does not clog when handling tarry or dirty fluids, and permits recovery of heat which formerly had to be wasted because no other type of heat transfer apparatus could withstand the severe operating conditions.

Fouling is prevented by its design that eliminates dead ends or pockets and provides continuously high velocity of fluids through passages of uniform cross-sectional area.

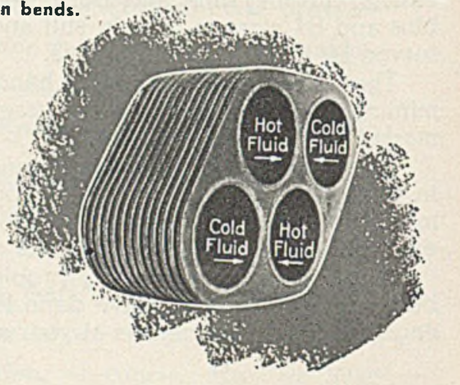
Internal leakage or contamination of fluids cannot occur because all joints are on the outside of the units.

Unequalled strength is provided by use of heavy gage tubes reinforced by closely spaced fins, permitting operating pressures up to 5000 psi.

If you have a high-temperature heavy or sediment-bearing fluid, the G-R Tubeflo Section will enable you to recover its heat effectively and economically. Bulletin 1621 describes this unit in detail, graphically shows its many distinctive features, explains several heat-saving applications, and quotes many service records. Write for your copy today.



Rear end of bank of G-R Tubeflo Sections showing return bends.



In the G-R Tubeflo Section each fluid flows through two parallel tubes arranged in two passes. The four tubes of the Section are expanded into closely-spaced diamond-shaped fins which bind the four tubes together and transfer the heat from the hot tubes to the cold tubes. All pipe connections are at one end of the unit, and the return end of the unit floats freely on change in temperature. The Sections are standard and interchangeable, and any number of sections can be connected together in series or parallel to form a compact installation for the desired duty.

THE GRISCOM-RUSSELL CO.
285 Madison Avenue • New York 17, N. Y.

GR-125

GRISCOM-RUSSELL

Pioneers in Heat Transfer Apparatus

INDONEX

REG. U. S. PAT. OFF.

PLASTICIZERS

hit the bull's-eye for many uses!

(Have you tried them?)

Grade	633½	634½	638½	VG
Color	Dark	Dark	Dark	Medium
Sp. Gr. (60°F.)	0.9958	0.9979	1.020	.9847
Flash °F.	450	460	510	460
Pour °F.	35	40	70	20
Viscosity 210°F., Saybolt, sec.	110	125	510	103
Dist. (1mm) °F. 5% . .	405	409	498	430
30%	442	445	540	458
Evap. Loss mg/10g (1hr. 100°C.)	5	5	3	4

RUBBER—The utility and low cost of the dark-colored INDONEX Plasticizers 633½, 634½, 638½ in compounding of GR-S, Natural Rubber, Neoprene, Butyl and Acrylonitrile Copolymers has been fully demonstrated. (Bulletin 13.) Circulars on special applications also available.

OTHER APPLICATIONS—All grades of INDONEX Plasticizers are compatible with a wide range of resins including various phenolics, modified phenolics, alkyds, acrylates, polyamides, cellulose derivatives, coal tar and petroleum resins, polystyrenes, rosin derivatives, and waxes. Many diverse applications as plasticizers, modifiers, or extenders are indicated. (Circular 105.) In compounding vinyl resins "INDONEX" VG is a satisfactory medium-colored partial replacement for dioctyl phthalate, tricresyl phosphate, etc. Because of its low volatility, retention of flexibility and physical properties on aging are excellent. (Circular 101.)

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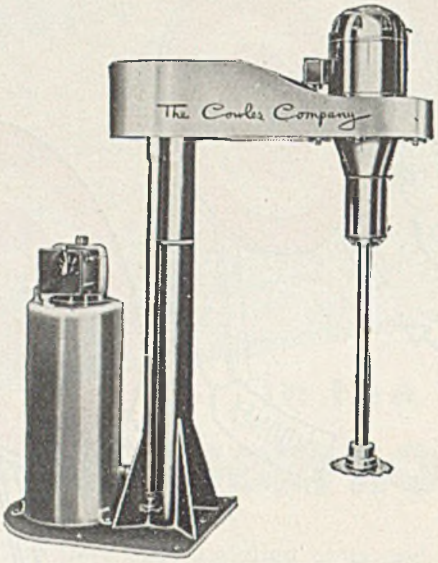
STANDARD OIL COMPANY (INDIANA)

CHEMICAL PRODUCTS DEPARTMENT

910 South Michigan Avenue Chicago 80, Illinois

2 TO 20 TIMES ——— FASTER!

ON TOUGH DISSOLVING & DISPERSING JOBS



With an impeller that elevates and swings in a 180° arc, model B is suited to rapid processing of batches brought to the machine in containers.

COWLES
Ultra-Fast
DISSOLVER
Faster because it develops laminar interface shear

Model A has a tank especially designed for the Cowles Ultra-Fast impeller. Available with a heat exchanger in the base, it increases solubility, reduces undissolved residues and is easy to clean.

Two to twenty times faster than conventional mixers, the Cowles Ultra-Fast Dissolver has an impeller of advanced design that sets up components of laminar flow, producing interface shear between multiple laminae with a high velocity gradient. The combined area of the many surfaces exposed to the shearing action plus the thinness of each laminae, subjects every particle in the batch to shear and scrubbing forces, greatly accelerating the dissolving and dispersing action.

Practically pure solutions and intimately-mingled colloidal dispersions are produced. There is no wait for undissolved residues or suspended solids to go into solution . . . no slow feeding . . . no clumping or balling of the dispersed medium in process. Splash and dead spots are virtually eliminated.

Safe, Silent, Long-Wearing

A high degree of balance in the rotating parts, coupled with rubber mountings, eliminates noise and destructive vibration. The rugged structure of the machine, the proved quality of the bearings and motor, all insure long life and low maintenance. For volatile and flammable solvents, solutes or sols, an explosion-proof motor, non-sparking tank and impeller—each adequately grounded for extra safety—are available.

Tanks and Removable Tank Models

The Cowles Dissolver is available from stock with tanks of 100 gal., 250 gal., or 500 gal. capacity; also in models for use in tanks or containers brought to the machine. Motor speed, horsepower and design of impeller are all adjusted to the gallonage, viscosity, physical and chemical properties of the materials you wish to process.

Tell us what your problem is. Write for a descriptive folder . . . or ask for a technical representative to discuss the matter with you. No charge. No obligation.

5 YEARS OF COMMERCIAL TEST SHOW COWLES DISSOLVER UP TO 10½ HOURS FASTER ON TYPICAL OPERATIONS

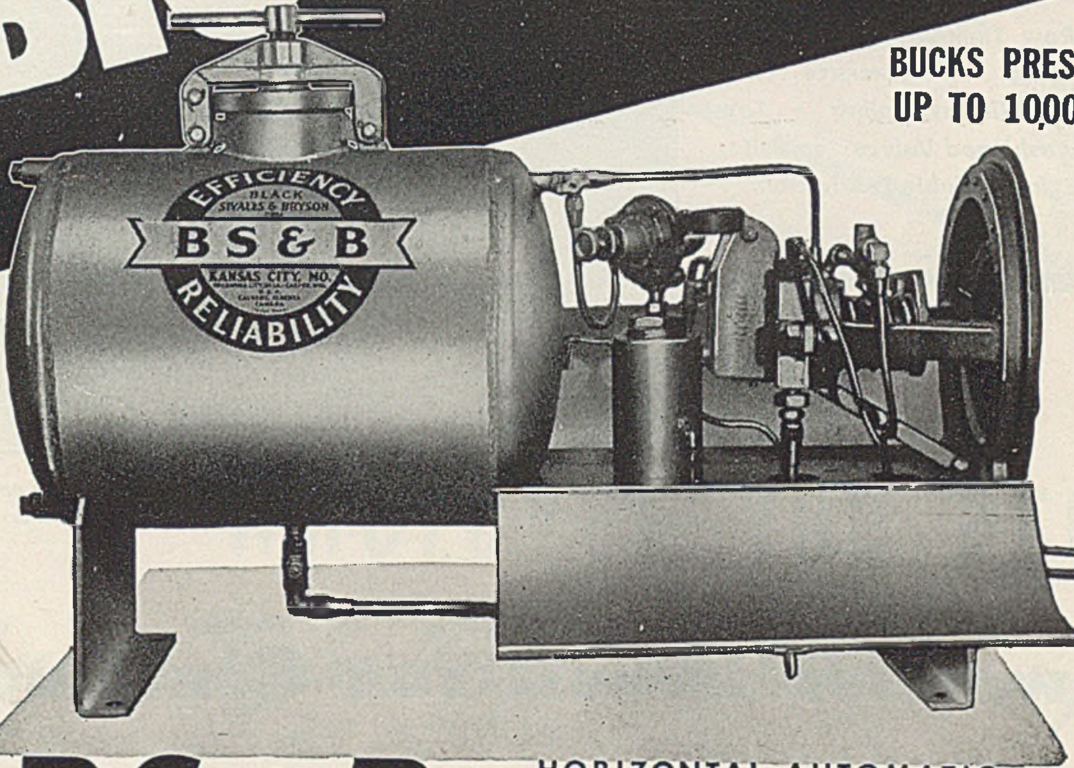
Type Operation	Material	Cowles Dissolver	Standard Mixer
Gum Cutting	Rosin	1½ Hrs.	12 Hrs.
Synthetic resin dissolving	Vinylite	1 Hr.	6 Hrs.
N/C solution	Nitrocellulose	12 Min.	90 Min.
Tinting	Enamel	5 Min.	30 Min.
Pigment dispersion	Heavy Enamel	6 Min.	150 Min.
Coating suspension	H. T. Clay	1 Hr.	9 Hrs.

The Cowles Company
INCORPORATED

Associate: Alexander Fleck, Ltd., Ottawa, Ont.

Little Fellow with the BIG "PUSH"

BUCKS PRESSURES UP TO 10,000 psi



The BS & B HORIZONTAL AUTOMATIC CHEMICAL FEEDER

Stumped by a problem of precise, timed feeding? A Black, Sivalls & Bryson Chemical Feeder accurately injects liquids into high-pressure lines, treating chemicals into flow lines, paraffin solvents into well casings, methanol into gas lines . . . handles many other similar jobs in refineries and process industries. Operates inexpensively on air or gas pressure of 20 to 50 psi. Achieves wide flexibility of discharge. Equally efficient with light or heavy viscous chemicals.

SPECIFICATIONS

Maximum Chemical Output per Day—$12\frac{1}{2}$ gallons with $\frac{3}{8}$" piston; 50 gallons with $\frac{3}{4}$" piston
Capacity of Chemical Tank—10 gallons
Piston Sizes—$\frac{3}{8}$" and $\frac{3}{4}$"
Overall Size—1′ 2″ wide—3′ 3″ long—2′ 1″ high.

Available for immediate shipment. Your nearest BS&B Sales Engineer has complete specifications and details. Call him today . . . or write the Executive Offices, Black, Sivalls & Bryson, Inc., Power and Light Building, Kansas City 6, Missouri.

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RELIABILITY

KANSAS CITY, MO.
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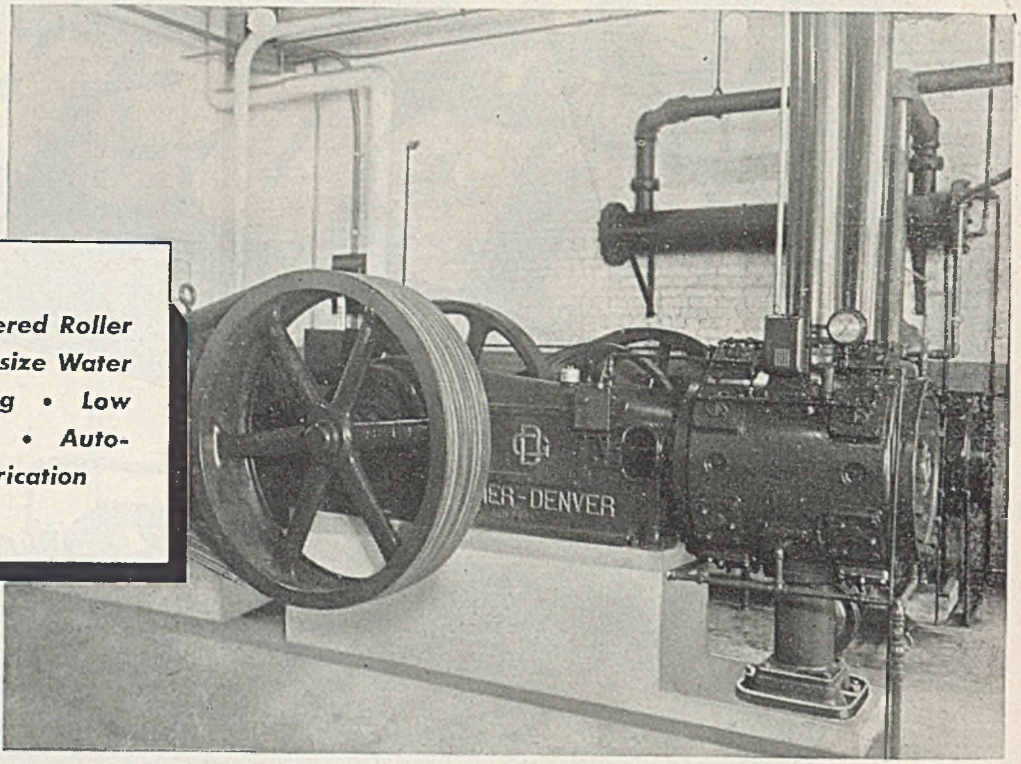
Double Row Timken Tapered Roller Main Bearings • Oversize Water Jackets for Efficient Cooling • Low Lift, Air Cushioned Valves • Automatic and Reliable Lubrication



Gardner-Denver RX, single-cylinder horizontal, double-acting, single-stage compressor—available in capacities from 89 to 1292 cubic feet displacement per minute.

No wonder it will run Continuously

Every part of a Gardner-Denver "RX" Air Compressor is built for heavy-duty, full-load, continuous service. And with such service goes high volumetric and mechanical efficiency—unusually low power costs! Here are additional features which make the RX a favorite in so many industries:

★ *Duo-plate cushioned valves—simple, durable, unusually quiet.*

★ *Large and unrestricted port areas help reduce heat of compression; insure effective lubrication with minimum oil consumption.*

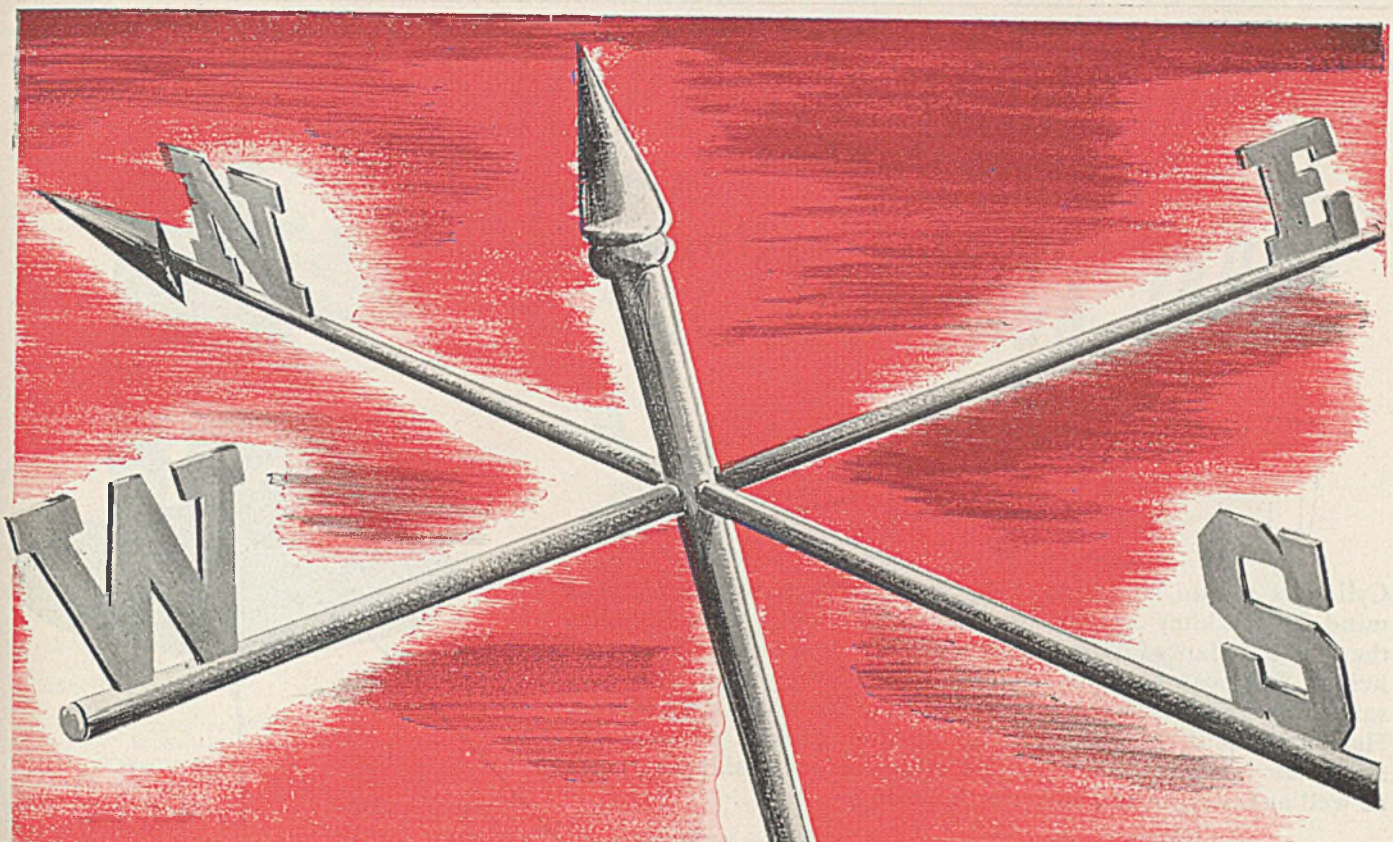
★ *Suction valve unloaders on all inlet valves result in lowest power consumption during unloaded period.*

★ *Oil-tight, dust-tight construction.*

For complete information about Gardner-Denver RX Compressors, write Gardner-Denver Company, Quincy, Illinois

USE COMPRESSED AIR FOR SAFETY CONVENIENCE FLEXIBILITY

GARDNER-DENVER
SINCE 1859



Wherever you are

...there's a Taylor Forge distributor near you

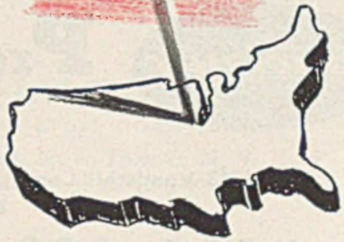
Just as WeldELLS "have everything," WeldELL distribution has everything! In every industrial trading center there is an Authorized Taylor Forge Distributor. One of them near you stands ready to give you prompt delivery from comprehensive local stocks of welding fittings and forged steel flanges for piping systems.

Your local distributor draws upon the accumulated wealth of Taylor Forge engineering knowledge and is in constant touch with strategically located district offices. Your distributor and his staff have been carefully chosen to give you practical advice and the best service in the shortest possible time.

It will pay you to know these people who represent the strong link between you and the finest of welding fittings and forged steel flanges. If you are not acquainted yet, write us.

WeldELLS

**TAYLOR FORGE
STEEL FLANGES**



TAYLOR FORGE & PIPE WORKS

General Offices & Works: P. O. Box 485, Chicago 90
New York: 50 Church Street Philadelphia: Broad Street Station Bldg.
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What to look for in choosing cylinders

design

Cylinders should be designed with the shippers' requirements in mind. In Hackney Anhydrous Ammonia Cylinders, for instance, there is a balanced relationship between diameter and over-all height. They can be easily, quickly and safely handled. And they save floor space as they can be safely stored in a vertical position. Hackney liquid chlorine, sulphur dioxide, as well as ammonia and other cylinders, are designed to assure lower shipping costs as well as faster, safer and easier handling.

light weight and strength

Strength and light weight should be balanced. One should not be sacrificed for the other. In Hackney Cylinders you are assured of a lightweight cylinder, yet one of adequate strength. This is made possible by the Hackney Deep Drawing Process, which assures uniform sidewall thickness and eliminates all excess material. Then, too, the physical qualities of Hackney Cylinders are improved by special heat-treating after complete fabrication.

appearance

While this feature may seem a factor of less importance in industrial selling, a wise shipper sees that his container reflects the high quality of his product. The Hackney Seamless Cylinder is handsome in appearance, for the cold drawing process results in a smooth, eye-appealing finish.

write for full details

Be sure to get the whole story on Hackney Seamless Cylinders. They are designed and constructed to give lowest transportation costs, full protection to product, ease of handling and ample resistance to transportation and handling abuse.

Hackney
MILWAUKEE

Pressed Steel Tank Company

Manufacturers of Hackney Products

Main Office and Plant: 1451 South 66th Street, Milwaukee 14
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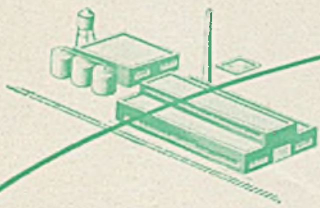
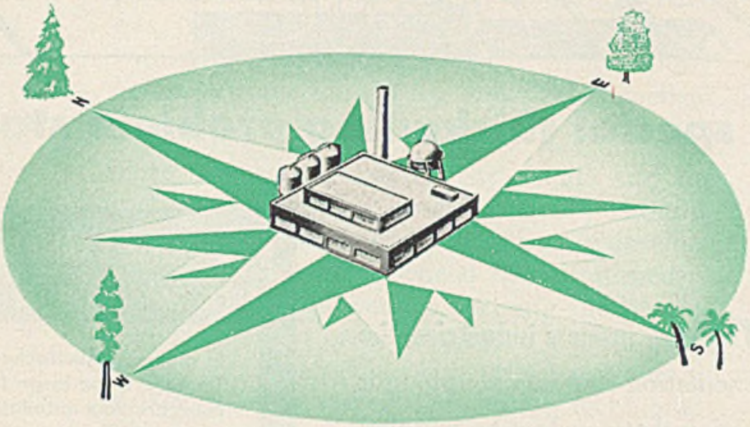
CONTAINERS FOR GASES, LIQUIDS AND SOLIDS

OUR PLANTS BLOOM THE YEAR 'ROUND

... IN YOUR BACK YARD!





... so when it's Basic Chemicals for American Industry

call on GENERAL CHEMICAL first!

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*General Chemical Company, Inc.

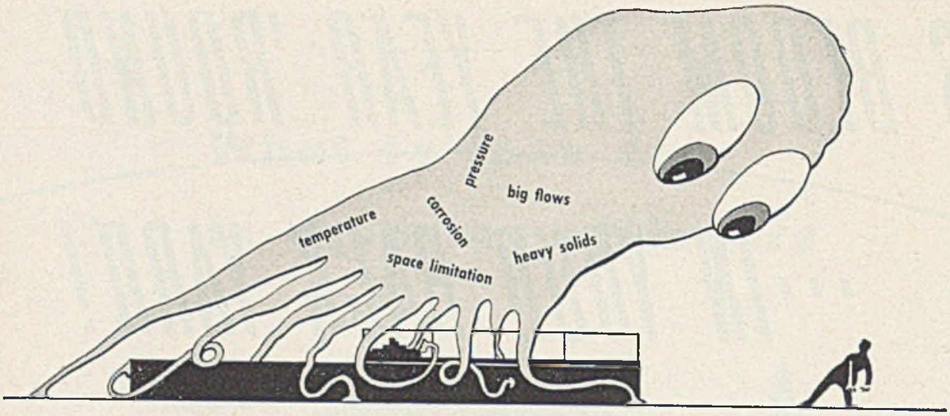
At every point in the compass . . . wherever Industry is centered . . . there is a General Chemical producing works or distributing station serving the territory. To supply Industry's requirements across the country, General Chemical has 33 major producing locations from which pour a steady stream of essential chemicals.

These include acids—alums—sodium compounds—fluorine derivatives—other heavy chemicals—as well as reagents, fine and pharmaceutic chemicals. Thus, coast to coast, a full flow of this broad and varied range of products, so necessary to peak production, is assured.

That is why . . . in every branch of Industry everywhere . . . the choice is General Chemical *first* in "Basic Chemicals for American Industry."

BASIC CHEMICALS
FOR AMERICAN INDUSTRY

GENERAL CHEMICAL DIVISION
ALLIED CHEMICAL & DYE CORPORATION
40 Rector Street, New York 6, N. Y.
Offices Serving Industry from Coast to Coast



is a special thickening problem staring YOU in the face?

In many process industries, the sedimentation step is a simple unit operation that can best be handled by a standard type of Dorr Thickener. But just as often, special conditions dictate innovations in thickening techniques and equipment to insure successful operation . . . or any operation at all! It is here that the Dorr ability to provide the *special* unit, tailor made for the *special* job, pays dividends.

At the right are a few instances of how this ability is paying off for users in a variety of process industries. If you have a thickening problem that involves special handling, why not check with Dorr . . . the oldest manufacturer of sedimentation equipment . . . *with the newest ideas.*

SOME EXAMPLES OF DORR THICKENER ADAPTABILITY

PROBLEM IN PIGMENTS

In pigment manufacture, Dorr Thickeners, too large for economical indoor installation, are covered with concrete domes for weather-proofing and to prevent contamination.

FLUE DUST AND SPACE SAVING

In blast furnace flue dust recovery, the tight space problem is being licked by the use of Dorr Torq *Tray* Thickeners . . . at no sacrifice in heavy duty durability.

CORROSION HEADACHES

In many process industries, special fabrication of Dorr Thickeners including lead, rubber, wood and alloys is commonplace to avoid corrosion from acid or abrasive slurries.

HIGH LIFTS FOR STORAGE PROBLEMS

For the storage of relatively light materials, motor operated lifting devices providing lifts of up to six feet are supplied on Dorr Thickeners.

BIG FLOWS AND ECONOMY

Where tremendous flows are encountered, excessive tank cost is often avoided by the installation of multiple units of Dorr Thickeners in a single basin . . . many times in earthen tanks.

PRESSURE SEAL FOR PETROLEUM

In separating catalysts from oil processed by cat-cracking, corrosive solutions at elevated temperatures under slight pressure are handled by Dorr Thickeners with a specially designed pressure seal for covered tanks.

DORRCO

THE DORR COMPANY, ENGINEERS
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Dorr Technical Services and Equipment Are Also Available Through Associated Companies and Representatives in the Principal Cities of the World. Names and Addresses on Request.

RESEARCH **DORR** **ENGINEERING** **EQUIPMENT**

CHEMICAL MAGIC

MEET THE MAGICIAN'S ASSISTANT

Out of such common materials as salt, sand and petroleum, the big new General Electric silicone plant at Waterford will produce unique materials; oils, greases, rubber, plastics and varnish to withstand heat and cold to a degree never before possible; one of the most water repellent films ever known . . .

That is chemical magic. The results and the methods of obtaining them are equally astounding. Now let's look behind the scene. In development of this project General Electric turned to Blaw-Knox for process engineering and process equipment. The magician needed a good assistant, someone he could lean on for real help in working out very special processing techniques. We did our part well. The magician is now using his assistant on other difficult jobs.

Let us help with your processing problems.

CHEMICAL PLANTS DIVISION
OF BLAW-KNOX CONSTRUCTION COMPANY
321 Penn Avenue, Pittsburgh 22, Pa.

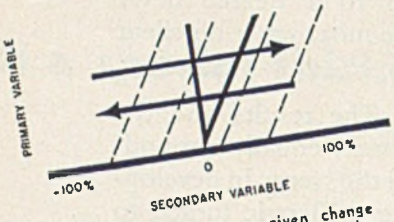
BLAW·KNOX

This NEW Device . . .

WHAT IS MEANT BY ZERO AND SPAN ADJUSTMENTS

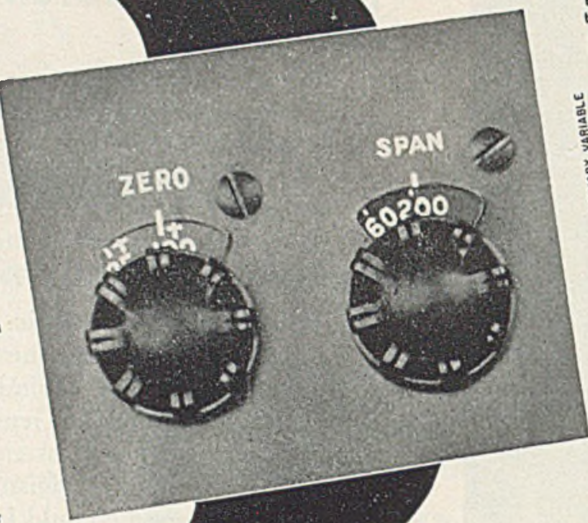
The ZERO adjustment is linear. It shifts the starting point for Indexet motion without changing the amount

FIG. 1



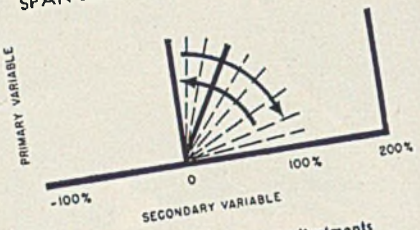
of index motion for a given change of air pressure from the primary instrument. ZERO adjustment is illustrated in Fig. 1.

The SPAN adjustment changes the amount of Indexet motion in the secondary instrument for a given change in air pressure from the primary instrument.

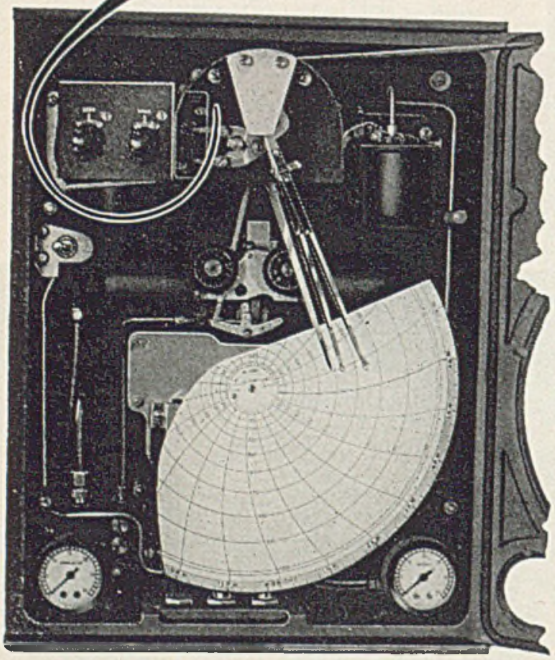


Any practical proportion can be set between an air pressure change from the primary instrument and the motion of the control index in the secondary. SPAN adjustment is shown in Fig. 2.

FIG. 2



Combining these two adjustments full flexibility of relationship is possible. ZERO can be adjusted from minus 100% to plus 100%; SPAN from 0 to 200%.



Puts REAL Flexibility in Process Relationships

THE Brown *Adjustable Indexet* is a new tool for handling tough control problems involving the relationship between two variables, such as temperature, pressure, flow or liquid level.

Essentially, it is a Pneumatic Receiver operating in response to a change in air pressure from a primary measuring instrument. This change in air pressure from the primary instrument causes the Indexet to change the control point setting in the secondary instrument. In addition, the ZERO and SPAN adjustments make this relationship fully adjustable...putting real flexibility in process relationships. (See explanation above.)

The ZERO and SPAN adjustment knobs are directly inside the instrument door and are accessible without disturbing the chart or the operation of the instrument in any way. A graduated scale above each knob shows the settings in percentage terms—making adjustment an easy matter. Adjustable limit stops may be set to prevent the control index from exceeding any desired limits. Write for Catalog 2221.

THE BROWN INSTRUMENT COMPANY, 4480 WAYNE AVE., PHILADELPHIA 44, PA.
DIVISION OF MINNEAPOLIS-HONEYWELL REGULATOR CO.
SUBSIDIARY COMPANIES IN TORONTO • MEXICO CITY • LONDON
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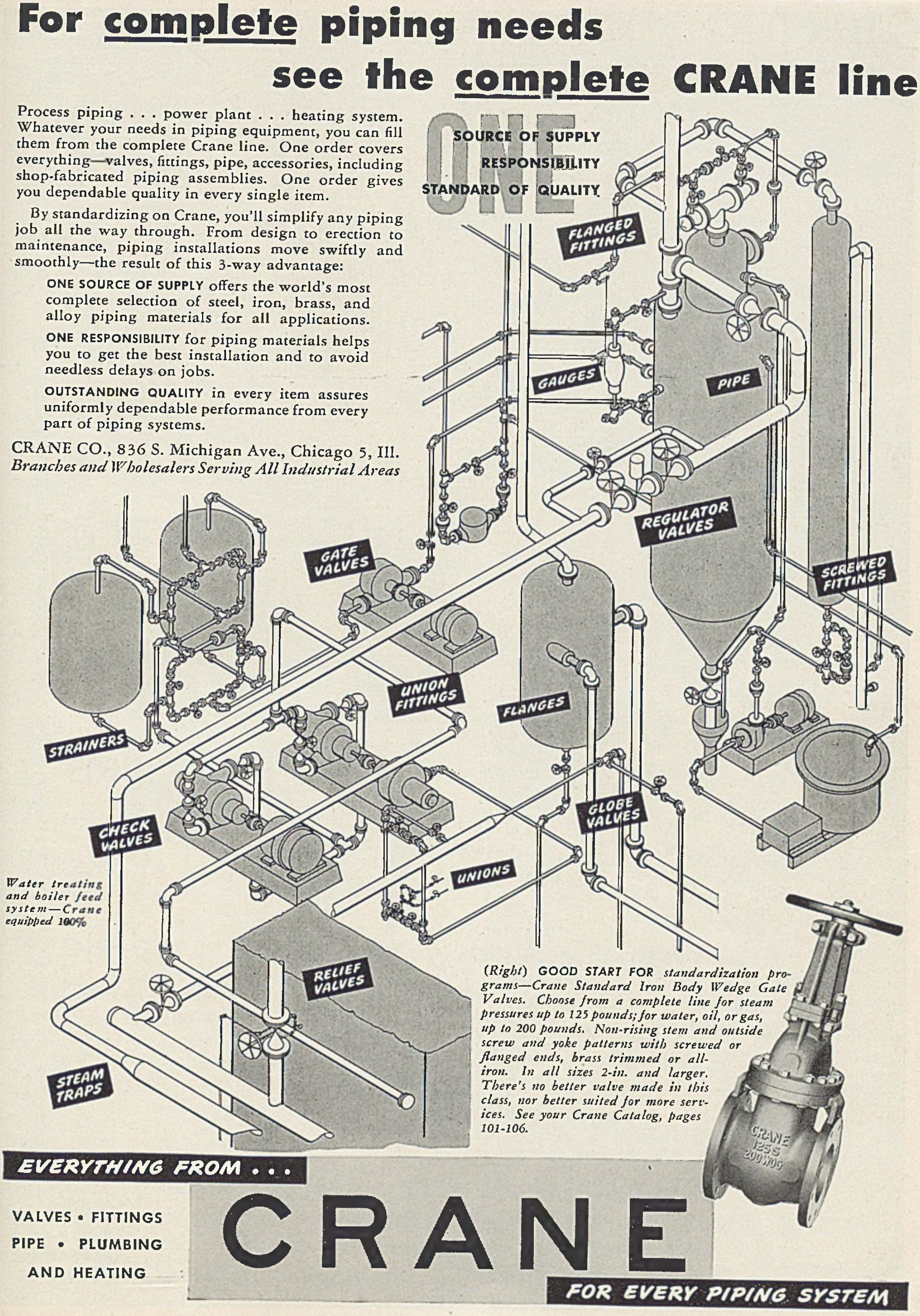
BROWN PNEUMATIC TRANSMISSION SYSTEM

FOR TEMPERATURES . . . . PRESSURES . . . . FLOWS . . . . LIQUID LEVELS



For complete piping needs see the complete CRANE line

Process piping . . . power plant . . . heating system. Whatever your needs in piping equipment, you can fill them from the complete Crane line. One order covers everything—valves, fittings, pipe, accessories, including shop-fabricated piping assemblies. One order gives you dependable quality in every single item.

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ONE SOURCE OF SUPPLY offers the world's most complete selection of steel, iron, brass, and alloy piping materials for all applications.

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OUTSTANDING QUALITY in every item assures uniformly dependable performance from every part of piping systems.

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Water treating and boiler feed system—Crane equipped 100%

(Right) **GOOD START FOR** *standardization programs—Crane Standard Iron Body Wedge Gate Valves. Choose from a complete line for steam pressures up to 125 pounds; for water, oil, or gas, up to 200 pounds. Non-rising stem and outside screw and yoke patterns with screwed or flanged ends, brass trimmed or all-iron. In all sizes 2-in. and larger. There's no better valve made in this class, nor better suited for more services. See your Crane Catalog, pages 101-106.*

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VALVES • FITTINGS
PIPE • PLUMBING
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CRANE

FOR EVERY PIPING SYSTEM

Palladium on Carbon Powder 5%

FOR
HYDROGENATION
AT LOW
TEMPERATURE
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LOW PRESSURE

Of the many industrial uses of the platinum metals, catalysis is of the greatest promise for future development. Our research departments devote a large part of their time to the development of new catalysts and new catalytic reactions.

Palladium has proven to be an unexcelled catalyst for liquid phase hydrogenation of terpenes, vitamins, alkaloids, and other organic compounds.

Our refinery is well equipped to insure complete recovery of the precious metals in exhausted catalyst material.

Our long experience and research of platinum metal catalysts is available to you. We shall be very happy to advise you upon the catalyst best suitable to your particular process.

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"Console" model: magnification 500 X and 5000 X; useful photographic enlargement to 100,000 diameters.

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HELPING GREAT COMPANIES PLAN TOMORROW'S PRODUCTS

RCA ELECTRON MICROSCOPES— multiply vision 100,000 times

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And so it goes. The RCA Electron Microscope reveals long-held secrets of particle size, shape and structure . . . down to macromolecular dimensions. Its enormous resolving power and depth of focus permit easy visual and photographic inspections hitherto impossible . . . up to 100,000 diameters' magnification!

Out of such research grows tomorrow's products . . . improved in countless ways through industry's widespread use of the electron microscope. RCA specialists are ready to advise you regarding the value of the electron microscope in any suggested application. Write Dept. 39-L.

RCA

SCIENTIFIC INSTRUMENTS
RADIO CORPORATION of AMERICA
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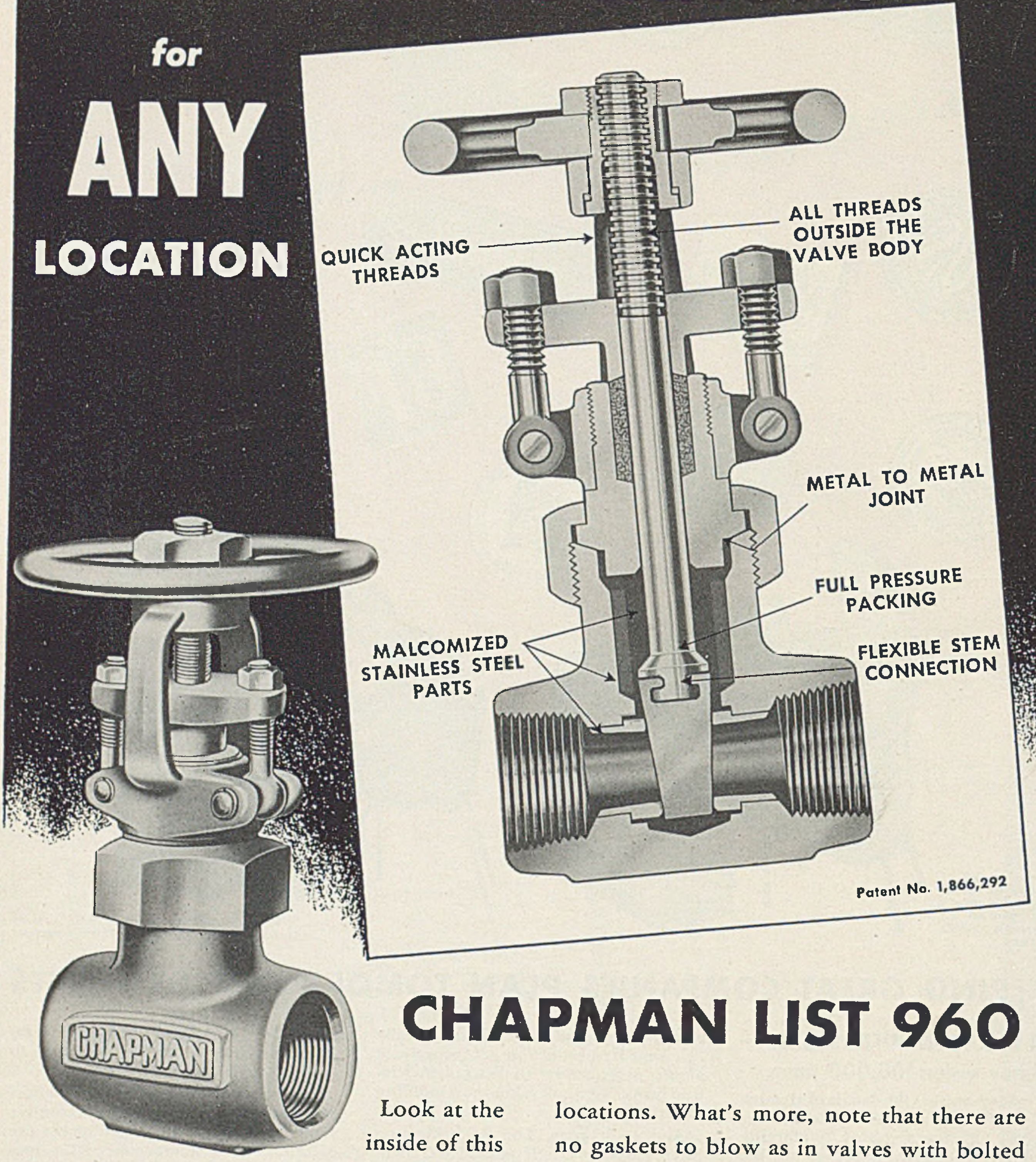
Here's the Gate Valve You Need for

EXPOSED LOCATIONS—

for

ANY LOCATION



CHAPMAN LIST 960

Look at the inside of this sturdy List 960 gate valve. Note its tough, compact construction and its forged steel body and yoke. See how it's fitted with a flanged forged steel packing gland which protects the threads on the valve yoke from rust and corrosion when the valve is used in exposed locations. What's more, note that there are no gaskets to blow as in valves with bolted bonnet connections.

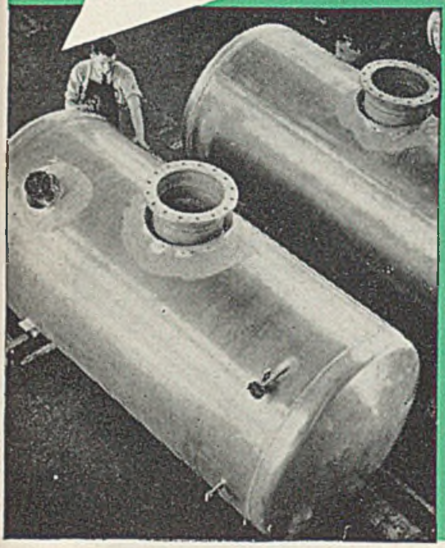
Available in sizes from ¼″ to 2″—in carbon steel for pressures to 800 pounds at 750° F. For higher pressures, specify List 990.

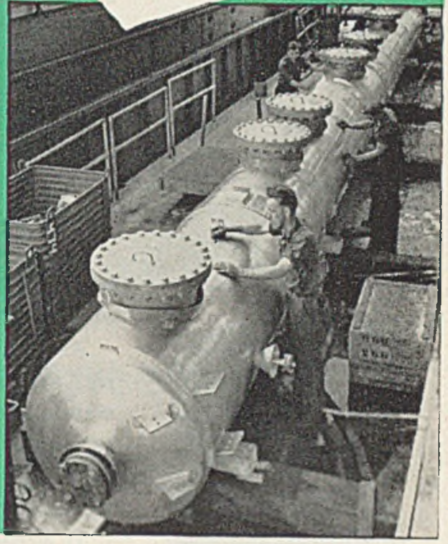
THE CHAPMAN VALVE MFG. CO.
INDIAN ORCHARD, MASS.

You Can Use Alcoa Aluminum

FOR

STORAGE TANKS ■ CONDENSERS ■ TOWERS





TO

Speed Reactions • Save Money

Reduce Depreciation • Prevent Contamination

Hydrogen sulfide, carbon dioxide, ammonia, and similar compounds generally cause no appreciable attack on Alcoa Aluminum refinery and process equipment, even when moisture is present. Depreciation costs are reduced, equipment shows more in-service time without repairs, and replacement is postponed for longer intervals.

Alcoa Aluminum Condenser Tubes are safe to use with many chemicals and most types of cooling waters. The high heat conductivity of aluminum permits rapid heat transfer, allows condensers, towers, and heat exchangers to work at high thermal efficiency.

Because aluminum does not rust, many chemical products that must be kept water-white and free from contamination are safely processed and stored in aluminum tanks.

Our engineers will be glad to tell you where Alcoa Aluminum is now being used, and help work out the details of using it in your plants. ALUMINUM COMPANY OF AMERICA, 2154 Gulf Building, Pittsburgh 19, Pennsylvania. Sales offices in 54 leading cities.

MORE PEOPLE WANT **MORE** ALUMINUM FOR **MORE** USES THAN EVER

ALCOA FIRST IN ALUMINUM

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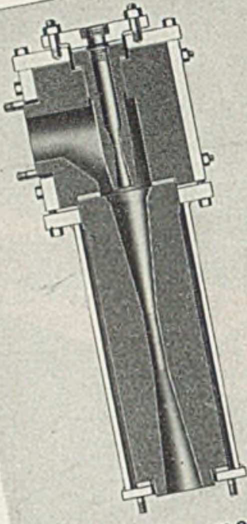
ALCOA ALUMINUM

IN EVERY COMMERCIAL FORM

HANDLING CORROSIVE VAPORS
at 150 Microns



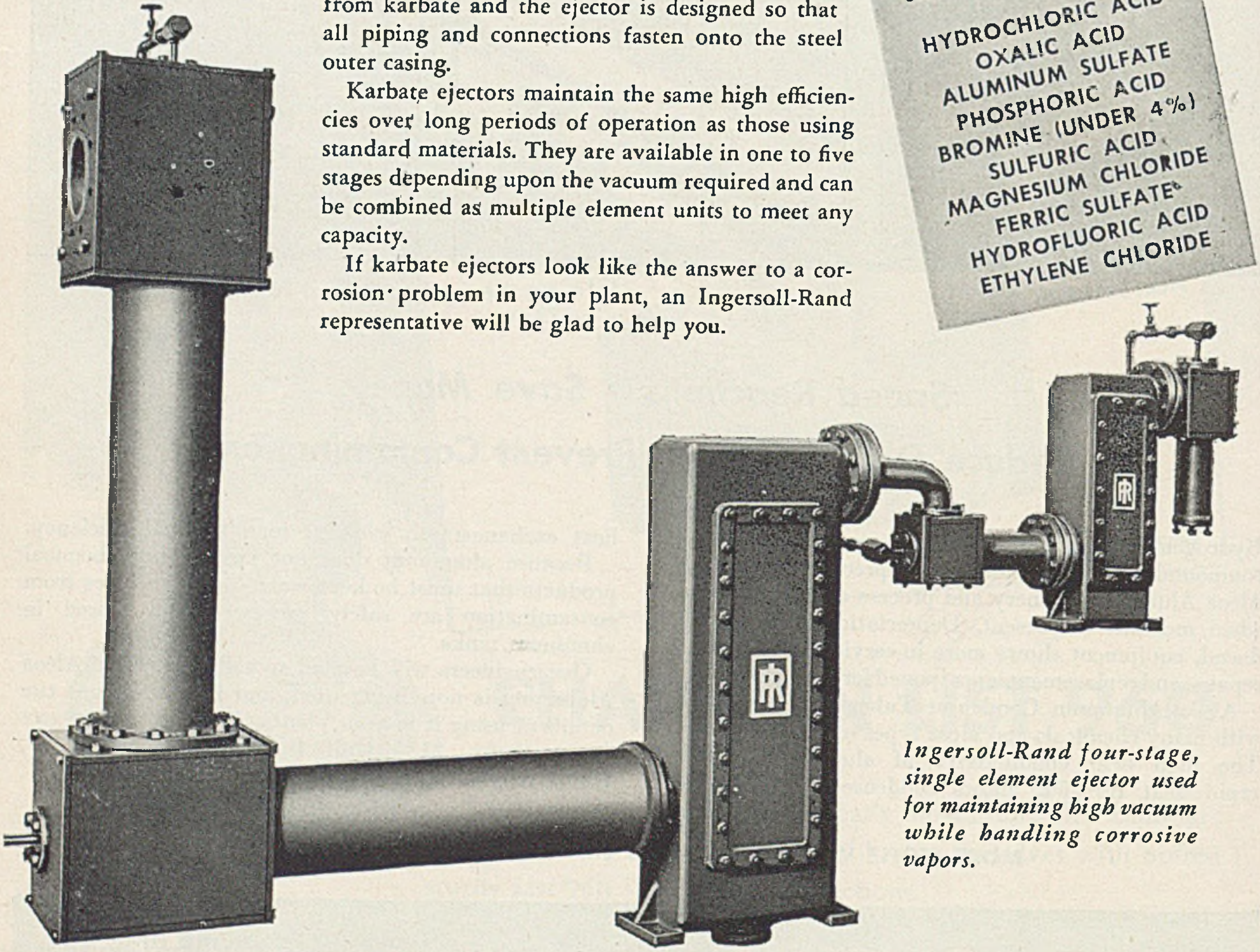
Here are some of the acids and active corrodants that karbate will effectively handle.

HYDROCHLORIC ACID
OXALIC ACID
ALUMINUM SULFATE
PHOSPHORIC ACID
BROMINE (UNDER 4%)
SULFURIC ACID
MAGNESIUM CHLORIDE
FERRIC SULFATE
HYDROFLUORIC ACID
ETHYLENE CHLORIDE

When it is necessary to pull extremely high vacuum (150 microns) while handling corrosive vapors, Ingersoll-Rand Karbate Ejectors will resist corrodants that attack stainless steel, monel, bronze and other common corrosion resistant materials. Karbate is a chemically inert, nonporous form of carbon that is highly resistant to corrosion, thermal shock and erosion. All ejector parts exposed to corrosive vapors are machined from karbate and the ejector is designed so that all piping and connections fasten onto the steel outer casing.

Karbate ejectors maintain the same high efficiencies over long periods of operation as those using standard materials. They are available in one to five stages depending upon the vacuum required and can be combined as multiple element units to meet any capacity.

If karbate ejectors look like the answer to a corrosion problem in your plant, an Ingersoll-Rand representative will be glad to help you.



Ingersoll-Rand four-stage, single element ejector used for maintaining high vacuum while handling corrosive vapors.

COMPRESSORS • AIR TOOLS
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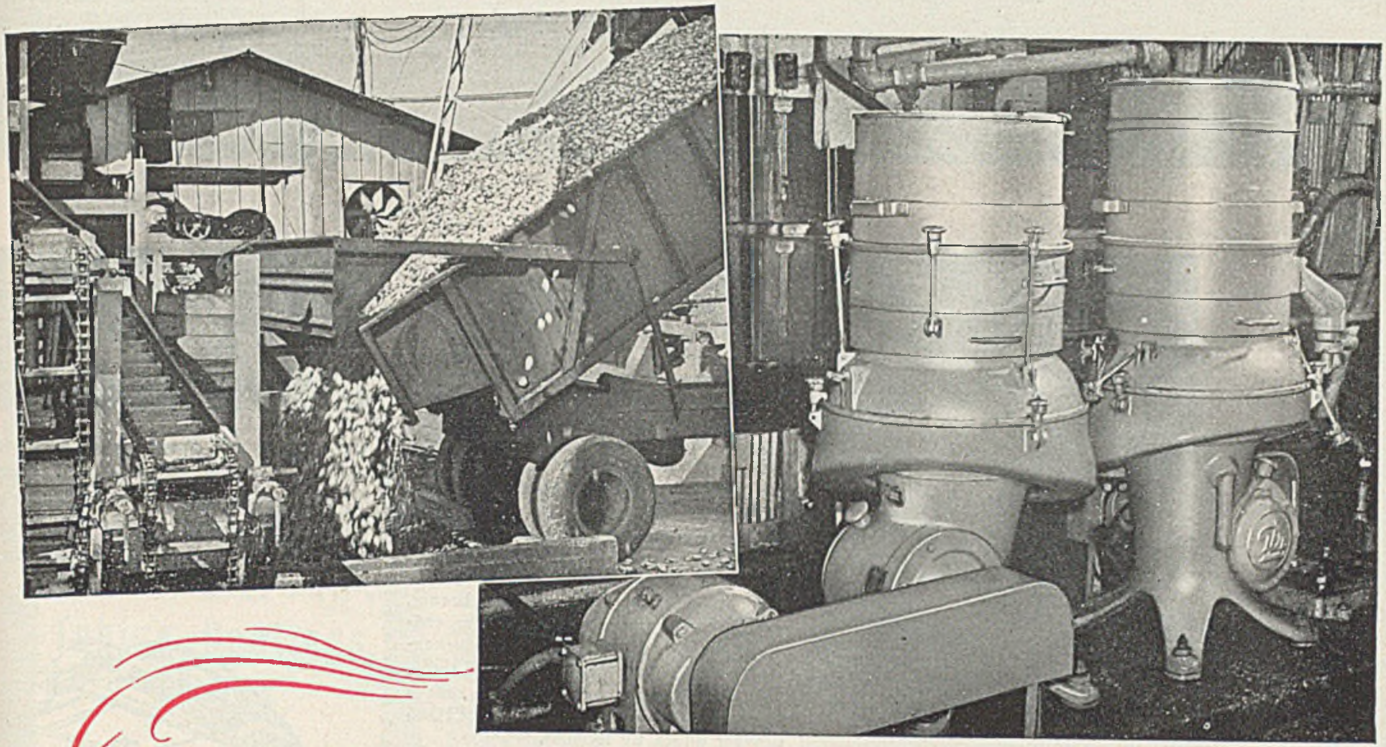


an ANCIENT process is speeded up by DE LAVAL CENTRIFUGALS

THE making of essential oils changed from a slow process to a continuous one when centrifugal force replaced settling tanks. Now two types of De Laval centrifugal machines are saving time and increasing production in this industry.

The De Laval "Nozzle-Matic" continuously separates oil emulsion, water introduced in the washing phase, and albido. Other De Laval Oil Purifiers polish the oil, leaving it dry and bright.

This is another in the ever-increasing list of processes that can be made much more profitable by being made continuous. The De Laval range of types and sizes is large, and includes a machine for practically every problem where centrifugal force may be used to advantage.

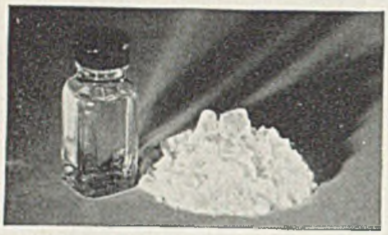
Write for additional information. It will help if you will outline your problem.

THE DE LAVAL SEPARATOR COMPANY
165 Broadway, New York 6 427 Randolph St., Chicago 6
DE LAVAL PACIFIC CO., 61 Beale St., San Francisco 5
THE DE LAVAL COMPANY, Limited, Peterborough, Ont.

DE LAVAL Centrifugal Machines

. . . FOR PROCESSING SYSTEMS

FOR YOUR INFORMATION



New Uses For
AROCLORS

Promise New Profits, New Performance

In the AROCLORS (chlorinated biphenyl and chlorinated poly-phenyls) Monsanto offers industry more than 25 starting points that can lead to many an improvement in profits, processing, product performance and production costs. Manufactured exclusively by Monsanto, the AROCLORS comprise a "family" of over 25 chemical compositions, unique in the field of synthetics. At present, they fill many and varied requirements not met by materials previously available. Their future potential is even greater—they possess numerous interesting properties that suggest wider fields of application still awaiting development. To help uncover new and profitable uses for the AROCLORS, a list of their principal characteristics and applications is included here.

New ideas for you from these suggested uses

Electrical Materials and Equipment . . . Nonflammability, high resistivity, high dielectric strength and low power factor of liquid resinous AROCLORS are extremely useful in many electrical applications. Coatings for underground cables are additionally protected by AROCLORS against corrosion and attack by termites.

Hydraulic Pressure Medium . . . The AROCLORS contribute an unusually high safety factor when used as hydraulic media in high-pressure operations such as zinc-alloy die casting. Possible line leaks or breaks, even in the presence of open flames, constitute no fire hazard because of the nonflammable characteristics of the AROCLORS.

Soil Poisoning . . . Added to fill-in soils in any type of construction, the AROCLORS prevent attack by termites.

Chlorinated Rubber Finishes . . . When used as plasticizers for chlorinated rubber, AROCLORS add toughness and flexibility. Valuable as finishes for alkaline surfaces such as brick, concrete, stucco, and for acid, alkali and moisture-resistant coatings.

Paints and Varnishes . . . AROCLORS are used to give great durability and adhesion and to vary the degree of hardness or flexibility in quick-drying paints.

Adhesives, water-insoluble.

Expansion Medium, in bellows controls and thermostats.

Liquid Heat Transfer Medium.

High Temperature Lubrication.

Ethyl Cellulose; Nitrocellulose, to impart weather resistance, luster, adhesion, decreased burning rate.

Properties of the AROCLORS

The AROCLORS range in form and appearance from mobile oily liquids to fine white crystals and hard transparent resins. They possess the following properties:

Adhesion . . . AROCLOR resins adhere strongly to glass, metal, or smooth varnished or lacquered surfaces.

Electrical . . . High resistivity, high dielectric strength and low power factor are characteristics of the AROCLORS.

Thermal Conductivity . . . Of particular value as high-temperature, low-pressure fluid heat transfer medium.

Non-Drying . . . When exposed to air, even in thin films, no noticeable oxidation or hardening occurs. Drying rate of lacquer films is not retarded.

Nonflammability . . . High safety factor in high-temperature, high pressure applications. When fluxed with resins and pitch-like materials, AROCLORS give a product having a decreased fire hazard.

Stability . . . AROCLORS have marked stability towards alkalies, acids, heat and oxidation.

Compatibility . . . AROCLORS are compatible with most of the common plastic materials.

Solubility . . . AROCLORS are easily soluble in most of the common organic solvents and drying oils. They are insoluble in water.

Thermoplasticity . . . No condensation or hardening appears upon repeated melting and cooling.

Vaporization . . . The AROCLORS have low vaporization losses.

Aroclors. Reg. U. S Pat Off

2, 4 D
2, 4 D Sodium Salt

Formulators and processors are invited to send for information on 2, 4 D and 2, 4 D Sodium Salt—now available in commercial quantities. Mail the coupon on the facing page—or write, outlining any special information you require.

Good News for the Petroleum Industry

Two recent developments by the Petroleum Chemicals Department of Monsanto are of special interest to the petroleum industry—SANTOPOID* 29 and SANTODEX,* both oil additives.

SANTOPOID 29 is an all-purpose gear-lubricant additive that simplifies blending and cuts distribution costs. Used with suitable base oil stocks, it is now possible to blend a single, all-purpose lubricant that will serve equally well in hypoid or conventional gears . . . in high-speed passenger car or heavy-duty truck service.

SANTODEX is a viscosity-index-improver that makes possible viscosity indices up to 140 or higher, depending on the base oil stock with which it is blended. It is an all-hydrocarbon material and improves the viscosity index of oils without the expense and waste of extreme refining. Readily soluble in mineral oil, does not stratify or separate from a lubricant; can be easily compounded in conventional refinery equipment.

Ask for technical data—use coupon on opposite page.

*Reg. U. S. Pat. Off.

News of Monsanto Chemicals for the Process Industries...December, 1947

NON-TOXIC...
Tubing, Coatings, Sheets

Where lack of toxicity is essential in a plasticizer to be used for such applications as tubing for the transfer of beer, beverages, milk and liquid foods—industry is turning more and more to the use of Monsanto Santicizers B-16, E-15 and M-17.

In addition to their non-toxicity, these glycollates impart no characteristic odor or taste. This makes them further useful in their application to can and cap liners. They are also used in hospital sheetings, acrylic dentures and similar products.

Quick Facts

SANTICIZER B-16...Compatible with most resins; imparts good flexibility and clear, brilliant films that are tough, moisture resistant, and have good weathering qualities. Especially good with vinyl resins and nitrocellulose.

SANTICIZER E-15 . . . An excellent plasticizer, particularly for nitrocellulose and cellulose acetate and for most resins. Light-fast and relatively non-volatile, even from the thinnest films. With both acetyl and nitrocellulose, gives clear, tough, flexible films with greatly increased resistance to moisture penetration.

SANTICIZER M-17 . . . A solvent plasticizer for vinyls and cellulosics, imparting a high degree of plasticity. Probably the best cellulose acetate plasticizer available. Insoluble in petroleum products—confers oil resistance to films in which it is used.

MORE INFORMATION . . . Send for literature, technical data, samples. If you wish specific information, a letter outlining your application problems will receive prompt attention.

Santicizer: Reg. U. S. Pat. Off.

MONSANTO CHEMICAL COMPANY, 1705 South Second Street, St. Louis 4, Missouri. District Sales Offices: New York, Philadelphia, Chicago, Boston, Detroit, Cleveland, Cincinnati, Charlotte, Birmingham, Houston, Akron, Los Angeles, San Francisco, Seattle. In Canada: Monsanto (Canada) Limited, Montreal.

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CHEMICALS AND PLASTICS

SERVING INDUSTRY . . . WHICH SERVES MANKIND

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Many pharmaceutical manufacturers, food manufacturers and users of gluconates for other industrial purposes *turn first to Pfizer*. With some, the deciding factor is their own experience with the consistently high quality of Pfizer products in general and gluconates particularly. With others it is the reputation of Pfizer for almost a century as manufacturing chemists, and the knowledge of the extensive modern plant facilities for gluconate production. Chas. Pfizer & Co., Inc., 81 Maiden Lane, New York 7, N. Y.; 444 West Grand Ave., Chicago 10, Illinois; 605 Third Street, San Francisco 7, Calif.

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SODIUM GLUCONATE
$NaC_6H_{11}O_7$
Molecular weight 218.13
White crystalline product
Soluble in water

PFIZER
CALCIUM GLUCONATE
$CaC_6H_{11}O_7 \cdot H_2O$
Molecular weight 448.27
White crystalline salt
Solubility in cold water:
3 grams per 100 cc of water
Readily soluble at high temperatures

PFIZER
COPPER GLUCONATE
$Cu(C_6H_{11}O_7)_2$
Blue crystalline powder

PFIZER
FERROUS GLUCONATE
$Fe(C_6H_{11}O_7)_2 \cdot H_2O$
Brownish yellow powder

PFIZER QUALITY

PFIZER
Manufacturing Chemists Since 1849

5104

Only POWELL makes a *complete* line of valves for the CHEMICAL & PROCESS INDUSTRIES

More than a century ago, the Wm. Powell Company adopted a definite, long-range policy, namely, to concentrate on making valves—and valves only—for all branches of industry. As a result Powell has been able, through the years, to meet each new flow control requirement as it has arisen. Thus at any given time in more than a hundred years, the Powell Line has always been *complete*.

As of today, the Powell Line includes Bronze and Iron Valves of all required types, designs and sizes; Cast Steel Valves of all types in pressure classes from 150 to 2500 pounds; and Valves for Corrosion Resistance, available in the widest range of metals and alloys ever used in making valves.

The Wm. Powell Co., Cincinnati 22, Ohio

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POWELL VALVES for Corrosion Resistance are available in the following Metals and Alloys.

Stainless Alloys
18-8S
18-8S Mo.
18-8S Cb.
Misco "C"
Durimet 20
11.5-13.5% Cr. Iron
18% Cr. Iron
28% Cr. Iron
25% Cr. 12% Ni.

Nickel and Nickel Alloys
Nickel
Monel Metal*
Inconel*
Hastelloy Alloys†
(A, B, C and D)
Illium
D-10

Bronzes—Acid, Aluminum, Silicon
Everdur
Herculoy
Ampco
Ampcoloy
76
90-10
88-10-2

Alloy Steels
Carbon Steel
4-6% Cr. .5% Mo.
3½% Nickel Steel
6-8% Cr. Mo.
8-10% Cr. Mo.

Cast Irons
Cast Iron
3% Nickel Iron
Ni-resist*

Aluminum
Alcoa No. 43
Alcoa No. B-214

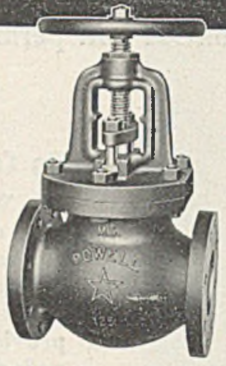
Silver

Hard Lead

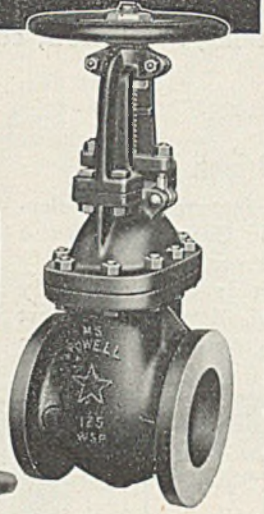
Molybdenum

*Registered trade-names of the International Nickel Co., Inc.

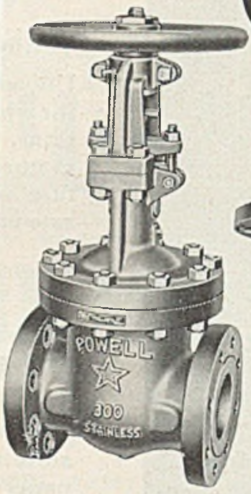
†A registered trade-name of the Haynes-Stellite Co.



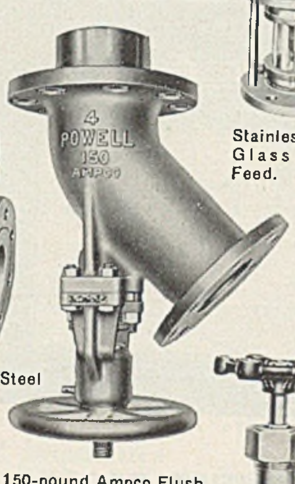
Large 125-pound Iron Body Bronze Mounted or All Iron Globe Valve.



Large 125-pound Iron Body Bronze Mounted or All Iron Gate Valve.



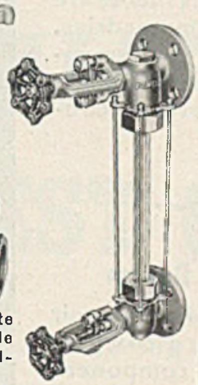
Class 300-pound Stainless Steel O. S. & Y. Gate Valve.



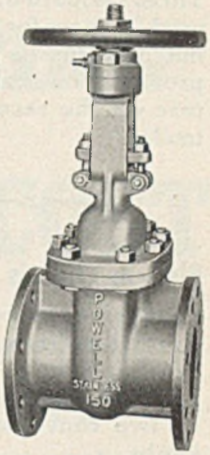
150-pound Ampco Flush Bottom Tank Valve.

Stainless Steel Glass Sight Feed.

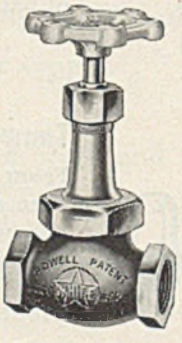
200-pound Bronze Gate Valve with renewable "Powellium" nickel-bronze disc.



O. S. & Y. Liquid Level Gauge, offset pattern, for 150 pounds W. P.

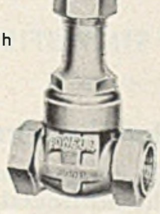


New, standard 150-pound Stainless Steel O. S. & Y. Gate Valve.

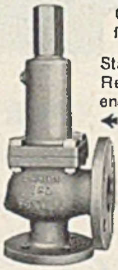


200-pound Bronze Globe valve with renewable stainless steel seat and regrindable, renewable "Powellium" nickel-bronze disc.

200-pound Nickel Swing Check Valve.

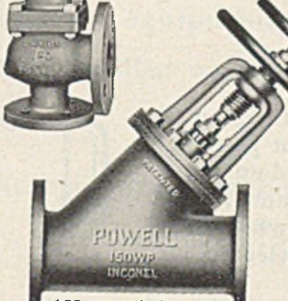


200-pound Monel Metal* Gate Valve.

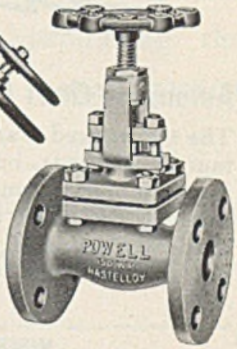


Stainless Steel Angle Relief Valve with enclosed spring.

Stainless Steel Needle Globe Valve.



150-pound Inconel* O. S. & Y. "Y" Valve with Powell Patented Seat Wiper.



150-pound Hastelloy† O. S. & Y. Globe Valve.

POWELL VALVES

CAPACILOG The New *Electronic* SCRIBER

AVAILABLE AS POTENTIOMETER—DEFLECTION—RESISTANCE THERMOMETER TYPES

The many exclusive features of the Wheelco Capacilog and its amazing simplicity make it the outstanding scriber for the measurement, indication, control and permanent record of variables in the process industries.

Electronic Principle

Instantaneous electronic action ... no physical contact between measurement and the electronically operated pen, eliminating pointer sticking or mechanical wear.

Standard Electronic Tubes

Three standard 6N7 tubes are used. Two are for motor drive, but only one is necessary—providing an extra safety feature on the recording controller.

Plug-in Chassis Design

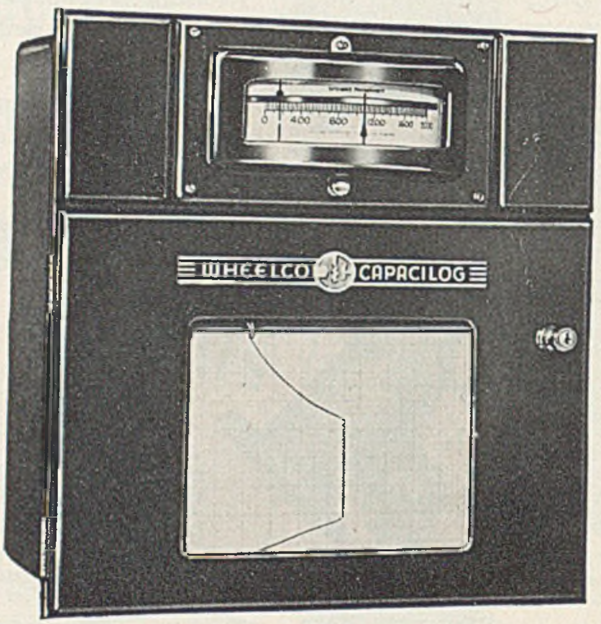
Drawer type plug-in, electronic chassis contain a compact arrangement of component parts. The circuit is adjusted by two conveniently located knobs.

Automatic Chart Reroll

The 10″ printed chart remains taut at all times, but permits inspection of wound-up portions of the chart and automatically rewinds when the pull-out section is released.

Power-Driven Pen

A unique feature of the deflection type Capacilog is the power-driven pen—the only one that is electronically synchronized with the direct reading pointer.



FOR SIMPLIFIED RECORDING

Back-lash Breaker

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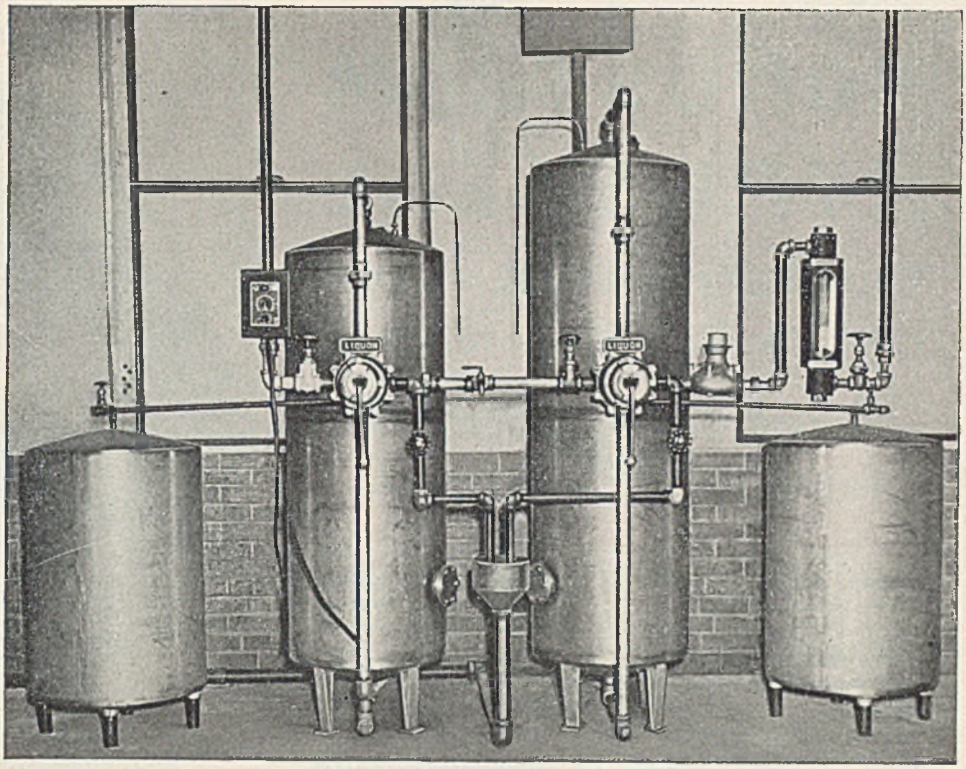

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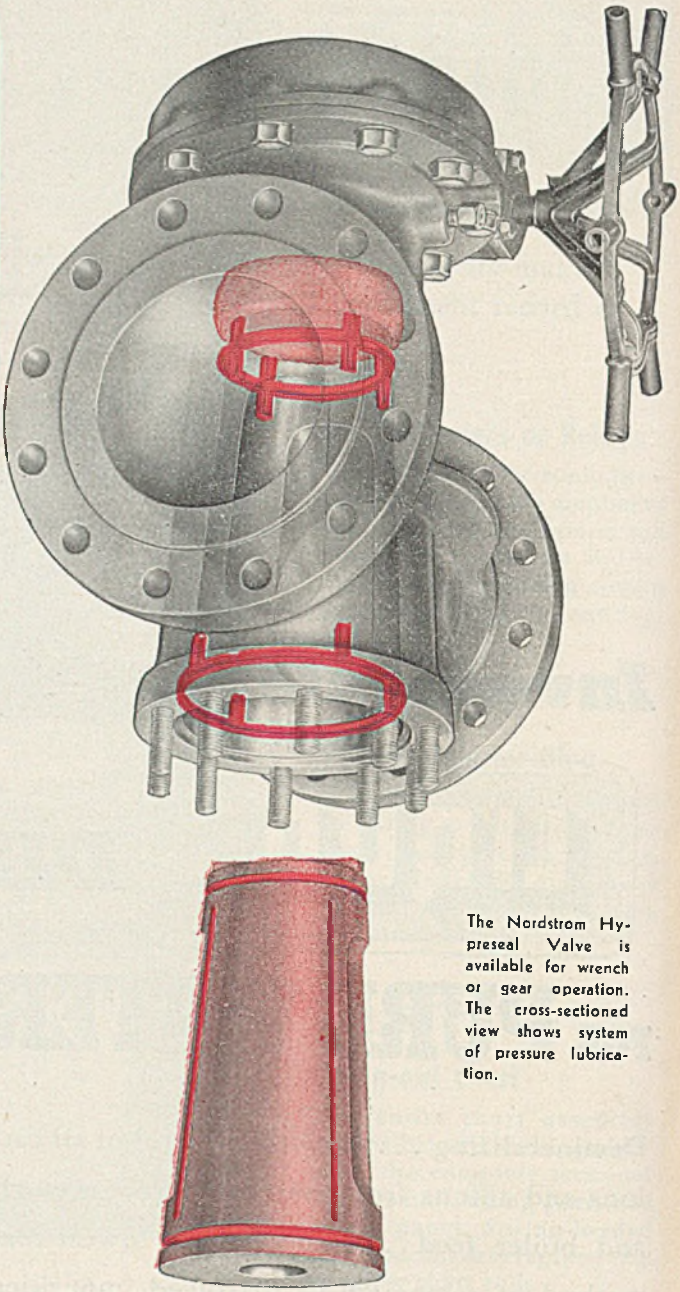

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   Renewable without disturbing valve positions or line pressure.
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    Compact construction, heavy sections, simplicity, insure durability.
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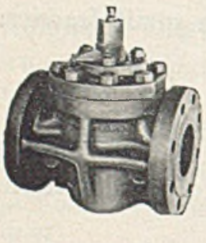
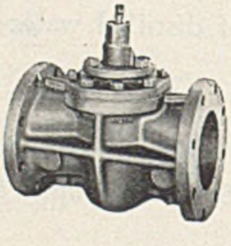
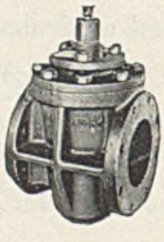
New Bulletin No. V-200 describing the various types of Nordstrom Lubricated Valves, with specifications and prices, will be sent upon request.



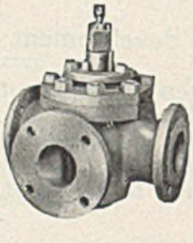
Regular Pattern



Venturi Pattern



Short Pattern



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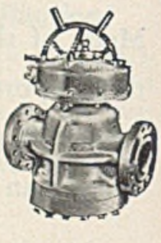


Round Opening

Nordstrom

LUBRICATED VALVES

As We See It . . .

On the Bench. Four papers from the Atlantic City A.C.S. spring symposium on bench scale techniques form an interesting group of articles appearing on page 1555 *et seq.* The principal emphasis is on equipment design, and the chemical engineer will find many ingenious developments that should stimulate his thinking when he has similar problems.

Clark, Golden, Whitehouse, and Storch lead off with the important topic of high pressure reactions. Their equipment was used in work on hydrogenation of coal, and was designed for conditions that are unquestionably rigorous. Pressures ranged from 1000 to 12,000 pounds per square inch and temperatures from 300° to 600° C., and the products handled were both corrosive and erosive in nature. The authors compare their designs with those evolved in Germany for similar investigations. Instruments and techniques of operation also are discussed.

Henriques next deals with the special needs for bench scale equipment used in study of vapor phase reactions with solid catalysts. His paper also involves designs for superatmospheric pressures, but the top of 50 atmospheres is substantially below the range discussed in the previous paper. Sampling techniques, feeding and metering devices, and pumps are considered.

Schools and other research organizations that may be required to operate on a limited budget will be especially impressed with the paper by Goldberg. He describes simple and inexpensive equipment for preparation of high molecular weight addition polymers that consists essentially of the conventional bottles, closures, and coolers used for carbonated beverages, yet has been found suitable for pressures of 5 to 10 atmospheres. Polymerization techniques are described.

Liquid-liquid and vapor-liquid extraction equipment and techniques are the subject of the fourth paper, authored by Knox, Weeks, Hibshman, and McAteer. Flow sheets of various systems are shown, the design of an 11-inch unit section for a 21-foot extraction tower for countercurrent solvent extraction is given, similar details for a vapor-liquid extraction system are presented, and operating procedures are described.

Peroxide Boom. When they begin shipping it in tank cars, there is little doubt that a chemical product has reached commercial stature. If you had not realized that 90% hydrogen peroxide has attained this position in the United States, a good long look at the lower right corner of page 1537 should be thoroughly convincing. The authors, Shanley and Greenspan, start the subject at its very beginning with the decomposition thermodynamics of hydrogen peroxide and present approximately seven pages of highly useful information about the commercial 90% product, its reactions, and its compounds. The aspects of handling hazard and decomposition factors are discussed extensively, and the region of detonable compositions is indicated graphically for the ternary systems containing hydrogen peroxide, water, and either ethanol, acetone, or glycerol. A regrettable omission from the paper is any description of the large scale technology of manufacturing the peroxide. However, the lack will not prove a serious handicap to the industrial chemist or chemical engineer who can utilize the article as a valuable reference guide.

Day-to-Day Data Date. Our new industrial data department, which you should have noticed by now in the rear advertising section, began at a time when we were so preoccupied with such matters as our materials of construction review that we did not give it the introductory fanfare it deserved. We hope you have discovered it and are finding that it serves a need. It certainly was not ignored, for in the first two weeks approximately 360 cards were received expressing interest in a total of 2300 items from the October issue alone. This youngest baby of our family of departments appears destined for a long and healthy life.

The modus operandi of a department of this type is simple in its basic outline and depends largely upon the knowledge that the enthusiasm of a company for a new product or service it has developed will promptly boil over in the form of a technical press release, usually accompanied by a booklet or folder describing the technical features of the development. We cull from this constant, daily stream those items of broadest interest and most practical value and once a month indicate the technical information available. Your comments for improvement of the feature will be heartily welcomed.

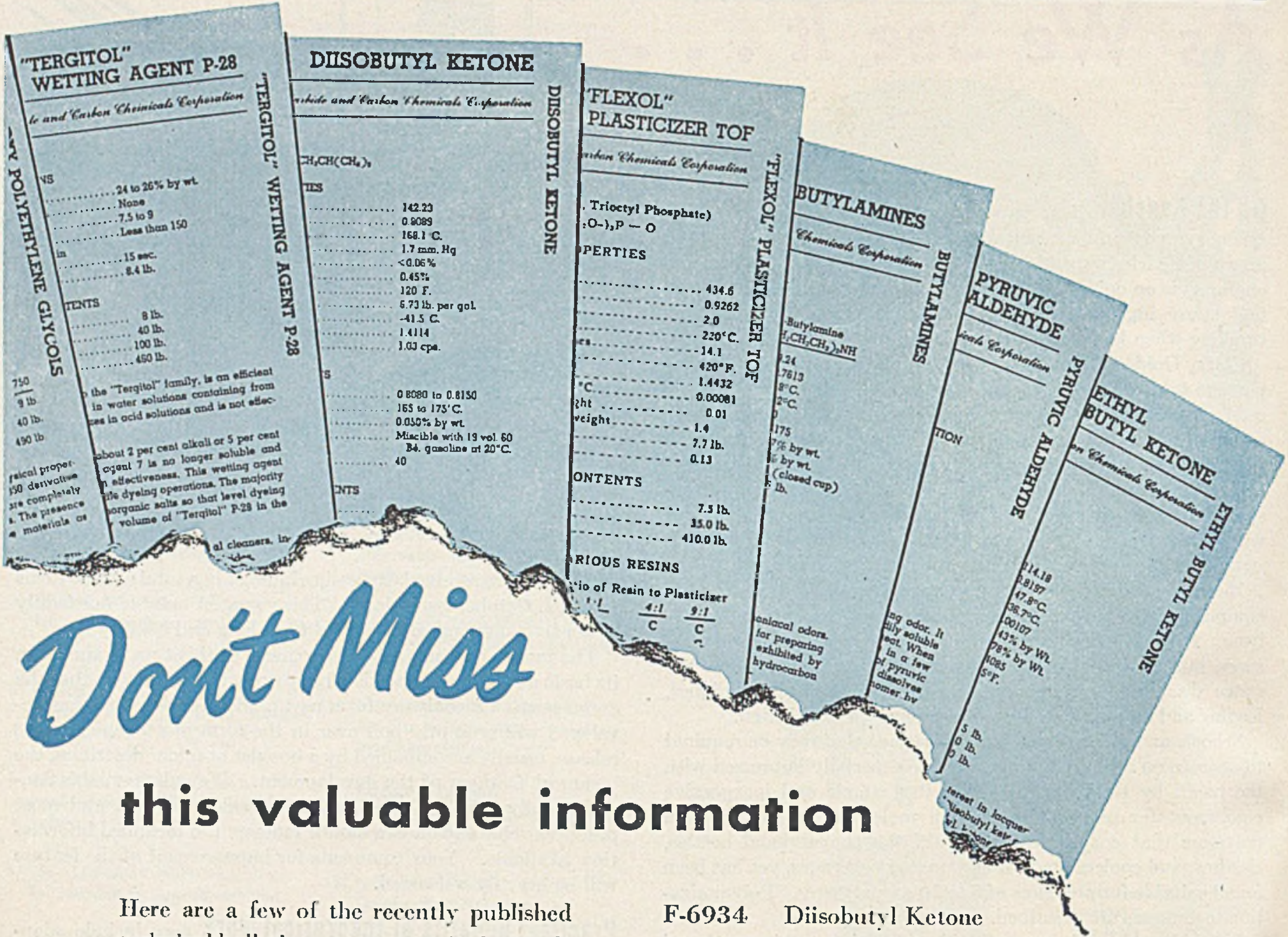
Practical benefits of theoretical work may include adoption in engineering equipment of designs originally necessitated by investigations of a highly theoretical nature. Brown cites as a beautiful example the incorporation of a leakless packing, first developed in apparatus used to study the physics of systems under extremely high pressures, into the design of a commercial high pressure valve. In addition, he describes a portable hydrogenation unit that should be of some interest as a useful and convenient unit in an organic process laboratory.

A short course in instrumentation that was given at Texas A.&M. in September 1946 is the topic Munch treats this month. He reviews the papers presented and commends the course as an effective effort to acquaint the technical man in industry with practical applications in the chemical process industries.

A heat-hardenable stainless steel is reported by Fontana in the column on corrosion. Described as a "starved" 18-8 steel containing titanium as the principal hardening agent, the material hardens upon being held at 950° F. and then cooled in air. Data from comparative corrosion tests with Type 304 steel in several acids are tabulated.

Continuous processes usually prove preferable to batch operations, says von Pechmann, and all too frequently an unthinking adherence to traditional methods blinds the plant operator to advances in processing equipment which would allow conversion to the continuous basis. The familiar fundamental arguments against the continuous alternative are considered one by one and firmly rejected as illogical.

D. O. Myatt



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A-12

December 1947

INDUSTRIAL and ENGINEERING Chemistry

WALTER J. MURPHY, Editor

DOES "LIFE BEGIN AT FORTY"?

A Forecast of Editorial Content in an Anniversary Year

BOTH Industrial and Engineering Chemistry and the Division of Industrial and Engineering Chemistry will celebrate their fortieth anniversaries in 1948.

As a result of discussions which began at the American Chemical Society meeting in Toronto, June 27 to 29, 1907, M. T. Bogert, President of the Society, appointed a committee in the fall of that year to consider the possibility of publishing a journal devoted to the special interests of industrial chemists and chemical engineers. At the December 1907 meeting of the Society in Chicago, its Industrial Chemistry Section enthusiastically approved the committee's recommendations that a journal be established and that a division of industrial chemists and chemical engineers be organized to serve the broad field of industrial chemistry.

The first issue of the Journal of Industrial and Engineering Chemistry, consisting of 60 pages, appeared in January 1909, with W. D. Richardson, an industrial chemist connected with Swift and Company, of Chicago, as Editor. During the journal's first year, 24 editorials and 168 papers were printed. In his annual report for 1909, the Editor stated that he had on hand 16 unpublished articles, had rejected 28, and that a total of 224 papers had been received. The monthly edition for the first year varied from 5200 to 4600 copies. The membership of the Society was 4502; today it is approximately 56,000.

Under the successive editorships of W. D. Richardson, M. C. Whitaker, Charles H. Herty, and Harrison E. Howe, Industrial and Engineering Chemistry grew in scope, esteem, and influence. This is neither the time nor the place to review the contributions of the publication and its offspring, *Analytical Chemistry* and *Chemical and Engineering News.* More appropriately the history of I. & E. C. will be recalled in a paper which will be presented in a Symposium on Technical Journalism during the spring meeting in Chicago under sponsorship of the Division of Industrial and Engineering Chemistry.

The tempo of research is expanding in all industrial fields. With more paginated pages allowed, I. & E. C. will expand in 1948 the number of original research articles presented. Such articles, reporting the original applied research performed in our colleges, universities, research institutes, and privately owned laboratories, are the lifeblood of the research structure in this or any country. Without this steady stream of published manuscripts research would wither and die. One of the most remarkable changes that has taken place during the 40 years of I. & E. C.'s existence has been the realization by most industrial organizations that exchange of scientific information through scientific publications benefits industry as a whole and does not penalize the donor.

Looking ahead, we present to our loyal readers a forecast for 1948:

JANUARY	The Third Annual Review of Unit Operations.
FEBRUARY	Furan Chemistry—a symposium celebrating 25 years of furan chemistry presented before the Division of Industrial and Engineering Chemistry in September 1947.
MARCH	Unit Process Symposium—a regular feature of the fall meeting sponsored by the Division of Industrial and Engineering Chemistry.
APRIL	Synthesis Gas—symposium presented at the September meeting in New York under the joint sponsorship of the Division of Gas and Fuel Chemistry and the Division of Petroleum Chemistry. Chemical Engineering in the Plastics Industry—a symposium presented last fall under the joint sponsorship of the Division of Industrial and Engineering Chemistry and the Division of Paint, Varnish, and Plastics Chemistry.
MAY	High-Vacuum Technology—a symposium held in Cambridge, Mass., October 30 and 31, under the joint sponsorship of the National Research Corporation and the Division of Industrial and Engineering Chemistry. A Statistical Review of the Chemical Process Industries—a new annual feature presented jointly by the Manufacturing Chemists' Association and the editorial staff of I. & E. C.
JUNE	Heat Transfer—the annual Christmas Symposium on Chemical Engineering, sponsored by the Division of Industrial and Engineering Chemistry.
AUGUST	Purification and Conditioning of Water Supplies—a symposium presented at the 1947 fall meeting by the Division of Water, Sewage, and Sanitation Chemistry.
SEPTEMBER	Unit Processes Review—a new feature and a worthy companion to the annual reviews on Unit Operations and Chemical Engineering Materials of Construction.
OCTOBER	Chemical Engineering Materials of Construction—Second Annual Review.
NOVEMBER	Pilot Plant Design and Construction—a symposium to be presented at the spring meeting in Chicago under the sponsorship of the Division of Industrial and Engineering Chemistry.


W. D. Richardson
1909–1911


Milton C. Whitaker
1911–1916


Charles H. Herty
1917–1921


Harrison E. Howe
1922–1942

Other symposia to be presented during 1948 include Insecticides in Food Production, Food Technology, Fluorine Chemistry, and several more of special interest to industrial chemists and chemical engineers. The regular departments—I. & E. C. Reports on the Chemical World Today, Equipment and Design, Instrumentation, Corrosion, and Plant Management—will be continued. Additional departments will be introduced during the year. Likewise the Pilot Plant series initiated in August this year will be continued, and, beginning in February, a monthly feature—process or plant production articles written by I. & E. C. staff members in collaboration with company engineers —will be introduced.

When M. C. Whitaker resigned his editorship in 1916, he prophetically pointed out that "the JOURNAL OF INDUSTRIAL CHEMISTRY, as the official organ of the AMERICAN CHEMICAL SOCIETY, should occupy a commanding position among technical publications of this country" and "should be in a position to cement and unify the interests of the chemical profession, to develop and improve the ethical standards of chemists, to collect and distribute all knowledge which will make for higher chemical engineering achievements, to draw us to —not to separate us from—other engineering professions, to take and to hold a position squarely representing the profession before the public, and to be a real factor in molding and directing national policies in which the chemical profession has a right to be heard."

Dr. Whitaker also pointed out that "the very fact of the journal's being owned by a great technical society should give it a position of strength for enhancing its influence and bestowing substantial benefits on the profession which supports it; that its policy and outlook should be big and broad enough to make its influence felt not only within the SOCIETY itself, but outside, not only on purely chemical matters, but matters of general technical and engineering value; not only in scientific matters, but the relations of the chemical profession to great public or national problems."

He felt that the turning point had been reached, and that, inasmuch as the industrial journal was then more than self-supporting, the time was ripe and the way clear to place it upon a foundation from which it could be developed into an influence and power. He therefore recommended that a full-time editor be appointed who could give his entire time "(1) to the study of the SOCIETY's problems, (2) to the consistent editorial development and discussion of its needs, (3) to the editorial treatment of questions of public and national interest in which the SOCIETY is concerned, and (4) to the general development of an editorial policy which would make the journal known both at home and abroad as the authoritative representative of the views, aims, ethics, and sphere of influence of the chemical profession in America."

He further recommended that "the news gathering facility of the journal be developed at once, by providing staff reporters to cover all technical and engineering society and convention meetings; that foreign and domestic engineering and industrial news should be reviewed promptly and regularly; that the trend of industrial progress should be forecast from a close study of foreign and domestic patent literature; and that competent staff writers should be provided to investigate and report upon important plant, process, and equipment improvements." He suggested that the journal publish each month at least one good illustrated article by a staff representative, describing some of the new plants or processes constantly being developed in the United States.

The ideas and aspirations voiced by Dr. Whitaker for his beloved journal have been largely, if not wholly, achieved. His blueprint required not one but three journals to meet the complete specifications and, under the long and able editorship of Harrison E. Howe, the *Analytical Edition* and the *News Edition* were established. Now, on the fortieth anniversary of the founding of INDUSTRIAL AND ENGINEERING CHEMISTRY, both of these offspring have become entirely separate publications. Each has its own special mission to perform for the members of the AMERICAN CHEMICAL SOCIETY and the chemical and chemical engineering professions.

The existence of any publication depends on the service it performs for its readers. INDUSTRIAL AND ENGINEERING CHEMISTRY has recorded the research achievements of the chemists and chemical engineers of America and the world at large, not superficially, but in a manner designed to stimulate further research resulting in more and more new processes and new products. For forty years INDUSTRIAL AND ENGINEERING CHEMISTRY has been an essential tool for the research chemist, chemical engineer, and chemical executive. Its objectives are the same today as they were in 1908. We believe they will be the same 100 years hence.

HIGHLY CONCENTRATED HYDROGEN PEROXIDE

Physical and Chemical Properties

EDWARD S. SHANLEY AND FRANK P. GREENSPAN
Buffalo Electro-Chemical Company, Inc., Buffalo 7, N. Y.

The physical properties of 90% hydrogen peroxide are summarized. The decomposition of hydrogen peroxide is discussed with relation to catalysis and stabilizers. Various typical reactions of high strength peroxide are outlined. These include applications to organic synthesis, bleaching, polymerization, and explosives technology. The handling of concentrated hydrogen peroxide is discussed with special reference to possible hazards.

HYDROGEN peroxide entered a new era of usefulness during World War II. Some of the intesting new uses for this material have already been described (*1, 2, 4, 8*). Hydrogen peroxide of high concentration (90%) is now commercially available. The purpose of this article is to describe a few of the properties of the material. A few of the physical properties are compiled in Table I.

STABILITY

Hydrogen peroxide solutions of high purity are very stable. For example, one commercial 90% product contains hydrogen peroxide and water and substantially nothing else. Typical rate of loss figures are noted in Table II.

The decomposition of hydrogen peroxide is a strongly exothermic reaction (*21*):

$$H_2O_2(g) \longrightarrow H_2O(g) + {}^1/_2O_2 \qquad (1)$$

$$\Delta H = -23 \text{ kg.-cal.}; \quad \Delta F = -30 \text{ kg.-cal.}$$

In spite of the large driving force, the rate of decomposition is very low in the absence of catalysts. Consideration of the free energy data indicates that no attainable pressure has any influence on the decomposition of hydrogen peroxide. For reaction 1,

$$\Delta F_{298} = -RT \ln K = -30{,}000 \text{ cal.}$$

$$\log K_{298} = \frac{30{,}000}{1{,}365} = 21.5$$

$$K = \frac{(p_{H_2O})(p_{O_2})^{1/2}}{(p_{H_2O_2})} = 10^{21.5} \text{ atm.}^{1/2}$$

Hydrogen peroxide is remarkable for the number and variety of decomposition catalysts and for the minute quantities required to give large effects. Table III shows the effect of adding certain heavy metals to a commercial hydrogen peroxide of mildly acid reaction. In all cases the metals were added as soluble salts. Many, but not all, heavy metals are active decomposition catalysts. The presumption is that only those metals having more than one valence state, correctly placed as to redox potential, can so act.

Many ferments and enzymes are able to decompose hydrogen peroxide—e.g., those contained in liver extract, saliva, yeast, etc. These materials are very effective in decomposing dilute hydrogen peroxide but are sometimes destroyed by concentrated solutions before causing much decomposition. Almost all varieties of dust and dirt will catalyze the decomposition of hydrogen peroxide.

Hydrogen peroxide solutions are generally more stable when acid and less stable when made alkaline. It is likely that the OOH^- ion is involved in the decomposition reactions, and this ion is present in higher concentrations in alkaline solution (*20*):

$$H\,OOH \rightleftharpoons H^+ + OOH^-$$

$$K_{298} = 2.4 \times 10^{-12}$$

Acids are, probably, the only known materials which actually increase the stability of hydrogen peroxide. Exact measurement of the effect of alkali on stability is made difficult by the extreme sensitivity of the solutions to catalysis. Traces of catalysts added with the alkali are responsible for a large part of the observed effects. Table IV shows the behavior of certain hydrogen peroxide solutions upon addition of sodium hydroxide

Table I. Properties of 90% Hydrogen Peroxide

Color	Clear, colorless
Odor	Slight at room temperature
Density	1.393 at 18° C. (*22*)
Viscosity	0.0130 poise at 18° C. (*22*)
Freezing point	−11° C. (*23*)
Boiling point	140° C. with decomposition
Refractive index	1.3998 n_D^{20} (*14*)
Dielectric constant	97 at 0° C. (*9*)

Table II. Stability of Hydrogen Peroxide at Various Temperatures

Temperature	Approx. Rate of Decompn.
30° C. (86° F.)	1% per year
66° C. (151° F.)	1% per week
100° C. (212° F.)	2% in 24 hours
140° C. (284° F.)	Decomposes rapidly with boiling

Table III. Effect of Contaminants on Hydrogen Peroxide

	Addition, Mg./L.	% of Original Active O Lost during 24 Hr. at 100° C.		Addition, Mg./L.	% of Original Active O Lost during 24 Hr. at 100° C.
None		2	Copper	0.1	85
Aluminum	10	2	Iron	1.0	15
Chromium	0.1	96	Tin	10	2
Copper	0.01	24	Zinc	10	10

Table IV. Effect of Purity on Stability of Alkaline Hydrogen Peroxide

Composition	Rate of Decompn. at Room Temp.
6% commercial H_2O_2 in water	2% per year (approx.)
6% com. H_2O_2 + 20% com. NaOH	79% in 24 hr.
6% com. H_2O_2 + 20% c.p. NaOH	53% in 24 hr.
6% com. H_2O_2 + 20% NaOH specially repurified by absorption process	5% in 24 hr.
6% triple-distd. H_2O_2 in H_2O	2% per year
6% triple-distd. H_2O_2 + 20% NaOH specially repurified as above	2% in 24 hr.

as well as the large part played by the impurities in the sodium hydroxide. With the purest alkali the contaminants in commercial hydrogen peroxide become of dominating importance. It is noteworthy that the commercial product contains only traces of catalytic impurities.

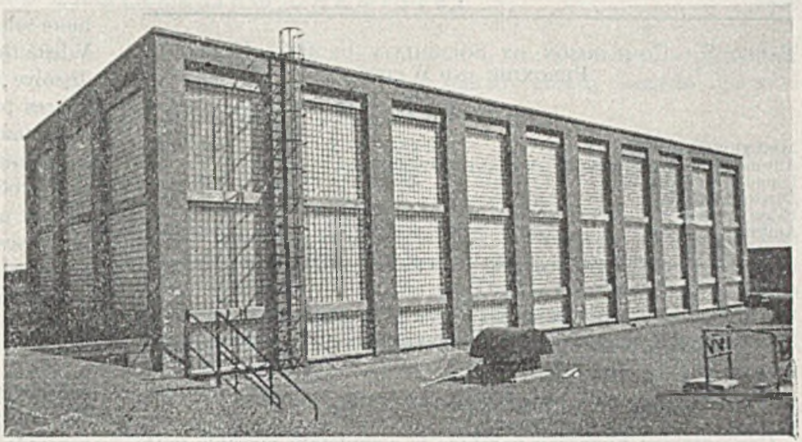
Alkaline hydrogen peroxide solutions, regardless of the degree of purity, are always much less stable than acid solutions of a comparable degree of purity. For example, if small amounts of heavy metal ions, such as copper, lead, manganese, or cobalt, are added to slightly acid hydrogen peroxide, the rate of decomposition may rise from one or two per cent per year to a few per cent per week. The same solutions made alkaline will decompose completely in some minutes or hours.

STABILIZATION

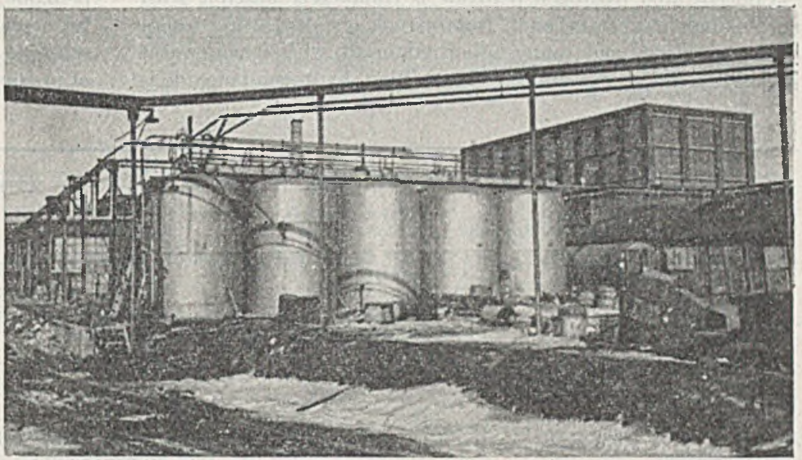
A great many materials have been suggested and tried as hydrogen peroxide "stabilizers." These materials, except for acids, probably have no influence on the hydrogen peroxide, but owe their action to removal or inactivation of decomposition catalysts. One group of stabilizers seems to owe its action to complex-forming ability, which serves to remove heavy metal ions from solution; in this group may be mentioned the pyrophosphates, fluorides, cyanides, and various organic substances such as 8-hydroxyquinoline and acetanilide. Another group of stabilizers probably owes its action to adsorptive powers; such substances as freshly precipitated alumina and silica, hydrous antimony oxide, and hydrous stannic oxide are effective to varying degrees in increasing the stability of hydrogen peroxide solutions. There is no one best choice of stabilizer for hydrogen peroxide solutions. The effect depends upon the nature of the catalyst, pH of the solution, temperature, and other factors. Thus the decomposing action of copper under certain circumstances is inhibited more by stannic oxide and less by pyrophosphate, while the opposite is true for chromium ions.

It follows from these considerations that high purity is the best guarantee of hydrogen peroxide storage stability. Stabilizers are usually necessary in stored hydrogen peroxide only to make up for deficiencies in the product or its container. A possibly more valid reason for using stabilizers is to furnish a degree of protection against accidental contamination of the solution. While some protection can be secured in this way, no additive will prevent rapid decomposition if gross contamination occurs. It has been common commercial practice to ship and store hydrogen peroxide solutions containing appreciable quanti-

Reading from top to bottom⟶

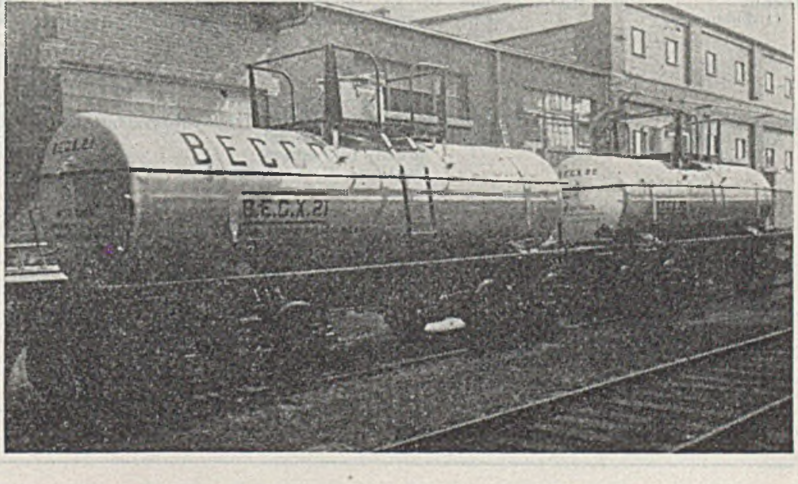


New Plant for Manufacture of Concentrated Hydrogen Peroxide



Hydrogen Peroxide Tank Farm

Nonspilling Vented Drum for Concentrated Hydrogen Peroxide



Tank Cars for Hydrogen Peroxide

Table V. Comparison of Solubility of 90% Hydrogen Peroxide and Water

	G. of 90% H_2O_2/ 100 G. Solvent	G. of H_2O/ 100 G. Solvent
Methyl methacrylate	18	1.0
Allymer CR-39 monomer	28	3.0
Dimethyl phthalate	28	1.6
Diethyl phthalate	2.5	1.0
Ethyl acetate	∞	3.5
Aniline	∞	3.5

ties of stabilizers—for example, phosphates or tin compounds or both. Present tendency is toward increased purity and less stabilizer.

SOLUBILITY

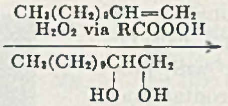
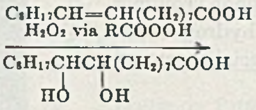
Concentrated hydrogen peroxide is completely miscible with such substances as ethanol, isopropanol, acetone, ethyl Cellosolve, pyridine, and many other materials with which water is miscible in all proportions. In addition, hydrogen peroxide is more soluble than water in a number of organic materials. Table V lists the number of grams of 90% hydrogen peroxide that will dissolve in 100 grams of a few solvents. The corresponding figures for water are listed for comparison. All data are for room temperature.

Precautions are called for in dealing with solutions of concentrated hydrogen peroxide in organic materials. Violent reactions upon mixing are exceptional but have been noted in a few cases. Solutions containing alcohols, ketones, sugars, etc., are relatively stable when undisturbed, but are subject to violent detonation under some conditions.

BEHAVIOR AS IONIZING MEDIUM

Ninety per cent hydrogen peroxide is reported to have a dielectric constant of 97 at 0° C. More dilute solutions of hydrogen peroxide show still higher values, reaching a maximum of 120 for a solution containing 35% by weight H_2O_2 (*9*). That these solutions are good ionizing media has been borne out by the work of previous investigators (*9, 17*).

Table VI. Reactions[a] of 90% Hydrogen Peroxide with Representative Organic Substances

Reactant	Oxidant[a]	Solvent	Experimental Conditions	Result	Reaction	Remarks	Reference
Aliphatic acids (acetic)	90% H_2O_2	....	22–23° C., 1% H_2SO_4 catalyst	Peracid formation	$RCOOH + H_2O_2 \rightleftharpoons RCOOOH + H_2O$	Rapid efficient reaction for peracid prepn.	(*10, 16*)
Alcohols (ethanol)	90% H_2O_2	....	100 p.p.m. Fe^{+++} catalyst, 40° C.	Acetic acid yield, 50% of theory approx.	$C_2H_5OH \xrightarrow{H_2O_2} CH_3COOH$	Tendency toward overoxidation with CO_2 evolution; in absence of catalyst, no reaction noted in cold or on refluxing	....
Aldehydes (hexaldehyde)	90% H_2O_2	....	80° C.	Hexanoic acid yield, 70% of theory approx.	$C_5H_{11}CHO \xrightarrow{H_2O_2} C_5H_{11}COOH$	....	....
Primary amines (ethylamine)	90% H_2O_2	....	22–23° C.	Vigorous decompn. of peroxide; reaction difficult to control; no products isolated	....	....	....
Sec. amines (diethylamine)	90% H_2O_2	....	Reaction bath cooled during H_2O_2 addition	Diethylhydroxylamine yield, 50% of theory approx.	$(C_2H_5)_2NH \xrightarrow{H_2O_2} (C_2H_5)_2NOH$	Reaction rate faster than for dil. H_2O_2; isolation of product simplified	Use of dil. H_2O_2 (*13*)
Tert. amines (triethylamine)	90% H_2O_2	....	60° C. for 10 hr.	Triethylamine oxide yield, 60% isolated product	$(C_2H_5)_3N \xrightarrow{H_2O_2} (C_2H_5)_3NO$	Product hygroscopic, isolation difficult, reaction appears to be quantitative with rate faster than for dil. H_2O_2	Use of dil. H_2O_2 (*7, 13*)
Paraffins (*n*-pentane)	90% H_2O_2	....	With & without catalysts (Fe, Va, Mn) at reflux temp.	No reaction	....	....	....
Alicyclics (cyclohexane)	90% H_2O_2	....	With & without catalysts (Fe, Va) at reflux	No reaction	....	....	....
Olefins (1-pentene)	90% H_2O_2	....	With & without catalysts (Fe, Va)	No reaction	....	....	....
Olefins (1-dodecene)	90% H_2O_2	Formic acid	40° C., followed by saponification	1,2-Dodecanediol yield, 75% approx.	 $CH_3(CH_2)_9CH{=}CH_2 \xrightarrow{H_2O_2 \text{ via } RCOOOH} CH_3(CH_2)_9\underset{HO}{CH}\underset{OH}{CH_2}$	....	(*5, 26*)
Monounsatd. acids (oleic)	90% H_2O_2	Formic acid	Catalyst, 1% H_2SO_4, 3 hr. at 40° C., followed by saponification	Dihydroxystearic acid	 $C_8H_{17}CH{=}CH(CH_2)_7COOH \xrightarrow{H_2O_2 \text{ via } RCOOOH} C_8H_{17}\underset{HO}{CH}\underset{OH}{CH}(CH_2)_7COOH$	Efficient hydroxylation, 99% conversion of double bond	(*15*); use of 30% H_2O_2 (*25*)
Aromatics (benzene)	90% H_2O_2	....	Fe^{++} catalyst + Al strips	Phenol in small yield	$C_6H_6 \xrightarrow[Fe^{++}]{H_2O_2} C_6H_5OH$	No reaction in absence of Fe^{++}, even at reflux	....
Aromatics (toluene)	90% H_2O_2	....	Reflux with & without catalysts (Fe, Va)	No reaction	....	....	....
		Acetic acid	22–23° C. and at reflux	No reaction	....	....	....

[a] As a general laboratory safety precaution it is recommended that, in the extension of any reaction of 90% H_2O_2 to new materials, work be initially conducted with approximately 3 ml. of total reactants.

In this laboratory it has been confirmed that many salts have similar conducting power in solutions ranging from 0 to 90% hydrogen peroxide. Acids behave differently, however, having a lower equivalent conductance in hydrogen peroxide solution. Figure 1 shows typical data. A detailed study of this effect is in progress.

ENERGY CONTENT

Hydrogen peroxide decomposition is an exothermic reaction (*24*):

$$H_2O_2\ (l) \longrightarrow H_2O\ (l) + {}^1/{}_2O_2(g) + 23{,}450 \text{ cal.} \qquad (2)$$

Upon complete decomposition, 1 liter of 90% peroxide yields 589 grams of oxygen gas and 801 grams of steam. Under adiabatic conditions the calculated temperature of these products is 750° C., and their calculated volume is about 5000 liters at this temperature and 1 atmosphere pressure. This system has obvious possibilities as a power source.

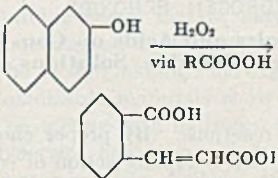
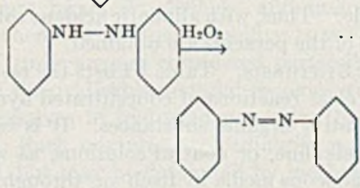
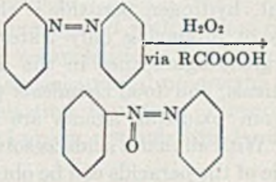
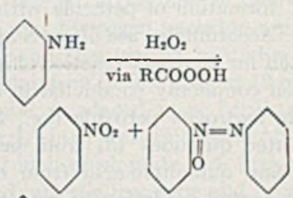
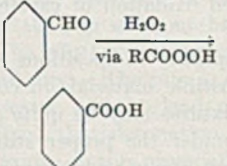
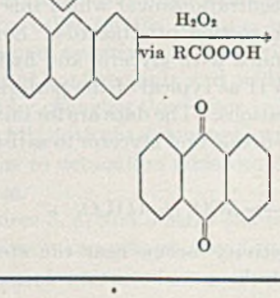
The oxygen from decomposition reaction 2 can be utilized for the combustion of fuel and thereby greatly increase the total energy yield per gram of fuel mixture.

OXIDIZING PROPERTIES

Concentrated hydrogen peroxide possesses the same general oxidizing action noted for more dilute solutions. However, it is a powerful oxidizing agent with distinct attributes of its own, indicative of the transition from the properties of an aqueous solution of hydrogen peroxide to the properties of pure hydrogen peroxide containing relatively small amounts of water. Enhanced solubility in organic media, increased concentration of effective oxidizing agent, and the relative absence of water lend themselves to increased efficiency when applied to existing processes employing hydrogen peroxide, as well as making possible many new applications.

Hydrogen ion concentration, presence and nature of catalyst, and temperature are important controlling and directing in-

Table VI (*Continued*)

Reactant	Oxidant[a]	Solvent	Experimental Conditions	Result	Reaction	Remarks	Reference
β-Naphthol	90% H_2O_2 in acetic acid	Acetic acid	40° C., catalyst 1% H_2SO_4	o-Carboxycinnamic acid yield, 71% of theory		....	(6, 15)
Hydrazobenzene	90% H_2O_2	....	22–23° C.	Azobenzene yield, 100% of theory		....	....
Azobenzene	90% H_2O_2	....	22–23° C.	No reaction	....	....	....
	90% H_2O_2 in acetic acid	Acetic acid	Catalyst 1% H_2SO_4, temp. raised to 70° C. after slow addition of oxidant	Azoxybenzene yield, 100% of theory		....	....
Aniline	90% H_2O_2	....	22–23° C.	Aniline black products	....	....	....
	90% H_2O_2 in acetic acid	....	22–23° C.; oxidant added to water slurry of aniline containing Na bicarbonate	85% azoxybenzene + 15% nitrobenzene		....	(15)
Benzaldehyde	90% H_2O_2 in acetic acid	....	Catalyst 1% H_2SO_4, 22–23° C.	Benzoic acid yield, 100% of theory		....	(11)
Anthracene	90% H_2O_2 in acetic acid	....	Finely divided anthracene dispersed in water, reaction mixture gradually heated to 50° C.	Anthraquinone yield, 70% of theory		....	(15)

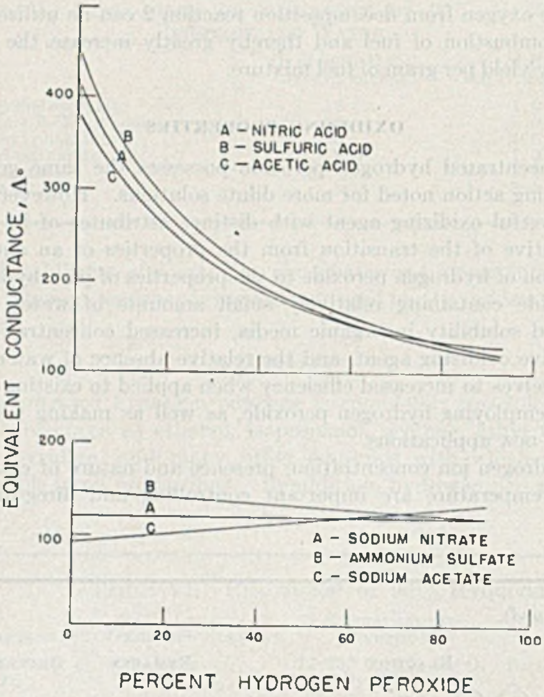


Figure 1. Effect of Salts and Acids on Conductance of Hydrogen Peroxide Solutions

fluences in hydrogen peroxide reactions. By proper choice of solvent, it is possible to modify the oxidizing action of concentrated hydrogen peroxide. Thus, with aliphatic acids as solvents, reactions characteristic of the peracids are obtained.

Oxidant in Organic Synthesis. Table VI lists the results of a study of the general class reactions of concentrated hydrogen peroxide with representative organic substances. It is capable of functioning in acid, alkaline, or neutral solutions, as well as being applicable to nonaqueous media by itself or through inert solvents. As an oxidixing agent, hydrogen peroxide is characterized by the distinct advantage of producing only water as a reaction by-product. This is of great significance in the manufacture of dyestuffs, pharmaceuticals, and food chemicals where metallic impurites resulting from oxidizing agents are often deleterious to the final product. With aliphatic acids as solvents, important reactions characteristic of the peracids can be obtained because of the high rate of formation of peracids with concentrated hydrogen peroxide. Accordingly, use of concentrated hydrogen peroxide suggests itself for increased reaction efficiency wherever oxidations have been commonly conducted in acetic acid medium with more dilute hydrogen peroxide (i.e., 30%), such as production of substituted quinones (*3*) from benzene and naphthalene derivatives and quinolinic acid from quinoline (*18*). Of interest is the reported oxidation of carotene to vitamin A (*19*).

Component of Explosives. Explosive compositions can be formed by dissolving certain combustible materials in concentrated hydrogen peroxide. Such mixtures may be quite stable in storage but detonate violently under the proper stimulus. The range of materials and concentrations over which this effect is observed is discussed in the section on Hazards. Some of the data on explosives compounded with glycerol and hydrogen peroxide are outlined in Table VII as typical of the performance to be expected from such compositions. The data are for mixtures made up with 90% hydrogen peroxide and glycerol to satisfy the equation:

$$C_3H_8O_3 + 7H_2O_2 \longrightarrow 3CO_2 + 11H_2O$$

The maximum power and sensitivity occur near the stoichiometric composition, even though the actual reaction does not go to completion as shown. The figures in Table VII indicate the possibility that useful explosives may be compounded with concentrated hydrogen peroxide.

Bleaching Agent. Concentrated hydrogen peroxide, because of increased solubility and higher effective oxidizing concentration at the interface, shows promise for the bleaching of oils, fats, and waxes. Experiments have shown that 90% hydrogen peroxide added to beeswax yields a superior bleach to that obtained when the same number of equivalents of 30% peroxide is employed. Similarly, excellent results have been obtained in the bleaching of soluble and insoluble commercial sorbitan esters of the Span and Tween type.

Discolored concentrated acids can readily be bleached with 90% hydrogen peroxide. In this way sulfuric acid and glacial acetic acid have been bleached to a colorless product. Bleaching with concentrated hydrogen peroxide suggests itself as a step in the recovery of spent acids.

POLYMERIZATION REACTIONS

Hydrogen peroxide is a common catalyst in emulsion polymerization of vinyl type compounds—for example, Buna S, styrene, and methyl methacrylate. In bulk polymerization of vinyl type compounds, one is limited to a monomer-soluble catalyst and thus aqueous hydrogen peroxide (30% concentration) is not applicable. Hitherto the bulk of such catalysts have been the organic peroxides—i.e., benzoyl peroxide.

Concentrated hydrogen peroxide (90%) is an effective catalyst for the bulk polymerization of many vinyl type substances (styrene, methyl methacrylate). Solubility tables show that 90% hydrogen peroxide is surprisingly soluble in many monomers (methyl methacrylate, allymer). Furthermore, although the solubility in compounds such as styrene is limited it is in the range of catalytic concentrations. Accordingly, it is not surprising that bulk polymerization can be effected with concentrated hydrogen peroxide (90%) in contrast to the experience with more dilute hydrogen peroxide (30%).

Recently, Delmonte (*12*) compared 90% hydrogen peroxide with a number of commonly used organic peroxides and found 90% hydrogen peroxide to be the most rapid-acting catalyst for polyester castings. Concentrated hydrogen peroxide (90%) has been successfully applied in this laboratory to the curing of partially polymerized polysulfides of the Thiokol type, which are useful in impregnating and caulking compositions.

HAZARDS

Concentrated hydrogen peroxide has obtained a somewhat exaggerated reputation for being hazardous. Like any material of high energy content, it requires intelligent care in handling, but given this care it can be used in safety.

Toxicity. Hydrogen peroxide solutions and vapors are nontoxic. Both are irritating, however. The vapor causes discomfort of the eyes and nose. The liquid at moderate concentration causes whitening of the skin and a more or less severe stinging sensation. In most cases the stinging subsides quickly and the skin gradually returns to normal without any damage. Highly concentrated hydrogen peroxide can cause blistering if

Table VII. Comparison of Peroxide Explosive with Nitroglycerol

	Glycerol + 90% H_2O_2[a]	Nitroglycerol
Impact sensitivity (drop wt. test), kg.-cm.	15	2
Total energy released, kg.-cal./gram	1.6	1.6
Total gas vol. released, liter/gram	1.0	0.7
Detonation rate, meters/sec.	6500	8000

[a] Stoichiometric mixture.

left on skin surfaces for any length of time. Contact with the material should be avoided, but immediate flushing with water will prevent any reaction in case accidental contact occurs.

FIRE. Hydrogen peroxide of high concentration can cause fire upon contact with combustible material. Calculations show that hydrogen peroxide of 65% concentration releases just enough energy upon complete decomposition to evaporate all the water present and formed. Consequently, decomposition of weaker hydrogen peroxide solutions would not be expected to lead to spontaneous ignition of inflammable materials. On the other hand, hydrogen peroxide solutions stronger than about 65% can release enough energy to heat the decomposition products to high temperature—i.e., 750° C. in the case of 90% hydrogen peroxide. Ignition of nearby inflammable material is then to be expected.

Actual experiments have been carried out which confirm the above line of reasoning. It is difficult to cause fires with 60% hydrogen peroxide except under conditions favorable to evaporation, when it may be assumed that the concentration exceeded 65% before ignition occurred. On the other hand, fires can be started at will by dampening combustible materials with hydrogen peroxide stronger than about 70%, provided that the proper catalyst is present. In the absence of catalysts—i.e., clean cotton or wood—even 90% hydrogen peroxide causes no vigorous reaction.

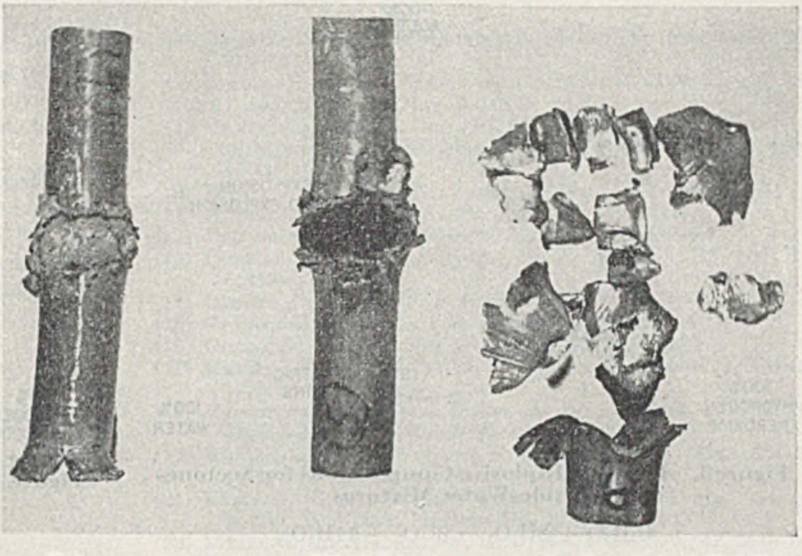
Most wooden flooring, straw, rags, clothing, etc., contain enough catalytic material to cause rapid ignition upon addition of 90% hydrogen peroxide. Proper precautions should be taken with this fact in mind. Storage areas for concentrated solutions should be of fireproof construction, and provision should be made for the flushing and draining of spillage. Workmen should be provided with rubber aprons, boots, and gloves resistant to hydrogen peroxide; the Koroseal type is suitable.

In case of spillage or any other emergency with concentrated hydrogen peroxide, water is the best remedy. If used in time it will prevent any vigorous reaction, and it is also the best extinguishing agent for fires resulting from spillage.

EXPLOSION. Apparently it is impossible to obtain a propagating detonation in pure 90% hydrogen peroxide. The material has been subjected to mechanical impact in drop weight testers, to rifle and machine gun fire, and to a variety of tests with blasting caps with and without booster charges. In no case has a propagating detonation been observed. Similar tests by other workers have tended to confirm these results (*4*).

Catalytic decomposition of hydrogen peroxide in a closed container may cause pressure rupture of the vessel. Containers for hydrogen peroxide should always be vented in order to obviate this possibility.

In case concentrated hydrogen peroxide becomes badly contaminated, the decomposition may become self-accelerating because of heating of the solution. This process goes slowly at first but can rise to a climax capable of rupturing the containing vessel in spite of the vent. Forewarning of this uncommon eventuality is given by a more or less protracted period during which a steady temperature rise occurs. The rate of temperature rise is a function of the degree of contamination. Unless heating can be arrested, contaminated peroxide should be flushed promptly to drain with adequate diluting water. It is desirable to provide thermometers on large storage vessels for concentrated hydrogen peroxide to provide forewarning of any possible difficulties. Mercury thermometers are not to be used in direct contact with strong hydrogen peroxide because of the vigorous decomposing action of this metal. (This caution applies, of course, to all measuring devices utilizing mercury.)



Water 90% H_2O_2 6 ml. ethanol, 4 ml. 90% H_2O_2

Figure 2. Appearance of Lead Pipes after Blasting Cap Tests with Various Mixtures

Substances especially easy to oxidize, or alkaline in nature, or containing heavy metals, may react violently upon mixing with concentrated hydrogen peroxide; therefore proper care should be used in making such experiments. On the other hand, many oxidizable materials show no particular evidence of reaction on mixing with hydrogen peroxide of any concentration. Such behavior has been noted with sugars, starch, cellulose, petroleum products, alcohols, and many other materials. In cases where the mutual solubility is very low (i.e., kerosene), the mixtures are not considered particularly hazardous. However, if the oxidizable material becomes well dispersed, especially if it dissolves in hydrogen peroxide, then an explosion hazard exists. Such mixtures are ordinarily quite stable when undisturbed, but may be detonated by mechanical shock, heating, or the impact of a blasting cap. A number of such solutions have been investigated with a view to determining the range of explosive compositions. Various procedures have been employed, such as mechanical drop-weight tests, rifle bullet impact studies, and blasting cap test. Since the latter provides the most severe impact, a standardized procedure has been adopted on this basis.

The test is carried out as follows: The desired quantities of "fuel" and hydrogen peroxide are measured into separate containers and then mixed behind a suitable barricade. The resulting mixture (usually about 10 ml.), in a 15 × 150 mm. Pyrex test tube, is placed in a 7-inch section of $^3/_4$-inch lead pipe having $^1/_4$-inch wall thickness. This pipe is supported upright on a 1-inch steel plate. A fuse-ignited No. 6 blasting cap is lowered into the test tube and supported in such a way that the shell of the cap is about half immersed. The cap is then set off. The effect can be judged by the sound and appearance of the lead pipe. The pipe is only bulged when the test tube contains water. If the lead pipe is broken into fragments, it is considered that detonation has occurred. Figure 2 shows the appearance of the pipes after some typical trials. This test, like any other for the purpose, is arbitrary to a certain degree. The impact sensitivity of liquids is particularly dependent on the degree of confinement, and widely varying results can be obtained by changing this factor. The test as described is a severe one. Mixtures not detonated by this procedure can be considered immune to detonation under any circumstances likely to arise in practice.

Figures 3, 4, and 5 show the range (in per cent by weight) of explosive compositions found in this fashion for solutions of

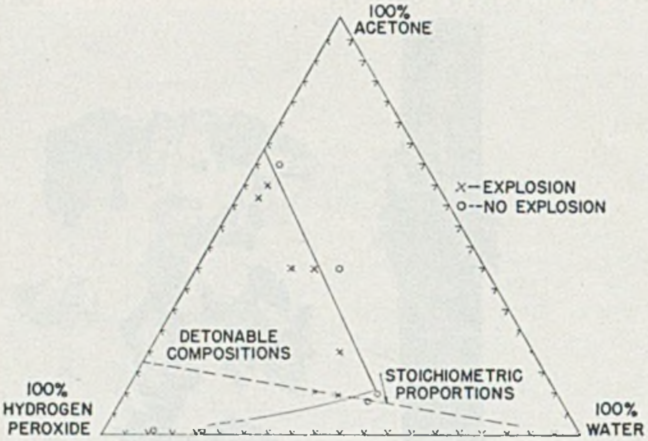


Figure 3. Range of Explosive Compositions for Acetone-Peroxide-Water Mixtures

$$C_3H_6O + 8H_2O_2 \rightarrow 3CO_2 + 11H_2O$$

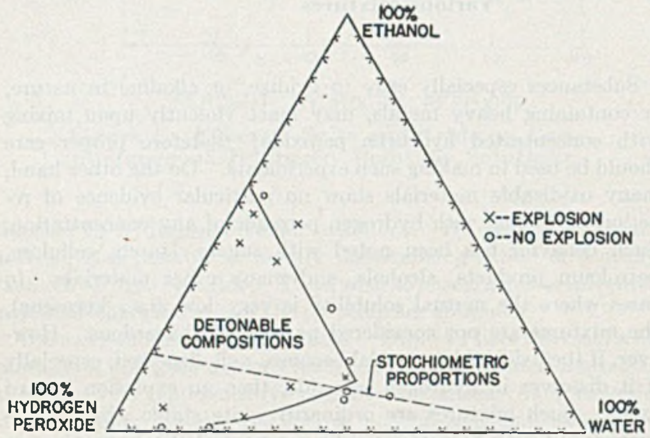


Figure 5. Range of Explosive Compositions for Ethanol-Peroxide-Water Mixtures

$$C_2H_5OH + 6H_2O_2 \rightarrow 2CO_2 + 9H_2O$$

hydrogen peroxide and three typical fuels (ethanol, glycerol, and acetone). It is indicated that the diagrams for other fuel mixtures are similar. In addition to these three systems exploratory tests have been carried out with a number of other soluble combustible materials. Particular attention has been devoted to determining the maximum amount of 90% hydrogen peroxide which is permissible in various solvents without entering the explosive range. The following materials have been tested: Acetone, acetic acid, acetic anhydride, aniline, carbitol, dioxane, ethanol, ethyl acetate, ethyl Cellosolve, ethylene glycol, glycerol, isopropanol, methanol, methyl methacrylate, and quinoline.

Detonations have been observed only when the 90% hydrogen peroxide formed over 30% by volume of the final mixture (more than 3 ml. of 90% peroxide in 10 ml. total). Most soluble fuel mixtures containing 4 ml. of 90% hydrogen peroxide (in 10 ml. total) are detonable in the lead pipe test. Hydrogen peroxide (90%) with addition of several per cent of a soluble fuel is usually detonable.

In case it is desirable to make up hydrogen peroxide–fuel solutions which fall within the explosive range, it is advisable to take extensive precautions. Some mixtures may be detonated rather easily—for instance, by dropping the container—and the explosion may sometimes be comparable with that of a corresponding quantity of nitroglycerol.

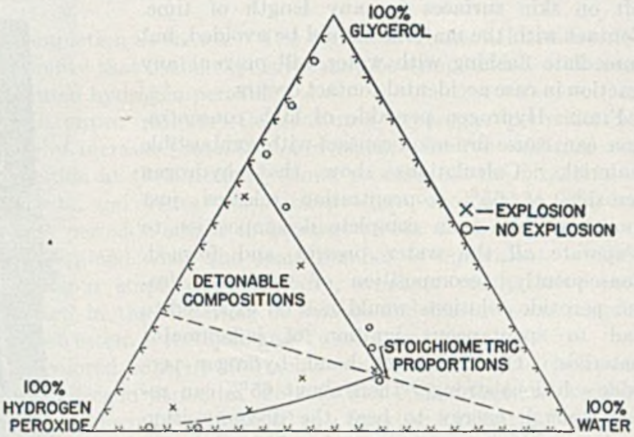


Figure 4. Range of Explosive Compositions for Glycerol-Peroxide-Water Mixtures

$$C_3H_8O_3 + 7H_2O_2 \rightarrow 3CO_2 + 11H_2O$$

STORAGE AND HANDLING

Hydrogen peroxide of high concentration can be handled and stored without hazard. Special methods are required in conformance with the properties of this material.

CONTAINERS. For long term storage of 90% hydrogen peroxide, containers are best made from high purity (99.6%) aluminum. In contact with 90% hydrogen peroxide of high purity, this material is unexcelled for resistance to attack and lack of decomposing action. Aluminum containers should be cleaned and pickled before being filled with hydrogen peroxide. Suitable cleaning can be obtained with a dilute sodium hydroxide solution. After this solution is drained, the container should be rinsed and then treated with acid. Several hours of contact with high purity 10% sulfuric acid is suitable. The acid should be flushed out with distilled water. A subsequent rinse with hydrogen peroxide may be desirable. In any event, the container usually improves with use; that is, fillings after the first are somewhat more stable than the first.

It is best to refill empty hydrogen peroxide containers without rinsing, unless contamination is known to have occurred or is suspected. In such cases the cleaning and pickling should be repeated.

Containers of chemically resistant glass are suitable for use with concentrated hydrogen peroxide because of their lack of attack and lack of effect on the product. Small samples of 90% hydrogen peroxide are regularly shipped in glass bottles provided with a protective outside metal container. Glass carboys are not advisable for use with 90% hydrogen peroxide because of the hazard from breakage.

Coated and lined equipment is generally not acceptable for hydrogen peroxide storage because of the deleterious effect of small flaws in the coating. Imperfections are likely to grow rapidly because decomposition on the backing furnishes a large amount of gas which tends to lift the coating. In special instances, flexible containers of the polyvinyl chloride type have been used to hold hydrogen peroxide.

All containers for concentrated hydrogen peroxide should be vented. Care should be taken to keep the venting arrangement in working order to prevent the possibility of pressure rupture due to unforeseen decomposition of the contents. It is essential to have the vent designed and arranged so as to minimize the possibility of introducing dust and dirt or other contaminants.

PUMPS AND PIPING. For 90% hydrogen peroxide pumps and piping can be made from aluminum. Porcelain and glass piping and fittings are satisfactory and stainless steel pumps can be used. Flanged joints are preferred, with polyvinyl chloride or similar gaskets. It is important to avoid the use of screwed fittings with "pipe dope" of conventional types because red lead and the like are active decomposition catalysts for hydrogen peroxide. The greatest care should be taken to exclude fittings of iron, brass, copper, Monel, etc.

The piping scheme should be arranged so that material once withdrawn from the storage tank cannot find its way in again. This bars the use of the conventional measuring tank setup with overflow back to storage. Storage spaces for concentrated hydrogen peroxide should be of fireproof construction and have adequate drains and flushing facilities to take care of any accidental spillage.

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China's Motor Fuels from Tung Oil

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Cracking the soap of vegetable oils thermally or cracking a vegetable oil itself thermally or catalytically decomposes the fatty acids into hydrocarbons. Subsequent cracking of these hydrocarbons is somewhat similar to petroleum cracking. During the war industrial batch-cracking processes were developed in China to produce motor fuels from vegetable oils. Tung oil, which could not be exported during the blockade, served as the main raw material. The average commercial yield of crude oil was 70% by volume of the original tung oil, the gasoline content in crude oil being 25% by volume.

THE wealth of vegetable oils in China has inspired its scientists to become pioneers in exploiting this unique renewable resource as raw materials of motor fuels which may be designated by the newly coined terms "veg-gasoline" and "veg-Diesel" oil. However, the manufacturing of motor fuels by cracking vegetable oils was dictated entirely by exigencies of the situation brought about by the war. It was a hastily developed enterprise which left much to be desired. The present paper deals mainly with its technical aspects and the use of tung oil in this industry is particularly emphasized.

EXPERIMENTAL DATA

Prior to its investigation in China, the cracking of vegetable oils had been studied by Kobayashi (*6*), Saito (*11*), Maihle (*9, 10*), Waterman and Perquin (*14*), Haga (*4*), and Egloff and Morrel (*3*). Chinese scientists began to take up the work at a much later date, shortly before going into war, and naturally pursued it with great interest. Normal steps for the systematic development of a novel industrial process ordinarily extend over many months or even years, but such a period was too long to be practical under the emergency conditions of war. Actually the pressure of time forced the hasty installation of cracking plants, built on the basis of laboratory data of a rather fragmentary nature. Among the laboratories undertaking this investigation may be mentioned the Research Laboratory of Applied Chemistry at Nankai University, the Sin Yuan Fuel Laboratory of the National Geological Survey of China, the Laboratories of the National Bureau of Industrial Research (N.B.I.R), the Laboratory of the Tung Li Oil Works, and the Research Laboratories of the China Vegetable Oil Corporation. The results are rarely published. Of the published papers, a digest has been made available by Koo (*7*).

Experimental methods adopted for the preparation of crude oil may be roughly classified as: (1) destructive distillation of a vegetable oil and the simultaneous or subsequent cracking of its vapors; (2) liquid-phase cracking of a vegetable oil with or without using catalysts; and (3) pyrolysis of the soap of vegetable oils.

DESTRUCTIVE DISTILLATION FOLLOWED BY VAPOR-PHASE CRACKING. Table I gives the distillation range according to A.S.T.M. procedure of the crude oils resulting from the cracking of rapeseed and tung oils by subjecting these oils to destructive distillation and passing the vapors at an optimum rate through a steel reaction tube maintained at 400° to 450° C. From either oil the yield of crude vegetable gasoline is approximately 20% by volume of the original oil.

Liquid-Phase Cracking of Vegetable Oils. Liquid-phase cracking is carried out either under elevated pressure in order to maintain the necessary pyrolysis temperature or under normal pressure in the presence of catalysts. As an illustration of the first type of liquid phase cracking, typical experimental data are presented in Table II.

As an illustration of the second type of liquid-phase cracking, typical experimental data are presented in Table III. These experiments were run under normal pressure at 300° to 350° C. The reactions usually started at 150° C. with exothermic effects.

Table I. Distillation Range of Crude Oils

	Source of Crude Oil	
	Rapeseed oil	Tung oil
Total yield of crude oil, vol.% of original oil	56	55
Distillation range of crude oil		
First drop, ° C.	45	40
Up to 200° C., vol.% of crude oil	36	36
Up to 300° C., vol.% of crude oil	86	89

Table II. Liquid-Phase Cracking without Catalysts

	Source of Oil	
	Cottonseed oil	Tung oil
Amount of oil used, ml.	1000	1000
Autoclave gage pressure, lb./sq. in.	280	280
Temperature, ° C.	450	470
Time, minutes	100	120
Products, % of original oil		
Crude oil		
Wt.%	55	54
Vol.%	65	66
Crude oil distilling below 200° C., %	41	45
Water, wt.%	3.5	2.7
Coke, %	10	12
Gas, liters per kg. of oil.	170	182

Table III. Catalyzed Liquid-Phase Cracking

	Vegetable Oil Used							
	Cottonseed Oil		Soybean Oil	Rapeseed Oil			Tung Oil	
	Catalyst Used							
	1% $AlCl_3$	10% $AlCl_3$	1% $AlCl_3$	10% lime	10% magnesia	10% caustic soda	1% $AlCl_3$	10% lime
Products in % of original oil								
Total crude oil, vol. %	82	81	83	75	82	72	75	72
Fraction up to b.p. 200° C., vol. %	20	19	24	34	25	30	21	24
Fraction up to b.p. 300° C., vol. %	58	57	63	59	50	53	56	55
Water, wt. %	5	5	4	4	4	4	5	4
Coke, wt. %	6	7	7	..	..	..	9	..
Gas, liter per kg. of oil	240	250	210	..	..	..	..	..

Table IV. Distillation of Calcium Soaps

	Volume % of Original Oil		
Products	Rapeseed oil	Peanut oil	Tung oil
Crude oil	74	72	72
Fraction below 200° C.	25	23	22
Fraction below 300° C.	63	62	65

Table V. Properties of Crude Oils

	Type of Experiment			
		Liquid-Phase Cracking		
	Vapor-phase cracking	Pressure cracking	Catalytic cracking	Calcium soap distillation
Sp. gr. at 15° C.	0.840–0.860	0.800–0.830	0.820–0.850	0.820–0.870
Acid value	5–18	25–40	3–30	0.20–1.50
Loss by concd. H_2SO_4, %	20–40	30–78	15–40	15–25
Calorific power, B.t.u./lb.	16,500–17,800	17,000–18,000	16,800–17,800	17,000–18,000

Pyrolysis of Soap of Vegetable Oils. Table IV gives typical data obtained from the distillation of the calcium soaps of rapeseed, peanut, and tung oils.

The properties of crude oils obtained from these experiments differ in certain respects, as shown in Table V. The crude oil samples prepared by laboratory methods after fractionation and refining invariably yield vegetable-gasoline, vegetable-kerosene, and vegetable-Diesel oils, as counterparts of the respective petroleum fractions. Since these oils contain practically no sulfur compounds, the refining process is relatively simple and involves only treatment of the fractions with concentrated sulfuric acid, removal of excess acid with water, neutralization of remaining acid with an alkaline solution, removal of excess alkali with water and finally redistillation. Characteristics of vegetable-gasoline vegetable-kerosene, and vegetable-Diesel oils as prepared and refined in the laboratory are given in Table VI, in which are also given for comparison the specifications of the corresponding petroleum products.

Although the investigation of cracking of vegetable oils to produce petroleumlike substances was soon folllwed by experiments to determine the performance data, such data are comparatively meager and somewhat inconsistent. It suffices to say that vegetable gasoline with the characteristics given in Table VI would develop approximately 90 to 95% of the brake horsepower developed by American motor gasoline under identical testing conditions and that under such conditions the distance covered per unit volume of vegetable gasoline consumed would also be approximately 90 to 95% of that in the case of gasoline.

By combining the data of the National Bureau of Industrial Research with those of these laboratories, a better idea may be obtained from Table VII (*7, 13*) about the performance of vegetable-Diesel oils.

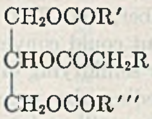
It is thus possible to use vegetable oils directly in Diesel engines, but their much higher viscosity as compared with Diesel oil, which requires a 20% increase in injection pressure for effective atomization, and their high carbon residue and tendency towards gum formation, particularly in the case of tung oil, interfere with smooth and economic operation to such an extent that these Diesel substitutes once advocated had yielded their ground to vegetable-Diesel oil, which had meanwhile become an important by-product from the vegetable-gasoline industry.

Table VI. Characteristics of Refined Vegetable Motor Fuels

	Veg-Gasoline	U. S. Gasoline
Sp. gr. at 15° C.	0.785	0.762
Sulfur	None	Max.
Corrosion test	Negative	Negative
Doctor test	Negative	Negative
A.S.T.M. distillation, ° C.		
I.B.P.	45	38
10%	86	82
20%	105	99
30%	115	110
40%	126	120
50%	134	128
60%	145	138
70%	156	149
80%	168	160
90%	185	177
E.P.	210	205
B.t.u./lb.	15,800	16,600
Octane No.	60	70
	Veg-Kerosene	U. S. Kerosene
Flash point, ° C.	118 min.	146 min.
Sulfur, %	None	0.06 min.
End point of distillation, ° C.	300	316
	Veg-Diesel Oil	U. S. Diesel Oil
Flash point, ° F.	150 min.	150 min.
Viscosity, Saybolt sec. at 100° F.	40	50
Sulfur, %	None	1
Carbon residue, %	0.2 max.	0.18 max.
Distillation test, 80% distilled over, ° C.	300	290

MECHANISM OF CRACKING REACTIONS

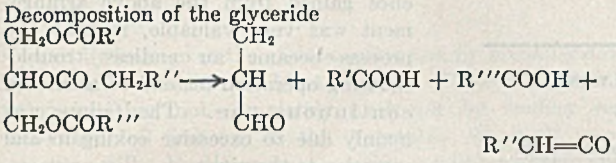
Starting with a vegetable oil which is mainly a mixture of fatty acid glycerides represented by the formula:



$$\begin{array}{l} CH_2OCOR' \\ | \\ CHOCOCH_2R'' \\ | \\ CH_2OCOR''' \end{array}$$

in which R′, R″, and R‴ are radicals. $C_nH_{(2n+1)}$ or $C_nH_{(2n-1)}$ or $C_nH_{(2n-3)}$ or $C_nH_{(2n-5)}$ (except in the case of castor oil) which may or may not be identical, the following types of reaction are possible:

Decomposition of the glyceride

 (1)

$$\begin{array}{l} CH_2OCOR' \\ | \\ CHOCO.CH_2R'' \\ | \\ CH_2OCOR''' \end{array} \longrightarrow \begin{array}{l} CH_2 \\ | \\ CH \\ | \\ CHO \end{array} + R'COOH + R'''COOH + R''CH{=}CO \quad (1)$$

Decomposition of fatty acids

$$RCOOH \longrightarrow CO_2 + RH \quad (2)$$
$$2RCOOH \longrightarrow CO_2 + H_2O + RCOR$$

Decomposition of ketenes and acrolein

$$2R''CH{=}CO \longrightarrow 2CO + RHC{=}CHR \quad (3)$$
$$CH_2{=}CHCHO \longrightarrow CO + C_2H_4$$
$$RCOCH_2R \longrightarrow R{-}R + CH_2CO$$
$$2RCOCH_2R \longrightarrow 2R_2 + CO + C_2H_4$$

Decomposition into elements

$$C_nH_{2n+2} \longrightarrow nC + (n+1)H_2 \quad (4)$$

Dehydrogenation of paraffins

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2 \quad (5)$$

Splitting decomposition of paraffins

$$C_nH_{2n+2} \longrightarrow C_{n-m}H_{2n-2m+2} + C_mH_{2m} \quad (6)$$

Alkylation of paraffins, the reverse of (6) (7)

Isomerization of paraffins

$$N - C_nH_{2n+2} \longrightarrow iso - C_2H_{2n+2} \quad (8)$$

Aromatic cyclization of paraffins

$$C_{(2n+6)}H_{(2n+14)} \longrightarrow C_nH_{2n+1} + 4H_2 \quad (9)$$

Polymerization of olefins

$$2C_nH_{2n} \longrightarrow C_{2n}H_{4n} \quad (10)$$
$$C_nH_{2n} + C_mH_{2m} \longrightarrow C_{(n+m)}H_{2(n+m)}$$

Depolymerization of olefins, the reverse of (10) (11)

Decomposition of olefins to diolefins (12)

Decomposition of olefins to acetylenic hydrocarbons (13)

Aromatization or cyclization of olefins (14)

Hydrogenation of olefins

$$C_nH_{2n} + H_2 \longrightarrow C_nH_{2n+2} \quad (15)$$

Isomerization of olefins

$$n - C_nH_{2n} \longrightarrow iso - C_nH_{2n} \quad (16)$$

The type of reaction represented by Equation 1 was studied by Hurd (*5*) for triacetin. The presence of acrolein in the cracking products of all vegetable oils, imparting to them the characteristic but disagreeable odor, is entirely in line with this mechanism. It is also qualitatively supported by the data of Lo and T'sai (*8*), who followed the changes in such properties as acidity and saponification value of the liquid condensates and the composition of the gases during the course of cracking cottonseed oil in an autoclave. The oil was heated in the autoclave until a pressure of 200 pounds per square inch was reached. Then a sample valve on the top of the autoclave was regulated to allow the vapor cracking products to distill through a condensing system, at the end of which condensable and gaseous samples were numbered consecutively and analyzed. Parts of these data are reproduced in Tables VIII and IX.

That the acid value and saponification value in the initial stage of the cracking process should go up beyond 100 and that both should steadily decrease as the reaction goes on is a strong evidence for reactions 1 and 2. Gas analysis indicates that about 40% of the total is evolved at the beginning, showing that the larger part of the acids, acrolein, and ketenes formed according to

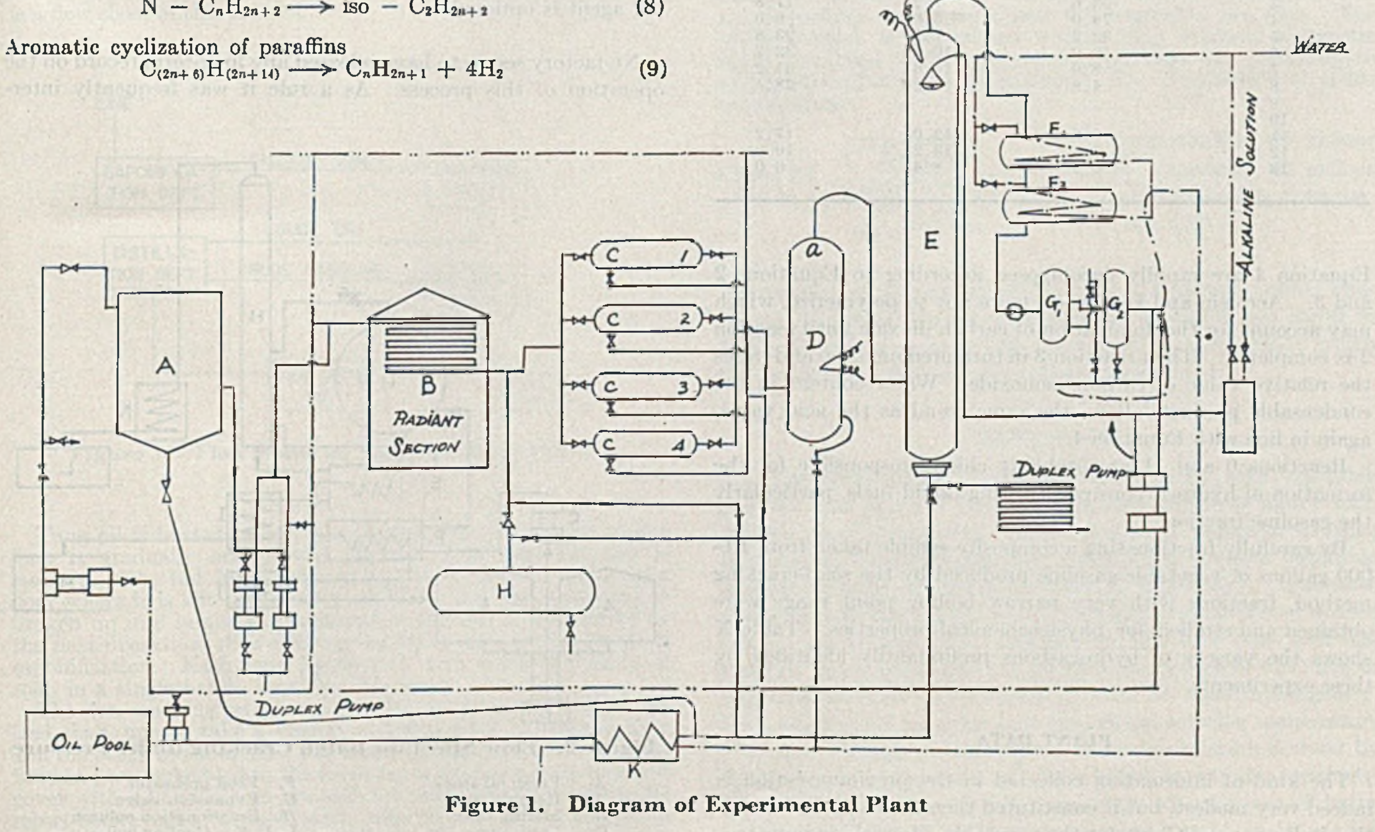


Figure 1. Diagram of Experimental Plant

A. Charging tank
B. Pipe still
C. Reaction chamber
D. Flash chamber
E. Fractionator
F. Condenser
G. Separator
H Surge tank
K. Cooling channel

——— Oil or gasoline line
—·—·— Steam line
—··— Water line
- - - - - Alkaline solution line
—▷◁— Valve

Table VII. Performance Data of Diesel Oils

Engine Speed, R.P.M.	Mineral Diesel Oil	Cottonseed Oil	Rapeseed Oil	95% Rapeseed, 5% Kerosene Oil	Tung Oil	Veg-Diesel Oil
			B.H.P. Developed from Testing Engine			
1000	25.8	23.2	23.5	23.8	23.4	24.4
1200	31.2	29.8	30.3	30.5	28.7	30.8
1400	35.7	35.2	34.5	34.4	33.5	34.7
1600	40.2	37.8	38.4	38.5	37.7	39.3
1800	43.7	40.5	41.4	41.3	38.7	42.1
2000	..	..	..	..	..	..
			Fuel Consumption, Grams/(B.H.P.-Hours)			
1000	225	314	311	307	321	257
1200	239	301	305	294	310	275
1400	254	321	320	318	325	296
1600	263	358	355	357	364	303
1800	289	365	367	364	371	331

Table VIII. Properties of Condensable Products from Pyrolysis of Cottonseed Oil in Autoclave

Sample No. of Distillate Fractions	Conditions			Yields			Characteristics	
	Temp., ° C.	Gage pressure, lb./sq. in.	Total time, min.	Total distilled over, g.	In Each Fraction Water wt. %	In Each Fraction Gas, vol. %	Saponification No.	Acid value
1	382	200	34	4.11	35.82	28.28	135.6	117.3
2	382	150	48	8.07	32.70	12.08	141.4	123.0
3	385	160	64	12.15	21.22	6.56	114.2	99.5
4	387	60	80	17.32	16.84	8.28	46.4	39.2
5	392	40	97	21.93	3.28	3.40	11.7	8.28
6	392	20	110	26.60	0	3.42	8.33	4.78
7	385	20	125	31.04	0	1.38	4.96	2.45
8	385	20	160	38.89	0	1.38	3.45	2.62
9	385	25	194	42.94	0	0.34	4.23	0.87
10	385	30	219	55.67	0	0.00	3.42	0.78
11	382	20	274	71.11	0	2.76	2.03	0.43
12	372	20	329	87.33	0	13.80	2.24	0.93
13	382	10	419	100.8	0	19.30	3.16	1.28

Table IX. Composition of Gas Fractions from Pyrolysis of Cottonseed Oil in Autoclave

Sample No. of Distillate Fractions (Table VIII)	Gas Analysis, Vol. %		
	CO_2	C_2H_4	CO
1	34.4	10.0	28.4
2	42.4	8.6	20.2
3	53.6	7.2	17.8
4	78.0	5.6	6.0
5	32.2	7.2	23.8
6	12.0	10.0	32.2
7	8.0	11.6	31.2
8	4.8	11.2	28.4
9	..	..	..
10	..	..	..
11	0.8	12.0	17.2
12	0.4	13.2	10.0
13	0.4	8.4	0.0

Equation 1 are rapidly decomposed according to Equations 2 and 3. Acrolein and ketene are more apt to polymerize, which may account for the domination of carbon dioxide until reaction 2 is completed. Then reaction 3 in turn predominates and raises the relative value of carbon monoxide. Water content in the condensable product follows the same trend as the acid value, again in line with Equation 1.

Reactions 6 and 11 are probably chiefly responsible for the formation of hydrocarbons constituting liquid fuels, particularly the gasoline fraction.

By carefully fractionating a composite sample taken from 10,000 gallons of vegetable gasoline produced by the soap-cracking method, fractions with very narrow boiling point range were obtained and studied for physicochemical properties. Table X shows the variety of hydrocarbons preliminarily identified by these experiments.

PLANT DATA

The kind of information collected in the previous section is indeed very modest, but it constituted the sole scientific foundation indigenous of China for the vegetable oil cracking industry. In the early days of the development it was assumed that much of the technique learned from the petroleum cracking industry in America could be used with little modification.

Figure 1 is the diagram of a plant designed by incorporating many features of petroleum cracking equipment such as the pipe still, the reaction chamber, the flash chamber, etc. It was expected that such a plant could convert a maximum of 10,000 gallons of a nondrying or semidrying oil per 24-hour day. The operation consists of feeding the vegetable oil together with recycle stock into the pipe still maintained at 425° to 450° C. and passing it through the reaction chambers, from which the cracking products expand into the flash chamber where the heavy oil leaves from below as recycle stock and the light portion goes on to a packed fractionating column. The experience gained from the above arrangement was very valuable, in that the process became an endless trouble-shooting operation instead of a smooth continuous one. The failure was mainly due to excessive coking in and corrosion to the pipes.

Batch cracking under pressure in shell stills was the next simpler design to be tried. Stills ranged in empty capacity from a few gallons to 1800 gallons and the process followed more or less the flow sheet in Figure 2.

Fresh oil mixed with recycle stock is pumped through preheater *F* into cracking still *D* while the cracked vapors expand through valve *C* into the fractionating column, *H*. The heavy oil in the still, after purging through reboiler *E* and preheater *F* to give up the major portion of its sensible heat, is further cooled by water and stored up for recycle or redistilled into Diesel oil. The light oil from the top of column *H* is condensed and cooled in coil *K*, while the heavy portion from the bottom of the column is stored as Diesel oil in *M* after cooling in coil *I*. The addition of lime in the still as an emulsifying and neutralizing agent is optional.

No factory seems to have released any long-term record on the operation of this process. As a rule it was frequently inter-

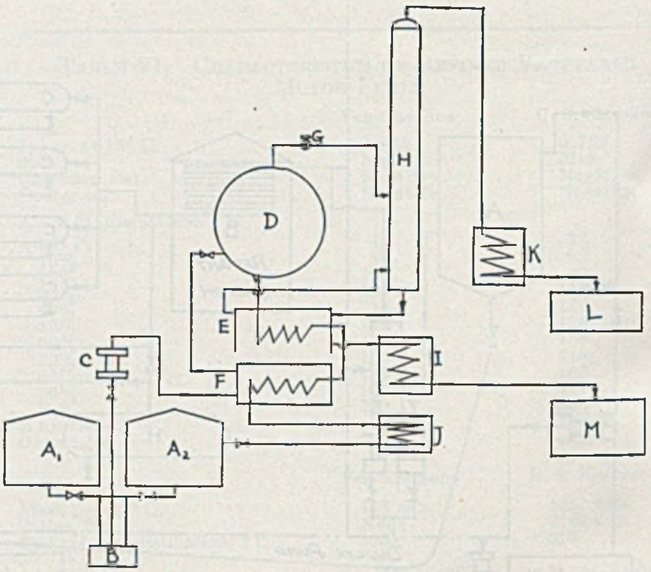


Figure 2. Flow Sheet for Batch Cracking under Pressure

*A*₁.	Fresh oil stock	*F*.	Feed preheater
*A*₂.	Recycle stock	*G*.	Expansion valve
B.	Mixing tank	*H*.	Fractionation column
C.	Feed pump	*I, J, K*.	Cooling coils
D.	Cracking still	*L*.	Crude gasoline stock
E.	Reboiler	*M*.	Crude Diesel oil stock

Table X. Hydrocarbons Identified from Vegetable-Gasoline (*13*)

	Boiling Point, ° C.	d_4^{20}	n_4^{20}
n-Hexane	69	0.6595	1.3754
n-Heptane	98	0.6839	1.3880
Hexene-2	68	0.6885	1.3990
Hexene-3	66	0.6790	1.3945
Heptene-2	98	0.7033	1.4022
Heptene-3	95	0.7015	1.4035
Hexadiene-2,4	90	0.7186	1.4490
Heptadiene-2,4	106	0.7329	1.4488
Methyl cyclopentane	73	0.7502	1.4102
Cycloheptane	119	0.8110	1.4433
Methyl cycloheptane	133	0.8055	1.4410
Cycloöctane	146	0.8306	1.4566

rupted by leakage at the various joints and by breaking down of stills due to corrosion or local heating. These difficulties were minimized but not completely overcome by feeding vegetable-Diesel oil instead of the vegetable oil itself into the cracking still. Furthermore, operating conditions, being entirely manually controlled, could not be set within reasonably narrow limits required for the collection of consistent data. The authors' own data (*2*) indicate that under the most practical working conditions, pressure and temperature could be maintained in the cracking still at 160 to 180 pounds gage and 480° to 500° C., to produce a 60% yield (by volume) of light oil plus 20% (by volume) yield of heavy oil for recycling, gasoline being 50% by volume of the light oil. Usually the vegetable-Diesel oil used as a starting material would be the product of a calcium soap-cracking plant.

While some were struggling with the troubles of pressure cracking, others had steadily developed an art in retorting the calcium soap. The soap-cracking process has always occupied the leading position in total output of vegetable liquid fuels and has outlived all other processes. It lacks features akin to modern chemical technology; yet it is so simple, practically standardized, and widely adopted that it is the only process which supplied production data that are of real statistical value. Figure 3 is a flow sheet of this process.

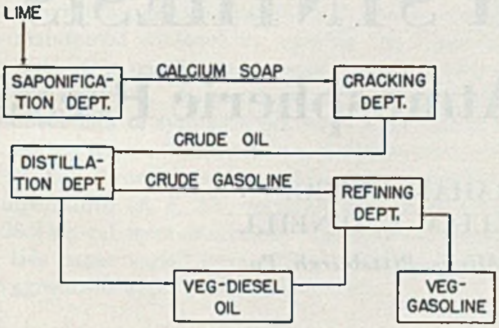


Figure 3. Flow Sheet of Soap-Cracking Process

Tung oil is heated in cast-iron kettles and commercial slaked lime is gradually added with stirring until saponification is stopped. The hot fused calcium soap is ladled onto a cement floor where it is left to cool and solidify. The hardened soap is broken up into lumps and removed to storage or transferred to the next operation, thus clearing the space for another batch of saponification. Each soap kettle may turn out 300 pounds of soap in a single batch, requiring 2.5 hours.

The iron cracking retorts are cast in two practically standardized sizes, one to take a charge of 100 pounds of calcium soap and the other 150 pounds. The retort consists of a hemispherical bottom part embedded in the furnace; a frustrated cone-shaped cover with a handhole on one side for charging and cleaning the retort before and after each batch, respectively; and a gooseneck connecting the top of the cover with a cooling coil through which the vapor products are condensed and led into a receiver. A number of retorts are arranged in a row and the cooling water is circulated. The sections of a retort are all joined together by plain flanges held tight with bolts and nuts and sealed with asbestos gaskets. A retort of 150-pound charging capacity produces on the average 13 gallons of crude oil in a cracking period of 6 hours. Two additional hours for charging and cleaning complete the 8-hour shift required by a single batch. Fuel consumption is on the average 300 pounds of bituminous coal per retort batch.

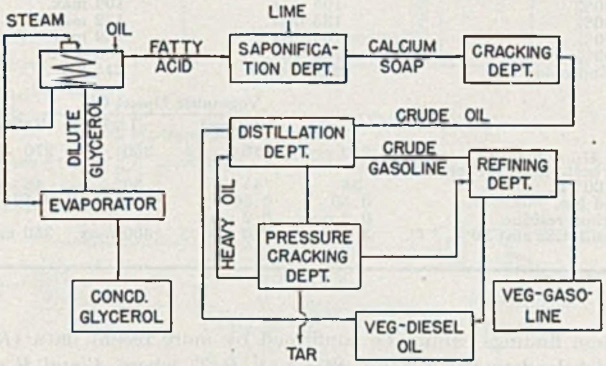


Figure 4. Flow Sheet of Vegetable-Gasoline Manufacture

Crude oil is sent to the refining section of the plant, where it is distilled with or without a fractionating column from horizontal shell stills constructed from $^3/_{16}$- to $^1/_2$-inch iron plates, seams being usually arc-welded. The capacity of the still is on the average about 600 gallons with a safe charging space of 400 gallons. The still is always provided with a manhole which is closed by a cover with grooved flanges for sealing with asbestos. Fractions of the distillate are separately collected as crude gasoline, light Diesel oil, and Diesel oil. The bottoms discharged from the still are collected as crude Diesel oil. These Diesel oils are marketable as they are, or the light Diesel oil may be redistilled and separated into Diesel and crude kerosene fractions. The latter after gum removal with 5% 66° Bé. sulfuric acid, scrubbing with water, neutralizing with a 10% solution of caustic soda, and again scrubbing with water, is redistilled and cut according to specifications for vegetable kerosene. The crude gasoline is neutralized with a 10% solution of caustic alkali, scrubbed with water, redistilled, and cut according to specifications for vegetable gasoline. The distribution of yields is as follows:

Crude oil, 1 ton	veg-gasoline, 60 gallons veg-Diesel oils, 0.73 ton tar, 0.05 ton	or	veg-gasoline, 60 gallons veg-kerosene, 40 gallons veg-Diesel oils, 0.60 ton tar, 0.06 ton

Tentative specifications announced for vegetable motor fuels by the National Bureau of Industrial Research are listed in Table XI in comparison with the actual average quality which the products of this corporation have maintained.

