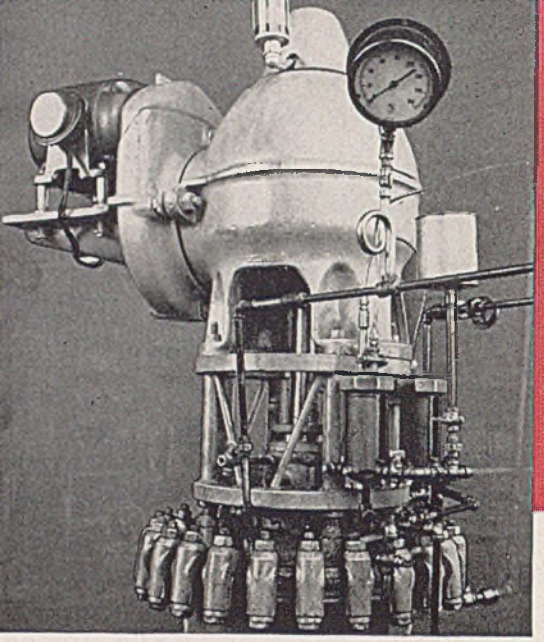
INDUSTRIAL AND ENGINEERING *Chemistry*

APRIL 1946



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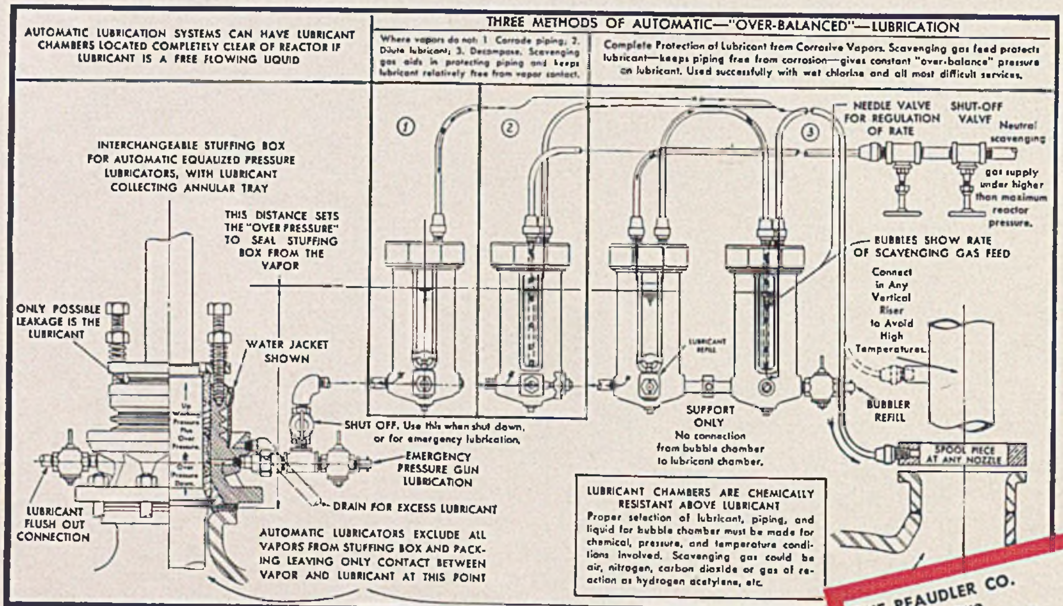

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ENGINEERS AND FABRICATORS OF CORROSION RESISTANT PROCESS EQUIPMENT

INDUSTRIAL AND ENGINEERING CHEMISTRY · INDUSTRIAL EDITION

VOLUME 38, NUMBER 4 ● ISSUED APRIL 16, 1946 ● CONSECUTIVE NUMBER 7

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37,600 copies of this issue printed

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We acknowledge with thanks the action of H. K. Porter Company, Inc., in releasing the front cover of this issue for editorial purposes.

The front cover shows a liquid-level controller used in a butadiene plant. It calls attention to our lead article this month on Averaging Liquid Level Control by J. G. Ziegler of the Taylor Instrument Companies.

Departments

*** Indicates page number in the advertising section.**

Technical Articles

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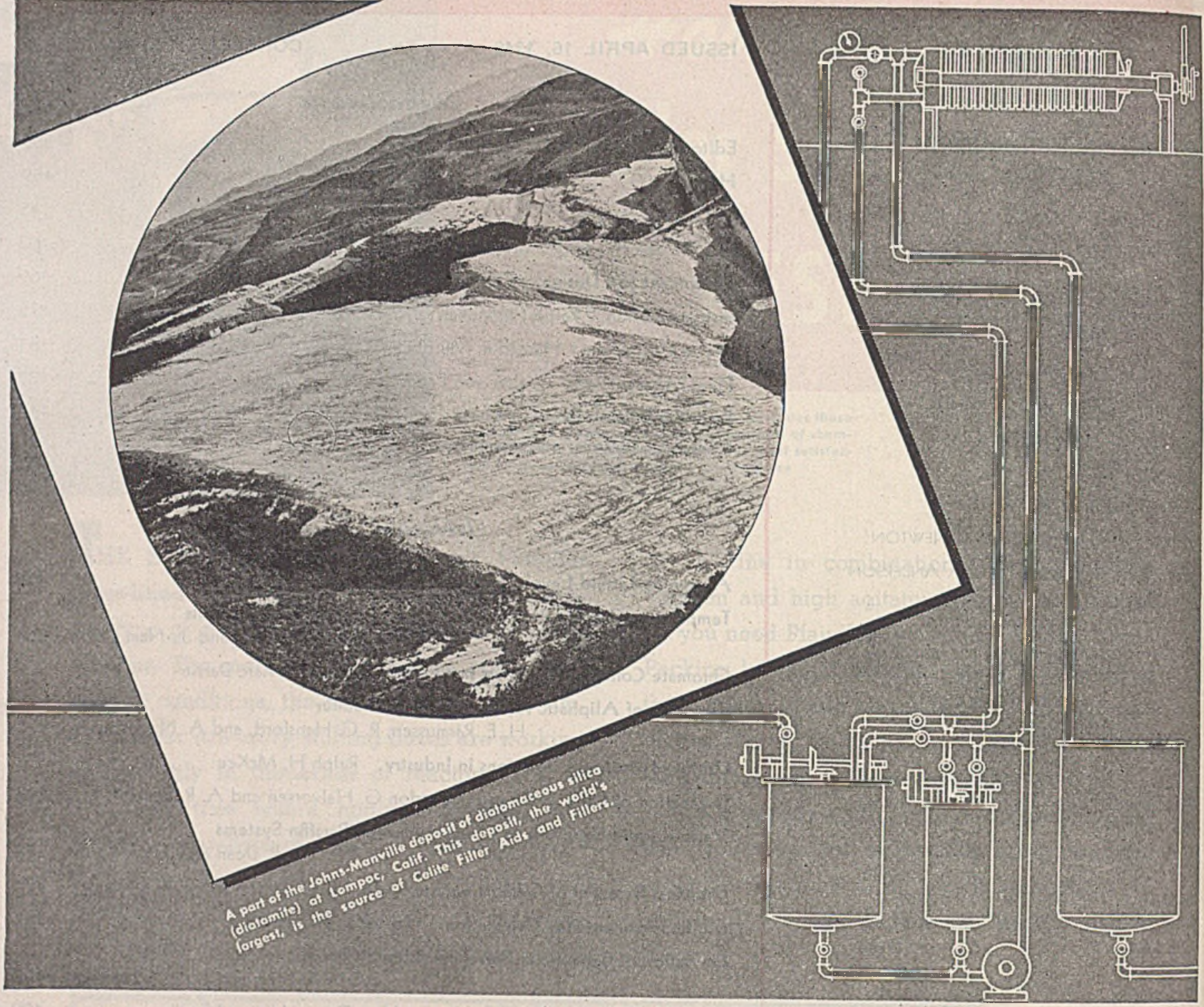


INDUSTRIAL AND ENGINEERING CHEMISTRY

REPORTS ON THE CHEMICAL WORLD TODAY

Resources

Marine Real Estate. The Geological Survey, Department of the Interior, has proposed that Congress soon appropriate the wherewithal for exploring what may be the last major mineral acquisition of the continental United States. When on September 28, 1945, President Truman asserted federal sovereignty over those portions of the continental shelf and overlying seas that border the United States and Alaska, he laid claim to about 900,000 square miles, comparable to the area we obtained in the Louisiana Purchase. Nearly two thirds of the shelf is in the shallow seas adjacent to Alaska. The remainder is divided as follows: Atlantic Coast, 155,000 square miles; Gulf of Mexico, 137,000 square miles; and Pacific Coast, 26,000 square miles. There is no question that this newest acquisition is of great economic value. In fact, rights to the shelf off the California coast already have become the prize in a heated dispute between federal and state governments and private oil interests.

A continental shelf surrounds every major land mass of the world. It is characterized by a terrain with a relatively gentle slope that extends to a depth of approximately 600 feet (100 fathoms). Beyond the edge of the shelf, the slope of the sea bottom becomes distinctly steeper. Continental shelves are not formed primarily by sedimentation, and geologists are pretty much at sea to explain their occurrence but think it may be a plastic slumping of the continental mass to equalize pressures.

From scanty evidence now at hand, mineral strata appear to extend beyond the shore line and into the continental shelf with a continuity similar to that found on land. Most of the limited explorations made thus far have been in the Gulf of Mexico by oil companies; and most of our knowledge of underwater deposits pertains to petroleum, sulfur, and salt. The Geological Survey is closemouthed about any other minerals believed to occur in the ocean bed, but is frank in stating that location of additional oil deposits is a major objective of the exploration. The saline content of ocean water itself also will be comprehensively measured, since it varies significantly from one location to another as a result of the seasons, evaporation, and discharge of fresh water streams. This information may reveal locations favorable for other chemical-from-sea water methods similar to Dow Chemical Company's present successful and familiar bromine and magnesium processes. The saline survey also is expected to be valuable in studies of marine life on the shelf.

Upon receiving Congressional approval, the Geological Survey expects to start its first work in the Gulf of Mexico. This area is particularly suitable because of its location, the substantial width of the shelf, and the information already available about it. The first year is expected to be fully occupied with perfecting survey instruments and methods. In the tentative program, actual collection of records for the next nine years is expected to yield a reasonably accurate over-all conception of the resources. The work planned includes study of samples already collected over a period of years by the Scripps Institute on the West Coast, by the Woods Hole, Mass., Oceanographic Institution, and by the United States Coast and Geodetic Survey. Both the Navy and the Geological Survey are anxious to have Navy craft used in the work. Thus, the expense of the survey, in one sense, is merely the salaries of the scientists involved and the costs of the special equipment.

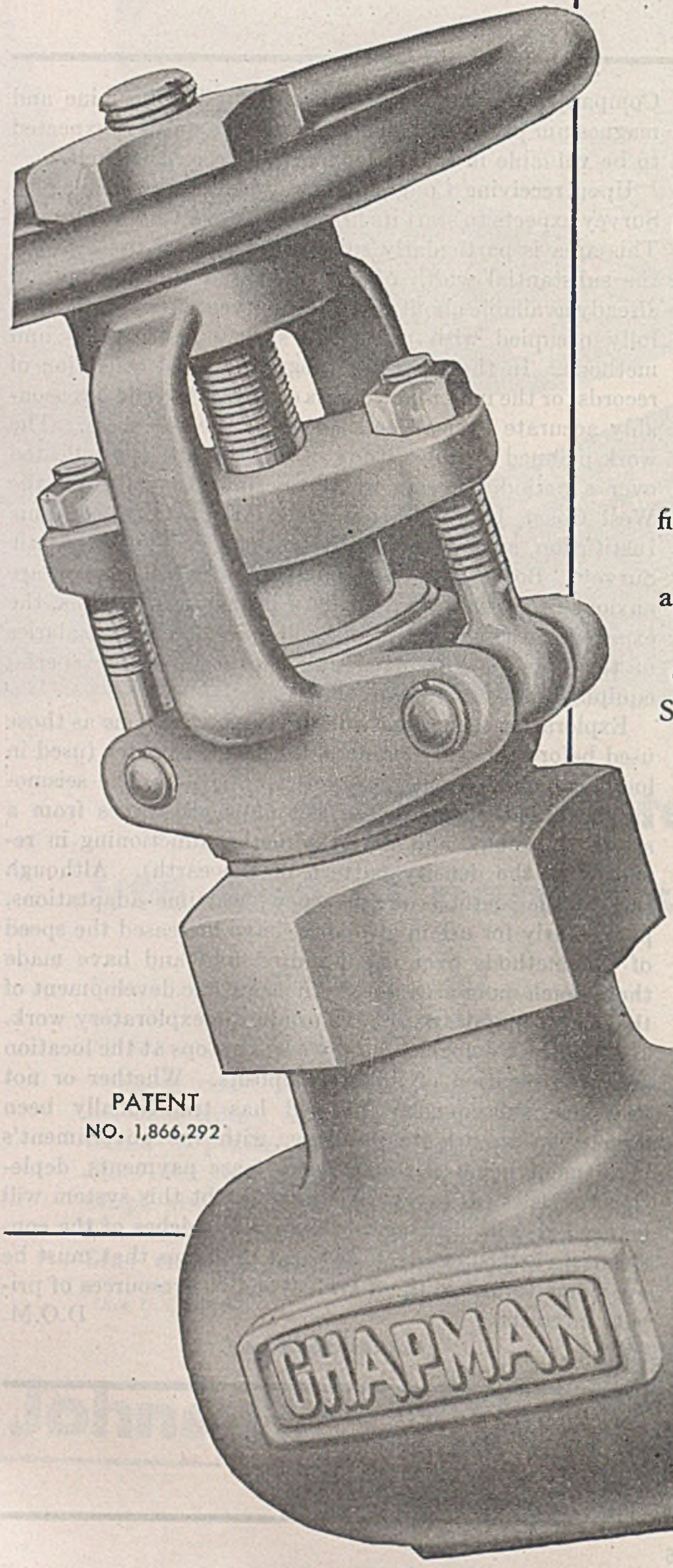
Exploration techniques will be largely the same as those used before the war—namely, the magnetometer (used in locating minerals with magnetic properties), the seismograph (based on characteristics of shock waves from a small explosion), and the gravimeter (functioning in response to the density pattern of the earth). Although these basic methods are not new, wartime adaptations, particularly for use in airplanes, have increased the speed of the methods over one hundred fold and have made them much more accurate. An electronic development of the war also appears to have use in the exploratory work.

All of the Geological Survey's work stops at the location and identification of mineral deposits. Whether or not they are subsequently utilized has traditionally been largely up to private industry, with the government's investment being repaid through lease payments, depletion royalties, or taxes. Without doubt this system will be used also in utilizing any discovered riches of the continental shelf, unless the physical problems that must be overcome to utilize them are beyond the resources of private interests.

D.O.M.

(*Continued on page 8*)

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



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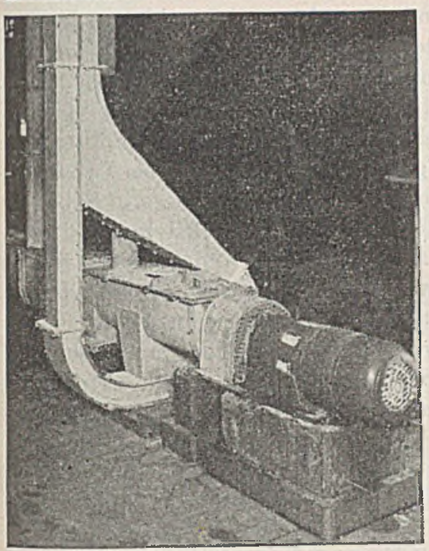
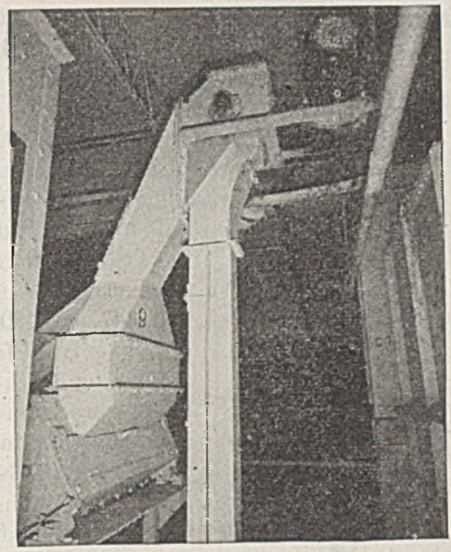


Loop type Bulk-Flo receiving salt moved from dryer by screw conveyor.

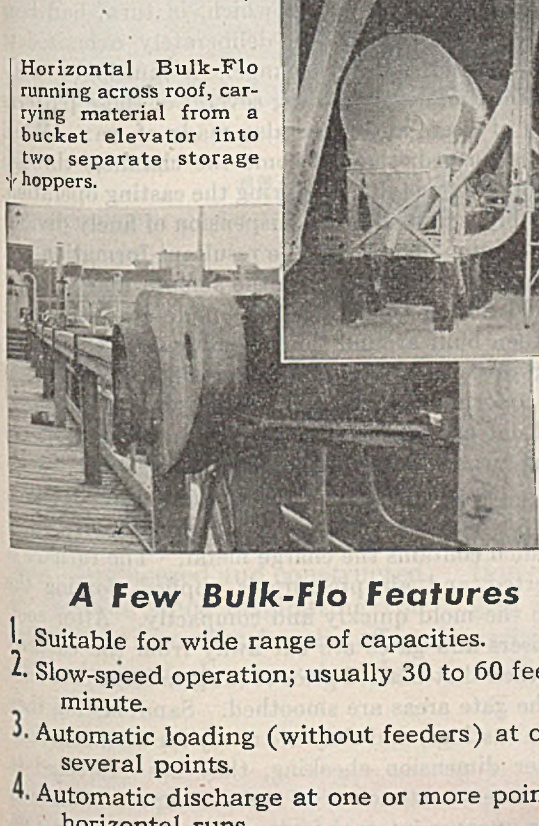


Top (discharge) end of Bulk-Flo unit. Material is discharged through chute onto a vibrating screen.

Discharge end of Bulk-Flo, which discharges into storage hopper, which in turn discharges into dryer.

Loading end of L-path Bulk-Flo receiving material discharged from drum type dryer. →

Horizontal Bulk-Flo running across roof, carrying material from a bucket elevator into two separate storage hoppers.



THE photographs on this page show how Link-Belt Bulk-Flo is being employed to move free-flowing bulk materials from one processing operation to another, and from one floor to another, in a great midwestern plant manufacturing food grade inorganic salts. This installation is typical of Bulk-Flo's flexibility and adaptability to a vast range of material-handling problems — whether large or small, simple or complicated — in the chemical and food industries.

Bulk-Flo provides a safe, efficient, low-cost method of moving practically *any* flowable granular, crushed, ground or pulverized material of nonabrasive, noncorrosive nature. It conveys material in compartments, horizontally, vertically, on any slant, around corners — wherever it is necessary to move them, even across the roof (see photo at bottom left) if desired! Bulk-Flo's gentle handling keeps degradation, breakage and dusting at a minimum.

Ask a Link-Belt Materials Handling Engineer for suggestions on Bulk-Flo and/or other types of handling equipment for your plant. Meanwhile, send for catalog No. 2075 today.

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A Few Bulk-Flo Features

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4. Automatic discharge at one or more points on horizontal runs.
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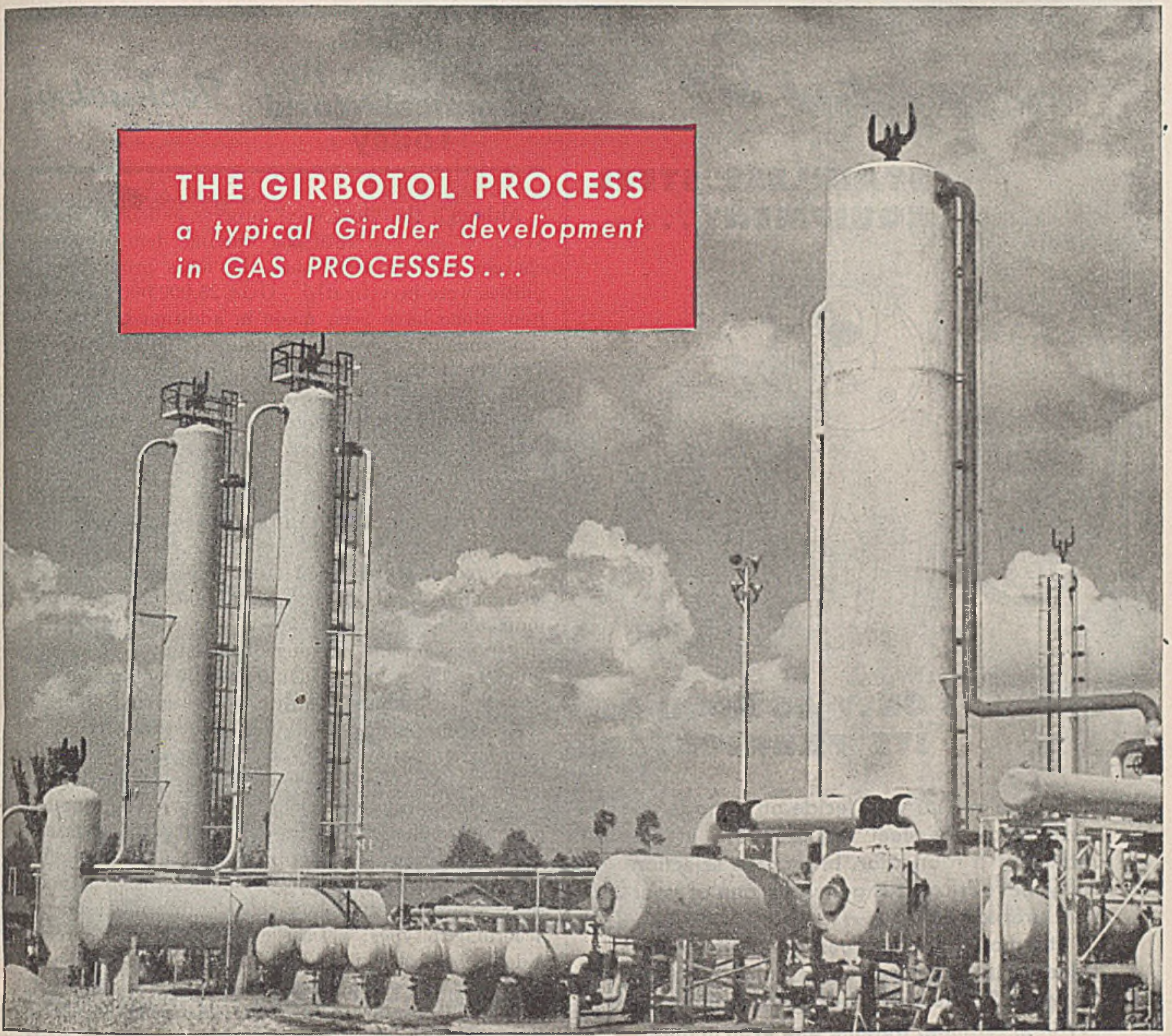
I. & E. C. Reports on the Chemical World Today

Technology

"Lost Wax" Wanes, Waxes. Perhaps only a schizophrenic would at first glance associate a modern jet-propelled P-80, winging its way across our continent in four hours, with the familiar American dentist's office. But if this be madness, let us have more of it: For, by taking the dentist's method of making well-fitted inlays for teeth, the Haynes Stellite Company was able to produce on a mass scale the much-needed cast buckets for aircraft superchargers. This "lost wax process" or the "precision casting process", as it is called by Haynes Stellite, makes possible the casting of alloys which have been considered difficult to forge or machine, to tolerances of −0.003 to −0.005. In addition to nickel-base Hastelloy and cobalt-base Stellite, two tough abrasion- and corrosion-resisting products, it is now possible to precision cast Types 316, 310, 347, and 410 stainless steels. The finished product requires only a few grinding operations and usually no machining operations before it can be used. To date the largest precision casting made by this process on a mass scale is a coupling for a Pratt and Whitney engine, fabricated of type 347 stainless steel and weighing approximately $1^1/_3$ pounds. However, this figure is not the maximum weight that can be produced. Already parts weighing up to 5 pounds have been cast on an individual basis, and as far as minimum limits are concerned, suffice it to say that items weighing only 0.002 pound have been successfully cast.

Essentially the precision of the whole process is based on the fact that, for each piece produced, a wax pattern is necessary. These patterns are made by injecting a suitable wax into a soft metal die which, in turn, had been cast from the master pattern deliberately oversized to allow for wax and metal shrinkage. A multipattern assembly is then made by welding several of these patterns to a series of risers and gates also made of wax. When the mold is formed, these become the channels through which the molten metal flows during the casting operation. This assembly is dipped into a suspension of finely divided silica and dehumidified, with the resultant formation of a tight-fitting film which becomes the smooth inner surface of the mold during the firing. A simple Hastelloy container is then built around this assembly, and chemically hardening investment material of a siliceous nature is poured in to form the actual mold. The wax is then "lost" or burned out of these molds by passing them through a continuous furnace heated from 1300° to 1900° F.

The actual casting is done by clamping the mold upside down over the pouring spout of a small, indirect arc heated furnace which contains the charge metal. The furnace is then inverted and air pressure is applied, forcing the metal into the mold quickly and compactly. After cooling, the risers and gates are cut away from the castings which are then shot-blasted prior to the grinding operations wherein the gate areas are smoothed. Sandblasting then finishes the castings, and they are ready for final examination. After dimension checking, they are subjected to Zyglo fluorescent tests to reveal surface imperfections and x-raying to uncover internal faults. *(Continued on page 10)*


THE GIRBOTOL PROCESS
a typical Girdler development
in GAS PROCESSES . . .

I. & E. C. Reports on the Chemical World Today

Technology

Although the "lost wax" process had been known for years, it was not until the wartime demand for supercharger buckets arose that the mass production possibilities were investigated. Over 25,000,000 pieces of this item alone have been made in addition to hundreds of thousands of other types of industrial and military parts. Precision casting has opened many new avenues to the design engineer. Now it is possible for him to plan shapes and contours, never before considered practical, from the desirable abrasion- and corrosion-resistant alloys.

"Lost wax" has found itself. R.L.D.

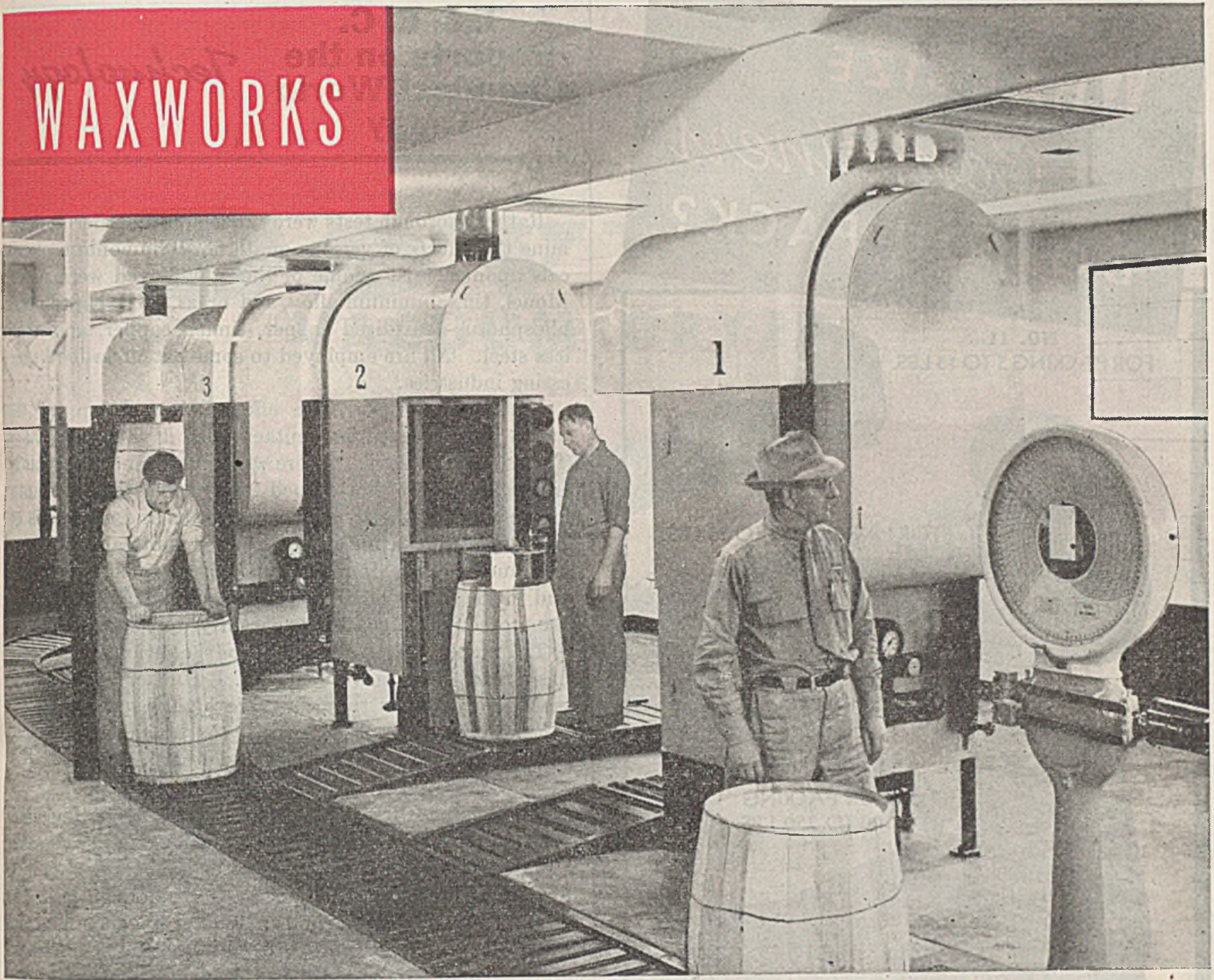
Bad News for Bugs. In the food industry, sterilization of equipment is a highly essential function. A recent development is the introduction of quaternary ammonium compounds as cationic germicides, and experimental work indicates that an important job is marked out for those in the processing and canning of foodstuffs. Thus far this industry has kept its manufacturing equipment free of bacteria with the use of steam, hot water, and chlorine, but there is now a possibility that industrial sterilization is entering a new phase.

At the New York State Agricultural Experiment Station chemists and bacteriologists are investigating quaternary ammonium compounds for sterilization in the food industry since they are odorless, they enter readily into solution, and their use does not involve corrosive action. On the other hand, they vary considerably in specific action according to types; yet the least efficient in the group provided a bacterial kill of 90 to 95%. This made it necessary for the experimenters to resort to a wide description of test cultures, including *Escherichia coli* (a heat-resistant strain), *Aerobacter aerogenes*, *Streptococcus cremoria* (a cheese starter organism), *Bacillus subtilis* M-23 (a mesophilic flat sour organism isolated from beets), and others.

When the number of quaternary ammonium germicides used in the test is considered, the magnitude of the task can be appreciated. At a recent meeting of the Institute of Food Technologists, a dozen of these germicides were described, and the results of the tests outlined. They are not easily committed to memory. The compound marketed under the trade name "Nopco QCL" is lauryldimethylbenzylammonium chloride. Hyamine 1622 is diisobutylphenoxyethoxyethyldimethylbenzylammonium chloride, CTAB is cetyltrimethylammonium bromide, and another called "Onyxide" or "Quartol" is oleydimethylethylammonium bromide. Similar to the latter chemically are BTC and Tetrosan.

The state agricultural chemists report that *Aerobacter aerogenes* was more sensitive to cationic germicides than *Escherichia coli*, a capsulated slimy strain found in paper mills. If the former was used as the test organism, complete killing was noted in much lower concentrations of the germicide than when *Escherichia coli* was employed in the standard test. The cationic germicide Isothan Q 15 completely killed both *Escherichia coli* and *Aerobacter aerogenes* in about the same concentration, 1 to 8000, after some 10 minutes of exposure.

(*Continued on page 12*)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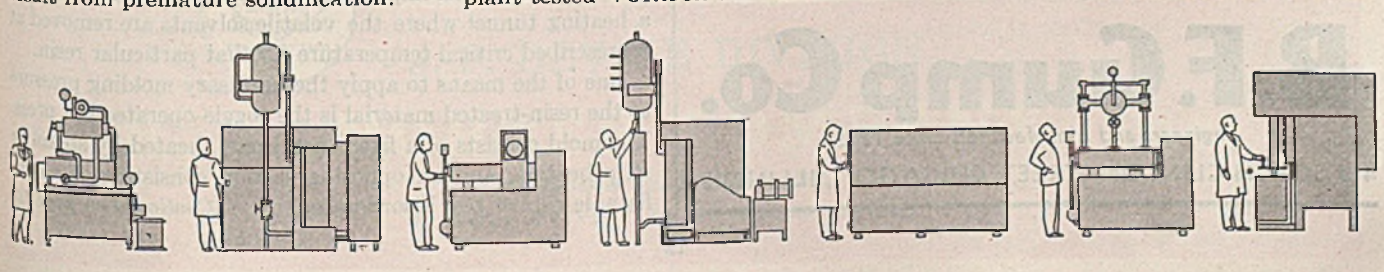


I. & E. C. Reports on the Chemical World Today

Technology

Rather thorough tests were carried out in order to determine the effects of various quaternary ammonium chemicals upon metals. Some of those employed were nickel, Monel, tin, aluminum alloy, red brass, 30% cupronickel, phosphorus-deoxidized copper, tinned copper, and stainless steel. All are employed to some extent in food processing industries.

Practically no corrosive effects were shown by test metal strips placed in contact with Hyamine 1622 or Tetrosan for 21 days. There were some minor exceptions. In the instance of hot-dipped tin some rusting was noted at the edges of the strips, where breaks and abrasions occur in the tin coating. Small pitted spots also appeared on tinned copper after 21-day exposure to the germicides and to the effects of water control. Here again breaks in the protective tin coating apparently were responsible.

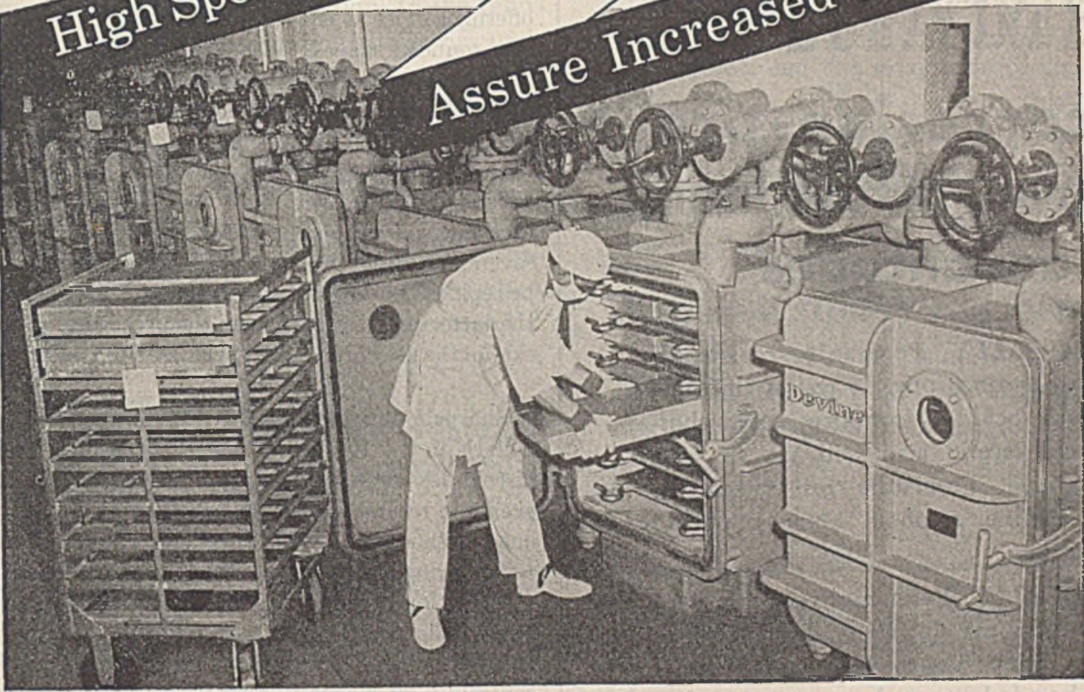
The highly selective character of the cationic germicides has already been mentioned. G. J. Hucker of the experiment station finds that they are highly specific against spore formers as well as against the organisms normally encountered in food processing and other industries. H.S.

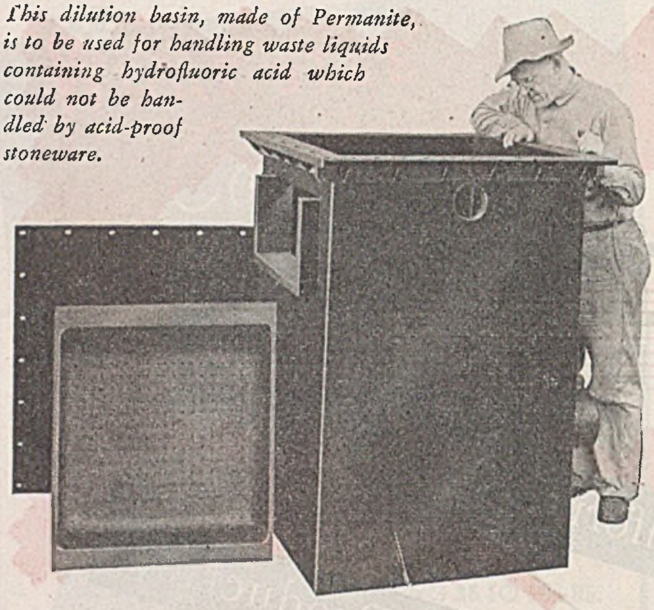
Plastic Sandwiches. The idea of incorporating other materials with plastics to increase their strength and make them more adaptable for wider uses is not new. Only a few months after the first phenol-formaldehyde resin was produced by Leo Baekeland in 1909, a phenolic laminate was made. However, prior to 1940 "plastic sandwiches" of resin and paper or other reinforcing materials were made under pressures of 1000–2500 pounds per square inch. This necessitated heavy, well engineered, and consequently expensive equipment for the lamination molding operations. These high working pressures also had the effect of limiting the area of the molded product that could be produced.