DISCUSSION

It has been suggested that alcohol blended with vegetable gasoline will improve the latter's properties as a motor fuel. Alcohol may increase the octane number of vegetable gasoline as it does in low-octane gasoline, but in other respects vegetable gasoline is the benefactor rather than the beneficiary. Ignorance about the solubility of the two often causes a great deal of wasted effort. Data have been obtained to illustrate how well one must be acquainted with the physical properties of mixtures of vegetable gasoline and alcohol in order to blend intelligently. Suen and Li (*12*) reported that the critical solution temperature of alcohol in vegetable gasoline follows the relation derived by Bridgeman and Querfeld (*1*) for alcohol in gasoline—namely, $\log S = a + b/T$, in which S is concentration of water, T is the absolute critical solution temperature, and a and b are constants.

Table XI. Vegetable Motor Fuel Specifications

	Chinese Government Specifications		China Vegetable Oil Corp. Standards	
	Vegetable Gasoline			
Color	Light yellow		Light yellow	
Sp. gr. at 15.5° C.	0.800 max.		0.790 max.	
Acid No.	0.20 max.		0.08 max.	
Corrosion test	Negative		Negative	
Gum content, mg./100 cc.	150		2	
A.S.T.M. distillation, ° C.				
Initial boiling point	65 max.		60 max.	
10%	85 max.		86 max.	
30%	105 max.		103 max.	
50%	135 max.		132 max.	
70%	165 max.		169 max.	
90%	200 max.		205 max.	
End point	225 max.		215 max.	
	Vegetable Diesel Oil			
	Light	Refined	Light	Refined
Sp. gr., A.P.I.	350	270	350	270
Saybolt viscosity, sec. at 100° F.	38	45	36	43
Acid No.	0.50	0.50	0.40	0.40
Carbon residue	0.2 max.	0.2 max.	..	
Distillation test 80%, ° C.	300 max.	350 max.	300 max.	350 max

These findings cannot be confirmed by more recent data (*13*), which lead to the relation $S^2 = A + B/T$, where A and B are constants.

Vegetable gasoline itself, if produced according to specifications, is an effective and reliable motor fuel having a higher calorific power and higher volatility than alcohol. Vegetable gasoline is an appropriate name because, being a mixture of hydrocarbons, it is a cousin not too distant in relation to gasoline.

Like gasoline, vegetable gasoline consists of both saturated and unsaturated hydrocarbons. The latter slowly oxidize and polymerize in the presence of air during storage, but are removable by the simple process of repeatedly treating with concentrated sulfuric acid until the refined distillate no longer reacts with the acid and remains colorless permanently. So refined, the oil also acquires a pleasant odor. Industrially, this procedure has not been followed because it will reduce output, increase production cost, and lower the octane value of vegetable gasoline.

Possible improvements in the process of manufacture have been tried. Thus in the soap-cracking process the vegetable oil is first steam-hydrolyzed to set free the fatty acids from the glycerol, which may become a valuable by-product for lowering the production cost of vegetable gasoline.

A pilot plant hydrolyzing tung oil under 120 pounds gage pressure at 170° C., using 3% by weight of quicklime for 10 hours to each batch, has shown that hydrolysis is 90 to 95% complete and from 8 to 9 pounds of glycerol (in terms of 99% glycerol) may be obtained from each ton of tung oil.

The other end of the soap-cracking process can be benefited by combining with pressure cracking, using the heavier portion of crude oil as its raw material. The latter, being a product of soap cracking, has low acidity and is suitable for the type of equipment now available. These possible improvements would call for an arrangement outlined in Figure 4.

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FISCHER-TROPSCH SYNTHESIS

Tests of Cobalt Catalysts at Atmospheric Pressure

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IN THE Fischer-Tropsch synthesis hydrogen and carbon monoxide are converted into mixtures of hydrocarbons, varying from methane to waxes on catalysts of cobalt, iron, nickel, or ruthenium. The synthesis has been reviewed by Storch (*22*, *23*), Golumbic (*12*), and others (*15*, *23*). Cobalt catalysts are usually operated in the temperature range of 175° to 200° C. at pressures from 1 to 20 atmospheres. Successful cobalt catalysts may be divided into two classes, skeletal and precipitated. Skeletal catalysts may be prepared by the method of Raney (*21*). Alloys of cobalt and silicon or aluminum were prepared by fusion in an induction furnace, and the silicon or aluminum was dissolved by aqueous caustic soda solutions (*9*, *18*, *26*, *28*, *29*). Although skeletal catalysts should be better conductors of the high heat of reaction of the synthesis to cooling surfaces of the converter, they were found to lose their activity more rapidly than precipitated catalysts. Skeletal types also require greater amounts of cobalt than precipitated catalysts; hence, they have not been used on a commercial scale.

Fischer, in 1932, described the development of the precipitated cobalt-thoria-kieselguhr (100:18:100) catalyst (*8*). The cobalt and thoria were precipitated with potassium carbonate from solutions of their nitrates, and kieselguhr was added at the time of precipitation. The amounts of thoria and kieselguhr could be varied over rather wide ranges without producing catalysts that were greatly inferior, but optimum proportions of cobalt-thoria-kieselguhr were considered to be 100:18:100. This type of catalyst has also been studied in England (*3*, *14*). In catalysts used in many of the Fischer-Tropsch plants, magnesia was substituted for part of the thoria, and the amount of kieselguhr was increased (*3*). The magnesia may be introduced in two ways.

Methods of preparing and testing a typical cobalt catalyst are described. Usually tests with the same catalysts were reproducible, but tests with different catalysts prepared in the same manner showed very much wider variations. Pelleted catalysts produced more light hydrocarbons and carbon dioxide than granular catalysts. Experiments were made in which the flow of synthesis gas was varied with the temperature adjusted to give the same per cent conversion. Under these conditions the degree of unsaturation increased with increase in flow and temperature. Except for the change in degree of unsaturation, the product distribution was not significantly different up to temperatures of 205° C. Over-all activation energies of 24 to 27 kg.-cal. per mole were found for the synthesis.

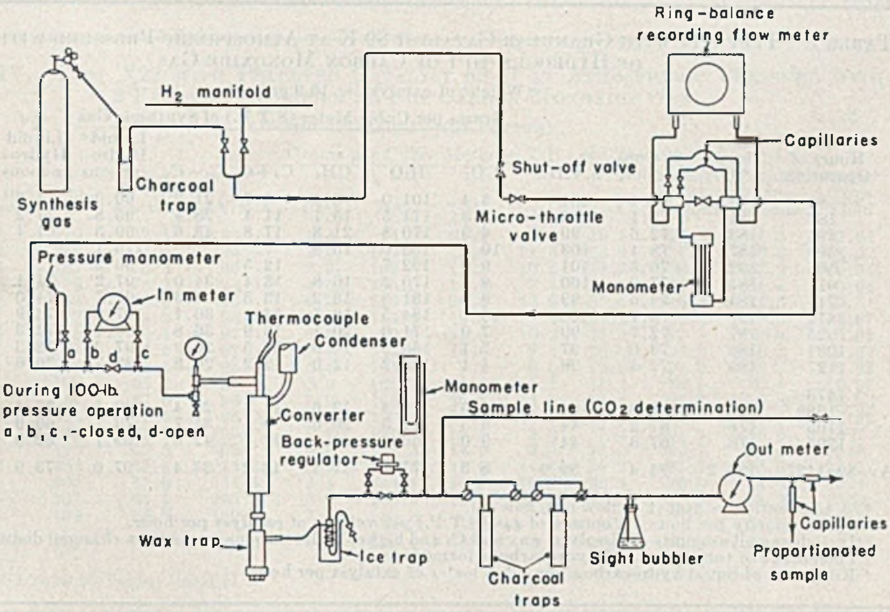

Figure 1. Flow Diagram of Catalyst-Testing Unit

In the first magnesium nitrate was added to the solution of cobalt and thorium nitrates, and the catalyst was precipitated with sodium carbonate, the kieselguhr being added at the time of precipitation. The optimum composition of this type of catalyst has been given as cobalt-thoria-magnesia-kieselguhr, equal to 100:6:8:200. In the second method of preparation precipitated magnesia as a fine powder and kieselguhr in an aqueous slurry are added at the time of precipitation. Typical catalysts of this type contain cobalt-thoria-magnesia-kieselguhr in the ratios 100:6:12:200 (*13*). The magnesia-containing catalysts are reported to have greater mechanical strength than the cobalt-thoria-kieselguhr catalyst and to produce less solid hydrocarbons.

In the present paper typical data for tests of cobalt-thoria-magnesia-kieselguhr (100:6:12:200) precipitated catalysts at atmospheric pressure are presented. In some of the tests the throughput of synthesis gas was varied, with the percentage of contraction maintained constant by varying the temperature. From these data it is possible to compute over-all activation energies for the synthesis. In a number of studies reported in the literature, the flow of synthesis gas was varied, but in most cases these studies were carried out at a constant temperature (*10, 16, 20, 27, 31*) From the studies of the rate of synthesis at different temperatures (*1, 5, 32*), apparent activation energies from 9.5 to 28.3 kg.-cal. were estimated. The activation energies reported in this paper varied from 24 to 27 kg.-cal. per mole, which are in agreement with those of Weller (*32*).

EXPERIMENTAL

The catalysts were tested in twelve small converters, a schematic drawing of one unit of which is shown in Figure 1.

The converters were constructed of standard steel pipe with a catalyst bed of 1.52-cm. inside diameter by 30 cm. in length, containing a steel thermocouple well of 0.65-cm. outside diameter. This annular space held about 50 cc. of catalyst. The catalyst tube was surrounded by an electrically heated boiler containing suitable boiling liquids such as tetralin for temperatures from 150° to 210° C. and Dowtherm A from 200° to 400° C. Temperatures were maintained by controlling the pressure of the boiler fluid with a mercury-containing manostat of the type described by Donahoe (*6*). The manostat used in this work was constructed of steel pipe with steel valves, and had a working range from −700 to +500 mm. of mercury pressure. Temperatures were measured by a Chromel-Alumel thermocouple placed within the well at the midpoint of the length of the catalyst bed and were recorded by multiple-point potentiometers. The temperature, as recorded at the midpoint, was usually the maximum temperature measured along the thermocouple well, as shown by the graph of temperature as a function of position in the bed in Figure 2. The temperature was lower at the top of the catalyst bed, the inlet side, than at the bottom. This was probably due to conduction of heat along the well, which extended out of the catalyst bed and tube at the top of the converter.

Synthesis gas of approximately 2 hydrogen to 1 carbon monoxide was prepared by passing a mixture of natural gas, steam, and carbon dioxide over a nickel catalyst at 900° C. (*24*), and was compressed into cylinders. The sulfur content of this gas was 0.5 grain per 1000 cubic feet, or less. The gas from the cylinder passed through a charcoal trap to remove carbonyls and organic sulfur compounds and on to a worm-geared needle valve.

The flow of synthesis gas was recorded and indicated by a ring balance recording flowmeter and an oil manometer, which measured the pressure drop across a capillary orifice. For operation at atmospheric pressure, an oil-filled wet-test meter was used to measure the inflow. The synthesis gas was passed down through the catalyst bed, and water, heavy oil, and wax collected in the wax pot, while some lighter hydrocarbons and water were condensed in the ice trap. The back-pressure regulator shown in Figure 1 was by-passed in tests at atmospheric pressure. The gas then passed through a charcoal scrubber, containing about 500 cc. of active carbon cooled to 0° C. The volume of the gas, which passed through the charcoal and which

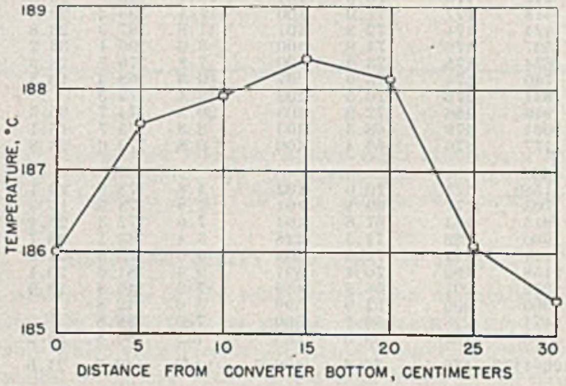

Figure 2. Vertical Temperature Gradient in Catalyst Bed

TABLE I. TEST X17 WITH GRANULAR CATALYST 89 K AT ATMOSPHERIC PRESSURE WITH 2 PARTS OF HYDROGEN TO 1 OF CARBON MONOXIDE GAS

(Weight of catalyst = 16.0 grams)

Hours of Operation	Av. Temp., ° C.	% Contraction[a]	S.V.H.[b]	Grams per Cubic Meter (S.T.P.) of Synthesis Gas						%[d]	
				CO_2	H_2O	CH_4	C_3+C_4	C_1-C_4	Liquid[c] Hydro-carbons	Liquid Hydro-carbons	Space[e] Time Yield
82	178	52.4	101	3.4	101.0	8.4	8.7	21.2	60.9	74.2	6.15
187	184	73.1	102	7.3	171.5	15.1	11.4	28.4	95.8	77.2	9.77
293	183	72.6	99	6.9	170.8	21.8	17.8	43.6	69.3	61.4	6.86
399	187	78.4	103	10.3	188.6	15.8	..	..	115.1	..	11.86
505	192	76.3	101	9.0	192.7	..	12.5	..	96.2	..	9.72
611	184	77.0	100	8.7	170.2	16.8	13.4	34.0	97.2	74.1	9.72
716	184	74.5	99	9.0	181.5	18.2	13.3	34.3	97.7	74.0	9.67
819	190	73.7	100	13.1	184.5	18.7	14.1	36.1	107.8	74.9	10.78
925	187	72.7	99	7.0	171.0	20.1	13.9	36.8	106.1	74.3	10.51
1031	186	73.0	97	7.1	156.9	15.0	10.5	26.9	97.2	78.3	9.43
1127	185	72.4	99	4.4	183.2	12.0	12.2	26.8	87.7	76.6	8.68
1473–1589	188	68.6	100	5.5	134.8	13.6	11.4	26.4	90.5	77.4	9.05
1705	176	67.2	44	9.5	162.5	20.6	9.1	31.7	73.7	69.9	3.25
1795	176	67.3	44	9.0	163.0	16.6	22.1	42.6	69.7	62.0	3.07
Av. 82–1127	186.2	74.4	99.9	8.3	177.1	17.1	13.2	33.4	97.0	73.9	9.70

[a] % contraction = 100 (1 − flow out/flow in).
[b] Space velocity per hour. Volumes of gas (S.T.P.) per volume of catalyst per hour.
[c] Includes small amounts of dissolved wax and C_5 and higher hydrocarbons in gas from charcoal distillation.
[d] Percentage of total weight of hydrocarbons formed.
[e] Kilograms of liquid hydrocarbon per cubic meter of catalyst per hour.

TABLE II. TEST X18 WITH GRANULAR CATALYST 89 K AT ATMOSPHERIC PRESSURE WITH 2 PARTS OF HYDROGEN TO 1 OF CARBON MONOXIDE GAS

(Weight of catalyst = 16.0 grams)

Hours of Operation	Av. Temp., ° C.	% Contraction[a]	S.V.H.[b]	Grams per Cubic Meter (S.T.P.) of Synthesis Gas						%[d]	
				CO_2	H_2O	CH_4	C_3+C_4	C_1-C_4	Liquid[c] hydro-carbons	Liquid Hydro-carbons	Space[e] Time Yield
79	177	47.3	104	4.4	81.0	9.7	6.1	19.6	51.6	72.4	5.36
186	187	72.1	98	7.2	190.0	18.3	10.8	32.1	71.0	68.8	6.96
292	187	72.6	98	7.0	169.6	21.4	13.1	35.1	65.4	65.0	6.41
397	186	77.8	102	10.3	159.8	17.3	10.3	29.0	87.4	75.0	8.92
503	192	75.1	101	9.0	186.0	20.2	11.2	34.3	103.3	75.1	10.44
609	190	77.2	99	8.8	186.0	..	..	..	105.0	..	...
715	188	72.7	101	9.0	171.0	15.7	12.0	32.4	103.9	76.2	10.50
818	189	68.9	99	8.6	188.2	19.5	11.9	34.0	87.3	72.0	8.64
924	188	73.8	101	5.1	179.3	14.7	3.4	18.6	96.0	83.7	9.70
1030	186	71.4	96	6.7	171.6	18.2	11.3	30.4	89.0	74.5	8.54
1121	186	73.2	101	8.5	172.8	13.5	9.8	25.5	86.6	72.5	8.75
1351–1467	190	64.3	99	7.8	132.5	14.3	8.9	24.9	88.0	77.9	8.70
1583	188	66.5	99	4.7	139.5	14.0	12.9	29.0	82.7	74.0	8.18
1699	178	66.4	43	6.1	165.3	..	27.0	..	81.1	..	3.49
1789	178	67.0	43	6.3	153.7	..	13.0	..	62.2	..	2.67
Av. 79–1121	187.9	73.5	99.6	8.0	177.4	17.6	10.4	30.2	89.5	74.8	8.91

[a] % contraction = 100 (1 − flow out/flow in).
[b] Space velocity per hour. Volumes of gas (S.T.P.) per volume of catalyst per hour.
[c] Includes small amounts of dissolved wax and C_5 and higher hydrocarbons in gas from charcoal distillation.
[d] Percentage of total weight of hydrocarbons formed.
[e] Kilograms of liquid hydrocarbon per cubic meter of catalyst per hour.

TABLE III. TEST X19 WITH PELLETED CATALYST 89 K AT ATMOSPHERIC PRESSURE WITH 2 PARTS OF HYDROGEN TO 1 OF CARBON MONOXIDE GAS

(Weight of catalyst = 38.8 grams)

Hours of Operation	Av. Temp., ° C.	% Contraction[a]	S.V.H.[b]	Grams per Cubic Meter (S.T.P.) of Synthesis Gas						%[d]	
				CO_2	H_2O	CH_4	C_3+C_4	C_1-C_4	Liquid[c] hydro-carbons	Liquid Hydro-carbons	Space[e] Time Yield
106	165	58.2	103	26.5	121.0	2.4	9.0	11.9	53.4	81.7	5.50
212	175	76.8	101	20.7	198.5	13.3	13.6	31.9	92.6	74.4	9.35
318	177	77.0	100	17.4	193.2	29.5	5.1	37.1	100.2	73.0	10.02
424	174	72.8	101	11.8	187.0	23.8	17.3	43.8	89.0	64.5	8.99
527	176	74.8	100	9.0	190.4	33.2	15.6	51.3	87.6	63.1	8.76
634	175	73.9	100	7.8	176.7	23.3	15.8	40.6	98.8	70.9	9.88
740	174	73.9	97	10.3	168.3	18.5	12.1	38.0	102.4	72.9	9.93
831	172	70.5	102	13.4	172.5	..	11.7	..	66.2	73.6	6.75
946	186	72.9	103	20.5	174.7	35.3	6.6	45.0	78.4	63.5	8.08
1061	176	68.3	103	8.8	175.7	15.1	11.0	30.4	93.2	75.4	9.60
1177	176	66.4	100	6.8	170.0	16.8	9.6	28.4	99.6	77.8	9.96
1499–1589	178	70.0	102	4.8	178.8	20.1	11.3	32.7	98.8	75.1	10.08
1703	177	69.8	101	7.8	178.6	15.4	7.3	23.6	91.2	79.4	9.21
1815	184	67.8	164	7.6	172.3	20.1	6.2	27.0	85.1	75.9	13.96
1930	189	71.5	228	3.4	183.1	38.7	14.9	61.6	99.8	61.8	22.75
2044	194	71.6	308	5.6	175.8	24.2	16.1	43.6	87.3	66.7	26.90
2158	199	70.4	391	9.4	181.6	20.1	15.1	38.4	90.2	70.1	35.27
2272	201	66.9	436	7.2	146.8	19.0	13.8	35.8	82.1	69.6	35.80
2360	209	57.9	599	5.0	143.8	..	..	..	72.9	..	43.67
2474	218	56.1	690	7.0	138.8	..	..	..	47.5	..	32.79
2588	197	69.6	175	4.2	180.8	22.2	19.9	44.7	100.1	69.1	17.52
Av. 106–1177	176.1	72.7	100.7	12.7	180.7	21.6	11.8	37.0	90.8	71.0	9.64

[a, b, c, d, e] Same as in Tables I and II.

contained unreacted syn
thesis gas, small percent
ages of methane, carbo
dioxide, and traces of C
C_3, and C_4 hydrocarbon
was measured by an oi
filled wet-test meter. Abou
1% of the exit gas was co
lected by a proportionatin
device for analysis by a Co
solidated mass spectromete
The charcoal was steam
distilled at temperatur
above 200° C. The liqu
products that collected i
an ice trap were combine
with the other liquid hydr
carbons, the volume of th
gaseous hydrocarbons wa
measured, and the gas wa
analyzed by the mass spe
trometer. Carbon dioxide wa
determined by a small Ha
dane apparatus on spo
samples withdrawn befo
the gas entered the charco
scrubber, as shown in Figu
1. Hydrocarbons greate
than C_4 are reported a
liquids in this paper. I
these tests at atmospher
pressure the wax (defined a
hydrocarbons insoluble in
mixture of 3 parts of aceto
to 1 part of methylene chl
ride at 0° C. with solve
to solute ratio of 3:1) di
solved in the liquid hydr
carbons was usually less tha
6%.

The catalysts were pr
pared by the following pr
cedure, in which the precip
tation and washing were a
complished as rapidly as po
sible:

A solution of C.P. coba
and thorium nitrates of abou
0.68 molarity of cobalt n
trate was heated to boilin
A boiling slurry of kieselgu
and finely divided magnes
and a boiling solution
sodium carbonate were add
simultaneously to the sol
tion of the nitrates. Th
solution was efficiently stirr
and the precipitation co
pleted as rapidly as possib
The precipitate, which w
not very gelatinous or co
loidal, settled rapidly.
was filtered and washed fr
of by-product electrolyt
with boiling water. Distill
water was used for the was
ing and in all the solution
The moist filter cake w
spread on glass plates a
dried in air at about 100°
The catalysts were prepar
in 200- to 400-gram batche
precipitation was acco
plished in Pyrex battery ja
and filtration on a lar
Büchner funnel.

For granular catalyst
the dried cake was broke
into pieces of 6- to 10-mes
size. Pelleted catalysts we
made from finely broke
filter cake, with a Stok

pelleting machine with 4% by weight of finely divided graphite added as a die lubricant. The pelleted catalysts used in this study were cylinders $^1/_8$ inch in diameter by $^1/_{16}$ inch long. The percentages of cobalt in the catalysts described in this paper were: 89 K, 24.6%; 89 O, 24.3%; and 89 Q. 23.8%. Catalysts 89 K and 89 Q contained a Portuguese kieselguhr which was obtained from C. C. Hall of the British Fuels Research Laboratory, where it had been used in Fischer-Tropsch catalysts. Catalyst 89 O contained as a carrier Johns-Manville Filter-Cel, which had been extracted with nitric acid for several hours, and the magnesia used had been washed with sodium hydroxide solution. Acid extraction of the kieselguhr was desirable, but the washing of the magnesia was probably not necessary. Electron micrographs and physical and chemical properties of the kieselguhrs used in these and other Fischer-Tropsch catalysts have been presented by Anderson, McCartney, Hall, and Hofer (2).

The catalysts were reduced in the converters, using high flows of dry hydrogen at space velocities [volumes of gas (S.T.P.) per volume of catalyst] per hour of 3000 for 2 hours at 400° C. All the catalysts were inducted and operated at atmospheric pressure with approximately 2 parts of hydrogen to 1 part of carbon monoxide synthesis gas. Two methods of induction were used: the slow method with contraction schedule and the slow method with temperature schedule. In the slow method with contraction schedule which was used in tests X18, X19, X22, and X27, the synthesis gas was introduced to the catalyst at 150° C. After about 30 minutes, the temperature was increased to give 45 to 50% contractions with 175° C. as an upper limit. After 48 hours, the upper limit on the temperature was a 45 to 50% contraction or 180° C., and after 24 additional hours the temperature was increased to give 70 to 75% contractions. In test X17 the slow method with temperature schedule was employed, in which the synthesis gas was introduced to the catalyst at 150° C., and in the first hour the temperature was increased to 175° C. After 48 hours the temperature was increased to 180° C., and after 24 additional hours to whatever temperature necessary to maintain 70 to 75% contraction. Both methods were probably more cautious than necessary, and both gave catalysts of equal activity and product distribution within the limits of reproducibility of the testing.

Table IV. Test X22 with Pelleted Catalyst 89 O at Atmospheric Pressure with 2 Parts of Hydrogen to 1 of Carbon Monoxide Gas

(Weight of catalyst = 28.5 grams)

Hours of Operation	Av. Temp., ° C.	% Contraction[a]	S.V.H.[b]	Grams per Cubic Meter (S.T.P.) of Synthesis Gas: CO_2	H_2O	CH_4	C_3+C_4	C_1-C_4	Liquid[c] hydrocarbons	%[d] Liquid Hydrocarbons	Space[e] Time Yield
103	179	32.1	94	5.4	74.2	21.2	13.4	39.2	27.8	41.5	2.61
210	183	74.4	94	3.6	169.0	12.9	11.5	26.9	87.4	76.4	8.22
316	182	76.3	95	6.2	198.5	17.1	10.6	29.7	100.5	77.2	9.54
407	178	74.2	94	4.0	195.2	14.9	7.5	24.1	105.8	81.4	9.94
522	183	68.4	96	9.3	176.0	20.9	12.9	35.6	109.8	75.5	10.5
637	177	63.3	94	5.1	158.5	19.4	6.8	29.2	95.4	76.5	8.97
752	178	69.1	97	5.0	180.0	21.5	10.2	33.3	97.1	74.4	9.42
868	177	69.5	97	4.8	183.6	14.6	9.6	26.6	95.2	78.2	9.24
984	178	68.1	95	5.1	161.5	7.2	8.5	18.9	97.0	83.7	9.22
1074	188	65.2	97	3.4	166.7	19.6	9.1	31.1	72.9	70.1	7.07
1164	187	67.0	96	9.2	165.3	21.1	13.1	34.7	97.5	73.8	9.36
1278	184	67.5	95	9.6	176.0	10.9	10.0	22.4	100.2	81.7	9.52
1390	192	67.2	156	7.1	181.4	13.5	3.0	17.5	107.1	85.9	16.7
1504	198	68.5	208	6.3	162.3	14.0	3.9	20.0	94.2	82.4	19.6
1618	202	67.4	271.3	5.2	177.8	17.0	14.6	34.2	83.2	70.9	22.6
1732	206	57.0	351.4	5.1	148.8	18.7	10.7	32.4	92.0	74.0	32.3
1846	207	63.1	295.5	5.8	164.5	18.2	15.2	35.9	80.9	69.2	15.8
1935	192	68.9	159.3	7.3	183.3	..	..	..	79.5	..	14.7
Av. 103–1164	181.1	69.6	95.5	5.6	175.4	16.9	10.0	29.0	95.9	76.8	9.15

[a,b,c,d,e] Same as in Tables I and II.

Table V. Test X27 with Pelleted Catalyst 89 Q at Atmospheric Pressure with 2 Parts of Hydrogen to 1 of Carbon Monoxide Gas

(Weight of catalyst = 34.2 grams)

Hours of Operation	Av. Temp., ° C.	% Contraction[a]	S.V.H.[b]	Grams per Cubic Meter (S.T.P.) of Synthesis Gas: CO_2	H_2O	CH_4	C_3+C_4	C_1-C_4	Liquid[c] hydrocarbons	%[d] Liquid Hydrocarbons	Space[e] Time Yield
115	176	58.5	102	14.8	142.7	7.7	11.5	20.5	71.9	77.8	7.33
230	179	68.1	101	5.0	178.8	12.1	10.7	25.3	81.2	76.2	8.20
346	181	65.8	100	7.6	156.5	..	10.7	..	93.6	..	9.36
462	179	65.6	101	4.6	158.1	22.2	14.2	38.8	90.3	70.0	9.12
578	179	70.8	100	8.7	155.7	18.5	7.9	29.8	69.5	70.0	6.95
668	182	67.3	102	5.2	175.4	12.4	19.7	32.8	97.0	74.7	9.90
758	182	70.0	101	3.5	189.1	20.2	12.3	35.4	100.5	74.0	10.15
872	183	68.6	99	7.0	180.8	23.5	17.4	40.7	89.4	68.7	8.85
984	185	68.3	100	10.7	180.2	14.3	9.6	24.6	95.1	79.4	9.51
1098	187	71.0	96	2.0	190.4	15.9	12.3	28.6	102.7	78.2	9.86
1212	186	72.2	104	6.6	178.9	14.9	13.0	29.4	98.2	77.0	10.21
Av. 115–1212	182	68.8	100	6.1	174.4	17.1	12.8	31.9	91.8	74.2	9.21

[a,b,c,d,e] Same as Tables I and II.

Table VI. Statistical Comparison of Catalyst Testing Data by Method of Student

(Averages of 2nd to 11th week of operation)

Run	Catalyst and Form[a]	Wt. of Catalyst	%[b] Contraction	Temp., ° C.	Grams per Cubic Meter: CO_2	H_2O	CH_4	$C_3 + C_4$	$C_1 - C_4$	Liquid hydrocarbons
17	89 K-G	16.9	74.4	186.0[c]	8.3	177.1	17.1	13.2	33.4	97.0[c]
18	89 K-G	16.0	73.5	187.9[c]	8.0	177.4	17.6	10.4	30.2	89.5[c]
18	89 K-G	16.0	73.5	187.9[d]	8.0[d]	177.4	17.6[c]	10.4	30.2[d]	89.5
19	89 K-P	38.8	72.7	176.1[d]	12.7[d]	180.7	21.6[c]	11.8	37.0[d]	90.8
19	89 K-P	38.8	72.7	176.1[d]	12.7[d]	180.7[c]	21.6[c]	11.8	37.0[c]	90.8
27	89 Q-P	34.2	68.8	182.0[d]	6.1[d]	174.4[c]	17.1[c]	12.8	31.9[c]	91.8
19	89 K-P	38.8	72.7	176.1[d]	12.7[d]	180.7	21.6[c]	11.8[c]	37.0[d]	90.8
22	89 O-P	28.5	69.6	181.0[d]	5.6[d]	175.4	16.9	10.0[c]	29.0[d]	95.9

[a] G = granules; P = pellets.
[b] Per cent contraction.
[c] Difference possibly significant.
[d] Difference probably significant.

The data of the catalyst testing are reported for weekly periods of operation. Operation of the converters was started about Monday noon and was continuous until Saturday morning, when the catalyst was reactivated by passing hydrogen over it at 10° C. higher than the synthesis temperature for 2 hours. Then the products were recovered and a very slow flow of hydrogen was passed over the catalyst until Monday, when the synthesis was resumed. In all testing the contractions were maintained between 70 and 75% by varying the operating temperature.

REPRODUCIBILITY OF CATALYST TESTS

In general, tests of the same preparation of catalysts were reproducible, while tests of similar preparations showed considerably wider variations of activity and product distribution. The widest variations within a test were found in the data for liquid hydrocarbons because of the difficulty of recovering small quantities of liquids (70 to 80 cc.) from two metal traps and the charcoal scrubber.

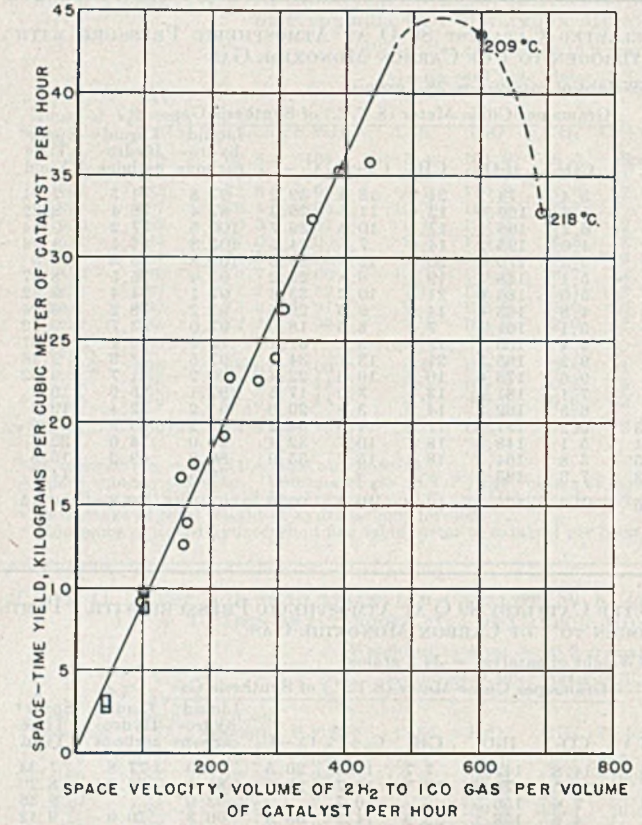

Figure 3. Plot of Space-Time Yield against Space Velocity for Cobalt Catalysts at Atmospheric Pressure

Temperature varied to maintain 70% contraction
○. Pelleted catalysts
□. Granular catalysts

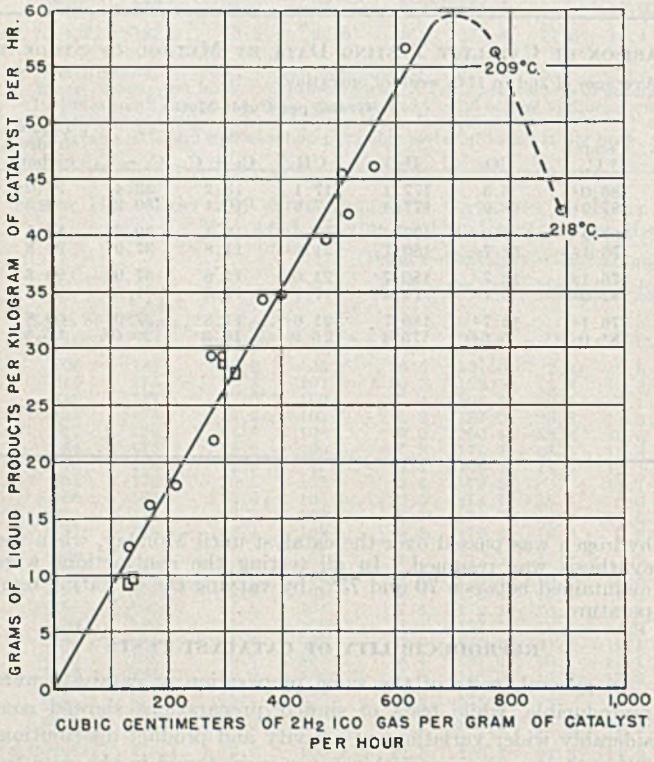

Figure 4. Plot of Weight-Time Yield against Flow of In-Gas per Gram

Temperature varied to maintain 70% contraction
○. Pelleted catalysts
□. Granular catalysts

In Tables I and II are presented data of tests X17 and X18 of granular catalyst 89 K. Different methods of induction were used in these tests, but these inductions are similar. The differences of the means of the data for the second to eleventh week of operation were tested for significance by a statistical method as developed by Student (*25*). With this method the probability that two groups of data may be samples of the same "parent group" is estimated. The probability of finding differences of means greater than observed, on the basis of two samples taken from the same parent group, was computed. If this probability was less than 8%, the samples were probably from different parent groups, and the difference was probably significant. For probabilities from 8 to 25% the differences were regarded as possibly significant, and for probabilities greater than 25%, differences were not considered significant.

In the comparison of tests X17 and X18, as shown in Table VI, none of the differences were probably significant. Pelleted catalysts 89 K and 89 Q were prepared in an identical manner with Portuguese kieselguhr as a carrier. In the tests of these catalysts, X19 and X27, as shown in Tables III and V, the means of the data for the two tests showed greater differences than those of X17 and X18. The statistical test showed significant differences in temperatures and amounts of carbon dioxide, methane, and $C_1 - C_4$ hydrocarbons. At least part of these differences may be attributed to higher density of catalyst 89 K.

Material balances for the tests were satisfactory, usually varying from 90 to 98% for the weekly operating periods. Hydrogen and carbon monoxide were used in a ratio of about 2.2, the average usage ratios for the first 1500 hours of operation being 2.20, 2.24, 2.11, 2.30, and 2.24 for tests X17, X18, X19, X22, and X27, respectively.

TESTS AT CONSTANT SPACE VELOCITY

In most of the testing the space velocity per hour of synthesis gas was 100. In tests X17 and X18 it is evident that the two methods of induction, at least in this case, gave almost identical activity and product distribution. In the statistical comparison of tests X18 and X19 (Table VI) with granular and pelleted catalyst 89 K, significant differences were found in temperature, carbon dioxide, methane, and $C_1 - C_4$ hydrocarbons. The greater amounts of carbon dioxide and light hydrocarbons were due to the higher density of the pelleted catalyst and not to the differences in temperature, since at higher temperatures greater yields of carbon dioxide and light hydrocarbons may be expected if any variation is found. The temperature difference was due to the greater weight of catalyst used in test X19. Although the product distribution was a function of catalyst density, it was also a function of variations of the method of preparation, since the product distribution of pelleted catalyst 89 Q about equaled that of granular 89 K. Usually, however, when differences in density occur, the denser catalysts will produce greater amounts of carbon dioxide and light hydrocarbons.

In statistical tests of X19 and X22 significant differences occurred in temperature, carbon dioxide, methane, and $C_1 - C_4$ hydrocarbons. Here again the catalyst of the lower density, 89 O, produced less carbon dioxide and light hydrocarbons and operated at a higher temperature.

With cobalt-thoria-magnesia-kieselguhr catalyst of the type described in this paper, Craxford (*4*) found large differences in product distribution when the space velocity was varied at 185° C. In these experiments the yields of liquid products and methane per cubic meter of in-gas increased proportionally as the space velocity was decreased until flows were reached at which the synthesis gas was fairly completely converted by the middle of the catalyst bed. In the part of the bed that was not actively engaged in the synthesis, liquid hydrocarbons were hydrocracked to methane and carbon monoxide was converted to carbon dioxide by the water gas shift reaction, thus increasing the yields of methane and carbon dioxide and decreasing the yield of liquid products. Although the flow of synthesis gas per gram of catalyst in the authors' experiments varied considerably owing to differences in catalyst density, the mechanism of Craxford was not operative, since all tests were made at contractions of 70%.

TESTS WITH VARIED SPACE VELOCITY

After 1200 or more hours of operation the catalysts in tests X17, X18, X19, and X22 were operated at several different space velocities with the temperatures varied to maintain contractions of 70 to 75%. The catalysts were tested for one week at each space velocity; the data for these tests are given in Tables I to IV. Up to temperatures of 205° C. the yields per cubic meter and distribution of products did not change appreciably. In Figure 3 the space-time-yield in kilograms of liquid hydrocarbons per cubic meter of catalyst per hour is plotted against space velocity, and in Figure 4 the weight-time-yield in kilograms of liquid hydrocarbons per kilogram of catalyst per hour is plotted against flow in cubic centimeters (S.T.P.) per gram. All the time yields scattered about straight lines, except the points for the operation at 209° and 218° C. in test X19. Points for the granular catalysts fall within the range of scattering of the points for pelleted catalysts. The maximum space-time and weight-time yields were 43.7 and 56.7 grams per kg. per hour for a space velocity per hour of 600 and a flow per gram of 616 cc. (S.T.P.) per gram per hour, respectively.

The fraction of olefins in both the gaseous and liquid hydrocarbons increased with higher temperature and flow of synthesis gas. In Table VII are presented the percentage of olefins in the C_3, C_4, and C_5 fractions of the gaseous products, and the bromine numbers of the liquid products of test X19. The bromine numbers of tests X17, X18, X19, and X22 can best be correlated to the flow per gram of catalyst as shown in Figure 5, in which bromine numbers are plotted against flow per gram of catalyst. The increase in unsaturation of products with flow may indicate that olefins are the primary product, and that the degree of saturation increases with increasing time of contact. The degree of unsaturation of products usually increases with increases of either flow or temperature. With a cobalt-nickel (1:1) skeletal catalyst at a flow of 0.4 liter per gram per hour, Tsuneoka and Murata (*30*) found the unsaturation increased with increased temperature, and with a similar catalyst at 190° C. Murata, Ishikawa, and Tsuneoka (*17*) observed that the iodine number of liquid products increased from 0 at 0.05 liter per gram per hour to 34.0 at 1.5 liter per gram per hour.

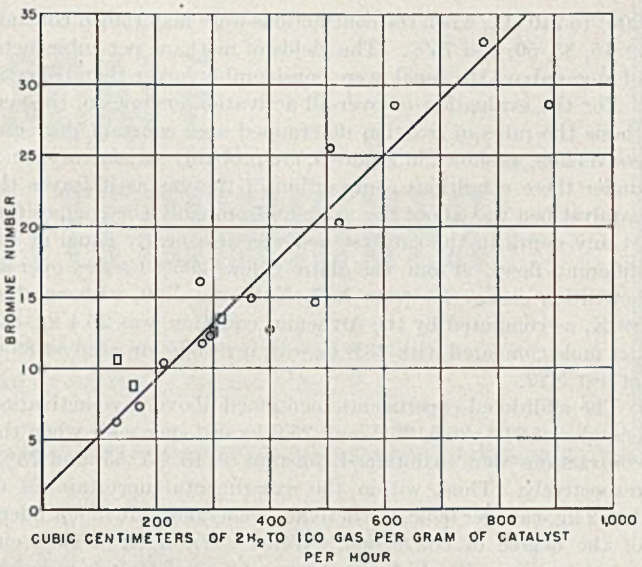

Figure 5. Variation of Bromine Numbers of Liquid Products of Cobalt-Thoria-Magnesia-Kieselguhr Catalysts at Atmospheric Pressure with Flow of Synthesis Gas per Gram of Unreduced Catalyst

Temperature varied to maintain 70% contraction
○. Pelleted catalysts
□. Granular catalysts

In Figure 6 the rate of synthesis in cubic centimeters of synthesis gas reacting per gram of catalyst per hour is plotted against temperature for tests X17, X18, X19, and X22. The points for granular catalyst 89 K in tests X17 and X18 fall along the curve of pelleted 89 K in test X19 indicating that granular and pelleted forms of the same catalysts were about equally active per gram. For tests X19 and X22 at temperatures higher than 205° C. the rate of synthesis did not increase as rapidly with increasing temperature as below 205° C. It is probable that the break in the rate-temperature curves was due to changes in the mechanism of reaction or the catalyst itself. In test X19 the catalyst was permanently damaged by the high temperature of operation (Table III), while in test X22 (Table IV) the activity was not impaired. Additional data, which are not described in detail, for pelleted catalyst 89 V, show that similar breaks in the rate of conversion-temperature curves occur in the temperature range

Table VII. Olefin Content of Gaseous and Liquid Products from Test X19

Flow		% Olefins in Gaseous Products			Bromine No. of Liquids
S.V.H.[a]	Cc./g.	C_3	C_4	C_5	
100	129	21.3	28.5	24.1	6.2
164	211	18.7	29.6	23.9	10.4
228	294	30.8	53.4	24.4	12.3
308	397	36.4	44.5	37.5	12.7
391	504	58.6	54.2	40.1	25.5
599	722	71.8	67.0	52.8	33.0
690	889	65.3	59.7	59.3	28.6

[a] Space velocity per hour. Volumes of gas (S.T.P.) per volume of catalyst per hour.

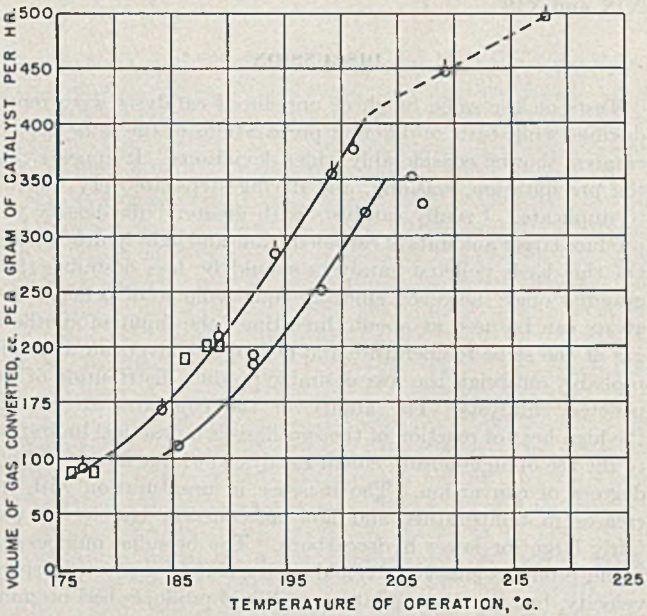

Figure 6. Variation of Volume of Synthesis Gas Converted per Hour

Temperature varied to maintain 70% contraction
ǫ. Pelleted catalyst 89 K in test X19
□. Granular catalyst 89 K in tests X17 and X18
○. Pelleted catalyst 89 O in test X22

200° to 210° C., when the contractions were maintained constant at 15, 35, 50, and 75%. The yields of methane per cubic meter of in-gas above the break were considerably larger than below it.

For the evaluation of over-all activation energies of the synthesis the rates of reaction determined at a constant degree of conversion, as shown in Figure 6, are probably satisfactory, since under these conditions composition of the gas as it leaves the catalyst bed was about the same and probably the composition at any depth in the catalyst bed was also nearly equal at the different flows. From the data below 205° C. the over-all activation energy for tests X17, X18, and X19, with catalyst 89 K, as computed by the Arrhenius equation, was 26.4 kg.-cal. per mole compared with 23.8 kg.-cal. per mole for catalyst 89 O in test X22.

The additional experiments mentioned above gave activation energies of 24.4, 26.6, 26.3, and 25.6 kg.-cal. per mole when the contractions were maintained constant at 15, 35, 55, and 75%, respectively. Thus, within the experimental uncertainties of 1 to 2 kg.-cal. per mole, the activation energies were independent of the degree of conversion. Weller (*32*), using a glass circulating system in which the degree of conversion per pass was 1 to 2%, found that the energy of activation for synthesis on cobalt-thoria-kieselguhr catalyst was 26.5 kg.-cal. per mole.

Craxford and Rideal (*5*) reported a value of 9.5 kg.-cal. per mole for synthesis on a cobalt catalyst, but this value may not be reliable, since it was determined in a static system. From data for iron catalyst, activation energies of 20 and 29 kg.-cal. per mole were computed. Eidus (*7*) found an activation energy of 29 kg.-cal. per mole for iron-copper-thoria–potassium carbonate–kieselguhr catalyst at 245° to 265° C. From data of Pichler (*19*), for an unpromoted iron oxide–gel catalyst, an activation energy of 20 kg.-cal per mole was computed. Thus, the more reliable temperature-rate data for both cobalt and iron catalysts give activation energies of the synthesis varying from 20 to 29 kg.-cal. per mole. Although the reaction mechanisms cannot be predicted from the activation energies, the high values probably exclude diffusion as the rate controlling step in the synthesis. This is in agreement with the observation that granular and pelleted forms of the same catalyst preparation were equally active when compared on an equal weight basis as in tests X17, X18, and X19.

DISCUSSION

Tests on the same batch of unreduced catalysts were reproducible, while tests of different preparations of the same type of catalyst showed considerably wider deviations. It appears that the precipitation, washing, and drying steps are very difficult to duplicate. Usually catalysts with greater bulk density will produce larger amounts of carbon dioxide and light hydrocarbons. On this basis pelleted catalysts should be less desirable than granular ones; however, since an equal volume of pelleted catalysts can be used at about three times the input of synthesis gas at the same temperature and degree of conversion, this will probably outweigh the less desirable product distribution of the pelleted catalysts. The ability of the converter to remove the high heat of reaction of the synthesis is a practical limitation to the use of high-density cobalt catalysts at large flows and high degrees of conversion. The increase in unsaturation with increases in temperature and flow at constant conversion was fairly large for lower hydrocarbons. The bromine numbers of liquid products changed fivefold with a sixfold increase in space velocity, but the most unsaturated liquid products had bromine numbers of only 30.

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BENCH SCALE EQUIPMENT AND TECHNIQUES

Presented before the Division of Industrial and Engineering Chemistry at
the 111th Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, N. J.

High pressure reactions . . . .

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THE design and operation of experimental equipment for the investigation of hydrogenation of coal as a source of synthetic liquid fuel is complicated by the rigorous requirements of the process. The use of high pressures (1000 to 12,000 pounds per square inch gage) and high temperatures (350° to 600° C.), coupled with the corrosive and erosive nature of the products, necessitates specialized and carefully planned equipment. Three types of experimental high pressure units are in use: batch autoclaves or, in general, units in which no flow of reactants or products takes place; semicontinuous units where part of either the reactants or products are in continuous flow; and completely continuous units wherein all reactants are fed into and all products removed from the reactors or converters. Various problems in design of these units, including suitable protection for operating personnel, are discussed. Materials of construction, vessel closures, internal liners and techniques of operation, and control for batch-type units are described. Examples are cited of piping joints, valves, and instruments of special design required for units wherein continuous flow is maintained of materials of corrosive or erosive nature. Comparisons are made between the equipment used in Germany for small scale and pilot plant research and the units here.

THE importance of small scale pilot plants in our present scheme of research and development work has been sufficiently stressed to have become almost factual. A well designed and carefully planned bench scale layout can permit tremendous savings of time and effort in investigating reactions and processes for both industrial and academic research. In the design of small scale equipment for operation at high temperatures and pressures the many mechanical problems, the necessity for stressing personnel safety, and the care required in assembly and operation present serious obstacles. There are in the literature many helpful references to work done at elevated pressures. Sage and Lacey (*4*) have described equipment used for accurate measurements at pressures up to 10,000 pounds per square inch and temperatures up to 240° C. The work of Bridgman (*2*) at the extremely high pressures of over 100,000 atmospheres but at relatively low temperatures mentions techniques and methods of sealing that are useful. In addition, the two excellent texts on high-pressure plants by Tongue (*5*) and Newitt (*3*) are informative.

This paper presents in some detail the type of equipment in use at the Bureau of Mines for investigating the high pressure hydrogenation of coal. These investigations have been in progress for ten years and are now being intensified as part of the Government synthetic fuels program. Reports of this work and brief general descriptions of the equipment in use may be found in Bureau of Mines publications and journal articles by H. H. Storch, L. L. Hirst, C. H. Fischer, and their co-workers. It is felt, however, that some detailed discussion of techniques and equipment for operation at high pressures and temperatures may be of interest to builders and users of bench scale apparatus.

The hydrogenation of coal imposes severe requirements for the designer, such as pressures up to 15,000 pounds per square inch, temperatures up to 500° C., and the presence of hydrogen sulfide, ammonia, and, in many cases, hydrogen chloride. In addition, the unreacted coal and ash residues mixed with oil are extremely erosive combinations, particularly for valves, pumps, and preheater coils. Obviously, under such conditions the selection of suitable materials of construction is important. The ideal material for the construction of equipment for the hydrogenation of coal at elevated temperatures and pressures should have the following characteristics: (*a*) high creep strength and good resistance to hydrogen, (*b*) high resistance to abrasion, (*c*) good corrosion resistance in the presence of appreciable quantities of ammonia, sulfur compounds, and water vapor, (*d*) good machining qualities, and (*e*) good weld properties for joining parts readily with presently available welding practices. Although all parts of the equipment may not be subjected to elevated temperatures which impose many of these requirements, it is considered advisable to use the same material for all tubing and fittings because of the constant revisions and rearrange-

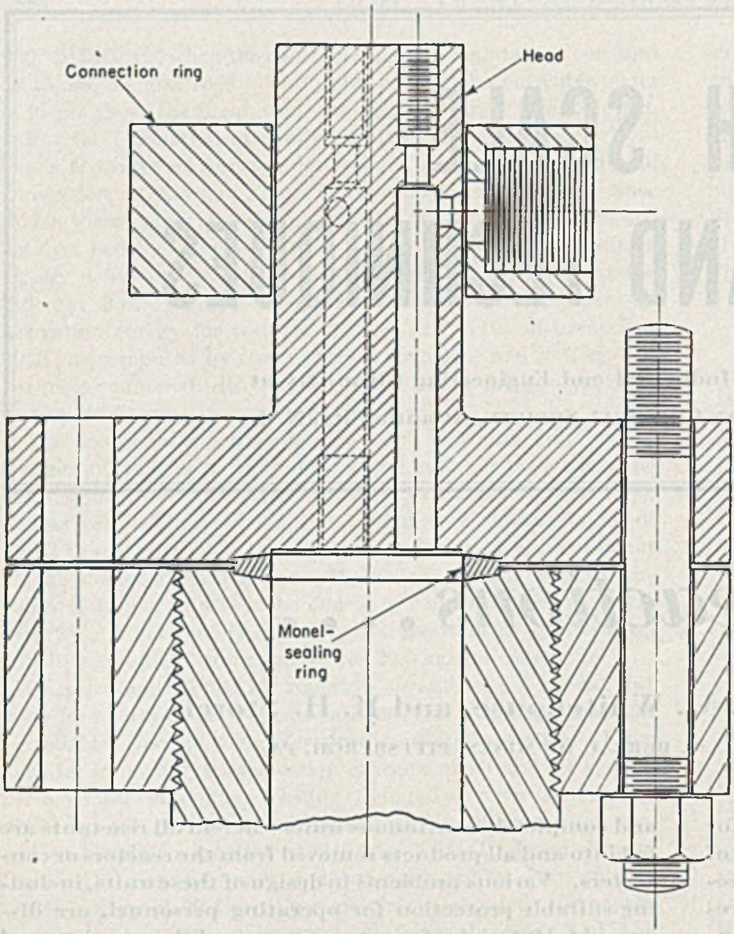

Figure 1. Assembly of Vapor Phase Converter Head

ments made in experimental work. The use of material suitable for the most severe conditions throughout the plant, although expensive originally, actually is cheaper because of savings in revision and maintenance.

Austenitic stainless steel (18 Cr–8 Ni) type 347, columbium-stabilized, was chosen for all vessels exposed to high temperatures and pressures, and for tubing and fittings that may be exposed to extreme conditions. Although expensive, this steel combines all of the desirable properties to a high degree. Solid test pieces of this type of steel and welded joints made with a 25% Cr–12% Ni-Cb electrode were tested in the liquid and gas phase of the existing pilot plant at the Pittsburgh station of the Bureau of Mines. After exposure for over 1100 hours at operating pressures of 3500 pounds per square inch and temperatures up to 440° C., more satisfactory resistance to surface corrosion was found than noted in other steels similarly tested. The weld metal used was also found satisfactory.

Material suitable for metal gaskets and sealing rings must have properties consistent with the service conditions. If the conditions permit a choice of two or more materials, that material having the higher yield strength should be used. In this work both copper and Monel metal have been found suitable for sealing pressure-vessel closures from the standpoint of corrosion and service temperature. Monel metal sealing rings have proved superior for securing the initial seal, maintaining the seal throughout temperature variations, and for the number of times the ring may be used before it must be discarded. It is believed that the elasticity of the Monel metal accounts for this superiority.

A few words on methods for calculating wall thickness or maximum working pressures may be of interest. Table I gives the permissible working pressures for a number of vessels, calculated by various theories. The first two vessels are to be constructed soon, the fourth is in progress of construction, and the third and fifth are now in use. Considerable variance in permissible working pressures may be noted, with the maximum shear stress theory the most conservative, and the classical Lamé or maximum principal stress theory the least conservative. The maximum strain energy theory is preferred for our use, although it is slightly less conservative than the maximum shear method of calculation. In addition, it should be noted that the maximum allowable fiber stress used in design is the creep strength, with only 1% deformation permitted in 10,000 hours. More detailed discussion and comparison of these theories are given in Boe's recent paper (*1*).

A definition of the safety factor is quite difficult under service conditions. At room temperature the safety factor averages 5 in most cases. At temperatures required for coal hydrogenation using short-time tensile properties, the safety factor is approximately 3. In most vessels machined reference points are periodically checked to detect any appreciable increase in diameter or change in creep rate. Vessels now in service after several thousand hours indicate no appreciable deformation. Careful records are maintained, as it is felt that appreciable changes in outside diameter can occur before failure of vessels constructed of ductile materials can take place.

BATCH AUTOCLAVE

The simplest type of bench scale equipment in use at the Bureau of Mines for high pressure–high temperature investigations is the batch autoclave. The autoclaves in use are 2 to 3 inches in internal diameter and 12 to 14 inches in length. For coal hydrogenation research, the required amounts of powdered

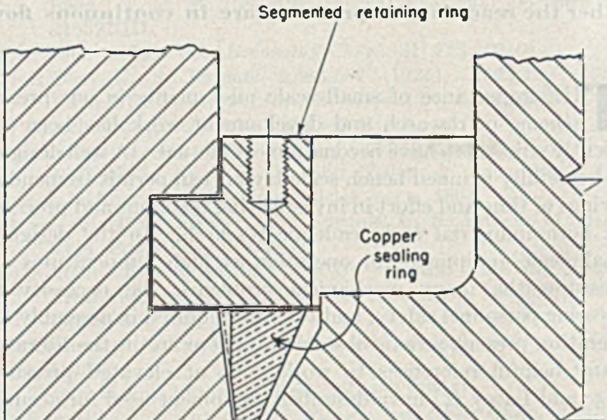

Figure 2. Detail of Pressure Seal

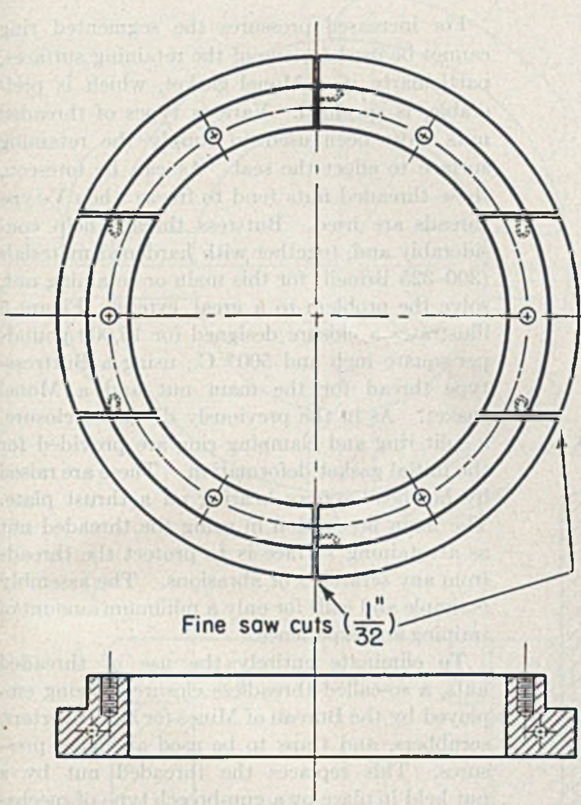

Figure 3. Segmented Retaining Ring

coal, catalyst, and oil vehicle are weighed into the autoclave; hydrogen is added to the required pressure, and then the temperature raised to the point required for the reaction. To provide mixing during the reaction period, the autoclave is rotated within the furnace. Furnace temperatures are controlled by a temperature controller manually set. The internal temperature of the autoclave is recorded by a thermocouple and temperature recorder with mercury pools used for contacts to the couple, which rotates with the autoclave. After the reaction time has elapsed, the gaseous products are recovered by venting the autoclave through a suitable absorption train and thus reducing the pressure to atmospheric. The autoclave is then opened for removal and examination of the liquid and solid products. An obvious precaution in handling experimental work of this type is accurate manipulation to permit good mass balances by keeping losses to a minimum. A suitable balance is used to weigh the autoclave and contents at several points in the charging and venting operations. The results are quite gratifying; they indicate losses of less than 0.5% in many cases. These indicate good sealing in both the autoclave closure and charging valve, as well as skillful and accurate manipulation.

Closures for high pressure vessels can be assembled by using sturdy bolts or studs and suitable flanges and gaskets. Such a closure for a converter 2 inches in internal diameter is shown in Figure 1. This type of flanged closure is commonly used in industrial work. The eight bolts are evenly tightened to suitably deform the Monel gasket. Torque wrenches are necessary to assure even deformation and good seal. There are several disadvantages in the use of this type of closure—increased pressure would tend to cause leakage, heating or cooling must proceed slowly to avoid the effects of thermal shock, and the eight bolts needed for the closure are quite a nuisance in assembly and maintenance. This type of closure was extensively used in German experimental work, probably because of the ease of machining and the possibility of inserting a side connection through the gasket wall. In these cases a gasket of some three inches in length and somewhat thicker than the vessel wall was employed. Although vessels with this type of closure are in use at the Bureau of Mines and are giving trouble-free service, the necessity for a great deal of care and the amount of work required for assembly makes them less satisfactory than other types of closures available.

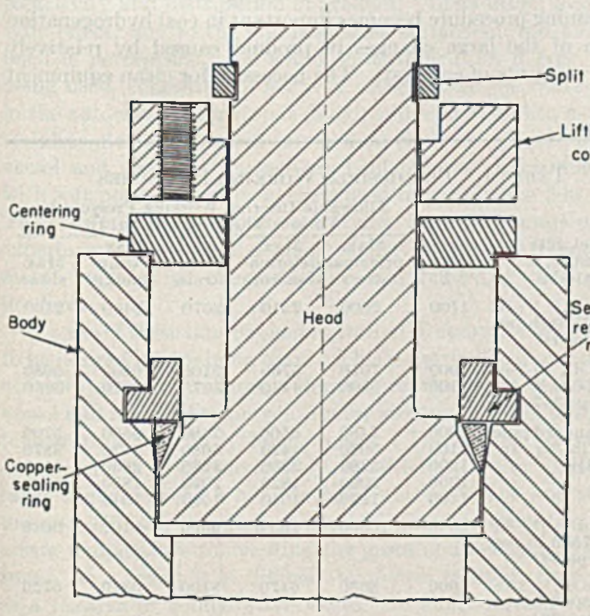

Figure 4. Assembly of Chamber Closure

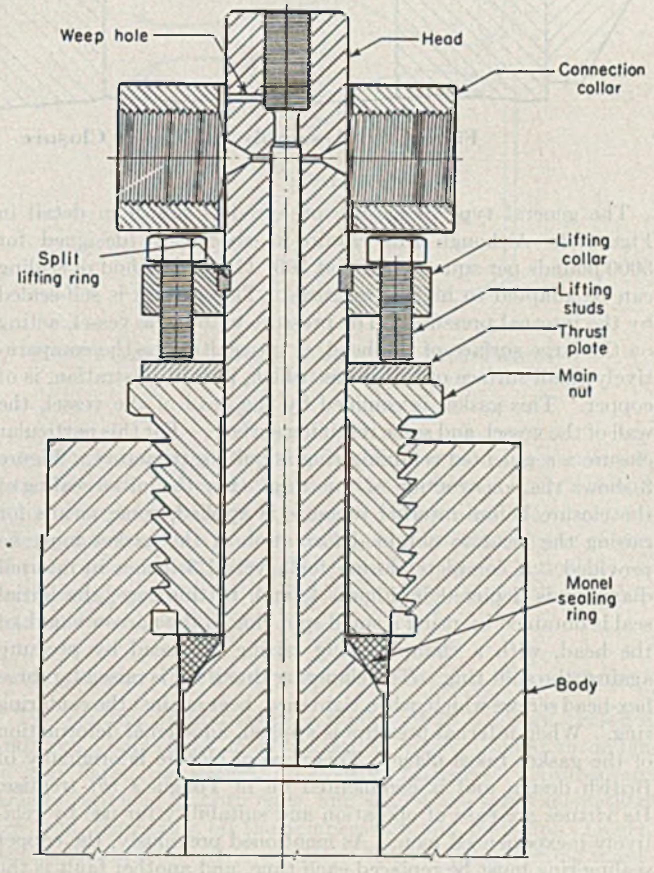

Figure 5. Autoclave Closure for 15,000 Pounds per Square Inch

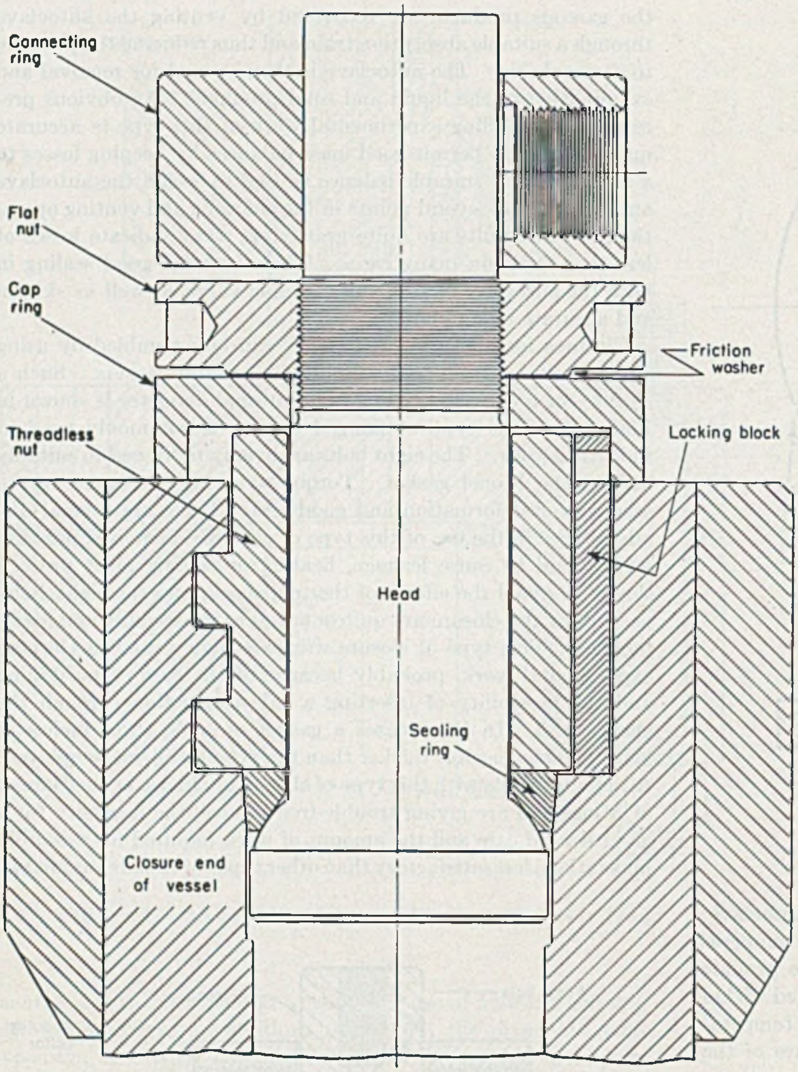

Figure 6. Assembly of Vessel Closure

The general type of closure preferred is shown in detail in Figure 2. Although this closure is specifically designed for 5000 pounds per square inch and 500° C., the method of sealing can be adapted to higher pressures. This closure is self-sealed by the internal pressure. The pressure within the vessel, acting on the large surface of the head, is transmitted to the comparatively small surface of the gasket which, in this illustration, is of copper. This gasket is confined by the head of the vessel, the wall of the vessel, and some retaining surface. For this particular closure a segmented retaining ring is quite satisfactory. Figure 3 shows the construction of this ring. For the initial sealing of the closure before internal pressure is applied, some means for raising the head to obtain deformation of the gasket must be provided. A complete closure for a vessel 3 inches in internal diameter is depicted in Figure 4, and, in this case, the initial seal is obtained by using a small split ring in the narrow shank of the head, with a clamping ring raising the head by pressure against the split ring. The clamping ring itself is raised by three hex-head screws which, when tightened, bear against the centering ring. When internal pressure is applied, additional deformation of the gasket takes place. This type of closure is originally of British design and is commented on in Tongue's (*5*) treatise. Its virtues are ease of operation and suitability for use by relatively inexperienced men. As mentioned previously, the copper sealing ring must be replaced each time, and another fault is the necessity for occasional overhauling due to deformation of the segmented retaining ring.

For increased pressures the segmented ring cannot be used for one of the retaining surfaces, particularly if a Monel gasket, which is preferable, is specified. Various types of threaded nuts have been used to supply the retaining surface to effect the seal. As can be foreseen, these threaded nuts tend to freeze when V-type threads are used. Buttress threads help considerably and, together with hardened materials (300–325 Brinell) for this main or retaining nut, solve the problem to a great extent. Figure 5 illustrates a closure designed for 15,000 pounds per square inch and 500° C., using a Buttress-type thread for the main nut and a Monel gasket. As in the previously discussed closure, a split ring and clamping ring are provided for the initial gasket deformation. These are raised by hex-head screws bearing on a thrust plate. The main precaution in using the threaded nut as a retaining surface is to protect the threads from any scratches or abrasions. The assembly is simple and calls for only a minimum amount of training and experience.

To eliminate entirely the use of threaded nuts, a so-called threadless closure is being employed by the Bureau of Mines for all converters, scrubbers, and traps to be used at higher pressures. This replaces the threaded nut by a nut held in place by a gun-breech type of mechanism shown in Figures 6 and 7. The nut is machined with three lugs fitting into three slots located in a projecting ridge in the vessel wall. Rotating the nut 60° effects the closure. A locking lug is inserted in one of the slots, and all that is needed is to compress the Monel gasket initially, which, in this case, is accomplished by a flat nut threaded on the head. A washer is provided between this flat nut and the threadless, main retaining nut to reduce friction. This closure is amazingly simple to use and offers few possibilities for error in its assembly.

During the research work with these autoclaves it was found that much time and effort are expended in removing the reactants from the autoclave and suitably cleaning the autoclave walls. The cleaning procedure becomes important in coal hydrogenation because of the large changes in product caused by relatively minute amounts of catalyst. The necessity for clean equipment

TABLE I. PERMISSIBLE WORKING PRESSURES

Vessel, Size, Pressure, & Material	Service Temp., ° F.	Allowable Internal Working Pressure by Various Theories, Lb./Sq. In.: Max. principal stress	Max. deformation work	Max. strain	Max. strain energy	Max. shear
6-in. o.d., $^1/_2$-in. wall, 2500 lb./sq. in., type 347	1100	2600	2510	2670	2400	2100
3-in. o.d., $^1/_2$-in. wall, 6000 lb./sq. in., type 347	1000	7070	5700	5100	6000	5080
	1100	5500	4430	3975	4670	3960
$^1/_2$-in. standard pipe, 1000 lb./sq. in., type 316	1000	7480	6500	7480	6500	5700
	1100	5080	4420	5080	4420	3870
	1200	3280	2860	3280	2860	2510
	1300	2090	1820	2090	1820	1600
	1400	1190	1040	1190	1040	912
6-in. o.d., 1$^1/_2$-in. wall, 7500 lb./sq. in., type 347	1000	10800	7550	9900	8100	6640
5-in. o.d., 1-in. wall, 5000 lb./sq. in., type 304	1000	8630	6470	8100	6840	5750

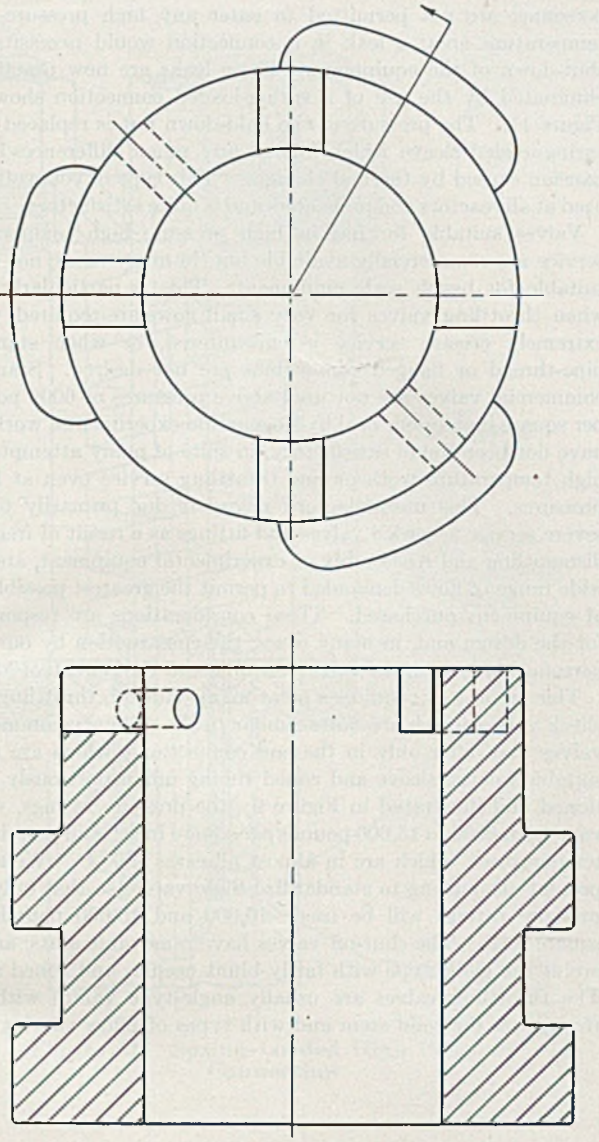

Figure 7. Threadless Nut

is increased further when various catalysts are being compared as to activity and distribution of product. In addition, some catalytic effect, due to the stainless steel surface of the autoclave itself is perceptible. To avoid these difficulties a liner is now being used, consisting of a Pyrex vessel which fits quite snugly in the autoclave. The top is flared, and a glass well to cover the stainless steel thermowell inserted as shown in Figure 8. The vessel and glass thermowell are held together by spring clips, with soft porous asbestos gaskets used to permit free flow of gas. The results have been quite gratifying, both as to more uniform experimental data and a great saving of time in cleaning the metal surfaces of the autoclave and removing the reaction products.

In spite of these improvements, the batch operation leaves much to be desired in obtaining data. This is particularly true of work at elevated temperatures. Because of the large mass of the vessel and the need to prevent undue stresses, heating to reaction temperature is a fairly long process. The reverse, or cooling-down time, is of approximately equal length. For example, it takes slightly over an hour to bring the autoclave and its contents to 450° C., the same amount of time is required to cool to a safe temperature for venting the gases and releasing the pressure. As a result it is difficult to define reaction time except as a relative or comparative value. In addition, the variation in hydrogen partial pressure during the course of the reaction in some instances makes interpretation of the results uncertain and limits definitely the size of the coal sample that may be used. The authors are thus limited to comparative data for the effects of most process variables. The use of the batch autoclave is, however, of great value in this investigation of reaction mechanism and catalyst activity.

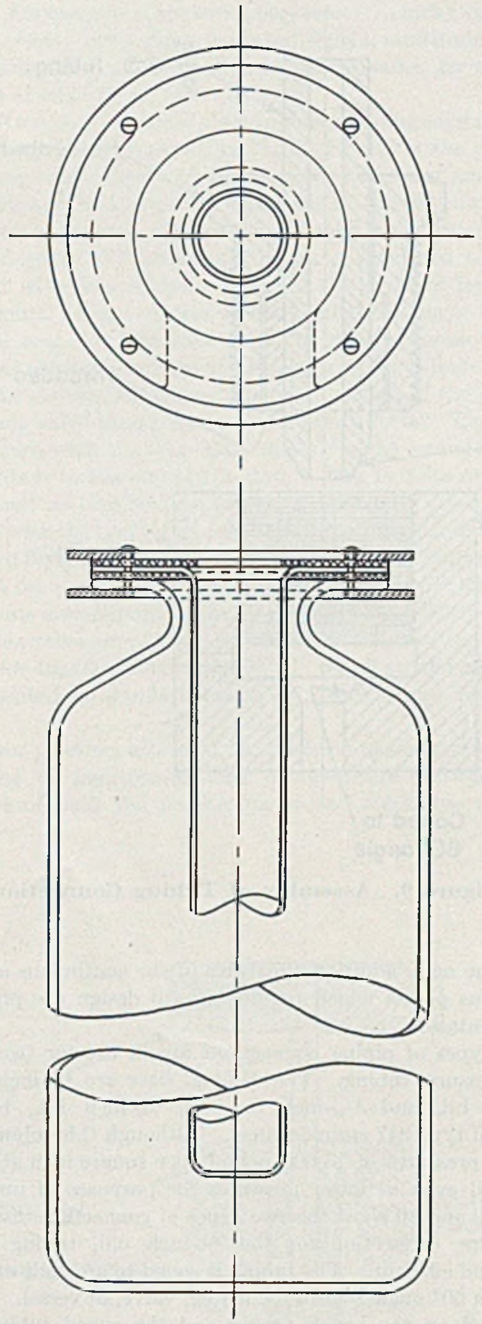

Figure 8. Glass Liner for 5000-Pound Autoclave

CONTINUOUS AND SEMICONTINUOUS BENCH SCALE UNITS

The continuous and semicontinuous units for high pressure and high temperature reactions utilize vessels similar in design to the batch autoclaves previously discussed. Closures are usually provided at both ends, and any of the types mentioned are used, depending on the temperature and pressure. Liners, usually of carbon steel, are quite successful in decreasing maintenance requirements. These liners are discarded after each

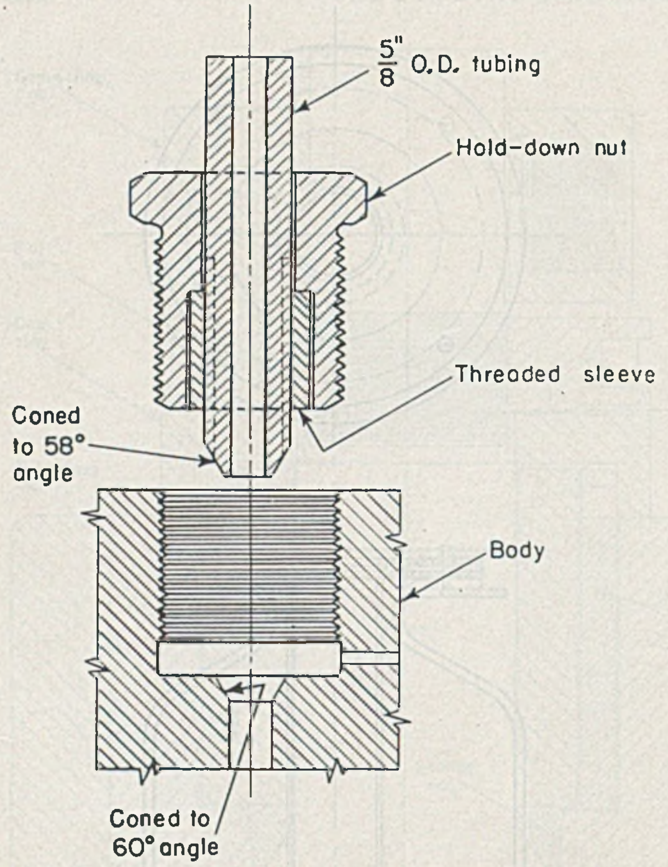

Figure 9. Assembly of Tubing Connections

run. The main additional features of the continuous and semicontinuous plants which require careful design are piping and instrumentation.

Two types of piping connections are in use for two sizes of high pressure tubing. The tubing sizes are $^5/_8$-inch o.d. by $^5/_{16}$-inch i.d. and $^5/_{16}$-inch o.d. by $^5/_{32}$-inch i.d., both fabricated of type 347 stainless steel. Although this tubing is suitable for pressures of 15,000 pounds per square inch at 500° C., it is used even at lower pressures for purposes of uniformity. Figures 9 and 10 show the two types of connections used. The sleeve-type connection for the $^5/_8$-inch o.d. tubing is quite simple and efficient. The tubing is coned to an angle of 58° and fits into a 60° angle seat in the fitting, valve, or vessel. A sleeve is screwed on the coned tubing and the coned tubing forced into the seat by using a hold-down nut 1$^5/_8$ inches in diameter. The make-up of this connection requires a certain amount of experience, and usually six to eight months of training are required before men are permitted to assemble high pressure piping without very careful supervision. Tees and crosses are made of stainless steel blocks suitably bored, threaded, and coned. The $^5/_{16}$-inch o.d. tubing is connected by the use of a steel cinch and a hold-down nut which forces the cinch to compress, grip the tubing and seal against a rounded seat. Figure 10 shows this type of connection for 7500 pounds per square inch. This type of connection has been adapted from the connection in use at the Fixed Nitrogen Laboratories for many years. For these pressures the cinch is screwed on the tubing and silver-soldered in place. The hold-down nut forces the angle of the cinch against a rounded seat in the fitting. For lower pressures (below 5000 pounds) the compression of the cinch is used to hold the tubing in place.

A great deal of trouble is experienced in keeping connections tight when subject to thermal shock. This applies particularly to the cone connection used for the $^5/_8$-inch o.d. tubing. Since personnel are not permitted to enter any high pressure–high temperature area, a leak in a connection would necessitate a shut-down of the equipment. These leaks are now practically eliminated by the use of a spring-loaded connection shown in Figure 11. The pressure of the hold-down nut is replaced by a spring-loaded sleeve which follows any minor differences in expansion caused by thermal changes. This type of connection is used at all reactors and preheaters and is quite satisfactory.

Valves suitable for use in high pressure–high temperature service are commercially available but, in many cases, not quite suitable for bench scale equipment. This is particularly true when throttling valves for very small flows are required, when extremely erosive service is encountered, or when standard pipe-thread or flanged connections are not desired. Standard commercial valves are not used above pressures of 6000 pounds per square inch in our coal hydrogenation experimental work and have not been found satisfactory, in spite of many attempts, for high temperature work or fine throttling service even at lower pressures. This unsatisfactory record is due primarily to the severe service accorded valves and fittings as a result of frequent dismantling and reassembly of experimental equipment, and the wide range of flows demanded to permit the greatest possible use of equipment purchased. These considerations are responsible for the design and, in many cases, the construction by our own personnel of most of the valves now in use at the Bureau of Mines.

This laboratory requires a great many shut-off, throttling, and check valves which are quite similar to the ordinary commercial valves and differ only in the end connections, which are made suitable for the sleeve and coned tubing union previously mentioned and illustrated in Figure 9; the pressure ratings, which vary from 5000 to 15,000 pounds per square inch; and permissible temperatures, which are in almost all cases 500° C. We are at present attempting to standardize these valves so that only two pressure ratings will be used—10,000 and 15,000 pounds per square inch. The shut-off valves have removable seats, and all are of the globe type with fairly blunt needles and coned seats. The throttling valves are usually angle-type valves with fine threads on the solid stem and with types of plugs varying with

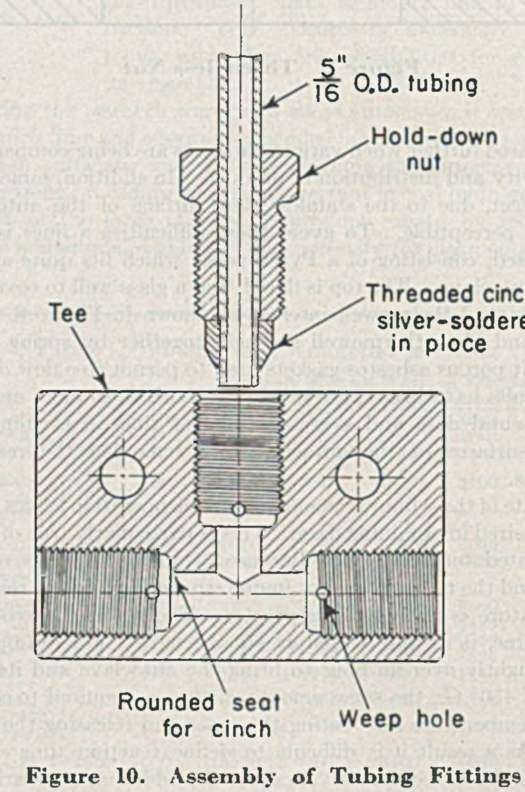

Figure 10. Assembly of Tubing Fittings

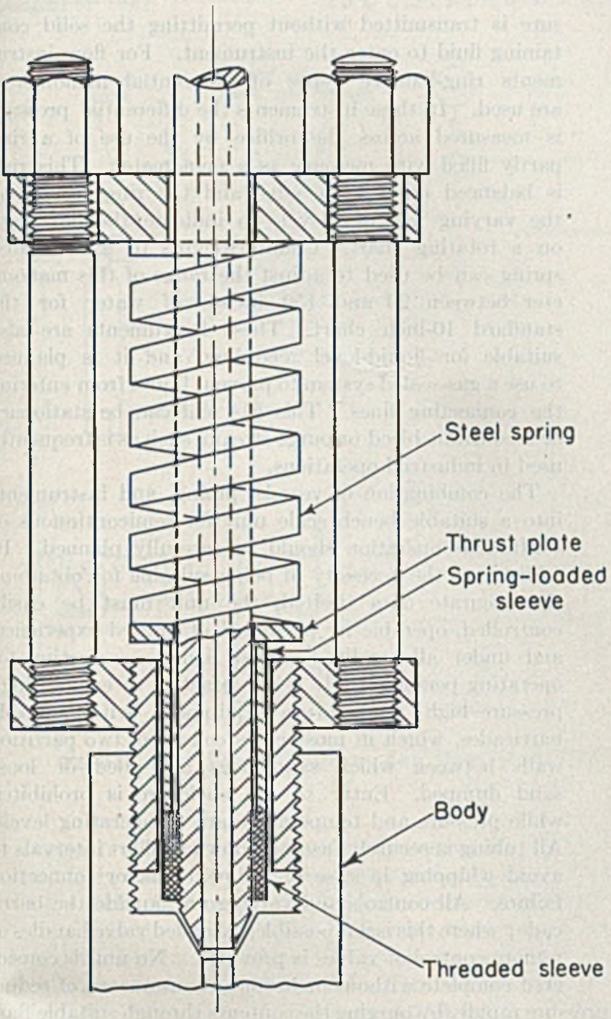

Figure 11. Spring-Loaded High Pressure Connection

the material handled—for a clear liquid, a straight plug ahead of the slow needle taper; for a gas, a smaller opening in the seat with the needle coned to suit. Ball-type check valves are used quite successfully and are of ordinary design. In addition to the high pressure valves mentioned, which are now standard usage in our coal hydrogenation work, two quite special valves are in use. The first type is a fine throttling valve suitable for high pressure service, and allowing high pressure drops across the valve and very close control of small flow rates. The second is specially designed for use with erosive fluids having high concentrations of solids.

The first of these two valves, the fine throttling valve, is shown in Figure 12 and is a small block valve provided with two holes for mounting. The problem of mounting valves, although not very severe for large industrial plants, becomes rather important in small bench scale units. A neat, well planned unit must be compact and accessible, and mounting of valves and instruments in high pressure work becomes somewhat difficult because of the massiveness of some of the equipment. This problem was specifically considered in the design of this valve. This valve may be fabricated from brass, cold-rolled steel, or alloy steel. The alloy-steel valve is suitable for 5000 pounds per square inch and will regulate gas flow to bubbles per second with several thousand pounds pressure drop. This is accomplished by the fine threads and long taper provided in the stem and coned seat. The packing gland, although small, is quite adequate, particularly where the flow enters at the bottom and proceeds upward through the seat. On account of the small-bore inlet ($^{1}/_{16}$ inch), this valve is suited for only fairly clean fluids but finds a multitude of uses in our bench scale equipment even at low pressures, for accurate regulation of small flow rates.

The valve preferred for use with fluids containing solid material of an erosive nature is shown in Figure 13 and is the result of many changes and much experimentation. The seat and needle are provided with inserts of Kennametal (tungsten titanium carbide) to withstand the erosion. Before this material was used, solid stems and seats and inserts of hardened tool steel were tried with little success; some of these valves lasted less than 24 hours. Some success with a hardened plunger fitting a cylindrical seat was obtained since, in spite of erosion, some seating was obtained because of the length of the cylinder, which could make contact with some uneroded portion of the plunger. The present valve shows almost no erosive effects. The needle does not turn with the stem but "floats" in the screwed sleeve, which holds it to the end of the stem. This is quite necessary, as the small seating surface caused a high unit stress which, combined with the turning of a nonfloating needle, caused tearing of the metal when the needle and seat met. The larger surface of contact between the stem and needle decreases the unit stress and prevents any damage to the needle and seat. The body and stem of this valve are of type 347 stainless steel, and the valve is designed for 10,000 pounds and 500° C., which are the conditions being accepted as standard for most of our future equipment design.

Wherever possible, attempts are made to use standard industrial types of instrumentation. Temperature recorders and controllers of both the potentiometer and electronic type are

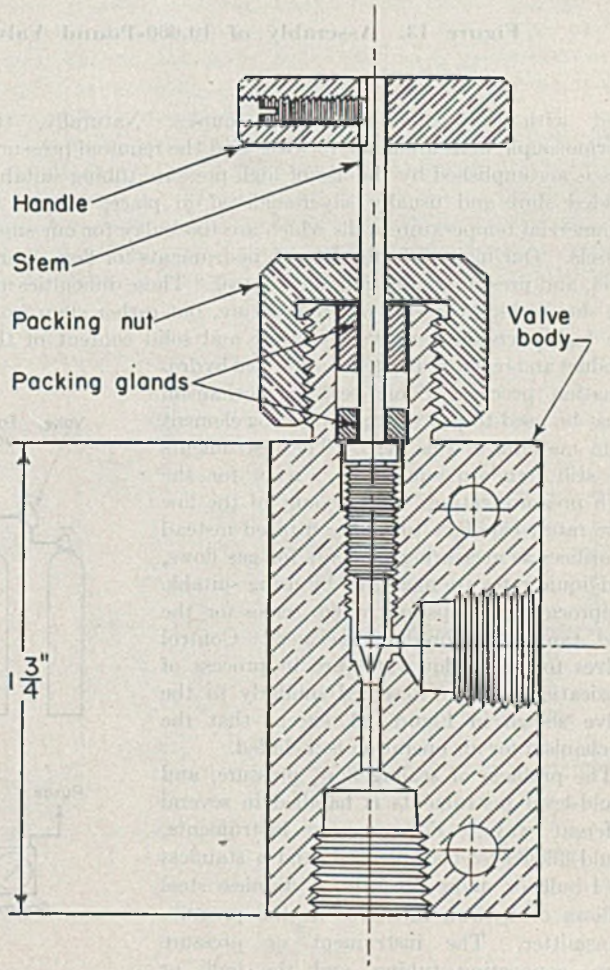

Figure 12. Cryogenic Type of Needle Valve

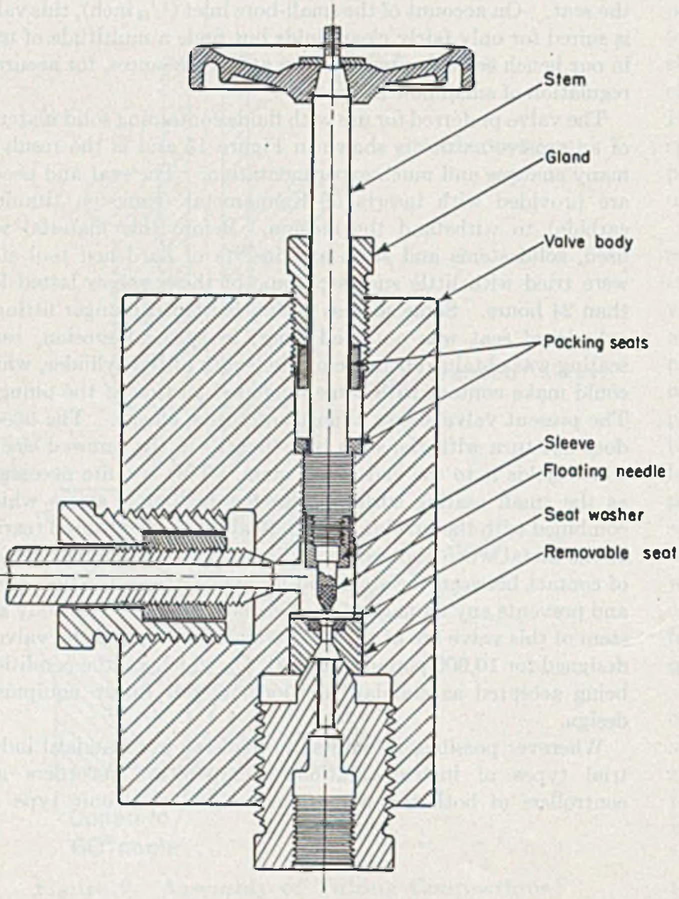

Figure 13. Assembly of 10,000-Pound Valve

used with chromel-alumel thermocouples. Naturally, the thermocouple wells are made to withstand the required pressure; this is accomplished by the use of high pressure tubing suitably welded shut and usually silver-soldered in place, instead of commercial temperature wells which are too bulky for our small vessels. Our main difficulty is with instruments for flow, liquid level, and pressure indication and control. These difficulties are not due to high pressure or temperature, but rather stem from the highly viscous, erosive character and solid content of the product and reactor "burden" in the coal hydrogenation process. Some sealing mechanism must be used to protect the indicating element from material of this type. The instruments are still standard equipment, except for the high pressure rating. On account of the low flow rates, capillary tubes are utilized instead of orifices as measuring elements for gas flows, and liquid rates are measured by using suitable reciprocating pumps and weigh scales for the feed tanks and product receivers. Control valves for small flow rates are in process of fabrication and are designed similarly to the valve shown in Figure 13, except that the mechanism for air operation is included.

The problem of sealing flow, pressure, and liquid-level instruments is handled in several different ways. For pressure instruments, liquid-filled systems are used, and a stainless steel bulb or, more recently, a stainless steel bellows or hydron functions as the pressure transmitter. The instrument or pressure gage, connecting tubing, and the bulb or hydron are filled with liquid, and the pressure is transmitted without permitting the solid containing fluid to enter the instrument. For flow instruments ring-balance types of differential manometers are used. In these instruments the differential pressure is measured across the orifice by the use of a ring partly filled with mercury as a manometer. This ring is balanced on a knife edge and the ring tipped by the varying mercury levels to indicate the flow rate on a rotating chart. Counterweights or a calibrated spring can be used to adjust the range of this manometer between 20 and 150 inches of water for the standard 10-inch chart. These instruments are also suitable for liquid-level recording, and it is planned to use a gas-sealed system to prevent liquid from entering the connecting lines. This gas seal can be stationary or a constant bleed or purge stream, such as is frequently used in industrial operations.

The combination of vessels, piping, and instruments into a suitable bench scale unit for semicontinuous or continuous operation should be carefully planned. In addition to the necessity of being suitable for obtaining the accurate data desired, the unit must be easily controlled, operable by personnel of limited experience, and under all conditions must include protection for operating personnel. It is our practice to enclose high pressure–high temperature equipment with suitable barricades, which in most cases consist of two partition walls between which sand bags are piled or loose sand dumped. Entry to the enclosure is prohibited while pressure and temperature are at operating levels. All tubing is securely fastened down at short intervals to avoid whipping in case of a line break or connection failure. All controls and valving are outside the barricade; where this is not possible, extended valve handles or remote control of valves is provided. No unit is considered complete without inclusion of some means of reducing pressure rapidly by purging the contents through suitable flare lines.

The flow diagram of a semicontinuous unit for coal hydrogenation is shown in Figure 14. In this unit a constant flow of hydrogen is maintained and metered by a ring-balance type of flowmeter which measures the differential pressure across a length of capillary tubing. The coal, mixed with vehicle and catalyst previously placed in a glass liner within the reaction vessel, is kept slightly agitated by the stream of high pressure

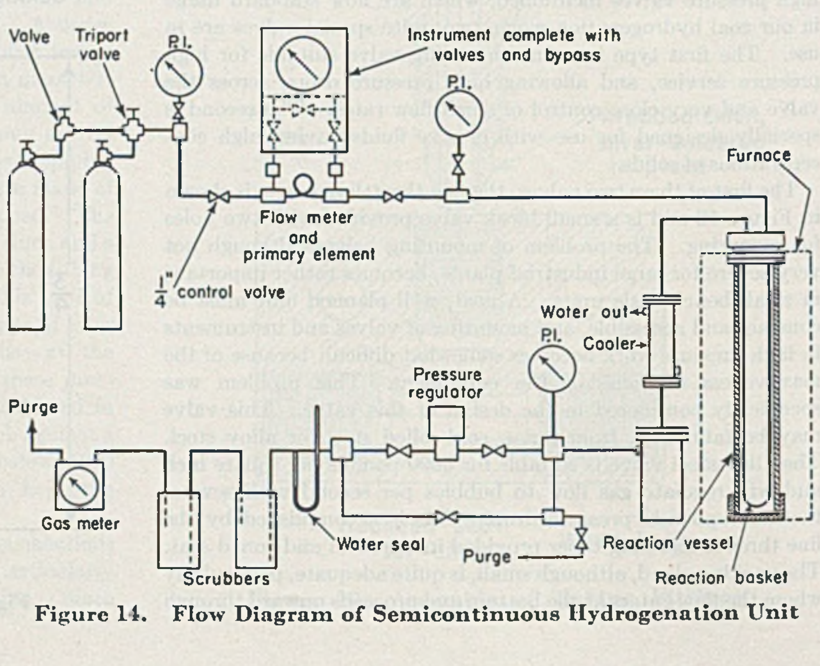

Figure 14. Flow Diagram of Semicontinuous Hydrogenation Unit

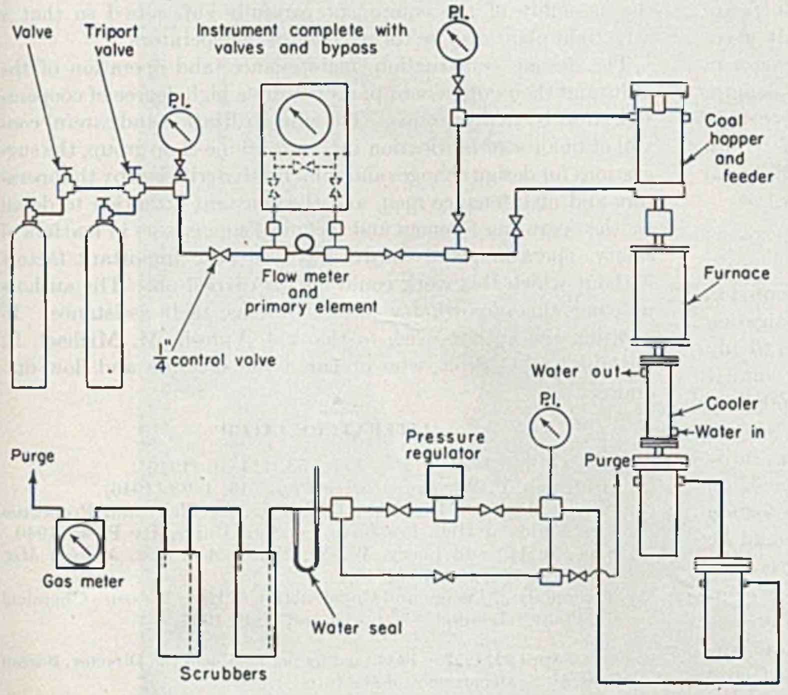

Figure 15. Flow Diagram for Powdered Reagent Feeder

hydrogen. The exit gases are cooled to remove any oil products and, after passing through a separator, are released by the back pressure valve to atmospheric pressure to be metered and sampled. Carbon dioxide and hydrogen sulfide are removed by suitable scrubbers before metering. The unit is protected by the purge valve in the high pressure line ahead of the back pressure regulator. A dip tube protects the wet-test meter and scrubbers against surges due to the possible improper functioning of the valve. Temperatures are controlled by internal and external thermocouples. For this plant the reactor or converter, cooler, and the gas separator are kept within the protective barricade. Suitable tubing through the barricade permits all valves to be located on the operator's side of the protective wall. Once hydrogen flow rates are manually set, only minor adjustments are needed to maintain operation.

While gas flow through this unit is continuously maintained, the coal and catalyst are handled batchwise, as is the case in autoclave experiments. The principal reasons for this type of unit are twofold—first, to maintain what is practically a constant partial pressure of hydrogen, which permits more accurate results and larger samples of coal to be used; second, the constant removal from the reaction zone of distillable oils and product gases present an excellent opportunity for reaction rate and mechanism investigations. While this is an improvement over total batch operation, some complications peculiar to the coal hydrogenation reaction are encountered. These complications are beyond the scope of this paper but unfortunately limit the value of this unit for obtaining process data that may be extrapolated. For data of this type the use of a completely continuous plant where both coal and hydrogen are fed at metered rates is necessary. Flow diagrams for two such units are shown in Figures 15 and 16. In both these units all reactants are continuously fed into the reaction zone and all products continuously removed. The heating and cooling periods necessary in the batch and semicontinuous units are eliminated. A finite time of contact which can be calculated from flow rates and reaction volume is thus maintained.

The unit shown in Figure 15 is designed for handling small quantities of powdered coal at temperatures up to 700° C. and pressures up to 3000 pounds.

A small powdered-coal hopper and feeder is mounted above the reaction tube; it is approximately $^1/_2$ inch in internal diameter and enclosed by a laboratory combustion furnace giving a heated length of approximately 12 inches. Hydrogen enters at top and bottom of the hopper feeder, and reaction products are collected in two receivers with exit gases scrubbed and metered after passing through a pressure-reducing valve. The hydrogen rate is metered by using a capillary tubing and differential flowmeter. The coal rate is controlled by varying the feeder speed. The coal particles are either permitted to fall through the reaction zone or retained there by inserting a small container fabricated of stainless steel. This permits investigation of very short contact times and the use of coal without any vehicle. The usual precautions are observed as to safety of personnel. The high pressure reaction tube and receivers are isolated by suitable barricades.

The unit illustrated by the flow diagram in Figure 16 is a small, simplified model of the pilot plant now in operation at the Bureau of Mines plant. The coal feed is mixed with a recycle oil from the plant, with usually 40 to 50% by weight of coal in the paste formed. This paste is injected by a high pressure, variable-stroke reciprocating pump through a preheater coil immersed in

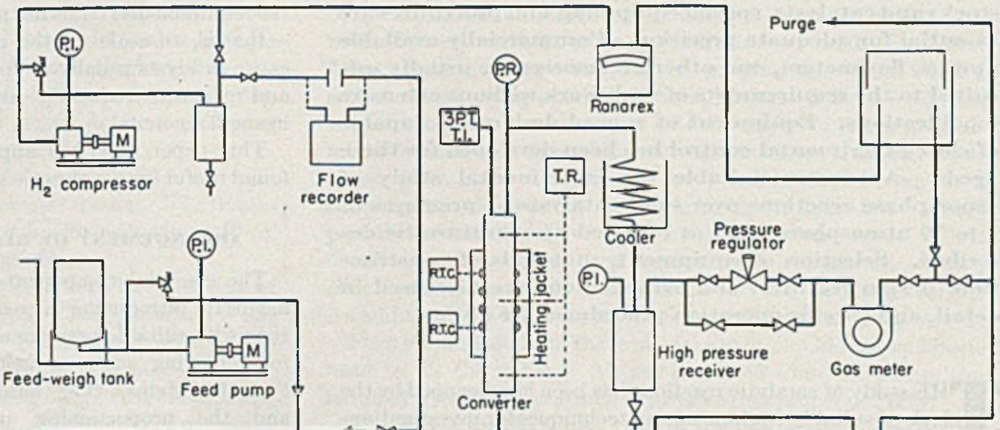

Figure 16. Flowsheet of Small Pilot Plant for Service at 6000 Pounds per Square Inch and 1100° F.

a lead bath and then into the reaction vessel. The products are cooled and collected in a receiver or catch pot, the exit gases being suitably scrubbed, sampled, and metered. The reactor in plant shown is 2 inches in internal diameter and 6 feet in length. The liquid products are discharged into a low pressure receiver. Part of the product is used to make up the feed paste. Both feed and products are suitably weighed or metered. The usual precautions for personnel safety are, of course, mandatory.

SUMMARY

The techniques of vessel, valve, and piping design presented in this paper, while designed specifically for use in the investigation of the high pressure hydrogenation of coal, are adaptable to any high pressure-high temperature investigation requiring similar process conditions. In particular, the precautions adopted for safety of personnel and the handling of corrosive and erosive liquids have been quite successful. It is a source of great satisfaction that bench scale and pilot plant researches at elevated pressures have been carried out by the Bureau of Mines for ten years without any injury to operating personnel that could be attributed to the type of investigation pursued. This record is even more impressive when it is realized that chemists or engineers are used in supervisory capacity only. Both maintenance and operation are, in most cases, handled by nontechnical personnel. Extreme care in maintenance is heavily stressed, and the assembly of the equipment carefully supervised so that a safe, tight plant may be turned over to the operators.

The design, construction, maintenance, and operation of the units and their component parts require a high degree of cooperative effort by many groups. The standardization and careful control of quality of fabrication by our machine-shop group, the suggestions for design changes and constructive criticism by the operators and maintenance men, and the constant attention to detail by the operating foremen and technical supervisors in matters of safety, operation, and control have all been important factors without which this work could not be carried on. The authors welcome this opportunity to acknowledge their assistance. In addition the authors wish to thank J. Vidosh, M. Michael, R. Parkins, and C. Siple, who prepared the sketches and flow diagrams.

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BENCH SCALE EQUIPMENT AND TECHNIQUES . . .

Evaluation of vapor phase reactions with solid catalysts

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TO STUDY catalytic reactions with small amounts of feedstocks and catalysts, special equipment and procedures are essential for adequate precision. Commercially available pumps, flowmeters, and other accessories are usually unsuited to the requirements of such work without extensive modifications. Equipment of rugged design and capable of close experimental control has been developed for these needs. Apparatus suitable for experimental study of vapor-phase reactions over solid catalysts at pressures of 1 to 50 atmospheres and at elevated temperatures is described. Selection of equipment, materials of construction, design features, and arrangement are discussed in detail, and specific operation procedures are given.

THE study of catalytic reactions has been handicapped by the lack of suitable equipment and techniques for investigations at elevated temperatures and pressures in flowing systems. Equipment must be small and as simple as compatable with the operations. It should be usable over a wide range of conditions and with a variety of materials. Controls should be simple, precise, and reliable. Laboratory batch apparatus has been in a fair state of development for some time, but it does not permit precise determination of reaction rates, primary and secondary products, and side reactions, or satisfactory control of reaction conditions. Some items of equipment may be miniature copies of industrial units, but usually they must be developed to suit the requirements. It is not possible to use the opposite approach—that is, to scale up the operations to fit the apparatus—because catalysts usually are prepared in laboratory-sized batches, and reactants frequently are special preparations or are purified in small amounts.

This paper describes apparatus, assemblies, and techniques found useful for bench scale studies of catalytic reactions.

ARRANGEMENT OF REACTOR SYSTEM COMPONENTS

The essential components of a catalytic reactor system are means for introducing the reactants at the proper rates, a reaction zone with suitable pressure and temperature controls, and means for removing and separating products. Figure 1 shows two typical systems. The burets on the white panel at the left and the proportioning pump beneath the near reactor furnace supply and meter liquid feed to both reactors. Gases are controlled by the valves at the upper center and metered by the rotameters just below them; they join the liquid feed at the left end of the reactor tube. Products pass through a condenser and a phase separator; liquids go to a receiver to be withdrawn periodically, and gases pass through a back pressure regulator (center) to a wet-test meter and a suitable sampling system. Temperature control and recording instruments are not shown. Vertically mounted furnaces may be used as well.

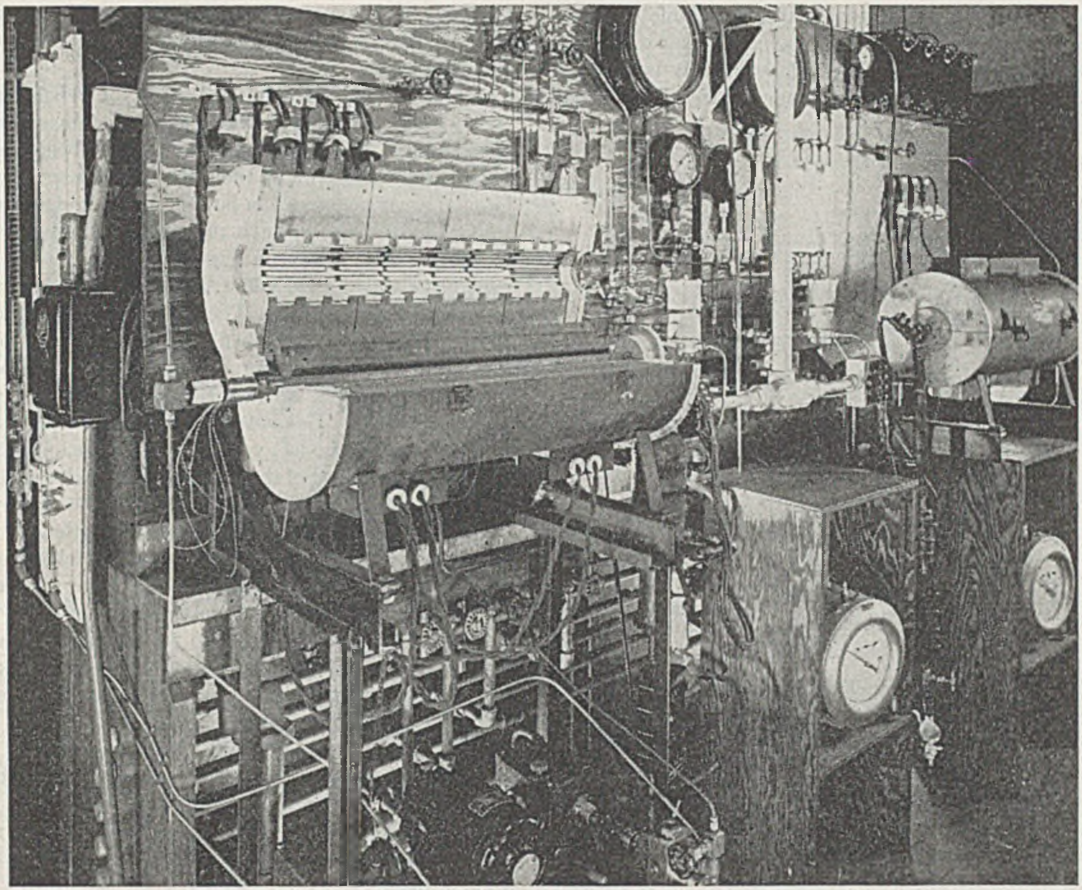

Figure 1. Horizontal Reactor Systems

FEEDING AND METERING DEVICES

Pumps. Liquid feed starts at the pump supply vessel. Figure 2 shows a supply and metering unit. The upper buret holds the main supply. The bulb holds a short time reserve and has an index mark below it. The metering pipet is connected to the feed vessel below a stopcock. At the start of a run the pump and lines are filled, the metering section is filled to the index line, and the supply buret is filled. The rate is measured by timing the emptying of the metering pipet with the stopcock closed. When a total is required, the level of the feed vessel is brought to the index line and the volume read from the buret. The connection to the pump is made through a glass-to-metal adapter. Rubber or other light tubing is not desirable because flexing produces significant errors in the rate measurement.

A number of small pumps now on the market have been tried; none of these are acceptable without some alteration. The Bosch-Diesel injection pump offers some promise for rates above 10 cc. per minute with kerosene or heavier materials.

Manzel Bros. and Hills-McCanna Company have models of small pumps that are nearly identical. This laboratory has used Hills-McCanna chemical proportioning pumps with extensive modifications of the design. The changes made were reduction of the plunger size, improvement of the stroke-adjusting mechanism for greater reproducibility, and provision of means for elimination of trapped gases. Attempts to reduce stroke frequency resulted in spurt feed and reactor instability. Figure 3 is a photograph of a modified triple unit. Such a pump will deliver hexane or heavier at 0.5 ± 0.05 cc. per minute, provided checks and adjustments are made at about 15-minute intervals. A gear-head motor (approximately 60 revolutions per minute) drives a crosshead through a $1^{1}/_{4}$-inch stroke on rigid vertical guides. The crosshead carries three fingers, one of which is visible where one of the bodies has been left off. Visible also is the means for guiding the plunger. The separate plunger, at one side, gives an over-all view of the stroke-adjusting parts. A small block has a slot milled through it for most of its length. The upper portion carries a knurled-head adjusting screw, and the lower portion is threaded to recieve the top of the plunger. The finger projecting from the crosshead fits in the space between the plunger and the adjusting screw. The projection at the side of the block is a full-stroke latch that permits operation at maximum delivery without changing adjustment, useful for quick filling of lines before a run and for purging air. Figure 4 is a sectional view of the pump body and plunger. A fine wire screen basket above the suction valve catches shreds of packing which might foul the valve; packing and suction valves are the greatest causes of trouble. The plunger is $^{1}/_{8}$ inch in diameter and is a running fit in the cylinder. Not visible in the figure is a $^{1}/_{16}$-inch port drilled into the top of the plunger space and closed with a needle valve, to permit free removal of entrapped air. An inclined passage connects the cylinder and the discharge valves. An additional air bleed is provided above the discharge valves.

Feed is admitted from the feed unit which should have sufficient head to lift the valves. All gas is vented from the pump, the motor started, and the stroke adjusted to get proper delivery.

The valves are SKF steel balls of the best grade. The seat is lapped to a knife edge and finally polished by alternate use of balls larger and smaller than that selected for the valve. One of the valve balls is then gently pressed onto the seat until the knife edge becomes a fine line, preferably in an arbor or bushing press. This ball is discarded, and another of the same size is installed for test. It is not possible to determine quality by inspection; consequently if the test is not satisfactory, the entire lapping operation is repeated. Optimum size of ball is in dispute; suction valves from $^{1}/_{4}$ to $^{9}/_{16}$ inch in diameter have been used. Seat diameters from $^{1}/_{2}$ to $^{3}/_{4}$ of the ball diameter will work. Discharge valves may be smaller and may be spring-loaded. Suction valves may be spring-loaded if feed is supplied under pressure.

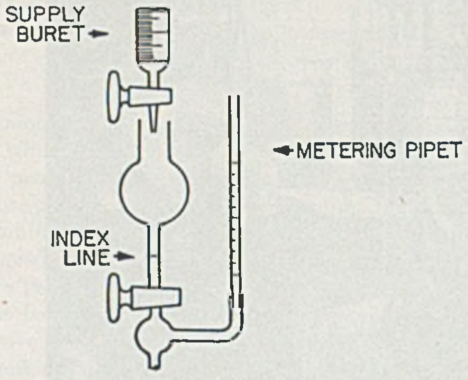

Figure 2. Feed Supply and Metering Unit

By use of heating or cooling jackets these pumps have been used to handle materials ranging from butane to wax; however, they are not advisable for liquefied gases, in view of the difficulty of detecting leaks.

A more satisfactory method for handling liquefied gases is to displace them from a closed vessel by pumping into it an immiscible liquid. Two such arrangements are shown in Figure 5; the simpler, at the left, employs a glycerol-water solution as the displacement liquid. Before starting operations the lines and feed tank must be filled to a point near the reactor. During such periods a surge tank provides expansion space. Immediately before the pump is started, the surge tank is isolated by closing the bottom valve. When glycerol water solution is not suitable, the scheme shown on the right may be used. Mercury is not pumped directly because steel ball valves float in it. On the other hand, kerosene behaves ideally in most pumps.

Molten waxes for the most part are rather mobile liquids and are easily pumped in heated pumping systems. Viscous liquids, including some asphalts, that do not permit free valve action have been pumped by using heated and pressured feed vessels and spring-loaded valves.

FLOWMETERS. Pumps have not been satisfactory for metering gases nor some liquids, so two types of inferential meters have been used.

The variable-area instruments, known commercially as rotameters, have been modified to be usable at laboratory rates and have been in service for several years. The changes have been in size only. Figure 6 shows one giving an idea of its size and general construction. The tapered tubes are made by collapsing heavy-walled glass tubes on tapered steel mandrels and annealing for stress relief. This method is used by several manufacturers of larger instruments. Floats are top-shaped miniatures ranging in weight from 2 to 80 mg. After testing to 100 atmospheres the design has been considered safe, but operating pressures have been held to 50 atmospheres. By proper choice of floats and tapers the range of 1.5 to 2800 cc. per minute of nitrogen at 1 atmosphere can be metered. It is always necessary to calibrate under conditions of use. If the desired rate can be obtained with more than one combination of float and taper, a solid float should be chosen, since hollow floats are easily damaged. When rotameters are used for liquids, the continuous flow results in smooth operation.

Liquids of low viscosity may be handled by supplying the feed at a pressure higher than reactor pressure. It is not practical to meter liquids more viscous than kerosene with instruments of this size except by dual displacement, as described for pumping liquefied gases.

Use of orifice and Venturi meters for bench scale reactors is nearly impossible because the minute resistance element is so easily obstructed. Capillary constrictions have been used successfully for several years. Using them the flow is nearly linear with head loss. Larger passages can be used in the resistance element, and routine cleaning after each run serves to prevent serious errors. The block unit shown in Figure 7 comprises, in one assembly, control valve, by-pass valve, capillary element, and connections to line and manometer. The hollow center of the block houses the capillary holder which fits in the center of the block. The cover nut is the closure. Hypodermic tubing permits a wide selection of ranges, and range change can be accomplished in about 1 minute. Gas enters through the upper left opening and is controlled by the left valve, passes to the lower left opening for the high pressure leg of the manometer and also to the upper end of the capillary, then through the capillary to the low pressure leg of the manometer (lower right) and the outlet line (upper right). The right valve by-passes the capillary chamber. There are only nine points where leakage might occur; a similar unit made from standard fittings would have about eighteen.

Manometers for pressures to 50 atmospheres are simple but cumbersome. Barton Instrument Company makes small dial-type differential pressure indicators employing the displacement of oil-filled metal bellows to drive the pointer. They are undamaged by overranging, even to the extent of applying full line pressure to one side only. Lubrication of bearing at the pointer drive every few weeks prevents leakage.

REACTORS. The reactor zone comprises furnace, catalyst and reaction chambers, and means for temperature indication and control.

The furnace should be large enough to permit several sizes of reaction chambers to be used. Figure 1 shows a furnace of 3-inch inside diameter by 24-inch heated length made by Hevi Duty Electric Company. The manufacturer has made minor modifications on a standard unit. Heat is supplied in two 5-inch, 700-watt end sections and two 7-inch, 1000-watt middle sections.

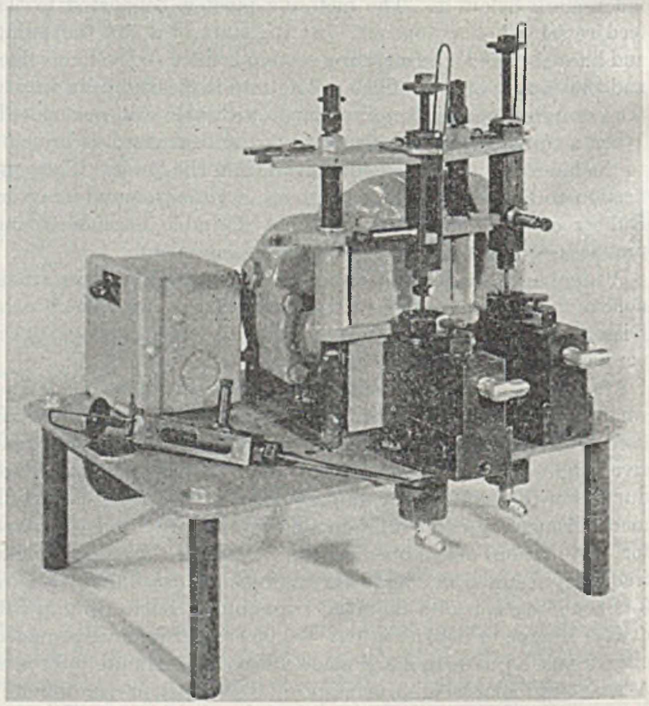

Figure 3. Small Proportioning Pump

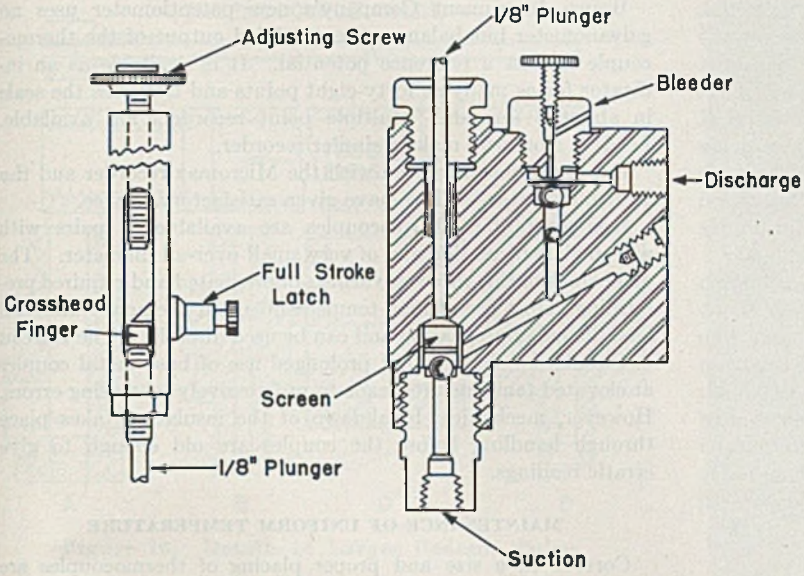

Figure 4. Sectional View of Pump Body and Plunger

Heat input is nearly uniform throughout the heated length, but independent control on each section permits compensation for different operating conditions. The furnace hinges allow for either horizontal or vertical mounting. The horizontal mount is somewhat easier on the operator, an important factor with women operators, and permits easier substitution of nonstandard tubes. Although comparative tests have indicated no differences due to reactor position, there is a possibility that catalysts may settle in a horizontal reactor and permit channeling. The vertical mounting is technically preferable unless head room is not available.

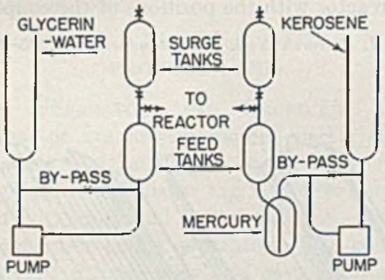

Figure 5. Dual Displacement Pumping Arrangement

To distribute heat uniformly it is necessary to use metal fillers or blocks. Where temperatures permitted, aluminum and copper were used in earlier work and are excellent but heat-resisting. Mechanite is now used because of its superior high temperature properties. The melting point of aluminum is too low; copper is excellent but short-lived as a result of serious scaling and warping. Certain copper alloys are somewhat better, but their thermal conductivities are low. Copper blocks treated by metal spraying or plating scaled less but warped badly. Mechanite is highly resistant to scaling, does not warp badly, and machines like gray cast iron. Figure 8 shows typical blocks. The bore is made $^{1}/_{32}$ to $^{1}/_{16}$ inch larger than the outside diameter of the tube. A thermocouple slot is milled as close to the circumference of the block as possible. Blocks for the 1-liter (2-inch pipe size) tubes were made by slitting lengths of $2^{1}/_{2}$-inch stainless pipe and allowing enough space for tack-welding a piece of $^{1}/_{4}$-inch stainless tubing to one of the sections for a thermocouple sheath. Temperature control is on-off, so the controller thermocouples must be close to the source of heat. In horizontal mounting the blocks rest on the end insulation of the furnace, and plugs of Transite are used to fill the ends of the furnace. In vertical furnaces steel brackets support the blocks through the hole shown in the end.

Reactor Tubes. The reaction space is a tube containing the catalyst, placed in the furnace and connected to supply and product lines. Figure 9 shows a tube design used for several years for 50 to 75 cc. of catalyst at 50 atmospheres. The tube itself is a length of $^{1}/_{2}$-inch pipe size stainless tubing, with ends machined from American Iron and Steel Institute type 304 steel bar stock, finished to an accurate crown at one end for the closure and left with a lip at the opposite end for alignment during welding. After welding, this lip is machined off, leaving a smooth bore to facilitate cleaning and inspection. The heads are machined from A.I.S.I. type 416 bar stock, finished for a crown seat on the inside. This seat is leak-free even at elevated temperatures and pressures, and is easily cleaned and refinished. The line connection is for a 60° cone seat. The thermocouple well is $^{1}/_{4}$-inch A.I.S.I. type 304 steel tubing welded into an adapter. The distance between end fittings and the style and size of connections are the same for tubes of other sizes.

For larger charges of catalyst, tubes have been made in sizes up to 1-liter capacity. The design shown at *A* and *B* in Figure 10 can be adapted to any size of tube by altering the size of the ends to suit. It has smaller end heat losses than that shown at *C* and *D*, but its ends are smaller than the bore and cleaning is difficult, and threads are in contact with the fluids in process. The design at *C* and *D* allows easy inspection and cleaning. Therefore the *A* head is used at one end and the *D* at the other.

Assembling and Charging Tubes. Before charging, all joints are cleaned and inspected. A thin film of graphite grease is applied to all contact surfaces, and the head carrying the thermocouple well is assembled to the tube, which is then supported open end up. Fillers or spacers of stainless steel are placed around the thermocouple well to center the well and place the catalyst in the middle portion of the furnace. A funnel is screwed to the open end of the tube, and the thermocouple well is held concentric with the tube. As the catalyst is added the tube is jarred with a

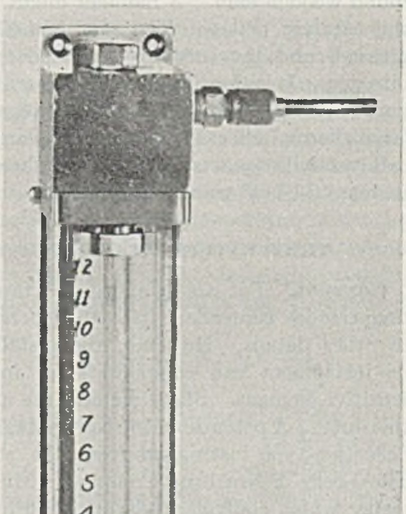

Figure 6. Miniature Rotameter

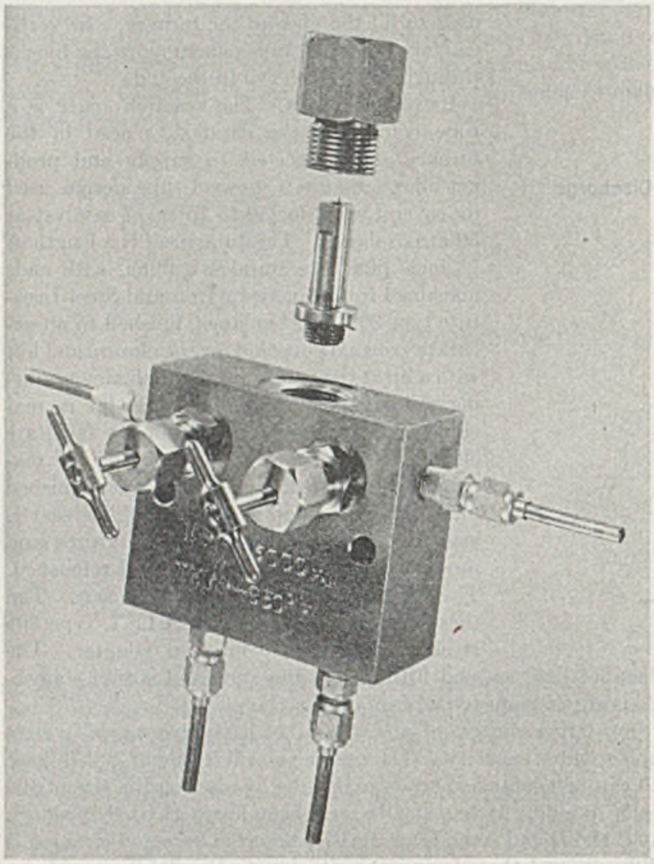

Figure 7. Flowmeter Block Assembly

round wooden club. A hammer might nick the tube and crack the catalyst pellets. The seat and threads are cleaned and greased, and the tube is assembled and pressure-tested with nitrogen. It is then installed in the furnace and the entire system purged and pressure-tested with nitrogen. For reactions having large thermal effects it is sometimes an advantage to dilute the catalyst with quartz chips to lengthen the reaction zone and increase the heat transfer area.

TEMPERATURE MEASUREMENT AND CONTROL

CONTROL. For an extended program the use of automatic temperature controllers frees the operator for closer attention to other details. However, the installation must be correct; no instrument can compensate for improper location of the sensitive element. Space dictates the use of a thermocouple for this duty. A potentiometric control instrument is preferred to a deflection-type instrument from the standpoint of reliability. The Leeds & Northrup Company's Micromax single point controller which controls loads up to 20 amperes directly and the C. J. Tagliabue Manufacturing Company's Celectray multiple point potentiometer controller are made for use over the entire useful range of the well-known couples. The latter will handle as many as six points, each with independent control, but requires the use of heavier external relays for loads of over 2 amperes. Both instruments have given satisfactory service.

MEASUREMENT. Although portable manual potentiometers are excellent for probing, automatic recording instruments provide a permanent record of the temperature of selected points in the reaction zone and simplify control by making temperature trends more evident. The Micromax strip chart recorder for this job can be had to record as many as sixteen points, with chart speed suited to the printing frequency. Newer models will traverse the entire chart and balance in a few seconds.

Brown Instrument Company's new potentiometer uses no galvanometer but balances the amplified output of the thermocouple against a reference potential. It is available as an indicator for as many as forty-eight points and traverses the scale in about 3 seconds. Multiple point recorders are available. Leeds & Northrup make a similar recorder.

Our experience has been with the Micromax recorder and the Brown indicator. These have given satisfactory service.

Iron-constantan thermocouples are available in pairs with woven glass insulation and of very small over-all diameter. The older stock of this wire was varnish-impregnated and required preburning before use at high temperatures, but the newer material has silicone impregnation and can be used directly. The Bureau of Standards[1] showed that prolonged use of base metal couples at elevated temperatures leads to progressively increasing errors. However, mechanical breakdown of the insulation takes place through handling before the couples are old enough to give erratic readings.

MAINTENANCE OF UNIFORM TEMPERATURE

Correct tube size and proper placing of thermocouples are necessary for satisfactory results. Tube size must be chosen to allow placing the catalyst in the middle 14 inches of the furnace as the ends may not be at correct temperature, and one end must serve to preheat feed. Short runs with different process variables for consecutive runs demand simple instruments that are easily adjusted, such as on-off controllers. The controller couples must be in thin-walled slots close to the heating elements. The controller must be set a few degrees higher than the temperature desired in the tube. The block will eliminate the variations in the temperature of the reaction zone. The controller thermocouples should be placed $^1/_2$ to 1 inch closer to the middle of the furnace than the midpoints of the sections they control, and the recorder couples slightly downstream from the corresponding controller couples. Figure 11 is a schematic diagram of a reactor with the positions of the couples indicated.

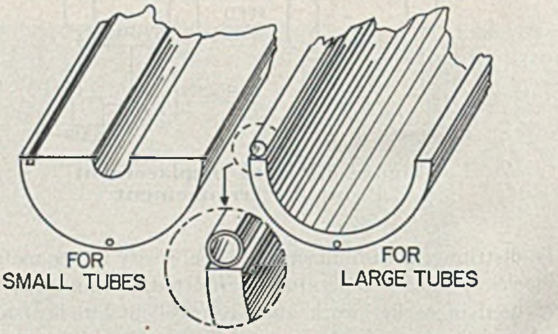

Figure 8. Heat Distributing Blocks

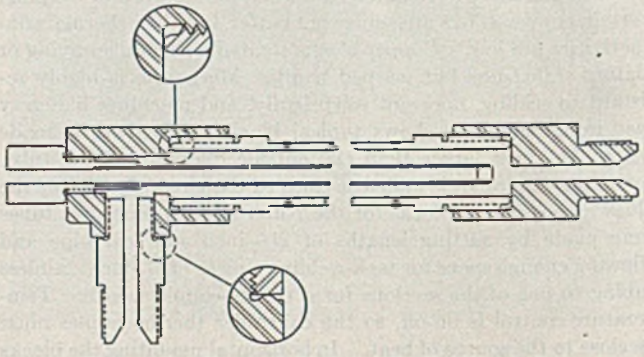

Figure 9. Reactor Tube of 50-Cc. Capacity

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[1] Dahl, A. I., *J. Research Natl. Bur. Standards*, 24, 205–24 (1940); R.P. 1278.

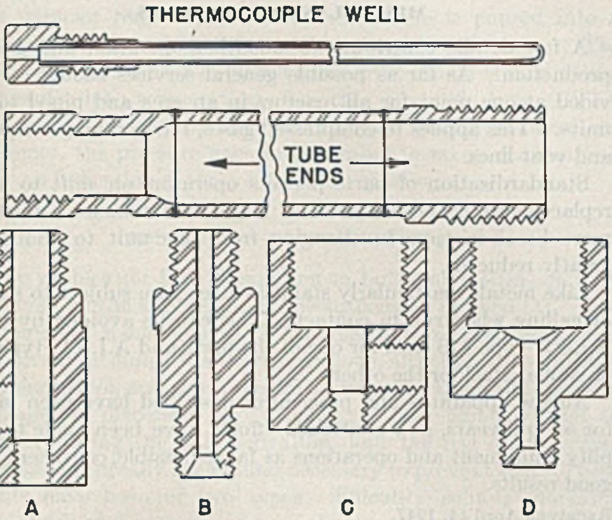

Figure 10. Details of Larger Reactor Tubes

The arrow shows the direction of flow. The dotted curve shows a temperature profile of the outer surface of the block and approximately that of the tube before feed has started. During operation the block temperature remains about the same, but the tube center assumes a new profile about that of the solid curve. Temperature of a 14-inch midsection of the tube should be uniform to within ±1° C. Often this can be bettered. For closer profile or for moderately exothermic reactions, recourse may be had to a jacketed tube heated by rapidly circulating a high boiling liquid, or by boiling a liquid at controlled pressure. For high preheat requirements an extra external preheater is advisable to avoid local high temperatures and general disturbance of the reaction zone.

PRODUCT ZONE

Condenser, Separator, and Receiver. The products leaving the reactor are mostly vapors, partly condensable at room temperature and possibly carrying some material solid at room temperature. Usually tap water is cold enough for condensers; if not, additional cooling may be supplied. Figure 12 shows a condenser and a separator. The condenser is designed for straight through flow and easy cleaning, and has a rugged joint for frequent removal. The condenser over-all is nearly 5 inches longer than the jacket to allow inspection of welded joints. It may be necessary to add heat in the condenser to prevent separation of solids, in which case it will be necessary to attach a cooled condenser to the gas outlet of the separator to return condensables that might otherwise be carried over.

The phase separator (and receiver) is a chamber allowing sufficient space for separation of gases and liquids, and having outlets for both. All openings should be as large as permissible with the type of fittings used, to allow free drainage. During removal of liquid product a slight tendency to froth will indicate that only a few drops remain, and, with care, a complete removal can be effected with no disturbance of the system, so that a sight glass is not needed. A large separator permits the liquid to be held to the end of the run, when the pressure is released and the liquid run directly to a stabilizer.

Pressure Recording and Control. The readability of a 10-inch recording pressure gage is not as good as that of a 3-inch pressure gage of the same range. Moreover an installed recording gage is difficult to exchange for another of more suitable range. Since indicating gages of several ranges may be kept at hand and changed at will, they have been accepted as standard.

Manual pressure control is difficult, chiefly because a change in any other of the operating variables almost immediately affects the pressure. From one of their small regulators the Grove Regulator Company evolved their model 155 relief pilot. It is small and light enough to be supported on the connecting piping. It is sensitive within its range, but for tight shutoff a manual valve should be installed in series. Range of control can be changed from 5 to 1500 pounds per square inch by changing a few parts. It will resume control at the same pressure after shutdown.

The newer Grove model 90 gives tight shutoff at close to the controlled pressure. It is even smaller than model 155. Being dome loading, it must be pressured to the desired value. The only moving part is the diaphragm, which floats between the reference pressure and the controlled pressure and itself seats on the outlet port. The Hycar diaphragms supplied are short-lived with some hydrocarbons, but substitutes made of Teflon show no signs of failing after nearly a year. On checking with a gage of fair quality, no difference between dome pressure and controlled pressure has been evident except at very low pressures.

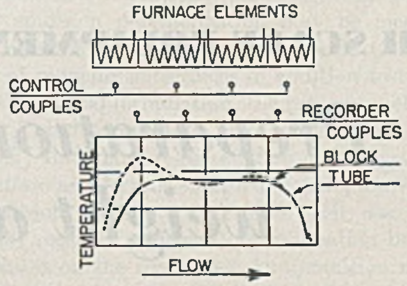

Figure 11. Reactor Temperature Profile

Metering Product Gases. It is advisable to install some form of positive low pressure relief in the line on the atmospheric side of the regulator for the protection of operators and apparatus. Following this should be absorbers for removal of any gases that might be harmful to the meters. A cold trap is at times advisable. The standard wet-test meter is usable for most work. For accurate work a saturator can be placed at the inlet side of the wet meter to ensure saturation and prevent loss of water from the meter. Wet meters are normally calibrated for a full revolution of the drum. The intermediate readings are only approximate; if they are important additional points should be calibrated.

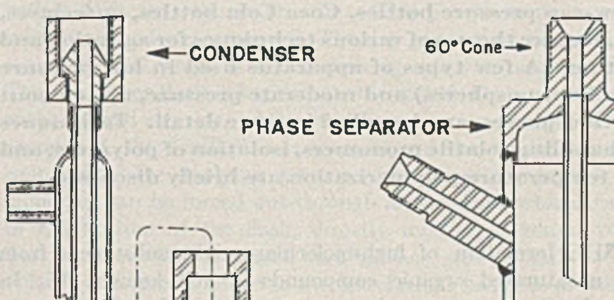

Figure 12. Condenser and Phase Separator

Calibrated gasometers may be used to measure product gases, but their best use appears to be to store product gases after metering and prior to sampling.

Sampling Product Gases. Samples of product gases may be taken as stream samples or as portions of the entire gas. Spot samples taken in evacuated 250-cc. bulbs can be collected in the minimum time. Continuous samples are representative only if the rate of collection is a constant fraction of the rate of production. Often the difference is not important. An evacuated bottle fitted with a gage, drying tube, and needle valve may be utilized to collect a dry sample, the rate of pressure rise giving an estimate of the rate of collection.

Stirred gasometers are useful for collection of good representative samples, especially if it is desired to blend in the gas produced during stabilization of the liquid sample. The stirrer is carried near the top of the gasometer bell on a shaft passing through the top of the bell. Experience in preparing samples of mixed gases showed that some form of agitation is needed if a representative sample is required in a reasonable time.

MISCELLANEOUS FACTORS

A few details contribute to smoother operation and greater production. As far as possible general services should be provided at one point for all reactors in an area and piped to the units. This applies to compressed gases, refrigerants, and power and vent lines.

Standardization of parts permits operators on shift to make replacements as needed and do minor maintenance. Furthermore break-in time in changing from one unit to another is greatly reduced.

Like metals, particularly stainless steels, are subject to siezing or galling when run in contact. This can be avoided by using A.I.S.I. type 416 steel for one of the parts and A.I.S.I. type 304 or similar steel for the other.

All the apparatus and procedures described have been in use for several years, and continued efforts have been made to simplify equipment and operations as far as possible, consistent with good results.

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BENCH SCALE EQUIPMENT AND TECHNIQUES . . .

Preparation of high-molecular-weight addition polymers

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HIGH-molecular-weight polymers may be prepared in various ways, such as bulk, solution, suspension, or emulsion. The equipment depends somewhat on the mode of preparation but is essentially a function of the physical properties of the monomers. Temperature control of polymerization reactions is especially important inasmuch as the average molecular weights, and therefore the physical properties, vary considerably with temperature. Because of the exothermic nature of the reaction, good heat transfer is required, which necessitates adequate agitation. The large number of volatile monomers existing in the gaseous state at the desired polymerization temperatures indicate the need for specialized equipment. Sealed tubes, screw-cap pressure bottles, Coca Cola bottles, autoclaves, etc., require the use of various techniques for agitation and heating. A few types of apparatus used in low pressure (5 to 10 atmospheres) and moderate pressure, up to about 30 atmospheres, are described in some detail. Techniques for handling volatile monomers, isolation of polymers, and low temperature polymerization are briefly discussed.

THE formation of high-molecular-weight substances from unsaturated organic compounds is well known (*6*). In general, these compounds are represented by the formula $RCR_1{=}CH_2$, and the reaction may conveniently be termed vinyl polymerization. The following discussion reviews the techniques that have been devised for carrying out such reactions in the laboratory.

Polymerization may be carried out in any of a number of ways such as bulk, solution, suspension, or emulsion. The laboratory equipment necessary is somewhat dependent upon the mode of preparation, but for the most part it is a function of the physical properties of the monomers. It is necessary to control the temperature of polymerization reactions fairly closely inasmuch as the average molecular weights, and consequently the physical properties, vary considerably with the temperature of the reaction. Furthermore, the polymerization involves a chain reaction which is exothermic in nature, with the evolution of about 20,000 calories per mole. Thus, it is necessary to exercise precautions to maintain the desired temperature during the reaction and adequate agitation is necessary to secure efficient heat transfer.

BULK POLYMERIZATION

Bulk or block polymerization is a term used to describe the polymerization of vinyl compounds, with or without catalyst, which is performed in the absence of solvents or other dispersing media. The dissipation of the heat evolved in the reaction is a major problem in bulk or block polymerization. As the reaction proceeds, the fluid monomer becomes more and more viscous. The heat transfer becomes poorer and poorer as the viscosity increases, and agitation becomes less and less effective. A temperature rise of 30° C. or more may be noted in bulk polymerizations even where precautions have been taken for heat dissipation. Such reactions are carried out in the laboratory by utilizing a high ratio of surface to volume. It is advisable to work with a monomer layer which is no more than one inch thick. Small quantities may be conveniently polymerized in test tubes about one inch in diameter. For the bulk polymerization of larger quantities (600 to 900 grams) the use of a pressure cooker has been found satisfactory for systems having a maximum pressure of 2 atmospheres. A pressure cooker utilizing a metal-to-metal seal has been used. The usual rubber gaskets will not withstand the action of hot monomeric substances, and a substitute gasketing material (silicone) should be secured for such types To facilitate polymer removal, the monomer charge is poured into a shallow baking pan that fits within the pressure cooker. The sealed pressure cooker is placed in an oven which is held at the polymerization temperature for the required time. When polymerization is desired at or near the boiling point of the monomer, the pressure gage incorporated in many cookers provides an indication of the course of the reaction.

SUSPENSION POLYMERIZATION

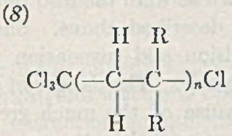
The problem of heat dissipation in bulk polymerization may be solved by the application of the suspension method (*4*). The monomer or monomers to be polymerized are suspended in a nonsolvent medium—water in most cases, although salt solutions, ethylene glycol, and glycerol have been used. Upon agitation the monomer is dispersed into droplets. These globules tend to coalesce during the polymerization, and the use of dispersing agents has generally been found necessary to prevent this. These agents have been of two types: difficultly soluble inorganic compounds such as magnesium carbonate, tricalcium phosphate, talc, and bentonite, or organic substances such as gelatin or polyvinyl alcohol.

The basic unit of laboratory equipment here, as well as in solution and emulsion polymerization for high boiling monomers, is the three-neck round-bottom flask equipped with thermometer, condenser, and stirrer. A typical formulation for suspension polymerization is: 300 grams water, 30 grams monomer, 0.3 gram suspending agent, and 0.3 gram catalyst (organic). A satisfactory procedure is to add the suspending agent to the water, and commence stirring and heating. When the polymerization temperature (usually between 60° and 90° C.) is attained, the solution of catalyst (e.g., benzoyl peroxide) in monomer is added. The polymer is isolated in the form of globules or pearls which vary in average size, depending upon the conditions of the reaction.

The maximum ratio of monomer to suspending medium depends upon the particular monomer, varying from 1:1 to 1:10 in accordance with the degree of heat dissipation found necessary. For example, styrene permits the use of high monomer ratios (1:2), whereas ethyl acrylate agglomerates unless lower ratios (1:10) are used. The amount of suspending agent required to avoid agglomeration depends upon such factors as the monomer-water ratio, the monomer, the suspending agent, etc.; in general 1% on the monomer is sufficient for efficient agents such as magnesium carbonate, tricalcium phosphate, etc. The problem here is to prevent coagulation of the pearls during polymerization, and one of the variables involved is the rate of stirring. To secure comparable stirring conditions, a variable-speed motor was connected to a drive shaft from which as many as six stirrers could be operated by beveled-gear transmission. By attaching a tachometer to the drive shaft, the actual stirring rate may be determined.

SOLUTION POLYMERIZATION

The solution method is the simplest means of preparing polymers in the laboratory. Good heat transfer is obtained by diluting the monomer with solvent. Usually, a homogeneous system is secured whose viscosity increase is relatively small when the monomer concentration is about 20%. In some cases the solvent takes part in the polymerization and acts as a chain transfer agent; in that case a solvent molecule such as carbon tetrachloride may be chemically incorporated into a polymer molecule to form (*8*)



$$Cl_3C(-\overset{H}{\underset{H}{C}}-\overset{R}{\underset{R}{C}}-)_nCl$$

Ionic catalyzed polymerizations involving the use of acidic catalysts, such as boron fluoride, titanium tetrachloride, etc., are among the fastest reactions known to the organic chemist. The reaction is characterized by a very low energy of activation, and once the reaction begins, it tends to proceed with explosive violence. Because of this high rate of reaction, the problem of dissipating the heat of polymerization becomes much more acute, so that these reactions are almost always carried out in solution. Furthermore, it has been found necessary in some cases to add the catalyst by spraying dilute catalyst solutions into the reaction chamber. These reactions are often carried out at low temperatures, from −50° to −130° C. Hersberger, Reid, and Heiligmann (*3*) recently presented a schematic diagram of an ionic catalyzed apparatus with a thorough description of the technique.

EMULSION POLYMERIZATION

The commercial production of huge quantities of emulsion-polymerized synthetic rubber during the past few years was preceded and accompanied by a large volume of laboratory work. Much of it has already been published (*2*, *4*, *9*, *10*, *11*), and the equipment and technique have been adequately described. The use of reduction-activation systems which further accelerate the rate of emulsion polymerization may be mentioned as a recent development by Evans and co-workers (*1*). By the incorporation of reducing substances in addition to the persulfate catalyst of the typical formulation, the rate of reaction increases many fold. This is applicable to other methods of polymerization as well; but many reduction-activation systems, such as sulfite-persulfate and ferrous sulfate-peroxide, are water soluble, and the emulsion procedure facilitates their use. Hohenstein and Mark (*4*) recently reviewed polymerization literature with special emphasis on the suspension and emulsion methods, and discussed the mechanism of such polymerizations.

POLYMERIZATION EQUIPMENT

Since many of the common monomers, such as butadiene, vinyl chloride, isoprene, etc., are in the gaseous state at the desired polymerization temperature, it becomes necessary to work under pressures above atmospheric. Some monomers, such as ethylene, tetrafluoroethylene, etc., require high pressure apparatus which is outside the scope of this discussion. The use of sealed tubes, screw-cap bottles, Coca Cola bottles, autoclaves, etc., necessitates the use of specialized equipment for agitation and heating.

The technique used in the handling of volatile monomers has already been described by Fryling (*2*), and there is little further that need be added. The method in use at these laboratories is to pass the gaseous monomer from the cylinder through acetone-extracted rubber tubing through two wash bottles containing 5% sodium hydroxide and then through two wash bottles filled with a desiccant such as Drierite. This process removes acidic substances and water vapor. The dry gas is then liquefied in a condenser coil which is sealed directly into the receiving flask. The condenser flask is kept in a wide-mouth Dewar bottle filled with crushed dry ice. After the necessary quantity has been condensed, the distillation is stopped and the condenser is disconnected. By applying pressure from a nitrogen tank, the monomer can be forced out through a glass tube which reaches to the bottom of the flask, directly into the reaction vessel. The reaction vessel is placed on a balance, and a small excess of volatile monomer is added to the vessel which has been previously filled with all the other less volatile ingredients. The excess is allowed to boil off, and the vessel is immediately cooled in a dry ice–solvent mixture. The reaction vessel is then capped or sealed with a hand torch.

The use of test tubes with necks which may be readily sealed has the advantage that, when properly sealed, there is no leakage. However, Coca Cola bottles which have been capped with a hand-capping machine are very convenient. The use of heavy-wall screw-cap bottles has also been found satisfactory (*7*).

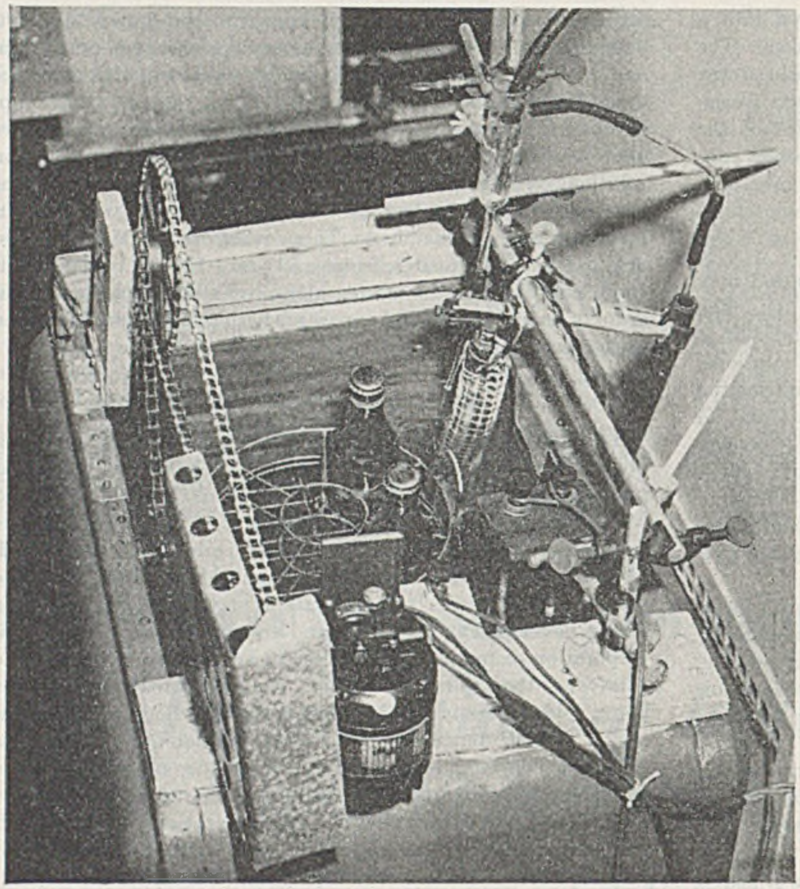


Figure 1. Polymerization Apparatus

However, their convenience is offset by the possibility of leakage. Most of these applications have been to butadiene copolymer systems which were polymerized at low temperatures and correspondingly low pressures. The capped bottles often leak, but where the heat dissipation is poor, the pressure may rise rapidly and serious explosions have been reported (7).

The polymerizations are conveniently carried out in a constant temperature cabinet or liquid bath. The latter (Figure 1) provides better heat transfer and makes it possible to detect leaks readily. The vessels are either rotated end over end or agitated in a forward and backward oscillatory manner. The apparatus may be conveniently constructed from a Coca Cola dispensing unit, serving as an insulated liquid bath equipped with an overflow which may be adapted to a constant level device. An axle to which an open framework has been soldered is supported by two bearing plates fixed to the sides of the tank. For end-over-end rotation, a small brass sprocket wheel is incorporated at one end of the axle and is connected through a cadmium-plated chain to a compound sprocket mounted above. This is chain-driven by a sprocket mounted on the shaft which protrudes from a gear box incorporated on the end of the motor. A $^1/_{50}$-horsepower motor with a 6:1 reduction gear box has been found satisfactory. The shaft rotates at 287.5 revolutions per minute, and it is customary to rotate the samples between 20 and 60 r.p.m.; thus the proper selection of sprockets provides the desired rate of rotation. The oscillating type of agitation may be secured by utilizing the equipment in a somewhat different manner. The large sprocket, mounted above the axle at about the same height as the motor, is linked to one end of the framework by a connecting rod. The amplitude of the crank arm motion depends on the off-center distance at which the connecting rod is pinned. This distance may be varied until the desired agitation is secured.

The reaction vessels may be inserted into wire screen containers which are wired to the framework. Polymerizations in such thermostated baths are quite convenient, but when it is necessary to go to higher temperatures and pressures, the following type of apparatus has been found useful. The wooden container compartment of an Equipoise type shaker is replaced by a $^1/_4$-inch Transite board to which are bolted four heating tubes. These are iron pipes, about 9 inches long and 3 inches in diameter, which are wrapped in asbestos and wound with 30 ohms of Nichrome wire. About 7 feet of 28-gage Nichrome provides the necessary resistance, and on a 120-volt line this provides a maximum power of 480 watts. After the Nichrome wire is embedded in asbestos cement, the heating tube is wrapped in asbestos paper and strapped down to the Transite board. A variable rheostat of about the same resistance as the Nichrome wire is connected in series as is a 6-ampere fuse; a pilot light is connected in parallel to serve as an input indicator. Four such heating chambers may be mounted on the board, and all four are connected in parallel through a 10-ampere variable transformer. (The rheostats mentioned may well be replaced by variable transformers.) The heating tubes are permanently sealed at one end, and the other end is stoppered with a cork through which a thermometer is inserted to indicate temperature. The transformer makes it possible to vary the range of temperature that can be secured. When it is necessary to raise or lower the temperature in all heating tubes to the same extent, it is convenient to alter the transformer setting. The temperature may be changed in a single tube or all four may be operated at different temperatures by varying the individual rheostats. It should be kept in mind that the described apparatus was designed for a maximum current of 10 amperes, and when it is necessary to utilize the full wattage, no more than two tubes should be used at one time. A temperature of 180° C. can be readily attained, which is about as high as one would generally go in polymerization reactions.

The temperature is set where desired while the machine is agitating; after temperature equilibrium is attained, the reaction vessels are inserted. As many as three reaction vessels, wrapped in glass wool, may be inserted in one heating tube when necessary, but it should be kept in mind that, if one explodes the others will undoubtedly be destroyed. The temperature control on such an apparatus is about ±5° C. Heat dissipation is relatively poor, and for reactions that are completed in a few hours, temperature control is difficult. The agitation is reciprocating in nature and is quite vigorous. This apparatus has been used for bulk, suspension, and emulsion methods of polymerization.

The preparation of larger quantities may be carried out in autoclaves. Liter stainless steel autoclaves that will withstand 1000 pounds per square inch can be secured. Pressure gages and thermometer wells should be incorporated in the cover which is bolted down. The use of Garlock gasket 681 has been found satisfactory in preventing leakage. The autoclaves may be heated and strapped down as were the iron pipes, and the entire assembly is agitated as described above. Such equipment has been used for the emulsion and suspension polymerization of 200-gram batches of polymer. The danger of explosions in such autoclaves is small because of the much greater likelihood of leakage at the gasket; nevertheless the use of safety blowout valves is desirable. For pressures higher than 30 atmospheres the use of commercially designed equipment is recommended.

POLYMER ISOLATION

Once the polymer has been prepared by any of the various techniques, it is necessary to isolate it in a form which is convenient for handling, analysis, and characterization. Both volatile and nonvolatile impurities are generally removed by dissolving the polymer in a solvent, preferably a poor one, and precipitating the dilute polymer solution in a large excess of nonsolvent with vigorous agitation. For such materials as polystyrene, the polymer is obtained in a form which is readily filtered and dried to constant weight. Rubberlike polymers, on the other hand, are difficult to isolate, and the use of the frozen benzene technique of Lewis and Mayo (*5*) has proved quite satisfactory. The original method has been modified in one respect. Instead of evacuating individual Erlenmeyer flasks, a vacuum desiccator containing several vessels of convenient shape is utilized. After the polymer is dissolved and precipitated two to three times, the thoroughly drained polymer is dissolved in benzene to make an approximately 10% solution. This is rapidly frozen at dry ice temperature in any convenient vessel. The use of Erlenmeyer flasks is advantageous in exposing a large surface for a given volume, but weighing bottles, vials, evaporating dishes, etc., may be used. These vessels are then transferred to a large vacuum desiccator which can hold as many as a dozen samples. The desiccator is connected to a vacuum pump capable of maintaining 2 mm. of mercury through two traps cooled with dry ice contained in thermos flasks. A 500-cc. suction flask may be used for the first trap. The sublimed benzene is led in through the side arm, and the vapors are congealed on the lower wall of the flask. A wide exit tube leading down to about 3 cm. from the bottom conducts the remaining vapors to a second trap. A manometer, incorporated between the desiccator and the first trap, indicates the vacuum and gives warning if the line is plugged at any point. The continuous sublimation of the benzene is necessary to absorb sufficient heat and keep the samples frozen, even when immersed in an ice bath. If the vacuum is broken, the benzene will melt, and the entire procedure must be repeated by adding more benzene to redissolve the polymer.

The sublimation is usually complete in 10 to 12 hours, but it is convenient after the first 8 hours to allow the process to continue overnight. It is then held at room temperature for a few hours and then at 50–60° C. until constant weight is attained. Rubberlike polymers tend to retain the original volume of the solution while cold. However, upon warming they contract, become rubbery, and are difficult to remove; the use of evaporating dishes simplifies their removal.

ACKNOWLEDGMENT

The author wishes to express his gratitude to the members of the High Polymer Institute who designed and constructed much of the apparatus described.

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BENCH SCALE EQUIPMENT AND TECHNIQUES . . .

Liquid-liquid and vapor-liquid extraction

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DETAILED descriptions of batch and continuous extraction equipment for studying liquid-liquid and vapor-liquid extraction processes are given. Operating techniques found helpful and typical data are also described. Included are a gage glass apparatus for visual observation of phase equilibria at high pressures, batch equipment for studying vapor-liquid extraction, countercurrent stage and tower equipment for liquid-liquid extraction, and continuous countercurrent tower equipment for vapor-liquid extraction.

THE purpose of this paper is to present information regarding the construction and successful operation of various types of laboratory scale extraction equipment as they have been developed by the Esso Laboratories of Standard Oil Development Company over the past decade. Although the applications of most of this apparatus have lain in the petroleum or allied chemical fields, it is believed that a discussion of the salient features of this equipment and operating techniques will prove valuable to a wide audience both within the petroleum industry and in nonrelated activities where extraction processes are being studied. Typical data are presented only for purposes of illustrating the usage of the equipment and are not intended to convey any conclusions regarding the reported experiments.

PHASE EQUILIBRIA AT HIGH PRESSURE

Treatment of crude petroleum residua with a liquefied normally gaseous hydrocarbon (the process known as deasphalting) results in a separation of the residuum into two phases, one mainly asphaltic, the other asphalt-free. It is also practicable to separate asphalt-free, high-molecular-weight petroleum stocks into fractions varying in molecular weight by this technique.

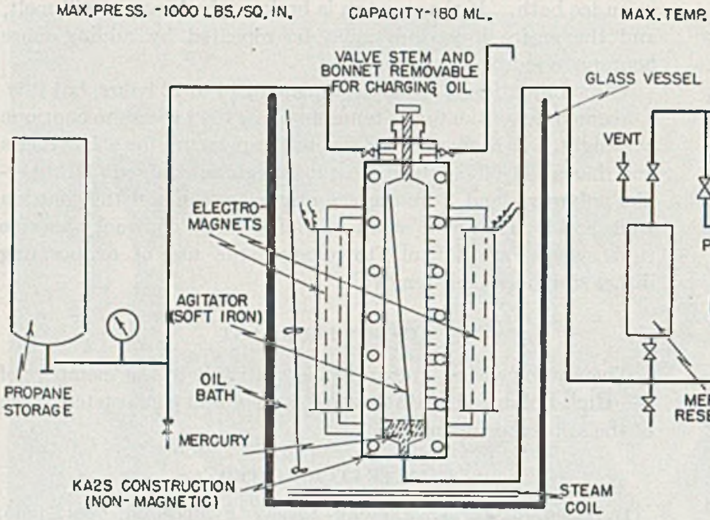

Figure 1. Gage Glass Equipment for Studying Phase Equilibria at High Pressure

Visual observation of this process, although relatively difficult because of the high pressures employed, has been made possible with a specially designed gage glass and suitable auxiliary equipment. With this equipment it has proved possible to study quantitatively the effect of solvent: oil ratio, temperature, and pressure on the phase equilibria within the system. This equipment has also proved valuable in phase equilibria study of nonpetroleum systems requiring high pressures.

EQUIPMENT. The equipment, a schematic drawing of which is shown in Figure 1, comprises essentially a specially constructed, Jerguson type of through-vision gage glass, 12 inches long, $2^3/_4$ inches deep, and $^3/_4$ inch wide, connected through a mercury reservoir to an inert gas pressure source by means of which pressure up to 1000 pounds per square inch gage can be applied to the system within the gage glass. The metal part of the gage glass is constructed of nonmagnetic stainless steel to permit the use of a perforated soft iron strip as a stirring device. This stirrer is actuated by a pair of electromagnets mounted on the exterior sides of the gage glass body and controlled manually through a mercury relay. The valve seat at the top is an integral part of the gage glass body and is situated only a slight distance above the top of the liquid chamber. The stem and bonnet of the valve are removable to allow the charging of oil to the gage glass through a pipet. The liquid volume capacity of the gage glass is 180 ml. and is measured by means of a brass scale attached to the edge of the gage glass body. Liquefied solvent (usually propane) is forced into the gage glass through a port in the main valve body from a storage reservoir. Pressure is obtained on the solvent by heating the reservoir with a steam coil. The complete gage glass and electromagnet assembly are suspended in an open glass battery jar which contains a pancake-type steam coil on the bottom. A low viscosity transparent white oil is used as the heat transfer medium, and uniform heating is obtained by gentle agitation of the bath with an air-driven stirrer. A strong light source behind the gage glass permits easy observation of phase changes. Blowout disks on the mercury and inert gas reservoirs protect against unsafe pressure rises. Temperatures are measured by three iron-constantan thermocouples peened into the gage glass body.

EXPERIMENTAL PROCEDURE. Typical operating procedure for the examination of the phase equilibria existing in a propane heavy-lubricating oil system is as follows: The valve stem and bonnet are removed, and the mercury level at the bottom of the gage glass is adjusted to the desired level by varying inert gas pressure on the mercury reservoir. The valve from the gage glass to the mercury reservoir is then closed. The desired volume of oil is charged to the chamber by means of a pipet. The valve stem and bonnet are replaced, and the valve stem is closed. Liquid propane is then admitted to the valve body and the valve stem slowly opened; this allows a measured volume of propane to be added gradually to the system. Because of the frequently experienced high temperature of the gage glass and oil, it has been found helpful at times to vent to the atmosphere the first propane delivered in order to chill the gage glass equipment to a temperature low enough to condense propane at the charging pressure. When the desired volume of propane is added, the main valve stem is closed; thus the system is isolated. The system pressure existing in the gage glass is then balanced against inert gas pressure applied to the mercury reservoir by carefully opening the valve from the gage glass to the reservoir and at the same time admitting sufficient gas pressure to hold the mercury level at the desired point. The system pressure is observed on a large pressure gage capable of indicating pressure differences of 5 pounds over the entire pressure range up to 1000 pounds per square inch gage. The system is then fully charged and ready for study.

The mercury meniscus at the liquid-mercury interface generally remains easily visible. However, with asphalt-containing residua the high viscosity asphaltic phase which is precipitated induces the breakup of the mercury into droplets, and this creates a false meniscus. The addition of a small amount of an asphalt solvent such as benzene eliminates this difficulty.