Low-pressure molding and lamination practice has been directly dependent upon the development of resins that possessed a high degree of flow and were curable at low pressures but still maintained good mechanical and electrical qualities. At present two kinds of thermosetting resins are used in low-pressure molding, phenol-formaldehyde and ester types. The bulk or density of this filler determines to some extent the lowest pressure that can be used; this, in turn, often governs the type and quantity of resin. It has been found that high-density papers and tight-woven fabrics mold at lower pressures than do the waterleaf type papers and loosely woven fabrics. When materials such as fabrics or papers are being treated for lamination, the resin is usually applied by immersing the material in a bath or by passing it through squeeze rolls. After impregnation, the sheet is passed through a heating tunnel where the volatile solvents are removed at a prescribed critical temperature for that particular resin.

One of the means to apply the necessary molding pressure to the resin-treated material is the toggle-operated hot press. The mold consists of a fixed metal part, heated by steam or strip heaters, and an opposing section consisting of an inflatable rubber bag incorporated

(*Continued on page 14*)





I. & E. C. Reports on the Chemical World Today

Technology

in the press head. The pressure, which may vary from 50 to 250 pounds per square inch, is applied on the material by bleeding water into the rubber bag through the press head.

The hydraulic press is valuable in the production of flat sheet laminates by low molding pressures which produce less strain and distortion in the filler material and, hence, tougher finished sheets which are less suceptible to warpage. The ability to mold large sheets of laminate by this method has made possible the use of decorative panels for construction work. A recent survey by *Architectural Forum* indicates that this market will probably reach $750,000,000 a year. These materials will soon be marketed under such names as Weldwood, Duramold, Lap-Ply, Metal-Ply, etc.; in addition to offering service as flat laminates, they can be contour-molded into rounded shapes. The latter property has been utilized in the fabrication of four molded boats, shown at the exhibit of the Society of Plastics Industry in Chicago. The largest, a continuous skin hull in one solid piece, was 17 feet long and moistureproof, wormproof, leakproof, and rotproof. These resistant qualities will make low-pressure reinforced plastics excellent substitutes for metals where climatic conditions are severe. It is not probable that high-pressure laminating will be replaced by low-pressure molding, but it is expected that the latter process, born from the urgency of war, will greatly extend the use of reinforced plastics in our daily life. R. L. D.

Sharpshooting with DDT. TVA's success in controlling malaria in the Tennessee Valley has been so resounding that discoveries of malaria-positive blood smears have become events in recent annual surveys averaging hardly more than one per thousand among those most likely to have malaria.

The principal control methods used by TVA have been a combination of lake level fluctuation and airplane dusting of large shallow-water areas with larvicide (usually Paris green). In addition, shore-line weeds that favor mosquito growth are controlled by mowing or cattle grazing, and the shore-line contour is shaped to eliminate pockets of stagnant water.

When DDT was added to our list of chemical "miracle" workers, its possible use for malaria control was not overlooked. At the suggestion of the Orlando (Fla.) Laboratory of the U. S. Bureau of Entomology and Plant Quarantine, TVA conducted preliminary airplane dusting tests in 1943 and much more extensive tests in 1944 and 1945, with the assistance of the former group and others from universities and the Government. Results were highly successful. DDT, dissolved in a thermal aerosol that was evaporated by the heat of the engine exhaust, was effectively distributed as a visible cloud by the propeller blast. Application of 0.12 pound of DDT per acre was more effective in killing mosquito larvae than the standard Paris green treatment of 1 pound per acre, and estimated comparative costs were 35 cents per acre for DDT compared to 85 for Paris green.

Two bays were isolated from a TVA lake and given this standard DDT treatment. Examination of the fish at the end of the season showed that no harm had been done. The damage to insect life was confined to mosquitoes. D.O.M.

(*Continued on page 18*)

Furfural has PHYSICALLY and CHEMICALLY PROPERTIES VALUABLE to YOU

FURFURAL, the cheapest pure aldehyde available today, does duty for the chemist on two counts—its physical properties and its chemical properties.

PHYSICALLY...

Because of its selective solvent properties, its preferential solubility for unsaturated compounds, Furfural is widely used to refine organic crudes with components of varying degrees of unsaturation. In the refining of lubricating oil, in the separation and purification of butadiene, in the manufacture of pale rosins from crude dark colored rosin, in the separation of fractions of high-iodine number from animal and vegetable glyceride oils, Furfural is especially effective and economical.

Other uses for Furfural, continually gaining in importance, are as a dispersant in resinoid-bonded abrasive wheels, dyes, lacquers, and varnish removers.

CHEMICALLY...

Its versatility as an aldehyde in condensation, oxidation and reduction makes it a useful raw material in organic syntheses.

PHYSICO-CHEMICALLY...

In the manufacture of phenolic resins, Furfural is being used because of its high boiling point, its high molecular weight, and the unique properties of its heterocyclic ring structure. Valuable in this connection too are its solvent properties. Ability to dissolve phenolic bodies and resinous condensation products makes it possible to maintain substantially homogeneous mixtures throughout the reaction process.

Furfural SUPPLY IS PLENTIFUL...

The supply of Furfural is ample to meet all present and anticipated needs and a program to keep production facilities ahead of increasing demands is already in operation.

LITERATURE AVAILABLE ON *Furfural*

Three Bulletins in a series on the Furans being published by the Quaker Oats Co. Chemicals Dept. are now available to those interested. They are:

Bulletin 201—*General Information About Furfural.*

Bulletin 202—*Introduction to the Chemistry of the Furans.*

Bulletin 203—*Physical Data on Furfural.*

Any one of these or all will be sent free of charge when requested on your letterhead. Samples will be gladly furnished to those who would like to work with Furfural and the Quaker Oats Technical Staff is ready to help in the application of Furfural to your problems.

PROPERTIES OF QUAKER FURFURAL

(Furfuraldehyde, C_4H_3O-CHO)

Amber-colored liquid of high stability and unusual purity

Molecular Weight	96.08
Freezing Point, °C	−37
Boiling Range (99%)°C	157 to 167
Specific Gravity (20/20°C)	1.161
Flash Point (open cup)°C	56
Refractive Index (20/D)	1.5261
Surface Tension at 20° C (dynes/cm)	49
Viscosity at 38°C (centipoises)	1.35

Solubility: Completely miscible with ethyl alcohol, ether, acetone, benzol, butyl acetate, china wood oil and most organic solvents except petroleum hydrocarbons and glycerol; 8.13% by wt. in water at 20°C.

Analysis:

Furfural, minimum %	*99.5
Water, maximum %	0.2
Organic Acidity, Maximum equiv/l	0.023
Ash, maximum %	0.006
Mineral Acidity	None
Sulfates	None
Ketones	None

*As determined by A.O.A.C. method.

Standard Containers: 9, 45, 90, and 520 lb. Drums

†Carload of Drums 80 to 88	41,600 to 45,760 lbs.
Tank car 8,000 gal.	78,000 lbs.
Tank car 10,000 gal.	98,000 lbs.

†ODT requires maximum loading

Drums non-returnable

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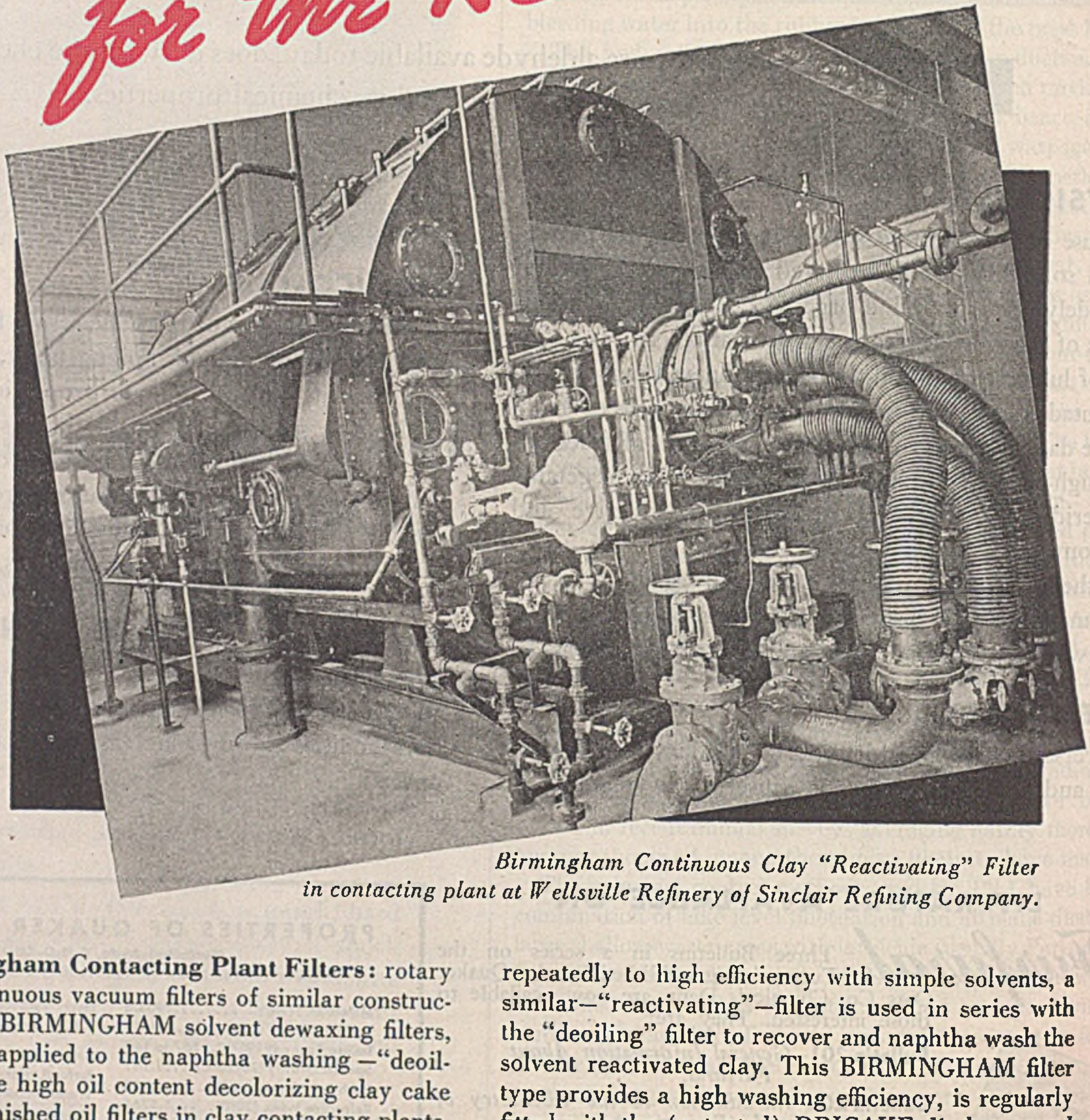
CONTACT PLANT FILTERS for the REFINERY...



Birmingham Continuous Clay "Reactivating" Filter in contacting plant at Wellsville Refinery of Sinclair Refining Company.

Birmingham Contacting Plant Filters: rotary drum continuous vacuum filters of similar construction to the BIRMINGHAM solvent dewaxing filters, have been applied to the naphtha washing—"deoiling"—of the high oil content decolorizing clay cake from the finished oil filters in clay contacting plants. In the continuous clay-reactivation process developed by Sinclair Refining Company's Wellsville Refinery, and employing the decolorizing adsorbent clay "Magnesol"* which is capable of being reactivated repeatedly to high efficiency with simple solvents, a similar—"reactivating"—filter is used in series with the "deoiling" filter to recover and naphtha wash the solvent reactivated clay. This BIRMINGHAM filter type provides a high washing efficiency, is regularly fitted with the (patented) DRICAKE discharge and compartment flushing device for separation of filtrate and wash. This filter is available in standard sizes from 50 to 500 square feet of filter area.

*Manufactured by The Magnesol Corporation.

GOSLIN-BIRMINGHAM MANUFACTURING CO., INC.

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ALKANE SULFONIC ACIDS


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A new Series — *Interesting in both the Organic and Inorganic Fields*

Available only in research quantities—potentially available commercially.

THE ALKANE SULFONIC ACIDS

Are strong, stable acids, non-reactive with paraffinic and aromatic hydrocarbons. Are effective but milder catalysts than sulfuric acid in typical reactions. Form many interesting organic derivatives. Form metal salts characterized by high water solubility, including those of lead and barium.

TYPICAL PROPERTIES

	Methane Sulfonic Acid	Ethane Sulfonic Acid	Mixed Alkane Sulfonic Acids
Molecular Weight	96	110	110-120
pH of 1% Solution	1.05	1.10	1.15
Solubility of Lead Salt (g./100 g. aq. soln.)	59.2	67.3	——
Color	Yellow	Light Amber	Amber

Available in ½ and 1 pound packages, prices on request. Methane and ethane sulfonic acids are in limited supply—mixed acids available in larger quantities.

For further information send for Bulletin No. 11 and for price list.

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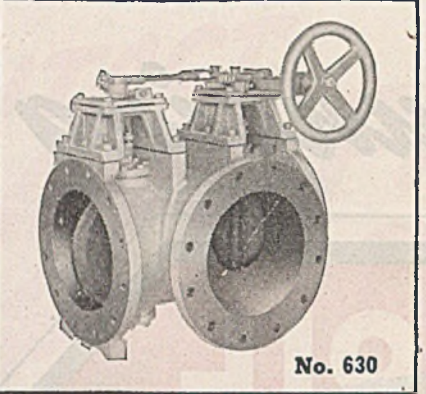

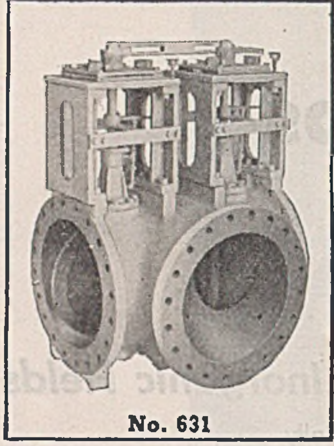

I. & E. C. Reports on the Chemical World Today

Education

War Baby's Epitaph. If old-fashioned, lengthy epitaphs were still in style, an impressive one could be inscribed for a war baby that barely lived to be four and a half years old. It was born December 9, 1940, when the first Engineering Defense Training (EDT) courses got underway to help relieve the shortage of engineers in specialized fields essential to national defense. Later the program was broadened to include courses for chemists, physicists, and production supervisors. On June 30, 1945 (end of the governmental fiscal year), the European war was over, the Japanese military machine was ready to crumble, and ESMWT (ET plus science, management, and war) breathed its last on the date usually provided for demise of federal agencies that are mortal. In the period intervening, a total federal expenditure of $59,967,040 had been made, and separate enrollments aggregating 1,795,716 were recorded. The principal burden was carried by the colleges and universities that did the on-the-spot job of administering the courses. A small central staff in the United States Office of Education coordinated the policy through its control of the purse strings. Teachers were drawn from school staffs and from industrial organizations.

Enrollment in courses classed as chemistry and chemical engineering totaled 39,000 and 52,000, respectively. Numerous additional workers in the chemical field undoubtedly participated in other courses with such general names as basic science for engineers (100,000), general engineering (208,000), industrial engineering (185,000), and production supervision (387,000). A high-school education or its equivalent was a minimum prerequisite for any course, but many specialized subjects were for college graduates. Total enrollments ranged from 151,000 at the University of California and 142,000 at Penn State, to 11 at Fisk, a negro college in Tennessee, and 24 in the East Texas State Teachers College. Courses were given in every state and in Alaska, Puerto Rico, and Hawaii. Women comprised nearly one sixth of the total enrollments.

As the inroads of Selective Service on the originally limited number of technically trained persons became deeper, industrial organizations were forced to make drastic readjustments. Jobs previously performed by professional employees were broken apart and carried on by technicians with narrower qualifications of experience and ability. ESMWT supplied the only specialized training received by many of these technicians before they took such jobs. Many others were upgraded into more responsible technical work after additional training in the courses.

The ESMWT program has been in its grave nearly a year, but some of the by-products of its operation remain as permanent benefits in the Nation's educational structure. Many schools first undertook extension services under the ESMWT program, and many others greatly expanded existing services. A substantial number continued the services when the ESMWT program ended.

The United States Office of Education plans a clearing house of information for and about the engineering schools that were the core of the program. Should this venture bear good fruit, similar efforts for other types of schools may follow. The American people will receive dividends from this sixty-million-dollar investment for years to come. D.O.M.

It's so much easier to get the RIGHT horsepower, the RIGHT shaft speed, RIGHT where you need it, when you use Master Gearmotors . . . they soon become a habit.

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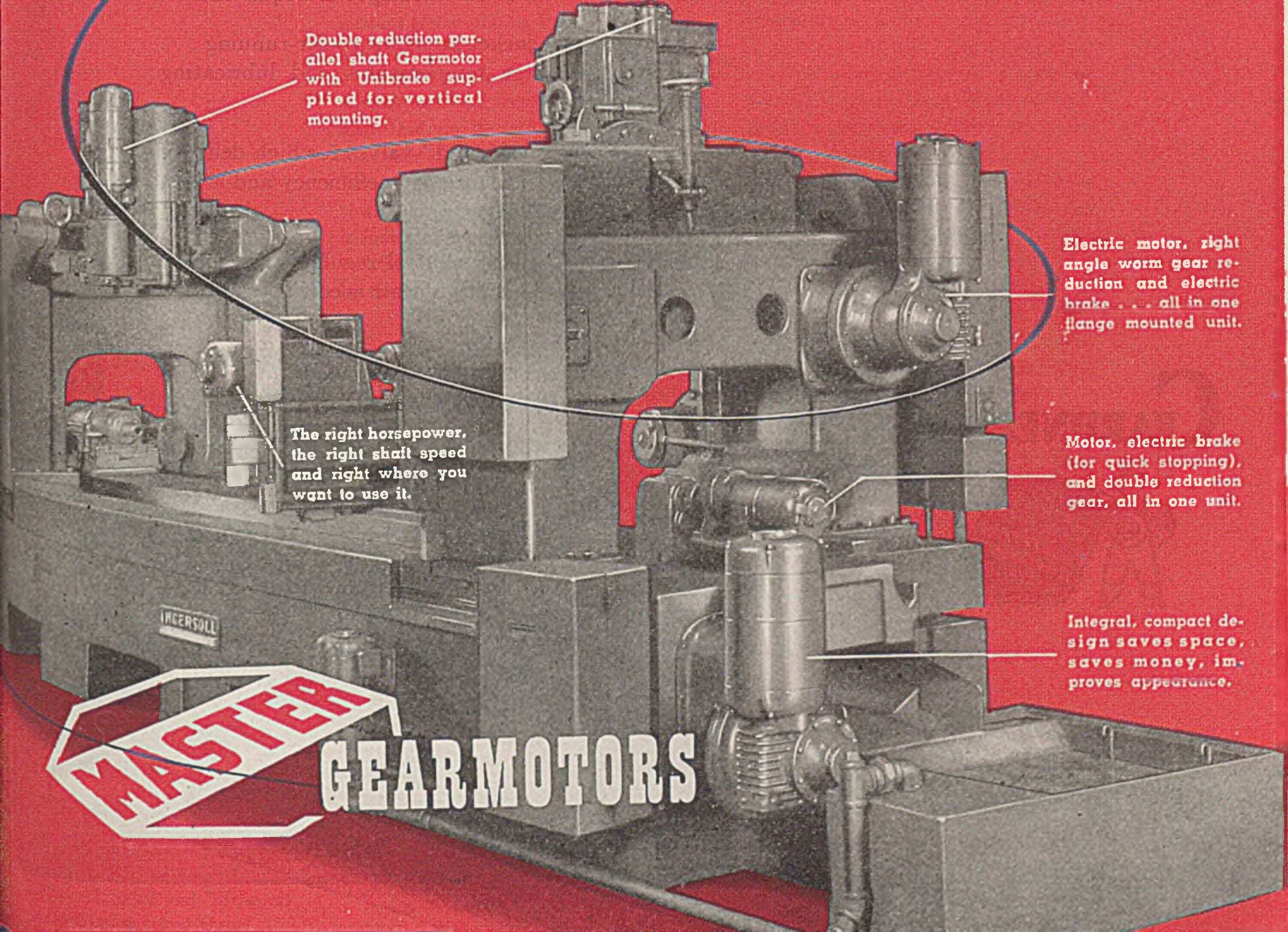
HEALTHY HABIT



Double reduction parallel shaft Gearmotor with Unibrake supplied for vertical mounting.

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The right horsepower, the right shaft speed and right where you want to use it.

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Integral, compact design saves space, saves money, improves appearance.

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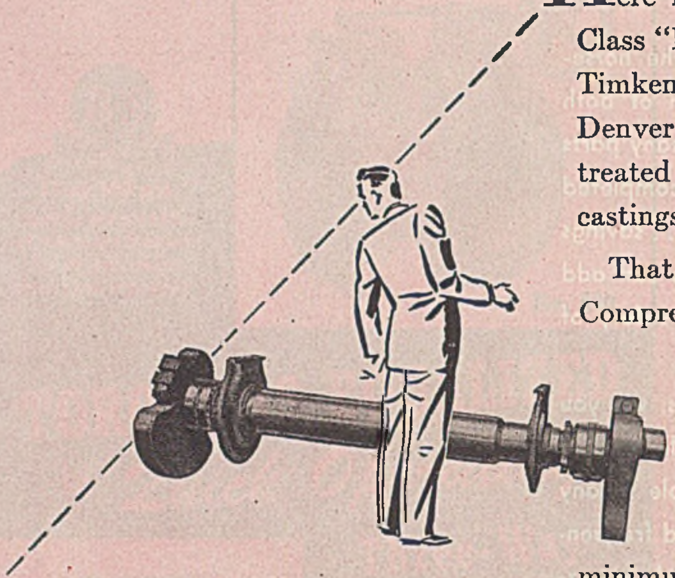


You can learn a lot about a compressor from its crankshaft!

Here is the main crankshaft of a Gardner-Denver Class "HA" Horizontal Air Compressor. Notice those Timken roller main bearings—an exclusive Gardner-Denver feature. The shaft is a steel forging, heat treated and finished all over. The crank discs are steel castings and counterweights are cast integral.

That crankshaft tells you a lot about an "HA" Compressor — because it is typical of the kind of construction used throughout. That's why the "HA" is a *heavy-duty* compressor in every sense of the word. That's why it gives year after year of continuous service — 24 hours a day if you like — with a bare minimum of maintenance.

If you're looking for a compressor that's a standout for service—and a miser on costs—let us tell you more about the "HA". For complete information, write Gardner-Denver Company, Quincy, Illinois.

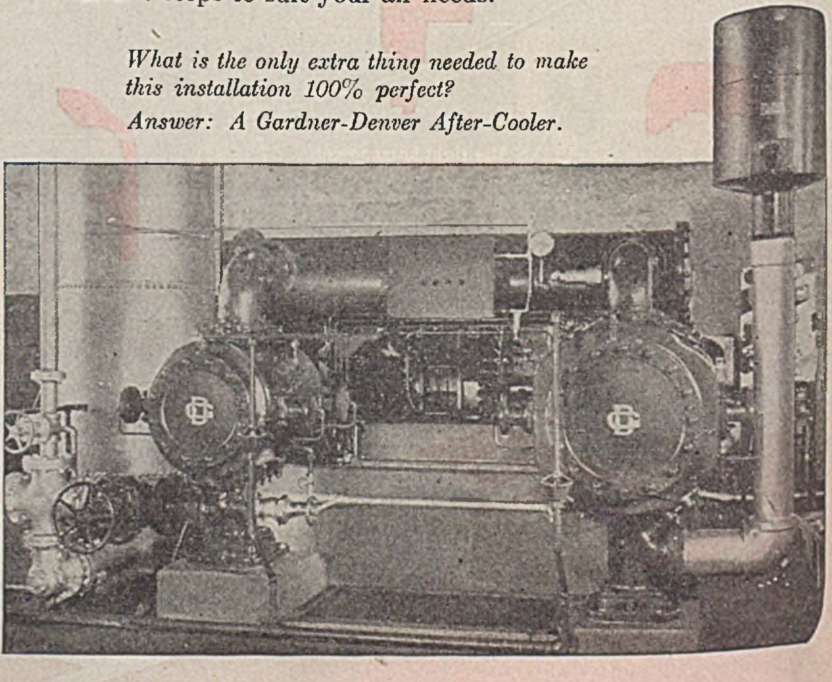
OTHER "HA" FEATURES

- Air cylinders designed for highest volumetric efficiency and lowest horsepower requirements.
- Large water jacket areas for cooler-running . . . lower discharge temperatures and lubricating economy.
- Duo-plate "cushioned" valves for high delivery capacity, high compression efficiency and lowest power consumption.
- Five-step capacity control regulates air output in five steps to suit your air needs.

What is the only extra thing needed to make this installation 100% perfect?
Answer: A Gardner-Denver After-Cooler.

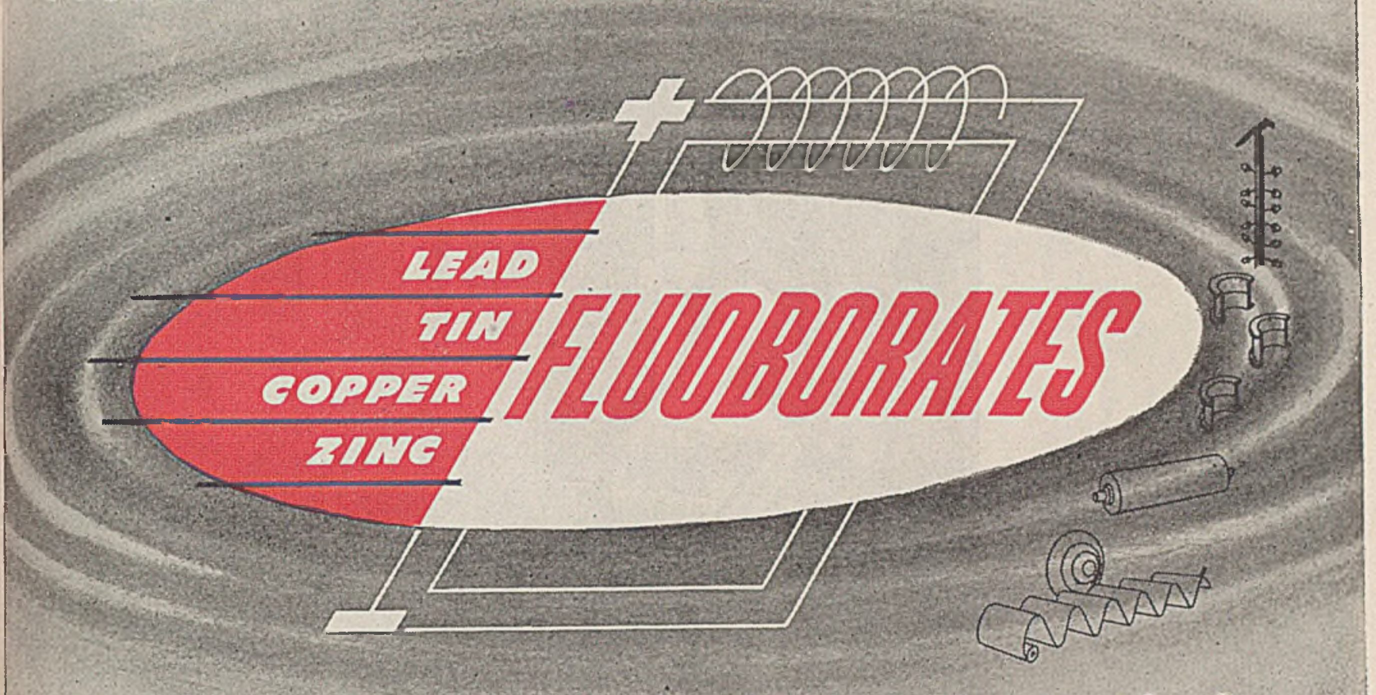
GARDNER-DENVER
Since 1859

USE COMPRESSED AIR FOR SAFETY CONVENIENCE FLEXIBILITY



Gardner-Denver Class "HA" Two-stage Horizontal Compressor. Available in capacities from 316 to 2012 cubic feet displacement per minute.

Products of General Chemical Fluorine Research



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To the electroplater, the Metal Fluoborates, generally, offer such advantages as: 1. Concentrated solution form; no mixing or dissolving necessary. 2. Simplicity of bath preparation and ease of control. 3. Stability of composition, high conductivity, and good covering power. 4. Fine-grained deposits of good color. 5. High-speed operation, with practically 100% anode and cathode efficiency.

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Metal Fluoborates BULLETIN 1015-A
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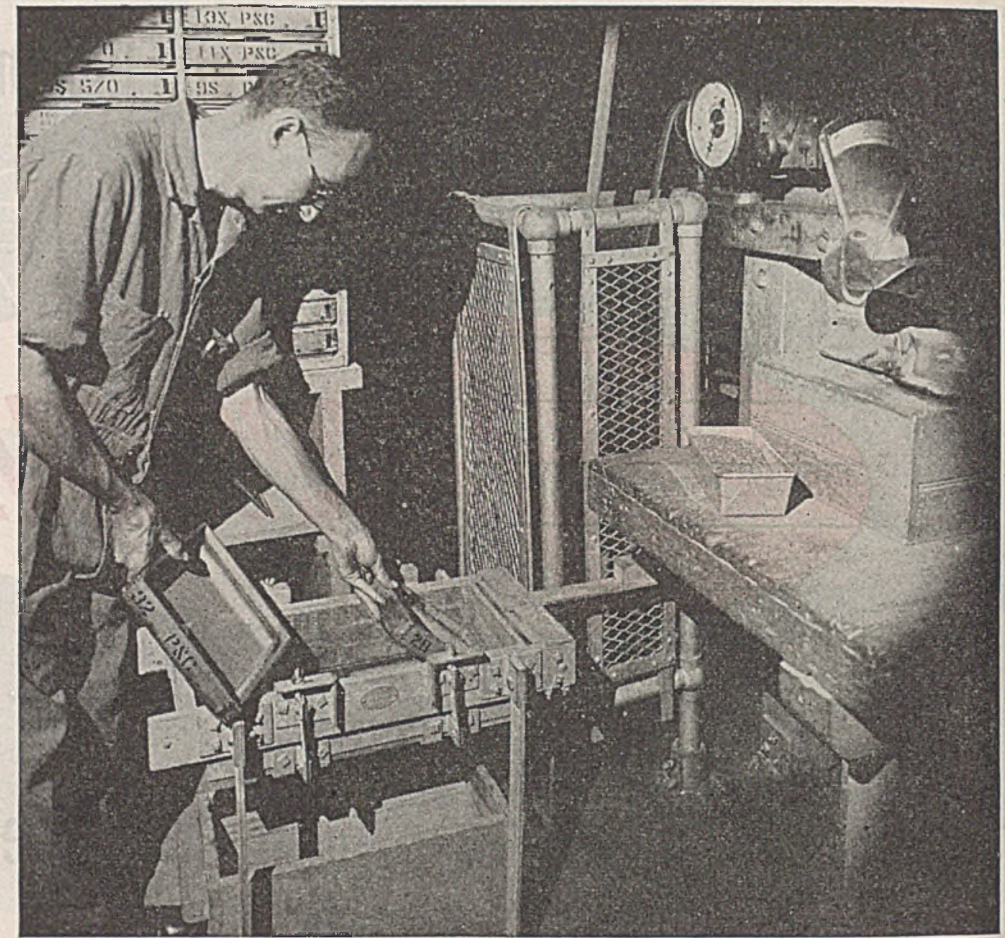

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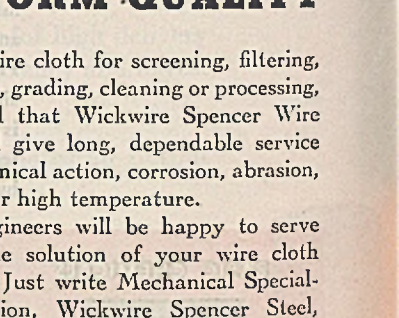

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—he's doing the best he can
NO CREDIT
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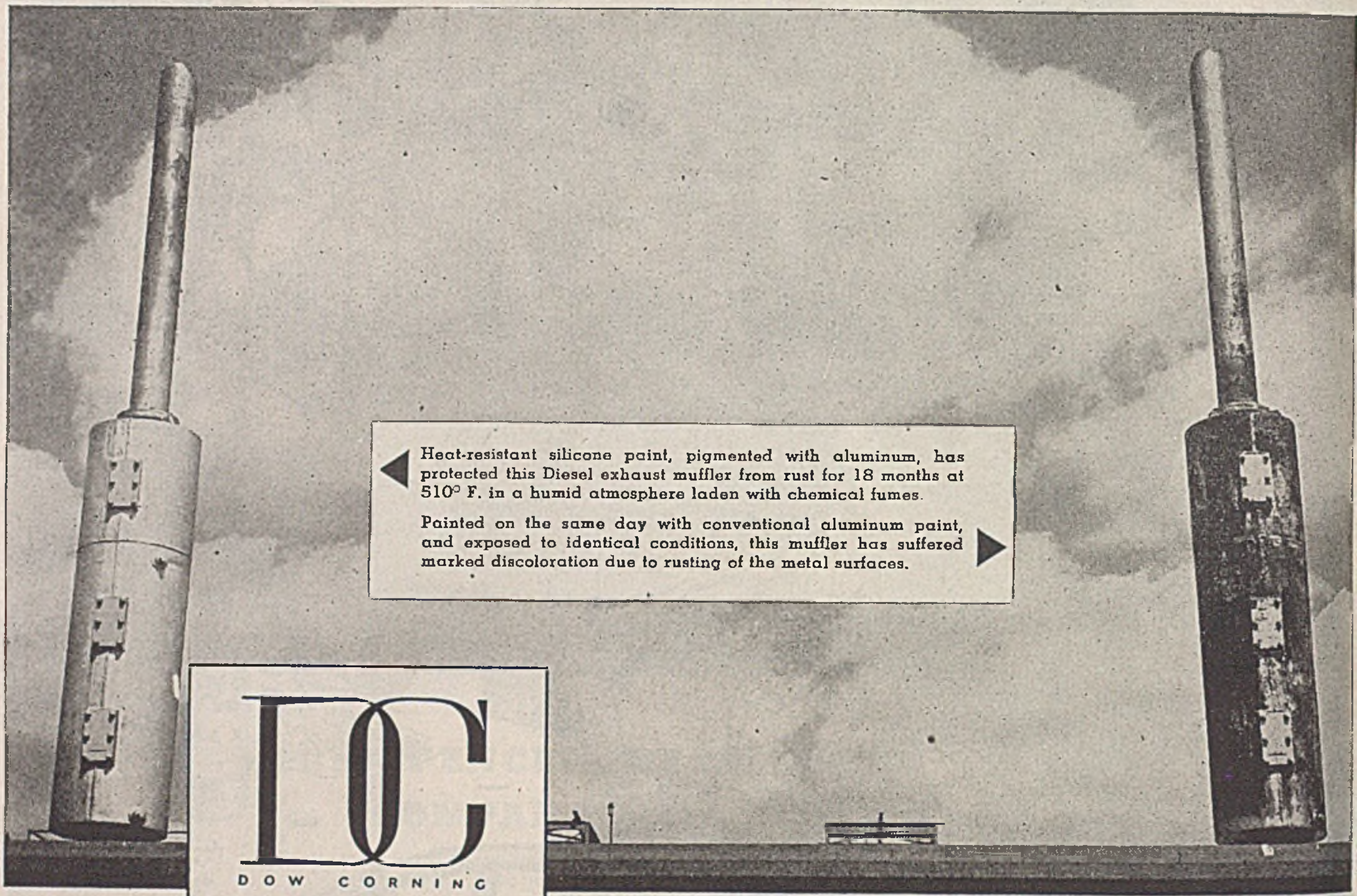
DC SILICONE RESINS

For paint that protects at 500° F.



Heat-resistant silicone paint, pigmented with aluminum, has protected this Diesel exhaust muffler from rust for 18 months at 510° F. in a humid atmosphere laden with chemical fumes.

Painted on the same day with conventional aluminum paint, and exposed to identical conditions, this muffler has suffered marked discoloration due to rusting of the metal surfaces.

DC
DOW CORNING
SILICONES

. . . Proof Against Moisture, Weathering, and Chemical Fumes

Now—with these *unique* silicone resins—you can readily formulate heat-resistant paints that fill the gap between organic paints and ceramic coatings. Available today, DC 801, 802, and 803 can be blended for practically every degree of hardness and flexibility. Though markedly different from all previous paint vehicles, these silicone resins can be formulated and mixed—like other paint resins—with inorganic pigments. DC 801, 802, and 803 are largely inorganic. That's why they resist heat, oxidation, ultraviolet rays, and chemical fumes. In addition, they are waterproof, water-repellent and non-yellowing. For further information, call on Dow Corning.

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MERCURY SWITCH CONTROL

MERCURY SWITCHES

- Glass enclosed — non-chattering
- Contact capacity: 30 amps. of 115 volts A.C.
- Open contacts and need for external relays eliminated.
- Trouble-free operation even in corrosive atmospheres.

The Brown *ElectroniK* Potentiometer... unsurpassed for outstanding performance ... has been made more versatile with Con-Tac-Tor Mercury Switches for the control of electric and fuel-fired furnaces.

Continuous Balance makes possible *Continuous* Correction—recording—signalling. Con-Tac-Tor (glass enclosed) mercury switches are worthwhile features that eliminate corrosion problems and the need for extra relays—and are available in fourteen different switching actions.

For applications where thermocouples or Radiamatics are used as the measuring element—the scope of the Brown *ElectroniK* Potentiometer plus Con-Tac-Tor mercury switch control is unlimited.

Salient features of this new *ElectroniK* Controller are:
FRONT SET CONTROL INDEX: knob provides quick and easy setting of control point.
"CONTINUOUS BALANCE" PRINCIPLE OF MEASUREMENT AND CORRECTION: an electronic detector *in place* of conventional galvanometer. SUPER SENSITIVITY, ACCURACY, AND RUGGEDNESS.
AUXILIARY MERCURY SWITCHES are available on both circular chart and strip chart *ElectroniKs* for signalling alarms, safety devices, etc.

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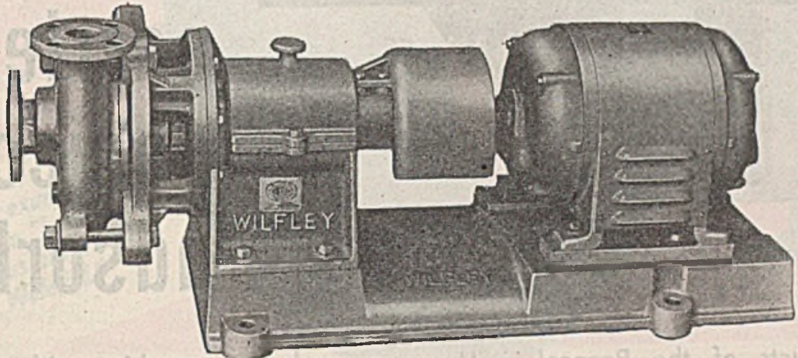
BROWN *ElectroniK* POTENTIOMETERS

For ACIDS



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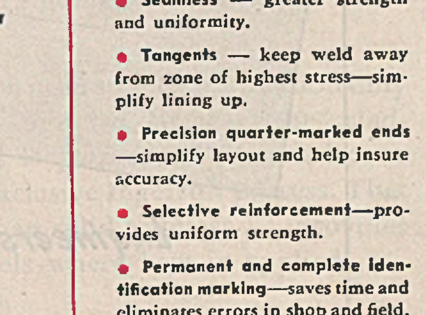

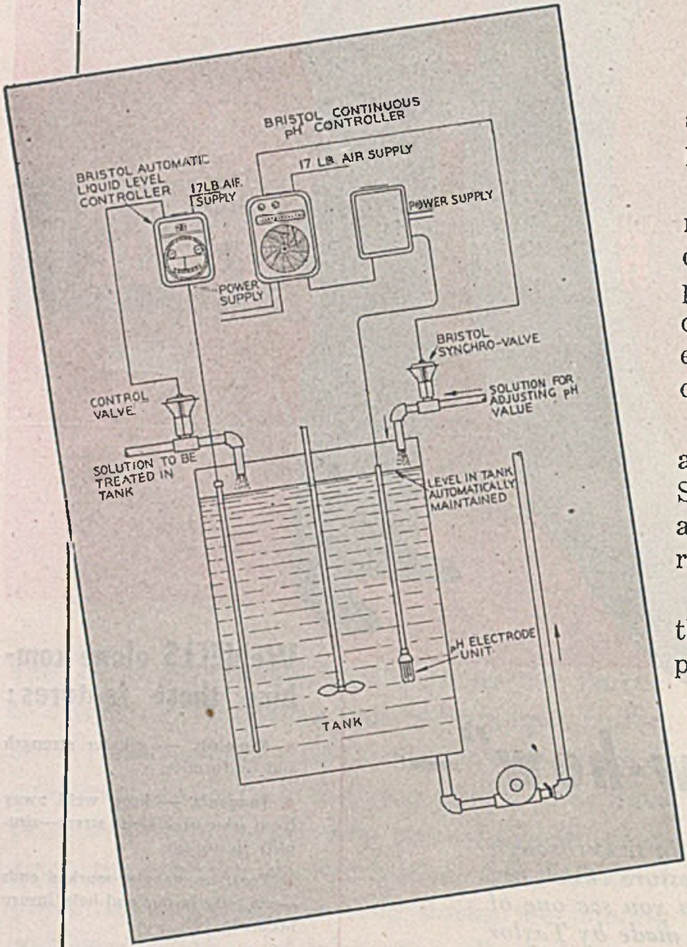
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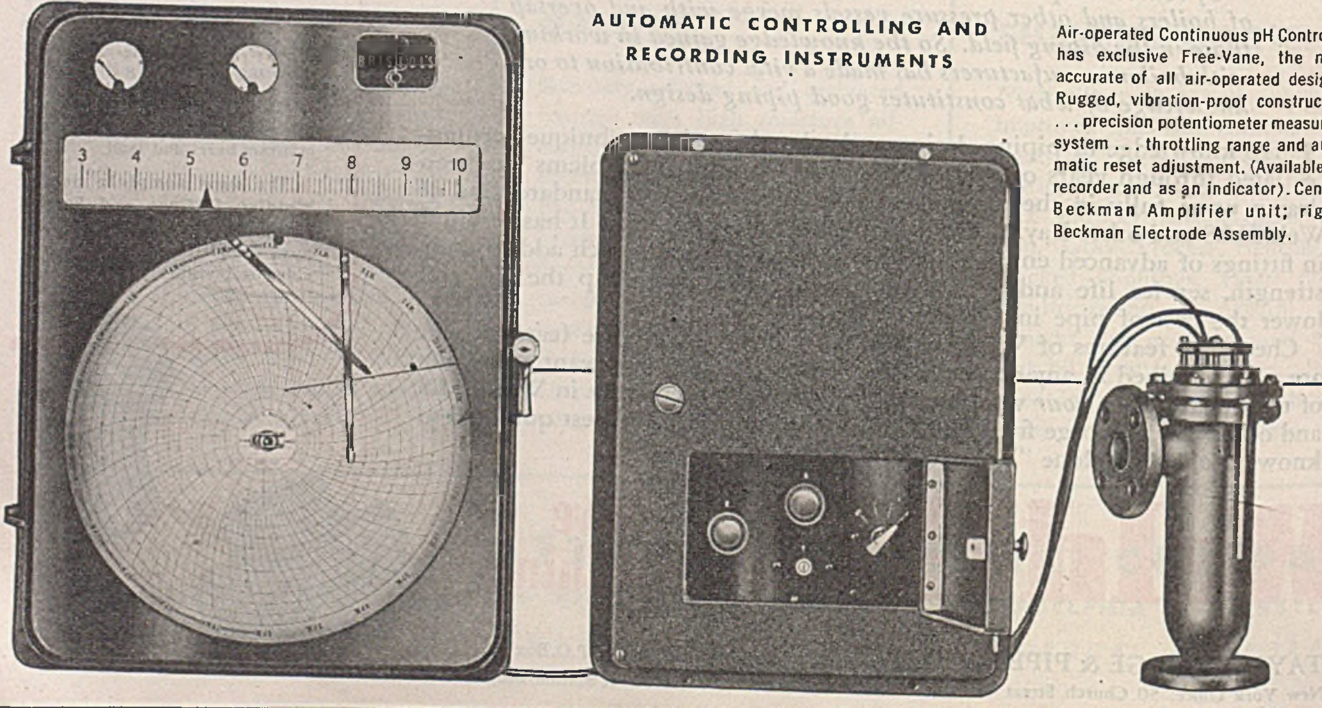
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BRISTOL'S

Smart Lad, that Waldo

Yes, little Waldo knows it's smart to *protect the side that's exposed.* Some day, when he's specifying materials for plant equipment, one of his "musts" will be IngAclad Stainless-Clad Steel. For this famous, time-tested Borg-Warner product provides full stainless protection on the side that's going to "take it."

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So look to IngAclad for maximum contact-side stainless protection at minimum cost. It's the *only* Stainless-Clad Steel proved by 14 years of continuous service. And since Ingersoll also produces Solid Stainless and Heat-Resisting Steels, you may be sure the recommendations of Ingersoll engineers will be completely impartial. Write, wire or telephone—no obligation.

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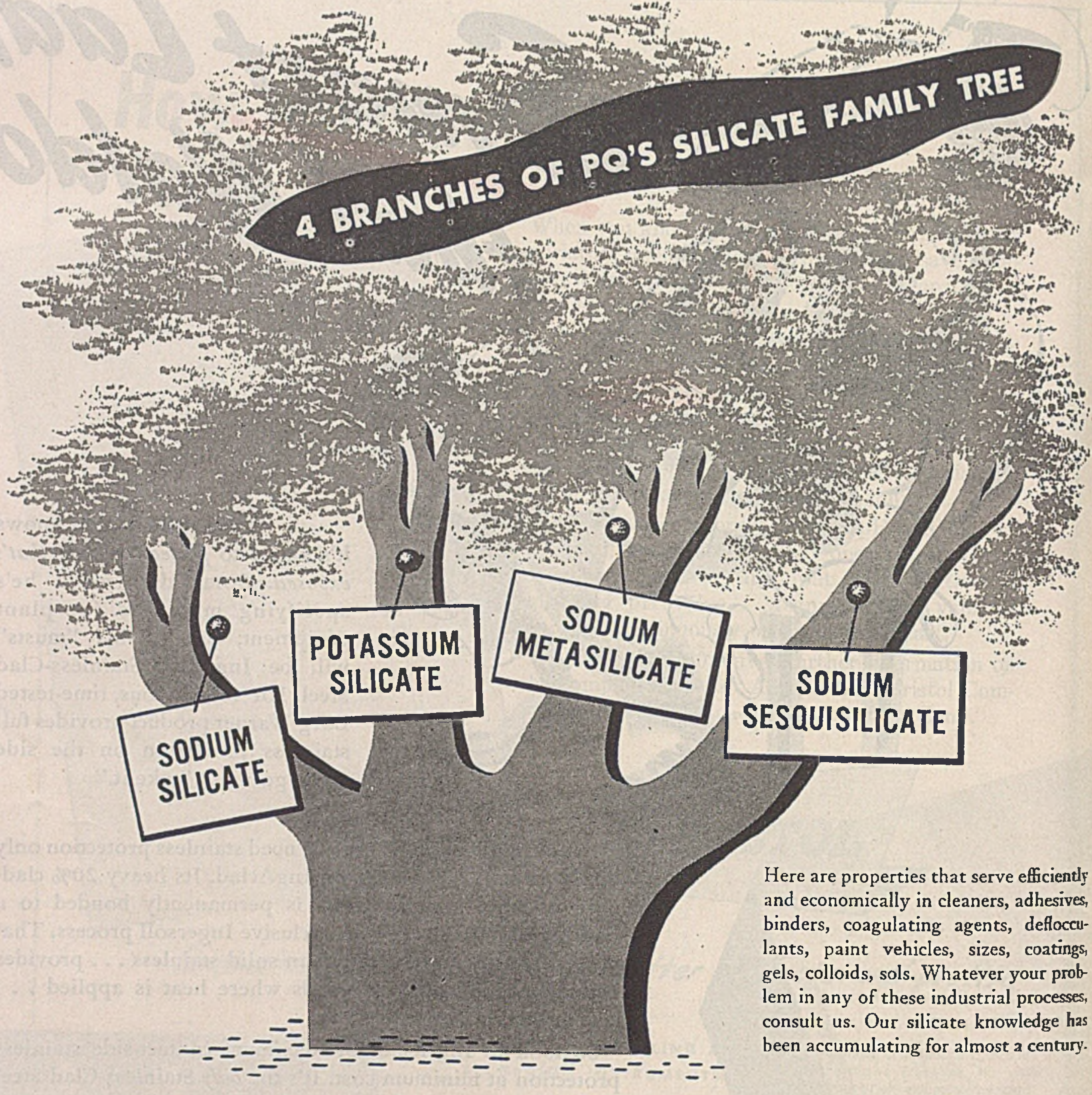
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Easier ROLLING-IN

Better FLOW CONDITIONS

Uniform HEAT TRANSFER

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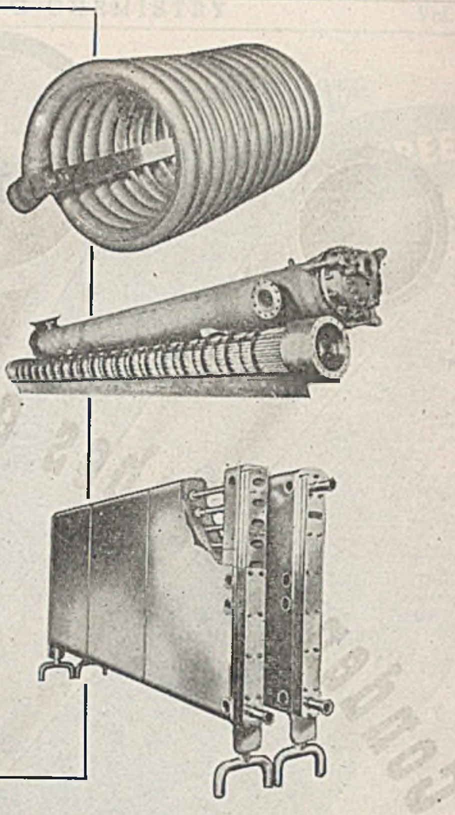

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IMPROVED FLOW CONDITIONS are provided by the smooth I. D. and O. D. surfaces which provide protection against sludge and scale deposit.

AND YOU SAVE 30 to 40% on cost of material alone when you use Carpenter "Heat Exchanger Quality" Stainless Tubing. Your savings increase as fabricating troubles disappear and equipment stays on the job longer.

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In convenient form, this slide chart gives you useful information on:

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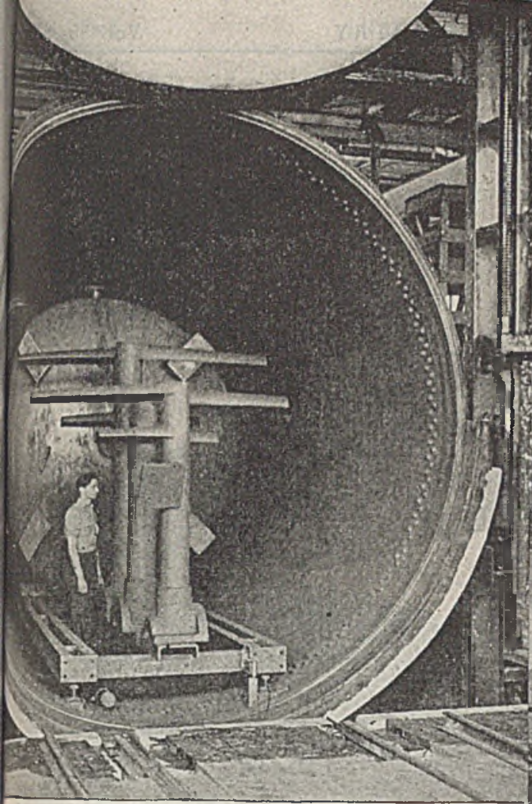
Cross Sectional Areas of Tubes
Sq. Ft. Internal and External Surface per Lineal Ft. of Tube
Physical Properties of Stainless Tubing

A note on your company letterhead will start your Stainless Tubing Slide Chart on its way. Write for your copy today.

THE CARPENTER STEEL COMPANY
Welded Alloy Tube Division • Kenilworth, New Jersey

Carpenter
WELDED
STAINLESS TUBING

Maximum Facilities in MANHATTAN'S RUBBER LINING DEPARTMENTS

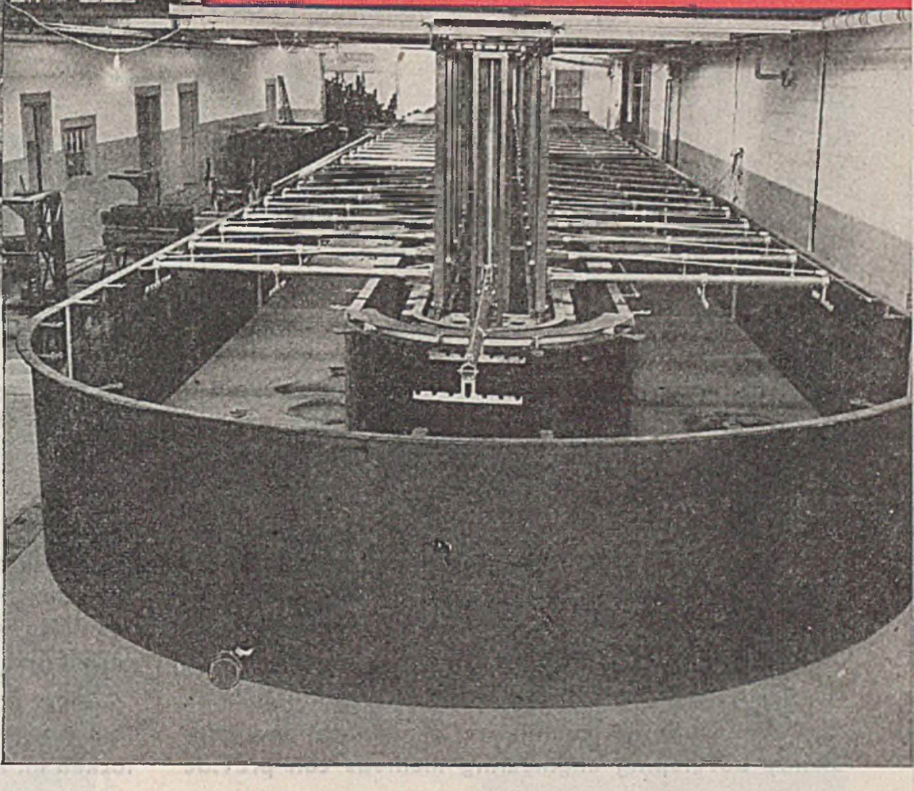


IANT OF VULCANIZERS

gest of Manhattan's extensive battery of rubber lining izers, this giant, 15 ft. in diameter, will handle any of equipment that can be shipped by rail, making pos- a complete service in this field and enabling Manhattan ake care of the increasing needs of industry for large ment. Vulcanizer is shown loaded with 2 huge rubber- tanks and 3 big rubber-covered castings.

anhattan Lined the WORLD'S LARGEST BBER-LINED NICKEL PLATING TANK ▸

ired 7 railroad flat cars to ship. Big in every dimension gth, breadth and width—it was easily accommodated Manhattan's spacious facilities.



anhattan's Record

ng the "impossible" has been the record of Manhattan's rubber lining departments for many years. Countless ecifications for unusual sizes and shapes of process handling and storing equipment have been met by Manhattan gineers backed by a technique that has steadily developed for 40 years.

separable Bond Developed

ing this period, a special process of rubber lining has been developed that places Manhattan Acid-Proof Rubber nings foremost in the field. Adhesion to metal has been attained so that mechanical separation cannot be effected.

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mpounded to give and take with the expansion and contraction of metal, Manhattan rubber linings can undergo treme temperature changes without cracking or oxidizing. Other qualities inherent in Manhattan lining compounds e utmost resistance to abrasion, to damage by electrolysis, and to corrosion and contamination.

wer Your Operating Costs

nsult Manhattan's engineers about rubber lining and rubber covering possibilities in your plant.

RAYBESTOS-MANHATTAN, INC.

MANHATTAN RUBBER DIVISION

Are you locking OUT

In a chemical world that is forever moving forward—and highly competitive!—it is natural that manufacturers should desire to keep control of the processes and plant designs their engineers have developed . . . often at great expense.

Badger offers chemical managements and their engineers the truly constructive outside viewpoint . . . with the assurance that confidence will not be violated—that private plans, processes or designs will not be disclosed or diverted into competitive reach.

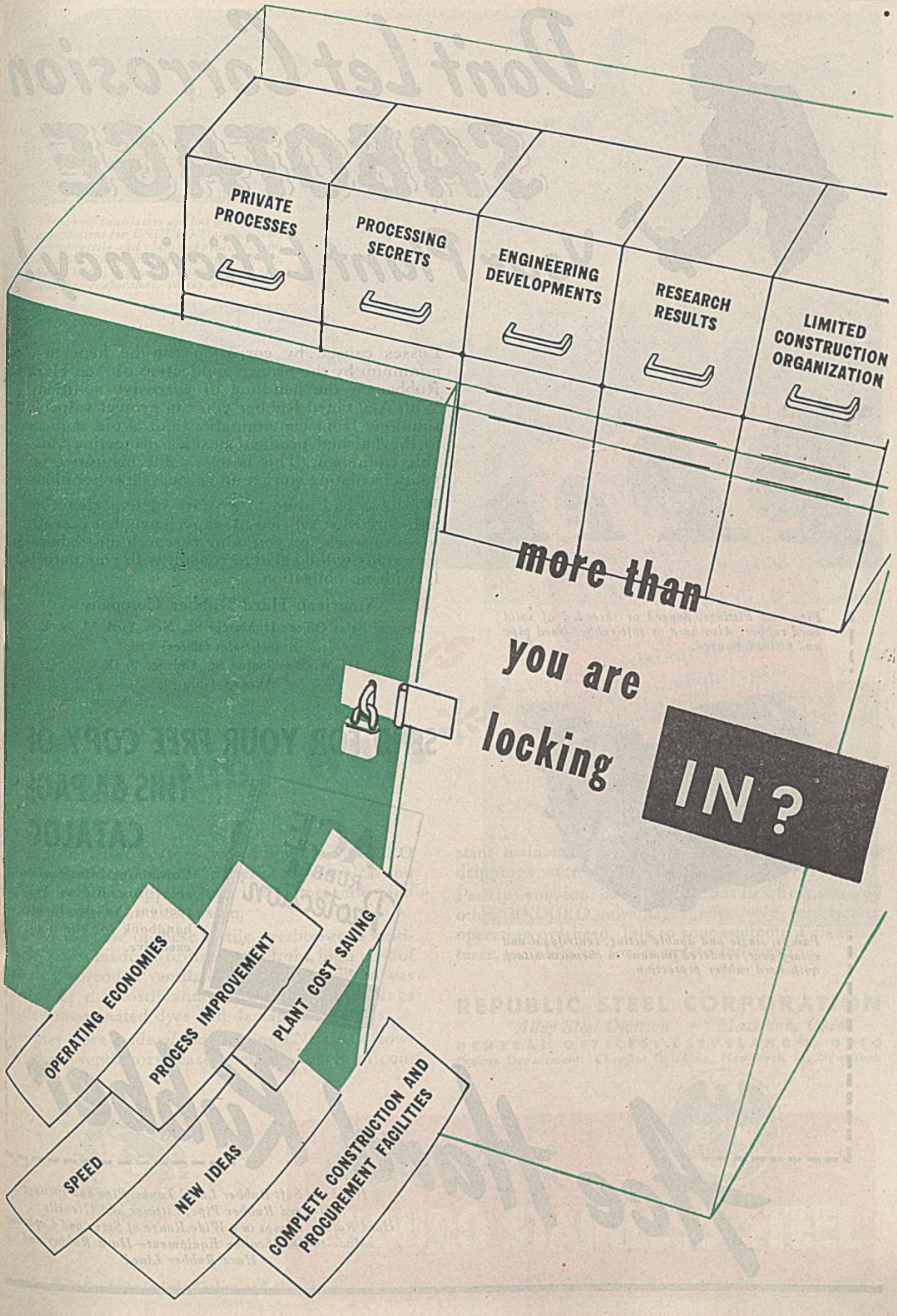
Badger's broad cumulative experience and constantly developing engineering methods can provide a fresh approach to old as well as to new problems . . . and the Badger design and construction organization is experienced in efficient co-ordination with its customers.

Making new processes work efficiently in large-scale production, improving designs and decreasing operating costs, saving time and initial plant costs . . . these are some of the pay-offs Badger has achieved for many a client.

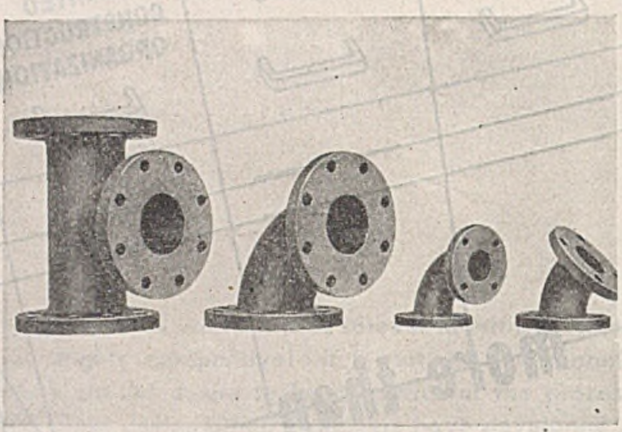
More and more important concerns are finding out that *they* have often locked out more than they have locked in. Have *you?*

E. B. Badger & SONS CO. Est. 1841
BOSTON 14 • NEW YORK
SAN FRANCISCO • LONDON

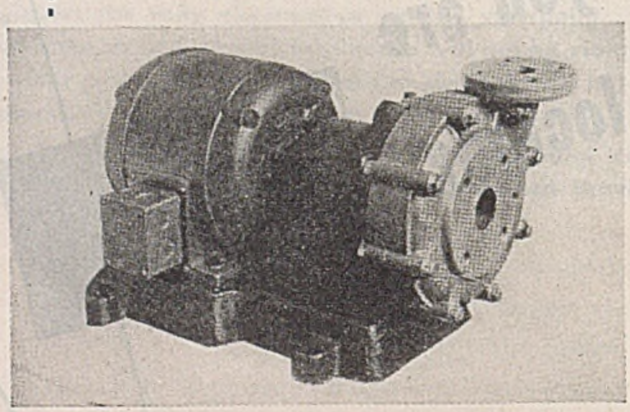
PROCESS ENGINEERS AND CONSTRUCTORS FOR THE
CHEMICAL, PETRO-CHEMICAL AND PETROLEUM INDUSTRIES


PRIVATE PROCESSES
PROCESSING SECRETS
ENGINEERING DEVELOPMENTS
RESEARCH RESULTS
LIMITED CONSTRUCTION ORGANIZATION
more than
you are
locking
IN?
OPERATING ECONOMIES
PROCESS IMPROVEMENT
PLANT COST SAVING
SPEED
NEW IDEAS
COMPLETE CONSTRUCTION AND PROCUREMENT FACILITIES

Don't Let Corrosion SABOTAGE Your Plant Efficiency!



Pipe and Fittings, flanged or threaded of solid hard rubber. Also hard or soft rubber lined pipe and fittings, flanged.



Pumps, single and double acting, centrifugal and rotary gear, rendered immune to chemical attack with hard rubber protection.

Losses caused by corrosion can be kept to a minimum by the proper application of Ace Hard Rubber in the handling of corrosive solutions. With Ace Hard Rubber you can protect valuable solutions from contamination and avoid damage to the finished product, besides protecting valuable equipment. This is invaluable insurance for your circulating, storage and processing operations.

We have had almost 75 years of experience in anti-corrosion service . . . experience that is ready to go to work for you. Our research and laboratory staffs will be glad to consult with you, natually with no obligation.

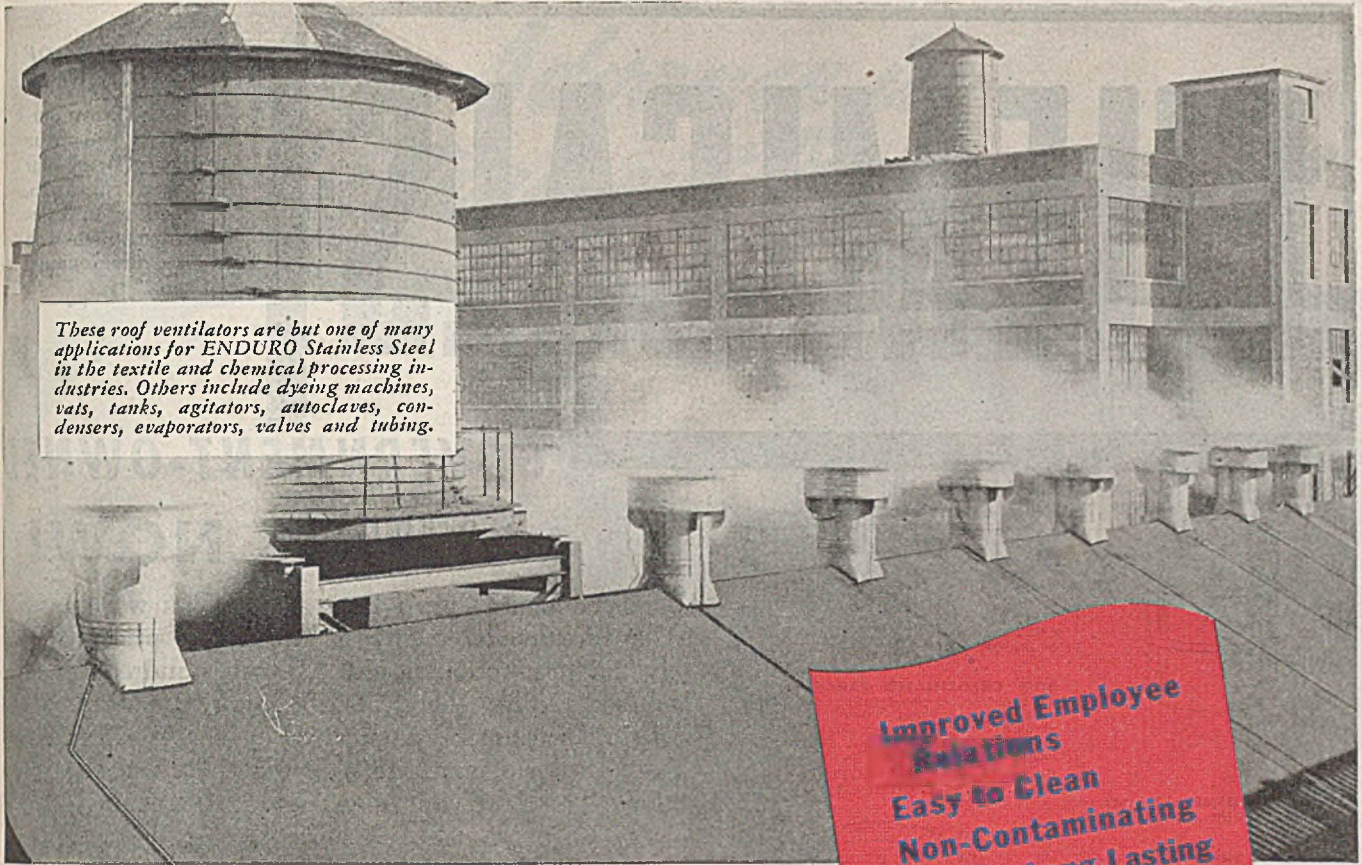
American Hard Rubber Company
General Sales Office: 11 Mercer St., New York 13, N. Y.
Branch Sales Offices:
111 W. Washington St., Chicago 2, Ill.
Akron 4, Ohio

SEND FOR YOUR *FREE* COPY OF THIS 64 PAGE CATALOG

Containing information about Ace Rubber Protection. An invaluable handbook for the plant executive.

Ace Hard Rubber

Hard and Soft Rubber Lined Tanks, Pipe and Fittings
All-Hard Rubber Pipe, Fittings and Utensils
Hard Rubber Pumps in a Wide Range of Sizes and Capacities
Made-to-Specification Equipment—Hard Rubber and Hard Rubber Lined



These roof ventilators are but one of many applications for ENDURO Stainless Steel in the textile and chemical processing industries. Others include dyeing machines, vats, tanks, agitators, autoclaves, condensers, evaporators, valves and tubing.

Improved Employee Relations
Easy to Clean
Non-Contaminating
Strong—Long Lasting
Resistant to Rust and Corrosion
Resistant to Heat
Easy to Fabricate
Universal Acceptance
Low Ultimate Cost

Enduro Pays
in many ways

Among the major reasons why Republic ENDURO Stainless Steel is a "natural" material for chemical and textile processing applications is its inherently high resistance to rust and corrosion.

Consider the case of these textile dyeshop roof ventilators. When made of ordinary steel, the high cost of replacing corroded ventilators every six months was dwarfed by the costly annoyance of rusty drippings which contaminated dyes and damaged materials.

After they were made of long-lasting ENDURO, however, these ventilators ceased being a source of constant maintenance and replacement expense. Rusty drippings were ended.

Perhaps you, too, have applications in which this and other ENDURO advantages effectively can reduce operating overhead. Talk to your equipment manufacturer, or write us for complete information:

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

MID AMERICA EXPOSITION CLEVELAND

Republic
ENDURO STAINLESS STEEL
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REPUBLIC STEEL SERVES THE WORLD

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

CHEMICALS

VETERANS OF WORLD WAR II:
To help you in purchasing surplus property from War Assets Corporation, a veterans' unit has been established in each of our Regional Offices*.

GOVERNMENT-OWNED SURPLUS NOW!

The chemicals shown here are surplus war material. They are available now at quick sale prices to meet civilian production needs. As with hundreds of other similar surplus chemicals they may be obtained by writing, wiring, or phoning your nearest War Assets Corporation office*. Make it *your* habit to check this source whenever your stock needs replenishing.

**In directories simply look up Reconstruction Finance Corporation. War Assets Corporation is an R.F.C. subsidiary.*

HYPOCHLORITE BLEACH—one year old material; manufactured with 30% available chlorine; grade 3; available as follows for 1½ cents per pound in carload lots; (F.O.B. location).

Birmingham — 305,600 lbs. in 400 lb. drums. Also one carload of grade 2, packed in 100 lb. drums.

Salt Lake City—8,785,572 lbs. in 43 and 50 lb. steel drums.

40% CHLORINATED PARAFFIN for fire proof, water proof and mildew proof coatings. Approximately 9 million pounds available for 2 cents per pound in car load lots or total amount at a single location, F.O.B. location as follows:

Boston, Cleveland, Detroit, Philadelphia, Richmond and Salt Lake City

MIXED XYLIDINES; 7 cents per pound, carload lots, F.O.B. location.

POTASSIUM SULPHATE available for 10 cents per pound, F.O.B. location as follows:

Minneapolis: 93,075 lbs. in 400 lb. (app.) wooden barrels.
Chicago: 53,355 lbs. in 35 lb. fiber drums.

CHECK AND MAIL TODAY

To War Assets Corporation:

Without obligation, please send me further information on the following products and place my name on your regular mailing list:

☐ Glacial Acetic Acid, C.P. in one gal. bottles.
☐ Copper Napthenate, 8% solution in drums.
☐ Sodium Sulphite
☐ Manganous Chloride
☐ Smokeless Powder
☐ D.N.T. (Dinitrotoluol)
☐ Silica Gel; in various small size fabric bags weighing from 15 grams to 10 lbs. each.
☐ Khaki Dyes (basic colors)

Firm……………………………………………………………………………

Street……………………………………………………………………………

City…………………………………………State…………………………

155-2

PAINTS

OIL TYPE, READY MIXED PAINT—SPEC. T-1215

Ready for use. This paint, containing linseed oil, may be brushed or sprayed to produce a flat finish which dries in a few hours. It is well suited to both interior and exterior walls wherever a medium grade low cost paint is permissible. It may be applied to wood, brick, masonry or concrete.

FOR INDUSTRIAL USES

Warehouses
Office Buildings
Shops & Garages
Housing
Fencing
Factories

COLORS

Light Green
Dark Green
Field Drab
Earth Yellow
Earth Brown
Sand
Olive Drab
Loam
Earth Red
Haze Gray
Black
White

For detailed information contact any of the War Assets Corporation Regional Offices below:
Price: 65 cents per gal., F.O.B. location; minimum sale, 200 gallons.

A DISPOSAL AGENCY DESIGNATED BY THE SURPLUS PROPERTY ADMINISTRATION for Surplus Producers' and Capital Goods, Aircraft and Plants formerly handled by Reconstruction Finance Corporation and for Surplus Consumer Goods formerly handled by United States Department of Commerce.

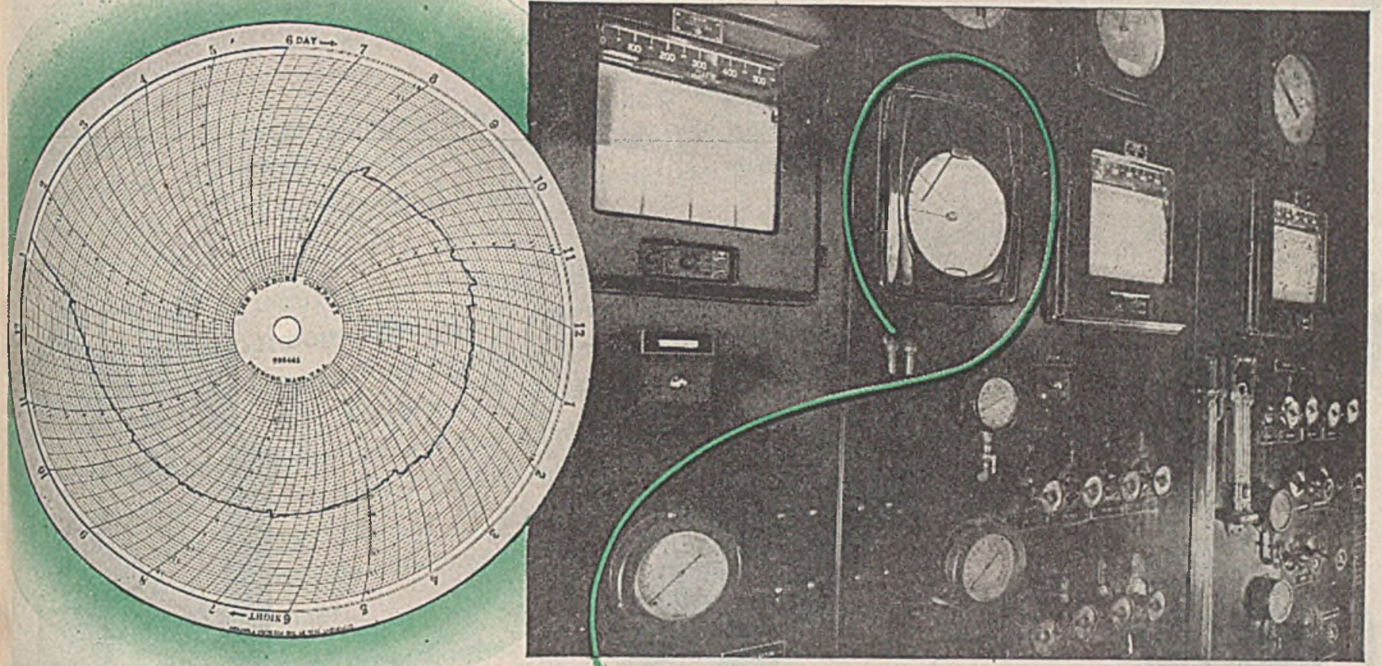
WAR ASSETS CORPORATION

(A SUBSIDIARY OF RECONSTRUCTION FINANCE CORPORATION)

RFC OFFICES (INCLUDING FORMER DEPARTMENT OF COMMERCE REGIONAL SURPLUS PROPERTY OFFICES) LOCATED AT: Atlanta • Boston • Chicago • Denver • Kansas City, Mo. • New York • Philadelphia • San Francisco • Seattle • OTHER RFC SURPLUS PROPERTY OFFICES LOCATED AT: Birmingham • Charlotte • Cleveland • Dallas • Detroit • Helena • Houston • Jacksonville • Little Rock • Los Angeles • Louisville • Minneapolis • Nashville • New Orleans • Oklahoma City • Omaha • Portland, Ore. • Richmond • St. Louis • Salt Lake City • San Antonio • Spokane • OTHER FORMER DEPARTMENT OF COMMERCE REGIONAL SURPLUS PROPERTY OFFICES LOCATED AT: Cincinnati and Fort Worth

155-3

3-Way Advance in Instrument Performance!