The types of observations possible on a given system at various temperatures and pressures are the volumes of the liquid and vapor phases, and the temperature and pressure values corresponding to a change in the number or volume of the phases. The usual procedure has been to examine the system at various pressures for a given temperature, since pressure can be adjusted almost instantly. Points representing a change in the number of phases can be more accurately fixed by approaching from the direction which causes the appearance, rather than disappearance of the phases. When varying the pressure at a constant temperature, this technique is used by starting at the maximum pressure and progressively lowering the pressure. Because of the small volume of the gage glass no phase samples are obtained. It is felt that the primary purpose of the gage glass equipment is to

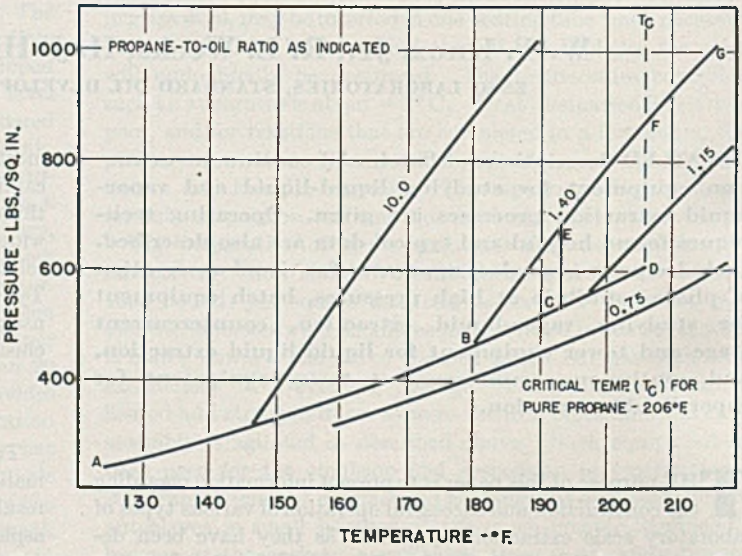

Figure 2. Pressure-Temperature Phase Boundary Diagrams for Asphalt-Free Lube Stocks and Propane

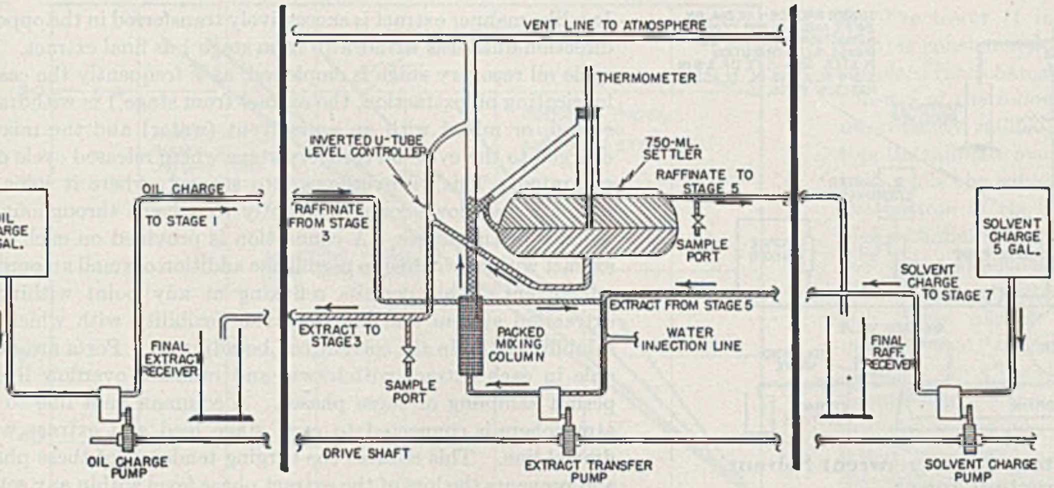

Figure 3. Countercurrent Extraction Unit Showing Details of Intermediate Stage 4

permit visual observation of the process, and samples may be obtained under the same P-V-T conditions from larger, all-metal equipment.

Typical Data. Results obtained for a typical phase study on a system comprising propane and an asphalt-free petroleum bright stock are shown in Figure 2. The nature of this diagram can be described by consideration of the phase relations existing for a system consisting of 100 parts oil and 140 parts propane. The curve *ABCD* is the bubble point curve for this system, which is practically identical with the bubble point curve for pure propane except at low propane to oil ratios. Point *B* represents the initial appearance of a precipitated phase as the system temperature is raised along the bubble point curve. With a further rise in temperature along this curve, precipitation is increased. Approaching point *D* (critical temperature for pure propane is 206° F.), precipitation becomes virtually complete, and the uppermost liquid phase is essentially oil-free propane. Section *AB* of the bubble point curve, therefore, represents equilibrium between one liquid phase and propane vapor. Section *BCD* of this curve represents equilibrium between two liquid phases and propane vapor. At temperatures above point *D* the uppermost liquid phase and the propane vapor phase become identical in the form of a noncondensable propane phase; thus the bubble point curve is terminated at point *D*.

If at any point *C* on the bubble point curve (above the initial precipitation temperature) the system pressure is increased, one of the two liquid phases (usually the lower phase) is caused to decrease in volume until, at point *E*, the system becomes homogeneous. The curve *BEF*, therefore, represents a boundary between one and two liquid phases, with two liquid phases existing throughout the area *DCBEF*.

Curve *FG* (extension of *BEF* above the critical temperature of propane) also represents a boundary between one and two phases, although in this case the two-phase area (below *FG*) comprised one liquid phase (oil plus dissolved propane) and the noncondensable propane phase. The curve *FG*, therefore, represents the minimum pressure necessary to dissolve in the oil phase all noncondensable propane present in the system.

The line *FD* (at propane critical temperature) indicates a nonobservable composition change as regards the uppermost phase, the area to the left of *FD* representing an uppermost noncondensable phase. Since this phenomenon does not involve the loss or gain of a phase, *FD* is shown as a broken line. The line *FD* does, however, complete the bounding of area *DCBEF* in which propane precipitation of heavy lube fractions can be obtained with this type of oil charge stock and with a propane-to-oil ratio of 1.40.

The reproducibility of data with the gage glass equipment is illustrated by the following table. Observations of operator *A* were those used to plot the 10.0 propane-to-oil ratio curve shown in Figure 2. Observations were also made by operator *B* for a similar propane-oil system. Individual results are shown to check the average within ±2% for bubble point determinations and to check within ±5% for boundary point determinations.

System temp., ° F.	157		172		180		190	
Operator	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Obsvd. pressures, lb./sq. in. gage								
Bubble point	360	360	425	420	465	475	525	545
Boundary point	480	475	750	695	875	860	1020	950

LIQUID-LIQUID EXTRACTION

The refining of lubricating oils by selective solvent extraction has become one of the most widely used processes for the production of premium quality lubricating oils. A number of selective solvents for lubricating oil refining are in commercial use today, among them being phenol, Chlorex (2-2′-dichlorethylether), furfural, nitrobenzene, and sulfur dioxide–benzene.

It has been found helpful to employ both a countercurrent extraction tower and a countercurrent stage extraction unit for establishing the effect of fundamental solvent extraction variables. The tower unit has also proved extremely useful in preparing moderate quantities of refined lubes for engine tests, and in piloting the design and operation of refinery solvent extraction units. The function of this equipment has not, however, been limited to the solvent refining of lubricating oil stocks, since the units have been flexibly designed, and the predominantly glass construction permits observation of the extraction process.

The countercurrent tower unit has to a large extent displaced the countercurrent stage extraction unit in refinery practice. In the laboratory the tower equipment has proved extremely valuable in preparing extracted materials with a minimum expendi-

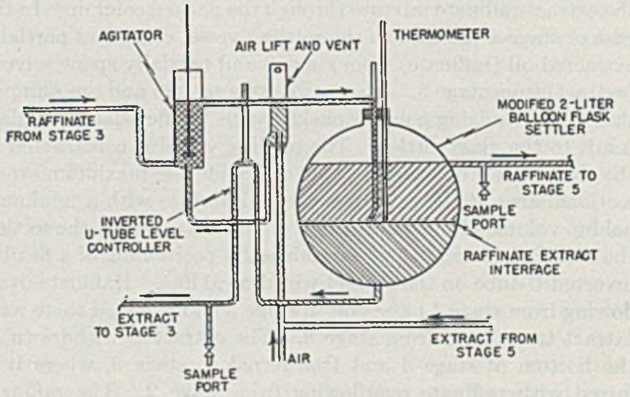

Figure 4. Air Lift Countercurrent Extraction Unit Showing Details of Intermediate Stage 4

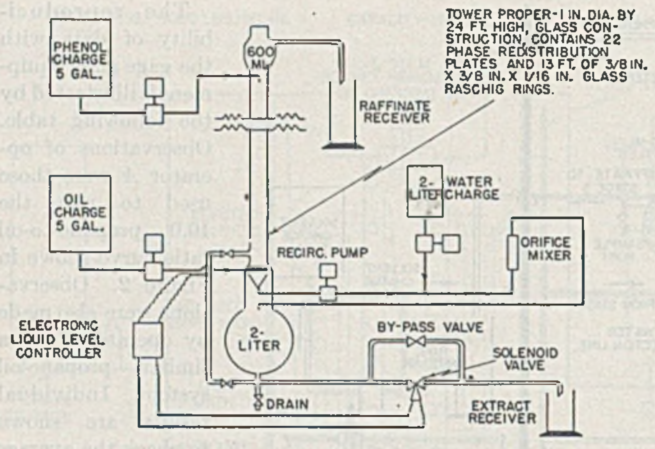

Figure 5. Laboratory Countercurrent Solvent Extraction Tower

ture of time, manpower, and charge stock. The stage extraction equipment serves two useful purposes: the determination of the stage equivalent of countercurrent tower units containing different contacting media and the determination of the quantities and qualities of the phases existing in successive stages of such equipment, which permits an analysis of phase composition changes occurring at analogous points in a countercurrent extraction tower.

COUNTERCURRENT STAGE EXTRACTION UNIT. A schematic diagram of the laboratory countercurrent stage extraction unit is shown in Figure 3. The unit normally comprises seven mixing and settling zones, although one or more stages may be added at the extract withdrawal end of the system for the recovery of cycle oil through the use of antisolvents. For purposes of simplicity, construction details have been shown in Figure 3 only for an intermediate stage (No. 4) since all other stages are of identical construction.

The mixture to be extracted and the solvent are charged to the system from 5-gallon-capacity calibrated glass vessels by means of Zenith gear pumps. These charge pumps and the intermediate stage transfer pumps are driven from a common drive shaft, pumping rates being controlled through the use of varying-ratio gear reducers. Charge rates are about 4 liters per hour of feed and solvent. The counterflow of the extracted material (raffinate) and solvent (extract) streams throughout the stage system, and the function of individual pieces of stage equipment can best be described in terms of a single stage as shown in Figure 3.

Each stage consists essentially of three parts: (*a*) a 750-ml.-capacity glass settling vessel with raffinate overflow and extract withdrawal connections, (*b*) a packed column wherein the raffinate and extract charge streams to the stage are intimately mixed prior to stratification, and (*c*) a transfer pump for forcing the extract-raffinate mixture through the packed column. In the case of stage 4 the feed to the settling vessel comprises partially extracted oil (raffinate) from stage 3 and partially spent solvent (extract) from stage 5. These two streams join and are pumped through the mixing column packed with $^1/_8$-inch-diameter glass beads to the glass settler. The settling vessel is constructed in the shape of an oblate spheroid to provide the maximum cross-sectional area at the raffinate-extract interface with a minimum holdup volume of the phases. Stratification occurs in the settler, the interfacial level being maintained by positioning of a flexible inverted U-tube on the extract withdrawal line. Raffinate overflowing from stage 4 passes on to stage 5 and is mixed there with extract transferred from stage 6. The extract is withdrawn at the bottom of stage 4 and transferred to stage 3, where it is mixed with raffinate overflowing from stage 2. The raffinate phase continues to flow countercurrently to the extract phase until it overflows from stage 7 and is collected as final raffinate. In a like manner extract is successively transferred in the opposite direction until it is withdrawn from stage 1 as final extract. If a cycle oil recovery stage is employed, as is frequently the case in lubricating oil extraction, the extract from stage 1 is withdrawn, cooled, or mixed with an antisolvent (water) and the mixture charged to the cycle oil recovery stage where released cycle oil is separated. This oil overflows into stage 1, where it joins the raffinate and flows countercurrently to solvent throughout the balance of the stages. A connection is provided on each stage extract withdrawal line to permit the addition of small amounts of antisolvent. This permits refluxing at any point within the extraction system and increases the flexibility with which the solubility of oil in the solvent can be adjusted. Ports are available in each extract withdrawal and raffinate overflow line to permit sampling of these phases. A common vent line to the atmosphere is connected to each stage feed and extract withdrawal line. This reduces the surging tendency of these phases and prevents the loss of the extract phase level within any settler by breaking the suction at the apex of the inverted U-tube level controller.

The laboratory stage extraction unit has also been successfully operated in the past using the gas lift principle to transfer the partially spent extract between stages. Details of one such stage (such as stage 4 in a seven-stage system) of this type of construction are shown in Figure 4. The principal components of this stage were: (*a*) a 2-liter glass balloon flask settler with raffinate overflow and extract withdrawal connections, (*b*) an agitating vessel in which the charge to the settler was intimately mixed by means of a stirrer, and (*c*) an air lift tube by which the extract was transferred to the preceding stage. Flow of raffinate was obtained by gravity by decreasing the height of each successive settler and auxiliary equipment. The extract-raffinate interface level within the settler was again controlled by the positioning of a flexible inverted U-tube. Although operability was satisfactory with this air-lift device, it was discarded in favor of mechanical gear pumps because of the fire hazard presented by mixtures of air and hydrocarbon vapors. The desired temperature is obtained by locating pairs of stages in insulated, individu-

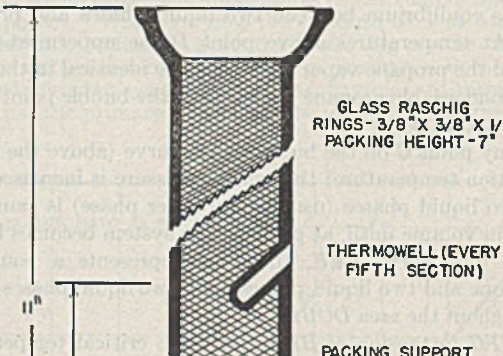

Figure 6. Countercurrent Tower Section

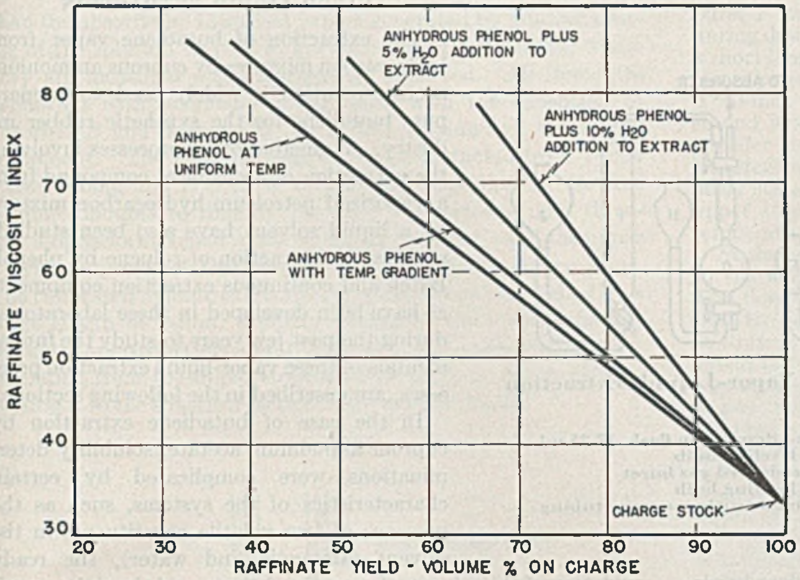

Figure 7. Phenol Extraction of Colombian 52V/210 Lube Distillate in Countercurrent Extraction Tower

ally heated compartments. The heat is supplied by electrical strip heaters individually controlled by rheostats, which allows good control of the compartment temperature and permits operation with a temperature gradient between the two ends of the system. A temperature range from 80° to 250° F. is possible with this equipment. Glass doors and suitable lighting are provided in each compartment to permit visual observation of the mixing and stratification.

The equipment is operated by pumping solvent into stage 7 and transferring solvent to succeeding stages until an extract level is obtained in stage 1, at which time the oil charge pump is started. When raffinate overflow is obtained from stage 7, the unit is operated "off condition" for a period of time (dependent on charge rates) sufficient to displace the system completely at least once.

The stage extraction equipment described here is capable of carrying out operations in a similar manner as in countercurrent tower type of equipment but requires considerably more time, charge stock, and operating supervision than does the tower equipment. Samples of intermediate raffinates and extracts are obtained, however, and data obtained from these interstage streams enable an interpretation of extraction conditions existing at analogous points within a countercurrent tower extraction system.

Prolonged, intimate mixing followed by settling of the interstage raffinate and extract streams blended in production proportions at the corresponding treating temperature was adopted to test for the existence of equilibrium. No yield or quality difference between the original and recontacted phases was observed. The existence of equilibrium conditions was further verified by the excellent data reproducibility experienced. For example, raffinate yields and quality (V.I.) obtained with varying oil feed rates (otherwise identical treating conditions) are as follows:

Run	Oil Feed Rate, Ml./Hr.	Raffinate Yield, Vol.%	Raffinate Viscosity Index
A	200	72.5	93
B	800	72.5	93
C	2000	73.4	92

These data indicate that, for feed rates within operating limits, equilibrium existed within the stages of the pilot unit.

COUNTERCURRENT TOWER EXTRACTION UNIT. A flow diagram of the extraction tower hookup is shown in Figure 5, with auxiliary equipment such as charge and recirculation pumps shown schematically. Details of the tower proper are shown in Figure 6. The tower (1 inch in diameter by 24 feet high) is constructed entirely of Pyrex pipe with standard interchangeable ground ball joints, and consists of the following main parts: (*a*) a 600-ml.-capacity raffinate settler bulb at the tower top, the raffinate overflowing from the top of the bulb while the solvent charge enters just below the bottom of the bulb; (*b*) a total of 21 feet of 1-inch-diameter glass pipe sections, each section being 11 inches in length and containing a plate for the collection and redistribution of the two liquid phases, with glass Raschig rings ($^3/_8 \times {}^3/_8 \times {}^1/_{16}$ inch) being used as a packing medium; (*c*) a bottom tower section 2 inches in diameter and 1 foot in length to which is connected the oil feed inlet and the extract recirculation withdrawal and return lines; and (*d*) a 2-liter balloon flask at the bottom to provide adequate extract settling capacity. Thermowells are provided in the raffinate and extract settlers and in every fifth tower section. Spent solvent is continuously withdrawn from the bottom of the extract settler by gravity flow, controlled by an electronic liquid level controller. By means of two electrodes fused about $^3/_{16}$ inch apart in a glass side arm on the extract settler, the electrical conductivity of the phase covering the electrodes is measured, and a solenoid valve in the extract withdrawal line is actuated through a relay and mercury switch from these electrodes. This controller affords a simple method of controlling the phase interface within narrow limits. In actual practice about 75% of the extract solution is continuously withdrawn through a manually operated by-pass valve; thus the frequency of the solenoid valve action is decreased. Although this instrument was constructed in the laboratory, similar instruments may be purchased from laboratory supply companies.

The tower proper is housed in an insulated box 1 foot square and 24 feet high. The back and sides of the housing are lined with $^1/_2$-inch-thick sheet asbestos; the front of the box is provided with glass doors to permit visual observation of oil and solvent counterflow. The glass tower is supported by two brackets which are attached to the sides of the tower housing. Light bulbs are placed behind the tower at 2-foot intervals to provide sufficient illumination for visual observation of the extraction. These bulbs introduce negligible amounts of heat. The tower housing is divided laterally into three sections, and each section is heated independently by electrical strip heaters controlled by rheostats. The temperature range possible is from 80° to 250° F.

The mixture to be extracted and the solvent are charged to the tower by Zenith gear pumps delivering 0.58 ml. per revolution. These pumps are motor-driven, and the pumping rates of each are controlled by variable-speed-friction drive transmissions. Charging rates of about 6 liters per hour total for feed and solvent are usually employed. A gear pump for adding an antisolvent such as water to the extract phase and another for the recirculation and mixing of the extract and antisolvent are driven from the same drive shaft as the phenol charge pump. With such a common drive, antisolvent addition rates of 2.5, 5, and 10% of the phenol feed are possible. The phenol charge, extract recirculating, and oil charge pumps are situated in a heated, insulated compartment to prevent solidification of phenol or waxy oil stocks in the pumps or connecting lines. All transfer lines are of $^1/_4$-inch-diameter copper tubing which is connected to the glass tower by neoprene tubing. The oil and phenol feed vessels are located in separate electrically heated compartments in order that different charging temperatures may be obtained when the tower is operating under temperature gradient conditions. Each vessel is of 5-gallon capacity, and suitably calibrated to permit measurement of oil and phenol charge rates.

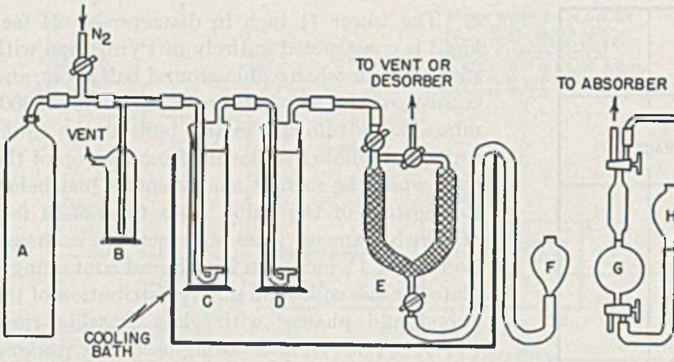

Figure 8. Equipment for Determination of Vapor-Liquid Extraction Equilibrium

A.	Feed cylinder
B.	50-ml. mercury safety bubbler
C, D.	500-ml. scrubber
E.	Absorption tube
F.	Mercury leveling bulb
G.	Calibrated desorption flask, 17.25 ml.
H.	Mercury leveling bulb
I.	500-cc. graduated gas buret
J.	Mercury leveling bulb
	Connections made with neoprene tubing

Steel platforms are located 8 and 16 feet above the floor level; thus all parts of the tower are readily accessible for observation and maintenance.

The unit was designed to be sufficiently flexible to permit several types of operation when lube stocks are extracted with a solvent such as phenol: (*a*) use of anhydrous phenol, aqueous phenol, or anhydrous phenol in conjunction with water addition to the extract; and (*b*) operation with uniform or temperature gradient conditions. Temperature gradient conditions are obtained by adjusting the temperature of the oil and phenol feed vessels and by varying the electrical input to the sectional strip heaters mounted in the tower housing. A Leeds & Northrup 8-point temperature indicator-recorder is used to indicate and record temperatures at different points throughout the tower. A small blower at the base of the tower can also be utilized to circulate an inert atmosphere throughout the tower housing during operation at uniform temperature.

In operations employing aqueous phenol the desired amount of water is premixed with the phenol charge. When employing water addition to the extract, the recirculating pump withdraws extract from a point just below the oil feed inlet to the tower. Water is added to the extract stream, and the two phases are forced through a small orifice mixer. The addition of water reduces the solubility of oil in the phenol which causes cycle oil to be released from solution.

In all types of operation solvent is first pumped into the empty tower until the solvent level reaches the feed inlet point. The feed charge pump is then started, and feed and solvent charge rates are adjusted as desired. The tower is usually operated, for lubricating oil extraction, with oil as the continuous phase and phenol as the discontinuous phase (interfacial level at the tower bottom). However, when extracting residual lube stocks of relatively high viscosity, better operability is obtained with phenol as the continuous phase (interfacial level at the top of the tower) because of the lower viscosity of the phenol phase. When raffinate overflows from the top of the tower the "off condition" period is started. The length of the "off condition" period is usually determined by the oil charge rate, it being considered desirable to displace the tower contents at least once before collecting representative "on condition" raffinate and extract samples.

Typical data obtained when extracting a Colombian medium lube distillate with phenol is shown in Figure 7. In this graph raffinate quality (as measured by viscosity index) is plotted against raffinate yield. Operations were carried out with (*a*) anhydrous phenol with uniform temperature and temperature gradient conditions, and (*b*) anhydrous phenol employing 5 and 10% water addition to the extract solution. A progressive increase in selectivity is noted (increased yield for a fixed quality raffinate) as operations vary from anhydrous phenol at uniform temperature (least selective) to anhydrous phenol plus 10% water added to the extract (most selective). These curves reflect the increased refluxing obtained by decreasing (either by cooling or addition of water) the solubility of oil in the extract solution.

VAPOR-LIQUID EXTRACTION

The extraction of butadiene vapor from hydrocarbon mixtures by cuprous ammonium acetate solution is widely used to prepare pure butadiene for the synthetic rubber industry. Numerous other processes involving the extraction of a chemical compound from a vaporized petroleum hydrocarbon mixture by a liquid solvent have also been studied, such as the extraction of toluene by phenol. Batch and continuous extraction equipment, as have been developed in these laboratories during the past few years to study the fundamentals of these vapor-liquid extraction processes, are described in the following sections.

In the case of butadiene extraction by cuprous ammonium acetate, solubility determinations were complicated by certain characteristics of the systems, such as the presence of two volatile constituents in the solvent (ammonia and water), the ready oxidation of the solvent when exposed to air, and the rather sensitive response of butadiene solubility to variations in solvent composition and temperature. Satisfactory static and dynamic procedures were devised, however, for obtaining the desired vapor-liquid equilibrium data.

Batch Vapor-Liquid Equilibrium Apparatus. The present discussion of equilibrium measurements on a vapor-liquid extraction system will be illustrated by a description of a dynamic method employed advantageously for obtaining vapor-liquid equilibrium on a butadiene–cuprous ammonium acetate system at temperatures in the neighborhood of 32° F. and at a total pressure of about 1 atmosphere. The apparatus may be used, however, at temperatures from −50° to 300° F. with ease.

The equipment satisfactorily employed for this purpose is represented in Figure 8. Vaporized feed is fed from a low pressure cylinder through a pressure-reducing valve which reduces total pressure to about 0 pounds per square inch gage. A mercury safety bubbler with 3-inch mercury head provides against pressure surges which might break the glass extraction equipment. The feed vapors may be saturated with ammonia vapors in the two bubblers before passing into the absorber, as in studying butadiene extraction, or the vapors may be sent directly to the absorber. Both bubblers and absorber are almost totally immersed in a thermostatically controlled bath. After saturation of the absorbing solution, the solution is transferred (employing mercury leveling bulbs) to the desorber, which is also held in a thermostatically controlled bath about 5–10° F. lower

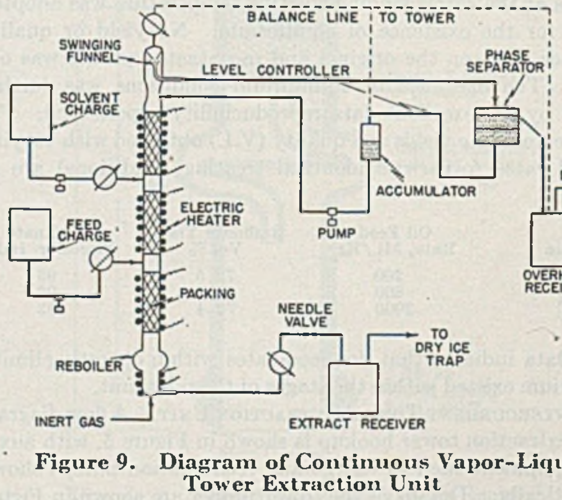

Figure 9. Diagram of Continuous Vapor-Liquid Tower Extraction Unit

than the absorber. Desorbed vapors generated by gradual heating of the solution to 180° F. are collected in a gas buret, where they are measured and subsequently analyzed. All items are connected with neoprene tubing, and, with the exception of absorber E and desorber G, all consist of standard laboratory equipment. The U-shaped absorber is constructed from 1-inch Pyrex tubing and is packed with 4-mm. glass beads. Its free volume amounts to roughly 125 ml. The two-way and three-way stopcocks attached to the upper part of the U- and the upper T-type stopcock of the desorber carry 2-mm. capillary arms. The calibrated cylindrical section of the desorber is attached by a short length of 2-mm. capillary tubing to the lower spherical section of approximately 50-ml. capacity. The calibrated section, extending from the upper stopcock to a mark on the neck connecting it to the spherical section, represents 17.25 ml.

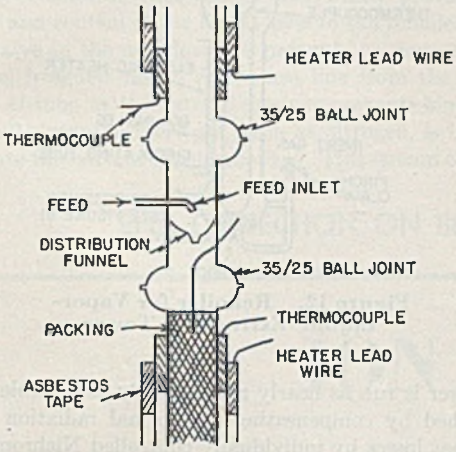

Figure 10. Feed Section for Vapor-Liquid Extraction Tower

In the butadiene–cuprous ammonium acetate system the ammonia concentrations employed produce partial pressures of ammonia and water vapor in the hydrocarbon stream nearly equal to those over the cuprous ammonium acetate solution. When employing cuprous ammonium acetate solution containing approximately 3.0 moles per liter of cuprous copper, 4.0 moles per liter of acetate ion, and 11.0 moles per liter of ammonia, the concentration of the ammonia solution in scrubber C is 11 N and that in D, 7 N.

The following procedure is used in carrying out a typical solubility determination with pure butadiene. A is the feed cylinder and B a 50-ml. mercury safety bubbler. Scrubbers C and D are filled with approximately 500 ml. of aqueous ammonia of the desired concentrations and immersed in the bath with empty absorber E. A slow stream of cylinder nitrogen is used to sweep out the air in the system, to minimize oxidation of the cuprous ammonium acetate during the initial portion of the absorption step. After the absorber is sealed from the scrubbers by the two-way stopcock, the residual gases in the absorber are displaced by mercury from leveling bulb F. Cuprous ammonium acetate solution is transferred batchwise to the absorber through a short length of 2-mm. capillary tubing by simultaneous application of a small pressure of nitrogen to the solution storage vessel and withdrawal of mercury from the desorber. After approximately 50 ml. of solution are introduced, the three-way stopcock of the absorber is closed and the connection to the storage vessel broken. The flow of butadiene feed is then begun and adjusted to a rate of about 50 to 100 ml. a minute. Mercury is withdrawn from the absorber until it recedes from the U. The three-way stopcock is adjusted to permit venting unabsorbed vapors from only the right-hand limb of the absorber. The hydrocarbon feed generally contacts a 5- to 6-inch layer of solvent confined in the right-hand limb for about 2 hours.

Approximately 15 ml. of a 5 weight % solution of sulfuric acid saturated with potassium sulfate are introduced into 500-ml. gas buret I for the purpose of absorbing ammonia vapors expelled during desorption. The gas buret is connected to the desorber by a short length of 2-mm. capillary tubing. All gases are displaced from the gas buret prior to the desorption step by mercury from J. A 10-inch length of 2-mm. capillary tubing is attached to the second arm of the desorber capillary stopcock to serve as the transfer line for the equilibrated solution. The desorber and transfer line are then filled with mercury from bulb H. As previously stated, the desorber is immersed to a point just above the upper stopcock in a bath maintained 5° to 10° lower than the temperature of the absorber.

At the end of the absorption period mercury from F is admitted to the absorber, trapping the solution in the right hand limb. The flow of feed is then discontinued, the absorber is shut off from the scrubbers, and the three-way capillary stopcock is turned to connect both limbs with the vent line. Additional mercury is added to raise the level of the equilibrated solution to the three-way stopcock, which is then closed to the vent line. Connection is now made to the transfer line which had been previously attached to the desorber and nearly completely filled with mercury. Where necessary, dry ice placed in a trough directly below the transfer line cools the line sufficiently to prevent evolution of absorbed vapor from the equilibrated solution. The three-way capillary stopcock on the absorber is turned to connect the solution with the transfer line and the flow of mercury from F and to H is simultaneously adjusted to transfer about 20 ml. of solution to the desorber. A small amount of air frequently collects in the desorber but is eliminated when the equilibrated solution level is adjusted to correspond to the calibration mark of the desorber. The desorber stopcock is then closed.

Desorption is begun by removing the cooling bath from the desorber. As the solution sample warms up, the solution is forced into the spherical section of the desorber by the desorbed vapors. When the mercury is completely displaced, the lower stopcock is closed and the desorber opened to the gas buret. A water bath is then placed around the desorber and the solution sample heated to 180° F. Approximately 20 minutes are required for the desorption operation, when butadiene adsorption is being studied. Mercury is again introduced, forcing the desorbed solution sample into the upper section of the desorber and displacing all vapors from it. No correction is required for the dead space in the capillary joining the desorber and gas buret. All connections are made with neoprene tubing.

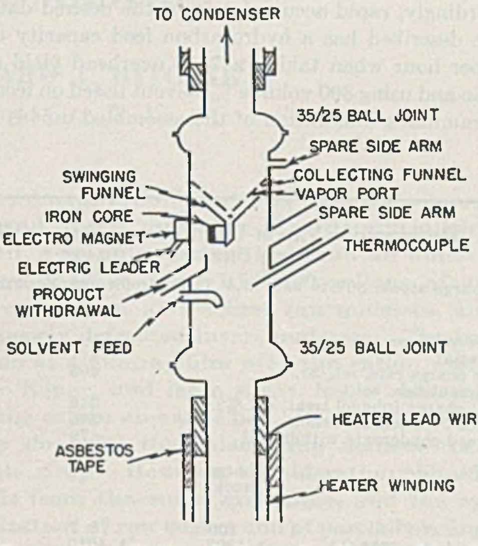

Figure 11. Reflux Splitter for Vapor-Liquid Extraction Tower

Readings of desorbed gas volume, temperature, and pressure are taken. In the butadiene–cuprous ammonium acetate process, previously determined values for the partial pressures of ammonia and water vapors above the cuprous ammonium solution are subtracted from the total pressure in order to calculate the equilibrium partial pressure of butadiene in the absorber. Values for the vapor pressure of water over saturated potassium sulfate solutions taken from the literature are used to obtain the corrected pressure of desorbed butadiene. Similar corrections are employed with other systems.

The following results for the solubility of 99% butadiene at 0° C. may be cited as typical of those obtainable with the given procedure. The composition of the cuprous ammonium acetate solution, expressed as moles per liter, was: cuprous copper 2.84, cupric copper 0.32, acetate ion 3.78, and ammonia 10.79.

Run	Barometric Pressure, Atm.	Adsorption: Butadiene Pressure, Atm.	Desorption Vol. of gas, ml.	Desorption Temp., ° C.	Butadiene Soly., Moles/Liter
3	1.009	0.945	385	35.0	0.870
4	1.004	0.940	385	31.0	0.880
			378	31.0	0.865

These butadiene solubility values are not corrected for deviation from ideal gas behavior. They are, moreover, based on the volume of saturated solution. One liter of saturated solution is produced from about 0.996 liter of lean solvent.

The data of runs 3 and 4 indicate that the precision or reproducibility of the butadiene solubility measurements obtained by this dynamic method is quite satisfactory. On the basis of these and additional experiments it appears that an over-all precision of ±2% can be expected. The estimation of the accuracy of the solubilities determined by this method is not so readily achieved. The values for the solubility of butadiene in these runs may be compared with the observed value of 0.90 mole per liter of saturated solution at 0.95 atmosphere butadiene partial pressure obtained from static vapor-liquid equilibrium measurements at 0° C. with a solution closely similar in composition to that employed here. It is believed that the present method is probably accurate within ±6%.

CONTINUOUS VAPOR-LIQUID EXTRACTION TOWER UNIT. A simple countercurrent tower for obtaining continuous vapor-liquid extraction data has been successfully employed to obtain operating variable data on a variety of extractions, including, for example, phenol extraction of benzene, toluene, and xylenes from appropriate petroleum fractions. Its simplicity and glass construction permit rapid initial assembly with a minimum of effort; its low holdup permits quick attainment of equilibrium and, accordingly, rapid accumulation of the desired data. The apparatus described has a hydrocarbon feed capacity of about 400 ml. per hour when taking a 75% overhead yield at a 4:1 reflux ratio and using 300 volume % solvent based on feed.

A diagrammatic illustration of the assembled unit is given in Figure 9. It consists of three 1-inch-diameter Pyrex pipe sections, each approximately 3 feet long, with appropriate means for admitting feed and releasing products, and for reboiling, condensing, and refluxing. The 1-inch glass tower is packed with $^3/_{32}$-inch stainless steel Fenske helices; the plate equivalent of each section is varied by changing the height of the packing. The top section is arranged so that it can be eliminated easily if desired; its principal function is to remove solvent from the overhead.

TABLE I. CONTINUOUS VAPOR-LIQUID EXTRACTION OF TOLUENE WITH PHENOL

(Charge stock, 80° to 250° F.V.T. Hydroformed Naphtha)

Run No.		34	35
Operating conditions			
Reflux ratio[a]		4:1	4:1
Naphtha charge rate, ml./hr.		405	398
Stream quantities, vol.[b]			
Phenol charge (phenol treat, vol.%)		316	327
Overhead condensate reflux		316	328
Overhead condensate withdrawal		79	82
	Charge Stock		
Overhead			
Yield, %	100	78.7	82.7
Refractive index (20° C.)	1.4208	1.4010	1.4059
Sp. gr. (20° C./20° C.)	0.7487	0.7156	0.7236
Specific dispersion	124	107	110
Aromatics, %	27	8	10
Bottoms			
Yield, %		21.3	17.3
Refractive index (20° C.)		1.4939	1.4972
Sp. gr. (20° C./20° C.)		0.8629	0.8711
Specific dispersion		183	184
Bromine No.		3.2	2.2
Olefins, %		2.2	1.5
Paraffins, %		1	0
Aromatics, %		96	99
Toluene recovery, %		95	80

[a] Reflux ratio $= \frac{\text{overhead condensate refluxed to tower}}{\text{overhead condensate withdrawn from system}}$.

[b] Based on 100 volumes of naphtha feed.

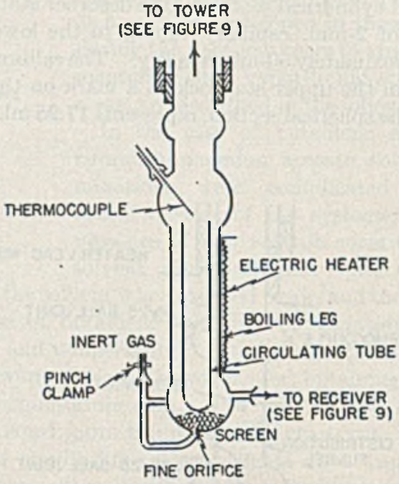

Figure 12. Reboiler for Vapor-Liquid Extraction Tower

The tower is run as nearly adiabatically as possible. This is accomplished by compensating for normal radiation and convection heat losses by individually controlled Nichrome electric heating elements which surround each tower section. These heaters are wound on glass tubes surrounding, and arranged concentrically with, the tower. The heating elements are protected and thermally insulated in each case by a larger, concentrically located glass tube. Thermocouples are suspended between the tube having the heating element and the tower itself. The energy supplied the heating elements is controlled in such a way as to minimize the difference in temperature between these thermocouples and the tower itself. This construction is seen in Figures 10 and 11.

The feed containing the material to be separated is introduced immediately above the first section and the solvent immediately above the second section. These feed sections are identical; one of them is shown in Figure 10. Feed enters from the left side through an insulated connector. Each feed section is equipped with a distributing funnel and thermocouple.

The feed is delivered by means of a bellows-type pump through a preheater. The temperature of the feed, measured just before its introduction into the tower, is closely controlled by means of an oil bath surrounding a U-shaped preheater. This preheater, which is approximately 18 inches long and made of $^1/_2$-inch glass tubing, functions satisfactorily when feeding either a liquid or vaporized feed; in this latter case the vaporization is done in the U-preheater. The solvent temperature is also closely controlled. In this case a low capacity preheater consisting of an electrically wound copper tube is used in order to permit rapid and sensitive temperature adjustment of the solvent entering the tower.

The reflux-product splitter section, mounted near the top of the column below the condenser, is shown in Figure 11. It consists of a conventional Ace Glass Company reflux head modified to permit simultaneous injection of several solvent and recycle streams, and to permit use of an interchangeable condenser. The "swinging" funnel acts as a splitter and is activated by a magnet connected to a Flexopulse timer. The setting of this splitter determines the reflux ratio. As shown in Figure 9, for those systems which produce a two-phase overhead product, facilities are provided for continuous recycle of one phase to the extraction tower. The rate of recycle is controlled in a positive, sensitive, and reproducible manner by means of a bellows pump connected to a Flexopulse timer controlling the pump motor current source. The time is set to deliver current over most of the pumping cycle in order to produce as nearly continuous pumping as possible. The use of the Flexopulse timer is far more satisfactory than attempting to adjust the pump stroke.

The reboiler, mounted at the bottom of the column, is shown in Figure 12. The electrically wound "boiling leg" was made 10 inches long and 2 inches in diameter to provide maximum heat input with minimum liquid holdup. Extract is removed from the bottom of the leg (shown at the bottom right-hand side in Figure 12) through a small conventional glass condenser acting as a cooler. The rate of withdrawal is controlled by means of a flexibly connected inverted U-tube which provides gravity overflow and control of the liquid level in the reboiler. A Hoke needle valve in the overflow line prevents pressure surges from producing irregular flow. A balance line from the top of the inverted U-tube to the extract receiver prevents siphoning. A very small stream of inert gas, such as nitrogen, is bled continuously into the bottom of the reboiler. This stream of gas passes up through the annular space between the heated boiling leg and an inner concentric tube open at the top. The inner tube is open at the bottom only at the sides. This arrangement ensures even, continuous boiling by initiating vapor bubbles and enhancing natural convection.

The operating procedure is as follows: The reflux ratio is set on the automatic timer and the naphtha feed started into the tower at the predetermined rate. The feed preheater is adjusted to give the desired feed temperature. After a liquid level has been built up in the reboiler, the reboiler heat is adjusted slowly to give approximately the desired overhead rate. Too rapid application of heat to the reboiler may result in flooding. Solvent feed is then started into the tower, while the overhead rate is maintained by appropriate adjustments in reboiler heat. During this period the tower jacket heaters are adjusted to maintain approximately adiabatic conditions. The solvent feed preheater is adjusted to correspond to the tower temperature at the solvent injection point. The reboiler heat is finally readjusted to give the exact overhead yield desired. The tower is usually operated slightly below the flooding rate to ensure high efficiency of tower operation and time utilization.

Typical operating conditions and results obtained with this equipment are shown in Table I. In this case high purity toluene was extracted from a hydroformed naphtha of 80° to 250° F. boiling range which contained about 27% toluene.

RECEIVED March 13, 1947.

END OF SECTION ON BENCH SCALE EQUIPMENT AND TECHNIQUES

ION EXCHANGE

Operation of Commercial Scale Plant for Demineralization of Cane Sirups and Molasses

EMANUEL BLOCH AND RICHARD J. RITCHIE

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A plant scale ion exchange demineralization unit was put into operation in order to purify cane sirups and invert molasses. The demineralizing system consists of a cation exchange unit, a granular carbon bed, and an anion exchange unit. Four such batteries were used to treat 1,500,000 gallons of a blend of partially inverted commercial cane sirup and a first run molasses, and for the processing of 715,000 gallons of poorly defecated invert molasses. The main problems encountered were formation of a gummy film over the cation exchange bed which prevented passage of the liquor, and large sugar losses due to bacterial infection in the upper layers of the cation exchange bed. With the present capacities of exchange materials it is doubtful that blackstrap molasses can be economically converted to an edible sirup. However, consideration should be given to the recovery of organic acids from the anion exchanger, and the application of this process in the demineralization of raw sugars and of partially refined sugars.

SEVERAL reports have been published describing the pilot plant operation of various ion exchange systems in treating sugar juices. These plants have been used to remove electrolytes from sugar juices in order to obtain a higher yield of sucrose and a minimum yield of molasses. Very little work on a commercial scale has been done on the purification of cane sirups and molasses, and, except for two beet campaigns, no extended operation of any full scale commercial plant has been reported. In 1944 this laboratory instituted studies in the utilization of ion exchangers for the purification of various grades of sirups and molasses. A number of exchangers were tested in both laboratory scale and pilot plant scale operations. The results from this work justified undertaking a full scale commercial operation. This plant was put into operation in January 1946 and was operated until August of that year. It is the purpose of this paper to describe the production methods and indicate some of the problems and possibilities of using ion exchangers.

DEMINERALIZING PROCESS

Since a number of able theoretical presentations of ion exchange theory have been recently published, only a brief presentation of the underlying principles will be given here (*2–5*). Basically a demineralizing system consists of two steps. In the first step a cation exchanger removes such ions as Na^+, K^+, Ca^{++}, and Mg^{++} from their salts in solution by replacing them with hydrogen ions. This results in the production of the corresponding acids—hydrochloric, sulfuric, carbonic, and various organic acids. This highly acidic solution is then brought in contact with an anion

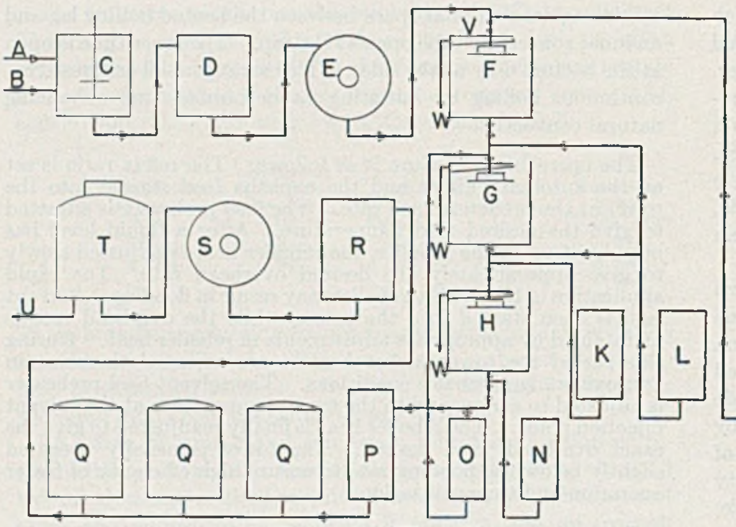

Figure 1. Flow Sheet

A. Water
B. 76° Brix sirup
C. Mixing tank
D. 33° Brix sirup tank
E. Filter press
F. Catex
G. Darco
H. Deacidite
K. Soda
L. Water for backwash
M. Acid
N. Soft water for backwash
O. Used soda
P. Blending tank
Q. Triple-effect evaporators
R. Activated carbon mixing tank
S. Filter press
T. Pan evaporator
U. To storage
V. Launder
W. To sewer

Solid arrow = sirup flow
Open arrow = water and regenerants

exchange resin where the entire acid molecule is probably adsorbed. A large percentage of the electrically charged colloids are also removed, and a solution relatively free of colloidal material and electrolytes is thus obtained. These reactions are reversible in that both beds can be regenerated and re-used. The cation exchanger is regenerated by means of a mineral acid, usually sulfuric, and the anion exchanger is regenerated by means of an alkali, such as sodium hydroxide, ammonium hydroxide, or sodium carbonate. A granular carbon bed may be placed between the exchangers to facilitate removal of undesirable odors, flavors, and color.

Equipment. The only full scale plant available at the time this work was started was built at the Isabella Sugar Company, Mount Pleasant, Mich., in 1941 and was used during two campaigns to demineralize beet juice (*1*, *6*). This demineralizing system consists of four batteries of demineralizing units. Each battery is composed of three cells with a hydrogen exchange cell located on the top floor, a granular activated carbon bed placed on the floor beneath, and below this the anion exchange cell.

The cells are rubber-lined, and all lines connecting the cells are of hard rubber. All other surfaces coming in contact with acidic or alkaline material are painted with resistant paints. The cation exchange cell has a diameter of 11 feet 6 inches and a height of 11 feet, and contains 610 cubic feet of Catex, a sulfonated coal. The granular carbon bed has a diameter of 10 feet and a height of 10 feet, and contains 340 cubic feet of 12–20 mesh Darco. The Anex or anion exchange bed has a diameter of 10 feet and a height of 10 feet, and contains 370 cubic feet of Anex. All cells have a 1-foot underlying bed of graded anthracite. Included in this installation are a number of tanks for the preparation of regenerants, and the storage of soft water and sweet water. Gravity flow is used to send the liquids through the battery.

All materials enter the bed through a common line and strike a baffle plate placed 8 inches above the bed level. The liquid is distributed in a spreading fan over the surface of the bed. On the bottom of the tank is a distributing system. This consists of a 6-inch header line with branching 1$^1/_2$-inch perforated lines. These lines serve to collect the liquid when it reaches the bottom and for the introduction of water for backwashing (Figure 1). The top of the tanks have a launder, as shown in Figure 2, for carrying off the water.

Demineralization of Blended Sirup. The first type of sirup treated during this operation was 1,500,000 gallons of a blend of partially inverted commercial cane sirup with a first-run molasses. The blend was received at 76° Brix and had to be diluted and filtered before entering the demineralizing plant. The extent of dilution and rate of passage through the exchangers depend largely upon the ash content of the material being processed. In this operation 5000 gallons of 33° Brix sirup treated at a flow rate of 100 to 125 gallons per minute gave an end product containing the desired properties of low ash and 6.25 to 6.50% nonsugar solids, dry basis. After filtration the sirup passed to the cation exchange cell. The acidic effluent then entered the bed of activated carbon. From this cell the effluent passed into the Anex bed, which removed the acidic components from the liquid. The initial effluent from the ion exchanger was highly alkaline, but with the gradual exhaustion of the bed the pH kept dropping until the final sweet water ran as low as 2.90. The data of a typical run are shown in Table I.

Processing Demineralized Sirup. From the demineralizing plant the juice entered large blending tanks, where the high and low pH products were blended to give a final product with a pH of 4.5 to 5.5, solids content of 12.0 to 14.0° Brix, and Solu-Bridge reading between 18 and 35 grains per gallon as sodium chloride. The liquid coming out of the demineralizers has a hazy, cloudy, muddy appearance. The dilute juice was sent from the blenders to the evaporators for concentration. After being boiled to 50° Brix, it was filtered through Vallez presses with 0.5% activated carbon and 2% filter aid, both on solids. This filtered sirup, further concentrated to the desired solids content, was ready for shipment.

Table I. Three Parts Commercial Cane Sirup to One Part First Molasses

	Influent (before Dilution)	Final Product
Brix, degrees	76.62	75.40
Sucrose, %	53.03	50.40
Invert, %	12.74	20.19
Total sugars, %	65.77	70.59
Nonsugar solids, %	10.91	4.81
N.S.S. (dry basis), %	14.27	6.38
Ash (conductivity), %	3.52	0.58
Solu-Bridge, grains/gal. as NaCl	350	28
pH	4.90	4.80
Taste	Molasses, malty	Bland
Odor	Molasses	None

5000-Gallon Cycle at 33° Brix

(Influent: 32.8° Brix; pH 4.90; Solu-Bridge, 250 grains/gal. as NaCl)

		Catex Effluent			Anex Effluent		
Vol. of Effluent, Gal.	Time (P.M.)	Degrees Brix	pH	Solu-Bridge, grains/gal. as NaCl	Degrees Brix	pH	Solu-Bridge, grains/gal. as NaCl
2,000	4:25	0.1	3.30	16	0.7	11.95	500
4,000	4:45	25.6	1.30	500	0.2	11.85	120
5,000	4:55	28.9	1.20	500	0.2	11.75	100
Sweetening Off Began with Sweet Water Followed by Raw Water							
1,000	5:08	29.0	1.20	500	0.2	11.65	70
3,000	5:14	18.5	1.95	225	16.8	9.60	30
5,000	5:30	3.2	2.95	26	27.2	3.85	18
7,000	5:43	1.9	3.30	22	19.4	3.40	21
9,000	5:55	1.2	3.30	18	16.3	3.30	15
15,000	6:30	0.0	3.90	14	0.3	2.90	12

The beds were sweetened off by passing whatever high Brix sweet water (5.0–2.0° Brix) was available from previous sweetening on and off into the beds first, followed by raw water. The low Brix sweet water (2.0–0.2° Brix) was used to dilute fresh batches of sirup. The total sweetening off required about 15,000 gallons of water.

After this the beds were backwashed until they ran clean. The backwash consumed 10,000 to 15,000 gallons of water per bed. The anion exchange bed was backwashed with soft water. This water was obtained during the sweetening on process and consisted of the residual water left in the beds from rinsing during regeneration. In addition, a zeolite softener was used to obtain further quantities of soft water. This was done to avoid the gelatinous iron and magnesium hydroxide precipitates which could foul the beds.

For regenerating the Catex the quantity of acid needed was made up to 1.5% solution. The anion exchange material was regenerated by making the needed amount of caustic into a 1.8% solution. Excess caustic (0.6–1.0%) washed from the anion exchange bed during the regeneration process was collected, heated to 160° F., and used for the regeneration of the carbon bed. The carbon bed was then acidified by using the acidic rinse water obtained from the regeneration of the Catex bed.

Demineralization of Invert Molasses. The second type of molasses processed was 715,000 gallons of poorly defecated invert molasses, which had been prepared originally for use in alcohol production and stored at Port Everglades, Fla. When received, this molasses contained large quantities of bagacillo, gums, and dextrins. It had previously been observed that unfiltered molasses tended to decrease the efficiency of the cation exchanger by 50 to 75%. Two factors were held to be primarily responsible for this drop in capacity: (*a*) Large colloid and gum particles apparently formed a coating around the granules, preventing contact with the ions in solution; because of this, no exchange took place. As a result, the solution passed through substantially unchanged. (*b*) An inpenetrable gummy film formed over the surface of the cation exchanger bed, which prevented the passage of the liquor. Whenever this occurred, normal regenerative procedures proved ineffective, and drastic treatment of the cation bed had to be undertaken. This consisted of treating the bed with hot caustic solution and then regenerating with double strength acid.

To prevent the occlusion of the particles and of matting, the molasses was first filtered through a bed of fine anthracite. (Sand can be used effectively for the same purpose.) This removed a substantial quantity of the undesirable material and gave a fairly clear molasses. The data of a typical demineralization on invert molasses are shown in Table II.

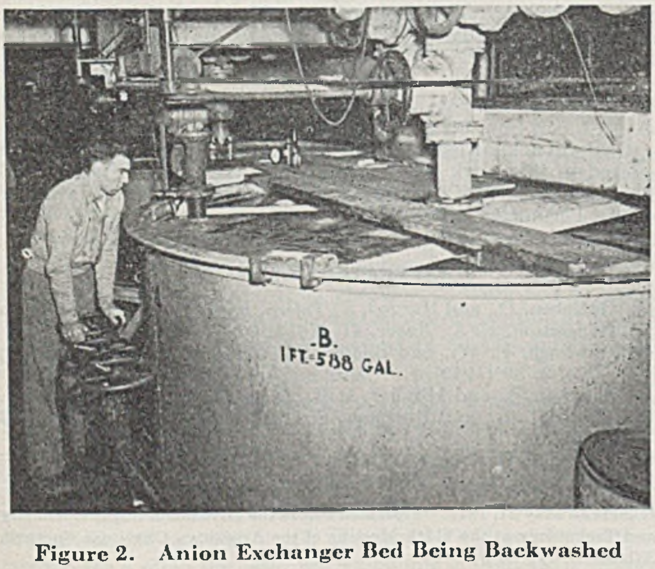

Figure 2. Anion Exchanger Bed Being Backwashed

INSTALLATION OF NEW ANION EXCHANGER

Before processing this latter type of molasses, an important change in the equipment was made. Tests had indicated that the cation exchanger beds were only about 35% exhausted during a 5000-gallon cycle, whereas the anion exchange material was completely exhausted at the end of the cycle. In order to utilize more fully the entire capacity of the system, the four beds of Anex were replaced by two beds of Deacidite, each having a volume of 320 cubic feet. By using two beds of Catex in parallel followed by one bed of Deacidite, satisfactory treatment of a 30,000-gallon cycle of 33° Brix sirup was possible (Table II). This decreased markedly the amount of regenerant chemicals needed with substantial saving of time and material (Table III).

CAPACITY LOSSES OF EXCHANGE MATERIALS

It is not possible to enter into a discussion of the exact cost figures, since equipment and material had to be used as found, with slight modification for our own use, and efficiency and cost were frequently sacrificed to increase production. With improved types of cells and exchangers, operating costs can be sharply reduced. One of the more important cost considerations is the extent of exchanger deterioration and loss of capacity. At the beginning of the first run the cation exchanger had a capacity of 9900 grains per cubic foot as calcium carbonate. At the

Table II. Everglades Molasses

	Influent (before Dilution)	Final Product
Brix, degrees	83.40	75.60
Sucrose, %	24.50	20.71
Invert, %	48.82	49.87
Total sugars, %	73.32	70.58
Nonsugar solids, %	10.08	5.02
N.S.S. (dry basis), %	12.09	6.64
Ash (conductivity), %	2.49	0.65
Solu-Bridge, grains/gal. as NaCl	350	26
pH	5.0	5.1
Taste	Molasses	Bland
Odor	Molasses	Very slight molasses

30,000-Gallon Cycle of 33° Brix Molasses

(Influent: 32.9° Brix; pH 5.0; Solu-Bridge, 275 grains/gal. as NaCl)

		Catex Effluent			Deacidite Effluent		
Vol. of Effluent, Gal.	Time (A.M.)	Degrees Brix	pH	Solu-Bridge, grains/gal. as NaCl	Degrees Brix	pH	Solu-Bridge, grains/gal. as NaCl
2,000	7:30	0.2	3.0	20	0.2	11.8	85
4,000	7:50	16.4	1.3	300	0.2	11.6	60
6,000	8:10	16.8	1.3	300	2.5	11.2	60
8,000	8:30	25.3	1.3	290	16.8	10.7	35
10,000	8:52	28.6	1.2	280	27.6	10.0	25
12,000	9:10	30.4	1.5	250	29.8	10.0	21
14,000	9:29	30.4	2.1	160	29.8	9.4	18
15,000	9:40	30.2	2.5	100	29.8	9.1	16

Switched to Second Catex Bed, Merging the Sweet Water from the First Bed with that of the New Bed

4,000	10:30	9.0	1.3	300	17.0	9.7	70
6,000	10:50	18.7	1.4	300	9.8	8.6	35
8,000	11:10	26.3	1.3	290	22.6	7.8	25
10,000	11:35	29.8	1.2	250	28.7	6.5	12
	(P.M.)						
12,000	12:05	30.0	1.2	200	29.5	5.9	7
14,000	12:25	30.1	1.9	190	29.6	5.1	6
15,000	12:45	30.0	2.4	170	29.6	4.8	9

Sweetening Off Began with Sweet Water Followed by Raw Water. Total Requirement, 11,000 Gallons of Water

Total Time/Cycle, Min.

Juice (30,000 gal.)	330
Sweetening off (11,000 gal.)	65
Backwash and rinse	130
Regeneration time	100
Total	625 = 10$^1/_2$ hours (approx.)

Table III. Material Used in Processing

Material	Quantity, Lb.	Lb./Lb. of Solids Removed
5000 Gal. of 33° Brix Sirup[a]		
NaOH	766	0.59
H_2SO_4	1011	0.79
Hyflo	282	0.22
Darco	71	0.055
30,000 Gal. of 33° Brix Everglades Molasses[b]		
NaOH	766	0.12
H_2SO_4	2022	0.32
Hyflo	1692	0.25
Darco	426	0.068

[a] Nonsugar solids removed per 5000-gallon cycle, 1282 pounds.
[b] Nonsugar solids removed per 30,000-gallon cycle, 6267 pounds.

completion of 223 cycles the capacity was reduced to 8900 grains per cubic foot, a capacity loss of 11%. The Anex showed a far greater reduction in exchange capacity and a secondary loss in volume due to the increase in fines caused by the wearing down of the resin. However, this particular type of anion exchange material is no longer used, because improved anion exchangers are available.

The Deacidite showed a capacity loss of 8% after the completion of 123 cycles. No definite evidence is available which would indicate whether the loss in capacity of exchange materials is due to a coating of the ion exchange material or to its taking up an ion which is not easily regenerated off. Undoubtedly a part of the relatively high loss in capacity experienced in these operations can be attributed to the fact that proper clarification of the raw material was difficult. It can be assumed that in processing sugar solutions generally, the capacity losses experienced will be higher than in water treatment, for large amounts of colloids and organic substances have totally different effects than do solutions containing only mineral salts. Therefore, before an exchanger resin is selected, determination should be made of its ability to stand up under the impact of impure sugar solutions for many cycles.

SUGAR LOSSES

At times large sugar losses were sustained because of bacterial infection. The cation exchange bed appeared to offer an extremely fertile medium for this growth. Examination showed that the infection was concentrated in the upper two inches of the bed. This is attributed to the conditions offered for growth. The beds are always slightly acidic; the juice enters at a temperature of 70–80° F.; and the proximity to the air provides the oxygen necessary for growth. Addition of small quantities of formaldehyde during regeneration seemed to retard the bacterial growth, but some infection was present at all times. There were many other sugar losses. The over-all loss in the operation was 15.0% of the total sugars. Some of this loss may be attributed to the difficulty encountered in sweetening off the filter presses. The degradation of invert sugar under the influence of a highly alkaline or acidic media must also be considered.

DILUTION

Dilution of the sirup entails consideration of an adequate water supply and increased evaporation costs. All sirups must be diluted to a point where they will diffuse through the beds at a maximum rate of flow. This would mean the addition of 0.48 gallon of water to every gallon of 75° Brix sirup in order to obtain a 33° Brix solution. By the time the sirup reached the blending tanks the dilution by sweet water had reduced the solution to 14° Brix.

With increased exchanger capacities the bed dilution would be decreased; this would result in a composite sirup of higher concentration than that obtained in this operation.

WATER REQUIREMENTS

The water requirements in sirup or molasses demineralization are high. Sirup and molasses are usually obtained in a concentration of 75° to 80° Brix. As previously stated, these high Brix materials must be diluted. In addition the following amounts of water were required per battery: preparation of regenerating solutions, 13,000; rinse water, 10,000; backwash water 40,000; the total water per battery, 63,000 gallons.

DISCUSSION

The operation of this plant on a commercial scale has indicated the possibilities of demineralizing cane sirups and molasses by ion exchangers. The authors have not discussed the production costs because this operation was carried on under unusual conditions, and many of the costs met at Mount Pleasant would normally not be encountered. The cost of demineralization will be based on the following:

1. Amount of nonsugars to be removed. The greater the amount of nonsugars, the more frequent the regeneration, with resulting increase in cost of regenerants.
2. Capacity of resins for the specific ash, organic, and colloid materials found in sugars
3. Per cent resin replacement
4. Cost of regenerants in area where plant is located
5. Cost of filtering sirups before they enter the demineralizing system. If a press is used the cost of filter aids must be considered
6. Cost of treating demineralized sirups with activated carbons and filter aids to obtain clarification
7. Evaporation costs
8. Labor

In addition an adequate water supply must be assured.

From the experience obtained during this operation it also appears improbable that complete demineralization can be obtained by one passage through the beds. The Solu-Bridge readings in Tables II and III show that at no time was the sirup free of mineral matter. To obtain a completely ash-free sirup it would be necessary to pass the liquor through at least two batteries.

CONCLUSIONS

Under normal conditions it is doubtful whether blackstrap could be economically converted to an edible sirup. The high ash and colloid content of that material would result in extremely short cycles and a corresponding increase in the amount of regenerative material. However, it appears to the authors that this process should at this time be considered as a possible method for reducing losses from frozen cane. In this connection the recovery of aconitic acid from the anion exchanger may prove to be a valuable by-product. The application of this process in the demineralization of raw sugars and washed raws may also prove to be fruitful.

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ADSORPTION

A Tool in the Preparation of High-Purity Saturated Hydrocarbons

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Mixtures of isomeric saturated hydrocarbons, including geometric isomers, can be separated by adsorption on silica gel or activated carbon; activated alumina gives very little separation. Data are given on the separation of many binary synthetic mixtures, including paraffin-paraffin, paraffin-naphthene, and naphthene-naphthene types. Most of these systems give S-type isotherms on silica gel and U-type isotherms on carbon. The effect of hydrocarbon type and molecular weight on adsorbability is discussed. The theoretical basis for the results obtained is considered; they may be reasonably explained in terms of Freundlich adsorption isotherms. Material of high purity may be obtained from many commercially available or synthetic hydrocarbons by the use of adsorption. 2,3,3-Trimethylpentane and 2,2,3-trimethylbutane were obtained in better purity than was previously possible by other methods. Unsaturated and high-molecular-weight hydrocarbons may also be separated by adsorption. Its rather wide applicability, speed, and the use of very simple and inexpensive apparatus make adsorption one of the most powerful and convenient tools available for the separation and purification of saturated hydrocarbons.

DURING the past decade the use of adsorbents, particularly silica gel, for the separation of hydrocarbons of different chemical types has become rather widespread. Previous work has shown that for hydrocarbons of similar molecular weight, the adsorbability, in general, increases with the number of double bonds per molecule. Thus, for example, small amounts of olefins or aromatics are removed from saturated hydrocarbons by percolation through silica gel.

Silica gel has also been used where it has been desired to remove small amounts of nonhydrocarbon impurity from hydrocarbons.

The possibility that saturated hydrocarbons, or more broadly that hydrocarbons of the same degree of unsaturation, could be separated from each other by means of adsorption has received little attention. [Since this manuscript was prepared, two papers discussing the separation of saturated hydrocarbons by adsorption have appeared (*7*, *17*).] In 1933, Hofmeier and Meiner (*13*) reported that a mixture of paraffins and naphthenes was not fractionated by silica gel. In 1935, Mair and White (*18*) percolated mixtures of *n*-heptane–methylcyclohexane, 2,2,4-trimethylpentane–methylcyclohexane, and *n*-octane–"nonanaphthene" through silica gel. In each case the concentration of naphthene was 10% by volume. It was found that in each experiment the naphthene was preferentially adsorbed.

Mair and White also percolated a 50-50 volume % mixture of *n*-nonane and *n*-tetradecane through silica gel, and found the *n*-nonane to be preferentially adsorbed. However, they reported no attempts to separate from each other two isomeric paraffins or naphthenes.

Several years later Willingham (*25*) reported on the separation by adsorption of hydrocarbons of high molecular weight. While aromatics were separable from paraffins or naphthenes, and a monocyclic aromatic from a dicyclic one, no separation at all was observed from a mixture of 10 weight % 5-(2-decahydronaphthyl)-docosane with *n*-dotriacontane.

In the first part of this paper the process of adsorption is extended to the separation of a number of mixtures of paraffin isomers or naphthene isomers as well as to paraffin-naphthene mixtures and to the effect of concentration on relative adsorbability. The results indicate a new general application of adsorption: the purification to a high purity of saturated hydrocarbons which contain (as is often the case) small amounts of isomeric or closely related saturated hydrocarbon impurity. The second part presents the results obtained in the purification of a number of hydrocarbons by adsorption.

In saturate-olefin or saturate-aromatic mixtures, the olefin or aromatic is adsorbed over the complete concentration range, and plotting the adsorption isotherm over the range of 0 to 100% unsaturate gives rise to what is commonly termed a U-type isotherm. However, a study of the effect of concentration on adsorbability in binary mixtures of saturated hydrocarbons on silica gel has disclosed the fact that in most cases each component is adsorbed over a portion of the concentration range, giving rise to what is often termed an S-type isotherm.

By way of illustration the results of percolating *n*-heptane–methylcyclohexane mixtures of various initial concentrations through 84 grams of 28- to 200-mesh silica gel in a column 38 × 0.5 inches at 0° to 2° C. are shown in Figure 1. An excess of hydrocarbon mixture (100 ml.) was added in each case. Methylcyclohexane is adsorbed from a mixture containing 10% of this hydrocarbon, confirming the earlier observation (*18*); however, more *n*-heptane is adsorbed from a 10% *n*-heptane solution than methylcyclohexane in the former case.

THEORETICAL CONSIDERATIONS RELATING TO S-TYPE ISOTHERMS

If an excess of a given binary mixture is poured through a column of adsorbent, the first portion of percolate will be richer in the component less easily adsorbed. After passage of a certain volume, the composition of the filtrate returns more or less sharply to the initial value and further portions of the mixture pass through unchanged.

The volume of hydrocarbon preferentially adsorbed can be calculated by a summation over all percolate fractions which differ in concentration from the charge to the column according to the equation

$$V = \frac{v(C_0 - C)}{100} \qquad (1)$$

where V is the volume adsorbed, C_0 the original solute concentration and C the concentration of the given cut, both expressed in volume per cent, and v the volume of the given cut. This volume is proportional to the area bounded by the line representing the

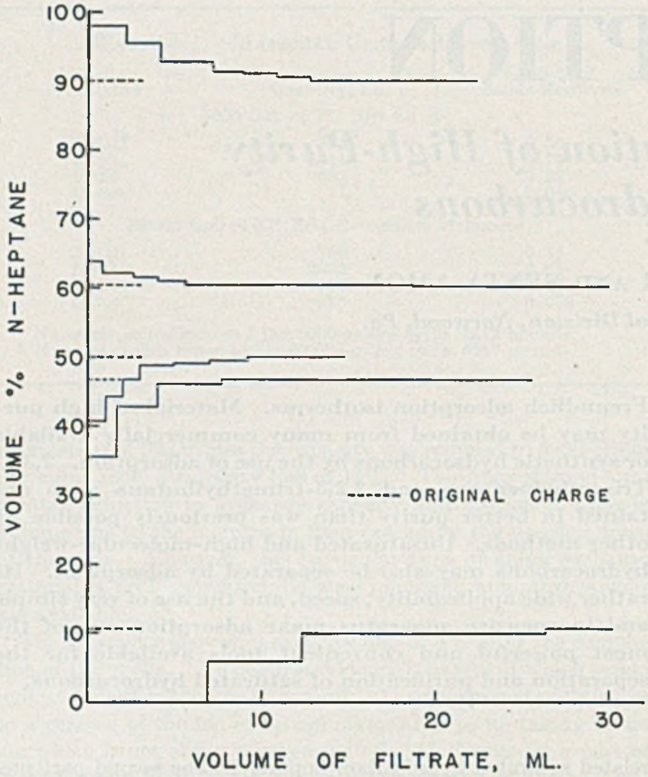


Figure 1. Fractionation of n-Heptane–Methylcyclohexane Mixtures of Various Initial Concentrations by Silica Gel

initial composition, the curve of composition versus volume of filtrate, and the composition axis.

The amount of preferential adsorption as calculated by Equation 1 is only an apparent value and not the true adsorption, as it neglects the change in volume caused by adsorption of the solute, as well as considering the amount of "solvent" adsorbed to be zero. In systems where the components do not greatly differ in adsorbability, such as those dealt with here, the latter assumption is considerably in error. In a solution of A and B whenever the ratio of the true adsorption of component A to that of component B becomes less than the ratio of A/B in solution, B will be apparently adsorbed, even though actually there is considerably more A than B in the adsorbed phase.

Correction for the change in volume caused by adsorption of the solute is relatively simple, as has been shown by Bartell and Sloan (*2*, *3*); and may be made by replacing the denominator of Equation 1 by $100-C_0$. However, in a system exhibiting an S-type isotherm, this correction becomes rather arbitrary unless sufficient data to permit correction for "solvent" adsorption are also available. Equation 1 is adequate for the comparison of the relative adsorption in various binary systems and on different adsorbents and is therefore employed in this paper.

The adsorption isotherm for the n-heptane–methylcyclohexane system calculated as above from the data in Figure 1 is shown in Figure 2. It is of typical S-shape, with the point of zero selectivity at about 57% n-heptane by volume (53.5 mole %). Each component is preferentially adsorbed over the region in which it is present in smallest amount; or stated otherwise, each component is negatively adsorbed in the region in which its concentration approaches 100%. This is a general characteristic of systems exhibiting S-type isotherms.

Bartell and co-workers (*2*, *3*) have shown how, by combining two modified Freundlich equations, the apparent adsorption isotherm can be calculated over the complete concentration range in systems exhibiting S-type isotherms. If we assume that the absolute adsorption of each component of a binary mixture follows the Freundlich isotherm $\frac{V}{m} = kc^n$ (where $n < 1$) throughout the whole concentration range, and further that the two components are equally adsorbable in the sense that the isotherms for each component dissolved in the other are identical, it can easily be shown using the equation of Bartell and Sloan that the curve for the apparent adsorption will be S-shaped, and further that the two loops of the S will be equal and symmetrical, each component being preferentially adsorbed over the region in which its concentration is 0 to 50%.

Considering now the effect of exponent n in the Freundlich isotherm upon a system in which the two components are equally adsorbed as defined above, it is apparent that when $n = 1$ (the so-called linear isotherm) there will be no preferential adsorption at any concentraion—i.e., the S is reduced to a straight line. In general, reducing the value of n will shift the points of maximum apparent adsorption toward the extremes in composition and increase the amount of selective adsorption.

The above considerations therefore lead to the conclusion that whenever two liquids have nearly equal adsorbabilities, and the adsorption isotherms are of the Freundlich type, with $0 < n < 1$, their mixtures should exhibit an S-type isotherm, and each component will be preferentially adsorbed in the region of low concentration. As a result of this fact, either component can be freed from small amounts of the other by percolation through a column of adsorbent, the purified material being in the first portion of the percolate. This is the basis for the rather wide applicability of silica gel to the purification of saturated hydrocarbons.

If one component is more strongly adsorbed than the other, it will be preferentially adsorbed over more than 50% of the concentration range. The greater the disparity in adsorbability, the greater will be the difference in size of the two loops of the S; when the difference in adsorbability becomes sufficiently great one loop will entirely disappear, giving rise to a U-type isotherm.

These conclusions are not limited to systems whose isotherms obey the Freundlich equation. Any type of isotherm which is concave to the composition axis will result in a qualitatively similar picture.

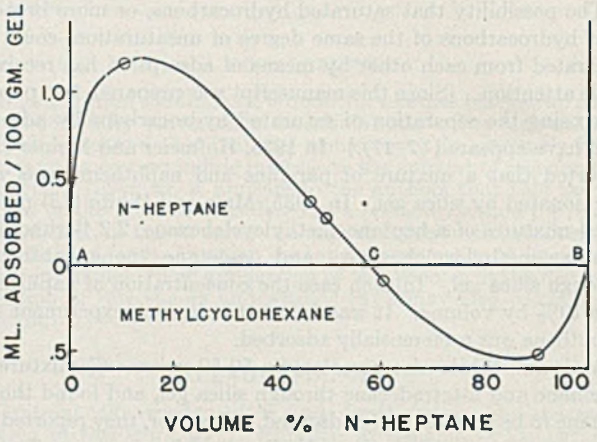


Figure 2. Isotherm (0° C.) for n-Heptane–Methylcyclohexane on Silica Gel

In systems whose components differ considerably in density or molecular weight, the shape of the isotherm will depend on the choice of volume, weight, or mole fractions as the units for expressing the composition. In this paper volume fraction is employed for convenience.

While the percolation of an excess of a given hydrocarbon mixture through an adsorption column has the advantage of simplicity, a greater degree of separation may be obtained in some cases if the quantity of hydrocarbon mixture is reduced to an amount sufficient to wet perhaps 50% of the column and, when the liquid level just reaches the top of the adsorbent, a suitable desorbing liquid is added. The desorbing liquid forces the hydrocarbon portion down the column, during which process it is fractionated according to the adsorbability of its components. The first portion of hydrocarbon filtrate is richer in the least adsorbed component than the charge, while the last portion of the hydrocarbon filtrate, just before the desorbing liquid reaches the bottom of the column, is richer in the most strongly adsorbed component. If a given binary mixture exhibits a U-type isotherm and the separating power of the adsorbent column is sufficiently great, a portion of each component may be obtained in substantially pure form. Thus, Mair (*16*), using this technique, has shown that a mixture of paraffins, naphthenes, olefins, and aromatics can be separated rather sharply into a paraffin plus naphthene portion, an olefin portion, and an aromatic portion.

In a binary system which exhibits an S-type isotherm, however, it is not possible to obtain both pure components starting with a given mixture, regardless of the separating power of the column. Referring to Figure 2, a mixture with composition between *C* and *B* could be separated into pure *n*-heptane and a mixture with composition *C*, while similarly a mixture initially between *A* and *C* could be separated into mixture *C* and pure methylcyclohexane. If the mixture were initially of composition *C*, no separation would be observed. The analogy of this situation to that of a constant-boiling mixture in distillation is obvious.

The position of the point of zero selectivity in a given case thus determines over what range of concentration a practical degree of separation can be obtained. The initial composition should preferably be substantially different from this composition. If the point of zero selectivity with a given adsorbent happens to fall near one end of the concentration scale, say at 95% of component *A*, then component *A* cannot be obtained in a state of high purity by the use of that adsorbent unless by other means the purity can be raised to 96 or 97%. Even then the amount of selective adsorption would be small.

There are a number of possible methods by which a mixture whose composition corresponds to the point of zero selectivity on a given adsorbent could be resolved into two portions, each of which could then be separated on that adsorbent into one or other of the pure components. Among these are:

1. Distillation (with or without entrainer)
2. Solvent extraction
3. Adsorption, using an adsorbent of different adsorptive properties
4. A change in the temperature of percolation. In many cases it would be expected that the effect of temperature on the adsorbability of the two components would be sufficiently different to alter the point of zero selectivity
5. Dilution with a third component separable by distillation, such that the adsorbabilities of the first two components are changed by different amounts

TABLE I. SELECTIVE ADSORPTION IN PARAFFIN-PARAFFIN SYSTEMS

Component A	Component B	Adsorbent	Equilibrium Concn., % of A	Component Adsorbed	Ml. Adsorbed per 100 Grams of Adsorbent	Composition of Point of Zero Selectivity, Vol. % (Approx.)
n-Heptane	2,4-Dimethylpentane	S[a]	6.0 94.5	A B	0.41 0.25	....
n-Heptane	2,3-Dimethylpentane	S	94.5	B	0.30	....
n-Heptane	2,2,4-Trimethylpentane	C	10.0 90.0	A A	>6.8 2.0	U-type, A ads.
2,4-Dimethylpentane	2,2,3-Trimethylbutane	S	10.0 90.0	A A	1.3 0.12	95–100% A
2,4-Dimethylpentane	2,2,3-Trimethylbutane	C	7.0 90.0	A A	1.7 0.70	95–100% A
2,4-Dimethylpentane	2,3-Dimethylpentane	S	10.0 90.0	A	0.45 0	90% A
2,4-Dimethylpentane	2,3-Dimethylpentane	C	13.0 91.0	B B	1.8 0.21	95–100% B
2,2,4-Trimethylpentane	2,3,3-Trimethylpentane	S	10.0 90.0	A A	1.3 0.18	95–100% A
n-Octane	2,2,4-Trimethylpentane	S	10.0 51.7 90.0	A A B	1.4 0.29 0.36	70% A
n-Octane	2,2,4-Trimethylpentane	C	10.0 86.0 91.9	A A A	9.2 3.7 2.2	U-type, A ads.
n-Octane	2,2,4-Trimethylpentane	A	6.6 86.9	A B	0.06 0.08	~50% A
n-Heptane	*n*-Pentadecane	S	10.0 90.0	A A	0.97 1.1	U-type, A ads.
n-Heptane	*n*-Hexadecane	C	10.0 90.0	B B	0.68 >7.6	U-type, B ads.
n-Heptane	*n*-Hexadecane	A	10.0 90.0	 B	0 0.14	90% B
n-Octane	*n*-Decane	S	11.7 90.3	A A	0.46 0.17	U-type, A ads.
n-Octane	*n*-Decane	C	10.0 90.0	B B	0.51 1.6	U-type, B ads.
n-Hexane	2,2,5-Trimethylhexane	C	9.2 50.4 91.1	A A A	74.2 5.4 3.1	U-type, A ads.

[a] S silica gel, C carbon, A alumina.

SEPARATION OF SYNTHETIC MIXTURES BY ADSORPTION

EXPERIMENTAL DETAILS. In order to determine the scope and possible limitations of adsorption as a procedure for purifying hydrocarbons, a considerable number of synthetic mixtures were prepared and percolated through adsorbent columns.

For this work a glass tube 0.5 inch in diameter was provided with a sintered-glass plate near the bottom and a reservoir at the top (column A). It was filled with adsorbent to a height of 36 to 38 inches; the column and reservoir were provided with a jacket through which ice water was circulated; the temperature of the efflux water was usually 3° to 6° C. The silica gel used was 28- to 200-mesh (Davison Chemical Corp. 659528-2000), 84-grams being used to fill the column. The activated carbon was 60- to 90-mesh (Columbia activated carbon grade L); 50 grams were used to fill the column to a height of about 34 inches. In the experiments with alumina 140 grams of a mixture of 3 parts of 20- to 40-mesh (Grade F-1, Aluminum Ore Co.) and 1 part of −80 mesh (grade A, Aluminum Ore Co.) was used.

The adsorbents were poured into the column and packed by tapping the outside of the column with a rubber mallet until no further change in level occurred.

The materials used were for the most part of known high purity (98% or better, often 99%+) and were percolated through silica gel prior to use. The first fractions were examined by refractive index to make sure that impurities adsorbable on silica gel had caused no substantial change. In many cases commercially available hydrocarbons were further purified by adsorption prior to use.

The dicyclohexyl was prepared by the hydrogenation of recrystallized diphenyl; the *n*-pentadecane by the hydrogenation of recrystallized palmitic acid. The "amylcyclohexane" was possibly a mixture of several isomers, obtained by hydrogenating the 192–3° C. fraction of commercial "amylbenzene," followed by

TABLE II. SELECTIVE ADSORPTION IN PARAFFIN-NAPHTHENE SYSTEMS

Component A	Component B	Adsorbent	Equilibrium Concn., % of A	Component Adsorbed	Ml. Adsorbed per 100 Grams of Adsorbed	Composition of Point of Zero Selectivity, Vol. % (Approx.)
2,2-Dimethylbutane	Cyclopentane	S	..	..	....	97-100% B[a]
2,2-Dimethylbutane	Cyclopentane	C	..	..	....	95-100% B[a]
n-Hexane	Methylcyclopentane	S	10.7	A	0.27	55-60% B
			50.0	B	0.08	
			90.7	B	0.31	
n-Hexane	Methylcyclopentane	C	10.0	A	3.1	U-type, A ads.
			89.7	A	0.50	
n-Hexane	Cyclohexane	S	11.2	A	>1.8	70% A
			50.7	A	1.1	
			90.0	B	0.27	
n-Hexane	Cyclohexane	C	7.4	A	>2.6	U-type, A ads.
			90.0	A	0.66	
2,2-Dimethylbutane	Cyclohexane	S	10.0	A	0.37	65% B
			47.7	B	0.12	
			90.0	B	1.9	
2,2-Dimethylbutane	Cyclohexane	C	0.5	A	0.10	98% B
			10.0	B	Minute	
			90.0	B	1.9	
n-Heptane	Methylcyclohexane	S	10.6	A	1.2	57% A
			46.7	A	0.37	
			50.0	A	0.29	
			60.5	B	0.11	
			90.0	B	0.52	
n-Heptane	Methylcyclohexane	C	10.0	A	4.2	U-type, A ads.
			90.0	A	0.78	
			97.0	A	0.22	
2,2,4-Trimethylpentane	Methylcyclohexane	S	10.0	A	0.13	75% B
			49.5	B	0.52	
			90.0	B	0.56	
2,2,4-Trimethylpentane	Methylcyclohexane	C	10.0	B	0.42	U-type, B ads.
			90.0	B	2.2	
2,2,4-Trimethylpentane	Methylcyclohexane	A	9.9	B	0.01	95-100% B
			90.0	B	0.16	
2,4-Dimethylpentane	Cyclohexane	S	10.0	A	1.1	70% A
			50.0	A	0.79	
			90.0	B	0.29	
2,2,3-Trimethylbutane	Cyclohexane	S	10.0	A	0.41	70% B
			50.0	B	0.33	
			90.5	B	0.75	
2,2,3-Trimethylbutane	Cyclohexane	C	10.0	A	0.61	65% B
			48.0	B	0.20	
			89.5	B	2.0	
n-Octane	Ethylcyclohexane	S	10.0	A	0.36	70% B
			50.6	B	0.38	
			90.0	B	0.55	
n-Octane	Ethylcyclohexane	C	10.0	A	>3.5	98-100% A
			90.7	A	0.46	
			95.6	A	0.01	
n-Octane	Ethylcyclohexane	A	9.6	A	0.13	U-Type, A ads.
			89.7	A	0.09	
2,2,4-Trimethylpentane	Ethylcyclohexane	S	3.0	..	0	90-100% B
			10.0	B	0.1	
			50.0	B	0.67	
			90.0	B	0.65	
n-Decane	Amylcyclohexane	S	10.0	A	0.22	70% B
			50.0	B	0.85	
			87.7	B	0.65	
n-Decane	Amylcyclohexane	C	90.3	A	0.50	U-type, A ads.
n-Dodecane	Amylcyclohexane	C	89.7	A	0.60	U-type, A ads
n-Dodecane	Dicyclohexyl	C	10.0	A	4.3	U-type, A ads.
			90.0	A	0.62	
n-Pentadecane	Dicyclohexyl	S	10.0	A	1.4	60% A
			90.0	B	0.88	
2,2-Dimethylbutane	Ethylcyclohexane	S	10.0	A	0.24	78% B
			47.1	B	0.77	
n-Octane	Cyclohexane	S	55.5	A	0.26	64% A
			80.3	B	0.54	
n-Decane	Cyclohexane		50	B	0.29	
n-Dodecane	Dicyclohexyl	S	10	A	1.08	56% A
			55	A	0.11	
			90.5	B	0.50	

[a] Estimated from percolation of impure cyclopentane containing several per cent 2,2-dimethylbutane.

fractional distillation of the product. The 2-butylcyclopentylcyclopentane was synthesized in these laboratories by A. P. Stuart.

In most cases 49 ml. of hydrocarbon mixture were added to the column, and when this had completely entered the adsorbent, a desorbing liquid was added to force the hydrocarbon down the column. When silica gel or alumina was used, methanol or ethanol was usually employed as the desorbing liquid, though occasionally benzene was used; for activated carbon, benzene was used for saturated hydrocarbons and olefins, and α-methylnaphthalene for aromatics. In a few cases the availability of the hydrocarbons restricted the volume of mixture to 24 ml.

The filtrate was collected in appropriate fractions up to the point at which the desorbing agent appeared. The composition was determined by refractive index, using a Valentine Abbe refractometer where the difference in n_D^{20} of the components was 0.0080 or more. In several cases with an index difference of 0.0040 a special spectrometer-type refractometer sensitive to 0.00001 or better was employed. The sample was placed in a metal 75° prism with glass windows. In a few cases, the composition was determined by measurement of freezing point; samples as small as 4 ml. could be analyzed in this way, when a calibrated 5-junction copper-constantan thermocouple was employed for temperature measurement.

The rate of percolation in the silica gel experiments was about 1 to 2 ml. per minute. The initial rate under gravity flow was appreciably faster than this; as the liquid front progressed down the column the rate of flow decreased, so that in most cases slight nitrogen pressure was used to keep the rate of travel from falling below 1 cm. per minute.

The coarser size of the activated carbon resulted in an average rate of about 1.5 to 2 cm. per minute under gravity flow. The filtrate was collected at 1 to 1.5 ml. per minute. The rate for activated alumina was about the same as for silica gel.

RESULTS. The results on the separation of synthetic mixtures are given in Tables I to III. In column 6, the extent of preferential adsorption as calculated by Equation 1 is given for each concentration studied. The data permit an approximate location of the point of zero selectivity for those systems exhibiting S-type adsorption curves (column 7). In many cases the uncertainty in this point is of the order of 5%, though occasionally it may be greater.

Table III. Selective Adsorption in Naphthene-Naphthene Systems

Component A	Component B	Adsorbent	Equilibrium Concn., % of A	Component Adsorbed	Ml. Adsorbed per 100 Grams of Adsorbent	Composition of Point of Zero Selectivity, Vol. % (Approx.)
Cyclopentane[a]	Cyclohexane	S	10.0 90.0	A A	>0.53 0.34	U-type, A ads
Cyclopentane[a]	Cyclohexane	C	10.0 90.0	A	1.1 Little change	90–100%
Methylcyclopentane	Cyclohexane	S	10.0 90.0	A A	0.58 0.37	U-type, A ads
Methylcyclopentane	Cyclohexane	C	10.0 90.9	A A	2.1 0.90	U-type, A ads
Cyclohexane	Ethylcyclohexane	S	10.0 56.0 90.0	.. B B	0 0.72 0.10	70% B
Cyclohexane	Ethylcyclohexane	C	14.3 88.6	B B	1.7 >3.4	U-type, B ads
Methylcyclohexane	Ethylcyclohexane	S	50.5	A	0.13	.....
Methylcyclohexane	Ethylcyclohexane	C	10.0 90.0	B B	1.0 2.2	97–100% B
Methylcyclohexane	Ethylcyclohexane	A	10.0 91.2	A B	0.01 0.13	85% B
Methylcyclohexane	Amylcyclohexane	S	9.9 49.6 90.1	A A B	0.29 0.22 0.25	65% A
cis-Decalin	*trans*-Decalin	S	..	..	....	98–100% B
Amylcyclohexane	Dicyclohexyl	S	10.0 90.0	A A	>0.48 0.68	98–100%
2-Butylcyclopentylcyclopentane	Dicyclohexyl	S	10.0 90.0	A A	0.61 0.10	95–100% A
Cyclohexane	Dicyclohexyl	C	10.0 90.0	B B	0.73 >4.3	U-type, B ads
trans-Decalin	Dicyclohexyl	C	11.0	A	0.27	

[a] Contained several per cent of 2,2-dimethylbutane.

This stated uncertainty applies only to the particular lot of silica gel used for a given system. The relative adsorbabilities of various saturated hydrocarbon types vary somewhat from lot to lot. For example, in the system *n*-heptane–methylcyclohexane the point of zero selectivity shown in Figure 2 is at 57% *n*-heptane; for two other more recently obtained lots the point of zero selectivity was found to be at 50 and 53% *n*-heptane, respectively. The extent of this variation is insufficient to affect conclusions as to the effect of hydrocarbon structure on adsorbability except in those few cases of nearly equal adsorbabilities.

For a number of systems, the composition of the point of zero selectivity is given as "95 to 100% *A*." In most of these instances it is probable that the isotherm is of a U-type but in the absence of experimental data at concentrations near 100% *A*, the possibility that the curve is S-type, with component *B* being adsorbed over a few per cent of the concentration range, cannot be excluded.

In some of the experiments, the absence of a plateau in the volume-composition curve at the initial concentration indicated that the quantity of hydrocarbon mixture was not sufficient to saturate the adsorbent. As a result, the true adsorption at equilibrium would be somewhat greater than the value calculated from the experimental curve. Such values in column 6 are prefixed by ">". An extreme example of such lack of saturation is the curve for 10% *n*-hexane in cyclohexane. Figure 3 illustrates the type of volume-composition curves obtained when a desorbing liquid such as alcohol is used to force the hydrocarbon portion through the column of silica gel, and compares the adsorbability of cyclohexane with *n*-hexane, neohexane (2,2-dimethylbutane), and methylcyclopentane. When a 10% cyclohexane–90% methylcyclopentane mixture is percolated through silica gel, the first portion of filtrate is of lesser purity than the charge, but the final portion of hydrocarbon just preceding the appearance of desorbing liquid is of increased purity. This is an example of a system with a U-type isotherm, and while theoretically it is possible to obtain pure methylcyclopentane in the last portion of filtrate from a column of sufficient separating power, in practice it is more difficult than when the purified hydrocarbon is in the first portion of filtrate. The considerable heat produced at the alcohol-hydrocarbon interface disturbs the separation; the alcohol tends to overrun the hydrocarbon somewhat, thus contaminating the purest portion of the filtrate; and impurities desorbed from the gel by the alcohol add to the contamination. There is also the possibility that some of the less strongly adsorbed component is held so tightly on the most active centers of the adsorbent that it is not readily desorbed by the more strongly adsorbed component, but is displaced by the alcohol. These difficulties are, of course, proportionately more serious as the amount of preferential adsorption decreases. Where there

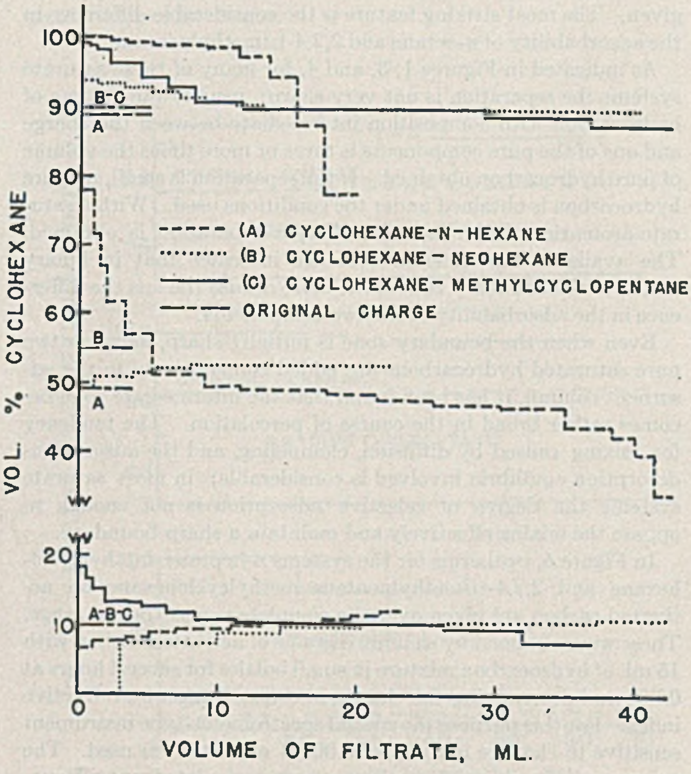


Figure 3. Separations Produced in Several Binary Systems by Silica Gel

Column A, 84 grams of gel, 25-ml. charge for cyclohexane–*n*-hexane at 10 and 89% concentration
49-ml. charge for other systems

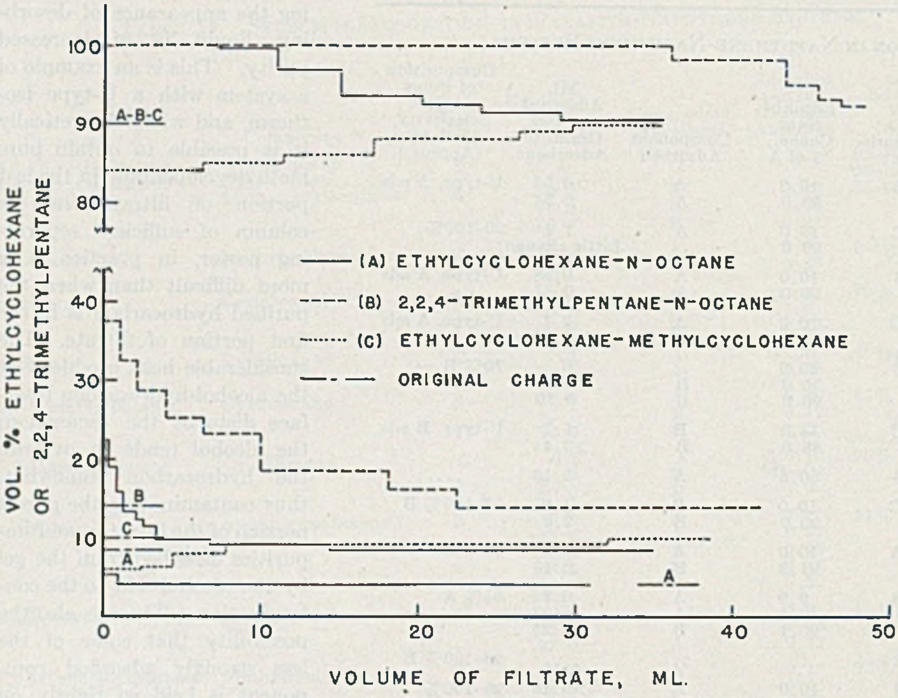


Figure 4. Separations Produced in Several Binary Systems by Activated Carbon

Column A, 50 grams of carbon, 150-ml. charge for 2,2,4-trimethylpentane–*n*-octane at 90% concentration
49-ml. charge for other systems

is a considerable difference in adsorbability, the more strongly adsorbed component can be obtained in substantially pure form in the last portion of hydrocarbon filtrate, as has been shown by Mair (*16*) for mixtures of aromatic and saturated hydrocarbons.

In Figure 4, a few curves obtained on activated carbon are given. The most striking feature is the considerable difference in the adsorbability of *n*-octane and 2,2,4-trimethylpentane.

As indicated in Figures 1, 3, and 4, for many of these saturate systems the separation is not very sharp; usually the volume of hydrocarbon with composition intermediate between the charge and one of the pure components is three or more times the volume of pure hydrocarbon obtained. If the separation is small, no pure hydrocarbon is obtained under the conditions used. With a saturate-aromatic mixture a much sharper separation is obtained. The available experimental evidence indicates that in binary mixtures the boundary zone is the more diffuse the less the difference in the adsorbability of the two components.

Even when the boundary zone is initially sharp, as when two pure saturated hydrocarbons are added consecutively to the adsorbent column, it has been found that the intermediate zone becomes rather broad in the course of percolation. The tendency for mixing caused by diffusion, channeling, and the adsorption-desorption equilibria involved is considerable; in most saturate systems the degree of selective adsorption is not enough to oppose the mixing effectively and maintain a sharp boundary.

In Figure 5, isotherms for the systems *n*-heptane–methylcyclohexane and 2,2,4-trimethylpentane–methylcyclohexane on activated carbon are given over the complete concentration range. These were obtained by shaking 5 grams of activated carbon with 15 ml. of hydrocarbon mixture in small bottles for several hours at 0° C. and determining the change in concentration by refractive index. For this purpose the special spectrometer-type instrument sensitive to changes in index of 0.00001 or better was used. The amount of adsorption from these curves (calculated using Equation 1) is somewhat greater than at the corresponding concentrations as given in Table II, which may indicate that the rate of percolation in the adsorption columns did not allow equilibrium to be fully attained.

While for a number of the systems in Tables I to III the boiling points are sufficiently different to make the components easily separable by distillation, in the following cases the boiling point differences (° C.) are small: 2,2,3-trimethylbutane–cyclohexane, 0.13°; 2,4-dimethylpentane–cyclohexane, 0.23°; 2,4-dimethylpentane–2,2,3-trimethylbutane, 0.36°; *n*-heptane–2,2,4-trimethylpentane, 0.81°; 2,2,4-trimethylpentane–methylcyclohexane, 1.7°; and *n*-heptane–methylcyclohexane, 2.51° (*1*).

Factors Affecting Relative Adsorbability. Based on the data in Tables I to III the following conclusions appear to be permissible:

The majority of the systems studied have S-type isotherms on silica gel, but on activated carbon they have preponderantly U-type isotherms. The data on activated alumina are too incomplete to permit a generalization. In some of the systems with U-type curves on silica gel, it was somewhat surprising to find that the differences in adsorbability of the two components were sufficient to result in this type of isotherm. Such, for example, were the systems *cis*-decalin–*trans*-decalin and 2,2,4-trimethylpentane–2,3,3-trimethylpentane.

In most of the systems studied, the component more strongly adsorbed on silica gel was also more strongly adsorbed on carbon and alumina. Usually, however, the isotherm was S-type on silica gel and U-type on carbon. There are some exceptions to the first generalization; thus in the system 2,4-dimethylpentane–2,3-dimethylpentane the former is adsorbed over 90% of the concentration range on silica gel, whereas on carbon the latter is adsorbed over 95 to 100% of the concentration range. The systems *n*-octane–ethylcyclohexane, *n*-decane–"amylcyclohexane," and *n*-hexane–methylcyclopentane also show this difference in selectivity between carbon and silica gel.

Both on silica gel and carbon, adsorbability in the liquid phase is in part a function of molecular weight. However, for silica gel the adsorbability in a homologous series appears in general to decrease as molecular weight is increased (certain alkylcyclohexanes excepted), whereas for carbon it is the reverse. The data for the system *n*-heptane–*n*-hexadecane on alumina, in which the latter is adsorbed over about 90% of the concentration range, indicate that alumina in this respect is similar to carbon. The effect of molecular weight on adsorbability is apparently more pronounced on carbon than on silica gel.

In vapor-phase adsorption, the boiling point or critical temperature becomes important, and the amount of adsorption increases with the ease of liquification of the vapor. Turner (*23*) has found that in the fractionation of the gaseous paraffin hydrocarbons from methane to pentane by activated carbon the hydrocarbons are desorbed in the order of their boiling points. That the same is true for silica gel is indicated by the work of Edse and Harteck (*8*). The authors have found that when a propane-pentane vapor mixture is passed through silica gel the propane emerges first.

The work of Claesson (*5*) has only recently become available to the authors. This paper includes data on the separation of a number of saturated hydrocarbons, including several heptane and octane isomers, on activated carbon in the vapor phase, using a method termed "displacement development." He found that when the adsorption affinity was plotted against boiling point, all

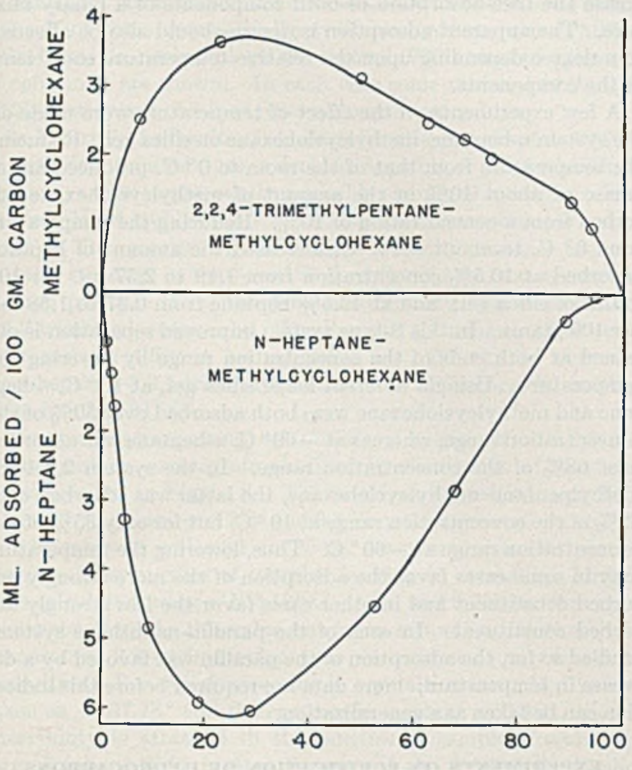


Figure 5. Isotherms (0° C.) for Systems *n*-Heptane–Methylcyclohexane and 2,2,4-Trimethylpentane–Methylcyclohexane on Activated Carbon

aliphatic hydrocarbons fell on a smooth curve, the adsorption affinity increasing with boiling point. Cyclohexane and methylcyclohexane had somewhat greater adsorption affinities than aliphatic hydrocarbons of the same boiling point. Hence close-boiling paraffin isomers would be difficult to separate by vapor-phase adsorption.

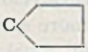
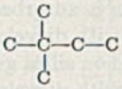
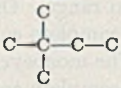
No such close relation of boiling point and adsorbability is found in the liquid phase. *n*-Hexane (b.p. 69°) is adsorbed over the complete concentration range in mixtures with 2,2,5-trimethylhexane (b.p. 124°) on activated carbon. In the systems *n*-heptane–2,2,4-trimethylpentane and 2,4-dimethylpentane–2,2,3-trimethylbutane the lower-boiling component is adsorbed over 95% or more of the concentration range on activated carbon, though here the differences in boiling point are only 0.81° and 0.36° C., respectively.

In at least the lower members of the *n*-alkylcyclohexane series, adsorbability increases as the molecular weight increases on silica gel. Ethylcyclohexane is more strongly adsorbed than cyclohexane or methylcyclohexane; however, methylcyclohexane is somewhat more strongly adsorbed than "amylcyclohexane." Here, increasing paraffinicity is a complicating factor; it is probable, based on the latter system, that with sufficiently great molecular weight differences the lower molecular weight homolog in this series will be preferentially adsorbed.

Some conclusions in regard to the effect of hydrocarbon structure upon adsorbability are indicated in Table IV. Since a change in temperature may alter relative adsorbabilities, the ones given are for temperatures near 5° C. For some preparations of silica gel or activated carbon the order of adsorbability may differ somewhat from that shown.

If we consider the pairs *n*-hexane–cyclohexane, *n*-heptane–methylcyclohexane, *n*-octane–ethylcyclohexane, and *n*-decane–"amylcyclohexane," the paraffin is adsorbed over 70, 57, 30, and 30% of the concentration range, respectively. Thus, above C_8, *n*-alkylcyclohexanes appear to be more strongly adsorbed than the corresponding *n*-paraffin on silica gel, reversing the order for C_6 and C_7. The first two columns of Table IV show the effect of structure on adsorbability above and below C_8 on silica gel.

Table IV. Relative Adsorbability as a Function of Structure in Order of Decreasing Adsorbability

Silica Gel		Activated Carbon
C_6 and C_7	C_8 and above	
	Alkylcyclopentane	C—C—C—C—C—C
C—C—C—C—C—C	Alkylcyclohexane	
	*n*-Paraffin	
	Isoparaffin	

For activated carbon, a somewhat different order of adsorbability is shown than for silica gel. The relative adsorbabilities of the higher homologs are the same as shown in column 3 for the C_8 hydrocarbons. The differences in adsorbability are, however, considerably greater on activated carbon than on silica gel, the case of *n*- and isoparaffins being especially noteworthy in that the degree of adsorption of the *n*-isomer approaches that of an aromatic hydrocarbon. Thus, from 10 volume % solutions in 2,2,4-trimethylpentane, 9.2 ml. of *n*-octane per 100 grams of carbon are adsorbed, compared to about 14 ml. of toluene.

In mixtures of cyclopentane and cyclohexane, the former is probably adsorbed over the complete concentration range on both silica gel and carbon.

The greater ease of adsorption of cyclopentane derivatives as compared with cyclohexane derivatives extends to the dicyclic compounds. Thus 2-butylcyclopentylcyclopentane (a C_{14} naphthene) is apparently adsorbed on silica gel over the complete concentration range in mixtures with dicyclohexyl, in spite of its greater molecular weight.

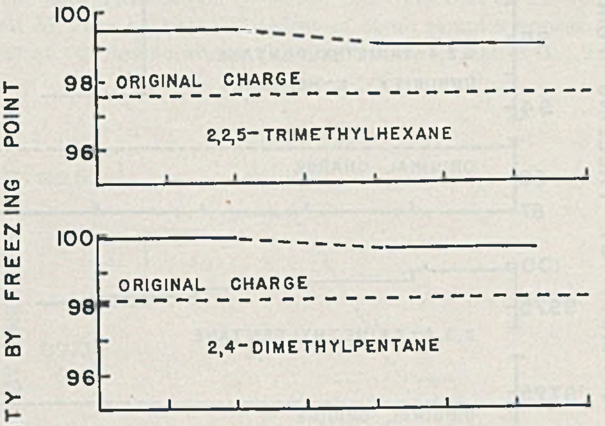


Figure 6. Purification of Three Technical Hydrocarbons by Percolation through Silica Gel

Column B, 750 grams of silica gel, 200-ml. charge

2,4-Dimethylpentane is adsorbed over 90% of the concentration range on silica gel in mixtures with 2,3-dimethylpentane; similarly, 2,2,4-trimethylpentane is adsorbed over 95 to 100% of the concentration range in mixtures with 2,3,3-trimethylpentane. Thus, on silica gel, isoparaffins with branching near the extreme ends of the molecule appear to be most strongly adsorbed.

While *n*-alkylcyclohexanes of more than eight carbon atoms appear to be more strongly adsorbed than the corresponding *n*-paraffin on silica gel, *n*-dodecane is somewhat more strongly adsorbed than dicyclohexyl, being adsorbed over 56.6% of the concentration range. On activated carbon, *n*-dodecane is adsorbed over the complete concentration range in mixtures with dicyclohexyl. The monocyclic amylcyclohexane is adsorbed on silica gel over the complete concentration range in mixtures with dicyclohexyl, a dicyclic compound.

An interesting point is the relative magnitude of the effects of molecular weight and molecular type on adsorbability. On silica gel, *n*-octane is more strongly adsorbed than cyclohexane; however, *n*-decane is less strongly adsorbed than cyclohexane. Ethylcyclohexane is also more strongly adsorbed than 2,2-dimethylbutane. Other systems in which the component of higher molecular weight is more strongly adsorbed on silica gel are *n*-pentadecane–dicyclohexyl, 2-butylcyclopentylcyclopentane–dicyclohexyl, 2,4-dimethylpentane–cyclohexane, and amylcyclohexane–*n*-decane. Thus, a molecular weight difference of two to four carbon atoms is required to offset differences in adsorbability caused by difference in molecular type. A similar situation obtains for activated carbon; *n*-decane–amylcyclohexane, *n*-heptane–2,2,4-trimethylpentane, methylcyclohexane–2,2,4-trimethylpentane, *n*-hexane–2,2,5-trimethylhexane, and cyclohexane–2,2,3-trimethylbutane are examples of systems in which the component of lower molecular weight is more strongly adsorbed.

Effect of Temperature. Since adsorption liberates a considerable amount of heat, lowering the temperature should increase the true adsorption of both components of a binary mixture. The apparent adsorption isotherm should also be affected, to a degree depending upon the relative temperature coefficients of the components.

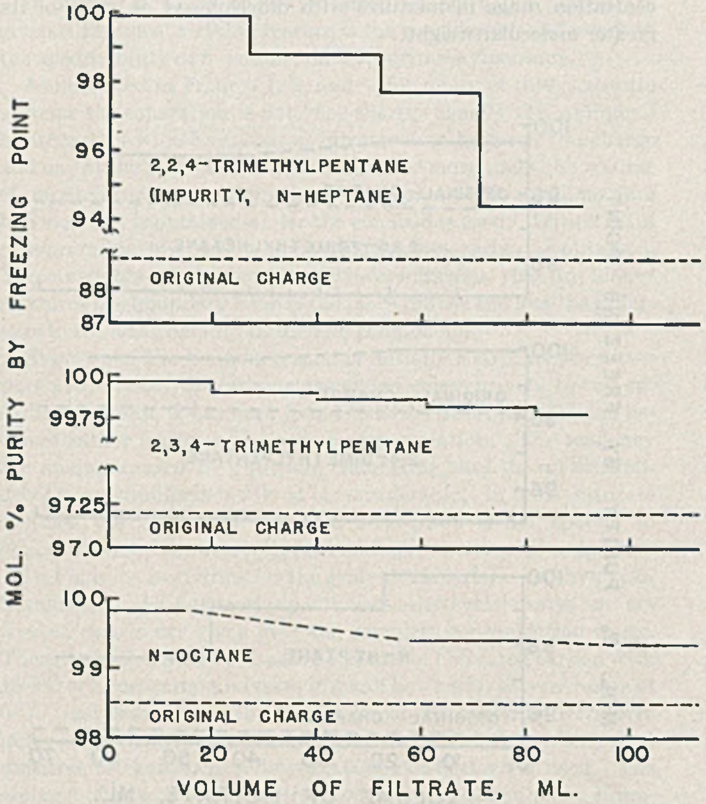


Figure 7. Silica Gel Purification of Three Impure Hydrocarbons

Column B, 780 grams of silica gel, 200-ml. charge for n-octane and 2,2,4-trimethylpentane; 100 ml. for 2,3,4-trimethylpentane

A few experiments on the effect of temperature were made on the system *n*-heptane–methylcyclohexane on silica gel. Reducing the temperature from that of the room to 0° C. produced an increase of about 10% in the amount of methylcyclohexane adsorbed from a concentration of 10%. Reducing the temperature from 0° C. to about −70° C. increased the amount of heptane adsorbed at 10.5% concentration from 1.19 to 2.57 ml. per 100 grams of silica gel; and at 46.5% heptane from 0.37 to 1.58 ml. per 100 grams. In this S-type system improved separation is obtained at both ends of the concentration range by lowering the temperature. Using a different lot of silica gel, at 10° C. *n*-heptane and methylcyclohexane were both adsorbed over 50% of the concentration range, whereas at −60° C. *n*-heptane was adsorbed over 68% of the concentration range. In the system 2,2,4-trimethylpentane–methylcyclohexane, the latter was adsorbed over 82% of the concentration range at 10° C. but for only 35% of the concentration range at −60° C. Thus, lowering the temperature may in some cases favor the adsorption of the more strongly adsorbed constituent and in other cases favor the less strongly adsorbed constituent. In each of the paraffin-naphthene systems studied so far, the adsorption of the paraffin was favored by a decrease in temperature; more data are required before this indication can be taken as a generalization.

EXPERIMENTS ON PURIFICATION OF HYDROCARBONS

Experimental Details. The first purification experiments were carried out in a water-jacketed glass column 1.3 inches in internal diameter and packed to a depth of about 44 to 46 inches with 28- to 200-mesh silica gel (column B). Gel from several lots varying considerably in bulk density was used; the weight of gel to fill the column varied from 675 to 780 grams. Packing of the gel was accomplished by tapping the column with a rubber mallet. A flow of ice water, or cold tap water, through the jacket was maintained during the run; the temperature of the water leaving the jacket was 5° to 10° C. Methyl or ethyl alcohols were added as desorbing agents after the hydrocarbon charge had entered the column. The recovery of hydrocarbon was improved if a few grams of fresh silica gel were added to the column just prior to addition of the alcohol (*16*).

Two columns permitting a gel depth of 8 feet were constructed, one 1.3-inch inside diameter (column C) the other 1-inch inside diameter (column D). These were cooled by flowing a film of water by gravity down the outside surface from a point just below the reservoir at the top of the column. A semiball joint at the bottom of the column made it possible to clean the column in situ after use by removing the lower portion of the joint and washing out the gel by means of a water jet forced up the inside of the column. A long piece of Saran tubing was employed for this purpose. The lower portion of the joint was tapered and a sintered-glass plate sealed as close as possible to the joint itself. A collecting ring for the coolant was placed just above the ball joint.

Columns C and D were used to contain approximately 1650 and 880 grams of 28- to 200-mesh silica gel, respectively; packing was accomplished by tapping as in the other cases. During this process the center portion of the column was supported by clamps; these were removed during use, so that the flow of water down the external surface would be uninterrupted. The column was then supported by clamps on the reservoir at the top of the column and on the collecting ring at the bottom. A rate of 1 to 2 cm. per minute was employed; a nitrogen pressure of a few pounds per square inch was sufficient.

Purities were determined by the freezing point method and are therefore in mole per cent. Unless otherwise stated, a platinum resistance thermometer and Mueller bridge were used for temperature measurement; 55-, 25-, and 10-ml. freezing point tubes were available. Some older data were obtained using a calibrated 5-junction copper-constantan thermocouple and Type K potentiometer; temperatures so measured are probably in error by 0.05° C. or less.

Results. In Figure 6, the data obtained on percolating about 200 ml. of three commercially available hydrocarbons (Phillips Petroleum Co. technical grade) through 780 grams of silica gel in column B are shown. In each case some material of 99.4 to 99.9% purity was obtained (thermocouple apparatus).

In Figure 7, the results of similarly treating a *n*-heptane–2,2,4-trimethylpentane mixture, a synthetic sample of 2,3,4-trimethylpentane, and a commercially available sample of *n*-octane (Connecticut Hard Rubber Co.) are illustrated (thermocouple apparatus). The results with the 2,3,4-trimethylpentane are especially striking, in that over 90% of the charge was recovered in high purity. Here, the principal impurity was identified as 2,3,3-trimethylpentane by the Raman spectrum; these two hydrocarbons differ in boiling point by 1.29° C. In the case of *n*-heptane–2,2,4-trimethylpentane the difference in boiling point is only 0.81° C.

The purification, using column C, of a sample of 2,3,3-trimethylpentane concentrate obtained by distillation of alkylate, is summarized in Figure 8. The principal impurities were 2,3,4-trimethylpentane and 2,3- and 3,4-dimethylhexanes. A charge of 522 ml. was collected in 25-ml. fractions with the results shown. [The purities of samples freezing in crystalline form I were calculated using −100.43° C. as T_{f0} and 0.006 for the cryoscopic constant, *A;* this value was taken assuming that dimethylhexanes and 2,3,4-trimethylpentane were about equally likely as impurities. For samples freezing in crystalline form II, T_{f0} was taken as −107.78° and the cryoscopic constant as 0.046. Some uncertainty is attached to the purities of samples freezing in form I (above 95% purity) because of the formation of solid solutions (*11*).] The first 17 cuts (425 ml.) were then rerun through fresh gel; the cuts were added one at a time in the order obtained, with the results noted in the upper plot. The first cut of this second run had a freezing point of −100.78° (resistance thermometer); by comparison the best lot (A.P.I-N.B.S. grade), obtained by Streiff *et al.* (*21*) employing azeotropic distillation in columns of 135 and 130 theoretical plates, froze at −101.034° C.

After two runs carried out as described above the volume of filtrate exceeding 99% purity is about three times the quantity obtained in the first run—that is, the additional amount obtained in the second run is twice that obtained in the first. Often, the ratio is even more favorable than this and results from the advantage taken of the considerable volume of partially purified hydrocarbon obtained in the initial run. The results (particularly in the first 200 ml. of filtrate) approximate those which would have been obtained in a single percolation through a column twice the height—i.e., 1.3 inches × 16 feet.

The results of the purification of methylcyclopentane (Phillips technical grade, purity 93.7%) in the same column are shown in Figure 9. Two runs were made; 500 ml. were charged to the first run and collected in 25-ml. fractions. The first 16 of these (actual volume 381) were added to fresh gel two at a time; 25-ml. cuts were again collected. The purities obtained in the second run are shown in Figure 9. The first cut is of lesser purity than succeeding ones because of contamination of the silica gel. (Certain lots of silica gel are contaminated as received from the manufacturer. Usually, such gel has a brownish or yellowish tinge; extraction with benzene removes most of the color. Evaporation of the benzene leaves a small amount of a reddish-brown sticky residue.)

Two purifications using column D are shown in Figure 10. In one, 200 ml. of *n*-dodecane (Connecticut Hard Rubber Co.) originally 89.6% pure were percolated through 800 grams of silica gel. The first 70 ml. averaged 99% purity.

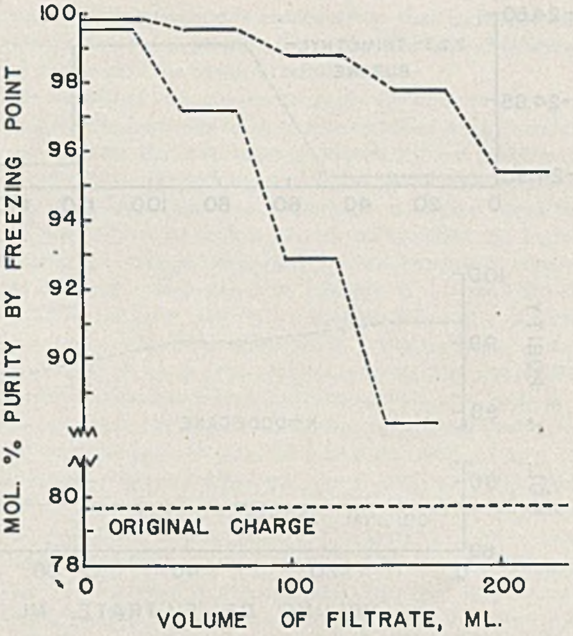


Figure 8. Silica Gel Purification of a 2,3,3-Trimethylpentane Concentrate Obtained by Distillation of Alkylate

Run 1. Column C, 1650 grams of gel, 522-ml. charge. Rate, 5 ml. per min.
Run 2. Column C, 1650 grams of gel, cuts 1 to 17 of run 1 (425 ml.) as charge. Rate, 5 ml. per min.

In the second case, 250 ml. of 2,2,3-trimethylbutane (obtained through the courtesy of General Motors Corp. Research Laboratories Division) were percolated through 850 grams of silica gel, and collected in 25-ml. fractions. The first nine (216 ml.) were added two at a time to 850 grams of fresh gel and again collected in 25-ml. cuts. It was then learned that the gel used in the second run was contaminated with hydrocarbon-soluble material; hence all the fractions were put through a third time, using a new lot of gel, and adding at the end the tenth cut of the first run (total volume 226 ml.). All the first 174 ml. of filtrate froze at temperatures (determined with platinum resistance thermometer) higher than the value calculated by Glasgow *et al.* (*9*) for the pure hydrocarbon (−24.96° C.). The best 50 ml. (cuts 4 and 5) froze at −24.82° (Most of these samples appear to freeze at two temperatures differing by 0.05° to 0.07° C. The

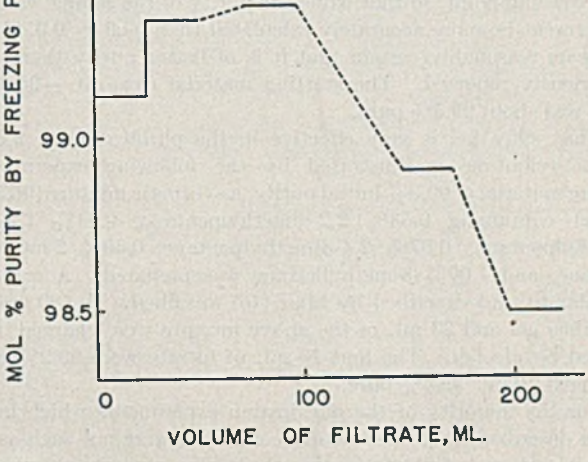


Figure 9. Purification of Technical Methylcyclopentane by Silica Gel

Initial purity 93.7%
Column C, 1650 grams of gel, 381 ml. (cuts from previous run) as charge. Rate, 6 to 8 ml. per min.

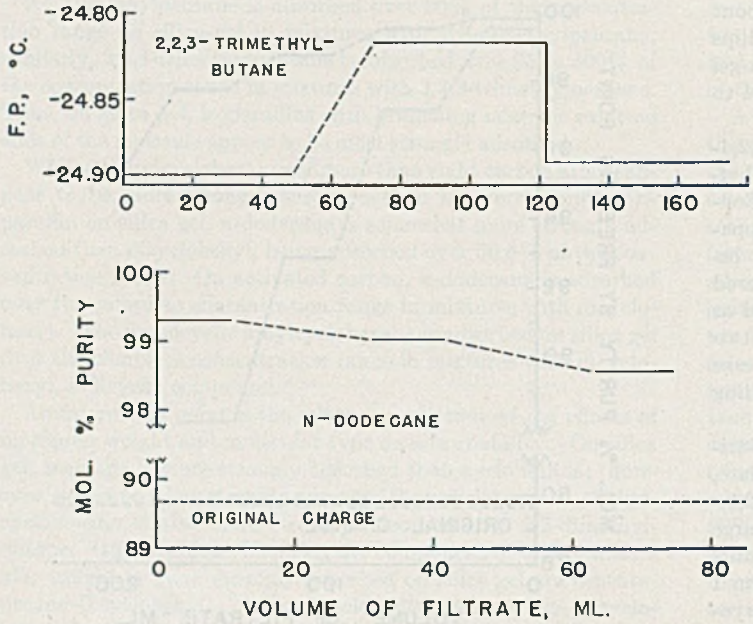


Figure 10. Purification of n-Dodecane and 2,2,3-Trimethylbutane by Silica Gel

2,2,3-Trimethylbutane. Column D, 850 grams of gel, 226-ml. (cuts from previous run) as charge
n-Dodecane. Column D, 800 grams of gel, 200-ml. charge

values used here are for the higher-melting form.), as compared with the best fraction of Glasgow *et al.*, which froze at −25.037°, and was obtained by azeotropic distillation at 165-1 reflux ratio in a column rated at 135 theoretical plates at total reflux.

Work on the determination of the freezing point of 2,2,3-trimethylbutane for zero impurity has not yet been completed (*12*), but the available data indicate a value near −24.4° C. Calculation of the purity from freezing point measurements is also complicated by the fact that this hydrocarbon forms with a number of the possible impurities solutions which depart considerably from ideality. A probable cause is solid-solubility. Formation of solid solutions with 2,4-dimethylpentane had been reported earlier by Tooke and Aston (*22*); in addition 2,2-, 2,3-, and 3,3-dimethylpentanes, 3-methylhexane (possibly 2-methylhexane), 3-ethylpentane, as well as cyclohexane, methylcyclopentane, and others are apparently solid-soluble (*12*). None of the above mentioned hydrocarbons were found to raise the freezing point, so that while the purity of the sample cannot at present be more accurately calculated than 99.9 ± 0.05%, it appears reasonably certain that it is of better purity than any previously reported. The starting material froze at −25.62°, and was about 99.5% pure.

That silica gel is very effective in the purification of 2,2,3-trimethylbutane is illustrated by the following experiment. Using material of 99.9% initial purity, a synthetic mixture (96.7% pure) containing 0.53% 2,2-dimethylpentane, 0.54% 2,3-dimethylpentane, 0.67% 2,4-dimethylpentane, 0.50% 2-methylhexane, and 1.00% 3-methylhexane was prepared. A column similar to that described by Mair (*16*) was filled with 180 grams of silica gel and 33 ml. of the above mixture were charged, followed by alcohol. The first 10 ml. of filtrate were 99.9% and the next 10 ml. 99.8% pure.

For the majority of the purification experiments which have been described, the experimental conditions were not such as to obtain any material representing the utlimate purity obtainable by adsorption. Only a limited number of such experiments have been carried out, but the results are very encouraging. Thus 2,2,4-trimethylpentane of 99.95% purity and cyclohexane of 99.93% purity have been obtained.

VARIABLES AFFECTING MAXIMUM SEPARATION

It might be supposed that the greater the ratio of adsorbent to hydrocarbon in a given case, the greater would be the separation. This is true only under certain conditions. With a given column, reducing the charge of hydrocarbon beyond a certain point was found to decrease rather than increase the maximum purity obtainable. Using column B, with 730 grams of 28–200-mesh silica gel and a rate of about 1 cm. per minute, a series of experiments charging 20, 50, 100, 200, and 500 ml. of a 90% 2,2,4-trimethylpentane–10% methylcyclohexane mixture was made. The desorbing agent was alcohol in each case. The amount of substantially pure 2,2,4-trimethylpentane consistently increased up to 200 ml. (none was obtained with 20 and 50 ml.); then decreased somewhat at 500 ml. The optimum charge is thus somewhere between 200 and 500 ml. in this particular case. About 700 ml. of hydrocarbon would be needed to fill the column.

To a considerable degree, the above results are probably the result of the fact that the smaller the amount of hydrocarbon, the greater the concentration gradient within the hydrocarbon portion for a given difference in concentration between the front and rear boundaries of the hydrocarbon zone. This high concentration gradient increases the effect of diffusion, which tends to nullify the separation accomplished by preferential adsorption, and also aggravates the effects of channeling and nonattainment of equilibrium. Reduction in adsorbent particle size, and increasing the uniformity of particle size and packing should reduce these disturbing effects, and influence the optimum charge to a column of given dimensions, and the optimum column dimensions for a given weight of adsorbent.

In Figure 11 the results of three runs on the separation of 90% 2,2,4-trimethylpentane–10% methylcyclohexane mixtures are shown. The first two were made with 1650 grams of silica gel in column C, using 300- and 600-ml. charges of hydrocarbon mixture, respectively. The latter gave much better separation; the improvement is relatively much better at high 2,2,4-trimethylpentane concentrations. The third run was made using 300 ml. of hydrocarbon in column D with 870 grams of silica gel. Runs 1 and 3 are essentially the same in the high-purity region, although the total separation in run 1 is somewhat greater. The separation per unit weight of adsorbent is much greater in the column of smaller diameter (larger height-diameter ratio), and considerably more sharp. Almost doubling the gel-hydrocarbon ratio by increasing the column diameter, with height unchanged, produces far from a corresponding increase in separating power.

For runs 2 and 3 the gel-hydrocarbon ratios are approximately the same. The separation in run 3 is just about half of that in run 2, so that per unit amount of adsorbent the two are nearly equivalent.

Since the volumetric capacity per unit length for column C is approximately twice that of column D, this means that when the hydrocarbon zones reached the bottom of each column, plots of 2,2,4-trimethylpentane concentration *vs.* the distance from the bottom of the column would be nearly the same for the two columns. This fact, with the fairly broad intermediate zone formed during percolation when two pure hydrocarbons are added consecutively to an adsorbent column, suggests that for any given system there is a maximum concentration gradient per unit length of column, independent of the diameter. Turner (*23*) reached a similar conclusion in the separation of gaseous hydrocarbons by adsorption. The smaller the difference in the adsorbability of two hydrocarbons the less the maximum concentration gradient.

When charged with the same amount of silica gel as column B, column D was filled to approximately twice the height. When separate portions of the same mixture were percolated through each column the taller column gave better separation.

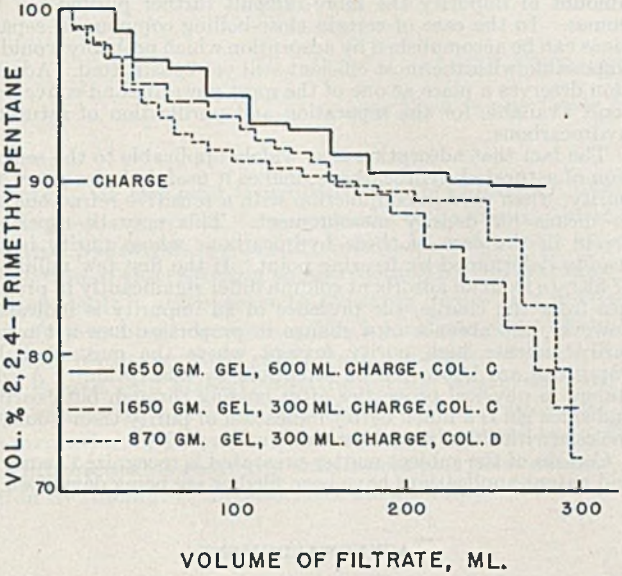


Figure 11. Effect of Gel-Hydrocarbon Ratio and Height-Diameter Ratio of Column on Separation of Saturated Hydrocarbons by Silica Gel

If the hydrocarbon volume and column diameter are held constant, and the gel-hydrocarbon ratio is increased by increasing the length of the column, it is probable that increased separation will usually be obtained. (This statement holds only within certain limits. If it were possible to extend the length of the column indefinitely, it is probable that beyond a certain point a further increase in length would produce no additional separation.) As indicated in the discussion of Figure 8, doubling the amount of adsorbent and column height would result in more than twice the volume of high-purity hydrocarbon obtained from a given charge. Other experiments described in connection with Figure 8 indicate that often about four times as much high-purity material would be obtained by doubling column height (and weight of adsorbent). This figure depends on initial purity and purity desired for the product.

If with a given weight of adsorbent, the adsorbent-hydrocarbon ratio is increased (by decreasing the hydrocarbon volume), increasing the height-diameter ratio of the column sufficiently will hold constant or even reduce the concentration gradient produced by a given separation. This consideration together with the results noted above strongly suggests that with a given amount of adsorbent the best separating power will be obtained by placing it in a column as tall and narrow as possible, within limits which will be determined largely by the size and uniformity of the adsorbent—i.e., reduction in column diameter requires a proportionately smaller particle size in order to prevent the liquid from running faster around the circumference of the column than through the body of the adsorbent.

There is both theoretical and experimental evidence that the smaller the selective adsorbability the greater the need for, and the more advantage from, an increased height-diameter ratio.

Since the taller the column the smaller the volume rate of throughput with a given linear rate and the greater the pressure required to maintain a given linear rate, and since the need for attainment of equilibrium restricts the increase in linear rate beyond a certain value, it is apparent that a suitable compromise must be made between maximum throughput and maximum efficiency. This situation is analogous to that in fractional distillation in which the greater the separating power (theoretical plates) the greater the required reflux ratio.

With an adsorption column of uniform diameter the concentration gradient increases as the hydrocarbon zone is forced down the column and the separation produced by the adsorbent becomes effective. Therefore, to obtain good separation while holding the column height to a minimum, a column which tapers toward the bottom in such a manner as to offset the increased concentration gradient produced by the increasing separation should be used. This principle (though in reversed direction) was used by Turner (*23*) in an apparatus for the analysis of gaseous hydrocarbons by adsorption. Alternatively, a column with two or more sections of progressively smaller diameter from top to bottom, such as described by Mair (*16*), may be used.

A few experiments were made with a much finer grade of silica gel, all of which was to pass 150-mesh and 50% to pass a 325-mesh screen (Davison Chemical Corp. 6595150, 50% through No. 325), made according to specifications of Mair (*16*) for analytical separation of aromatic hydrocarbons from saturates. The amount of separation for a *n*-heptane–methylcyclohexane mixture was found to be considerably less than with 28 to 200-mesh gel, though the adsorptive capacity for benzene in 2,2,4-trimethylpentane was about the same. This poorer efficiency is not to be attributed to the particle size as such, but to a lowered adsorptive capacity caused by some unknown factor during manufacture, and were the absorptive capacities the same, sharper separation would be obtained with the finer adsorbent.

SEPARATION OF HIGH-MOLECULAR-WEIGHT HYDROCARBONS

Most of the data so far discussed have related to hydrocarbons of relatively low molecular weight, but separations can be accomplished in materials of much higher molecular weight, including high polymers. A hydrogenated Pennsylvania oil of 30 carbon atoms and an aromatic-free naphthenic white oil of 35 carbon atoms per molecule could each be separated by silica gel into fractions with considerably different properties. The filtrate fractions had lower viscosities and density, higher viscosity index and molecular weight, and a smaller number of rings per molecule than the original oils; the adsorbate fractions were the reverse. The data in Table V for the naphthenic white oil illustrate the wide difference in the properties of the most and least adsorbed fractions. It is not clear whether the separation was based primarily on molecular weight or paraffinicity. A high-melting microcrystalline wax has also been separated into cuts of different melting point. The preliminary data obtained so far indicate that adsorption can be a powerful aid in the separation of high-boiling saturated petroleum fractions into cuts of greatly improved homogeneity (with respect to number of rings per molecule), in order to learn more of the constitution of these materials. [Since this manuscript was prepared, the authors have found that Nederbragt and deJong (*20*) recently reported good separations of di-*sec*-butyldecahydronaphthalene used in

Table V. Fractionation of an Aromatic-Free White Oil by Silica Gel

Property	Original Oil	Least Adsorbed Fraction	Most Adsorbed Fraction
Viscosity at 100° F., cs.	106.8	80.0	1127
Viscosity at 210° F., cs.	10.51	10.1	22.5
Viscosity index	87	114	−115
Density, d_4^{20}	0.8842	0.8550	0.9446
Refractive index, n_D^{20}	1.4825	1.4719	1.5087
Molecular weight[a]	490	539	393
Rings per molecule[b]	3.2	1.75	4.45
Weight % naphthene ring[c]	39	24	72

[a] Calculated from viscosities (*10*).
[b] Calculated from specific refraction and molecular weight by methods of Waterman (*24*).
[c] Calculated from density and molecular weight (*15*).

binary mixtures with tetracosane and octadecylcyclohexane by percolation through large quantities of floridin.]

A commercial polybutene of about 1500 molecular weight was percolated in pentane solution through columns of activated carbon and silica gel. On carbon, the components of higher molecular weight are preferentially adsorbed, while on silica gel the fractions of lower molecular weight are preferentially removed. This observation is in agreement with results obtained on mixtures of hydrocarbons of low molecular weight.

Mark and Saito (*19*) have reported the fractionation of nitrocellulose and cellulose acetate on several adsorbents; the best results were obtained with blood charcoal. Levi and Giera (*14*) confirmed the fractionation of cellulose acetate on charcoal and reported that experiments on the fractionation of both natural rubber and Buna synthetic rubber were in progress, but gave no details of these latter experiments. Cajelli (*4*) has reported that when a solution of natural rubber is passed through a column of charcoal, a fractionation occurs in which the fractions most strongly adsorbed are those of highest viscosity. In the fractionation of cellulose acetate on charcoal (*14*, *19*), the fractions of low viscosity (presumably also of low molecular weight) were preferentially adsorbed, in contrast to polybutenes and rubber.

Claesson and Claesson (*6*) report that for polyvinylacetate, nitrocellulose, and synthetic rubber, adsorption increases with decreasing molecular weight on activated carbon. These conclusions were based on the adsorption isotherms (expressed in weight per cent) of fairly homogeneous fractions, rather than on the percolation of a heterogeneous mixture through an adsorbent column. The rate of adsorption was found to be a function of molecular weight.

Fractionation of the polybutene was also accomplished by shaking its pentane solution with activated carbon and silica gel for two days; as in the percolation experiments the low-molecular-weight fractions were adsorbed by silica gel and the high-molecular-weight fractions by carbon. This eliminates a possibility that percolation results were affected by a rate of adsorption effect and do not represent adsorbability at equilibrium.

Several other polymeric materials have been fractionated by adsorption. It seems probable that in some instances adsorption could give separations as good as, or better than, obtained by fractional precipitation. As yet, no data comparing the polydispersity of fractions found by adsorption with those by fractional precipitation have been obtained.

PURIFICATION OF UNSATURATED HYDROCARBONS

Since we should expect S-type isotherms whenever we have mixtures of two hydrocarbons with nearly equal adsorbabilities, mixtures of two unsaturated hydrocarbons having the same degree of unsaturation should also exhibit this phenomenon. This is the case. Isomeric olefins, diolefins, and alkylbenzenes have been separated by adsorption, though the selectivity is not always as great as for the saturates. The authors hope to discuss this phase of the problem more fully later.

DISCUSSION

While insufficient data have been presented to explore fully the scope and possible limitations of adsorption as a procedure for the separation and purification of saturated hydrocarbons, a sufficient variety of systems has been investigated (including many not dealt with here) to justify the conclusion that it will be of wide, though certainly not of universal applicability. Geometric as well as structural hydrocarbon isomers have been separated. It is fortunate that the majority of systems give S-type isotherms on silica gel, for this greatly extends the possible applicability of the method. In most instances, more than one impurity must be removed. Were all isotherms of U-type, it is probable that often some components would be less and others more strongly adsorbed than the major constituent, which would complicate the purification. On the other hand, if the most weakly adsorbed component of a mixture is to be purified, carbon will often give a much greater separation than silica gel.

The technique of adsorption has several important advantages over other means of purification. The apparatus required is very simple and inexpensive and requires little skill. The time required is only a few hours for a single percolation. The smaller the amount of impurity originally present, the greater is the yield of product of high purity. In this respect adsorption is well suited to supplement other methods in which the smaller the amount of impurity the more difficult further purification becomes. In the case of certain close-boiling compounds, separations can be accomplished by adsorption which probably would be impossible with the most efficient still yet constructed. Adsorption deserves a place as one of the most powerful and convenient tools available for the separation and purification of saturated hydrocarbons.

The fact that adsorption is so widely applicable to the separation of saturated hydrocarbons, makes it useful also as a test for purity, when used in conjunction with a sensitive refractometer, or means for density measurement. This may be especially useful in the case of those hydrocarbons whose purity is not readily determined by freezing point. If the first few milliliters of filtrate from an adsorbent column differ significantly in properties from the charge, the presence of an impurity is indicated; however, the absence of a change in properties does not necessarily indicate high purity (except where the most probable impurities are known to be separable by adsorption). A constancy in physical properties after passing through both carbon and silica gel is a much better indication of purity than would be the case with either adsorbent alone.

Certain of the subject matter presented is recognized as novel, and patent applications have been filed or are being developed.

ACKNOWLEDGMENT

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Fermentable Sugars from Unfermented Reducing Substances in Cane Molasses

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In a study of the acid hydrolysis of the unfermentable reducing substances in cane molasses it has been found that the hydrolysis proceeds simultaneously with the destruction of the reducing sugars formed by the reaction. The net result is an increase in reducing power to a maximum, followed by a decrease. The hydrolytic effect of the acid and its destructive effect both increase with time, temperature, and acidity, but the former decreases with rising concentration of solids, while the latter increases. The formation of fermentable sugars by the hydrolysis of the unfermentable reducing substances has been demonstrated by the higher alcohol yield obtainable.

SATTLER and Zerban (*8*) have shown that the greater part of the unfermentable reducing substances in cane molasses is derived from the reducing sugars in the cane juice. At the temperature prevailing during the manufacturing process these sugars are initially converted into anhydrides, so-called reversion products, and also condense with the amino acids present in the juice. It was found that fructose yields anhydrides more readily than glucose. Both glucose and fructose react with aspartic acid, glutamic acid, asparagine, and glutamine, which are the principal amino compounds in sugar cane. Upon prolonged heating, the anhydrides and nitrogenous condensation products undergo further changes by progressive condensation and polymerization, with the further loss of water and, in the final stages, of carbon dioxide. The resulting dark-colored substances, termed "caramels" when obtained from sugars alone and "melanoidins" when formed from sugars and amino compounds, represent complex mixtures of products of varying degree of anhydridization and polymerization (*11*). They reduce Fehling solution, but their reducing power is smaller than that of glucose and fructose.

Wohl (*9*) discovered that high solids concentration favors the formation of reversion products from reducing sugars, but that at low concentration the reversion products are partially hydrolyzed by acid to the original sugars. Later Reindel and Frey (*5*) reported that the unfermented residue from cane molasses after hydrolysis with acid has a higher reducing power than before, and that a second fermentation decreases the reducing power. They ascribed these results to the presence of a sugar which is difficultly fermentable because of the high concentration of ash and other inhibiting substances. Attempts to identify this sugar failed.

Sattler and Zerban (*8*) pointed out the similarity of the hydrolysis curves of the unfermentable residue from cane molasses with those obtained upon hydrolysis of the unfermentable substances produced by heating fructose and glucose solutions in the presence or absence of asparagine. Upon prolonged heating with acid the reducing power of the hydrolysis products tended toward a maximum, and in some cases the curve descended after having reached the maximum; this indicated destruction of the hydrolysis products. The present investigation was undertaken to study the effect of temperature, acidity, and time on the course of the reaction, to determine under what conditions the maximum reducing power is reached, and to find whether the increased reducing power is actually due to the formation of fermentable sugars as disclosed by increased alcohol production.

Similar hydrolysis experiments have previously been made with polysaccharides occurring in nature. Saeman (*7*) showed that the acid hydrolysis of cellulose and the decomposition of the glucose formed from it are essentially first-order reactions. The reducing values give a curve which ascends to a maximum and then descends again. The net sugar yield can be calculated from the velocity constants of the two reactions. With cotton cellulose and wood cellulose freed from hemicelluloses, the observed sugar yields agreed quite well with those calculated, but crude cellulose showed a marked difference between the rate of hydrolysis of the portion that was easy, and that of the portion that was difficult, to hydrolyze.

The hydrolysis of starch and the reversion of the glucose formed from it have been studied extensively, and it has been found that the over-all reaction is complex (*3*). Even if corrections are applied for secondary reactions, the rate of hydrolysis is at the beginning greater than, then equals, and finally becomes smaller than that calculated on the basis of a first-order reaction, assuming a strictly random hydrolysis of equivalent linkages in the starch molecule. Various theoretical and empirical equations have been formulated for the course of the reaction, but either the theoretical equations have not been verified experimentally or the empirical equations are valid only over a limited range. Sadovyĭ (*6*) observed that when starch is hydrolyzed under given conditions the amount of dextrose destroyed is very much greater than when pure dextrose is treated with acid under the same conditions. It was also found that at high initial concentration of starch the destruction of the glucose formed is much greater than at low initial concentration; this confirms the earlier observations of Wohl.

In a study of the hydrolysis of inulin, Jackson, Silsbee, and Proffitt (*2*) found that the reaction is approximately monomolecular, although there were small, erratic variations in the velocity constant. Later Mathews and Jackson (*4*) investigated the stability of fructose under varying conditions of temperature and acidity. The results showed that the destruction of this sugar follows the first-order equation until the reducing power has fallen to about 80% of the original. If that rate were maintained, the equilibrium value would be reached at a reducing power of about 74% of the initial value. This equilibrium figure is practically constant between pH −2.6 and +1, falls to about 73% at pH 3, and then begins to drop more rapidly. The actual course of the reaction after the initial decrease of reducing power to 80% of the initial value was not investigated because the solutions became very dark as a result of secondary reactions.

The unfermented reducing substances in molasses represent a highly complex mixture of reaction products formed from at least two sugars, glucose and fructose, and possibly mannose and allulose, and at least four amino compounds, asparagine, glutamine, aspartic acid, and glutamic acid, and possibly others; consequently it cannot be expected that the course of the reaction upon treatment with acid can be expressed by a simple formula. For this reason any conclusions drawn from this investigation

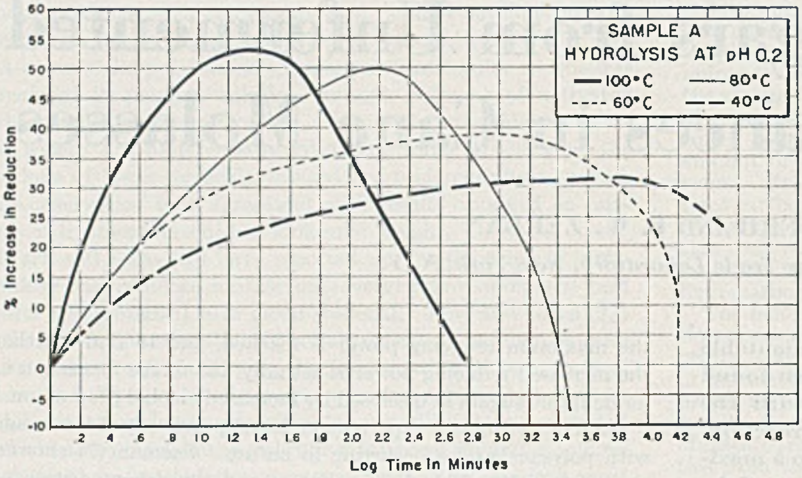

Figure 1

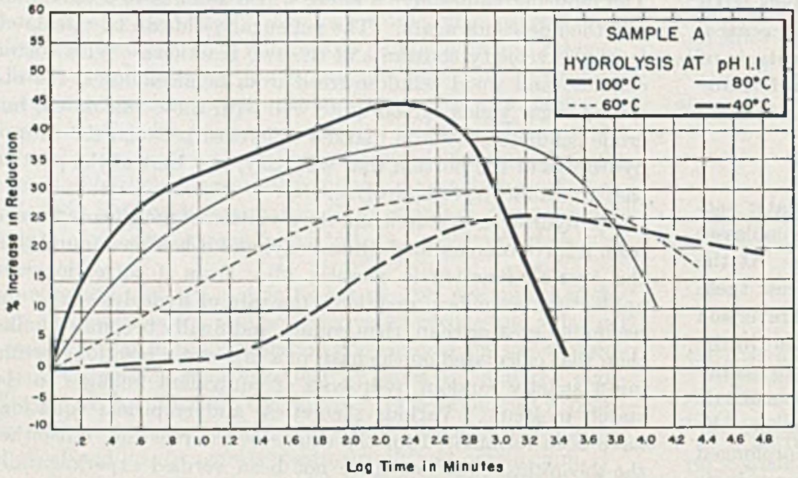

Figure 2

will have to be based on the experimental results themselves. A theoretical interpretation must await the study of simpler systems.

EFFECT OF ACIDITY, TEMPERATURE, AND TIME ON HYDROLYSIS AND DESTRUCTION

Samples of distillery residue were secured from three different distilleries whose cooperation is gratefully acknowledged. The first (*A*) was a dried slop with 96.91% solids, marketed by U. S. Industrial Chemicals, Inc., as BG-CLT and supplied by F. M. Hildebrandt. The other two, furnished by G. T. Reich of the Pennsylvania Sugar Company (*B*) and by C. L. Gabriel of Publicker Commercial Alcohol Co. (*C*), respectively, were slops concentrated by evaporation at low temperature and containing 73.65 and 52.01% solids, respectively. All had a pH around 5. The apparent invert sugar content on dry substance, calculated from the reducing power, was 12.58% in sample *A*, 12.45% in sample *B*, and 13.36% in sample *C*. These values are not a measure of the total quantity of hydrolyzable sugar derivatives present or of the potential reducing substances obtainable from them by hydrolysis, because the reducing power of the individual components of the mixture before hydrolysis varies greatly, and some of them, such as difructopyranose anhydride, do not reduce Fehling solution.

The hydrolysis experiments were carried out with solutions of three samples at four temperatures—40°, 60°, 80°, and 100° C.—and at three acidities—pH 0.2, 1, and 2. The heating was continued beyond the maximum hydrolysis point until the reducing power reached again approximately the initial value through destruction of the reducing substances formed. An amount of material containing the desired quantity of solids was weighed into a 500-ml. volumetric flask, about 300 ml. of hot water were added, and the flask was shaken mechanically until all the soluble material had gone into solution. The volume was completed at 20°, and the solution filtered from the small amount of insoluble residue, Filter-Cel being used as a filter aid. One hundred milliliters of the filtrate were pipetted into a 250-ml. flask, and 20 ml. of hydrochloric acid were added of such strength as to give the desired pH. The necessary acid concentration was determined by preliminary experiments. The flasks were then placed in a constant temperature bath for increasing lengths of time. For the 100° temperature a briskly boiling water bath was used, which had a basket of 0.5-inch wire screen inserted in it to ensure that the flasks were always immersed to the same depth. The bath was provided with a siphon arrangement to keep the water at a constant level. Four Bunsen burners were placed under the bath for the purpose of uniform heating. The experiments at 60° and 80° were carried out in a water thermostat, and those at 40° in an incubator, which was also used in some cases at 60°.

The time of heating was measured from the moment when the contents of the flask reached the desired temperature. The weight of the flasks was checked from time to time, and enough water added to make up for evaporation. At the completion of the heating period the flask was rapidly cooled, and the free acid neutralized by careful addition of the predetermined quantity of sodium hydroxide solution. The solution was then made up to volume at 20°, clarified by the addition of dry potassium oxalate to remove the calcium salts, and filtered. No lead acetate was added because it is known that some of the reducing substances are precipitated by this reagent. The reducing power was determined, at least in duplicate, in 50-ml. aliquots of the filtrate by the Munson and Walker method, which is most generally used in this country for this purpose. Collaborative experiments under the auspices of the Association of Official Agricultural Chemists (*10*) have shown that this method, when applied to unfermentable reducing substances, leaves much to be desired if carried out by different analysts, but when the analyses are made under carefully controlled conditions by the same operator, closely checking results are obtained in replicate determinations.

In this series of experiments each 100 ml. of the original solution contained 5.000 grams (4.846 grams solids) of dried slop *A*, 2.500 grams solids of slop *B*, or 2.500 grams solids of slop *C*. At the lower temperature, especially 40°, and at the higher pH levels the complete destruction of the reducing substances formed by

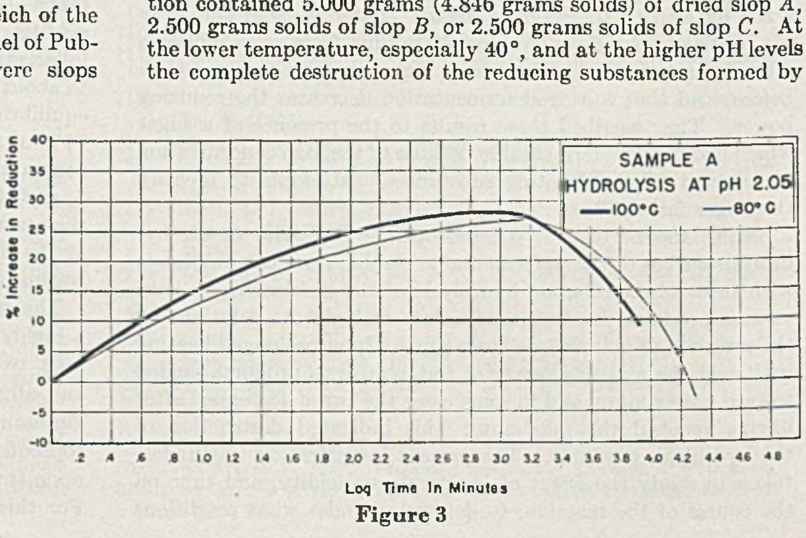

Figure 3

hydrolysis required such a long time that the heating had to be discontinued before this time was reached, in order to make the equipment available for other runs. For the same reason, and partly also for lack of available material, some of the experiments at the lower temperatures and lower acidities were omitted.

The experimental results have been tabulated[1]. The data obtained are shown graphically in Figures 1 to 9. The percentage increase in apparent invert sugar over that found in the original material, not treated with acid, was plotted against the logarithm of the time, because this provides a clearer picture than if the time as such had been used as abscissa. In the latter case the curves for low pH and high temperature would have been unduly steep, and those for high pH and low temperature excessively extended in the horizontal direction.

The curves were fitted as closely as possible to the experimental values, but there was a certain amount of scattering which was attributable to manipulative difficulties. It was impossible to shake the flasks constantly during the longer periods, and imperfect heat distribution within the solution, caused by convection currents, probably affected the results. The rate of heating from room temperature and the cooling back to 20° could not be closely controlled with changing atmospheric conditions. Local destruction of reducing substances during the neutralization of the acid solutions with sodium hydroxide is another source of error to be considered. Nevertheless, the general shape of the curves permits the drawing of valid conclusions.

The results confirm previous findings that at any given pH or temperature the reducing power first increases, reaches a maximum, and then decreases again to the original value and beyond. The curve is evidently the net result of two opposed reactions proceeding at the same time, hydrolysis of the original reducing substances, and destruction of these and of the products formed by hydrolysis.

The rate of hydrolysis, the maximum reducing power, and the rate of destruction are all the greater the higher the acidity and the higher the temperature. This is in line with the observations of Saeman (*7*) on the acid hydrolysis of cellulose. At any pH or temperature the rate of destruction is much slower than the rate of hydrolysis. In three cases the hydrolysis curves are apparently S-shaped, but this is probably due to experimental error.

There are differences in the hydrolysis curves of the three samples compared to one another, but direct comparison can be made only between samples *B* and *C*, the solutions of which had the same dry substance concentration. Sample *C* shows a higher hydrolysis maximum than sample *B* for all three acidities at equal temperature and for both temperatures used on the two samples at equal acidity. This is to be ascribed to differences in the composition of the mixture of unfermentable reducing substances in the two samples, as might be expected. However, the rate of destruction in the later stages is, under equal conditions of temperature and acidity, essentially the same in both cases; this indicates that the same substances, presumably glucose and fructose, are formed upon hydrolysis.

Attempts have been made to interpret the experimental results on the basis of reaction rates, but so far without success, probably because of the complex nature of the mixtures and the effect of secondary reactions.

Some experiments were also run with a blackstrap molasses containing 57.27% of total sugars (expressed as invert sugar) and 4.07% of unfermentable reducing substances (expressed in the same manner). Solutions containing 15.88 grams of this molasses (9.09 grams of total invert sugar) in 100 ml. and acidified to pH 0.2 with 20 ml. of hydrochloric acid were heated at different temperatures for varying lengths of time, and the reducing power was determined. The results are shown in Table I.

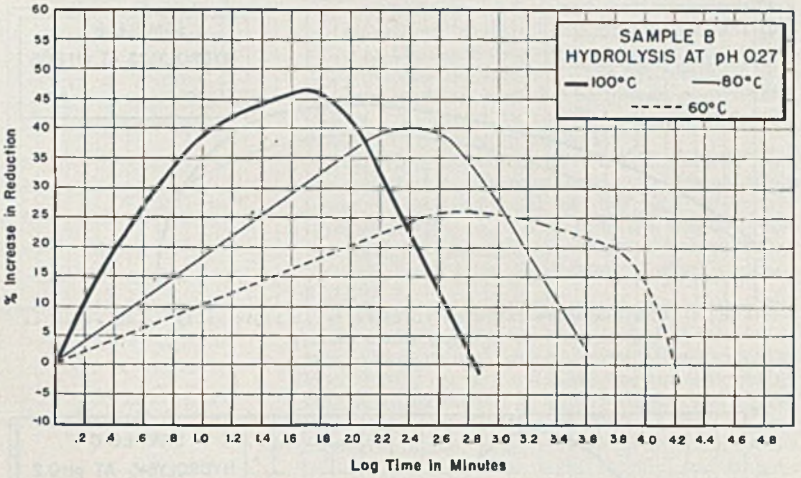

Figure 4

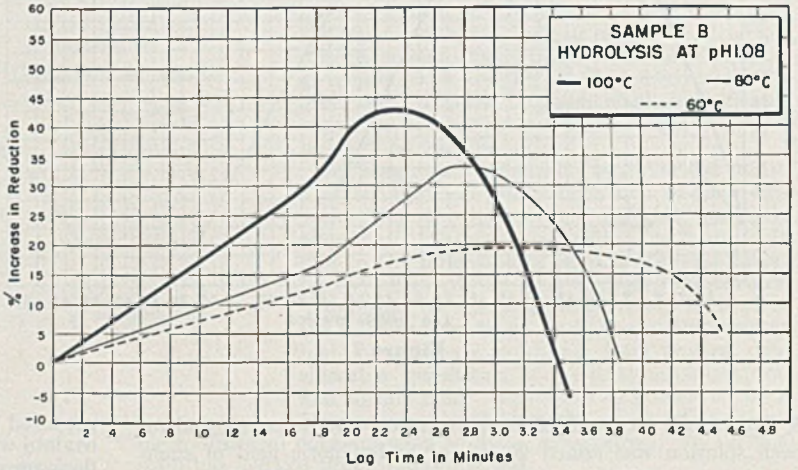

Figure 5

There is a small increase in reducing power, followed at the higher temperatures by a decrease after the maximum has been reached; this confirms the results obtained with the distillery slops. The acid at high temperature undoubtedly attacks the sugars present in the molasses and decreases the net amount of additional sugar formed by hydrolysis of the unfermentable reducing substances.

EFFECT OF CONCENTRATION ON HYDROLYSIS AND DESTRUCTION

In the study of this question 100-ml. solutions of sample *A*, containing 2, 5, 7.5, 10, and 15 grams, and of sample *C*, containing

Table I. Hydrolysis of Blackstrap Molasses at pH 0.2

30° C.		60° C.		80° C.		100° C.	
Time, hr.	Invert sugar, %	Time, min.	Invert sugar, %	Time, min.	Invert sugar, %	Time, min.	Invert sugar, %
0	57.27	0	57.27	0	57.27	0	57.27
6	57.61	5	57.58	5	57.70	3	57.30
24	57.56	10	57.58	10	57.61	5	57.67
48	57.70	20	57.58	15	57.90	10	56.55
		30	57.64	20	57.53	15	56.07
		45	57.61	30	57.30	20	55.05
		60	57.64	45	56.98		

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[1] The complete tables will be sent upon request to anyone interested in the details.

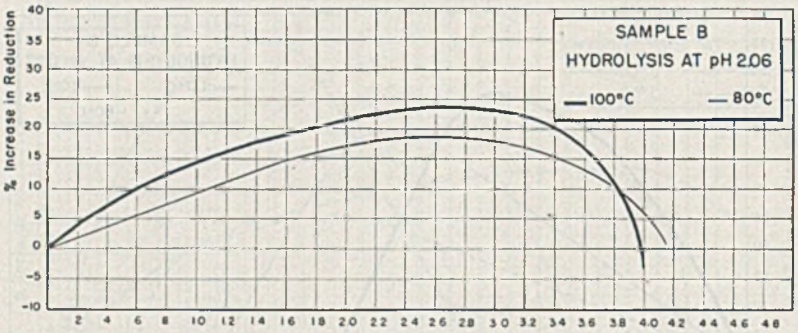

Figure 6

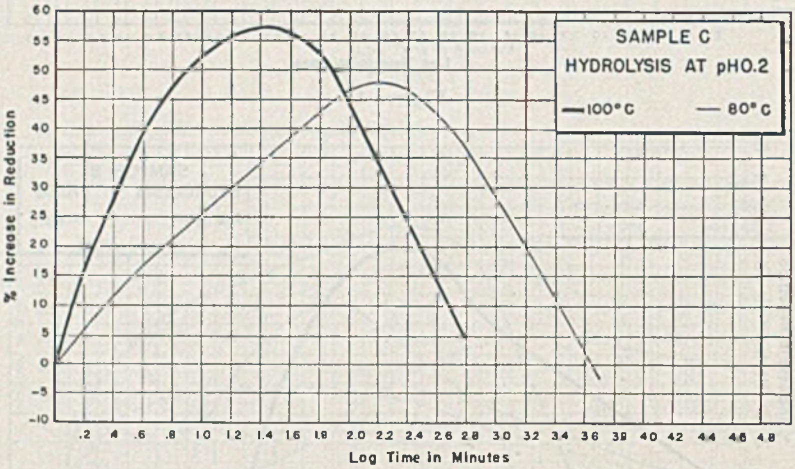

Figure 7

5, 7.5, 10 and 15 grams of dry substances were prepared, and to each solution was added 20 ml. of hydrochloric acid of such strength as to raise the acidity to pH 0.2. The solutions were heated for increasing lengths of time, up to 6 hours at 80° and up to 1 hour at 100° C., in both cases well beyond the point of inversion by hydrolysis. The reducing power after each treatment was determined as described previously.

The results, expressed again as the percentage increase in apparent invert sugar over that in the unhydrolyzed material, have been tabulated[1]. The plotted curves are all of the same pattern as the previous ones showing a rapid rise to a maximum and then a slower descent. The important criteria for judging the effect of concentration are the increase in apparent invert sugar at the point of maximum hydrolysis and that after the elapse of the longest heating period. The former are shown in Table II and the latter in Table III.

The figures for maximum hydrolysis (Table II) indicate a downward trend with increase in concentration. In order to eliminate the effect of experimental errors, the values for the four series have been averaged in the table. These averages show a steady decrease, as was found by Wohl for reversion products. The decrease becomes smaller with each added unit of dry substance.

The results given in Table III showing the destruction of reducing substances, are less consistent than those for maximum hydrolysis. The decreases in the apparent invert sugar found experimentally per unit of dry substance are quite irregular but on the average the first two units of added dry substance decreased the apparent invert sugar by 4.76 per unit and the next three by 2.24 per unit.

Table IV shows a comparison between the behavior of samples *A* and *C* upon hydrolysis under comparable conditions. The results are again expressed as the increase in apparent invert sugar over that found in the original samples.

It is found that different fermentation residues behave differently even under comparable conditions. At all concentrations but the lowest, sample *C* was less readily hydrolyzed and suffered greater destruction of the reducing sugar than sample *A*. It is evident that the nature and proportion of the various hydrolyzable components varies from case to case.

EFFECT OF HYDROLYSIS ON ALCOHOL YIELD

Although the analytical data shown furnish presumptive evidence that simple sugars are obtained by the hydrolysis of the unfermented sugar derivatives, it was still necessary to prove their fermentability. The alcohol yield was therefore determined by fermentation with yeast before and after hydrolysis under various conditions. Because of the small quantities of potential alcohol obtainable, these experiments were carried out with larger quantities of raw material than the previous ones.

Sample *A*. Portions containing 25 grams of dry substance were dissolved in hot water to a total volume of 125 ml., 20 ml. of hydrochloric acid were added to give the desired pH, and the flask, provided with a reflux condenser, was placed in a boiling water bath and heated for varying lengths of time within the range where maximum hydrolysis was expected to be reached. The flask was then rapidly cooled, and the solution was neutralized with the calculated quantity of sodium hydroxide solution, transferred to a 500-ml. volumetric flask, and diluted to the mark with water. If the reducing power was to be determined, dry potassium oxalate was added and the solution filtered with the aid of Filter-Cel. For the fermentation tests the solution was prepared in the same manner, but clarification with potassium oxalate was omitted. The solution was transferred to a 1-liter flask provided with a fermentation trap; this was designed by Louis Sattler of this laboratory and is shown in Figure 10. It serves the same purpose as that described by Davis (*1*). The pH of the liquid was adjusted to about 5, and 5 grams of Fleischmann's baker's yeast was added. The fermentations were car-

Table II. Maximum Increase in Apparent Invert Sugar at Varying Concentration

Relative Concn.	*A*, 80° C.	*C*, 80° C.	*A*, 100° C.	*C*, 100° C.	Av.	Decrease/Unit Added Dry Substance
1	53.12	49.00	53.77	57.89	53.45	...
2	49.60	45.51	52.70	53.25	50.27	3.18
3	48.85	40.41	51.15	53.89	48.58	1.69
4	47.54	40.76	52.46	50.00	47.69	0.89
6	45.57	41.06	53.12	47.80	46.89	0.40

Table III. Increase in Apparent Invert Sugar at End of Heating Period, at Varying Concentration

Relative Concn.	*A*, 80° C.	*C*, 80° C.	*A*, 100° C.	*C*, 100° C.	Av.	Decrease/Unit Added Dry Substance
1	40.33	42.50	47.54	51.70	45.52	...
2	44.36	44.61	46.98	41.49	44.34	1.18
3	42.62	30.81	41.64	28.74	35.95	8.39
4	39.67	27.71	41.64	30.84	34.97	0.98
6	33.44	26.98	29.84	26.69	29.24	2.87

Table IV. Comparison between Samples *A* and *C*

Relative Concn.	Av. Increase at Max. Hydrolysis, 80° & 100° C.		Av. Increase at End of Heating Period, 80° & 100° C.	
	A	*C*	*A*	*C*
1	53.45	53.45	43.94	47.10
2	51.15	49.38	45.67	43.05
3	50.00	47.15	42.13	29.78
4	50.00	45.38	40.66	29.28
6	49.35	44.43	31.64	26.84

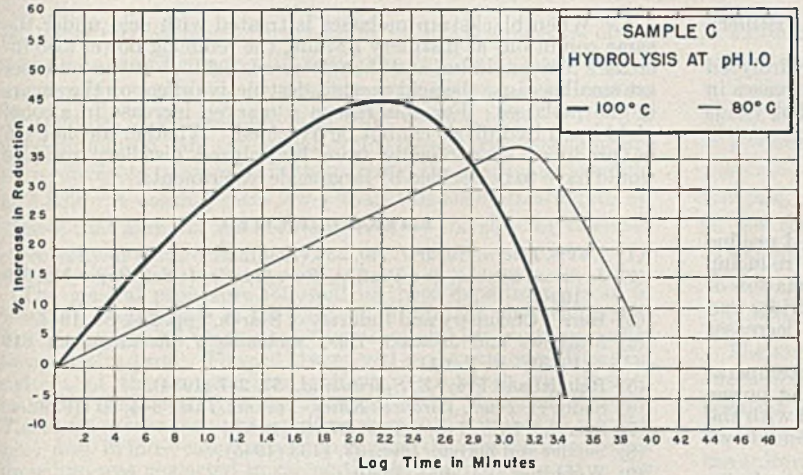

Figure 8

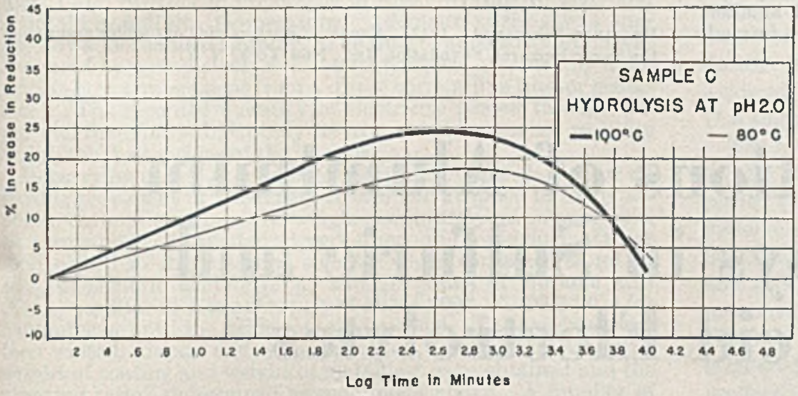

Figure 9

ried out at room temperature until there was no further loss in weight, and during this time the pH was adjusted periodically. The hydrolyzed samples, but not the original material, evolved considerable quantities of volatile products which imparted a dark color to the acid in the fermentation trap. If the fermentation was sluggish, more yeast was added. When the fermentation was complete, the entire content of the flask was distilled.

Upon distillation of the hydrolyzed solutions more of the volatile products just mentioned were given off. This made it necessary to carry out the distillations in a current of steam, repeated two or three times, and to place a Kjeldahl bulb between the distillation flask and the receiver. In the final distillation the solution in the flask was neutralized with sodium hydroxide to keep volatile acids from distilling over. The specific gravity of the final distillate was determined with the pycnometer, and the result converted into grams of alcohol. For comparison with the hydrolyzed portions, a solution of the original material was fermented and distilled in the same manner, but a quantity of sodium chloride equivalent to the hydrochloric acid used was added in order to obtain comparable values. The results of the experiments with sample *A* are given in Table V.

Table V. Reducing Power and Alcohol Yield before and after Hydrolysis at pH 0.2, Sample *A*

Time of Heating, Min.	Invert Sugar, % of Dry Substance	Addnl. Invert Sugar Formed, %	Alcohol Yield, % of Dry Substance	Addnl. Alcohol Yield, %
Not hydrolyzed	12.58	...	1.73	...
15	.....	...	2.64	0.91
30	18.59	6.01	3.05	1.32
45	18.39	5.81	3.38	1.65
60	17.71	5.13	2.81	1.08

Table VI. Yield of Alcohol from Samples *B* and *C*

	Alcohol, % Dry Substance			
	Sample *B*		Sample *C*	
Treatment	Yield	Addnl. yield	Yield	Addnl. yield
pH 0.2, not hydrolyzed	2.20	...	2.80	...
Heated 15 min.	3.04	0.84	3.68	0.88
Heated 30 min.	3.40	1.20	4.12	1.32
Heated 45 min.	4.64	2.44	3.84	1.04
pH 1.0, heated 2 hr.	4.28	2.08	...	...

The original material gave 1.73% alcohol; this showed that it still contained some fermentable sugar. The additional alcohol yield after hydrolysis for 30, 45, and 60 minutes, respectively, was 22.0, 28.4, and 23.8% of the additional sugar formed, contrasted to Pasteur's ideal yield of 51.12%.

A similar calculation can be made on the basis of the reducing power before and after fermentation. The original material gave, after fermentation, 9.20% on dry substance of unfermentable substance expressed as invert sugar, and therefore contained 12.58 − 9.20 = 3.38% of fermentable sugar. The portion hydrolyzed for 30 minutes was found to contain 9.95% unfermentable sugar, and thus 18.95 − 9.95 = 8.64% fermentable sugar. Hence, the fermentable sugar present in the original material gave an alcohol yield of 1.73/3.38 = 51.2% of alcohol, the potential yield within the limit of error. But the additional sugar formed by hydrolysis for 30 minutes gave only (3.05 − 1.73)/(8.64 − 3.38) = 25.1% additional alcohol on additional fermentable sugar, in fair agreement with the 28.4% found by the first calculation.

Although the fermentable sugar in the unhydrolyzed material gave a high alcohol yield, the yield from the hydrolyzed material was only about half of the potential yield. This is probably due to the formation of fermentation inhibitors by the effect of the acid at high temperature, manifested by the volatile products noticed in the fermentation trap. It is known that acid at high temperature produces, from sugars, considerable quantities of hydroxymethylfurfural and formic acid. The latter is known to be a fermentation inhibitor; the effect of hydroxymethylfurfural does not seem to have been studied, but furfura itself has marked fungicidal properties.

Samples *B* and *C*. With these samples only the amount of alcohol before and after hydrolysis was determined because of lack of material. Sample *B* was hydrolyzed at pH 0.2 and 1.0, sample *C* only at pH 0.2, using always 25 grams of dry substance. The hydrolyses, fermentations, and distillations were carried out as described previously, but both samples were found to be more difficultly fermentable, and 25 grams of yeast had to be used to produce active fermentation. The results are shown in Table VI and confirm the previous findings that fermentable sugars are formed by hydrolysis of the unfermentable sugar derivatives.

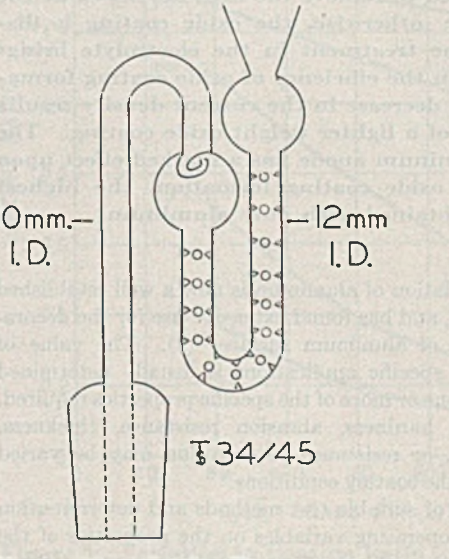

Figure 10. Sattler Fermentation Trap

Another experiment was carried out with a fresh distillery slop furnished by Louis Lang of the National Sugar Refining Company. It was found to contain 15.08% unfermentable reducing substances (expressed as invert sugar) in the dry substance. Hydrolysis at pH 0.3 for 30 minutes increased the invert sugar to 22.12%. The corresponding increase in alcohol yield was 1.4%, or 19.9% of the increase in invert sugar, a little less than that obtained under similar conditions from the concentrated distillery residues.

Some fermentation tests were also set up with unhydrolyzed and hydrolyzed blackstrap, but because of the small increases in the invert sugar upon hydrolysis the additional alcohol yields were erratic. Experiments of this nature would have to be made on a much larger scale to furnish reliable results.

CONCLUSIONS

1. When the reducing substances in the unfermented residue from blackstrap molasses are heated with acid, the reducing power first increases to a maximum because of the formation of fermentable sugars by the hydrolysis of the sugar anhydrides and sugar-amino acid condensation products, and then decreases again through the destruction of the fermentable sugars.
2. Within the experimental limits of pH 0.2 to 2 and temperatures between 40° and 100° C. the maximum reducing power increases with the acidity at constant temperature, and with the temperature at constant acidity. The rate of destruction follows the same rule.
3. Increase in the concentration decreases the rate of hydrolysis and increases the rate of destruction.
4. Upon fermentation with yeast the sugars formed by hydrolysis yield alcohol, but the alcohol recovery is much smaller than the theoretical because fermentation inhibitors are formed from the sugars by the effect of acid at high temperature.
5. When blackstrap molasses is treated with acid under the same conditions as distillery residue, the reducing power also increases to a maximum and then decreases again, but the increases are small because the acid exerts a destructive effect on the sugars in the molasses. For this reason a marked increase in alcohol yield upon hydrolysis cannot be expected. Whether alcohol can be produced economically from hydrolyzed distillery residues would have to be decided by large scale experiments.

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Anodic Reactions of Aluminum and Its Alloys in Sulfuric and Oxalic Acid Electrolytes

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This article describes factors, such as temperature, concentration and agitation of electrolyte, time of treatment, current density, and type of alloy treated, which affect the formation of aluminum oxide produced by the anodic treatment of aluminum in sulfuric and oxalic acid electrolytes. Electrolytes used at elevated temperatures or in a more concentrated form tend to produce oxide coatings of lighter weight. The electrolyte must be sufficiently agitated to remove the heat developed at the aluminum anode; otherwise, the oxide coating is dissolved. Long time treatment in the electrolyte brings about a decrease in the efficiency of oxide coating formation. Likewise, a decrease in the current density results in the formation of a lighter weight oxide coating. The purity of the aluminum anode has a marked effect upon the efficiency of oxide coating formation, the highest efficiency being obtained with pure aluminum.

THE anodic oxidation of aluminum is now a well established coating process, and has found extensive use for the decoration and protection of aluminum surfaces (*4*). The value of anodic coatings for specific applications is usually determined by measurement of one or more of the specific properties required. Properties such as hardness, abrasion resistance, thickness, adsorptive capacity, or resistance to corrosion may be varied widely by changing the coating conditions.

The development of suitable test methods and determination of the effect of the operating variables on the properties of the coatings have been the subject of considerable research. Some of the reports (*2, 3, 4, 7*) on this work have indicated the accuracy of these test methods and their field of application. Although these methods have been found satisfactory, the information they supply on the mechanism of coating formation and the variables involved in the anodic oxidation procedure is limited.

In connection with the development of procedures for measuring coating thickness by stripping methods, R. B. Mason (*5*) discovered that a solution of phosphoric and chromic acids quickly dissolves the oxide coating and has practically no effect on the aluminum. The weight of the coating can thus be readily and accurately obtained. The value of such a method to determine the efficiency of anodic oxidation and to show the effect of either minor or major changes in the coating procedure was immediately apparent. Edwards and Keller (*6*) used the method to determine the apparent current efficiency of the anodic process; they showed that, while the aluminum was oxidized and dissolved at approximately 100% efficiency, only about 70% of the aluminum lost was accounted for by the weight of the coating, assuming that it consisted entirely of aluminum oxide. The authors pointed out, however, that this assumption is only an approximation because the coating, when it is formed in sulfuric acid, is known to contain some sulfate and water.

GENERAL PROCEDURE

Preliminary experiments indicated that even very small changes in the operating conditions were readily detected by changes in the weight of coating or in the weight of metal removed. A convenient unit for expressing the results was obtained by dividing the weight of coating formed under the conditions of test by the weight of metal removed during the for-

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mation of the coating. This "coating ratio"[2] is a measure of the over-all anode efficiency with respect to coating formation. No assumptions regarding the possible composition of the coating are required in the calculation of this "coating ratio." If, with pure aluminum, all the metal which reacts electrochemically were converted to alumina in the coating, the coating ratio would be 1.889. A coating ratio lower than this theoretical figure indicates that alumina has been dissolved by the electrolyte either chemically or electrochemically.

The general procedure followed in these experiments was to weigh the ingredients of the electrolyte into the glass cell which was either cooled or heated, as required, by running water through a lead coil. The coil also served as the cathode. The acid content of the concentrated sulfuric acid which was used to make up the electrolyte was determined by chemical analysis. The sheet specimens to be anodized were 2 × 3 inches (5.1 × 7.6 cm.), and, in most cases, were thin gage so that the surface area of the edges was neglected in calculating the current density. The temperature of the electrolyte was maintained as close to the desired figure as possible and in no case varied more than ±1° F. (0.5° C.). Stirring is important in order to remove heat and maintain a uniform temperature. Adequate stirring was supplied by a mechanical agitator. The time of anodic oxidation was measured by a stop clock, and the current was obtained by a potentiometer arrangement from a direct current line (motor generator). The recorded quantity of electricity passed through the cell was therefore subject only to errors in the ammeter readings and to the fluctuations in the line current.

In carrying out an experiment, the specimen was cleaned by an etching treatment or anodically coated and stripped in the phosphoric-chromic acid mixture, weighed accurately on an analytical balance, anodically treated, rinsed, dried, and reweighed. It was then placed in the stripping solution which contained 35 ml. of 85% phosphoric acid (H_3PO_4) and 20 grams of chromic acid (CrO_3) per liter at a temperature of about 200° F. (93.3° C.) for 5 minutes or until the oxide was all dissolved. The specimen was then rinsed, dried, and weighed again. By subtraction the weight of coating and weight of metal lost were obtained and the "coating ratio" determined as mentioned above. A number of different variables were studied by this procedure.

Surprisingly consistent results were obtained when all the conditions were carefully maintained. Indeed, the weight of metal dissolved from 99.9% aluminum sheet employed as anode in sulfuric acid was so consistent that it appeared to be a more accurate measure of the quantity of electricity than was obtained with the ammeter and stop clock. Since a high purity aluminum anode acts as its own coulometer in the sulfuric acid electrolyte, it is desirable to use the weight of aluminum dissolved as a measure of the current actually employed in the electrochemical reaction. This method eliminates errors from leakage losses in the coated aluminum clips used for suspending the sample in the electrolyte as well as errors because of initial current surges.

ALLOY COMPOSITION AND SURFACE PRETREATMENT

The composition of the metal was expected to have an important effect on the coating ratio. A few experiments were made for comparative purposes, but this point is not considered in detail here. In these experiments the aluminum anodes were suspended in the sulfuric acid by means of tantalum clips which show no leakage loss in the sulfuric acid electrolyte at the voltages employed. For the measurement of current, a copper coulometer was connected in series with the aluminum-lead cell. Table I shows the variation in coating ratio caused by alloy composition and indicates the importance of this variable. The specimens were oxidized in 15% sulfuric acid at 12 amperes per square foot (1.3 amperes per sq. dm.) for 30 minutes at 70° F. (21.1° C.).

The metal, which approaches 100% purity, is consumed anodically at close to 100% efficiency. Aluminum of commercial purity (2S) has been checked a number of times and found to dissolve at an anode efficiency of about 97.5%. However, the effect of metal composition is brought out strikingly by the 17S-T and 24S-T specimens. It was known previously that coatings on alloys of this type were not so thick or abrasion resistant as those on pure metal. These figures show that the coating ratio is markedly decreased and also that only about 80% of the current is effective in reacting with the aluminum.

The pretreatment of the surface was also considered as a possible source of variation in the coating weight. Specimens of 2S-H sheet were cleaned by various treatments and oxidized in 15% sulfuric acid for 30 minutes at 70° F. and 12 amperes per square foot. The different surface cleaning treatments did not affect the efficiency of the anodic treatment. The small differ-

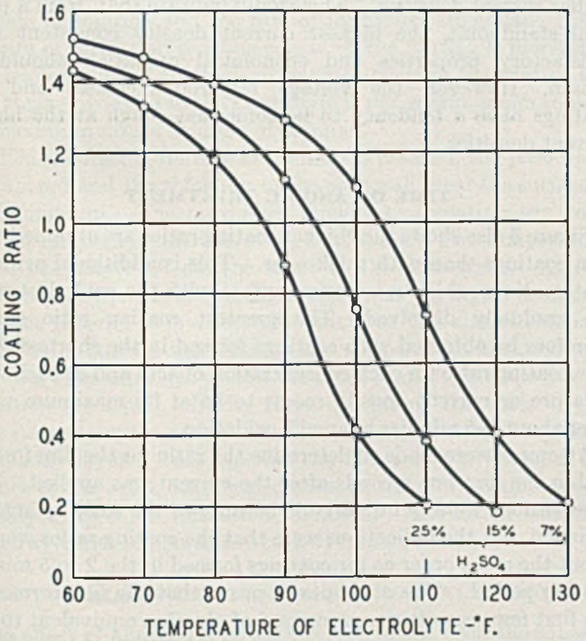

Figure 1. Variation in Coating Ratio with Temperature of Electrolyte for 99.9% Aluminum Anodically Treated for 30 Minutes at 12 Amperes per Square Foot

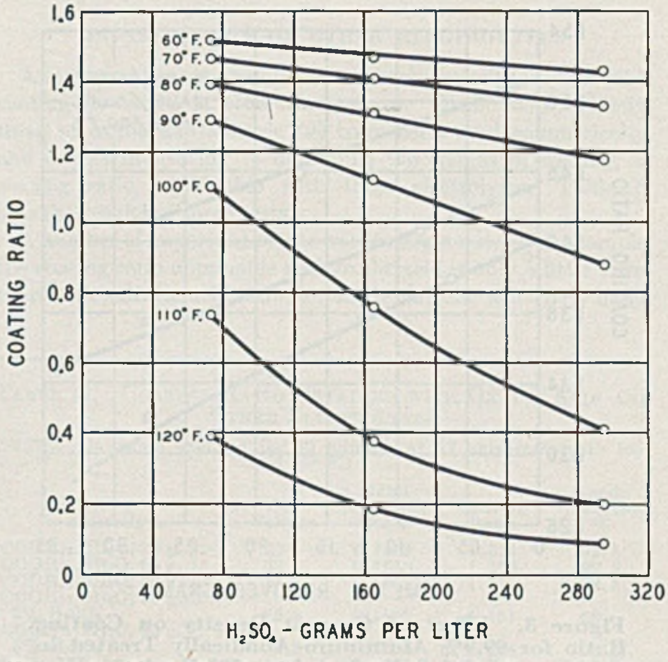

Figure 2. Variation in Coating Ratio with Concentration of Electrolyte for 99.9% Aluminum Anodically Treated for 30 Minutes at 12 Amperes per Square Foot

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[2] The practical film efficiency of Tarr, Darrin, and Tubbs (8), multiplied by 1.899, equals the "coating ratio."

Table I. Effect of Composition of Metal on Anode Efficiency and Coating Ratio

Nominal Alloy Composition[a], %	Anode Efficiency[b], %	Coating Ratio
99.95 Al	100.05	1.399
99.85 Al	99.74	1.370
99.75 Al	99.36	1.367
2S-H (99.2 Al)	97.63	1.352
3S-H (1.2 Mn)	95.17	1.351
52S-H (2.5 Mg, 0.25 Cr)	99.67	1.338
17S-T (4.0 Cu, 0.5 Mn, 0.5 Mg)	80.42	0.918
24S-T (4.5 Cu, 0.6 Mn, 1.5 Mg)	80.83	0.917
75S-T (5.6 Zn, 2.5 Mg, 1.6 Cu, 0.2 Mn, 0.3 Cr)	94.77	1.078
14S-W (4.4 Cu, 0.8 Si, 0.8 Mn, 0.4 Mg)	80.60	0.957

[a] In the last six alloys the balance of the composition is aluminum of commercial purity.

[b] $\% \text{ anode efficiency} = \frac{\text{wt. metal removed}}{\text{theoretical wt. Al}} (100)$.

ences noted were not significant, being approximately in the range of experimental error. There is an indication, however, that severe etching of the surface might cause a slightly lower coating ratio because of a lower current density per unit of actual area.

CONCENTRATION AND TEMPERATURE OF SULFURIC ACID

With this background it was possible to consider a number of other factors. The influence of the strength and temperature of sulfuric acid, the current density, and time of anodic oxidation are interrelated. A series of experiments was made in which these variables were investigated separately with careful control of the other factors. In the first group, specimens of 99.9% aluminum were oxidized for 30 minutes at 12 amperes per square foot and temperatures of 60° to 130° F. (15.6° to 54.4° C.) in electrolytes containing 7, 15, and 25% by weight of sulfuric acid. The weight of coating and the coating ratio were determined for each condition. The relation existing between these factors is most conveniently shown graphically. Figure 1 presents curves of coating ratio against temperature for the three sulfuric acid electrolytes. These curves have the expected form, since it was known that the hardest and most dense coatings are formed at low temperatures and at low acid concentration. The sharp drop in coating ratio obtained for all three concentrations of acid as the temperature was raised above 90° F. (32.2° C.) indicates that thinner, more porous coatings are formed because of the increased solvent action of the warmer acid.

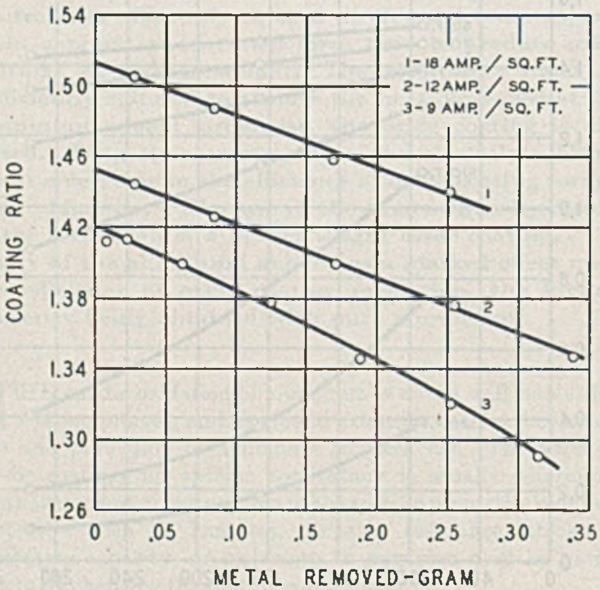

Figure 3. Effect of Current Density on Coating Ratio for 99.9% Aluminum Anodically Treated in 15% Sulfuric Acid at 70° F.

For a 30-minute coating the metal removed is equivalent to 0.168 gram.

The same data are plotted in a different manner in Figure 2, to show how the coating ratio decreases with increasing electrolyte concentration. The relation is practically linear up to 100° F. (37.8° C.), and the increasing slope of the lines with rising temperature is evidence of the increased solvent action of the acid under those conditions. The solubility of alumina formed by anodic treatment is influenced by the concentration of the acid and the temperature of the electrolyte.

The curves for electrolyte temperatures of 100°, 110°, and 120° F. (37.8°, 43.3°, and 48.9° C.) graphically show what happens to the coating ratio as the concentration of the acid is raised. Under these conditions the coatings decrease substantially in thickness and abrasion resistance. The fact that the coating ratio is approaching zero at 120° F. in the 25% electrolyte indicates that little or no coating would be produced at about 140–160° F. (60–71.1° C.). The shape of the 120° F. curve seems to indicate that increasing the concentration of the acid beyond 25% would have less effect on the solubility of the oxide coating than raising the temperature 10° or 20° F. (5.6° or 11.1° C.).

For electrolytic brightening, the anodic oxide coating should be removed approximately as fast as it is formed, and this condition is being approached in the 25% sulfuric acid at 120° F. If the current density were decreased, the anodically formed alumina would have a better chance to dissolve and the coating ratio would also decrease (Figure 3).

CURRENT DENSITY

As might be expected, a heavier (and denser) coating is obtained at higher current densities. The reasons for this are: (*a*) the coating is formed at a faster rate; and (*b*) for the passage of the same quantity of electricity, the coating remains in contact with the solution for a shorter time and is subject to less chemical attack. Therefore, the slope of the curve (metal dissolved *vs.* coating ratio) should be steeper at the lower current densities. Figure 3 shows this to be the case.

The metal removed is a measure of the ampere-minutes used in the cell, and the curves show that for the same quantity of electricity, the heavier (and denser) coatings are formed at the higher current densities. This would indicate that, from a practical standpoint, the highest current density consistent with satisfactory properties and economical operation should be chosen. However, the voltage required increases and the coatings have a tendency to be somewhat rough at the higher current densities.

TIME OF ANODIC TREATMENT

Figure 3 also shows that higher coating ratios are obtained with thin coatings than with thick ones. This is additional evidence that coatings which remain in contact with the acid electrolyte are gradually dissolved. The greatest coating ratio should therefore be obtained with coatings formed in the shortest time. The coating ratio for each concentration of acid and at each temperature or current density seems to be at its maximum value after about 2–5 minutes of anodic oxidation.

Attempts were made to determine the ratio for the film formed within the first few seconds after the current was applied. The observations were quite variable because of the small quantities involved, but the indications were that the coating ratios were of about the same order as for coatings formed in the 2 to 5 minute coating period. The attempts to prove that the film formed in the first few seconds was composed of alumina equivalent to the aluminum removed were not successful since the maximum ratio obtained was considerably below the theoretical ratio of alumina to aluminum. If this theoretical figure is reached instantaneously or within a few seconds, it is not possible to detect it with this technique. The difference between the theoretical ratio of alumina to aluminum and the observed coating ratio might mean that some of the aluminum which was anodically dissolved did not form oxide but went directly into the electrolyte to form aluminum sulfate (*1*) or some similar compound.

EFFECT OF TEMPERATURE AND TIME ON COATING WEIGHT

The fact that alumina can be dissolved by the electrolyte at the same rate at which it is formed can be shown readily by plotting the weight of metal removed, which is proportional to the ampere-minutes, against the weight of the coating formed. Figure 4 shows a family of such curves. The conditions of anodic oxidation were carefully controlled, the only variable being the temperature which was maintained at 70°, 80°, 90°, and 100° F. (21.1°, 26.7°, 32.2°, and 37.8° C.) for the corresponding curves. The shape of the curves indicates the progress of oxidation and emphasizes the importance of the electrolyte temperature in determining the characteristics of the coating. A constant current density was used, and therefore the oxide coating was formed at the same rate at all four temperatures.

The curves clearly show, however, that the oxide coatings were dissolved at different rates, depending on the temperature of the electrolyte. The weight of the oxide coating, therefore, depends on the balance that is reached between the rate of formation and the rate of solution. During the anodic process this is continuously changing, up to the point where the solution rate is equal to the oxidation rate. When this point is reached, no further increase in the weight of coating can occur, which is indicated by the flat portion of the curves. The action is then merely anodic solution of aluminum, through the intermediate oxidation stage, and can be continued until all the aluminum is consumed. The solvent action is no doubt controlled by the area exposed to attack and by the temperature of the acid.

The temperature seems to be the more important variable, since each 10° F. rise results in a considerably lower equilibrium value. In the present experiments the curves of Figure 4 indicate that the equilibrium weight of coating is reduced by about one half for every 10° F. rise in temperature.

At a given temperature the total amount of anodically formed alumina going into solution per unit time in the sulfuric acid is determined by the total area exposed. For example, the 100° F. curve in Figure 4 shows that after about 30-minute treatment the rate of solution and the rate of formation are equal. Since the rate of formation remains constant, the coating is increasing in thickness during the first 30 minutes because the area of the pore surface exposed to the electrolyte is not great enough to give the maximum rate of solution of alumina.

When the maximum rate of solution is reached, the pore walls are tapered and the thickness of the pore walls near the surface is at a minimum. The maximum thickness of coating has been reached for the specific operating conditions. The temperature of the electrolyte affects the taper of the pore walls. At low temperatures there is only a slight taper; at the higher temperatures the taper is proportionately greater. The size of the pore at the outer surface increases as the temperature is raised and reaches a maximum size when the rate of solution and the rate of formation are equal. Under these conditions the walls of the pores near the outer surface are likely to break down to form a soft chalky layer. This explains the fact that the abrasion resistance of the oxide coating decreases as the temperature of the electrolyte used for formation is raised. Also oxide coatings formed at higher temperatures sorb dyes more readily.

EFFECT OF ALUMINUM IN SULFURIC ACID ELECTROLYTES

The effect of aluminum in the electrolyte has been the subject of some speculation, since it is known that the aluminum content of the acid increases with continued operation of the bath. The weight of coating method seemed to offer promise as a means of detecting any differences in the coatings which might result from aluminum or other additions to the electrolyte.

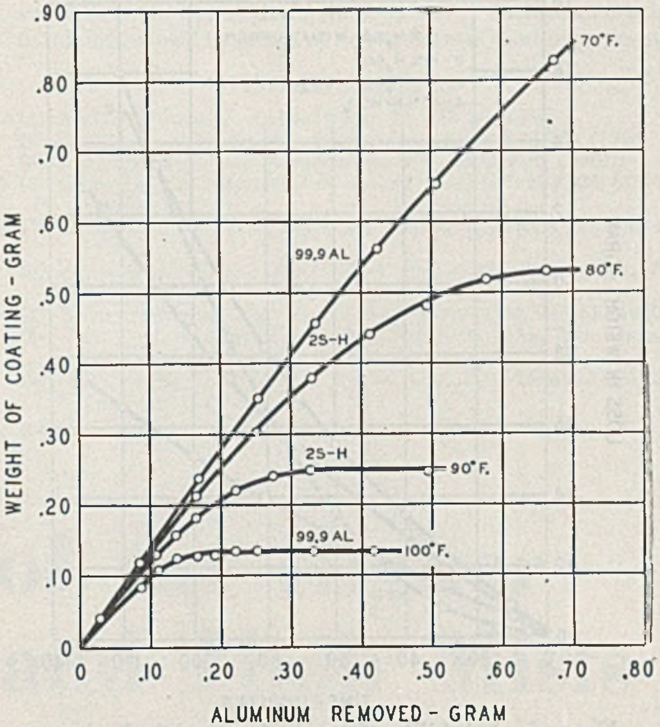

Figure 4. Relation between Aluminum Removed and Weight of Coating Formed at Different Temperatures

Specimens of aluminum 2 × 3 inches, having a surface area of 12 square inches, anodically treated for varying times in 15% sulfuric acid at 12 amperes per square foot.

The presence of aluminum sulfate in amounts up to 20 grams per liter aluminum has no detectable effect on the coating ratio. However, the concentration of the sulfuric acid may have a marked effect on the coating ratio (Figure 2). When aluminum is anodically coated in sulfuric acid, a certain amount of the acid is used up to form aluminum sulfate. While the aluminum sulfate has no effect on the coating ratio, an appreciable decrease in concentration of the acid causes an increase in the coating ratio.

INVESTIGATION OF OTHER ELECTROLYTES

A few experiments were made to check the efficiency of oxide coating formation in other electrolytes. Oxalic acid and mixtures of oxalic and sulfuric (*9*) have been used commercially, and it was interesting to determine the weight of coating, or coating ratio, obtainable with these electrolytes. Table II lists the results of these tests.

A number of important points were brought out. For example, the coating ratio obtainable with oxalic acid is only a little lower than with sulfuric acid, but the anode current efficiency, based

Table II. Coating Ratio Obtained with Oxalic Acid and Other Electrolytes

(99.75% aluminum oxidized for 30 minutes at 12 amperes/square foot and 70° F.)

Electrolyte	Cell Voltage	Metal Removed, Gram	Coating Ratio	Anode Efficiency, %
$(COOH)_2.2H_2O$, 30 g./l.	70	0.1558	1.354	92.5
$(COOH)_2.2H_2O$, 60 g./l.	62	0.1558	1.366	92.5
$(COOH)_2.2H_2O$, 90 g./l.	57	0.1565	1.374	92.8
$(COOH)_2.2H_2O$, 90 g./l. + 3% H_2SO_4	25.8	0.1651	1.461	98
$(COOH)_2.2H_2O$, 90 g./l. + 6% H_2SO_4	20.8	0.1665	1.454	98.8
H_2SO_4, 15% by wt.	16.5	0.1664	1.381	98.7
$NaHSO_4.H_2O$, 465.5 g./l.	20	0.1672	1.477	99.2

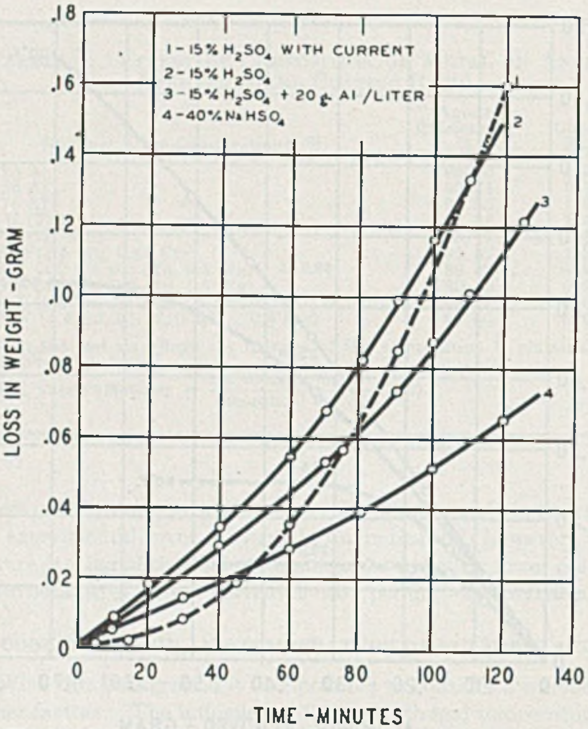

Figure 5. Solubility of Anodic Coatings in Various Electrolytes

on weight of aluminum removed, is only 92.5%. This indicates that 7.5% of the current must be consumed in some other electrochemical reaction, possibly oxidation of the oxalic acid.

The addition of sulfuric acid to oxalic raises both anode current efficiency and coating ratio to approximately the figure expected with sulfuric acid alone. The voltage is also lowered considerably. Oxidation with the mixture resembles that with sulfuric acid in operating characteristics. It is known, however, that the oxalic-sulfuric mixtures may be operated at higher temperatures than sulfuric acid alone without the formation of soft coatings. An experiment was therefore conducted to compare the coating ratios of these solutions at several temperatures (Table III).

TABLE III. COMPARISON BETWEEN SULFURIC AND SULFURIC-OXALIC ACID ELECTROLYTES AT SEVERAL TEMPERATURES

(99.9% aluminum oxidized for 30 minutes at 12 amperes/square foot)

	7% H_2SO_4		9% $(COOH)_2.2H_2O$ + 6% H_2SO_4	
Electrolyte Temp., ° F.	Cell voltage	Coating ratio	Cell voltage	Coating ratio
70	22	1.467	21.5	1.465
90	17.5	1.291	16.4	1.318
100	15	1.103	13.8	1.199

These results show that, although the coating ratios at 70° F. are practically identical, at 90° F. the coating ratio is appreciably higher when the mixture of sulfuric and oxalic acids is used. The presence of the oxalic acid seems to reduce the attack of the electrolyte on the oxide coating at the higher temperature, the result being a heavier (and denser) coating.

The inhibiting action of certain salts on the solvent action was also noted in the experiments with the sodium acid sulfate electrolyte. Solutions of sodium acid sulfate were made up, and the equivalent free acid was calculated from the reaction:

$$2NaHSO_4 \rightleftarrows Na_2SO_4 + H_2SO_4 \qquad (1)$$

For example, a solution equivalent in sulfate content to 15% sulfuric acid contained 232.7 grams of hydrated sodium acid sulfate per liter, and this according to Equation 1 was equivalent to 82.6 grams of free sulfuric acid per liter. The coating ratio obtained with the sodium acid sulfate bath was 1.500 (at 70° F. and 12 amperes per square foot for 30 minutes) on 99.9% aluminum, which is somewhat higher than would be expected with an 82.6 gram-per-liter sulfuric acid bath (7–8% sulfuric acid).

SOLUBILITY OF COATING IN ELECTROLYTE

The solvent action of the electrolyte has been mentioned as having an influence on the oxide coating characteristics and in determining the properties of the coating. Since this action is taking place simultaneously with the forming action, the rate of solution is changing continuously up to the equilibrium value for each set of conditions, and its effect is difficult to separate from the oxide coating effect. However, it is possible to measure the solubility of the coatings in the various electrolytes without current flowing and, in this way, determine the relative effect of the acids.

TABLE IV. SOLUBILITY OF ALUMINA IN SULFURIC ACID DURING FORMATION OF ANODIC COATING

(99.9% aluminum oxidized in 15% H_2SO_4 at 12 amperes/square foot and 70° F.; area of specimen, 12 sq in.)

Time, Min.	Metal Removed, Gram	Actual Wt. of Coating, Gram	Coating Ratio[a]	Calcd. Theoretical Coating Wt., Gram	Coating Dissolved, Gram
5	0.0285	0.0412	1.442	0.0413	0.0001
15	0.0851	0.1213	1.425	0.1234	0.0021
30	0.1705	0.2386	1.399	0.2472	0.0086
45	0.2552	0.3511	1.376	0.3700	0.0189
60	0.3391	0.4566	1.347	0.4917	0.0351
75	0.4255	0.5602	1.317	0.6170	0.0568
90	0.5086	0.6526	1.283	0.7375	0.0849
120	0.6795	0.8248	1.214	0.9853	0.1605

[a] Coating ratio (no chemical solution) = 1.45 (from Figure 3).

Specimens of 99.9% aluminum with a surface area of 12 square inches were oxide-coated for 30 minutes at 12 amperes per square foot and 70° F. in 15% sulfuric acid. The dried and weighed pieces were then immersed in the electrolytes under consideration at 70° F. with mechanical agitation, and weighed at intervals to determine the weight loss. As Figure 5 shows, a definite difference in solvent action was obtained. The presence of sulfates in the acid partially inhibits the attack of the oxide coating in this static test. The same relation no doubt holds while the coating is in process of formation, and aluminum sulfate in the sulfuric acid electrolyte would perhaps decrease the chemical solvent action on the oxide coating.

The data of Table IV were used to calculate the amount of alumina dissolved during the formation of the anodic coating. If the curve in Figure 3 for a current density of 12 amperes per square foot is extrapolated to cut the y-axis for zero time, a coating ratio of 1.45 is obtained. Any coating ratio obtained under these operating conditions which is lower than 1.45 indicates that some oxide coating has dissolved by standing in the electrolyte. The coating ratio of 1.45 is considerably less than the theoretical value of 1.889. This indicates that some aluminum may pass into the electrolyte without forming oxide.

From the coating ratio values extrapolated to zero time, it is possible to calculate for each time of treatment the weight of oxide coating which would be present if no chemical solution of the coating had occurred. This can be done by determining the amount of metal that has reacted during the oxidation treatment and by multiplying this value by the proper factor (for a current density of 12 amperes per square foot the factor is 1.45). The difference between the computed value and the actual weight of the oxide coating that is obtained is the weight of coating that has dissolved in the electrolyte. Such values are given in the last column of Table IV and are shown graphically in Figure 5 for comparison with other solubility values.

Less coating is dissolved while the coating is being formed by the current than when the coated specimen is merely standing in the electrolyte. The presence of aluminum sulfate in the sulfuric acid has been shown to decrease the solubility of anodically formed alumina. Knowing the method of formation for thick anodic coatings, it is concluded that the high concentration of aluminum sulfate within the pores causes a decrease in the solubility of the coating. It would appear that the electrolyte within the pores contains aluminum sulfate.

Many other experiments of a similar nature were made; all pointed to the usefulness of the weight of coating method for studying the mechanism of oxide coating formation, investigating new electrolytes, and accurately determining the effect of variables in the anodic oxidation procedure. Further knowledge in this field should be gained by an extension of these experiments.

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Flammability of the Higher Boiling Liquids and Their Mists

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This investigation concerns the flammability of the higher boiling organic fluids and petroleum oils. The explosive hazard due to oil mists in the atmosphere was of especial interest. A new apparatus was devised for the measurement of the flammability of oil mists and was applied to numerous fluids. These fluids were also exposed to incendiary fire tests and the results were recorded by color photography. Measurements and comparisons were made of the flash and fire points and the spontaneous ignition temperatures of the same fluids. Fluids investigated were: hydrocarbons, chlorinated hydrocarbons and ethers, castor oil-base hydraulic fluids, aliphatic diesters, organic phosphates and carbonates, silicones, polyalkylene glycols, and some of the glycols, glycol ethers, and their aqueous solutions. The glycols, their aqueous solutions, the higher polyalkylene glycols, properly stripped silicones, several carbonates, and the highly chlorinated hydrocarbons were the most resistant to oil mist explosions. Of the phosphate compounds studied, those having the highest ratio of the number of phosphorus atoms to the number of carbon atoms were the most resistant to such fire hazards. It was found that the spontaneous ignition temperature of the various types of silicones differed enough to permit their qualitative analysis.

ALTHOUGH the flammability of lubricating and hydraulic oils has long constituted a hazard, their use has been made a more serious problem in modern warfare by the use of high velocity and incendiary ammunition. Information on the flammability of such fluids is much too limited (*19*), since past investigations of liquids in the lubricant and hydraulic fluid range have been concerned mainly with the flash point, the fire point, and the spontaneous ignition temperature. The more elaborate studies of flammability reported in the literature were concerned with liquids and gases suitable for solvents or fuels or with dispersions of dusts in the atmosphere rather than with the higher boiling fluids. The accepted methods of measuring the flammability of liquids have been reviewed by the Underwriter's Laboratories (*18*), which determined the flammability characteristics of a variety of old and new liquids under fire hazard conditions of interest.

EVALUATION OF FIRE HAZARDS

FLASH AND FIRE POINT. The evaluation of the fire hazards of light petroleum fractions by means of the Tag closed cup flash point test (*1*, A.S.T.M. Method D56-36) or the Pensky-Martens closed cup flash point test (*1*, A.S.T.M. Method D93-42) has been much used, particularly on liquids in the gasoline, kerosene, and light fuel oil ranges of volatilities. The usefulness of the Cleveland open cup flash point test (*1*, A.S.T.M. Method D92-45) for predicting the fire hazard of relatively nonvolatile petroleum fluids is not well established. This limitation of the flash point test for the evaluation of fire hazard has been recognized by the A.S.T.M. Committee on Petroleum Products and Lubricants (*2*).

FIRE POINT. The Cleveland open cup fire point (A.S.T.M. Method D92-45) is defined as the temperature at which "the liquid ignites in the presence of a specified source of ignition and continues to burn for at least 5 seconds." With many low-boiling petroleum or other organic liquids the fire points are only a few degrees above the flash points. Higher boiling, less volatile oils and fluids exhibit a wider difference between the flash and fire points.

SPONTANEOUS IGNITION TEMPERATURE. Methods of determination and the significance of spontaneous ignition temperatures (also referred to as the "autogenous ignition temperature) (*2*, A.S.T.M. Method D286-30) have been reviewed by Helmore (*12*). The spontaneous ignition temperatures given here were

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[2] Research Laboratory, General Electric Co., Schenectady, N. Y.

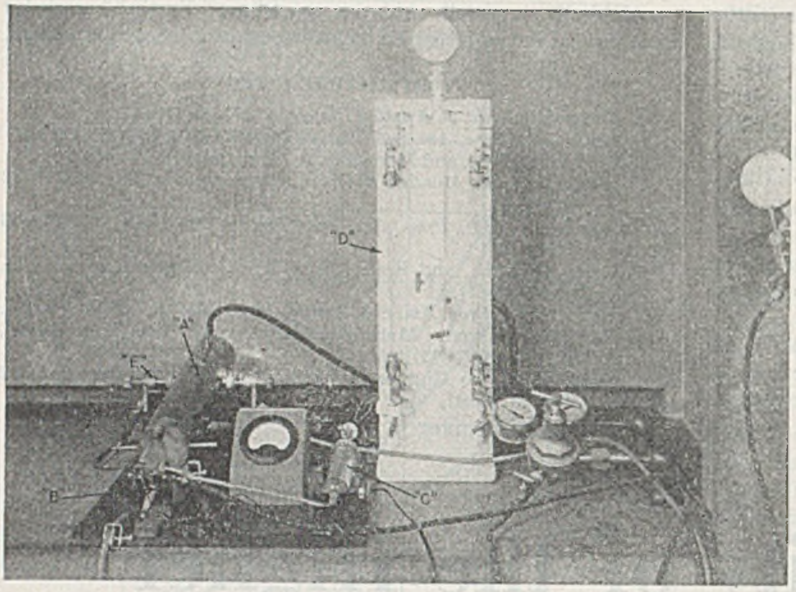

Figure 1. Spray Flammability Apparatus

obtained with the convenient apparatus described by Sortman, Beatty, and Heron (*17*).

The air flow rate was kept at 125 cc. per minute while a 1-ml. hypodermic syringe advanced with a micrometer screw served as an excellent method of introducing oil drops of known volume. By using a No. 20 hypodermic needle, droplets of about 10 mg. were obtained. The rate of temperature rise did not exceed 2° F. per minute. Enough time was always allowed between successive drops to avoid missing a spontaneous ignition occurring with a time lag of one minute (and usually several minutes). This was ample to permit the observation to be free from the complications arising from the well-known time-lag effects (*12*).

In any related fire hazard condition occurring in practice, the spontaneous ignition temperature will be determined by conditions such as the nature of the hot surface, the quantity of oil impinging on it, the volume of space enclosed, and the ventilation. Hence, the relative values of the empirically defined spontaneous ignition temperature may serve as rough indications of the relative temperatures at which such a type of ignition becomes a practical hazard.

Spray Flammability. The rupture of a high-pressure feed line or pressurized tank or the impact on an oil tank by a missile often results in the production of an oil mist or spray. The fire hazard involved during the existence of that mist was studied on a laboratory scale by a spray flammability method developed for that purpose.

The propagation of flames in gases has been intensively studied and reviewed in classic references like those of Bone and Townsend (*6*) and Gibbs (*11*). Flame propagation speed tests have been used by the Underwriters' Laboratories on mixtures of combustible gases used as refrigerants as a method for the evaluation of flammability (*19*). Diesel engineers have been interested in the spray flammability of fuels in the light petroleum oil range, but their method of ignition (adiabatic compression) and their goal (a good Diesel fuel) are removed from the object of this investigation. There has been interest but relatively little work on the electrical ignition of the higher boiling liquid fuel sprays or mists in contact with air (*14*). Dust explosions have been much investigated and reviewed (*11*, *15*), and here there is an obvious relation to the explosiveness of dispersions of liquids in air. In a liquid spray most of the combustible material will be present as small particles dispersed in a gaseous medium; however, volatile components of the fluid will enter the surrounding medium to form an easily ignited gas. The greater ease of dispersing liquids and their greater ease of coalescence or condensation make important differences between the fire hazards due to oil and dust aerosols.

APPARATUS

The present apparatus evolved from a crude spray flammability apparatus consisting of a cylindrical tin can mounted with its axis vertical and with the upper end closed by a loose-fitting cap. Through the top a burning rod of magnesium was held suspended on a wire. A hole was provided in the side of the can close to the bottom and through it was sprayed a fine mist of oil and air produced with a household insecticide sprayer. Petroleum hydraulic oils fired readily in this apparatus and the resulting rapid combustion and explosion always blew the cap off the can. This apparatus was improved by mounting within the can a carbon arc which ignited the spray more conveniently. Later it was found desirable to use a high-voltage spark discharge to start a copper arc having a fixed gap. The early experiments were conducted in the air. In order to make a quantitative comparison possible, controlled mixtures of oxygen and nitrogen were used instead. By starting with a low oxygen concentration and increasing it in a series of successive exposures to ignition, the minimum percentage of oxygen required to propagate the flame in the oil spray was determined. This minimum or limiting oxygen concentration was used as a measure of the flammability of the spray or mist of each fluid studied and was named the "spray flammability limit."

A number of other improvements or refinements were found necessary to obtain adequate reproducibility and convenience. The apparatus finally evolved (Figure 1) consisted of the following elements: the flame propagation chamber, *A;* the oil atomizer, *B;* the oil pump and metering device, *C;* the gas mixer and flowmeter system, *D;* and the electrical ignition system, *E*. The over-all dimensions were chosen to make a compact apparatus capable of quickly giving a flammability determination with from 25 to 100 ml. of the fluid to be tested.

Flame Propagation Chamber. The main part of the apparatus (Figure 2) consisted of a water-cooled cylindrical flame propagation chamber constructed from two concentric tubes, *B* and *C*. The top view of the chamber shows the integral parts and the dimensions of the tube as constructed. *A* and *M* are brass tubes of 0.25-inch (0.6-cm.) inside diameter, serving as water outlet and inlet, respectively, for the cooling jacket. Brass tubing of 0.625-inch inside diameter, *D*, serves as a holder for each of the two porcelain insulators, *E*, fitted on opposite ends of the tube. Electrodes, *F*, of $^5/_{16}$ inch diameter copper rod are fitted securely into threaded brass holders. The hexagonal nuts, *G*, are fastened to the base, and the nuts designated *I* are soldered to the threaded brass electrode holder. The arc gap width can be computed from the pitch of the screw thread. The broken lines shown as *L* indicate the lead wires from a thermocouple having its hot junction at point *K*, midway between the electrodes and the rear end of the tube. The lower end of the chamber is closed with a tightly fitted brass cap, *N*, which holds a porcelain thermocouple insulator in the top and a brass rod, *O*, passing through the center of the gap to serve as a handle. A hole 0.235 inch in diameter is made near the bottom of the cap to accommodate the nozzle of the spray gun. The forward end of the tube is left open to the atmosphere to decrease the explosion danger (the velocity of air through the tube being sufficient to prevent appreciable diffusion in from the atmosphere). The chamber is rigidly supported to give a slope of about 5° upward to the open end. A hole $^1/_{16}$ inch in diameter underneath the cap near the lower edge provides an outlet for excess oil drippings which collect in the lower end of the tube.

Oil Atomizer. The spray gun used was a Paasche artist's air brush, model ML-8. It was selected because it gave satisfactory results when used on low gas pressures (20 to 30 pounds per square inch); it had a short liquid passage to the tip; the rate of liquid flow required for the production of a finely atomized spray was small and was more in keeping with the amount of oxygen contained in the propagation chamber; and the tip of the air brush was particularly adaptable to the chamber used, since the orifice tip could be easily fitted to the brass cap, allowing no atmospheric air to enter and dilute or enrich the carefully regulated gas mixture. The brush was operated at maximum air and liquid flow rates and the silver needle adjusted so that the resulting spray pattern was conical in shape, equaling the diameter of the propagation chamber approximately 0.5 inch before reaching the arc gap. The spray gun was mounted with the longitudinal axis in line with the midpoint of the spark gap. It was observed that this spray gun adjustment produced the most reproducible measurements of the minimum oxygen concentration.

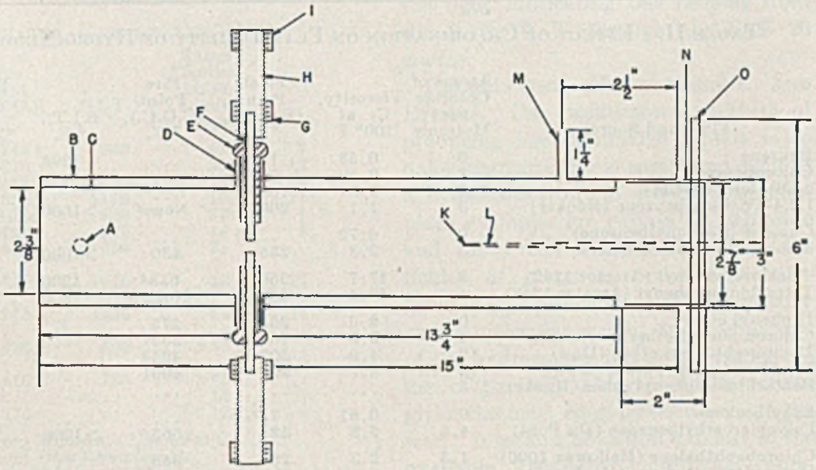

Figure 2. Top View of Propagation Chamber

Scale, 6 inches = 1 foot

Oil Pump and Metering Device. When a constant pressure and a fixed flow rate were used on the spray gun, the amount of oil passing through the gun and the condition of the spray were dependent upon the amount of liquid drawn through the orifice of the spray gun tip by the aspirator effect. The volume of oil aspirated per unit time decreased with increasing viscosity of the oil. This difficulty was avoided by the use of an oil pump which delivered a known volume per minute.

The pump was made from a motor-driven 100-ml. Becton-Dickinson 707G glass syringe. A hole was placed in the back end of the plunger and was closed with a one-hole rubber stopper. A 7 r.p.m. electrical motor having a long screw 0.25 inch × 20 threads per inch on the end of the shaft and threaded into a nut tightly fitted into the hole in the stopper served to advance the plunger.

The gas introduced in the propagation chamber through the spray gun at the rate of 10 liters per minute was sufficient to prevent appreciable diffusion or dilution with atmospheric air through the open end of the chamber. A simple calculation neglecting turbulence shows that the column of spray moves at a rate of 350 cm. per minute. The oxygen and nitrogen used were piped through flowmeters to a mixing chamber formed from a labyrinth of concentric brass cylinders which provided the turbulence necessary to assure proper mixing of the gases. A pressure gage and regulator was used at this point to regulate the pressure on the spray gun as well as the rate of flow. A pipe connection was then made to a T which carried the spray gun gas connector. A T connection in the line permitted the use of compressed air to sweep out the exhaust gases produced in each run. Unless otherwise stated, in all these experiments, the oil was atomized with a gas pressure of 25 pounds per square inch while the gas flow rate at atmospheric pressure was 10 liters per minute.

Electrical Ignition System. The system of spark ignition of the arc used was essentially the same as that described for spectroscopic work by Brockman and Hochgesang (8). Carbon electrodes were tried but were found to burn too rapidly, and copper electrodes having hemispherical and polished tips were adopted. An electrode spacing of 0.10 inch (two screw turns) was found to give satisfactory operation. When the gap was much wider the arc was often blown out by the less flammable sprays. A study was made of the effect of spark gap width on the spray flammability of two liquids. It was not found to be a critical adjustment, although if the gap width was increased more than twofold the spray flammability decreased appreciably.

Experimental Procedure. The syringe was filled with the liquid under study. With the remainder of the system open, the needle valves were adjusted to produce the desired oxygen-nitrogen mixture. The gas was allowed to flow for at least 45 seconds to sweep out the chamber. Fifteen seconds after commencing the operation of the spray gun, the arc was started and allowed to burn for 5 seconds. If the thermocouple millivoltmeter reading within 5 seconds was less than 1 millivolt (under 90° C.), the test was considered negative. Accordingly, the oxygen concentration was raised and the flammability measurement was repeated until the thermocouple reading was 1 millivolt or more. In this manner the minimum percentage of oxygen necessary for flame propagation in the oil mist could be ascertained. These measurements could be reproduced to within ±1% oxygen in the lower oxygen percentages and ±2% in the higher ranges. A positive test was usually accompanied by a muffled report, the intensity of which increased as the minimum required concentration of oxygen was exceeded. Before the flammability test or at each new concentration, the chamber was swept out with air or the gas to be used for from 1 to 5 minutes, depending on the type of oil under study. The electrodes were removed, cleaned, filed free of pits, and respaced for each fluid and at least once for every ten arc discharges in using the same fluid. It was found necessary, however, to clean them more often when consistent results could not be obtained otherwise. This precaution was necessary when studying oils which charred readily on the hot electrodes. It was necessary to clean the apparatus carefully before making tests on each liquid.

Table I. Flammability of Petroleum-Base Oils and Hydrocarbons

Fluid	Viscosity, Centistokes at 100° F.	Flash Point (C.O.C.), ° F.	Fire Point (C.O.C.), ° F.	S.I.T., ° F.	Liquid Flow Rate, Ml./Min.	Spray Flammability Limit, % Oxygen	Incendiary Test, Flame Height, Feet
Benzene (analytical grade)	0.62	12[a]	...	1295	17.6 3.0	30–35 12	0
n-Hexadecane (Conn. Hard Rubber Co.)	3.1	275	285	465	12 5	12 12	..
Aviation hydraulic oil AN-VV-O-366b	14.4	215	220	..	10 5	12 12	20
Naval Ordnance hydraulic oil O.S. 2943	28.5	230	250	504	10 5 10 6 5	12 12 12 12 12	20
Naval Ordnance hydraulic oil O.S. 1113	41.8	315	340	505	3 1.8	13 14	15
Army Ordnance recoil oil AXS-808 (Rev. 1)	59	235	250	..	10	12	16
Naval lubricating oil N.S. 2135	66	365	420	685	10 5 1	34 36 38	12
Naval lubricating oil N.S. 5190	1050	555	615	..	10	50	4

[a] Tag closed cup flash point.

Table II. Effect of Chlorination on Flammability of Hydrocarbons

Fluid and Source	Atoms of Chlorine per Molecule	Viscosity, Cs. at 100° F.	Flash Point (C.O.C.), ° F.	Fire Point (C.O.C.), ° F.	S.I.T., ° F.	Spray Flammability Limit, % Oxygen
Benzene	0	0.58	12[a, b]	...	1295	12[c]
Chlorobenzene	1	0.59	90[a, b]	...	..	14[c]
o-Dichlorobenzene	2	0.84	165[b]	...	..	29
1,2,4-Trichlorobenzene (Hooker)	3	1.1	260	None[d]	>1000	44
Cumene (isopropylbenzene)	0	0.72	...	...	..	12
Trichlorocumene (Hooker)	3	2.3	235	430	>1000	37
Trichlorodiphenyl (Aroclor 1242)	3	17.7	350	633[d]	1230	45
Tetrachlorodiphenyl (Aroclor 1248)	4	45.4	380	None	1300	64
Diphenyl ether	0	2.6	265	275	..	11
Chlorodiphenyl ether (Dow)	1	3.0	260[d]	335[d]	..	27
Dichlorodiphenyl ether (Dow)	2	4.9	300[d]	465[d]	..	33
Trichlorodiphenyl ether (Dow)	3	8.7	325[d]	4901	..	42
Pentachlorodiphenyl ether (Hooker)	5	...	...	...	..	80
Ethylbenzene	0	0.61	75[a, b]	...	..	12
Polychloroethylbenzene (Du Pont)	4.5	6.8	325	565	>1000	50
Chloronaphthalene (Hallowax 1000)	1.3	2.3	285	345	..	27
Hexachlorobutadiene (Hooker)	6	1.48	None	None	>1000	77[c]

[a] Tag closed cup flash point.
[b] (5).
[c] Did not ignite under incendiary fire.
[d] Manufacturer's data.

Empirical Nature and Significance of Results Obtainable with Spray Flammability Apparatus. The reproducibility found was adequate for the purpose of this investigation. However, only empirical results are obtained. Appreciable differences in the measurements will result from large increases in the electrode spacing and probably will arise from any large variations in the applied potential difference or the length of the exposure to the electric arc. With some fluids important differences in the results may be found if the nature of the electrode material is changed. Considerable changes in the wall temperature of the combustion chamber or the temperature of the liquid sprayed may cause significant alterations in the relative ratings of some oils. One of the most important variables in flame propagation phenomena is the composition of the mixture. For some vapor-air mixtures the range of fuel concentrations permitting explosions is narrow. It is hence to be expected for them that the weight concentration of the liquid dispersed in the gas would be an important variable. The smaller the liquid drop size, the greater the area of contact of oil and oxygen and the greater the oxidation rate. Hence, the drop size and distribution of sizes will be important. In these experiments the concentration and dispersion variables are controlled empirically by the oil feed rate, the gas pressure on the oil dispersing device, and the design and adjustment of that device. The empirical conditions were chosen to give the most flammable condition obtainable in this apparatus when fluids were used in the light lubricating or hydraulic fluid range of volatilities and viscosities.

Table I reveals the wide flammability limits of the mists of some commonly used lubricant and hydraulic fluids. However, when the liquid flow rate was below 1 to 2 ml. per minute, appreciable variations in the spray flammability limit often resulted. The effect of overrich fuel-air mixtures is exemplified by the results on a low-boiling fluid such as benzene. When atomized at the rate of 10 ml. per minute, benzene required from 30 to 33% oxygen. At a rate of 3 ml. per minute and the same gas flow rate the spray flammability limit dropped to 12% (the same value obtained for the light oils). Therefore, when the apparatus is used to measure the flammability of more volatile fluids than those of interest in this investigation, the liquid flow rate should be decreased below 10 ml. per minute (possibly to 1 to 2 ml. per minute) to get the proper fuel-air ratio.

INCENDIARY FIRING TEST

Numerous firing tests on fluids of interest were conducted at the Naval Proving Ground, Dahlgren, Va. The earliest tests, made by shooting 50-caliber M-1 incendiary bullets directly through 1-gallon cans filled with petroleum-base hydraulic fluids, gave erratic results. Reproducible flammability results were obtained only if the incendiary bullet was fragmented and ignited before it reached the oil container. The procedure adopted was to fire a single incendiary bullet at a range of 15 feet through two baffle plates of $^1/_{16}$ inch cold-rolled steel spaced 1 foot apart and 1 foot from a 1-gallon tin completely filled with the fluid to be tested. The filled and capped can (dimensions 4 × 6.5 × 9.5 inches) was placed behind the baffles in such a manner that the bullet passed through the longest of these dimensions. This procedure assured the bullet's being fragmented and ignited in passing through the steel plates. These high-velocity fragments penetrating the can of fluid created a pressure sufficient to burst the container and scatter the contents as a fine spray for a radius of from 15 to 20 feet.

Colored motion pictures (16-mm.) were taken at 64 frames per second to record the results of each test. It was found advantageous to use color photography, since otherwise the flame could not always be distinguished from the smoke and spray. The burning of the incendiary bullet, which lasted about 0.01 second, occurred between the two baffle plates and in the sample and occasionally flared up 6 to 8 feet behind the sample as the fragments hit the ground. Unless otherwise stated, the oil tested was at atmospheric temperature (60° to 80° F.). In a firing test on a typical aviation petroleum hydraulic oil the first motion picture frame showed the intense flash of the incendiary, followed in later frames by the production of a liquid spray and the first appearance of fire in the third frame. The fire soon overtook the spray (about 0.1 second later) and reached its maximum height of 20 feet in the fortieth frame (in about 0.7 second).

OBSERVATIONS ON FLAMMABILITY OF FLUIDS

Petroleum Oils. Since petroleum oils constitute the large proportion of the lubricating and hydraulic fluids in use, they were the first class studied, and the results are given in Table I. Observations on different samples of each fluid showed unimportant deviations from the values given.

The flash and fire points of the high viscosity index hydraulic oils were low, varying from 215° and 220° F. for the aircraft hydraulic oil (AN-VV-O-366b) to 315° and 340° F. for Naval Ordnance hydraulic oil (O.S. 1113), while those of the lubricating oils N.S. 2135 and N.S. 5190 varied from 365° and 420° to 555° and 615° F. The spontaneous ignition temperatures of all these petroleum oils were under 700° F. The spray flammability limits were all 12% oxygen, except for the several high-boiling oils N.S. 2135 and N.S. 5190, for which values of 34 and 50% were obtained. When oxygen concentrations a few per cent above the spray flammability limit were used, violent explosions resulted. Several of the polymer-thickened hydraulic fluids were not much less viscous than the unthickened oil N.S. 2135, yet they required only one third the oxygen concentration. Clearly the flammability of a spray or mist of a polymer-thickened oil is dependent mainly on the nature and volatility of the base stock.

Incendiary firing tests on a number of samples of each oil of Table I established the essential reproducibility of the results and allowed a rough estimate to be made of the degree of flammability by the maximum height of the flame recorded on the motion picture (last column of Table I).

All the polymer-thickened hydraulic oils were practically equally flammable, the average maximum height of the flame be-

TABLE III. FLAMMABILITY OF ORGANIC PHOSPHATES, CARBONATES, ETC.

Fluid	Viscosity, Cs. at 100° F.	Flash Point (C.O.C.), ° F.	Fire Point (C.O.C.), ° F.	S.I.T., ° F.	Spray Flammability Limit, % Oxygen	C/P
Trimethyl phosphate[a]	..	225[b]	245[b]	903	47	3
Tributyl phosphate[c]	2.6	285	370	..	27	12
Trioctyl phosphate[d]	8.1	380	465	680	13	24
Tricresyl phosphate[e]	29	500	685	1170	19	21
Hexamethyl tetraphosphate[d]	38.3	>510	None	920	31	1.5
Tetrabutyl pyrophosphate[d]	8.9	465	720	845	14	8
Dioctylphenyl phosphonate[d]	11.5	435	480	630	21	..
Diphenyl mono(*p-tert*-butyl phenyl) phosphate[f]	40.3	465	720	1076	12	22
Di-(*o*-chlorophenyl) monophenyl phosphate[f]	34.3	510	>760	1296	21	18
Diethylene glycol bis(*n*-butyl carbonate)[g]	10.1	360	400	800	>85	..
Diethylene glycol bis(2-*n*-butoxyethyl carbonate)[g]	18.0	355	410	785	>85	..
Aniline[h]	2.6	...	...	..	14	..
β-(Methoxymethoxy) ethanol[i]	2.0	175	175	..	12	..

[a] Laboratory preparation, J. O'Rear (carefully purified by distillation and selective adsorption).

[b] Data supplied by manufacturers.

[c] From Commercial Solvents Corp.

[d] From Victor Chemical Works.

[e] From Monsanto Chemical Co.

[f] From Dow Chemical Co.

[g] From Pittsburgh Plate Glass Co.

[h] From Eastman Kodak Co.

[i] From Ammonia Dept., Du Pont Co.

ing 20 feet and the explosion lasting 1.2 seconds. Lubricating oil N.S. 2135 was also very flammable, for it flamed to a height of 12 feet. When the temperatures of the oil samples were changed, the expected differences in the flammability were observed. Hydraulic oil O.S. 1113 was fired while at 0°, 55°, and 180° F. into the atmosphere whose temperature was 55° F. At 0° F. the flame height was half that at 55° F., while at 180° F. it was so greatly increased that the largest fires of all were encountered (over 25 feet height). Similarly, N.S. 2135 flamed 10 feet high at 0° F. and 25 feet high at 180° F.

The decreased flammability of the more viscous oils revealed in the spray and incendiary tests may be attributed to two factors: (1) The lower vapor pressures of the more viscous oils reduce the amount of combustible material leaving the oil droplets sufficiently to prevent the formation of an ignitable vapor-phase mixture. (2) The viscous oils are less finely dispersed by the spraying device and therefore exposed smaller surface areas to the atmosphere. The result is a decreased rate of attaining equilibrium vapor pressure and also a decreased rate of oxidation.

Unsuccessful attempts were made to relate the flash and fire points and the results of the spontaneous ignition temperature spray, and incendiary tests. Many oils having widely different flash and fire points showed the same flammability in the other tests. However, the results of the spray flammability and incendiary fire experiments can be correlated if allowance is made for the fact that the incendiary bullet carries its own supply of oxygen which must be added to the 21% of oxygen in the air. No fluid requiring over 45 to 50% oxygen in the spray test ever caused a fire in the incendiary test.

The modern demand for hydraulic oils having the highest possible viscosity indices has caused the use of very low-boiling petroleum-base fractions thickened to the desired viscosity and viscosity index by the addition of linear polymers. Thereby much has been sacrificed with regard to resistance to fire hazards, and when such oils are sprayed or dispersed in the atmosphere they create an exceedingly dangerous fire and explosion hazard. This conclusion also applies in a gradually decreasing degree to the light lubricating oils ranging from the SAE 10 W through the SAE 20 grades.

CHLORINATED HYDROCARBONS AND ETHERS. One well-known method of producing less flammable liquids is to halogenate an organic compound such as a hydrocarbon or an ether. Commonplace examples are carbon tetrachloride and the Freon refrigerants. The difficulty of preparing completely halogenated hydrocarbons increases greatly as the molecular weight and complexity of the hydrocarbon increase. Hence the use of partially halogenated fluids was given the most consideration prior to the war. A serious objection to many of the available partially chlorinated compounds is their hydrolysis and the resulting evolution of hydrochloric acid. The rate of hydrolysis appears to be very low in compounds in which the chlorine is directly attached to an aromatic ring. Where halogen and hydrogen atoms are both attached to the same carbon atom as in aliphatic compounds, the rate of hydrolysis is sufficient to cause serious corrosion in hydraulic systems. For these reasons the commercially available halogenated fluids discussed here are confined to partially chlorinated aromatics or fully chlorinated aliphatics.

It was evidently valuable to determine the influence of the number of halogen atoms per molecule on the resistance to ignition. The results of such a study using the available materials are given in Table II. Where possible the flammability data on the hydrocarbon before halogenation are also added for comparisons. The only fully chlorinated compound (hexachlorobutadiene) did not have a flash or a fire point, the spontaneous ignition temperature was over 1000° F., and the spray flammability limit was 77% oxygen. During incendiary firing tests no smoke or flame was observed other than that due to the incendiary bullet alone. As for the partially chlorinated compounds studied, it is evident from a comparison of the second and last

TABLE IV. FLAMMABILITY OF THE SILICONE FLUIDS

Description of Fluid	Manufacturer's Designation	Viscosity, Cs. at 100° F.	Flash Point[a] (C.O.C.), ° F.	S.I.T., ° F.	Spray Flammability Limit, % Oxygen	Incendiary Fire Test, Flame Height, Feet
Polymethylsiloxane	D.C. 190	22.6	240	860	39	..
	D.C. (190–200)	201	475	...	65	..
		393	460	...	79	..
	D.C. 500	0.57	Below 100	920	12	..
		2.5	225[b]	905	..	..
		8.1	350[b]	875	23	..
		17.0	455(545)	860	..	..
	G.E. (0–73)	24.7	...	890	31	12
	G.E. (0–69)	25.0	...	...	..	10
	G.E. (0–73)[c]	34.3	...	...	55	..
	D.C. 500	44.9	470	900	..	..
		57.8	465	905	..	8
	D.C. 500[d]	65.0	...	...	>70	0
	D.C. 200	82.5	600[b]	890	..	..
	G.E. (A-199B)[d]	84.4	505	905	>70	0
	D.C. 200	120	615	890	..	8
		272	625[b]	910	..	6
Polyethylsiloxane	D.C. 400	10.5	255(280)	610	13	..
		19.3	...	540	..	..
	D.C. 400B	38.3	320(380)	505	30	..
	D.C. 400B[c]	50.0	360(445)	590	70	..
	D.C. 400	96.0	295(325)	610	..	..
oly(methyl, phenyl) siloxane	D.C. 700	2.8	305(325)	940	13	..
		17.8	435(540)	975	42	..
		32.0	...	990	55	..
		61.5	435(495)	980	58	..
	D.C. 703	38.6	440[b]	...	70	..
	D.C. 703[c]	39.0	...	...	76–80	..

[a] When available, fire point is given in parentheses.

[b] Data supplied by producers, Dow Corning Corp. and General Electric Co.

[c] Stripped of volatiles by this laboratory.

[d] Stripped of volatiles by producer.

Table V. Flammability of Ucon Fluids

	Viscosity, Cs. at 100° F.	Flash Point (C.O.C.), ° F.	Fire Point (C.O.C.), ° F.	S.I.T., ° F.	Spray Flammability Limit, % Oxygen	Incendiary Fire Test, Flame Height, Feet
50HB-260	56	455	500	743	43	6
50HB-260 (without antioxidant)	49	...	...	...	..	3
50HB-260 plus 10% water	53.1	...	...	...	48	..
50HB-260 plus 15% water	...	...	...	...	..	1
50HB-260 plus 20% water	...	...	...	...	51	..
50HB-260 plus 25% water	38.4	...	...	770	..	2
50HB-260 plus 30% water	...	...	...	...	57	..
50HB-260 plus 35% water	...	...	...	...	..	1
50HB-260 plus 40% water	...	...	...	...	62	..
50HB-260 plus 50% water	13.8	...	...	815	67	0
LB-60	10.7	310	325	653	20	..
LB-80	17.2	380	420	698	30	..
LB-100	20.8	390	435	750	35	..
LB-135	33.8	380	445	720	54	6
LB-135 (without antioxidant)	31.8	...	...	720	54	6
LB-250	59.7	465	570	725	54	2
LB-250 (without antioxidant)	56.1	455	500	725	54	3
LB-400	102.6	...	...	752	54	..
LB-400 (without antioxidant)	96.9	445	470	727	54	5

columns of Table II that a high proportion of the hydrogen atoms must be replaced by halogen to raise the spray flammability limit to over 40% oxygen. When the spray flammability limit is plotted against the number of chlorine atoms per molecule, smooth curves result. The partially chlorinated fluids all evolved much smoke during the spray and incendiary fire tests. These were unpleasant and probably toxic. Since some of the liquids studied are commercial preparations likely to contain small concentrations of volatile impurities (as evidenced by the low flash points of several), it is possible that a somewhat higher resistance to ignition could be developed for the same degree of chlorination by a more careful removal of the volatile impurities present. It is of interest to note the close agreement in the spray flammability limits of trichlorodiphenyl and trichlorodiphenyl ether. The higher fire point of the former compound may be evidence of the increased rate of oxidation of the ether as compared with the hydrocarbon.

Incendiary firing tests were made on benzene, chlorobenzene, and *o*-dichlorobenzene at atmospheric and fluid temperatures of 30° F. No flame was observed from the tests on either benzene or chlorobenzene, but in the case of the *o*-dichlorobenzene a flame 8 feet high resulted. These observations are very indicative. The lack of fire for the first two fluids is presumably due to the formation of an overrich fuel-air mixture. The boiling point of the *o*-dichlorobenzene is enough higher than that of the monochlorobenzene to bring this ratio down below the upper limit of flammability. Finally, mixtures of 60% by weight of ethyl polychlorobenzene and 40% 1,2,4-trichlorobenzene were exposed twice to incendiary tests at 55° F. No fire was observed but a dense gray irritating smoke was evolved.

Castor Oil–Base Hydraulic Fluids. Because of the many excellent and well-known properties of castor oil–base hydraulic fluids, their flammability properties were also investigated. Such fluids are usually blends of blown castor oil thinned with various proportions of organic solvents such as alcohols, ethers, or alcohol-ethers. Polymers are sometimes added to improve the viscosity index, and small concentrations of corrosion inhibitors are usual. Kenneth B. Walker of the Ammonia Department of E. I. du Pont de Nemours and Co., who has had much experience in the development of such fluids, was kind enough to cooperate by preparing a number of experimental batches of these fluids with the object of increasing the resistance to spray flammability and to incendiary fire hazards. The blown castor oil, used in concentrations of from 10 to 55%, was thinned by the addition of various proportions of one or more of the following fluids: β-(methoxymethoxy) ethanol, β-butoxyethanol, and propylene glycol.

Flammability Results. The flash points were all between 160° and 200° F. The spontaneous ignition temperature ranged from 785° to 865° F., while all but two fluids had spray flammability limits of from 12 to 25%. One fluid thickened with a resin required 30% and another containing the highest proportion of blown castor oil (55%) required 50% oxygen. The fluids containing much less than 55% blown castor oil were exposed to incendiary firing tests and proved to be very flammable, the flames observed ranging from 10 to 20 feet high. The higher the spray flammability limits of these fluids, the smaller the flames. Very little smoke was evolved in the firing of such fluids. One fluid which was blended to meet specification 3586-C of the Army Air Corps for aircraft hydraulic fluids (castor oil–base) was about as flammable as petroleum hydraulic fluids of the same 100° F. viscosity. Since the diluents used are all very flammable when dispersed as liquid sprays or mists (see Tables III and VI), the failure to obtain the desired fire-resistant properties is understandable.

Diesters. The flammability of the aliphatic diesters has been discussed to some extent in a recent publication of this laboratory (*7*). The synthetic fluids used were carefully stripped of volatile impurities. The kinematic viscosities varied from 4.6 cs. (neglecting a few of the most volatile diester fluids) up to 60 cs. at 100 °F. The spontaneous ignition temperature ranged from 700° to 850° F. The spray flammability limit varied from 13 to 18% for all but the few comparatively viscous compounds like di-(tetradecyl) adipate and di-(heptadecyl) adipate, for which the limits were 25 and 45%, respectively. Dibutyl sebacate and di-(2-ethylhexyl) sebacate were distilled under diminished pressure and further purified by percolation through adsorption columns of alumina and silica gel. Incendiary firing tests were made on four samples of each fluid. The liquids were fired while at 55° F. into the atmosphere at 55° F. and while at 180° F. into the atmosphere at 55° F. In spite of the fact that these diesters had around $^1/_{50}$ the volatility of petroleum oils of the same viscosity, they were just as flammable to indendiary fire. Flame heights of 10 and 20 feet were obtained with the first fluid, and 7 and 28 feet with the second. These results are what might have been predicted from the observed low values of the spray flammability limit.

It can be concluded that the diesters have higher flash and fire points and spontaneous ignition temperatures than petroleum oils of the same viscosity, but their aerosols are only slightly less flammable. Since these diesters are so much less volatile than comparable petroleum oils, it is evident that the spray flammabilities of finely dispersed fluids are not much affected by large differences in the volatilities. These conditions are not surprising, for other work of this laboratory (*4*, *7*) on a number of other physical and oxidation properties has shown that these fluids behave very much like aliphatic hydrocarbons of the same over-all structure. Here the data can be interpreted to indicate that the ester groups have little influence on the thermal oxidation processes involved in the flammability tests (*4*).

Organic Phosphates and Carbonates. Because of the high flash point and reputed flame-resistant properties of tricresyl phosphate, the flammabilities of a group of homologous phosphates were studied. The results obtained using a number of such compounds in commercially available grades of purity will be found in Table III. The sources are given in order better to identify the commercial materials used. Although the flash points varied from 225° to 510° F. and the fire points from 245° to over 760° F., the flammability limit ranged from 13% to only 21% except in the case of the two phosphates having the highest proportions of phosphorus.

There are no evident relations between the flash and fire points and the spray flammability limits or between the viscosities at 100° F. and the spray flammability limits. In the series of alkyl phosphates it appears that as the ratio of the number of carbon atoms to the number of phosphate groups per molecule increases the spray flammability limit decreases. The aryl phosphates were somewhat more resistant to fire, as evidenced by all the flammability properties given. It is noteworthy that although the flash and fire points of both diphenyl mono-(*p-tert*-butylphenyl) phosphate and di-(*o*-chlorophenyl) monophenyl phosphate are high (over 435° F.), the spray flammability limit is only 12% for the former and 21% for the latter. It is suggested that the former is low like hydrocarbons of the same viscosity, owing to cracking of the butyl side chains on the phenyl groups, while the latter is only a little more fire-resistant than tricresyl phosphate, the two chlorine atoms giving too low a molecular proportion of chlorine to cause much of a decrease in the flammability. Of the phosphorus compounds studied it is concluded that aromatic phosphates are somewhat more resistant than aliphatic, while alkyl substitution on the benzene ring decreases the flammability. It is also concluded that the higher trialkyl orthophosphates and the triaryl orthophosphates are too flammable in the form of oil mists in the atmosphere for use in developing nonflammable hydraulic oils.

TABLE VI. FLAMMABILITY OF GLYCOLS AND AQUEOUS MIXTURES

Fluid	Viscosity, Cs. at 100° F.	Flash Point[a] (C.O.C.), ° F.	S.I.T., ° F.	Spray Flammability Limit, % Oxygen	Incendiary Fire Test, Flame Height, Feet
Ethylene glycol	8.7	240	856	40	3–8
Plus 10% water	6.9	...	862	..	..
Plus 15% water	6.0	...	...	..	3
Plus 20% water	5.1	...	871	48	..
Plus 25% water	4.4	...	...	..	1
Plus 30% water	3.8	...	880	..	..
Plus 35% water	3.2	...	885	67	2
Plus 40% water	2.8	...	892	..	..
Plus 50% water	2.2	...	903	>80	..
Plus 60% water	1.6	...	918	..	..
Plus 70% water	1.3	...	934	..	..
Plus 80% water	1.1	...	956	..	..
Diethylene glycol	16.0	280(300)	900	42	..
Plus 20% water	..	...	...	50	..
Plus 35% water	..	...	...	>80	..
Propylene glycol	19.6	230(235)	835	38	..
Dimethoxy tetraethylene glycol	2.5	285[b]	...	12	..
Plus 45% water	..	...	...	>80	..
Diethylene glycol monoethyl ether	2.8	210[b]	790	12	..
Plus 45% water	..	...	...	60	..
Ethylene glycol monomethyl ether	1.3	115	...	12	..
Plus 45% water	..	...	...	29	..
Plus 45% water plus 25% glycol	..	...	...	>80	..
Ethylene glycol monoethyl ether	2.2 at 68°	135[b]	...	12	..
Plus 45% water	..	...	...	51	..
Plus 45% water plus 25% glycol	..	...	...	>80	..
Ethylene glycol monobutyl ether	2.4	165[b]	...	12	..
Plus 45% water	..	...	...	56	..
Plus 45% water plus 25% glycol	..	...	...	>80	..

[a] When available, fire point is given in parentheses.
[b] Manufacturer's data.

Although only a few organic carbonates were studied, it was found that two carbonates made available at the end of the war had spray flammability limits of over 85% oxygen (see Table III). These are derivatives of diethylene glycol which deserve further study. They exemplify the lack of correlation between flash and fire points, spontaneous ignition temperature, and spray flammability.

SILICONE POLYMER FLUIDS. Much interest has been aroused in the silicone polymer fluids or polyorganosiloxanes (*5*, *16*). Their possibilities for use in lubrication and hydraulics have been investigated (*9*, *10*) because of their remarkably low temperature coefficients of viscosity and their unusual resistance to thermal oxidation in the air. The two manufacturers of these fluids have been most cooperative in making available a variety of samples of interest in this investigation, and Table IV lists the flammability data obtained. Each fluid is identified by a brief chemical description of the results of the analyses of this laboratory and by a reference serial number of the producer.

The flash points are much higher than those of petroleum oils of the same 100° F. viscosity, for they range from 225° to 625° F., increasing with the viscosity. The flash points of all the polyethylsiloxanes are over 100° F. lower than those of the other polysiloxanes of comparable viscosities. This large difference may be due to a higher vapor pressure or a lower oxidation stability. That it is not due to the presence of a volatile impurity is shown by the low value obtained for the stripped sample. The silicones do not have fire points when determined by the usual procedure. They can be made to burn after continued flaming with a Bunsen burner, but the flame burns poorly and tends to extinguish itself after the external source of flame has been removed. If the products of oxidation are allowed to accumulate in a closed container for long enough, the resulting vapors can explode upon admission of a source of ignition. This has happened in oxidizing silicones in an oven at 250° C. Among the products evolved from the combustion of the polymethylsiloxanes are silicon dioxide, carbon dioxide, formaldehyde, and formic acid. Usually the fire points were not measured because they were not considered sufficiently significant.

The spontaneous ignition temperatures were higher (except for the polyethylsiloxanes) than were those observed with any of the petroleum oils. All the polymethylsiloxanes had spontaneous ignition temperature values of from 880° to 910° F. regardless of viscosity or source. The values of 504° to 608° F. obtained for the polyethylsiloxanes are so much lower that they are believed to originate in fundamental differences in molecular structure. In the thermal decomposition of the polymethylsiloxanes both the C—H bond in the methyl group and the Si—O bond in the polysiloxane chain are so much more stable that a Si—C bond probably is the first to be broken. In the polyethylsiloxanes besides the Si—C bond there are the C—C bonds and also the C—H bond of the —CH_2— group in the ethyl side chain. These are more likely to break than the Si—O bond or the C—H bond in —CH_3. The poly(methyl, phenyl) siloxane copolymers have spontaneous ignition temperatures approximately 80° F. higher than the polymethylsiloxanes, presumably due to the greater stability of the Si—(aromatic C) bond than the Si—(aliphatic C) bond. The appearance of the ash left in the cup of the spontaneous ignition temperature apparatus was consistent with identification given these three classes of polysiloxanes, since the polymethylsiloxanes left a pure white ash consisting of silica particles, while the poly(methyl, phenyl) siloxanes left a gray ash consisting of particles of silica and of carbon black so typical of the cracking of aromatic hydrocarbons.

The results of the measurements of the spray flammability limits of the earlier silicones were very scattered, the limits varying from 31 to 79%. It was merely concluded that the spray flammability limit decreased with increasing viscosity. It was observed later that individual samples under periodic observation gradually become less flammable. Information about the precise composition of the samples was not then available, and the pungent odor frequently found in the early samples had been assumed to be inherent. It was finally concluded that volatile material was present, whose gradual escape was causing the upward drift in the spray flammability limit. To test this plausible hypothesis a sample of fluid O-73 having a spray flammability limit of 31% oxygen was warmed under diminished pressure to remove volatiles. Approximately 10% of the fluid evaporated, the pungent odor disappeared, the viscosity at 100° F. increased from 25.2 to 34.3 cs., and the spray flammability limit rose to 55% oxygen. Following this experience both producers of silicones were asked to make available fluids for this and related investigations, using all possible care to obtain them as free as possible from volatile impurities or components. Such "stripped" fluids were much less flammable, the higher spray flammability limits exceeding 70% oxygen. But when the spray flammability limit was exceeded, the resulting explosion was rather violent.

An early polymethylsiloxane (sample O-69) having a viscosity at 100° F. of 25 cs. was found to flame 10 feet high in the incendiary firing test. The early D.C. 200 fluids (having viscosities at 100° F. of 57.8, 120, and 272 cs.) flamed 8, 8, and 6 feet high in this test. However, when the fluids which had been stripped of the more volatile materials were fired, they were nonflammable, for the only flames seen in the motion picture records were due to the highly localized ignition of the incendiary bullets.

The properties of properly stripped polymethylsiloxanes or poly(methyl, phenyl) siloxanes having viscosities at 100° F. in excess of 20 cs. are summarized as follows: The flash points are high; when the liquids are ignited the flames are readily extinguished; the spontaneous ignition temperatures are high; the spray flammability limits are high; and they are practically nonflammable to incendiary fire. Obviously these fluids have much promise in applications where unusual resistance to fire hazards is necessary.

Ucon Polymer Fluids. Two new series of polymer fluids have been made available by the Carbide and Carbon Chemicals Corporation (*13*). These are both polyalkylene glycol derivatives possessing several properties which make them interesting lubricants and hydraulic fluids. Fluids of the first series (designated by the manufacturer as the Ucon LB series) are able to dissolve only a few per cent of water at 100° F. The second series (designated as the Ucon 50HB series) is very soluble in cold water. Both classes of fluids require the addition of an antioxidant when used in aerated systems persistently maintained over 150° F. Unless otherwise stated the Ucon fluids in question contain 2% by weight of the oxidation inhibitor recommended by the manufacturer.

The Ucon LB fluids were furnished this laboratory in six viscosity grades ranging from 10 to 100 cs. at 100° F. Their behavior in the flammability tests is summarized in Table V. As the flash and fire points varied from 310° to 570°, they were somewhat above those of petroleum fluids of the same 100° F. viscosities. The viscosity grades over 20 cs. at 100° F. had only small variations in the spontaneous ignition temperature. The spray flammability limit was 54% oxygen for all viscosities above 30 cs. at 100° F. Several incendiary firing tests were made on each of three viscosity grades. The least viscous fluid (LB-135) caused a flame 6 feet high, the most viscous (LB-400) gave no flame, and the intermediate fluid (LB-250) caused a flame 2 feet high. The presence of the antioxidant did not appear to have a particularly significant effect on the flammability as observed in this test.

The one grade of the Ucon 50HB fluid examined had a viscosity at 100° F. of 56 cs., and its flash and fire points as well as the spontaneous ignition temperature were nearly the same as those of the Ucon LB series fluids of the same viscosity. However, the spray flammability limit was 43% as compared with 54% for the LB series. The incendiary firing tests on the 50HB-260 fluid revealed it to be only slightly more flammable than the LB-250 fluid. Even when fired at 180° F. it caused a flame only 5 feet high.

Since the 50HB-260 fluid will dissolve a high proportion of water at ordinary temperatures, data were obtained on the flammability characteristics of a series of mixtures containing from 10% up to 50% water. The spontaneous ignition temperature increased from 743° F. when no water was present up to 815° F. with 50% water, and the spray flammability increased linearly with the water content, reaching 67% oxygen in the 50% aqueous solution. Incendiary firing tests showed that the addition of 15 to 25% water cut the flame height down to only 1 to 2 feet, while over 35% water eliminated all evidence of flame propagation.

Hence, the two classes of Ucon polymer fluids have higher flash and fire points and spontaneous ignition temperatures than petroleum oils of the same 100° F. viscosity. They have spray flammability limits so much higher that they can be described as very resistant to the fire hazards caused by incendiary fire.

Glycols and Their Aqueous Solutions. The dissolving of water in an organic liquid is a well-known method of decreasing its flammability. Ethylene glycol is especially promising for use as the organic component because of its availability, its low viscosity at 100° F., its limited action on packing materials, and its effectiveness as a freezing point depressant. Various proportions of ethylene glycol and water were examined by the flammability tests described (see Table VI). By adding water to ethylene glycol the spontaneous ignition temperature could be raised from 856° F. (for the pure glycol) to 956° F. when 80% water was present. While the spray flammability limit of pure ethylene glycol was rather high (40% oxygen), it was not considered high enough for safety. When 35% water was present the spray flammability limit had risen to 57% oxygen, and with 50% water present over 80% oxygen was necessary.

Incendiary firing tests were made on a number of ethylene glycol–water solutions. Ethylene glycol alone was somewhat flammable to incendiary bullets, for flames were from 3 to 8 feet high. The flame height decreased with the increase in water content, and when 40% or more water was present no evidence of flames or smoke was ever found.

Observations were made on a number of other glycols and their derivatives and some appeared promising for use in aqueous and other special lubricant and hydraulic compositions. Attention is called to the much higher resistance to spray flammability of the diethylene glycol than the propylene glycol or the monoethers of ethylene and diethyl glycol (Cellosolve and Carbitol).

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Submerged Culture of Fungal Amylase

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Improvements are described for the production and culturing of submerged mold for commercial use as a conversion agent of grain mashes. Distillers' dried solubles were found superior to stillage as a substrate for submerged mold amylase production; calcium carbonate was used to replace sodium hydroxide for adjusting the pH of the mold media. By-products from mold-converted grain mashes are comparable to those from malt-converted mashes as a substrate for mold growth. In the culturing procedure, 0.5% mycelial transfer is sufficient for inoculation; the mold culture may be transferred serially through several 24-hour submerged stages prior to the final propagation stage. Submerged mold cultures prepared by a method incorporating the improvements described may be used to replace barley malt completely as a converting agent and results in an alcohol yield increase of 0.2 to 0.3 proof gallon per bushel of grain.

THE literature contains many references to the use of fungal amylases in supplementing or replacing malt for the conversion of grain starches for alcoholic fermentation. Takamine (*10*) was the first in the United States to suggest the commercial possibility of such a process. Underkofler and associates have published numerous papers describing laboratory and commercial scale production and use of fungal amylase in the form of mold bran (*4, 11, 12, 13*). Hao and Jump (*5*) and Roberts *et al.* (*7*) have also reported successful application of the mold bran process to the conversion of starchy grains.

Recently, these laboratories (*1*) and others have reported on methods for the preparation of fungal amylase in submerged culture employing a medium consisting of stillage from grain mash fermentations. During these studies it became apparent that stillage as a mold medium presents a problem that may vary with plant operating conditions. Erb and Hildebrandt (*2*), working with species of *Rhizopus*, reported a toxic substance in stillage which could be removed by carbon treatment or by the addition of traces of aluminum powder. Van Lanen and Le Mense (*14*) successfully cultured *Aspergillus niger* in stillage and reported no indication of any toxicity.

In the authors' laboratories it was found that growth and amylase production by a strain of *A. niger* in plant stillage (produced in a low temperature distillation unit) were definitely inferior to those in stillage from laboratory-prepared mash. Charcoal treatment and the addition of aluminum powder were ineffective in improving the growth-promoting quality of plant stillage.

The present paper deals with the selection of a more uniform substrate for submerged mold amylase production and improvements in culturing procedure designed to facilitate commercial application of the process.

The specific problems to be considered are:

1. A comparison of distillery by-products as media for mold propagation.
2. The effects of variation of the conversion temperature on conversion of grain mash with mold amylase.
3. Procedures for the neutralization of mold media.
4. The re-use of stillage from mold-converted mashes as mold media and as backset. (Backset is defined as stillage added to converted mash as a nutrient prior to fermentation.)
5. Procedures for culturing mold in the intermediate stages between the laboratory culture and the final plant propagator.

PREPARATION AND EVALUATION OF MATERIALS

A strain of *A. niger* obtained from the Northern Regional Research Laboratory (N. R. R. L. No. 337) was employed in all the studies discussed in this paper.

Submerged mold cultures were grown in stillage or distillers' dried solubles at a solids concentration of 5 grams per 100 ml. fortified with 1 gram per 100 ml. of corn meal. The pH was adjusted and 1 liter of the medium was sterilized in a 2-liter cone-shaped flask and inoculated with 2.0% by volume of a surface-grown mold culture. The culture was then placed in a 30° C. water bath and aerated (by means of an Aloxite sparger) for 48 hours at a rate of 0.2 cubic foot per minute per liter. Variations from this procedure are discussed below.

Enzyme activities of the mold amylase preparations were measured by three methods. Alpha-amylase determinations were run on a portion of the samples by the Sandstedt, Kneen, and Blish 30° C. method (*8*) and results reported as alpha dextrinizing units per 100 ml. of mold filtrate.

All cultures were analyzed for saccharifying power by an unpublished method of Hao (*3*, revised in 1946). In this determination the saccharification value is defined as the number of grams of starch saccharified by 100 ml. of mold filtrate in one hour at 40° C. This method lacks the value of wide acceptance but has the advantage of speed and is particularly valuable when large numbers of analyses are to be made.

All mold amylase preparations were evaluated finally on the basis of alcohol yields from laboratory test fermentations by an adaptation of the method of Stark *et al.* (*9*).

Corn was cooked at atmospheric pressure for one hour, autoclaved at 22 pounds' pressure for one hour, and cooled to conversion temperature (130° F.), and an amount of the submerged mold culture equivalent to 10% of the final mash volume was added. The mash was agitated for 5 minutes and cooled to setting temperature. Ten per cent by volume of stillage was then added as backset, the pH adjusted to 4.8, and the total volume of the mash adjusted to a concentration of 38 gallons per bushel of grain. Control fermentations were run with each experiment using 1% premalt, 7% conversion malt, and 145° F. conversion temperatures. Twenty per cent by volume of stillage was added to the control mashes as backset.

The yields of the malt controls are based on total grain and in all reported experiments the control yields are at a level considered optimal.

Throughout this paper the quality of each mold amylase preparation is evaluated in terms of the yield of alcohol from test fermentations employing the mold preparation as the sole conversion agent.

EXPERIMENTAL WORK

The standard malt used throughout these studies had a starch content of 47.1%; Lintner, 166°; α-amylase, 46.8 units; β-amylase, 14 units; and saccharification value, 6.3 S. V. units

Table I. Distillery By-products as Media for Mold Propagation

Mold Medium	S. V.[a]	Alcohol Yield, Proof Gal./Bu., Dry Basis	Plant[b] Efficiency, %
Laboratory stillage	..	6.11	91.6
Evaporator sirup	63.5	6.15	92.2
Distillers' dried solubles	95.0	6.10	91.4
Control (malt converted)		5.99	90.5

[a] Saccharification value is defined as the number of grams of starch saccharified by 100 ml. of mold filtrate in one hour at 40° C.

[b] Plant efficiency is defined as per cent of theoretical alcohol yield based on starch in grain used.

Table II. Distillers' Dried Solubles Produced by Different Companies as Media for Mold Propagation

Source of Solubles for Mold Media	S. V.	α-Amylase, Units/100 Ml.	Alcohol Yield, Proof Gal./Bu., Dry Basis	Plant Efficiency, %
Company 1	80	2783	6.06	90.8
Company 2	80	2390	6.06	90.8
Company 3	80	2351	6.02	90.2
Company 4	95	2941	6.05	90.7
Company 5	80	2606	6.01	90.1
Control (malt converted)			5.95	91.3

per gram. [Beta-amylase content of the malt was determined by the method of Kneen and Sandstedt (*6*).] Two standard lots of corn having starch contents of 67.7 and 69.3% were used.

Selection of Medium for Mold Propagation. In commercial distillery operations, stillage from the distillation column is screened to remove most of the suspended solids, evaporated to a solids concentration of approximately 30%, and finally dried on drum dryers. The end product is known as distillers' dried solubles.

When the inferiority of plant stillage to laboratory stillage was established, both evaporator sirup and distillers' dried solubles were investigated as media for mold propagation (Table I). The yields of alcohol from fermentations converted with mold amylase produced in both evaporator sirup and solubles were comparable to the yields from laboratory stillage media. The yield in all cases was over 0.1 proof gallon per bushel higher than with the malt-converted control. (Proof gallon per bushel is a term used to denote gallons of 100° proof alcohol yield from 56 pounds of grain as received, unless stated as "dry basis.") In this and succeeding tables each yield figure represents an average of at least three fermentations.

Since evaporator sirup has shown some tendency to vary in quality from time to time, attention was concentrated on solubles as the medium for further refinement of the mold amylase process.

Distillers' dried solubles throughout numerous experiments have proved remarkably consistent in quality as reflected in mold growth and amylase production. In order to test this material further, however, solubles were obtained from five separate companies representing a wide divergence in grain bills and processing equipment. These samples were compared as media for mold propagation (Table II). The saccharogenic values of the mold cultures grown in these solubles and the alcohol yields from fermentations converted with these mold cultures were practically identical. There was a wider variation in the α-amylase analyses, though not enough to be reflected in plant efficiency at the concentrations used. (The term "plant efficiency" is used to denote the per cent of the theoretical alcohol yield based on the starch in the grain used.)

Conversion Temperature. The submerged culture of *A. niger* was normally added to the cooked grain at 130° F. This conversion temperature has been generally accepted as optimum for fungal amylase action, although the high mash viscosity at 130° F. poses a problem in plant operation.

Since the existing cooling equipment in most distilleries is designed for conversion at 145° F., it was thought advisable to test the use of mold amylase at this higher temperature. The effect of conversion temperatures on alcohol yield is shown in Table III. The higher conversion temperature substantially decreased the viscosity of the mash and in addition resulted in higher alcohol yields. Although the increase from 6.07 to 6.15 proof gallons per bushel would not be considered significant on the basis of one test, numerous experiments have proved that such an increase is obtained. As a result of these tests 145° F. was adopted as the standard conversion temperature and all the following experiments were conducted at the higher temperatures. In all subsequent data the difference between the alcohol yield from malt- and mold-converted cooks is appreciably greater than in previously discussed experiments.

Adjustment of pH of Mold Medium. Adjustment of the pH of the mold medium was also investigated from the standpoint of application to plant processing problems. Prior to this time media for laboratory scale mold propagation were adjusted with sodium hydroxide and 0.5% calcium carbonate added as a buffer. The results of several variations in this procedure are presented in Table IV. In the first instance the solubles medium was adjusted to pH 6.0 with sodium hydroxide and 0.5% calcium carbonate was added. In the second case, sufficient calcium carbonate was added to adjust the pH to 5.0 and 0.5% excess was added. In the third case the pH was adjusted to 5.0 with calcium carbonate but no excess was used. Mold growth and amylase values were identical with each of the above procedures. The alcohol yields from fermentations converted with these amylase cultures give further evidence that calcium carbonate is satisfactory in replacing sodium hydroxide. In all cases the alcohol yield of the experimental fermenters was 0.25 proof gallon per bushel higher than the malt-converted control. There is a definite advantage in the use of calcium carbonate in plant operation. The danger of overadjustment due to operational error is minimized and the time required for pH adjustment is reduced.

Re-use of Stillage from Mold Converted Mashes as Mold Media In the commercial production of mold amylase the distillery by-products used as mold media and as backset would obviously be produced from mold-converted mashes. In all the experiments previously described, the submerged mold cultures have been grown in by-products from malt-converted fermentations. It was deemed necessary to determine whether stillage from mold- and malt-converted mashes differ in regard to suitability as substrates for mold amylase production. Experiments were run in which laboratory stillage from mold-converted mashes was compared with malt stillage as mold media and as backset (Table V).

Two controls were employed. The first was the malt-converted control and the second, the mold control in which 10% by volume of a culture grown in stillage from a malt-converted mash was used as the conversion agent. Ten per cent by volume of malt stillage was added as backset. In one set of fermentations malt stillage was again used as the submerged culture medium

Table III. Effect of Conversion Temperature on Alcohol Yield

Conversion Agent	Temperature, ° F.	S. V.	Alcohol Yield Proof Gal./Bu., Dry Basis	Plant Efficiency, %
Malt control	145	..	5.99	91.9
Mold culture	130	63.5	6.07	91.0
Mold culture	145	63.5	6.15	92.2

Table IV. Sodium Hydroxide and Calcium Carbonate as Neutralizing Agents for Mold Media

Neutralizing Agent	Excess $CaCO_3$, G./100 Ml.	S. V.	Alcohol Yield, Proof Gal./Bu., Dry Basis	Plant Efficiency, %
NaOH	0.5	95	6.26	93.8
$CaCO_3$	0.5	95	6.26	93.8
$CaCO_3$	None	95	6.24	93.6
Control (malt converted)			6.01	92.2

TABLE V. STILLAGE FROM MOLD- AND MALT-CONVERTED MASHES AS MOLD MEDIA AND AS BACKSET

Conversion Agent	Type of Stillage		S. V.	Alcohol Yield, Proof Gal./Bu., Dry Basis	Plant Efficiency, %
	Mold medium	Backset			
Malt (control)	...	Malt	..	6.13	94.0
Mold culture (control)	Malt	Malt	80	6.32	94.7
Mold culture	Malt	Mold	80	6.38	95.6
Mold culture	Mold	Malt	80	6.27	94.0
Mold culture	Mold	Mold	80	6.38	95.6

TABLE VI. EFFECT OF VARYING AMOUNTS OF 24-HOUR MYCELIAL TRANSFERS AS INOCULA FOR MOLD AMYLASE PRODUCTION

Propagating Procedure		S. V.	α-Amylase, Units/100 Ml.	Alcohol Yield, Proof Gal./Bu., Dry Basis	Plant Efficiency, %
Type of inoculum	Amount of inoculum, %				
Sporulated	2.0	95	2180	6.10	90.3
Mycelial	2.0	80	2020	6.11	90.4
Mycelial	0.5	80	2042	6.11	90.4
		Control (malt converted)		5.94	90.0

TABLE VII. TYPICAL LABORATORY FERMENTATIONS WITH MOLD AMYLASE PREPARED BY PROPOSED PROCEDURE[a]

Conversion Agent	S. V.	Alcohol Yield, Proof Gal./Bu., Dry Basis	Plant Efficiency, %
Malt control	..	5.95	91.3
Mold culture	63.5	6.27	94.0
Mold culture	80.0	6.20	92.9
Mold culture	80.0	6.16	92.3

[a] Incorporating all improvements described in this paper.

but stillage from a mold-converted mash was used as backset. Mold stillage was also used as the mold medium with malt and mold stillage backset. It was found that the amylase production as measured by the saccharification values was identical in all cases. The alcohol yields indicate that the elimination of malt will not affect the by-products in regard to re-use for mold propagation. The average alcohol yield with the mold amylase preparations was approximately 0.3 proof gallon per bushel higher than the malt-converted control.

SERIAL SUBMERGED CULTURE TRANSFER. Another problem which has been investigated from the standpoint of industrial application is the procedure for culturing mold in the intermediate stages between the laboratory and the final plant-scale mold propagator. Inoculations of laboratory submerged cultures have been made from heavily sporulated surface cultures. On a commercial scale it is necessary to use intermediate submerged culture stages and the size of these vessels and the length of the incubation period at each stage are of course important from the economic standpoint.

A group of experiments was run in which varying amounts of inocula from serially transferred submerged cultures were compared with 2.0% by volume of sporulated surface cultures as inocula for the final submerged mold amylase preparation (Table VI). Serial transfer of submerged cultures is termed mycelial transfer, since sporulation is negligible in submerged growth at the incubation periods studied.

The first propagating procedure listed is the standard control method in which the medium was inoculated with a sporulated surface culture, aerated for 48 hours, and used for conversion of a test mash. In the second propagating procedure one flask was inoculated as above but transfer was made to a second submerged culture which was aerated for 24 hours. Two per cent of this culture was used to inoculate the third and final stage which was aerated for 48 hours. The last propagating procedure was varied from the above in that only 0.5% inoculum was employed.

The amylase values and alcohol yields with the various inoculation procedures were practically identical. Although amylase production in submerged culture was low at 24 hours, the mold growth had developed sufficiently for use as inoculum; 0.5% by volume of such a transfer is comparable to a heavily sporulated surface culture.

TYPICAL FERMENTATION DATA USING IMPROVED CULTURE METHODS. Table VII contains typical data from laboratory fermentations in which the submerged mold amylase cultures used for conversion were prepared by a procedure incorporating all the developments which have been described. The medium consisted of 5 grams per 100 ml. of distillers' dried solubles and 1 gram per 100 ml. of corn meal, neutralized with calcium carbonate. The culture was transferred serially through three stages with 0.5% by volume inoculum. The first two stages were aerated for 24 hours and the last stage for 48 hours. An amount of this material equivalent to 10% of the final mash volume was used as the sole conversion agent in test fermentations. Conversion was conducted at 145° F. With this procedure the alcohol yields varied from 6.16 to 6.27 proof gallons per bushel as compared to the malt-converted control yield of 5.95 proof gallons per bushel. Plant efficiencies (based in the starch analysis of the grain) with mold conversion are equal to or higher than the efficiencies with malt conversion.

CONCLUSIONS

As a result of the wide variation of stillage in regard to mold growth-promoting quality, distillers' dried solubles which consistently support mold growth and amylase production are recommended. Improvements have been made in submerged culturing methods which will be reflected in simplification of operating procedure and in a reduction of operating cost. These improvements may be summarized as follows:

1. Adjustment of the pH of the mold medium with calcium carbonate, instead of sodium hydroxide, and the elimination of excess calcium carbonate.
2. The use of 24-hour submerged cultures as intermediate stages between the laboratory culture and the final plant mold propagator.
3. The use of 0.5% mycelial transfer for inoculation of submerged cultures.
4. Elevation of the conversion temperature from 130° to 145° F.

With submerged mold amylase prepared by this procedure as the sole conversion agent for grain mashes, a consistent alcohol yield increase of 0.2 to 0.3 proof gallon per bushel can be obtained over malt-converted fermentations.

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KIESELGUHRS

Suitability as Carriers in Catalysts

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The properties of a number of kieselguhrs used as supports in cobalt Fischer-Tropsch catalysts have been studied. Data on chemical analysis, x-ray diffraction, surface areas, and pore volumes, together with electron micrographs at a magnification of 2000 and 20,000 diameters, are presented and correlated.

In the search for a suitable carrier for cobalt Fischer-Tropsch catalysts the properties of a number of kieselguhrs were determined. Since these data may be of general interest to chemists as well as of specific interest to those preparing catalysts, they are presented here; in later papers the influence of these kieselguhrs on the properties and activity of Fischer-Tropsch catalysts will be discussed. The data include chemical analyses of representative samples, x-ray diffraction patterns, electron micrographs, surface areas by nitrogen adsorption, and pore-volume studies.

There is not a great deal of information in the literature that may enable one to determine the suitability of a given kieselguhr as a carrier in catalysts. The properties and uses of kieselguhrs have been summarized by Calvert (*4*), Skinner (*12*), and others. Only a few papers have appeared on the application of the electron microscope to catalysts or constituents of catalysts. Ries (*9*) has discussed electron microscope and adsorption studies of a typical commercially available kieselguhr. Turkevich (*14*) has described electron micrographs of a number of catalysts, and Shekter, Roginskiĭ, and Isaev (*11*) have published electron micrographs of catalysts prepared with asbestos as a carrier.

Kieselguhrs are composed chiefly of diatoms. (In this country the names diatomaceous earth or diatomite are more common, but in Fischer-Tropsch literature the name kieselguhr is generally used.) Kieselguhrs may be of either marine or fresh water origin but they are always composed of amorphous silica plus small amounts of alumina, iron oxide, and traces of other oxides. Kieselguhr particles exhibit a variety of interesting forms that reflect to some extent the source of the material. Kieselguhrs formed in swamps sometimes contain rather high percentages of carbonaceous material, which is usually removed by calcination. In preparing commercial kieselguhrs the crude material is crushed and then separated into fractions of varying particle sizes by screening, settling in water, air separation, or combinations of these. Some commercial kieselguhrs have been heat-treated (calcined) and alkali-heat-treated (flux-calcined) to produce varying degrees of sintering to improve their properties as filter aids, etc.

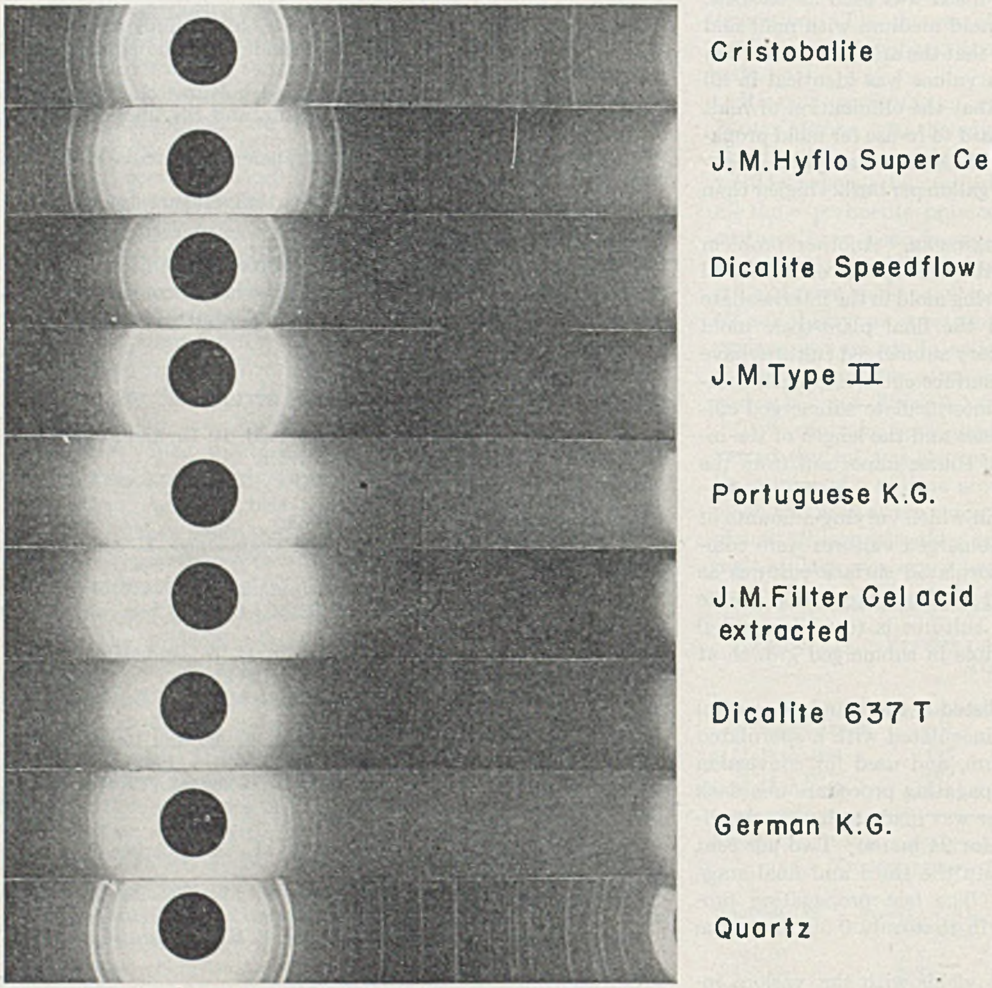

Figure 1. X-Ray Diffraction Patterns of Kieselguhrs, Quartz, and Cristobalite

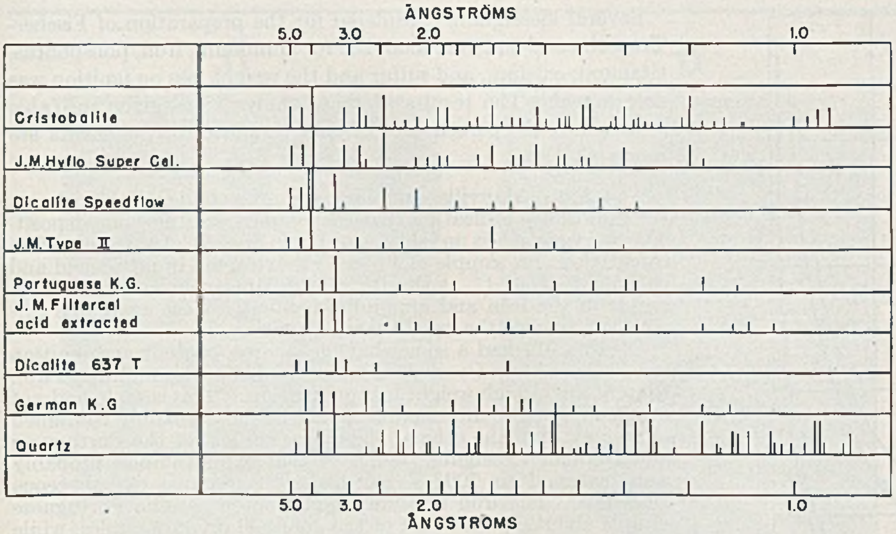

Figure 2. X-Ray Diffraction Data for Kieselguhrs, Quartz, and Cristobalite

EXPERIMENTAL

Specimens of each type of kieselguhr were prepared for observation with the electron microscope by the following technique.

A supporting film was obtained by dipping a clean microscope slide into a 0.5% solution of Formvar (polyvinyl formal) in dioxane. The kieselguhr particles were dusted onto the dried film and dispersed by exposure to a high-frequency, high-voltage spark discharge from a Tesla coil (an ordinary vacuum-leak tester). The film was scored around the edges of the slide and crosswise into 0.25-inch squares, then moistened by the breath, and the slide was lowered obliquely into water so that the film floated off onto the water surface. A square of film with adhering kieselguhr particles was picked up on a loop and lowered onto a 200-mesh screen placed on the specimen holder. When dry, the mount was ready for observation in the electron microscope.

The electron micrographs shown here were made in an R.C.A. Type B microscope. Those in Figures 5 to 9, which were selected by six or more persons as most representative of eight or more micrographs of each sample, were made at a magnification of 2000. This was sufficiently high to reveal the structure of larger pores, and the larger field that could be viewed at this magnification permitted study of the external shape of the particles. However, finer detail of possible significance is revealed by enlargement to 20,000 as illustrated in Figure 10.

The x-ray diffraction studies were made by the powder method.

All the samples were sufficiently fine to be used without further grinding. Each specimen was prepared by packing the powder into small 20-mm. lengths of stainless steel tubing 0.7 mm. in inside diameter; it was then partly extruded to a length of about 5 mm. by pushing a closely fitting stainless steel wire through the bore. No binder such as collodion was used to increase the strength of the sample; compacting alone gave the specimen sufficient cohesion to withstand all subsequent treatment. The use of binders, even if amorphous and of low scattering power, is undesirable in studying amorphous or semiamorphous catalyst materials. The tube with the extruded cylinder of compacted powder was mounted in a Debye-Scherrer camera of 71.6-mm. diameter. A sealed off x-ray tube of the Coolidge type equipped with beryllium windows and an iron target was used. K_β radiation was removed with a manganese dioxide filter. Exposures were for 3 hours at 48 kilovolts and 7 milliamperes. Phase identification was effected by means of the Hanawalt index cards of x-ray reflections (*1*) and by comparison with patterns from authentic samples of cristobalite, tridymite, and quartz.

Nitrogen adsorption isotherms were determined on the kieselguhr samples, by a volumetric method described by Emmett (*5*). The surface areas were estimated by the use of the simple Brunauer, Emmett, and Teller equation (*3*), where the cross-sectional area of the nitrogen molecule is assumed to be $16.2\ \text{Å}^2$. All samples were dried in an oven at 100° C. for 1 hour and then evacuated for 1 hour at 100° C. before the isotherms were determined.

Pore-volume studies were made by determining the bulk density, and densities by the displacement of helium and mercury. Bulk densities were determined on samples dried at 100° C. for 1 hour by measuring the volume occupied in a 100-cc. graduate after it was tapped on a table 100 times. Helium density measurements at 30° C. by the method of Smith and Rossman (*13*) were made on dried samples pumped for 1 hour at 100° C. The accuracy of this method, as applied in this study, was only about ±1.5% because of the small volumes of helium displaced by fairly large volumes of kieselguhr. Mercury densities were determined by introducing mercury at an absolute pressure of 1140 mm. into samples which were dried and pumped as in the helium density method. Mercury-density measurements on a finely divided material may be uncertain because (*a*) particles may pack so closely under the pressure of the mercury that mercury cannot penetrate between the particles, and (*b*) the mercury may require a long time to penetrate all the pores available to it. If the first effect is pronounced, the mercury density should vary considerably in repeated determinations, especially if the size of bulb is changed. Significant variations did not occur in experiments with Dicalite 911 in which the mercury density was 0.371 and 0.375 on repeated determinations in the same bulb and 0.378 in a bulb 50% larger than the first. The effect of time of contact of the mercury was not pronounced, as indicated by determinations on Dicalite, Grade 1, in which the mercury density after several minutes of contact was 0.348 compared with 0.361 after 6 days. At atmospheric pressure mercury will penetrate only pores (cylindrical) whose openings are larger than 5 microns (*10*). The macropore volume (pores larger than 5 microns) is the difference of the reciprocals of the bulk and mercury densities, while the micropore volume (pores smaller than 5 microns) is the difference of the reciprocals of the mercury and helium densities. The macropore volume probably consists almost entirely of spaces between the particles of kieselguhr, and the micropore volume consists of volume between and within the particles.

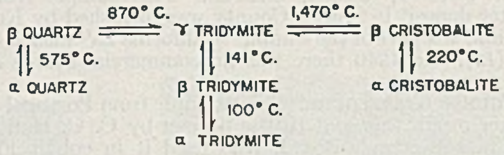

Figure 3. Transitions of Silica (*7*)

DESCRIPTION OF SAMPLES

JOHNS-MANVILLE SAMPLES. All are from the Lompoc, Calif., deposit, which is of marine origin. Filter-Cel and Hyflo Super-Cel are examples of filter aids, the Filter-Cel being a natural material, while Hyflo Super-Cel is a flux calcined product. Snow Floss is a natural kieselguhr characterized by a very small particle size. Samples I to IV are described as catalyst supports; III and IV are natural kieselguhrs, II is a calcined material, and I is flux-calcined. At the bureau, a sample of Filter-Cel was treated with hot nitric acid for 6 hours to reduce the percentages of materials other than silica, then filtered and dried at 120° C., and finally heated at 650° C. for 2 hours.

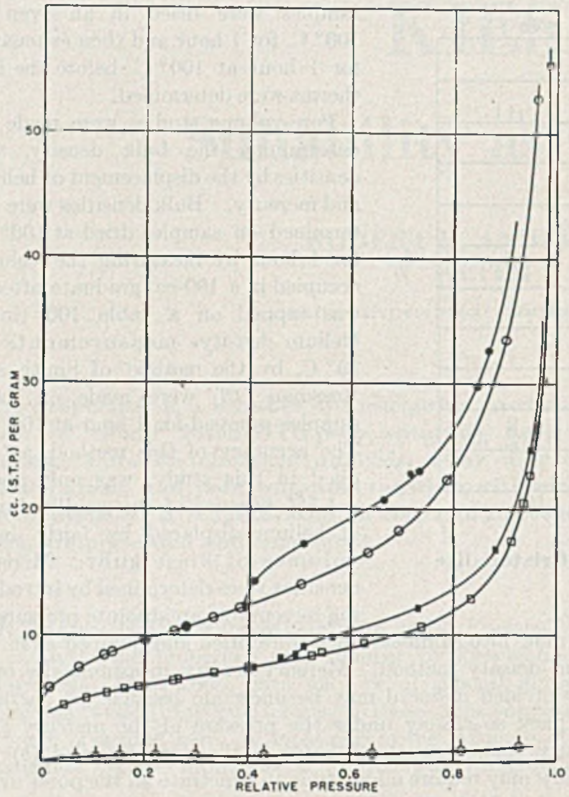

Figure 4. Adsorption of Nitrogen on Kieselguhrs at −195° C.

○. Shasta County kieselguhr
□. Filter-Cel
⦶. Hyflo Super-Cel
Solid points represent desorption

Dicalite Samples. Samples 911 and Grade 1 are natural materials of the fresh-water deposit at Terrebonne, Ore. Samples SA5 and 637T are fresh-water kieselguhrs from Nevada, while 658T is a fresh-water material from the state of Washington. Speedflow and PS filler are flux-calcined materials, probably from the Lompoc deposit in California.

Shasta County, Calif., Sample. This sample from the fresh-water deposit in Shasta County was furnished by Kenneth Skinner, and is a part of the sample "California 2a" mentioned by Skinner (*12*). In 1940 there was no commercial source of this material.

Portuguese Kieselguhr. This sample from Portugal and of fresh-water origin was sent to the bureau by C. C. Hall of the British Fuels Research Board, who used it in cobalt Fischer-Tropsch catalysts.

German Kieselguhr. This was taken from the catalyst factory, Ruhrchemie A.-G., Sterkrade, on April 19, 1945. Probably this is the German Röstguhr. It is thought to have come from a fresh-water deposit near Hannover and to have been calcined to 700° C. or higher, possibly to remove carbonaceous material. Another sample of kieselguhr was obtained by extracting with hot nitric acid constituents other than kieselguhr from a German cobalt Fischer-Tropsch catalyst.

CHEMICAL ANALYSES OF KIESELGUHRS

In the preparation of some types of catalysts small percentages of certain elements are undesirable. In addition to hydrated silica, kieselguhrs contain small amounts of other compounds, aluminum and iron oxides being the chief impurities. Skinner (*12*) presented analyses of a number of kieselguhrs from Washington and Oregon. In this bulletin Skinner assumed that any aluminum came from clay present as an impurity. Calvert (*4*) has given analyses of a number of kieselguhrs from the United States and Germany. In the tables of Skinner and Calvert the amounts of silica varied from 70 to 90%, with weight losses upon ignition of 3 to 12%. From 0.5 to 10% of alumina and of iron oxide were reported.

Several kieselguhrs considered for the preparation of Fischer-Tropsch catalysts were analyzed for aluminum, iron, phosphorus, titanium, calcium, and sulfur and the weight loss on ignition was determined. The results of these analyses are given in Table I, in which the percentages of these impurities as elements are reported.

The Johns-Manville samples gave almost identical analyses, the uniformity indicating that they came from the same deposit. The low weight loss on ignition of Hyflo Super-Cel was due to flux calcination. A sample of Filter-Cel, extracted in nitric acid and calcined to 650° C. at the Bureau of Mines, showed a 50% decrease in the iron and aluminum content. Here again the calcination reduced the weight loss on ignition.

Dicalite 911 had a somewhat higher iron content and ignition loss. The Shasta County kieselguhr had high aluminum and iron content and a high weight loss on ignition. This sample had not been subjected to any separating method and possibly contained more clay than the others. The ignition loss of the Portuguese and German kieselguhrs indicates that these samples probably were calcined to 700° C. or higher to remove carbonaceous materials. The iron and aluminum content of the Portuguese sample about equaled that of the Johns-Manville samples, while the aluminum content of the German kieselguhr was very low and the iron high.

The percentages of phosphorus and titanium in all the samples were low—less than 0.3% in all cases—and the calcium content was always less than 0.5%. The sulfur content was less than 0.1% for all samples except Shasta County and German kieselguhrs.

Table I. Elements Other Than Silica in Kieselguhrs

	Weight Loss on Ignition, %	Percentages Computed as Elements					
		Al	Fe	P	Ti	Ca	S
Johns-Manville							
Hyflo Super-Cel	0.33	1.90	0.87	0.07	0.12	0.19	0.03
Filter-Cel	3.47	1.87	0.85	0.10	0.13	0.31	0.03
Filter-Cel (acid-extracted)	0.60	0.9	0.49	[a]	[a]	[a]	[a]
Dicalite 911	4.28	2.29	1.49	0.01	0.16	0.46	0.09
Shasta County	6.42	4.88	2.24	0.02	0.28	0.49	0.31
Portuguese	1.58	2.06	0.87	0.006	0.08	0.03	0.05
German	1.66	0.58	3.86	0.01	0.08	0.27	0.19

[a] Not determined.

X-RAY DIFFRACTION STUDIES OF KIESELGUHRS

By means of x-ray diffraction patterns of kieselguhr the crystalline phases may be identified, and moreover the width or diffuseness of the diffraction lines gives an indication of crystallite size. The reactivity of kieselguhrs—for example, the solubility in solutions from which catalysts are precipitated—depends among other things upon the crystalline phase and crystallite size.

Table II. X-Ray Diffraction Data on Kieselguhrs

	Diffuseness	Phase
J.M. I	A	Cristobalite
II	C	Cristobalite
III	X	Amorphous
IV	X	Amorphous
FC	C^-	Amorphous, quartz, unknown
FC acid-extracted	C^-	Amorphous, quartz
HSC	A	Cristobalite
Dicalite SF	B	Cristobalite, quartz
637T	X	Amorphous
658T	X	Amorphous
SA5	X	Amorphous
911	X	Amorphous
Grade 1	X	Amorphous
PS	C^-	Cristobalite
Shasta County	C^-	Amorphous, unknown
Portuguese	C^-	Amorphous, quartz
German	C	Quartz

A. Sharp.
B. Somewhat diffuse.
C. Diffuse
C^-. Diffuse to the point where phases are difficult to ascertain.
X. Amorphous.

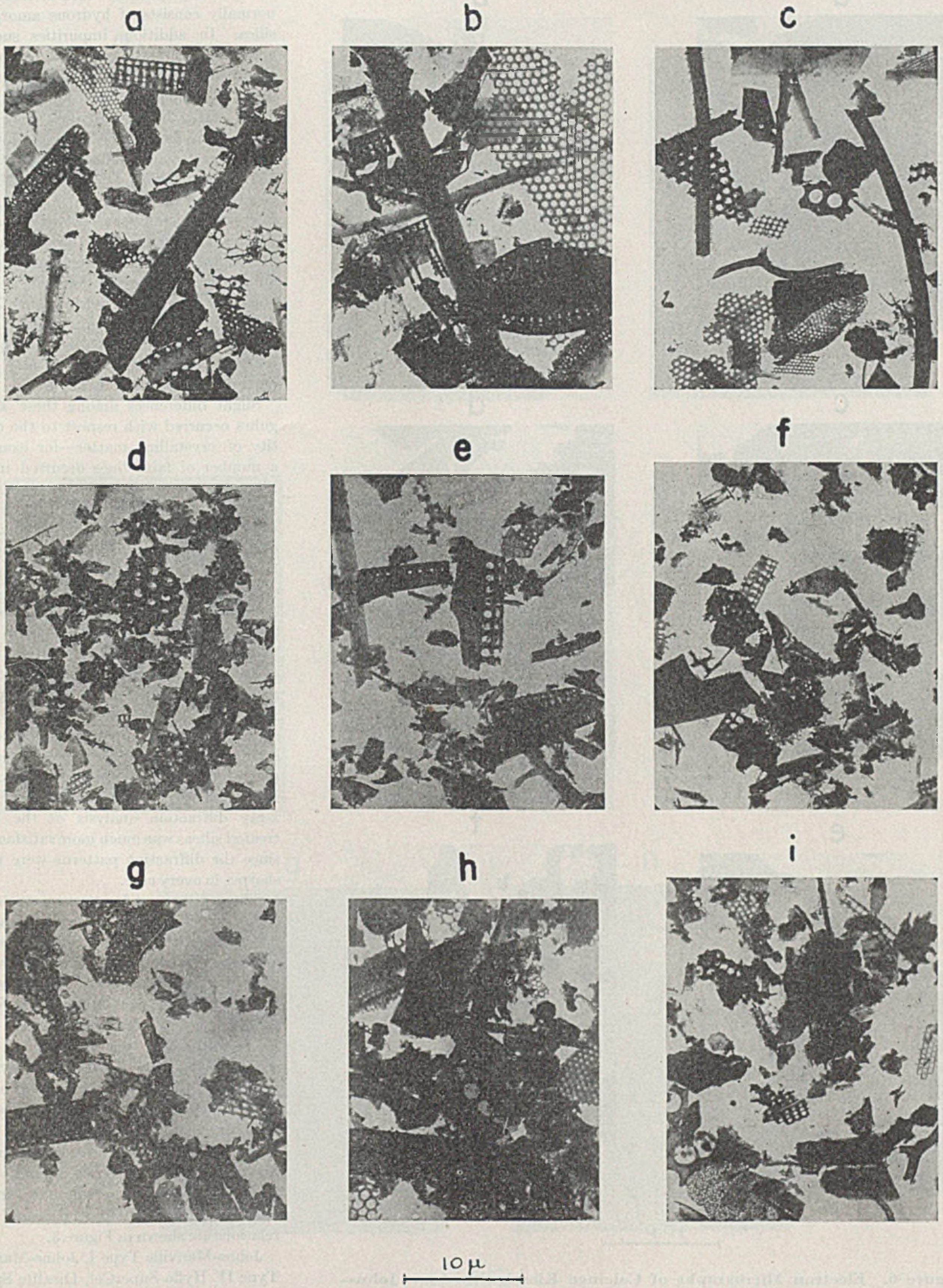

Figure 5. Electron Micrographs of Uncalcined Kieselguhrs from Johns-Manville Corporation (2000 ×)

a, b. Filter-Cel
c. Filter-Cel acid-extracted
d, e. Snow Floss
f, g. JM-III
h, i. JM-IV

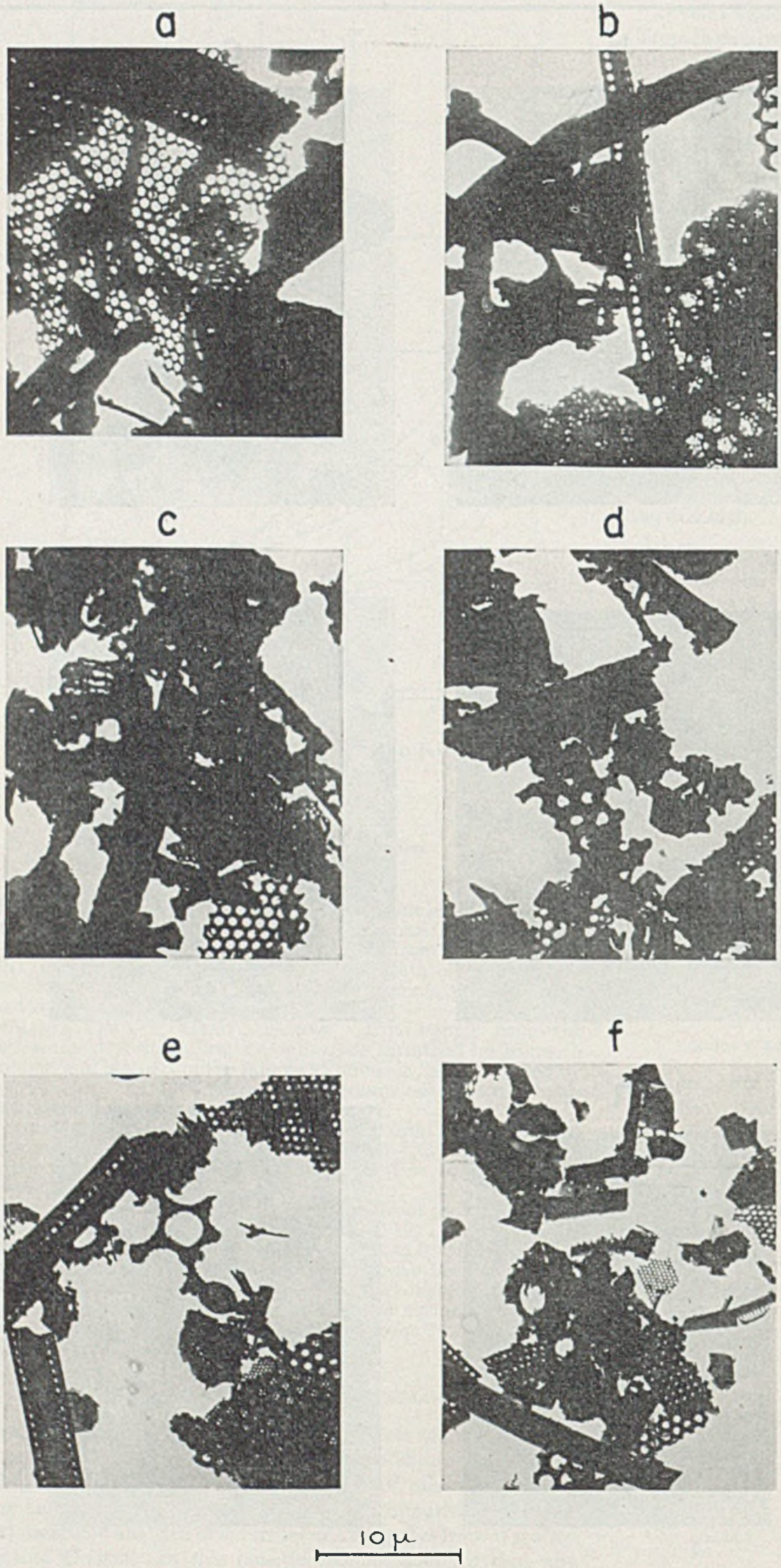

Figure 6. Electron Micrographs of Calcined Kieselguhrs from Johns-Manville Corporation (2000 ×)

a, b. Hyflow Super-Cel *c, d.* JM-I *e, f.* JM-II

Crystallographically natural kieselguhr normally consists of hydrous amorphous silica. In addition, impurities such as clay, and crystalline quartz often are found in perceptible quantities. In the series of samples studied, Johns-Manville Type III, Johns-Manville Type IV, Johns-Manville Filter-Cel, both raw and acid-extracted, Dicalite 637T, Dicalite 658T, Dicalite SA5, Dicalite 911, Dicalite Grade 1, Shasta County, and the Portuguese kieselguhr all belong essentially to this normal group. In spite of the low water content, the Portuguese kieselguhr showed no crystallization, such as one might expect from calcination. X-ray diffraction patterns of various kieselguhrs and samples of cristobalite and quartz are given in Figures 1 and 2, and these patterns are described in Table II.

Slight differences among these kieselguhrs occurred with respect to the quantity of crystalline matter—for example, a number of faint lines occurred in the Filter-Cel patterns, some of which disappeared on acid extraction. Those lines which remained seem to be those of quartz. The pattern of the Portuguese kieselguhr, as far as the faint lines were concerned, was very similar to the acid-extracted Filter-Cel. The pattern of the Shasta County kieselguhr contained faint lines which cannot be assigned to quartz or any other crystalline silica. The large amount of impurities 8.0% as compared with 2.9% for Filter-Cel and 1.4% for acid-extracted Filter-Cel, suggest that the strange lines were due to crystalline impurities. The other amorphous kieselguhrs gave very few faint lines. The x-ray diffraction analysis of the heat-treated silicas was much more satisfactory, since the diffraction patterns were much sharper in every case.

Silica exists in at least seven crystalline forms, which may be naturally classified into a quartz series, a tridymite series, and a cristobalite series. Transitions from one series to another are sluggish, whereas within each series transitions are in general very rapid. At room temperature only one member of each series usually exists: α-quartz, α-tridymite, and α-cristobalite. The last two owe their existence to the slowness of the transition from one series to another. The only forms of silica which have an accessible region of thermodynamic stability are α-quartz, β-quartz, γ-tridymite, and β-cristobalite. The various forms and their relations are shown in Figure 3.

Johns-Manville Type I, Johns-Manville Type II, Hyflo SuperCel, Dicalite Speedflow, and Dicalite PS filler all contained cristobalite. In addition, Dicalite Speedflow contained α-quartz, indicating incomplete conversion from quartz to cristobalite. Normally one might ex-

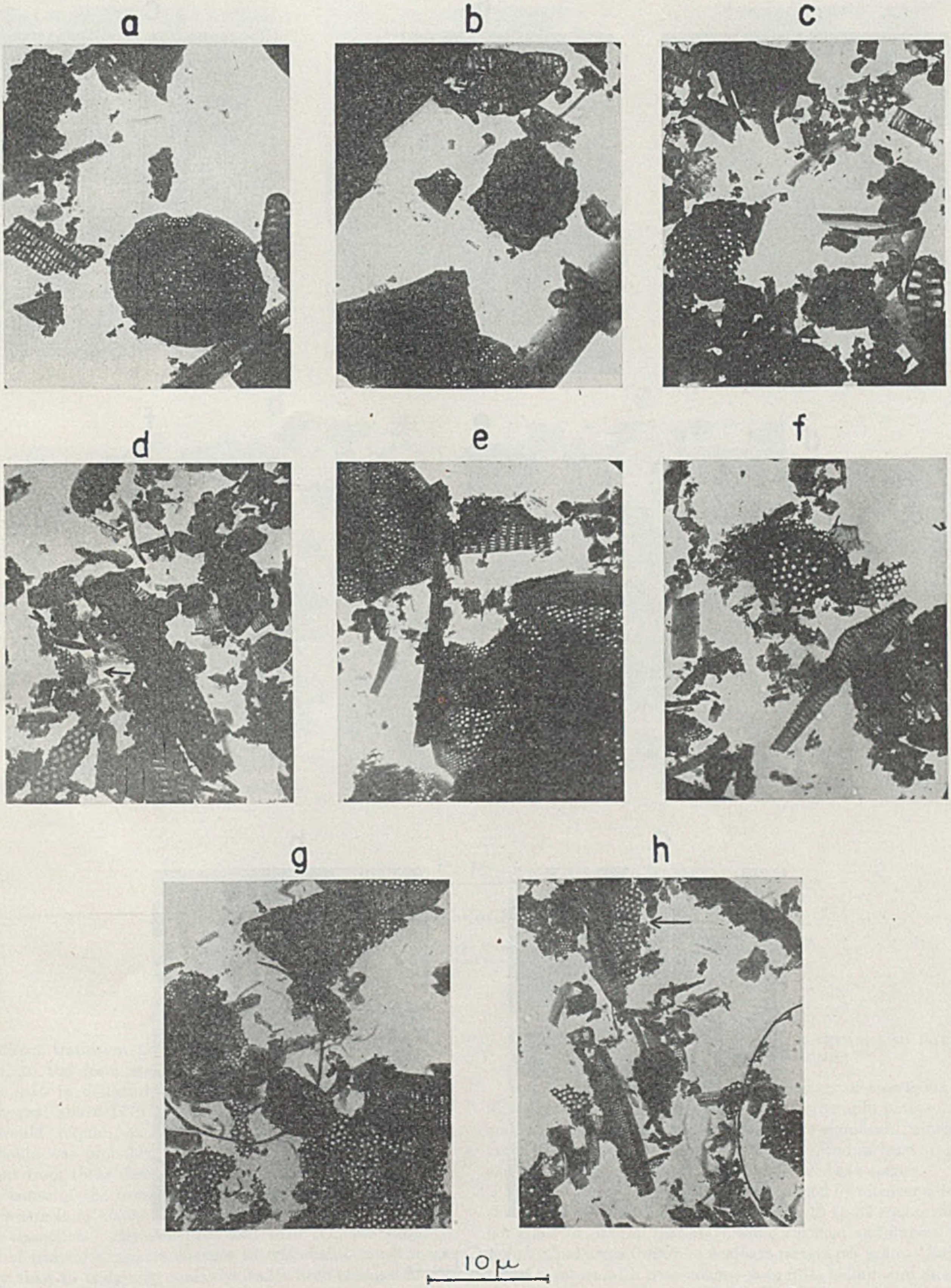

Figure 7. Electron Micrographs of Kieselguhrs from Dicalite Company (2000 ×)

a, b. Grade 1
c, d. 911
e, f. SA-5
g, h. 637T

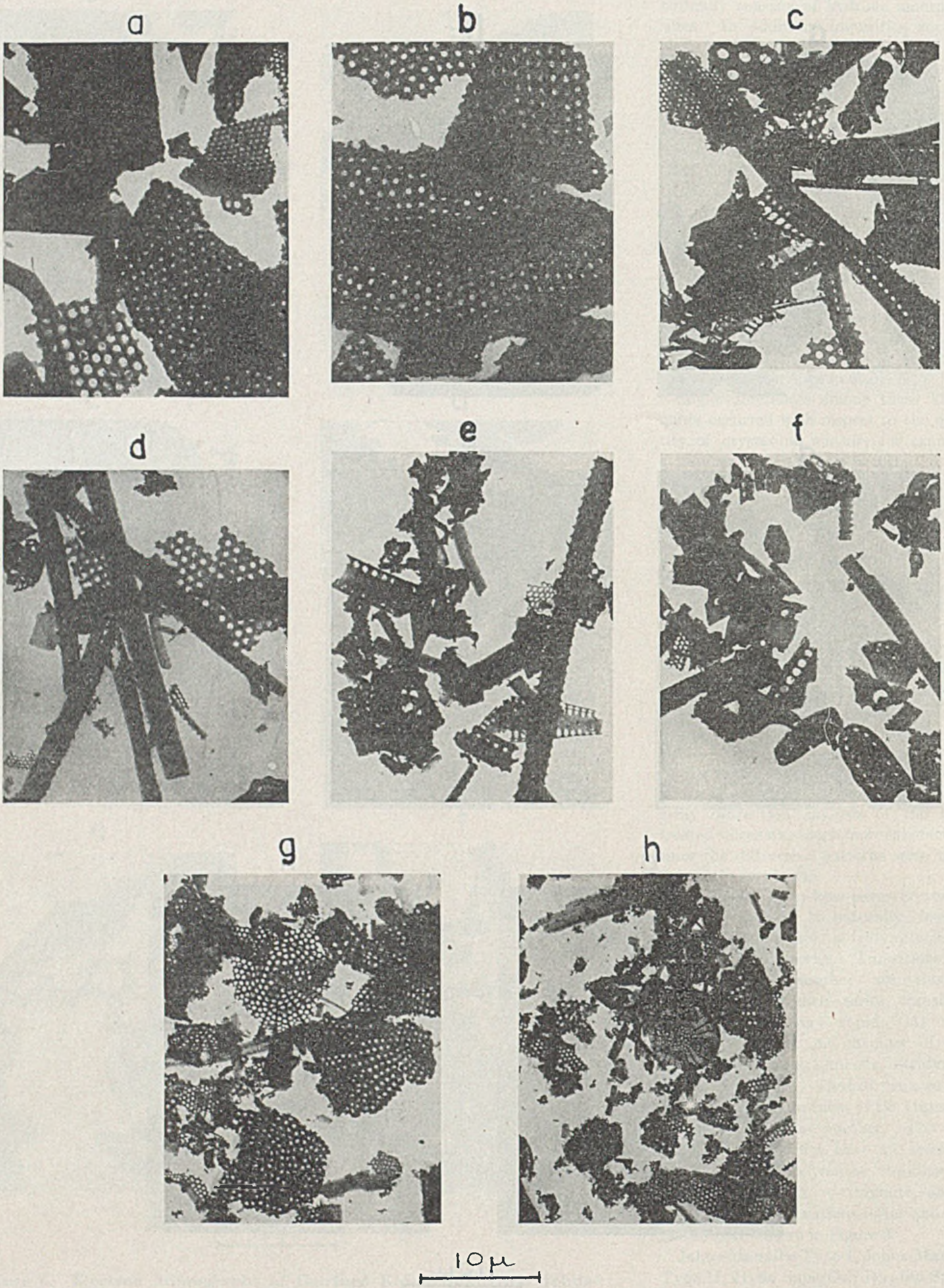

Figure 8. Electron Micrographs of Kieselguhrs from Dicalite Company and from California Deposit

a, b. 658T
c, d. Speedflow
e, f. PS filler
g, h. Shasta County, Calif.

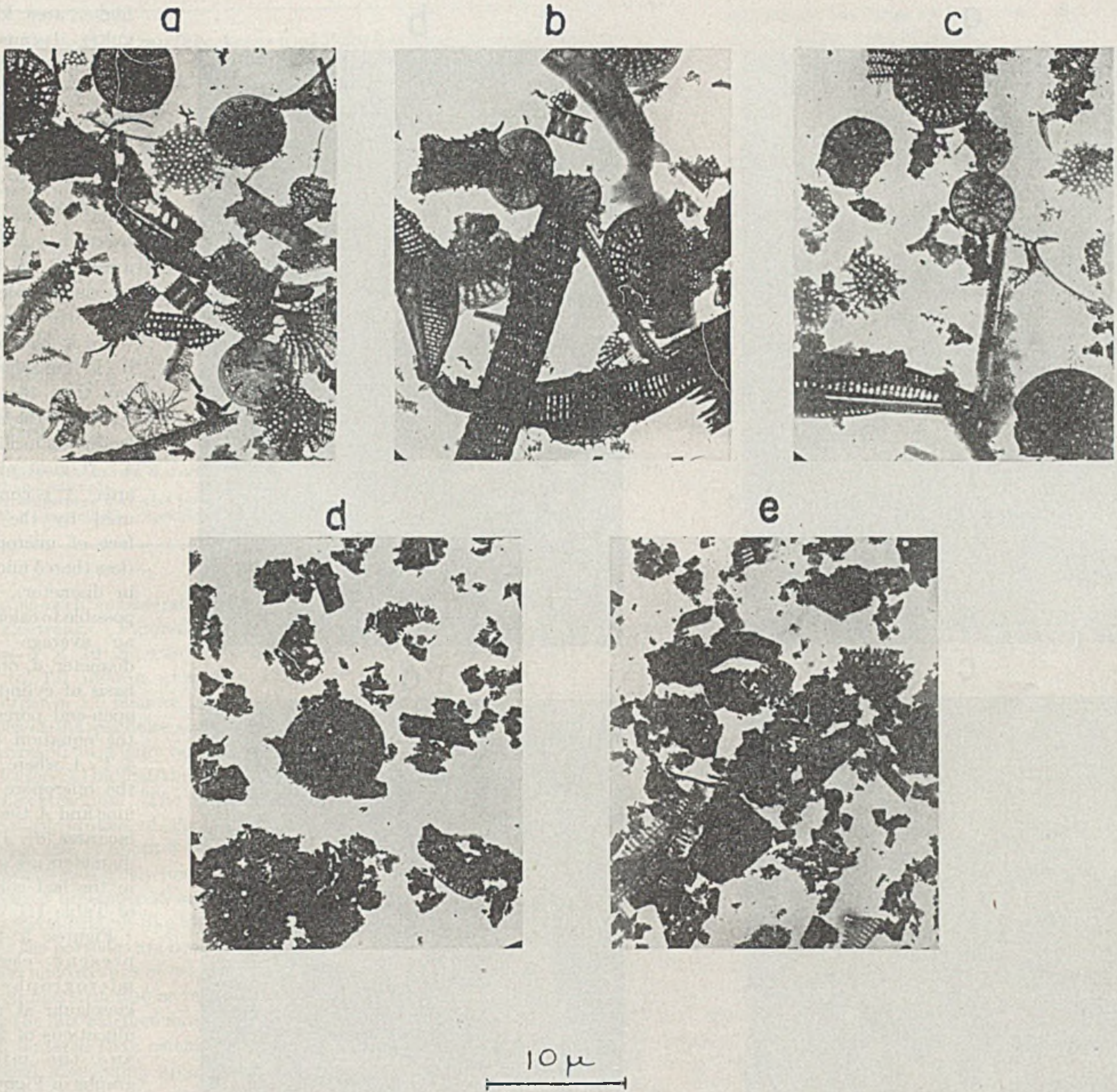

Figure 9. Electron Micrographs of Foreign Kieselguhrs (2000 ×)

a, b. German near Hannover
c. From German cobalt catalyst
d, e. Portuguese

pect direct transition from the low-temperature stable form, quartz, to the form stable above the transition point, tridymite. It is doubtful if any of the calcined kieselguhrs were heated above 1470° C., where cristobalite is stable, since this would require exceedingly expensive equipment. The cristobalite was probably formed under conditions not greatly different from those described by Skinner (*12*).

The cause of the formation of cristobalite in a temperature range where it is known to be metastable lies in the kinetics of the transition. Between 870° and 1470° C., the stability region of tridymite, quartz changes to cristobalite much more rapidly than to tridymite, and cristobalite itself changes to tridymite very slowly.

The sharpness of the lines of German kieselguhr was probably due to calcination, but no indication of the presence of cristobalite could be found. Therefore, 870° C. probably was not exceeded during calcination.

ELECTRON MICROGRAPHS, SURFACE AREAS, AND PORE VOLUMES OF KIESELGUHRS

A reasonably good picture of the geometry of kieselguhr particles can be presented from electron-micrograph, pore-volume, and surface-area studies. These data are significant, since the pore structure and density of catalysts depend at least to some extent on the properties of the kieselguhr used as a carrier.

Surface areas of kieselguhrs, as determined by nitrogen-adsorption isotherms at −195° C., varied from 15 to 37 square meters per gram for natural materials, while calcined and flux-calcined samples had areas from 2 to 6 square meters per gram. Surface areas, together with pore-volume data from helium and mercury densities, are given in Table III. These data are computed per gram of kieselguhr after evacuation at 100° C. as previously described. The adsorption isotherms were of the S-type (Type II of Brunauer's classification (*2*), which would be expected for a system of pores averaging larger than about 1000 Å. in diameter.

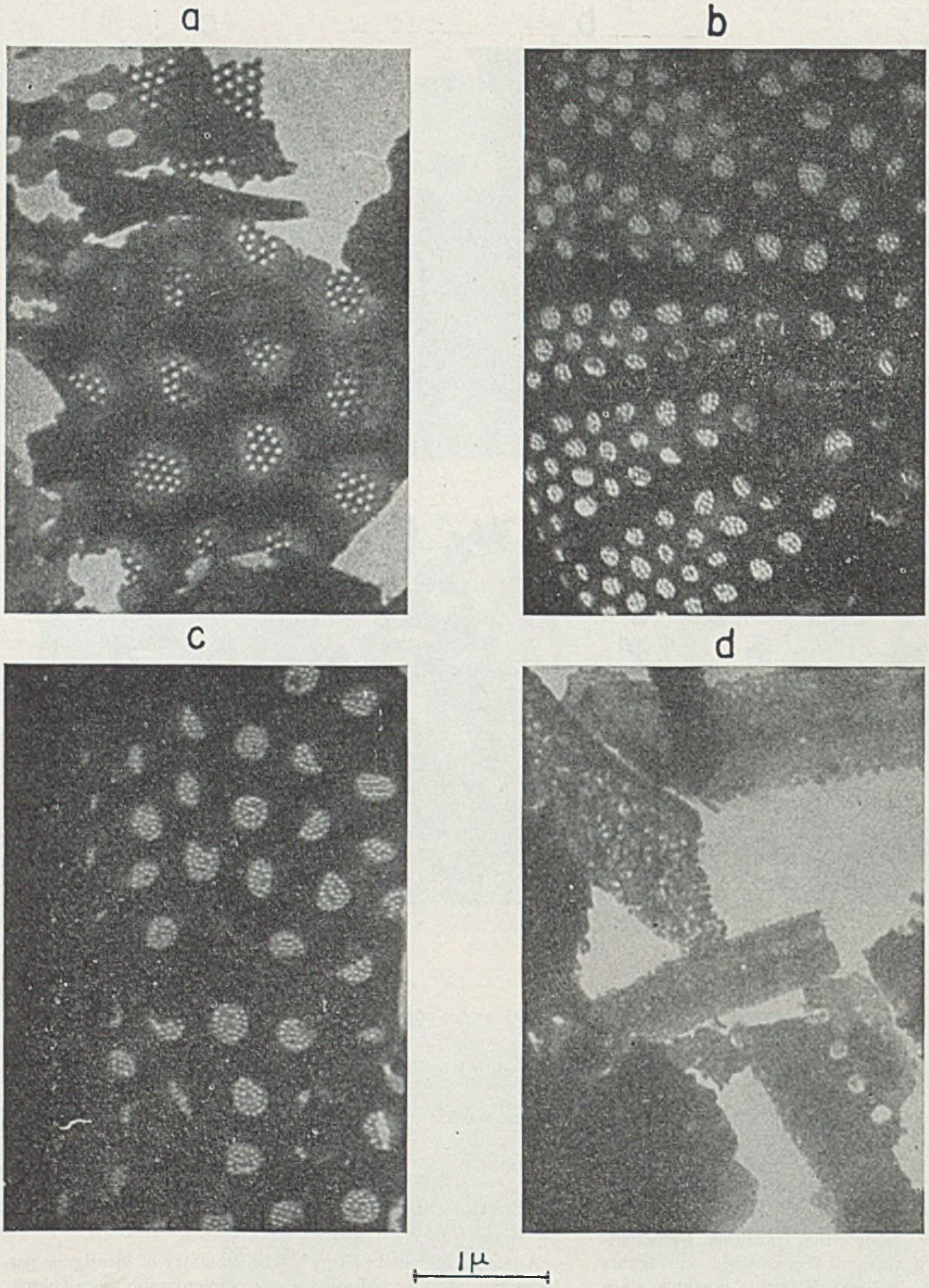

Figure 10. Electron Micrographs of Kieselguhrs, Showing Fine Pore Structure Visible at High Magnification (20,000 ×)

a. Johns-Manville Snow Floss
b. From German cobalt catalyst
c. Dicalite 637T
d. Dicalite 911

Isotherms to fairly high relative pressures of Shasta County, Filter-Cel, and Hyflo Super-Cel are given in Figure 4. Desorption points determined on the Shasta County kieselguhr and Filter-Cel show definite hysteresis, indicating the presence of some pores of diameters in the range 15 to 100 Å. Isotherms of this type have been discussed by Ries (*8*). The accuracy of the Hyflo Super-Cel isotherm was less than for higher area kieselguhrs, because of the low ratio of surface area to dead space. This lack of accuracy makes it impossible to state with certainty whether the isotherm has a slight amount of hysteresis or none at all. However, if there is hysteresis, it is considerably less than that observed in the other isotherms in Figure 4. If most of the area, A, is contributed by the surface of micropores (less than 5 microns in diameter), it is possible to calculate an average pore diameter, d, on the basis of cylindrical open-end pores by the equation $d = 4\ V/A$ where V is the micropore volume and A the surface area (*6*). These diameters are given in the last column of Table III.

Figures 5 to 9 present electron micrographs of kieselguhr at magnifications of 2000, and the micrographs in Figure 10 are enlarged to 20,000 diameters. The general characteristics of the particles at magnifications of 2000, such as external shape and large pores, are discussed below. Some of these larger pores contain smaller pores evident only at higher magnifications.

The pictures of the Johns-Manville samples, Figures 5 and 6, showed similar types of particles which are termed a "rod and perforated plate" structure, the perforated plates probably being fragments of larger disks. This structure appeared to be characteristic of the marine deposit at Lompoc, Calif. The untreated Johns-Manville samples (Figure 5), Filter-Cel, Filter-Cel extracted, Snow Floss, JM III, and JM IV had somewhat similar micrographs. The par-

Table III. Surface Areas and Pore Volumes of Kieselguhrs

	Surface Area, Sq. M./G.	Bulk Density G./Cc.	Hg Density, G./Cc.	He Density, G./Cc.	Macro-pore[a] Volume, Cc./G.	Micro-pore[a] Volume, Cc./G.	Av.[b] pore Diameter, Microns
Johns-Manville							
Filter-Cel	22.8	0.149	0.299	2.19	3.32	2.81	0.51
Filter-Cel acid-extracted	20.8	0.17	...	..	..	..	..
Snow Floss	19.4	0.186	0.343	2.33	2.46	2.48	0.52
Hyflo Super-Cel	1.9	0.22	0.361	2.27	1.77	2.33	4.9
JM I	3.2	0.26	0.381	2.43	1.22	2.21	2.8
JM II	5.5	0.20	0.346	2.24	2.12	2.46	1.8
JM III	19.2	0.174	0.323	2.35	2.64	2.67	0.56
JM IV	12.4	0.228	0.406	2.22	1.92	2.01	0.66
Dicalite							
911	29.7	0.245	0.373	2.25	1.41	2.29	0.31
Grade 1	20.3	0.179	0.348	2.35	2.71	2.44	0.49
SA5	37.7	0.203	0.372	2.05	2.23	2.20	0.24
637T	34.2	0.196	0.369	[c]	2.39	2.28	0.28
658T	25.4	0.215	0.335	2.20	1.67	2.55	0.40
Speedflow	3.5	0.214	0.372	2.34	1.94	2.26	2.6
PS	3.2	0.245	0.372	[c]	1.39	2.26	3.0
Shasta County	33.6	0.35	0.425	2.39	0.51	1.92	0.23
Portuguese	17.5	0.345	0.508	2.36	0.90	1.54	0.40
German	14.9	0.137	0.272	2.29	3.63	3.24	0.87

[a] Macropores have a diameter greater than 5 microns and micropores have a diameter less than 5 microns.

[b] Average pore diameter computed by $d = 4 \times$ micropore volume/surface area.

[c] Not determined. Assumed to be 2.3 for pore volume estimations.

ticles showed considerable fine structure, and were transparent to electrons. Filter-Cel had perforated plates averaging about 5 × 10 microns, with holes varying from diameters of 0.1 to 1.0 micron averaging about 0.4 micron and rods of the order of 1.5 microns by 30 microns in length. The irregular shapes of the particles accounted for the low bulk density. The micrograph in Figure 5c and the surface area of the acid-extracted Filter-Cel indicated that no serious change had been produced by the extraction. The particles of Snow Floss were the smallest and most broken of the Johns-Manville kieselguhrs, with an average size of about 3 × 3 microns. The surface area of this material was slightly lower than that of Filter-Cel, but this may be only a difference in sampling. The surface area per gram of a porous substance like kieselguhr will increase only very slightly when the particles are broken into smaller pieces.

The micrographs of calcined kieselguhrs (Figure 6) showed the loss in fine structure as indicated by surface-area measurements, with the flux-calcined materials, JM I and Hyflo Super-Cel, being more sintered than calcined sample JM II. As the particles of calcined kieselguhrs appeared more opaque to electrons, these particles may have a greater thickness than the uncalcined samples. With Hyflo Super-Cel the perforated plates were larger than in Filter-Cel, with holes averaging about 1 micron in diameter and some as large as 2 microns.

The Dicalite samples in Figures 7 and 8 were from several different deposits, each having somewhat characteristic forms. Dicalite Grade 1 and 911 were from a fresh-water deposit in Terrebonne, Ore. Grade 1 was characterized by rods, large perforated disks about 17 microns in diameter, and some elliptical particles. Sample 911 was similar in structure to Grade 1, but the porous disks were of smaller diameter (about 8 microns), and all the particles were smaller and more broken in 911. Both samples had a considerable amount of fine structure with holes averaging about 0.3 micron in diameter. The surface areas and pore volumes were in qualitative agreement with the micrographs, in that the area of 911 was higher than that of Grade 1 while the pore volume was smaller than for Grade 1.

Samples SA5 and 637T, which were from a fresh-water deposit in Nevada, had high surface areas. Both samples contained chiefly perforated disks or fragments of these, which averaged about 18 microns in diameter for SA5 while those of 637T were somewhat smaller. The particles of 637T were more uniform than those of SA5. The holes, which averaged about 0.3 micron in diameter, were numerous in both samples; this probably accounts for the large surface area. Both samples have similar pore volumes.

Sample 658T, from a fresh-water deposit in Washington, occurs in large, opaque, porous pieces, which were probably fragments of larger disks. The average size of these pieces was about 30 × 45 microns. The holes were uniform in size, averaged about 0.5 micron in diameter, and were not very numerous. Some contained fine structure, which may account for the fairly high surface area. The structure of this sample, with large pieces and large pores, was reflected in the somewhat lower macropore volume and higher micropore volume than most of the samples.

Speedflow and PS filler were probably flux-calcined samples, possibly from the Lompoc deposit. A rod structure was predominant, and the material appears sintered. The surface areas were low.

In the kieselguhr from the fresh-water deposit in Shasta County, Calif. (Figure 8, *g* and *h*), the most common structure was disks or fanshaped fragments. The disks averaged about 10 microns in diameter with holes from 0.1 to 0.3 micron. This material had a high surface area and high bulk density. The symmetrical shape of the particles and the absence of rods probably accounted for the high bulk density. The high area may be due to small amounts of high area clays present as impurities, since the amount of alumina was high. It is, of course, possible that high area impurities may influence the surface areas of some of the other kieselguhrs.

The German kieselguhr (Figure 9, *a* and *b*), which was reported to be from a fresh-water deposit near Hannover, had the most perfect diatoms encountered in this study. The most prominent forms were disks and perforated rod or ladderlike structures. The disks have diameters of about 6 microns, with holes averaging about 0.05 micron. The rodlike structures average about 5 × 15 microns, with holes 0.3 to 0.5 micron in diameter. Because of the proportion of elongated forms, the bulk density was the lowest of any sample studied and both macro- and micropore volumes were large. The surface areas were lower than anticipated from the apparent fine structure; this was probably due to the calcination to 700° C. or higher. In Figure 9*c* is a micrograph of kieselguhr from a German cobalt Fischer-Tropsch catalyst. This kieselguhr was similar if not identical to the previous sample.

A large portion of the diatoms of the Portuguese fresh-water kieselguhr (Figure 9, *d* and *e*) was broken into small fragments of about 1 × 2 microns, the average particle size being the smallest of any sample discussed in this paper. Some particles of circular cross section about 5 microns in diameter are found. Some of the unbroken diatoms of this sample were similar to those of the German kieselguhr. It is possible that this sample had been calcined to about 650° C., for its surface area was lower than most of the fresh-water kieselguhrs. The fact that this sample was considerably broken was reflected in the high bulk and mercury densities of this material.

Micrographs of natural kieselguhrs at magnifications of 20,000 in Figure 10 show considerable fine structure not apparent in Figures 5 to 9. The particles in Figure 10, *c* and *d*, can also be seen in Figure 7, *h* and *d*, as indicated by the arrows. The fine structure is of two types: small holes within larger holes as shown in Figure 10, *a*, *b*, and *c*, and fine structure apparent in thin pieces and at the edges of thick pieces (Figure 10*d*). These micrographs show pores as small as can be detected, about 100 Å. Although this fine structure is not apparent on the majority of the pieces of natural kieselguhr, it is found frequently.

Micrographs of calcined and flux-calcined kieselguhrs at magnifications of 20,000 showed significantly less fine structure than natural samples. In micrographs of flux-calcined samples, Hyflo Super-Cel and JM I, there was no evidence of fine structure. The sample appeared sintered, as indicated by drop-shaped portions and smooth outlines of all particles. Some larger pores were eroded and enlarged until they merged with adjacent pores and all small pores had disappeared. Speedflow and PS filler showed more fine structure than the samples just described, and the degree of sintering and erosion was less. Calcined sample JM II showed slightly more structure than Speedflow or PS filler. The surface areas, fine structure of electron micrographs, and diffuseness of x-ray diffraction patterns are in qualitative agreement for these calcined samples.

Adsorption isotherms of natural kieselguhrs showed hysteresis above relative pressures of 0.4, but the isotherm of Hyflo Super-Cel showed little, if any, hysteresis in this range. Since pores as small as detectable in these micrographs (100 Å.) were found in the natural kieselguhrs but not in the flux-calcined samples, it may be inferred that natural kieselguhrs also contain pores smaller than 100 Å. in diameter and flux-calcined materials do not. This agrees with the current belief that the hysteresis is associated with pores smaller than 100 Å. in diameter.