One of many recent DYNALOG installations. It gives speedy, accurate temperature records on chart with full-width range of only 12° C.

Only DYNALOG* Instruments Give This Combined

SPEED

Almost instantaneous! Only 3 seconds for full-scale travel of pen or pointer.

ACCURACY

¼ of 1% of scale for all ranges.

SENSITIVITY

So high that full calibration accuracy is maintained, even for extremely narrow scales.

Until the development of Foxboro's *DYNALOG* Instruments, you could not get industrial bridge-type instruments with this unique combination of performance characteristics!

The reason is: *DYNALOG* Instruments were specifically designed as *electronic instruments* . . . not merely supplemented by electronic improvements. In them, electronic circuits permit complete replacement of usual slide-wire mechanisms with a simple variable capacitor. Moving contacts are entirely eliminated!

Further, wholly-electronic design also replaces customary rotary drive-motors with a simple push-pull magnetic motor. Positive dynamic balancing is supplied, automatically, on bridge-unbalance voltages of less than 15 microvolts!

These are only high-lights of *DYNALOG* Recorders and Multi-Point Indicators. If your process demands unusually-exacting thermal measurements, call in a Foxboro Engineer. Or write for detailed information. The Foxboro Company, 40 Neponset Ave., Foxboro, Mass., U.S.A.

* Reg. U. S. Pat. Off.

FOXBORO
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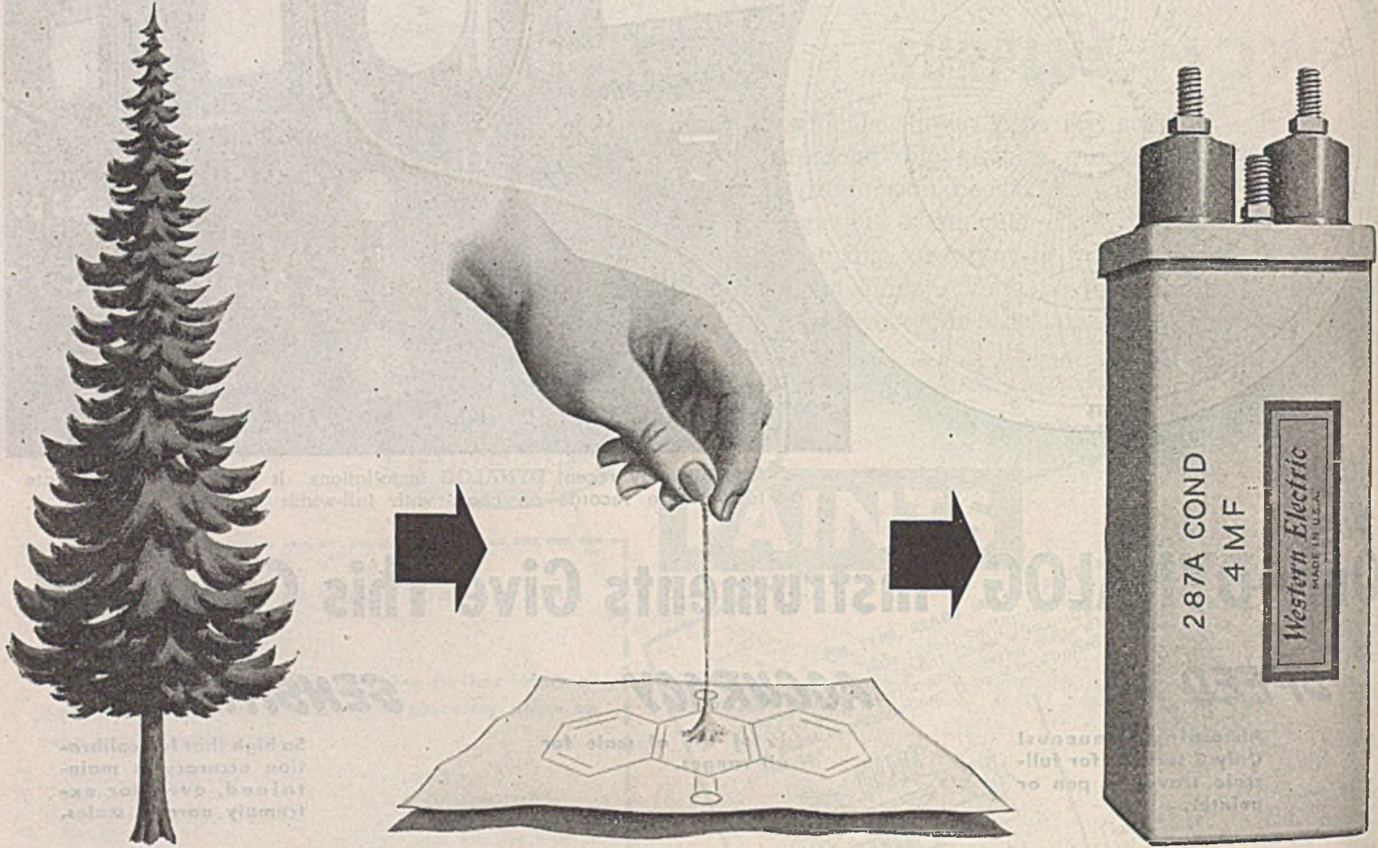
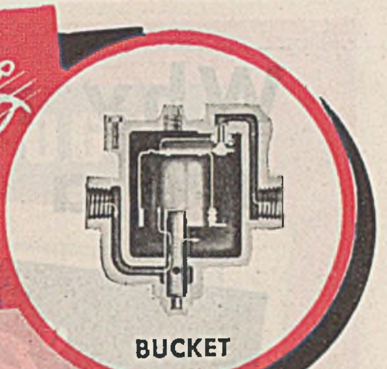
ELECTRONIC INSTRUMENTS


287A COND
4 MF
Western Electric
MADE IN U.S.A.

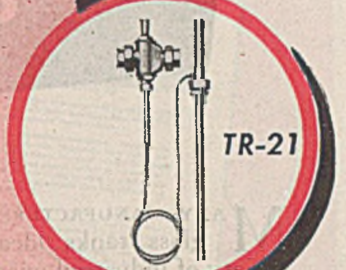
WHAT MESSAGE HAS THIS TANK . . . FOR YOU?

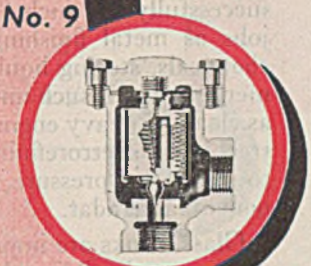


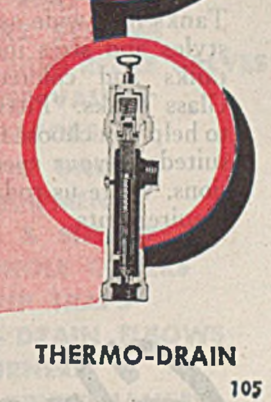
In dozens of industries there are large tanks of liquid which cannot be pumped unless heated. Pumping is at a high rate one minute and then no action at all for hours. The liquids should be pumped at the exact temperatures.

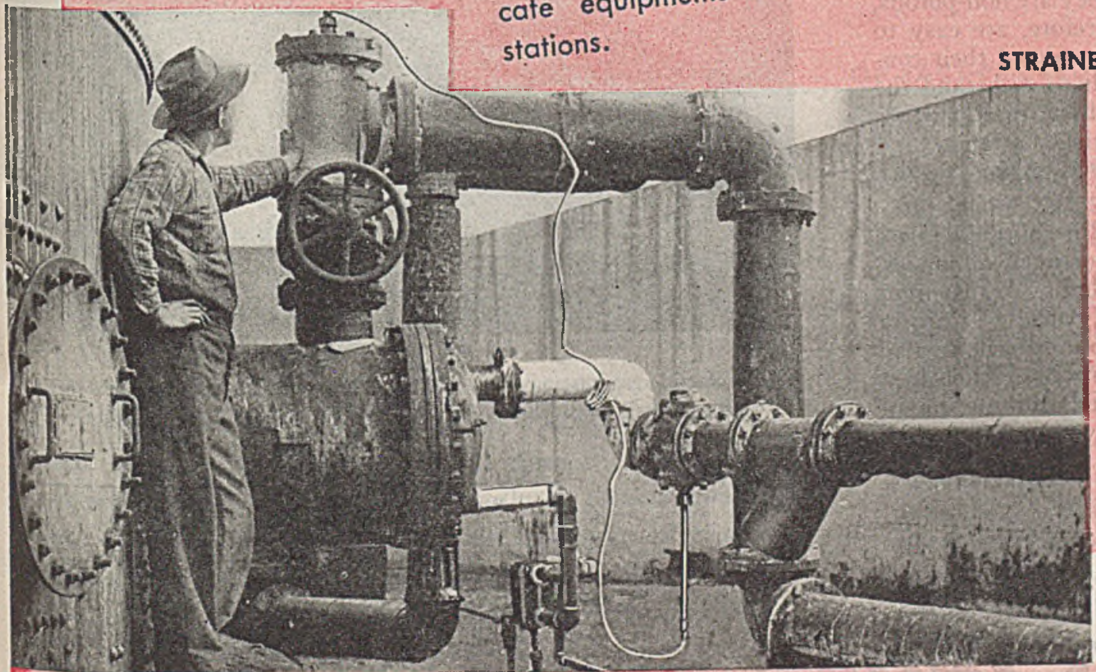
In the fuel oil industry, it's a "must" because false meter readings may occur at temperatures above 120 degrees. So the accurate and reliable Sarco TR-21 temperature regulator is hooked up to a nest of fin type heating coils inside the tank and of sufficient surface to heat the oil as it flows. The regulator valve is protected by a Sarco strainer. Condensate is removed from the heater coils by a Sarco bucket steam trap fitted with a Sarco Thermodrain set at 40 degrees to prevent freezing. Steam supply line is dripped by a Sarco No. 9 thermostatic steam trap with a Sarco ¾" strainer.

It's a message of co-ordinated efficiency. Seven different, but "blood related" Sarco products working together on one job and the cost according to the manager is already forgotten because of the improved service. They are ordering duplicate equipments for other distributing stations.









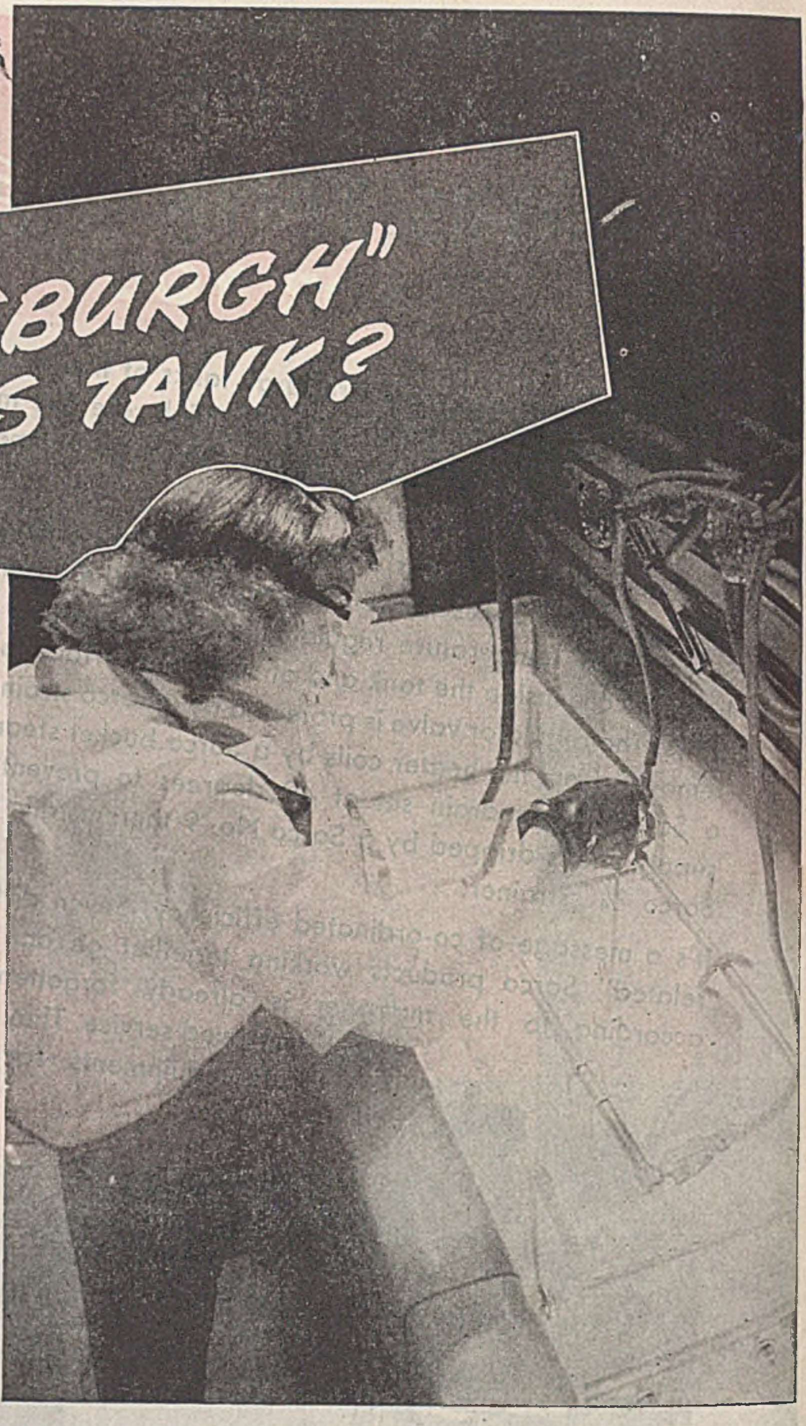
105

FOUR STARS
ON OUR E PENNANT
TESTIFY TO SARCO
PERFORMANCE
IN THE WAR EFFORT

SARCO SAVES STEAM

Represented in Principal Cities

SARCO COMPANY, INC., 475 FIFTH AVE., NEW YORK 17, N.Y. • Sarco Canada, Ltd., 85 Richmond St., W., Toronto 1, Ont.



A manufacturer speeds up production of electronic equipment with the help of Pittsburgh Glass Tanks. The tanks resist the acid and stop electric losses.

Why not use a "PITTSBURGH" GLASS TANK?

Many manufacturers are finding glass tanks ideal for a wide variety of industrial operations. "Pittsburgh" Glass Tanks have been used successfully for such "run-of-the-mill" jobs as metal finishing, compounding chemicals, storing liquids, making cosmetics, and for such unusual operations as cleaning heavy engine parts, pickling steel bars, electrorefining of copper and to check air pressure in several components for radar.

Glass Tanks are impervious to acids, alkalis, nearly all liquids, including even hot chromic acid. They are non-porous, non-absorptive; therefore, are easy to clean and don't contaminate their contents. They are built to withstand the shock of sharp temperature changes and they have the rugged strength and sturdiness which mean long service under hard usage.

You can get "Pittsburgh" Glass Tanks in a wide assortment of shapes, styles and sizes including transparent tanks and colored, opaque Carrara Glass Tanks. "Pittsburgh" will be glad to help you choose the Glass Tanks best suited to *your* special working conditions. Write us today about your tank requirements.

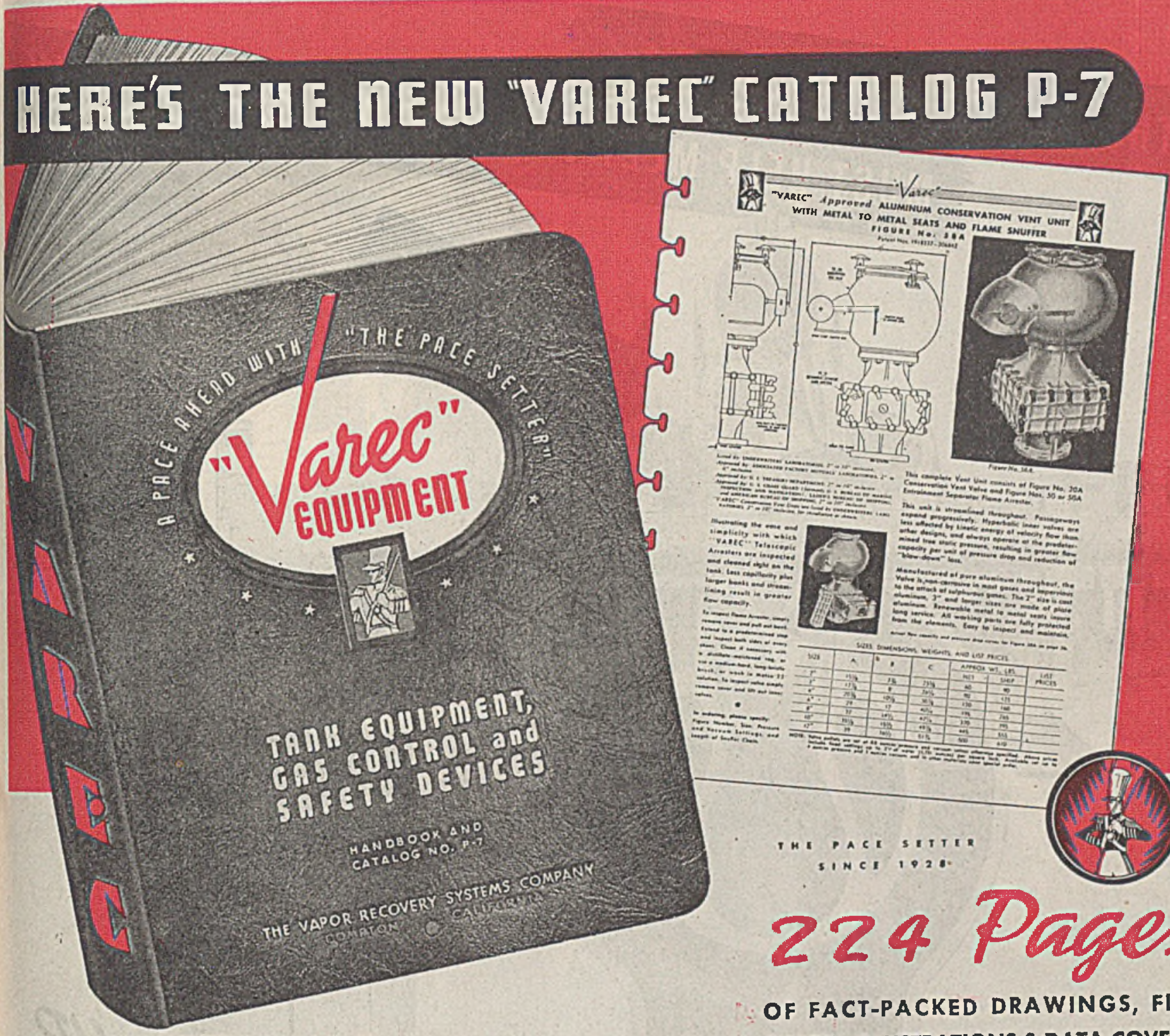
Pittsburgh Plate Glass Company
2102-6 Grant Building, Pittsburgh 19, Pa.
Please send me, without obligation, your free folder giving full details about Glass Tanks by "Pittsburgh."
Name____________________________
Address__________________________
City________________ State__________

Glass Tanks

"PITTSBURGH" stands for Quality Glass and Paint

PITTSBURGH PLATE GLASS COMPANY

HERE'S THE NEW "VAREC" CATALOG P-7



THE PACE SETTER
SINCE 1928

224 Pages

OF FACT-PACKED DRAWINGS, FLOW-CHARTS, ILLUSTRATIONS & DATA COVERING:

- ✓ FLAME ARRESTERS
- ✓ PRESSURE RELIEF VALVES
- ✓ CONSERVATION VENT VALVES
- ✓ VAPOR RECOVERY SYSTEMS
- ✓ PRESSURE & VACUUM RELIEF VALVES
- ✓ EXPLOSION RELIEF VALVES
- ✓ PRESSURE REGULATORS
- ✓ AUTOMATIC TANK GAUGES
- ✓ SWING LINE EQUIPMENT
- ✓ TANK WINCHES & SHEAVES
- ✓ GAUGE & MANHOLE COVERS
- ✓ SEDIMENT & DRIP TRAPS
- ✓ MANOMETERS — DRAIN ELBOWS
- ✓ WASTE GAS BURNERS
- ✓ OTHER TANK APPURTENANCES

Ever on the alert to constantly improve the design of tank equipment, "VAREC" takes full advantage at all times of every proved advance in technological research, manufacturing methods, and material of construction. Here's the information brought up to date with drawings, illustrations, descriptions, and engineering data on all "VAREC" Products so that your specific requirement can be determined at a glance. "VAREC" fact-packed P-7 Catalog and Handbook shows clearly what "VAREC" Equipment to use and how, why, and where—also incorporated is a corrosion table covering approximately 120 chemicals and products and the metals most suitable for use under various conditions.

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THE VAPOR RECOVERY SYSTEMS COMPANY
COMPTON · CALIFORNIA

Consultants, Designers, & Manufacturers of Gas Control & Tank Equipment

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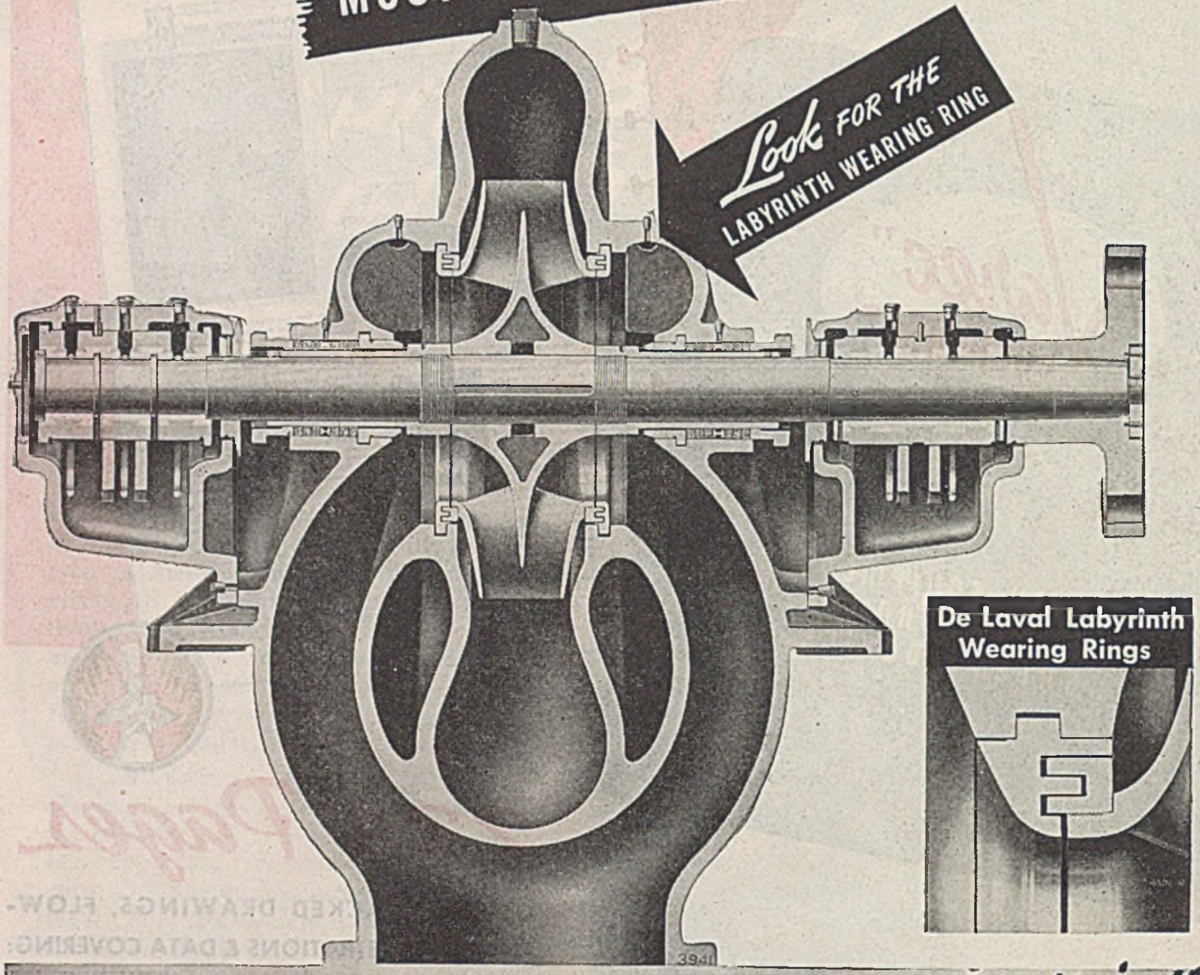
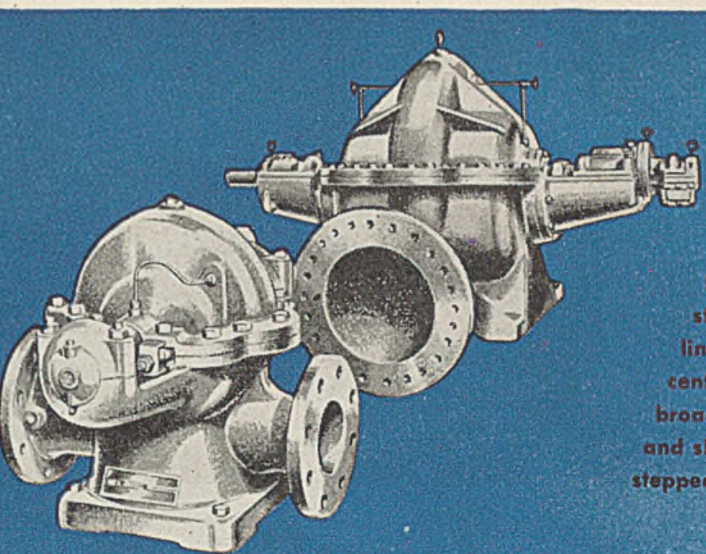
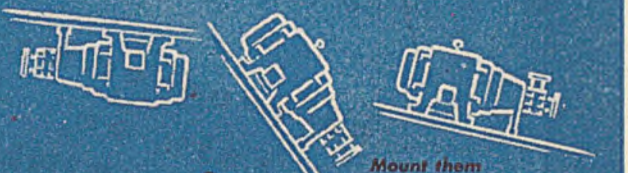

Look FOR THE
LABYRINTH WEARING RING
De Laval Labyrinth
Wearing Rings
3941

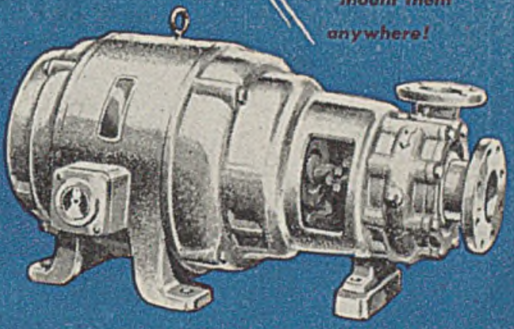


The older they are the farther they fall in attempting to meet standards that are being set by the line of Fairbanks-Morse split-case centrifugal pumps. Here's a line that's broad enough to include the type and size which most closely meets your stepped-up needs.

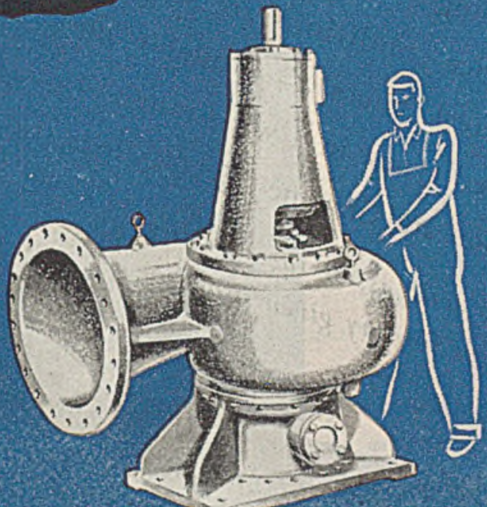
Time to Forget . . . and Remember!

Now is the time to forget your old pumps whose efficiency is that of a bygone era and whose daily services are costing you money! Remember—pumps are commonly designed and built to answer specific conditions of head and capacity: When these conditions change, the increase in pumping costs may be appreciable.





Replace tired-out, hard-to-get-at pumps with Fairbanks-Morse Builtogether pumps—packaged units, with pump and motor on a single shaft. Used industry-wide, they move up to 1200 gallons per minute at heads up to 260 feet.



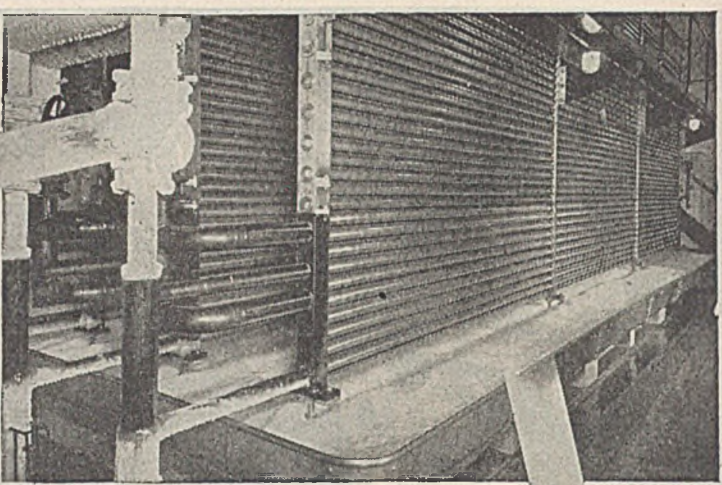
Name your pumping job— there's a modern Fairbanks-Morse "high-efficiency" pump ready to handle it. For instance, the line of vertical Angle-Flow pumps for moving lots of water—up to 80,000 g.p.m.—at a cost that, even compared with modern standards, is extremely low.

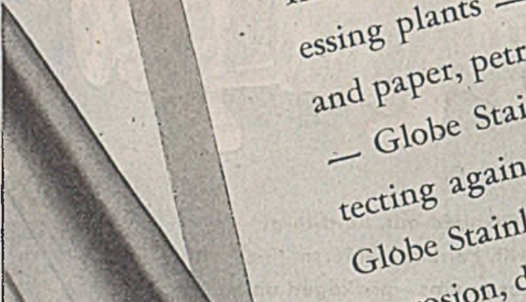
Three famous names— Fairbanks-Morse, Pomona and Westco are gilt-edged evidence that when you see your Fairbanks-Morse dealer or call at your Fairbanks-Morse branch office, you're taking the right step toward lowest liquid-moving costs.

FAIRBANKS-MORSE

A name worth remembering

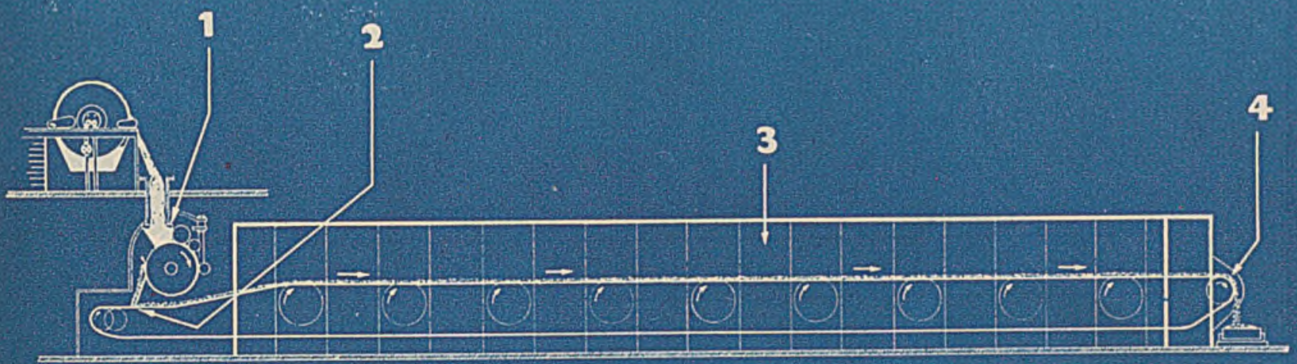
DIESEL LOCOMOTIVES • DIESEL ENGINES • MAGNETOS • GENERATORS • MOTORS • PUMPS
SCALES • STOKERS • RAILROAD MOTOR CARS and STANDPIPES • FARM EQUIPMENT





PROCTOR *Aero-Form* DRYER

with Fin Drum Feed—Speeds Output of CALCIUM CARBONATE



ONE OF MANY TYPICAL APPLICATIONS FOR THIS MODERN CONTINUOUS DRYING SYSTEM

1. Calcium carbonate is delivered from continuous filter to hopper of fin drum feed of dryer with moisture content of approximately 110% (B.D.W.B.*).

2. Partially dried on fin drum feed, material is pre-formed, into small sticks of uniform size and thickness and discharged to conveyor of dryer.

3. Loaded to a uniform depth on moving conveyor, material passes through 9-unit dryer. Temperatures begin at 270°F. in first compartment, increase to 280°F. in second compartment and to 290°F. in third compartment.

4. Calcium carbonate, uniformly dried, is discharged from dryer with moisture content of 0.25% (B.D.W.B.), at the rate of 2,750 lbs. (C.D.W.†) per hour.

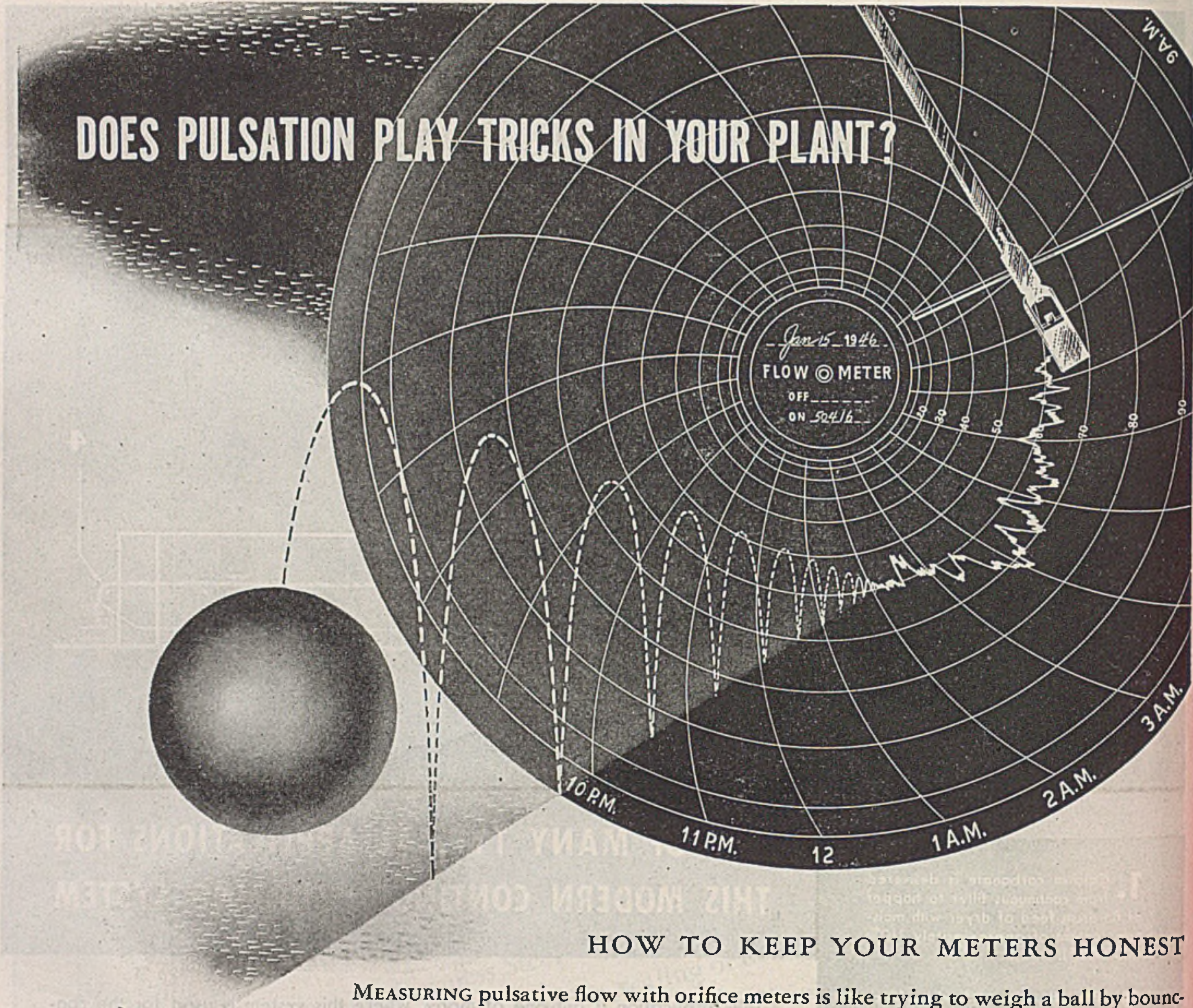
*Bone Dry Weight Basis
†Commercial Dry Weight.

Close-up of "fin drum sticks" shows form in which material enters dryer ...allowing through-circulation.

This application is but one of many, where this system is used for the continuous drying of wet-solids. In each case, the material comes to the feed hopper after mechanical dewatering. It is then pressed, by means of rollers, into the grooved surface of the internally heated, revolving fin drum which forms the feeding device. In this way, the material is dried sufficiently to be discharged, from the drum, to the conveyor of the dryer in the form of small sticks—of uniform thickness. It is then possible to circulate heated air *through* the bed of material on the conveyor and rapid, uniform, thorough drying results. This particular pre-forming and drying system may or may not be suited to the physical characteristics of your product. However, it demonstrates what we mean when we say Proctor drying systems are scientifically engineered to meet individual plant and product requirements. This system—in fact every Proctor system in operation—was installed only after it was conclusively proven in the laboratory that it was the ideal system for the individual problem. Proctor engineers may well save you hours of production time and reduce your costs materially—if you let them consider your drying problem today!

P&S

PROCTOR & SCHWARTZ · INC ·
SEVENTH STREET and TABOR ROAD · PHILADELPHIA 20 · PA ·



HOW TO KEEP YOUR METERS HONEST

MEASURING pulsative flow with orifice meters is like trying to weigh a ball by bouncing it on the scales. Downward-upward thrusts give inaccurate readings . . . they happen so fast the measuring instrument can't keep up with them. To keep your orifice meters honest, pulsative flow must be converted into a steady stream. The FLUOR Pulsation Dampener is the practical answer to this problem.

For example — a large Eastern Gas Company pumps gas into underground storage during the summer and withdraws it during the winter when consumer load is heaviest. As storage reservoir pressure drops, it becomes necessary to compress the gas to maintain pressure in the mains. Pulsations set up in the gas stream by the compressors threw the meters off by such substantial amounts that the Company was unable to determine how much gas was being pulled out of the reservoir. FLUOR Pulsation Dampeners installed in the suction lines between the meters and compressors eliminated this condition and made accurate measurement possible.

The FLUOR Pulsation Dampener changes pulsative flow into smooth, steady flow . . . with beneficial effect on frictional losses, horsepower savings and rate of flow. If vibration plays *tricks* in *your* plant, it may be due to pulsations in air, gas or vapor lines. In that case, the FLUOR Pulsation Dampener is your answer.

fc
SINCE
1890

FLUOR PULSATION DAMPENER

THE FLUOR CORPORATION, LTD. 2500 South Atlantic Boulevard, Los Angeles 22
NEW YORK • PITTSBURGH • KANSAS CITY • HOUSTON • TULSA • BOSTON

ENGINEERS • MANUFACTURERS • CONSTRUCTORS

TO HELP YOU OVERCOME YOUR INSULATION PROBLEMS

Methods of applying insulation have progressed so rapidly that many changes and advancements have taken place in just the past few months. These most recent advancements have revealed new ways of making insulation more efficient and longer-lived (Amosite asbestos fibres have been found to afford more resilient strength and lower conductivity) at lower applied cost (sectional insulation is now available for large size piping and you can use one insulation in single-layer construction to 1200°).

AN UNBIASED REPORT IS YOURS FOR THE ASKING . . . all recommendations will be backed up by technical reports, K factor charts and actual operating figures on piping that is similar to your own.

FILL IN, TEAR OFF, AND MAIL

UNION ASBESTOS
MEANS PROGRESS IN INSULATION
AND RUBBER CO.

A nationwide organization of Field Engineers, qualified distributors and contractors — strategically located to most effectively serve you.

UNION ASBESTOS & RUBBER COMPANY
1821 SOUTH 54TH AVENUE • CICERO 50, ILLINOIS

Gentlemen: Send me the latest data and technical information on the following. No obligation on my part, of course.

PIPING

LENGTH OF RUN________
PIPE SIZE________ EXPANSION JOINTS________ BENDS________
TEMPERATURE________ INDOOR ☐ OUTDOOR ☐
FLANGES________ FITTINGS________
BOILER FEED PIPING________

BOILERS

PRESSURE________
TEMPERATURE________ BOILER WALLS________
SETTINGS________ FLUES________
DRUMS________ HEADERS________

TANKS, VESSELS AND EQUIPMENT

RECEIVERS________
HEATERS________ EVAPORATORS________
LARGE OUTDOOR TANKS AND VESSELS________

REMARKS

*Position*________
*Name*________
*Company*________
*Address*________
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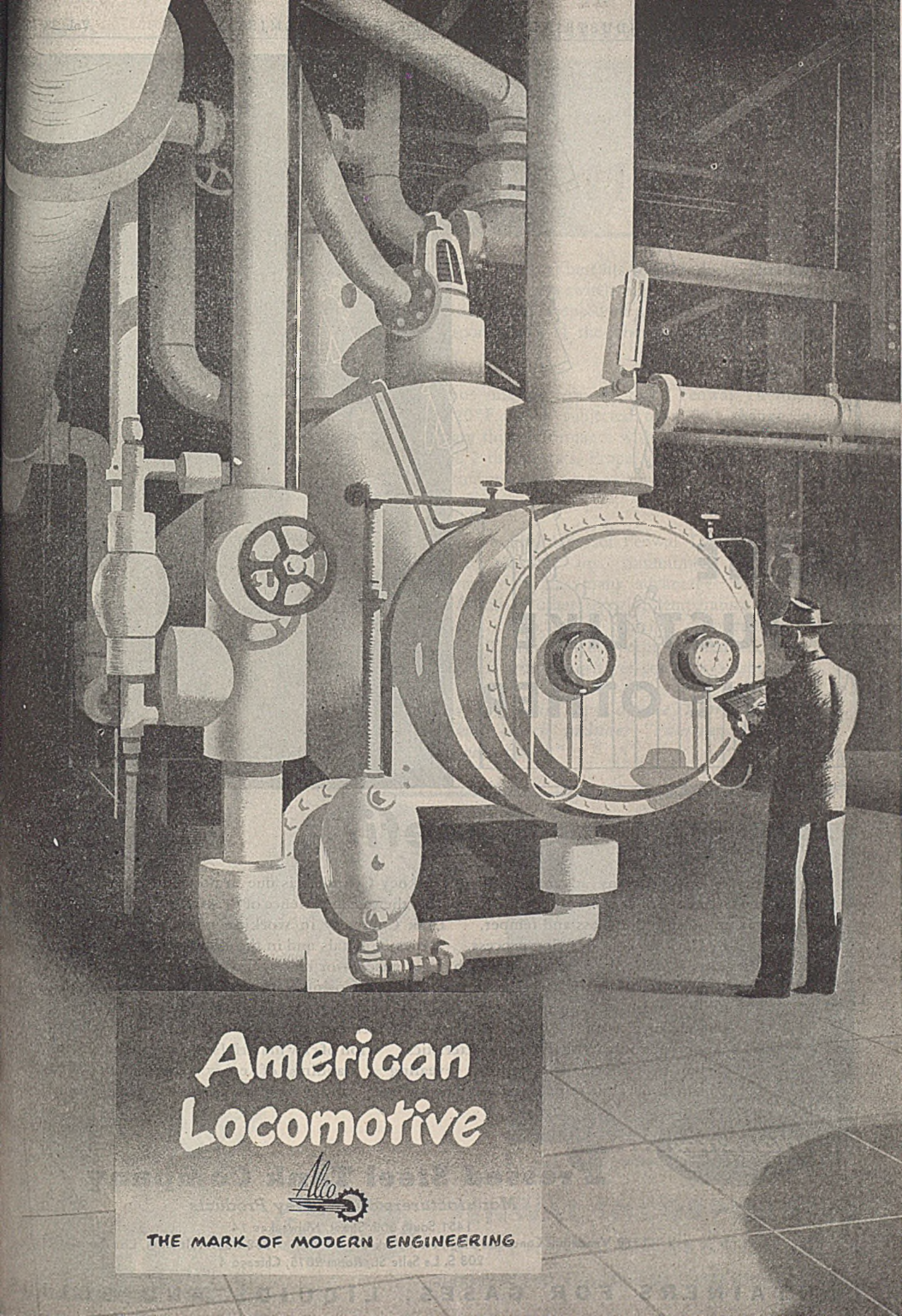
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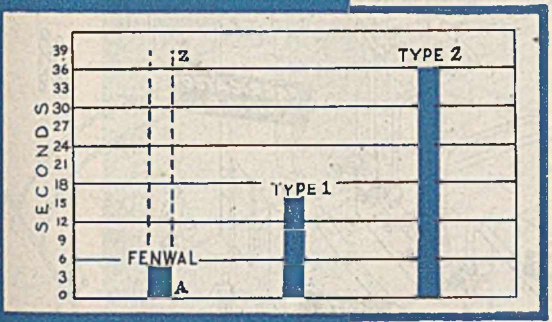

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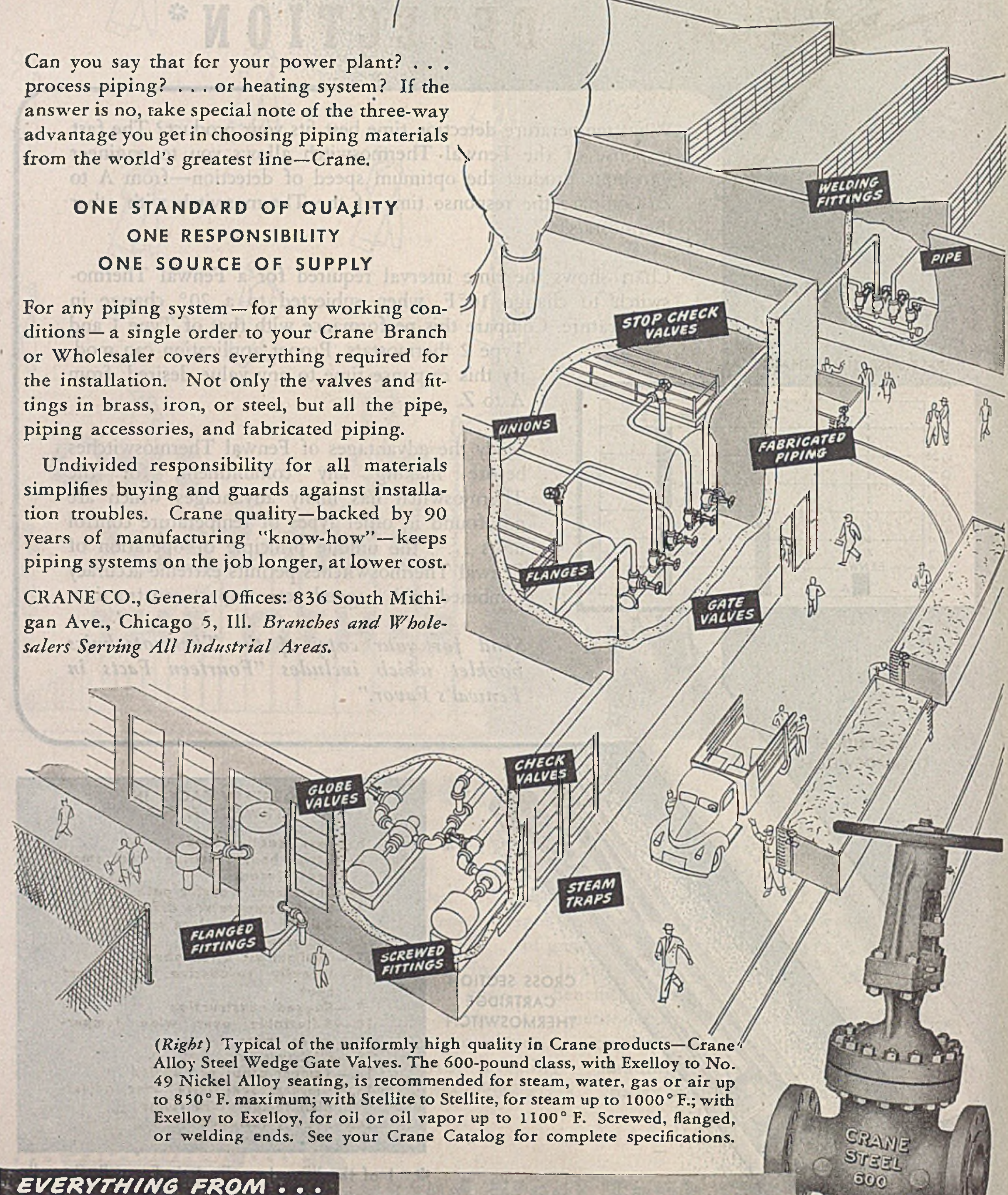

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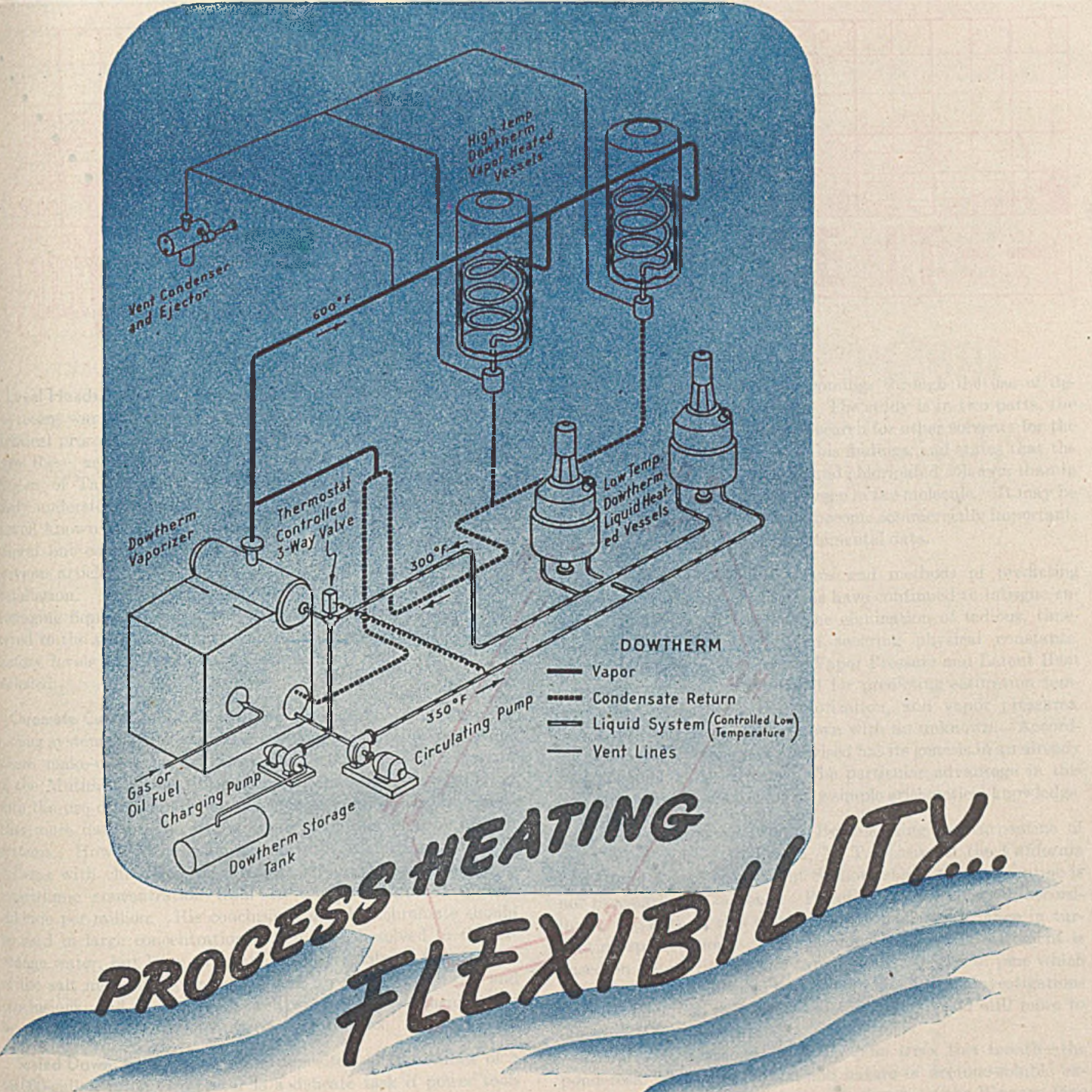
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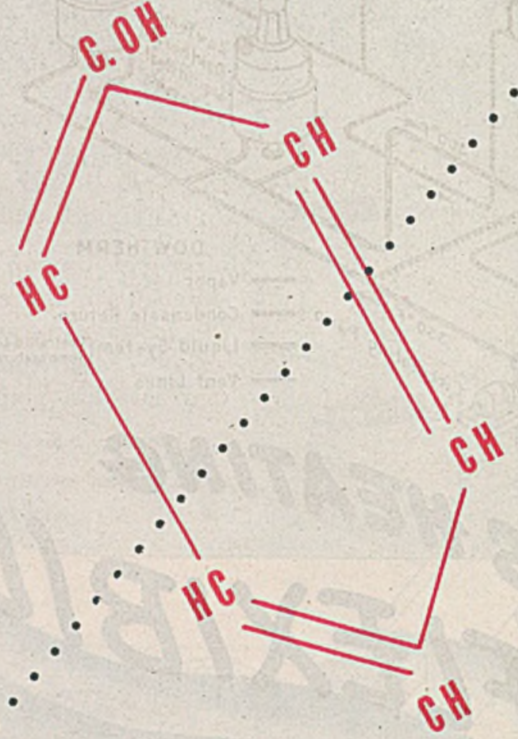
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AS WE SEE IT- -

Level Heads. Out of the enormous construction program of the recent war will come new and perfected techniques for every chemical process plant. One of the fields that benefited greatly from these activities is that of automatic control, and from Ziegler, of Taylor Instrument Companies, we have snared an easily understood article on the control of liquid level. Ziegler is well known to instrument engineers, and the users of these helpful but complicated mechanisms have often turned to his previous articles for help on the tougher problems of instrument installation. In this article he tangles with the mysteries of averaging liquid level control. Ziegler explains, with equations keyed to the sensitivity of the controller, how to maintain satisfactory levels in columns and tanks. Numerical examples are included.

Chromate Cures Chloride Corrosion. Recirculation of water in cooling systems has its own little problem of corrosion, especially where make-up water is heavy with chloride salts. Darrin, of the Mutual Chemical Company of America, long associated with the use of chromate salts as corrosion inhibitors, now supplies more data on the use of these chemicals in recirculation systems. However, he examines only the protection of ferrous systems with chromate for a series of four waters—ranging in logarithmic concentration from 10 to 1000 parts of sodium chloride per million. His conclusions are that chromate should be used in large concentrations when first dissolved in the exchange water, but later when the protective film is formed, use of the salt may be decreased. There are other conditions and conclusions, and the article is well worth serious consideration by those annoyed with such corrosion problems.

Scaled Down. Removing scale deposited on the tubes of a 50,000-gallon brine evaporator is a delicate task if power tools are used and the tubes are made of soft copper, chances being that the tool will puncture the tube wall. Wasco and Alquist, of The Dow Chemical Company, tell how sodium hydroxide, in certain concentrations and for certain periods, was used for descaling without so much as a nicked tube resulting. In the case under consideration by the authors, two individual treatments with 45% caustic removed 95,000 pounds of calcium sulfate incrustation and improved the performance of the evaporator from a steam condensation rate of 55,000 to 85,000 pounds per hour. The two authors found that the best concentrations of sodium hydroxide were in the range 30 to 50%, and the best working temperatures were above 175° F. Nine heat exchange units were treated by this method, and in all at least 85% of the deposit was removed. In several cases the authors state that all the scale disappeared.

Cotton Wax. In case anyone needs a new wax of medium-high melting point, it will be wise for him to investigate this article by W. H. Tonn, Jr. The fibers of cotton are coated with a thin layer of waxy material, and Tonn, through the use of huge quantities of cotton and a hot benzene extraction, managed to gather about 25 pounds of the material for study. It had a disagreeable odor and a dark color, but Tonn was able to overcome both of these commercial shortcomings through the use of decolorizing and bleaching agents. The study is in two parts, the second reporting on the author's search for other solvents for the wax. He was able to generalize his findings, and states that the wax is more soluble in aromatic and chlorinated solvents than in aliphatic materials containing oxygen in the molecule. It may be that the process at some time will become commercially important, and for that day stand these fundamental data.

Arithmetical Correlation. Means and methods of predicting data by mathematical operations have continued to intrigue engineers since it always means the elimination of tedious, time-consuming laboratory work in securing physical constants. Seglin in an article, Correlating Vapor Pressure and Latent Heat Data, has worked out a method for predicting saturation temperatures, latent heats of vaporization, and vapor pressures, based on a comparison of a known with an unknown. According to the author, the system devised has its genesis in an already well documented procedure. The particular advantage in this new scheme is its demand for only simple arithmetical knowledge.

The Not-So-Lonesome Pine. By analyzing the turpentine of the Coulter pine of California, N. T. Mirov, of the California Forest and Range Experiment Station, shows that turpentine is not necessarily all terpenes. Paraffins are present and, according to the author, this may some day lead to a change in turpentine specifications. The reasoning behind the statement is based on the inevitability of tapping other species of pine which give mixed-type turpentines. More analytical investigations are contemplated, and the data obtained will add still more to our knowledge of oleoresins.

We present a second study on pine trees this month—the ponderosa. The distribution and nature of acetone-soluble extractives are described by Arthur Anderson, of the Western Pine Association, and the paper is part of an extensive study being made of western pines. (This family is becoming quite accustomed to scientists poking around its interior, for one of I. & E. C.'s famous editors, Charles Herty, first became noted for his work on the proper method of tapping pine trees for turpentine.)

Salting-in Effect. Ralph H. McKee, of Columbia University, is the author of an industrial article this month on Hydrotropic Solutions in Industry. Hydrotropic solutions, usually of a salt, dissolve more of a slightly soluble material than a similar amount of pure water. In simpler language, it is the opposite of "salting out". McKee sees a great future for the use of the principle, and states that chemical operations may now have the advantage of solvent extraction without the disadvantage of volatile solvents. There is more detail about the future applications in the pulp, dyestuff, and organic chemical industries.

F. S. Van Antwerpen

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INDUSTRIAL AND ENGINEERING CHEMISTRY
Editorials
PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY
WALTER J. MURPHY, EDITOR

The Priestley Medal

AS THE time approaches for the Atlantic City meeting of the American Chemical Society, and the presentation of the Society's highest honor, the Priestley Medal, to the renowned British organic chemist, Sir Ian Morris Heilbron, we are eager to supplement our knowledge of the man for whom America's most outstanding medal in the broad field of chemistry is named. The American Chemical Society is undoubtedly indebted to the late Francis C. Phillips, of the University of Pittsburgh, for first calling the attention of the Pittsburgh Section of the American Chemical Society and later of the national Society, to the serious lack of effort on the part of American chemists to perpetuate the memory of Priestley as a great investigator in the field of chemistry. As a result of his interest and enthusiasm, the Council in April, 1916, appointed a committee to consider a Priestley Memorial and designated Professor Phillips as its chairman. Activities toward raising funds for such a memorial were suspended during World War I and it was not until April, 1922, that the committee presented its final report, and recommended that a medal, to be known as the Priestley Medal, be awarded.

By a bit of coincidence, we have just received from J. V. N. Dorr a copy of Sir Harold Hartley's instructive and entertaining lecture on Priestley, delivered at the Royal Society's rooms March 15, 1933, on the occasion of the bicentenary of the birth of the man whose theological opinions were described rather disparagingly by Samuel Johnson "as tending to unsettle everything and yet settle nothing".

Sir Harold speaks of Priestley, the minister and schoolmaster, as "the great pioneer in pneumatic chemistry, whose discoveries played so important a part in the revolution of chemical thought at the end of the 18th century". The expression "pneumatic chemistry" (meaning the chemistry of gases) rarely, if ever, is used in this country, but we must admit it is a satisfactory generic term.

Priestley's first scientific contribution of any importance was the publication in 1767 of a "History of Electricity". Most of the material was obtained from books belonging to Benjamin Franklin, then in London trying to secure the repeal of the Stamp Act, but in all fairness it should be recorded that Priestley independently contributed a number of remarkable experiments. Later in the same year he moved to Leeds and lived (as he described it) "in a house that was contiguous to a large common brewery". Here he became interested in "fixed air" (carbon dioxide). The first practical result of his early chemical investigations was the invention of soda water.

A study of the phenomena of combustion and respiration in confined volumes of air and observation of the contraction in volume and the vitiation of the air led him to conclude that Nature must have some means for maintaining the purity of the atmosphere. Unfortunately, he could never quite free his mind of the phlogiston theory, and so he let the discovery of oxygen slip through his fingers, not once but several times. Priestley became convinced ultimately that he had obtained a new species of air which he called "dephlogisticated air", because it could, as he claimed, take up more phlogiston than ordinary air, but it was left for Lavoisier to sense that the gas discovered by Priestley was the final clue he needed to explain the theory of combustion.

In 1791 Priestley's chapel was wrecked, his home burned, and his papers and instruments destroyed by a Birmingham mob who feared and hated him for his espousal of liberal ideas and particularly for a pamphlet supporting the principles of the French Revolution. Three years later he came to America and ultimately settled in the little town of Northumberland on the banks of the Susquehanna River in Pennsylvania. Here he remained until his death in 1804.

Unfortunately, Sir Harold's otherwise excellent review does not dwell at any length on Priestley's life and work in America nor on the reason why the name "Priestley" was selected to be associated with the highest award of the American Chemical Society.

Bernard Jaffe's fascinating book "Crucibles" tells of Priestley's discovery of carbon monoxide in 1799, and, as many ACS members know, the first suggestion for a national society was made on July 31, 1874, when the chemists of America assembled in Northumberland to celebrate the one hundredth anniversary of the discovery of oxygen by Joseph Priestley. The idea met with favor, and in 1876 at the Centennial in Philadelphia the American Chemical Society was founded.

The Priestley Medal of the American Chemical Society has always had special international significance. As C. A. Browne pointed out in 1921, in presenting the Priestley portrait at the public meeting of the American Chemical Society in New York, "The hold of Priestley upon the thoughts of English-speaking people is tremendous and it is destined to endure as long as the English language is spoken. He is one of those common possessions, which, belonging to England and America alike, work for unity of thought and feeling." The international aspects of this medal have never been more significant than at this moment when it is being bestowed upon one of Great Britain's foremost chemists.

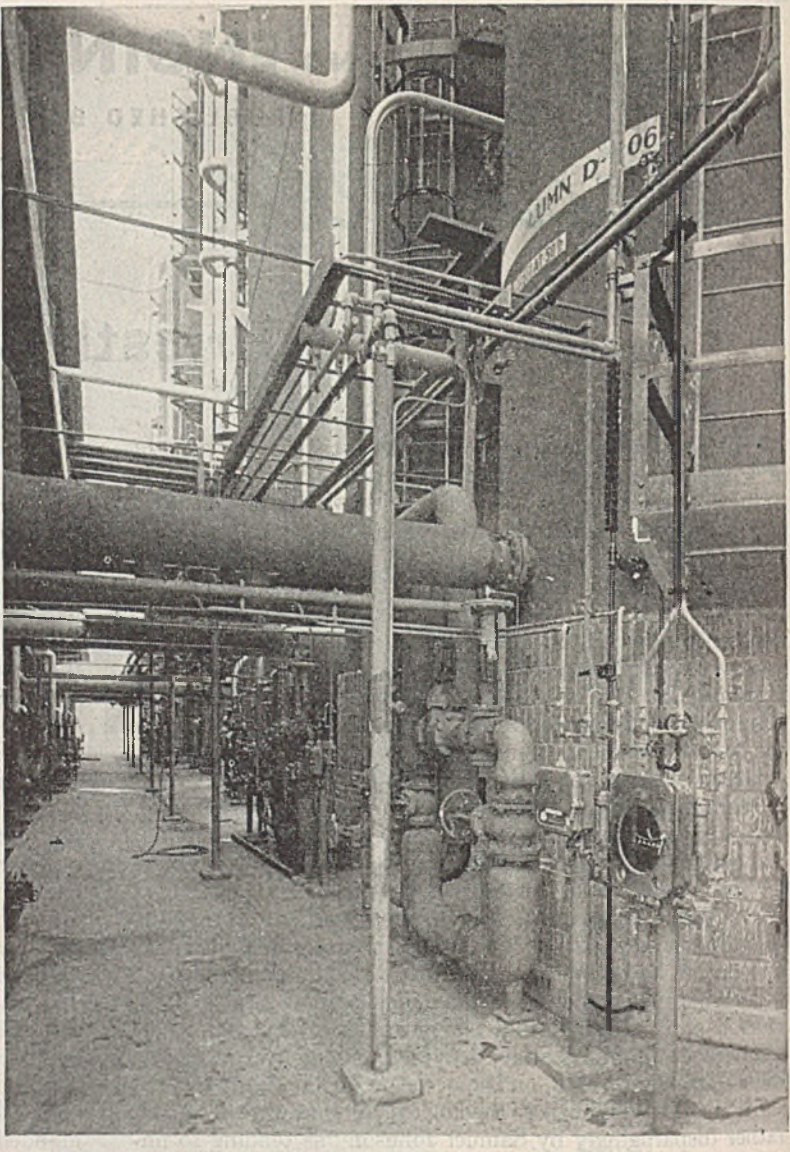
Science advances only when it is free—free from the stifling influences of political and geographical considerations, free from all artificial barriers. Scientists must strive for a world in which knowledge belongs to all peoples—is not withheld by or from any nation or group of nations. When such a philosophy prevails throughout the world, and only then, can we say that we are of "One World".

Momentous decisions in world affairs are about to be reached. Will nations, will world leaders and statesmen, continue to follow the pattern of the past with narrow nationalistic fears and desires, inevitably leading to another world holocaust, or will good sense, good will, mutual trust, and complete understanding at the international level prevail? If the scientists could speak for their respective countries we know what the answer would be. The 1946 Priestley Medal award is a manifestation of the scientists' viewpoint.

AVERAGING LIQUID LEVEL CONTROL

J. G. ZIEGLER
TAYLOR INSTRUMENT COMPANIES
ROCHESTER, N. Y.

A logical method is presented for determining such factors as the required feed tank capacity, the type of instrumentation required, and the probable instrument settings for specific, continuous process installations of averaging liquid level controls. The photograph on this page shows a liquid level controller (right) installed at the base of a large fractionating column. →



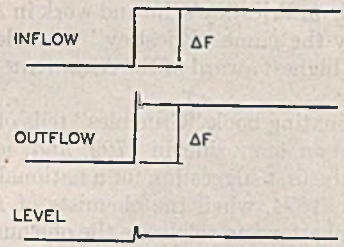


Figure 1. Effect of Flow on Liquid Level in a Fractionating Column

In automatic control of industrial processes the problem is usually one of maintaining a variable as close as possible to some optimum value. The process factors which cause deviations from the desired set point of the controller are the unavoidable variations in process demand called "load changes". When these changes occur, the controller corrects at the expense of a deviation for a certain length of time, and the best settings of the controller responses are those which hold the deviations and their duration to a minimum. But there are examples of automatic control in which deviation of the measured variable is not so detrimental to successful process operation as the abrupt disturbances in flow which a controller can make in correcting for load changes. The most common case of this kind is probably that of surge vessel control.

In the base of a fractionating column it is customary to install a liquid level controller which operates a valve in the line carrying bottom product away from the column. The actual liquid level carried in the column base is not important so long as it does not fall below the top of the heating surface or does not rise high enough to flood the bottom plate; therefore the controller set point is normally positioned for a level somewhere between these two limits. Level control itself is generally very easy. In the example cited, the controller could be set so that very small changes in level would make large output changes. When so adjusted, the course of level and flow transients following a sudden increase in column downflow would be about as shown in Figure 1. Level would be held essentially constant, and the outflow transient would almost duplicate the inflow transient. The sudden change in bottom-product outflow would matter little if the material were flowing to a storage tank; but if it were fed to another column in which control was important, the sudden change in feed flow might make operation of the second column difficult or impossible. In that case it would be much better to change the outflow slowly, to allow the level in the base of the first column to vary within the tolerable limits. This is called "averaging control".

Controllers of two types are used for averaging control—the simple proportional response type and the proportional plus reset type. The results obtainable with each and the optimum response settings are discussed in this paper. To state the problem, let us assume that the tolerable change of volume in a surge tank is C gallons; an inflow varying from 0 to Q gallons per minute enters the tank, and a level controller operates a valve in the outflow line as shown in (Figure 2). Optimum controller settings will be taken as those which, following the largest normal sudden change of inflow, ΔF, cause an outflow transient with the lowest possible maximum rate of change of outflow $(dF)_{max}$.

PROPORTIONAL RESPONSE CONTROLLER

To ensure that the level does not exceed minimum or maximum limits, a proportional response controller would be adjusted so that a level change equivalent to C would move the valve enough to change the outflow from 0 to Q gallons per minute (Figure 3). The sensitivity would then be:

$$S = Q/(m)(v)(C) \tag{1}$$

where S = controller sensitivity, lb./sq. in. output change per in. of pen travel
Q = maximum inflow and outflow, gal./min.
m = measuring sensitivity, in. of pen movement per gal. in tank
v = valve sensitivity, gal./min. change in outflow per lb./sq.-in. change in controller output
C = tank capacity between limits, gal.

For example, if a change in controller output of 8 lb./sq. in. opened a diaphragm valve from the closed position to the one at which Q gallons per minute passed, and the tolerable level change were equivalent to 4 inches of pen travel, the sensitivity would be set at 2 lb./sq. in. per in. It should be noted that the optimum sensitivity is not necessarily equivalent to 100% "throttling range", since a control valve will generally pass more than the maximum required flow at full opening.

With a proportional response controller set in the optimum sensitivity, the greatest rate of change of outflow will occur immediately after the largest sudden change in inflow, ΔF, and will be equal to:

$$(dF)_{max} = \frac{(\Delta F)(Q)}{C} \text{ gal./min./min.} \tag{2}$$

The outflow will change exponentially until it equals the inflow, as Figure 4 shows. The time constant of the level and outflow curves is equal to C/Q minutes.

PROPORTIONAL PLUS RESET CONTROLLER

When the sudden changes in inflow, ΔF, are small compared to the maximum throughput, Q, considerable reduction in $(dF)_{max}$ can be effected by the use of a proportional plus reset controller. The action of this instrument is such that under steady-flow conditions the level is maintained midway between the limits. Following a sudden sustained change in inflow, the tank level changes but is gradually set back to mid-tank, ready for the next inflow change in either direction.

In order to arrive at realistic optimum settings on this type of averaging controller, it is necessary to assign for the largest normal sudden inflow change, ΔF, the value which can occur every hour or so, not that which happens once a week or month. For example, in starting a piece of equipment, the flow might suddenly be changed from 0 to 200 gallons per minute; but once in continuous operation, no sudden changes in flow greater than 30 gallons per minute would ever occur even though the throughput during a week or month run might vary gradually over a very wide range. The largest normal sudden change in inflow, ΔF, in this case would be 30 gallons per minute.

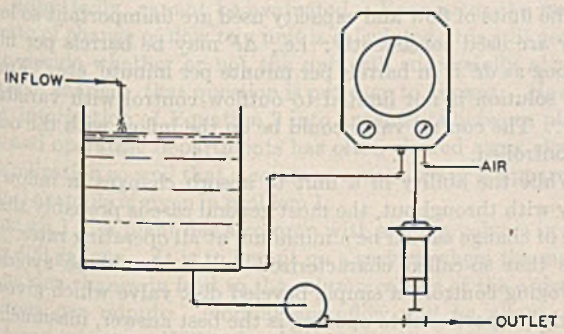
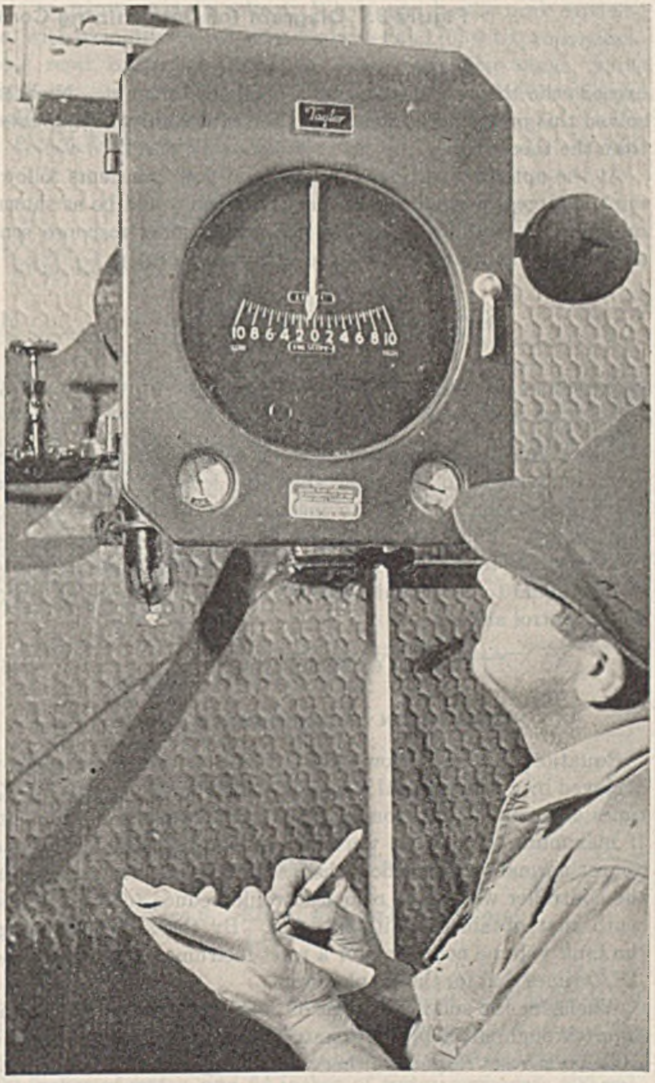


Figure 2. Simple Control System for Liquid Level

The optimum settings for the proportional plus reset controller are taken as those which produce the lowest maximum rate of outflow change following the largest normal sudden inflow change. In order to make the fullest use of the available tank volume, the controller should allow the level to rise just to the tank limit following this largest normal inflow change, ΔF.

Inflow changes larger than ΔF could cause the tank level to exceed its limits, were it not for limit stops built into the controller which automatically bring the outflow equal to inflow when either limit is reached. This modification of a standard proportional plus reset controller has been called an "averaging liquid level controller".