In many cases the average pore diameters from the ratio of pore volume to surface area (Table III) were of the same order of magnitude as those estimated from the larger pores of the micrographs, and for the high-area kieselguhrs the agreement was very good. This agreement is believed to be fortuitous because: (*a*) the micropore volume was larger than the volume of the holes shown in the micrograph because it probably contained considerable volume between particles for which the pore diameters might be less than 5 microns, the limit of mercury penetration, and (*b*) a sizable fraction of the area of the natural kieselguhrs probably came from very small pores of diameters, less than 200 Å. as shown in Figure 10; hence the surface area was larger than that observed in the micrographs. In most natural kieselguhrs these effects apparently cancel, and the calculated pore diameters approximately equaled those observed. With highly sintered kieselguhrs the micropore volumes were not seriously changed, but the surface areas were decreased considerably owing to removal of the ultrafine structure. For these samples the calculated pore radii were several fold larger than those observed in the micrographs.

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Resistance of Resin-Impregnated Cotton Fabrics to Microorganisms

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Cotton cloths were impregnated with urea-formaldehyde and melamine-formaldehyde resins and subjected to pure culture mildew tests, using *Metarrhizium glutinosum* and *Aspergillus flavipes*, and to soil burial tests. Complete resistance to the pure culture mildew tests was exhibited by cloths containing 6.4% Resloom, 5.5% Aerotex, and 5.0% RHonite resins, respectively. In the more severe soil burial test, cloth impregnated with Aerotex gave the best performance. Whereas the untreated cloth lost all of its tensile strength in less than 7 days, an impregnated cloth containing 5.9% Aerotex M-3 retained all of its strength for the duration of the test of 14 days. Although the preliminary experiments presented do not give any indications as to the effectiveness of resin-impregnation relative to other antimildewing treatments, they suggest another purpose to which the many varied resin preparations can be directed.

PRELIMINARY histological investigations on the penetration of cotton fibers by fungi and bacteria (*3, 4*) indicate that the organisms attack from the outer surface inwards in an apparently highly localized manner. Accordingly, it seems logical to assume that any inert physical barrier preventing the fungi and bacteria from coming into intimate contact with the cellulose may protect the cotton fabric against the microbiological attack. It was thought that such a microbiologically resistant coating can be applied in the form of a resin impregnation. The present paper describes preliminary studies in the mildew resistance of resin-impregnated cloths.

Table I. Resistance of Cloth Impregnated with RHonite Resin to Microbiological Attack

				Microbiological Tests																
				Aspergillus flavipes, 12 days						*Metarrhizium glutinosum*, 6 days						Soil burial, 7 days				
				Uninoculated cloth		Inoculated cloth				Uninoculated cloth		Inoculated cloth				Not buried		Buried		
Sample No.	Merceri-zation	Resin Applied	% Resin on Cloth	Repli-cations	Av. tensile strength, lb.	Repli-cations	Av. tensile strength, lb.	Loss in strength, %	Amt. visual growth	Repli-cations	Av. tensile strength, lb.	Repli-cations	Av. tensile strength, lb.	Loss in strength, %	Amt. visual growth	Repli-cations	Av. tensile strength, lb.	Repli-cations	Av. tensile strength, lb.	Loss in strength, %
1	−	RHonite 609[a]	5.0	10	32.6	10	32.0	2	+	3	29.6	3	28.6	4	++	10	33.1	2	14	58
2	−	RHonite 609	15.0	10	32.4	10	30.8	5		5	30.4	5	32.0	0	0	10	32.3	2	27.7	14
3	−	RHonite QJ85[b]	5.0	10	30.7	10	31.6	0	+	4	33.0	3	33.0	0	+	10	28.8	2	21.0	27
4	−	RHonite QJ85	15.0	10	23.1	10	24.8	0	0	5	26.3	4	24.2	8	0	10	24.7	2	23.1	6
5	+	RHonite 609	5.0	10	30.4	10	32.0	0	+	5	29.4	4	20.3	27	+++	..	..	..	..	...
6	+	RHonite 609	15.0	10	28.1	10	28.4	0	0	5	29.6	5	27.1	8	0	..	..	..	..	...
7	+	RHonite QJ85	5.0	10	27.6	10	29.8	0	+	4	31.9	5	28.1	12	++	..	..	..	..	...
8	+	RHonite QJ85	15.0	10	20.3	10	20.9	0	0	5	26.8	5	25.0	7	0	..	..	..	..	...
27	−	None	0.0	10	38.8	10	10.7	72	++++	5	33.6	5	0.0	100	++++	10	42.8	12	0	100
28	+	None	0.0	10	32.1	10	7.3	77	++++	4	33.2	5	0.0	100	++++	..	..	..	..	..

[a] Monomeric urea-formaldehyde resin produced by Rohm & Haas Company.
[b] Monomeric melamine-formaldehyde resin produced by Rohm & Haas Company.

MATERIALS AND METHODS

Bleached 3.3-ounce cotton print cloth was impregnated with resin either with or without previous mercerization. Mercerization was applied without tension. Samples 1 to 18 were impregnated with different percentages of RHonite and Resloom resins. The resin solutions were padded on the respective samples, dried, cured for 10 minutes at 300° F., and finally washed for 3 minutes with water at 120° F. For samples 19 to 26 he different resin formulations were padded on the cloth with a load of 8.6 tons, frame-dried at 180° F., cured at 300° F. for 6 minutes, rinsed thoroughly in water, then finally dried. A mixture containing 16% Acrotex 450, 0.28% Accelerator 187, and 0.10% Decerosol OT 25% was used for samples 19 and 23. The same constituents in amounts of 32%, 0.56%, and 0.10%, respectively, were used for samples 20 and 24. Samples 21 and 25 were padded with a mixture of 5.3% Aerotex M-3, 0.165% Accelerator 187, 0.10% Decerosol OT 25%, and 7.40% accelerator 190A. Similarly a formulation containing 11.0% Aerotex M-3, 0.33% accelerator 187, 0.10% Decerosol OT 25%, and 7.4% accelerator 190A was employed for samples 22 and 26.

In tests for the resistance of the cloth to microbiological attack the samples were ravelled along the direction of the warp to a width of 1 inch and cut to 6-inch lengths. For pure culture tests the strips were autoclaved for 20 minutes at 15 pounds pressure, placed one each on the surface of Greathouse formula A mineral agar (*2*) in Petri dishes, and inoculated with a heavy spore suspension of the fungus. After incubation at 85° F. and 80% relative humidity for the indicated number of days, the strips were harvested, exposed overnight to formaldehyde vapors to kill the fungus, washed with tap water, air-dried, conditioned at 70° F. and 60% relative humidity for 24 hours, and finally broken on a Scott tensile strength tester. The decrease in tensile strength of the inoculated strips was taken as a convenient index of the degree of microbiological degradation. The organisms used for pure culture tests were *Aspergillus flavipes* PQMD 24a and *Metarrhizium glutinosum* USDA 1334.2.

Inasmuch as there may be criticisms against relying solely on pure culture mycological tests as a basis for determining the resistance of fabrics to microorganisms, the various resin-impregnated samples were also subjected to soil burial tests (*1*). For the latter test the strips were buried at a depth of 1.5 inches in rich garden soil with moisture content adjusted to 32% in Pyrex trays.

RESULTS

The summarized data on the resistance of the various resin-impregnated samples are presented in Tables I and II.

The data show a high degree of resistance to microorganisms imparted to the cloth by the resin impregnations. In the pure culture tests, while the untreated cloth lost all of its tensile strength, cloths containing 6.4% Resloom, 5.5% Aerotex, and 5.0% RHonite resins retained all of their strength. Inasmuch as these were the lowest concentrations tried, the figures do not represent the minimum threshold values. A photograph showing the growth of *Metarrhizium glutinosum* on impregnated and nonimpregnated cloths is given in Figure 1. Whereas the nonimpregnated cloth is completely covered with growth, only scant growth which did not affect the tensile strength of the cloth is evident in the cloth containing 5% resins. The large dark splotches on the strips are merely the result of wet contact between the cloth and the under support during the photographing.

In the more severe soil burial tests, however, a much higher percentage of resin content was required to withstand the test. Whereas the untreated cloth lost all of its tensile strength in less than 7 days, cloth containing 6.4% Resloom NC-50 lost 35% of its strength in 7 days. No strength was lost by cloth containing 7.4% Resloom HP in the same test. For RHonite impregnations a content of 15.0% resin was necessary before a negligible loss of tensile strength by the cloth was obtained during the 7-day soil burial. The best resistance to the soil burial test was given by cloths impregnated with Aerotex M-3 melamine resin. In this case cloths containing only 5.9% Aerotex M-3 withstood soil burial completely for the duration of the 14-day test.

From the data it is not possible to conclude whether the resistance of resin-impregnated cloth to microorganisms was brought about through a blocking of the cellulose by means of an inert physical barrier, or whether it is due to the presence of antiseptic compounds in the resins. In the use of resins with a high formaldehyde content the latter cause may contribute to the final resistance of the cloth. On the other hand, unpublished data show the greater susceptibility of depectinized cotton to microorganisms than raw cotton; this suggests that the physical prevention of the organism from making contact with the cellulose may be a very important factor in rendering resin-impregnated

Table II. Resistance of Cloths Impregnated with Resins to Microbiological Attack

				Uninoculated control cloths		Microbiological Tests: *Metarrhizium glutinosum*, 6 days				Microbiological Tests: Soil burial		
Sample No.	Merceri-zation	Resin Applied	% Resin on Cloth	Repli-cations	Av. tensile strength, lb.	Repli-cations	Av. tensile strength, lb.	Loss in strength, %	Amt. visual growth	Repli-cations	Av. tensile strength, lb.	Loss in strength %
											Buried 7 Days	
9	+	Resloom NC-50[a]	6.4	9	32.4	9	31.2	4	0	3	21.1	35
10	−	Resloom NC-50	6.5	9	36.3	9	35.2	3	0	3	29.8	18
11	+	Resloom NC-50	17.8	9	29.3	9	31.1	0	0	4	31.8	0
12	−	Resloom NC-50	18.0	9	32.6	9	33.7	0	0	4	32.2	1
13	+	Resloom HP	7.7	9	27.1	9	27.2	0	0	5	30.1	0
14	−	Resloom HP	7.4	9	32.4	9	31.9	2	0	5	34.9	0
15	−	Resloom HP	16.8	9	32.3	9	31.7	2	0	5	34.9	0
16	+	Urea formaldehyde[b]	15.4	9	28.9	9	29.6	0	0	5	27.5	5
17	−	Urea formaldehyde	16.8	9	32.3	9	29.7	8	0	6	33.8	0
18	−	Urea formaldehyde	7.4	9	30.3	9	31.1	0	0	6	31.0	0
27	−	None	0	9	35.3	9	0	100	++++	11	0	100
28	+	None	0	9	31.4	9	4.0	87	++++	11	0	100
											Buried 14 Days	
19	−	Aerotex 450[c]	5.5	10	32.0	10	33.2	0	+	4	15.9	50
20	−	Aerotex 450	11.1	10	30.8	10	30.9	0	+	4	31.7	0
21	−	Aerotex M-3[c]	3.0	10	35.0	10	27.2	22	++	4	5.8	83
22	−	Aerotex M-3	5.6	10	35.9	10	36.4	0	+	4	32.2	10
23	+	Aerotex 450	5.5	10	28.9	10	24.6	15	+	3	10.4	64
24	+	Aerotex 450	12.1	10	27.5	10	28.0	0	+	4	31.7	0
25	+	Aerotex M-3	3.0	10	28.9	10	17.2	40	++	4	0	100
26	+	Aerotex M-3	5.9	10	28.6	10	27.7	3	+	4	31.2	0

[a] Melamine resin high in formaldehyde prepared by Monsanto Chemical Company.
[b] Dimethylol urea resin.
[c] Urea and melamine resins, respectively, prepared by the American Cyanamid Company.

COURTESY, PHILADELPHIA QUARTERMASTER DEPOT AND ROHM & HAAS COMPANY

No Resin		5% RHonite 609		5% RHonite QJ85	
Control	Inoculated	Control	Inoculated	Control	Inoculated

Figure 1. Effect of Resin Impregnation on Mercerized (*above*) and Unmercerized (*below*) Bleached Cotton Sheeting to *Metarrhizium glutinosum*

cloths resistant to fungi. Further work is necessary, however, before this and other issues, such as, mildew resistance of resin-impregnated cloths in actual use, can be settled.

SUMMARY

Mildew tests using *Metarrhizium glutinosum* and *Aspergillus flavipes* as well as soil burial tests were conducted on cotton cloths impregnated with urea-formaldehyde and melamine resins. In general, a high degree of resistance to microbiological degradation was imparted to the cloth through the application of resins. Complete resistance to the pure culture mildew tests was exhibited by cloths containing 6.4% Resloom, 5.5% Aerotex, and 5.0% RHonite resins, respectively. In the more severe soil burial test, impregnated with Aerotex M-3 cloth gave the greatest resistance to degradation. Although the untreated cloth lost all of its tensile strength in less than 7 days, a sample containing 5.9% Aerotex M-3 retained all of its strength for the duration of the 14-day test.

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TURKISH TOBACCOS

Characteristics and Chemical Composition of Imported Types

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The chemical analyses of twenty-four constituents or groups of constituents of imported oriental tobaccos are presented. The analyses are for tobaccos of varying grades from eighteen areas scattered over four of the main growing regions of Greece and Turkey; the tobaccos were grown in 1937 and 1938. These analyses show significant differences in chemical composition among the tobaccos from the four regions and among grades. They also show some differences among tobaccos from neighboring areas within the regions. These differences indicate a basis for the commercial practice of dividing oriental tobaccos into types and divisions of types along geographical lines, and in turn reassembling these to obtain a blend of more constant composition. A discussion of chemical analyses as they appear to be related to the commercial usages and evaluation of these tobaccos is presented. Also the chemical analyses are correlated, to the extent possible, with the existing climatic and soil conditions and the cultural practices in vogue in each geographical region.

DURING recent years, except for a period during the war, over 50 million pounds of tobaccos of the Turkish type were imported into the United States annually (*23*). These tobaccos are normally grown in Turkey, Greece, Bulgaria, and southern Russia. Except for some regions in Bulgaria, they are grown in areas relatively close to the shores of the Black, Aegean, and Mediterranean Seas. These tobaccos differ primarily from domestic tobaccos in that their leaf size is small and the intensity of their aroma is greater.

A large proportion of these tobaccos is imported to be incorporated in blends of popular brands of blended cigarets to improve their burning quality and aroma. These tobaccos cost the American manufacturer more than the average domestic tobaccos. Part of this increased cost is the import duty.

In view of the importance of this crop to the cigaret industry as a whole, and because of the significance that a more detailed knowledge of these tobaccos might hold for the American tobacco farmers, a program of research was initiated in 1939 at Duke University to study these tobaccos. This included an investigation of the possibility of producing a type of tobacco in the United States with properties similar to those of imported Turkish tobaccos. It also included a study of the chemical composition of imported types and of domestically grown aromatic tobaccos to permit comparisons between the two types and to increase our knowledge of each. To do this numerous samples of tobacco which were grown in Turkey and Greece in 1937 and 1938 were obtained from the importers and analyzed. The absence of chemical data in the literature for Turkish tobaccos imported into this country, and the significance of these data for a large and important industry, indicate the desirability of publishing this information.

These tobaccos are grown in areas surrounding villages and towns in which the people live who produce them. The tobaccos are usually named after one of the main towns in the area. They may also be known by the name of the seaport from which they are shipped or the city in which they are prepared for shipment.

Thus, the tobaccos grown in the numerous villages near Serres, Greece, are known as Serres tobacco, and those grown in the villages in the general area of Drama, Greece, are known as Drama tobacco. These tobaccos, as well as others, are shipped out of the port of Cavalla and are often known in the trade as Cavalla tobaccos. The name may also arise from the topography of the region in which they grow; thus Djebel refers to mountainous country, and Yaka refers to the hills in the mountainous regions. The name may also be derived from the name of a section of territory such as Souyalassi or Pravi.

The small leaf size of these tobaccos is obtained by growing the plants on relatively poor soils and by planting a large number of plants—40,000 to 70,000—per acre. If fertilizer is used it commonly consists of goat or sheep dung. The growing season after transplanting and during curing is usually dry and warm in these regions.

The tobacco is harvested by priming, the leaves being picked a few at a time as they ripen. After priming they are strung by piercing the large end of the midrib with a large needle and pulling the leaf onto the string. After the strings of leaves are allowed to wilt for 1–3 days in a cool shady place, they are placed in the sun and air and cured by means of these agents. During wilting and curing the leaves change from green to a brown or yellow color and lose most of their natural moisture content. After the leaves are cured they are stored in a protected place until they take up moisture again with the coming of damp autumn weather. They are then made into temporary bales and delivered by the grower to the dealer or exporter.

The tobaccos from the top part of the stalk are usually considered to be the best in quality, and those from the base the poorest. From 20–50% of the production of the plants of most crops is not imported into the United States because its quality does not warrant the payment of import duty.

The tobacco is delivered by the grower to the dealer or exporter for "manipulation." This consists of sorting, grading, and baling the tobacco in the preferred manner, for shipment and to facilitate fermentation. In recent years most Turkish tobaccos imported into the United States are baled in the so-called Tongas bale. This consists in placing the loose leaves in bales under pressure and sewing burlap covers securely to the bales. The bales vary in weight from 70 to 125 pounds.

The tobacco is usually stored for two or more years before it is used by the manufacturer. During storage it undergoes fermentation. In most instances this begins with the coming of warm weather and proceeds for a period of varying length depending upon the temperature conditions and the tobacco. It ceases with the arrival of cooler weather. The tobacco may undergo fermentation each summer until it is used. The temperature of the tobacco usually exceeds that of its surroundings during fermentation.

REVIEW OF LITERATURE

The literature contains but few data on the chemical composition of tobaccos of the Turkish type. Because of the limited scope of most of the investigations recorded in the foreign literature, they are not comparable, in many instances, to the data presented in this paper, nor do they aid in the interpretation of these data.

Grading Room in Turkey

Andreadis and Toole (*3*), working with Greek tobaccos, show that the nicotine increases from the lower to the intermediate leaves on the stalk and again decreases in the top leaves. In another paper (*2*) the same authors show that the total nitrogen content follows the course of the nicotine and that protein nitrogen increases in the leaves from the base to the top of the stalk.

The work of Pyriki (*19A*) indicates that the better grades of Turkish tobaccos have a lower pH value than the poorer grades. Vladescu and Dimofte (*24*, *25*, *26*) determined total nitrogen, protein nitrogen, nicotine, soluble carbohydrates, and ash for Turkish, Greek, and Bulgarian tobaccos. Their data indicate that the better grades of tobacco possess the lower ash and nicotine content and the higher carbohydrate content. They also indicate, with some exceptions, a higher total nitrogen content in the poorer grades of tobacco. These authors find the total nitrogen, protein nitrogen, and nicotine content of the Bulgarian tobaccos to be lower than that of the Greek and Turkish tobacco, whereas the carbohydrate content of the former is higher. The ash content of the Greek tobaccos is somewhat greater than that of the other two. Their data show that the Smyrna tobaccos are lower in content of nitrogenous materials and higher in carbohydrates than the Samsun tobaccos. Also the Djebel tobaccos from both the Greek and Bulgarian regions are lower in nicotine content and higher in sugar content than any other tobaccos of the respective regions.

Kadir (*13*) discusses the blending of Turkish tobaccos for cigaret manufacture and gives the analysis of tobaccos of average grade from many sections of Turkey. His figures show that the composition of tobaccos growing in different major regions, such as Samsun on the Black Sea and Izmir in Southern Turkey, may vary widely and, furthermore, that there may be considerable differences in the composition of tobaccos from different areas within the same region.

Koseraif (*14*) gives some analyses of Turkish tobaccos which lead to similar conclusions as those drawn from Kadir's data.

METHODS OF ANALYSIS

MOISTURE. Two-gram samples in aluminum dishes were dried over concentrated (above 91%) sulfuric acid at 30° C. for 14 days.

HYGROSCOPICITY. The dried samples from the moisture determination were placed in an atmosphere of 72% relative humidity at 30° C. for a period of 14 days. The increase in weight on a percentage basis was termed the hygroscopicity.

PETROLEUM ETHER EXTRACT. Five-gram samples of the ground material were extracted for 23–24 hours with petroleum ether (boiling point 30–60° C.) on a Bailey-Walker extraction apparatus (*27*). The residue was dried to a constant weight at 95–98° C. in an electric oven.

ALCOHOL EXTRACT. The residue from the petroleum ether extract was extracted 23–24 hours with 95% ethyl alcohol on a Bailey-Walker extraction apparatus (*27*). The residue was dried to constant weight at 100–102° C. in an electric oven.

STARCH. The residue from the alcohol extract was used for the determination of starch by the diastase method with subsequent acid hydrolysis (*4*, p. 120).

NICOTINE. The Keller method as modified by Garner was used (*10*, *11*).

PROTEIN NITROGEN. Two-gram samples were boiled for 10 minutes with 50 cc. of 0.5% acetic acid, and the mixture was filtered when cool. The residue was washed with hot 0.5% acetic acid until the filtrate was colorless. The nitrogen in the residue was determined by the Kjeldahl-Gunning-Arnold method (*4*, p. 8).

TOTAL NONVOLATILE ACIDITY. Five grams of tobacco and 6 cc. of 6 M hydrochloric acid were mixed into a homogeneous mass, and finely divided neutral pumice stone was later worked into it until a semidry mixture was obtained. This mass was extracted with alcohol-free ether for 40 hours or more in a Soxhlet extractor. The ether was removed by the addition of boiling water, and the acid-containing solution was boiled for 5 minutes to remove any volatile acids. The solution was made to a volume of 250 cc. at room temperature. Aliquots of 10 cc., to which 100 cc. of water had been added, were titrated for acidity with 0.1 N alkali using phenolphthalein as indicator. Chlorine was determined on other 10-cc. aliquots by the Mohr (*16*) method and its acid equivalent subtracted from the alkali titration. The results are expressed in the number of cc. of 0.1 N alkali required to neutralize the acidity in 1 gram of tobacco.

The amino nitrogen, water-soluble nitrogen, total reducing substances, total reducing sugars, and total sugars were determined on an extract made by extracting 25 grams of tobacco with 375 cc. of water in a Mason jar, with the addition of 1 cc. of chloroform at room temperature for 12 to 14 hours, with occasional shaking for the first hour. The pH was determined on an extract of the same proportions of tobacco and water but with the omission of the chloroform. The extracts were filtered through a linen cloth or a plug of glass wool.

HYDROGEN ION CONCENTRATION. The Coleman glass electrode was used. The results were expressed in terms of pH.

REDUCING AND TOTAL SUGARS. Reducing sugars were determined before and after hydrolysis by the Munson-Walker method (*4*, p. 190), and the results expressed in terms of glucose. The extract was clarified with neutral lead acetate.

TOTAL REDUCING SUBSTANCES. Total reducing substances were determined on the extract without clarification and after hydrolysis by the Munson-Walker method (*4*, page 190). The difference between the total reducing substances and the reducing sugars was called polyphenols[1].

TABLE I. REGIONS, AREAS, AND TOWNS OR VILLAGES

REGION	AREA	TOWNS AND VILLAGES
Samsun (Black Sea)	Djannik	Kehyali, Haji, Ismailoglou, Sitma, Suyu, Tash Demir, Baldjali, Yagh Bassan, Hamzalu, Kara Oglan, Kokdje, Kishla, Buyuklu, Kir Pidjli
	Maden	Teke Keuy, Yokari Tsinik, Papaz Mahallessi, Tsinik, Dvgherish, Assar Agatch, Okse, Andria Mah, Tsirakman, Ilyaskeuy
	Evgaf	Kertme, Dagh Keuy, Duz Keuy, Karagol, Tavlan, Manados, Kavadjik, Oyoumdja, Aksoular, Alanos, Tchobanli, Ballatch, Deredjik, Kadi Keuy
	Bafra	Ak Teke, Elifli, Kara Keuy, Teke Sarmousak, Dedeli, Orendjik, Ak Ghuneyi, Elmadjik, Koushlaghan, Kovanlik, Martakala, Dervent, Sourmeli, Deressi, Dar Boyaz, Kush Kayassi, Domuz Aghi
Smyrna (Aegean Sea)	Akhisar	Soma, Kirkagac, Akhisar, Gordus, Manisa, Sindirgi, Yenice, Selendi, Marmara, Alibeyli, Hartu, Yayakoy, Suleymanli, Derekoy, Gelenbe
	Foca	Menemen, Foca, Dikili, Bergama, Ayvalik, Gomec, Jonuzlor, Demirtas, Acan, Sanakoyu, Kozah, Camamli, Akcenger, Kasaly, Guzelhisar
	Izmir	Izmir, Torbali, Buca, Seydikoy, Cumaovasi, Develi, Tarbali, Kayas, Burnova, Dikardas, Urlan, Cesme, Karaburun, Salman, Alcati, Denizyiren
	Mugla	Selcuh, Milas, Mugla, Bodrum, Akcaalan, Yahkavak, Kurukoy, Asin, Aydin, Yoran, Akkoy, Soke, Ula, Alacam, Sozkoy, Karacahisar, Kemikler, Kazikli
Eastern Greece	Comontini	Komotini, Doukatan, Kasmion, Pandrossas, Geneti, Messi, Xylagani, Krovyti, Maronia, Proskymital, Keresli, Yeni Kioi, Bulat Kioi, Tsipeli, Semetli, Sendeli, Haskioi, Kiouplu, Esserdjili, Aghiasma, Yalendjali, Tchohadjiler
	Xanthi (2nd Yaka)	Kasos, Ghenissaia, Evlalon, Tsimenli, Karakiozolou, Daoutlu, Kipseli, Kiosse Ali
	Djebel	Kechrokambo, Lekani, Dipotumon, Platamonia, Ptelea, Makaklov, Aronaout, Sarnovista, Yasriani, Issidje
	Souyalassi	Kallithea, Dafnon, Stavroupolis, Sarnitz, Ada, Kourlar, Yenikioi
	Drama	Drama, Doxaton, Koudounia, Choristi, Kabanbaki, Fotolivi, Boriani, Radovista, Tsataldja, Karatsali
	Prava	Drysna, Fteri, Amfipolis, Pravi, Avli, Kipia, Eleftherai, Pangaion, Messoropia, Bostandjil, Nikissiani, Dranitsa
	Zihna	Alistrati, Sfelinos, Zihna, Tholos, Dratsova, Vitasta, Anghista, Rodolivos, Kotsakioi, Myrkinos, Nikissiani, Rahova, Draviskos, Vultsista, Kioupkioi, Horovista
	Serres	Kastri, Kutsos, Rahmanli, Achinos, Nigrita, Dimitritsi, Serrai, Neos, Skopas, Homondos, Christos, Dranova, Lacos, Sidirokastron, Kimissis, Karmaroto, Valtero, Strymonikon, Staros, Subaskioi, Dovista, Vesnik, Sormousakti, Rahovistia, Topaliani
	Prossotsian	Granitis, Gornitsa, Egri-Dere, Prossotsian, Revika, Vissatian, Plevna, Drama, Koublista, Kirlibova
Agrinion (Western Greece)	Agrinion	Agrinion, Stamna, Angkelokastron, Spoluita, Papadatais, Gavalou, Analipsis, Thernon, Drymonas, Lepena, Neochori

TOTAL NITROGEN. Kjeldahl-Gunning-Arnold method modified to include nitrates (*4*, p. 9) was used.

WATER-SOLUBLE NITROGEN. Kjeldahl-Gunning-Arnold method (*4*, p. 8) was used.

AMINO NITROGEN. Van Slyke method (*4*, p. 245) was used.

SOLUBLE ASH. Five-gram samples in tared porcelain crucibles were heated at 250° to 300° C. for 3 to 4 hours, then heated to a temperature of dull redness in a muffle for 14 to 16 hours, cooled to room temperature in a desiccator over calcium chloride, and weighed as total ash. The sand was determined, the difference between the total ash and sand considered to be soluble ash.

SAND, SILICA, OXIDES OF IRON AND ALUMINUM, CALCIUM, AND MAGNESIUM. These were determined by the official methods (*4*, pp. 39–41).

PHOSPHORUS. Two-gram samples were dissolved in 30 cc. of concentrated nitric acid and 6 cc. of concentrated hydrochloric acid; organic matter was destroyed by boiling and phosphorus determined by the volumetric method (*4*, p. 3).

SULFUR. The magnesium nitrate method was used (*4*, p. 45).

CHLORINE. This was determined by the official volumetric method (*4*, pp. 43–4).

POTASSIUM. This was determined by the Lindo-Gladding method (*4*, p. 42).

SAMPLES

Each sample was taken from one individual bale, selected at random from a large number of bales available from each of the regions considered. The covers were removed from the bale and a section (1/20–1/10) of the bale was removed and taken to the laboratory. Part of this section was ground on a Wiley mill to pass a 30-mesh sieve, thoroughly mixed, and sealed in a glass jar until used for analysis.

The stock of bales available for selection consisted of bales of grades 1, 2, and 3, grade 1 being the best in quality. The number of bales of grade 3 was greater than the number of grades 1 and 2.

The tobacco in each of the bales selected for analysis was probably a mixture of leaves from numerous growers from several villages in the area surrounding the town for which the tobacco is named. It is possible, however, that the tobacco in any bale may have come from a restricted locality. The tobaccos of grade 1 may or may not have been from the same part of any community as those of grades 2 and 3.

TERRITORIES

For this work tobaccos from four marketing areas in each the Samsun and the Smyrna tobacco-producing regions of Turkey, nine areas in the Macedonian and Thracian regions of Greece, and one area in the Agrinion region of Greece were selected.

Tobaccos representative of the areas of Djannik, Maden, Evgaf, and Bafra of the Samsun region, and Akhisar, Foca, Izmir, and Mugla of the Smyrna region, were selected as being typical of those grown in Turkey. Tobaccos representative of Comontini, Xanthi (2nd Yaca), Souylassi, Djebel, Drama, Pravi, Zihna, Serres, and Prossotsian in Eastern Greece and Agrinion in Western Greece were selected as being typical of those grown in Greece. The geographical locations of these areas are shown in the accompanying maps (Figures 1 and 2), and some of the towns and villages located in each area are given in Table I. All towns named are not necessarily tobacco-producing centers.

The villages from which the tobaccos in the Samsun region were obtained all lie within 30 miles of the seacoast except for a few scattered villages in the Bafra area. In the Maden, Djannik, and Evgaf areas most of the tobacco is grown on hilly land, whereas in Bafra part of it is grown on the plain. The region in which Smyrna tobacco is grown is much larger, some of the areas extending inland from the sea as far as 60 to 80 miles. In this region most of the tobacco is grown on hillsides or high tablelands; a part of it, however, is grown on flatland in well drained valleys.

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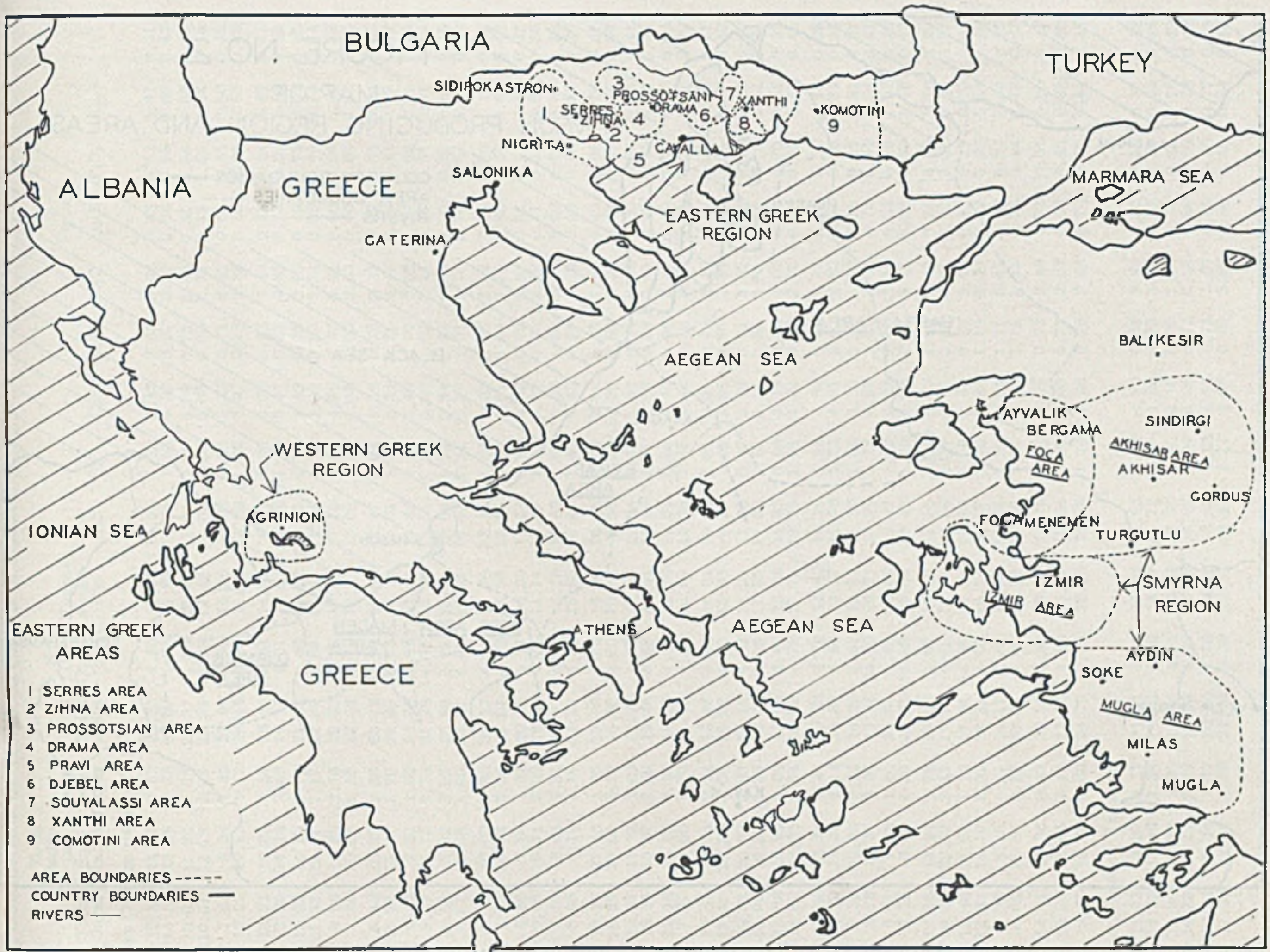
[1] Wright (*29*) points out that an alternative interpretation of the so-called polyphenol content is possible in view of the statements in the literature. Pyriki (*19*) states that "it is perhaps correct" to consider that the difference between the total reducing substances and the total sugars are the polyphenols. Our data include values for both the reducing sugars and total sugars, which makes it possible to calculate the polyphenol values either way.

After reviewing the confused state of this matter in the literature we are of the opinion that a more correct value for the content of phenolic compounds would be obtained if the extract were hydrolyzed first to convert all soluble sugars and soluble phenolic compounds into forms in which they would reduce Fehling's solution, and then determine the reducing power before and after clarification. If the clarification procedure removed all reducing materials other than soluble reducing sugars, the difference between the two values thus obtained for reducing power should more correctly represent the polyphenol content.

TABLE II. PERCENTAGE[a] CHEMICAL COMPOSITION OF TOBACCOS GROWN IN TURKEY

Area	Grade	Crop	Total N	Protein N	Water-Sol. N	Amino N	Nicotine	Petroleum Ether Extract	Alcohol Extract	Starch	Reducing Sugar	Total Sugar	Total Reducing Substances	Polyphenols	Total Acids[a]	H Ion Concn. (pH)	Hygroscopicity	Sol. Ash	SiO$_2$	CaO	MgO	K$_2$O	Fe$_2$O$_3$ + Al$_2$O$_3$	P$_2$O$_5$	Cl$_2$	S
SAMSUN REGION																										
Djannik	1	1937	2.53	1.06	1.43	0.347	0.70	4.65	33.49	3.87	6.22	7.48	8.05	1.83	21.63	4.83	15.05	12.21	1.48	3.32	0.96	4.03	0.82	0.81	0.68	0.40
		1938	2.62	1.06	1.39	0.365	0.76	3.95	27.49	2.77	5.13	5.56	7.82	2.69	25.50	4.99	14.58	14.08	1.44	4.19	1.00	4.09	0.59	0.76	0.65	0.33
	2	1937	2.55	1.04	1.51	0.354	0.90	4.85	29.71	3.24	6.34	6.66	8.09	1.75	21.61	4.86	14.71	15.39	1.19	3.73	1.01	4.07	0.60	0.87	0.59	0.33
		1938	2.66	1.05	1.45	0.361	0.90	5.27	25.30	2.51	4.13	5.62	5.47	1.34	24.98	5.07	14.12	15.22	1.23	4.60	1.13	3.86	0.62	0.77	0.54	0.36
	3	1937	2.92	1.21	1.72	0.407	0.67	4.40	28.09	3.43	5.11	5.32	6.93	1.82	22.51	4.99	14.55	16.74	1.60	4.35	1.20	4.05	0.92	0.86	0.78	0.35
		1938	2.97	1.24	1.57	0.491	0.83	5.28	23.15	2.39	3.83	4.23	5.09	1.26	23.37	5.13	13.72	15.48	1.16	4.65	1.26	5.00	0.55	0.77	0.71	0.38
Bafra	1	1937	2.82	0.98	1.70	0.374	1.32	5.48	31.69	3.19	5.86	7.05	7.21	1.35	24.36	4.76	15.58	12.18	1.38	3.74	0.91	3.59	0.44	0.70	0.66	0.43
		1938	2.75	1.05	1.62	0.350	1.11	4.28	29.93	2.68	4.79	5.31	6.77	1.98	22.80	4.88	13.85	13.23	1.23	3.83	1.07	4.21	0.51	0.76	0.36	0.44
	2	1937	2.98	1.03	1.89	0.420	1.50	5.34	28.92	2.73	4.36	4.75	5.83	1.47	26.16	4.79	14.82	14.50	0.91	4.38	0.92	4.07	0.40	0.77	0.55	0.40
		1938	2.69	0.95	1.61	0.350	1.52	5.41	29.85	2.96	5.58	6.24	7.59	2.01	24.09	4.90	13.12	13.54	1.47	5.04	1.00	3.69	0.54	0.71	0.42	0.40
	3	1937	3.08	1.09	1.88	0.460	1.49	4.53	31.76	3.27	5.34	5.57	6.60	1.26	21.86	4.82	14.87	13.72	0.91	4.40	1.03	3.47	0.38	0.77	0.83	0.44
		1938	3.28	1.20	1.94	0.533	1.55	4.91	26.36	2.38	3.71	4.13	5.06	1.35	25.16	4.93	12.86	14.36	1.81	4.36	1.15	3.48	0.74	0.68	0.72	0.43
Maden	1	1937	2.84	1.03	1.61	0.382	1.31	4.83	34.65	3.73	5.65	6.31	6.99	1.34	22.77	4.80	14.13	11.94	1.45	3.77	1.00	3.40	0.64	0.68	0.76	0.41
		1938	2.81	1.03	1.62	0.382	1.16	4.96	29.90	2.79	4.81	5.61	6.75	1.94	23.89	4.89	14.05	13.48	1.41	4.21	1.13	4.18	0.69	0.66	0.62	0.39
	2	1937	2.83	1.02	1.75	0.437	1.48	6.20	30.78	2.99	5.08	5.33	7.55	2.47	23.31	4.90	14.99	13.93	0.71	4.18	1.23	3.78	0.64	0.96	0.70	0.38
		1938	2.73	0.94	1.65	0.377	1.47	5.19	29.52	2.89	5.95	6.73	7.98	2.03	24.29	4.89	13.54	13.67	1.65	4.38	1.22	4.01	0.69	0.70	0.46	0.40
	3	1937	3.35	1.31	1.93	0.529	1.47	5.43	31.75	1.94	3.99	4.31	5.82	1.83	23.25	4.82	14.73	13.37	1.05	4.43	1.37	3.49	0.68	0.80	0.85	0.38
		1938	3.05	1.22	1.73	0.421	1.50	5.08	26.69	2.51	3.97	4.73	5.38	1.41	23.81	4.90	13.06	14.44	1.92	4.85	1.24	3.43	0.86	0.74	0.63	0.44
Evkaf	1	1937	2.74	0.99	1.59	0.377	1.54	5.22	32.30	3.36	5.84	6.51	7.76	1.92	23.74	4.80	13.83	12.34	1.89	4.22	0.89	3.32	0.57	0.63	0.62	0.49
		1938	2.92	1.02	1.75	0.406	1.33	4.62	30.29	2.70	4.63	5.20	6.54	1.91	25.70	4.85	13.20	13.23	1.53	4.13	1.00	4.13	0.74	0.67	0.62	0.43
	2	1937	2.81	0.97	1.72	0.405	1.72	6.45	30.02	2.86	4.74	5.11	5.94	1.20	23.03	4.80	13.30	13.32	1.07	4.60	0.89	3.58	0.66	0.77	0.42	0.44
		1938	2.99	0.99	1.81	0.345	1.40	5.68	29.59	2.24	4.80	5.44	6.47	1.67	25.05	4.93	13.48	13.81	1.18	4.52	1.19	3.95	0.58	0.81	0.47	0.36
	3	1937	3.10	1.15	1.80	0.469	1.57	5.55	30.00	2.85	4.80	5.23	6.34	1.54	22.45	4.80	13.36	13.95	1.25	4.72	1.17	3.50	1.01	0.77	0.72	0.42
		1938	3.43	1.22	2.04	0.527	1.73	5.63	25.26	2.15	2.93	3.12	4.56	1.63	25.41	5.10	13.40	14.96	1.85	4.48	1.22	3.96	0.87	0.69	0.71	0.42
SMYRNA REGION																										
Axhisar	1	1937	1.52	0.84	0.69	0.106	0.88	5.29	37.31	9.28	13.58	13.81	15.85	2.27	19.17	5.09	14.40	12.01	2.51	3.69	0.95	2.82	0.85	0.59	0.48	0.36
		1938	1.50	0.81	0.68	0.124	0.75	3.99	37.90	6.84	15.56	16.92	19.01	3.45	22.11	5.23	13.67	12.42	2.33	4.25	0.84	3.12	0.81	0.51	0.16	0.35
	2	1937	1.63	0.81	0.83	0.135	0.98	5.45	34.74	7.25	14.56	15.75	16.02	1.46	19.09	5.00	14.85	12.57	1.80	4.25	0.83	3.62	1.08	0.52	0.29	0.34
		1938	1.50	0.75	0.78	0.125	0.77	5.29	37.16	6.01	16.58	17.42	19.91	3.33	18.71	5.10	13.95	12.57	2.70	4.02	0.76	2.82	0.72	0.60	0.15	0.25
	3	1937	1.83	0.96	0.86	0.129	1.13	5.92	33.31	7.41	11.89	12.41	13.18	1.29	19.46	5.01	13.66	13.38	2.11	5.55	1.14	2.59	1.22	0.54	0.52	0.34
		1938	1.67	0.88	0.83	0.152	0.90	4.83	35.22	5.29	12.21	13.68	15.09	2.88	17.28	5.13	13.00	13.93	3.12	4.25	1.01	2.88	0.99	0.58	0.26	0.37
Izmir	1	1937	1.72	0.92	0.80	0.123	1.04	4.87	38.40	7.37	13.94	14.31	16.37	2.43	18.33	5.11	14.68	11.76	2.75	4.16	0.79	2.25	0.83	0.48	1.00	0.39
		1938	1.61	0.85	0.75	0.112	0.83	4.20	38.19	5.63	16.03	16.57	18.17	2.14	16.30	5.10	14.29	12.48	2.55	4.03	0.75	2.91	1.17	0.47	0.56	0.35
	2	1937	1.72	0.83	0.87	0.110	1.21	5.64	37.88	6.88	14.45	15.54	16.53	2.08	17.97	5.01	13.85	12.26	1.49	4.62	0.76	2.55	1.01	0.54	0.62	0.31
		1938	1.69	0.82	0.87	0.126	1.01	5.31	37.29	5.66	14.75	15.76	17.34	2.59	20.76	4.99	13.56	12.39	1.13	4.28	0.71	2.50	0.66	0.48	0.62	0.33
	3	1937	2.00	0.99	0.99	0.157	1.29	6.15	32.61	6.62	12.88	13.41	14.74	1.86	18.66	5.02	13.73	12.75	1.54	4.94	0.98	2.28	1.04	0.51	1.02	0.35
		1938	1.86	0.97	0.92	0.146	1.08	5.58	32.80	4.89	12.34	13.15	15.05	2.71	18.57	4.99	12.46	13.23	1.32	5.16	0.87	2.39	0.75	0.50	0.82	0.35
Foca	1	1937	1.59	0.84	0.71	0.102	1.00	6.46	35.24	8.31	14.28	14.85	17.23	2.95	16.93	4.98	15.27	11.18	2.33	3.52	0.85	2.36	0.67	0.44	1.10	0.38
		1938	1.65	0.84	0.75	0.115	0.91	4.92	35.83	6.20	14.23	14.74	15.61	1.38	16.96	4.89	12.59	12.04	1.99	3.80	0.77	3.08	0.77	0.47	0.95	0.42
	2	1937	1.64	0.83	0.79	0.109	1.06	6.82	35.80	8.51	13.35	14.82	15.01	1.66	17.91	4.99	14.19	12.04	1.61	3.89	0.83	2.97	0.87	0.54	0.96	0.34
		1938	1.63	0.81	0.76	0.109	1.01	5.64	35.88	6.06	14.96	16.13	17.97	3.01	17.64	4.93	13.58	12.26	2.17	3.70	0.79	2.87	0.52	0.57	0.57	0.35
	3	1937	1.91	0.96	0.92	0.128	1.24	6.21	28.59	7.11	11.41	12.12	12.77	1.36	23.02	5.00	13.83	13.64	1.73	5.02	1.06	2.90	1.00	0.45	0.86	0.38
		1938	1.90	0.96	0.94	0.130	1.12	5.77	34.17	4.45	15.38	16.33	17.55	2.17	18.39	4.91	13.31	13.54	2.39	3.92	0.94	2.96	0.59	0.58	0.72	0.38
Mugla	1	1937	1.51	0.83	0.68	0.100	0.78	5.31	36.45	8.69	14.41	14.87	17.56	3.15	17.48	5.19	14.26	11.75	2.86	4.60	0.66	1.96	0.92	0.44	0.74	0.33
		1938	1.44	0.79	0.65	0.111	0.57	3.45	36.68	7.48	16.90	17.49	18.78	1.88	17.00	5.09	12.81	13.15	2.94	3.79	0.75	2.91	1.19	0.56	0.48	0.34
	2	1937	1.56	0.81	0.75	0.127	0.78	5.92	34.09	8.55	15.30	15.95	16.76	1.46	17.65	5.10	13.37	12.01	1.36	4.79	0.63	2.20	1.00	0.53	0.62	0.28
		1938	1.51	0.78	0.69	0.117	0.74	5.52	35.37	6.18	15.68	16.27	18.14	2.46	16.35	4.94	14.05	13.71	2.15	3.81	0.68	2.62	0.69	0.60	0.51	0.30
	3	1937	1.88	0.97	0.87	0.122	1.04	5.48	32.55	7.62	11.22	12.28	12.56	1.34	21.90	5.00	12.54	13.75	2.02	5.12	0.96	2.50	1.37	0.54	0.86	0.28
		1938	1.74	0.92	0.76	0.127	0.76	5.67	32.45	5.66	12.28	13.31	14.87	2.59	19.72	5.00	13.31	13.59	2.66	4.55	0.90	2.37	1.01	0.61	0.67	0.32

[a] Expressed as cc. of 0.1 *N* alkali required to neutralize the acid in 1 gram of tobacco.



MAP OF GREEK AND SMYRNA PRODUCING REGIONS AND AREAS
FIGURE NO.1

The areas in the Eastern Greek region from which tobaccos were selected lie within 35 miles of the Aegean sea or its arms, with the exception of parts of the Serres and Prossotsian areas. In general, this territory is mountainous, but much of it is constituted of small valleys. The tobacco-growing land extends from the banks of the streams and small rivers that flow through the valleys to the sea, into the hills and mountains that border these valleys.

The city of Agrinion is located in the tobacco-growing region of that name in Western Greece. The tobacco was obtained from an area within a radius of 15 miles of Agrinion. The region is generally mountainous with some flatland lying west of Agrinion.

DISCUSSION

The data for twenty-four chemical constituents or properties of each of the samples analyzed are given in Tables II and III.

As would be expected, there is rather wide variation in some cases between the content of certain constituents in tobaccos of the same grade from year to year and from area to area in each of the regions. The average content of the constituents for the whole group of samples is quite similar for each of the two years. This similarity holds for each grade from year to year. These average data are given in Table IV. Also the trend from grade to grade is definite when the data on all samples are considered as a whole. This trend, however, fails to hold in many individual cases. The data show that the tobacco from each of the three main regions is quite different chemically. They also show that tobaccos from different areas within a specific region may be quite similar in chemical make-up in some cases and different in others.

Information on such points as weather, production, fertilization, and soil fertility, from which an adequate explanation of these differences could be formulated, is not at hand. The practice of many importers—obtaining tobaccos from as many areas as possible within a region and then blending the tobaccos from each—indicates that these differences in chemical compositions reflect real differences in the tobaccos and that these are recognized in commercial practice.

Nitrogenous Constituents. The data for the individual samples in Tables II and III show that the content of the nitrogenous components varies over a wide range. On the other hand, the data in Table IV show that the average content for these constituents is essentially the same for each of the 1937 and 1938 crops. Isolated cases, however, can be found in Table III where the contents of these materials are rather divergent for the two years. For instance, they are highest in the Souyalassi tobaccos of the 1938 crop, whereas they are highest in the Comotini tobaccos of the 1937 crop.

With the exception of the protein nitrogen, the average content of these constituents is least in the tobacco of grade 1 and most in that of grade 3. The average protein nitrogen content of the tobacco of grade 3 is greater than that of the tobacco of grades 1 and 2; these are essentially the same, with slightly less in grade 2 than in grade 1. This decreased nitrogen content in the tobacco from the upper portion of the stalk (grade 1 is considered to be

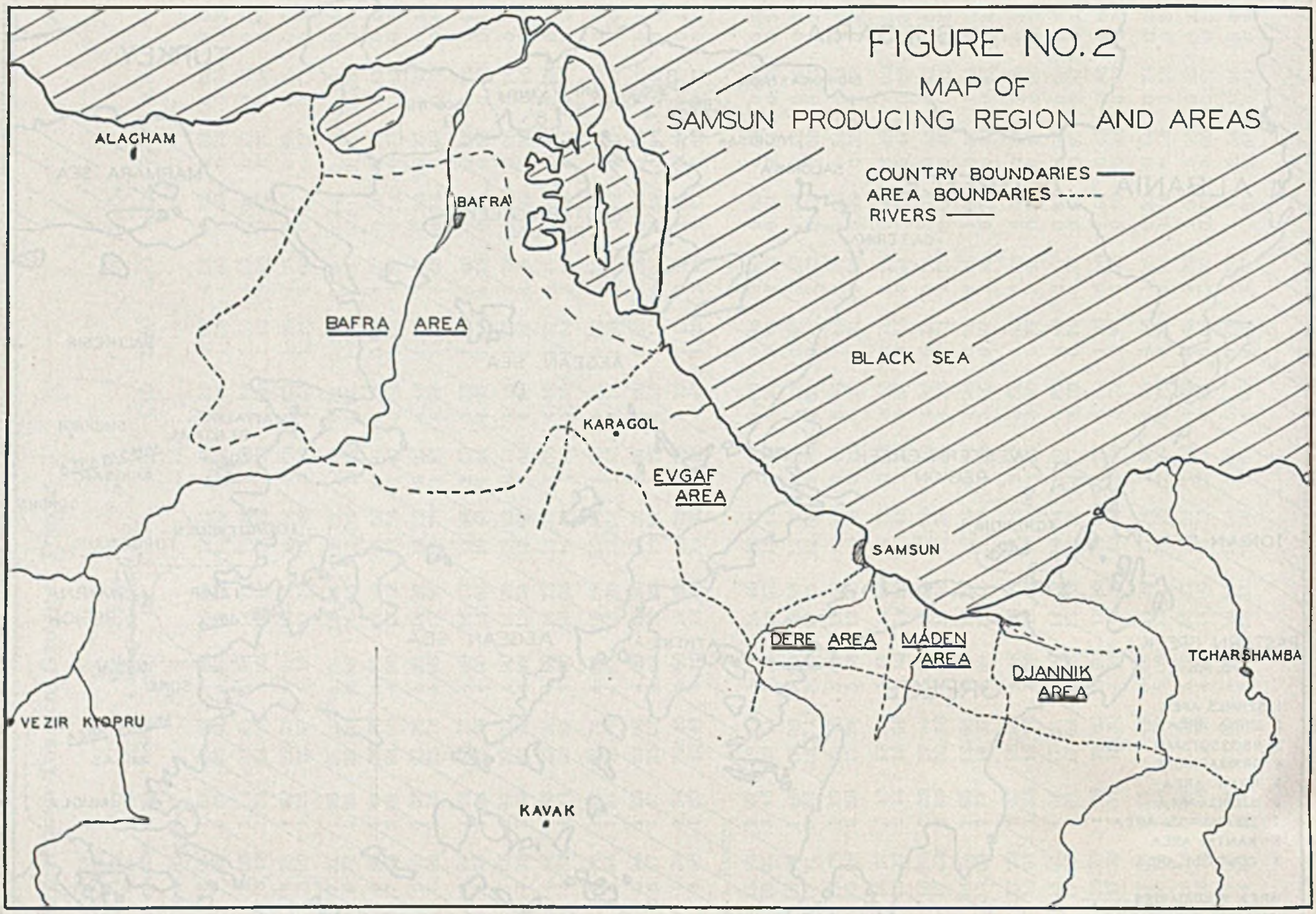


FIGURE NO. 2
MAP OF
SAMSUN PRODUCING REGION AND AREAS

mainly from the top of the stalk) is at variance with the behavior of cigar tobaccos (*1*) and flue-cured cigaret tobaccos (*7*) where the nitrogen content is usually maximal in the tobacco grown on the top part of the stalk. However, in respect to grade it is in accordance with the findings for cigaret tobacco (*7*), the better cigaret tobaccos being of a low and medium nitrogen content. Perhaps this decreased nitrogen content in the top leaves may be due to the limited supply of nitrogen available to the plant, this being due in turn to the low level of fertility of the soil and the loss of nitrogen from these leaves to the seed head. The seed head is formed late in the life of the plant and frequently is not removed from the plant.

The average content of protein nitrogen in the tobaccos varies but little between the four major regions represented.

The average nicotine content of the tobaccos from the Samsun, Eastern Greece, and Agrinion regions is similar, varying from 1.29 to 1.34%. That of the tobacco from the Smyrna region, however, is much less, being only 0.96%. The average content of total nitrogen, water-soluble nitrogen, and amino nitrogen of these tobaccos varies considerably from region to region. The data in Table IV, with the exception of nicotine, show that as one of these constituents varies the others vary; the gradation of these constituents from Samsun to Smyrna through the Greek tobaccos is shown in Figure 3. In this figure an arbitrary linear scale was selected for the total nitrogen content of these tobaccos from the different geographical regions; the Samsun tobacco was arbitrarily given a value of 1, Eastern Greek tobaccos a value of 2, the Agrinion tobacco 3, and the Smyrna 4. If the other nitrogen constituents are plotted against the same arbitrary index, the striking result is found that (with the exception of nicotine) essentially linear relations exist for these constituents.

This same index of gradation in tobacco composition from region to region also gives surprisingly good linear relations for the carbohydrate type of constituents. This is shown by the curves for carbohydrate constituents in Figure 3. The juxtaposition of the curves for nitrogenous constituents and carbohydrate constituents in Figure 3 emphasizes again the relations found in previous work as characteristic of the flue-cured type of tobacco (*6, 7, 8*). These may be stated briefly as follows: (*a*) If one nitrogen constituent is high the others are high; (*b*) if nitrogenous constituents are high, the sugar constituents are low; and (*c*) if total nonvolatile acids are high the carbohydrate constituents are low. The large amount of data presented in Tables II, III, and IV (much of which will not be mentioned specifically in the discussion) indicates quite clearly that the Turkish tobaccos show similar trends in their chemical composition.

This indicates that those factors influencing growth, which originate from the soil and climatic differences existing in the middle East region where these tobaccos were grown, operate in essentially the same manner as those influences which determine the differences in flue-cured types from different regions (*6*). If this principle is valid, as it seems to be, it is of considerable importance, as it will permit application of the extensive knowledge already available (*6, 7, 8*) regarding the effects of varying cultural and fertilization practices on tobaccos of the flue-cured type, and lead to more intelligent procedures in producing tobaccos of the Turkish type.

This knowledge has already been applied in field work now in progress. Thus it has been possible to reduce greatly the amount of phosphorus available to the plant so as to delay flower formation. This results in a slower maturing plant, which in turn gives the grower a longer period over which to spread the manual work required in harvesting.

The percentage of total nitrogen which is water soluble is greatest

TABLE III. PERCENTAGE[a] CHEMICAL COMPOSITION OF TOBACCOS GROWN IN GREECE

Area	Grade	Crop	Total N	Protein N	Water-Sol. N	Amino N	Nicotine	Petroleum Ether Extract	Alcohol Extract	Starch	Reducing Sugar	Total Sugar	Total Reducing Substances	Polyphenols	Total Acids[a]	H Ion Concn. (pH)	Hygroscopicity	Sol. Ash	SiO_2	CaO	MgO	K_2O	$Fe_2O_3 + Al_2O_3$	P_2O_5	Cl_2	S
											EASTERN GREECE REGION															
Zihna	1	1937	2.15	0.96	1.11	0.231	0.87	6.11	35.57	4.66	11.85	12.33	14.47	2.62	20.85	4.80	13.65	10.95	1.52	5.45	0.65	2.02	0.45	0.52	0.81	0.51
		1938	2.31	0.96	1.16	0.219	1.04	4.56	35.83	4.28	12.73	14.55	15.08	2.35	20.37	4.86	12.85	11.25	1.50	4.89	0.69	2.51	0.64	0.55	0.60	0.42
	2	1937	2.54	0.94	1.47	0.303	1.70	6.86	30.70	2.17	9.63	10.05	11.86	2.23	25.37	4.80	15.47	11.59	0.92	5.38	0.73	2.36	0.55	0.58	0.62	0.40
		1938	2.53	0.91	1.55	0.305	1.68	6.39	31.15	2.65	9.85	10.61	12.78	2.93	25.73	4.95	13.49	14.66	1.24	6.05	0.69	2.73	0.48	0.54	0.43	0.45
	3	1937	2.83	1.05	1.64	0.410	1.65	6.55	26.58	1.66	6.99	7.55	8.54	1.55	27.09	4.98	15.36	13.02	0.83	5.33	0.71	2.42	0.61	0.55	0.50	0.46
		1938	2.55	0.96	1.47	0.272	1.34	5.40	31.72	3.08	11.23	12.07	12.95	1.72	24.48	4.93	14.91	14.28	1.26	5.97	0.78	2.33	0.50	0.51	0.63	0.42
Pravi	1	1937	2.36	1.11	1.14	0.207	0.93	5.88	35.24	5.01	12.79	13.21	16.35	3.56	18.84	4.61	14.82	9.94	1.43	3.75	0.93	2.44	0.43	0.64	0.89	0.47
		1938	2.76	1.17	1.41	0.248	1.39	4.40	34.73	4.26	11.68	13.05	14.14	2.46	19.11	4.61	13.06	11.08	1.68	3.51	0.88	2.85	0.73	0.69	1.00	0.38
	2	1937	2.56	1.06	1.40	0.218	1.49	7.04	32.84	4.77	11.46	12.22	14.17	2.71	21.83	4.60	14.72	10.25	0.71	3.82	0.75	2.93	0.49	0.72	0.67	0.42
		1938	2.92	1.19	1.54	0.251	1.51	7.25	33.45	2.90	10.50	11.52	12.67	2.17	22.34	4.66	12.86	11.54	1.08	3.95	0.87	2.54	0.66	0.69	0.75	0.34
	3	1937	2.69	1.05	1.53	0.303	1.18	6.92	28.36	3.19	9.43	9.90	11.59	2.16	22.93	4.75	16.00	11.79	0.88	4.39	0.97	3.01	0.50	0.66	0.82	0.38
		1938	3.36	1.39	1.82	0.341	1.61	5.67	30.22	2.65	8.52	9.38	10.07	1.55	22.44	4.70	12.41	12.09	1.25	4.46	1.06	2.63	0.56	0.66	0.82	0.36
Serres	1	1937	2.52	1.00	1.39	0.268	1.64	6.79	31.51	3.33	7.89	8.30	10.25	2.36	23.12	4.91	13.18	12.47	2.08	5.38	0.78	2.31	0.97	0.55	0.71	0.39
		1938	2.39	0.95	1.33	0.217	1.43	4.13	28.42	4.20	11.37	12.92	13.47	2.10	22.80	4.78	13.15	11.61	1.55	5.24	0.85	2.41	0.69	0.51	0.77	0.42
	2	1937	2.85	0.95	1.79	0.379	2.17	7.52	27.70	2.05	6.19	6.52	7.21	1.02	23.65	4.92	14.04	12.85	1.61	5.48	0.79	2.90	0.77	0.62	0.69	0.49
		1938	2.63	0.92	1.58	0.246	2.23	7.13	30.67	2.78	8.39	9.09	11.13	2.74	21.28	4.85	12.66	15.51	1.20	5.80	1.03	2.14	0.70	0.51	0.81	0.44
	3	1937	2.92	0.98	1.81	0.433	2.27	7.39	25.77	1.77	4.40	4.82	5.32	0.92	26.88	5.01	13.31	13.98	1.24	5.84	0.82	2.53	0.99	0.59	0.80	0.42
		1938	2.80	1.02	1.77	0.297	2.26	6.18	28.60	2.83	7.99	8.61	9.68	1.69	22.01	4.90	12.82	16.41	1.24	6.37	1.01	2.70	0.74	0.51	0.81	0.39
Drama	1	1937	2.58	1.11	1.38	0.269	1.69	6.58	31.82	3.75	7.37	7.96	10.00	2.63	22.17	4.74	13.76	12.14	1.69	4.62	0.90	2.45	0.66	0.72	1.13	0.37
		1938	2.64	0.99	1.45	0.253	2.08	5.38	27.70	2.74	8.48	9.84	10.63	2.15	25.01	4.79	13.50	12.55	0.95	5.61	0.90	2.70	0.82	0.60	0.89	0.40
	2	1937	2.58	1.02	1.51	0.305	1.77	8.31	28.47	2.90	6.19	6.86	7.80	1.61	20.76	4.77	14.39	11.54	0.92	4.59	0.79	2.61	0.52	0.77	0.80	0.37
		1938	2.72	1.04	1.57	0.231	1.98	7.21	31.48	2.05	8.69	9.06	10.71	2.02	19.81	4.78	14.14	13.37	1.41	5.22	0.85	2.59	0.71	0.57	0.98	0.36
	3	1937	2.79	1.06	1.65	0.370	1.81	7.12	24.57	2.03	4.73	5.08	6.04	1.31	25.91	4.99	14.15	13.80	1.22	5.59	1.02	2.96	0.69	0.70	0.83	0.38
		1938	2.83	1.10	1.64	0.249	2.16	7.24	29.48	2.54	7.71	8.06	9.19	1.48	24.21	4.81	12.65	14.46	1.69	5.43	0.93	2.23	0.90	0.60	0.83	0.36
Djebel	1	1937	1.88	0.87	0.91	0.140	0.48	4.24	38.48	6.48	18.83	19.13	21.48	2.65	17.08	4.65	16.38	10.04	1.74	2.74	0.65	2.97	0.49	0.65	0.50	0.51
		1938	1.92	0.90	0.96	0.161	0.45	3.69	37.59	5.94	17.90	18.25	20.00	2.10	18.20	4.60	15.30	9.85	1.32	3.20	0.88	2.33	0.59	0.64	0.76	0.39
	2	1937	2.10	0.93	1.11	0.167	0.82	4.94	33.45	6.20	15.62	16.81	17.24	1.62	16.22	4.67	14.83	11.84	0.55	3.32	0.74	2.85	2.50	0.66	0.63	0.41
		1938	2.67	1.11	1.48	0.207	0.94	5.82	33.87	4.81	12.38	13.15	15.07	2.69	19.58	4.58	14.91	11.28	1.17	3.33	0.89	2.61	0.49	0.65	0.74	0.50
	3	1937	2.44	1.07	1.31	0.264	0.98	5.07	31.85	4.64	11.15	12.16	13.73	2.58	18.79	4.87	13.70	12.02	0.66	4.13	0.90	3.84	0.49	0.65	0.67	0.58
		1938	3.41	1.30	1.95	0.451	1.32	6.12	30.19	3.07	6.90	7.37	8.60	1.70	21.96	4.81	15.09	15.29	1.45	4.42	1.19	3.49	0.71	0.68	1.17	0.50
Souyalassi	1	1937	1.96	0.96	0.95	0.195	0.47	5.58	38.63	3.94	16.95	17.64	19.69	2.74	15.95	4.60	16.01	10.00	1.81	2.91	0.78	2.10	0.48	0.68	0.85	0.47
		1938	2.33	1.08	1.10	0.210	0.62	4.30	38.86	6.11	16.89	17.42	20.89	4.00	16.92	4.52	15.00	9.99	1.63	2.86	0.80	2.82	0.50	0.65	0.77	0.42
	2	1937	1.98	0.90	1.08	0.178	0.61	4.39	37.33	5.30	17.75	18.32	20.58	2.83	16.12	4.62	14.21	11.00	0.47	3.13	0.61	3.02	0.34	0.70	0.52	0.40
		1938	2.69	0.96	1.65	0.255	0.85	5.48	34.48	4.21	13.32	14.95	16.57	3.25	20.22	4.59	17.35	11.90	1.16	3.17	0.85	2.81	0.74	0.70	0.63	0.34
	3	1937	2.29	1.04	1.17	0.238	0.61	4.95	35.20	4.94	14.80	15.38	16.84	2.04	15.80	4.69	13.58	11.82	0.66	3.19	0.75	3.09	0.45	0.70	0.65	0.52
		1938	3.02	1.18	1.69	0.272	0.95	5.21	32.29	2.59	10.71	11.02	13.05	2.34	19.92	4.72	17.73	14.25	1.24	4.24	0.97	2.85	0.65	0.65	0.83	0.42
Xanthi (2nd Yaca)	1	1937	2.62	1.20	1.33	0.237	1.19	5.82	35.86	5.44	11.33	11.66	13.74	2.41	19.80	4.72	14.80	11.18	1.93	4.84	0.89	2.45	0.77	0.52	1.10	0.39
		1938	2.72	1.14	1.46	0.283	1.11	5.53	34.56	3.39	9.14	9.79	13.28	4.14	20.87	4.59	13.27	11.98	1.75	4.01	1.08	2.82	0.83	0.65	1.34	0.45
	2	1937	2.90	1.13	1.64	0.285	1.74	8.76	29.30	3.67	7.98	8.31	10.73	2.75	19.20	4.67	12.21	11.59	1.09	4.30	0.90	3.12	0.75	0.58	0.81	0.37
		1938	2.95	1.03	1.76	0.340	1.53	7.65	31.71	2.16	8.29	8.70	10.33	2.04	19.87	4.60	16.71	13.99	1.18	4.59	1.21	3.06	0.75	0.54	1.34	0.41
	3	1937	3.26	1.23	1.86	0.375	1.71	7.72	27.03	3.25	6.08	6.51	7.88	1.80	22.84	4.83	15.48	13.41	1.12	5.38	1.00	3.12	0.54	0.59	1.01	0.46
		1938	3.32	1.18	2.12	0.394	2.01	7.96	27.97	1.63	5.47	5.72	6.67	1.20	24.21	4.90	16.02	16.47	1.30	4.88	1.13	3.11	0.88	0.59	1.13	0.47
Comotini	1	1937	2.29	1.08	1.11	0.195	0.93	5.57	35.50	4.90	12.06	12.45	13.84	1.78	20.00	4.62	14.36	11.50	2.23	3.79	1.00	2.17	0.75	0.58	1.10	0.37
		1938	1.87	0.92	0.89	0.148	0.47	2.82	37.18	7.31	18.50	19.48	20.92	2.42	17.79	4.69	15.25	9.30	1.29	3.45	0.63	2.31	0.40	0.67	0.54	0.31
	2	1937	2.44	0.99	1.37	0.182	1.46	7.40	33.80	5.78	12.83	13.43	14.93	2.10	17.91	4.69	17.25	10.63	0.79	3.65	0.87	2.71	0.53	0.72	0.70	0.33
		1938	2.35	0.97	1.35	0.251	1.04	6.41	33.55	3.61	12.27	12.82	15.19	2.92	18.31	4.60	14.74	13.27	1.46	3.83	1.10	2.56	0.72	0.56	1.12	0.46
	3	1937	2.84	1.11	1.57	0.381	1.43	7.72	27.31	2.45	6.78	7.28	8.05	1.27	24.47	4.89	16.65	14.35	1.20	4.84	1.11	3.41	0.88	0.64	0.99	0.42
		1938	2.50	1.01	1.38	0.273	1.22	6.70	30.89	3.21	10.17	10.64	12.54	2.37	20.31	4.80	14.76	15.46	1.73	4.40	1.14	3.33	0.78	0.66	1.12	0.47
Prossotsian	1	1938	2.31	0.98	1.21	0.203	1.02	5.33	35.34	4.52	13.09	14.42	16.36	3.27	20.06	4.52	13.80	11.75	0.71	4.99	0.75	2.40	0.77	0.61	0.60	0.41
	2	1938	2.61	0.90	1.63	0.288	1.50	7.23	30.17	2.29	9.60	10.31	11.04	1.44	23.26	4.82	15.99	13.94	1.00	5.03	0.79	2.97	0.60	0.62	0.36	0.48
	3	1938	2.67	1.02	1.53	0.327	1.34	6.31	26.92	2.72	9.10	9.60	10.70	1.60	24.70	4.90	15.95	14.96	1.14	5.68	0.96	2.64	0.70	0.52	0.54	0.45
											WESTERN GREECE REGION															
Agrimon	1	1937	2.01	0.81	1.13	0.208	1.33	5.23	34.03	4.00	11.10	11.73	14.27	3.17	21.81	4.99	15.22	14.95	1.08	4.40	0.63	3.79	0.42	0.51	0.83	0.58
		1938	2.05	0.94	1.02	0.186	1.28	4.59	40.95	5.56	11.42	12.26	13.46	2.04	19.20	4.89	14.77	11.77	0.72	4.82	0.75	3.00	0.61	0.52	0.94	0.42
	2	1937	2.08	0.92	1.13	0.212	1.06	7.16	33.88	4.26	11.38	12.26	13.63	2.25	17.85	4.81	15.06	13.70	1.05	4.10	0.70	2.95	0.39	0.54	0.78	0.43
		1938	2.04	0.87	1.12	0.184	1.20	6.38	33.43	4.06	12.89	14.73	15.11	2.22	18.89	4.93	17.47	13.67	0.94	4.05	0.72	3.14	0.50	0.50	0.78	0.41
	3	1937	2.37	1.04	1.26	0.190	1.51	7.07	31.33	3.75	9.67	10.64	11.44	1.77	20.46	4.90	14.49	12.58	1.23	4.53	0.74	3.07	0.49	0.50	0.77	0.39
		1938	2.24	0.98	1.19	0.218	1.49	6.47	31.46	4.55	10.96	11.68	12.86	1.90	22.12	5.00	16.73	15.43	1.21	4.67	0.82	3.07	0.80	0.46	0.84	0.46

[a] Total acids expressed as cc. of 0.1 *N* alkali required to neutralize the acid in 1 gram of tobacco.

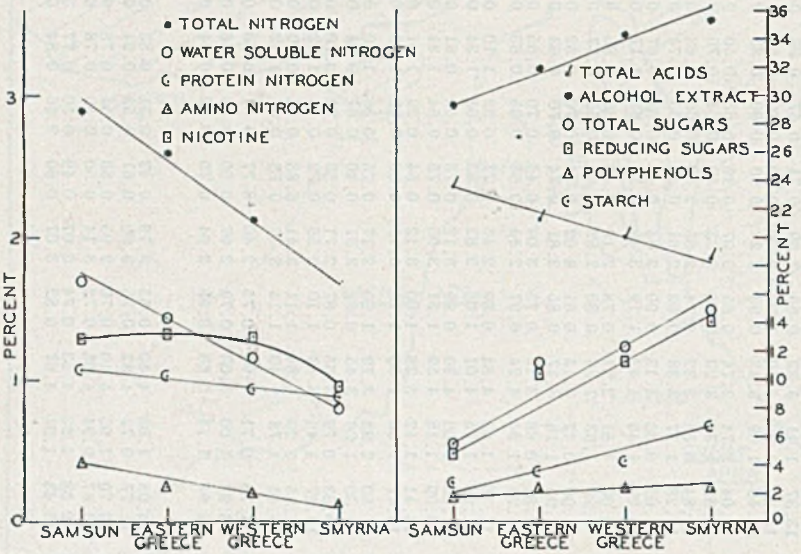


FIGURE NO.3

in the tobaccos grown in the Samsun region, least in those grown in the Smyrna region, and intermediate for those grown in Greece. Unpublished work of this laboratory indicates that most of the nitrogen content of tobaccos of these types is in the insoluble form when the leaves are harvested, and that the nitrogen in soluble form tends to increase in amount until the moisture content of the tobacco becomes too low. The work of Smirnov (*21*) also indicates a loss in protein nitrogen during curing.

The tobaccos grown in the Smyrna region were probably cured more rapidly, because of the hot, dry climate of that region, than those grown in the Samsun and Greek regions. This condition may have reduced the moisture content to unfavorable proportions for the conversion before a larger percentage of the nitrogen was changed to the soluble form.

The lower total nitrogen and amino nitrogen content of the Smyrna tobaccos would seem to indicate that they were grown with less nitrogen available to the plant or that the leaves were more mature at the time of harvest: probably both were contributing factors. The high total nitrogen content of the Samsun tobaccos probably originates from the facts that they were produced on better soils and harvested when less mature. High amino nitrogen content indicates immaturity, a conclusion supported by unpublished work of this laboratory.

The contents of the nitrogenous constituents of the tobaccos from each of the four areas in the Smyrna region are not very different from one another; this indicates a uniformity in soil types, climatic conditions, and cultural practices in the entire region.

The content of nitrogenous constituents of the tobaccos from the Bafra, Maden, and Evgaf areas of the Samsun region is somewhat greater than that of the tobaccos from the Djannik area.

The content of the nitrogenous constituents varies considerably from area to area in the Eastern Greek region. It is greater, however, in the tobaccos produced in the Zihna, Pravi, Serres, Drama, and Prossotsian areas, which are in the western part of the region, and less in the Souyalassi, Dejebel, and Comotini areas, which are in the eastern part of the region. This may be a partial explanation for the division of the tobaccos into Cavalla and Xanthi types as is frequently practiced by the trade. The content of nitrogenous constituents, however, is larger in the tobacco from the Xanthi (2nd Yaca) area than in any other tobacco produced in the region. There is no apparent reason for this exception.

Petroleum Ether Extract. Low boiling petroleum ether removes wax and fatlike materials from the tobacco tissue. These substances are primarily protective materials, and their content may be affected considerably by the weather conditions (*7*) which prevail shortly before harvest. The absence of weather data precludes any adequate discussion or valid correlations in this case.

The data in Table IV show that tobacco of the 1937 crop was 0.55% higher in the extract than that of the 1938 crop, and that grade 1 contains 1% less of the extract than grades 2 and 3. They also show that the tobacco from the Samsun region contains the least amount of the extract, whereas that from the Greek regions contains the greatest amount.

The data in Table II show that the extract content is consistently less in the tobaccos of the 1938 crop from the Smyrna region. This would tend to indicate that dryer, hotter weather prevailed in 1937 in this region. For the Samsun region they show that the variation in extract content is not consistent within the region or for the grades within a specific area of the region.

The data in Table III show a general definite trend toward a greater content of the extract in the 1937 crop for the Eastern Greek tobaccos. They also show that the tobacco from the Djebel and Souyalassi areas contains much less of the extract than the tobaccos from any other area of the region. Table III shows that the content of the extract varies from 2.82 to 8.76% for individual samples. These variations among samples are much greater for the tobaccos from the Eastern Greek region than for those from the Samsun and Smyrna regions, which probably indicates that either the weather conditions were more variable or the grading practice was less efficient in the Eastern Greek region.

Other factors being equal, the smaller the petroleum ether extract the better the burning quality and the poorer the aromatic qualities. If this is correct, the data tend to lend validity to the contention that the Samsun tobaccos are most desirable for general blending qualities, while the Smyrna and many of the Eastern Greek tobaccos are desired if a greater intensity of aroma is required in the blend.

Carbohydrate and Acid Constituents. Tables II and III show the wide range in content of carbohydrate material found in these tobaccos; Figure 3 shows the relation of other carbohydrate constituents to one another when they are plotted in an arbitrary manner, as was done for the nitrogenous constituents. As the sugar type materials increased the acids decreased.

The alcohol extract contains a conglomerate mixture of materials. The main part, however, consists of sugar, acid, protein, gum, and resinlike substances. The data in Table IV and Figures 3 and 4 show that in general the larger the amount of alcohol-soluble material found in a tobacco, the larger the amount of soluble sugar materials and the smaller the amount of nitrogenous materials it contains.

Figure 4 also indicates, as has been observed previously for the flue-cured type of cigaret tobacco (*7*), that as the soluble sugar content increases the total acid content decreases. In the case of the alcohol extract, sugar, starch, and polyphenols, Figures 3 and 4 show that as one of these constituents varies, each of the others do also. Unpublished work of this laboratory indicates that the aromatic principle of tobacco of this type is included in the alcohol extract. The specific constituents from which the aroma arises, however, have not been identified.

The difference between the total sugars and reducing sugars is a measure of the disaccharides present in the tobacco. In general, the greater the total sugar content the greater the content of disaccharides.

The gradation of the sugar-containing constituents from Smyrna to Samsun and from grade 1 to grade 3 is clearly shown in

Figures 3 and 4, and the data in Table IV show the average content to be essentially the same for each of the two years.

The average content of these materials for each of the areas in the Samsun and Smyrna regions varies but little. In the case of the Eastern Greek region, however, a division occurs; the tobaccos from the western part or those from the Serres, Drama, Zihna, Pravi, and Prossotsian areas contain less of these constituents than do those from the eastern part. This again supports the practice of dividing geographically the tobaccos from this region into two classes, Cavalla and Xanthi, as is usually done in the trade. Again, as in the case of the nitrogenous materials, the tobacco of the Xanthi area is not similar in carbohydrate composition to tobaccos from neighboring areas.

The average starch content of the tobaccos from the Smyrna region is greater than that of the tobaccos from the other regions, that of the Samsun region being least. The starch content is greatest in grade 1 tobacco and least in grade 3. The tobacco of the 1937 crop contained more starch than that of the 1938 crop. The starch content of tobacco from each area in the Samsun region is low, that of each area in the Smyrna region is high, and that of the areas in the Eastern Greek region is rather variable. In general, it is higher in those tobaccos grown in the eastern part of the region.

It is generally conceded (*9*, *28*) that the starch content of freshly harvested tobacco is high while the soluble sugar content is low, that the soluble sugars are formed by the conversion of starch to sugars, and that the cured tobaccos are higher in sugar and lower in starch content; unpublished work on curing in this laboratory confirms this. Air-cured tobaccos, when cured over a prolonged period, are low in soluble sugar content (*5*, *12*), whereas flue-cured tobaccos, when cured rapidly, are high in soluble sugar content (*6*).

It was pointed out previously that the 1937 growing and curing season was probably dryer and warmer than the 1938 season, and that the Smyrna region is generally much dryer and warmer than the Samsun region. Thus it would be expected that the tobacco would cure much faster in the former region and that it probably cured faster during the 1937 season than during the 1938 season. If such were the case it is logical to attribute the variation in content of starch and sugars of these tobaccos, at least in part, to the difference in length of the period required for curing.

In the hot, dry Smyrna region the length of time in curing during which the tobaccos contained sufficient moisture to allow the starch to be converted to soluble sugars was relatively short; this resulted in a rapid and incomplete conversion of starch, as well as a short period of life in the green tissue during which the sugars could be lost by respiration. This would result in both higher starch and higher sugar contents, as found in the Smyrna tobaccos. The color of Smyrna tobaccos usually contains some green, which indicates rapid drying and an incomplete loss or conversion of chlorophyll.

In the Samsun region the climate is cooler and more moist. The period of curing is probably much longer, and the tobacco loses moisture more slowly. Consequently the period during which the conversion of starch to sugars can take place, and also the period during which the loss of sugar (by respiration) can occur, is longer. Therefore, it would be expected, as found, that a cured tobacco of less starch and sugar would result. In contrast to the Smyrna tobaccos, the Samsun tobaccos, which are usually some shade of brown or red, contain no traces of green.

The total reducing substances were determined and the polyphenols calculated by obtaining the difference between the total reducing substances and reducing sugars. The polyphenol coefficient (*22*), in grams of polyphenol per 100 grams of total reducing substances, was calculated for each sample. The average values are given in Table IV. Smuck (*22*) claims that the polyphenol content is related to flavor and aroma, and the polyphenol coefficient is related to color and quality; the greater the polyphenol content the better the flavor and the greater the aromatic properties; and the higher the polyphenol coefficient the darker the color.

The polyphenol content of the tobaccos studied here is least in the Samsun tobaccos and greatest in the Smyrna and Eastern Greek tobaccos. Among the grades the polyphenol content is largest in grade 1 and least in grade 3. The polyphenol coefficient is highest in the Samsun tobaccos which were darkest and least in the Smyrna tobaccos which were the lightest in color.

Total acidity content, expressed in terms of cc. of 0.1 *N* alkali required to neutralize the acid in 1 gram of tobacco, is, on the average, just the reverse of the alcohol extract and sugars in relative magnitude (Figure 3). The Samsun tobaccos are lowest in extract and sugar content and highest in acids, whereas the Smyrna tobaccos are highest in extract and sugar content and lowest in acids. This relation in connection with flue-cured tobaccos has been pointed out previously (*7*, *8*). The work of Richards (*20*) would indicate that organic acids are by-products of respiration as carbohydrates are broken down. If this be true, a part of the increased acid content of the Samsun tobaccos may be due to this process which results in a decreased sugar content.

The average acid content of tobacco of grades 1 and 2 is less than that of grade 3 (Figure 4). This agrees with the observation of Piatnitzki (*17*, *18*) who worked with Russian tobaccos of the aromatic type. He concluded that the content of organic acids bears an inverse relation to quality as judged by tobacco classification.

The acid content of the tobacco from each of the areas of the Samsun region is essentially the same. This is true also for each of the areas of the Smyrna region. In the Eastern Greek region the same geographical division that seems to be correlated with differences in nitrogenous and sugar constituents holds, those tobaccos grown in the western part of the region being higher in acids than those grown in the eastern part.

The hydrogen ion concentration is expressed as pH. The average pH value is largest for Smyrna tobaccos and least for the Eastern Greek tobaccos. It is less for the tobaccos in grades 1 and 2 than it is for those of grade 3. This agrees with the ob-

FIGURE NO. 4

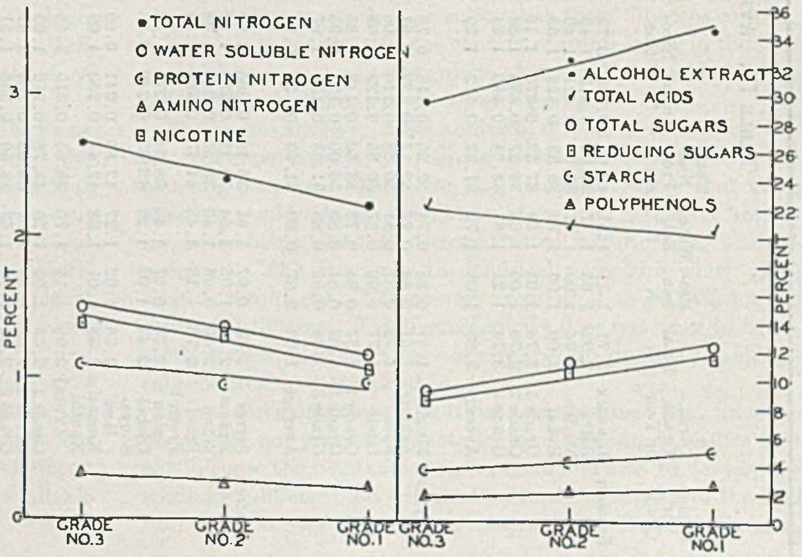


Table IV. Average Percentage[a, b] Analysis of Greek and Turkish Tobacco of 1937 and 1938 Crops

Region or Grade	Area, Grade, or Year	Total N	Protein N	Water-Sol. N	Total N as Protein N	Amino N	Nicotine	Petroleum Ether Extract	Alcohol Extract	Starch	Reducing Sugar	Total Sugar	Total Reducing Substances	Polyphenols	Starch + Total Sugar	Total Acids[a]	H Ion Concn. (pH)[b]	Hygroscopicity	Sol. Ash	SiO_2	CaO	MgO	K_2O	Fe_2O_3 + Al_2O_3	P_2O_5	Cl_2	S	Polyphenol Coefficient
Samsun	Djannik	2.71	1.11	1.51	40.95	0.388	0.79	4.73	27.87	3.04	5.13	5.81	6.91	1.78	9.19	23.27	4.98	14.46	14.86	1.35	4.14	1.09	4.19	0.69	0.81	0.66	0.36	25.75
	Bafra	2.92	1.05	1.77	35.96	0.413	1.40	4.99	29.75	2.87	4.96	5.50	6.51	1.57	8.71	24.07	4.85	14.19	13.58	1.29	4.29	1.01	3.75	0.50	0.74	0.59	0.43	24.16
	Maden	2.94	1.09	1.72	37.07	0.421	1.40	5.27	30.55	2.81	4.91	5.50	6.75	1.84	8.63	23.55	4.87	14.08	13.47	1.36	4.30	1.20	3.71	0.70	0.76	0.67	0.40	27.26
	Evkaf	3.00	1.06	1.79	35.33	0.422	1.55	5.53	29.58	2.69	4.63	5.11	6.27	1.65	8.11	24.23	4.88	13.43	13.62	1.46	4.44	1.06	3.74	0.74	0.72	0.60	0.43	26.32
	Grade 1	2.76	1.03	1.59	37.32	0.376	1.16	4.74	31.22	3.14	5.38	6.13	7.24	1.87	9.62	23.80	4.85	14.26	12.84	1.48	3.93	1.00	3.87	0.63	0.71	0.62	0.42	25.83
	Grade 2	2.78	1.00	1.68	35.97	0.380	1.36	5.55	29.21	2.81	5.13	5.73	6.87	1.75	8.87	24.07	4.90	14.01	14.19	1.18	4.27	1.08	3.88	0.59	0.80	0.52	0.39	25.47
	Grade 3	3.14	1.21	1.83	38.54	0.480	1.34	5.10	27.88	2.62	4.22	4.58	5.72	1.51	7.49	23.48	4.94	13.82	14.63	1.44	4.53	1.21	3.80	0.75	0.76	0.75	0.41	26.40
	Average	2.89	1.08	1.70	37.33	0.412	1.29	5.13	29.44	2.86	4.91	5.48	6.61	1.71	8.66	23.78	4.90	14.03	13.89	1.37	4.24	1.10	3.85	0.66	0.76	0.63	0.41	25.87
Smyrna	Mugla	1.61	0.85	0.74	52.80	0.118	0.78	5.23	34.60	7.36	14.30	15.03	16.45	2.15	23.20	18.35	5.05	13.39	12.99	2.33	4.45	0.77	2.43	1.03	0.55	0.65	0.31	13.07
	Axhisar	1.61	0.84	0.77	52.17	0.129	0.91	5.13	35.94	7.01	14.06	15.00	16.51	2.45	22.79	19.30	5.12	13.92	12.82	2.43	4.42	0.92	2.98	0.95	0.56	0.31	0.34	14.84
	Foca	1.72	0.87	0.81	50.58	0.116	1.06	5.96	34.25	6.71	13.94	14.84	16.02	2.09	22.30	18.48	4.95	13.80	12.45	2.04	3.98	0.87	2.86	0.74	0.51	0.86	0.38	13.05
	Izmir	1.77	0.90	0.87	50.85	0.129	1.08	5.30	36.20	6.18	14.07	14.79	16.37	2.31	21.66	18.43	5.04	13.77	12.48	1.80	4.53	0.81	2.48	0.91	0.50	0.77	0.35	14.11
	Grade 1	1.57	0.84	0.72	53.50	0.113	0.85	4.81	37.01	7.48	14.87	15.45	17.32	2.46	23.76	18.04	5.09	14.00	12.10	2.53	3.98	0.80	2.68	0.90	0.50	0.69	0.37	14.20
	Grade 2	1.62	0.81	0.80	50.00	0.121	0.95	5.70	36.03	6.89	14.96	15.96	17.21	2.26	23.61	18.26	5.01	13.93	12.48	1.80	4.24	0.75	2.77	0.82	0.55	0.55	0.32	13.13
	Grade 3	1.84	0.95	0.88	51.63	0.137	1.07	5.71	32.72	6.13	12.45	13.33	14.48	2.01	20.14	19.63	5.01	13.23	13.48	2.09	4.82	0.99	2.61	1.00	0.54	0.72	0.35	13.88
	Average	1.68	0.87	0.80	51.79	0.124	0.96	5.41	35.25	6.83	14.09	14.91	16.34	2.25	22.50	18.64	5.04	13.72	12.69	2.14	4.35	0.85	2.69	0.91	0.53	0.65	0.35	13.77
Eastern Greece	Serres	2.68	0.97	1.61	36.19	0.305	2.00	6.53	28.78	2.83	7.71	8.38	9.51	1.80	11.52	23.29	4.90	13.20	13.81	1.49	5.69	0.89	2.50	0.81	0.55	0.77	0.43	18.93
	Drama	2.68	1.05	1.54	39.18	0.280	1.92	6.97	28.92	2.67	7.20	7.81	9.07	1.87	10.77	22.95	4.82	13.76	12.98	1.32	5.18	0.90	2.59	0.72	0.66	0.91	0.38	20.62
	Zihna	2.49	0.96	1.40	38.55	0.290	1.38	5.98	31.92	3.08	10.38	11.19	12.62	2.24	14.62	23.65	4.89	14.26	12.63	1.21	5.52	0.71	2.40	0.54	0.54	0.60	0.45	17.75
	Pravi	2.78	1.16	1.48	41.73	0.262	1.35	6.20	32.48	3.80	10.73	11.55	13.17	2.44	15.76	21.25	4.66	13.96	11.12	1.17	3.98	0.93	2.74	0.56	0.68	0.83	0.39	18.53
	Prossotsian	2.53	0.97	1.46	38.34	0.273	1.29	6.29	30.81	3.18	10.60	11.44	12.70	2.10	14.97	22.67	4.75	15.25	13.55	0.95	5.23	0.83	2.67	0.69	0.58	0.50	0.45	16.54
	Djebel	2.41	1.02	1.29	42.32	0.242	0.83	4.98	34.24	5.19	13.80	14.48	16.03	2.23	20.23	18.64	4.70	15.04	11.72	1.15	3.53	0.88	3.02	0.55	0.66	0.75	0.48	13.91
	Souyalassi	2.38	1.02	1.27	42.86	0.241	0.69	4.97	36.14	4.52	15.07	15.79	17.94	2.87	20.81	17.49	4.63	15.65	11.50	1.09	3.25	0.79	2.78	0.53	0.68	0.71	0.43	16.00
	Komatini	2.38	1.01	1.28	42.44	0.253	1.09	6.06	33.04	4.44	12.10	12.69	14.25	2.14	17.62	19.80	4.72	15.50	12.42	1.45	4.00	0.98	2.75	0.68	0.64	0.93	0.40	15.02
	Xanthi (Yaca)	2.96	1.15	1.70	38.85	0.319	1.55	7.24	31.07	3.26	8.05	8.45	10.44	2.39	12.07	21.14	4.73	14.76	13.10	1.40	4.67	1.04	2.95	0.75	0.58	1.12	0.40	22.89
	Grade 1	2.33	1.02	1.20	43.78	0.216	1.05	5.11	34.90	4.71	12.89	13.71	15.61	2.72	18.95	19.94	4.72	14.28	11.08	1.53	4.24	0.83	2.47	0.65	0.62	0.83	0.42	17.43
	Grade 2	2.59	0.99	1.51	38.22	0.264	1.47	6.84	31.91	3.45	10.48	11.27	12.84	2.36	15.10	20.82	4.73	14.78	12.48	1.03	4.43	0.85	2.75	0.61	0.63	0.72	0.42	18.38
	Grade 3	2.85	1.10	1.62	38.59	0.338	1.51	6.48	28.99	2.72	8.41	8.93	10.12	1.71	11.95	22.98	4.86	14.81	14.05	1.18	5.01	0.97	2.91	0.68	0.61	0.82	0.44	16.90
	Average	2.59	1.04	1.44	40.15	0.273	1.34	6.14	31.93	3.63	10.59	11.30	12.86	2.27	15.33	21.25	4.77	14.62	12.54	1.25	4.56	0.88	2.71	0.65	0.62	0.79	0.43	17.65
Western Greece	Agrinion	2.13	0.93	1.15	43.66	0.200	1.31	6.15	34.18	4.36	11.24	12.25	13.46	2.23	17.09	20.05	4.92	15.71	13.69	1.04	4.43	0.73	3.17	0.54	0.51	0.82	0.45	16.57
	Grade 1	2.03	0.88	1.08	43.35	0.197	1.31	4.91	37.49	4.78	11.26	12.10	13.87	2.61	17.41	20.50	4.94	15.00	13.36	0.90	4.61	0.69	3.40	0.52	0.52	0.88	0.50	18.82
	Grade 2	2.06	0.90	1.13	43.69	0.198	1.13	6.77	33.66	4.16	12.14	13.50	14.37	2.24	18.12	18.37	4.87	16.51	13.69	1.00	4.08	0.71	3.05	0.45	0.52	0.78	0.42	15.59
	Grade 3	2.31	1.01	1.23	43.72	0.204	1.50	6.77	31.40	4.15	10.32	11.16	12.15	1.84	15.78	21.29	4.95	15.61	14.01	1.22	4.60	0.78	3.07	0.65	0.48	0.81	0.43	15.14
Grade 1	1937	2.21	0.98	1.16	44.34	0.227	1.06	5.52	35.07	5.25	11.17	11.74	13.59	2.42	17.57	20.23	4.84	14.67	11.68	1.89	4.05	0.84	2.73	0.66	0.60	0.82	0.43	17.81
Grade 1	1938	2.26	0.97	1.18	42.92	0.227	1.02	4.39	34.30	4.74	11.85	12.74	14.32	2.47	18.11	20.59	4.82	13.83	11.96	1.58	4.16	0.86	3.04	0.73	0.61	0.70	0.39	17.25
	Average	2.24	0.98	1.17	43.63	0.227	1.04	4.96	34.69	5.00	11.51	12.24	13.96	2.45	17.80	20.41	4.83	14.25	11.82	1.74	4.11	0.85	2.89	0.70	0.61	0.76	0.41	17.55
Grade 2	1937	2.34	0.95	1.33	40.60	0.254	1.32	6.41	32.32	4.71	10.48	11.05	12.35	1.87	16.28	20.33	4.82	14.49	12.42	1.07	4.28	0.82	3.08	0.65	0.67	0.65	0.38	15.14
Grade 2	1938	2.48	0.94	1.38	37.90	0.252	1.29	6.13	32.43	3.67	10.48	11.36	12.86	2.38	15.45	21.18	4.84	14.43	13.35	1.42	4.34	0.92	2.97	0.63	0.62	0.65	0.39	18.51
	Average	2.41	0.95	1.36	39.42	0.253	1.31	6.27	32.38	4.19	10.48	11.21	12.61	2.13	15.89	20.76	4.83	14.46	12.89	1.25	4.31	0.87	3.03	0.64	0.65	0.65	0.39	16.89
Grade 3	1937	2.61	1.07	1.46	41.00	0.316	1.36	6.13	29.80	4.00	8.27	8.82	9.90	1.63	13.26	22.25	4.90	14.35	12.56	1.25	4.81	1.00	3.07	0.78	0.64	0.79	0.41	16.46
Grade 3	1938	2.70	1.10	1.52	40.74	0.318	1.40	5.89	29.77	3.25	8.69	9.26	10.37	1.68	12.88	22.12	4.92	14.12	14.59	1.65	4.82	1.03	3.05	0.75	0.61	0.78	0.41	16.20
	Average	2.66	1.09	1.49	40.97	0.317	1.38	6.01	29.79	3.63	8.48	9.04	10.14	1.66	13.07	22.19	4.91	14.24	14.08	1.45	4.82	1.02	3.06	0.77	0.63	0.79	0.41	16.37
Average 1937 crop		2.39	1.00	1.32	41.84	0.266	1.25	6.02	32.40	4.65	9.96	10.56	11.95	2.00	15.72	20.94	4.86	14.50	12.50	1.41	4.38	0.89	2.96	0.70	0.64	0.75	0.40	16.74
Average 1938 crop		2.48	1.01	1.36	41.06	0.266	1.24	5.47	32.17	3.89	10.32	11.12	12.56	2.25	15.42	21.29	4.86	14.13	13.30	1.55	4.44	0.93	3.02	0.70	0.61	0.71	0.40	17.91
Grand Average		2.43	1.00	1.34	41.45	0.266	1.24	5.75	32.28	4.27	10.14	10.84	12.26	2.13	15.57	21.12	4.86	14.32	12.90	1.48	4.41	0.91	2.99	0.70	0.63	0.73	0.40	17.37

[a] Total acids expressed as cc. 0.1 N alkali required to neutralize the acid in 1 gram of tobacco.

[b] Since pH values are logarithmic and may not be averaged like ordinary numbers, the pH values were converted to moles per liter. These values were averaged, and the results were reconverted to pH units.

servation of Pyriki (*19A*) that the better grades of Turkish tobacco have a lower pH value than the poorer grades.

Ash and Mineral Constituents. The work of Darkis and collaborators (*7, 8*) with flue-cured tobaccos shows that the mineral constituents in some tobaccos are localized in certain parts of the plant and that the water supply available to it affects the amount of ash constituents taken from the soil by the plant. The interpretations placed on the data for the mineral constituents in the following discussion are subject to error because of the absence of rainfall data, yield data, soil analyses, and analytical data for all parts of the plant.

The total ash data obtained are included here in order to afford a complete picture of the mineral constituent of these tobaccos. In the absence of the complementary data on weather and soil an adequate interpretation of the significance of the mineral content of these tobaccos is not possible at this time. However, experiments are in progress wherein the nutrition of the plant is controlled and known and the whole of the plants produced is being subjected to analysis. Complete weather and soil data are available. When the complete data from these experiments become available it is believed that it will be possible to give at least a partial interpretation of the significance of the different trends in the mineral content of the tobaccos of the various types discussed in this paper.

The following condensed figures show the wide range over which mineral constituents vary: soluble ash 9.30 to 16.74, silica 0.47 to 3.12, calcium oxide 2.74 to 6.37, magnesium oxide 0.61 to 1.26, potassium oxide 1.96 to 5.00, $Fe_2O_3 + Al_2O_3$ 0.34 to 1.37, P_2O_5 0.44 to 0.96, chlorine 0.15 to 1.34, and sulfur 0.25 to 0.58%.

The average ash content as well as the average content of silica, calcium, magnesium, and potassium is slightly greater in the tobacco of the 1938 crop than in that of the 1937 crop. This would probably be expected (*7, 8*) if the 1937 season was dryer than the 1938 season, as suggested.

The average content of soluble ash, magnesium, and potassium is somewhat higher in the tobaccos from the Samsun region than it is in those from the Smyrna and Greek regions. The average silica content is highest in those tobaccos grown in the Smyrna region, the average calcium content highest in the Greek tobaccos. The higher calcium content of the latter may be due to the high calcium content of the soils on which the tobacco was grown. The soils of Macedonia originate from the limestone formations of which the Rhodope mountains are composed (*15*).

The calcium contents of the tobaccos of each area in the Samsun region are about equal. This same relation holds for the tobaccos of each area in the Smyrna region; this indicates that soils of areas within each region have about an equivalent content of available calcium. The calcium content of the tobaccos from the different areas of the Eastern Greek region is quite variable and seems not to be correlated directly with geographical locations. It probably reflects, however, the content of available calcium in the soil of each area.

The average content of potassium in the tobacco varies rather widely among the areas within each region as well as among the regions. This is typical of the potassium content of tobaccos (*7, 8*). The generally increased potassium content of the Samsun tobaccos, however, would indicate a larger content of available potassium in the soils of that region.

Workers Grading Tobacco in Greece

The generally increased ash content of the tobaccos from the Samsun region is probably due, in part, to the increased loss of carbohydrate during the curing of these tobaccos, which in turn would give an apparent increase in content of mineral materials.

The tobaccos of grade 1 are lowest and those of grade 3 highest in average soluble ash, calcium, magnesium, and potassium content. These differences in relation to grade would be expected to follow this pattern because of the increased percentage of carbohydrate materials in the tobaccos of better grade.

In general the content of iron and aluminum in most of these tobaccos is high (*8*), that of the tobaccos from the Smyrna region being the highest. This would indicate that the soils used for the production of these tobaccos were high in available iron or aluminum. Many of these soils are red (*15*), a color indicating a high iron content.

The phosphorus content of the Samsun tobaccos is greatest, and that of the Smyrna tobaccos smallest. In general, the phosphorus content tends to be low; this would indicate soils of low available phosphorus content.

The average content of chlorine is high. This would be expected because of the fact that the soils on which the tobaccos are generally grown are fertilized by excrement of sheep and goats, which furnishes considerable chlorine to the soil.

The average sulfur content of these tobaccos is low (*8*). As the plant will take up much more sulfur than these tobaccos contain, it is logical to assume that the content of sulfur is low in the soils on which the tobaccos were grown. Little sulfur is added to the soil by the excrement of the sheep and goats.

The hygroscopicity, or the ability of a tobacco to take up water, is of importance in determining the suitability of a tobacco for blending purposes. Therefore, the amount of water that these tobaccos would take up in an atmosphere of 72% relative humidity, after being dried over concentrated sulfuric acid, was determined. This is purely an empirical procedure which gives relative results only. These vary from 12.21 to 17.73% for the acid-dried tobacco. The hygroscopicity does not seem to be directly correlated with any one or any specific group of the chemical constituents determined.

In the foregoing discussion it has been assumed that these tobaccos did not possess characteristics of any innate nature that would cause the plants from each region and area to develop according to different physiological patterns, in respect to the final chemical make-up of their physical structure. If such is the case, the assumption could probably be made that seed of tobacco from each area and region, if planted in the same locality, grown, and cured under similar conditions, should give a product rather similar in chemical composition to that of each of the others.

Incomplete and inconclusive unpublished work of the writers indicates that characteristics of an innate nature do exist between Samsun and Smyrna tobaccos. If such is the case these characteristics probably originated as a result of the selection of natural crosses by the growers during the period, since tobacco was first introduced into Turkey shortly after the discovery of America.

The presence of innate characteristics may cast much doubt on the validity of any of the theoretical speculations offered. They do not, however, change the fact that differences among the chemical compositions of these tobaccos exist. Therefore, the practice of the trade in attempting to get tobaccos of each type to blend in making blended products is justified.

The data presented here show that the tobaccos of the Turkish type may vary within wide limits in chemical make-up and that the tobacco from any area may not be of constant chemical composition from year to year. It also shows that the tobaccos of a given main region tend to be dissimilar in chemical composition from those from other regions. The similar data obtained for the 1937 and 1938 crops, when the analyses of all samples of the specific crops are averaged, indicate that an experienced tobacco blender could maintain a blend of rather constant chemical composition, if a sufficient supply of tobacco from several crops from many areas of the different regions was available.

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VACUUM DRYING OF PAPER

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The removal of water, of importance in many technical processes, is of especial importance in the manufacture of radio parts employing electrical insulating paper. Vacuum treatment of tightly rolled, interleaved layers of metal foil and paper has been employed for drying the tissue. The interrelation of the physical phenomena of moisture sorption and the practical problems involved in its removal by vacuum pumping systems are presented. Drying may be supplanted at high temperatures by what appears to be a decomposition of some paper constituent.

PAPER exposed to room conditions normally contains at least 5% water sorbed throughout its structure. The exact amount to be found on any particular type of paper depends on the relative humidity of the surrounding atmosphere and also on the previous history of the paper sample, the temperature, and the pulp composition (*4, 5, 14, 15, 16, 22, 26, 30, 31*). This moisture exerts a marked effect on the physical properties of papers, although its exact role is not known (*1, 2, 3, 6, 9*). The serious decrease of electrical insulating quality with increasing moisture content is of importance in the numerous uses of dielectric paper (*7, 8, 11, 24, 31*). Tissue paper (*23, 27*) used in the manufacture of rolled electrical capacitors was examined in the present investigation.

Evacuation under heat has been the method used to dry radio parts containing paper. This process presents several problems, but the two major factors considered are the extent of the drying that results from various times of treatment under factory conditions with varying loads in commercial vacuum tanks, and the extent of damage attending exposure to elevated temperatures.

The removal of water from materials with large surface area is usually achieved by lowering the relative humidity or partial pressure of water in the gas surrounding the sorptive material. The effectiveness of various reductions in humidity has not been thoroughly studied but will probably depend upon temperature and the partial pressure of water vapor. Inert gas pressure should be of importance only as it affects the rate of drying (*11, 13*).

In vacuum drying these same considerations hold. The rate of water removal and the limiting desiccation attained depend upon the temperature and the atmosphere within the system. The vacuum tank atmosphere, in turn, is dependent upon the load, the leaks in the system, and the pump speed.

In order to obtain data relative to paper drying and decomposition, sorption isotherms for kraft paper at the full range of temperatures were studied by successively evacuating and reestablishing equilibrium within a large volume connected to paper samples through a large vacuum stopcock. Details of this method of estimating both the composition of the sorptive system and the partial pressures of water at the temperatures of testing are presented later.

Since the ultimate drying conditions seemed to present the most serious drying problem, the sorption isotherms at lower partial pressures were determined most carefully. In most experiments the paper was first held at room conditions and then subjected to progressively higher temperatures and lower pressures, so that the highest temperature isotherms of about 150° C. were determined after a history of lower temperature measurements. Furthermore, the equilibria established at the higher temperatures occur in the presence of products of decomposition of the paper and, for this reason, are uncertain. The nature, extent, and over-all effect of this decomposition have not been established (*7, 8, 18, 24, 25, 28*).

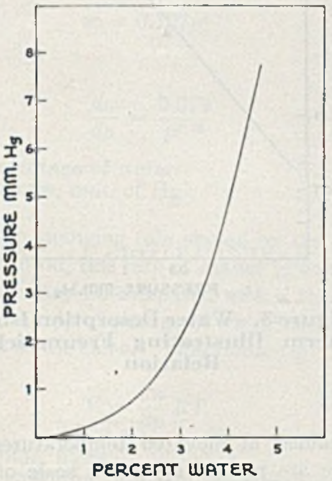

Figure 1. Desorption Isotherm of Kraft Capacitor Tissue at 27° C.

Equilibrium moisture curves for paper at room conditions are of the typical sigmoid shape (*5, 17*). Figure 1 represents the lower portion of the desorption isotherm of kraft capacitor tissue. It shows the amounts of water to be removed in drying such paper and the limits to which the paper may be dried under various conditions at room temperature. The portion for lower water contents is of significance in these applications and indicates, for example, that for zero humidity the equilibrium water content will be zero. However, the problem of approaching complete dryness presents considerable difficulty, since the rate of approaching this condition falls off toward zero for any given drying condition as the water content decreases. The drying rate will vanish for water contents having partial pressures of water equal to that of the desiccant used or, in the case of vacuum drying, equal to the system vapor pressure. In the case of paper at room temperature exposed to fresh calcium chloride, equilibrium would correspond to more than 1% water. In order to obtain electrically insulating paper of low water content, severe drying conditions must be employed (*17*).

MOISTURE SORPTION BY PAPER

In order to determine the factors influencing both the equilibria and the rate of drying radio capacitors, specimen parts consisting of tightly wound layers of paper and aluminum foil were placed in large Pyrex test tubes, which were then drawn down for sealing to an all-glass high vacuum system. In several experiments samples of paper only were placed in the sample tubes. After the samples were sealed onto the system, they were usually allowed to come to equilibrium with the room atmosphere.

The sample was shut off from the remaining volumes of the system, which were evacuated with a diffusion pump. This permitted an adjustment of the residual air pressure throughout the whole system. Any leaks in the system would be indicated at this time by an increasing partial pressure of air. It was usually possible to conduct a whole series of rate and equilibrium measurements at essentially the same air pressure, in the micron range.

By the use of suitable dry ice or liquid air cold traps with intervening vacuum stopcocks, water could be pumped away from the paper, measured, and condensed in a reservoir trap. If necessary this accumulated water could be readmitted to the paper or it could be evacuated and eliminated from the system by direct pumping on the reservoir section. A few measurements of adsorption equilibria were made by readmitting portions of this accumulated water to the paper.

Figure 2 is a sketch of portions of the vacuum system. Paper sealed in *A* may be exposed to cold traps in sections *B*, *C*, or *D*, and evacuated through *E*. The volumes of sections *A*, *B*, *C*, and *D* are 85 ml., 490 ml., 300 ml., and 1350 ml., respectively.

Vacuum measurements (*10, 19, 20, 29*) in such a system that contains condensable vapors are subject to very large errors unless special precautions are taken. The partial pressure of air was determined by two suitably trapped McLeod gages. These were constructed in different sizes with overlapping ranges and were found to agree when they were used to measure dry gases. The water partial pressure was estimated from measurements of the total pressure. Two gages of overlapping ranges were used in this case also. The first was useful for pressures up to 30 mm. of mercury and consisted of an inverted hollow floating metal tube such as that described by Germann and Gagos (*12*). The second consisted of a differential oil manometer suitable up to pressures of about 10 mm. of mercury; when employed against a high vacuum utilizing a cathetometer, it was useful down to 20 microns pressure. The errors inherent in these gages seem to range from a fraction of a millimeter of the oil manometer scale reading up to about 1 mm. of mercury at the highest pressures with the floating barometer gage. The use of short scale McLeod gages cannot be recommended for measuring total pressure, since adsorption may occur on the gage walls and precede condensation so that low readings result. This effect is present with gages having surface films of any nature but is particularly troublesome with gages cleaned with strong solutions that leave a coating of silica gel on the glass walls.

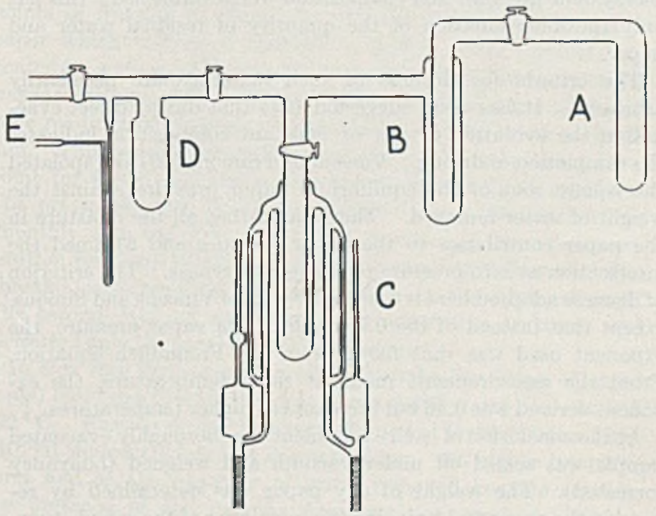

Figure 2. Outline of Vacuum System

The pressures of the water vapor in the system, together with the volume of the chambers, permitted calculation of the weights

Table I. Dehydration of Paper at 27° C.

Water, %	*P*, Mm.	Rate of Water Withdrawal, Cc./Min. 0.40 mm. air	Rate of Water Withdrawal, Cc./Min. 0.02 mm. air
4.1	5.0	7100	..
3.4	3.3	6800	..
2.9	2.2	4800	..
2.1	1.0	2000	..
1.9	0.8	1000	..
1.6	0.6	..	4300
1.5	0.5	700	2900
1.3	0.4	500	..
1.2	0.3	..	2200
1.0	0.2	400	2100
0.7	0.1	400	2000
0.6	0.08	400	2000
0.4	0.05	400	2000
0.2	0.02	400	2000

Table II. Desorption Pressure of System Kraft Paper–Water

Water, %	Temp., ° C.	*P*, Mm.
1.2	52	1.2
1.2	89	15
1.2	93	21
0.9	82	8
0.9	102	20
0.8	62	1.2
0.8	78	4.1
0.8	102	17
0.35	82	2.0
0.35	105	6.5
0.35	122	15
0.1	104	1.4
0.1	122	3.2
0.1	131	5.0
0.07	102	0.35
0.07	120	1.0
0.07	145	3.0

of water removed. At convenient intervals during measurements of the rate of water removal, the sample chamber was allowed to come to equilibrium for the measurement of the apparent equilibrium partial pressure of water. After repeated steps in this process, the quantities of water removed become smaller, and the partial pressures diminish also. By this means the system pressure and composition were established; this left only the determination of the quantity of residual water and paper.

The criteria for dryness of such materials are necessarily arbitrary. It has been suggested (*24*) that during direct evacuation the evolution of gas of constant composition indicates the completion of drying. Vincent and Simons (*30*) extrapolated the square root of the equilibrium vapor pressure against the weight of water removed. They stated that all the moisture in the paper contributes to the vapor pressure and assumed the intersection at zero pressure to represent dryness. The criterion of dryness adopted here is essentially that of Vincent and Simons, except that instead of the 0.5 power of the vapor pressure, the exponent used was that found from the Freundlich equation. From the measurements made at room temperature, the exponent derived was 0.46 but increased at higher temperatures.

At the conclusion of each experiment the thoroughly evacuated sample was sealed off under vacuum and weighed (buoyancy corrected). The weight of dry paper was determined by removing the paper and weighing the remainder of the sample tube.

Having this weight permitted the calculation of the percentage composition throughout each experiment. Table I lists data obtained in this way for typical experiments at 27° C. The desorption pressures may be expressed by the equation:

$$w = 2.1p^{0.46} \qquad (1)$$

where w = percentage of water
p = pressure, mm. of Hg

Table I gives not only the desorption isotherm but also the rates at which it was possible to withdraw water from the edge of the paper roll. These values represent the time rate of removal of water vapor when the sample was opened to an adjacent dry ice trap. The rate was nearly constant at each pressure. Substitution of a liquid air trap slightly increased the rate of withdrawal. A fivefold increase in the rate of water withdrawal was achieved by decreasing the foreign gas pressure to one twentieth of its former value. The data of Table I are presented graphically in Figures 1, 3, and 4.

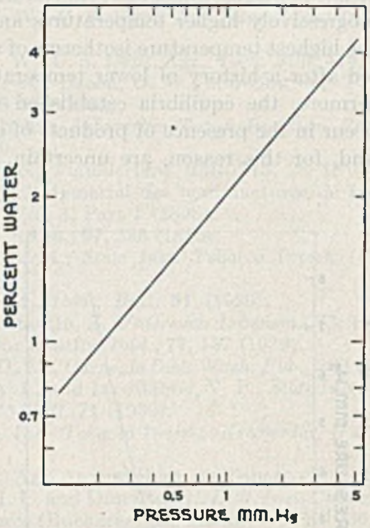

Figure 3. Water Desorption Isotherm Illustrating Freundlich Relation.

The data obtained at elevated temperatures are listed in Table II. These are plotted against a scale of the reciprocal of absolute temperature in Figure 5. From the slopes one obtains an estimate of the heat of the desorption reaction (*16*). This is 14 kilocalories per mole of water for average water content, approximately the value found in the literature (*10, 16*).

Knowledge of the vapor pressure–composition relations at the temperatures employed in the vacuum drying is important in accounting for the results of various vacuum treatments. When large quantities of paper are to be dried in a vacuum tank, the composition and pressure of various parts will vary with their temperature. Under temperature differences the various parts will tend to have different compositions such that their partial pressure of water will be the same. In addition, the volumes of vapor which the vacuum pump must withdraw in order to produce any given change in composition will vary with the temperature and the pressure at which the water vapor is removed.

Knowledge of the water vapor pressure in equilibrium with paper is of thermodynamic interest as evidence of the state of the sorbed water (*3, 5, 10, 14, 20, 21, 26*). It is of practical signifi-

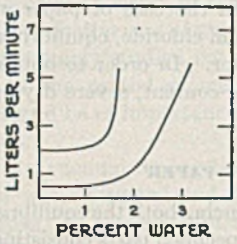

Figure 4. Drying Rates for 6.5-Gram Roll of Paper at 0.4 Mm. Hg Air Pressure (*lower curve*) and 0.02 Mm. Hg Air Pressure (*upper curve*)

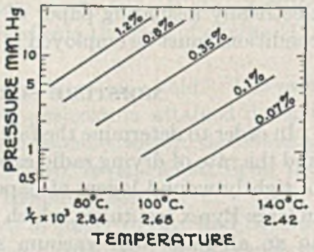

Figure 5. Equilibrium Desorption Pressures for Moist Kraft Paper at Elevated Temperatures

cance in defining the limits within which dehydration by exhaustion may be accomplished.

VACUUM PUMP LOAD IN SORPTIVE SYSTEMS

In order to reduce the pressure in an all-gas system, only a portion of the gas must be removed. In a sorptive system with condensed vapor present, however, a portion of this condensed vapor must be removed. The amounts of this sorbed water vapor which must be removed and the pressures existing within the system during its removal are related to the sorption isotherm for the temperature of drying.

One may obtain the changes in composition required to produce given reductions in the pressure of the system from the sorption isotherm. For 100° C. this equation is

$$w = 0.107p^{0.74} \tag{2}$$

so that

$$\frac{dw}{dp} = \frac{0.079}{p^{0.26}} \tag{3}$$

where w = percentage of water
p = pressure, mm. of Hg

For estimating the changing role played by the sorbed water as the pressure is reduced, this rate of change of water content with change in pressure may be compared with a volume of vapor of such a size that its rate of change of water content with change in pressure would be the same. This volume is

$$V = \frac{dn}{dp} RT \tag{4}$$

where V = volume, liters
R = gas constant, liter-mm./mole degree
T = absolute temperature
$\frac{dn}{dp}$ = molal change in water content with pressure

Since it is customary to state the speed of vacuum pumps in terms of a volume per unit time, this apparent volume is a convenient way of measuring the variable load on the pumps. If the load were not variable but consisted of 1 pound of water to be removed at 0.1 mm. mercury by a commercial pump having a speed of 100 cubic feet per minute, the exhaustion would require about 35 hours. However, with the sorptive system the pressure will fall as the drying proceeds, and the apparent volume presented to the pump by the residual water will vary. For the case under consideration

$$\frac{dn}{dp} = \frac{Q}{100\,M}\frac{dw}{dp} \tag{5}$$

where Q = weight of paper
M = molecular weight of water

so that the apparent volume of the sorptive system is

$$V = \frac{RTQ}{100\,M}\frac{0.079}{p^{0.26}} \tag{6}$$

This equation and that for pump speed give the minimum exhaustion required to reduce the moisture content of paper to that corresponding to any given pressure at 100° C.

The curves of Figure 6 give the apparent volumes calculated by this equation for 1800 grams of paper containing initially 1.5% water.

DIFFUSION AND DECOMPOSITION RATES

The actual drying rates will be lower than those predicted from these equations. This is because of slowness in diffusion and also the influx of heat necessary to maintain uniform temperature at sites of desorption.

The rate of regain of water by a dehydrated sample unit when opened to room conditions is shown in Figure 7. When the vacuum-sealed unit weighing 6.5 grams was opened, air filled the interstices, and the slow gain in weight resulted from the diffusion of water into the layered roll. A sudden increase in weight was noted when the unit was unrolled.

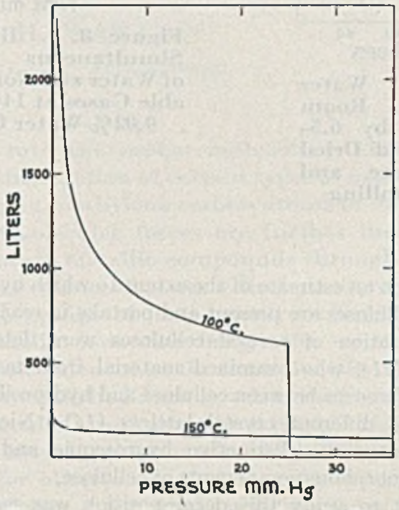

Figure 6. Volumetric Loads Presented to Vacuum System by Water Present on 1800 Grams of Paper in 25-Liter Tank

The thermal insulation of the sample when held in a vacuum requires that considerable time be taken for the adjustment of test temperatures. Figure 8 illustrates this and several other points of interest in the work. A capacitor with 6.43 grams paper which had been reduced to 0.02% water content was heated by a thermal bath at 144° C. Within 1 hour the pressure was increasing rapidly. One of the two McLeod gages employed gave readings of pressure that exhibited a sharp break at 0.063 mm. This corresponds closely with the calculated condensation point for the condensation of water in the McLeod capillary. The pressures given by the manometer gages (broken line) fit smoothly with the first curve. The presence of gaseous decomposition products is indicated by the increasing values after the "break" corresponding to condensation in the McLeod gage. The second McLeod gage had walls adsorptive to water and measured only the other gases being liberated.

In this case decomposition (or rather the liberation of other gases) had been first detected at about 0.3% water content and 122° C. Further drying had been effected at lower temperatures without added evidence of decomposition. At higher temperatures and as the quantity of water removed became smaller, the presence of the gaseous decomposition products became more noticeable. Upon continued evacuation the composition of the gases evolved became more constant and, as estimated from the condensation at low temperatures, using baths of liquid air and dry ice in a manner similar to that of Murphy (*24*), approximated equal portions of carbon dioxide and carbon monoxide with water and smaller amounts of other gases.

In general, as the temperature of such paper is raised, some paper constituent undergoes decomposition (*8, 18, 24, 25, 28, 31*). This is presumably the cellulose, and gives gaseous decomposition products of carbon dioxide, carbon monoxide, and water, together with small amounts of other gases and condensed products. Adsorption of some of the products on the remaining paper surfaces masks their evolution and makes difficult the direct study of this reaction. The complicated chemistry of cellulose does

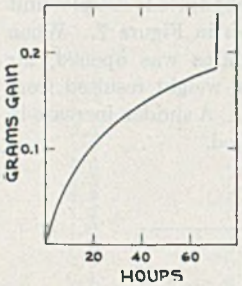

Figure 7. Water Uptake at Room Conditions by 6.5-Gram Roll of Dried Paper Before and After Unrolling

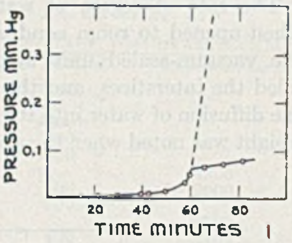

Figure 8. Illustrating Simultaneous Evolution of Water and Noncondensable Gases at 144° C. and 0.02% Water Content

not permit even an estimate of the extent to which hydrocellulose or oxidized celluloses are present and partake in reactions. The heats of hydration of several celluloses were determined by Lauer *et al.* (*21*), who examined material from many sources and found differences between cellulose and hydrocellulose which they relate to different crystal lattices (*14*). Nickerson and Habrle (*25*) attribute distinctive hygroscopic and hydrolytic behavior to amorphous components of cellulose.

An attempt to study this decomposition was made by observing the rate of pressure increase in a system having the paper samples under heat. After thorough and repeated evacuation, this rate of pressure increase was reproducible at any temperature.

The natures of the reactions giving rise to these gases and of whatever residues remain in the paper are not known. A liquid of very low vapor pressure accumulated outside the heated zone. This is either a product of repolymerization of decomposition products or a distillate from the paper. The slowest process in their evolution seems to be one of constant rate at fixed temperature, although the rate may fall off slightly as the process reaches higher pressures.

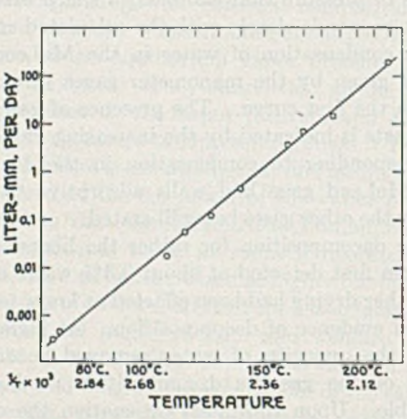

Figure 9. Rate of Decomposition of Paper at Elevated Temperatures as Measured by Gas Evolution

Table III. Rate of Evolution of Gases from 6.5 Grams of Heated Paper

Temp., ° C.	Liter-Mm./Day	Temp., ° C.	Liter-Mm./Day
219	173	127	0.12
186	13	117	0.05
169	7.2	110	0.02
162	3.6	71	0.0005
140	0.44	70	0.0003

Measurements of the rate of evolution of these gases at impregnation temperatures and at pressures from 0.001 to 10.0 mm. mercury exhibit the temperature variation of the rate and are listed in Table III. The decomposition rate per gram may be represented by

$$\ln K = 33 - \frac{14710}{T} \qquad (7)$$

where T = absolute temperature
K = rate in liter-mm./day

Figure 9 gives these data plotted on the scale of the reciprocal of absolute temperature. The activation energy of this process as given by these results is 29 kilocalories, which is 10 kilocalories lower than the value obtained by Murphy (*24*).

CONCLUSIONS

The sorption of water by kraft paper and the decomposition of the paper were studied under conditions comparable to those present in impregnation processes. Decomposition accompanies severe drying and at high temperatures supplants the final drying. The interrelation of these processes and the effect of these processes on the electrical insulating qualities of paper are only imperfectly understood.

A method of estimating the minimum load presented to a vacuum pump by such sorptive systems is given.

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Mechanism and Theory of Vulcanization

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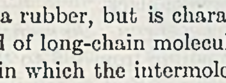
X-ray and stress-strain data have been obtained which indicate that accelerators and divalent metallic compounds, as well as sulfur, react with the rubber molecules during vulcanization and become a part of the rubber vulcanizate. The vulcanization reaction was found to behave like a normal chemical reaction in solution, which is influenced by the temperature, solubilities of the reacting ingredients, relative strengths and concentrations of the acids present, pH, and chemical nature of the vulcanizing agent. On the basis of these results and the known characteristics of vulcanized rubber, the original hypothesis of Goodyear and the more recent conclusions of Midgley, Henne, and Shepard were developed into a theory of vulcanization which postulates that vulcanization is a process by which the intermolecular forces are increased through the introduction of polar groups, generally acidic in nature, into the rubber molecules. This is accomplished by the reaction of certain types of oxidizing agents with the alpha methylene carbon atoms or double bonds. These intermolecular forces are further increased with soluble divalent metallic compounds through the formation of ionic valences between divalent metallic ions and polar acidic groups of the rubber vulcanizate. These divalent metallic ions may bridge the rubber molecules through ionic valences in the form of a salt. Intermolecular forces established during vulcanization give rigidity to the molecular structure, which retards plastic flow and crystallization of rubber molecules. They also are responsible for other characteristics of vulcanized rubber. The molecules in vulcanized rubber are presumably not joined by primary valence bonds through sulfur or oxygen bridges but retain their individual existence.

RUBBER was used commercially prior to the discovery of vulcanization because of its elastic properties. Guth and Mark (*11*), Kuhn (*16*), Wall (*25*) and others have shown that this elasticity is neither dependent upon vulcanization nor peculiar to Hevea rubber, but is characteristic of any material which is composed of long-chain molecules with freely rotating valence bonds and in which the intermolecular forces are comparatively weak. Thus, it was not the search for elasticity but rather the search for a means to overcome the undesirable thermoplastic properties of rubber that led to the discovery of vulcanization.

As a result of extensive experimentation (and not by accident as popularly believed), Goodyear (*10*) found in 1839 that rubber would not become hard and stiff (frozen) at low temperatures or soft and sticky at high temperatures if 100 parts of rubber, mixed with 20 parts of sulfur and 28 parts of white lead, were heated at 270° F. He believed that the rubber combined both with the sulfur and with the lead compounds to form a triple compound in the process and that the lead could be added in the form of its salts or oxides, although some were more effective than others. Following Goodyear, no other hypothesis was advanced for the vulcanization reaction until the work of Henriques (*12*) and Weber (*26*). Since then many theories of vulcanization, both physical and chemical, have been advanced. These theories have been ably reviewed by Kindscher (*15*), Williams (*27*), Fisher (*9*), LeBras and Compagnon (*17*), and van Amerongen and Houwink (*1*). Of the theories proposed, the one most prevalently held today assumes: (*a*) a cyclic structure for hard rubber vulcanization of the type  $-\overset{H}{\overset{|}{C}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}-$ (bridged by S); and (*b*) some form of sulfur or oxygen bridge linking the rubber molecules by primary valence bonds in soft rubber vulcanization—for example, R—S—R—S—R.

In order to explain the effects of inorganic and organic accelerators on the vulcanization reaction, elaborate theories have been proposed, most of which assume that these materials act as catalysts in a reaction mechanism that effects the linking of rubber molecules by sulfur bridges or other types of primary valence forces. As pointed out by Williams (*27*), the theories of vulcanization that have been proposed do not explain the facts adequately and are subject to many objections. In view of the inadequacy of existing theories, studies on the mechanism of the vulcanization reaction were undertaken in 1939 in The B. F. Goodrich Company laboratories.

In surveying the literature on vulcanization, the present authors noted that there were at least two, and generally three, requirements for vulcanization of any natural or synthetic rubber. Preliminary experiments confirmed this conclusion. These requirements which must be explained in any adequate theory of vulcanization are as follows:

1. Ethylenic double bonds (—C═C—) must be present in the polymer molecule. Completely saturated polymers, such as polyethylene, polyisobutylene, polystyrene, and hydrogenated natural or synthetic rubber, cannot be vulcanized with the usual vulcanizing agents, whereas natural rubber, polyisoprene, polybutadiene, and copolymers of isoprene or butadiene, which are unsaturated polymers to varying degrees, can be vulcanized.
2. An oxidizing agent is required which will add in some manner to the double bonds or alpha methylene carbon atoms in the polymer molecule to produce strong polar groups on the molecule. In addition to sulfur, some of the oxidizing agents that are suitable for vulcanization, are certain of the thiuram disulfides, accelerator-sulfur complexes, organic nitro compounds, and quinones. Judging from published data, peroxides apparently cause a polymerization type of reaction rather than vulcanization in the sense used in this paper.
3. A divalent metallic compound is required to develop the best properties of the vulcanizate. In some instances vulcanizates can be prepared with only an unsaturated polymer and an oxidizing agent; nevertheless, the properties of the vulcanizate are greatly enhanced when a soluble divalent metallic compound is present. With many oxidizing agents the use of such compounds is imperative.

It was evident from the published data that vulcanization is a typical chemical reaction and obeys all the laws for such reactions. It appeared from a study of the literature and the data reported

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TABLE I. EFFECT OF ZINC ION IN RUBBER-TUADS RECIPE

Recipe	Zinc/ Tuads Mole Ratio	Tensile, Lb./Sq. In.	Elongation, %	700% Modulus, Lb./Sq. In.
Control (basic recipe[a])	0	2200	1060	200
Zn stearate ≈ 0.25 Tuads	0.05	2500	980	350
Zn stearate ≈ 0.50 Tuads	0.1	2300	960	300
Zn stearate ≈ 1.00 Tuads	0.2	2200	910	500
Zn stearate + ZnO ≈ 2.00 Tuads	0.4	2400	850	800
Zn stearate + ZnO ≈ 5.00 Tuads	1.0	2800	710	2600
Zn stearate + ZnO ≈ 8.00 Tuads	1.6	2900	710	2700

[a] Pale crepe 100 parts, Tuads 5 parts. Other recipes had the ingredients indicated added to the basic recipe. Equivalents indicated were on a molecular basis. All compounds were cured 30 minutes at 280° F., which was near or at the optimum cure in all instances.

TABLE II. EFFECT OF SULFUR IN RUBBER-ZIMATE COMPOUNDS

Sulfur[a]	Tensile, Lb./Sq. In.		Elongation, %	
	Original	Aged 4 mo.	Original	Aged 4 mo.
0.5	400	1200	1250	1120
1.0	600	1300	1240	1230
1.5	600	1300	1220	1060
2.0	400	1600	1210	1130

[a] Recipe, pale crepe 100 parts, Zimate 1 part, plus sulfur indicated. Data given for vulcanizates cured 30 minutes at 280° F.

later in this paper, that the principal factors which affect the vulcanization reaction are: (*a*) the temperature of the reaction; (*b*) the pH of the system; (*c*) the solubility of the oxidizing agent and the divalent metallic compounds; (*d*) the effective concentration of these substances if they are below the saturation level; and (*e*) the chemical nature of the vulcanizing agent.

Further, it became apparent that cross linking of rubber molecules by primary valence bonds is not the explanation of ordinary vulcanization. Consequently, the conclusions of Goodyear (*10*), Midgley, Henne, and Shepard (*19*), Williams (*29*), and of the study reported here were developed into a theory of vulcanization whereby the sulfur, accelerator, and divalent metallic ion (or the vulcanizing ingredients in other types of vulcanization) react with and become a part of the rubber molecule. Through the increase in the intermolecular forces resulting from dipole interaction and ionic valences of the polar groups so introduced into the rubber molecules, the effects of vulcanization on the physical properties are explained.

PROCEDURE

Most of the studies were made on first-grade pale crepe, since this material was more uniform and had less objectionable impurities than any other material available at the time this work was done. Particular care had to be taken to avoid contamination of the compounds with dust from the mill room. Traces of zinc compounds were found to have a pronounced effect on the properties of the vulcanizate. The rubber vulcanizates were prepared by mixing on a 6 × 12 inch laboratory rubber mill and cured into 6 × 8 × 0.030 to 0.100 inch tensile sheets in the usual manner.

The vulcanization reaction was followed by means of the stress strain properties of the vulcanizate and the x-ray diffraction patterns of the curing ingredients in the rubber compound at various stages of vulcanization. The x-ray diffraction patterns were obtained by a technique similar to that used by Clark, Le Tourneau, and Ball (*4*).

The acid-base characteristics were determined in a few of the compounds by passing the vulcanizate twice through tight rolls of a cold laboratory mill, extracting the crumb so obtained with freshly distilled cyclohexanone for 16 hours at room temperature, and measuring the pH of the extract with a glass electrode and a Leeds & Northrup pH electrometer. These pH measurements were in agreement with those obtained by dissolving the uncured compound in freshly distilled cyclohexanone and heating the solution 60 minutes at 150° C. to effect cure. Most of the measurements were made by the latter technique, since the pH could be measured after various times of heating.

RESULTS

VULCANIZING AGENT CONSTANT WITH VARIABLE ZINC. As seen in Table I, the stress at 700% elongation increased thirteenfold, and the ultimate elongation decreased by one third as the concentration of zinc ions (the term "ions" used throughout this paper refers to both those that are free and those combined in the form of salts) increased from zero to an amount molecularly equivalent to the 5 parts of Tuads (tetramethylthiuram disulfide) in the compounds. When the vulcanizates indicated in Table I were examined by x-rays, diffraction patterns of crystalline Zimate (zinc dimethyldithiocarbamate) were obtained in all instances except with the control compound and with the one containing the smallest quantity of zinc stearate. In addition, patterns for zinc oxide were observed in the two vulcanizates containing the highest concentration of zinc ions.

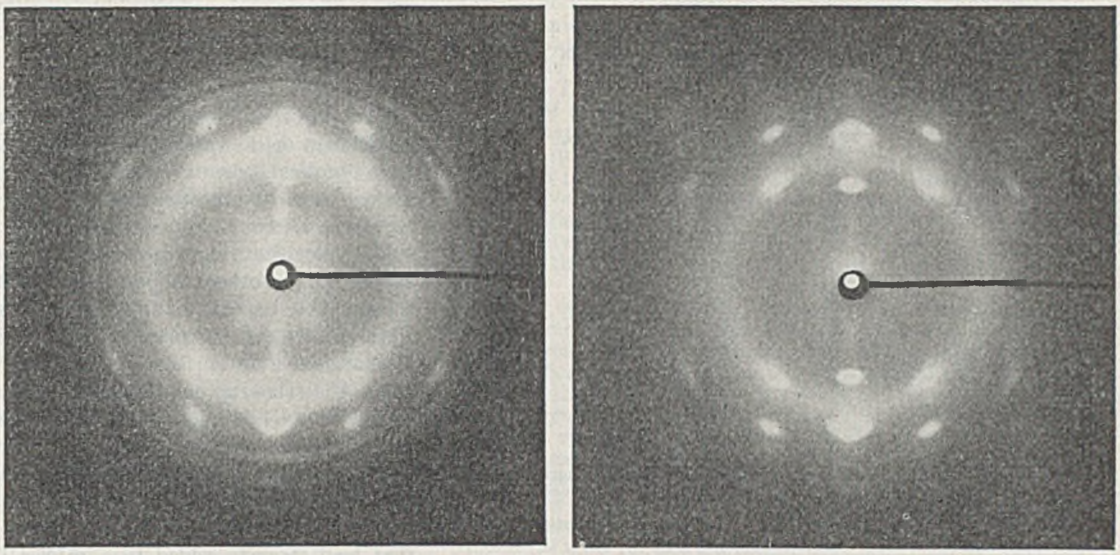
In similar studies on compounds containing pale crepe 100 parts, sulfur 10 parts, and varying quantities of zinc oxide, the stress at 700% elongation doubled and the ultimate elongation decreased by one tenth as the concentration of zinc oxide increased from 0 to 0.75%.

It was noted that, in the x-ray diffraction patterns of the stretched rubber-sulfur stock (without zinc), the A_1 and A_2 spots were approximately circular in shape (Figure 1*A*), whereas in those of the stretched rubber–Tuads compound (without zinc) these spots were elliptical (Figure 1*B*) with the minor axis perpendicular to the direction of the stretch. The presence of zinc ions increased the eccentricity of the spots for both types of vulcanizate (Figures 1*C* and *D*) in a manner similar to but smaller in magnitude than that due to carbon black.

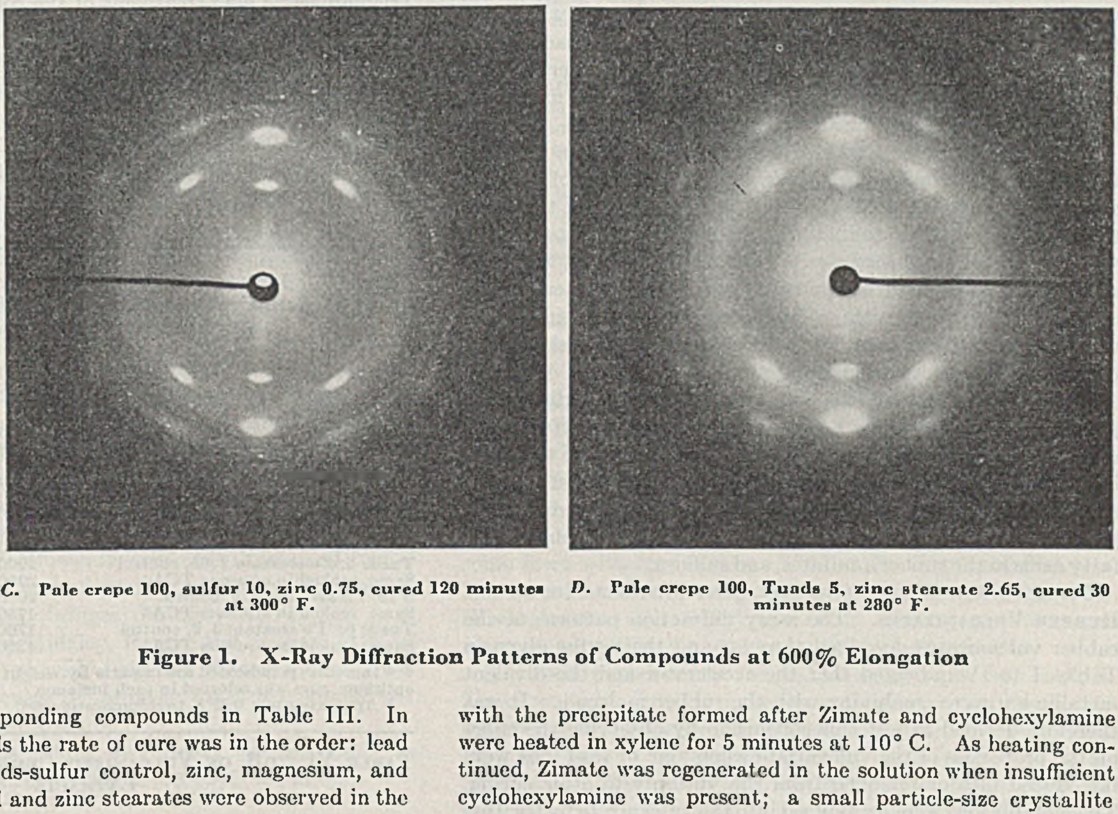
ZINC CONSTANT WITH VARIABLE SULFUR. As seen in Table II, increasing the concentration of sulfur from 0.5 to 2 parts per 100 parts of pale crepe had little or no effect on tensile properties when the zinc ion in the form of Zimate was kept constant. It was interesting to observe that the stress-strain properties immediately after curing were very poor when Zimate was the only source of zinc ion. However, after the vulcanizates had aged for four months at room temperature, tensiles of 1200 pounds per square inch or more were obtained. The tensile of vulcanizates cured 5 minutes at 280° F. increased from 400 or less to 1500 pounds per square inch for the compound containing 0.5 part sulfur and 2200 pounds or more for the others.

The x-ray diffraction patterns indicated that Zimate had disappeared completely in all compounds cured 30 minutes at 280° F., and by amounts proportional to the sulfur present in those cured 5 minutes at 280° F. Figure 2 shows the disappearance of Zimate during cure. The circular arcs in Figure 2*A* are the diffraction patterns of Zimate in an uncured stretched rubber specimen containing 2.5% of Zimate and 1% of sulfur. These arcs have disappeared in Figure 2*B*, which is the diffraction pattern of the same compound cured 30 minutes at 280° F. and then stretched. At the end of four months Zimate could not be detected in any vulcanizate except the one containing 0.5 part sulfur cured 5 minutes at 280° F. In another compound containing 1.3% Zimate and 0.2% sulfur the pattern for Zimate completely disappeared when the compound was heated 30 minutes at 280° F. This was the smallest amount of sulfur that made the patterns for Zimate disappear; this indicated a probable combining ratio of 2 atoms of sulfur to 1 molecule of Zimate.

COMPARISON OF DIVALENT METALLIC OXIDES. A comparison of the relative effects of zinc, lead, calcium, and magnesium oxides was made in both rubber-Tuads and rubber-Tuads-sulfur com-



A. Pale crepe 100, sulfur 10, cured 120 minutes at 300° F. *B.* Pale crepe 100, Tuads 5, cured 30 minutes at 280° F.



C. Pale crepe 100, sulfur 10, zinc 0.75, cured 120 minutes at 300° F. *D.* Pale crepe 100, Tuads 5, zinc stearate 2.65, cured 30 minutes at 280° F.

Figure 1. X-Ray Diffraction Patterns of Compounds at 600% Elongation

pounds. Table III presents the data for the rubber-Tuads compounds. Except for lead oxide, all of these oxides increased the modulus and tensile strength. The calcium and magnesium oxides increased the rate of cure markedly, and the overcures reverted badly. The lead oxide was completely converted to Ledate (lead dimethyldithiocarbamate) and lead stearate. Figure 3 is an x-ray diffraction pattern of a stretched rubber-Tuads-lead oxide compound heated 45 minutes at 300° F., showing the formation of oriented Ledate.

Similar results were obtained for the rubber-Tuads-sulfur stocks, except that the compound containing lead oxide cured and had higher modulus and lower elongation than the control. The recipes for these compounds were: pale crepe 100 parts, Tuads 3 parts, sulfur 0.75 part, plus the oxide under test and stearic acid in the same quantities as given for the corresponding compounds in Table III. In both series of compounds the rate of cure was in the order: lead (slowest), Tuads or Tuads-sulfur control, zinc, magnesium, and calcium (fastest). Lead and zinc stearates were observed in the patterns, whereas calcium and magnesium stearates were not. When caproic acid was substituted for the stearic acid, no pattern of lead or zinc caproate was observed, and the rate of cure was markedly increased.

Effects of Various Anions. The results obtained in studying the effect on the physical properties of rubber-Tuads compounds, when the metal is added in the form of different salts, are given in Table IV. Zinc added in the form of any salt increased both modulus and tensile. In all instances Zimate was formed, and the added zinc compound disappeared completely except for traces of zinc sulfide. Both the sulfide and sulfate retarded cure but enhanced the physical properties. In the vulcanizates which were cured 5 minutes at 280° F. and contained either zinc oxide or zinc stearate, the x-ray diffraction patterns gave evidence that a new compound was formed, which has not yet been identified. A similar pattern was also obtained with the precipitate formed after Zimate and cyclohexylamine were heated in xylene for 5 minutes at 110° C. As heating continued, Zimate was regenerated in the solution when insufficient cyclohexylamine was present; a small particle-size crystallite was formed with larger amounts of cyclohexylamine.

Table III. Influence of Oxides of Calcium, Magnesium, Zinc, and Lead in Rubber-Tuads Compounds

Recipe	Tensile, Lb./Sq. In.	Elongation, %	700% Modulus, Lb./Sq. In.
Control (basic recipe[a])	1200	800	600
Stearic acid 5	800	860	400
Stearic acid 2, Ca(OH)$_2$ 3.5	2400	830	1200
Stearic acid 2, MgO 2	2300	900	700
Stearic acid 2, ZnO 3.5	2700	730	2100
Stearic acid 2, PbO 10	...	...	...

[a] Pale crepe 100 parts, Tuads 5 parts. Other recipes had the ingredients indicated added to the basic recipe in parts by weight. The quantities of metallic oxides were equivalent on a molecular basis. All compounds were cured 25 minutes at 280° F.

Table IV. Effect of Zinc and Lead Added in Form of Different Salts and in Conjunction with Acid on Properties of Rubber-Tuads Compounds

Recipe	Cured at 280° F., Min.	Tensile, Lb./Sq. In.	Elongation, %	700% Modulus, Lb./Sq. In.
Control *A* (basic recipe[a])	30	1200	940	300
ZnO	30	2600	870	800
ZnS (alpha)	30[c]	2200	930	400
$ZnSO_4.7H_2O$	30[c]	1700	870	500
Zn stearate	30	2500	820	1000
PbO	45	900	820	500
PbS	45	700	1100	200
$PbSO_4$	45	800	1050	200
Pb stearate	30	1300	1050	300
Trichloroacetic acid	30	1200	960	300
Trichloroacetic acid + ZnO	30	2500	860	900
Trichloroacetic acid + PbO	45	700	1000	200
Benzoic acid	30	1400	1100	300
Benzoic acid + ZnO	30	2300	820	1000
Benzoic acid + PbO	45	600	820	250
Control B[b]	30	600	1050	150

[a] Pale crepe 100 parts, Tuads 5 parts. Other recipes had ingredients as indicated in an amount equivalent to 2.5 parts Tuads on a molecular basis, added to the basic recipe.

[b] Control *B* had 2.5 parts instead of 5 parts of Tuads in the recipe.

[c] Below optimum cure.

A pattern for stearic acid was obtained in the compound to which zinc stearate had been added. In another experiment in which the zinc was added in the form of Zimate instead of zinc stearate, a similar increase of the stress-strain properties was noted, except that double the quantity of zinc ion on a molecular basis was required to obtain an equivalent effect.

All the compounds with lead had higher tensiles and moduli than control *B* containing 2.5 parts of Tuads, but not so high as those of control *A* with 5 parts of Tuads, except for the modulus of the compound containing lead oxide. The rate of cure was less in all instances also. The patterns for all the lead compounds added had disappeared, and Ledate patterns were observed in every instance. Trichloroacetic or benzoic acid in combination with zinc or lead oxide caused effects similar to those with the corresponding stearates.

The particle size and the intensity of the x-ray diffraction patterns of the Zimate or Ledate formed gave a qualitative indication of the solubility rate and hence indirectly of the solubility of the zinc or lead compound added. The finest particle size, related to the greatest solubility, was observed for the stearates, followed by the oxides (presumably made soluble by the fatty acids in the rubber), sulfates, and sulfides.

Addition and Removal of Divalent Metallic Ions from Rubber Vulcanizates. The x-ray diffraction patterns of the rubber vulcanizates described thus far and the results given in Tables I to IV indicated that the accelerator and the divalent metallic ion were combining with the rubber molecule. It was therefore decided to test this conclusion by observing the effect on the properties of the vulcanizate when zinc or lead ions were introduced into or removed from the vulcanizate after curing. The metallic ions were introduced into the vulcanizate by treating the surface with a metallic stearate, as follows: A rubber-sulfur or rubber-Tuads vulcanizate at optimum cure was coated on the surface with the stearate and then heated for 30 minutes at a temperature 50° F. below the curing temperature. The control was similarly heated but not treated with the stearate. The stearates were molten at these temperatures and partially dissolved in the thin sheets (0.030 inch approximately). The metallic ions were removed from the molecular structure by soaking the vulcanizate in a dilute aqueous solution of hydrochloric acid or trichloroacetic acid for several days at room temperature, while the control was similarly treated with distilled water. After soaking, the specimens were allowed to dry thoroughly before testing. Hydrochloric acid was not very effective for this purpose, evidently because of its complete ionization in water, which prevented penetration of the acid into the rubber vulcanizate. This experiment should be repeated with the hydrochloric acid dissolved in anhydrous alcohol.

Table V presents the results obtained by surface treatment of vulcanizates with zinc and lead stearates, and by soaking vulcanizates in trichloroacetic acid. When a vulcanizate containing no divalent metal was surface-treated with zinc, increased moduli were obtained, whereas when a vulcanizate containing zinc was soaked in trichloroacetic acid, decreased moduli resulted. Similar effects were noted in the case of lead. However, the rubber-sulfur vulcanizate surface-treated with lead stearate did not respond like the others, apparently because of the formation, with the unreacted sulfur, of insoluble lead sulfide near the surface, since no attempt was made to extract the free sulfur remaining after cure before surface treating with lead stearate. Larger effects than those given in Table V for rubber-Tuads vulcanizates surface-treated with lead stearate, were obtained in other experiments.

Traces of Zimate and Ledate were noted in the x-ray diffraction patterns of the rubber-Tuads vulcanizate that was surface-treated with the corresponding stearates. It was interesting to observe that lead stearate added to a rubber-Tuads compound before vulcanization retarded cure and decreased the modulus, whereas lead stearate added after vulcanization increased the modulus. Trichloroacetic acid treatment of the control, containing Tuads and zinc stearate, reduced the intensity of the sharp crystalline x-ray diffraction pattern of the rubber so that it was similar to one for a rubber-sulfur vulcanizate. The Zimate pattern was barely visible.

Influence of pH. A qualitative correlation was noted between the rate of vulcanization and the pH of the heated cyclohexanone cement or the extract of the vulcanizate given in

Table V. Introduction by Surface Treatment and Removal by Acid Treatment of Zinc and Lead in Rubber-Tuads and Rubber-Sulfur Compounds

Recipe[a] and Treatment	Tensile, Lb./Sq. In.	Elongation, %	700% Modulus, Lb./Sq. In.
S 10, control	2400	860	900
Same, Zn stearate on surface	2400	830	1000
Same, Pb stearate on surface	1700	800	900
Tuads 5, control	1500	1130	200
Same, Zn stearate on surface	1800	820	600
Same, Pb stearate on surface	1500	950	350
S 10; Zn stearate 4.5, control	2000	750	1400
Same, soaked in aqueous TCA[b]	3000	310	...
Tuads 5, Zn stearate 2.65, control	2900	900	600
Same soaked in aqueous TCA[b]	2200	900	350
S 10, Pb stearate 5.5, control	2000	980	400
Same soaked in aqueous TCA[b]	1750	960	350
Tuads 6; Pb stearate 3.2, control	1700	1090	200
Same, soaked in aqueous TCA[b]	1300	1100	150

[a] Ingredients indicated are in parts by weight per 100 parts of pale crepe; optimum cure was selected in each instance.

[b] Approximately 0.2 *N* trichloroacetic acid.

Table VI. pH of Vulcanized Cements and Vulcanizate Extracts

Recipe[a]	pH of 5% Cement in Cyclohexanone: Control unheated	pH of 5% Cement in Cyclohexanone: Heated at 305° F. 60 min.
S 10	4.9	3.6[b]
S 6, PbO 10, stearic acid 1	7.2	3.6
S 6, DPG 1	5.6	3.9
S 6, DPG 1, ZnO 2	6.2	4.6
S 1, ZnO 2, S.A. 1, Captax 1	6.3	5.3
Same plus cyclohexylamine 1	6.9	7.3
S 1, ZnO 2, S.A. 1, Captax 1, Tuads 0.2	6.0	6.1[c]
S 1, PbO 6, S.A. 1, Captax 1, Tuads 0.2	6.7	5.9[d]
Tuads 5	7.0	7.1
Tuads 5, ZnO 2	7.0	7.1

[a] Basic recipe, pale crepe 100 parts plus ingredients indicated.

[b] pH of cyclohexanone extract of vulcanizate cured 60 minutes at 320° F., 3.8; pH of cyclohexanone extract of similar vulcanizate but containing 4.5 parts of zinc stearate in addition, 4.4.

[c] pH cyclohexanone extract of vulcanizate cured 30 minutes at 280° F., 6.2. pH cyclohexanone extract of vulcanizate cured 60 minutes at 300° F., 6.4.

[d] pH cyclohexanone extract of vulcanizate cured 30 minutes at 280° F., 5.8. pH cyclohexanone extract of vulcanizate cured 60 minutes at 300° F., 5.8.

Table VI. The compound containing cyclohexylamine cured in the least time but reverted quickly. With other compounds not reported here, there were indications that, above a pH of 8, reversion would occur so soon that a satisfactory vulcanizate could not be obtained. On the contrary, the compound containing only sulfur cured the slowest, and there were indications that acids which reduced the pH below 3 retarded vulcanization so markedly that cure could not be attained. It is to be emphasized that a given pH in cyclohexanone solution is not necessarily equivalent to the same pH in an aqueous solution.

Hydrogen sulfide was liberated from the cement, when heated, in every instance in which free sulfur was present, and no hydrogen sulfide could be detected in the two cases given in Table VI where Tuads but no sulfur was present. The total amount of hydrogen sulfide liberated correlated qualitatively with the amount of free sulfur added; however, the rate at which it was liberated increased with pH. In rubber cements containing litharge and sulfur it was noted that lead sulfide was formed, but in those containing zinc oxide no zinc sulfide was detected.

DISCUSSION

EVIDENCE AGAINST CROSS LINKING THROUGH PRIMARY VALENCES. The experimental results indicate that divalent metallic compounds have a definite influence on the crystalline structure and physical properties of rubber in a manner independent of any effect they may have on the rate of cure. The effect of these substances in Tuads vulcanizates indicates further that vulcanization is not solely a cross linking of rubber molecules with sulfur or other primary valence bonds, but rather that both the Tuads and metallic ion become a part of the structure of the rubber molecules. In fact, the experiments of Williams (*28, 29*) indicate that, even in a rubber-sulfur vulcanizate, cross linking of rubber molecules by primary valence bonds does not occur. He found that smoked sheet containing 6% of sulfur, vulcanized for 75 minutes at 150° C., swells in benzene but does not lose its shape or dissolve in 15 days. Adding to the benzene such compounds as piperidine, mercaptobenzothiazole, the piperidine salt of mercaptobenzothiazole, butyraldehyde-butylamine reaction products, or other accelerators causes either a marked visible effect or a homogeneous solution in the same period of time. Soluble zinc salts added to the benzene retard the action of these materials. If a three-dimensional network through primary valence bonds formed during vulcanization, it is difficult to explain these results. However, even if it is assumed that a few rubber molecules are cross-linked by primary valence bonds through sulfur or oxygen bridges during vulcanization, it is evident from the work of Midgley, Henne, and Shepard (*19*), in which rubber was treated with Grignard reagents, that cross linking of rubber molecules by primary valence bonds is not essential to obtain vulcanization.

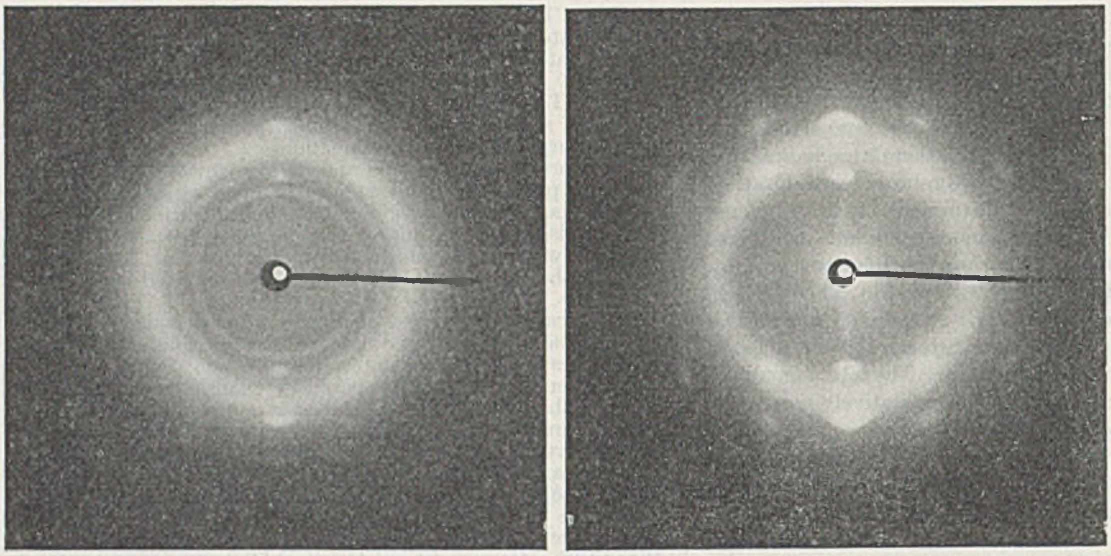
Evidence against cross linking by primary valence bonds, in addition to that presented by Williams (*27, 29*) is as follows:

1. In polymers with very few double bonds—for example, GR-I—it is improbable that a sufficient number of double bonds or alpha methylene carbon atoms in different molecules will be adjacent and properly oriented so that they can be bridged by sulfur to form a satisfactory vulcanizate.
2. The sulfur bridge would have to be formed in two or more steps since trimolecular reactions have not been demonstrated. It should be possible to prevent the cross linking, therefore, by the addition of reactive compounds, particularly if a free-radical chain mechanism were involved. Although many compounds have been found which accelerate vulcanization, no compound, except those lowering the pH, has been found which retards the sulfur type of vulcanization reaction. In Tuads vulcanization even acids do not decrease the rate.
3. The fibrous structure which develops on stretching would be expected to decrease as the number of primary cross linkages increased during vulcanization. Well cured compounds, particularly those containing channel black, still develop fibrous structures as pronounced as those in crude rubber. The forces between the fibers or molecules are very small compared to those between atoms in the molecules themselves. This can be easily demonstrated by inserting a pin in a piece of stretched rubber and moving it both parallel and perpendicular to the direction of stretch. The force required to move the pin parallel to the direction of stretch is negligible compared with that required to move it perpendicular to this direction.
4. If organic accelerators and divalent metallic ions do not become a part of the rubber molecule along with the sulfur but only activate the sulfur to cross link the rubber molecules, these compounds should not improve the properties of a three-dimensional network already formed by vulcanization. This is contrary to the results in Table V and those reported by Williams (*28*).
5. In cases where cross linking by primary valence bonds is fairly certain, the polymers lose their rubberlike elasticity and become resinous. For example, resinification of polybutadiene or butadiene copolymers, prepared by emulsion polymerization, occurs if the polymerization catalyst is not completely destroyed after polymerization. Certain types of photovulcanization and peroxide vulcanization are probably also polymerization rather than vulcanization reactions. Divalent metallic oxides do not assist these reactions and frequently retard them.
6. The stress-strain temperature effects, particularly the large hysteresis of the first cycle of flexing, noted by Roth and Wood (*22*), Meyer and Ferri (*18*), and Holt (*13*), indicate that it is relatively easy to rearrange the intermolecular forces, and that the forces involved must be relatively small and of several strengths. The changes observed were reversible to a first approximation. It is difficult to understand how primary valence bonds could be so easily broken and rearranged without showing evidence of more drastic and permanent changes in the stress-strain properties, such as those produced by oxygen on aging. Particularly, it does not seem reasonable to expect an increase in stress with time following a reduction of elongation if primary valence bonds are responsible.
7. It is not reasonable to assume that primary bonds between rubber molecules are formed in the early stages of vulcanization and then broken during overcure and reversion.
8. As pointed out by van Dalfsen (*6*), the properties of films from vulcanized latex must result from secondary valence forces and not from those of primary valence bonds.

REACTION OF RUBBER WITH COMPOUNDS OTHER THAN SULFUR. In the presence of a number of reactive compounds, either naturally occurring in or added to the rubber, it is not valid to assume that the rubber molecule reacts exclusively with the sulfur. As mentioned previously, the data indicate the converse—namely, that the rubber does react with compounds other than sulfur. These conclusions are further substantiated in vulcanization with aromatic nitro and azo compounds, during which Blake (*3*) and Fisher (*9*) have shown that nitrogen is combined in some form with the rubber. With sulfur compounds, such as Tuads, evidence of this type has not been reported. However, Wistinghausen (*30*) found that both diphenylguanidine and mercaptobenzothiazole disappeared during vulcanization.

The results reported herein, and those obtained by Clark, Le Tourneau, and Ball (*4*) indicate conclusively that the carbon disulfide accelerators react during the early stages of vulcanization with the metallic compounds to form the metallic salt of the accelerator. The question still remains how these salts of accelerators react with the sulfur and form a compound with the rubber molecule. There appears to be little doubt that they do, however, since it was noted that (*a*) when the various salts, Zimate, Zenite, Ledate, etc., were added to rubber as such or were formed in the rubber by interaction between the acid form of the accelerator and a metallic compound, their x-ray diffraction patterns decrease in intensity after the early stages of cure and disappear completely in the latter stages if excess quantities are not added; (*b*) neither the metallic ion or accelerator anion could be detected in other crystalline compounds; and (*c*) the diffraction pattern of the rubber crystallites became altered in shape. Even lead oxide, when heated with acetone-extracted pale crepe, reacts with the rubber or unextractable materials in it to form a new compound.

An interesting observation in connection with the reaction of compounds other than sulfur has been made during the vul-



A. Uncured

B. Cured 30 minutes at 280° F.

Figure 2. X-Ray Diffraction Patterns of Compounds Containing Pale Crepe 100, Zimate 2.5, Sulfur 1 and Stretched to 600% Elongation

canization of balata using the same recipes and conditions found to be optimum with Hevea. It was noted that vulcanization of balata with sulfur and diphenylguanidine (DPG) or di-*o*-tolylguanidine (DOTG) had a more striking effect on the retention of rubberlike elasticity at room temperature than vulcanization with sulfur, either in the presence or absence of carbon disulfide accelerators and/or zinc oxide. Heating balata with DPG or DOTG in the absence of sulfur under equivalent conditions of time and temperature failed to produce a soft structure after cooling to room temperature. To achieve an equivalent effect with other vulcanizing agents, a higher degree of cure was required. These observations indicated that more than a combination of balata and sulfur was involved, and that the DPG, sulfur, and balata had combined in some manner to form an integrated structure.