An Averaging Controller

The theoretical minimum rate of change of outflow following the largest inflow change, ΔF, would be:

$$(dF)_{max} = \frac{(\Delta F)^2}{C} \text{ gal./min./min.} \tag{3}$$

This would be realized if the controller increased the outflow at a constant rate, the two flows balancing just as the level reached the upper or lower limit. It is possible to adjust a proportional plus reset controller so that the maximum rate of outflow change

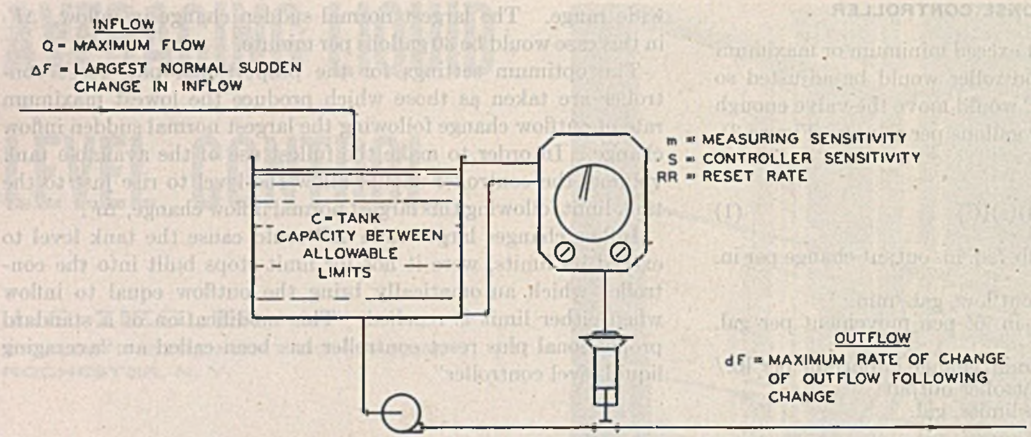


Figure 3. Diagram for Determining Controller Sensitivity

exceeds the theoretical value by a negligible amount. Nichols[1] solved this problem and found that the rate is only 3.6% greater than the theoretical.

At the optimum settings the level and flow transients following the largest normal sudden inflow change would be as shown in Figure 5, and these settings for proportional response sensitivity S and automatic reset rate RR are very nearly:

$$S = \frac{\Delta F}{(m)(v)(C)} \text{ lb./sq. in. per in.} \tag{4}$$

$$RR = (1.5)\frac{\Delta F}{C} \text{ per minute} \tag{5}$$

Or more simply, the sensitivity should be set so that a pen movement equivalent to the total allowable level change makes a valve movement sufficient to increase the outflow ΔF gallons per minute. The reset rate is set equal to 1.5 divided by the time required to fill the tank between allowable limits at a rate of flow equal to ΔF. This time unit is useful in work on averaging control and is:

$$\theta = C/\Delta F \text{ minutes} \tag{6}$$

COMPARISON OF CONTROLLER TYPES

Equations 2 and 3 show that the rate of change of outflow achieved by a proportional plus reset controller will be only $\Delta F/Q$ times as great as that from a proportional response instrument. If maximum throughput were 100 gallons per minute and the largest normal sudden inflow change were 10 gallons per minute, the controller with reset response would reduce $(dF)_{max}$ to one tenth that obtainable without reset. By the same reasoning, the tank volume necessary for a reset instrument would only be $\Delta F/Q$ times that for the simpler form.

Whenever the sudden changes in flow are less than the maximum throughput, a proportionate advantage is realized by the addition of reset response either in reducing the rate of change of outflow or in reducing the required tank size. However, there are certain disadvantages attending the use of the proportional plus reset instrument which can sometimes outweigh the advantages of smoother outflow or smaller equipment.

OVERPEAK. Figure 2 shows that the proportional response instrument does not allow the outflow change to exceed the inflow change, but that the reset type of instrument allows the outflow to exceed inflow in order that the level can be returned to the middle of the tank (Figure 5). This overpeak amounts to about 0.38 ΔF; ordinarily it is not serious but could be intolerable if the unit fed by the outflow were very near its maximum capacity—e.g., a column near the flooding point.

LIMITS. The averaging type of liquid level controller has stops which prevent the level from exceeding allowable limits. When inflow changes larger than ΔF occur, these stops operate to balance inflow and outflow abruptly (Figure 6). At times this sudden change in outflow, even though it occurs infrequently, can outweigh the advantage of slower changes. Of course this involves the choice of maximum ΔF; the largest should be taken if the limit effect can be undesirable.

BALANCING. If abrupt flow changes are to be avoided on start-up or shut-down of units, the averaging type controller must be balanced in manually. This requires certain manipulation which is not necessary on the straight proportional response instrument and, consequently, can necessitate some supervisory assistance to the regular operators at these times.

HIGHER COST. Although the additional cost of the reset mechanism is not great, at times it may give some weight to the selection.

There is no exact answer to the question of instrument type although a good practice rule might be that reset should be considered if the value of $\Delta F/Q$ is less than 0.5.

MISCELLANEOUS CONSIDERATIONS

It might be well to point out that the shape of the surge vessel is of no importance; only the available volume between limits is to be considered. Obviously, results would be altered slightly if a horizontal cylindrical vessel were used since the cross section changes with level. However, the slope of the calibration curve of such a vessel varies little between 20 and 80% of the diameter.

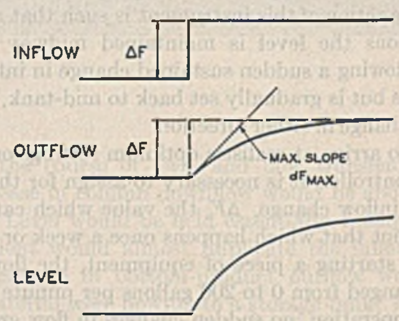


Figure 4. Effect of Flow on Liquid Level for a Proportional Response Controller

The units of flow and capacity used are unimportant so long as they are used consistently; i.e., ΔF may be barrels per minute as long as dF is in barrels per minute per minute, etc. Further, this solution is not limited to outflow control with variable inflow. The control valve could be on the inflow with the outflow uncontrolled.

While the ability of a unit to absorb changes in inflow may vary with throughput, the most general case is probably that the rate of change should be a minimum at all operating rates. This says that so-called characterized valves should be avoided in averaging control; a simple beveled disk valve which gives flow nearly proportional to opening is the best answer, inasmuch as it assures minimum rate of change of flow at large as well as at small throughputs.

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[1] Nichols, N. B., Am. Assoc. Advancement Sci., Gibson Island Instrumentation Conference, 1942.

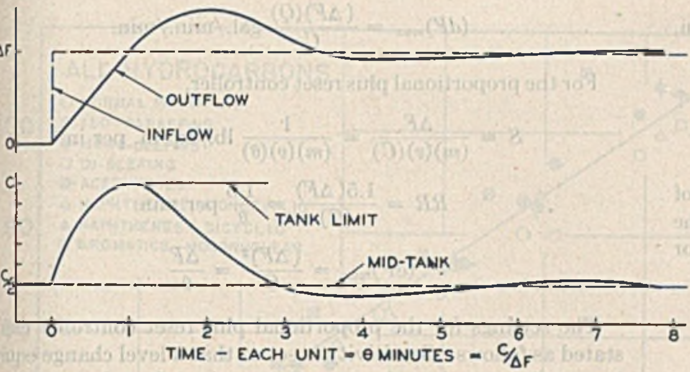

Figure 5. Effect of Reset Response on Liquid Level

Often an averaging level controller does not operate a valve directly but changes the set point of a flow controller on the outflow line. This has the advantage of eliminating the abrupt flow changes which would result if partial plugging of the control valve could occur or if the pressure drop across the valve could change abruptly. The disadvantage to this system is that most flow controllers have nonlinear scales, the flow varying as the square root of the differential. This system, then, in giving linear changes in differential-pressure set point actually causes faster rates of change of flow at low throughputs than at high. In calculating settings from Equations 1 or 4, constant v should be taken as the actual change in the flow set point per lb./sq. in. change in level controller output. Furthermore, the constant should be taken around the point on the flow scale representing maximum expected throughput. If taken at the average flow, the settings would be conservative at low flows, but the upper limit stop could be reached at high flows.

It is apparent that the level measuring device must cover the total allowable level change or more. Similarly, good practice would dictate that a valve positioner be used to eliminate the dead spot caused by valve friction, and a valve positioner with the widest input pressure range should be used to reduce end effects.

One other point can be important when the surge tank is very small compared to the throughput or, better, when ($\theta = C/\Delta F$) is very small. Under these conditions rapid correction in outflow may be required. In this case the lag of level measurement and the lag of operating the valve can become appreciable and affect the control results. It is, then, very important that a level measuring device with small lag be used, such as the direct-float operated instruments or bellows type (aneroid) manometer. In extreme cases it may be necessary to use booster relays to cut valve lag. In general, however, the required rates of valve movement are so slow that valve and measuring lags are not great enough to alter the calculated results appreciably.

EXAMPLES

This paper has attempted to apply numbers to quantities which, admittedly, cannot be evaluated. Even after the maximum rate of change of flow to a unit is calculated, it is still necessary to decide whether or not the unit will successfully absorb this rate of change; that question is not easy to answer. Nevertheless, interjection of Equation 3 into arguments between plant design and operating departments has often cleared away clouds of generalization so well that a common-sense answer is apparent. A typical example is given in problem 1.

Problem 1. A plant has a column with a surge volume in the base of 400 gallons. It is to be put on a service where the maximum sudden change in feed to the column can be of the order of 20 gallons per minute. Normal downflow will be about 100 gallons per minute. Will a level controller be able to absorb this change in flow without upsetting the following column which is to be fed with the bottoms from the first? Or will an expensive high-pressure tank be required to augment the existing capacity?

Solution. From Equation 3 $(dF)_{max}$ will be 1 gallon per minute per minute. Almost any column will be able to accept a 1% per minute change in feed rate. Therefore no auxiliary tank is required.

Problem 2. Flow to a surge tank varies from 30 to 180 gallons per minute. Sudden changes in throughput will not be greater than 50 gallons per minute, and the rate of outflow change regulated by a level controller must not exceed 5 gallons per minute per minute. Pressure drop through the control valve is 25 pounds per square inch. Specific gravity of the liquid is 1.0. Minimum holdup is desirable.

Questions of design, instrumentation, and adjustment must be solved: What must be the tank capacity (*a*) with proportional response controller and (*b*) with proportional plus reset controller (design)? What controller range, valve size, etc., should be selected (instrumentation)? What is the estimate of the controller settings (adjustment)?

Solution. From Equation 1,

$$C = \frac{(\Delta F)(Q)}{(dF)_{max}} = \frac{(50)(180)}{5} = 1800 \text{ gallons}$$

From Equation 3,

$$C = \frac{(\Delta F)^2}{(dF)_{max}} = \frac{(50)^2}{5} = 500 \text{ gallons}$$

The need for minimum holdup indicates that the proportional plus reset instrument should be used. A vertical cylindrical tank, 4 × 6 feet, would hold 500 gallons in 64 out of 72 inches and thus leave 4 inches above and below limit stops.

The nearest standard manometer range above 72 inches is 100 inches of water. A 2-inch, single-seat, beveled-disk diaphragm valve with a capacity of 200 gallons per minute and a valve positioner with an input range of 16 pounds per square inch would be selected.

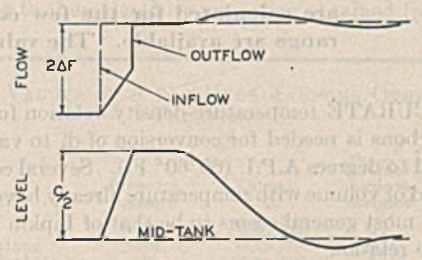

Figure 6. Effect of Limit Stops on Liquid Level

The controller sensitivity can be estimated from Equation 4 after evaluating two constants. Measuring sensitivity m is the pen movement per gallon. The 5-inch controller scale represents 100 inches of water, and 64 inches of water represents 500 gallons; therefore,

$$m = \frac{(64)(5)}{100\ (500)} = 0.0064 \text{ in. of pen movement per gal.}$$

Valve sensitivity v is the flow change per unit change in controller output. Since a linear valve is used, and 16 pounds per square inch change in positioner input makes a flow change of 200 gallons per minute,

$$v = \frac{200}{16} = 12.5 \text{ gal. per min. per lb./sq. in.}$$

The problem gave ΔF as 50 gallons per minute, and C has been determined to be 500 gallons; therefore,

$$S = \frac{\Delta F}{(m)(v)(C)} = \frac{50}{(0.0064)(12.5)(500)} = 1.25 \text{ lb./sq. in. per in.}$$

From Equation 5 the reset rate should be:

$$RR = \frac{(1.5)(\Delta F)}{(C)} = \frac{(1.5)(50)}{500} = 0.15 \text{ per min.}$$

The controller limit stops should be set at 4 and 64 inches of level. Figure 5 shows that after a sudden change in inflow the level will return to mid-tank in a time of about (5) $(C)/(\Delta F)$ or 50 minutes.

SUMMARY OF EQUATIONS

For the proportional response controller,

$$S = \frac{Q}{(m)(v)(C)} \text{ lb./sq. in .per in.}$$

$$(dF)_{max} = \frac{(\Delta F)(Q)}{C} \text{ gal./min./min.}$$

For the proportional plus reset controller,

$$S = \frac{\Delta F}{(m)(v)(C)} = \frac{1}{(m)(v)(\theta)} \text{ lb./sq. in. per in.}$$

$$RR = \frac{1.5(\Delta F)}{(C)} = \frac{1.5}{\theta} \text{ per min.}$$

$$(dF)_{max} = \frac{(\Delta F)^2}{C} = \frac{\Delta F}{\theta}$$

The settings for the proportional plus reset controller can be stated as follows: Sensitivity is set so that a level change equivalent to C moves the valve enough to make a flow change equal to ΔF. Reset rate is set equal to 1.5 divided by the time required to fill the tank at a rate of flow equal to ΔF.

Temperature-Density Relation for Gasoline-Range Hydrocarbons

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The temperature coefficient of density (α) in the equation, $d_4^t = d_4^{20} + \alpha(t - 20)$, for pure hydrocarbons from C_6 to C_{12} is correlated with hydrocarbon structure or type and molecular weight at temperatures near 20° C. by the formula, $-\alpha = m(1/M - 0.002) + 6 \times 10^{-5}$, where M is molecular weight and m is a constant depending only on structural type. This permits an exact conversion of d_4^{20} to A.P.I. gravity whenever the type of compound is known. For application to wider temperature ranges, values of β in the equation, $d_4^t = d_4^{20} + \alpha(t - 20) + \beta(t - 20)^2$, are calculated for the few compounds on which data of sufficient accuracy and range are available. The values of β vary with structure in an unknown manner.

AN ACCURATE temperature-density relation for pure hydrocarbons is needed for conversion of d_4^t to various temperatures and to degrees A.P.I. (60/60° F.). Several correlations of density and of volume with temperature already have been presented. The most general seems to be that of Lipkin and Kurtz (*8*). For the relation,

$$d_4^t = d_4^{20} + \alpha(t - 20) + \beta(t - 20)^2 \qquad (1)$$

where d = density, grams/ml.
t = temperature, ° C.

these authors plotted α against molecular weight for various types of hydrocarbons, and β against molecular weight for normal paraffins. A single curve gave a fairly good representation of α for all types of hydrocarbons, although only a fraction of the values fell exactly on the curve.

CORRELATION OF ALPHA

The Lipkin and Kurtz plots show that the shape of the curves is at least approximately hyperbolic. If this is true, a plot of α against the reciprocal of molecular weight will yield a straight line. This was found to be the case, and Figure 1 shows values of α calculated from the most recent and reliable data (enumerated later). Figure 1 shows that divergence from a single straight line is greatest at the lowest molecular weights, that the data tend to converge at higher molecular weights, and that all aromatics fall above the line and all n-paraffins fall below the line; therefore, by differentiating between these types, a more accurate correlation is obtainable. Calingaert *et al.* (*1*) reported obtaining a linear correlation for paraffins on the coordinates of αM *vs.* N, where N is the number of carbon atoms from heptane to eicosane (C_7 to C_{20}). A type form equation linear in αM and N may be transformed algebraically into an equation linear in α and $1/M$ for any given series of hydrocarbons.

Recent data for the individual types were plotted separately with the results shown on Figure 2. The data include n-paraffins from C_5 to C_{16}, isoparaffins through C_9, naphthenes through C_{10}, olefins and aromatics through C_{12}, and a few heavier compounds. On the isoparaffin and olefin plots, points for several isomers of the same molecular weights sometimes superimpose. The data for each individual type are best represented by a straight line. With the exception of isoparaffins, the best lines for all series extrapolate through a hypothetical common point at 500 molecular weight and $\alpha = -60 \times 10^{-6}$. The isoparaffins may also be represented by a line through this common point with less error than occurs between certain isomers of the same molecular weight in other types. Isoparaffins, naphthenes, olefins, diolefins, and acetylenes may all be represented by the same line. A general equation for all types may be written in terms of molecular weight and slope:

$$-\alpha = m(1/M - 0.002) + 60 \times 10^{-6} \qquad (2)$$

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[1] Present address, University of Michigan, Ann Arbor, Mich.

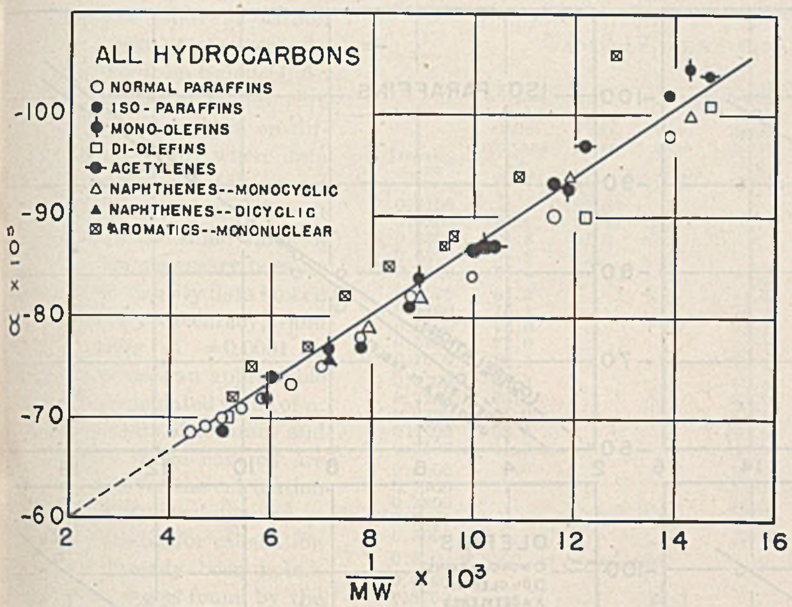

Figure 1. Values of α Calculated from Recent Data

where α is the coefficient in Equation 1, M is molecular weight, and m is the slope that depends on structure:

Hydrocarbon Type	Slope m
n-Paraffins	0.0315
Isoparaffins, naphthenes, olefins, diolefins, acetylenes	0.0333
Aromatics	0.0383

EVALUATION OF β

Data of a high order of accuracy and covering a fairly wide temperature range are needed for calculation of β. Very few of the temperature-density data reported in the literature are adequate for this purpose. The only data comprehensive for a series are on n-paraffins. These form a straight line from C_5 to C_{16} when β is plotted against the reciprocal of molecular weight (Figure 3). The equation for the line is:

$$-\beta_{\text{n.p.}} = (800/M - 3.0)10^{-7} \qquad (3)$$

Calingaert *et al.* (*1*) calculated β for n-paraffins from pentane through dodecane, and also β for several isoparaffins using data from other sources (*3, 12*). It was noted that values for isoparaffins were different from those for n-paraffins, but this was ascribed to inaccuracies of the data.

Lipkin and Kurtz (*8*) recommended that β values of n-paraffins be used for all hydrocarbons. Data have appeared since which show that β for n-paraffins should not be implicitly used for other types, even for isoparaffins. Data on styrene (*11*), on 2,3-dimethylbutane (*7*), and on undecyne may be used to obtain values of β of at least approximate accuracy. Table I gives the calculated values. The styrene reference data are presented only as a calculated table, and the value of β may not be accurate. For all other compounds the values range from equal to several times greater than those for the corresponding n-paraffins. As far as the authors know, Equation 1 is merely the conventional power series type of empirical equation commonly used to represent physical data. It does not correlate densities accurately over wide temperature ranges without the addition of a cubic term as used in International Critical Tables (*6*). Therefore no simple and general correlation of β may be expected. However, a rough value may be selected from Table I for use with compounds other than n-paraffins.

Table II compares the present values of α and β with those of Lipkin and Kurtz. The differences are appreciable in many places and are due partly to the later and more accurate constants now available, and partly to the improved method of correlation.

SCOPE OF EQUATION 1

Since values of β are known for relatively few compounds and no β correlation is indicated between various types, the scope of Equation 1 reduced to linear form by omission of the squared term should be defined. Values of β for the n-paraffins cover a range; using the constants for pentane through decane, values of $\beta(t - 20)^2$ were set equal to 0.0001, 0.0002, and 0.0005, and solved for $(t - 20)$. The resulting figures are the number of degrees above and below 20° C. at which the stated density error occurs if the squared term in Equation 1 is dropped entirely. The results (Table III) show that the density error accruing from neglect of the β term is negligible between 15° and 25° C., and frequently between much wider temperature limits. This agrees with the conclusion of Deanesly and Carleton (*2*) that for n-paraffins the temperature coefficient of density is substantially linear over the range 20° C. ± 20° C.

GRAVITY CONVERSION TABLE

Densities of pure hydrocarbons are commonly reported in the literature as d_4^{20}, whereas the petroleum industry favors A.P.I. gravity (at 60°/60° F.). A rapid and exact conversion between the two is of great convenience. The data required for the conversion are temperature coefficients of density for the hydrocarbons and for water. For the more common pure hydrocarbons, Equation 1 with the β term omitted was used with the proper α value to convert d_4^{20} to density at 15.56° C. (60° F.) relative to water at 4° C. This was then converted to density at 15.56° C. relative to water at 15.56° C. by dividing by the relative density of water at 15.56° C. to water at 4° C. The A.P.I. gravities corresponding to these densities were then obtained from a table

Table I. Values of β for Hydrocarbons Other Than n-Paraffins

Compound	Pressure, Atm.	Temp., ° C.	$\beta \times 10^6$ Subject hydrocarbons	$\beta \times 10^6$ n-Paraffin[a]
Styrene	1	0 to 145	0	−0.47
2,3-Dimethylbutane	Satn.	0 to 200	−2.4	−0.63
2,2,4-Trimethylpentane	1	10 to 100	−2.17	−0.40
3-Ethylpentane	1	−20 to 90	−0.89	−0.50
2,2-Dimethylpentane	1	−20 to 80	−0.50	−0.50
1-Undecyne	1	15 to 90	−0.4	−0.21

[a] From Figure 3 at mol. wt. of subject compound. (For compounds other than isoparaffins, these molecular weights are not those of actual paraffins. This procedure gives slightly better correlation than the basis of equal number of carbon atoms.)

Table II. Comparison of α and β with Lipkin and Kurtz Values

	$-\alpha \times 10^5$				$\beta \times 10^7$	
		Authors				
Mol. Wt.	Lipkin and Kurtz	n-Paraffins	Aromatics	Others[a]	Lipkin and Kurtz	Authors[b]
72	97.4	97.5	....	99.6	−8.1	−8.8
85	91.5	90.8	97.4	92.5	−6.4	−6.4
100	86.7	85.2	90.6	86.6	−5.0	−5.0
120	82.0	80.0	84.3	81.1	−3.7	−3.7
140	78.5	76.2	79.7	77.2	−2.6	−2.7
160	75.8	73.4	76.3	74.2	−1.8	−2.0
180	73.7	71.2	73.6	71.8	−1.2	−1.4
200	71.9	69.4	71.5	70.0	−0.7	−1.0
225	70.3	67.7	69.4	68.2	−0.2	−0.6
250	69.0	66.3	67.7	66.7	+0.2	−0.2
275	67.9	65.1	66.3	65.4	+0.5	+0.1
300	66.8	64.2	65.1	64.4	+0.8	+0.3

[a] Isoparaffins, naphthenes, olefins, diolefins, and acetylenes.
[b] Recommended for n-paraffins only.

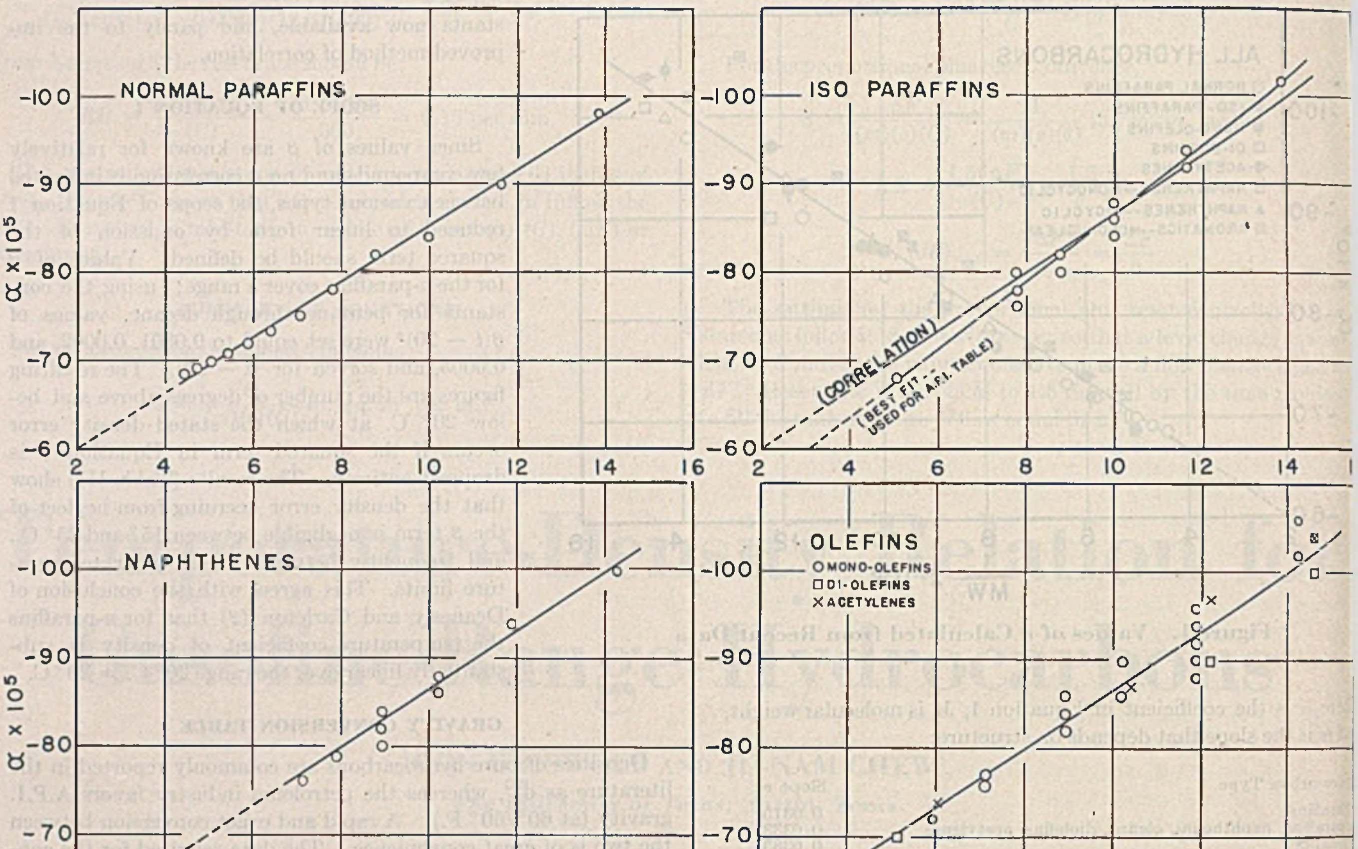

Figure 2. Values of α Separated According to Type of Hydrocarbon

(*13*). Values of α read from the curves of Figure 2 were used for calculating the A.P.I. gravity, except for benzene for which the actual experimental value was used. Benzene is the only common pure hydrocarbon not satisfactorily correlated. The best curve (as noted on Figure 2) was used for isoparaffins.

Table IV lists the conversion values. The density range includes all known hydrocarbons in the classes indicated, from C_5 through the C_8 compounds. Intermediate values may be readily found by interpolation, so the table is usable for hydrocarbons of various degrees of purity.

SOURCES OF DATA AND PROCEDURES

In an effort to use the most dependable density data, those from the National Bureau of Standards (*10*) were used when possible. For the normal paraffins the Bureau of Standard data were used for pentane through nonane; from decan on, those of Deanesly and Carleton (*2*) were used.

The temperature coefficient of density (dd/d*t*) is c Where densities were given at various temperatures, th α values were calculated by the abbreviated form of Equa tion 1 (β term omitted) and data near 20° C. (usually valuc at 20° and 25° C.).

A representative number of isomeric compounds of the vari ous classes were selected, and their α values calculated and plotted One point on a plot may represent more than one isomer. Dat for high-molecular-weight compounds not reported by the Burca

Table III. Effect of Omission of $[\beta(t - 20)^2]$ Term i Density Equation

Compound	$\beta \times 10^7$	$(t - 20)$ for Error of: ±0.0001	±0.0002	±0.0005
n-Pentane	−7.9	11.3° C.	15.9° C.	25.2° C.
n-Hexane	−6.3	12.6	17.8	28.2
n-Heptane	−5.0	14.1	20.0	31.6
n-Octane	−4.0	15.9	22.5	35.7
n-Nonane	−3.25	17.8	25.2	39.9
n-Decane	−2.5	20.0	28.3	44.7

Table IV. Gravity Conversion Table for Hydrocarbons

	A.P.I. Gravities										
Density, d_4^{20}	Olefins and cyclopentane C_5 (70)[a]	Pentanes C_5 (72)	Benzene C_6 (78)	Olefins and naphthenes C_6 (84)	Hexanes C_6 (86)	Toluene C^7 (92)	Olefins and naphthenes C^7 (98)	Heptanes C^7 (100)	Alkyl aromatics C^8 (106)	Olefins and naphthenes C^8 (112)	Octanes C^8 (114)
0.6100	..	98.5	..	..	..	..	..	..	..	..	..
0.6200	94.9	94.9	..	..	..	..	..	..	..	..	..
0.6300	91.3	91.3	..	..	..	..	..	..	..	..	..
0.6400	87.8	..	..	..	87.9	..	..	..	..	..	..
0.6500	84.5	..	..	84.6	84.6	..	..	..	..	..	..
0.6600	81.2	..	..	81.3	81.3	..	..	..	..	..	..
0.6700	78.1	..	..	78.2	78.2	..	..	78.3	..	..	..
0.6800	75.0	..	..	75.1	..	..	75.2	75.2	..	..	75.3
0.6900	72.0	..	..	72.1	..	..	72.2	72.2	..	..	72.3
0.7000	69.1	..	..	69.2	..	..	69.3	69.3	..	69.4	69.4
0.7100	66.3	..	..	66.4	..	..	66.5	..	..	66.6	66.6
0.7200	63.6	..	..	63.7	..	..	63.8	..	..	63.8	63.9
0.7300	61.0	..	..	61.1	..	..	61.1	..	..	61.2	61.2
0.7400	58.4	..	..	58.5	..	..	58.5	..	..	58.6	..
0.7500	55.9	..	..	56.0	..	..	56.0	..	..	56.1	..
0.7600	..	..	..	53.5	..	..	53.6	..	..	53.6	..
0.7700	..	..	..	51.1	..	..	51.2	..	..	51.2	..
0.7800	..	..	..	48.8	..	..	48.8	..	..	48.9	..
0.7900	..	..	..	..	..	..	..	..	..	46.6	..
0.8000	..	..	..	..	..	..	..	..	..	44.4	..
0.8100-0.8500 (no compounds)											
0.8600	..	..	..	..	..	32.1	..	..	32.1	..	..
0.8700	..	..	30.1	..	..	30.2	..	..	30.3	..	..
0.8800	..	..	28.3	..	..	..	..	..	28.4	..	..
0.8900	..	..	..	..	..	..	..	..	26.6	..	..
0.9000	..	..	..	..	..	..	..	..	..	..	..

[a] Figures in parentheses are molecular weights.

of Standards (above 9 carbon atoms in most cases) were obtained mostly from Egloff (*4*, *5*). In the selection of values, care was taken to use those on different samples only where data by different investigators agreed or where data from different sources gave the same value of α. This was necessary because much of the density data lacked the necessary accuracy, and even an error of ±0.0001 in density produces an appreciable error in the calculated value of α.

Requirements of accuracy and temperature range covered are more rigorous for the calculation of β than for calculation of α. The data suitable for calculation of β have already been noted. From these, β was found by the graphical procedure used by Calingaert (*1*).

Density data are available for C_4 and lighter gaseous hydrocarbons. These were not included, since the liquid density depends on pressure, and the gaseous hydrocarbons under high pressures do not correlate well with the higher hydrocarbons at atmospheric pressure.

TEMPERATURE-DENSITY-REFRACTIVE INDEX

Temperature, density, and refractive index are fundamentally related to molecular structure. For *n*-paraffins (and their mixtures) at 20° C. the density-refractive index relation (*2*) is:

$$n = 0.52167d + 1.03104 \qquad (4)$$

Ward and Kurtz (*14*, *15*) discussed the theoretical relations and noted that the ratio of differences of refractive index to density between two temperatures was substantially constant, or

$$\Delta n = C\Delta d \qquad (5)$$

For heavy petroleum fractions (A.S.T.M. groups 0 and 1) the value of C was 0.59, and for all lighter petroleum oils and wax, C was 0.60. Mibashan (*9*) found that C for *n*-paraffins from C_6 to C_{18} was 0.565 at temperatures near 20° C. Equation 5 is useful in connection with Equations 1, 2, and 3 to correct refractive indices for temperature. While Equation 5 was developed from data near 20° C., the temperature limits over which it is valid are unknown.

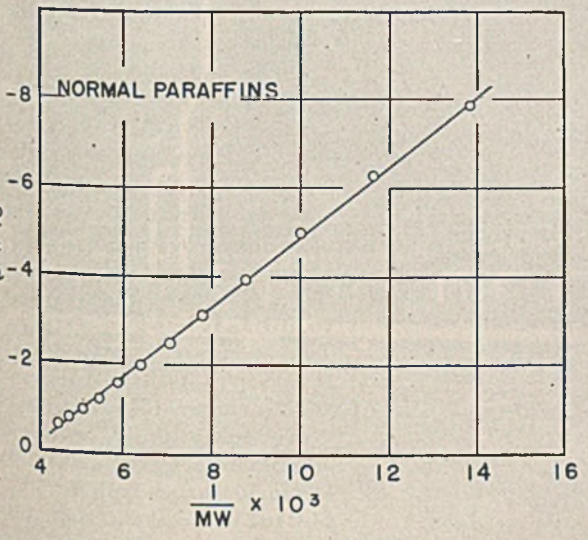

Figure 3. Values of β for *n*-Paraffins

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Liquid Holdup and Flooding in Packed Towers—Correction

Attention is called to an inconsistency in the units specified for the quantity U_L in the table of nomenclature (page 445) of this article by J. C. Elgin and F. B. Weiss [Ind. Eng. Chem., **31**, 435 (1939)]. U_L, the superficial liquor velocity based on entire cross section, should be correctly ft./sec. rather than ft./hr. as printed. With this change the superficial mass velocity of liquor, lb./(hr.)(sq. ft.) = 3600 $U_L \rho_L$. The chart of Figure 10 as printed is correct, as long as consistent time units are employed.

Chromate Corrosion Inhibitors

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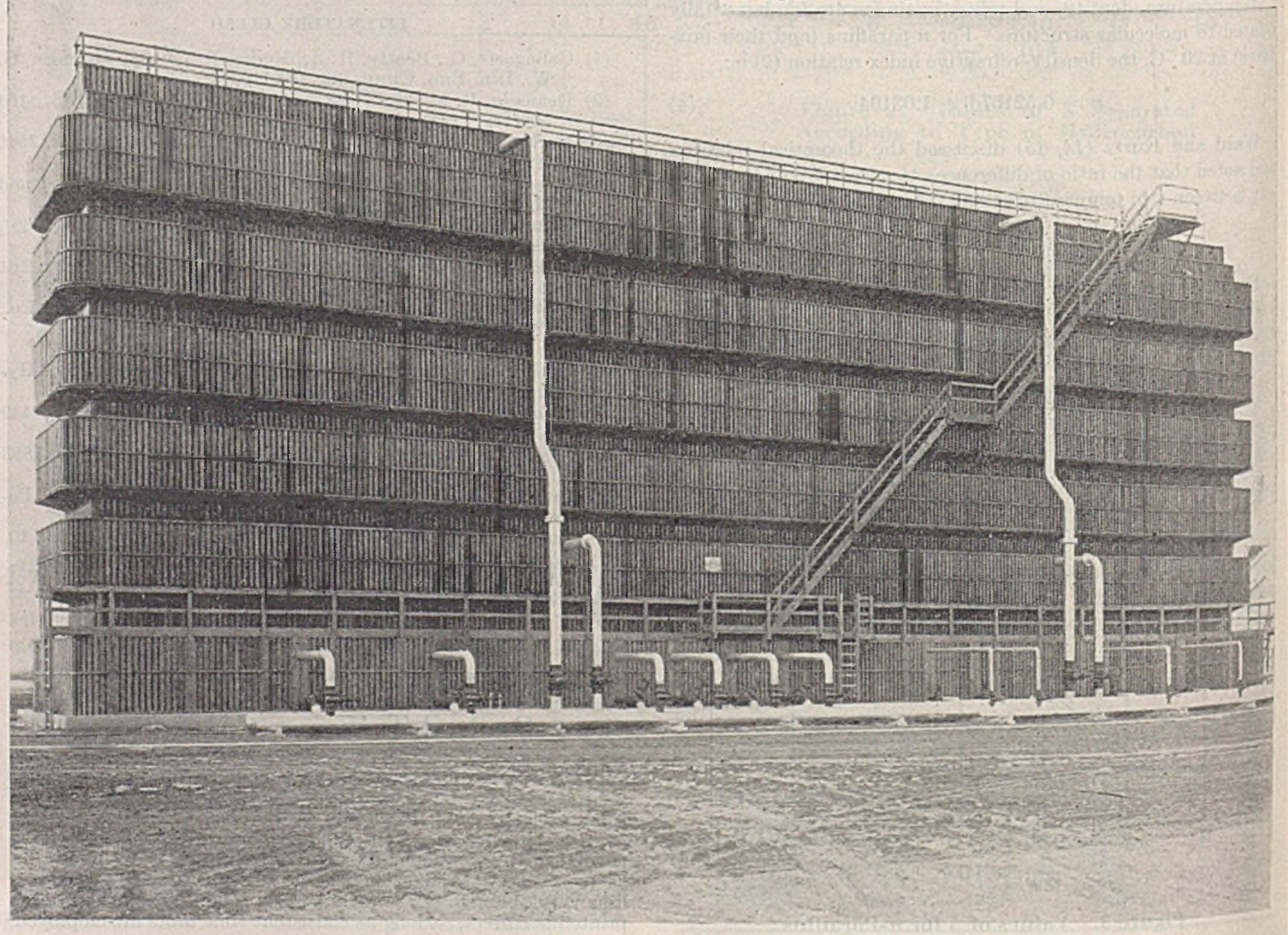
ROETHELI (*8*), Speller (*9*), and others (*2-6*) have shown that chromates and bichromates effectively inhibit the corrosion of iron in chloride-containing water. In closed water systems, such as are used for cooling locomotive Diesels (*7*), there is almost no mechanical loss of water, and it is not important to employ low concentrations of chromate; in fact, it is more convenient to use a comparatively high concentration (*4*). With open cooling towers and spray ponds which are employed for air conditioning and many industrial purposes, the situation may be very different. In general, somewhat lower concentrations of chromate are used, the optimum varying for individual installations. When there is little mechanical loss and the water contains much chloride, periodic drawoffs must be made to waste in order to keep the chloride content low; since this causes a simultaneous loss of chromate, it is most economical to employ the lowest concentration of chromate which effectively inhibits corrosion. It is better, however, to employ too much than not enough, since excess chromate not only increases the safe limit of salt concentration but in general reduces the amount of chromate consumed in the protection of metal surfaces. For this reason it is best to start the chromate treatment with a comparatively high concentration, 500 to 1000 p.p.m., and gradually reduce the amount of chromate over a period of months to the lowest concentration at which the particular installation is effectively protected against corrosion.