Solubility and Rate of Cure. There is a direct correlation in rubber-Tuads compounds between rate of cure and solubility of the metallic salts as judged by the particle size of the Ledate or Zimate formed; for example, zinc stearate produced the finest particle-size Zimate, best physical properties, and fastest rate of cure, whereas zinc sulfide produced the largest Zimate particles, poorest properties, and slowest rate of cure. None of the zinc or lead compounds studied is completely insoluble and inert in rubber. Consequently by altering conditions it is possible to shift the equilibrium; for example, Ledate in the presence of excess sulfur forms lead sulfide with no Ledate remaining, whereas lead sulfide in the presence of excess Tuads forms Ledate with no lead sulfide remaining. Jones and Depew (*14*) were led to similar conclusions regarding the effect of solubility of lead and zinc compounds on rate of cure. These workers found that even the order of adding ingredients will affect the rate of cure when an ingredient is formed in the rubber compound which is only slightly soluble, and that the equilibrium can be shifted by increasing the concentration of the more soluble components. In compounds accelerated with mercaptobenzothiazole these workers effectively showed that the properties of the vulcanizate depend upon the amount of soluble zinc available for reaction, which is a function of the amount both of fatty acid or zinc soap and of amines such as diphenylguanidine or butyraldehyde-aniline in the rubber compound. Cotton and Westhead (*5*) showed in an extensive study of the influence of various metallic oxides on vulcanization that zinc and lead oxides are not unique in their effect on vulcanization and that some oxides are more effective than others. It is probable that the differences in the effects of the various oxides result from differences in the solubilities of the various metallic salts formed during the vulcanization reaction.

The most pronounced difference between zinc and lead compounds in rubber containing sulfur is in the formation of the sulfide. Lead compounds form lead sulfide with ease, which is readily precipitated because of its low solubility. Zinc compounds, on the other hand, apparently do not form zinc sulfide, since no patterns of alpha or beta zinc sulfide have been observed despite the relatively low solubility of these materials when added to rubber. The results obtained with rubber in xylene indicate that this is due to the strength of hydrogen sulfide as an acid, and lead and zinc stearates as bases. These observations are not in accord with the conclusions of Armstrong, Little, and Doak (*2*), who assumed that the hydrogen sulfide liberated during the digestion of a vulcanizate with glacial acetic and concentrated hydrochloric acids is derived from zinc sulfide. They suggested that the zinc sulfide is derived from a zinc mercaptide of the rubber, momentarily formed as an intermediate during the vulcanization process. Therefore, they assume that the amount of zinc sulfide formed is a measure of the number of thioether or disulfide linkages between the rubber molecules. From our observations we cannot concur in the opinion that significant quantities of zinc sulfide are formed or that rubber molecules are linked by primary valence bonds. As will be seen, we propose a zinc mercaptide of the rubber in our theory of vulcanization but not under the conditions stated by Armstrong, Little, and Doak (*2*).

A correlation between solubility and rate of cure is noted, also, with butadiene copolymers. Zimate is most soluble in the acrylonitrile copolymers, next in vinylidene chloride copolymers, and least soluble in methyl methacrylate copolymers. The rate of cure corresponds to these solubilities. In each polymer cyclohexylamine increased the solubility of Zimate and the rate of cure. The lack of amino compounds in synthetic rubbers for solubilizing zinc salts is probably responsible for the commercial use of multiple accelerators, generally a carbon disulfide accelerator, a basic amine, and zinc oxide.

The solubilities observed in these studies are those at room temperature. In order to make a quantitative analysis of the physical-chemical system during vulcanization it is necessary to measure these solubilities at vulcanizing temperatures.

Other Physical-Chemical Factors. When solubility is not the principal limiting factor, the relative strengths and concentrations of the various acids and bases in the system have a direct bearing on the rate of cure and the physical properties of the final vulcanizate. In order to ensure a satisfactory cure and good physical properties, it is necessary that a sufficient quantity of divalent metallic ions be available for the rubber. The quantity of available ions is governed not only by the total number present but also by the concentration and relative strengths (pK values) of the other competing acids in the system. In low zinc stocks—for example, where the zinc has been introduced only as a salt of an organic accelerator—it has been found that poor physical properties result when stearic or other acids, competing with the rubber, combine with the zinc ions to form zinc salts. X-ray diffraction patterns of such vulcanizates have confirmed the formation of zinc stearate. By adding sufficient zinc to satisfy all the acids present, the best properties are obtained.

Besides the strength of the acid, the pH of the system is the other factor governing the proportion of the acid which will combine with zinc if all components are soluble. It has long been known that acids retard and bases accelerate sulfur vulcanization. However, the first quantitative correlation between pH and rate of cure was reported by Newton (*20*) and Newton and Willson (*21*) who showed that the rate of cure of crude rubbers increased with the pH of their aqueous extracts, with their buffer capacity, and with the pH of phosphate buffers added to the rubber. Their results and those reported here indicate that in a rubber-sulfur system pH and buffer capacity are next in importance to temperature in governing rate of cure.

When the work was interrupted, the studies on the effect of monovalent metallic compounds had not been started. Work reported in the literature showed that some of these compounds have a profound effect on rate of cure and the physical properties of the vulcanizate. Although definite conclusions cannot be drawn at this time, it is believed that the monovalent metallic compounds affect vulcanization primarily through their influence on the pH of the system. No trivalent metallic compounds were studied, but such compounds, if soluble, should behave like divalent compounds.

THEORY OF VULCANIZATION

The observations made and conclusions reached in the course of these studies led to the formulation of a theory of vulcanization. It is believed that crude rubber is a highly unsaturated fatty acid of high molecular weight. Other studies on the pH titration and viscosity of cements prepared from pale crepe milled for various times indicate that there is a —COOH group on at least one end of the rubber molecule, which makes the adjacent terminal double bond or alpha methylene carbon atom more reactive, so that it probably reacts first in vulcanization. The thixotropic effect observed with crude rubber is probably due in large part to the association (hydrogen bonding) and disassociation of these terminal acid groups. The effect of polar substances, particularly basic ones, on the viscosity of uncured rubber solutions in hydrocarbon solvents results from their effect on the disassociation of these groups, which causes the rubber particles to become monomolecular.

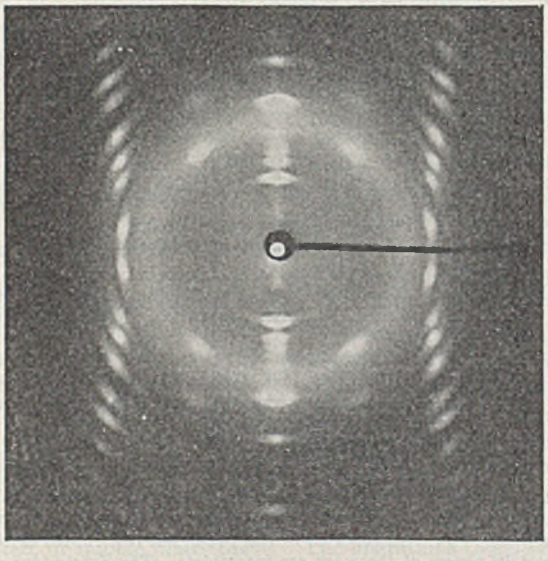
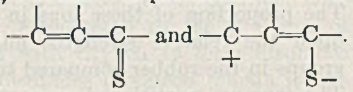


Figure 3. X-Ray Diffraction Pattern of Compound Containing Pale Crepe 100, Tuads 5, Lead Oxide 2.3, Cured 45 Minutes at 300° F. and Stretched to 600% Elongation

The elasticity of rubber is related to the thermal motion of the molecules. However, the weak van der Waals forces between the molecules of crude rubber result in a very low modulus and permit plastic flow and rotation around single bonds, so that the molecules become aligned easily and crystallize.

VULCANIZATION IN ABSENCE OF DIVALENT METALLIC IONS. When sulfur is mixed with rubber and the mixture heated, the sulfur reacts with the rubber molecule, probably at the alpha methylene carbon atom, to form a thioketone. This assumption has support from infrared studies by Sears (*23*) and Sheppard and Sutherland (*24*) who reported a band at 10.4μ, which could be assigned to a C═S bond. It is noted that these workers also reported no apparent decrease in the intensity of the band assigned to the C═C bond. Further, it is observed that no one has been able to detect thiol (—SH) groups in vulcanized rubber. To explain these observations, resonance is postulated between two or more structures, such as



$-\overset{|}{C}=\overset{|}{C}-\underset{\overset{\|}{S}}{C}-$ and $-\underset{+}{\overset{|}{C}}-\overset{|}{C}=\underset{\overset{|}{S-}}{C}-$.

In any case, the polar groups introduced into the rubber molecules during vulcanization markedly increase the intermolecular forces by dipole interaction. When a sufficient number of polar groups are present, plastic flow becomes extremely small, the modulus is markedly increased, and free rotation of the molecules is retarded so that they will not align and crystallize unless an external stress is applied.

When vulcanization is effected with Tuads, an accelerator-sulfur mixture, organic nitro or azo compounds, etc., most, if not all, of the oxidizing agent adds to the rubber molecule forming strong acidic groups on it. Benzoyl and other organic peroxides probably act differently in that they effect true cross linking of molecules by polymerization (rather than vulcanization) as indicated by Farmer and Michael (*8*). On the other hand, the organic basic amino compounds that act as accelerators probably play a dual role, namely, (*a*) to increase the pH of the system, and (*b*) to combine with the rubber molecule and sulfur to form a strong polar group capable of hydrogen bonding. The combination of polar organic compounds with rubber causes the intermolecular forces to be increased probably by both dipole interaction and hydrogen bonding, so that very few groups need to combine with the rubber.

VULCANIZATION IN PRESENCE OF DIVALENT METALLIC IONS. If a soluble divalent metallic compound is present in rubber-sulfur vulcanization, the mercaptide structure is enhanced which further increases the intermolecular forces through the ionic mercaptide valences—for example, (rubber)—S^- Pb^{++}—(soap anion). It is possible that some of the molecules become bridged through the ionic valences of a metallic mercaptide salt, thus: (rubber)—S Pb^{++}—S—(rubber). Accordingly, fewer sulfur atoms need add to the rubber molecules to obtain the same modulus and other properties. Farmer (*7*) suggests a similar mercaptide bridge in rubber-sulfur–zinc oxide vulcanizates. However, like Armstrong, Little, and Doak (*2*), he assumes the mercaptide to be an intermediate in a cross-linking reaction.

When vulcanization is effected with polar organic compounds, the resulting acidic groups in the rubber molecule are stronger than the mercaptide groups in rubber-sulfur vulcanizates and form salts with the divalent metallic ion more readily. Accordingly, divalent metallic ions are much more effective with this type of vulcanization than with rubber-sulfur vulcanization, so that minimal quantities of vulcanizing agents are required, probably only the quantity needed to react with the terminal reactive groups of the rubber molecule. As with rubber-sulfur vulcanizates, two or more molecules may be bridged through the ionic valences of a divalent metallic salt, thus: (rubber)—(accelerator–S complex)$^-$Zn^{++}—(accelerator–S complex)—(rubber).

FACTORS INFLUENCING VULCANIZATION. The main factors influencing vulcanization either in the presence or absence of divalent metallic compounds are (*a*) temperature, (*b*) relative solubilities of the various components in the system, (*c*) nature and effective concentration of the vulcanizing ingredients, (*d*) relative strengths and concentrations of the acid groups in the system, and (*e*) pH of the system. The rate of cure is governed primarily by temperature, pH, and concentration of the vulcanizing ingredients, the rate increasing with an increase in the value of each of these variables. In the case of delayed-action accelerators, the active vulcanizing ingredient is released after vulcanizing temperatures are reached, so that the effective concentration is very low during the initial vulcanization period. The properties of the vulcanizate are governed primarily by the nature of the vulcanizing agent, the degree of cure, and the concentration of divalent metallic ions in the rubber structure. The proportion of these ions in the rubber structure depends upon the relative strengths and concentrations of the acid groups in the rubber compared to those of other acids present. The ions are partitioned among the acidic groups of the rubber and other acids present according to the laws of physical chemistry.

Thus, vulcanization is essentially a process whereby the intermolecular forces are increased by the introduction of polar groups into the rubber molecules at the double bonds or alpha methylene carbon atoms. The individual molecules retain their identity with respect to length and approximate weight, although they may be joined to other molecules through the salt of a divalent metallic ion. The forces between the individual molecules give a rigidity to the molecular structure that retards plastic flow and crystallization, but are sufficiently weak to rearrange under the influence of mechanical or thermal effects. These forces are of several strengths, the weakest being van der Waals, then those due to dipole interaction, hydrogen bonding, and ionic salt type valences. Only under a high stress are the latter forces rearranged.

With this concept of vulcanization, the known facts of both natural and synthetic rubber behavior can be explained. Some of these are:

1. Effect of acids and bases on the vulcanization reaction
2. Action of accelerators
3. Effect of metallic oxides and salts in vulcanization
4. Quantity of combined sulfur required for optimum properties of various types of vulcanizates.
5. Reversion and reclaiming of rubber vulcanizates
6. Bonding of rubber to metal
7. Solubility changes on vulcanization
8. Vulcanization of polychloroprene (neoprene)
9. Vulcanization and properties of butadiene and isoprene polymers and copolymers
10. So-called history or memory effects of rubber vulcanizates
11. Reversible and irreversible stress-strain temperature effects, including the large hysteresis loop of the first cycle of extension and retraction
12. Reinforcement of rubber with carbon black and other fillers, which is believed to be due in part to dipole interaction between polar groups on the surface of the black and those of the vulcanized rubber. Thus, particle size, particle shape, and chemical nature of the surface become factors effecting carbon black reinforcement

In conclusion, vulcanization may be considered as a process whereby the properties of rubber are changed toward the middle of the continuum of high molecular weight linear polymers, at one end of which are polyisobutylene and crude rubber, with very weak intermolecular forces, and at the other end cellulose and nylon, with very strong intermolecular forces. Plasticization may be considered a reverse process to vulcanization, whereby strong intermolecular forces are weakened; for example, polyvinyl chloride is very rigid because of the strong intermolecular forces, but it becomes "rubbery" when these forces are weakened with plasticizers. There is one significant difference, however, in that the intermolecular forces are increased markedly at only a few points in vulcanization, whereas they are decreased uniformly along the whole chain in plasticization.

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RECEIVED September 30, 1946. Presented before the Division of Rubber Chemistry at the 110th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill. The work reported in this paper was interrupted in 1942, so that certain phases of the work are incomplete. The conclusions seemed sufficiently definite, however, to warrant publication. In the Charles Goodyear Memorial Lecture given at the same meeting of the AMERICAN CHEMICAL SOCIETY [IND. ENG. CHEM., 39, 901–6 (1947)], Williams presented conclusions similar to those of the present authors.

Tannins and Allied Chemicals in Mercaptan Removal Processes

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Alkali-soluble catalysts have been found with which a rapid economical regeneration of treating solutions, used for removal of mercaptans from gasoline, can be effected through air blowing. Representative of the groups of compounds which have been investigated and found to be effective for this purpose are tannins, gallic acid, hydroquinone, and pyrogallol. The influence of temperature concentrations and other variables upon oxidation rates of mercaptans is given. Methods of using the catalysts in mercaptan removal processes are discussed. The use of catalysts for regeneration of treating solutions presents a new approach to methods of mercaptan removal from gasolines and should result in wider application of this method of gasoline treatment.

A MAJORITY of the recently developed gasoline sweetening processes are directed toward mercaptan removal rather than conversion to disulfides. The benefits of this type of treatment, and various processes for accomplishing mercaptan removal, have been described at length in the literature and were reviewed in a previous paper by the authors (*1*). Both conventional sweetening and mercaptan removal processes eliminate the objectionable odor in gasoline associated with mercaptans. The extraction processes have the added advantage that improvements in octane number and lead susceptibility result because of the reduction in sulfur content. Therefore, a considerable saving in refinery operating cost results.

In general the mercaptan removal processes depend upon two distinct operations which are equally important—that is, extraction of mercaptans from the oil being treated, and regeneration of the treating solution. Naphthas vary widely in mercaptan type and content, depending on the sulfur contents of the crudes and the refinery processing steps involved in their production. Cracked gasolines usually contain a higher proportion of low-molecular-weight mercaptans as compared with straight-run naphthas of the same boiling range. The former are more readily removed by extraction. In general, the extraction step utilizes aqueous solutions of alkali metal hydroxides to which are added certain compounds which increase their ability to remove mercaptans. Ordinary caustic soda solutions are not very effective in removing the heavier mercaptans (above butyl). Solutions which have accumulated limited amounts of natural organic acids are much more suitable. For example, a 30 weight % sodium hydroxide solution which has picked up 20 volume % of organic acids may be used to advantage. Not all gasolines contain enough acids to cause them to build up to 20% of the caustic solution; then the outside addition of solutizers is necessary. Still higher extraction coefficients are obtainable by the the use of such materials as the Shell K-2 solutizer solution, which is 6 *N* potassium hydroxide and 3 *N* potassium isobutyrate. The treating solutions are usually regenerated by steam stripping in a packed, or bubble plate, tower. The operations (regeneration and extraction) are interrelated in that a reduction in efficiency of the former results in an additional burden upon the latter.

Although considerable progress has been made in the direction of extraction of mercaptans from gasolines through the use of solubility promoters, the technique of regenerating treating solutions has not been similarly improved. Unfortunately, too, the agents which have increased the mercaptan extraction power of caustic solutions have adversely affected the ease of regeneration by stripping. Shell has shown (*6*) that some saving in steam, during regeneration, can be realized by dilution which also affects a good recovery of gasoline entrained in the treating solution. Regeneration by stripping, however, is still an expensive operation, and simplifying it should materially increase the applications of mercaptan removal processes to gasoline treating.

It has been known for some time that caustic solutions containing mercaptides could be regenerated in the presence of gasoline or alone by reaction with oxygen to form disulfides (*2*). In the former case the disulfides produced remain in the gasoline, just as in the case of conventional sweetening processes. The rate of oxidation under normal conditions, however, is usually too slow for practical use. Some investigators (*3*) advocated the use of insoluble metal salts for catalyzing this reaction, but none of these catalysts has found commercial use. A study was undertaken to ascertain how the rate of this reaction could be more effectively increased. It was found in this work that a number of compounds are capable of promoting a rapid, economical regeneration of treating solutions containing mercaptans by air blowing at slightly above atmospheric temperatures. Disulfides, formed by the oxidation of mercaptans, are only slightly soluble in the treating solution and may be separated by settling. If complete disulfide removals are desired other means may also be employed.

DESCRIPTION OF PROCESS

A typical flow diagram showing the catalytic air regeneration system is shown in Figure 1.

Extraction of mercaptans is conducted in the usual manner using countercurrent stages or a packed tower. The fat solution is heated to 115–125° F. to reduce its viscosity and, if necessary, passes through a coalescer to remove any entrained gasoline. The fat solution is fed to a packed tower or to other convenient apparatus for securing intimate contact with air, where it is regenerated by air oxidation of mercaptides to disulfides. The solution is then transferred to a settler where the disulfides are separated. The regenerated solution is returned to the extraction system. In the case of the conventional solutizer process a steam stripper is substituted for the air regenerator and settler.

Disulfides are soluble to a small extent in the treating solution; as a consequence, when the air regeneration method is used, a small amount of disulfides will be returned to the gasoline being treated. This solubility varies from several tenths to one per cent by volume of the treating solution circulated, being higher in solutions containing the highest concentration of solubility promoters. Gasoline is also soluble in the treating solution to about the same extent, so that the RSSR re-entry is less than the disulfide solubility. In order to reduce the amount of disulfides returned to gasoline, auxiliary wash systems have been installed at some plants. Naphtha is generally used as the washing me-

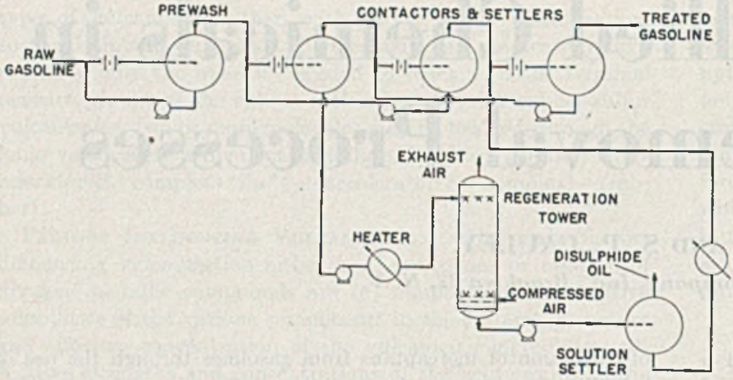

Figure 1. Typical Flow Diagram of Treating Process Using Catalytic Regeneration System

dium and may be periodically rejected or rerun to remove disulfides. Such naphtha wash streams may also be reformed by thermal or catalytic cracking; this results in conversion of the major proportion of the disulfide to hydrogen sulfide, which is readily removed.

PROPERTIES OF REGENERATION CATALYSTS

The types of catalysts which have been found thus far to be most effective for regeneration of treating solutions are tannic acid or tannins, phenolic acids, and polyhydroxybenzenes. All of these catalysts are soluble in the treating solution, insoluble in the gasoline, and relatively stable under the conditions of extraction and regeneration.

These catalysts are themselves readily oxidized in alkaline solutions, but it has been found that such oxidation is inhibited by the presence of mercaptans. The concentration of mercaptans required to protect the different catalysts varies somewhat, depending upon the activity and concentration of the catalyst used.

Tannic acid or tannins may be derived from a wide variety of sources, such as nut galls, bark, wood, leaves, roots, etc. All of the commercial grades of tannin tested have been found to have a beneficial effect upon regeneration. The most active of those tested thus far are derived from wattle bark, chestnut bark, tara pods, and Sicilian sumac bark. The tannins are complex compounds whose exact chemical composition and structure are not entirely known. Standard methods of classification and analysis (*4*) have been developed for them, and their chemistry has been studied in some detail by Russell (*5*).

CATALYTIC OXIDATION OF MERCAPTANS

The rate of oxidation of mercaptans in alkaline treating solutions depends upon a number of variables: (*a*) type of mercaptan, (*b*) concentration of catalyst used, (*c*) concentration of oxygen (with air at atmospheric pressure this is constant at the inlet), (*d*) temperature of contacting, (*e*) kind of solutizer solution, and (*f*) method of contacting.

In order to study the effects of these variables it was necessary to adopt a standard laboratory testing procedure. Extreme care was essential in view of the relatively high regeneration rates found. The procedure followed, after considerable preliminary work, was as follows:

> All solutions containing oxidation catalysts are prepared in the presence of nitrogen to prevent uncontrolled oxidation of mercaptans. The catalysts are added after the mercaptan concentration of the solutions has been adjusted to the proper initial concentration so as to avoid possible oxidation of the catalyst.
>
> A sample of the solution to be used is mechanically shaken at a rate of two shakes per second in a separatory funnel for periods of 1 minute each. The initial mercaptan sulfur concentrations are 1.0 ± 0.10%. The air-to-solution ratio is 6:1 by volume. After each minute of regeneration the free space in the separatory funnel is purged with low pressure air for a period of 20 seconds. This procedure is conducted with a minimum of time between shakings and is continued until the mercaptan concentration is reduced to 0.1–0.2%. The time required for regeneration is determined approximately by a preliminary run.

Experience has shown that the regeneration rates during a test were essentially constant, in the range of mercaptan sulfur concentrations used, so that the difference in initial and final concentrations divided by the number of regenerations may be taken as the regeneration rate. Mercaptan sulfur contents of solutions were determined by potentiometric titration. Final analyses of solutions, under test for regeneration rates, were made as soon as possible after the final shaking operation. It was recognized that the laboratory method used in contacting solutizer solutions with air would give only comparative results, since in plant operations quite different contacting methods would be employed. However, it is believed that this method gives reproducible results and is thus useful in studying the other variables involved.

Tables I to VI show the effects of different variables and catalysts on regeneration rates. The data given in the tables on regeneration rates, although not absolute, give the relative effectiveness of the various types of oxidation catalysts. Another factor, not shown in the tables, is the regeneration effected after all contacting of air and solution has ceased. Experimental work has shown that the mercaptan sulfur concentration of a solution becomes constant 15–30 minutes after regeneration at atmospheric temperatures. At higher temperatures less time is required. This effect is probably due to the continued reaction of air dissolved in the treating solution to the point where oxygen has been completely consumed.

A marked effect is possible by the use of small amounts of various catalysts, as shown in Table I. Rates using 1% of chestnut and wattle tannins are 200–250 times as great as those obtainable with straight caustic solutions, and even higher rates are shown for pyrogallol, although the use of the latter has certain disadvantages, as will be explained. Data given in Tables II–IV indicate that the heavier mercaptans are more readily oxidized than those of low molecular weight. The more rapid regeneration of methyl mercaptan may be due to the higher volatility of methyl disulfide, the removal of which would favor higher conversion rates. Solutions containing solutizers (Tables III and IV) have lower regeneration rates than caustic alone. These solutions also have higher viscosities, but it is likely that the effect of type and concentration of solutizer used would also be important. Increases in temperature markedly increase the rate of regeneration (Table V). Unfortunately temperature

Table I. Effect of Catalyst Concentration on Regeneration Rates

(Solution, 10% NaOH; mercaptan, *n*-butyl; temperature, 80° F

Catalyst Concn.[a], Wt.%	Regeneration Rate, % S (RSH)/Min. C.P. tannic acid	Chestnut extract	Wattle extract	Gallic acid	Pyrogallol	Hydroquinone
0.00	0.001	0.001	0.001	0.001	0.001	0.001
0.25	0.07	0.09	0.09	0.08	0.32	0.11
0.50	0.09	0.16	0.18	0.14	0.39	0.19
1.00	0.16	0.21	0.25	0.19	0.55	0.25
3.00	0.18	0.35	0.31	0.25	...	...

[a] Catalyst concentrations of extracts are based on tannin content as furnished by manufacturers.

increases also accelerate corrosion, and one of the important advantages of catalytic regeneration is the ability to avoid operation at elevated temperatures or pressures. The data in Table VI indicate the relative activity of various types of tannin. Chestnut and wattle, which are readily available, are also seen to have high catalytic activity.

PROTECTION OF CATALYST

In order to prevent oxidation of the catalyst during regeneration, it is necessary that a certain minimum amount of mercaptan be kept in the solution. The absolute quantity of mercaptan required for stabilization of the catalyst is important, since it has a bearing on the selection of catalyst to be used in a given installation. Experiments were therefore performed to determine the approximate concentration of mercaptan sulfur required to protect the various catalysts. The laboratory procedure in conducting the above tests was as follows:

> A solution containing five gram moles per liter of free sodium hydroxide, one gram mole per liter of sodium cresylate, and a given concentration of catalyst is prepared. A concentration of *n*-butyl mercaptan, greater than that necessary for catalyst stabilization, is then added to the solution. The solution is alternately regenerated by contacting with air and refortified with mercaptan for a total of seven such operations. The degree of regeneration is controlled so that the variation in mercaptan sulfur concentration is approximately 0.2% by weight during each cycle. At the end of seven cycles the solution is analyzed for its catalyst content. If no reduction in catalyst concentration is noted during these operations, the process is repeated with the same solution but a lower mercaptan concentration. Whenever the catalyst content is found to have been reduced by 10% of its original value during this procedure, it is considered that the mercaptan concentration was not sufficient for catalyst stabilization. Relative catalyst concentrations are measured by a colorimetric method developed especially for this purpose which is based upon the reducing effect of the catalyst on tungsten molybdenum phosphate.

The approximate minimum mercaptan sulfur concentrations which were found necessary for catalyst protection are given in Table VII.

SELECTION OF OXIDATION CATALYST

Selection of the best oxidation catalyst for a particular operation involves consideration of a number of factors, such as unit cost of the catalyst, effect of catalyst on characteristics of mercaptan solubility promoters, catalytic activity of catalyst, and oxidation stability of catalyst.

Taking a regeneration rate of 0.16% sulfur (RSH) per minute for *n*-butyl mercaptan in a 10% sodium hydroxide solution as a basis of comparison, and assuming that sufficient mercaptan is present to protect all of the catalysts, the initial catalyst costs for preparation of treating solution would be as shown in Table VIII, based on the data given in Table VII.

TABLE II. REGENERATION RATES OF MERCAPTANS IN 10% CAUSTIC SODA SOLUTION CONTAINING 1% TANNIN

(Viscosity at 100° F., 1.36 centistokes; temperature, 80° F.)

Mercaptan	Regeneration Rates, % S (RSH)/Min. Wattle	Chestnut
Methyl	0.20	0.18
Ethyl	0.13	0.13
Propyl	0.15	0.16
Butyl	0.25	0.21

TABLE III. REGENERATION RATES OF MERCAPTANS IN 5 *N*–1 *N* SODIUM CRESYLATE (*p*-CRESOL) SOLUTION CONTAINING 1% TANNIN

(Temperature, 80° F.; viscosity at 100° F., 4.6 centistokes)

Mercaptan	Regeneration Rates, % S (RSH)/Min. Wattle	Chestnut
Methyl	0.12	0.10
Ethyl	0.11	0.08
Propyl	0.10	0.08
Butyl	0.11	0.14
Amyl	..	0.16
Hexyl	..	0.16
Heptyl	..	0.16

TABLE IV. REGENERATION RATES OF MERCAPTANS IN SHELL SOLUTIZER SOLUTION (6 *N* POTASSIUM HYDROXIDE–3 *N* POTASSIUM ISOBUTYRATE) CONTAINING 1% TANNIN

(Viscosity at 100° F., 4.0 centistokes; temperature, 80° F.)

Mercaptan	Regeneration Rates, % S (RSH)/Min. Wattle	Chestnut
Methyl	0.03	0.05
Ethyl	0.04	0.05
Propyl	0.03	0.04
Butyl	0.05	0.05
Amyl	0.03	0.05
Hexyl	0.03	0.05
Heptyl	0.04	0.05

TABLE V. INFLUENCE OF TEMPERATURE ON REGENERATION RATES OF *n*-BUTYL MERCAPTAN IN 10% CAUSTIC SODA SOLUTIONS CONTAINING 1% TANNIN

Temp., ° F.	Regeneration Rates, % S (RSH)/Min. Wattle	Chestnut
37	0.09	0.07
80	0.25	0.21
114	0.37	..
127	..	0.32

TABLE VI. COMPARISON OF CATALYTIC ACTIVITY OF VARIOUS TANNINS

(Solution, 10% NaOH; mercaptan, *n*-butyl; temperature, 80° F.; tannin concentration, 1.0 weight %)

Tannin	Regeneration Rates, % S (RSH)/Min.
Wattle, extract	0.25
Chestnut, extract	0.21
Logwood, crystals	0.21
Sumac (Sicilian), liquid	0.21
Tara, liquid	0.21
Mangrove, liquid	0.16
Oak, liquid	0.14
Cutch	0.11
Quebracho (cold water-soluble), solid	0.11
Ulmo	0.11
Quercitron, crystals	0.09
Quebracho (hot water-soluble), solid	0.07
Gambier	0.05
Osage orange, crystals	0.03

TABLE VII. MINIMUM MERCAPTAN SULFUR CONCENTRATIONS REQUIRED FOR PROTECTION OF REGENERATION CATALYSTS

(Mercaptan, *n*-butyl; temperature, 80° F.)

Catalyst	Catalyst Concn., Wt.%	Mercaptan Sulfur Concn., %
Pyrogallol	0.25	0.35
	0.50	0.45
	1.0	0.60
	1.5	0.75
Hydroquinone	0.5	0.55
	1.0	0.55
	1.5	0.65
Gallic acid	0.5	0.20
	1.0	0.25
	1.5	0.30
Tannic acid, C.P.	0.5	0.20
	1.0	0.20
	1.5	0.20
Wattle, extract	1.0	0.08
Chestnut, extract	1.0	0.08

TABLE VIII. COMPARATIVE COST OF CATALYSTS FOR EQUIVALENT REGENERATION RATES

(Solution, 10% NaOH; mercaptan, *n*-butyl; basis, 0.16% S (RSH)/minute regeneration rate; temperature, 80° F.)

Catalyst	Required Catalyst Concn., Wt.%	Catalyst Cost, Dollars/100 Gal. of Soln.
Tannic acid, C.P.	1.00	0.26
Chestnut tannin extract	0.50	0.50
Wattle bark tannin extract	0.45	1.40
Gallic acid	0.70	5.56
Pyrogallol	0.13	1.54
Hydroquinone	0.38	2.88

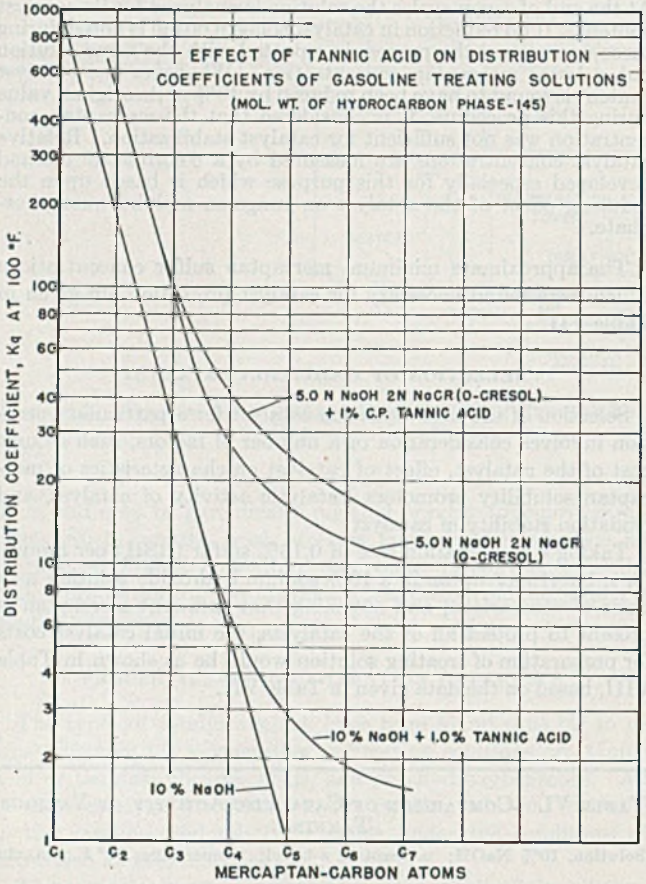

Figure 2

The effect of a catalyst upon the characteristics of a mercaptan solubility promoter (if present) in the treating solution is important. Tests on the oxidation stability of mercaptan solubility promoters, in the presence of the oxidation catalysts considered, indicate that, with the possible exception of hydroquinone and pyrogallol, no substantial interaction occurs.

The catalytic activity of a catalyst will influence the design of a regeneration system, or conversely the existing regeneration facilities will influence the choice of catalyst to be used.

The oxidation stability of a catalyst determines the minimum mercaptan concentration which can be carried in the treating solution and limits the treating application in which a given catalyst may be used. When it is desired to produce a treated gasoline of low mercaptan content (less than 0.001% by weight RSH), the maintenance of a low mercaptan concentration in the treating solution is important. In such cases it may be desirable to use a catalyst which will be protected by less than 0.2% by weight mercaptan sulfur. Assuming, as was done in the preparation of Table VIII, that a regeneration rate of 0.16% RSH per minute is desired for *n*-butyl mercaptan, it is apparent from the data in Table VII that only the tannins or gallic acid would be usable, without excessive catalyst loss due to oxidation. Lower mercaptan concentrations can be maintained in the treating solution provided that lower catalyst concentrations are maintained. In order to accomplish this, more effective means of contacting the solution with air are necessary. In any case the relative advantages of various catalysts remain the same.

When the proper mercaptan concentration is maintained, consumption of catalyst is only by mechanical loss or spillage, and this is ordinarily very small.

Taking everything into consideration, it was felt that the tannins showed the greatest promise of successful application. They were therefore employed in commercial scale operations and found to give practical confirmation of the above data.

In addition to their use as catalysts in the oxidation of mercaptans to disulfides, the tannins also exhibit some mercaptan solubility promoting effects. These effects are limited to *n*-butyl and heavier mercaptans, as shown in Figure 2. Although this feature is a secondary one, it is of interest in treatment of gasolines containing small amounts of heavy mercaptans which do not require the use of special solutizing treating solutions.

COMMERCIAL APPLICATION

Processes using the tannin catalyzed regeneration operation are at present employed in eight plants in the United States and Canada and total some 36,000 barrels per day treating capacity. The first of these plants has been in operation over four years. Also several large plants are at present in the design and construction stage. These units treat a wide variety of hydrocarbon fractions including butane-butene, low-end-point naphtha, and full range 400 extreme pressure gasoline; cracked and straight run stocks; and naphthas derived from naphthenic and paraffinic crudes.

Application of the process for the treatment of C_4 fractions is quite attractive, since methyl mercaptan is difficult to remove from treating solutions by steam stripping, and the tannin caustic system may be operated without the use of exchangers or coolers. Two full scale plants using a 10% sodium hydroxide solution containing 1% tannin are in operation for the treatment of such stocks.

In treating gasolines, cresylates or other solutizers are employed, and often potassium hydroxide is used in preference to sodium hydroxide. Typical solutions will employ 5 *N* hydroxide and 2 *N* sodium alkylphenol or 6 *N* potassium hydroxide and 2.5 *N* potassium alkylphenol. For the same viscosity, not exceeding 10 centistokes, higher concentrations are possible when using potassium hydroxide. Gasolines containing up to 0.2 weight % mercaptan sulfur are treated to obtain a reduction of mercaptan content of about 90%. Gasolines containing approximately 0.006% mercaptan sulfur can be readily scrubbed down to less than 0.001% and will then sweeten completely in storage. However, little lead saving is accomplished by scrubbing much below 0.002–0.003% mercaptan sulfur. Gasolines of this mercaptan content are generally satisfactory to the consumer, and tests indicate that their performance is in no way impaired.

Extraction equipment used has varied to a considerable extent, as several of the units in operation were converted from existing doctor sweetening units during the war, when it was difficult to obtain new equipment. Stage mixers and settlers are at present the most common type of contactors, and a typical installation will employ one such stage for precaustic washing followed by three countercurrent extraction stages. Packed towers and perforated tray towers have also been employed.

For contacting regeneration air with the treating solution, turbomixers and drilled pipe distributors have been employed with success. The air requirement is usually no more than 2–3 times the theoretical for oxidation of the mercaptans. The use of porous ceramic or graphite diffusers, such as are used in water aeration, has also been recently tried with success.

By the use of the naphtha wash mentioned previously, it is possible to prevent disulfide return almost completely, so that the mercaptan removed in the extraction stage is credited to lead savings.

Control of the process is not difficult, the only operating adjustment being the regeneration air. In practice it is found that this is not critical and that satisfactory protection of the treating solution can be accomplished without frequent adjustments or the need for skilled personnel.

The advantages of regeneration of treating solutions by air blowing in the presence of catalysts such as tannins are as follows: The cost of regeneration, through use of air, is very low; existing doctor or mercaptan removal treating plants may be easily converted to new type of operation; low temperature regeneration allows use of ordinary steel and keeps corrosion at a minimum; and odor nuisance during regeneration is eliminated, since disulfides are formed as a by-product.

CONCLUSIONS

The use of mercaptan oxidation catalysts, soluble in alkaline treating reagents, offers an attractive, economical means of regenerating solutions used in the removal of mercaptans from gasoline. The ease of regeneration possible through the use of oxidation catalysts materially improves operations of mercaptan extraction systems.

ACKNOWLEDGMENT

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Sorption of Nitrogen and Water Vapor on Textile Fibers

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Measurements were made of the adsorption of nitrogen and water vapor on six purified textile fibers and titanium dioxide. All the fibers had a relatively low capacity for adsorption of nitrogen as compared with capacity for adsorption of water vapor. The surface area values ranged from 0.31 square meter per gram for nylon to 0.98 square meter per gram for viscose rayon. The values of the free surface energies of adsorption as calculated by the Gibbs adsorption equation were the same for wool, cotton, silk, and rayon fibers but differed for the two synthetic polymers, nylon and acetate rayon.

THERE is evidence that surface characteristics of textile fibers have some effect on the properties of the finished textile fabrics. Examples of such evidence of surface properties are apparent in the phenomenon of water-repellency (*7*, *28*), in the loss of light-reflectance (*32*), and in the difference in moisture-sorption capacities of fabrics (*22*, *23*, *25*) after various treatments. While the importance of surface characteristics and properties has long been recognized in the technology of colloids and other sciences, the relation of these surface properties to the properties of fabrics is not well understood.

Several workers (*2*, *3*, *13*, *26*, *27*, *29*, *30*) have interpreted the adsorption of water by some textile materials (such as cellulose, wool, nylon, etc.) as a phenomenon in multimolecular (*12*) adsorption. If one assumes that the adsorption is a multilayer phenomenon, one may calculate that the surface area accessible to the first layer is in the range from 100 to 200 square meters per gram. This range of values is several orders of magnitude greater than the value (0.60 square meter per gram) calculated by Emmett and DeWitt (*18*) from nitrogen adsorption measurements on paper cellulose. On the other hand, it is not appreciably greater than the value (53.0 square meters per gram) reported by Purves *et al.* (*2*) working with nitrogen on a swollen cotton cellulose.

In order to obtain reliable surface area measurements of textile materials it is necessary to measure the surface area under conditions ensuring true physical adsorption. Brunauer, Emmett, and Teller (*12*) and Harkins and Jura (*21*) have shown that the adsorption isotherms of nitrogen at −195° C. (the boiling point of nitrogen, at which temperature nitrogen is physically adsorbed on solids) may be used to calculate the true surface areas of a great many crystalline and amorphous materials.

Knowledge of the molecular area or surface area (*8*) is believed necessary in order to evaluate such properties as the free surface energy (*5*) of adsorption and the work of adhesion (*20*) between the liquid and the solid phase. It therefore seemed highly desirable to measure the surface areas of the more common textile fibers—cotton, wool, viscose, silk, nylon, and cellulose acetate—and to obtain the water adsorption isotherms of the same samples used in the nitrogen adsorption experiments. The work presented here represents a portion of the preliminary work of a larger program sponsored and supported by the Office of the Quartermaster General, War Department. It is intended to provide comparative data on the adsorption of the two vapors on six different purified textile materials.

MATERIALS AND THEIR PREPARATION

Six purified textile fibers and a sample of titanium dioxide (anatase) were used in this study.

The cotton, wool, silk, and rayon were from the samples studied by Wiegerink (*31*). The titanium dioxide was employed as a reference standard. The cotton was purified by extracting 8 hours with alcohol and 8 hours with ether, followed by four washings in distilled water at 50° to 60° C. The wool was extracted with ether and alcohol until the extracting liquid was free of residue traces, then washed at 50° to 60° C. in distilled water. The raw silk was degummed in soap solution, extracted with alcohol and ether, then thoroughly washed in distilled water. The viscose rayon was washed four times in a 1% water solution

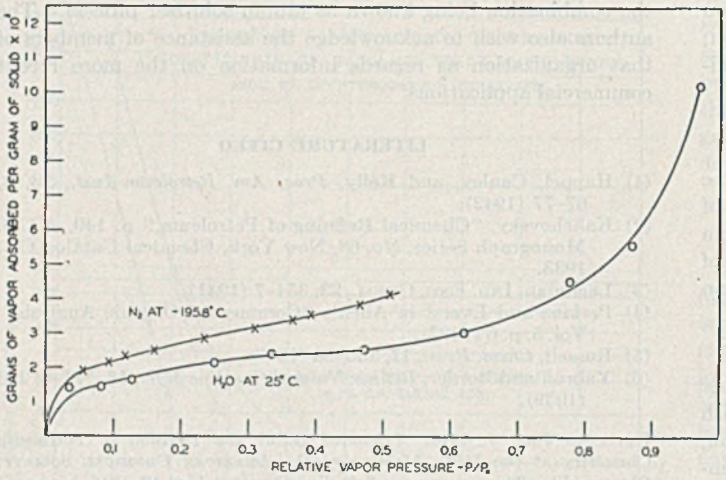

Figure 1. Adsorption Isotherms of Water and Nitrogen on Titanium Dioxide

of ammonia at 50° to 60° C. and then washed four times with distilled water at the same temperature.

The sample of nylon used in this study was supplied by E. I. du Pont de Nemours & Co. and was 40-denier 13-filament yarn having one half turn per inch of Z twist. Six hours' extraction with ethyl ether proved sufficient for complete removal of the 0.4% of oil-base lubricant applied during spinning. The acetate rayon was 150-denier 46-filament yarn having 2.5 turns per inch and was supplied by the American Viscose Co. The sample was washed four times in distilled water at 50° to 60° C.

TEST METHODS

The sorption of water by the textiles was determined gravimetrically. An analytical balance was used in conjunction with the conditioning apparatus described by Carson and Worthington (*14*). In this apparatus the partial pressure of the water is maintained by means of saturated salt solutions and the samples may be weighed without removal from the conditioned atmosphere. The moisture vapor pressures were obtained from wet- and dry-bulb temperatures and also by means of a Dunmore (*1*) electric hygrometer. The dry weights of the 5-gram samples of yarn were obtained by placing them over phosphorus pentoxide until constant weight was obtained—about 5 days. No loss of weight occurred from the fifth to the thirtieth day. After this drying period, the fibers were in equilibrium with an atmosphere whose relative water vapor partial pressure was less than 0.01. After the dry equilibrium point had been attained, the moisture content of the sample was determined at a series of increasing relative water vapor pressures. The rate of change of weight was plotted against time at each partial pressure and the equilibrium value, usually attained within 24 to 48 hours, was indicated by the rate curve.

The adsorption of nitrogen was determined by a method similar to the one used by Brunauer and Emmett (*16*). The saturation vapor pressure of the nitrogen was determined by use of a vapor pressure thermometer, using the purified gas employed for the adsorption experiment.

The low temperature adsorption tests were made on 20- to 50-gram samples of the fibers. The sample bulb was packed as tightly as possible for each determination to reduce the dead space correction. For the experiments reported in this article, the textile fibers were evacuated for 16 to 20 hours at room temperature (about 25° C.) to a pressure of about 10^{-6} mm. of mercury. Other preliminary tests were made in which the temperature of evacuation was higher and one experiment was made of the cotton-fiber surface available to oxygen. For the low temperature adsorption of titanium dioxide the temperature of evacuation was 200° C. Helium was used in evaluating the dead space in the sample bulb.

ADSORPTION MEASUREMENTS

As shown in Figures 1, 2, and 3, the adsorption isotherms of both water vapor and nitrogen were sigmoid-shaped, corresponding to type II of the five types classified by Brunauer (*11*). This type of adsorption curve is characteristic of physical adsorption on rigid solids with pore diameters larger than the molecular diameters of the adsorbed molecules (*17*). However, it

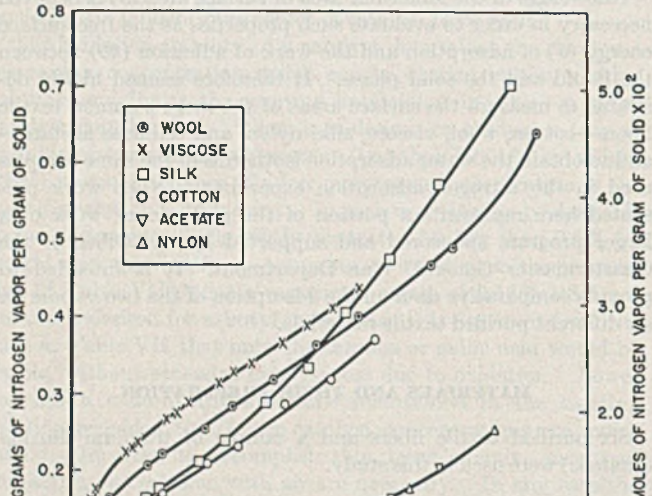

Figure 2. Adsorption Isotherms of Nitrogen on Six Textile Fibers at — 195° C.

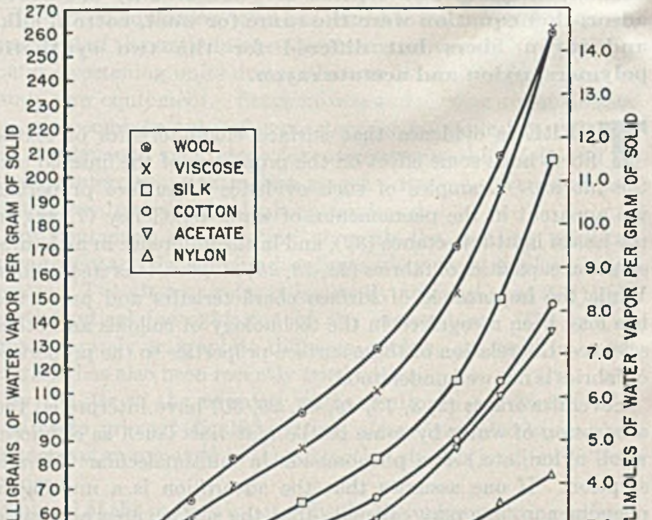

Figure 3. Adsorption Isotherms of Water on Six Textile Fibers at 25° C.

also occurs with nonrigid solids in which the adsorption sites are not restricted to the surface.

It may be noted from Figure 1 that the millimoles of water vapor and nitrogen adsorbed by the titanium dioxide differ only by a small percentage (*15*). This is true despite the fact that the nitrogen was adsorbed after thorough evacuation, whereas water vapor was adsorbed from mixtures in air after the sample had been dried over phosphorus pentoxide. On the other hand, comparing the adsorption isotherms of the textile fibers in Figures 2 and 3 and the data in Table I reveals that the orders of magnitude of adsorption capacity of nitrogen and water vapor are not the same. All the fibers had relatively low capacity for the adsorption of nitrogen as compared with the relatively high capacity for adsorption of water vapor.

The wool and viscose rayon fibers had slightly greater nitrogen-adsorption capacities than silk and cotton, and the adsorption capacities of the acetate and nylon fibers were the lowest. In the adsorption of water vapor, the wool and viscose rayon fibers also had greater adsorption capacity than silk and cotton, and the acetate and nylon had the lowest capacities. There was, however, a certain lack of parallelism and shifting of relative position. Sufficient study has not been made to indicate the significance of these differences.

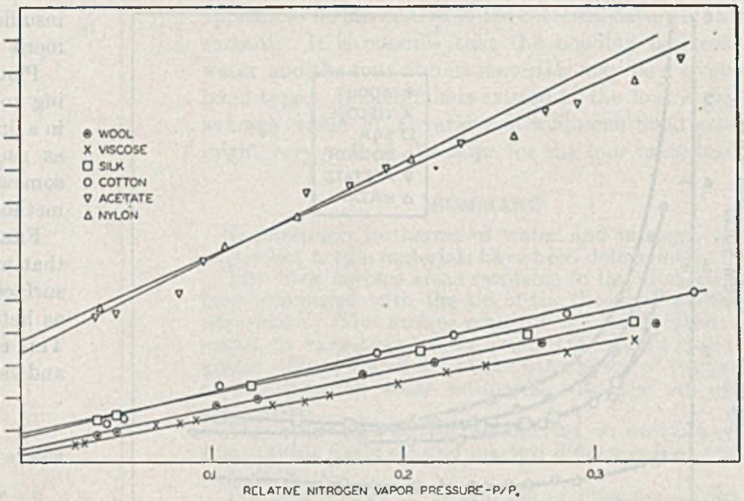

Figure 4. B.E.T. Plots for Obtaining Surface Areas Accessible to Nitrogen

Table I. Sorption of Nitrogen and Water Vapors on Textile Fibers

P/P_0	Wool	Viscose rayon	Silk	Cotton	Acetate	Nylon
	Millimoles of Water Vapor per Gram of Solid					
0.034	1.3	1.2	0.7	0.7	...	0.2
0.081	1.9	1.8	1.1	1.1	...	0.4
0.130	2.3	2.1	1.4	1.3	0.8	0.6
0.252	3.6	3.2	2.3	1.9	1.3	1.0
0.335	4.6	4.0	2.9	2.4	1.7	1.3
0.471	5.7	4.8	3.6	2.9	2.3	1.7
0.620	7.1	6.2	4.6	3.7	3.2	2.1
0.778	9.5	8.4	6.4	5.4	4.8	2.9
0.866	11.6	10.8	8.3	6.4	6.0	3.5
0.968	14.4	14.5	11.5	8.2	7.5	4.2
	Millimoles of Nitrogen Vapor × 10^2 per Gram of Solid					
0.05	1.1	1.4	0.7	0.8	0.3	0.3
0.10	1.4	1.7	1.1	1.1	0.4	0.4
0.15	1.7	2.0	1.4	1.3	0.5	0.5
0.20	1.9	2.2	1.7	1.6	0.6	0.6
0.25	2.2	2.5	2.0	1.8	0.7	0.7
0.30	2.4	2.7	2.3	2.0	0.8	0.8
0.35	2.7	2.9	2.7	2.3	0.9	0.9
0.40	2.9	..	2.9	2.6	1.1	1.1
0.45	3.1	..	3.6	...	1.3	1.3
0.50	3.4	..	4.1	...	1.4	1.4
0.55	3.8	..	4.6	...	1.7	1.7

Table II. Surface Areas of Textile Fibers

(Area available to nitrogen molecules at −195° C.)

Material	Area Available, Sq. M./Gram
Wool	0.96
Viscose rayon	0.98
Silk	0.76
Cotton	0.72
Acetate rayon	0.38
Nylon	0.31
Titanium dioxide (TiO_2)	7.90

Table III. Calculated Surface Areas Accessible to Water Vapor and Nitrogen Vapor

Material	Area I Available to Water Molecules at 25° C.	Area II Available to Nitrogen Molecules at −195° C.	Ratio of Area I to Area II
	Sq. Meters per Gram		
Wool	206	0.96	215
Viscose rayon	204	0.98	208
Silk	140	0.76	184
Cotton	108	0.72	150
Acetate rayon	58.8	0.38	154
Nylon	45.0	0.31	145
Titanium dioxide (TiO_2)	7.0	7.90	0.9

CALCULATED QUANTITIES

Surface Areas. The surface areas of the fibers available to the nitrogen vapor were calculated according to the B.E.T. equation (*10*) now commonly used for calculating the surface areas of solid materials. In evaluating the quantities of gas required for a monolayer on each of the textile fibers, the customary method of plotting $P/V\ (P_0 - P)$ *vs.* P/P_0 was employed (*10*). The plot is presented in Figure 4. The calculated surface area values are presented in Table II. All the surface areas were less than 1 square meter per gram. The value obtained for cotton cellulose—0.72 square meter per gram—compares favorably with the value of 0.60 square meter per gram reported by Emmett and DeWitt (*18*), but differs markedly from the value of 53.0 (*2*) reported by Purves for a sample of swollen cotton cellulose. The surface area available to the nitrogen vapor may be greatly dependent upon the source and treatment, as the comparison with Purves' single experimental value suggests. The surface area of cotton cellulose thus appears to vary from at least 0.60 to 53.0 square meters per gram, depending upon its history. The value for cellulose of 0.60 square meter per gram is only slightly larger than values (0.1 to 0.3 square meter per

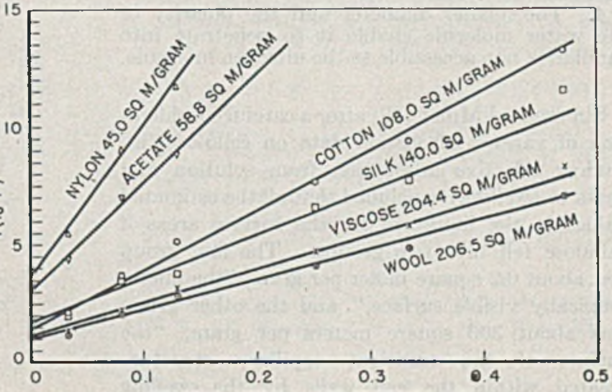

Figure 5. B.E.T. Plots for Obtaining Surface Areas Accessible to Water Vapor

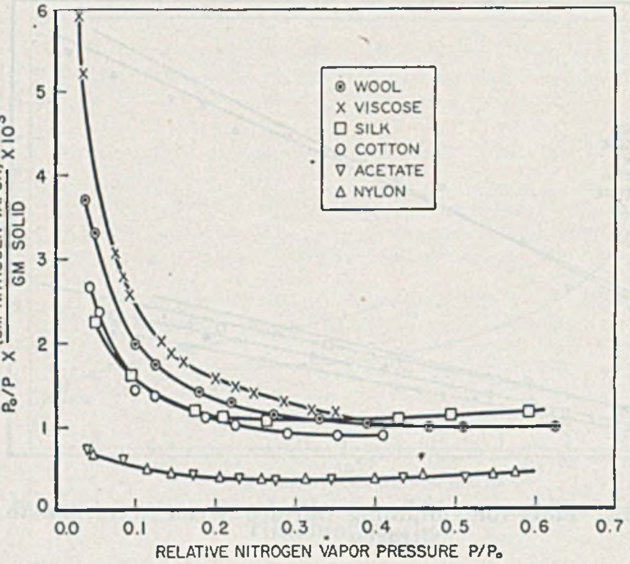

Figure 6. Plot of Nitrogen Adsorption Data in Accordance with Modified Gibbs Equation

gram) obtained by estimation of areas observed with the microscope and reported by Stamm and Millett (*30*) and Howell and Jackson (*24*). It is likely, therefore, that the surface area, as determined with nitrogen, represents a lower limit.

In view of the large differences between the adsorption capacities observed in the water isotherm and the nitrogen isotherm, it was of interest to calculate the "water" areas of the same samples. This calculation was carried out, even though the authors were aware of the possibility that the data could be interpreted from another point of view. The plot of $P/V\,(P_0 - P)$ *vs.* P/P_0 is shown in Figure 5 and the areas which may be calculated from them, by assuming all adsorbing sites were on the surface, are tabulated in Table III. It may be noted in this table that the calculated surface areas of the textile fibers were from 150 to 200 times as great when determined by water adsorption as when determined by nitrogen adsorption.

This apparent discrepancy may be explained in a number of ways:

1. The adsorbing sites are not restricted to a surface.
2. If the adsorbing sites are restricted to a surface there may be an additional internal surface specific to certain adsorbates as well as an external surface.
3. The internal surface within the fibrous structure exists only in the presence of a swelling agent such as water.
4. The smaller diameter and the polarity of the water molecule enable it to penetrate into capillaries not accessible to the nitrogen molecule.

Stamm and Millet (*30*) after a careful consideration of various adsorption data on cellulose (including selective adsorption from solution and heats of swelling) concluded that all the estimated values in the literature for the surface areas of cellulose fell into two groups. The first group was about 0.2 square meter per gram, "the microscopically visible surface," and the other group was about 300 square meters per gram, "the surface of the transient capillary structure created within the cell walls by the swelling agents."

All four of the above factors may operate to account for the apparent discrepancy. There is insufficient evidence at present for evaluating the relative merit of the four hypotheses suggested heretofore.

Plotting the nitrogen and water vapor adsorption data according to the method suggested by Harkins and Jura (*21*) resulted in a line or series of lines concave to the X axis rather than convex as usually found for other materials. In the two instances somewhat lower surface area values were obtained when this method of plotting was used.

Free Energy of Adsorption. In view of the possibility that we are here dealing with an internal as well as an external surface, it seemed of interest to attempt to treat both systems as heterogeneous and to apply the relationship of Gibbs (*19*). This equation is applicable to interfaces between solid surfaces and vapors; it was written by Gibbs as follows:

$$\sigma = E_s - tn_s - \mu_1\Gamma_1 - \mu_2\Gamma_2 \qquad (1)$$

where

σ = the work spent in forming 1 sq. cm. of clean new surface
E_s = surface total energy
t = temperature
n = surface entropy
μ_1 = chemical potential of the solid at boundary
μ_2 = chemical potential of the vapor at boundary
Γ_1 = surface concentration of the solid
Γ_2 = surface concentration of the vapor

Under isothermal conditions (*4*) and under conditions in which Γ_1 is set at zero (by choosing the Gibbs boundary so that the surface concentration of the solid is zero) Equation 1 reduces to:

$$d\sigma = -\Gamma_2 d\mu_2 \qquad (2)$$

Under appropriate conditions $d\mu_2$ may be replaced by its equivalent $d(RT \ln P)$ where P is the vapor pressure and we have:

$$\frac{d\sigma}{d(RT \ln P)} = -\Gamma_2 \qquad (3)$$

or

$$\int_0^\sigma d\sigma = RT \int_0^P \Gamma_2 d \ln P \qquad (4)$$

and

$$\int_0^\sigma d\sigma = \frac{RT}{MS} \int_0^P qd \ln P \qquad (5)$$

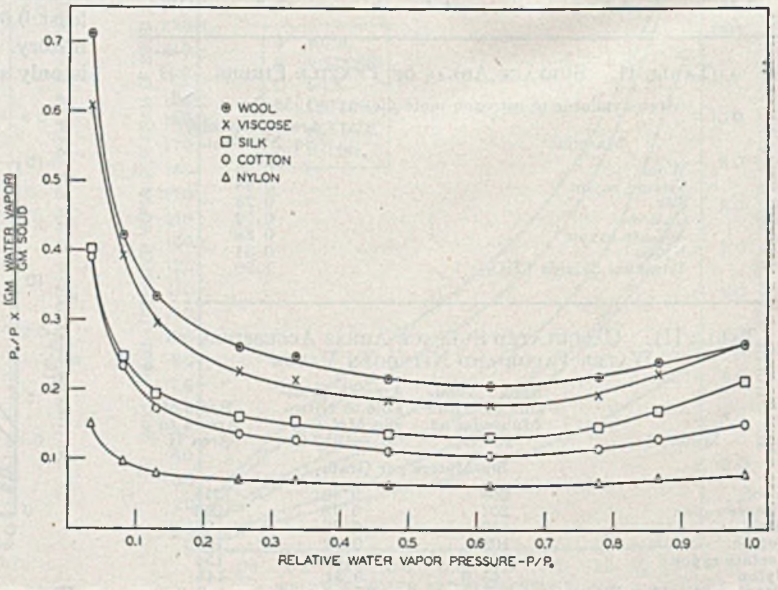

Figure 7. Plot of Water Adsorption Data in Accordance with a Modified Gibbs Equation

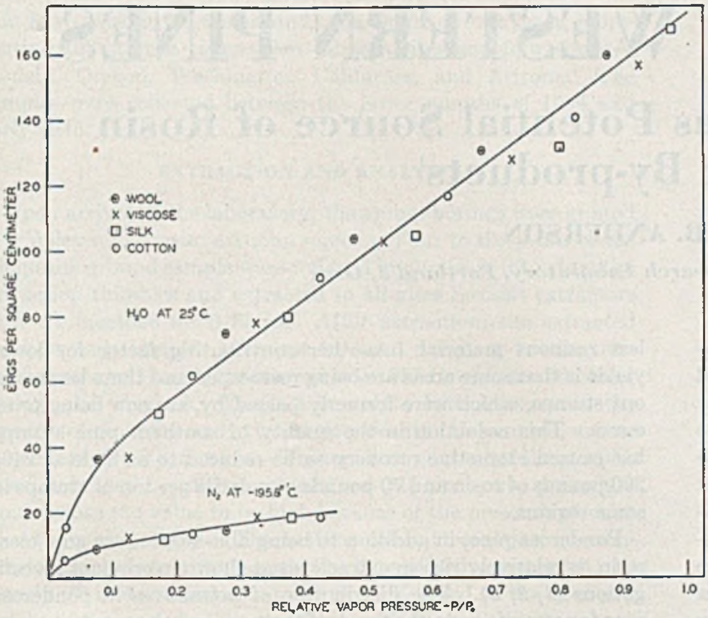

Figure 8. Free Surface Energy of Adsorption as a Function of Relative Vapor Pressure

Where Gibbs' surface concentration, Γ_2, is expressed (*6, 9*) as the number of moles of vapor adsorbed per sq. cm.:

$$\Gamma_2 = q/MS \tag{6}$$

q = grams of absorbate
M = its molecular weight
S = total surface area

Since σ is the work required to form 1 sq. cm. of surface, it is also the free surface energy; therefore, covering the surface with a vapor lowers the value of σ. This change of the free surface energy which accompanies adsorption is referred to here as the free energy change of adsorption and designated ΔF as follows:

$$\Delta F = \frac{RT}{MS}\int_0^P q/p\,dp \tag{7}$$

The ΔF of Equation 7 may be evaluated after experimental determination of S, q, and p. The integral $\int q/p\,dp$ can be obtained by graphical integration by estimating the area under the curve which is obtained when one plots values of q/p *vs.* P.

Plots of the data of Figures 2 and 3 in this manner are shown in Figures 6 and 7 (*13*). Since the plots do not lend themselves easily to extrapolation, the method used by Boyd and Livingston (*9*) was employed in obtaining the areas. The ΔF values thus obtained were in turn plotted against the relative vapor pressure, P/P_0, and the resulting curves are shown in Figure 8.

It is noted that the free energy of adsorption of water is the same at all relative vapor pressures for wool, silk, viscose, and cotton. The free energies of the two synthetic polymers, nylon and acetate, did not fall on the common curve. As was the case in the surface area measurements, the free energy of adsorption of these two fibers was in a separate class (see Table IV). With the exception of nylon and cellulose acetate, whose fiber-water contact angles are greater than zero, the free energy of adsorption appears to be insensitive to the chemical nature of the adsorbent. It is possible that the bonding between the water and the four fibrous materials may be a hydrogen bond type. If such bonds existed in the four cases, the average value of a variety of hydrogen bond energies might very well be the same for the four materials.

Table IV. Free Energy of Adsorption of Water and Nitrogen on Textile Polymeric Materials

Material	Water, Ergs/Sq. Cm.		Nitrogen, Ergs/Sq. Cm.	
	P/P_0 0.40	P/P_0 1.0	P/P_0 0.40	P/P_0 1.0
Wool	89	170	20	..
Viscose rayon	89	170	20	..
Silk	89	170	20	..
Cotton	89	170	20	..
Acetate rayon	114	247	14	..
Nylon	113	223	12	..

SUMMARY

The sorption isotherms of water and nitrogen on six important textile materials have been determined.

The fiber surface areas available to the nitrogen have been computed with the aid of the theory of multilayer adsorption. The surface areas of the textile fibers were found to vary between 0.31 and 0.96 square meter per gram. These values are of the same order of magnitude as the reported areas estimated with the aid of the microscope.

The water and nitrogen isotherms on samples of the same textile fibers showed marked differences in sorptive capacities.

The free energy of adsorption of nitrogen on the six fibrous materials have been calculated.

The implications of these calculations are discussed.

ACKNOWLEDGMENT

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CHEMISTRY OF WESTERN PINES

Ponderosa Pine Stumps as Potential Source of Rosin and Other By-products[1]

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The determination and analysis of extractives from ponderosa pine stumps indicate that this forest waste material may be a potential commercial source of resin acids, fatty acids, and other extractive by-products. Ponderosa pine stumps which have seasoned up to five years yield approximately 17.0% acetone-soluble extractives. This extract contains the following components, named in approximate order of quantity present: (1) resin acids, (2) unsaponifiables, (3) esters, (4) free fatty acids, and (5) volatile terpenes. Stump removal for extractive recovery and other uses would not only make the cutover and selectively logged areas more adaptable to advanced forest management and improved reforestation practices, but would likewise be another step in further utilization of western pine forest areas.

IN THE commercial production of extractives from southern pine trees, four different methods are employed in this country. These processes include solvent extraction of pine stump wood, collection of oleoresin from the living tree, recovery of tall oil from the sulfate pulping process, and the destructive distillation industry. All these industries, in the main, are confined to the southeastern states, predicated upon the fact that southern pines, largely longleaf and slash, are the richest source materials for these products and are particularly adaptable to these processes. The average annual value of these combined pine extractive products gives them a foremost place among southern industries.

Some thirty-two years ago Betts (*4*) and Schorger (*9*) found that it is possible to obtain considerable yields of naval stores from living ponderosa pine. In any case, no consequential commercial installation for turpentining ponderosa pine has been put in operation, perhaps because it could not compete with the well established southern pine naval stores industry. Perhaps another contributing factor was the beginning some thirty years ago of the recovery of rosin, turpentine, and pine oil from southern pine stumps which augmented the naval stores supplied by the living tree. It is of interest that the genesis of the stump wood extraction industry was based largely on the premise, since proved erroneous, that the living tree would soon cease to be a commercial source of rosin and turpentine.

The practice of the wood rosin processing industries is to allow the stump to remain in the ground ten years or so, which permits the bark and relatively anemic sapwood to slough off and leave the rosins and other extractives in the more concentrated heartwood. The harvested stumps are shipped to the plant, hogged, and extracted with a suitable volatile solvent, usually a petroleum naphtha cut. Solvent, turpentine, intermediate terpene cuts, and finally pine oil are fractionally separated, and a residue of crude wood rosin remains. The crude rosin is composed of approximately 85% resin acids, 5% esters, and 10% resenes (*6*). These seasoned pine stumps are reported to analyze approximately 18% water, 5% terpene oils, 22% rosin, and about 4% of a gasoline-insoluble resin (*7*). It appears that these percentages have been materially reduced in some instances, particularly where younger stumps are being used which contain more moisture and less resinous material. Another contributing factor for lower yields is that some areas are being restumped and these less resinous stumps, which were formerly passed by, are now being processed. This reduction in the quality of southern pine stumps has caused extractive recovery to be reduced to as little as 240–260 pounds of rosin and 70 pounds of volatile per ton of stumps in some regions.

Ponderosa pine, in addition to being able to produce gum oleoresin, is relatively rich in extractives as shown in previous investigations (*1*, *2*, *3*). The distribution of extractives in ponderosa pine is not uniform in the trunk of the tree, and the greatest quantity of this component was found at the butt log nearest the stump (*2*). This suggested that ponderosa pine stumps might contain sufficient quantities of extractives to warrant their removal and subsequent processing for extraneous components. This would be conducive to better forest practices and management since stump removal would, among other things, make the area more adaptable for reforestation by natural propagation or tree farming methods. This investigation is concerned with the quantity and nature of acetone-soluble extractives from ponderosa pine stumps. Acetone was chosen as the solvent, since it has good extractive power for the various extraneous components in this conifer.

METHOD OF SAMPLING

Since the distribution of extractives is not uniform, a method of stump sampling had to be devised which would be representative. After several attempts the following sampling procedure was found satisfactory. Three holes were bored, at ground level, to the pith of the stump with an auger and bit, each hole being about 120° apart. This was repeated at the middle and top levels of the stump (Figure 1). The borings from the nine holes were thoroughly mixed and sent in moisture-tight containers to the laboratory for analysis. From five to ten stumps were sampled at each site. Trained and experienced foresters collected these samples, and after the site was decided upon, the stumps for sampling were chosen at random to give as nearly as possible the total percentage of extractives that would be obtained if all the stumps at that site were removed and processed. The best forest practice would necessitate the removal of all the stumps and not just a portion of them. In the event that such a procedure would be prohibitive because of the too low over-all extractive yield, it would be relatively simple to select only the richer stumps, whether it amounted to 50%, more or less, of the stumps in any one particular area. Whichever procedure would eventually be employed, whether it be total or partial removal, its adoption would be beneficial to forestry practice in addition to supplying additional revenue from the cutover and selectively logged areas. The western pine stumps are now wasted, and any profitable use to which they could be put would be advantageous from many points.

It is important to note here that these samples represent the entire stump, including sapwood as well as heartwood, since most stumps which have seasoned up to five years are sound throughout. In the case of southern pine stump extraction, as previously noted, only the richer heartwood is included in the main. This initial report on ponderosa stump extractives deals with stumps

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[1] The first three articles in this series appeared in 1944 (*1*) and 1946 (*2*, *3*).

that have seasoned in the ground a maximum of four years, representing 108 stumps taken from thirteen sites and four states—namely, Oregon, Washington, California, and Arizona. The samples were collected between the latter months of 1944 and early 1945.

EXTRACTION AND ANALYSIS

Upon arrival at the laboratory, the stump borings were ground in a Wiley mill to pass a 2-mm. screen. Four to six grams of the composite ground sample were weighed in duplicate into alundum extraction thimbles and extracted in all-glass Soxhlet extractors with C.P. acetone for 8 hours. After extraction, the extracted residues and thimbles were put in tared weighing bottles, air-dried for several hours, transferred to a 105° C. oven for 16 hours, cooled, and weighed. The loss in weight here represented the amount of moisture and extractives present in the sample, uncorrected for solvent retention. The moisture content of the samples was determined by the toluene method (*10*) since oven procedure would cause the value to be high because of the presence of volatile oils in the stump. The acetone solvent retention in oven-dried extracted stump wood was also determined, as reported previously (*2*) and was found to average 0.5% based on the oven-dry weight of the extracted wood residue. The quantitative analyses reported here have been corrected for solvent retention.

The extract from all the samples from each site was combined and analyzed for water and ether insolubles, water solubles, resin acids, free fatty acids, volatiles, esters, and unsaponifiables, according to the procedure adopted for the analysis of acetone-soluble extractives from various parts of the ponderosa pine tree (*2*). The amount of each of these components is reported in per cent based on weight of extract and in per cent based on the green weight of the stump (Table III).

QUANTITY OF EXTRACTIVES

Table I summarizes the amount of acetone-soluble extractives found in ponderosa pine stump sapwood and in heartwood. Eleven stumps which had seasoned for 2 months to 5 years in the ground were sampled separately for sapwood and for heartwood to determine the amount of extractives which each of these parts of the stump would yield. The average of the heartwood sections yielded 26.9% extract, based on the moisture-free stumps, while the sapwood gave 9.1% extract, or approximately one third as much as the former. Thus it is apparent that if only the richer heartwood were used in extraction, a material increase in extractive yield would be realized over that obtained from the whole stump.

Table II lists the yields of extractives from 108 whole stumps (sapwood and heartwood). There is a wide variation of extractive content in the various stumps, the poorest containing 5.8% extract, while the richest analyzed 34.3% extract based on the green weight of the stump. However, from the standpoint of commercial stump extraction, the over-all average yields which any particular stump site might give is of greater significance for interpreting end value. The poorest site, Wahler Creek, Calif., averaged 11.6% extract; the richest site, Bates, Oreg., averaged 21.8% extract (green stump weight). The average for all the sites was 17.0% or 340 pounds of extract per ton of stumpwood. If this latter figure is compared with the yield of 31% extractives from the ten-year-old heart stumpwood of southern pine, the average of these western pine stumps will give a little over half the amount of extractives reported for southern pine stumps (*7*). However, this comparison in extract yield from each of these pines is hardly justified, because of the many contributing factors which affect extract yield; among them may be mentioned percentage of heartwood processed, age of stump, amount of moisture present, nature of stump site, and degree of stump selection.

Table I. Extractives in Sap and Heart Stumpwood

Seasoning Time	Diam., Inches	Extractives, %[a] Heart	Sap
2 months	22	19.1	10.3
2 months	16	23.3	13.7
1 year	36	29.6	12.1
1 year	22	20.7	10.4
1 year	30	26.8	5.2
1 year	29	22.0	10.4
2 years	32	26.5	10.5
2 years	28	36.8	10.9
3 years	40	26.2	1.1
3 years	40	28.9	..
4 years	26	36.8	6.3
	Average	26.9	9.1

[a] Based on moisture-free wood.

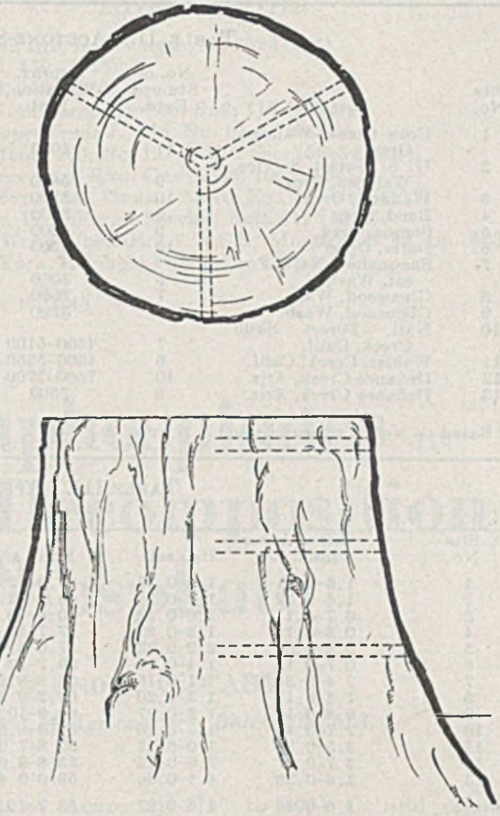

Figure 1. Method of Sampling Stumps

NATURE OF STUMP EXTRACTIVES

Table III gives the approximate composition of ponderosa pine stump extract. The first figure represents percentage composition based on weight of the extractives; the second figure represents percentage yield based on green weight of the stump. On the whole, the nature of the extractive isolated from each site does not vary a great deal in composition. In general, the composition of stump extractives is not expected to be effected materially from freshly cut to five-year-old stumps. Thus the average ponderosa pine stump extractive composition may be summarized briefly as follows (Table III):

H_2O–Ether Insoluble. This fraction may consist of phlobaphenes, natural pigments (*8*), and perhaps some resenes. This component is a minor entity, amounting to only 1.6% of total extractives, and may be in the same category as the gasoline-insoluble resenes found in southern pine stump extract.

H_2O Soluble. Perhaps this component would include sugars, cycloses, simple carbohydrates, and salts, if present (*8*). This constituent is likewise a minor one and, again, may be comparable to the water solubles in southern pine stump wood. The quantity present is only 1.6% of total extract.

Resin Acids. This is the major entity in ponderosa stumpwood extract, amounting to 58.7% of the extract. This fraction

Table II. Acetone-Soluble Extractives from Ponderosa Pine Stumps

Site No.	Location	No. of Stumps Extd.	Approx. Elevation, Feet	Year Trees Felled	Diam. of Stump, Inches	Approx. Ring Count	Extractives, %[a] Dry basis Range	Dry basis Av.	Green basis Range	Green basis Av.
1	Crow Creek, Wallowa, Oreg.	11	4000	1943	18–38	150–200	16.1–28.2	21.5	14.5–25.8	19.4
2	U. S. Forest Service, Wallowa, Oreg.	9	5800	1943	22–36	150–300	10.9–29.9	21.8	10.0–27.9	20.2
3	Wallowa, Oreg.	10	3800	1944	18–40	130–250	12.2–39.9	20.6	10.6–34.3	18.0
4	Bend, Oreg.	9	3800	1944	20–36	200–250	10.7–37.9	20.6	10.2–33.8	18.3
5	Seneca, Oreg.	9	4800	1944	18–32	250–300	14.1–22.9	17.2	12.2–19.9	14.9
6	Bates, Oreg.	10	4200	1944	32–49	250–300	19.8–32.9	26.5	17.1–29.5	21.8
7	Snoqualine Natl. Forest, Wash.	5	3000	1944	24–30	225–305	10.1–26.8	17.5	7.9–23.4	14.7
8	Glenwood, Wash.	7	2000	1942	20–36	125–175	7.2–35.6	17.0	6.4–32.4	15.3
9	Glenwood, Wash.	7	3200	1941	14–42	100–300	8.8–35.1	19.5	8.0–32.7	17.9
10	Natl. Forest Skull Creek, Calif.	7	4600–5100	1941–43	28–48	130–300	8.0–23.0	16.8	5.8–19.4	15.6
11	Wahler, Creek, Calif.	6	4000–5350	1942–44	31–42	200–380	9.1–18.8	16.5	6.7–15.7	11.6
12	Defiance Creek, Ariz.	10	7600–7700	1944	18–39	173–488	10.7–26.7	19.0	9.8–24.2	17.3
13	Defiance Creek, Ariz.	8	7600	1943	13–39	213–428	13.4–25.0	17.6	12.1–23.0	16.2
						Average	11.6–29.9	19.4	10.1–26.3	17.0

[a] Based on weight of stumpwood.

Table III. Approximate Composition of Stump Extractives

Site No.	Per Cent[a] H_2O + ether insol.	H_2O sol.	Resin acids	Free fatty acids	Volatile	Esters	Unsaponifiable	Extractives, % Dry basis	Green basis
1	1.6–0.31	1.2–0.23	62.0–12.03	8.8–1.71	4.2–0.81	9.3–1.80	12.8–2.48	21.5	19.4
2	1.6–0.32	1.2–0.24	60.1–12.32	8.4–1.70	5.4–1.09	11.0–2.22	12.1–2.44	21.8	20.2
3	0.7–0.13	1.0–0.18	60.4–10.87	8.9–1.60	4.3–0.77	11.3–2.03	13.4–2.41	20.6	18.0
4	0.8–0.15	1.2–0.22	57.7–10.56	10.9–1.99	5.7–1.04	8.1–1.48	15.5–2.83	20.6	18.3
5	0.6–0.09	2.2–0.33	57.0–8.49	9.7–1.45	4.6–0.69	11.4–1.70	14.5–2.16	17.2	14.9
6	0.7–0.15	1.4–0.31	59.2–12.90	9.0–1.96	6.3–1.37	8.9–1.94	14.5–3.16	26.5	21.8
7	2.4–0.35	1.1–0.16	55.8–8.20	9.1–1.34	5.9–0.87	12.1–1.78	13.5–1.98	17.5	14.7
8	1.1–0.17	1.3–0.20	60.2–9.21	8.3–1.27	3.9–0.60	11.7–1.79	13.5–2.07	17.0	15.3
9	0.8–0.14	1.5–0.27	60.9–10.90	6.9–1.23	8.9–1.59	7.9–1.41	13.2–2.36	19.5	17.9
10	2.7–0.42	1.3–0.20	54.9–8.56	10.1–1.58	8.0–1.27	9.6–1.50	13.4–2.09	16.8	15.6
11	2.5–0.29	1.0–0.12	60.8–7.06	10.0–1.16	4.7–0.54	9.5–1.11	11.5–1.33	16.5	11.6
12	2.7–0.47	2.6–0.45	55.8–9.65	9.5–1.64	4.1–0.71	14.0–2.42	11.3–1.95	19.0	17.3
13	2.4–0.39	4.1–0.66	58.0–9.40	8.1–1.31	5.2–0.84	9.8–1.59	12.3–2.01	17.6	16.2
Average	1.6–0.26	1.6–0.27	58.7–10.01	9.1–1.53	5.4–0.94	10.3–1.75	13.2–2.25	19.4	17.0
Lb./ton of stumps	5.2	5.4	200.2	30.6	18.8	35.0	45.0	340	

[a] First figure in each column, per cent based on weight of extractives; second figure, per cent yield based on green weight of stumps.

would include both the oxidized and unoxidized resin acids, together with some resin acid transformation products. Resin acids are likewise the major component of southern pine stump heartwood extract, amounting up to as much as 18.7% of the stump weight; ponderosa pine averages about 10.0% of resin acids, based on the green stump weight.

Free Fatty Acids. The quantity of free fatty acids in ponderosa pine stumps amounts to 1.53% or 30.6 pounds per ton of raw material. This constituent appears to be foreign to southern pine stump extract. The source of free fatty acids from southern pines occurs in tall oil processing, yielding about 25 pounds of this product per ton of air-dry pulp manufactured which requires about 2 tons of wood (*5*).

Volatiles. Approximately 5.4% of the extract is in the form of terpene fraction, amounting to about 0.9% of the stump weight or approximately 18 pounds per ton of raw material. Southern pine stumps, on the other hand, are reported to yield up to 100 pounds of terpenes per ton of stumps (*7*).

Esters. This is the third greatest entity in ponderosa pine stumpwood, amounting to 10.3% based on extract, 1.75% on stump weight, or 35 pounds per ton of stumps. Since southern pine rosin averages about 5% esters, a ton of this stumpwood would yield about 22 pounds of this fraction (*6*).

Unsaponifiable. The second greatest component of ponderosa pine stump extract is unsaponifiable material, amounting to 13.2% of total extract, 2.25% on stump weight, or 45 pounds per ton of stumps. On the other hand, southern pine rosin contains 10% of resenes or 44 pounds per ton of stumps.

To summarize briefly, whole ponderosa pine stumps which have seasoned up to five years will yield about 17% or 340 pounds of extract per ton of stumpwood. Hence from extract yield standpoint the younger ponderosa stumps do not yield so much as the older southern pine stumps; however, it appears that the more seasoned, sound ponderosa pine stumps (heartwood) will approach the extractive yield of the southern pine stump. In addition to quantity of extract, the nature of each entity must be taken into consideration, irrespective of stump species which play an important role in evaluating stump extraction processes. Thus characterization of each component isolated will help to evaluate in part ponderosa pine stump extractives, and this investigation is underway at this laboratory. In addition to amount and nature of extractives, many other contributing factors enter into the commercial feasibility of stump extraction processes.

APPLICATION OF RESULTS

The determination and analysis of acetone-soluble extractives from ponderosa pine stumps indicated that this forest waste material is a potential commercial source for rosin and other extractive by-products, including free fatty acids, esters, volatile terpenes, and unsaponifiable material. If this new industry is established in the western pine region, which includes twelve western states, not only will the cutover and selectively logged areas become more adaptable to advanced forest management and improved reforestation practices but the value of western pine forest areas will likewise be enhanced. As the result of the cardinal research activities by the leading naval stores industries and some of the Federal Government research laboratories during the last decade, rosin and the other extractives from the pine tree have found a myriad of new uses; it seems probable that the demand for these pine extractive products will continue. It has been estimated that the wood naval stores industry is responsible for annually clearing approximately 200,000 acres of cutover southern pine lands and releasing them for agricultural uses (*7*). This source is not renewable, since the present southern lumber production is largely from young second-growth stands, and the stumps left from second-growth material, which consists largely of sapwood, are not being used by the wood naval stores industries because of their low extractive content. Millions of acres of ponderosa pine stumps are an untapped potential source for the commercial production of extractives, and other millions of acres of virgin ponderosa pine forests will be available to ensure an adequate supply of raw material for many years to come.

A pilot plant with an extractor capacity of 680 cubic feet per charge has been erected for the purpose of extracting ponderosa, sugar, and Idaho white pine lumber, stumps, and other western pine forest and mill wood waste with solvents to determine whether such extraction processes are practical on a commercial basis.

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Acid Pyro- and Metaphosphates Produced by Thermal Decomposition of Monocalcium Phosphate

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Information on the products formed by heating monocalcium phosphate at temperatures below 600° C. has a practical significance in connection with the thermal treatment of superphosphate to produce mineral feed of low fluorine content. Monocalcium phosphate monohydrate is known to undergo partial fusion when it is heated rapidly in the open at 150° to 200° C., and the resultant mixture is converted to stable β-calcium metaphosphate at 600° to 700° C. Fusion can be avoided by first heating the charge at 125° to expel water of crystallization, but further heating in the range 200° to 600° yields an unpredictable mixture of phases, consisting of glasslike amorphous material and one or more of at least three crystalline phases. On the other hand, the anhydrous salt, obtained either by drying the hydrate or by crystallization from solution, readily loses water in an atmosphere of steam at 275° to 300° C. and changes smoothly into calcium acid pyrophosphate with the formation of little or no amorphous material. An essentially pure amorphous material can be prepared by heating extremely thin flakes of monocalcium phosphate monohydrate. At 325° to 350° in steam crystalline acid pyrophosphate is converted into a mixture of two crystalline compounds with more or less amorphous material. The latter, soluble in water, can be leached from insoluble crystalline compounds. One of these compounds is tetracalcium dihydrogen hexaphosphate; the other, γ-calcium metaphosphate. Formation of another crystalline metaphosphate from calcium acid pyrophosphate is enhanced by the presence of sulfate. This modification is structurally similar to, and apparently forms a solid solution with, anhydrous calcium sulfate (anhydrite).

PRODUCTION of feed-grade phosphate by thermal defluorination of superphosphate has raised questions about compounds formed from monocalcium phosphate when it is heated alone or in the presence of calcium sulfate (*4*). The reactions involve loss of water with formation of such compounds as calcium acid pyrophosphate, $CaH_2P_2O_7$, and calcium metaphosphates. As the temperature is increased pyro- and orthophosphates can be formed with accompanying loss of sulfur trioxide when calcium sulfate is present. Preliminary attempts to identify the compounds in laboratory and commercial preparations indicated a complexity to the reactions that is generally characteristic of metaphosphate salts. Further work reported here was undertaken to obtain reliable information on the compounds that may be formed from monocalcium phosphate.

Several monocalcium phosphates from various sources, thought to be typical of both laboratory and commercial food-grade preparations, were used as starting materials. These materials (Table I) differ with respect to the nature and amounts of impurities, crystal habit, and compounds produced upon heating. The laboratory preparations were crystallized from aqueous phosphoric acid solutions essentially as described in a previous article (*8*). Materials No. 1a, 1b, and 1c differ only in the extent to which free acid was removed and represent, respectively, (*a*) material separated from mother liquor with the aid of a porcelain-basket centrifuge, suspended in acetone and centrifuged again, (*b*) the same after two suspensions in acetone with intervening centrifugation, and (*c*) the same after four similar washings with acetone.

Sometimes monocalcium phosphate monohydrate crystallizes in extremely thin flakes which, being undesirable for most purposes in commercial practice, are customarily discarded or redissolved. One crop of crystals (No. 2) obtained in the laboratory showed unusual uniformity in this respect and was included in the study. When this fluffy material was found to change completely into the amorphous state at 300° C., conditions for its ready preparation were successfully worked out. Several lots of fluffy monocalcium phosphate that yielded good amorphous material were prepared by heating 500 ml. of 45% phosphoric acid and 200 grams of monocalcium phosphate monohydrate in a covered beaker in an oven at 110° C. until the solution was saturated, decanting the clear hot solution into a 600-ml. beaker, and allowing it to cool in air. The crust that formed at the surface as the solution cooled was broken up by occasional gentle stirring until presently the solution turned rapidly to a

TABLE I. COMPOSITION OF MONOCALCIUM PHOSPHATES

Prepn. No.	Prepd.	Character of Crystals	Free Acid P_2O_5[a], %	Total P_2O_5, %	CaO, %	SO_3, %	F, %	$Na_2O[K_2O]$, %	Total H_2O[b], %	Total %
1a	In lab.	Euhedral, thin plates, variable	3.37	54.39	19.91	<0.005	0.001	<0.01	25.76	100.06
1b		Euhedral, thin plates, less variable	0.43	55.67	21.61	<0.005	0.001	<0.01	22.27	99.55
1c		Euhedral, thin plates, still less variable	0.05	55.75	22.20	<0.005	0.001	<0.01	21.70	99.65
2	In lab.	Euhedral, extremely thin plates, brownish	0.25	55.47	22.33	0.49	0.001	<0.01	21.75	100.04
3	Commercially	Anhedral, thick plates[c]	0.55	55.56	23.72	<0.005	0.001	<0.01	20.88	100.24
4		Brownish particles and aggregates[c]	0.60	54.14	22.19	0.24	0.086	0.69	21.73	98.48
5		Round granular aggregates[d]	0.46	54.99	23.68	0.43	0.001	<0.01	21.05	100.15
6	In lab.	Large aggregates of small crystals	1.38	60.03	23.32	<0.005	0.001	<0.01	16.57	99.92
7		Large elongated crystals[c]	0.30	60.37	24.24	<0.005	0.001	<0.01	15.50	100.11
8	Commercially	Clean uniformly small prisms[d]	0.12	58.71	24.34	<0.005	0.001	0.20	15.93	98.98

[a] Determined by extraction with acetone (*6*).

[b] Ignition loss determined by heating the sample at 125° for 2 hours and then at 200°, 400°, and 700° C., respectively, for 30-minute periods.

[c] Thin flakes absent.

[d] Aggregates composed of fine grains, needles, and plates.

TABLE II. X-RAY DIFFRACTION DATA FROM IDENTIFIED PHASES

$CaH_2P_2O_7$			$Ca_4H_2P_6O_{20}$		δ-$Ca(PO_3)_2$			γ-$Ca(PO_3)_2$		
Spacing A					Spacing A			Spacing A		
This work	Bale *et al.* (*2*)	Intensity	Spacing A	Intensity	This work	Bale *et al.* (*2*)	Intensity	This work	Boullé (*3*)	Intensity
...	...	..	4.72	0.05	(6.0)	(6.1)	(0.05)	5.72	..	0.05
4.36	4.45	0.15	4.29	0.05	(5.5)	(5.6)	(0.05)	5.48	..	0.05
3.70	3.76	0.70(3)[a]	3.57	0.70(2)[a]	..	(5.3)	(0.05)	5.12	..	0.10
3.30	3.35	1.0 (1)[a]	3.28	0.10	(4.4)	(4.45)	(0.06)	4.73	4.74	0.50
3.15	3.18	0.80(2)[a]	3.13	1.00(1)[a]	(3.90)	(4.00)	(0.06)	4.15	4.16	0.50
2.68	2.70	0.15	2.96	0.02	3.49	3.55	1.00(1)[a]	3.98	..	0.05
2.49	2.50	0.12	2.86	0.07	..	(3.40)	(0.06)	3.58	3.60	0.50
2.31	2.32	0.12	2.77	0.10	..	(3.20)	(0.06)	3.48	3.48	0.70(2)[a]
2.28	...	0.12	2.68	0.20	(2.90)	(3.00)	(0.06)	3.38	3.39	0.50
2.21	2.21	0.20	2.61	0.08	2.80	2.83	0.70(2)[a]	..	3.12	($Ca_4H_2P_6O_{20}$)
2.16	...	0.10	2.50	0.08	2.48	2.50	0.20	3.10	..	0.03
2.04	2.05	0.10	2.25	0.15	..	(2.44)	(0.06)	3.00	2.98	0.40
1.92	1.93	0.18	2.15	0.30(3)[a]	2.28	..	0.10	2.86	2.86	0.40
1.902	...	0.18	2.05	0.04	2.19	..	0.25	2.75	2.76	1.00(1)[a]
1.852	1.84	0.08	2.00	0.07	2.14	..	0.05	2.60	..	0.05
1.818	...	0.10	1.898	0.07	2.07	..	0.05	2.56	..	0.05
1.755	...	0.18	1.845	0.08	2.00	2.02	0.30	2.45	2.45	0.50
1.742	1.72	0.18	1.804	0.05	(1.92)	(1.93)	(0.05)	2.36	..	0.20
1.700	...	0.05	1.784	0.05	1.860	1.87	0.40(3)[a]	2.33	..	0.20
1.659	1.66	0.10	1.758	0.07	1.806	..	0.03	2.27	..	0.05
1.626	...	0.10	1.700	0.15	1.759	1.77	0.35	2.20	..	0.10
1.570	1.585	0.20	1.666	0.12	..	(1.69)	(0.04)	2.12	2.11	0.15
1.568	...	0.20	1.641	0.14	1.645	1.65	0.30	2.09	..	0.05
			1.608	0.18	1.570	1.58	0.25	2.06	..	0.10
			1.544	0.03	1.559	..	0.20	1.99	..	0.05

[a] Numbers indicating orders of intensities of lines.

paste of shiny plates. When the mixture had cooled to room temperature, the crystals were filtered off with the aid of suction, washed repeatedly with acetone until free of acid, dried in air, and rubbed gently in a mortar to break up aggregates.

Laboratory preparations of superphosphate were made in approximately 100-gram lots by mixing the requisite amounts of acid and ground phosphate rock in a beaker and curing the mixture 5 hours on the steam bath (*8*).

EXPERIMENTAL METHODS

The experimental work was concerned mainly with heating the various monocalcium phosphates under different conditions as to temperature, duration of heating, and atmosphere, and with examination of the resultant products by means of x-ray powder diffraction photography, differential thermal analysis, petrographic microscopy, and solubility in water and neutral ammonium citrate solution. In the exploratory work a 1- to 5-gram charge, spread out in a 25-ml. platinum dish, was heated in a small muffle furnace provided with an automatic pyrometer regulator that kept the temperature variation in the charge within ±10° C. of the indicated value. The loss in weight of the charge on heating was noted, and optical and other examinations of the heated material were conducted promptly.

Samples were heated either in ordinary air or in steam. Charges of partially dehydrated materials, such as anhydrous monocalcium phosphate and calcium acid pyrophosphate, were placed in the dry furnace at 200° C. and allowed to come to this temperature before the steam was turned on and the furnace temperature brought to the desired setting. This precaution is necessary in order to avoid hydration of the material at the beginning of the run. Charges heated in steam were cooled in warm air a few minutes before they were placed in a desiccator.

Varying results were obtained, depending upon whether charges were heated directly or in a stepwise fashion to the selected temperature. Stepwise heating gave somewhat more reproducible results, particularly when hydrated monocalcium phosphate was used as a starting material. This salt, when it is heated rapidly, melts incongruently near 150° (*13*), and the accompanying rapid loss of water vapor causes frothing, frequently with loss of material from the container, and formation of a tough mass.

Differential thermal analyses were carried out on starting materials and hydrous products. This method was particularly useful in indicating the various steps involved in the loss of water. The apparatus was similar to the one described by Norton (*11*) with addition of a photographic recording device (*5*). The heating rate was 10° to 15° C. per minute, and the sample weighed about 0.5 gram. The behavior of hydrated monocalcium phosphate, as mentioned in the preceding paragraph, was particularly troublesome. This difficulty was eliminated by limiting analyses to anhydrous monocalcium phosphate or less hydrous materials.

X-ray powder diffraction photographs served to detect the major constituents in the various samples. They were made with CuKα radiation in cameras having a 6.25-cm. radius that gave fiducial markings for film shrinkage corrections. Examination under the petrographic microscope by the standard immersion technique served to characterize the various compounds, and aided in detection of minor constituents and amorphous materials. These examinations were often carried out with difficulty because of the very fine-grained character of most of the products and the admixture of several phases having similar optical properties.

The various compounds were usually first detected by x-ray diffraction photographs of preparations that were mixtures of two or more phases. Such photographs and differential thermal analyses of products were then used together in the search for conditions giving a particular phase in moderate purity. After sufficient knowledge had been obtained about the various phases their solubilities in water, neutral ammonium citrate, 2% citric

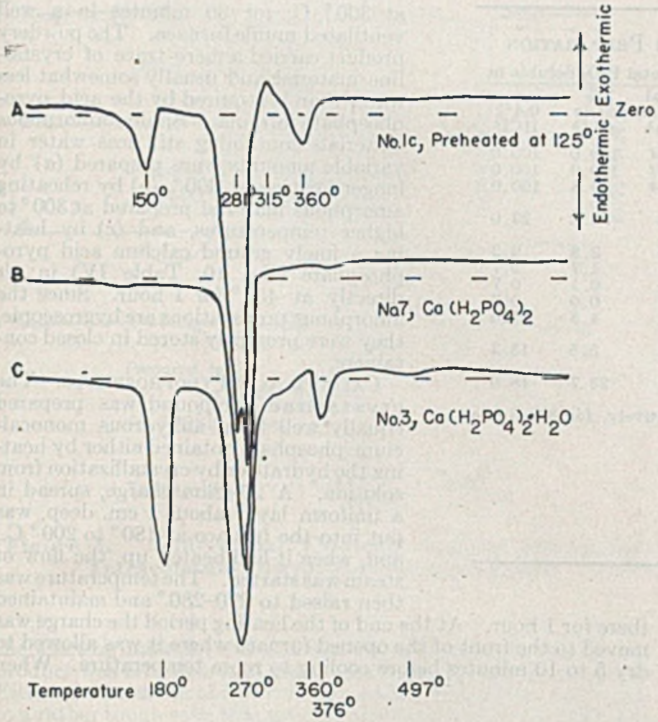

Figure 1. Differential Thermal Analysis Curves for Monocalcium Phosphate

acid, and 0.4% hydrochloric acid could be used for further characterization and also to effect purification.

DIFFERENTIATION OF PHASES

X-RAY DIFFRACTION CHARACTERISTICS. X-ray powder diffraction data from four compounds encountered in the work are listed in Table II together with measurements from recent literature. Two of these compounds are modifications of anhydrous calcium metaphosphate and are here designated as gamma and delta to distinguish them from the alpha and beta forms which have previously been described as stable phases in the system calcium oxide-phosphorus pentoxide (*7*). The gamma modification was described by Bouiié (*3*) and Bale *et al.* (*2*) listed measurements on a material that in the light of our data consisted chiefly of the delta form with some hydrous hexaphosphate ($Ca_4H_2P_6O_{20}$) as an impurity.

Diffraction data from two hydrous crystalline phases are also listed in Table II. Calcium acid pyrophosphate has previously been measured by Bale *et al.* (*2*) and has been prepared on a semicommercial scale by at least one concern. Interplanar spacing values for both the acid pyrophosphates and δ-metaphosphate listed by Bale *et al.* (*2*) are about 1% higher than the authors' values in the range above 2.0 Å.

THERMAL ANALYSIS CURVES. Differential thermal analysis records from three of the ten monocalcium phosphates used in this work are reproduced as Figure 1. Both endothermic and exothermic reactions are indicated, and variations among the several samples are to be noted. Absence of the endothermic peak in the region of 150–180° C. in sample 7 (curve *B*) and its presence in sample 3 (curve *C*) indicates that it corresponds to the reaction.

$$Ca(H_2PO_4)_2.H_2O \longrightarrow Ca(H_2PO_4)_2 + H_2O$$

The endothermic peak in the region 270–300° corresponds to loss of water from monocalcium orthophosphate. This, as will develop, can give rise to various products, the nature of which determines the water loss in the reaction region, the temperature range of the region, and the behavior of the sample at higher temperatures. Breaks in this peak as shown on curve *A* are due to frothing of the material, as previously discussed. Water loss in the region of 360–400° is later correlated with the presence of crystalline acid pyrophosphate, which is formed only to a minor extent under the conditions of analysis for samples 1c and 3 (Figure 1) and is essentially absent for sample 7. The exothermic peak (curve *A*) corresponds to recrystallization of amorphous materials.

Differential thermal analysis records from essentially pure samples of calcium acid pyrophosphate are shown in Figure 2. A difference in behavior is indicated for the two samples, the exothermic reaction of the one (curves *B* and *C*) being absent from the other (curve *D*). In curve *B* the exothermic process started before completion of the endothermic reaction and thus caused two apparent endothermic regions. Acid pyrophosphate can lose water to give β-, γ-, or δ-metaphosphate as well as some hexaphosphate and amorphous material. Amorphous material is readily identified by microscopic examination, and is indicated by exothermic reactions and by the presence of water-soluble phosphorus.

Amorphous material was obtained from (*a*) acid pyrophosphate at about 450° C., (*b*) coarsely crystalline anhydrous monocalcium phosphate at about 300°, and (*c*) extremely thin flakes of monocalcium phosphate monohydrate at 300°. It contained appreciable water, and the thermal stability depended upon the water content. Differential thermal analyses records from three samples are shown in Figure 2.

An odd result, not reproduced in several additional trials, was obtained on one sample of monocalcium phosphate (curve *A*, Figure 2) for which differential thermal analysis was carried out in an atmosphere of steam. Loss of water first gave an amorphous product (280° C. peak) which recrystallized in part to acid pyrophosphate (300° peak). At a slightly higher temperature (350° peak) the acid pyrophosphate in turn lost water to form amorphous material in part (360° peak) and then continued to give one of the metaphosphate modifications (380° peak). This formation of a double peak in decomposition of acid pyrophosphate was very confusing at first, and much effort was devoted to identification of a possible new hydrous phase, until it was demonstrated that the effect was really due to alternative courses of decomposition of the acid pyrophosphate.

In the early stages of the work small endothermic reactions were noted at temperatures greater than 500° C., as shown by curves *B* and *C* of Figure 3. The phase responsible for this high temperature peak was finally prepared relatively pure and gave curve *A* in Figure 3. Chemical analyses indicated that the formula of the compound is probably $Ca_4H_2P_6O_{20}$.

Peaks on differential thermal analysis curves were not observed for transitions of calcium metaphosphate. However, x-ray diffraction photographs indicated that samples heated to 700° were always the beta form, and transition of the gamma modification to the beta form was found to take place at temperatures as low as 500° C. Absence of peaks is due to the sluggish nature of the transitions and to the small amounts of heat involved. All results indicated that the gamma and delta modifications of calcium metaphosphates are monotropic forms.

TABLE III. OPTICAL CONSTANTS OF CRYSTALLINE COMPOUNDS

Compound	Indices of Refraction			2V	Optical Character	Habit
$CaH_2P_2O_7$	1.510	...	1.578	..	...	Oval plates
$Ca_4H_2P_6O_{20}$	1.592	...	1.606	..	...	Square or oblong plates with rounded corners
δ-$Ca(PO_3)_2$	1.583	...	1.594	60°	(+ ?)	Plates
γ-$Ca(PO_3)_2$	1.568	1.570	1.572	75°	(+ ?)	Irregular plates, blades; extinction ‖ moderate cleavage
β-$Ca(PO_3)_2$	1.573	1.587	1.596	80°	(−)	Prisms
α-$Ca(PO_3)_2$	1.587	1.591	1.595	90°	(−)	Plates, laths, 2 perfect cleavages

Table IV. Chemical Composition and Solubility of Phase Preparation

Sample No.	Compound	H_2O[a], %	CaO, %	SO_3, %	Total P_2O_5, %	% of Total P_2O_5 Soluble in: Neutral ammonium citrate[b]	2% citric acid[b]	0.4% HCl[c]
9	Calcium acid pyrophosphate	8.95	26.00	...	64.87	100.0[d]	100.0	100.0
10[e]	Calcium acid pyrophosphate	12.33	25.40	...	61.60	97.4[f]	100.0	100.0
11	Amorphous phase	5.50	26.66	...	66.27	100.0[g]	99.8	100.0
12	Tetracalcium dihydrogen hexaphosphate	2.35	32.78	...	64.27	72.1	4.3	23.0
	Calcium metaphosphate							
13	Delta	1.00	23 50	2.0	60.67	86.2	3.8	9.2
14	Gamma	1.45	29.84	.	68.22	89.4	1.7	5.7
15	Beta	0.00	28.9	...	70.8	19.1	0.1	0.7
16	Alpha	0.00	28.9	...	70.8	10.4	0.0	0.7
17	Vitreous	0.00	29.0	...	70.8	98.8	4.5	24.0
18	Calcium sulfate–metaphosphate complex	0.07	35.63	32.98	28.23	65.4	3.5	13.2
19	Calcium sulfate–metaphosphate complex	0.90	33.11	31.30	23.96	73.7	23.7	48.0

[a] Ignition loss determined by heating the sample at 400° and 600° C., respectively. for 30-minute periods.
[b] Official method for available phosphates in fertilizers (*1*) was used.
[c] Method of Reynolds *et al.* (*12*) was used.
[d] Water-soluble P_2O_5 99.9% of total.
[e] Material was supplied by a commercial concern.
[f] Water-soluble P_2O_5 68.0% of total.
[g] Water-soluble P_2O_5 92.9% of total.

OPTICAL CONSTANTS OF PHASES

Results of optical measurements on the several compounds as well as previously reported values (*7*) for α- and β-calcium metaphosphate are given in Table III. Values listed by Bale *et al.* (*2*) for calcium metaphosphate are those for the alpha form, which is not tetragonal as they indicate, whereas their x-ray diffraction data, as previously noted, correspond to the delta modification.

The high birefringence of the acid pyrophosphate makes it the most readily recognizable phase. The small size and habit of the crystals, however, prevent reliable measurement of the intermediate index and the optical character. This also is true for the hexaphosphate. Observed values for the index of the amorphous phase ranged from 1.535 to 1.545.

PREPARATION AND COMPOSITION OF PHASES

Material best adapted to optical measurements was obtained usually in small amounts. Often the sample represented a small portion of a particular zone in a 1- to 5-gram charge. In order to obtain 20- to 100-gram lots of relatively pure samples of the compounds proper conditions had to be determined, and the resulting product sometimes required subsequent treatment. Thus, while heating in air did not result in step-wise decomposition of monocalcium phosphate beyond the anhydrous salt, heating in an atmosphere of steam was found to bring about a definite and smooth change into crystalline calcium acid pyrophosphate. The acid pyrophosphate could in turn be heated at higher temperatures to form the several metaphosphates. Formation of appreciable quantities of amorphous material was controlled by selection of crystal character of the monocalcium phosphate used as a starting material and by choice of heating temperature. Some amorphous material always appeared in large charges heated above 275° C. Fortunately, this phase and also any residual calcium acid pyrophosphate could be removed from the hexaphosphate and metaphosphates by leaching with water. The materials described below were prepared in platinum vessels. Shallow trays made of stainless steel are also satisfactory containers for use at temperatures up to 600° C.

Chemical analyses of typical quantity preparations of the several compounds are given in Table IV. The proper conditions for the preparation of the gamma and delta forms of metaphosphate and the hexaphosphate are not well enough understood to permit an extension of the methods to larger charges without difficulty.

Amorphous Phase. Ten grams of a fluffy monocalcium phosphate monohydrate consisting of extremely thin plates (No. 2) was spread out in a layer 0.5 cm. deep and heated in air directly at 300° C. for 30 minutes in a well ventilated muffle furnace. The powdery product carried a mere trace of crystalline material and usually somewhat less water than is required by the acid pyrophosphate formula. Similar amorphous materials containing still less water in variable amounts were prepared (*a*) by longer heating at 300°, (*b*) by reheating amorphous material prepared at 300° to higher temperatures, and (*c*) by heating a finely ground calcium acid pyrophosphate (No. 10, Table IV) in air directly at 450° for 1 hour. Since the amorphous preparations are hygroscopic, they were promptly stored in closed containers.

Calcium Acid Pyrophosphate. The crystalline compound was prepared equally well from anhydrous monocalcium phosphate obtained either by heating the hydrate or by crystallization from solution. A 20-gram charge, spread in a uniform layer about 1 cm. deep, was put into the furnace at 180° to 200° C., and, when it had heated up, the flow of steam was started. The temperature was then raised to 270–280° and maintained there for 1 hour. At the end of the heating period the charge was moved to the front of the opened furnace where it was allowed to dry 5 to 10 minutes before cooling to room temperature. When

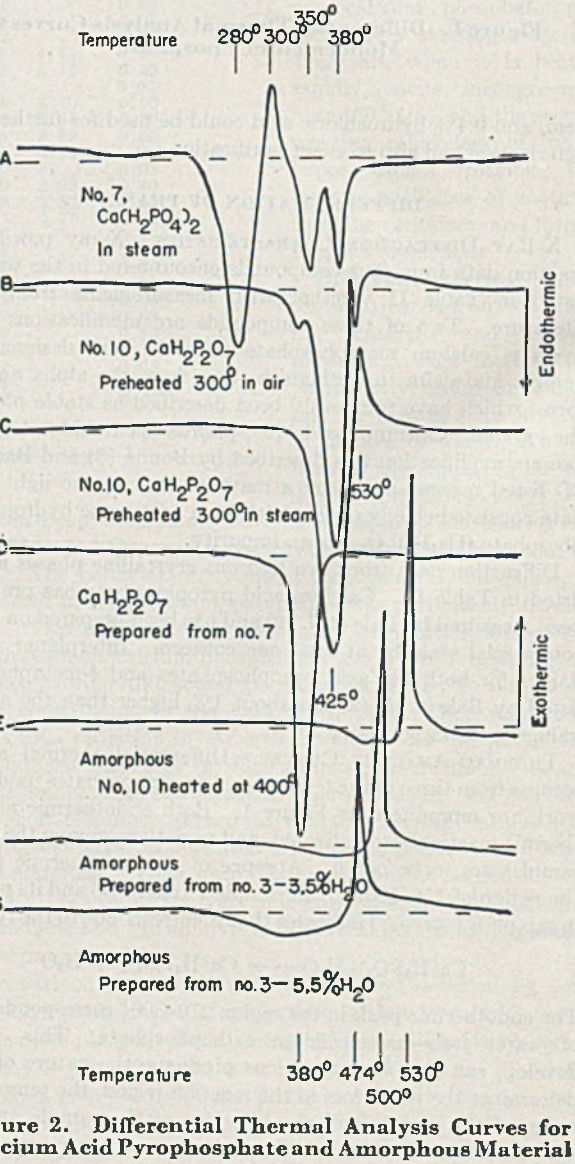

Figure 2. Differential Thermal Analysis Curves for Calcium Acid Pyrophosphate and Amorphous Material

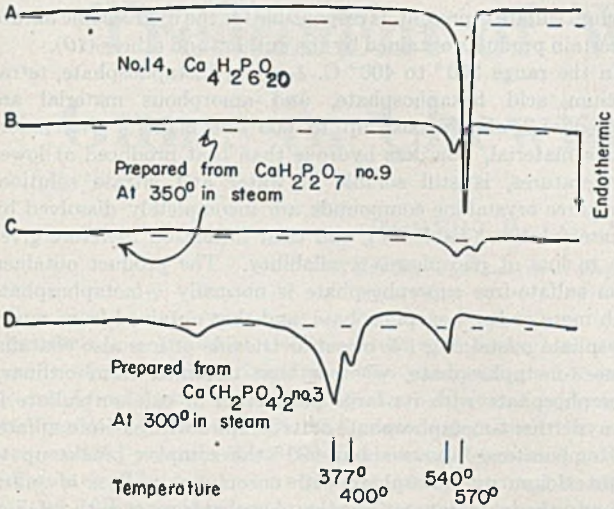

Figure 3. Differential Thermal Analysis Curves for Tetracalcium Dihydrogen Hexaphosphate

the starting material did not contain free phosphoric acid, the product was a friable cake nearly devoid of amorphous material. Either the presence of free acid or a higher temperature gave rise to a rather tough cake that usually contained a notable amount of amorphous material.

Small charges of a monocalcium phosphate with the phosphorus-calcium ratio required by the formula gave optically homogeneous products that carried almost exactly the water required (8.34%) for $CaH_2P_2O_7$. Material obtained by heating larger charges of other monocalcium phosphates contained more water (No. 9, Table IV) and was slightly hygroscopic—a condition that is attributable to the presence of amorphous material. The water content of the commercial acid pyrophosphate (No. 10) was reduced to 8.5%, with an accompanying improvement in crystallinity, by heating it in the manner already described.

TETRACALCIUM DIHYDROGEN HEXAPHOSPHATE. A 10- to 30-gram charge of crystalline calcium acid pyrophosphate in a layer 1 to 2 cm. deep was heated rapidly to 300° C. in air; then, with steam flowing into the furnace, the temperature was raised to 325° and maintained there for 1 hour. Under these conditions 30 to 60% of the heated charge was unaltered acid pyrophosphate, which was removed by leaching the charge repeatedly with cold water until the extract was only slightly acid and then several times with hot water. The resultant water-insoluble product, which contained 80 to 99% of the hexaphosphate with some γ-metaphosphate, was washed once with acetone and dried at 105° C.

The chemical analysis of an optically homogeneous preparation of this phase is: P_2O_5 63.38%, CaO 32.90%, and H_2O (between 400° and 700° C.) 3.2%. The hydrous nature of the compound is indicated by a sharp break at 560° in the thermal analysis curve of this sample (curve *A*, Figure 3). The analysis gives a P_2O_5–CaO weight ratio of 1.925 in comparison with the value of 1.898 required by the formula $Ca_4H_2P_6O_{20}$.[1] The observed value for water exceeds the formula requirement by 0.5%.

δ-CALCIUM METAPHOSPHATE. A 30-gram charge of sulfate-containing double superphosphate, spread in a layer 1 to 2 cm. deep, was heated in air at 200° C. for 1 hour and then at 500° for 1 hour. This was Tennessee brown-rock double superphosphate (No. 1362): P_2O_5 48.37, CaO 18.48, Al_2O_3 0.98, Fe_2O_3 (total Fe) 1.25, and F 1.15%, respectively (*8*). The heated material was leached with water, as described for preparing the hexaphosphate, to remove the relatively small amount of water-soluble phosphate (amorphous material), washed with acetone, and dried at 105°. The product (No. 13) carried practically all of the aluminum, iron, sulfur, and silica contained in the superphosphate; it gave a good x-ray diffraction pattern, which, aside from quartz lines, was identical with the pattern of the type specimen (Tables II and III) of δ-metaphosphate prepared from pure monocalcium phosphate.

γ-CALCIUM METAPHOSPHATE. Crystalline calcium acid pyrophosphate prepared from sulfate-free monocalcium phosphate was heated in steam and then leached with water, as described for preparing the hexaphosphate, with the exception that the final temperature was 340° to 360° C. The slightly caked charge broke down into a sandy product that was practically free of amorphous material only when the initial acid pyrophosphate was wholly crystalline. The final product contained more or less hexaphosphate as an impurity, the amounts of which appeared to depend upon the parent monocalcium phosphate. The low phosphorus-to-calcium ratios of γ-metaphosphates prepared in this manner are due mainly to the presence of hexaphosphate. As the identifiable amounts of the latter compound decrease, the ratio approaches the theoretical value of metaphosphate.

OTHER CALCIUM METAPHOSPHATES. Preparation of the samples of β-, α-, and vitreous metaphosphates, respectively, is described elsewhere (*9*). The vitreous metaphosphate was obtained by fusing a substantially anhydrous material produced by the stepwise heating of monocalcium phosphate to 400° C.; the beta modification by crystallization of the vitreous form at 900°; and the alpha form by inversion of the beta modification at 970° C.

CALCIUM SULFATE–METAPHOSPHATE COMPLEX. Ordinary superphosphate (20% P_2O_5) that had been heated in air at 600° C. for 1 hour or longer was leached with water to remove the free calcium sulfate. Twenty grams of the heated material were agitated with 500 ml. of water for 1 hour, allowed to settle, and decanted through a filter. This treatment was repeated with 30-minute agitations four to six times, or until the ratio of sulfate to phosphate in the supernatant liquid attained a constant value within the precision of the analytical methods. The leached product was washed with acetone and dried at 105°. Two such materials are listed in Table IV; No. 18 was prepared from bone-ash superphosphate, the other from Florida land-pebble superphosphate.

The first indication of the formation of a complex of calcium sulfate and metaphosphate was the absence of diffraction lines of a phosphate component in x-ray powder diffraction patterns of superphosphates that had been heated to 300° to 600° C. (*9*). This evidence was weakened by the later recognition of a delta modification of calcium metaphosphate so closely similar to calcium sulfate (anhydrite) as to be indistinguishable with certainty in patterns of mechanical mixtures of the two compounds. Consequently, the principal evidence for the existence of a complex resides in the change in solubility of the calcium sulfate constituent (Table V) when superphosphate is heated at 600° and 785°, respectively, whereas heating anhydrite under the same conditions does not appreciably alter its solubility. Thus, heating superphosphate at 600° markedly reduces the amount of sulfate that can be readily extracted with water. Further heating at a higher temperature destroys the complex with accompanying formation of calcium pyrophosphate, and the calcium sulfate again becomes readily extractable with water.

SOLID PHASE REACTIONS

The gamma and delta forms of calcium metaphosphate are probably monotropic phases metastable with respect to the beta form, into which they change with moderate rapidity near 600° C. Both are formed in solid phase reactions that involve water loss from calcium acid pyrophosphate, anhydrous monocalcium phosphate, or hydrous amorphous materials. The phase resulting from such reactions is determined by the composition and a

TABLE V. EFFECT OF IGNITION OF SUPERPHOSPHATE ON AMOUNTS OF CALCIUM SULFATE REMOVED BY WATER EXTRACTION

Treatment	X-Ray Identifications	Total SO_3, %	SO_3 Removed in Successive Extractions[a], % of Total		
			1st	2nd	3rd
	Superphosphate No. 2325-b Made from Bone Ash				
Unheated	$Ca(H_2PO_4)_2.H_2O$, $CaSO_4$	31.0	60.0	34.0	5.5
Heated at 600° C.	$CaSO_4$	36.9	6.3	0.9	0.5
Reheated at 785° C.	β-$Ca_2P_2O_7$, $CaSO_4$	27.7	22.6	12.0	6.7
	Superphosphate No. 2261 Made from Florida Land Pebble				
Unheated	$Ca(H_2PO_4)_2.H_2O$, $CaSO_4$	30.8	44.8	32.5	13.2
Heated at 600° C.	$CaSO_4$	35.0	1.5	0.6	0.8
Reheated at 785° C.	β-$Ca_2P_2O_7$, $CaSO_4$	27.8	24.7	14.9	8.2

[a] In the first extraction 3 grams of material were agitated with 400 ml. of water for 1 hour; in subsequent extractions the residue was agitated with 250 ml. of water for 0.5 hour.

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[1] A reviewer suggested that the compound may more properly be designated as a triphosphate, $Ca_2HP_3O_{10}$, against which view the authors have no evidence. The name and formula, however, have not beeh changed.

principle of possible rearrangement of the parent material to that of the product. Ring groups are removed from the reacting system when a solid that can best accommodate them persists irrespective of whether it is the stable phase. This rearrangement from a hydrous phase into an anhydrous one aids in the elimination of water and is aided by the presence of water vapor.

Tetracalcium dihydrogen hexaphosphate, $Ca_4H_2P_6O_{20}$, seems to be a product derived from acid pyrophosphate. Since the $CaO-P_2O_5$ ratio of the hexaphosphate is greater than that of calcium metaphosphate, the acid pyrophosphate decomposition must have also yielded a product with a ratio smaller than that of metaphosphate. The accompanying product appears to be the amorphous phase in all cases. A completely amorphous product can be produced, and in a sense the hexaphosphate can be considered in its formation as competing for pyrophosphate groups that alternatively form more condensed groups.

Amorphous material apparently forms when a dehydration rate is sufficiently rapid to condense many groups before rearrangement into crystalline compounds is effective. It serves to retain water, and its persistence with respect to metaphosphates depends upon the care with which water is removed as the temperature is increased. Magnitudes of heat effects upon recrystallization of amorphous materials indicate that these materials are highly metastable with respect to the metastable metaphosphates. The amorphous materials, moreover, contain in part groupings necessary for formation of crystalline metaphosphates.

Considerable interest attaches to loss of sulfur trioxide from heated superphosphate at temperatures as low as 600° C. Anhydrite when heated alone does not lose sulfur trioxide below 1000° C. Reactions at interfaces with calcium phosphates having $CaO-P_2O_5$ ratios less than that of tricalcium phosphate, however, appear to take place rapidly at somewhat lower temperatures.

COMPOSITION OF HEATED SUPERPHOSPHATE

The establishment of the existence of two low temperature forms of calcium metaphosphate, two hydrous crystalline compounds, and a hydrous amorphous phase, all derivable from monocalcium phosphate, gives a new insight into the probable phosphate compounds in heated superphosphate. Thus, material heated at temperatures under 300° C. may contain crystalline acid pyrophosphate, amorphous material, and, under some conditions, anhydrous monocalcium phosphate in addition to the usual complement of aluminum and iron phosphates, etc. Since both calcium acid pyrophosphate and the amorphous material are soluble in water and citrate solution (Table IV), their formation should not cause loss of phosphorus availability. Amorphous material, which seems to account for most of the phosphate when calcium sulfate is present, is responsible for the hygroscopic nature of certain products obtained by the authors and others (*10*).

In the range 300° to 400° C. δ- and γ-metaphosphate, tetracalcium acid hexaphosphate, and amorphous material are formed and may persist up to 600° or higher. The amorphous material, now less hydrous than that produced at lower temperatures, is still soluble in water and citrate solution. The three crystalline compounds are incompletely dissolved by citrate solution (Table IV), and their formation therefore gives rise to loss of phosphorus availability. The product obtained from sulfate-free superphosphate is normally γ-metaphosphate with more or less hexaphosphate, and that obtained from superphosphate containing 1% of sulfur trioxide or less also contains some δ-metaphosphate, whereas that obtained from ordinary superphosphate with its large proportion of calcium sulfate is always either δ-metaphosphate or its complex with calcium sulfate. At temperatures above about 600° the complex breaks up to form calcium pyrophosphate with accompanying loss of sulfur (*4*), and the low temperature metaphosphates react with calcium sulfate, when it is present, to form calcium pyrophosphate or change to β-metaphosphate.

ACKNOWLEDGMENT

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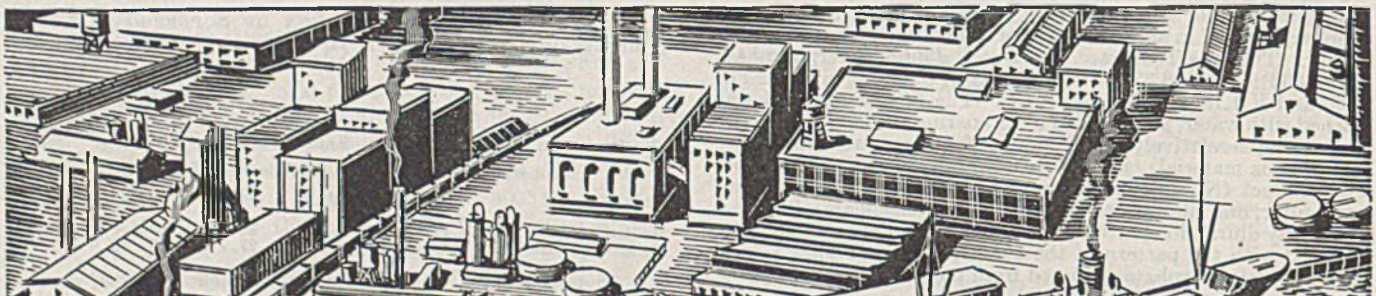

Treatment of Wastes from Natural Gums in Chewing Gum Manufacture

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Studies were made of the chemical and biological treatment of waste resulting from the processing of natural gums for chewing gum manufacture containing, respectively, 31.5 pounds B.O.D., 75.7 pounds total volatile matter, and 8.1 pounds of suspended material per 1000 gallons of waste. The total waste production amounted to about 25,000 gallons a day with a B.O.D. population equivalent of 4700, and 1200 on the basis of suspended solids. Chemical treatment was ineffective. Primary treatment is possible by anaerobic digestion or aerobic sludge treatment, but anaerobic treatment is more easily controlled, is more uniform, more stable, and requires simpler equipment than does aerobic sludge treatment. Reductions of 85–90% of the original B.O.D. may be expected in a 10-day digestion period. Further treatment of the digester effluent may be given by intermittent sand filtration. Effluents with 50 parts per million B.O.D. or less are readily obtained. Chlorination of the sand filter effluent to the extent of 600 p.p.m. reduces the color by approximately 85% and the remaining B.O.D. by 40%. The over-all process reduces the B.O.D. to any desired degree to as high as 98.5 to 99.5% of the original.

BEFORE natural gums are used in the manufacture of chewing gum, they must be cleaned of all sand, dirt, bark, and other undesirable natural material found in the gum as received from its sources.

A wide variety of natural gums from the tropical rain forests of the world is received at the processing plant. They are compounded according to various formulas, thoroughly dry-mixed, steam-cooked, and washed several times with a hot detergent solution containing trisodium phosphate. The cleansed gum is further processed before shipment to the chewing gum manufacturer. The waste involved in the processing of the natural gums prior to chewing gum manufacture is the detergent wash water.

Tests showed that the nature of the wash varied when individual gums were washed. However, due to the facts that many varieties of gum are used and that holding tanks are employed to retain the waste prior to discharge, a degree of equalization is obtained. Extreme variations are found when circumstances necessitate using one of the specific gums in greater quantities than is usual.

The purpose of the work described here was to develop a treatment process for wastes resulting from mixed gums which may vary to a certain extent and are capable of producing an effluent with a biochemical oxygen demand (B.O.D.) of less than 35 parts per million (p.p.m.) and substantially free from suspended solids and color. If such a process could be developed for mixed materials, it would probably work for wastes produced from specific gums.

CHARACTERISTICS OF WASTE

The waste studied is discharged at a temperature of about 140° F. It is colored a deep red and contains large pieces of gum, sand, grit, twigs, and debris. Most of this coarse suspended matter is easily removed by settling from $^1/_2$ to 1 hour in a detention tank, and does not constitute a problem of disposal other than that of removing and disposing of the accumulated sludge at regular intervals. The amount of sludge involved is small.

The data (Table I) show that the waste is of a high pollutional character, as indicated by the fact that the biochemical oxygen demand amounts to 31.5 pounds per 1000 gallons of waste. The major portion of the organic solids present is in the dissolved state, amounting to 75.7 pounds per 1000 gallons, whereas the suspended solids amount to 8.1 pounds per 1000 gallons.

For the entire waste of 25,000 gallons the population equivalents on the B.O.D. basis amount to 4700 and on the suspended solids basis, 1200. Evidently the most important problem is the reduction of the soluble organic substances with high B.O.D. The waste as discharged has a high pH value because of the detergent, but is not well buffered. On standing, natural bacterial fermentation takes place and results in a rapid drop in pH, which reaches neutrality within a few days.

In the manufacturing process each batch of gum is washed several times in succession with clean water. A study was made to determine the distribution of the pollutional load in the separate washes with a view to decreasing the total by elimination of one or more washes. For test purposes batches of gum were washed with five washes, and the washes segregated and analyzed. The results of the analyses are shown in Table II. Approximately 50% of the B.O.D. and an equivalent amount of volatile matter are contained in the first wash. The elimination of the first wash would halve the load placed on a treatment device. However, in most of the processes studied the entire waste was used. The possibilities of eliminating the first wash will be considered in pilot plant studies and will depend on the economics of evaporation, incineration, or hauling away of the initial wash.

Table I. Analysis of Gum Waste

	Typical Anal.	Variations
B.O.D., 5-day at 20° C., p.p.m.	3800	2500–4800
Total solids, p.p.m.	13760	8000–15000
Ash, %	33.9	...
Suspended solids, p.p.m.	970	250–1000
Ash, %	32.0	...
Total alkalinity, p.p.m.	1800	...
Total nitrogen, p.p.m.	220	...
pH	10.5	...

Table II. Analytical Data on Separate Washes

No. of Wash	1	2	3	4	5
B.O.D., 5-day at 20° C., p.p.m.	8700	4200	2175	1066	532
Total solids, p.p.m.	30,100	14,200	7840	4280	2420
Volatile matter, %	74.1	70.9	69.6	70.7	73.1
Flow, gallons/kettle	45	50	56	51	58
B.O.D./kettle, lb.	3.27	1.75	1.02	0.45	0.26
Volatile solids/kettle, lb.	8.35	4.15	2.55	1.25	0.85

TREATMENT PROCESSES

It was apparent from the analyses that at least two processes probably would be required to produce the desired effluent. In any event, the treatment would have to be simple and should require a minimum of control. The amount of waste to be treated was relatively small, 25,000 gallons daily. Economical use of chemicals, therefore, was not of prime importance.

The processes studied were chemical coagulation, aerobic sludge, anaerobic digestion, intermittent sand filtration of the partly treated waste, and chlorination of the filter effluent.

Table III. Results with Chemical Coagulation

Chemical	Dosage, P.P.M.	Reduction in Oxygen Consumed, %	Sludge Formed, %
$Ca(OH)_2$	8350	5	12
$Ca(OH)_2$	6250	5	11
Fe as $FeCl_3$	150	..	..
$Ca(OH)_2$	6250	9	22
$Al_2(SO_4)_3$	150	..	..

Chemical Coagulation. Although the soluble organic nature of the waste made it extremely unlikely that chemical coagulation would prove sufficiently effective, this process was investigated because of the probable presence of colloidal gum.

Experiments with reasonable dosages of 1400 to 2000 p.p.m. calcium hydroxide, of 1400 p.p.m. calcium hydroxide with 112 p.p.m. ferric chloride, and 1400 p.p.m. calcium hydroxide with 102 p.p.m. alum gave no settleable floc and produced virtually no reduction in oxygen consumption. Only when dosages were increased considerably was any floc formed. As an example some typical results are shown in Table III. Increased dosages of chemicals produced larger quantities of sludge but no further increase in reduction of oxygen consumed.

A series of experiments using increasing quantities of gaseous chlorine resulted eventually in very high dosages; the waste was bleached to a light yellow and contained an extremely flocculent precipitate which rose to the surface of the waste. The precipitate amounted to 80% of the total volume; it showed no tendency to compact on prolonged standing and filtered with difficulty. The filtrate from this treatment had an oxygen consumed value equal to about 40% of the original waste. The volume of sludge produced, the relatively low degree of purification, and the cost involved made this method impracticable. Since direct chemical treatment of the waste did not produce the desired results, biological treatment was next investigated.

Aerobic Treatment. A culture for the aerobic treatment of the waste was developed by aerating soil suspended in the waste for several days. The liquid seed thus obtained was fed with waste and aerated for 24 hours. Whatever sludge developed was allowed to settle; the supernatant was removed, and the process repeated. Within a week a flocculent, light tan sludge developed. The sludge was not wasted intentionally, but the daily decanting of the supernatant caused some loss. This apparently took care of the excess sludge, as there was no undue accumulation.

A waste of 2500 p.p.m. B.O.D. was used. Reductions of 21–54% of the B.O.D. were obtained in 24 hours. Analysis of the treated liquor showed only 2.5 p.p.m. of NH_3-N remaining. It was apparent that the high rate of cellular build-up encountered in aerobic sludge necessitated addition of nutrient nitrogen. Accordingly, 125 p.p.m. of NH_3-N as ammonium chloride was added, and a considerable improvement in performance resulted. For comparison the following average 24-hour reductions over a 1-month period with and without added nitrogen are given: average reduction of B.O.D. without added nitrogen, 34.3%; average reduction of B.O.D. with 125 p.p.m. added NH_3-N, 63.3%.

It was concluded that the waste was amenable to aerobic sludge treatment, provided an additional source of nitrogen was added. However, results were extremely variable. With one batch of waste the 24-hour reductions varied from 22 to 85%. Furthermore, use of a different sample from a slightly different manufacturing process resulted in complete dispersion of the sludge, although there was no radical change in the nature of the waste.

Several objections to the use of aerobic sludge were raised. Additional nutrient nitrogen must be added, and changes in the nature of the waste, due to production schedule changes, would possibly upset the process and introduce control difficulties. Moreover, the waste had a tendency to foam, and, despite the aerobic nature of the process, odors were prevalent. Consequently, the investigation was directed toward a study of anaerobic processes.

Anaerobic Digestion. To determine the feasibility of using anaerobic digestion to treat the waste, a series of three laboratory digestion containers was set up, each seeded to half its capacity with well digested sewage sludge. Daily additions of waste amounting to 5, 10, and 20% of the total digester volume were made, corresponding to theoretical 20-, 10-, and 5-day digestion periods. When the digesters were full, supernatant withdrawals equal in volume to the additions were made daily. The mixtures were incubated at 20° C.

The effluents from the digesters were colored deep red but showed a considerable decrease in suspended matter. During the course of digestion the reaction of the digesting waste held steadily at pH 6.5–7.0, the lower value being evident in the 5-day digestion. The pH of the raw waste was about 10; this indicated that the waste was not sufficiently buffered at the high pH to cause difficulties during digestion or to retard the biological processes.

Wastes with B.O.D. values ranging from 2500 to 4800 p.p.m. were used over a 1-month period, and the following average B.O.D. reductions were obtained: 5-day digestion, 61.4%; 10-day digestion, 84.8%; and 20-day digeston, 89.8%.

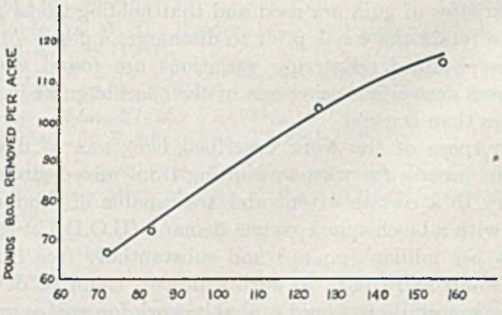

Figure 1. B.O.D. Removal by Sand Filter

An optimum digestion period of about 10 days was indicated. Longer digestion did not give commensurately greater reductions. No control difficulties were encountered. After about three months of operation it appeared that the addition of supplementary nitrogen was unnecessary.

In a continuation of the 10-day digestion for an additional month with wastes of a similar strength, average B.O.D. reductions of 91.7% were obtained. The value of acclimatization is indicated by the fact that the efficiency improved from 84.8 to 91.7% in one month.

Although 10 days was tentatively chosen as the optimum period of digestion for a mixture of all wash waters, further experiments, using a waste from which the first wash had been eliminated, indicated that satisfactory results might be obtained with a 5-day period. For example, with a waste of 2100 p.p.m. B.O.D. a 10-day digestion showed 92.5% reduction, and a 5-day period gave 91.5% B.O.D. reduction. Closer evaluation of digester loadings will be studied on a pilot plant scale.

Studies on gas production by anaerobic digestion showed that from 5.5 to 6.0 cubic feet of gas per pound volatile solids, or from 4300 to 4700 cubic feet a day, may be expected.

Thermophilic digestion was also investigated but was found to be less efficient than mesophilic digestion. B.O.D. reductions were not so high, and larger amounts of suspended matter appeared in the digester effluent.

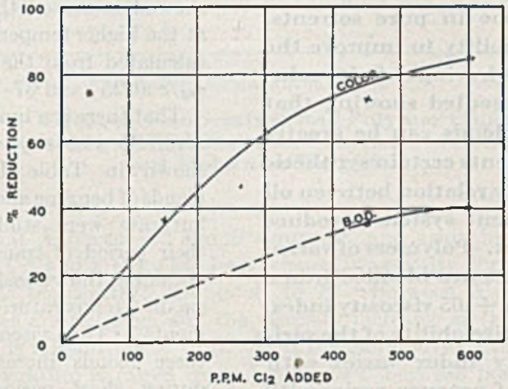

Figure 2. Chlorination of Sand Filter Effluent

Mesophilic digestion of this waste was found to be a process that promised stability and ease of control, and produced effluents relatively low in suspended solids, with B.O.D. values of the order of 250–500 p.p.m. Since a major portion of the B.O.D. could be removed by digestion, further reduction and stabilization were needed by a secondary device to meet the high degree of purification required. For this purpose sand filters were chosen as most likely to produce the desired results.

SAND FILTRATION OF DIGESTED WASTES

Experimental sand filters were used containing 24 inches of mature sewage filter sand over 1 inch of glass beads to support the sand, placed in a 2½-inch glass tube. Effluents from the digesters and aerobic sludge units were placed on the filter three times daily to simulate intermittent filtration. Filters of this size leave much to be desired, but, nevertheless, information of considerable value was obtained from them.

Table IV. Average Results of B.O.D. Removal by Sand Filters

Application Rate, Gal./Acre/Day	Influent, P.P.M.	Effluent, P.P.M.	Removal, %
20,000	432	29.2	96.6
40,000	249	38.6	84.5
60,000	251	43.6	82.7
75,000	250	64.0	74.5

Effluents from the aerobic sludge treatment caused clogging difficulties because of dispersed sludge, and the use of filters receiving this effluent was abandoned.

No clogging was experienced at any time with filters treating digester effluent. The effluent was devoid of suspended matter although it had a deep red color.

Loadings of 20,000, 40,000, 60,000, and 75,000 gallons per acre per day were applied. Average results of one month's operation are shown in Table IV. The results indicate that when adequate digestion was practiced to produce digester effluents of the order of 250 p.p.m. B.O.D., loadings to approximately 40,000 gallons per acre per day could be applied.

The relation between loadings in pounds B.O.D. per acre per day and the quantities removed by filtration is graphically shown in Figure 1. The higher the loadings the greater the removal—in other words, the sand filters could be operated to produce any desired degree of purification within the limits shown.

The effluents contained considerable quantities of nitrates (80 to 100 p.p.m.). The high nitrate content showed the effluents to be very stable. The effluents were satisfactory in all respects except color. Sand filter effluent color was consistently high, having a value of the order of 5000 compared to the platinum cobalt standards of the American Public Health Association.

When a combination of 10-day digestion and sand filtration at loadings up to 40,000 gallons per acre per day was used, over-all B.O.D. reductions of 98.5–99.5% were obtained in treating wastes ranging from 3100 to 4800 p.p.m. B.O.D.

Since the color was obviously not amenable to biological action, chlorination of the sand filter effluent was studied as most likely to produce the desired results.

COLOR REMOVAL IN EFFLUENT

Investigation proved that the high color of the sand filter effluent stemmed from two sources: (*a*) an acid-insoluble material with humic acid characteristics, and (*b*) an acid-soluble fraction. It was estimated that two thirds of the color was due to the former material. This would explain the stability against biological treatment.

Table V. Chlorination of Sand Filter Effluents

Cl_2 Added, P.P.M.	Color Reduction, %	B.O.D., P.P.M.	B.O.D. Reduction, %
0	0	73.3	0
150	37	...	..
300	63	...	..
450	72	46.6	35
600	84	44.6	39

To determine the effect of chlorine on the color of sand filter effluents, samples were treated with varying dosages of chlorine for half-hour contact periods. The percentage reductions of color were obtained by comparing the chlorinated samples against an untreated sample in a colorimeter. Where B.O.D. was determined, proper precautions were made to eliminate all residual chlorine. In all cases corrections were made for dilution. Some results are given in Table V and shown graphically in Figure 2. The results indicate that still higher reductions might be expected with higher dosages or more effective chlorine applications than were possible under laboratory conditions.

The B.O.D. reductions, although small in relation to the dosage, indicate that the sand filters can be operated at higher loadings than 40,000 gallons per acre per day. For example, where a final effluent of 35 p.p.m. B.O.D. is required, a sand filter effluent of approximately 60 p.p.m. will suffice when it is desired to remove color by chlorination. This allows virtual doubling of the load on the filters.

Even though massive doses of chlorine were applied, the residual after one half hour never exceeded 12 p.p.m. No precipitation occurred during the chlorination. The cost of such large doses would not be excessive with a low volume waste of this type.

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POLYMERS AND VISCOSITY INDEX

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A graphical interpretation is presented of viscosity index improvement by certain polymers, using data obtained during a study of the effect of temperature on the viscosity of high-molecular-weight polybutene in pure solvents. An explanation is given as to why ability to improve the viscosity index is limited to polymers having definite solubility characteristics. Data are presented showing that the viscosity index of polymer-oil blends can be greatly enhanced by adding as third components certain synthetic chemicals which reduce the solubility relation between oil and polymer. These three-component systems produce oils of abnormally high viscosity index. Polymers of varied composition and solubility properties are blended into a number of oils varying from −324 to +105 viscosity index. Data and curves show that the relative ability of the various polymers to improve viscosity index varies with chemical structure, and the order of potency varies with the viscosity index of the oil in which they are blended.

AMONG the important characteristics desired in motor oils are low consumption and ease of starting. Increasing high temperature viscosities to improve oil consumption and piston seal, and decreasing low temperature viscosities to improve ease of starting can be combined in the same oil only by improving the viscosity-temperature relation—in other words, by raising the viscosity index. It is generally known that certain polymers of high molecular weight can be added in small amounts to lubricating oils to improve the viscosity index (*2*). Paratone (*7*), a mineral oil blend of polybutene, is an example of a commercial product marketed for this purpose.

A cursory examination of the patent literature shows that not all polymers are capable of producing this effect, not even all of the polymers that are soluble in lubricating oil. Therefore, some explanation of the phenomenon of viscosity index improvement by certain polymers seems necessary in order to understand why other similar polymers are unable to exert this effect.

Considerable data (*3*) have already been given to illustrate the viscosity-concentration relation of polybutene in a number of pure solvents. The data indicate that when a standard polymer was used, the relative solvating properties of solvents could be estimated from the calculated η_{sp}/c at a specified concentration. It was shown that in the case of complete solubility the Arrhenius equation might be applicable at high concentrations:

$$\log \frac{\eta'}{\eta} = Kc$$

where η' = viscosity of solution
η = viscosity of pure solvent
K = experimentally determined constant
c = concentration of polymer in solvent

The equation did not hold, and deviations from it increased as the solvating power of the solvent decreased. In the case of such poor solvents for polybutene as benzene and toluene, the deviation became quite marked. These published curves indicate that, at low concentrations of polymer in solvent, the polymer is completely dispersed and exerts its optimum thickening effect. However, as the concentration of polymer in solvent is increased, the relative thickening power decreases until, at higher concentrations, further addition of polymer has less effect on viscosity.

This range of reduced thickening effect is characterized by abnormal sensitivity to temperature changes. First, viscosities of a number of blends were determined at 25° and 37.78° C. (77° and 100° F.), and the results are given in Table I. Benzene yielded polymer blends that increased in viscosity at the higher temperature; toluene, xylene, and isoamyl caproate gave blends which, in addition, showed increased thickening at the higher temperatures as calculated from the ratio of η_{sp}/c at 25° and 37–78° C.

That there is a limit to this reversed viscosity effect is shown in Table II where blends of benzene and isoamyl butyrate were studied over their period of transition by obtaining the viscosities over small temperature increments. The viscosities of these blends increase only during short periods, after which they again decrease. Similar data have been shown by other workers.

The effect of increasing concentration of polymer in *n*-butyl ether on viscosity at 20° and 37.78° C. was shown in Figure 7 of the previous article (*3*). These curves showed, that, although the viscosities remain widely divergent at the lower concentrations, the lower temperature curve approaches the higher as the range of decreased relative thickening power at the lower temperature is reached.

The blends just described are of theoretical importance only as solvent-polymer blends of this type have little practical significance. However, the use of polymers in lubricating oils to improve their viscosity-temperature relation is not new, and the preceding data have a direct bearing on these oil-polymer blends in that they have aided in explaining the underlying principles of viscosity index improvement by means of certain polymers.

On a graph (Figure 1) having as its axes log viscosity and concentration, three diagonal parallel lines *A*, *B*, and *C* are drawn; they represent the change in viscosity of a polymer-oil blend as the concentration increases at three temperatures *A*, *B*, and *C*, provided the polymer has a constant thickening power over the range of concentration covered. From the preceding observations on polybutene in pure solvents, it can be assumed that this is not the case, but rather the thickening power decreases with increasing concentration. Some point is reached where it agains reverses itself and the thickening power becomes pronounced. A flat S-curve results. Such a curve might be drawn as *A′* (Figure 1). If we can assume from the data that deviation will be less at each concentration at a higher temperature because of greater solubility but that an equivalent deviation will occur at some higher concentration, it should be possible to draw curve *B′* as shown, remaining closer to *B*, yet breaking away at the higher concentration. The same reasoning was used to draw curve *C′*.

At low concentrations of polymer in oil curves *A′* and *B′* tend to coincide with *A* and *B*, respectively. As the concentration of polymer in oil increases, the relative thickening power of the polymer decreases and the curves in each case tend to slope away horizontally from the respective straight lines.

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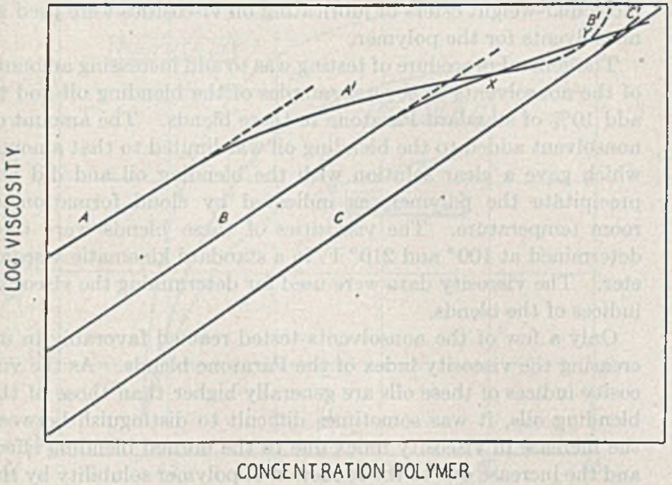

Figure 1. Effect of Temperature and Polymer Concentration on Viscosity of High Polymer Solutions in Solvents of Low Molecular Weight

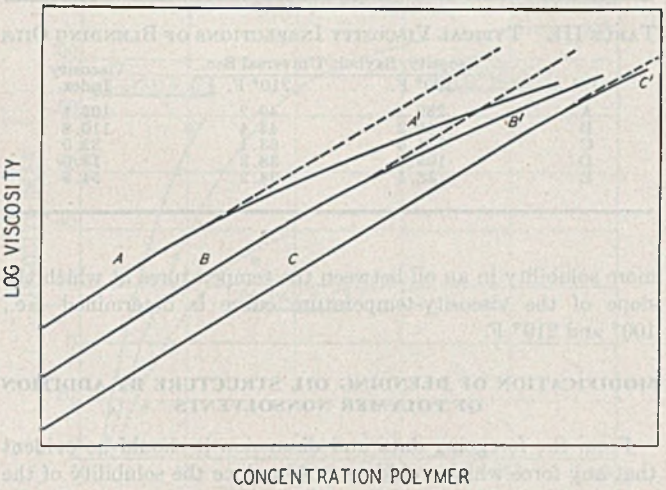

Figure 2. Effect of Temperature and Polymer Concentration on Viscosity of Low Polymer Solutions in Lubricating Oils

At point *X* curves *A′* and *B′* intersect, and again intersect at *Y*. At *X* and *Y* there can be no change in viscosity during the increment temperature change *A′* to *B′*. Between *X* and *Y* the curves are reversed, and the viscosity increases as the temperature is raised from *A* to *B*. It is therefore obvious that, as the temperature is raised from *A* to *B* to *C* between points *X* and *Y*, the viscosity of the polymer blend first increases in viscosity from *A* to *B* and then decreases in viscosity from *B* to *C*.

It should be remembered that the data used to draw the above series of curves were taken from experiments on pure solvents and a polymer nearly ten times the average molecular weight of that used in lubricating oil blends. It would be expected, therefore, that the stability of such blends would be far more critical than those of an oil of relatively high average molecular weight and a polymer of lower average molecular weight. Figure 2 shows a similar series of curves, based on oil and lower-molecular-weight polymer, which are less accentuated than those in Figure 1. These curves corroborate the relation better known to exist in practice.

THEORIES OF FLATTENING OF VISCOSITY-CONCENTRATION CURVE

One explanation for the flattening of the viscosity-concentration curve and the unusual temperature-viscosity characteristics of the blends is the view expressed in an earlier paper (*3*): The polymer exists in two phases—a molecularly dispersed polymer in solvent phase and a mechanically dispersed solvent in polymer phase within the first phase. It must be pointed out that this view is considered to be the very extreme case for the present viscosity-temperature or viscosity index theory.

A second explanation for the flattening of the viscosity-concentration curve and the unusual temperature-viscosity characteristics of blends follows. The intrinsic viscosity of a polymer in a poor solvent is lower than in a good solvent. However, there is little change in intrinsic viscosity with temperature in a good solvent, whereas there is a considerable increase in intrinsic viscosity in a poor solvent. It is necessary, therefore, that any polymer capable of improving the viscosity index of an oil to a great extent must pass through this reduced solubility transition at the temperature of measurement—e.g., within the range 100–210° F. It must show reduced viscosity-improving effect at 100° F. and act normally at 210° F. This is not always possible, and some polymers which pass through this period of transition at other temperatures would do so unobserved by the measurement of "viscosity index."

"Reduced solubility" in the polymer-solvent system mentioned in the preceding paragraph defines a region where at a given temperature the polymer molecules are highly convoluted in solution. At present it is held that the molecules are convoluted because of the very strong self-association factors for the polymer in a poor solvent. Under the convoluted condition the polymer exhibits a low intrinsic viscosity. Also, the convoluted polymer may be easily removed from solution by the addition of a rather small amount of a strong polymer nonsolvent. Experimental proof of this has been given (*3*).

We conclude, therefore, that a polymer capable of improving the viscosity index of an oil must undergo a period of less to

Table I. Viscosity-Temperature Relations of Polybutene[a] in Solvents

Solvent	Viscosity, Centistokes 25° C.	Viscosity, Centistokes 37.78° C.	η_{sp}/c 25° C.	η_{sp}/c 37.78° C.	Ratio
Benzene	2.28[b]	2.47	0.221	0.296	1.34
Toluene	3.49	3.27	0.429	0.440	1.02
Xylene	5.67	5.24	0.678	0.688	1.01
n-Propylbenzene	7.06	6.66	0.690	0.690	1.00
Mesitylene	6.28	5.55	0.690	0.689	0.997
Cymene	9.76	7.89	0.714	0.689	0.966
Amylbenzene	13.75	10.33	0.784	0.740	0.944
Isoamyl caproate	4.86	4.00	0.150	0.182	1.21

[a] Staudinger mol. weight, 104,000; true mol. weight, 1,650,000 by Flory method (*4*). Ten grams polybutene were used per liter of solvent; all solvents formulated clear solutions of polybutene at viscosity test temperature.

[b] Not a true solution at 20° C. (68° F.). A slight blue haze developed when this polymer solution was held at 20° C. for 15–30 minutes. However, at 25° C. a clear solution was obtained and viscosity results could be checked. No precipitation of polymer could be detected within the range of viscosity measurements.

Table II. Viscosity of 10 Grams of Polybutene[a] per Liter of Benzene or Isoamyl Butyrate

C.P. Benzene Temp., ° C.	C.P. Benzene Viscosity of solution, centistokes[b]	Isoamyl Butyrate Temp., ° C.	Isoamyl Butyrate Viscosity of solution, centistokes
25.0	2.31	37.8	35.6
37.8	2.47	40.6	36.2
39.0	2.56	42.2	36.1
40.0	2.58	55.0	35.6
41.0	2.65	60.0	34.0
42.0	2.62		

[a] Intrinsic viscosity of polymer in diisobutylene solution at 20° C. was 3.25:

$$[\eta] = 2.303 \log \text{relative viscosity}/c$$

where $[\eta]$ = intrinsic viscosity
c = grams polymer/100 ml.

This result indicates that the viscosity average molecular weight of the polybutene used was 1,650,000 by Flory method (*4*).

[b] Viscosities were measured in calibrated Ubbelohde suspended-level viscometers.

Table III. Typical Viscosity Inspections of Blending Oils

Oil	Viscosity, Saybolt Universal Sec. 100° F.	Viscosity, Saybolt Universal Sec. 210° F.	Viscosity Index
A	239.2	49.2	102.1
B	158.2	44.4	110.8
C	764.0	63.1	32.0
D	105.8	38.3	13.0
E	58.1	34.2	54.5

more solubility in an oil between the temperatures at which the slope of the viscosity-temperature curve is determined—i.e., 100° and 210° F.

MODIFICATION OF BLENDING OIL STRUCTURE BY ADDITION OF POLYMER NONSOLVENTS

From the foregoing data and discussion it should be evident that any force which would serve to reduce the solubility of the polymer in the blending oil at 100° to a greater extent than at 210° F. should further increase the observed viscosity index of the blend. Such a force might be a chemical which would be completely soluble in the blending oil and be less compatible with the polymer. Some work has been done to check this observation; a few of the experiments are described here.

To make the work as practical as possible, several lubricating oils of different viscosities were used as the polymer solvents. Paratone (7), a blend of polymer in oil, was used as the viscosity index improver, and various vegetable oils and synthetic high-molecular-weight esters of lubricating oil viscosities were used as nonsolvents for the polymer.

The general procedure of testing was to add increasing amounts of the nonsolvents to several samples of the blending oil and to add 10% of standard Paratone to these blends. The amount of nonsolvent added to the blending oil was limited to that amount which gave a clear solution with the blending oil and did not precipitate the polymer, as indicated by cloud formation at room temperature. The viscosities of these blends were then determined at 100° and 210° F. in a standard kinematic viscometer. The viscosity data were used for determining the viscosity indices of the blends.

Only a few of the nonsolvents tested reacted favorably in increasing the viscosity index of the Paratone blends. As the viscosity indices of these oils are generally higher than those of the blending oils, it was sometimes difficult to distinguish between the increase in viscosity index due to the normal blending effect and the increase due to the reduction of polymer solubility by the nonsolvent. In some experiments this was eliminated by first blending the nonsolvent with secondary petroleum oils so that the blending oil and nonsolvent would have similar analyses.

In all cases the relative viscosities

$$\eta = \text{relative viscosity} = \frac{\text{viscosity of polymer blend}}{\text{viscosity of oil}} = \text{a measure of thickening effect of polymer at } 100° \text{ and } 210° \text{ F.}$$

of the several blends were calculated so that the change in polymer solubility as measured by relative viscosity could be observed.

Table IV. Viscosity Data[a] on Various Blends

Composition of Blend	A V. of Solvent Mixt. at 100° F., Cs.	B V. of Mixt. + 10% Paratone at 100° F., Cs.	C R.V. at 100° F., *B/A*	D V. of Solvent Mixt. at 210° F., Cs.	E V. of Mixt. + 10% Paratone at 210° F., Cs.	F R.V. at 210° F., *E/D*	G % Change in R.V., *F − C/C*	H V. of Solvent Mixt. at 100° F., S.U.S.	I V. of Mixt. + 10% Paratone at 100° F., S.U.S.	J V. of Solvent Mixt. at 210° F., S.U.S.	K V. of Mixt. + 10% Paratone at 210° F., S.U.S.	L V.I. of Solvent Mixt.	M Mixt. + 10% Paratone
					Nonsolvent = 30% Castor Oil plus 70% Oil A								
Oil A	51.7	109.2	2.12	7.05	13.79	1.96	−7.56	239.2	504.0	49.2	73.1	102.1	124.0
Oil A + 0.075% nonsolvent	52.4	101.2	1.94	7.11	12.79	1.80	−7.22	242.3	467.0	49.4	69.3	102.3	122.8
Oil A + 0.30% nonsolvent	56.5	98.6	1.75	7.32	12.66	1.73	−1.14	261.3	455.5	50.1	68.8	97.0	123.2
Oil A + 1.00% nonsolvent	51.4	90.2	1.76	7.08	11.71	1.66	−5.68	237.8	416.7	49.3	65.3	104.2	122.0
					Nonsolvent = Butyl Acetyl Ricinoleate								
Nonsolvent	21.4	...	..	5.30	...	.	....	103.4	...	43.3	..	175.2	...
Oil B	33.9	71.6	2.11	5.55	10.96	1.98	−6.16	158.2	330.8	44.4	62.6	110.8	134.4
Oil B + 10% nonsolvent	30.7	63.9	2.08	5.35	10.32	1.93	−7.21	144.0	295.0	43.7	59.9	119.1	136.5
Oil B + 20% nonsolvent	28.6	61.7	2.16	5.10	10.18	2.00	−7.41	134.7	285.2	42.9	59.4	118.6	139.5
Oil B + 30% nonsolvent	27.9	56.2	2.01	5.10	9.66	1.89	−5.97	131.7	259.9	42.9	58.0	125.0	141.7
Oil B + 40% nonsolvent	27.3	52.9	1.94	5.09	9.40	1.85	−4.64	129.0	244.7	42.9	57.2	127.0	144.2
Oil B + 60% nonsolvent	26.1	35.0	1.34	5.07	8.77	1.73	+29.1	123.7	163.2	42.8	55.0	135.0	169.0
					Nonsolvent = 90% Dibutoxy Ethyl Phthalate Plus 10% Oil C								
Oil D	21.96	48.01	2.20	3.63	7.48	2.06	−6.37	105.8	222.2	38.3	50.6	13.0	124.4
Oil D + 10% nonsolvent	19.92	44.3	2.22	3.41	6.97	2.04	−8.12	97.2	205.2	37.6	48.9	8.8	122.4
Oil D + 20% nonsolvent	19.27	44.6	2.31	3.37	7.24	2.15	−6.93	94.4	206.6	37.4	49.8	14.2	128.1
Oil D + 30% nonsolvent	18.33	37.1	2.02	3.26	6.48	1.99	−1.48	90.6	172.6	37.1	47.4	11.2	132.9
Oil D + 40% nonsolvent	18.11	25.6	1.41	3.15	6.07	1.93	+36.9	89.6	121.5	36.7	46.0	9.7	171.7
Oil D + 60% nonsolvent	18.12	23.2[b]	1.28	3.27	7.42	2.27	+77.30	89.7	111.2	37.1	50.4	18.1	188.4
					Nonsolvent = Hydrogenated Castor Oil								
Oil A	51.7	109.1	2.12	7.05	13.79	1.96	−7.56	239.2	504.0	49.2	73.1	102.1	124.0
Oil A + 0.1% nonsolvent	64.6	136.6	2.12	7.08	13.71	1.94	−8.50	298.6	631.1	49.3	72.8	64.5	103.8
Oil A + 0.3% nonsolvent	101.2	192.0	1.90	7.11	13.89	1.95	+2.63	467.5	887.0	49.4	73.5	−43.1	67.1
					Nonsolvent = *n*-Butyl Phthalate								
Nonsolvent	9.70	...	..	2.37	...	..	....	57.8	...	34.2	..	...	...
Oil A	51.7	109.2	2.12	7.05	13.79	1.96	−7.56	239.2	504	49.2	73.1	102.1	124
Oil A + 10% nonsolvent	38.51	71.89	1.87	6.03	10.42	1.72	−8.04	179.0	331.7	46.0	60.7	111.9	128.7
Oil A + 20% nonsolvent	29.89	59.51	1.99	5.06	9.27	1.83	−8.05	140.0	275.1	42.8	56.7	106.0	132.3
Oil A + 30% nonsolvent	26.97	53.56	1.99	4.72	8.75	1.85	−7.04	127.3	247.5	41.7	54.9	102.1	135.5
Oil A + 40% nonsolvent	22.45	36.85	1.64	4.10	6.73	1.64	0.00	107.7	171.2	39.7	48.2	84.3	140.6
Oil A + 50% nonsolvent	18.84	26.82	1.43	3.68	6.19	1.68	+17.5	92.6	126.8	38.4	46.4	81.1	167.0
					Nonsolvent = Triethylene Glycol Di-2-ethyl Butyrate								
Nonsolvent	6.78	...	..	2.00	...	..	....	48.0	...	32.8	..	84.0	...
Oil E	9.79	19.41	..	2.38	4.41	..	....	58.1	95.0	34.2	40.7	54.5	155.0
Oil E + 10% nonsolvent	...	18.30	..	..	4.40	..	....	...	90.4	..	40.7	...	172.0
Oil E + 20% nonsolvent	...	16.60	..	..	4.21	..	....	...	83.5	..	40.0	...	181.0
Oil E + 30% nonsolvent	...	14.92	..	..	3.96	..	....	...	76.9	..	39.3	...	186.0
Oil E + 40% nonsolvent	...	13.27	..	..	3.73	..	....	...	70.6	..	38.6	...	190.0

[a] V. = viscosity, R. = relative, I. = index, Cs. = centistokes, S.U.S. = Saybolt Universal seconds.
[b] Sample cloudy at 15° C.

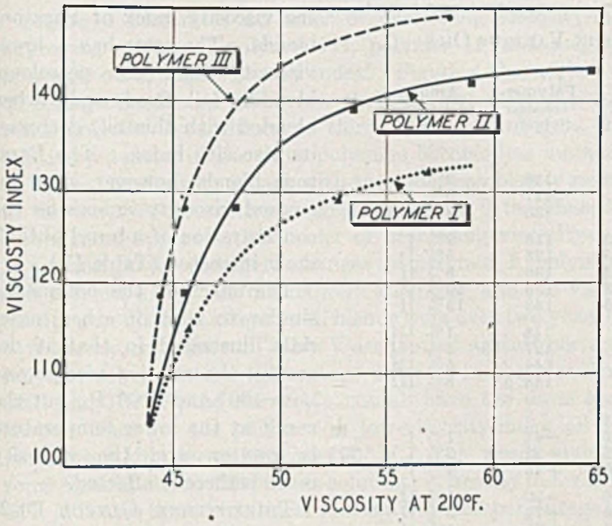

Figure 3. Blends of Additives in Oil F

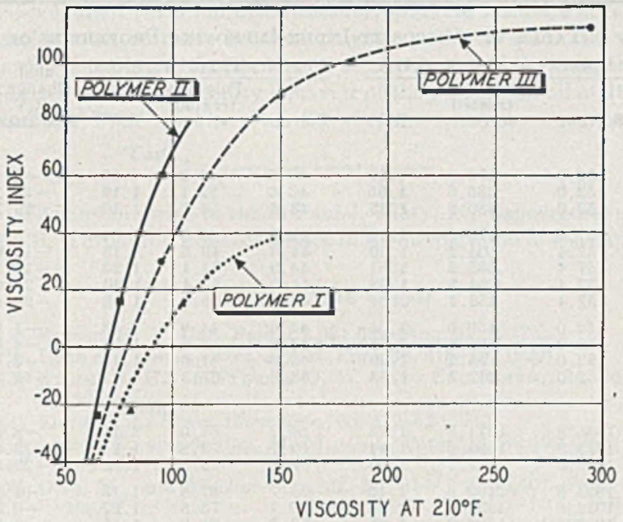

Figure 4. Blends of Additives in Oil G

The calculated percentage change in relative viscosity

$$\% \text{ change} = \left(\frac{\eta_{210°} - \eta_{100°}}{\eta_{100°}}\right) 100$$

is indicative of the selectivity of the nonsolvent for suppressing the viscosity at 100° with less effect at 210° F. Table III gives viscosity data for the petroleum lubricating oils.

Castor Oil. This was one of the first nonsolvent oils studied. A few preliminary experiments determined the solubility limit. For accuracy in blending, the castor oil was first diluted to 30% in oil A. Viscosity data are summarized in Table IV.

For some unknown reason, progressive additions of the nonsolvent through 0.30% slightly increased the viscosity of oil A at both 100° and 210° F., after which at 1% nonsolvent the viscosities nearly returned to those of the original oil. This effect is not in evidence in the Paratone blends of these mixtures, as the viscosities decreased in proportion to the amount of castor oil present. These irregularities are reflected in the percentage change in relative viscosity from 100° to 210° F.