By way of illustration, let us assume that the evaporative loss from a recirculating cooling system is 1000 gallons per day, that the raw water contains 100 p.p.m. of sodium chloride, and that

Atmospheric Water Cooling Tower Constructed for a Large Oil Company (Courtesy, Fluor Corporation)



in Chloride Systems

RATE OF CONSUMPTION OF CHROMATE

the maximum concentration of chloride permissible in the system is 1000 p.p.m. It would be necessary to replace the evaporation with raw water and to run to waste 100 gallons per day, in order not to exceed a concentration of 1000 p.p.m. of sodium chloride. Since this 100-gallon drawoff contains the maintained concentration of chromate—for example, 250 p.p.m. (0.025%)—it would be necessary to add an equivalent amount of chromate to the make-up water. In this case: 0.025 × 8.33 = 0.21 pound of chromate per day. Since the volume of the make-up water is ten times that of the drawoff, the required concentration of chromate in the make-up would be 25 p.p.m. in order to maintain 250 p.p.m. of chromate in the circulating system.

The same relative proportions apply to other additives, such as caustic soda to control alkalinity. The general method of calculating drawoff and chromate addition is similar for all manner of open coolers, spray towers, cascade towers, natural draft towers, mechanical draft towers, evaporative condensers, spray ponds, natural ponds, or any other device which operates through atmospheric evaporation (*1*).

ESTIMATION OF CHROMATE CONSUMPTION

In addition to the chromate which is run to waste, some is consumed in forming a protective film. This may be estimated (*7*) by means of Figure 1 which shows pounds of sodium chromate consumed per 1000 square feet of completely submerged ferrous surface for various periods at room temperature (70° F.), aerated, with the pH maintained at 7.5 to 9.5. Within this pH range there is no measurable change in corrosion rate. At higher temperatures the consumption of chromate is somewhat increased. With partial submersion, there may be greater corrosion at the water line, but this can be avoided by proper design or heavy painting of water-line areas which are seldom located where painting would hinder heat transfer.

Figure 1 includes examples of a good water containing 10 p.p.m. of sodium chloride, a fair to poor water containing 100 p.p.m., a very bad water containing 1000 p.p.m. such as might result from concentration in an evaporative cooling system, and an extreme condition, 10,000 p.p.m. of sodium chloride. From the practical viewpoint these graphs show that in all cases the rate of consumption of chromate is relatively high at first but rapidly falls off until it is stabilized within 1 to 3 months. In general, the consumption of chromate is highest at a concentration of about 50 p.p.m. of chromate and lowest at about 500 p.p.m.; for practical purposes there is little difference, after conditions have been maintained for 3 months, with chromate concentrations from 250 to 1000 p.p.m. The general effect of chloride is to increase the consumption of chromate, especially during the first 10 days while the protective film is forming.

The chromate-inhibition of monometallic ferrous systems is reported in the presence of chloride, in amounts commonly encountered in water-cooling systems. Data show the rate of consumption of chromate at different maintained concentrations and changes in the rate with passage of time. The advantage is shown of starting with a comparatively high concentration of chromate and maintaining it until the protective film is stabilized. This procedure is particularly applicable to cooling towers or spray ponds where part of the recirculated water is run to waste to avoid excessive concentration of mineral salts. Graphs are included which will be of practical assistance to the engineer. Incidentally, the data may prove helpful to a better understanding of the dual nature of passivation and thus lead to further technological improvements.

Table I. Comparison of Test Panels

Panel No.	NaCl, P.P.M.	Chromate, P.P.M.	Max. Depth of Pits[a], In.	No. of Pits[b]	Penetration[c], In. per Year	Score	Panel Condition	Fe Equiv. of Chromate Consumed[d]	Grams Fe Oxidized by Air
1	10	0	0.004	>5	0.01346	23	Bad	None	5.21
3		25	0.008	>5	0.00020	72	Poor	0.02	0.08
5		50	0.003	>5	0.00027	75	Fair	0.02	0.09
7		100	0.004	5	0.00005	85	Good	0.01	0.01
9		250	None	4	0.00001	90	Good	0.00	0.00
11		500	None	1	0.00000	97	Exc.	0.00	0.00
13		1000	None	0	0.00000	100	Exc.	0.00	0.00
15	100	0	None	0	0.00444	62	Bad	None	1.72
17		25	0.015	>5	0.00124	53	Bad	0.04	0.55
19		50	0.009	>5	0.00082	60	Bad	0.04	0.34
21		100	None	>5	0.00009	79	Fair	0.01	0.03
23		250	None	5	0.00008	80	Fair	0.01	0.02
25		500	None	4	0.00005	85	Good	0.00	0.02
27		1000	None	2	0.00004	90	Good	0.01	0.01
29	1,000	0	None	0	0.00569	57	Bad	None	2.20
31		25	0.017	>5	0.00118	58	Bad	0.04	0.52
33		50	0.010	>5	0.00093	58	Bad	0.06	0.38
35		100	0.008	>5	0.00017	77	Fair	0.02	0.05
37		250	None	>5	0.00013	79	Fair	0.02	0.03
39		500	None	4	0.00010	85	Good	0.01	0.03
41		1000	None	>5	0.00008	85	Good	0.01	0.02
43	10,000	0	None	0	0.00711	57	Bad	None	2.75
45		25	0.009	>5	0.00087	63	Bad	0.05	0.37
47		50	0.017	>5	0.00090	58	Bad	0.06	0.37
49		100	0.002	>5	0.00044	70	Poor	0.03	0.15
51		250	None	3	0.00022	78	Fair	0.02	0.06
53		500	0.004	5	0.00014	78	Fair	0.02	0.03
55		1000	0.005	>5	0.00012	83	Fair	0.01	0.03

[a] Exclusive of pits on or near edges.
[b] Inclusive of edge pits.
[c] Calculated from weight loss.
[d] 324.0 grams Na_2CrO_4 consumed (reduced to trivalent state) is equivalent to the oxidation of 111.7 grams Fe to Fe_2O_3.

From Figure 1 and the daily drawoff, the most economical chromate concentration may be estimated—namely, the concentration at which the sum of the chromate drawn off and that consumed has a minimum value. It is not advisable ordinarily to maintain chromate concentrations below 100 p.p.m. in the circulating system. Furthermore, it is best to start the treatment with a comparatively high concentration of chromate (500 to 1000 p.p.m.) and later lower the concentration as the protective film becomes stabilized.

If conditions encountered in practice are more corrosive than those on which the charts are based (due to higher temperature, bimetallic contacts, old rust, etc.) the figures obtained from the curves may be multiplied by a suitable safety factor. Excess chromate is desirable also because there may be a small additional consumption of chromate by reducing substances which may be present in the raw water or in the air with which it comes into contact. No correction is required for leakage and similar mechanical losses of chromate (provided they do not exceed the calculated drawoff) since these losses are compensated in practice by a reduced drawoff.

EXPERIMENTAL PROCEDURE

Panels. Test specimens having a surface area of 12 square inches were cut from a mild steel plate known as type A tank (about 0.1% carbon). All were cut from the same sheet and were uniformly polished, cleaned, and inspected for defects prior to testing. At the end of the exposure and before cleaning, photographs were taken (Figure 2) and corrosion scores obtained:

Designation	Score	Degree of Corrosion
Perfect	100	No indication
Excellent	Above 95	Minor, but very satisfactory
Good	85 to 95	Definite, but satisfactory
Fair	75 to 84	Questionable
Poor	65 to 74	Probably unsatisfactory
Bad	Less than 65	Severe

The scores are the composite observations of four men. There were no significant differences between the scores reported by different men or between duplicate panels. After the exposed panels were cleaned with a soft bristle brush, their weight loss and condition were evaluated, additional photographs were taken (Figures 3, 4, and 5), and depth of pits were measured optically.

Media. Twenty-eight media were employed (Figure 2). Large amounts of these media were prepared in advance, the pH was adjusted to 8.0–9.0, and chromate analyses were run by precise electrometric titration. The first series (10 p.p.m. sodium chloride) was prepared from Baltimore city water, which was

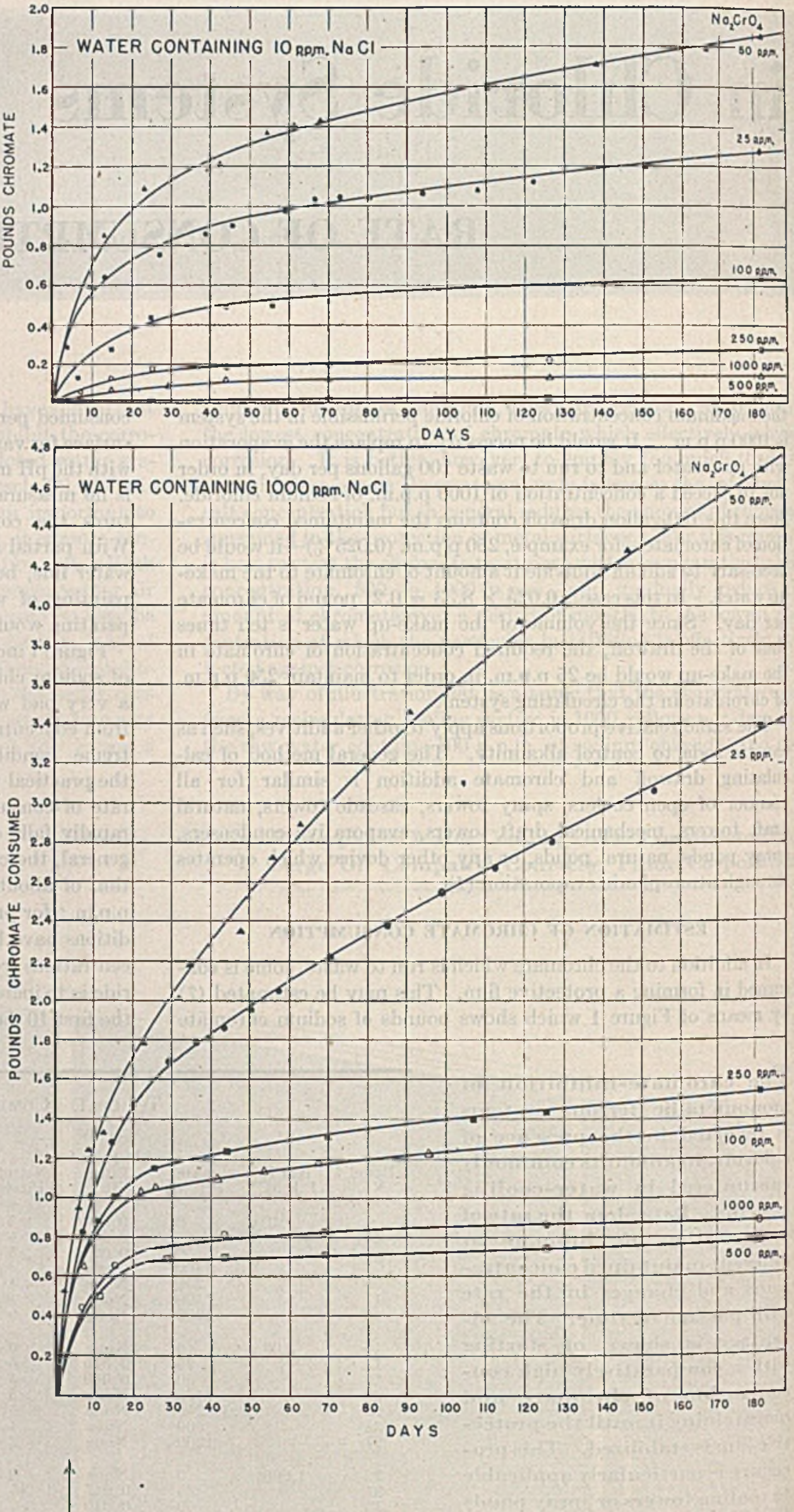
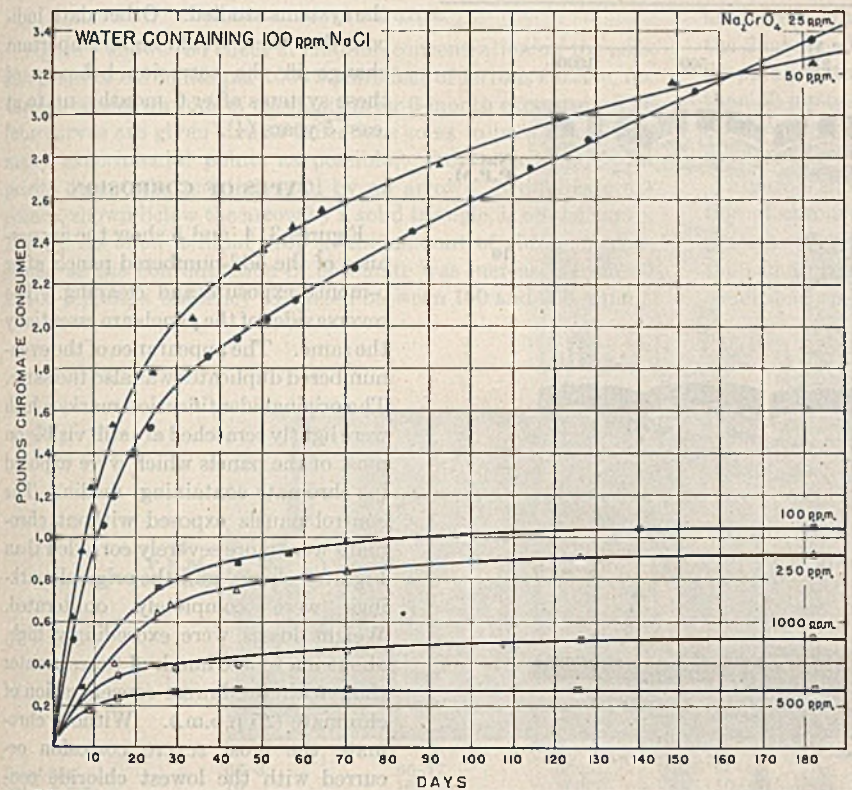
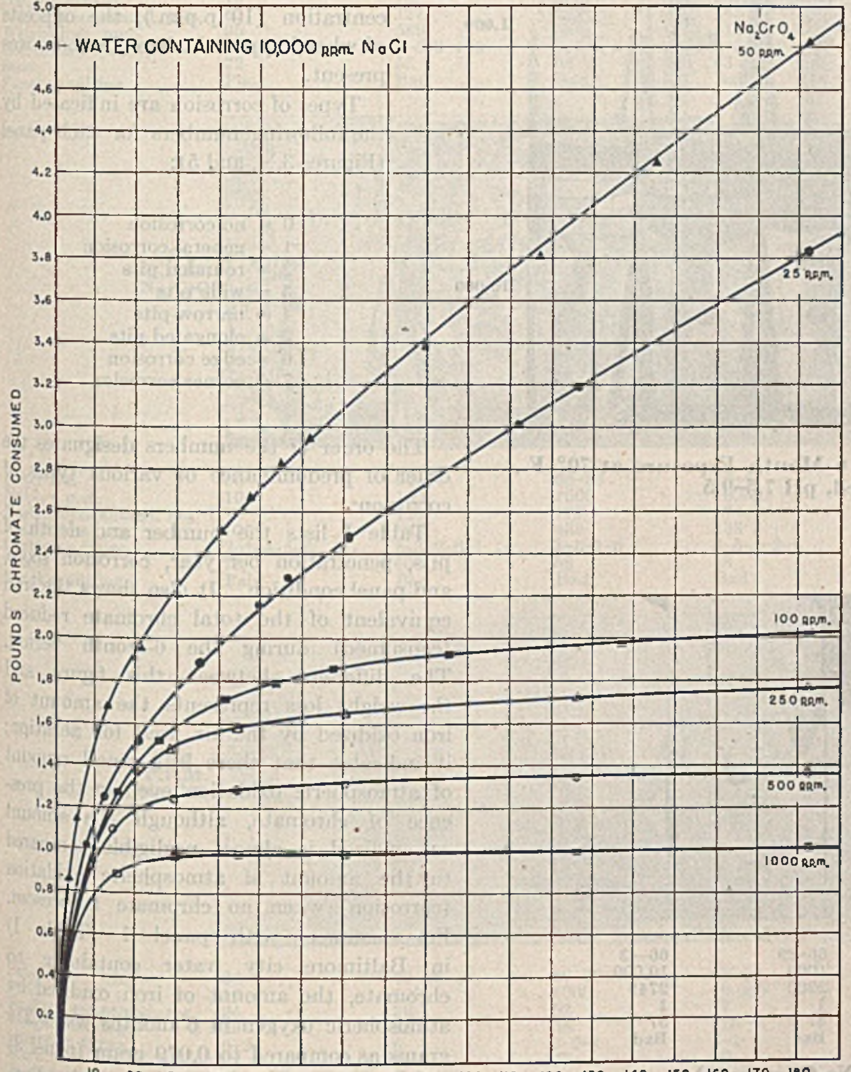


Figure 1. The Cumulative Consumption of Chromate per 1000 Square Feet by Waters Containing Various Amounts of NaCl





found to contain this amount of chloride at the time the solutions were prepared. The other three series were prepared by addition of calculated amounts of C.P. sodium chloride to Baltimore city water.

Exposure. Duplicate specimens were exposed in each medium at room temperature (70° F.). Individual jars were employed for each panel, which was completely submerged and aerated with an excess of water-washed air. Other details were the same as previously described (*4, 5*).

Analyses. During the period of exposure, at frequent intervals so as to avoid important changes in chromate concentration, the panels were transferred to other jars containing fresh media, and the old media analyzed. The difference between the total chromate in each jar, before and after each transfer, was recorded as the amount consumed. At first the chromate consumption was so rapid that daily analyses were required. Analyses for chloride and pH determinations showed no appreciable change, and these data are omitted. The fact that chloride analyses were constant precludes the possibility of any appreciable loss of chromate other than on the ferrous surface.

EFFECT OF TIME

Figure 1 shows the cumulative consumption of chromate for the odd-numbered panels by daily increments up to 182 days (6 months). Similar data, obtained for the duplicate even-numbered panels, are not shown. As a result of minor differences during the first few days the curve level of most of the duplicate panels was either a little above or below those shown in Figure 1, but their relative positions and shapes were the same (Figure 6). During the first 2 weeks a great many more points were obtained than are indicated on the graphs. They are omitted for clarity, but each is included as an increment of the cumulative curve. For instance, the solid triangular point for 10 days and 50 p.p.m. chromate (Figure 1, graph for 10 p.p.m. chloride) is the sum of the consumption during each of the previous days. Although all points are satisfactorily close to the smoothed-out curves, few points are precisely on the curves. There appears to be a periodic trend for points to fall above the curve and then below, the deviation becoming less with lapse of time. During the first few days these deviations were so great that increments for an upper curve were sometimes less than for a lower curve. For this reason misleading conclusions might be drawn by comparing rates based on analyses a few days apart. Instead, conclusions should be based on the slope of the smoothed-out curves. Inspection of the points on these graphs indicates that it is impossible to establish the average shape of the curves without data extending over 30 to 90 days. Data beyond 90 days are chiefly confirmative for

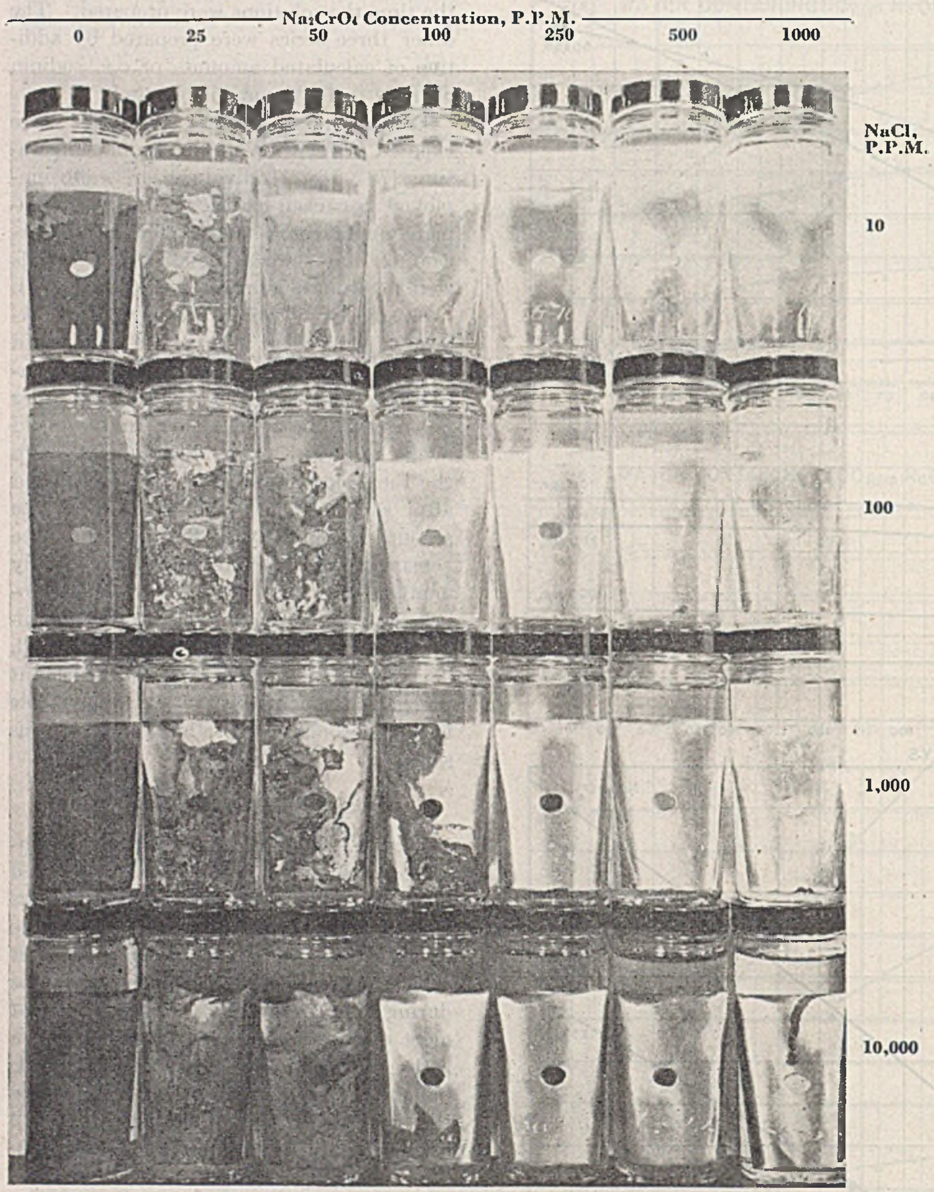
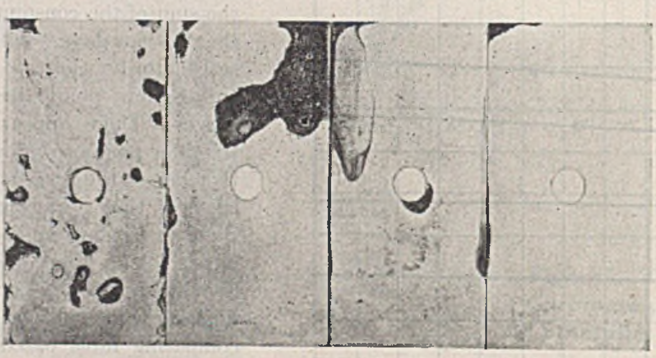


Figure 2. Condition of Iron Panels after 6-Month Exposure at 70° F., Total Submergence, Aerated, pH 7.5–9.5



Panel No.	66-1	66-15	66-29	66-43
NaCl, p.p.m.	10	100	1000	10,000
Weight loss, mg.	5214	1722	2200	2749
Corrosion types	1-5-3-6	1	1	1
Score	23	62	57	57
Panel condition	Bad	Bad	Bad	Bad

Figure 3. Control Panels (No Chromate)

the systems studied. Other data indicate that there would be no important change in the corrosion behavior of these systems after 6 months, up to at least 5 years (*4*).

TYPES OF CORROSION

Figures 3, 4, and 5 show the appearance of the odd-numbered panels after 6-month exposure and cleaning. The reverse sides of the panels are essentially the same. The appearance of the even-numbered duplicates was also the same. The original identification marks which were lightly scratched are still visible on most of the panels which were exposed in chromate-containing media. The control panels exposed without chromate were more severely corroded than Figure 3 shows, and the original markings were completely obliterated. Weight losses were exceedingly high, about ten to one hundred times greater than with the lowest concentration of chromate (25 p.p.m.). Without chromate the most severe corrosion occurred with the lowest chloride concentration (10 p.p.m.), the opposite of what happened when chromate was present.

Types of corrosion are indicated by the following numbers for each panel (Figures 3, 4, and 5):

0 = no corrosion
1 = general corrosion
2 = rounded pits
3 = wide pits
4 = narrow pits
5 = elongated pits
6 = edge corrosion
7 = corner corrosion

The order of the numbers designates the order of predominance of various types of corrosion.

Table I lists the number and depth of pits, penetration per year, corrosion score, and panel condition. It also shows the iron equivalent of the total chromate reduced (consumed) during the 6-month period. The difference between this figure and the weight loss represents the amount of iron oxidized by the air used for aeration; it indicates that there is a small amount of atmospheric oxidation even in the presence of chromate, although the amount so oxidized is almost negligible compared to the amount of atmospheric oxidation (corrosion) when no chromate is present. For instance, with panel 1 (Table I) in Baltimore city water containing no chromate, the amount of iron oxidized by atmospheric oxygen in 6 months was 5.214 grams as compared to 0.079 gram (panel 3) when a concentration of 25 p.p.m. of sodium chromate was maintained.

EFFECT OF CHLORIDE

Figure 7 shows the effect of chloride concentration on the consumption of chromate per 1000 square feet of ferrous surface, for various concentrations of chromate after 6-month exposure. The four curves are given similar inflections so as to pass through as many experimental points as possible; they pass through all points except the one indicated by an arrow. A duplicate exposure, shown below the arrow by a solid triangle, is on the curve. The curves show a rapid drop in the amount of chromate consumed as the concentration of chromate was increased from 50 to 100 p.p.m., a tendency to flatten between 100 and 250 p.p.m., and a rapid drop to a minimum at about 500 p.p.m. except for the highest chloride concentration which tended to continue dropping with increase in chromate concentration. For less than 50 p.p.m. the consumption of chromate dropped, but corrosion became quite noticeable; however, the amount of corrosion was much less than without chromate.

Figure 8 shows the effect of time of exposure on the consumption of chromate, for various concentrations of chromate in the presence of 100 p.p.m. of sodium chloride. These curves follow the same form as those of Figure 7. After 10 days under the conditions specified, the consumption of chromate was almost stabilized for concentrations of 500 to 1000 p.p.m.; after 30 days it was fully stabilized for 500 p.p.m. and about 90 days were required for lower concentrations of chromate.

DUAL NATURE OF PASSIVATION

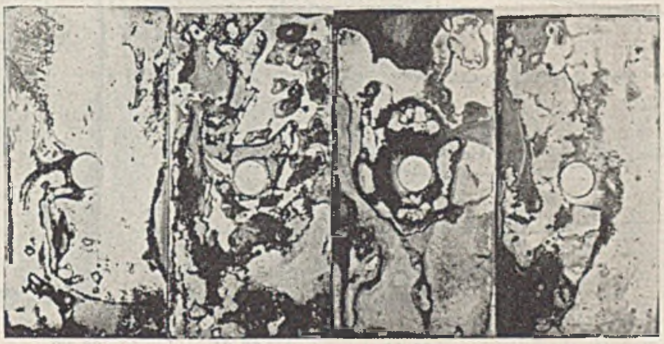
These data provide evidence that the mechanism of chromate inhibition has a dual character. The initial, almost instantaneous passivation or anodic polarization of the metal surface is followed by the slow formation of a more protective layer which becomes stabilized within 30 to 90 days under the conditions described. For the most part this film is invisible, but in time it may impart a color to the surface.

This evidence tends to reconcile the two general theories regarding the mechanism of passivation: (*a*) induced changes in the nature of the metal surface and (*b*) oxide film theory as anticipated by Faraday and later observed by Evans and co-workers (*2*, *6*, *9*). Both mechanisms may be essentially correct and may occur in the order named. Whatever the nature of the initial induced changes which cause a barrier in or on the metal surface, this barrier (be it force or molecular) is slowly reinforced by deposition of hydrous ferric-chromic oxides. During the time this outer layer is forming, there is a comparatively rapid consumption of chromate (reduction from hexavalent to trivalent). It is during this period that localized corrosion may occur if the chromate concentration is low and the chloride high. Afterward there is no corrosion of practical importance with a maintained chromate concentration above 100 p.p.m., nor is there much harmful corrosion with a maintained chromate concentration as low as 25 p.p.m. The foregoing is based on behavior at 70° F. As would be expected, some preliminary tests showed that the protective layers formed more rapidly at higher temperatures.

25 P.P.M. Na_2CrO_4

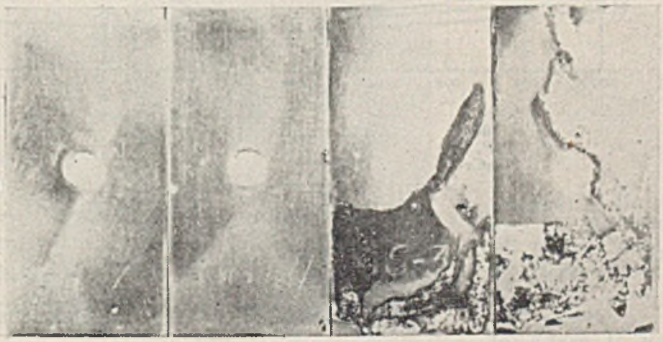
Panel No.	66–3	66–17	66–31	66–45
NaCl, p.p.m.	10	100	1000	10,000
Na_2CrO_4 consumed, mg.	47	127	128	145
Weight loss, mg.	95	589	561	416
Corrosion types	2–6–1	2–5–3–1–6	3–5–1–2	3–5–6–1
Score	72	53	58	63
Panel condition	Poor	Bad	Bad	Bad

50 P.P.M. Na_2CrO_4



Panel No.	66–5	66–19	66–33	66–47
NaCl, p.p.m.	10	100	1000	10,000
Na_2CrO_4 consumed, mg.	71	123	177	174
Weight loss, mg.	106	382	439	433
Corrosion types	2–1–4–5–6	5–3–2–6–1	3–5–1–6	3–5–1–2–6
Score	75	60	58	58
Panel condition	Fair	Bad	Bad	Bad

100 P.P.M. Na_2CrO_4



Panel No.	66–7	66–21	66–35	66–49
NaCl, p.p.m.	10	100	1000	10,000
Na_2CrO_4 consumed, mg.	24	39	52	77
Weight loss, mg.	19	36	65	176
Corrosion types	6–2	6	3–2–1	3–1
Score	85	79	77	70
Panel condition	Good	Fair	Fair	Poor

Figure 4. Effect of Low Concentrations of Chromate

Apparently, with concentrations of sodium chromate between 100 and 500 p.p.m. the induced changes on the metal surfaces are uniform, but during the inceptive period there may be some unevenness in the deposition of the outer film. Presumably, after building to a certain extent, it is ruptured and a little iron dissolves from or through the inner barrier (which is probably anodic to the outer layer); this dissolved iron, together with simultaneously reduced hydrous chromic oxide, is deposited to rebuild the outer layer. This mechanism repeats itself in a cyclic manner with decreasing amplitude and frequency with lapse of time until conditions are substantially constant. During the inceptive period it is simpler to consider that the iron dissolves directly from the surface of the metal than through a special kind of oxide film, from which it follows that the initial passivation probably resides in some induced changes in the nature of the metal surface rather than in a highly resistant oxide layer. The oxide layer demonstrated by Evans appears to be a product of the second stage which starts very quickly since the first stage is completed almost instantly.

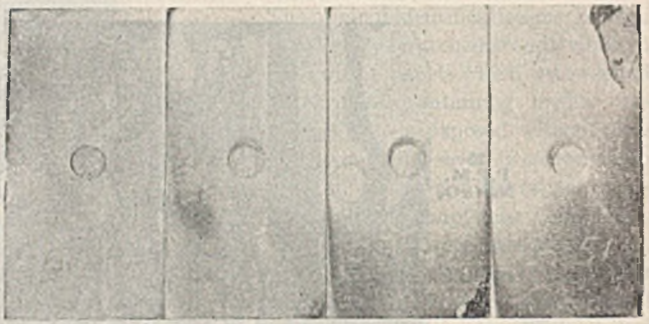
As the concentration of chromate was increased from 50 to 500 p.p.m., there was a rapid decrease in the rate of reduction of chromate and the rate of oxidation of iron. This means that the induced changes on or in the metal surface are more perfect with increase in chromate concentration.

When the chromate concentration was low (25 to 50 p.p.m.), the behavior fluctuated widely during the inceptive period, apparently as a result of imperfect or uneven primary passivation of the metal surface; this condition became stabilized with time but more slowly than with higher concentrations of chromate. The total amount of iron oxidized was of the same order for chromate concentrations of 25 and 50 p.p.m., although the reduction of chromate was usually a little less, and the proportion of iron oxidized directly by air a little greater, for 25 than for 50 p.p.m. of chromate. There is some additional but less definite evidence that, when the chromate concentration is high (above 500 p.p.m.), the opposite effects occur. With a chromate concentration of 1000 p.p.m. there was almost no fluctuation from the start; although the total amount of iron oxidized was usually slightly less than with 500 p.p.m. of chromate, the reduction of chromate was somewhat greater.

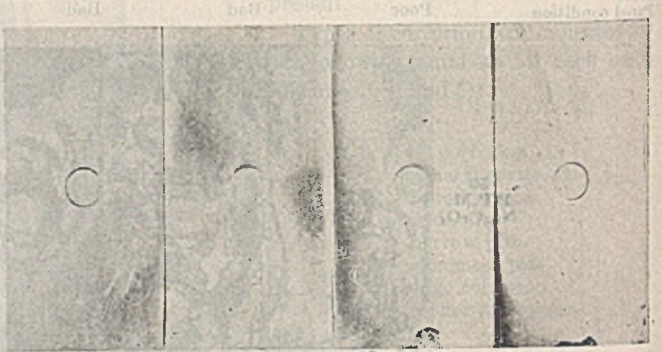
SUMMARY

Experimental data presented here are consistent with a dual theory for the mechanism of passivation. The nature of the time functions appears to preclude a simpler mechanism, but the possibility of a more complex mechanism is not excluded.