One per cent castor oil considerably decreased the relative viscosities at both 100° and 210° F.—e.g., from 2.12 to 1.76 at 100° and from 1.96 to 1.66 at 210° F. However, because the reduction in relative viscosity is nearly equivalent at both 100° and 210° F., there is no change in the viscosity index of the original blend. It was assumed that, so strong were the nonsolvent properties of castor oil, a negligible improvement in its solubility resulted on increasing the temperature from 100° to 210° F.

Butyl Acetyl Ricinoleate. Viscosity data are summarized in Table IV. Butyl acetyl ricinoleate has both a lower viscosity and a higher viscosity index than the blend oil used, and the improvement in viscosity index might be attributed to normal blending of stocks of high and low viscosity index.

Up to 20% butyl acetyl ricinoleate in the blend of Paratone and oil B, there is no noticeable effect on relative viscosity at either 100° or 210° F. There is a slight increase in the viscosity index, however, which is interpreted as the effect of normal blending of the high-viscosity-index butyl acetyl ricinoleate. Between 20 and 40% butyl acetyl ricinoleate affects relative viscosity at both 100° and 210° F., and to nearly the same degree. The increase in viscosity index is attributed to the reason given above.

At 60% butyl acetyl ricinoleate the relative effectiveness of the nonsolvent at 100° and 210° F. is marked, and the viscosity index and percentage change in relative viscosity at the two temperatures increases markedly.

Dibutoxy Ethyl Phthalate [Di(β-butoxy ethyl)-phthalate]. To eliminate the effect of viscosity and of viscosity index of the nonsolvent on the polymer blends, dibutoxy ethyl

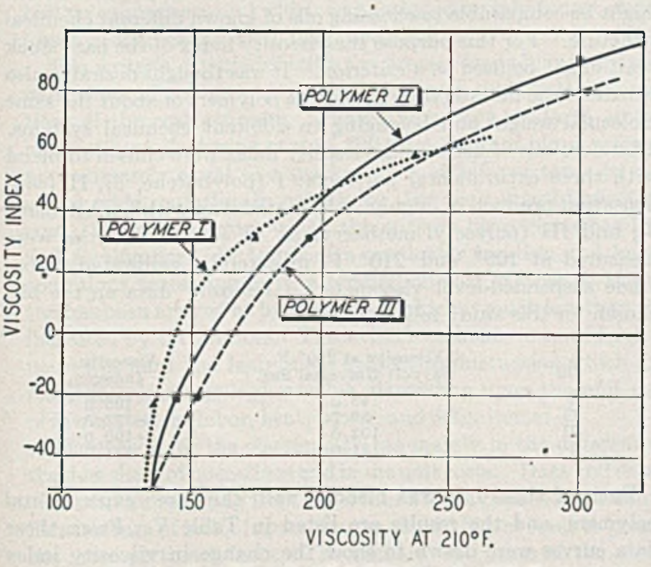

Figure 5. Blends of Additives in Oil H

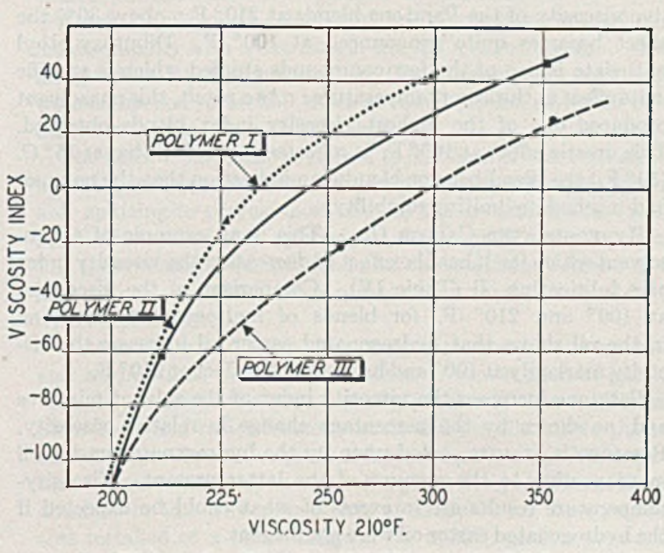

Figure 6. Blends of Additives in Oil I

Table V. Viscosity-Index-Improving Properties of Polymers in Various Oils

Viscosity at 100° F., S.U.S.			Viscosity at 210° F., S.U.S.			Calcd. % Change in R.V. 100–210° F.	V.I. of Solvent	V.I. of Polymer-treated Solvent	Amount of Polymer Used
Solvent	Polymer-treated solvent	R.V.	Solvent	Polymer-treated solvent	R.V.				
				Oil F					
152.0	176.9	1.16	43.6	46.2	1.06	−8.6	105	116	2% I
152.0	235.6	1.55	43.6	52.1	1.19	−23.2	105	127	5% I
152.0	280.6	1.85	43.6	56.6	1.30	−29.7	105	130	8% I
157.4	173.6	1.10	44.0	45.9	1.04	−5.4	105.5	116	2% I
157.4	205.2	1.30	44.0	49.6	1.13	−13.0	105.5	128	5% II
157.4	238.3	1.51	44.0	54.1	1.23	−18.5	105.5	136	8% II
157.4	264.5	1.68	44.0	57.4	1.30	−22.6	105.5	138	10% II
157.4	353.4	2.24	44.0	69.6	1.58	−29.4	105.5	143	15% II
152.0	159.5	1.05	43.6	44.9	1.03	−1.9	105	118	1% III
152.0	168.6	1.11	43.6	46.5	1.06	−4.5	105	127	2% III
152.0	196.2	1.29	43.6	51.6	1.18	−8.5	105	144	5% III
152.0	232.7	1.53	43.6	57.3	1.31	−14.3	105	148.5	8% III
				Oil G					
1035.8	1271.8	1.23	59.7	67.0	1.12	−8.9	−77.6	−42	1% I
1035.8	1493.6	1.44	59.7	73.8	1.24	−13.9	−77.6	−22	2% I
1035.8	2061.2	2.00	59.7	92.6	1.55	−22.5	−77.6	+16	4% I
1035.8	1192.9	1.15	59.7	67.8	1.13	−1.7	−77.6	−20	1% II
1035.8	1331.5	1.28	59.7	75.8	1.27	−0.8	−77.6	+14	2% II
1035.8	1707.8	1.65	59.7	98.2	1.65	0.0	−77.6	+60	4% II
1035.8	1687.2	1.63	59.7	88.5	1.48	−9.2	−77.6	+33	1% III
1035.8	2863	2.76	59.7	155.7	2.61	−5.4	−77.6	+90	2% III
1035.8	4947	4.78	59.7	310.4	5.19	+8.7	−77.6	+114	4% III
				Oil H[a]					
5678.9	6610	1.16	102.0	139.2	1.36	+17.2	−190	−48.9	5% I
5678.9	7510	1.32	102.0	196.0	1.92	+45.4	−190	+38.0	10% I
5678.9	8390	1.47	102.0	231.0	2.26	+53.6	−190	+59.3	15% I
5678.9	6760	1.19	102.0	148.9	1.47	+23.5	−190	−23.0	5% II
5678.9	8510	1.50	102.0	214.0	2.00	+33.0	−190	+42.5	10% II
5678.9	9930	1.75	102.0	308.1	3.02	+72.5	−190	+83.5	15% II
5678.9	6980	1.23	102.0	152.7	1.50	+22.0	−190	−22.2	5% III
5678.9	8740	1.54	102.0	206.0	2.02	+31.2	−190	+30.0	10% III
5678.9	9390	1.65	102.0	289.2	2.83	+71.6	−190	+80.0	15% III
				Oil I					
13,307	15,550	1.16	131	193	1.47	+26.7	−324	−105	5% I
13,307	15,565	1.19	131	237	1.81	+52.1	−324	−13.8	10% I
13,307	15,585	1.20	131	295	2.25	+87.6	−324	+39.0	15% I
13,307	16,300	1.22	131	372	2.84	+133.0	−324	....	20% I
13,307	16,000	1.20	131	208	1.59	+32.5	−324	−63.6	5% II
13,307	18,900	1.42	131	349	2.66	+87.4	−324	+52.0	14% II
13,307	19,200	1.44	131	367	2.55	+78.0	−324	....	15% II
13,307	20,100	1.51	131	478	3.17	+111.0	−324	....	20% II
13,307	22,800	1.71	131	282	2.15	+29.8	−324	−22	5% III
13,307	23,680	1.78	131	349	2.06	+49.4	−324	+29	6.5% III
13,307	29,700	2.22	131	656	5.00	+125.0	−324	....	15% III

[a] Gravity = 1.35, color = 12, aniline point = 127° F., refractive index = 1.543, V.I. = −190, viscosity at 210° F. = 102 S.U.S.

phthalate was first blended with 10% oil C; this mixture gave a viscosity and viscosity index comparable to oil D, the blending oil. Proportionate blends of these two oils gave comparable viscosities and viscosity indices throughout (Table IV).

Dibutoxy ethyl phthalate has practically no effect on the relative viscosity of the Paratone blends at 210° F.; above 30% the effect becomes quite pronounced at 100° F. Dibutoxy ethyl phthalate is one of the few compounds studied which is specific in its effect at the lower temperature. As a result, this nonsolvent produced one of the highest viscosity index blends obtained. This drastic effect at 100° F. is reflected in the fact that at 15° C. (59° F.) the blend became cloudy, an indication that the polymer had reached its limiting solubility.

Hydrogenated Castor Oil. This is an example of a nonsolvent which itself has the effect of decreasing the viscosity index of a lubricating oil (Table IV). Comparison of the viscosities at 100° and 210° F. for blends of hydrogenated castor oil in the oil shows that hydrogenated castor oil increases the viscosity markedly at 100° and has nearly no effect at 210° F.

Paratone increases the viscosity index of the solvent mixtures and, as shown by the percentage change in relative viscosity, Paratone is, in turn, acted upon by the hydrogenated castor oil in proportion to the amount of the latter present. Viscosity-temperature results are in excess of what could be expected if the hydrogenated castor oil were not present.

n-Butyl Phthalate. This ester also has a marked effect on the viscosity index of Paratone blends. The ester has a lower viscosity than the petroleum blending oil used and, when blended with this oil, decreases its viscosity index. The Paratone blends, however, show increased viscosity indices as the concentration of *n*-butyl phthalate is increased (Table IV).

The effect on the polymer is similar to that of other materials illustrated in that it decreases the relative viscosity at both 100° and 210° F., but the result at the lower temperature is greater, and the viscosity index is thereby affected.

Triethylene Glycol Di-2-ethyl Butyrate. Although the data on this ester are abbreviated (Table IV), its effect on the viscosity index is obvious.

Conclusion. The viscosity index improvement derived by adding certain polymers to petroleum lubricating oils can be greatly enhanced by adding a natural or synthetic oil to a polymer-oil blend as a third component. Such an oil should be soluble in the petroleum oil within the range of its addition and be less compatible with the polymer than the lubricating oil. It must further have the ability to reduce the solubility of the polymer as measured by its relative viscosity to a greater extent at 100° than at 210° F., and thereby fulfill the requirements of viscosity index improvement.

POLYMER-OIL STUDIES

From the results of the foregoing study it was postulated that addition of agents to reduce the solubility of the polymer in oils might be comparable to choosing oils of known different chemical structure. For this purpose the viscosity index of the base stock itself might be used as a criterion. It was thought desirable also to extend the investigation to include polymers of about the same molecular weight and belonging to different chemical systems. Therefore oils of decreasing viscosity index were chosen to blend with three experimental polymers: I (polybutene, *6*), II (condensation product of highly chlorinated wax with naphthalene, *5*), and III (polycetyl methacrylate, *1*). The viscosities were measured at 100° and 210° F. in carefully calibrated Ubbelohde suspended-level viscometers. Viscosity data on the oils chosen for this study follow:

Oil	Viscosity at 210° F., Saybolt Universal Sec.	Viscosity Index
F	43.6	105.0
G	59.7	− 77.6
H	102.0	−190.0
I	131.0	−324.0

Each of these oils was blended with the three experimental polymers, and the results are listed in Table V. From these data curves were drawn to show the change in viscosity index with viscosity increase (Figures 3 to 6).

Figure 3 illustrates an order of decreasing viscosity-index-improving powers of polymer III, polymer II, and polymer I in a base oil of high viscosity index. Figure 4 shows that with oil *G* polymers II and III reverse their original order of potency, while polymer I continues as third choice. In Figure 4 the relative potencies of the three polymers become less marked for oil H (−190 viscosity index) with the order completely reversed in the lower concentration range. In Figure 6 the change becomes more apparent; the order of decreasing viscosity-index-improving power definitely changes to polymer I, polymer II, and polymer III. The blends were all stable, and the viscosity results were checked after the oil blends were over two years old.

If the viscosity data in Table V are plotted against percentage polymer concentrate or percentage polymer in the blend oil at 100° and 210° F., the curves do not all have the same general shape. That for the polymer in low-viscosity-index oil I departs from the linear form at 100° F. This result may be of some significance to the present solubility–viscosity index theory, as it indicates there is no linear relation between percentage polymer and viscosity at 100° F. Polymer I does not thicken oil I at 100° F. to any great extent. These data are of value in supporting the present solubility theory for viscosity index.

CONCLUSIONS. Graphical analysis of viscosity index data for oil-polymer blends indicates that for optimum results a specific choice must be made between polymer and base oil. The viscosity-index-improving property of a polymer always depends in part upon the solubility behavior of the polymer in oil at 100° and 210° F.

ACKNOWLEDGMENT

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CORRESPONDENCE

Production of Iron-Free Alum

SIR: An article on "Production of Iron-Free Alum" by Gee, Cunningham, and Heindl (*2*) discusses pilot plant operations on a new process based upon the crystallization of aluminum sulfate with aqueous ethyl alcohol, employing hot, concentrated solutions of the salt. The initial development was made by the writer (*3*), who had carried out extended laboratory work and directed an initial pilot plant through the point where a very satisfactory product was obtained (*4*). The article by Gee *et al.* covers a subsequent second pilot plant, with which the writer had no connection, and which was designed mainly to test alcohol losses, a significant item in the process cost.

The writer's experience with the process leads him to disagree with some of the process conditions chosen and with some portions of the cost estimate. The authors have set forth an estimate of manufacturing cost of $39.91 per ton of alum, which is approximately equal to a market price of $40 per ton. In view of the wide variation in conditions that may greatly affect the cost, the explicit figure which the authors have given has little real significance. In terms of a particular location and known conditions pertaining to it, a production cost of close to $23 per ton has been arrived at by the writer, which is much less than that indicated by the authors. The writer's estimate is considered by no means hard and fast, but is subject to fluctuation which may result in a lower or higher value, depending upon the unit costs of raw materials, labor, heat, power, and other items.

The reason for the discrepancy lies mainly in the difference in the flow sheet of operations and in the unit costs. Data and details of procedure resulting from the writer's work cannot be presented here because of lack of space, but he should like at least to present the more pertinent facts. The authors' operation of the second pilot plant was carried out with an Al_2O_3 content of 8.87% and at a temperature of about 50° C., presumably because of mechanical difficulties such as plugging of lines, etc., when higher concentrations were used. Successful experiments were, however, carried out in the laboratory and in the first pilot plant with an Al_2O_3 concentration as high as 11.4% at 80° C. if the solution, which was quite thick after precrystallization, was made fluid by a short period of agitation. The viscosity following this treatment was 410 centipoises, so that the solution could be readily pumped for continuous operation. Consistent and excellent purifications were obtained by this method.

As can be shown by calculation, the requirement of alcohol increases rapidly with a decrease in the Al_2O_3 concentration. Operating with a 8.87% concentration, Gee, Cunningham, and Heindl were compelled to use 2.0 times as much alcohol as would be required in the case of an 11.4% solution.

The authors have also preferred to distill all of the wash alcohol solution, whereas the writer has found that it is feasible by suitable splitting to recycle most of it to the crystallization without distillation and without appreciable contamination of the product. For these reasons, the still feed and the heat requirement of the authors are over three times greater than those involved in the writer's procedure.

The writer is in disagreement with a number of the estimates and assumptions pertaining to costs. From a general point of view, he questions the accuracy of a procedure that applies pilot plant costs and ratios for accessories and installation to the estimate of a plant cost. A preferred procedure is a reliable contractor's estimate based upon a suitable plant design. The writer has obtained in this way an estimate of $125,000 for the equipment cost installed of a plant designed for a 20% greater production capacity than the authors'. The $240,000 difference from the authors' figure is due to difference in design and in estimates of unit costs. For example, comparing installed cost estimates:

1. Still, $22,000. Design for one third authors' capacity; use of a packed column for about 80% alcohol, instead of a stainless steel bubble cap, about $7000.
2. Ten-inch stainless steel screw conveyer from filter to nearby evaporator dryer, $5800, as against $900.
3. Hooded rotary vacuum filter of stainless steel, 30 square feet, $17,400, as against $11,400.

In regard to the manufacturing cost estimate, while the unit costs given for bauxite, alcohol, and steam appear low, the other items are considered high and in the aggregate give rise to a high estimate of manufacturing cost. A relatively significant item is the cost of sulfuric acid. The manufacturing cost is about $10 per ton, and the acid may frequently be purchased at less than the given $16.50 per ton. Alum manufacturers are almost invariably also manufacturers of sulfuric acid.

An estimated capital cost that is twice as high as another capital cost as noted results at once in a cost of depreciation, maintenance, taxes, and insurance that also is twice as high. In addition, the estimated tax rate of 4% and insurance rate of 2% appear high.

The estimated power requirement and cost appear to be excessive. In comparison with the authors' estimate of 24 h.p. for stirring 1000 gallons of crystal slurry during cooling, the writer has found that when agitation is used, as referred to earlier, the slurry viscosity does not exceed 140 centipoises. The writer has calculated correspondingly that the power required is about 6 h.p. The authors have estimated 15 h.p. for filtering with a 30 square foot hooded rotary vacuum filter, while the estimate of a contractor familiar with this type of equipment was 9 connected h.p. including power for vacuum pump, filter drive, and air blower. The authors' unit cost for power of 3 cents per kw.-hr. is evidently high.

The estimated maintenance cost is $3.60 per ton of product, which corresponds to approximately 9% of the selling price. In comparison, published information (*1*) on commercial aluminum sulfate gives a value for repairs and maintenance of 2.1% or approximately $0.50. While the addition of the vapor-tight crystallization and distillation steps obviously will increase the maintenance charges for the present process, the increase from $0.50 to $3.60 appears excessive.

The assumptions on other minor items such as cooling water also appear extremely conservative.

The writer's interest in this process has been not especially in its application to the production of iron-free alum, but rather in its possible application to the production of metallurgical grade alumina. It is for this reason that he has preferred to consider the process in relation particularly to kaolin clays as well as high-silica bauxites. The reaction of raw kaolin clay with strong sulfuric acid has been found to be favored by the process requirement of a slightly acid end point. Other favorable factors are considered to be the need of no raw material other than clay, except for make-up acid and alcohol, and a relatively low fuel requirement. The writer has been doing further work along pertinent lines. It is gratifying that the authors have confirmed previous laboratory and pilot plant work indicating the chemical feasibility of the process, and have achieved a low percentage alcohol loss in the pilot plant of less than 0.5% at the optimum.

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(2) Gee, E. A., Cunningham, W. K., and Heindl, R. A., IND. ENG. CHEM., 39, 1178 (1947).
(3) Roller, P. S., U. S. Patent 2,402,668 (1946).
(4) U. S. Bur. Mines, unpublished reports, 1943.

PAUL S. ROLLER

CHEVERLY, MD.

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SIR: The authors' comments concerning the points raised in Roller's communication follow:

Although the authors feel their conclusions are correct and, being based on published experimental data, require no further justification, the points raised will be briefly considered.

It is obvious that product cost varies with the particular raw materials, labor, and transportation involved, as well as management policy concerning depreciation, maintenance, insurance, etc. As the authors saw little likelihood of the industrial adoption of the process, no specific area or location was selected. For this reason every assumption involved in the cost estimate was published, so that actual values could be easily substituted.

The small pilot plant constructed and operated by the authors never succeeded in utilizing 11.4% alumina solutions, although tests at such concentrations were carried out. Under such conditions the slurry crystallized in the piping pumps. The process is sensitive to temperature and variations of a few degrees can cause premature crystallization and solidification. Alcohol losses also increase at higher temperatures, which are concomitant with increasing alum concentrations. The authors are completely familiar with the small scale studies and confirm that laboratory batches were handled successfully; they concluded, however, that continuous operation at such concentrations was not feasible.

It is not believed practical to recycle the wash for several reasons.

1. Experience demonstrated that plant washing is not by direct displacement. Excessive amounts of iron were recycled in the wash liquor when any substantial portion was utilized. This caused a prohibitive lowering of the product purity, which is a direct function of the iron content of the feed.
2. In pilot plant tests on blending 60% alcohol wash with strong distillate to produce 68% crystallization feed, hydrous aluminum sulfate separated, which caused plugging of lines and pumps. An additional filtration operation would be required to overcome this difficulty.
3. The process is complicated by separating wash on the relatively small filter; subsequent blending and filtration require additional labor.

The published equipment costs were estimated nearly a year ago in conjunction with reliable manufacturers and the difference is believed to be principally one of design. The mechanical problems associated with this process are complex and the authors would at the present time revise upward the majority of their equipment costs. An independent estimate of this process by a large chemical company at the specified production capacity places the capital cost at $286,000, in comparison with the published figure of $240,000. The former allows for recent inflation and is probably a truer figure. As stated in the text, no allowance was made for buildings, which would be a substantial item if no existing structure were available.

The published list price of sulfuric acid 66° Bé. is $16.50 per ton (f.o.b. works). Unquestionably such acid is manufactured at a lower cost and in many cases is purchased at lower cost. This again is a function of the specific situation involved and the authors based their figures on a conservative estimate of the probable circumstances. It should be emphasized that industrial accounting practices differ with respect to interplant transfer of chemical products. An outsider starting in business would, after deductions for contract purchase and payment of transportation, approximate the published figure. This conclusion is substantiated by a sulfuric acid manufacturer.

The power requirements for agitation and pumping were estimated from pilot plant operation. The horsepower for crystallization, including eight motors for agitating the slurry and eight motors for pumping between units, will approximate 24 h.p. It is interesting to note that the viscosity of the slurry varies between rather wide limits for minor variations in temperature, etc., and batches approximating the consistency of paste were frequently encountered.

The 30 square foot filter has five auxiliary centrifugal pumps, one vacuum pump, one compressor for refrigeration, one blower, one agitator, and a motor drive; hence no decrease in the specified 15 h.p. is indicated.

Power may be calculated at a lower figure and costs from 0.5 to 3.0 cents per kw.-hr. are reported, depending upon the specific locality and the magnitude of the load (*1*). The validity of this point is acknowledged.

Maintenance is based on pilot plant observations and one large producer of crude aluminum sulfate has advised that 10% of capital cost is indicated, representing an increase of 1% over the published figure. In any totally enclosed unit with volatiles, packings must be frequently replaced, leaks quickly repaired, and moving surfaces adequately protected by stuffing boxes.

With respect to the comment regarding cooling water requirements, the values chosen were believed to be a correct balance between the two factors of heat exchange surface and cooling water volume.

In conclusion, the authors wish to thank the critic for stimulating interest in the process, and if this Bureau of Mines development has industrial application, they should be pleased to assist in its exploitation. It is the authors' opinion that conservatism in the preparation of cost estimates based upon pilot plant investigations is a desirable policy.

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Radial Chromatography in Industry

SIR: In a paper entitled "Radial Chromatography in Industry" [IND. ENG. CHEM., 39, 938–40 (1947)] Hopf describes an apparatus invented by him and called "chromatofuge." This apparatus combines the use of the principles of chromatographic adsorption and centrifugal power.

In July 1943, I published an article on chromatographic adsorption in which I described an apparatus invented by myself and constructed on the same principles. It was distributed by the Baroid Sales Division, National Lead Company, Los Angeles, Calif.

OTTO KÖNIG

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SIR: König's 1943 publication, based on a previous publication by Brown, unfortunately was not available to scientists in Europe and, I believe, some parts of the United States.

The apparatus described by him certainly uses the same principles described by me, although it seems to have been intended solely as an analytical aid. The idea of using centrifugal forces as an aid to the passage of liquid in chromatography has been worked on to my knowledge in several laboratories all over the world. I believe, however, I am correct in saying that my work contains the first successful adaptation of the principle to an industrial problem that has been published in an internationally read journal.

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Synthesis of DDT with Chlorosulfonic Acid as the Condensation Agent

SIR: Our attention has been called to three recent references on the preparation of technical DDT by the sulfuric acid–oleum method, one by Mosher, Cannon, Conroy, Van Strien, and Spalding (*4*), another by Neil, Ames, and McIlhinney (*5*), and the last a British patent source (*1*). The latter describes several experiments wherein the conditions approximate those employed by Neil and co-workers (*5*), with but one significant difference: An initial 25% oleum concentration is employed in contrast to the 10.2% initial oleum concentration taken by Neil and associates. The purity of the technical product in the British report varies from 75 to 97% actual DDT and no data are given for the yields of technical product obtained. The article by Mosher and associates (*4*) embraces a complete account of the W.P.B. DDT Report Series, 44-1 through 44-12. From their reported yields of technical products and respective setting points, together with the corresponding percentage purity values established from Fleck and Preston's (*3*) setting point composition curve, calculated equivalent percentage theoretical yields of pure DDT varying from 34.7 to 75.2% are established. The conclusions of these authors (*4*) in reference to the experimental conditions leading to a maximum yield of 97% technical product of 77% pure DDT content have been called attention to in our paper (*2*).

The pilot plant data and observations by Neil and associates (*5*) of the Canadian Chemical Warfare Laboratories are even more significant for comparison purposes. Thus, these authors claim average yields of 70% technical DDT (which analyzed 71.2% pure DDT) and actual yields of 85% technical DDT in the latter stages of their production operations. These data correspond to calculated equivalent percentage theoretical yields of 50 to 60% pure DDT. Moreover, the pilot plant studies of Neil and co-workers (*5*) show clearly, when the operating plant ratio of acid to organic reagents was increased from 2:1 to 5:1 or as expressed otherwise, when the mole ratio of sulfuric acid to chloral was increased from 8:1 to 20:1, a yield of 90% technical product or a calculated equivalent 64% theoretical yield of pure DDT was obtained. However, Neil and associates admit that operations under such conditions "are not economically sound, as the slight gain [in yield] did not justify the cost of the excess acid used." Therefore, from a consideration of all published references to the sulfuric acid–oleum process wherein complete data are available, it would appear that an economic operating limit, corresponding to a 50 to 62% (and an optimum average, approximating 60 to 62%) theoretical yield of pure DDT, is about all that may reasonably be expected of this process. By contrast, our one-step chlorosulfonic acid method wherein essentially metathetical quantities of reactants were employed, gave under variable operating conditions 50 to 69% and under optimum experimental conditions 67 to 69% theoretical yields of pure DDT.

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Vapor Pressure of Pure Substances—Correction

Since the publication of the vapor pressure data in the April issue (*12*), a number of errors of various kinds have come to my attention. They have been pointed out by interested parties in a most constructive way and it is gratifying to thank each one for his cooperative part.

Table I. Corrections of Vapor Pressure Data

Formula	Name	Temperature, ° C. 1 mm.	5 mm.	10 mm.	20 mm.	40 mm.	60 mm.	100 mm.	200 mm.	400 mm.	760 mm.	M.P.	Citation No.
$C_4H_8Cl_2$	1,1-Dichloro-2-methylpropane	−31.0	−8.4	+2.6	14.6	28.2	37.0	48.2	65.8	85.4	106.0d	...	..
C_5H_{10}	1-Pentene	−80.4	−63.3	−54.5	−45.0	−34.1	−27.1	−17.7	−3.4	+12.8	30.1	...	..
C_6H_5ClO	2-Chlorophenol	12.1	38.2	51.2	60.9	82.0	92.0	106.0	126.4	149.8	174.5	7.0	..
C_7H_9NO	2-Methoxyaniline	61.0	88.0	101.7	116.1	132.0	142.1	155.2	175.3	197.3	218.5	5.2	..
$C_8H_{12}O_4$	Diethyl fumarate	53.2	81.2	95.3	110.2	126.7	137.7	151.1	172.2	195.8	218.5	+0.6	..
C_8H_{18}	2,2,3,3-Tetramethylbutane	−17.4	+3.2	13.5	24.6	36.8	44.5	54.8	70.2	87.4	106.3	+100.7	(*1*)
C_9H_{12}	3-Ethyltoluene	7.2	32.3	44.7	58.2	73.3	82.9	95.9	115.5	137.8	161.3	−95.5	(*1*)
C_9H_{20}	Nonane	+1.4	25.8	38.0	51.2	66.0	75.5	88.1	107.5	128.2	150.8	−53.7	(*1*)
$C_{10}H_{14}$	1,2,3,4-Tetramethylbenzene	42.6	68.7	81.8	95.8	111.5	121.8	135.7	155.7	180.0	204.4	−6.2	(*1*)
$C_{10}H_{14}$	4-Ethyl-1,3-xylene	26.3	53.0	66.4	80.6	97.2	107.4	121.2	141.8	164.4	188.4	...	(*1*)
$C_{10}H_{14}$	5-Ethyl-1,3-xylene	22.1	48.8	62.1	76.5	92.6	103.0	116.5	137.4	159.6	183.7	...	(*1*)
$C_{10}H_{14}$	2-Ethyl-1,4-xylene	25.7	52.0	65.6	79.8	96.0	106.2	120.0	140.2	163.1	186.9	...	(*1*)
$C_{10}H_{14}$	1,2-Diethylbenzene	22.3	48.7	62.0	76.4	92.5	102.6	116.2	136.7	159.0	183.5	−31.4	(*1, 7*)
$C_{10}H_{14}$	1,3-Diethylbenzene	20.7	46.8	59.9	74.5	90.4	100.7	114.4	134.8	156.9	181.1	−83.9	(*1*)
$C_{10}H_{14}$	1,4-Diethylbenzene	20.7	47.1	60.3	74.7	91.1	101.3	115.3	136.1	159.0	183.8	−43.2	(*1*)
$C_{10}H_{14}$	Cymene	17.3	43.9	57.0	71.1	87.0	97.2	110.8	131.4	153.5	177.2	−68.2	(*3*)
$C_{10}H_{14}$	Butylbenzene	22.7	48.8	62.0	76.3	92.4	102.6	116.2	136.9	159.2	183.1	−88.0	(*1*)
$C_{10}H_{14}$	Isobutylbenzene	14.1	40.5	53.7	67.8	83.3	93.3	107.0	127.2	149.6	172.8	−51.5	(*1*)
$C_{10}H_{14}$	*sec*-Butylbenzene	18.6	44.2	57.0	70.6	86.2	96.0	109.5	128.8	150.3	173.5	−75.5	(*1*)
$C_{10}H_{18}O_6$	Dipropyl-*d*-tartrate	115.6	147.7	163.5	180.4	199.7	211.7	227.0	250.0	275.6	303.0	...	..
$C_{10}H_{20}$	1-Decene	14.7	40.3	53.7	67.8	83.3	93.5	106.5	126.7	149.2	172.0	...	..
$C_{10}H_{22}$	Decane	16.5	42.3	55.7	69.8	85.5	95.5	108.6	128.4	150.6	174.1	−29.7	(*2*)
$C_{11}H_{16}$	3,5-Diethyltoluene	34.0	61.5	75.3	90.2	107.0	117.7	131.7	152.4	176.5	200.7	...	(*4*)
$C_{11}H_{16}$	*sec*-Amylbenzene	29.0	55.8	69.2	83.8	100.0	110.4	124.1	145.2	168.0	193.0	...	(*9*)
$C_{11}H_{24}$	Hendecane	32.7	59.7	73.9	85.6	104.4	115.2	128.1	149.3	171.9	195.8	−25.6	(*10*)
$C_{12}H_{26}$	Dodecane	47.8	75.8	90.0	104.6	121.7	132.1	146.2	167.2	191.0	216.2	−9.6	(*3, 8*)
$C_{13}H_{20}$	Heptylbenzene	64.0	94.6	110.0	126.0	144.0	154.8	170.2	193.3	217.8	244.0	...	(*5*)
KBr	Potassium bromide	795	940	982	994	1050	1087	1137	1212	1297	1383	730	..

Table I lists all numerical corrections up to date. In cases where these corrections result from more information, the source is cited. Other corrections follow:

Page 518. $CHBr_3$ represents tribromomethane instead of tribromoethane as listed.

Page 520. C_3H_9Ga is trimethylgallium.

Page 521. $C_4H_7Cl_2$ is not 1,1-dichloro-2-methylpropane; the whole line should be deleted.
$C_4H_8Cl_2O$ is di(2-chloroethyl) ether.

Page 523. The line named *tert*-butyl formate with formula $C_5H_{10}O_2$ should be deleted in its entirety.
$C_6Cl_4O_2$, named chloranil, is still solid at its normal boiling point.

Page 526. The substance listed incorrectly as 2,5-dimethyl-3-pentanone with formula $C_7H_{14}O$ is really the 2,4-dimethyl-3-pentanone.
C_8H_5NO is not benzonitrile as listed, but is phenylglyoxylonitrile, and the second compound with formula C_8H_7NS is benzylisothiocyanate and not phenyl isothiocyanate as listed.

Page 527. $C_8H_8O_4$ is dehydroacetic acid. Dichloroethylphenylsilane with formula $C_8H_9Cl_2Si$ should be entirely deleted.

Page 528. C_8H_{16}, the compounds listed as *cis*- and *trans*-1,3-dimethylcyclohexane are inverted. Thus the *cis* compound is the lower boiling in this case.
$C_8H_{16}O_2$, listed as amylisopropionate, actually is amyl propionate.
$C_8H_{18}O_4$ is not suberic acid and the whole line should be stricken out.

Page 529. $C_9H_{18}O$, incorrectly listed as 2-nonane, is 2-nonanone.

Page 531. $C_{11}H_{14}O$, incorrectly listed as isobutyrophenone, is isovalerophenone.

Page 532. $C_{12}H_{18}$, named 1,3,4-triethylbenzene, should be deleted. $C_{12}H_{18}$, marked 1,2-diisopropylbenzene, should be 1,4-diisopropylbenzene (*6*).

Page 533. Anthraquinone should have the formula $C_{14}H_8O_2$ instead of $C_{14}H_{18}O_2$ as given.
$C_{14}H_{22}$ represents 1,2,4,5-tetraethylbenzene instead of the 1,2,3,4-tetraethylbenzene given (*11*).
$C_{15}H_{16}O$, incorrectly given as isocapronaphthone, is 1-isovaleronaphthone.

Page 534. The formula for diphenyl-2-tolyl thiophosphate is $C_{19}H_{17}O_3PS$ and not $C_{18}H_{17}O_3PS$ as given.

Page 536. C_4H_6, 1,3-butadiene, at 40 atmospheres should be 158° C. C_4H_{10}, 2-methylpropane, at 10, 20, and 30 atmospheres should be 66.8°, 99.5°, and 120.5° C., respectively.
$C_{12}H_{26}$, dodecane: at 1 atmosphere, 216.2° C. and at 2 atmospheres, 249.2° C.

Page 539. Reference 368 should read: Schierholtz and Staples, *J. Am. Chem. Soc.*, 57, 2709–11 (1935).

Page 542. Citation 270 listed with CsF, cesium fluoride, should be changed to 370.

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(4) Gibbons and co-workers, *J. Am. Chem. Soc.*, 68, 1130–1 (1946).
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(6) Heise and Töhl, *Ann.*, 270, 155–71 (1892).
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Distribution in Hydrocarbon-Solvent Systems—Correction

In the article entitled "Distribution in Hydrocarbon-Solvent Systems" [Hunter and Brown, Ind. Eng. Chem., 39, 1343 (1947)], there is an error in Table I in that the refractive indices, n^{20}_D and n^{25}_D, observed for *n*-heptane are reversed. The name of the second author should be T. F. Brown rather than T. Brown.

PILOT PLANTS

Thermofor Catalytic Cracking Unit

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The Thermofor catalytic cracking pilot unit described is used primarily for the study of process variables and the evaluation of charge stocks. These studies provide the information required to conduct commercial operations at the highest economic level, thereby obviating expensive full-scale experimentation. The pilot unit is used also to compare new catalysts with those in present commercial service. It is one of several pilot units which were employed in the original development of the Thermofor process to obtain basic engineering information on catalyst flow characteristics, cracking yields, and catalyst regeneration. This engineering information was used to design an integrated unit to produce 500 barrels per day, which preceded the first full-scale commercial installation of the process in 1943.

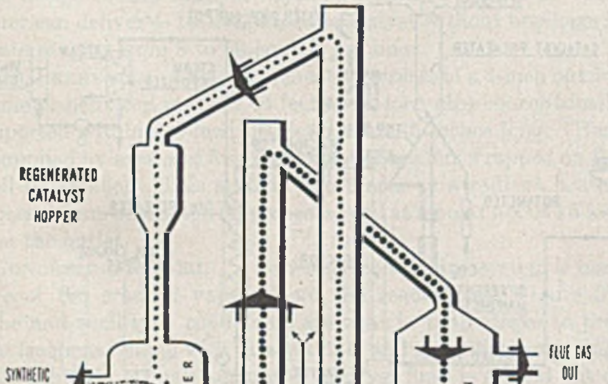

Figure 1. Simplified Flow Diagram of Reactor and Kiln

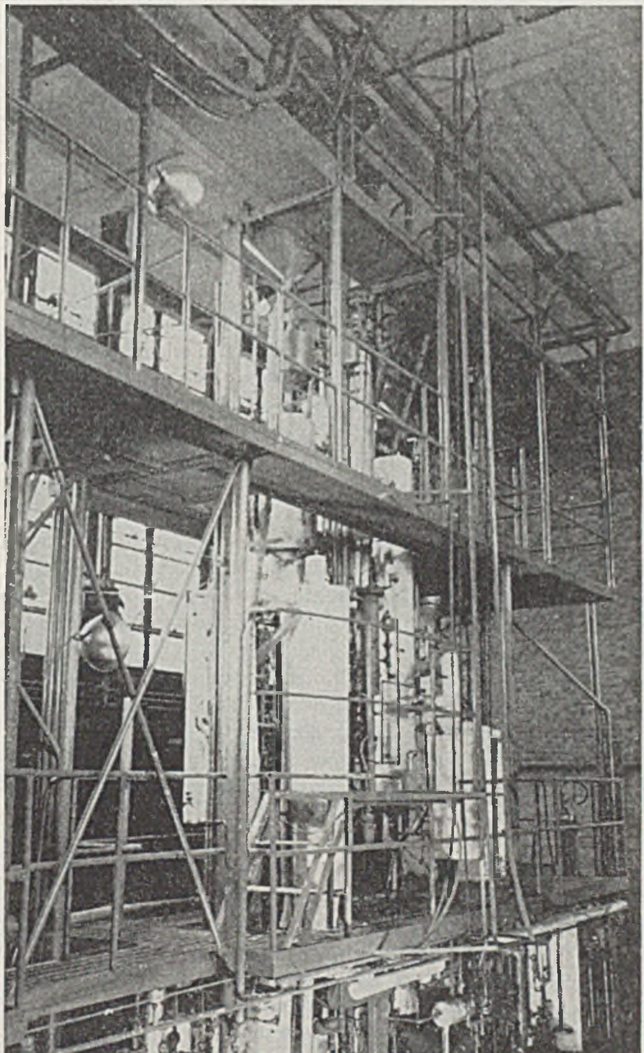

Figure 2. Pilot Unit

THE Thermofor catalytic cracking process has been described in detail (*2, 3, 4*). Its essential elements are a reactor for continuously contacting hydrocarbon feed with a moving bed of granular catalyst to effect partial conversion of the hydrocarbons, and a kiln for removing carbon which is deposited on the catalyst in the cracking operation, by controlled combustion with air. The catalyst flows by gravity through both vessels, which stand side by side, and is transferred from the bottom of one to the top of the other by means of bucket elevators. The system is illustrated by the simplified flow diagram shown in Figure 1. Commercial units have charging capacities ranging from 4000 to 20,000 barrels per day and catalyst circulation rates ranging from 75 to 150 tons per hour.

The pilot unit is designed to simulate and study the reactor part of the commercial Thermofor catalytic cracking system. The related operations are conducted batchwise in separate laboratory equipment for simplicity and economy. Thus, the spent catalyst is regenerated for re-use in a small Thermofor kiln which is operated intermittently and the liquid product from the reactor is fractionated in batch stills to provide the desired fractions for yield and quality determinations. Furthermore, the time required to establish equilibrium conditions on the pilot unit is minimized by divorcing the catalyst regeneration and product fractionation from the reactor operation.

PILOT UNIT

The pilot unit occupies a floor space 13 feet square and has an over-all height of 28 feet. It has a maximum oil charge capacity of 2 barrels per day, a catalyst throughput rate up to 60 pounds per hour, and can be operated at pressures up to 50 pounds per square inch gage and temperatures up to 1100° F. The minimum quantity of catalyst required to operate the unit continuously is 450 pounds. The oil charge requirement varies between 15 and 30 gallons for each run.

The general layout of the pilot unit is shown in Figure 2 with the oil feed system on the lower left side, the reactor in the center, and the gas meter and fractionating towers on the right. The operator is adjusting the variable-speed drive which controls the catalyst rate through the unit.

The flow of oil and catalyst through the pilot unit is shown diagrammatically in Figure 3 and described below.

CATALYST FLOW. Catalyst flows by gravity from the supply hopper at the top of the unit through the catalyst preheater and reactor. A catalyst meter below the reactor discharges the catalyst at the desired rate into the spent catalyst receiver. All the piping between vessels is 1.5 inches in inside diameter or larger to assure free flow of 4- to 10-mesh commercial catalysts used in the Thermofor process. As the unit is operated under pressure (5 to 20 pounds per square inch gage), a pressure lock system is provided at the top and bottom of the unit to permit charging and discharging catalyst without interrupting the operation of the reactor.

Figure 4 shows the laboratory Thermofor kiln used for regenerating the spent catalyst from the pilot unit.

OIL FLOW. The oil feed is charged by means of a Hills McCanna Type RM2F pump from burets through the oil preheater and into the reactor. Process steam is added at regulated rates as desired by pumping water from a buret through a vaporizer to join the oil stream in the preheater. The hot vapors from the reactor are condensed and the total liquid condensate, or "synthetic crude," is separated from the cracking gas. The cracking gas passes through a back-pressure control valve to a gas meter and is vented after sampling. The synthetic crude flows through a water separator and, if the operation is of the once-through type, is discharged through a level control valve into a product accumulator. In the case of recycle operation, the synthetic crude is fed into a two-tower fractionating system where a recycle stock is separated and returned to the reactor. Carbon dioxide is employed as seal gas on the catalyst inlet and outlet lines to prevent the escape of oil vapors from the reactor at these points. The carbon dioxide feed to the top seal leg enters at the bottom of the catalyst preheater and a portion of it is withdrawn from the top to dehydrate the descending catalyst, thereby simulating freshly regenerated catalyst typical of commercial operation.

EQUIPMENT

The equipment operating above 600° F.—i.e., the catalyst and oil preheaters, reactor, and connecting piping—is fabricated from 18-8 stainless steel. The other parts of the unit are constructed of carbon steel. The major pieces of equipment are described below.

CATALYST PREHEATER. The design of the catalyst preheater is shown in Figure 5. Heat is supplied by four 1.5-kw. heaters,

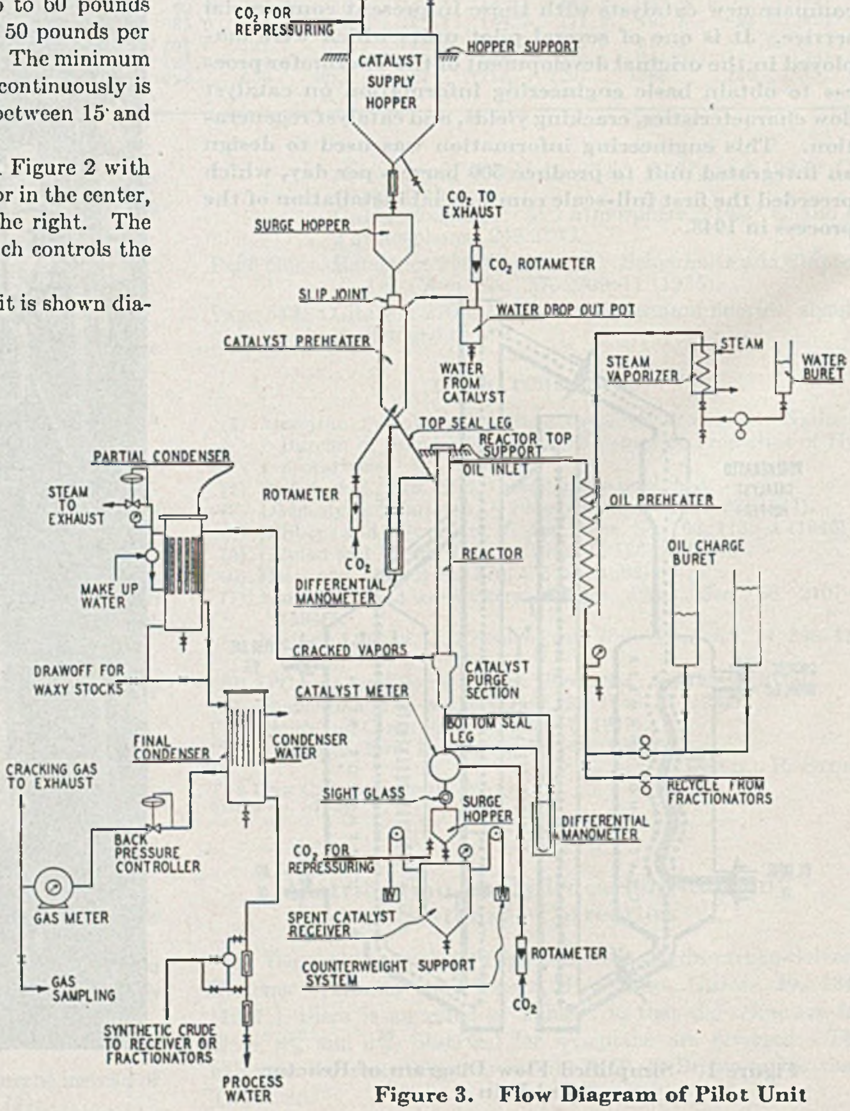

Figure 3. Flow Diagram of Pilot Unit

one of which is provided with voltage control, so that the heat input can be varied manually from 0 to 6.0 kw. This preheater has 9.2 square feet of heat transfer surface including the internal fins, and is capable of heating 60 pounds per hour of catalyst (0.25 average specific heat) from 100° to 1100° F.

Reactor. The design of the reactor assembly is shown in Figure 6. The reaction zone is 3 inches in diameter by 48 inches long and has a volume of 1.75 gallons. This reactor is designed to operate adiabatically along its entire length, so as to duplicate the temperature pattern that occurs in a commercial Thermofor catalytic cracking reactor as the result of the endothermic heat of cracking. This is accomplished by dividing the reactor zone into five sections of equal length and providing each section with an individually controlled electric heater wound on the first layer of insulation to prevent heat loss from the reactor proper. At the mid-point of each adiabatic section one thermocouple is attached to shell of reactor and another is embedded in the center of first layer of insulation on the reactor. The electric heater is adjusted so that the temperature readings at these two points are balanced to within 10° F. The average cracking temperature is obtained by integrating the temperature pattern through the reactor.

The reactor is designed to permit operation with either concurrent or countercurrent flow of oil and catalyst. With vaporized feed stocks either type of flow may be used. However, only concurrent flow is employed with stocks which are not completely vaporized and a nozzle is used to distribute the oil on the catalyst. The nozzle with auxiliary equipment is shown in Figure 7.

The purge section below the reaction zone (Figure 6) simulates commercial operation as to catalyst residence time and temperature, the only difference being that carbon dioxide is used instead of steam in the pilot unit.

Catalyst Meter. A special catalyst meter is used to control the rate of flow of catalyst through the reactor. Commercially this is accomplished by a valve in the catalyst discharge line from the reactor. The use of a special mechanical device in the pilot unit is necessitated by the fact that the desired small flow rates cannot be controlled by orifices. Such a device must also be capable of handling commercial-size catalysts without crushing. The design of the catalyst meter is shown in Figure 8. This meter can deliver 4- to 10-mesh size catalyst without breakage at a rate ranging from 8 to 60 pounds per hour.

Oil Preheater. The oil preheater consists of a 4-inch outside diameter helix coil made of 44 feet of $^{1}/_{4}$-inch pipe concentrically supported within a 6-inch diameter shell 45 inches long. Heat is supplied by means of five 2-kw. electric heaters wrapped on the shell in parallel. This shell in effect acts as a radiant heater. Process steam enters the oil preheater coil at a point about 15 feet from the outlet.

Condensing System. A two-stage condensing system is used to cool the cracked vapors from the reactor (see Figure 3). Tube and shell-type condensers are used in both stages to prevent frequent fouling with catalyst fines and to facilitate cleaning. Although only a small amount of catalyst fines is carried out of the reactor by the cracked vapors, it would be sufficient to plug a helical coil condenser. The first stage or "partial condenser" operates at about 260° F., while the second stage or "final condenser" operates at cooling water temperature. Both condensers are operated with the pressure in the shell side higher than that in the tube side, so that any leaks which develop immediately show up as unaccounted for water in the product.

When processing waxy stocks the condensate from the first condenser is withdrawn hot to a separate receiver; otherwise this stream passes to the second condenser where the total liquid product and cracking gas are separated. The liquid product from the final condenser passes through a water settler and the water-free synthetic crude is discharged by a float control valve to a product accumulator.

Fractionating Towers. Two packed towers which have a fractionating efficiency equivalent to about 10 theoretical plates are used in recycle operations to prepare the desired boiling range recycle fraction continuously from the synthetic crude. In this type of operation the condensed synthetic crude is fed through a preheater into the first tower where unstabilized gasoline is taken overhead. The bottoms flow into a second tower where a gas oil fraction is taken overhead for recycling while the bottoms are rejected. If desired, the total bottoms from the first tower may be recycled to the reactor without use of the second tower. All recycling is done continuously and automatically with a minimum of liquid holdup in the system.

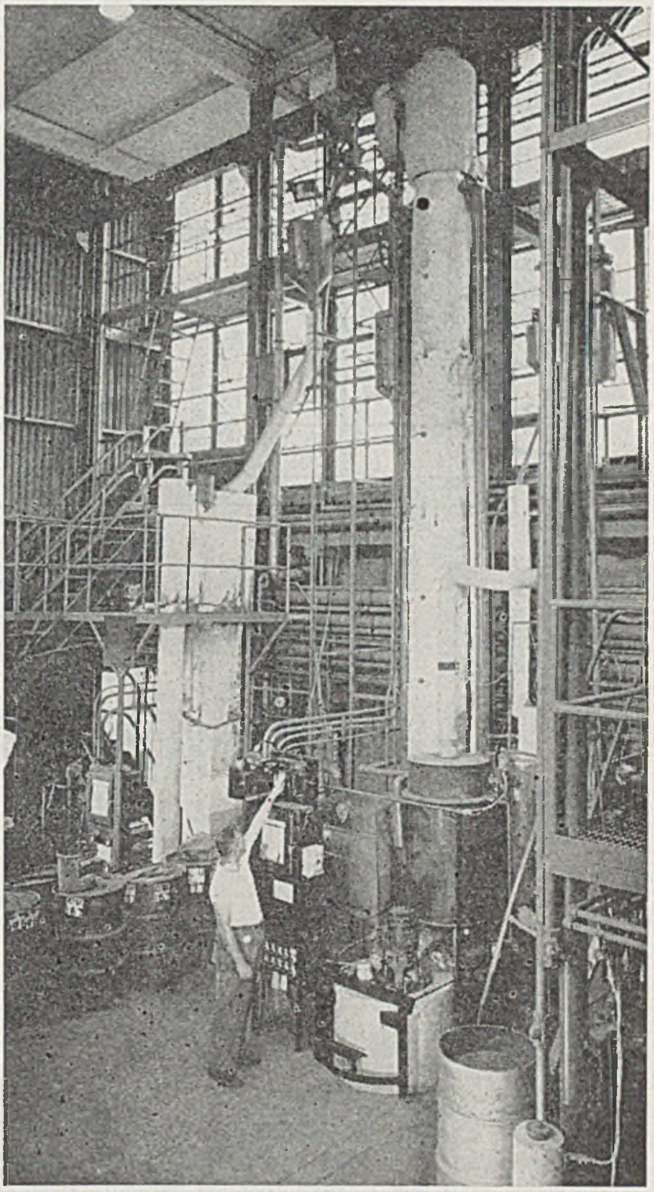

Figure 4. Thermofor Kiln

Unit Support. The unit is supported rigidly at the top of the catalyst supply hopper and at the top of the reactor. The catalyst feed line from the supply hopper enters the catalyst preheater through a packed slip joint, permitting upward expansion above the reactor. Expansion downward from this point is provided for by counterweight suspension of the bottom of the unit. Auxiliary equipment such as oil preheater, product condensers, and fractionating towers are suspended from the main support of the unit. Heat loss from the reactor is minimized by inserting $^{1}/_{4}$-inch mica between the reactor and its supports.

Kiln. A Thermofor kiln is used to regenerate catalysts for several pilot units. It will regenerate about 300 pounds per hour

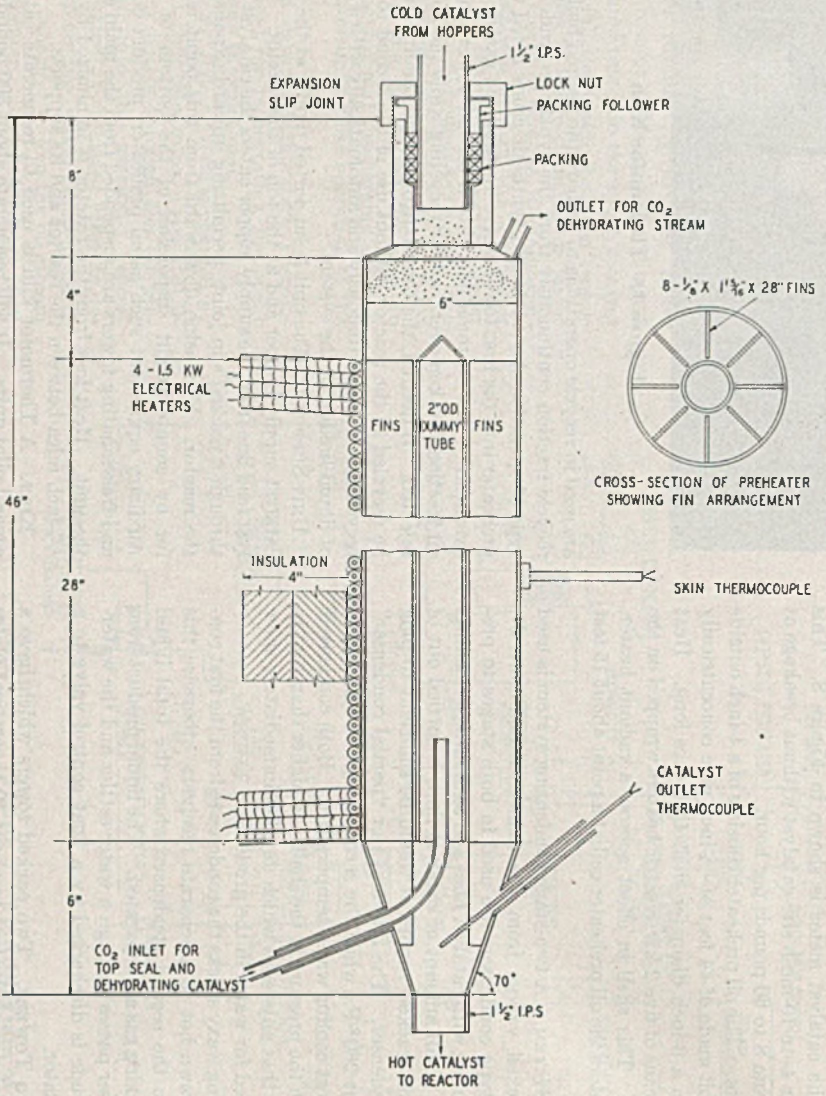

Figure 5. Catalyst Preheater

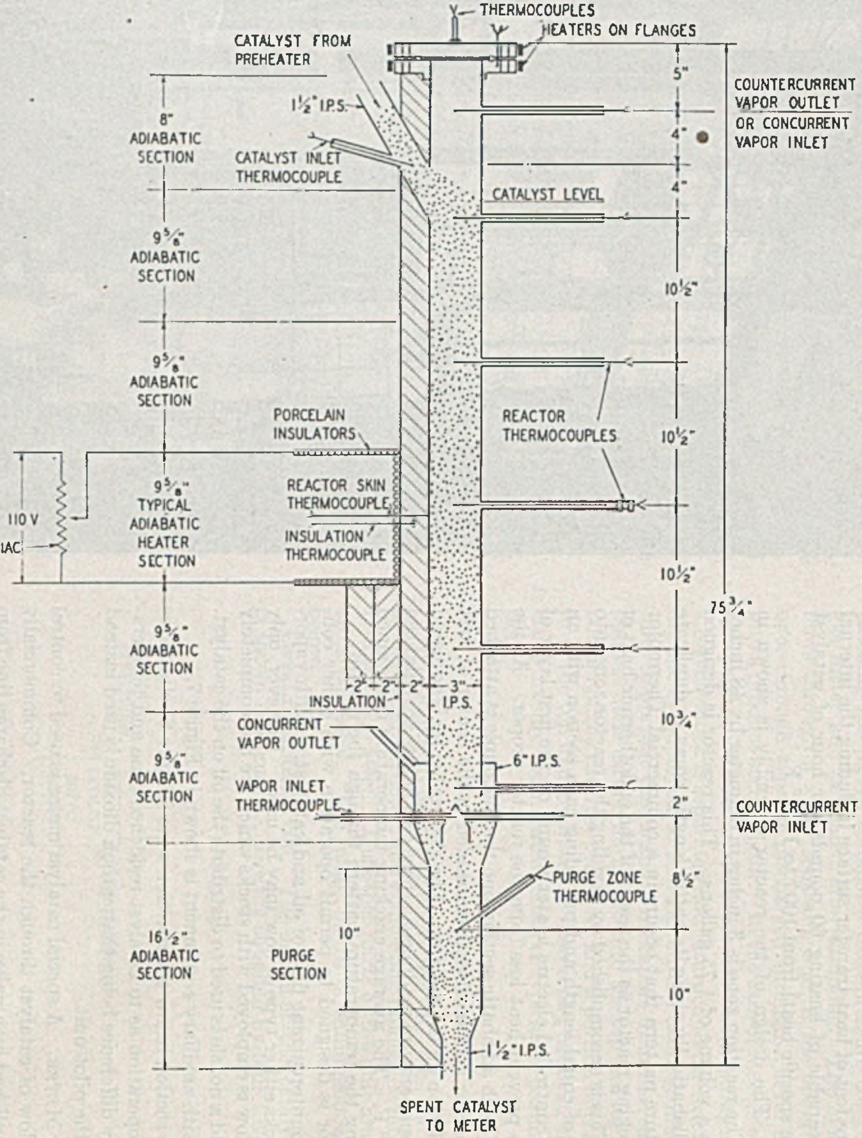

Figure 6. Pilot Unit Reactor

Table I. Comparison of Commerical and Pilot Unit Thermofor Catalytic Cracking Data

(Concurrent flow operation)

Comparison	1		2		3		4	
	Paraffinic		Paraffinic		Paraffinic		Naphthenic	
Charge stock	Light gas oil		Light gas oil		Heavy gas oil		Heavy gas oil	
Gravity, A.P.I.	33.5		34.1		31.0		27.4	
Aniline point, ° F.	170		172		174		155	
Sulfur, % wt.	0.31		0.32		0.43		0.31	
Carbon residue, % wt.	0.03		0.02		0.70		0.01	
A.S.T.M. distillation, ° F					[a]		[a]	
I.B.P.	370		395		392		472	
10%	512		511		483		548	
50%	601		590		609		640	
90%	712		672		801		817	
End point	730		714		..		..	
Unit	Plant	Pilot	Plant	Pilot	Plant	Pilot	Plant	Pilot
Type of feed	Vapor	Vapor	Vapor	Vapor	Mixed phase	Mixed phase	Mixed phase	Mixed phase
Catalyst activity	37.1	36.0	36.6	36.0	31.0	30.0	35.6	36.0
Operating conditions								
Catalyst inlet temperature, ° F.	935	939	955	955	1000	1001	967	972
Oil inlet temperature, ° F.	848	851	866	866	870	877	827	833
Total space velocity, V/hr./V	1.10	1.10	1.69	1.62	0.78	0.78	1.03	1.08
Recycle ratio, recycle/fresh feed	0.59	0.59	0.74	0.74	0.09	0.09	0	0
Catalyst/total oil, volume	1.84	1.87	1.22	1.26	2.77	2.80	2.25	2.17
Oil partial pressure (av.), p.s.i.g.	5.4	6.0	9.5	7.2	5.8	5.3	5.9	6.9
Total pressure, p.s.i.g.[b]	5.4	10.0	9.5	10.0	5.8	8.2	5.9	10.0
Yields, based on fresh feed								
C_4-free 356 F. at 90% gasoline, % vol.	55.3	54.2	49.0	47.8	36.7	35.7	39.9	42.0
Cycle stock, % vol.	26.6	25.8	36.1	36.0	48.2	47.6	52.8	46.2
Isobutane, % vol.	9.7	11.5	7.6	9.2	5.4	6.3	4.7	8.1
n-Butane, % vol.	3.3	4.8	3.2	3.0	1.7	3.4	2.0	2.1
Butylenes, % vol.	4.3	3.7	3.9	4.0	5.4	4.6	2.7	3.1
C_3-free liquid recovery, % vol.	99.2	100.0	99.8	100.0	97.4	97.6	102.1	101.5
Dry gas, % wt.	6.7	6.4	6.2	6.0	7.2	7.3	3.9	5.2
Coke, % wt.	4.7	5.1	3.5	3.3	3.2	4.2	3.0	3.8
10 RVP 356° F. at 90% motor gasoline								
Yield, % volume of fresh-feed	58.3	56.3	51.3	48.1	38.6	37.7	42.9	44.5
Octane ratings								
F—2 clear	79.8	80.8	80.0	80.3	80.5	80.0	79.6	80.9
+ 1 cc. TEL	84.7	84.9	84.6	85.2	84.4	82.9	84.1	85.0
+ 3 cc. TEL	87.2	88.3	87.9	87.9	86.0	86.1	87.2	87.7
F—1 clear	89.8	90.7	89.9	89.8	92.2	89.2	88.1	91.3
+ 1 cc. TEL	94.4	94.8	94.4	94.0	95.4	93.8	93.5	95.7
+ 3 cc. TEL	96.7	97.5	97.1	96.4	97.6	96.5	96.2	98.4

[a] Vacuum assay.

[b] Includes purge carbon dioxide present in pilot unit reactor.

of catalyst and requires little attention but is not intended to simulate commercial Thermofor kiln operation. The Thermofor kiln is used commercially to regenerate percolation clays (*5*). Published information is also available on the design and operation of commercial Thermofor catalytic cracking kilns (*1*).

Instrumentation. The instrumentation includes a pilot-operated back-pressure control valve for controlling unit pressure, a 10-point Micromax for recording the most important temperatures, and a 48-point Electronik potentiometer for reading other temperatures.

OPERATING PROCEDURE

The pilot unit is operated continuously on a 5-day schedule. During the week-end shutdown, partial heat is maintained on the unit in order to reduce the time required to reach operating temperatures. Oil is started to the reactor when catalyst temperatures have reached 800° F. and the unit is considered to be on-stream when the desired rates and temperatures have been established. The complete start-up period following a normal shutdown averages 5 hours, while a period of about 8 hours is required to bring a cold unit to on-stream conditions. In recycling operations the time required to establish equilibrium is about 24 hours.

The unit is operated at on-stream equilibrium conditions for a minimum of 6 hours or until 10 gallons of synthetic crude product are collected in once-through operations and for a minimum of 24 hours or until 5 gallons of unstabilized gasoline are produced in recycle operation. Occasionally, runs of several days' duration are conducted to meet special demands.

Personnel Requirements. The personnel required to conduct Thermofor catalytic cracking studies listed below are based on the operation of two units simultaneously, which is the practice in this laboratory.

Supervisory staff	Operating staff (nontechnical)
6 chemical engineers	9 unit operators, 3 per shift
	1 kiln operator (day shift)
	1 calculator (day shift)
	1 maintenance man (day shift)

The supervisory staff consists of two project leaders, each of whom is assisted by two chemical engineers who are responsible for programming work on the unit, seeing that proper samples are prepared and tested, correlating results, and preparing formal reports. In so far as possible, each engineer is responsible for a particular job from the beginning to the end, so that he possesses full knowledge of the problems involved and can process the work most efficiently.

The personnel requirements for batch distillation, light hydrocarbon analysis, and testing of products are approximately 150% of those for pilot unit operation.

Recording of Data. The important data are recorded hourly by the unit operators and include the oil and catalyst temperatures entering the reactor, catalyst bed temperatures, pressure, flow rates, gravity of the synthetic crude, and carbon dioxide content of the cracking gas.

Sampling Procedure. The spent catalyst leaving the unit is sampled by riffling the total quantity withdrawn every 2 hours. A representative sample of the charge catalyst is obtained in a similar manner. A composite sample of cracking gas from each run is obtained by continuously withdrawing a small stream during the full length of the run. A composite sample of synthetic crude is obtained by withdrawing a small fixed volume from the product accumulator each hour during the run.

The catalyst samples are analyzed for carbon content, while the gas and synthetic crude samples are analyzed by mass spectrometer and Podbielniak distillation, respectively, from which the yield of light hydrocarbons can be calculated. Five to 10 gallons of synthetic crude are batch-distilled to prepare gasolines and fuel oils of specification boiling range for testing.

In normal cracking operations 70% of the pentane and 85% of the hexane are condensed with the synthetic crude. The gasolines prepared for testing are adjusted for 100% recovery of pentane and hexane by blending the dehexanized gasolines, hexanes, and pentanes from the distillation step in the proper ratio. Since the composition of both the pentane and hexane fractions condensed in the synthetic crude varies somewhat from that of the corresponding fractions in the cracking gas, this procedure is not fundamentally correct; however, the effect on unsaturation and octane rating of the gasolines is within the experimental accuracy of individual cracking evaluations. In operations where gas yield is unusually high the recovery of pentanes and hexanes in the synthetic crude is relatively low and the gas is passed through a dry ice condenser to recover the butane and heavier material for inclusion in the synthetic crude.

COMPARISON OF PILOT UNIT AND COMMERCIAL THERMOFOR RESULTS

The pilot unit described above was designed to duplicate the performance of a commercial Thermofor catalytic cracking reactor. The degree to which this has been achieved is shown in Table I, which presents four sets of comparative pilot unit and commercial Thermofor data on identical charge stocks and catalysts. The commercial data were obtained during 1946 and 1947 on the 10,000-barrel-per-day unit at the Paulsboro, N. J., refinery of the Socony-Vacuum Oil Company. With vapor feed the pilot-plant results agree within experimental accuracy with those from the commercial plant with respect to product yields and quality. With liquid or mixed-phase feed the agreement is not so precise but it is expected that this will be improved by further study.

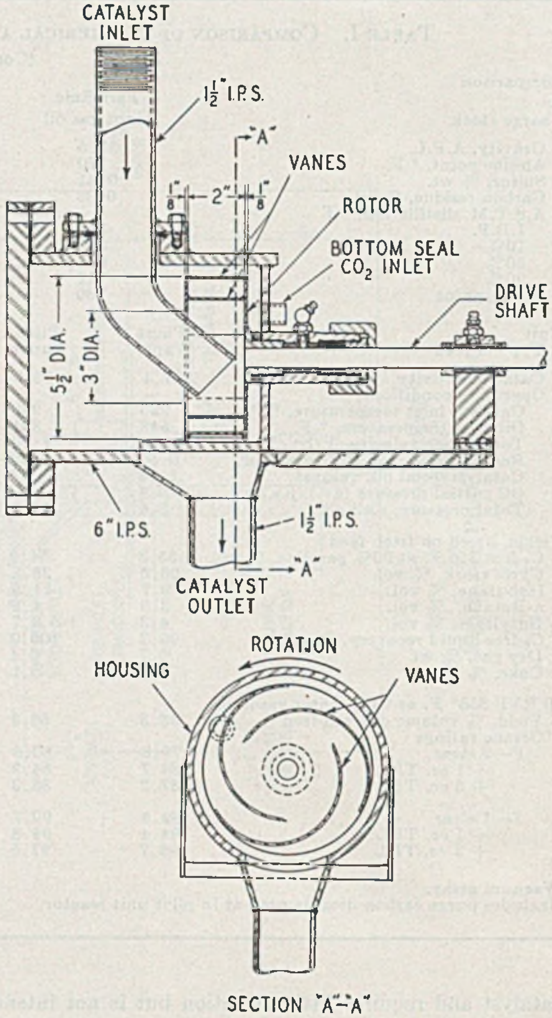

Figure 8. Catalyst Meter

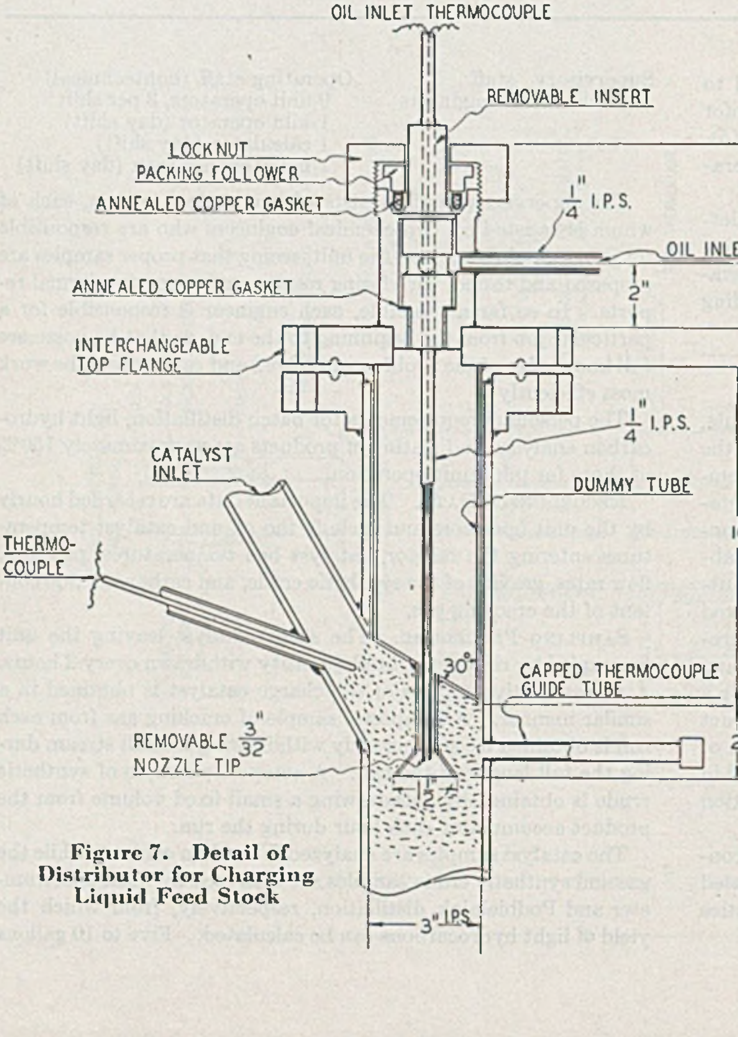

Figure 7. Detail of Distributor for Charging Liquid Feed Stock

OTHER APPLICATIONS OF PILOT UNIT

Although the Thermofor pilot unit has been described from the standpoint of studying catalytic cracking reactions, it can be applied readily to other studies. Thus, it can be used to study any operation (within limitations of the equipment) where vapor is brought in contact with a catalyst or heat-transfer material to produce a chemical reaction. With modifications the unit could be adapted to studying reactions in the liquid phase or at higher pressures.

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(1) Hagerbaumer, W. A., and Lee, R., *Petroleum Refiner*, 26, 551 (1947).
(2) Simpson, T. P., Evans, L. P., Hornberg, C. V., and Payne, J. W., *Proc. Am. Petroleum Inst.*, 23 (III), 59 (1942).
(3) *Ibid.*, 24 (III), 83 (1943).
(4) Simpson, T. P., Eastwood, S. C., and Shimp, H. G., *Ibid.*, 25 (III), 42 (1945).
(5) Simpson, T. P., Nicholls, E. S., and Payne, J. W., *Trans. Am. Inst. Chem. Engrs.*, 36, 846 (1940).

RECEIVED October 11, 1947.

November's HEADLINES...

Events of Interest to Chemists, Chemical Engineers, and Executives∼∼*Reviewed by the Editors*

¶ NOVEMBER 1. Glenn T. Seaborg, University of California, co-discoverer of plutonium, is announced as winner of Wm. H. Nichols Medal of New York Section, ACS, presentation to be made March 5, 1948[1].∼∼Goodyear Tire & Rubber announces Pliofilm is again available to fabricators.∼∼President's Council of Economic Advisers in report suggests U. S. increase its exports of nitrogenous fertilizers to Europe which would mean restoration of domestic end-use controls.∼∼Du Pont sets up mobile laboratory to test petroleum chemicals in motor fuel at El Monte, Calif.

¶ NOVEMBER 3. Leonard P. Schultz, a Smithsonian Institution scientist, says fish life in the area of Bikini atoll has returned practically to normal.∼∼W. E. Cake, assistant managing director, plantation division, U. S. Rubber, reveals that natural rubber latex is being produced in sufficient quantity in Malaya and Sumatra to indicate maintenance of expanding deliveries. ∼∼B. F. Goodrich Co. announces new "winter type" camel back for recapping tires.

¶ NOVEMBER 4. New England Textile Foundation announces it will award as many as thirty $500 freshman scholarships in 1948 in the four textile schools of New England.∼∼W. G. Skelly, former president Mission Corp. and Pacific Western Oil Corp., files to block suit of proposed merger of Mission and Sunray Oil Corp.∼∼U. S. Department of Agriculture plans long-time project under Research and Marketing Act to search for new and improved antibiotics from agricultural sources that will be effective against various diseases.

¶ NOVEMBER 5. Commerce Department reports exports of rubber products and materials declined in September for fourth month.∼∼Government officials deny London reports that U. S. has agreed to cut use of synthetic rubber in tires.∼∼Bureau of Agricultural Economics reports September dry casein production highest for month since 1941.∼∼Interstate Commerce Commission adds ammonium nitrate fertilizer and trifluorochloroethylene to list of explosives and other dangerous articles.∼∼Ethel L. French, chairman Rochester Section, ACS, announces that Carl F. Cori and Gerty T. Cori, co-winners of the 1947 Nobel Prize in Medicine, will give third Harrison Howe lecture[2].

¶ NOVEMBER 7. George W. Merck, president Merck & Co., at meeting in New York, receives 1947 Chemical Industry Medal of American Section Society of Chemical Industry for "outstanding accomplishment in the field of pharmaceuticals carried out under his leadership by Merck & Co., and for his wartime contributions to chemical industry."∼∼General Aniline and Film Corp. awards contract for construction of 3-story manufacturing building at Rensselaer, N. Y.[3]

¶ NOVEMBER 8. Sun Oil builds independent research department at Newtown Square, Pa., to house all its study work in petrochemical and physical research[4].

¶ NOVEMBER 9. Foreign Liquidation Commissioner Donald H. Connolly, extends deadline for submitting bids for parts of two German chemical plants offered as reparation to American industrialists.

¶ NOVEMBER 10. Parke Davis & Co., chemists, isolate new weapon against tuberculosis, chloromycetin, related to streptomycin, but said to be capable of being taken by mouth without harmful results.∼∼U. S. Department of Agriculture makes first annual presentation of honor awards in recognition of exceptional contributions of its employees to efficient and constructive public service; a number of chemists receive awards.∼∼Supreme Court upholds Justice Department antitrust suit against International Salt Co. and says company must cease requiring leased machines to use its products.∼∼Commerce Department reports chemical products machinery, dairy products, and textile manufactures led September export decline.∼∼Goodyear Tire & Rubber announces production of its 25 millionth tire.∼∼Interchemical Corp. acquires $150,000 3-acre tract to erect plant for manufacture of printer's ink in Elizabeth, N. J.

¶ NOVEMBER 11. Dewey & Almy Chemical Co. opens new solvent plant at Acton, Mass., H. S. Ferguson, general manager, announces.∼∼American Potash & Chemical Corp. completes $300,000 research laboratory office building in Los Angeles and subdivision of 47 homes at its Trona plant[4].∼∼Lawrence Ollinger, president U. S. Plywood, announces U. S. Plywood and Harbor Plywood Corp. will begin construction immediately on a $2,000,000 plywood plant at Anderson, Calif.∼∼National Research Council reports Merck Fellowships for the academic year 1948–49 are available.∼∼Chem-Tech Producers Corp. is formed for export of chemicals and chemical plant equipment, Martin Bernhardt, general manager, says.∼∼U. S. Rubber announces new rubber compound for sealing concrete highways.∼∼U. S. Rubber ceases operations at its synthetic rubber plant at Institute, W. Va., plant manager P. E. Rice announces.∼∼Manson Benedict, director of process development, Hydrocarbon Research, Inc., and Louis C. Rubin, manager of research, M. W. Kellogg Co., receive William H. Walker Award for wartime achievements in aiding in distillation of toluene at meeting of American Institute of Chemical Engineers in Detroit.∼∼Warren R. Austin, permanent U. S. delegate to UN, at 30th annual dinner of Foreign Press Association in New York, says Soviet Union probably is a long way from producing atomic bombs.

¶ NOVEMBER 12. Preliminary statistics of Commerce Department show manufacturers' consumption of natural rubber in September exceeded imports and use of synthetic rubber in excess of domestic consumption.∼∼Eagle-Picher completes new plant at Clark, Nev., to process diatomaceous earth, T. C. Carter, vice president in charge of insulation and diatomaceous earth, announces.∼∼Weller Noble, chairman Board National Fertilizer Association, and president Pacific Guano Co., at group's southern convention warns that any fertilizer shipped abroad under Marshall plan will limit to that extent amounts available to American farmers.∼∼Agricultural Research Administration says substantial new uses of soybean glue are in offing.

¶ NOVEMBER 13. Sir Robert Robinson, authority on synthesis and co-discoverer of artificial sex hormones, stilboestrol and hexoestrol, wins 1947 Nobel Prize in Chemistry, and Sir Edward Victor Appleton, the Nobel Prize in Physics; latter gives credit to J. H. Bellinger, National Bureau of Standards, who cooperated in investigations that helped lay groundwork for radar[5].∼∼Charles Edison, former Secretary of the Navy, speaking before annual national conference on Government of National Municipal Leagues, urges atomic bomb controls, and declares present curbs could pass too easily into hands of enemies.∼∼John M. Hancock, former member U. S. delegation to UNAEC, says report that So-

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[1] *Chem. Eng. News*, 25, 3201 (Nov. 3, 1947).
[2] *Ibid.*, 3567 (Dec. 1, 1947).
[3] *Ibid.*, 3508 (Nov. 24, 1947).
[4] *Ibid.*, 3506 (Nov. 24, 1947).
[5] *Ibid.*, 3510 (Nov. 24, 1947).

viet Union has tested an atomic bomb in Siberia is a ruse to get technical information.∼∼Navy Captain Shields Warren, medical researcher in atomic energy, says survivors of atomic bombing at Nagasaki are about normal now.∼∼George A. Sloan, president Nutrition Foundation, announces at annual meeting of board of trustees in New York that grants-in-aid exceeding $1,510,000 for fundamental research in the science of nutrition have been made to date to 57 universities and medical centers in the U. S. and Canada.∼∼L. W. Flett, new products division director, National Aniline Division, Allied Chemical & Dye, predicts annual production of synthetic detergents will reach 3,000,000,000 lb. within 10 to 15 years.

¶ NOVEMBER 14. The Royal Society, Britain's oldest scientific body, bestows its Davy Medal on Linus C. Pauling for distinguished contributions to the theory of valency and for their application to systems of biological importance.∼∼Representative Shafer tells House Armed Services subcommittee at first public hearing in Ohio that major rubber companies are nearing an agreement on disposal of government's synthetic rubber plants. ∼∼Representatives of U.S., Canada, and the United Kingdom begin 3-day conference in Washington on atomic security problems.

¶ NOVEMBER 15. USAEC issues regulation effective Nov. 20 requiring license of persons intending to manufacture or export facilities capable of producing any fissionable material.∼∼U. S. Bureau of Mines says experiments have proved that 915,000,000,000 tons of lignite in North Dakota, Montana, and South Dakota are potential producers of fuel gas for industry.∼∼A. D. Duncan, vice president Glidden Co., says $1,000,000 modernization program is under way at four of its major paint and varnish plants.

¶ NOVEMBER 16. Plastic Manufacturers Association and Commodity Standards Division, National Bureau of Standards, adopt commercial standard for molded urea plastics.∼∼Special mission of European fertilizer experts says western Europe is producing nitrogen fertilizers at current capacity.∼∼U. S. Department of Agriculture pushes 160 projects in research in first year's work under Research and Marketing Act.

¶ NOVEMBER 17. Representative Jamie L. Whitten (Miss.) asks House Appropriations Committee to investigate fully domestic shortage of nitrogen fertilizers before Congress votes emergency aid to Europe.∼∼Office of International Trade lifts quinine exports curb for first time since embargo was established in April 1942.

¶ NOVEMBER 18. Robert C. Elderfield, professor of chemistry Columbia University, at meeting of Western New York Section, ACS, says new antimalarial drug which will effect cures in 95% of relapse cases when used with quinine is practically ready for commercial production.

¶ NOVEMBER 19. Roy A. Bradt, president American Washer and Ironer Manufacturers Association, says record production of washing machines is due in part at least to substitution of aluminum for hard-to-get steel.∼∼Rayomer, Inc., adds to its holdings more than 2,000,000,000 ft. of timber in Far West, including three pulp mills. Company officials say new $5,000,000 wood naval stores plant of Newport Industries, Inc., at Oakdale, La., is rapidly approaching capacity production.∼∼Aluminum Oregon Co. announces plans for a $750,000 plant for manufacture of fluoride chemicals in East St. Louis, Ill.

¶ NOVEMBER 20. James J. Newman, vice president B. F. Goodrich Co., says American synthetic rubber plants have more than paid for themselves.∼∼Leighton R. Smith, research chemist Lever Brothers, and Charles E. Ruby, Boston attorney and chemical engineer, file suit in U. S. Court of Claims for $6,000,000 from U. S. for alleged government use of their patented processes to render wool shrink-resistant[6].∼∼American Cyanamid announces new insecticide said to be 5 to 25 times more effective than DDT.

¶ NOVEMBER 21. Reynolds Metals protests reductions in U. S. tariff on raw aluminum and its fabricated products.

¶ NOVEMBER 23. Linde Air Products Co. announces it will soon begin construction of $200,000 plant for oxygen and acetylene production near Woodrow, Ark.∼∼House of Representatives Select Committee on Foreign Aid points out that European nations should pay at least in part for American help by giving U. S. access to rich iron deposits in Labrador, oil holdings in Venezuela, and chrome and nickel deposits in New Caledonia.

¶ NOVEMBER 24. Commerce Department says newsprint is only paper expected to be in short supply in the spring.∼∼Revised report of American Petroleum Institute shows East Coast oil situation has deteriorated.∼∼Department of Agriculture recommends extension of government export controls on nitrogen and other fertilizer materials, pigments, paints, and varnishes, soap and allied products, and basic industrial chemicals for two years beyond Feb. 29, 1948.∼∼Representative Dawson says prospects are favorable for purchase of Salt Lake City Kalunite plant by American Potash and Chemical Co.∼∼B. F. Goodrich Chemical Co. announces plans for construction of new manufacturing unit to produce insecticide materials in its chemical plant in Akron.

¶ NOVEMBER 26. Military tribunal in trial of I. G. Farbenindustrie executives admits to evidence mass of documents placing on individual defendants ultimate responsibility for manufacture of cyclone B gas used to exterminate millions of concentration camp inmates.∼∼AEC investigates reports that a mining company owned by Gene Tunney and others has found rich uranium deposits in Northwestern Canada; British Columbia provincial government officials confirm such discoveries.

¶ NOVEMBER 27. Stevens M. Spencer, associate editor *Saturday Evening Post* and George A. Keaney, *N. Y. World Telegram* feature writer, win George Westinghouse science writing awards in annual competition of American Association for Advancement of Science.∼∼Davison Chemical Corp. buys silica gel plant constructed by Government during war for corporation at Curtis Bay, Baltimore, Md.∼∼B. F. Goodrich Chemical Co. announces plans for installation of new manufacturing unit for production in quantity of agricultural spray material, Good-Rite p.e.p.s. (polyethylene polysulfide).

¶ NOVEMBER 28. Office of International Trade increases dollar limits of some industrial pigments for shipment under general license procedure.∼∼Food and Drug Administration reports nationwide shortage of penicillin.∼∼D. E. Lilienthal, chairman AEC, addressing National Conference of American Education Fellowship in Chicago, urges educators to provide leadership in nationwide program of self-education in "the basic facts and the essential meaning of atomic energy" lest democracy perish.

¶ NOVEMBER 29. E. L. Bortz, president American Medical Association, speaking at Middle States Association of Colleges and Secondary Schools meeting in Atlantic City, says basis of modern defense program is greater training in science and recommends training small groups of highly skilled technicians for national defense.

¶ NOVEMBER 30. American Section, Society of Chemical Industry, announces selection of Clarence W. Balke, pioneer worker in rare metals, to receive 1948 Perkin Medal.∼∼Henry J. Kaiser's Permanente Metals Corp. is successful bidder for first German reparations plant to be offered U. S. industry; aluminum foil plant will be brought here from Teningen Baden[7].∼∼Reader poll conducted by *Chemical Bulletin*, publication of Chicago Section ACS, selects "ten ablest chemists and chemical engineers" now working in the U. S. in each of 20 specialized fields.

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[6] *Chem. Eng. News*, 25, 3578 (Dec. 1, 1947).

[7] *Ibid.*, 3434 (Nov. 17, 1947).

ANOTHER VOTE FOR *Fluid*

Improvements to Sohio's Lima, Ohio, refinery will include installation of a UOP-engineered fluid catalytic cracking unit. Result: flexibility in the processing of 16,000 barrels of fresh charge per stream day.

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Alloy (Annealed)	Temperature, °F.	Tensile Strength, psi.	Elongation, % in 2 in.	Impact Resistance—ft/lb, Izod Specimens
Deoxidized Copper	Room	31,400	48	43
	—292	58,000	58	50
Cupro Nickel, 30%	Room	70,800	41	90
	—292	112,700	51	97
Cartridge Brass, 70%	Room	51,100	49	66
	—292	73,500	75	79

(Tests on 0.25 in. diameter specimens)

Other Revere alloys, such as Herculoy (High-Silicon Bronze, A) show similar excellent properties at depressed temperatures.

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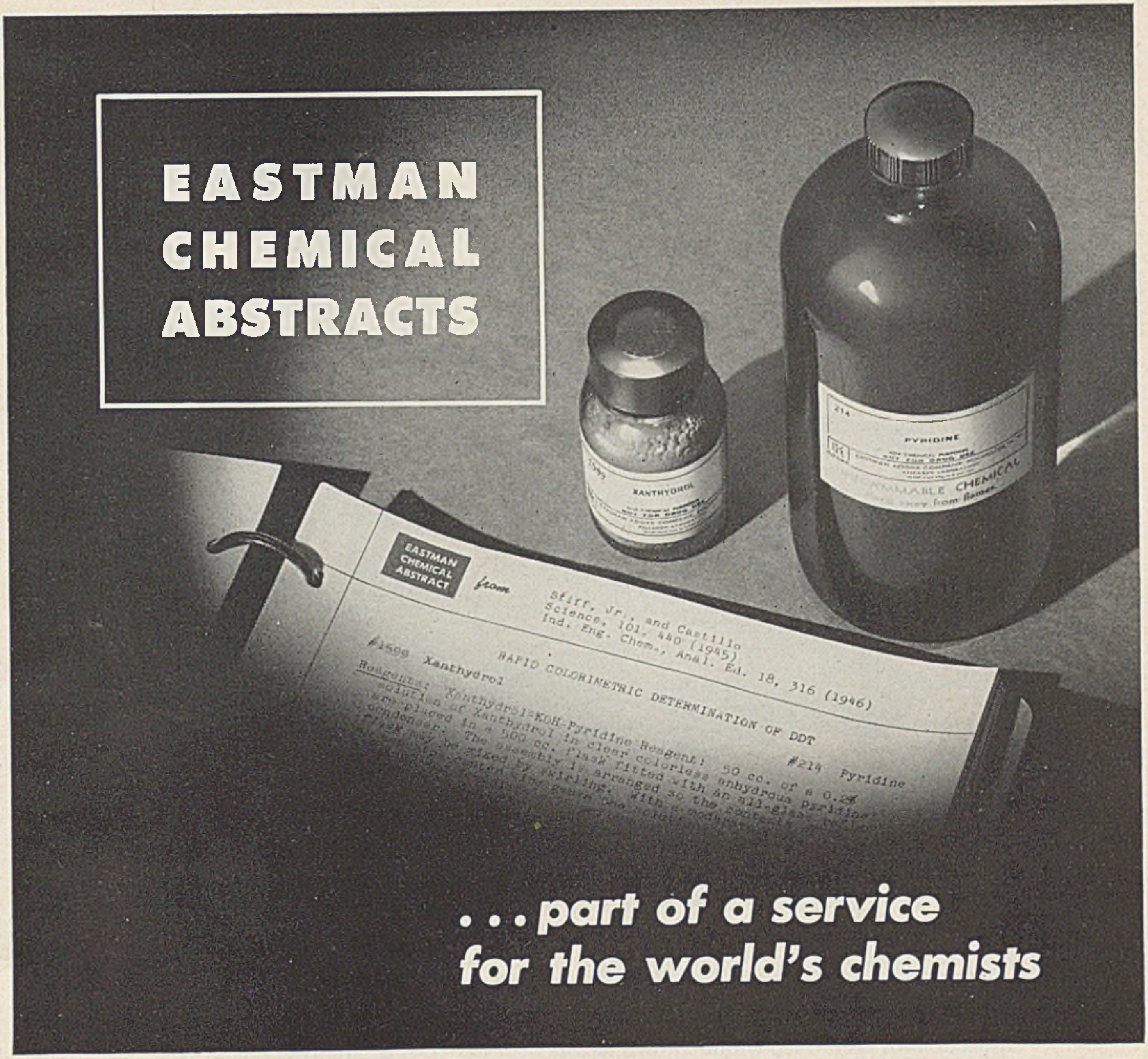

EASTMAN CHEMICAL ABSTRACT from

Stiff, Jr., and Castillo
Science, 101, 440 (1945)
Ind. Eng. Chem., Anal. Ed. 18, 316 (1946)

#1509 Xanthydrol

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#214 Pyridine

Reagents: Xanthydrol-KOH-Pyridine Reagent: 50 cc. of a 0.2% solution of Xanthydrol in clear colorless anhydrous pyridine are placed in a 500 cc. flask fitted with an all-glass reflux condenser. The assembly is arranged so the contents ... flask may be mixed by swirling. With a moderate ...

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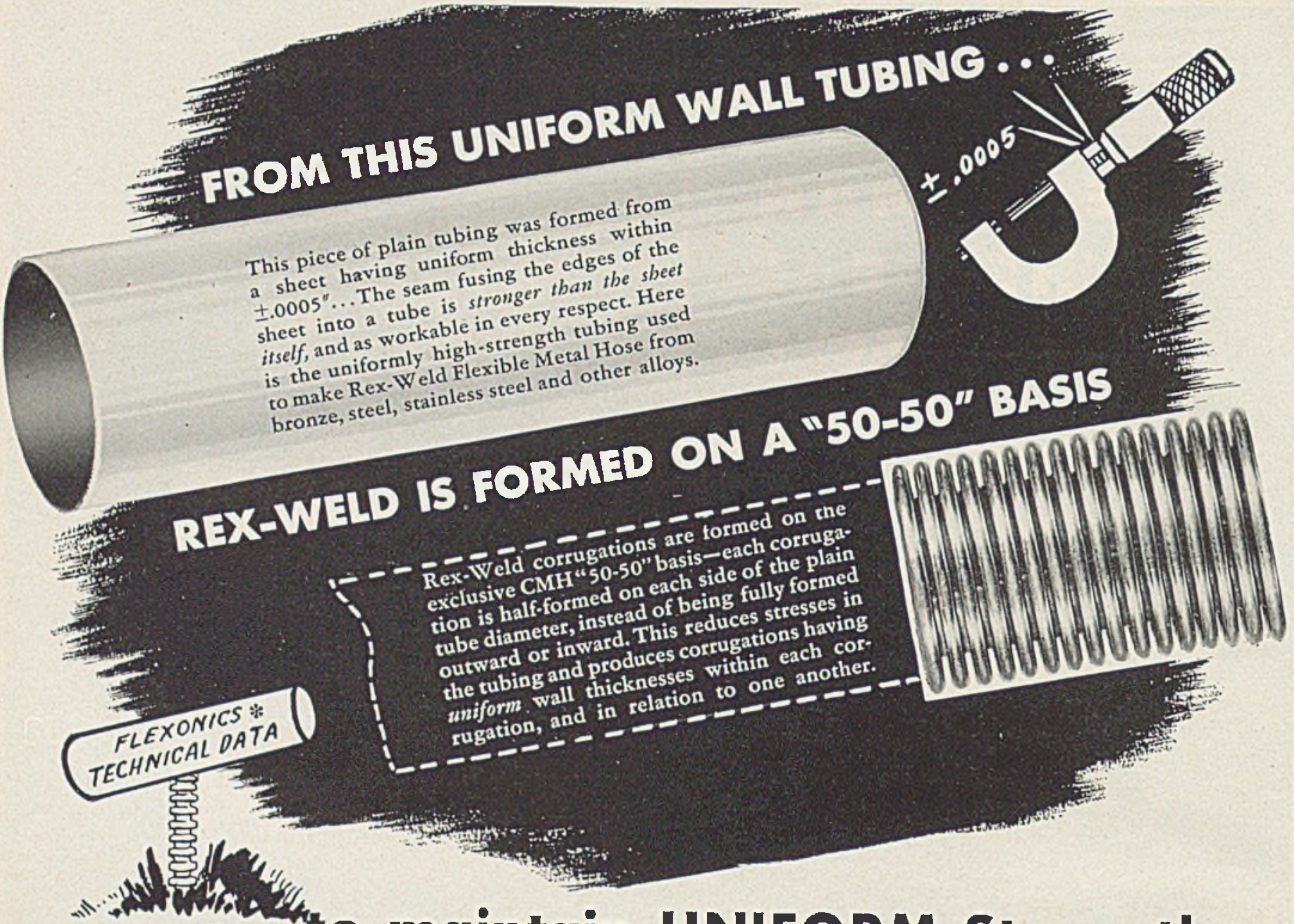

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- Laboratory tests show that when Rex-Weld samples are subjected to abnormally elevated pressures, failure of the tubing occurs at undeterminable points anywhere in the tube.
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Equipment and Design

The application of pure science to industry can readily be seen in today's commercial equipment.

by Charles Owen Brown

IT IS often a very instructive lesson to follow the history of equipment design from the origin, in a pure scientific research, to commercial production equipment. The pure science work, of course, precedes the commercial applications by many years; just how many is indicated by a new type of valve, recently announced, which forms the basis for this story. The evolution could be described from little steel test tubes to huge vessels and back to small valves.

Pressure equipment

At the turn of the century P. W. Bridgman decided to continue the work of Amagat in the physics of high pressures. His first task was to devise fundamentals, joints, packings, vessels, and closures which would withstand very high pressures. His ambitions embraced stresses many times higher than any pressure previously used, and his ingenuity and ability were sufficient to carry the work far beyond his original plans. After completing the basic pieces of a high pressure system, Bridgman next devised instruments and auxiliaries with which to follow the work. Of all these examples of brilliant design, including the high pressure window for reaction vessels and the electrical resistance method of measuring high pressures, Bridgman gives most credit to the gasketed joint he devised based upon the principle of an unsupported area. Of this extremely simple device (Figure 1) Bridgman writes in his book[1], "Finally, there is my own work done at Harvard University since 1906. A good part of the remainder of this book is to be devoted to it, so that no more need be said here, except to give the one characterization that all this work grew out of the development of a packing technique which makes it possible to reach without leak any pressure allowed by the mechanical strength of the wall of the containing vessel."

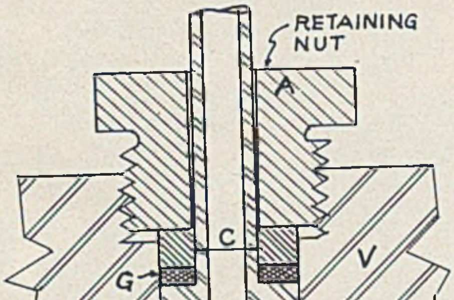

Figure 1. Bridgman's Gasketed Joint

This packing technique is so simple it can be accurately shown in the pipe connection sketch of Figure 1. Packing nut *A* is screwed into a machined and threaded opening in the wall of vessel *V*. This nut must always have an opening in the center creating the unsupported area *C*. Even when merely closing an opening with a plug, the nut is actually a ring. The gasket must be totally confined under the nut and above a piece completely closing opening *B*. The gasket area *B-C* is never larger than the area of metal in the nut or plug. Internal pressure forcing the bottom piece (which closes the opening) upward compresses the gasket proportional to the whole area *B* divided by the gasket area *B-C*. Usual and convenient design permits a gasket pressure of 5 to 8 times the unit working pressure without special effort.

The first commercial equipment to use the same design employed in Bridgman's 20- to 25-cc. vessels was at relatively low pressures in the eliptical manhole cover used in most boilers. The eliptical shape and low pressures permitted the cover to be inserted in the boiler from the outside, using the small diameter, then a 90° turn, and it covered the opening completely. Although limited to moderate pressures, this joint has only two pieces, the cover and the gasket. Under very high pressures this eliptical type would not be practical, because, for maximum strength, the vessel must be round; then three pieces are required—the cover, the gasket, and the nut. It is fortunate that this type of closure is self-sealing by the internal pressure, because the screwed nut retaining the gasket on large diameter, high pressure vessels is a very heavy affair with enormous thread friction. It would be most difficult to tighten this nut against the pressure as ordinary joints are tightened. In Bridgman's design all nuts and bolts, when used, are positioned and tightened before any pressure is applied to the system. The nut, or retaining ring, with bolts, gasket, and cover for a vessel 48 inches in inside diameter will weigh about 18 tons. These large closures have been made up to 60 inches in inside diameter, and trouble has never been known in this type of joint. Quite as remarkably, these massive closures are easily opened and yet are leakproof. In the whole world there are probably less than 350 heavy vessels using this closure, although an important industry is based on it.

This condition is soon to change, because of the rather belated appreciation of the advantages by the Crane Company now using this joint, as a means of closing the opening in a valve body. This application, although not so small as Bridgman's laboratory vessels, is still only a few inches in diameter but will place tens of thousands of these joints in service. The Crane Company describes this old design as follows: "The bonnet joint is inside the

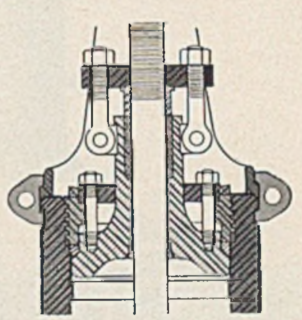

Figure 2. Crane Company's Leakproof Bonnet Joint

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[1] Bridgman, P. W., "Physics of High Pressures," p. 14, New York, Macmillan Co., 1931.

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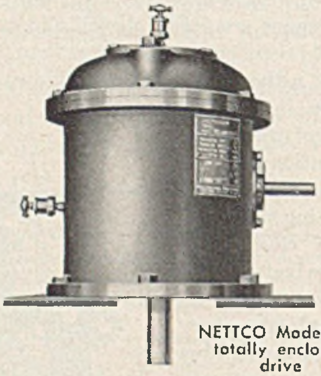

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valve, sealed with a wedge-shaped seal ring. Fluid pressure in valve automatically keeps bonnet joint tight. No bolts to retain pressure. Leakage is impossible." The method of applying this joint to an O. S. and Y. valve is shown in Figure 2. The space saved by using this joint on a 1500-pound 8-inch steel gate valve is $4^3/_4$ inches in length and 11 inches in height; the weight saving is over 15%.

Hydrogenation unit

A portable hydrogenation unit has been developed in the instrument shop of Bristol Laboratories, Inc., Syracuse, N. Y., supervised by Ernie Smith. The design has been described by Douglas E. Cooper and is shown in Figure 3. The assembly is completely portable except for a standard electrical cord, which supplies heat, power, and control energy. Space is provided for storage of liners, tools, and other accessories.

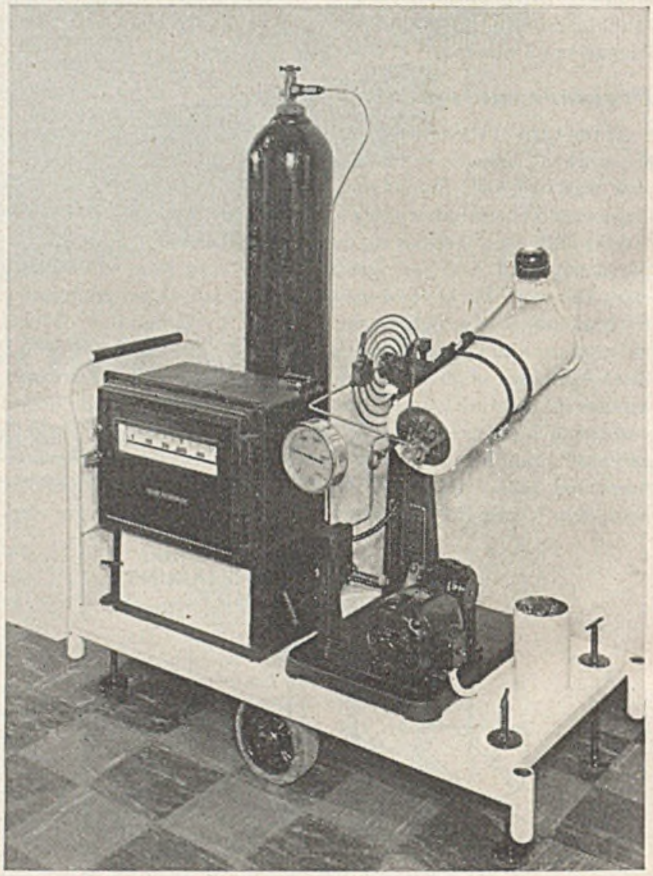

Figure 3. Portable Hydrogenation Unit

Most of the equipment is standard. The bomb shaker assembly is model 406-OIC of American Instrument Company, also supplying the Brown temperature controller and bomb tools. The truck is a Lewis-Shepard model SM-3060. The standard hydrogen cylinder is held upright by a 14-inch length of 10-inch steel pipe with L-strap braces bolted to the truck platform. Storage for liners is in the box supporting the Brown instrument, and other tools are kept in the box at the end of the truck. When in use the truck is anchored and leveled by hand screws at each corner, guided by two spirit levels placed at right angles. Gage faces are fitted with Plexiglas. This assembly is compact and conveniently moved from one laboratory to another, ready to be put to work without loss of time.

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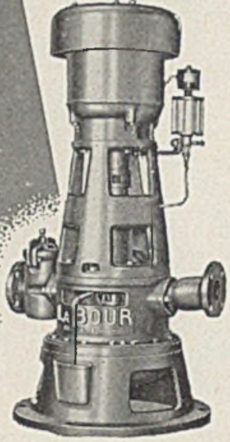
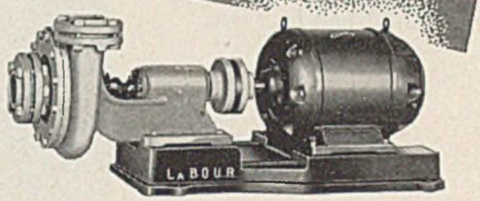


REQUIRED---

A simple, efficient centrifugal pump, not necessarily self-priming but able to free itself of minor volumes of air or vapor, to handle various acids and caustics.

Answer: LaBOUR Type Q



REQUIRED---

A dependable, self-priming centrifugal pump at minimum cost for quality equipment, to handle acids, caustics, "dry" liquids, and liquids containing small solids or fibres.

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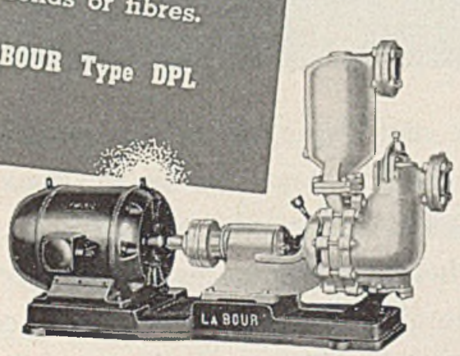

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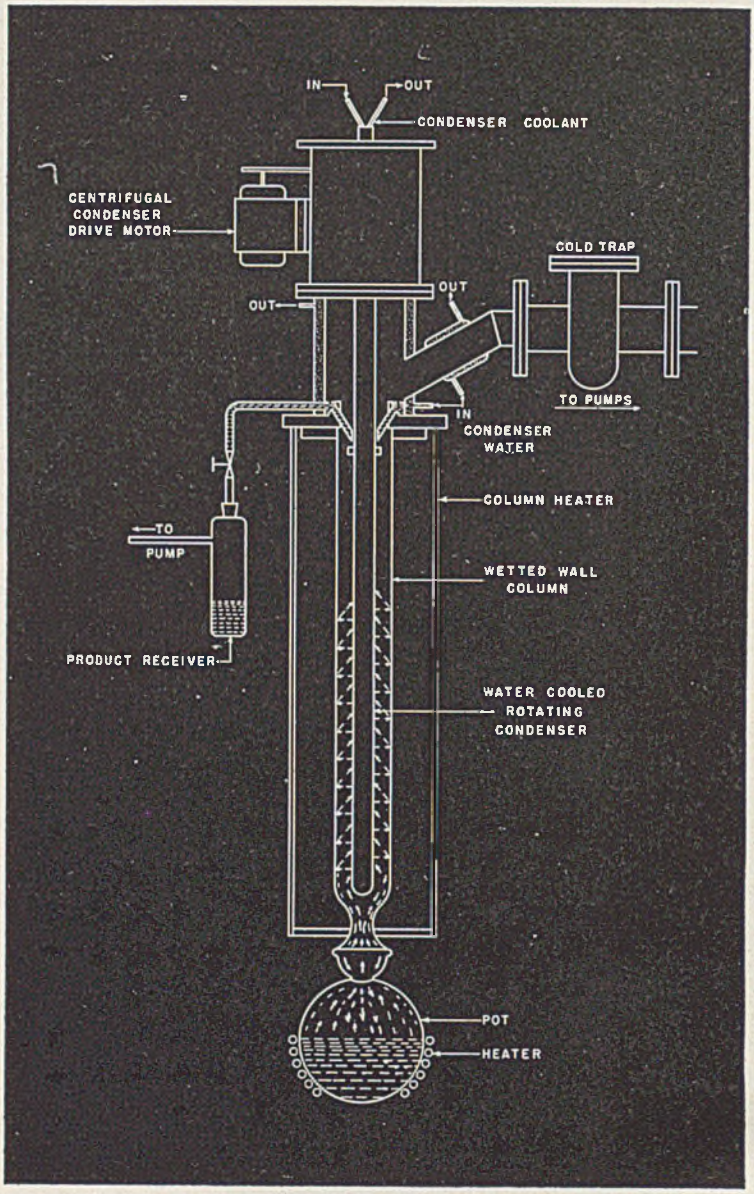

The unique principles of the centrifugal condenser type still are illustrated above. Rising vapor from the pot condenses on the cooled rotating cylinder. Condensate is then hurled off the condenser surface by centrifugal force and re-vaporized from the heated column. This cycle is repeated many times as the vapor moves up the annular space between the column and condenser, setting up a concentration gradient, with the more volatile components at the top where they are removed.

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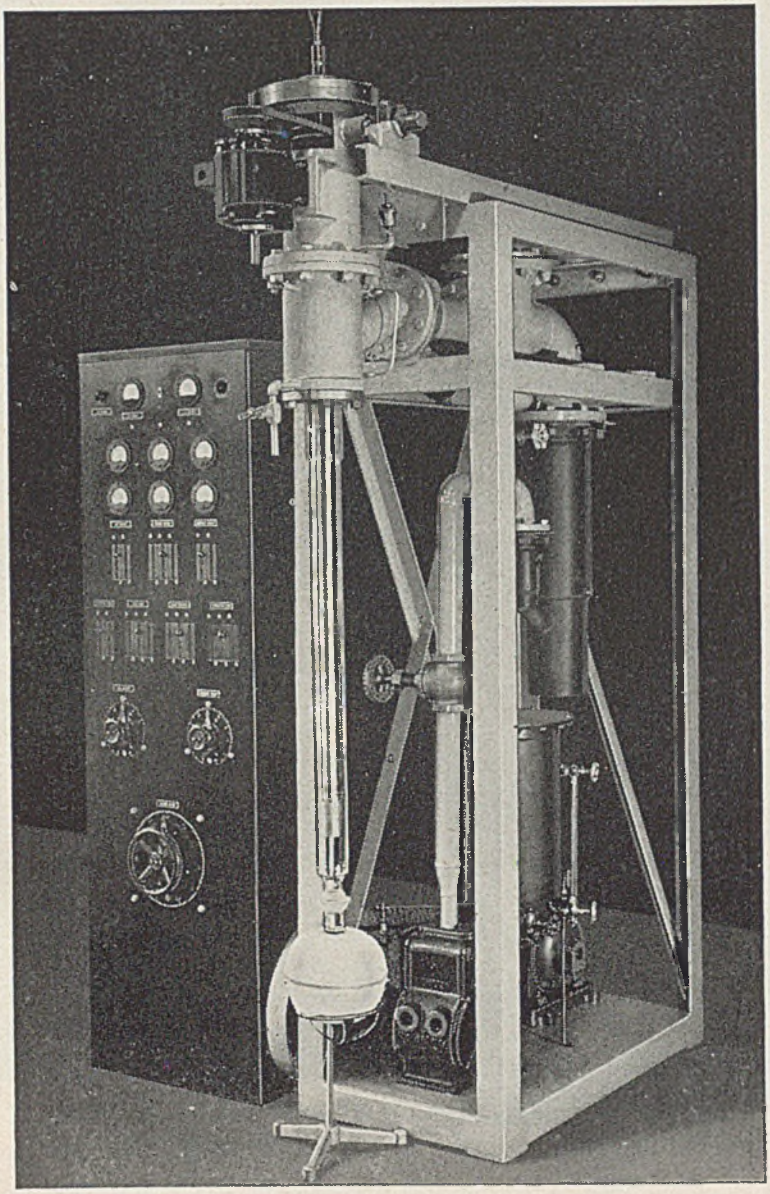

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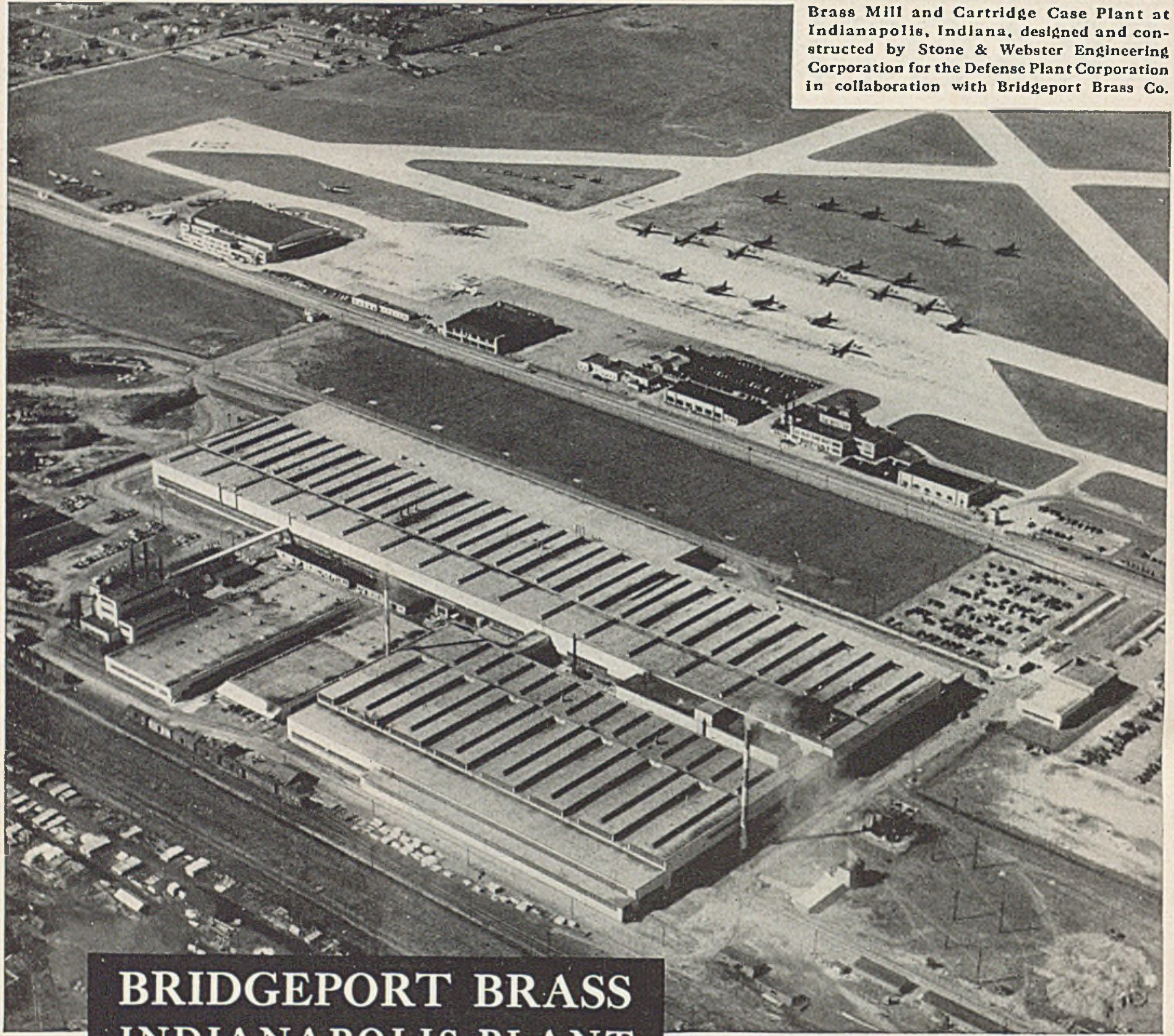

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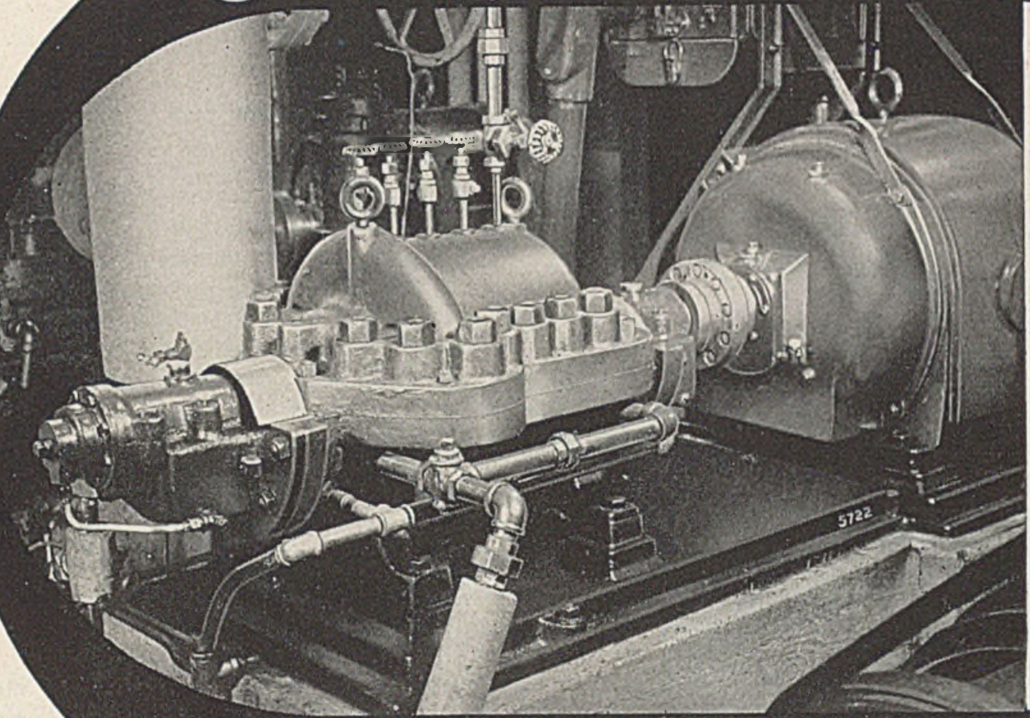

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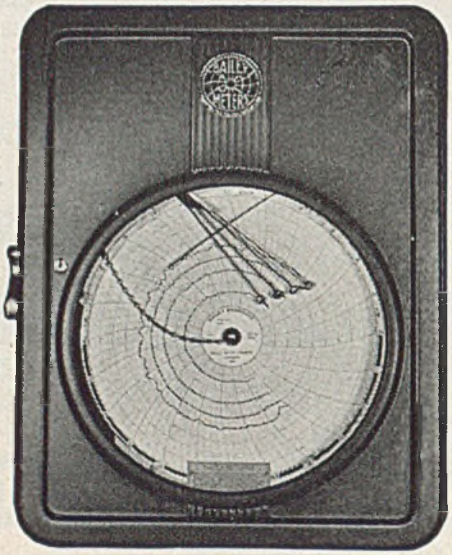

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Instrumentation

A summary is given of the proceedings of the 1946 Texas A. & M. short course on instrumentation for the process industries.

by Ralph H. Munch

INSTRUMENTATION can advance only if sufficient numbers of mathematicians, scientists, engineers, and technicians well trained in the field are available. Because it is a new field, there are no institutions with specialized courses leading to degrees in instrumentation. The experts in the field are those who started with good broad fundamental training in science and engineering and added considerable amounts of experience in the application of instruments in plants. As we have noted previously, educational institutions are giving a great deal of thought to the problem of how best to furnish men suitably trained to take advantage of the opportunities available in the field of instrumentation. Various possible means of solving the problem are being tried out. After these have been in operation long enough, they will probably supply the trained personnel needed. In addition to the need for men trained to enter the field of instrumentation, there is a very real need to give those already in the field an opportunity to better their knowledge of the subject.

To fill this need, the School of Engineering of the Agricultural and Mechanical College of Texas has started a series of annual short courses. The first of these was held September 3 through 6, 1946. The proceedings of this symposium have recently been published as Bulletin 100 of the Agricultural and Mechanical College of Texas. This bulletin, entitled "Instrumentation for the Process Industries," can be obtained from the Texas Engineering Experiment Station, College Station, Tex., at $2.00 per copy.

To quote from the foreword of the bulletin, "In the 1946 course the object was to present a summary of the fundamentals of the subject and a survey of methods of application to actual measurement and control in plant practice.

"The course is intended to be on the engineering level, with the major emphasis on the practical rather than the theoretical side. Since it is the theory, however, which largely provides the unifying thread, some theoretical aspects of instrumentation are covered.

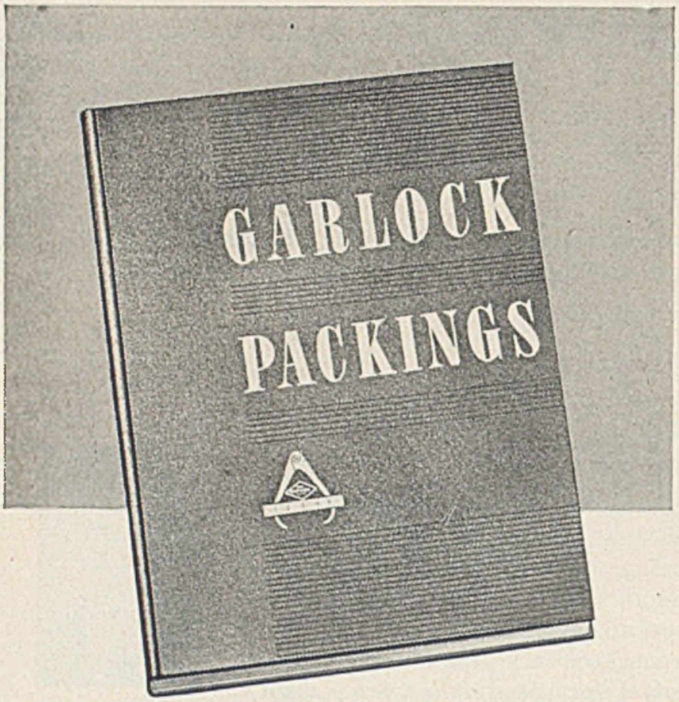
"The subject of instrumentation, if taken in its entirety, would be so broad that adequate coverage could not be given it. The field has been limited by placing primary emphasis on applications to continuous fluid flow processes. Measurement of gas flow is not done in great detail. Even with these limitations the field is so broad that it cannot be covered completely in any one year; hence it must be expected that thorough treatment of the entire subject will be obtained only in the course of several years' meetings."

The symposium opened with a paper by C. S. Comstock of Monsanto Chemical Company entitled "Some Economic Considerations of Instrumentation." It begins by citing the advantages of instrumentation—to make production possible, to improve product purity and uniformity, to reduce the dangers of operation, and to reduce costs of production. Next, costs of instruments and labor are developed. It is shown that the cost of owning an instrument—depreciation, return on investment, and cost of operating—amounts to $281 for the average control instrument, and that the cost of a man per shift for a year is about $15,000. In spite of this, labor costs cannot be reduced beyond a certain point by substituting instruments for operators. The advisability of designing process equipment and instrumentation simultaneously to take full advantage of instrumentation is discussed. Finally the functions of an instrument department are described.

"Measurement of Flow and Liquid Level" was the title of a paper by L. K. Spink of the Foxboro Company. It is a rather complete introduction to these two closely related subjects. The major types of flowmeters are described, but emphasis is put on variable head meters using the concentric flat-plate sharp-edged orifice. The piping hookup, arrangement of seal pots, and precautions to be observed to ensure accurate results are described in detail for many applications. Many piping diagrams are given as well as graphs showing Reynolds number corrections for various orifice-to-pipe diameter ratios and flows. A description of the commonly used types of liquid level instruments concludes the paper.

V. L. Parsegian of the C. J. Tagliabue Division of Portable Products Corp. described the measurement of temperature and pressure. This paper gives an excellent résumé of the theory and practice of temperature measurement but does not cover pressure measurement thoroughly. The author makes a point in this paper which is all too often forgotten; he reminds his readers that the complexity and price of instruments go up very rapidly as the accuracy or speed requirements are made more rigid. For example, he states that, using the thermocouple method, one may measure the temperature of a furnace to within an accuracy of $\pm 3\%$ at 1000° F. without spending more than a few dollars for a simple millivoltmeter. To increase the accuracy to within $\pm 0.5\%$ would multiply the cost of the meter by a factor of perhaps 10, while to increase it further to $\pm 0.2\%$ would require the use of potentiometric type instruments and considerable care in the choice and use of the thermocouples, at a cost 20 to 30 times the original. Therefore one should choose equipment sufficiently good but not too good for any particular application.

A survey of electrochemical measuring devices was presented by W. N. Greer of Leeds & Northrup Company, who gave an interesting survey of electrolytic conductivity methods, pH methods, and oxidation-reduction potential methods. He was careful to call attention not only to the potentialities of these methods but to their limitations.



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IEC-12

Instrumentation

The Taylor Instrument Companies' contribution to the program was a talk on some aspects of the theory of process control, by J. G. Ziegler. Ziegler points out that a good deal can be done to many processes to make them more easily controllable, and that an understanding of the effects of load changes in any process is necessary for the design of a good control system. He discusses methods for determining experimentally the best settings for controllers using the response curve of the system.

In an analysis of control of light ends fractionation E. D. Mattix of Cities Service Corporation discussed the control of fractionating equipment, known in petroleum refining circles as a debutanizer. He gives the liquid-vapor equilibrium diagram for the *n*-butane–*n*-pentane system and also shows the liquid composition for each tray in the tower. The latter diagram indicates that, to control this column, the temperature should be measured on the ninth tray rather than at the top or bottom. Mattix then goes on to describe two complete methods of controlling the operation of the debutanizer.

J. B. McMahon and R. W. Landon of Republic Flow Meters Company spoke on the control of primary operating variables. They emphasized the fact that one must exercise considerable judgment in applying mathematical methods to instrumentation, since the neglect of what appear to be unimportant details may lead to completely erroneous results. They analyzed problems in flow, temperature, liquid level, and pressure control to demonstrate their point.

Winfield B. Heinz of Penn Industrial Instrument Corporation is an exponent of pneumatic circuits for measurement and control. Few people are aware that pneumatic circuits are closely analogous to electronic circuits. Pneumatic relays can be used in suitable circuits in much the same way that vacuum tubes are used in electronic circuits. The author of this paper tabulates the analogous properties of pneumatic and electric circuits, and describes a group of useful pneumatic circuits.

Much has been written on valve characteristics. At this symposium T. B. Burris of Fisher-Governor Company gave the subject a new twist in a paper entitled "The Relations of Valve Characteristics," in which he describes the many details of valve design which can completely destroy the desired equal percentage characteristic of a valve. Valve body design, stem and packing-gland design, and the design of the diaphragm motor all are important if the valve is to have an equal percentage characteristic.

The final paper on the program was by D. M. Considine of the Brown Instrument Company on measurement as a factor in process instrumentation. It is a survey of primary measuring devices. Because most of those attending the meeting were familiar with the more conventional primary measuring devices, the author chose to emphasize some of the newer, less frequently used, primary measuring elements. Among these are the Pirani gage and the ionization gage for measuring low pressures, instruments for automatically recording dew point, the polarograph, infrared and ultraviolet spectrophotometers, and the x-ray spectrometer.

Those in charge of the Texas A. & M. short course on instrumentation for the process industries, and those who contributed papers for the program, are to be congratulated for the excellent job they have done. Almost everyone who is interested in instrumentation will find much stimulating new information in these proceedings.

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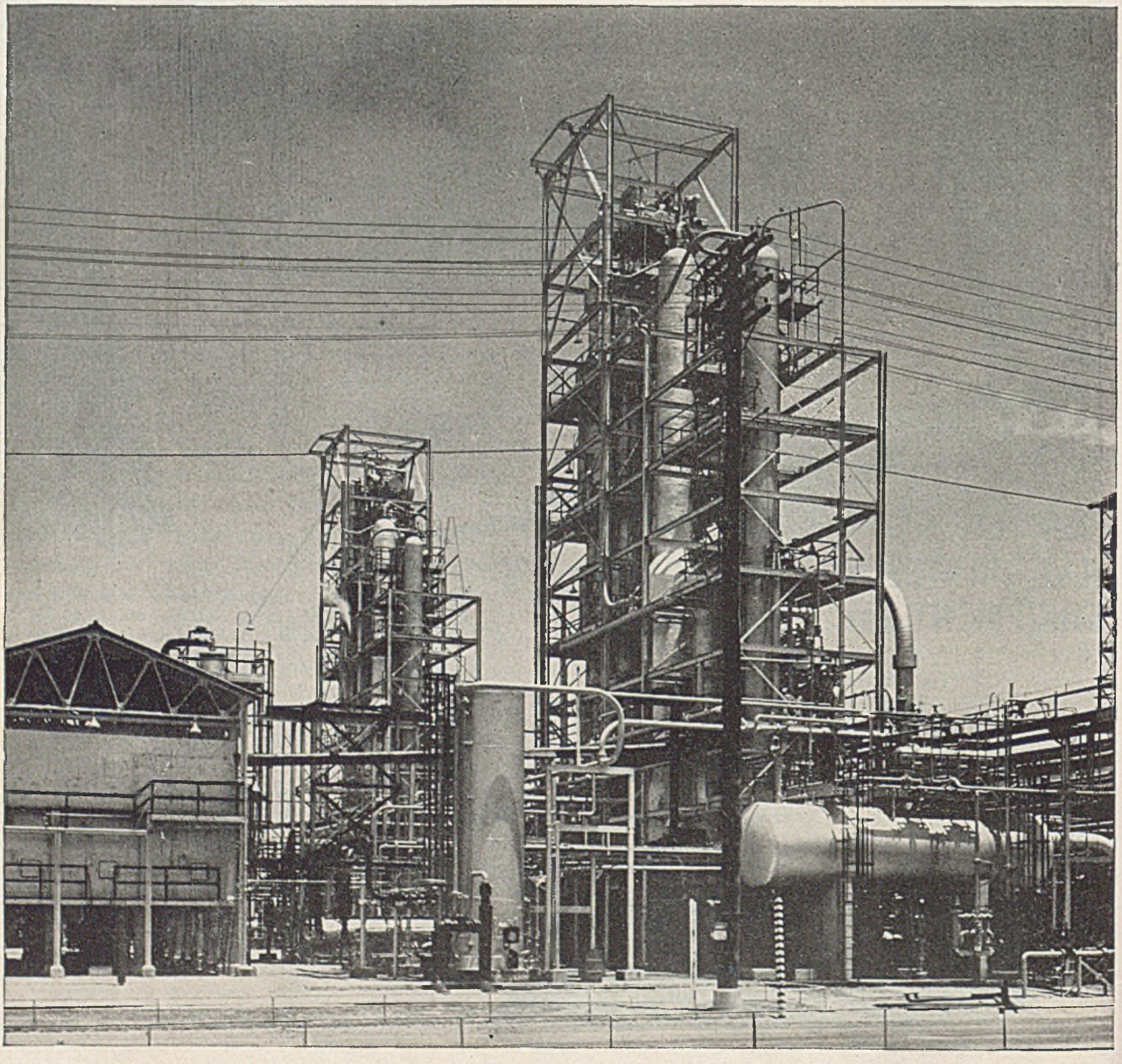

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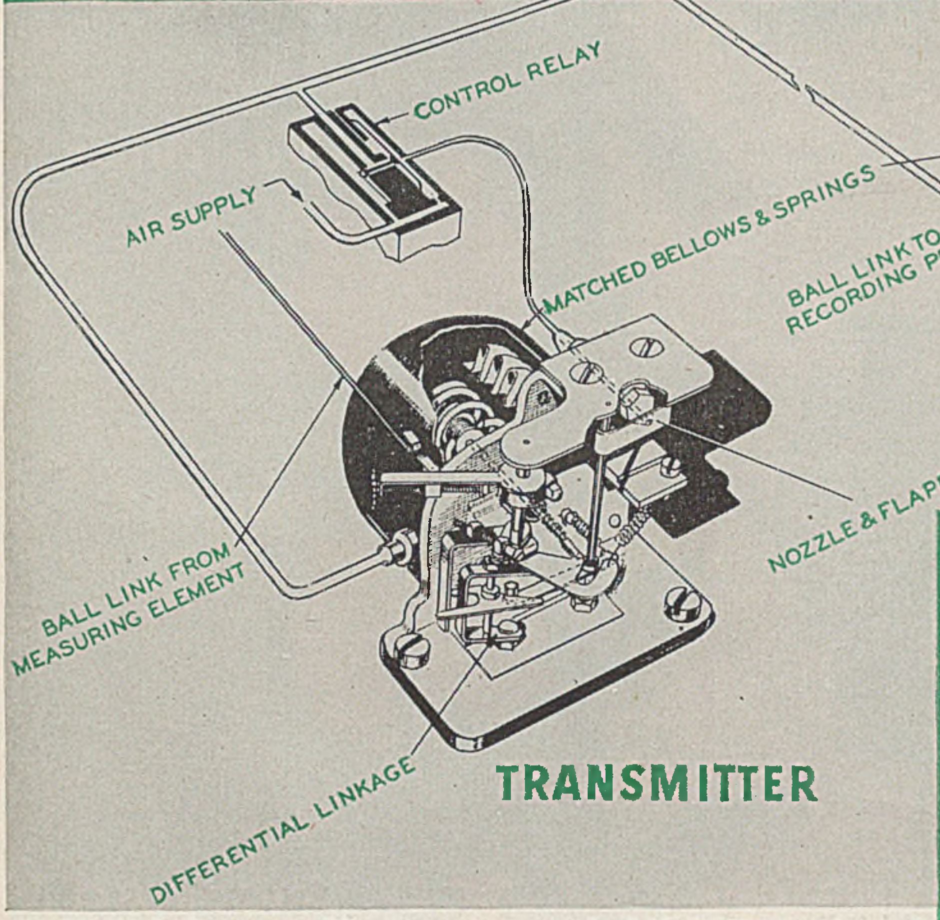
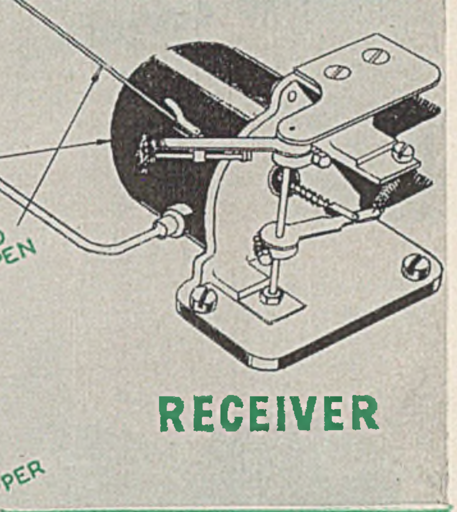

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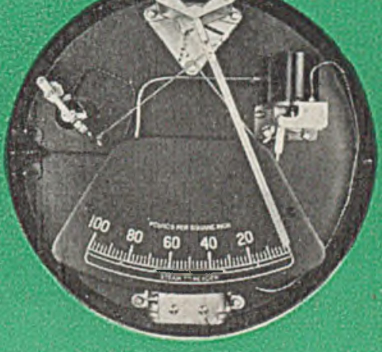

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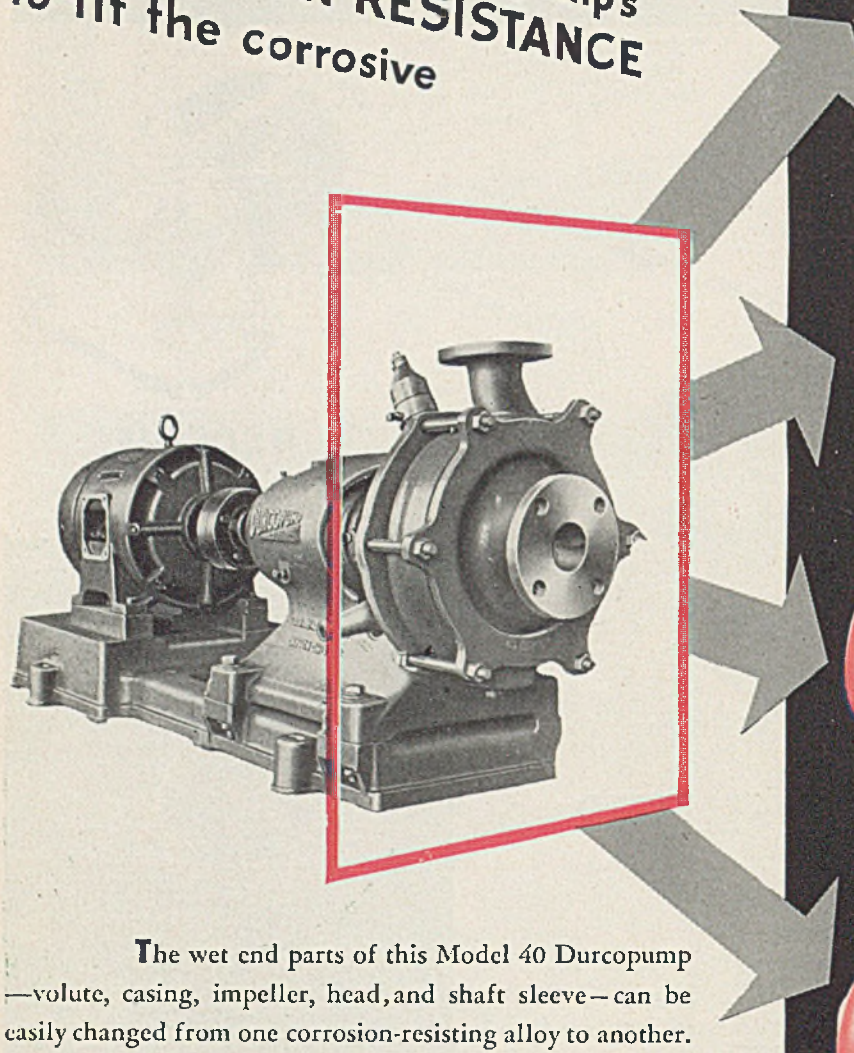

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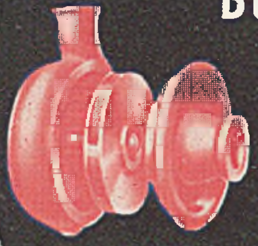

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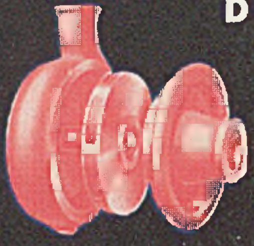
a high-silicon iron, containing approximately 14.5% silicon. Handles almost any commercial corrosive. Practically unaffected by sulfuric, nitric and acetic acid at any strength or temperature. Ask for bulletins 11 and 810.



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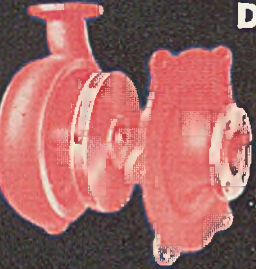
a high-silicon iron similar to Duriron but with much greater resistance to hydrochloric acid and its compounds, especially at higher temperatures and concentrations. Ask for bulletins 50 and 810.



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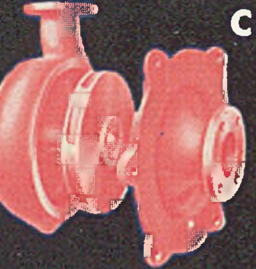
a high nickel—high chromium—molybdenum—copper—silicon—low carbon stainless steel. Some of the corrosives it successfully handles include sulfuric and sulfurous acid, oleum, caustic and bleach solutions. Ask for bulletins 110-2 and 811.



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#2—nickel base, high molybdenum alloy; #3—nickel base, high molybdenum, high chromium alloy. Both of these are high strength, machinable alloys. Chlorimet #2 handles hydrochloric acid in all concentrations and temperatures. It is excellent for hot sulfuric acid under reducing conditions and for wet hydrogen chloride gas. Chlorimet #3 handles most acids under oxidizing conditions, various salt solutions, also hot sulfuric in concentrations of less than 35%. Ask for bulletins 111 and 811.

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Corrosion

Corrosion resistance, mechanical properties, and some uses of a new heat-hardenable 18-8 stainless steel.

by Mars G. Fontana

The austenitic stainless steel commonly designated as 18-8S or Type 304 is a relatively soft material in the annealed condition, and it can be hardened or strengthened only by cold working methods. A steel, with approximately the corrosion resistance of 18-8, that could be hardened by heat treatment alone would be very desirable, particularly in cases where high strength and hardness and/or resistance to wear, galling, or seizing are required. In addition, the fields of application of this type of material could be greatly expanded because it could be used in shapes and equipment that are not readily amenable to cold working. In general, cold working is applied to only such shapes as wire, sheets, tubing, and strip.

Investigations of heat-hardenable or age-hardening 18-8 type steels was begun quite a few years ago, but it was not until recently that a material of this type became commercially available. The writer recalls obtaining a piece broken from an 18-8 high titanium ingot in 1939 and testing this piece in plant rayon coagulating bath (10% sulfuric acid). This sample practically dissolved, but regular 18-8S showed comparatively little attack. Tremendous advancements have been made since that time, however, and a commercial alloy designated Stainless W is being produced by the Carnegie-Illinois Steel Corporation. This alloy is also tentatively identified as Type 322 stainless steel.

The nominal composition of this alloy is as follows: 17% Cr, 7% Ni, 0.7% Ti, 0.2% Al, 0.07% C, 0.5% Si, 0.5% Mn, 0.01% P, and 0.01% S. It could be described as a "starved" 18-8 containing titanium and aluminum with titanium as the principal hardening agent. In the soft or solution-annealed state it shows a tensile strength of 120–150,000 pounds per square inch, an elongation of 8–14%, and a hardness of 235–270 Brinell. The material is precipitation-hardened or age-hardened by holding at 950° F. or a little higher, and then cooling in air. The hardened material shows a tensile of 195–255,000 pounds per square inch, an elongation of 8–14%, and a Brinell hardness of 370 to 460. Stainless W can be produced in cast or wrought form. The alloy parts could be rough-turned or even finish-machined prior to the hardening treatment, since little oxidation occurs at the aging temperature involved. Stainless W electrodes are produced for welding this alloy. Stainless W is ferritic or magnetic in the age-hardened condition and austenitic or nonmagnetic at elevated or annealing temperatures. The material precipitation hardens because the hardening constituents are soluble in the austenite and comparatively insoluble in ferrite.

Hardened Stainless W is not as resistant as annealed 18-8S to severe corrosion conditions, but for the more mild services the two materials can be considered equivalent as far as corrosion is concerned. This situation is fortunate from the corrosion standpoint, when one considers that Stainless W was developed primarily for high strength purposes.

Corrosion tests in sea water, salt spray, various atmospheres, hydrogen sulfide gas, sulfur dioxide gas, and hot milk indicate no essential differences in corrosion resistance between Stainless W and 18-8. The Stainless W did not show susceptibility to intergranular attack in a modified Strauss test (boiling solution of copper sulfate and sulfuric acid). Stainless W in the precipitation-hardened state is considerably inferior to annealed 18-8S in the boiling 65% nitric acid test; this means, of course, that Stainless W should not be used in applications involving boiling 65% nitric acid. The boiling 65% nitric acid test does not, however, indicate the corrosion resistance or applicability of the material for service in other corrosive media, including nitric acid at lower concentrations and/or temperatures.

Stainless W is under investigation at the Corrosion Research Laboratory at The Ohio State University. William E. Few studied this material for his senior thesis in metallurgical engineering, and other students have also investigated this alloy. We are interested in the corrosion resistance of Stainless W to corrosives that are considered between mild and severe for 18-8—or, in other words, media that are in the medium range, more or less. We are attempting to explore the field in order to find the conditions under which Stainless W and Type 304 could be con-

TABLE I. CORROSION TESTS ON STAINLESS W AND 18-8S

Material	Heat Treatment	Corrosive Media	Corrosion Rate for Each 48-Hr. Period, Mils/Year					
			1st	2nd	3rd	4th	5th	Cumulative
Type 322	Aged at 950° F.	Boiling 75% HAc	24	1	0	0	0	..
Type 322	A.C. from 1700° F.[a]		105	1	0	0	0	..
Type 304	W.Q. from 1950° F.[b]		110	1	0	0	0	..
Type 304	Air-cooled after 1 hr. at 1200° F. (sensitized)		94	96	0.1	0	0	..
Type 322	Aged at 950° F.	10%, 30%, and 40% HAc at 75° F.	0	0	..	..	..	..
Type 304	W.Q. from 1950° F.		0	0	..	..	..	..
Tyce 322	Aged at 950° F.	10% H_2SO_4 at 75° F.[c]	6[d]	0	..	..	..	..
Type 322	A.C. from 1700° F.		530	0	..	..	..	..
Type 304	W.Q. from 1950° F.		25	0	..	..	..	..
Type 304	Sensitized		75	0	..	..	..	..
Type 322	Aged at 950° F.	15% H_2SO_4 at 75° F.	7	0	..	..	..	..
Type 322	A.C. from 1700° F.		550	0	..	..	..	..
Type 304	W.Q. from 1950° F.		105	75	..	..	..	..
Type 304	Sensitized		220	540	..	..	..	..
Type 322	Aged at 950° F.	Boiling 3% H_2SO_4	370	280	250	85	300	275
Type 322	A.C. from 1700° F.		1085	1	1700	1	1600	..
Type 304	W.Q. from 1950° F.		1250	1	875	1	2	..
Type 304	Sensitized		1600	1600	..	..	..	..
Type 322	Aged at 950° F.	2% HCl at 75° F.	10	8	..	..	..	9
Type 304	W.Q. from 1950° F.		7	6	..	..	..	6
Type 322	Aged at 950° F.	5% HCl at 75° F.	40	37	..	..	..	38
Type 304	W.Q. from 1950° F.		9	8	..	..	..	8
Type 322	Aged at 950° F.	10% HCl at 75° F.	155	220	..	..	..	200
Type 304	W.Q. from 1950° F.		28	31	..	..	..	28
Type 322	Aged at 950° F.	15% HCl at 75° F.	440	520	..	..	..	500
Type 304	W.Q. from 1950° F.		95	120	..	..	..	115
Type 322	Aged at 950° F.	Boiling 65% HNO_3	90	195	215	255	205	200
Type 322	A.C. from 1700° F.		26	46	50	72	75	55
Type 304	W.Q. from 1950° F.		8	7	5	5	5	6
Type 304	Sensitized		13	47	205	435	670	275

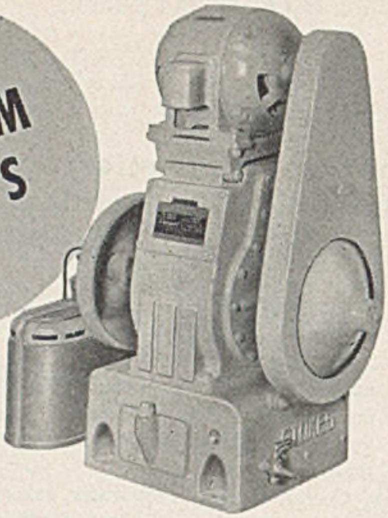
[a] Air-cooled.

[b] Water-quenched.

[c] Tests for which only two periods are shown were run for one 48-hour period and a second 120-hour period.

[d] Average of duplicate tests in 10% H_2SO_4.

VACUUM PUMPS



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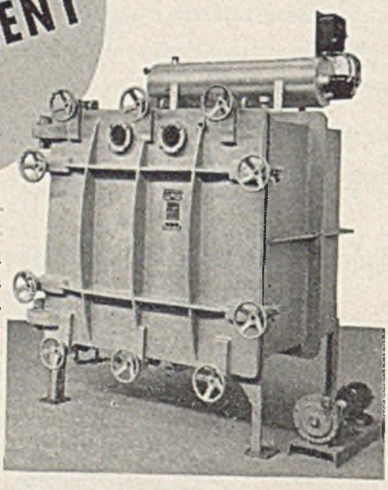

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Corrosion

sidered equivalent from the corrosion standpoint. Table I shows the results obtained in sulfuric, acetic, hydrochloric, and nitric acids of several concentrations and temperatures.

Boiling 75% acetic acid is considered to be a fairly aggressive condition for 18-8. The hardened Stainless W showed better corrosion resistance than quench-annealed Type 304 and the other materials in these tests. In 10%, 30%, and 40% acetic acid at room temperature none of the materials showed measurable rates of attack. The hardened Stainless W showed better resistance than the other materials tested in 10 and 15% sulfuric acid at room temperature. Boiling 3% sulfuric acid is apparently too severe for both Stainless W and Type 304.

The 18-8 type materials would not normally be used in solutions containing appreciable amounts of hydrochloric acid. Tests were made in this acid, however, to determine differences in corrosion resistance between these two alloys. The data in Table I show little difference in 2% hydrochloric acid and superiority for quench-annealed Type 304 in the stronger acids.

The quench-annealed Type 304 is superior in boiling 65% nitric acid, with both the aged Stainless W and the sensitized Type 304 showing high rates of attack. The corrosion resistance of Stainless W could have been improved if the material had been water-quenched from 1950° F. instead of air-cooled from 1700° F., not only in nitric acid but probably in the other acids also. The differences in corrosion between Stainless W and Type 304 in nitric acid of lower concentrations and/or temperatures would probably be negligible.

The data in Table I are, of course, subject to check, and additional tests will be made. These data were obtained from ordinary static immersion tests. Most of the data were obtained on two lots of Stainless W of the following compositions: (*a*) 17.02% Cr, 6.72% Ni, 0.62% Ti, 0.068% Al, and 0.059% C; (*b*) 16.18% Cr, 7.42% Ni, 0.60% Ti, 0.19% Al, and 0.044% C. Aging the former material resulted in a Brinell hardness of 405.

Stainless W and Type 304 both show tendencies to become passive in acetic and sulfuric acids. The results in Table I show that the second or subsequent period shows practically no corrosion of the specimens. For example, aged Stainless W shows 24 mils per year in the first period, one mil per year in the second, and no attack in the third, fourth, and fifth periods. A discussion of passivation of stainless steel was given in this column (page 103 A) for September 1947.

The effect of age-hardening on the erosion-corrosion resistance of Stainless W should be of great interest. It is generally assumed that a hard material should show better performance than a softer material under conditions of erosion-corrosion, provided both materials exhibit about the same corrosion resistance to a given solution under static conditions. This assumption may not hold true in many instances and may be an entirely erroneous assumption, particularly under fairly corrosive conditions. For examplc, annealed 18-8SMo with a hardness of about 180 Brinell showed about ten times longer life than Type 329 stainless steel hardened to 450 Brinell in a centrifuge handling a sulfuric acid slurry. Both alloys showed negligible corrosion in static tests.

Several tests were made on annealed and hardened Stainless W in 1%, 5%, and 10% sulfuric acid at 125° F. Practically no difference was found in the 1% acid, but in the two stronger acids the hardened material showed much greater rates of attack. These results should be regarded as preliminary, and additional tests along this line will be made. In these tests the specimens were exposed to the acids moving at high velocity. The erosion-corrosion test is described on page 87 A for June 1947.

Hardened Stainless W can be considered equivalent to Type 304 for many corrosive conditions. For a given application corrosion tests in the media involved should be made if directly applicable information is not available. Stainless W should find application as plugs, disks, seats, and stems in valves; pump shafts; bolts, tie-rods and other hardware; services requiring both corrosion resistance and high strength; high pressure applications; etc.

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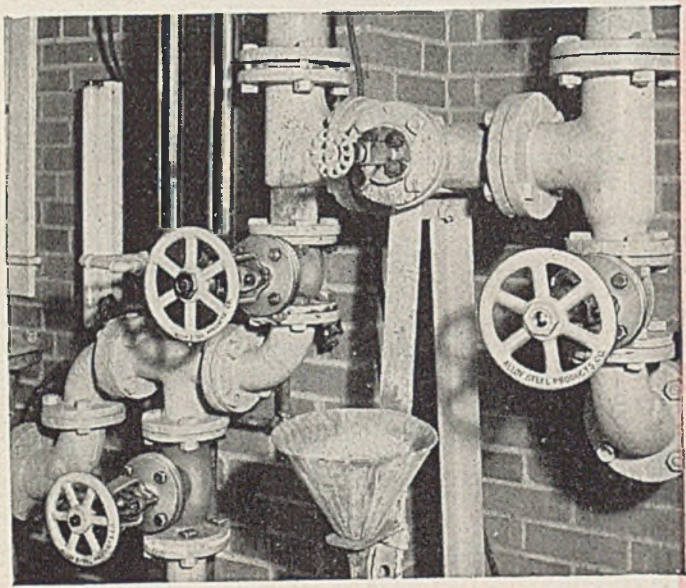
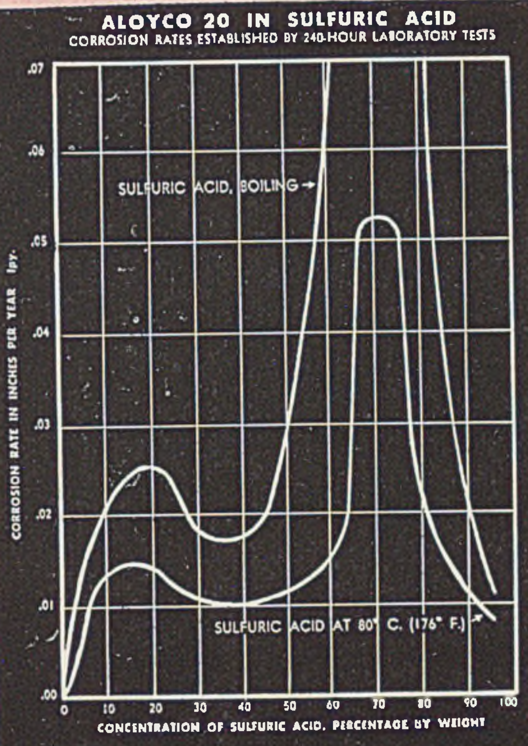


Nest of Aloyco 20 Valves used in recovery of alkylation spent acid.

The above photo shows one of several groups of Aloyco 20 Valves in the plant of Consolidated Chemical Corporation, Houston, Texas. It is part of an alkylation spent acid recovery installation made by the Chemical Construction Company. This system reclaims full strength H_2SO_4 from 85-90 percent spent acid, a waste product of the alkylation process of producing high octane gasoline with sulfuric acid as the catalyst.


ALOYCO 20 IN SULFURIC ACID
CORROSION RATES ESTABLISHED BY 240-HOUR LABORATORY TESTS

CORROSION IN BOILING ACID			CORROSION IN 80° C. (176° F.) ACID		
0.5%	H_2SO_4	— 0.0036 Ipy.	0.5%	H_2SO_4	— Nil Ipy.
2.5	"	— 0.0084 "	2.5	"	— Nil "
5	"	— 0.0130 "	5.0	"	— 0.0027 "
10	"	— 0.0132 "	10	"	— 0.0137 "
20	"	— 0.0264 "	20	"	— 0.0138 "
30	"	— 0.0181 "	30	"	— 0.0108 "
40	"	— 0.0174 "	40	"	— 0.0105 "
50	"	— 0.0276 "	50	"	— 0.0120 "
60	"	Not Recommended	60	"	— 0.0152 "
70	"	Not Recommended	70	"	Not Recommended
80	"	Not Recommended	80	"	— 0.0220 "
90	"	— 0.0220 "	90	"	— 0.0110 "
93	"	— 0.0110 "	93	"	— 0.007 "

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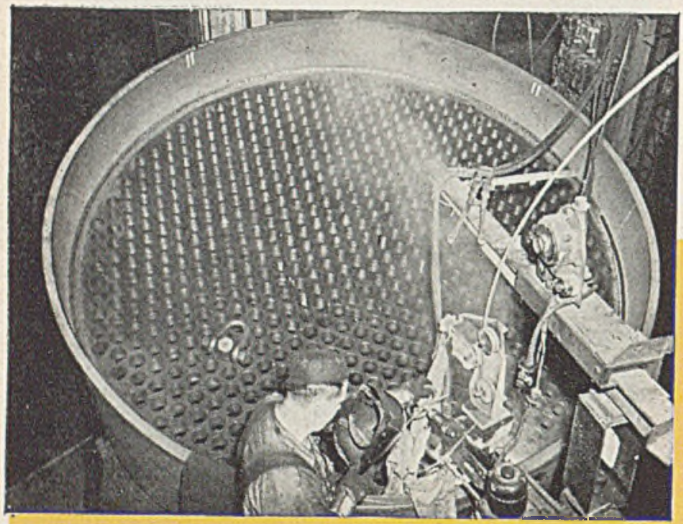

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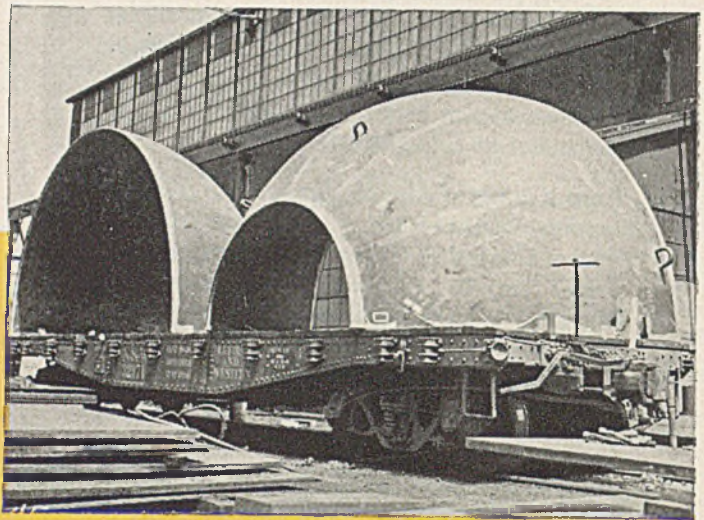
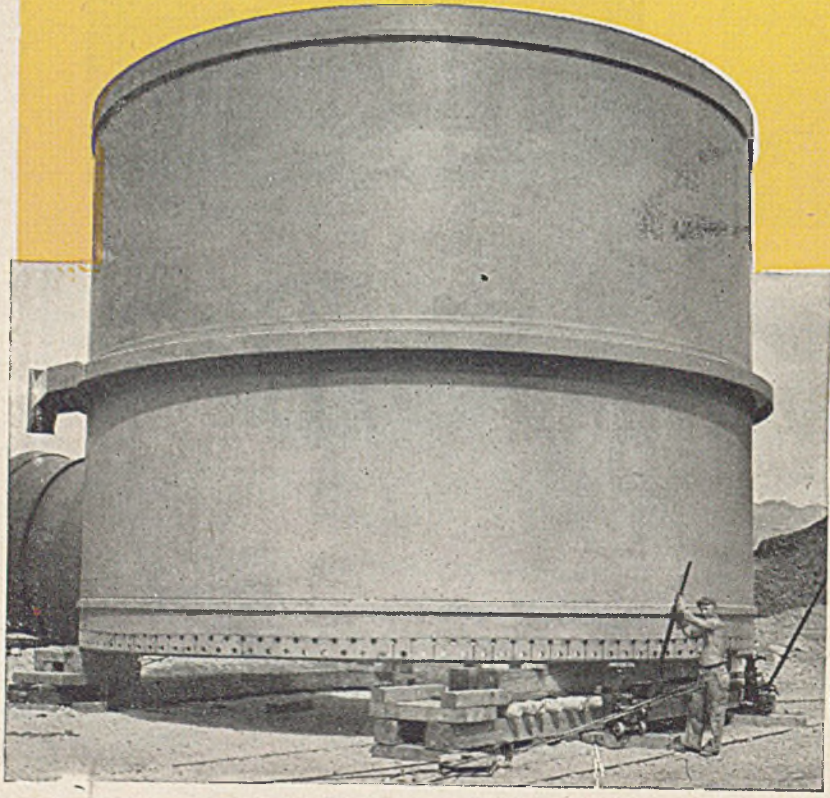


Field Construction Simplified

Short-cuts in fabricating 100 ft. x 20 ft. catalyst reactor in B&W shops saved erection time on location.

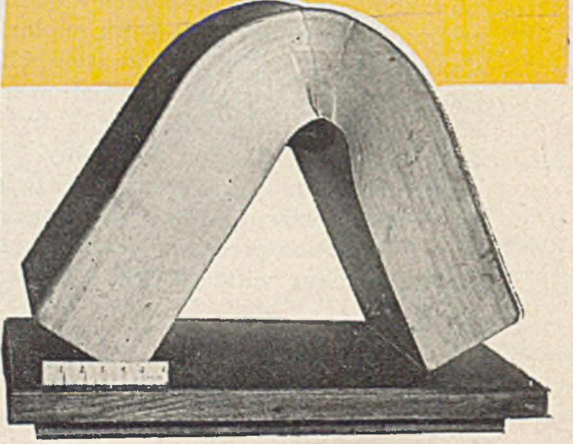


World's Largest Pipe Fabricated

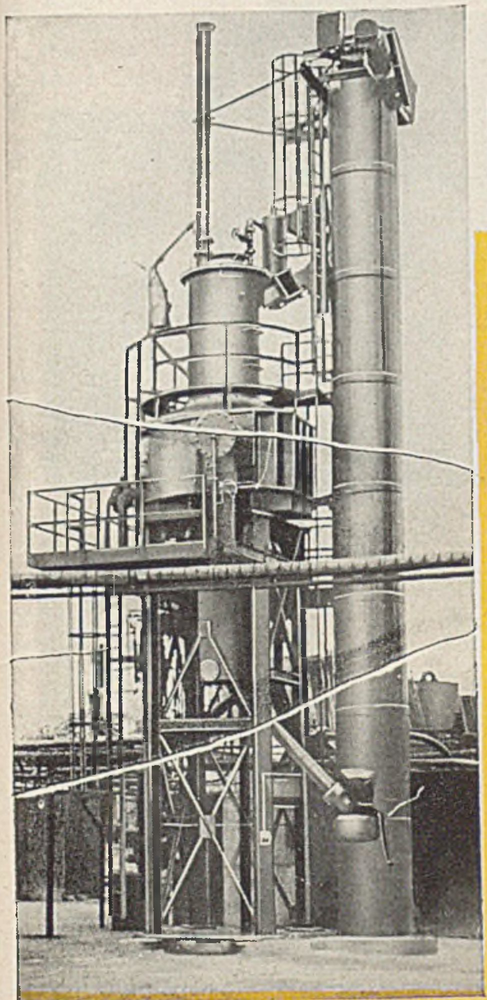
Supplying 45,000 tons of welded steel-plate pipe—8½ to 30 ft. in diameter—for Hoover Dam presented many new problems of fabrication, transportation, handling and installation solved by B&W.

The Weld That Held

Butt welding 6½ in. A .70 firebox plate into unfired pressure vessel of unusual design was successfully accomplished by B&W Fusion Welding Process. Strength of welds greatly exceeded code requirements. Sample of butt-welded plate after face bend test is shown below.

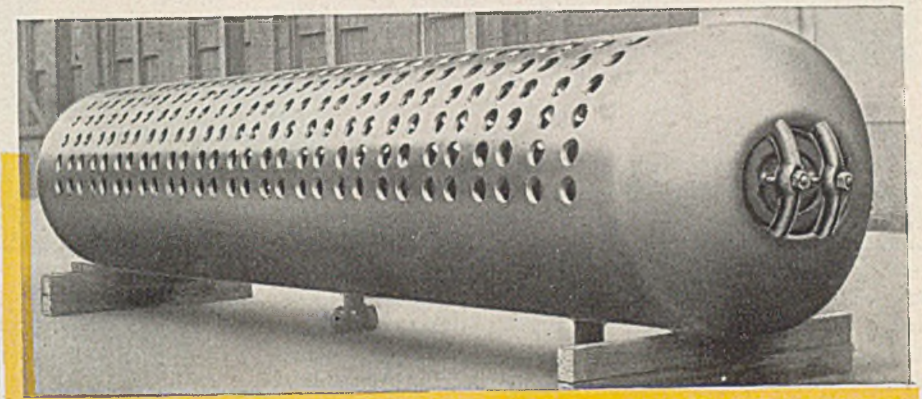


in pressure vessels...
STORY AT B&W



Air Hot Enough to Melt Bricks

Pebble Heat Exchanger developed by B&W heats gases to over 2000F and far above the temperature limits of metallic heat exchangers—hot enough to melt bricks.



Fusion-Welded Boiler Drums — a B&W First

The first welded boiler drums used in both marine and stationary boilers were built by B&W in 1930.

Designing and fabricating pressure vessels, drums, tanks, towers, tubes, piping and related products is a major activity at B&W — and has been for many years. Here, practical solutions for new problems encountered in the application of high pressure, high temperature equipment are constantly being developed. In fact, B&W pioneered many pressure vessel fabrication techniques such as fusion welding, x-ray inspection, stress relieving, welded drums and streamlined openings.

Shown on these pages are a few examples of how B&W pressure vessels and fabricating techniques have solved new and difficult problems.

S-74T

B&W

PROCESS EQUIPMENT — Alloy, Clad, and Bonded Pressure Vessels . . . Heat and Abrasive-resistant Alloy Castings . . . Special Process Equipment.

* * *

OTHER B&W PRODUCTS — Stationary and Marine Boilers . . . Boiler Components . . . Chemical Recovery Units . . . Pulverizers . . . Fuel Burning Equipment . . . Refractories . . . Seamless & Welded Tubes for All Pressure and Mechanical Applications.

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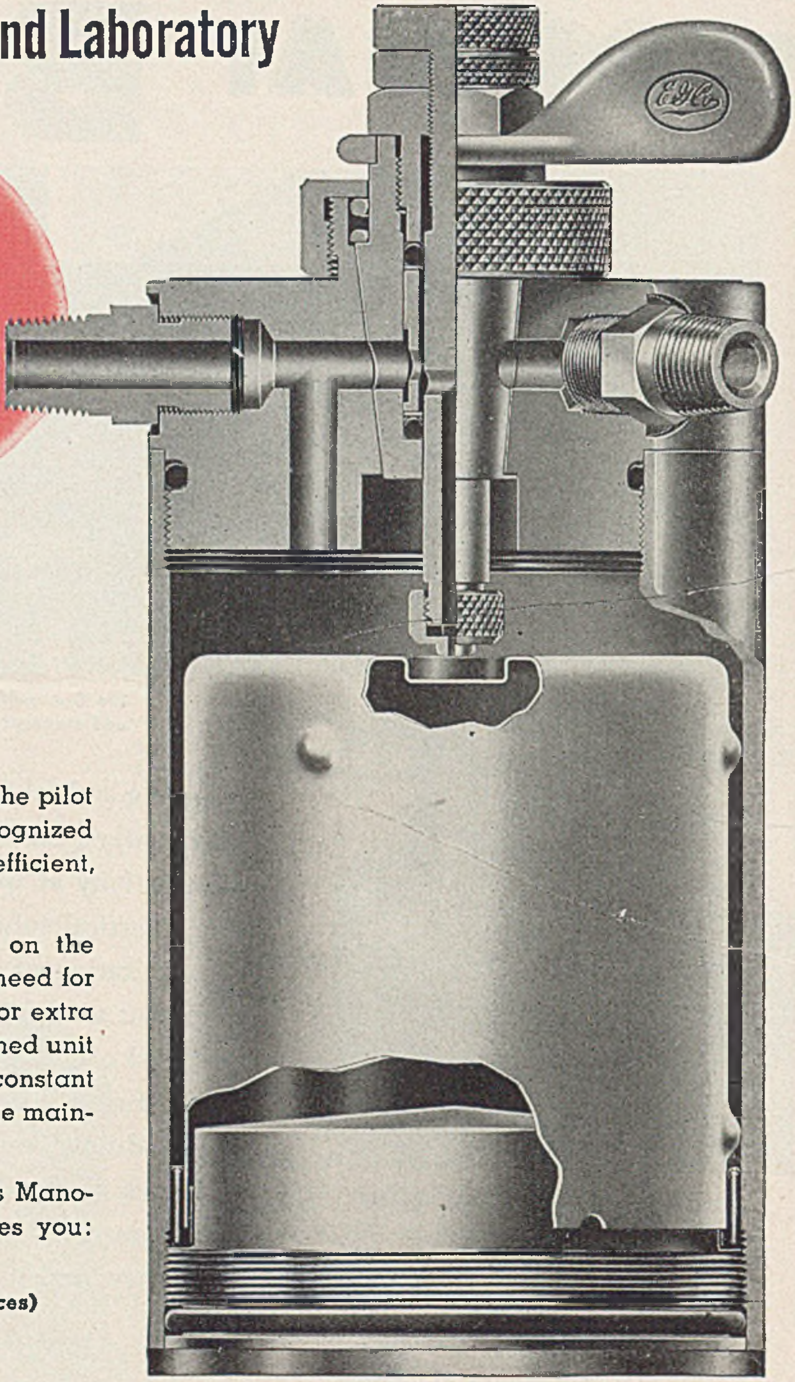

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- Just set it and forget it!
- Slashes operating costs!

TESTED in the laboratory and successful in the pilot plant, our new Cartesian Manostat is recognized by industry as *the* answer to the problem of efficient, effortless and economical pressure control.

Completely automatic, this Manostat works on the physical principle of the Cartesian Diver. No need for complicated electrical or mechanical systems or extra equipment of any kind. Just put this self-contained unit in your system—SET IT AND FORGET IT. A constant pressure or vacuum to within 1/10 to 1% can be maintained with this heavy duty, all metal unit.

Incorporating all the advantages of our Glass Manostat, this revolutionary Model No. 5 also gives you:

1—Larger Capacity
2—Wider Range (supplied with 3 interchangeable orifices)
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5—Control of both Pressure and Vacuum
6—Simplified Operation
7—Fool-Proof Design
8—Stainless and Chrome Steel
9—Low Price

For complete information, including performance and operating data, write for Bulletin ICM-96.

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TRADE MARK

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Complete with 3 interchangeable orifices and mercury, $95.00.
Size: 7½" overall. Diameter: 3¼". Weight: approximately 8 lbs.

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Plant Management

More consideration should be given to the possibility of employing continuous manufacturing processes in the chemical industry.

by Walter von Pechmann

A new chemical concern manufactures its products by a continuous instead of a batch process. This would not warrant any special attention were it not for the fact that this type of product has been made for almost a decade in batch form, and many people in the same field of manufacturing still contend today that this product never can or never will be made on a continuous basis because it would be impractical or too expensive. The manner in which the problem in this particular factory was solved is so simple that it makes one wonder if all the batch processes employed in the chemical industry today are really necessary as such.

The chemist, by virtue of his work and education, is more "batch conscious" than the chemical engineer. Also, manufacturing in batch form is traditional in the chemical industry, and consequently many plant men consider the continuous process a more or less revolutionary way of manufacturing. Continuous manufacturing processes require, in addition to chemical knowledge, a complete familiarity with all the latest improvements in the field of chemical engineering. Persons in charge of manufacturing operations sometimes do not keep up with all the latest improvements and are therefore inclined to underestimate the achievements of modern types of machinery.

There is another reason why many people seem unable to pry themselves loose from the idea that chemicals, which have to be brought together in a certain relationship, mixed, and possibly heated, have to be made in batch form—habit. Wherever one turns one sees cooking, baking of bread, mixing of cement, etc., carried out in batch form, and one cannot imagine that it might be done any other way. It often does not occur to the plant man that materials can just as well be heated, cooled, or moved while being mixed. For example, a certain manufacturing process required 2.5 hours of chilling the material to bring it from a fluid to a solid stage prior to cutting. Up to the present time the product has been poured onto shallow pans surrounded by brine, then cut into flakes, and then into cubes. Although ice cream and frozen custard are chilled, moved, and extracted in one continuous process, there are a number of chemical manufacturers who still use the batch chilling on similar processes. When asked why they did not employ the more simple and economical continuous chilling process, they usually justify their reluctance to accept modern machinery by stating apparent disadvantages of the continuous manufacturing process which can easily be disproved.

One of the most common objections raised is that continuous manufacturing does not allow flexibility in production. This is not true. Continuous manufacturing processes do not always require the construction of special machinery which can be used for only one certain type of product. There is no reason, for example, why equipment which heats a fluid when it passes through a pipe system cannot be used for the manufacture of many products. Pipes can be jacketed, and either hot water, steam, or brine can be used as the medium of heat exchange.

It is also often stated that continuous manufacturing processes are entirely controlled by mechanical means and that the exclusion of the human factor in chemical manufacturing is not advisable. The actual fact is that instruments of production control which are not manipulated by hand are much more accurate and dependable than work performed by people. For example, everyone will agree that a thermostatically controlled heating process is subject to less variation than an operation controlled by an employee by means of a control valve and thermometer. If this is brought to the attention of the people who object to complete mechanical control, it is usually claimed that mechanical devices lack sufficient flexibility to work under varying conditions. This, again, is not true. The writer was once confronted with the problem of eliminating a hand operation which required the addition of a certain solution at varying rates of flow. The problem was solved by plotting the various rates of flow on a disk chart and then using the chart as a pattern to cut a cam. A rod which traveled on the perimeter of the cam was connected with the valve allowing the solution to enter the reaction unit, automatically opening and closing the valve according to requirements. This instrument proved to be much more accurate than the old method of making the addition with a calibrated scale, a time clock, and a valve.

An argument against trying to develop a continuous manufacturing process is that, even if the entire process could be made on a continuous basis, there is one operation which requires the accumulation of an inventory or a holdup because of production control requirements. "If the process cannot be made continuously, there is no need of doing it partially." This way of thinking is holding up progress. Even if a few operations have to be performed individually, the advantages gained by accepting the continuous process system usually outweigh the disadvantages of the batch process. Admittedly continuous operations sometimes require a complete change of formulation, and laboratory facilities frequently do not allow one to determine in advance what will happen if new manufacturing techniques are employed. The construction of pilot plant equipment and close cooperation between the mechanical or chemical engineer and the plant operator, however, usually make it possible to overcome these difficulties. In some instances experimenting in the laboratory may have to be given up and trials might have to be made on a comparatively large scale in production—and this is a costly procedure. Nevertheless, the writer believes that such expenditures are justified if there is a reasonable chance of achieving the desired results.

People who oppose continuous manufacturing processes sometimes claim that the batch mixing process is more desirable because the individual batches can be tested separately and, if necessary, reworked, blended, or discarded; if something goes wrong in a continuous manufacturing process, however, an entire day's output may be spoiled. This is not logical. The reason why many batches do not measure up to required standards is that they cannot always be produced under identical conditions. Continuous manufacturing processes are almost entirely controlled by mechanical devices, and thus variations caused by the human element can be eliminated.

WHEREVER THERE ARE MATERIALS IN PROCESS, THERE IS A TRAMP-IRON HAZARD . . .

Sources of tramp-iron contamination are as numerous as the uses of ferrous metals in industry. And the damage caused by tramp-iron ranges from finely-divided impurities in finished products through fires, explosions, and major equipment wreckage.

Dings has been successfully fighting tramp-iron hazards for nearly half a century. Specializing in the development of positive magnetic iron-removal equipment has provided Dings units which fit the requirements of most modern industrial applications. Special tramp-iron removal problems are welcomed in Dings Magnetics Laboratories . . . Solutions of current new problems in magnetics have frequently turned out to be standard practice in progressively better production methods.

Research and development facilities of Dings Laboratories are offered to you without obligation—as a proven means of securing mutual benefits in more effective magnetic separation equipment. Write for specific information on your particular problems.

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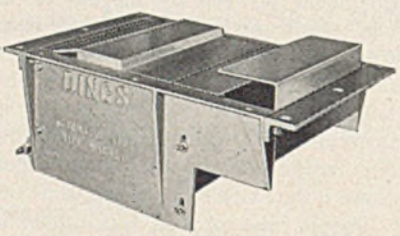
For installation in chutes, troughs, ducts or spouts carrying materials in process. "High Intensity" double-gap magnet design insures positive iron-removal at full flow volume. Automatic safety gate discharges iron outside chute when current is interrupted. Simple installation; low-cost operation. Illustration shows magnet with safety gate open.



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Plant Management

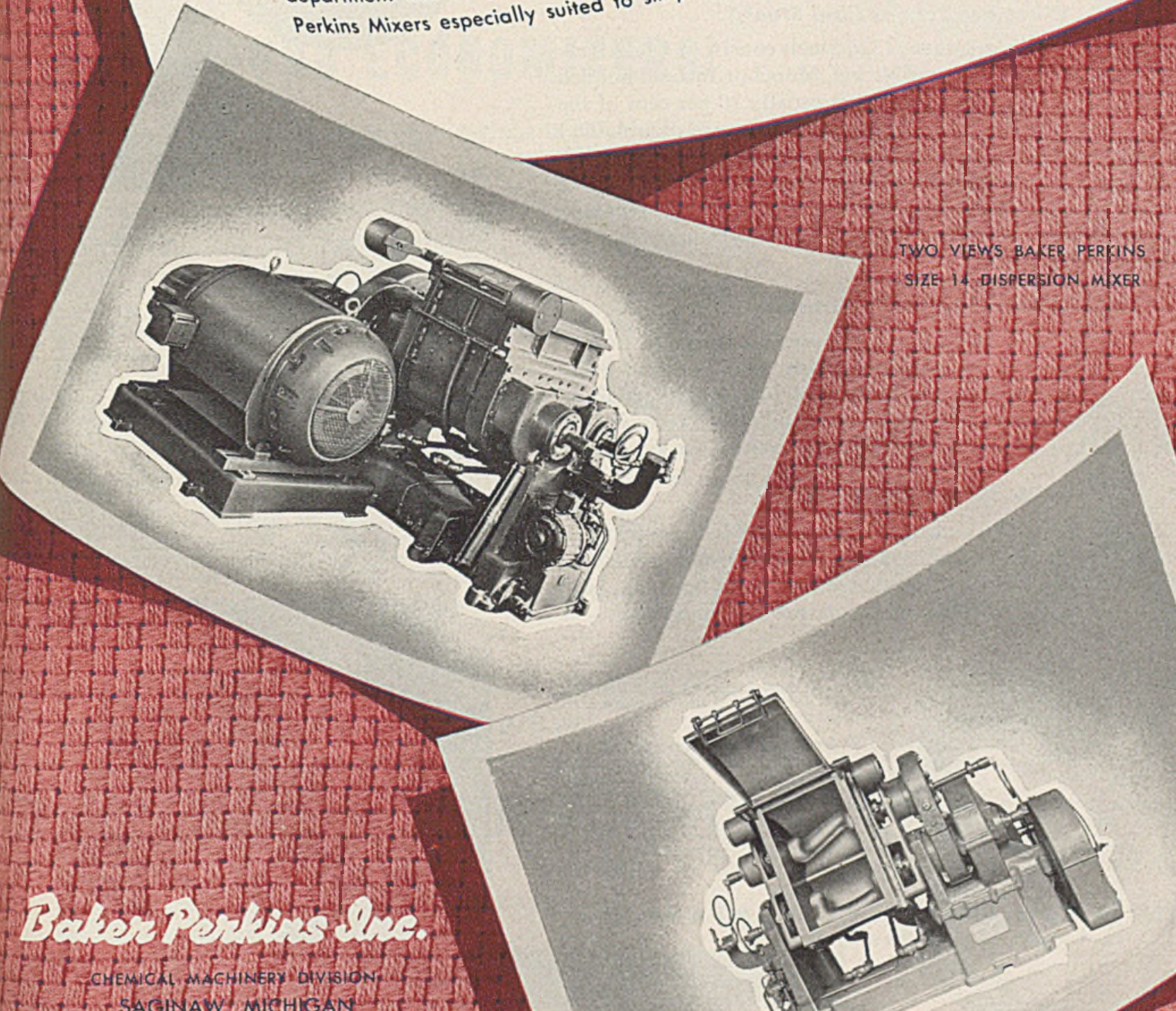
There is one advantage claimed for the batch mixing method which is hard to disprove. Samples can be taken during the several stages of production, and adjustments can be made during the manufacturing process. In the continuous process, manufacturing continues during the time of testing, and the product might have reached a new phase of production by the time results are obtained. However, many tests now conducted on batch mixing operations can be eliminated in the continuous process. Where tests are absolutely essential, it is frequently possible fully to mechanize testing methods or to by-pass the regular system until results are obtained. Instead of sampling the batch and making a conductivity test, the electrodes are installed in a pipe line through which the product passes. This is a typical example of installing testing instruments into a production line. There are instruments on the market today which not only allow constant reading but also give warning signals when allowable variations are exceeded. By-passing of the regular system is usually accomplished by the installation of so-called buffer tanks in which the product remains until it has been tested. The time of testing is arranged so that results from tank *B* are known before tank *A* is completely empty. One might say that this is no longer a continuous process; one must remember, however, that the goal of the continuous process is to produce at a constant rate of flow, that these tanks can be automatically opened and closed, and that interference by human hands is necessary only if testing results are negative.

It is sometimes claimed that fully mechanized equipment is undependable and hard to keep clean. It is especially stressed that a minor defect on the machinery may cause stoppage of the entire manufacturing process. This holds true for a machine in the chemical industry as well as for an airplane. Today's machinery is being built to reduce breakdown to a minimum, and there is no reason to refuse to accept the continuous manufacturing process merely because stoppage in production is a possibility. In regard to the cleaning of equipment, fully mechanized equipment can usually be kept cleaner than batch vessels. The methods of cleaning, should, of course, be adjusted to the specific equipment. If hot water, for instance, is being used to clean a mixing vessel, it would be wrong to conclude that a piping system cannot be cleaned so easily because hot water does not do a good job. The complaint that mechanical equipment cannot be cleaned so easily as mixing vessels originated mainly from the failure to take individual requirements into consideration.

The cost of constructing continuous processing equipment is high, but so are the savings which can be effected. For example, let us assume that a daily output of 1000 gallons is required. The present method of manufacturing is to make two batches daily in four kettles holding 125 gallons each. A continuous flow of only slightly over 2 gallons per minute is required to accomplish the identical output. Instead of using kettles, the entire production would pass continuously through a piping system which would take up no more floor space than a single kettle. The number of operators required would be reduced from four to one. There would be no weighing or measuring operations or cleanups between batches. Contamination by dust or foreign matter during the manufacturing process would be reduced to a minimum despite the fact that the new equipment would be installed in a room without air conditioning. The product would be of better quality, and an adjustment here or there would change operating conditions when required, such as temperatures, time of digestion, etc. This may sound fantastic, but the writer has seen it work. Why not investigate the possibility of a continuous manufacturing process in your plant if it is not already in existence?

FAST GROWING AMERICAN-MARIETTA COMPANY KEEPS PAINT PROCESSING AT PEAK WITH BAKER PERKINS DISPERSION MIXERS

American-Marietta Company of Chicago is one of the nation's fastest-growing producers of fine industrial finishes, maintenance paints, resins, bonding agents, and other chemical products. Among the latest-type equipment that is helping this progressive firm to attain a dominant position in its field are several Baker Perkins Dispersion Mixers, including the two illustrated. What Baker Perkins Mixers have accomplished for American-Marietta in fast, thorough, homogeneous dispersing of chemical components, they can do for you in your processing operations. Baker Perkins Mixers for the chemical industry are available with working capacities ranging from 0.25 to 2650 gallons. Design and construction are based on more than 50 years of engineering and production experience. Our chemical research department will be glad to analyze your mixing problems and recommend the Baker Perkins Mixers especially suited to simplify and speed your processing.

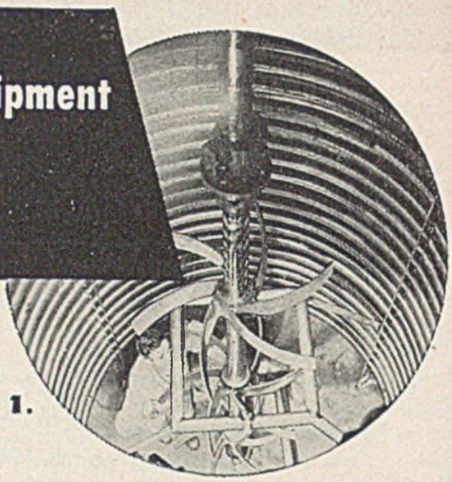


TWO VIEWS BAKER PERKINS SIZE 14 DISPERSION MIXER

Baker Perkins Inc.

CHEMICAL MACHINERY DIVISION
SAGINAW, MICHIGAN

What every user of heavy process equipment Should know about clad steels



1.

A 10% layer of Nickel, Monel or Inconel brings you full product protection at substantially lower cost

In Lukens Clad Steels, a 10 per cent thickness of Nickel, Monel* or Inconel* does the work of a *solid* plate.

As a result, the construction material cost drops. Savings of one-third to one-half are entirely possible.

And you get these savings without sacrificing a single property of the cladding metal.

The photos show a few of the ways in which Lukens Clad Steels are regularly used to combat corrosive attack and to prevent harmful metallic contamination.

What are Lukens Clad Steels?

Produced by hot-rolling, Lukens Clad Steels consist of a relatively thin layer of corrosion-resistant Nickel, Monel or Inconel bonded to a heavy steel plate. (The cladding is usually 10 per cent of the plate thickness, but greater or lesser thicknesses are obtainable.)

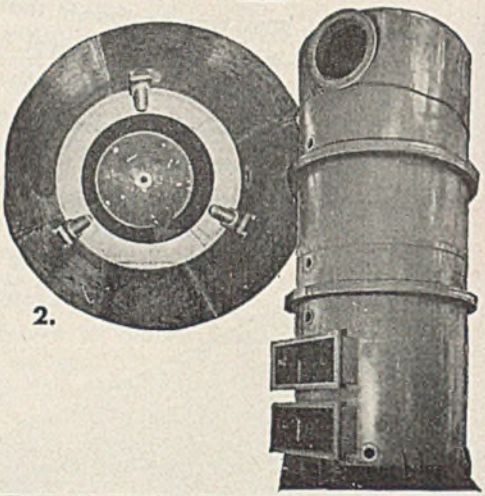
Because of the high temperatures employed in bonding, a solid-solution, high strength alloy of cladding metal and steel is formed at the plane of contact. Neither fabricating operations, pressure, vacuum, mechanical shock nor changes in temperature will separate the two metals.

Some typical applications

Versatile Lukens Clad Steels find wide use in evaporator bodies, hoppers, mixers, digesters, reaction vessels, tank cars and other heavy equipment where the properties of Nickel and its alloys are desired. They afford ample resistance to many corrosive agents, and safeguard the products handled from contamination or discoloration.

Write for FREE booklets

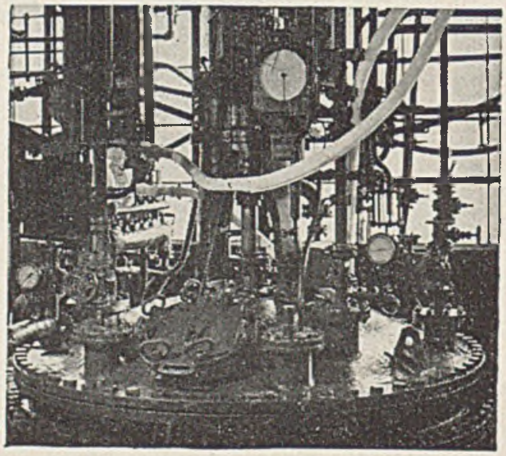
Further information and technical data are given in the booklet, ***Lukens Clad Steels***, and in Bulletin T-4, ***The Fabrication of Lukens Clad Steels***. Write for them. Both are free. And both can help you plan and build corrosion-resistant process equipment—*at lower material cost.*



2.

THESE ARE THE ADVANTAGES of Lukens Clad Steels

1. Effective corrosion resistance at lower cost.
2. High tensile strength (55,000 psi minimum).
3. Availability in extra-large plate sizes permits fabrication with a minimum of welds.
4. Ordinary welding methods produce continuous corrosion-resistant surfaces. No special treatment needed after welding.
5. Shearing, bending, flanging, forming, riveting or welding cause no buckling, cracking or peeling.
6. The thickness of cladding can be selected to meet individual service conditions.



3.

1. SAFEGUARDS FOR PENICILLIN—Thorough cleaning and checking of this penicillin fermentation tank follow each harvest of the drug, for even a slight trace of inorganic contamination can spoil an entire batch. The tank is made of Lukens Inconel-Clad Steel. Agitators, aerators and coils are of solid Inconel.

2. FOR GLUCOSE—This strike pan is built of Lukens 20% Nickel-Clad Steel. Total plate thickness is half an inch. The pan is 10 feet in diameter and 24 feet high, and has a 50,000-pound capacity. *(Inset)* View looking upward toward the centrifugal separator shows the three drain valves at its base for the discharge of glucose recovered from vapor.

3. IN DYESTUFF MANUFACTURE—This reaction vessel is used in processing organic compounds. Ten per cent sulfuric acid is but one of the many corrosive agents employed. Made of Lukens Nickel-Clad Steel, the 1850-gallon kettle is designed to operate under pressure or vacuum and may be steam heated or brine cooled.

THE INTERNATIONAL NICKEL COMPANY, INC.
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NICKEL MONEL* INCONEL*

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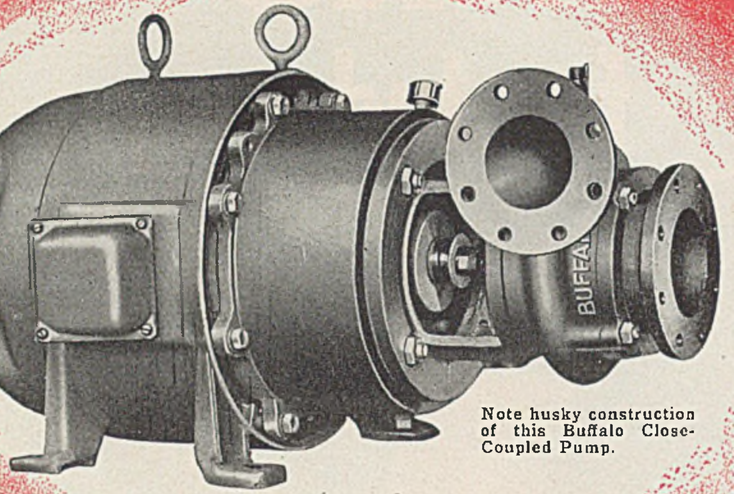
What Users Say about "Buffalo" CLOSE-COUPLED PUMPS



Note husky construction of this Buffalo Close-Coupled Pump.

ALL-AROUND ECONOMIZERS!

Right from installation on, you'll see the savings in "Buffalo" Close-Coupled Pumps! Amazingly compact, they fit into close quarters — and are easily mounted in horizontal or vertical position. Discharge angle is readily adjustable. AND — once operating, these sturdy little workhorses do a "lot of pumping on a little power" and require "practically no attention for years and years," as users tell us.

5 to 1600 G.P.M. — Powered to Suit the Head

With the "Buffalo" line of Close-Coupled Pumps, you never need to buy "too much pump" or "too little pump" for the job! There's a pump to handle exactly the head — and exactly the G. P. M. capacity required. And you can rely on "Buffalo" ratings when it comes to "on the job" performance.

As a first step towards finding how these "Buffalo" Pumps can help you, why not write for Bulletin 975-B?

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153 Mortimer St. Buffalo, N. Y.
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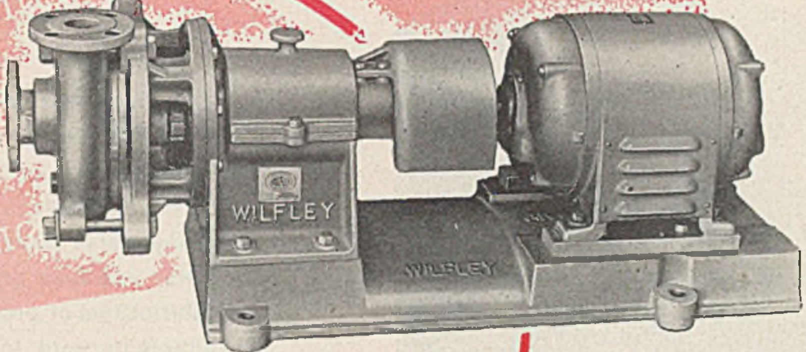
FOR *Acids*



Records made by WILFLEY pumps in modern chemical plants all over the world prove that this trouble-free acid pump is a prime factor in reducing costs. It handles acids, corrosives, hot liquids, mild abrasives on a 24-hour schedule without attention. Works on continuous as well as intermittent operations. 10- to 2,000-G.P.M. capacities; 15- to 150-ft. heads and higher. Individual engineering on every application. WILFLEY is the pump to buy when you want dependable, trouble-free, cost-saving efficiency. Write or wire for details.

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centrifugal PUMPS

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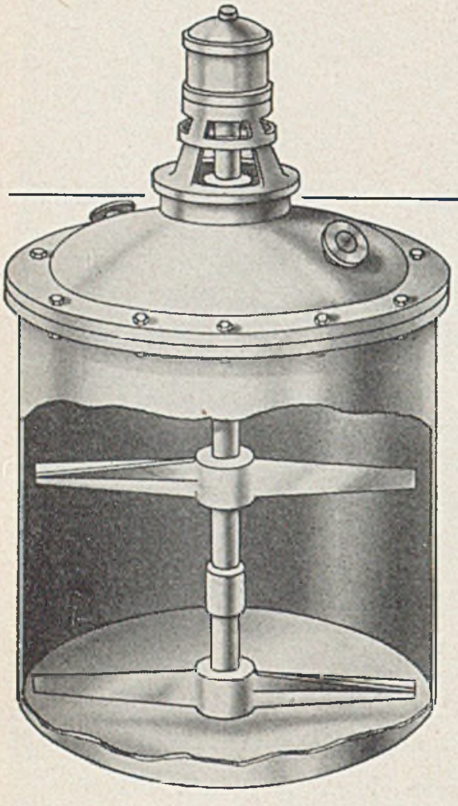
Specify HASTELLOY Alloy for Equipment that must Resist Corrosion

TRADE-MARK

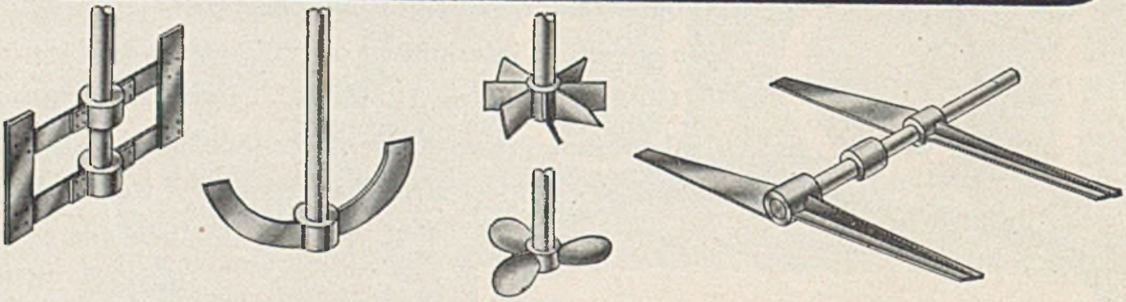


This glass-lined autoclave for mixing corrosive organic and hydrochloric acids in the manufacture of aniline dyes is equipped with an agitator unit of HASTELLOY alloy B. The agitator effectively resists the corrosive action of the hot hydrochloric acid, and there is no danger of breakage, since HASTELLOY alloy B is unusually strong.

There are four grades of HASTELLOY alloy to provide the best combinations of properties for different types of service. They are available in many forms and can be fabricated into a wide variety of chemical processing equipment, such as the standard and special agitators shown here. Mixing or agitating equipment can be built to specifications by Haynes Stellite Company, or can be supplied by the leading manufacturers of this type of equipment.

For further information, write for the booklet "HASTELLOY High-Strength Nickel-Base Corrosion-Resistant Alloys."

HASTELLOY ALLOY AGITATORS—



Haynes Stellite Company
Unit of Union Carbide and Carbon Corporation
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Chicago — Cleveland — Detroit — Houston — Los Angeles — New York — San Francisco — Tulsa

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HASTELLOY
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THE SMOKE GOES UP THE CHIMNEY...

JUST THE SAME!

THE INTERNATIONAL NICKEL COMPANY OF CANADA, LIMITED BEATS TOUGH CORROSION CONDITION

This 554-foot chimney was built* in 1936 for International Nickel of Canada to handle gases from copper reverberatories and converters. Now, after ten tough years, the smoke goes up this chimney just the same as the day the stack was built!

TEN YEARS WITHOUT REPAIR

The gases contain SO_2 with moisture content slightly above atmospheric humidity. Despite this corrosive condition, up to the present time no repairs have been made to this stack, and no evidence of deterioration has been noticed.

HERE'S WHY:

The entire lining of this stack was built with acid-proof brick laid in Penchlor Acid-Proof Cement.** In addition the top fifty feet of this stack was further protected by using Penchlor Acid-Proof Cement for pointing the outside surface joints. Penchlor Acid-Proof Cement is a superior sodium silicate cement that is quick-setting and self-hardening. Its outstanding record of satisfactory service has been proved in chemical plants, steel mills, paper and pulp mills, oil refineries and smelting plants.

SEND FOR CASE REPORT

If you have a corrosion problem, you'll be interested in further details about this Penchlor installation, as well as an illustrated brochure on Penchlor. Write for Case Report Number 68-3.

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PENNSYLVANIA SALT MANUFACTURING COMPANY
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CHEMICALS
97 Years' Service to Industry

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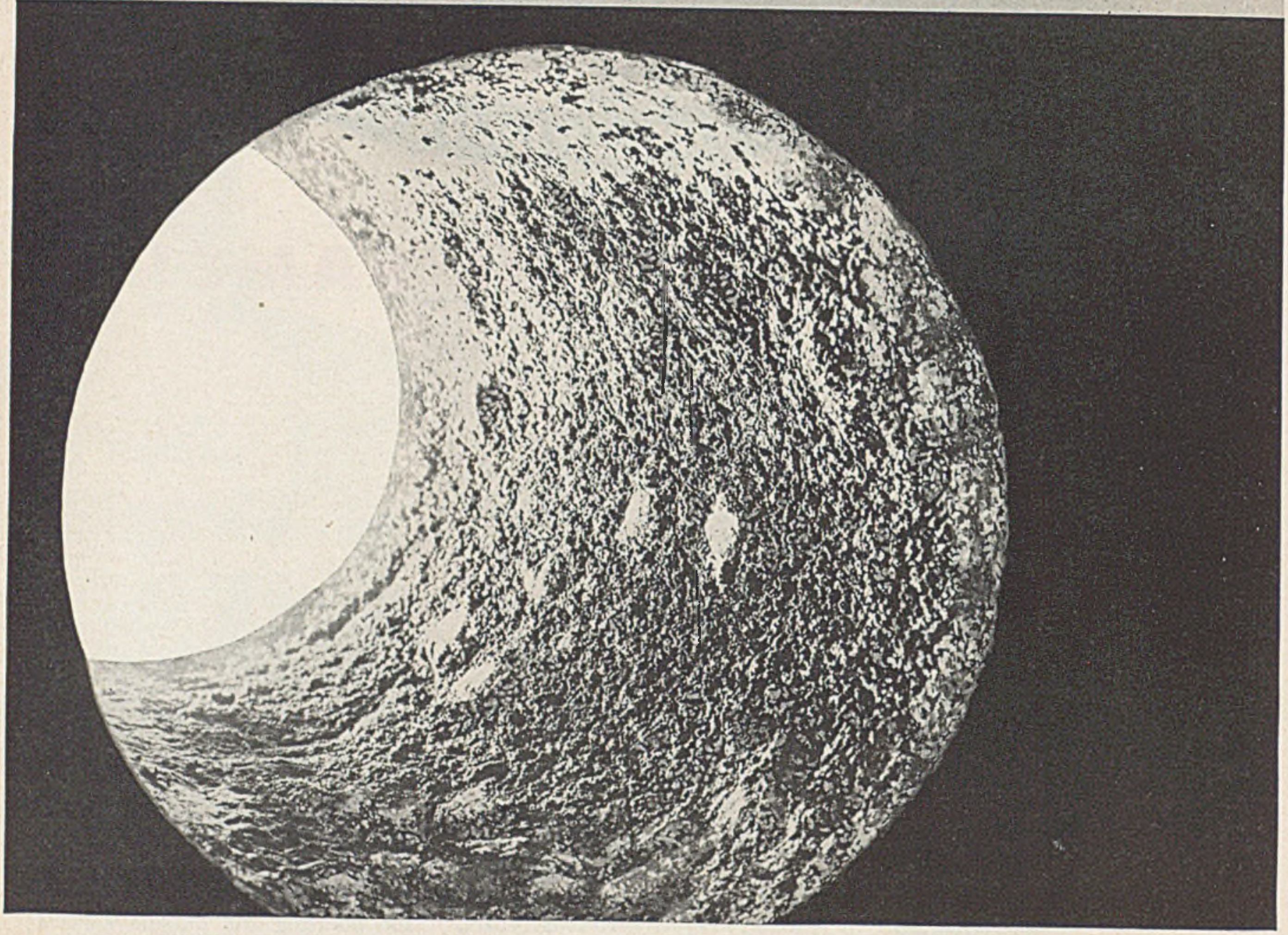
*Built by Custodis Canadian Chimney Company, Limited, Montreal

**Penchlor Acid-Proof Cement was furnished by our Canadian Associates G. F. Sterne & Sons, Ltd., Brantford, Ontario

UNITED STATES RUBBER COMPANY

SERVING THROUGH SCIENCE



For Want of a Lining the Pipe was Lost...

Hungry acids and gases chewed up the inside of this pipe, caused it to be discarded before its time.

This used to be a common occurrence, before "U. S." engineers developed Permobond Linings.

Permobond protects pipes from the corrosive action of acids, gases, chemicals and solutions. It is impermeable, and can be bonded and applied to any standard fitting and to almost any fabricated metal section, big or small, simple or complex.

Our engineers will gladly talk over your particular problems of pipe corrosion. Write Mechanical Goods Division, United States Rubber Company, 1230 Avenue of the Americas, New York 20, N. Y.

U. S. PERMOBOND RUBBER LININGS

You're Dollars Ahead with Lithium Soaps & Chemicals

Many researchers and producers have made these two important discoveries: First: the use of lithium chemicals and soaps in many instances improved their products and processes. Second: with this improvement came a saving in money.

DEHYDRATION, GLASSWARE, CERAMICS

Lithium chemistry has jumped from the test tube into overalls. And in so doing is elbowing out a few of the chemical giants. One instance is a growing preference for lithium salts over sulphuric acid or calcium chloride in the dehydration and purification of gases. Another, the substitution of lithium salts for those of sodium, potassium and lead in glassware and ceramics.

Still another is the use of lithium soap for the manufacture of all-weather, all-purpose automotive and aviation greases.

But this is only the beginning.

COSMETICS, POWDER METALLURGY, INSECTICIDES

Lithium stearate is the basis of better looking, longer-lasting cosmetics; as a lubricant it facilitates the removal of breakdown products in the sintering phase of powder metallurgy; is used as a jelling agent to transform liquid insecticides to paste.

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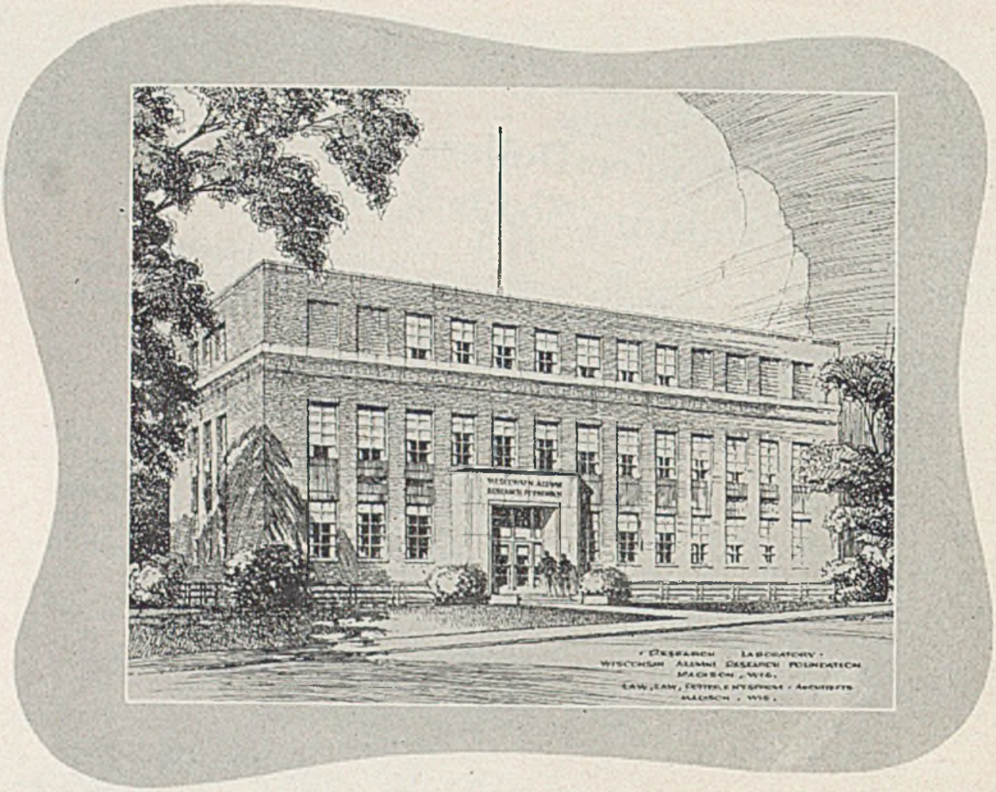

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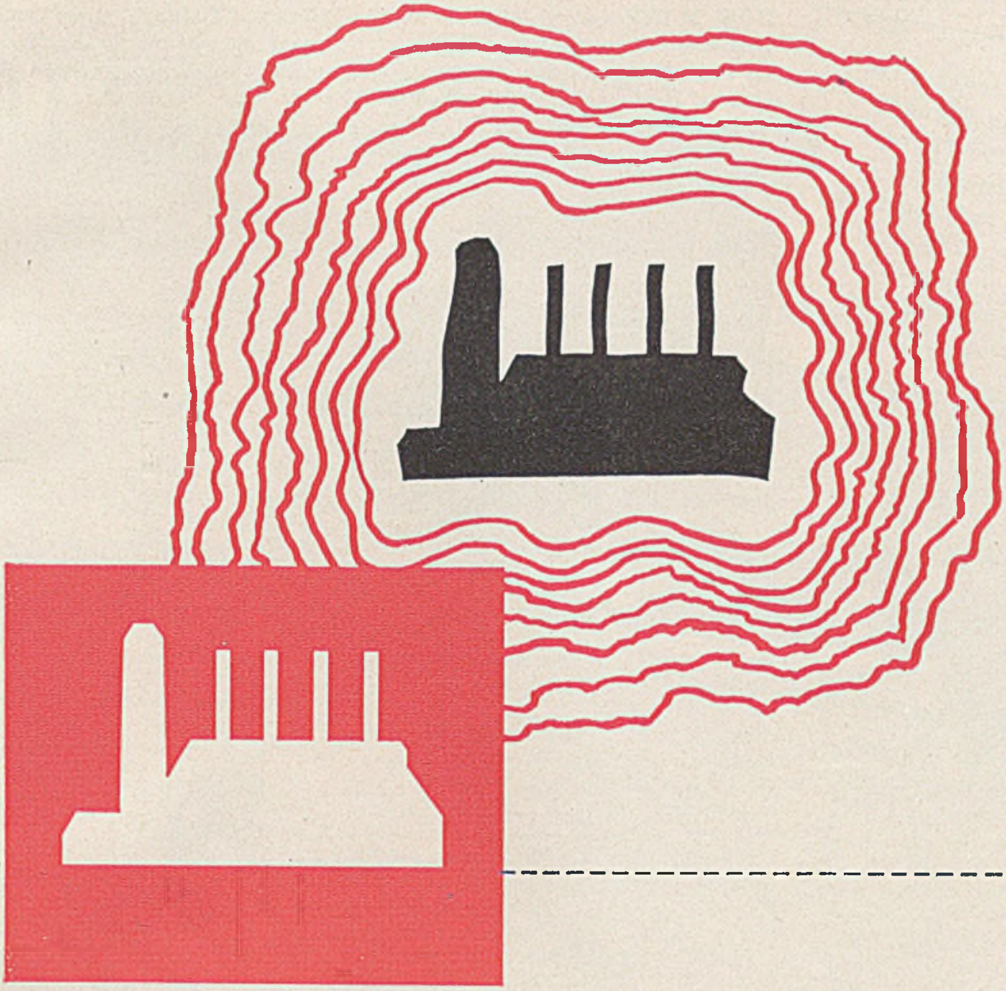

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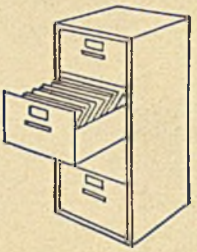

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MANUFACTURERS' LITERATURE

CHEMICALS & MATERIALS

RUBBER LATICES. Technical service brochure on American rubber latices. Particle size approximately 0.06μ in diameter. Negative charge. Suspending medium is water with some fatty acid soap to insure colloidal stability. Recommended for normal resistance to oils, gasolines, petroleum products, animal fats and oils, alcohols, glycols, paint and ink driers, lacquer solvents, etc. B. F. Goodrich Chemical Co. *(Bulletin 47-H1)* 1

LOW PRESSURE AEROSOLS. Bulletin, "Low Pressure Aerosols," gives introduction and history of insecticidal aerosols. Treats effectiveness, propellant gases, nonvolatile ingredients, formulations, dispensers, etc. Continental Can Co., Inc. *(Bulletin 14)* 2

FURNACE BLACKS. Report, "Reinforcing Furnace Blacks," compares 4 standard grade furnaces and channel black and 3 reinforcing furnace blacks with material being developed. Witco Chemical Co. *(Technical Service Report)* 3

PIGMENTS IN RUBBER. Bulletin, "Pigments in Rubber," covers physical properties of pigments and behavior in various natural rubber stocks and blends of natural rubber and GR-S, in chart form. Witco Chemical Co. *(Bulletin 47-1)* 4

CHLORINATED PARAFFIN. Booklet covers revised information on use of chlorinated paraffin as flameproof and weatherproof textile coatings, results of tests of vinyl coatings and vinyl plastics containing paraffin, and applications. Hercules Powder Co. *(Clorafin)* 5

CHEMICAL COMPOUNDS. Manual, "Chemicals by Glyco," lists and describes company's organic chemical compounds, and gives formulas for basic uses of chemicals. Glyco Products Co., Inc. 6

SUGAR SYRUPS. Booklet, "Better Sugar Syrups by Ion Exchange," describes process making possible reclamation of waste and off-grade fruit juices and molasses. Gives results obtained in treating various syrups on commercial and laboratory scale. Pictures commercial installations, outlines principles of ion-exchange, and includes chemical analyses of various syrups before and after ion-exchange treatment. American Cyanamid Co. 7

EQUIPMENT & SUPPLIES

BUNG WRENCH. Folder describes and illustrates all-purpose wrench and 15 closures it opens. Length, 15 in. over-all; weight, $2^{1}/_{8}$ lb. Ampco metal, beryllium-copper, or Monel metal. Rustproof and nonmagnetic. Ampco Metal, Inc. *(Bulletin 86)* 8

CATHODIC PROTECTION. Booklet, "Fighting Corrosion with Corrosion," on application of cathodic protection to submerged steel structures. Story of history and theory of protection with information covering successful design and application of systems. Electro Rust-Proofing Corp. 9

pH MEASUREMENT. Booklet, "pH, Its Measurement and Industrial Importance," illustrates models for industrial convenience and accuracy, precise laboratory work, and battery-operated portable. Describes electrodes and accessories. Fisher Scientific Co. 10

WORM GEARING. Advantages: compact right angle drive, large gear ratios, simple design, high shock load capacity, quiet power, long life through bronze gear teeth, ease of maintenance, interchangeability, etc. Bulletin describes and illustrates service classification, bearing load formulas, quality control and precision manufacturing, selection practice, hp. ratings, worm thread and gear tooth data for various ratios, dimensions, and details of standard worm mountings and dimensions, gear dimensions, and dimensions of standard flanged rims. De Laval Steam Turbine Co. *(Bulletin WG 1220-5-46)* 11

pH TABLES. Bulletin, "pH Tables for Electroplaters," is tabulation of plating baths listing permissible pH range with optimum pH for each bath. R. P. Cargille. 12

Circle Desired Items

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76	77													

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(DECEMBER 1947)

PLEASE TYPE OR PRINT

BELT GRINDING. Folder explains centerless belt grinding method, discussing and illustrating benefits and specifications. Constant or intermittent duty. Range, $^{3}/_{32}$ to $2^{1}/_{4}$ in. in diameter; operates on $3^{1}/_{4}$ h.p. and standard 220 v., 60 cycle, 3 phase; adapted for through work, short pieces, and lengths from $^{3}/_{4}$ in. to 2 ft., shoulder operations, and taper jobs up to 4 in.; speed, 6 to 8 ft./min. on $1^{1}/_{2}$ in. diameter, 16 ft. lengths; feed range, 0 to 18 ft./min. Height, length, and width, 57, 28, and 48 in., respectively. Porter-Cable Machine Co. 13

X-RAY DIFFRACTION. Folder, "X-Ray Diffraction Camera for Microtechniques," shows construction and explains application of camera adapted to fiber analysis. Beam diameters limited from 100 to 25μ. North American Philips Co., Inc. 14

MAGNETIC EQUIPMENT. Bulletin, "Blueprint for Tramp Iron Removal," describes and explains nonelectric, permanent magnetic equipment. Includes specific applications, pertinent data, and engineering drawings, showing size, weight, and construction of units. Eriez Mfg. Co. (*Bulletin 102-B*) 15

HEATING EQUIPMENT. Booklet, "Heat for Metals," describes company's activities in metallurgical research, and designing and manufacturing of heating equipment for metal producing and working industries. Treats latest developments in heating equipment for steel mills, history of development of gas chemistry and heat treatment, prepared gas atmospheres and heating equipment applications to processing, etc. Describes standard industrial furnaces and burner systems and equipment. Surface Combustion Corp. 16

STOCK DRIVES. Catalog, "Pre-Engineered Texrope Drives," compiles engineering data devoted to 22,000 stock drives for various applications from 1 to 150 h.p. Drives for motor speeds, ratios, and driven speeds systematically indexed according to h.p. Allis-Chalmers Mfg. Co. (*Bulletin 20-B-6956*) 17

SOUND SYSTEMS. Bulletin, "Sound . . . A Modern Control System," describes and illustrates line of voice-paging and music systems featuring "one button" and plate voltage controls, and electronically matched components. Executone, Inc. 18

SLIDE RULE. Tool for judging corrosion resistance of nonferrous and stainless steel alloys. Classifies resistance of 13 nonferrous and stainless steel alloys in 142 corrosive applications with degrees of excellent, good, fair, and no good. H. M. Harper Co. 19

COOLING TOWER. Folder describes and illustrates cylindrical mechanical draft cooling tower. Air enters tower from all points of 360° circumference. Individual or multicell units, redwood or steel construction. Santa Fe Tank & Tower Co. (*SFR 148*) 20

MAGNETIC PULLEY. Bulletin describes permanent Alnico magnetic head pulley for belt conveyor systems. Includes dimensions, capacities, weights, etc. Dings Magnetic Separator Co. (*Perma-Pulley*) 21

BLOWERS AND EXHAUSTERS. Booklet, "Multistage Centrifugal Blowers and Exhausters," describes applications of centrifugal equipment on production operations requiring air pressure from 1 to 8 lb./sq. in. on vacuum from 2 to 11.5 in. mercury. Uniform pressure, variable volume, and continuous service. Design features shown graphically, operating characteristics, capacity ranges, and conversion factors described. U. S. Hoffman Machinery Corp. (*A-650*) 22

SOLVENT EXTRACTION PROCESS. Bulletin, "Continuous Solvent Extraction Process," summarizes experience gained in engineering, installing, and operating various solvent extraction plants. Lists advantages, analyses economies, and suggests applications. Describes equipment supplied to oil extraction industry. Allis-Chalmers Mfg. Co. (*Bulletin 13B6757*) 23

ILLUMINATED MAGNIFIER. Catalog illustrates and describes portable, illuminated magnifier for inspection use, plus other models. Electric or battery models with magnification powers from 5 to 40. E. W. Pike Co. (*Flash-O-Lens*) 24

BENT TUBE BOILER. Booklet describes and illustrates units installed in various plants. Ranges: 25,000 to 125,000 lb. steam/hr. capacity, 8 ft. 6 in. to 19 ft. 6 in. furnace width, and 11 ft. 6 in. to 23 ft. over-all width of setting. Chain grate, underfeed, or spreader type stokers. Henry Vogt Machine Co., Inc. (*Class LE*) 25

METAL TUBING CIRCUITS. Data on selection, sizing, layout, and installation of metal tubing circuits. "Tube Fitter's Manual" contains basic data underlying specialized techniques required for design and installation of leakproof systems. Parker Appliance Co. (*Handbook No. 111. Price, $1.00*) 26

Y AND ANGLE VALVES. Folder describes corrosion-resisting Y and angle valves, showing internal construction. Lists features and explains service requirements. Provides dimensional data. Tells how to equip valves with air operated diaphragm motors for automatic regulation of flow of corrosive solutions. Duriron Co., Inc. (*Series 35 and 36. Bulletin 615*) 27

PLUG VALVE. Folder illustrating lubricated plug valve for accurate and positive control of fluid flow, in sizes 1, 1.5, 2, 2.5, 3, or 4 in. Working pressures vary from 200 to 500 lb./sq. in. Semi-steel, carbon steel, stainless steel, or bronze. H. K. Porter Co., Inc. 28

STAINLESS ELECTRODES. Bulletin, "What Electrode to Use to Weld Specified Stainless or Alloy Steel," divides subject into sections. Provides information on base metal identification of solid and clad materials, recommended types of electrodes, special considerations involving corrosion, heat, or strength properties, etc. Includes chart of trade names of stainless alloys. Arcos Corp. (*Bulletin 1047*) 29

RESIN PLANTS. Booklet, "Resin Plants and Equipment," describes and illustrates variety of plants and equipment for resin industry and allied fields. Treats: varnish cooking, oil bodying, resins, preparation of molding powers, electrical resistance heating, high and low temperature heating systems, design features, instrumentation, etc. Blaw-Knox Co. (*Bulletin 2087*) 30

MISCELLANEOUS

HANDLING FIRES. Booklet, "Watchman, What Would You Do?", uses question-answer method to illustrate important fundamentals in controlling fires as aid to plant managements. Contains page for recording official names and phones. Associated Factory Mutual Fire Insurance Companies. 31

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332 WEST 42nd ST.
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NEW PRODUCTS

CHEMICALS & MATERIALS

Thread Compound. Compound prevents freezing and galling of metal surfaces up to 1800° F. Developed for high temperature and high pressure applications. Felt Products Mfg. Co. (*Hi-Temp C-5*) 32

Fatty Esters. Line of products extends through range of polyoxyethylene fatty esters, from liquids of low freezing point to waxy solids, and from water to hydrocarbon solubility. Applicable to manufacture of emulsions, dry cleaning soaps, cosmetics, pharmaceuticals, lubricants, textiles, and plastics. Glyco Products Co., Inc. 33

Germicide. Chemical compound in small capsules for use in general disinfecting, sanitizing, and various preserving and sterilizing requirements. Contents of 1 capsule in 1 gal. water produces germicide 27 times more powerful than carbolic acid. Harmless to skin, materials, and painted surfaces. Nontoxic, nonpoisonous, odorless, colorless, and stainless. Service Industries. (*Steryl*) 34

Coating. Gloss coating resistant to fruit acids, vinegar, grease, alkali, and mineral spirits. 1-coat application. Dries in 5 to 10 min. for handling, 1 to 2 hr. for packing. For use on wood and metal. Hilo Varnish Corp. (*Clix*) 35

Hycar American Rubbers. Oil resistant rubbers designated as easy processing and nonstaining. Both band on processing mill rolls quickly, have good extrusion, fusion, and mold flow characteristics, high temperature mixing, and increased building tack for laminated products. To obtain equivalent state of cure to regular rubber, sulfur should be increased by 0.25 part sulfur to 100 parts rubber polymer. B. F. Goodrich Chemical Co. (*Hycar OR-25 EP and OR-25 NS*) 36

Metal Coating. Weather-protective, self-healing, spray coating for long-term metal protection. Effective 10 years or more. Aluminum color. Arco Co. (*Dum Dum for Metal*) 37

Chlorinated Rubber Base. Base for concrete paints and other protective coatings. Quick-dry, film-forming thermoplastic resists alkalies, acids, etc.; protects concrete and metal finishes. Hercules Powder Co., Inc. (*Parlon*) 38

Acetone Cyanohydrin. α-Hydroxyisobutyronitrile, containing 2 functional groups, tertiary hydroxyl and nitrile. Available in commercial quantities. Reactions discussed in bulletin. Rohm & Haas Co. 39

Soybean Nutrient. Development of nutrient increases streptomycin production. Consumed by streptomycin-producing mold during involved process, resulting in greater yield. Takes place of complex growth-producing substances. Cost, 0.1 that of protein complex materials. Nutrient alters neither fundamental streptomycin qualities, nor chemical processing production. A. E. Staley Mfg. Co. 40

EQUIPMENT & SUPPLIES

Steam Cleaner. Full-powered, heavy-duty, all-purpose utility model steam cleaner. Features: quick starting, simplicity of design and operation, welded unit construction, accessibility of all working parts, continuous electric spark ignition, nonclogging heating coil, and pressure atomizing oil burner. Oil or natural gas burner; electric motor or gasoline engine driven mechanism. Net weight and dimensions, 520 lb. and 55 × 25 × 47.25 in., respectively. Homestead Valve Mfg. Co., Inc. 41

Universal Expansion Joints. Joints designed for refineries, power plants, and chemical process plants. Capable of absorbing movement of high temperature lines axially, laterally, or angularly, or combination of these. Consists of 2 corrugated elements linked by section of pipe. Expansion elements of nonequalizing type for pressures up to 30 lb. or self-equalizing for higher pressures. Zallea Bros. & Johnson. (*Zallea Catalog 47*) 42

Adhesive Gauze Tape. Tape designed to protect fingers, etc., from painful skin burns, bruises, and other injuries. Oil-resistant combination of gauze and tape treated as to adhere to itself without leaving gummy deposits on skin. Rolls 1 in. wide, 15 yd. long to 2 in. wide, 10 yd. long. Modern First Aid Necessities Co. (*Gauztape*) 43

Condensate Return System. High pressure centrifugal pump saving up to 25% fuel by return of condensate at higher temperatures. Cochrane Corp. (*Cochrane C-B*) 44

Rotocycle Pump. Rotary, positive displacement pump of fixed volume double-acting type. Operating parts held in hydraulic and dynamic balance. Run in either direction. Volumetric efficiency, 90 to 95%, over-all operating efficiency, 85 to 90%. Rockwell Mfg. Co. 45

Lubricated Plug Valves. Valves available in semi-steel, carbon, alloy, and stainless steels. Features: leak-proof shutoff, elimination of leaks through stuffing box, and ease of operation. H. K. Porter Co., Inc. 46

Electronic Speed Control. Controls speed of boiler draft fans and centrifugal pumps, compressors, and blowers on which magnetic drive is used. Rectifies 3-phase supply current; adjusts value of current to hold operating speed of load to within ±1% selected speed. Guards against effects of overvoltage, undervoltage, short-time power failure, and improper operation of tubes or amplifier. Electric Machinery Mfg. Co. (*Regutron*) 47

Calculator. Pocket-size calculator makes available benefits of sequential sampling. Tells operator how many samples to take, how long to continue sampling, and finally indicates whether lot should be accepted or rejected. Based on tailor-made program drawn up to meet inspection needs of user. Functions on basis of: acceptable and unacceptable quality level, factory and customer risk, and average outgoing quality limit. Metal or plastic. Lightning Calculator Co., Inc. 48

Variable Speed Motor. Motor variable from 1500 to 6000 r.p.m. Maintains constant maximum torque at all speeds; adjustable, stepless speed control. Side lever stops and starts motor, mechanically controls pair of centrifugal vibrating contacts which accomplish speed variation. Motor, $^1/_5$ h.p., ball bearing, universal wound, reversible, 115 v., single phase, 9 × 7 × 5 in. Single and double reduction gears and flexible shafts. Guernet Electrical Machinery, Inc. 49

Alloy Globe and Gate Valves. Two lines of valves in sizes 2.5, 3, 4, and 6 in., with flanged ends. Available in 18-8 Mo and Monel metal for working pressures of 150 lb./sq. in. liquid or gas and working temperatures up to 350° F. Crane Co. 50

Linear Ball Bearing. Unlimited travel antifriction ball bearing for linear or reciprocating motion. Self-contained. Consists of: steel sleeve ground to close tolerances, pressed steel retainer fabricated in long continuous strips rolled inside sleeve, and pair of rings pressed in ends of sleeve to secure retainer to sleeve. Bushings available for shafts 0.25, 0.5, 0.75, and 1 in. in diameter. Low friction coefficient. Thomson Industries, Inc. 51

Hydraulic Gate Loader. Tail gate loader for trucks speeds up loading and unloading. Lift platform operates over distance from ground to truck floor level, lifting loads up to 1200 lb. Pump driven from truck's power take-off, controlled by lever. Simple installation. Day Co. 52

Gate Valve. Union bonnet valve incorporates first application of full cylindrical body sections to bronze gate valves. Maximum distortion resistance. 200-lb. bronze, double disk valve has rising stem and screwed ends. Features include: silicon alloy stem material reduces stem-thread failures, hexagon head gland, beveled disk wing guides and body guide channels for easy assembly. Circular shows principal features, dimensions, etc. Lunkenheimer Co. (*Circular 534*) 53

FLEXIBLE TUBING. Hose of innercore and braid for temperatures up to 1700° F. Innercore wall, 0.005 to 0.015 in. thick. Flat ribbon or round wire braid. Titeflex, Inc. (*Inconel*) 54

SELECTOR AND SHUTOFF VALVES. Series of nonlubricated and shutoff valves for chemical and process service. Handle air, gases, or hot liquids up to 400° F., and at nonshock pressures up to 500 lb./sq. in. Available in variety of metals. Nonlubricated rotors of inert graphite. Shutoff valve sizes from 0.5 to 2 in. pipe size, selector series from 0.5 to 1.25 in. Parker Appliance Co. 55

CONTINUOUS MIXER. Mixer handles products from viscosity and density of bread dough to properties of water. Control rate, 5 to 1000 gal./hr. Stainless and sanitary. Marco Co., Inc. (*Roto-Feed*) 56

METALLIZING GUN. Metal spray gun powered by electric motor for production line spraying. $^{1}/_{20}$ h.p. constant speed induction motor. Adjustments for gas and air. Available in 25, 50, and 60 cycles. Metallizing Co. of America. (*Mogulectric*) 57

SLIP-PROOF BELT. Belt with rubber teeth provides strength, flexibility, and noiseless operation. Reinforced with steel cables embedded in oil-resisting synthetic rubber. Speed up to 10,000 ft./min. Sizes to fit machine designer requirements. Suitable for power transmission and synchronization. U. S. Rubber Co. (*Gilmer Timing Belt*) 58

FORK TRUCK. Truck handles 4000- to 8000-lb. loads. Features controller which functions as electric counterpart of automotive automatic gearshift, high pressure hydraulic system, and silicone insulation and lubrication. Collapsed height, 83 in. Lift to 124 in. Automatic Transportation Co. (*Skylift Brawny*) 59

PORTABLE WELDER. Arc welder provides 1.5 kw. alternating current at 115 v., single phase. Trailer or stationary model. 200 amp. 1 control for any desired heat. Harnischfeger Corp. (*P&H Model WN-200*) 60

BOX FURNACE. Box-type laboratory furnace with temperatures up to 3000° F. top heat and 2500° F. continuous operation. Operation, 230 v., 60 cycle, single phase a.c. 8 kw. capacity variable voltage transformer. Lindberg Engineering Co. (*Model G-10. Bulletin 980*) 61

STACKING PALLET. Structural aluminum alloy unit for handling and stacking loads. 4 tubular columns at outside corners for supporting tiered loads fold when not in use. Weight, empty, 53 lb. Dimensional load, 48 × 36 in. × 4 ft. high. Capacity, 3000 lb./unit. Tobey International Co. (*Stak-Rak*) 62

BOOSTER FANS. Series of heavy-duty fans with propeller diameters 16, 20, 24, 30, and 36 in. Shafts and motors ball bearing mounted. Vertical or horizontal operation. Nonferrous metal blades. Chelsea Fan & Blower Co., Inc. (*Series DXB*) 63

MIDGET SOLDERING IRON. Soldering iron designed for precision soldering. Lightweight. Length and weight, 8 in. and $1^{3}/_{4}$ oz. with cord, respectively. Rated at 25 w., 6 v., and used with 115/6-v. transformer. Driver-Harris Co. (*Calrod Midget*) 64

IMPACT-CUSHIONING IDLER. Nonpneumatic idler for belt conveyors. Rubber rings mounted on idler core afford maximum deflection. Resilient rings decelerate lump. Goodyear Tire & Rubber Co. 65

INSTRUMENTS

RUGOSIMETER. Instrument for measuring rugosity or surface roughness of calendered raw rubber sheet or similar samples. Consists of constant-pressure air valve, large needle valve with calibrated scale, manometer, and annular test plate. Measurement principle is resistance to flow of air between rough surfaces and annular test plate which rests upon surface under test. Precision Scientific Co. 66

DEW POINT APPARATUS. Simple device for measuring moisture content of air and gases at approximately atmospheric pressure. Consists of outer container with inlet and outlet connections and glass window, inner container having highly polished outer surface visible through window, and thermometer. Use of acetone and dry ice mixture makes possible checking to −76° C. Pittsburgh Lectrodryer Corp. 67

PRECISION INSTRUMENTS. Midget meters and allied equipment, smallest D'Arsonval meters, offer accuracy, quality, durability, and dependability of larger meters. 6 basic ranges from 0 to 100, 200, 500, 1.0, 5.0, and 10 ma. International Instruments, Inc. 68

PLUG-IN SCALE. Scale consists of 6AL5 and 6J6 tube in Higginbotham circuit built in cast aluminum housing measuring 2 × 2 × 2 in., mounted on standard amphenol 9-prong tube-base plug. Useful as micro-second stopclock, production line counting and control equipment, and constant frequency divider in processes where events occur too rapidly to allow actuation of mechanical register. Tracerlab, Inc. (*Duoscale*) 69

CO_2 INDICATOR. Lightweight, portable indicator, containing no liquids or corrosive agents, determines CO_2 in less than 1 min. Gas sample drawn from stack and forced into barrel by means of rubber hand pump. Operating principle involves chemical absorption of CO_2 by dry cartridge. Indicator gage calibrated directly in percentage CO_2 in sample. Burrell Technical Supply Co. (*Bulletin 206*) 70

PNEUMATIC TRANSMITTER. Indicator-type instrument with eccentric or concentric scale. Transmitting and receiving mechanisms matched and linear in calibration. 12-in. round-form case. Useful for measurements of flow, static or differential pressure, liquid level, temperature, or humidity. Foxboro Co. (*Bulletin 409*) 71

ELECTRIC TACHOMETER. Hand-held tachometer weighing 3 lb., designed for accurate and direct readings of linear speeds from 10 to 10,000 ft./min., and of rotational speeds from 100 to 10,000 r.p.m. Consists of head and indicating unit. Not damaged by overspeeding. Measures clockwise and counter-clockwise rotation. General Electric Co. (*GEA 4895*) 72

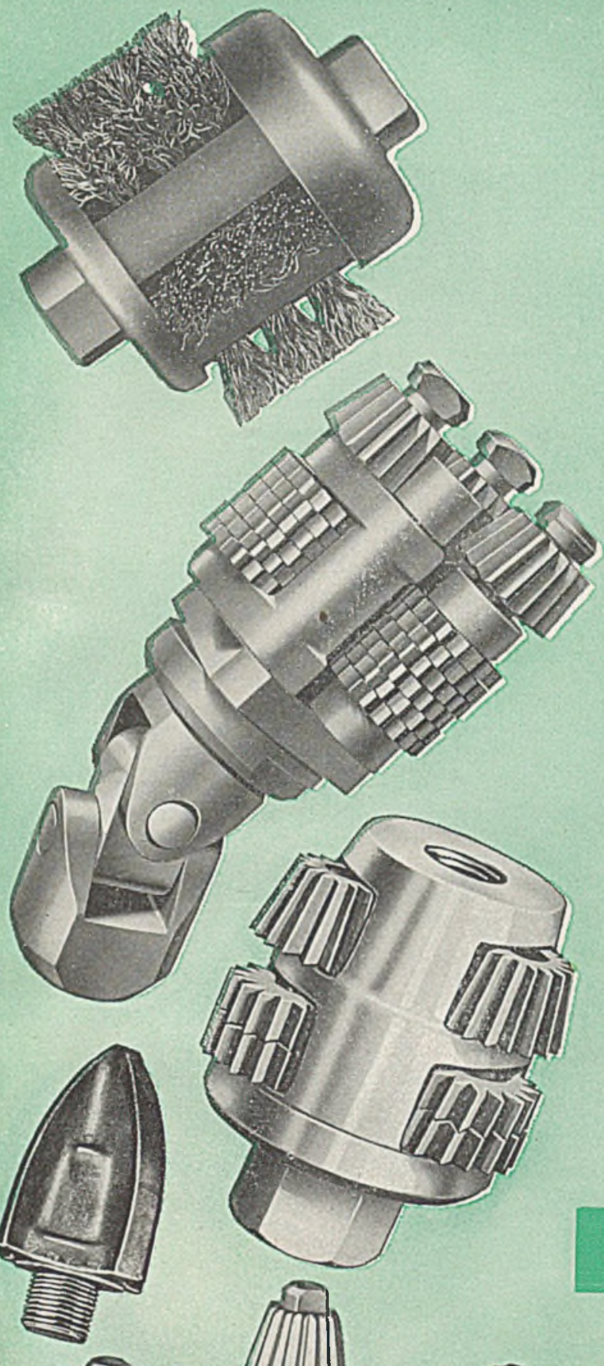
TIME SWITCH. Self-contained unit operates on 110 v., a.c. Self-starting clock, sweep second hand. Switch dial revolves once a day. Sheet steel case, black crackle finish. Input, 5-ft. cord with heavy rubber plug. Pilot light on front of case indicates condition of relay. Palo-Myers, Inc. (*Palo Switch Sr.*) 73

ELECTRONIC TIMER. Repeat cycle timer for process control, life testing, and laboratory use. Independently variable *on* and *off* intervals ranging from 0.1 sec. to 4.0 min. Housed in chassis 3 × 4 × 5 in. Operates on 115 v., 60 cycles. Timer for 115 v., d.c. operation available; relay contacts with 2 transfers rated for 10 amp. at 115 v., a.c. provided. G. C. Wilson & Co. 74

MEASURING INSTRUMENTS. Continuous dew point recorders and recording controllers. Main feature is measuring element, a perforated metal cylinder 9 in. in length and 2 in. in diameter. Pneumatic or electric control systems. Recorders require no refrigeration, water supply, or air circulating system. Thermal bulb measures temperature, which is transmitted to recording instrument and read on chart in degrees of dew point temperature. Foxboro Co. (*Bulletin 407*) 75

SAMPLE CHANGER AND PREAMPLIFIER. Lead shielded manual sample changer and preamplifier. Permits fast and accurate counting of radioactive samples. Consists of: 2 in. lead shield, outside dimensions, $11^{5}/_{8}$ in. in height × $6^{1}/_{2}$ in. in diameter; preamplifier circuit; tube; and stainless steel sample holder. Geometrical reproducibility within 0.1%. Tracerlab, Inc. (*SC-9A*) 76

AUTOMATIC TITRATOR. Dual automatic recording device for plotting automatic titration curves. Provides permanent and complete curve record; one sample titrated while second is prepared for analysis. Aqueous and nonaqueous media. Silver, antimony, platinum, calomel, or glass electrodes. Consists of reagent-feeding device and recording potentiometer. 200 w. power. Continuous duty. Change in 115 v., a.c. line results in d.c. voltage change of 0.1%. Precision Scientific Co. (*Precision-Dow Recordomatic*) 77



LESS TIME
FOR TUBE CLEANING
WITH THESE
WILSON ACCESSORIES

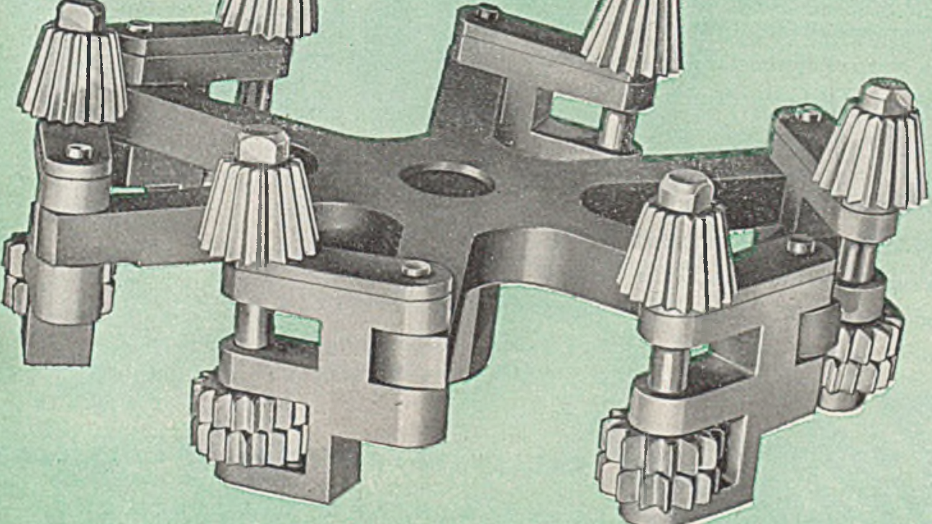
Years of research and development engineering by Thomas C. Wilson, Inc. have enabled process plant operators throughout the country to save production time through reduced down-time for tube cleaning.

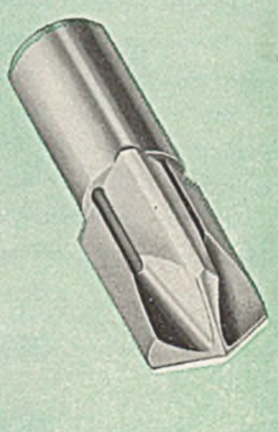
Progressive Wilson Engineers, always on the lookout for possible design improvements, have developed a complete line of up-to-the-minute accessories for the process industry. Developed for use with air, steam, water or electrically driven Wilson Tube Cleaner Motors, fast-acting, thorough-cleaning Wilson accessories make short work of the toughest chemical tube deposits.

The proper combination of standard Wilson motor and accessories will meet most process plant requirements. When unusual operating conditions are encountered, however, Wilson has the facilities and experience to provide special equipment designed to meet your particular requirements. Write for information on standard Wilson equipment and on special equipment to solve special problems.

THOMAS C. WILSON, INC. • 21-11 44th Ave., Long Island City 1, N. Y.
Cable address: "TUBECLEAN", New York

WILSON
TUBE CLEANERS





TW-733

Scientific advancements are pointing the way to new opportunities for American businesses who have the need and desire to pioneer new fields, and perfect present techniques. • Filtrol's process engineers have the "know-how" in the broad field of adsorbents which has led to the perfection of many new processes in the chemical industry. This "know-how" is offered to you. • Filtrol Corporation is the world's leading manufacturer of catalysts, adsorbents and other highly activated, chemically treated materials—all vitally important to the petroleum industry, the fatty oil industry, agricultural insecticides and in the drying of liquids and gases, purification of solvents, and in protective packaging.

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General Offices: 634 So. Spring St., Los Angeles 14, Calif.
Plants: Vernon, California, and Jackson, Mississippi

PRODUCT OF **Filtrol***
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RESEARCH AND DEVELOPMENT

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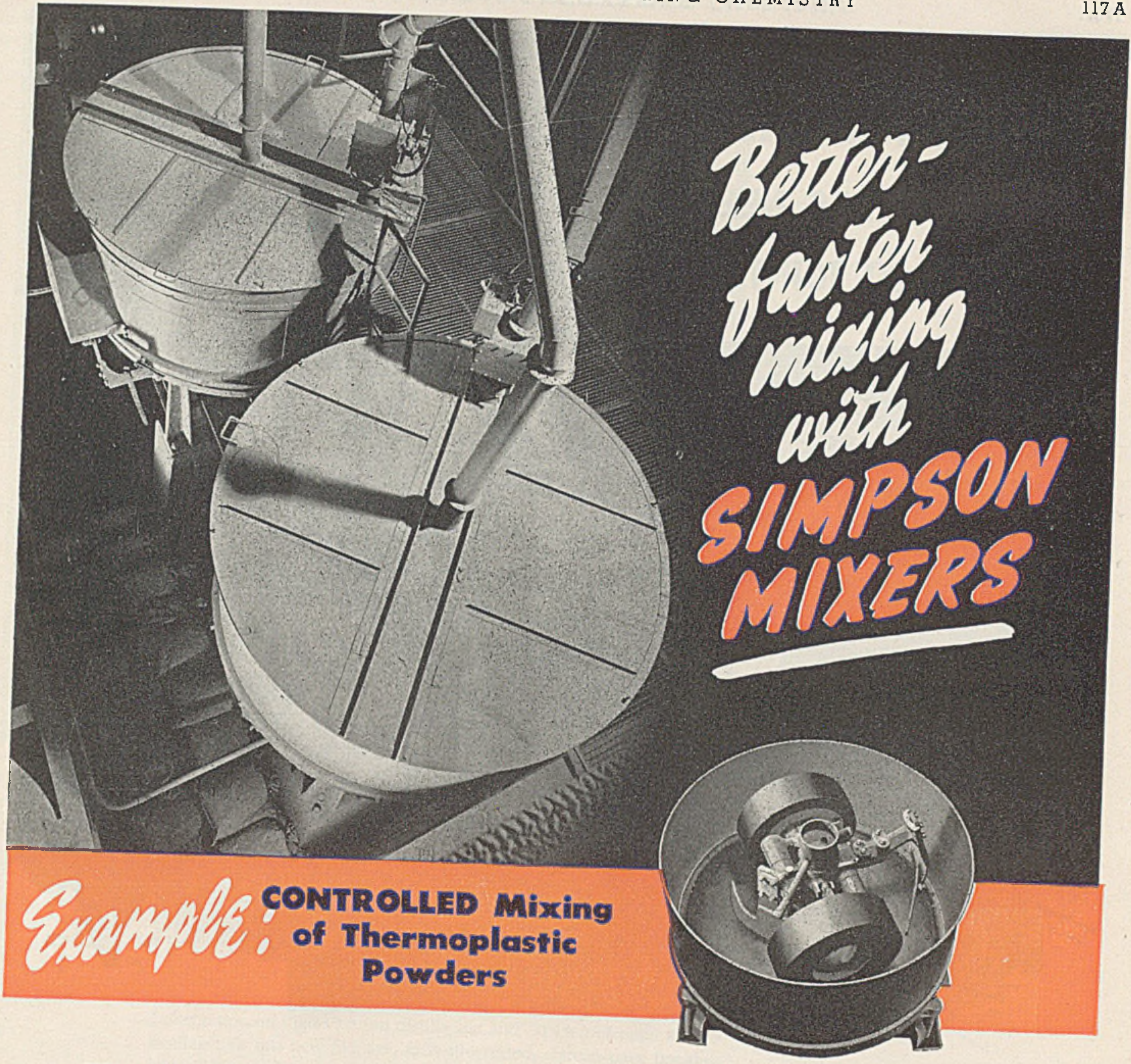

Example: CONTROLLED Mixing of Thermoplastic Powders

When it comes to better, faster, lower cost mixing of thermoplastic powders, you can't beat the Simpson method of *controlled* "mulling," to provide the desired impregnation of plasticizers and fillers into the resins.

Simpson Mixers are available in sizes to handle batches from 1/5th to 50 cu. ft., and may be steam or water jacketed to provide heat for more rapid blending of plasticizers. All models are virtually self-cleaning, and offer the well-known automatic discharge feature.

Write for further details about Simpson Mixers now in use on scores of difficult mixing jobs on dry, semi-dry and plastic materials. National Engineering Service is yours for the asking.

Ask to have a National Engineer show you how Simpson Mixers can solve your mixing problems involving dry, semi-dry and plastic materials

SIMPSON
Intensive Mixers

NATIONAL ENGINEERING COMPANY
609 Machinery Hall Bldg. • Chicago 6, Ill.

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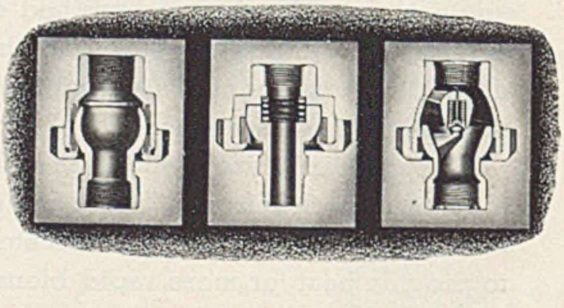
TO ABSORB SHOCKS

FUEL LINES NEED BARCO JOINTS

Fuel lines don't last long unless, like this hockey goalkeeper, they are protected from impact and shocks. Barco Flexible Joints, by responsive movement through every angle, absorb shocks and stresses in fuel lines, compensate for expansion and contraction. For over 30 years, these valuable time and cost savers have been guarding fluid-conveying systems from the deadly effects of vibration, preventing leakage and fractures. Whatever your special installation may be, you'll find the right joint for it in the Barco line. Write for complete facts. Barco Manufacturing Company, Not Inc., 1823 Winnemac Avenue, Chicago 40, Illinois. In Canada: The Holden Co., Ltd., Montreal, Can.



BARCO FLEXIBLE JOINTS

Not just a swivel joint ...but a combination of a swivel and ball joint with rotary motion and responsive movement through every angle.

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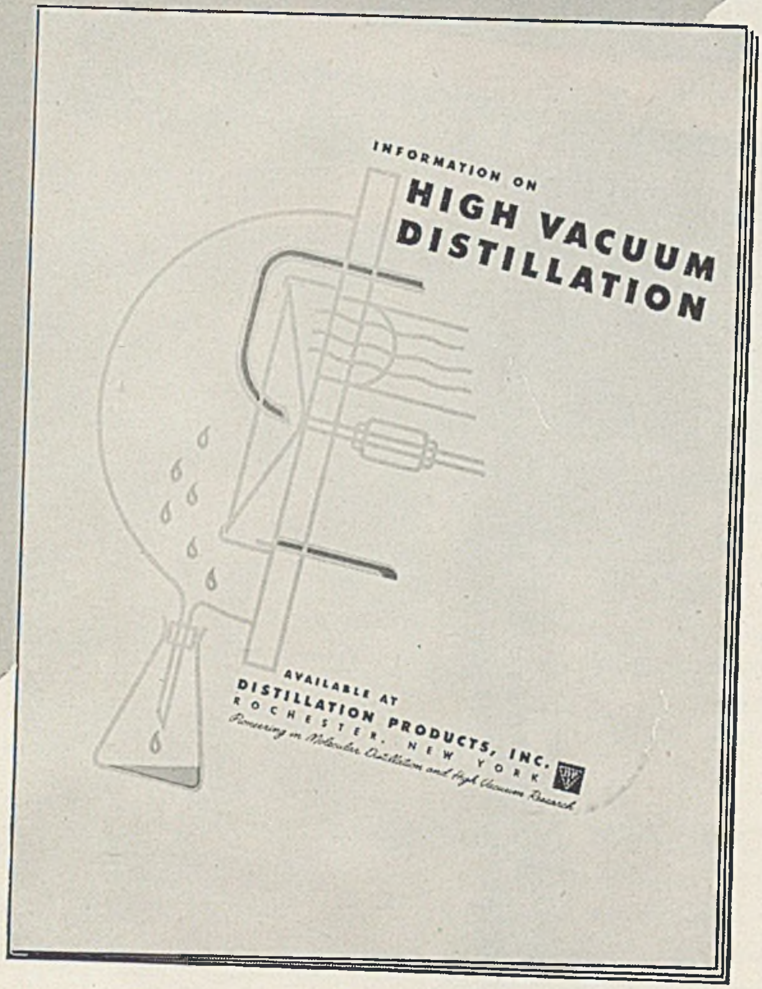
"MOVE IN

EVERY

DIRECTION"



INFORMATION ON
HIGH VACUUM
DISTILLATION

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Information on high vacuum distillation and DPI's molecular stills is available in this new file size, fully-illustrated, sixteen-page booklet, just off the press.

The booklet includes:

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"500"

RECORDING THERMOMETERS AND GAUGES

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. . . That Give You Minute-By-Minute Reports On
What *Is* Happening . . . What *Has* Happened

A NEW DESIGN . . .
FOR NEW, HIGHER STANDARDS

If *accuracy, convenience, dependability and service-performance* influence your choice of instruments, you'll certainly want to know more about Bristol's New "Series 500" recording thermometers and gauges. These instruments represent the very latest design based upon the same principles that have made Bristol Instruments so successful over the past 50 years. In this new design, Bristol Engineers have created instruments with . . .

1. Unsurpassed Accuracy. 2. Ruggedness and Simplicity. 3. Ease of Use. 4. Convenience in Servicing. 5. Ready Convertibility from One Type to Another.

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For the inside story on the new Bristol "Series 500" Instruments send for Bulletin T835. THE BRISTOL COMPANY, 110 Bristol Road, Waterbury 91, Conn.; The Bristol Co. of Canada, Ltd., Toronto, Ont.; Bristol's Instrument Co., Ltd., London N. W. 10, England.

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Engineers process control for better products and profits

AUTOMATIC CONTROLLING AND RECORDING INSTRUMENTS

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Mixing Equipment

is a major factor wherever efficient product processing is required

The innumerable agitation problems which Struthers Wells designers have successfully solved, gives them an enviable soundness of judgment in the selection of agitating equipment best suited to specific operating conditions.

Acknowledged as pioneers in the welded fabrication of ferrous and non-ferrous alloys and superbly equipped for autoclave and pressure vessel construction, Struthers Wells designing and manufacturing facilities are fully adequate to meet the most severe requirement.

Look to Struthers Wells when you have an agitating equipment problem.

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PLANTS AT WARREN AND TITUSVILLE, PA.
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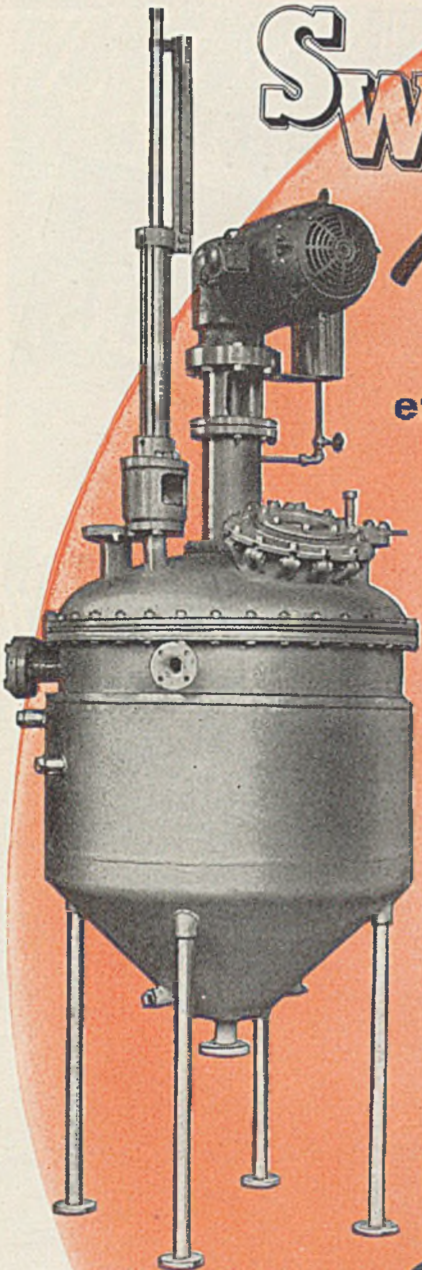
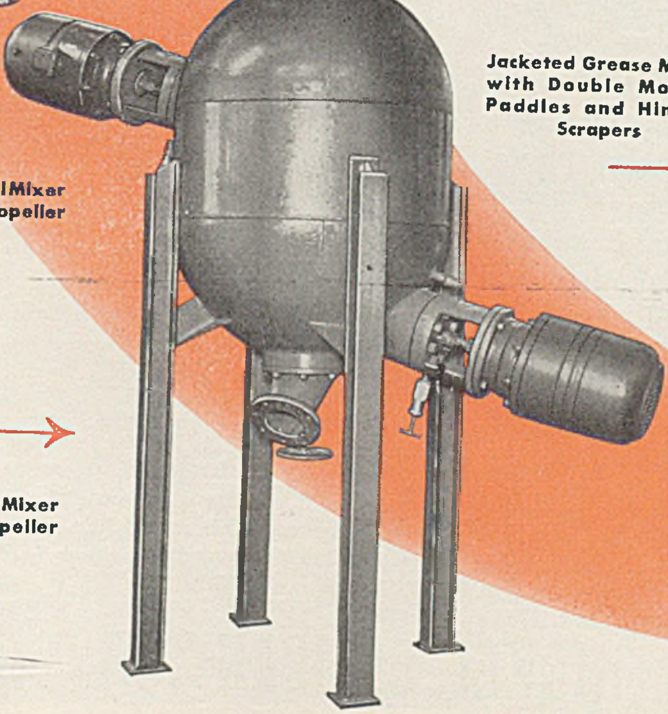
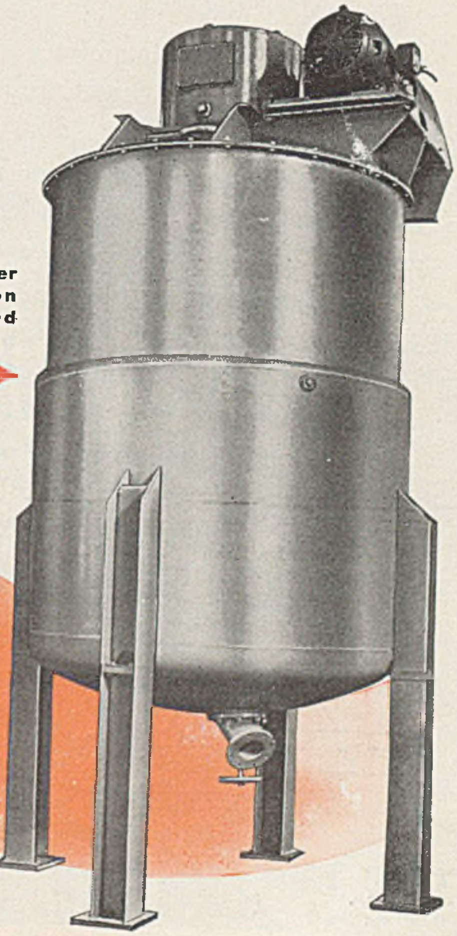


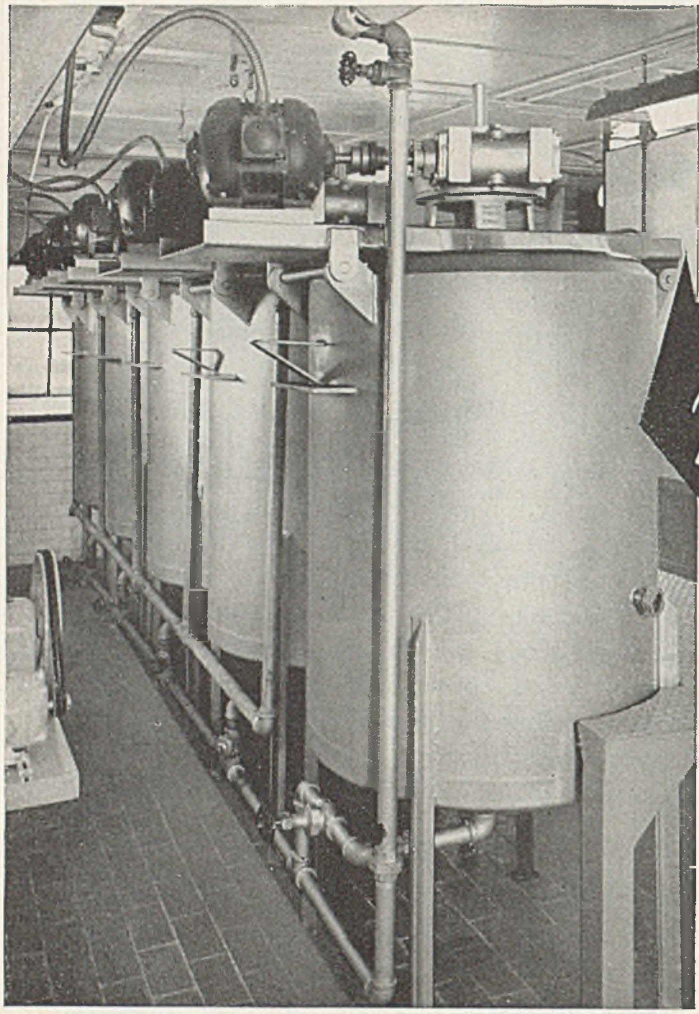
Jacketed Vertical Mixer with Radial Propeller Agitator



Rubber Cement Mixer with Marine Propeller Agitator



Jacketed Grease Mixer with Double Motion Paddles and Hinged Scrapers



STAINLESS STEEL helps *New* DIXIE COOKERS

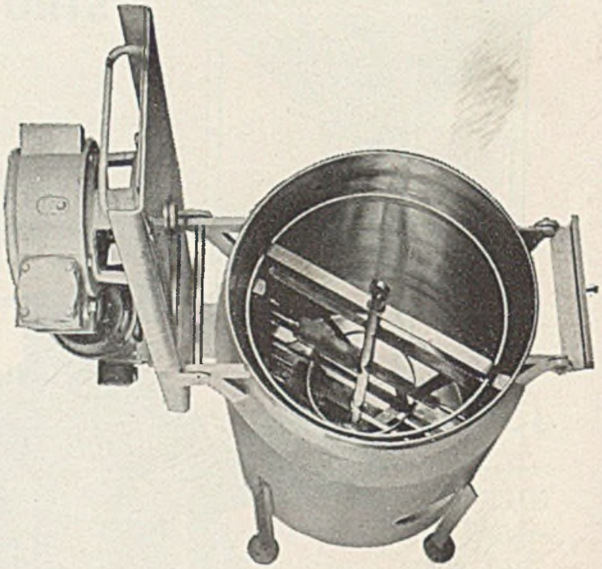
- SAVE LABOR
- DEFEAT CONTAMINATION
- SIMPLIFY CLEANING

See the newest starch cookers and coolers built by Dixie Manufacturing Company, Baltimore, Maryland.

Interiors of these 125-gallon tanks, as well as the scraper-agitators, are made from Type 316 austenitic chromium-Nickel stainless steel.

Type 316 is easy to clean and keep clean. Resistant to virtually all oxidizing-acid conditions, chromium-Nickel stainless steel in this application resists corrosive attacks from acetic acid.

Leading steel companies produce stainless steel containing Nickel in tubular, sheet and strip form. A list of the sources of supply will be furnished on request.



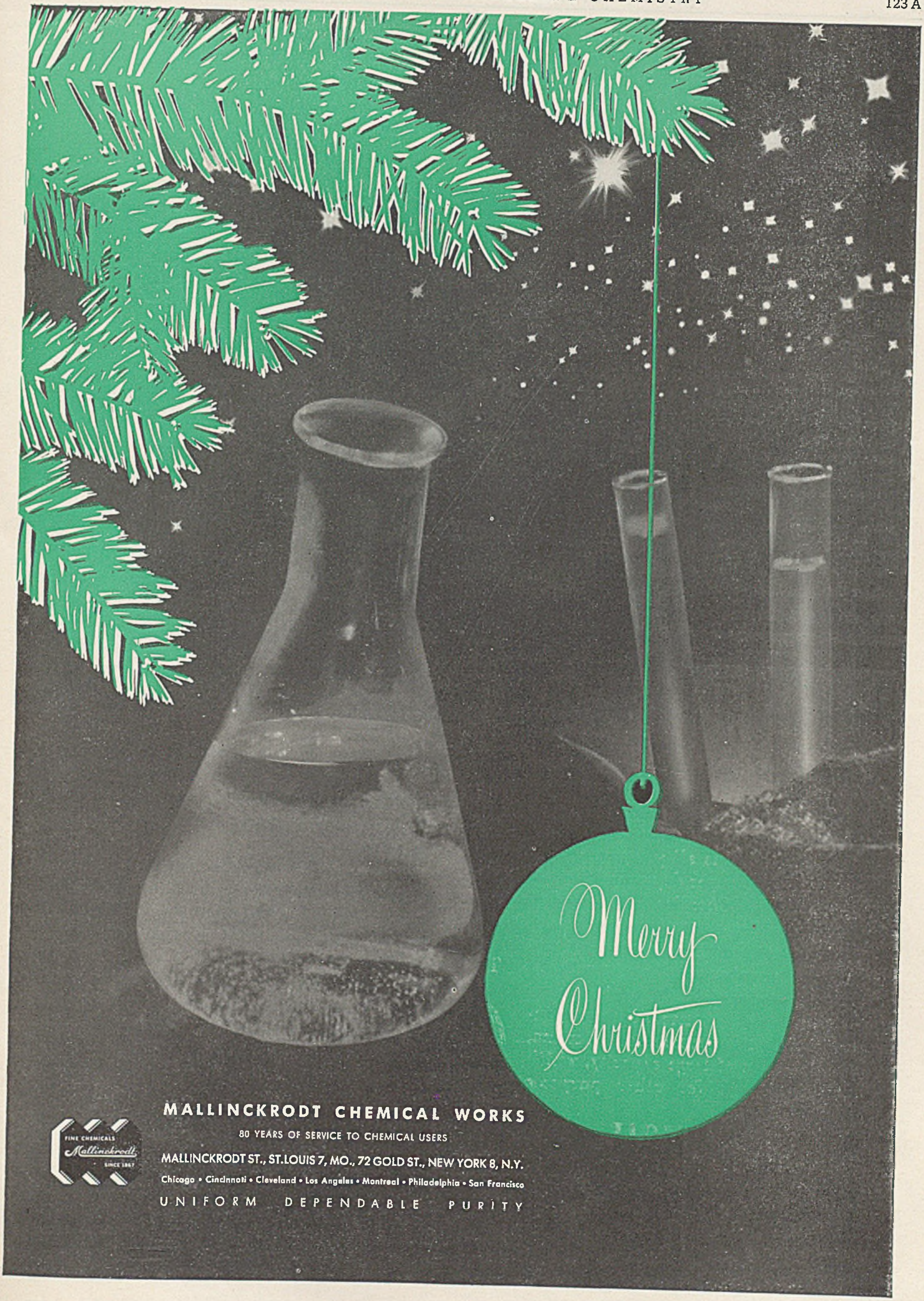
NO CRACKS OR ROUGHNESS *remain to gather ferments or bacteria in the stainless steel interiors of Dixie Manufacturing Company starch cookers and coolers. Dixie grinds the entire inside surface, including welded areas, to a smooth finish.*

EMBLEM OF INCO SERVICE
TRADE MARK

Over the years, International Nickel has accumulated a fund of useful information on the selection, fabrication, treatment and performance of engineering alloy steels, stainless steels, cast irons, copper-base and other alloys containing Nickel. This information is yours for the asking. Write for "List A" of available publications.

THE INTERNATIONAL NICKEL COMPANY, INC.

67 WALL STREET
NEW YORK 5, N. Y



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80 YEARS OF SERVICE TO CHEMICAL USERS
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UNIFORM DEPENDABLE PURITY

FINE CHEMICALS
Mallinckrodt
SINCE 1867

Chemico plants are efficient HERE'S PROOF

Here's evidence for you . . . black-and-white facts that prove the efficiency of Chemico-built heavy-chemical plants.

Take economy of manpower, for example. A 2-man crew is all you need to operate a 10 or a 300-ton per day capacity contact acid plant *built by Chemico.* This is made possible by centralized control, modern processes and equipment, and simplified plant layout.

Power requirements are negligible. The steam produced by the heat of burning sulfur drives most of the machinery with a substantial excess of steam, from plants of large capacity, which can be used for other purposes and credited against operating costs.

The improved vanadium catalyst assures high conversion efficiency and high over-all yield. Such items are guaranteed by Chemico.

Cost-saving efficiency is an integral part of *all* Chemico-built plants . . . in hundreds of heavy chemical installations which Chemico has designed and built in the last three decades.

For your acid plant needs, you can commission Chemico with confidence. Preliminary discussion of your problems and needs involves no obligation.

CHEMICO CHEMICAL CONSTRUCTION CORP.

CHEMICAL CONSTRUCTION CORPORATION

EMPIRE STATE BLDG., 350 FIFTH AVE., NEW YORK 1, N. Y.
European Technical Representative: Cyanamid Products, Ltd.,
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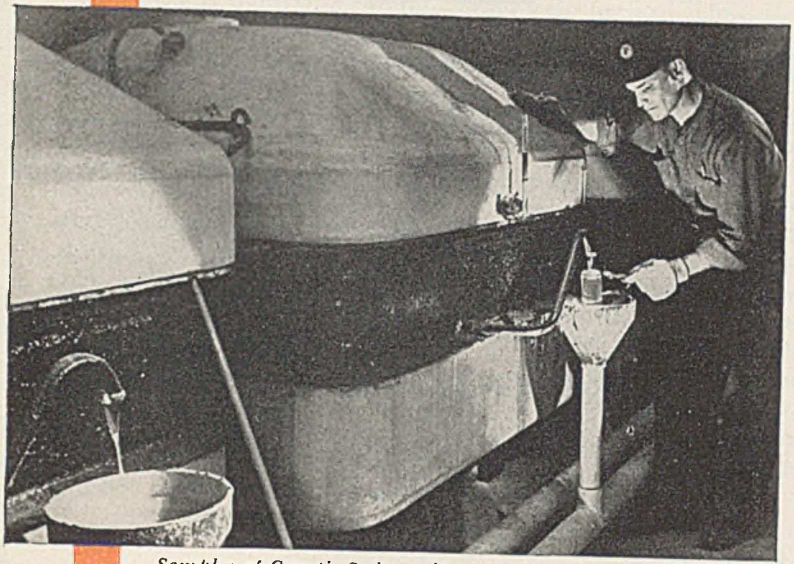
"Chemico plants are profitable investments"

CC-142

Three Hooker Chemicals That Help Make Thousands



Samples of Caustic Soda, as it comes from the Hooker "S" Cell, are checked carefully in the laboratory for strength and purity.

- ✓ LIQUID CHLORINE
- ✓ CAUSTIC SODA
- ✓ MURIATIC ACID

Hooker chemicals numbering over a hundred, and thousands of other products get their start from Caustic Soda, Liquid Chlorine and Muriatic Acid made by Hooker. Your supplies of these basic heavy chemicals are made possible to a large extent by the Hooker Type "S" electrolytic cell, designed and developed by our own engineers.

Caustic Soda, Liquid Chlorine and Muriatic Acid are produced and shipped from our plants at Niagara Falls, New York, and Tacoma, Washington. Helpful technical service and prompt shipping are corollary to the uniform high quality of these Hooker products.

Data sheets and other literature describing Hooker Chemicals are available upon request. If you don't have our latest General Products List, Bulletin 100, why not write today for your copy?

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Aluminum Chloride Paradichlorbenzene Monochlorbenzene Sodium Benzoate Sulfur Chlorides Sodium Sulfide Sodium Sulfhydrate

ROBINSON

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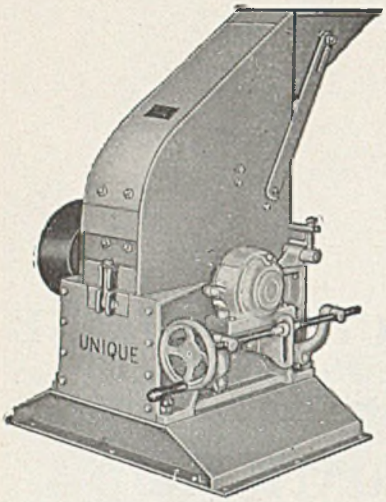
PROCESSING EQUIPMENT

HAMMER MILLS



Continuous full capacity production. Hard iron, interchangeable grinding plates. Self-aligning bearings. Automatic electro-magnet separator prevents tramp metals from entering grinds. Sturdy construction. Designed by experienced engineers whose reputation is founded upon doing things right. Literature available. Inquiries invited.

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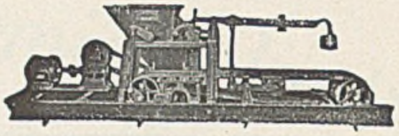

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THE AUTOMATIC FEEDER-WEIGHER-CONVEYOR

For Speed & Accuracy in Weighing—Blending—Feeding

Today's standard equipment for speeding up weighing and proportioning of crushed, granular or pulverized materials.

Poidometers are built for precision and durability. They insure years of continuous service and contribute to economy of production. Available with remote control recording and operating devices. Repair parts supplied for machines now in service.

Install Schaffer Poidometers and Watch Results
Write for catalog No. 3

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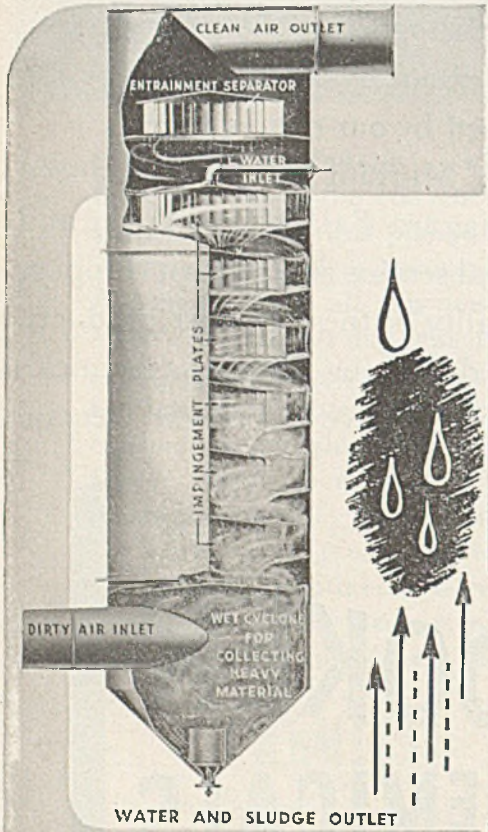
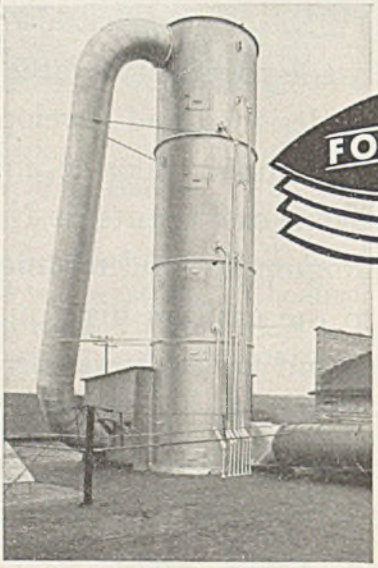


CONTAMINATION CYCLONE — Here's the Schneible Multi-Wash Collector Action that assures positive removal of dust, fumes, and odors.



A SCHNEIBLE SYSTEM VERSUS UNUSUAL AIR CONTAMINANTS

In marches Schneible to whip this plant's problem of multiple air contaminants (hydrogen sulphide, ammonia and other traces) with a multiple-liquid, Multi-Wash Collector. Four separate solutions, piped into the Collector at different levels, meet the churning uprush of fouled plant air with a chemically active liquid curtain and spray that envelops and floods contaminants out for settling and disposal.

Your problem — be it fine dust, condensible vapors, or multiple contamination—will fall as readily before a Schneible engineered system. Schneible Collectors, adaptable to every condition, feature no moving parts and exhaust fan on the clean air side. Schneible ducts, hoods, pumps, tanks, etc., complete a system tailor-made to keep your plant air fresh, clean, and safe.

Write for bulletins . . . better yet, visit Booths 421-422 at the Chemical Industries Exposition.

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for
DUST COLLECTION ABSORPTION
CONDENSATION AND TEMPERATURE REDUCTION

SCHNEIBLE

WHEN LARD COMES OVER THE MOUNTAINS

Here's the inside story—Some of America's most particular people protect every load of lard that travels in a GATX tank car.

Shippers—smart and careful—order a car for lard. They say, "Clean it thoroughly. Rub the walls down with lard before loading to avoid contamination from rust."

Eagle Eyes—*the U.S. inspectors*—look over every inch of the car. Then they write, "O.K. for loading" on the release.

. . . So, thousands and thousands of GATX cars are serviced each year for safe bulk transportation of a perishable food.

. . . This is typical of the work done for the railroads and shippers who use the GATX fleet of more than 37,000 specialized tank cars of 207 types.

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GATX
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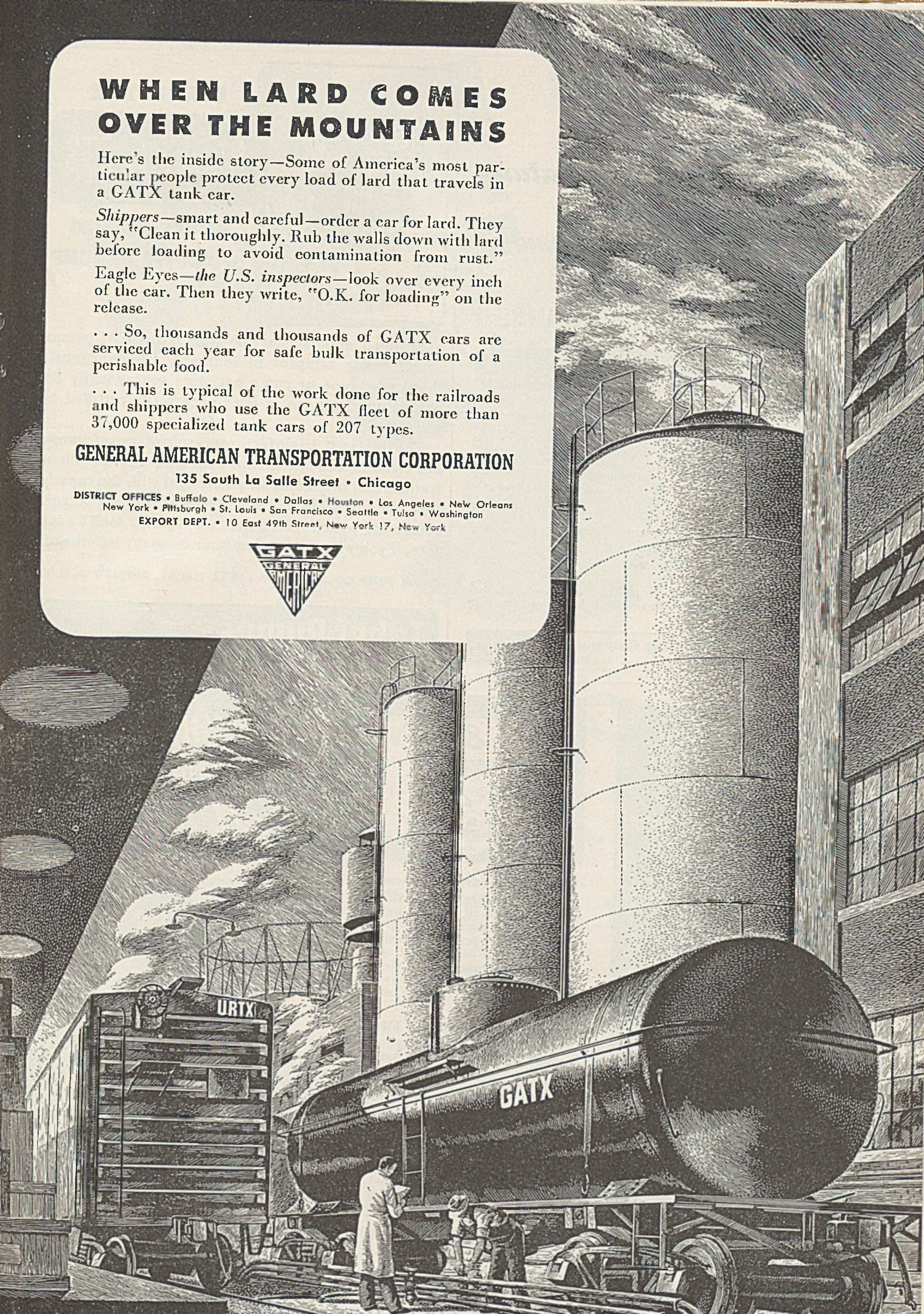
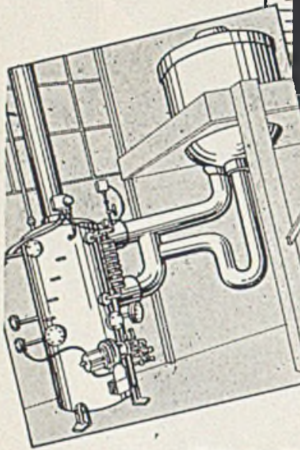


For Heat Transfer Applications Requiring UP TO 700° HIGH temperatures at LOW pressures McKee Eclipse with DOWTHERM VAPORIZERS

With Economical Gravity Return of Condensate



In addition to all the economy and safety advantages of high temperature heat application at low pressures, the suggested "set-up" provides economical Gravity Return. Condensate flows back to vaporizer by gravity, eliminating need for costly pumps and traps.

Write for FREE bulletin and case histories of interesting Dowtherm applications.

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Eclipse Fuel Engineering Company McKee Eclipse
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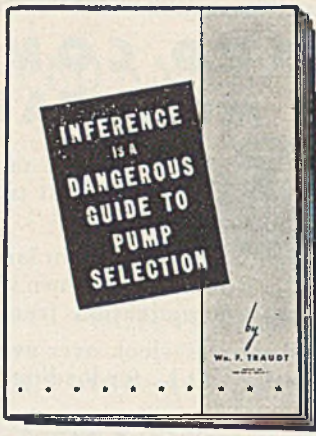


INFERENCE IS A DANGEROUS GUIDE TO PUMP SELECTION
by Wm. F. TRAUDT

5429A

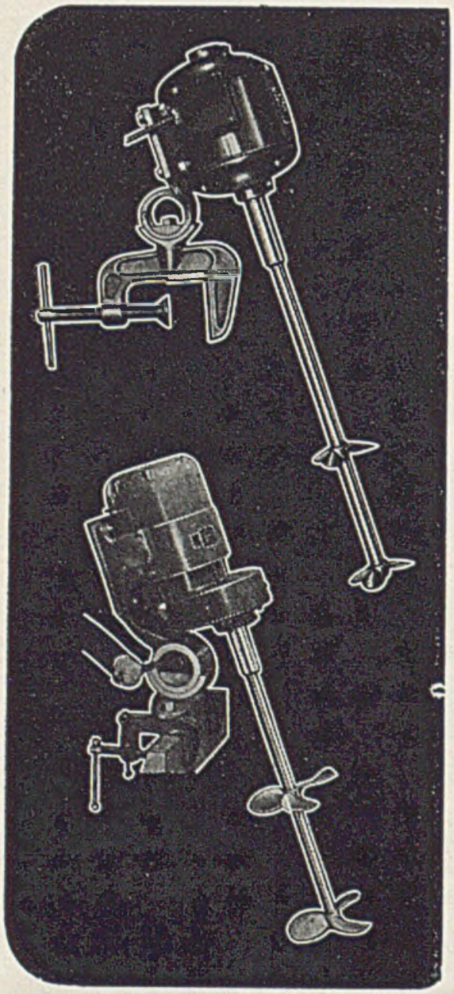
LEARN THE BASIC FACTS BEFORE DECIDING UPON TYPE OF PUMP

Fault-filled enthusiasms for certain types of pumps now running rampant in industry, are dangerous. Because a *type* of pump performs sensationally on somebody else's job, it isn't necessarily certified to your use.

The unbiased, basic facts concerning types of pumps are contained in our special bulletin S-146. Big illustrations and briefed descriptions deal with the capacities and adaptability of such types as piston, plunger, rotary and centrifugal pumps. We'll gladly send a copy free, if you will request it on your company letterhead.

TABER PUMP CO. • *Est. 1859* • 293 ELM ST., BUFFALO 3, N. Y.

Taber Pumps for Higher Practical Performance



Save TIME and LABOR

ALSOP "Hy-Speed" MIXERS AND FILTERS *for all liquids*

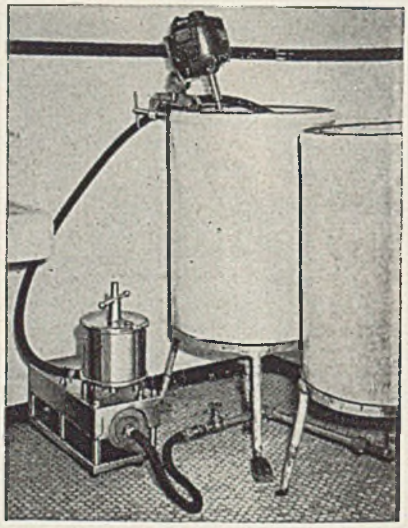
"Hy-Speed" Portable Mixers

Designed to meet your mixing and blending requirements on all liquids—based on 25 years' mixing experience, the Alsop "Hy-Speed" Portable Mixer provides dependable, accurate and economical service that needs no supervision. Simply mount it to your present tank, its special clamp provides easy adjustment for any mixing action and makes every tank a mixing tank.

Compact "Sealed-Disc" Filters

Provide positive filtration at all times with low operating, cleaning and maintenance cost. These unique filters are air-tight and leak-proof, recommended for intermittent or continuous operation on chemicals, liquid plastics, plating solutions, alcohol, acids, drugs, syrups, water, etc. Available in Stainless Steel, Monel, Nickel Plated Brass and Bronze, in sizes from 1 g.p.m. to thousands of g.p.h.

Write for catalog #745 showing our complete line of Top Entering Type Mixers and Fixed Side-Entering Agitators. The Alsop Engineering Corporation, 212 Black Road, Milldale, Connecticut.



ALSOP ENGINEERING CORPORATION
Filters, Filter Discs, Pumps, Tanks, Mixers, Agitators

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TRY WAA FIRST!

ELECTRIC GENERATOR SETS (Gasoline-Engine Driven)

INDUSTRIAL FURNACES & OVENS

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MOTOR STARTING & CONTROL EQUIPMENT

INDUSTRIAL TRUCKS (Hand and Powered)

CONVEYORS (All Types)

INDUSTRIAL FANS

WELDING EQUIPMENT (Arc, Resistance & Gas)

Millions of dollars' worth of industrial equipment and supplies still remain in War Assets inventories of surplus war material. Some of the equipment is unused; some of it is used. All for sale at extremely attractive prices.

Are you considering the purchase of additional equipment for your plant? Before you place an order, check with the nearest WAA Customer Service Center—it will have listings of current offerings of all items featured in this advertisement. Among these you are likely to find exactly the item you want, at a price that will save you a substantial amount of money.

All items are subject to prior sale

Our inventory includes: Industrial Furnaces & Ovens • Welding Equipment (Arc, Resistance & Gas) • Conveyors (All types) • Industrial Trucks (Hand & Power) • Hoists (Chain & Electric) • Electric Generator Sets (Gasoline-Engine Driven) • Motor Starting & Control Equipment • Industrial Fans

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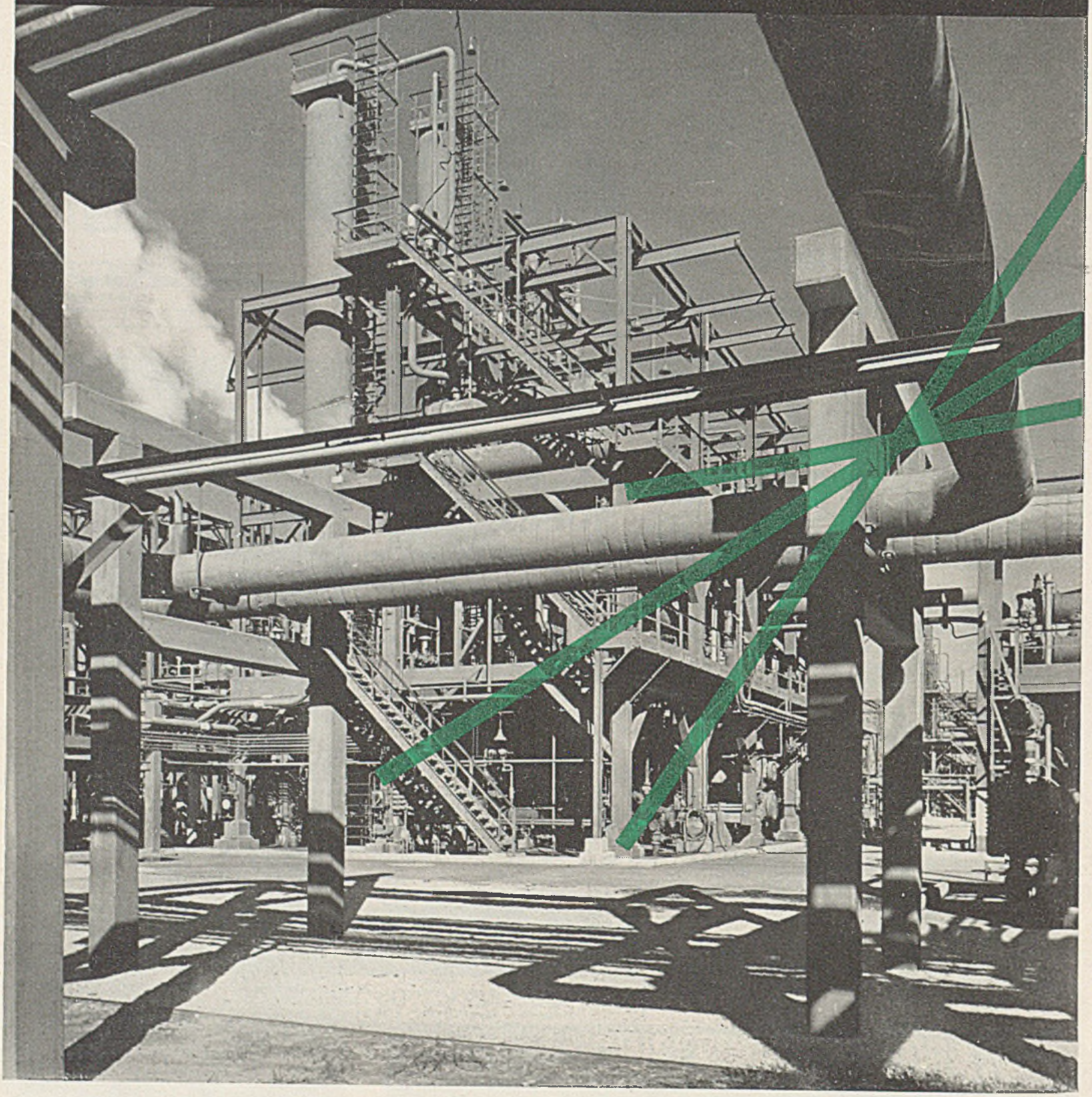
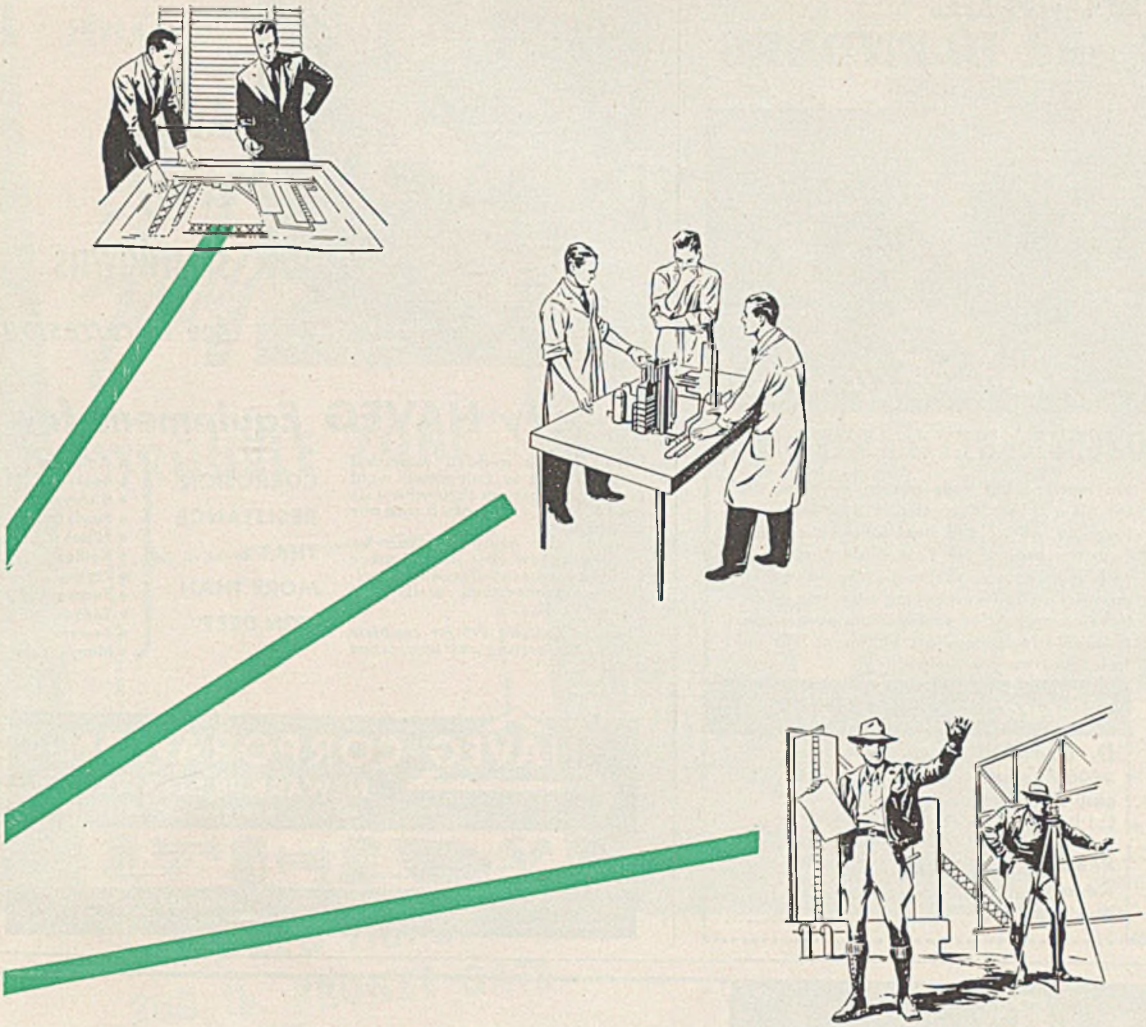
Badger brings you MANY SKILLS IN ONE COMPLETE SERVICE





To conceive, plan, schedule and execute, in time-saving sequence, the myriad details involved in the engineering and construction of a processing plant calls for many skills.

They must be specialized skills. Diversified skills—more than many refining or chemical manufacturing concerns can economically carry on their own payrolls for use in infrequently recurring construction or reconstruction projects.

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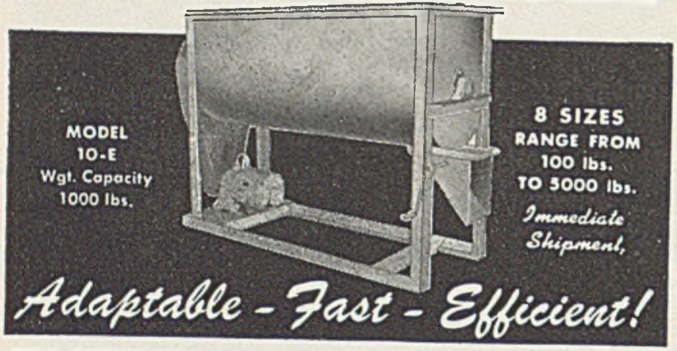

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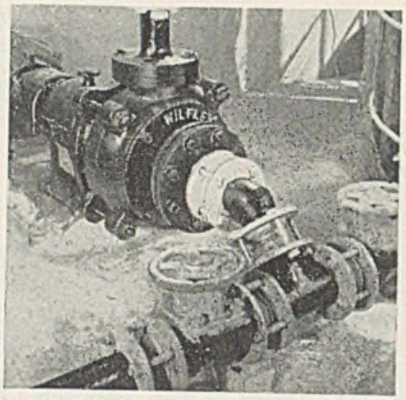

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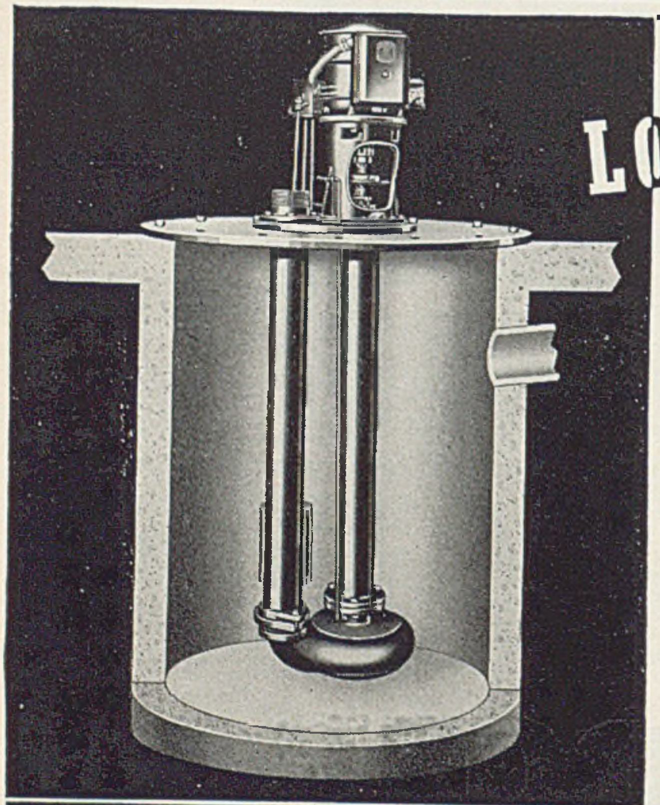

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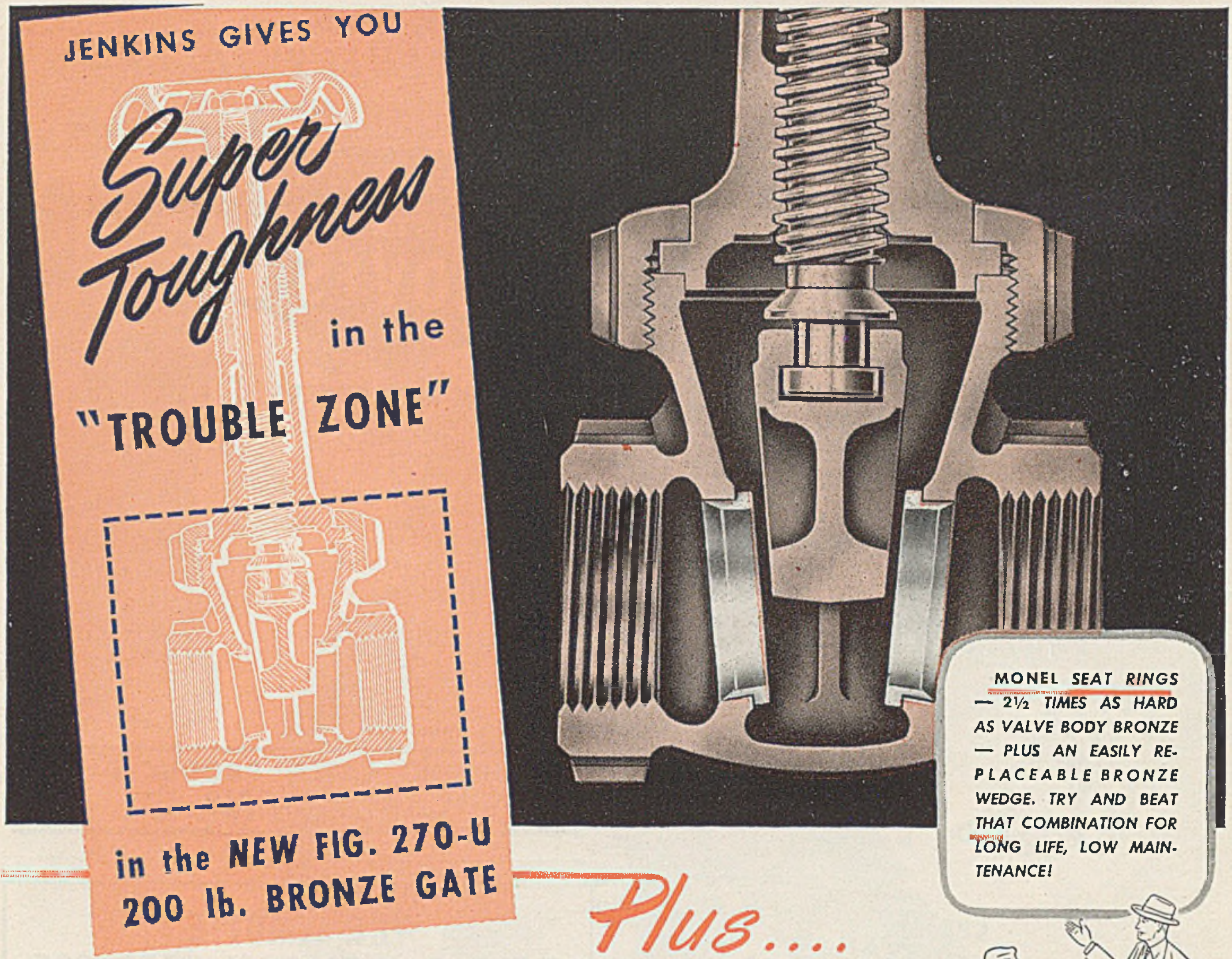

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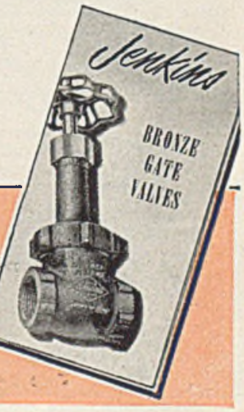

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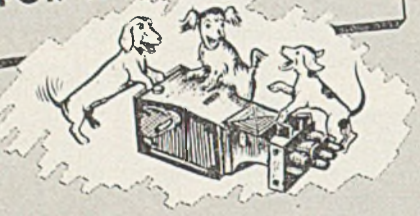

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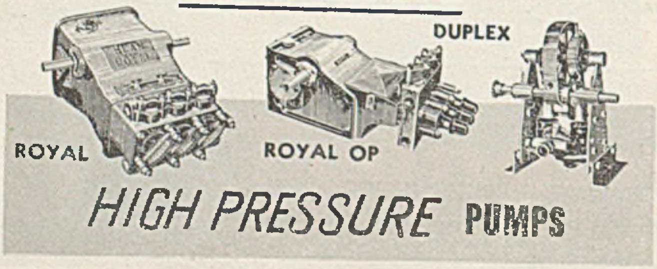

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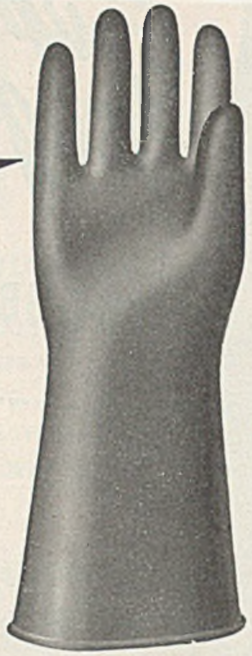

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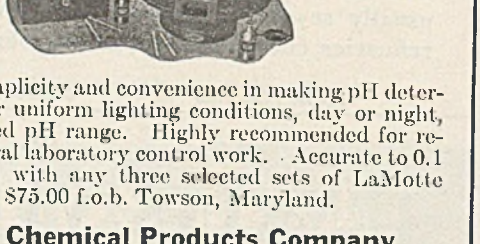

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Parts not visible in front view of ozonator shown at right are a pop safety valve to prevent excessive pressures in ozonator shell, a pressure safety switch to open circuit when gas is not under pressure inside the ozonator shell, and a water cooling jacket.

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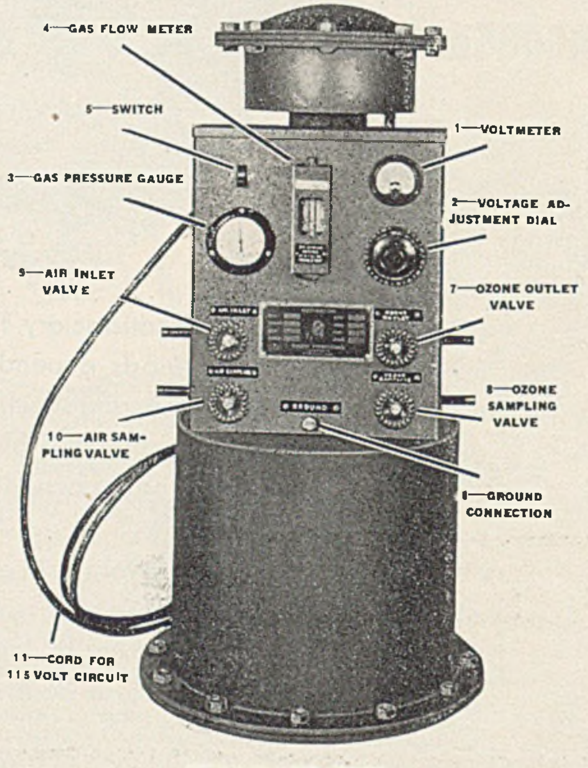
AIR	OXYGEN				
0.1	0.2	0.1	0.2	2	140



STANDARD TYPE
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Amperes: 118
Watts: 100
60 CYCLE

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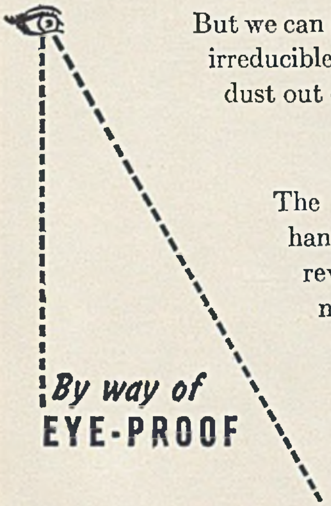

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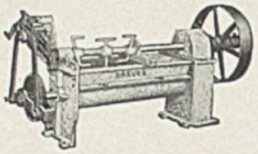

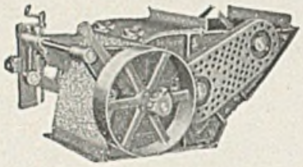

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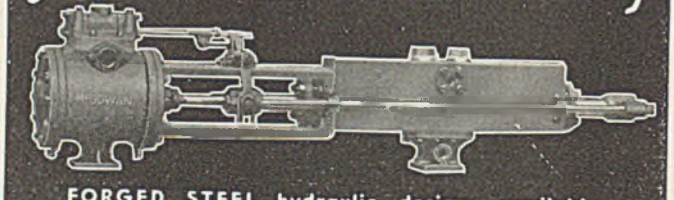

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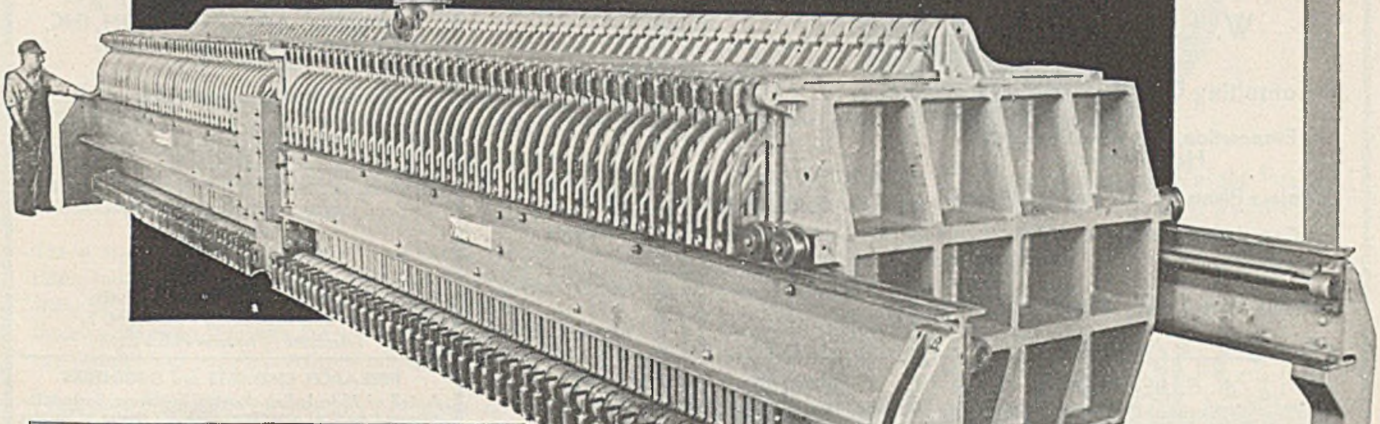
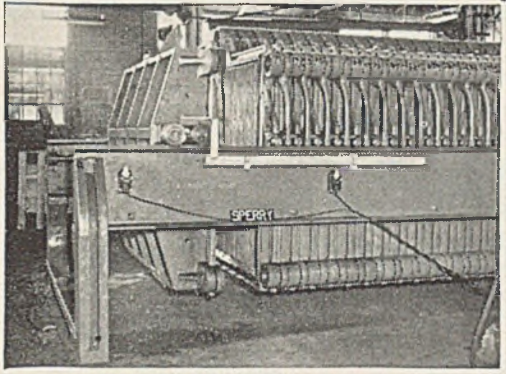
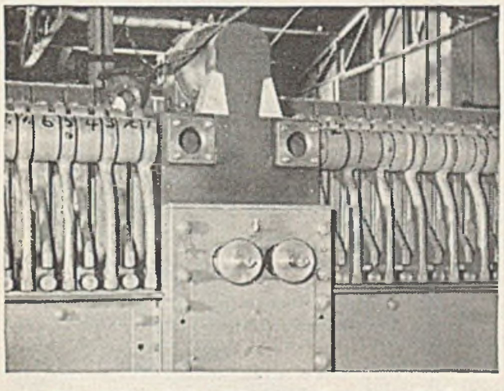




Detail view of the electrical opening and closing limiting mechanism showing head in open position.



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Equipment and Materials MARKETPLACE

Beginning with the January issue of INDUSTRIAL AND ENGINEERING CHEMISTRY a new Directory will appear in this section called . . .

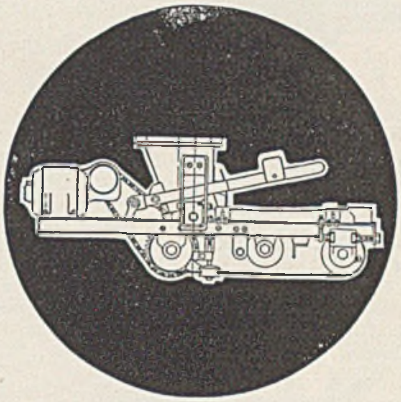
EQUIPMENT AND MATERIALS *Marketplace*

Here you can buy and sell—through low-cost advertising—all manner and form of industrial equipment and materials. Here you can tell your product story to the 35,000 men who subscribe to each issue of INDUSTRIAL AND ENGINEERING CHEMISTRY.

These men read I&EC because its editorial content covers their industrial needs completely and thoroughly. And, with *Equipment and Materials Marketplace* available, their purchasing interests are even more finely screened in the direction of your advertising interests.

Contact a Reinhold representative or write us at 332 West 42nd St., New York 18, N. Y., and start making sales with the next issue of INDUSTRIAL AND ENGINEERING CHEMISTRY.

Feed by WEIGHT . . . not by volume!



The revolutionary Hardinge Constant-Weight Feeder regulates feeding of materials at a constant weight-rate—automatically compensating for variations in *specific gravity* and *moisture content.*

Bulletin 33-D

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This instrument retains all of the advantages of the well established Hercules method without any of its disadvantages. Range extended to cover from 75 to 1,000,000 centipoises Constant temperature jacket built-in. Automatic timer can be furnished upon request. Write for bulletin No. 451.

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the New Improved
PLY NO 3
$10.00 per doz., 12 oz. jar, net weight

We are glad to announce to our many friends this new improved water repellent cream. PLY NO 3 will now meet workers' requirements for protection against water or water soluble oils or other solutions which do not exceed Ph 6 acid or Ph 8 alkali. Where the acid or alkali content exceeds these specifications, other types are available.

There are thirteen other PLY formulae which provide specific protection against more than 2000 industrial dermatitis hazards. Write us describing your requirements. A FREE sample for testing will be furnished.

FREE

Ask for a copy of "The Answer To Industrial Dermatitis," the only reference book of its kind. Everyone interested in combating dermatitis should have a copy.

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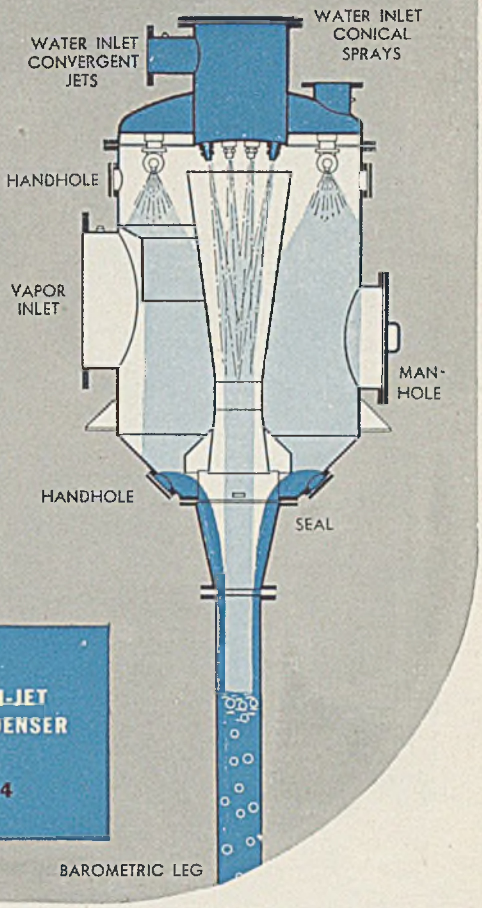
(All page numbers listed below are complemented with the letter "A" on the respective pages.)

ACME BAROMETRIC CONDENSERS *Engineered* FOR SPECIFIC PURPOSES

Barometric condensers provide an economical means of condensation for most high vacuum processes. Operating by means of gravity, a barometric condenser requires no costly pump for the elimination of the condensate, merely sufficient headroom for a 34-foot tailpipe. Barometric condensers are especially adaptable where there is no need to recover the condensate—where there is a high percentage of incondensible gases—where there are unusual fluctuations in the load—where the water supply is dirty or vapors contain solids. Two that have proven most successful in actual operation are the Acme Counter-Current and the Acme Patented Multi-Jet, described below.

THE ACME PATENTED MULTI-JET BAROMETRIC CONDENSER

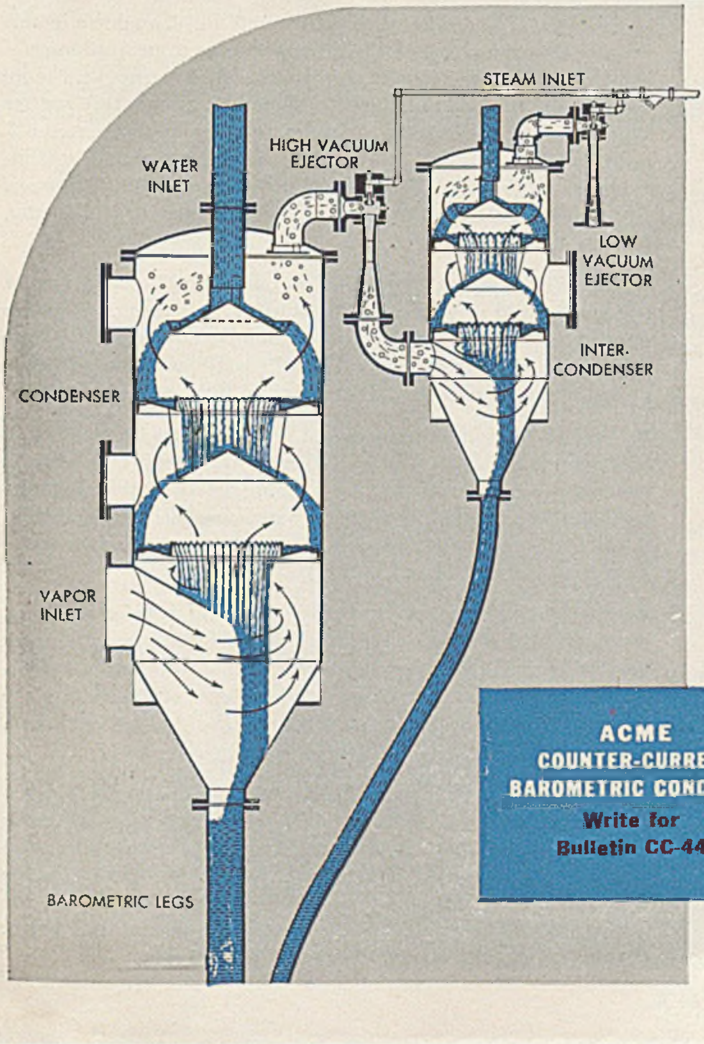
. . . The most economical condenser where vacua not exceeding 27″ Hg. are to be attained. Vapors entering the condenser rise through a cold spray from a series of converging jets, adjustable for maximum condensation. This countercurrent movement assures more complete condensation. The jets, in turn, wash the incondensible gases, along with the condensate, down through the tailpipe, without the use of an ejector or intercondenser. This process is made possible only through a patented arrangement with sealed baffles that permit the use of jets, while preventing the escape of vapors, thus forced to the top of the condenser.



ACME
PATENTED MULTI-JET
BAROMETRIC CONDENSER
Write for
Bulletin MJ-44

THE ACME COUNTER-CURRENT BAROMETRIC CONDENSER

Where vacua exceeding 27″ Hg. are to be attained, we recommend use of the Acme Counter-Current Condenser. Besides the advantages previously noted, this unit is less expensive to construct and more compact in design than other comparable equipment. It consumes less water and is scientifically proportioned for minimum pressure drop. Construction is simple and all parts are readily accessible. Available in many combinations with ejectors and intercondensers, Acme barometric condensers are specifically designed for any desired vacua and for most efficient operation in any particular process or under any set of operating conditions.



ACME
COUNTER-CURRENT
BAROMETRIC CONDENSER
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Bulletin CC-44

ACME
Processing Equipment

ACME COPPERSMITHING & MACHINE CO., ORELAND, PA.

PQ SILICATE REACTED WITH ALUMINUM SULPHATE

PQ Silicate is the paper-maker's friend (yours too as a consumer of paper). The precipitate it forms with aluminum sulphate catches in the fibres; keeps the short ones from escaping. This silicate size also increases retention of the clay and other fillers in the sheet — hence, improved quality and increased output, as much as 30 lbs. per ton.

Can you use this principle in one of your processes to improve results or cut costs? Other reactions of PQ Silicates with hydrochloric acid, chlorine, hydrogen peroxide, calcium chloride, etc. may solve the problem for you. Get more data from PQ Silicate headquarters.

Philadelphia Quartz Co.
Dept. C, 119 South Third Street
Philadelphia 6, Penna.

Sidelights and TRENDS

December 1947. The United States oil industry is setting a record this year in drilling footage. The previous high, 100,000,000 feet of hole in 1941, will be exceeded in 1947 with an estimated monthly average of 11,500,000 feet of hole per month, or 138,000,000 feet for the entire year. The Texas–New Mexico area accounts for almost half of the country's drilling footage. (*Oil and Gas Journal*, p. 124, Oct. 11, 1947)

■ A smooth, flexible paper with high tensile strength and tear and puncture resistance has been produced by reinforcing waterproof paper with Fiberglas. The glass yarns, laid parallel to one another between two sheets of kraft paper, do not absorb moisture and therefore cut down vapor transmission from one paper layer to the next. The small diameter of the glass yarns permits use of a minimum amount of asphalt to secure a firm bond, and the end product has a high vapor-barrier value. (*Modern Packaging*, p. 158, Aug. 1947)

■ An accurate and rapid method has been developed to determine the volume of water in paints and varnishes. The titrimetric method, which requires only small samples, allows determination to 0.1% of the amount of water in any varnish, and almost any paint, in only one hour. [Office of Technical Services, Department of Commerce, PB 52027 (1947)]

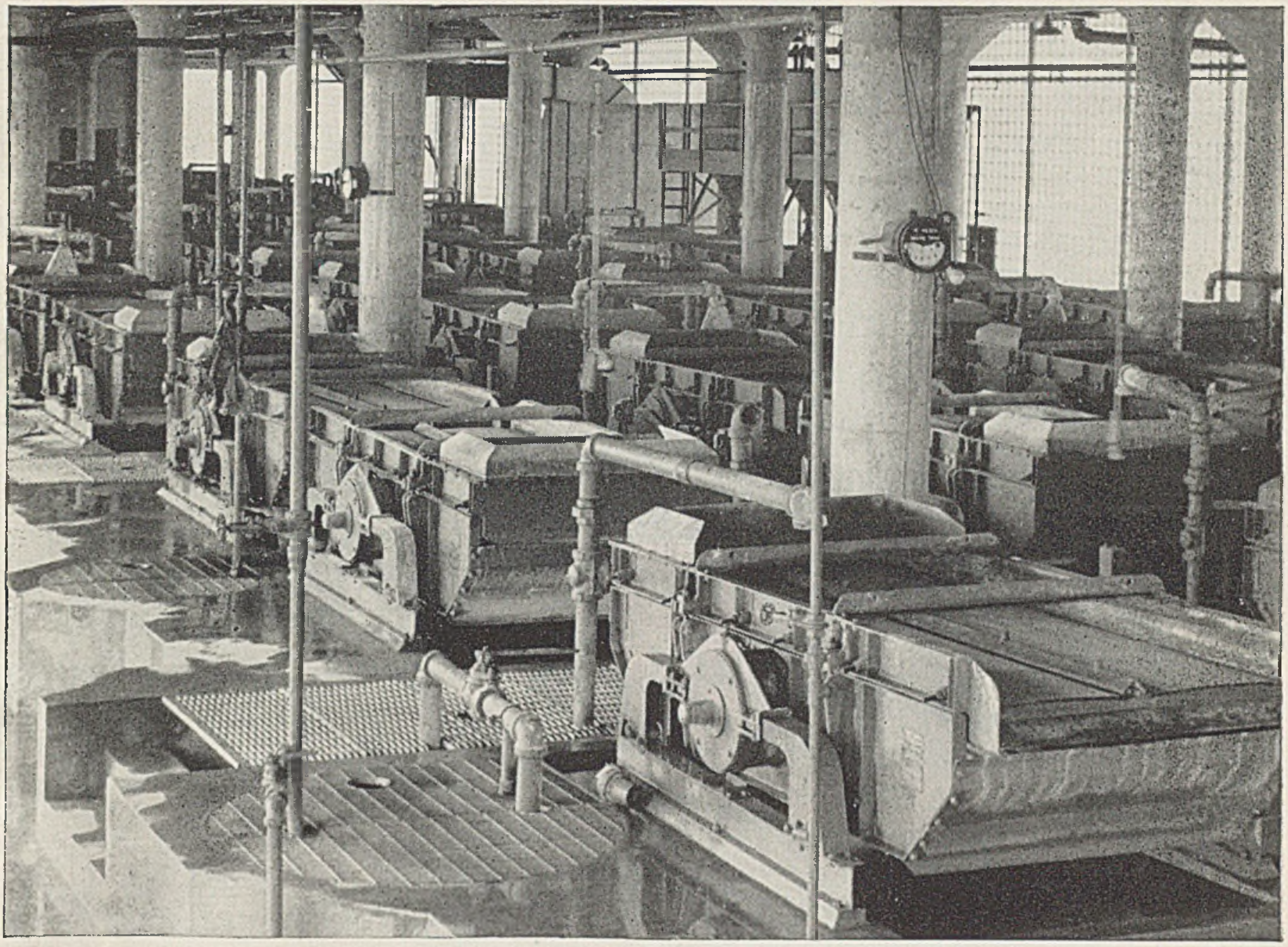
■ Manufacturers' sales of chemicals and allied products in this country dropped almost $400,000,000 in May from April sales of $850,390,000. The value of shipments was, however, still more than two and a half times greater than average monthly prewar shipments of $330,700,000. Manufacturers' inventories rose 6% in May to a total of $1,584,600,000; in August of this year inventories were up 41% compared to August 1946. (*Chemical Age*, p. 229, Aug. 16, 1947, and *Oil, Paint and Drug Reporter*, p. 35, Oct. 27, 1947)

■ The "light-piping" ability of a Lucite acrylic resin is now being employed in signboards for outdoor advertising. Signs are designed so that the sun's rays illuminate both sides for easy readability. At night two cold cathode tubes mounted inside provide even illumination. (Du Pont Co. Release, Nov. 14, 1947)

■ Preharvest drop of oranges and grapefruit has been cut 50 to 70%, apparently with no injury to the fruit or leaves, by use of a water-spray solution containing 8 p.p.m. 2,4-D. Fruit stem dieback has been reduced 60 to 80% by spraying with the same solution. Cost of the chemical is 19 cents per acre. (University of California Release, Nov. 13, 1947)

■ Extruded cellulose acetate butyrate tubing is being used as a conductor of fuel gas to replace steel in some states. Advantages are its availability, reasonable installation costs, light weight, ease of handling and bending on the job, ease of joining, and resistance to deterioration in most soils. (*Pacific Plastics*, Vol. 5, No. 6, June 1947)

■ An optical thickness micrometer has been developed to measure any transparent sheet material where physical access to one side only is available. It is a hand-held, self-contained battery-powered unit designed for use in any location. Based on the depth-of-focus principle as applied to a microscope system, the instrument accuracy is 0.0005 inch on thicknesses up to 0.275 inch. (*Review of Scientific Instruments*, p. 803, Oct. 1947)



Taking the starch out of shutdowns!

That's exactly what was done by these Robins Hydrex Screens. In fact, they reduced shutdown time 98%!

The problem arose in a plant that extracted starch from sweet potato pulp. The glutinous nature of the pulp clogged the mesh of several types of screening mechanisms tested in pilot plant operations. Shutdowns were numerous. Live steam had to be used to free the coagulated starch particles. Up to an hour was lost during each shutdown!

Then Robins engineers designed these special Hydrex Screens with removable deck frames. The operator merely releases four toggle bolts, lifts off the entire deck, and slips another in its place . . . *in less than a minute!*

Sixty of these Hydrex Screens operate in closed circuit with eight interlocked screening stages. They are able to remove the last ounce of starch from 600 tons of sweet potatoes a day!

Not only that, but the decks of these Hydrex Screens are *interchangeable.* Thus any size of opening—from 20 to 200 mesh—can be used in any part of the screening room at any desired time.

This is but one of many examples of how Robins Hydrex Screens save time and money. Whether it's potato starch, powdered coffee, reclaimed rubber, starch milk, fish oil, vegetable oil, clay slip, shellac or other material, you will find Hydrex Screens stepping up production.

Robins Hydrex Screens process pulps, slurry and sludges . . . can be used for hot or cold materials, for acid or alkaline.

No matter what your sizing or separation problem, why not let a Robins engineer help you choose the Hydrex Screen that meets your needs? Drop us a line today.

HEWITT-ROBINS INCORPORATED HR

ROBINS
HYDREX SCREEN

ROBINS CONVEYORS DIVISION
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Here at Buflovak you will find modern equipment to study and test your new process, at savings to you!

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Buflovak OFFERS ITS PRACTICAL RESEARCH AND TESTING LABORATORIES TO SOLVE YOUR PROCESSING PROBLEMS

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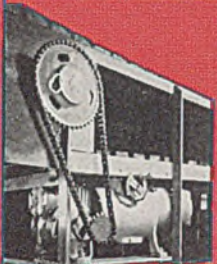
FOR WIDE
RANGE OF WORK

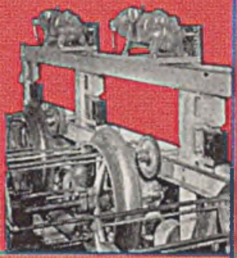
FOR CHANGES
IN VISCOSITY



REGULATES
CONVEYOR SPEEDS

FOR CHANGES
IN DIAMETER

FOR CHANGES
IN TEMPERATURE

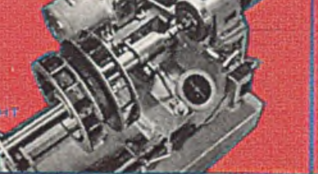


MAINTAINS
CONSTANT
TENSION

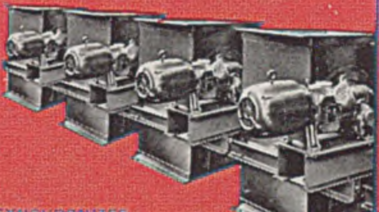
MAINTAINS
LINEAL
SPEEDS

FOR CORRECT POSITIONING

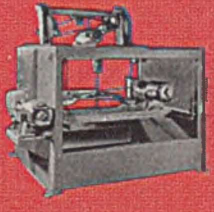
CHANGES
ERIPHERAL
SPEED



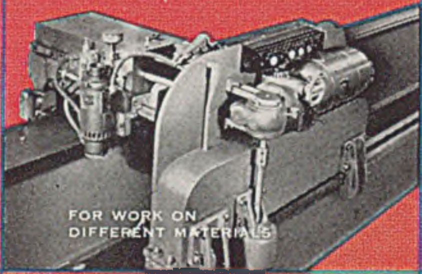
CHANGES
IN SIZE
AND WEIGHT



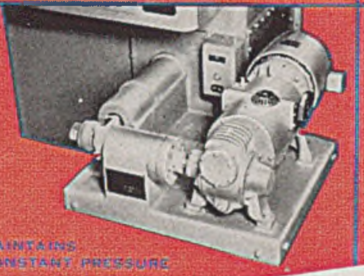
SYNCHRONIZES
MACHINES IN SERIES



TEXTILE MACHINERY



FOR WORK ON
DIFFERENT MATERIALS



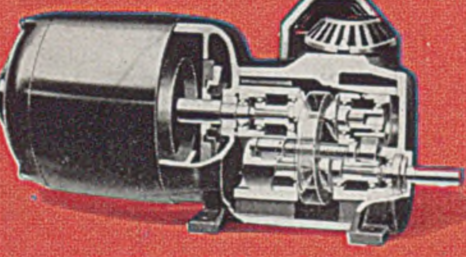
MAINTAINS
CONSTANT PRESSURE

These are only a few of the many types of applications where Master Speedrangers are providing the correct range of variable speed for every operation . . . for every operator . . . or for each change in the consistency or shape of the material being processed.

Such variable speed operation pays off in higher rates of production, a better quality product and more efficient performance of your equipment and your operators.

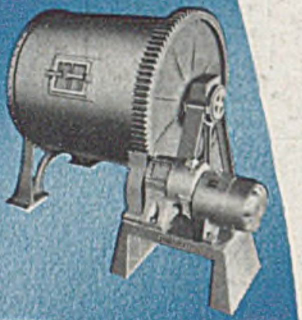
Write for Data 7525 . . . its 24 pages will show you how the compact, all metal construction of Master Speedrangers makes it easier for you to enjoy the many advantages of variable speed operation.

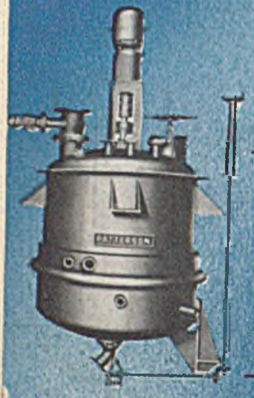
THE MASTER ELECTRIC COMPANY • DAYTON 1, OHIO



The power of precision-

... for INDUSTRIAL CHEMISTRY'S PROCESSES



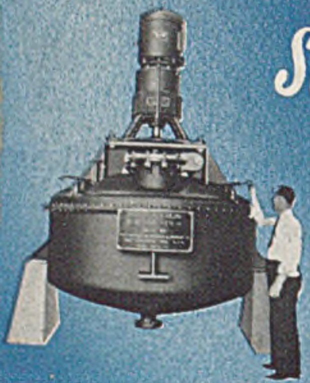


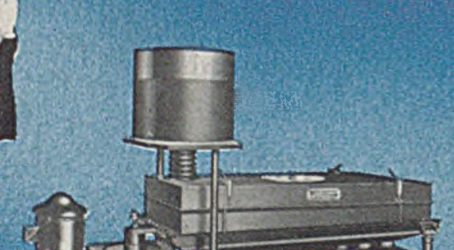
PATTERSON

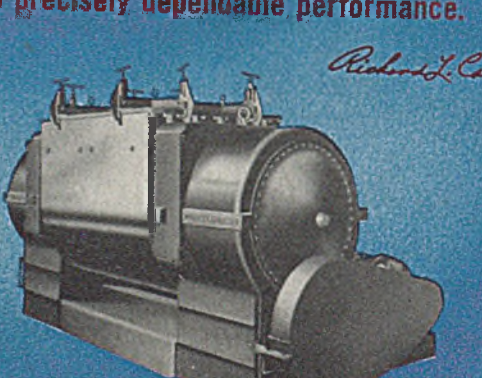
satisfactory MACHINERY

Patterson's precision in manufacture translates effective equipment design into precisely dependable performance.

Richard L.
President







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East Liverpool, Ohio, U. S. A.
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