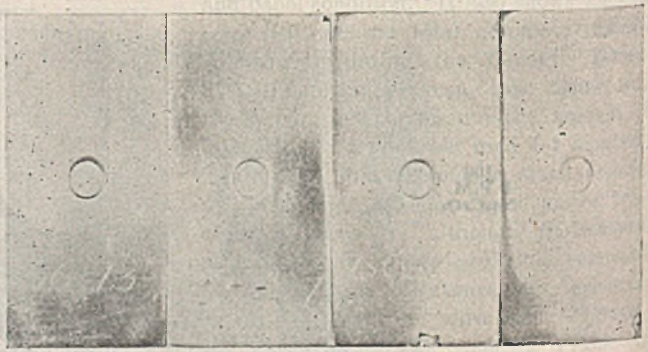
Fundamental data (Figure 1) show that, when chromate is used to inhibit corrosion in water systems under the conditions specified: (*a*) Rate of consumption of chromate is relatively high at first, but rapidly falls off until it is stabilized within 1–3 months. (*b*) Consumption of chromate is highest at a concentration of about 50 p.p.m. chromate and lowest at about 500 p.p.m. (*c*) There is little difference, after conditions have been maintained for 3 months, with chromate concentrations from 250 and 1000 p.p.m. (*d*) As the chloride content of the


250 P.P.M. Na_2CrO_4

Panel No.	66-9	66-23	66-37	66-51
NaCl, p.p.m.	10	100	1000	10,000
Na_2CrO_4 consumed, mg.	10	35	58	67
Weight loss, mg.	4	30	51	83
Corrosion types	6	7–6	7–6	3–6
Score	90	80	79	78
Panel condition	Good	Fair	Fair	Fair


500 P.P.M. Na_2CrO_4

Panel No.	66-11	66-25	66-39	66-53
NaCl, p.p.m.	10	100	1000	10,000
Na_2CrO_4 consumed, mg.	1	11	29	48
Weight loss, mg.	1	18	37	53
Corrosion types	6	6	6–7	5–3–7–6
Score	97	85	85	78
Panel condition	Exc.	Good	Good	Fair


1000 P.P.M. Na_2CrO_4

Panel No.	66-13	66-27	66-41	66-55
NaCl, p.p.m.	10	100	1000	10,000
Na_2CrO_4 consumed, mg.	5.0	20.1	33.2	38.1
Weight loss, mg.	0.0	15.5	29.9	46.5
Corrosion types	0	7–6	6–7	3–7–6
Score	100	90	85	83
Panel condition	Perfect	Good	Good	Fair

Figure 5. Effect of High Concentrations of Chromate

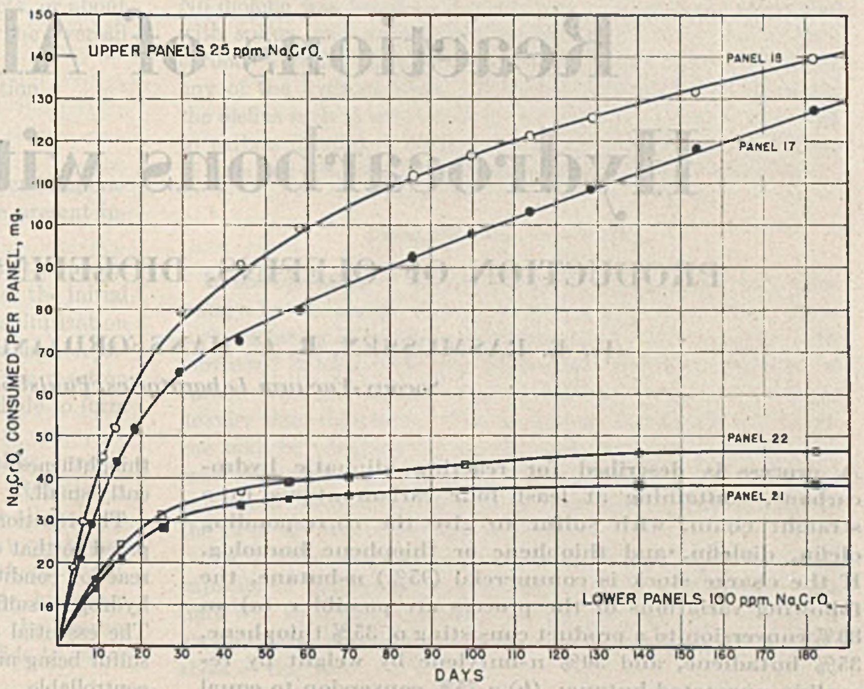


Figure 6. Duplicability of Results

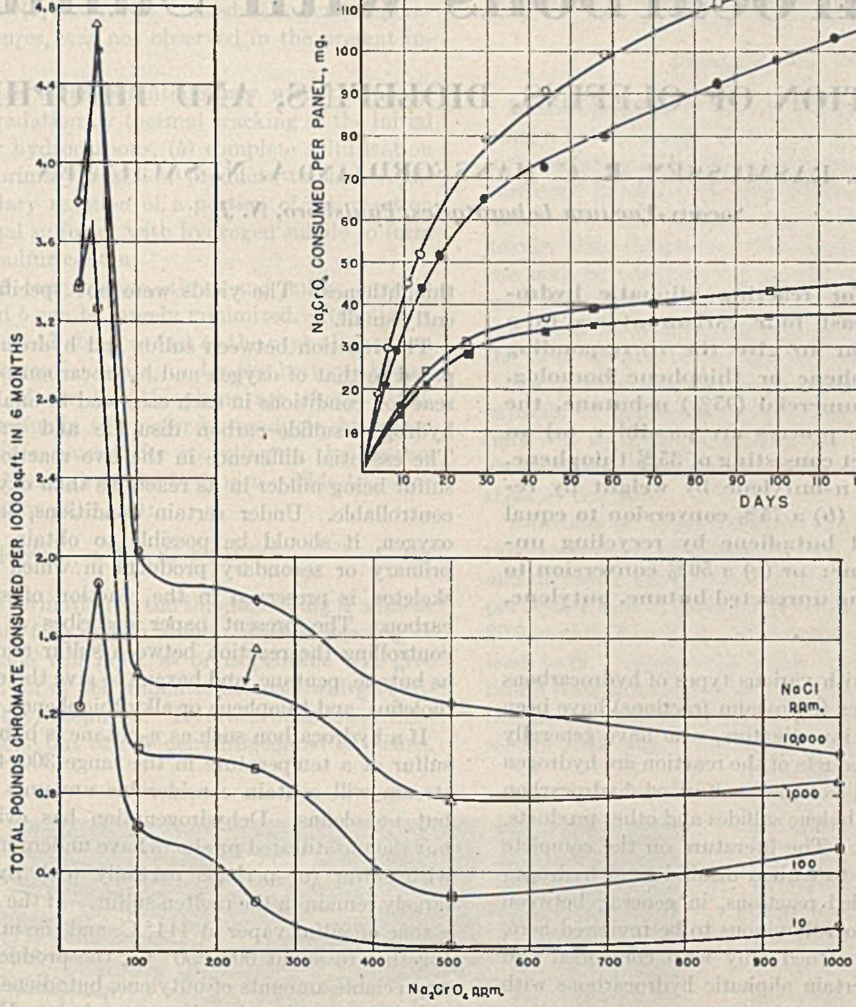


Figure 7. Effect of Chloride after 6-Month Exposure

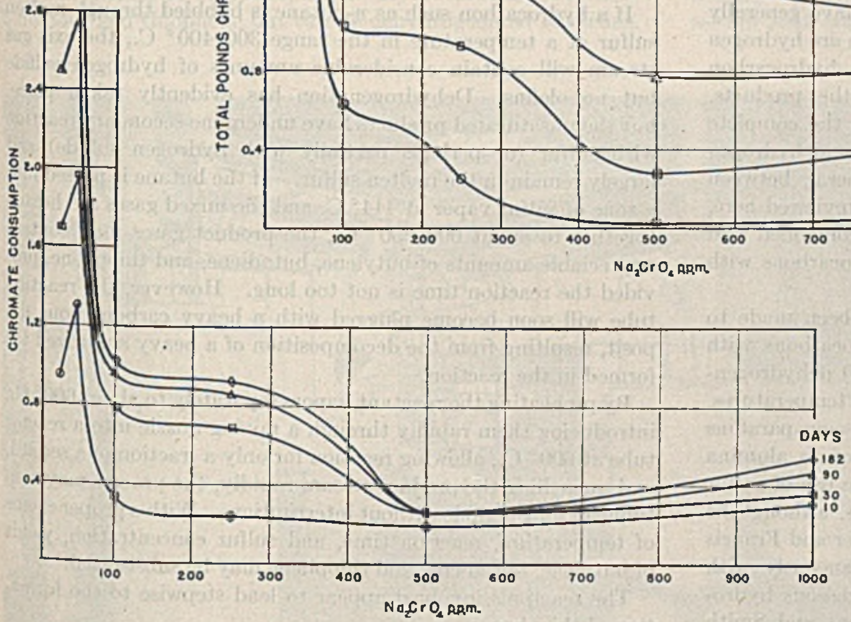


Figure 8. Effect of Time in the Presence of 100 P.P.M. Sodium Chloride

water is increased, the consumption of chromate increases, especially during the first 10 days while the protective film is forming. (*e*) Rate of consumption of chromate fluctuates in a cyclic manner, but the amplitude and frequency decrease with lapse of time until conditions are substantially constant.

These data have important practical applications. They show that it is most advantageous to start treatment of a water system with a comparatively high concentration of chromate and to maintain such a concentration until the protective film is formed. This concentration may be lowered later. An example was given to illustrate how the optimum concentration of chromate may be estimated for inhibiting corrosion in recirculating water systems such as are commonly employed for air conditioning and other cooling purposes.

ACKNOWLEDGMENT

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Reactions of Aliphatic Hydrocarbons with Sulfur

PRODUCTION OF OLEFINS, DIOLEFINS, AND THIOPHENE

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A process is described for reacting aliphatic hydrocarbons, containing at least four carbon atoms in a straight chain, with sulfur to give the corresponding olefin, diolefin, and thiophene or thiophene homolog. If the charge stock is commercial (95%) *n*-butane, the following variations of the process are possible: (*a*) an 80% conversion to a product consisting of 35% thiophene, 35% butadiene, and 30% *n*-butylene by weight by recycling unreacted butane; (*b*) a 75% conversion to equal weights of thiophene and butadiene by recycling unreacted butane and butylene; or (*c*) a 50% conversion to thiophene alone by recycling unreacted butane, butylene, and butadiene.

THE reactions of sulfur with various types of hydrocarbons and hydrocarbon mixtures (petroleum fractions) have been extensively studied by many investigators, who have generally reported that the principal products of the reaction are hydrogen sulfide, carbon disulfide, and complex sulfurized hydrocarbon derivatives, including polymethylene sulfides and other products, mostly of unknown structure. The literature on the complete sulfurization of hydrocarbons to carbon disulfide and hydrogen sulfide and on the uncontrolled reactions, in general, between hydrocarbons and sulfur is too voluminous to be reviewed here, particularly since we are concerned only with controlled and more selective reactions of certain aliphatic hydrocarbons with sulfur.

Some comparatively successful attempts have been made to dehydrogenate selectively specific types of hydrocarbons with sulfur. Ruzicka, Meyer, and Mingazzini (*14, 15*) dehydrogenated naphthenes with sulfur at moderately high temperatures. Monroe and Ipatieff (*12*) produced olefins from gaseous paraffins by dehydrogenation with sulfur in the presence of an alumina catalyst at 550–650° C. Wulff (*18*) suggested the use of sulfur in the production of acetylene from hydrocarbons, although he actually used chlorine in his experiments. Wheeler and Francis (*17*) claimed to have produced benzene, simultaneously with carbon disulfide, by the reaction of sulfur with gaseous hydrocarbons at temperatures above 1000° C. Gibbons and Smith (*8*) dehydrogenated ethylbenzene to styrene with sulfur at 500–700° C.

Thiophene and derivatives have been synthesized from hydrocarbons and sulfur in a number of ways. The reaction of acetylene and sulfur with and without catalysts has constituted the major preferred prior art (*2, 11, 13*). Shepard, Henne, and Midgley (*16*) bubbled butadiene through molten sulfur and obtained a yield of 6% thiophene; using isoprene, the yield of methylthiophene was 47%. Baker and Reid (*1*) reacted *n*-butane and *n*-octane with sulfur in a bomb at 300° C. for 24 to 48 hours and obtained traces of thiophene and alkylthiophenes, respectively. Friedmann (*5, 6, 7*) reacted a variety of paraffins and olefins with sulfur under pressure at 300° C. for long periods to give various thiophane and thiophene derivatives and thiophthenes. The yields were not specified but were apparently small.

The reaction between sulfur and hydrocarbons may be compared to that of oxygen and hydrocarbons, in that uncontrolled reaction conditions in each case lead to analogous end products: hydrogen sulfide–carbon disulfide and water–carbon dioxide. The essential difference in the two reactions is one of degree, sulfur being milder in its reactions than oxygen and hence more controllable. Under certain conditions, less critical than for oxygen, it should be possible to obtain attractive yields of primary or secondary products in which the original carbon skeleton is preserved in the reaction of sulfur with a hydrocarbon. The present paper describes a feasible method for controlling the reaction between sulfur and such hydrocarbons as butane, pentane, and hexane to give the corresponding olefins, diolefins, and thiophene or alkylthiophenes.

If a hydrocarbon such as *n*-butane is bubbled through molten sulfur at a temperature in the range 300–400° C., the exit gas stream will contain considerable amounts of hydrogen sulfide but no olefins. Dehydrogenation has evidently taken place, but the unsaturated products have undergone secondary reaction with sulfur (or perhaps partially with hydrogen sulfide) and largely remain in the molten sulfur. If the butane is passed into a zone of sulfur vapor at 444° C. and the mixed gases are heated together to about 600–650° C., the product gases may contain appreciable amounts of butylene, butadiene, and thiophene, provided the reaction time is not too long. However, the reaction tube will soon become plugged with a heavy carbonaceous deposit, resulting from the decomposition of a heavy sulfurized tar formed in the reaction.

By preheating the reactant vapors separately to about 600° C., introducing them rapidly through a mixing nozzle into a reactor tube at 600° C., allowing reaction for only a fraction of a second, and quenching the product stream rapidly, the process may continue for long periods without interruption. With a proper choice of temperature, reaction time, and sulfur concentration, yields of butylene, butadiene, and thiophene may be substantial.

The reactions involved appear to lead stepwise to the formation of thiophene:

$$C_4H_{10} + {}^1/_2\,S_2 \longrightarrow C_4H_8 + H_2S \qquad (1)$$

$$C_4H_8 + {}^1/_2\,S_2 \longrightarrow C_4H_6 + H_2S \qquad (2)$$

$$C_4H_6 + S_2 \longrightarrow C_4H_4S + H_2S \qquad (3)$$

Actually, these equations represent the ideal case, but other reactions also occur. Some of them may be controlled and minimized, resulting practically in about an 80% conversion[1] of butane according to Equations 1, 2, and 3—that is, withdrawing

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[1] Except where otherwise indicated, conversion here refers to moles of hydrocarbon charge converted to product indicated per mole charged, times 100. Thus a 50% conversion of butane to thiophene would be 0.50 mole of thiophene per mole of butane charged or about 72 pounds of thiophene per 100 pounds of butane charged.

butylene, butadiene, and thiophene as useful products, or about 50% conversion of butane to thiophene alone for the over-all reaction.

The formation of thiophanes according to the reaction,

$$C_4H_{10} + S_2 \longrightarrow C_4H_8S + H_2S$$

reported by Friedmann (*5*, *6*, *7*) who worked at lower temperatures and higher pressures, was not observed in the present investigation.

Other reactions which occur simultaneously with the above reactions are: (*a*) degradation by thermal cracking of the initial hydrocarbon to lighter hydrocarbons, (*b*) complete sulfurization of a portion of the primary reaction products to carbon disulfide, and (*c*) secondary reaction of a portion of the reaction products with additional sulfur or with hydrogen sulfide to form a complex tar of high sulfur content.

By proper choice of temperature, time, and sulfur concentration, reactions *a* and *b* can be largely minimized. Reaction *c*, however, appears to proceed about as fast as the over-all reaction leading to thiophene formation since, under the best conditions attained, the amount of tar and thiophene are about equal. Practically all of the sulfur in the major by-products, hydrogen sulfide and tar, can be recovered for recycling to the process by burning the tar and enough of the hydrogen sulfide to sulfur dioxide to give the reaction (*3*, *9*, *10*):

$$2H_2S + SO_2 \longrightarrow 1^1/_2 S_2 + 2H_2O \qquad (4)$$

A prerequisite to the formation of the thiophene ring is a linear chain containing at least four carbon atoms. *n*-Butane will give thiophene, but isobutane will not; *n*- or isopentane will give methylthiophenes, and all of the aliphatic hexanes will give dimethylthiophenes or ethylthiophene. Hydrocarbons lower than C_4 do not yield thiophene but can be dehydrogenated to olefins.

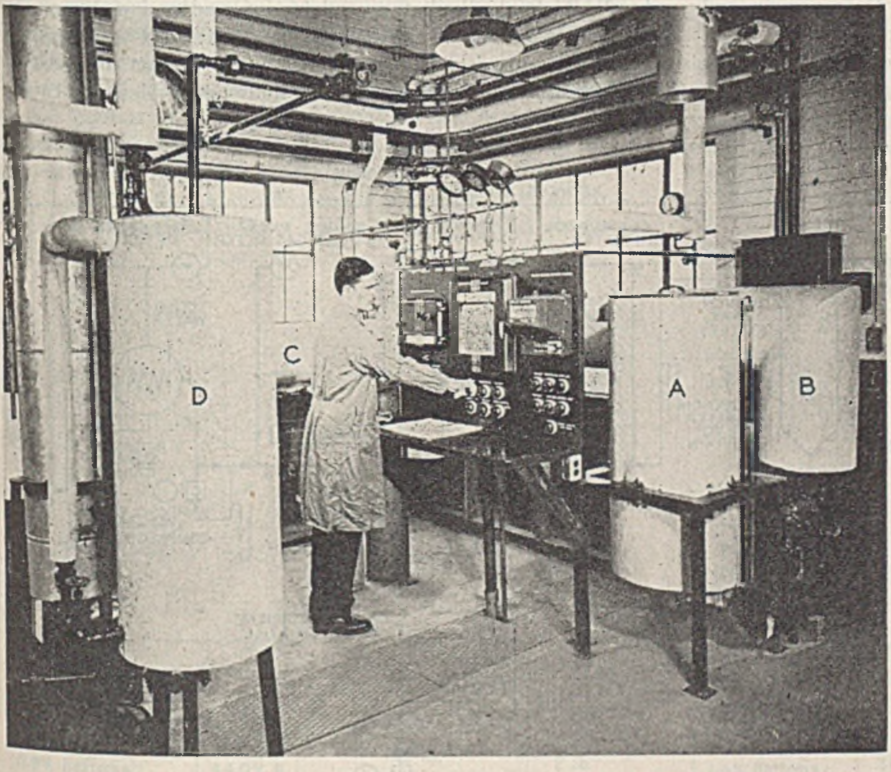

Figure 1. **Hundred-Pound Unit for the Reaction of Aliphatic Hydrocarbons with Sulfur**

A, liquid sulfur reservoir and sight glass; *B*, sulfur vaporizer-preheater, with sulfur charge pump below; *C*, reactor; *D*, thiophene receiver, with quench tower, glass-wool filter and caustic scrubber just beyond. The hydrocarbon storage tanks are located outside the building. The hydrocarbon vaporizer-preheater lead bath is hidden from view beyond the control panel board.

No diolefin was found in the reaction of propane or propylene with sulfur, and no appreciable amounts of acetylenic hydrocarbons were found in the range of conditions investigated with any of the hydrocarbons. The lower hydrocarbons, especially the olefins such as ethylene and propylene, are readily converted to carbon disulfide. Methane requires more severe conditions of time and temperature and forms principally carbon disulfide.

PROCESS AND APPARATUS

In the operation of the process under the preferred conditions using *n*-butane charge, there appears in the product stream a mixture consisting of butylene, butadiene, and thiophene along with unreacted butane, hydrogen sulfide, tar, and minor amounts of carbon disulfide, lighter cracked hydrocarbons, and bottoms heavier than thiophene. The thiophene, butadiene, and butylene may be withdrawn from the product stream, and the unreacted butane recycled; or the thiophene alone or the thiophene and butadiene or butylene may be withdrawn and the balance of the C_4 in the product stream recycled.

The process was conducted in a small continuous unit with a capacity of 20 pounds of thiophene per day. Subsequently the unit was enlarged to produce 100 pounds per day. Figure 1 shows the larger unit in operation, and Figure 2 is a process flow sheet of the unit.

n-Butane of approximately 95% purity, obtained as a by-product from an alkylation unit, was charged through a rotameter and metering valve from a blow case, maintained at 120 pounds per square inch by nitrogen pressure, to a preheater consisting of 20 feet of 0.15-inch i.d., 18–8 stainless steel tubing immersed in a lead bath. Commercial grade sulfur was pumped as molten liquid from a surge pot to a 20-foot section of $^1/_8$-inch, standard iron pipe size, 27% chromium stainless steel tubing immersed in a second lead bath. The sulfur pump body was constructed of 27% chromium steel, and the $^3/_8$-inch plunger, of 18–8 steel. The body was jacketed with 70 pounds of steam. Hills-McCanna double-action, vertical-composite check valves with SS 304 seats and SS 440 balls were used on the pump. The check valves, sulfur lines, and other valves in the lines were traced with 70 pounds of steam. The check valves were protected against fouling by a steam-jacketed glass-wool filter. The pumping rate was controlled by adjusting the plunger stroke and stroking rate. The sulfur rate was metered by pumping periodically from an internally steam-traced, calibrated sight glass adjoining the surge pot through a manifold valve arrangement. Rates from 1 to 100 cc. per minute could be obtained and accurately held. The jacketing or tracing of sulfur lines and reservoirs with 70 pounds of steam eliminated pumping eccentricities (noted by some observers) due to the peculiar viscosity characteristics of liquid sulfur (6.7 centipoises at 157° C. as compared to about 93,000 centipoises at 190°).

The preheated butane and sulfur vapors were then sent through a mixing nozzle to the reactor which consisted of 27% chromium steel (or other alloy) coils of varying size immersed in a third lead bath. The reactor was changed at frequent intervals to give different reaction times. Usually, turbulent flow was maintained in the reactor; when charging rates were changed, the simultaneous change in pressure drop across the reactor resulted in nearly the same reaction time. Thus a different size reactor coil was needed each time a different reaction time was desired. The pressure drop across the reactor and auxiliary equipment varied from about 1 to 20 pounds gage, depending upon reactor coil size and charging rates.

Temperature was measured by thermocouples in the lead baths and in the transfer lines at the exits of preheaters and reactor. The latter thermocouples were placed inside thermowells, made by welding an 8-inch-long tube through a header into a larger diameter section of the transfer line. Dimensions of the tube and of the enlarged section were chosen to give approximately the same annular space as cross section of the transfer line. Temperature was controlled by Transtats on the preheaters and a Micromax controller on the reactor.

Upon leaving the reactor, the reaction products were immediately quenched with a water spray to a temperature where no further reaction took place, usually about 120° C. Quench water was withdrawn from the side of the quench column near its boiling point to minimize the solubility of hydrogen sulfide and butadiene in the water. Shock cooling of the products, such as is obtained with a quench, was found necessary to arrest the reaction and to prevent undue degradation and coking.

Most of the tar formed was thrown down in the quench tower and drained off the bottom periodically. Upon leaving the quench tower, the gaseous products were passed through a glass-wool filter to remove suspended tar mist. Tar was also withdrawn periodically from the bottom of the filter. The pressure drop across the filter was about 0.5 to 1.0 inch of mercury.

The filtered product vapors were then sent to a countercurrent caustic scrubber where hydrogen sulfide was removed. Hot caustic was circulated through the tower from a reservoir. Fresh make-up caustic was continuously pumped to the reservoir, and the same amount of spent caustic removed from the bottom of the scrubber. The pressure drop across the scrubber was about 1 to 2 inches of mercury. The caustic was kept at about 70° C. by a steam coil in the reservoir to keep the thiophene from condensing out.

The product stream, free of hydrogen sulfide and tar, was then cooled to about 5° C. and sent to a gas separator where most of the crude thiophene was thrown out. The remaining uncondensed gases were metered and sent to the vent stack in the single-pass operation or in the recycle operation to a Frigidaire SO_2 compressor to be compressed to 80 pounds per square inch. The rate of compression was controlled by bleeding back to the compressor intake the proper amount of compressed gases through a metering valve. By this expedient the pressure on the system at the intake to the compressor was maintained at 0.0 inch of mercury.

The main stream of compressed gases was sent first to an oil separator and then through a water-cooled heat exchanger (for liquefaction) to a liquid C_4 reservoir. Pressure on the reservoir was maintained at 80 pounds per square inch by continuously bleeding off through a metering valve the proper amount of light gases formed as a result of degradation. The light gases were metered and sent to the vent stack.

The liquid level in the C_4 reservoir was kept constant by metering the proper amount of C_4 recycle to the butane preheater to repeat the cycle and by readjusting the fresh-feed butane rate.

In making a run, data were not taken until the recycle stream and recycle level in the reservoir had attained equilibrium (usually in 1–2 hours). The run proper then lasted about 4–6 hours. Temperature and pressure readings were taken every half hour. Sulfur, butane, and recycle rates were checked at the same time. Hydrogen sulfide control analysis on the gases going into the scrubber was made every 15 minutes. Samples of light gas and recycle stream (or product gas if operation was single pass) were withdrawn over the whole run for analysis. Material balances were obtained from charge data, from the above analyses, and from the weights and analysis of the tar and crude thiophene. The gaseous products and recycle stream were analyzed by Podbielniak distillation and by infrared and mass spectrographic examination; butadiene was determined by absorption in maleic anhydride. The crude thiophene was analyzed by fractionation through a packed column equivalent to twenty

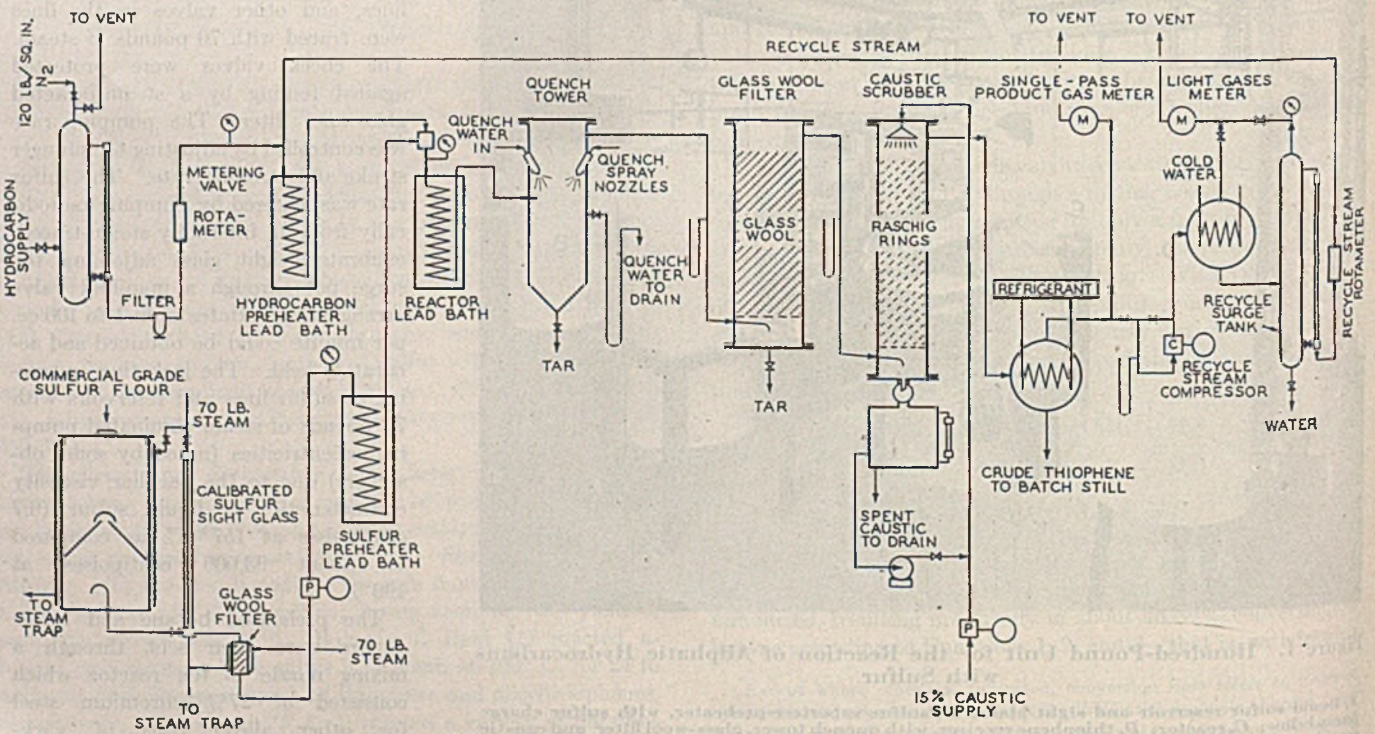

Figure 2. Flow Diagram of Unit for Reaction of Hydrocarbons with Sulfur

theoretical plates. Ultimate analyses were made on the tar and thiophene bottoms. Figure 3 is a material-balance flow sheet of a typical recycle run for the production of thiophene. Figures 4 and 5 are the material-balance flow sheets calculated from single-pass runs for the operation where (*a*) butadiene and (*b*) butadiene and butylene as well as thiophene are withdrawn as useful products.

No attempt was made to obtain sharp fractions in the separations by complicated fractionation equipment. As a result the crude thiophene contained some C_4 and the recycle C_4 contained some lighter ends, as well as some thiophene and carbon disulfide, and the light bleed-off gases contained appreciable amounts of C_4. These overlappings were taken into account in calculating yields.

EFFECT OF TIME AND TEMPERATURE

The relation of temperature range (450° to 760° C.) to reaction time was studied. Other variables investigated were the effect of changing the ratio of sulfur to hydrocarbon in the feed and the effect of pressure on the reaction.

The study was carried on in two parts—the single-pass operation and the recycle operation described above. In addition to *n*-butane, other charge materials investigated were *n*-butenes and butadiene as well as C_1–C_6 paraffins and certain selected olefins from the group. Pure butadiene per se could not be used because of its reactivity and secondary coking in the preheater. However, mixtures of butadiene and butane, of butylene and butane, and of all three were studied. Isobutane does not react to give thiophene, but experiments showed that it is dehydrogenated to isobutylene. Rather large amounts of isobutylene are lost to secondary tar formation, however (Table I). *n*-Butane refinery cuts usually contain minor amounts of isobutane and sometimes small quantities of isopentane. The isobutane in small proportions is not detrimental, although it contributes nothing useful to the process unless the isobutylene formed is withdrawn—for example, by polymerization to di-isobutylene with a suitable catalyst. The pentane contributes methylthiophene to the final product which can be withdrawn as a useful derivative.

The yield of thiophene per pass varies from 8 to 23 pounds per 100 pounds of *n*-butane charged as the temperature is changed from about 480° to 710° C., at a fixed ratio of sulfur to hydrocarbon of 1.0 and a reaction time of 0.07 second (Figure 6, curve I) and from 0 to about 45 pounds per 100 pounds of butane charged as the weight ratio of sulfur to hydrocarbon charge is increased from 0 to 4.5 at a constant reaction temperature of 677° C. and reaction time of 0.07 second (Figure 7, curve I).

For the reaction time of 0.07 second, the ultimate yield of thiophene in the recycle operation increases as the reaction temperature increases until it reaches a maximum at about 700° C.; then it falls off rapidly as a result of degradation and carbon disulfide formation (Figure 6, curve II). Similarly, the sulfur-hydrocarbon ratio variable shows an optimum peak which for a reaction time of 0.07 second at 677° C. is in the vicinity of 1 to 2 (Figure 7, curve II).

From the shape of the two curves in Figure 7 it is obvious that the ratio of sulfur to hydrocarbon charged may be varied over wide limits. An increase in the proportion of sulfur at a fixed temperature and reaction time increases the conversion per pass to desired products. Too much sulfur, however, results in poor efficiency of sulfur conversion per pass and at higher temperatures tends to favor the formation of carbon disulfide. This is the reason for the downward deflection of curve II. Too low a proportion of sulfur, on the other hand, lowers the conversion per pass and the ultimate yield due to increased over-all degradation. Best results are obtained with a weight ratio of sulfur to hydrocarbon in the range 0.5 to 4.0; about 1.0 is preferred for the recycle operation.

The consumption of sulfur—that is, pounds of sulfur charged per pound of thiophene produced—is highest at the lowest

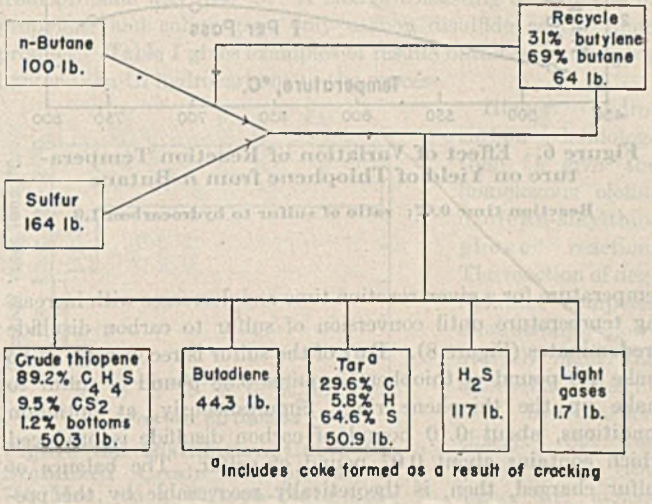

Figure 4. Material Balance for Thiophene and Butadiene from *n*-Butane and Sulfur

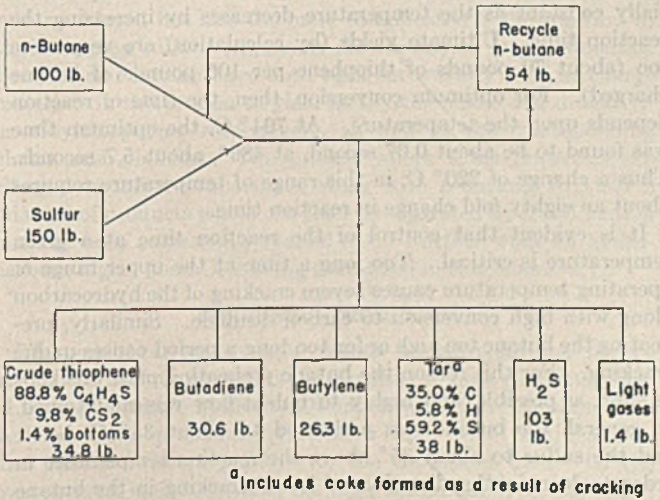

Figure 5. Material Balance for Thiophene, Butylene, and Butadiene from *n*-Butane and Sulfur

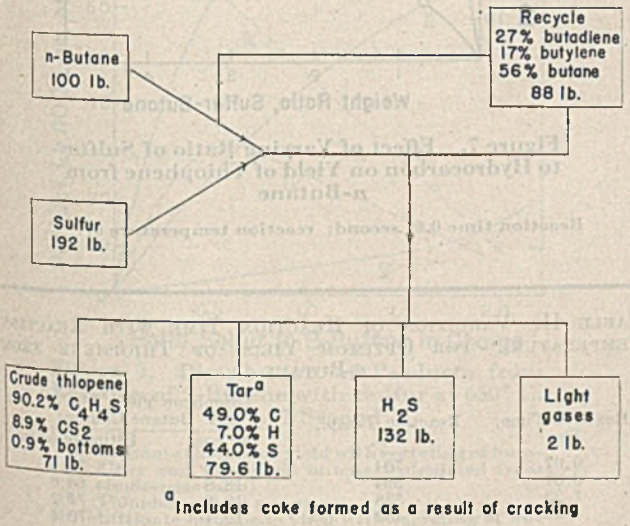

Figure 3. Material Balance for Thiophene and *n*-Butane and Sulfur

Table I. Results of Charging Hydrocarbons and Mixtures to the Process

Hydrocarbon Charged	Reaction Temp., ° C.	Approx. Reaction Time, Sec.	Wt. Ratio, S to Hydrocarbon in Charge	Conversion[a] of Hydrocarbon Charged per Pass	Products and Yields[b] per Pass
n-Butane	650	0.07	1.0	25.4	15.5 C_4H_4S
2-Butene	650	0.07	1.0	53.7	28.7 C_4H_4S
Mixed *n*-butylenes	652	0.07	1.0	53.3	27.2 C_4H_4S
30% butadiene + 70% *n*-butane	651	0.07	1.1	42.4	22.1 C_4H_4S
Isobutane	649	0.07	0.5	22.8	14.8 iso-C_4H_8
Propane	704	0.1	2.0	17.6	15.0 C_3H_6
Ethane	760	0.1	2.0	15.9	14.4 C_2H_4
Propylene	704	0.1	2.0	8.9	8.2 CS_2
Ethylene	760	0.1	2.0	8.3	7.9 CS_2

[a] Expressed as moles of hydrocarbon used to form the product indicated and degradation products per mole charged, × 100.

[b] Expressed as moles of hydrocarbon charge converted to the product indicated per mole charged, × 100. The difference between columns 5 and 6 represents degradation to other products than those indicated, chiefly tar; column 6 divided by column 5 in each case would be an approximate calculated ultimate yield.

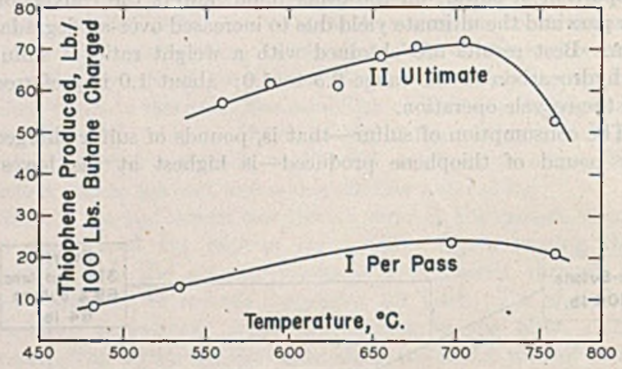

Figure 6. Effect of Variation of Reaction Temperature on Yield of Thiophene from *n*-Butane

Reaction time 0.07; ratio of sulfur to hydrocarbon 1.0

temperature for a given reaction time and decreases with increasing temperature until conversion of sulfur to carbon disulfide predominates (Figure 8). Part of the sulfur is recoverable. To make 1.0 pound of thiophene requires 0.38 pound of sulfur to make up the thiophene ring. Simultaneously, at optimum conditions, about 0.10 pound of carbon disulfide is produced which contains about 0.07 pound of sulfur. The balance of sulfur charged, then, is theoretically recoverable by the previously mentioned process (Equation 4).

Table II shows the relation between reaction time and reaction temperature; the yield of thiophene per pass can be kept essentially constant as the temperature decreases by increasing the reaction time. Ultimate yields (by calculation) are very close too (about 70 pounds of thiophene per 100 pounds of butane charged). For optimum conversion, then, the time of reaction depends upon the temperature. At 704° C. the optimum time was found to be about 0.07 second, at 480°, about 5.7 seconds. Thus a change of 220° C. in this range of temperature requires about an eighty fold change in reaction time.

It is evident that control of the reaction time at a given temperature is critical. Too long a time at the upper range of operating temperature causes severe cracking of the hydrocarbon along with high conversion to carbon disulfide. Similarly, preheating the butane too high or for too long a period causes undue cracking. For this reason the butane preheating path was kept as short as possible, and highly turbulent flow was maintained. In general, the butane was preheated to about 35° C. below and the sulfur to about 35° above the reaction temperature in order to lean in the direction of lesser cracking in the butane preheating step. Equally divergent preheating temperatures do not result in convergence to reaction temperature upon mixing the reactants, since the specific heats of reactants are different (0.28 for S_2 and 0.81 for butane at 670° C.). Superheating sulfur well above reaction temperatures would be advantageous, both for supplying part of the butane preheating load and thus minimizing cracking, and for supplying part of the reactor heat load. Corrosion of alloy sulfur preheaters, however, increases perceptibly at temperatures above 700° C. Preheating the sulfur for the purpose of dissociating the polymeric forms to S_2 or S_1 does not seem to be a prerequisite for good reaction; about the same yields are obtained with a sulfur preheat of 700° as with 540° C. if the same reaction temperature and time are maintained (runs 4 and 5, Table III). The reactor heat load is greater in the latter instance.

Unduly long reaction times at the lower range of reaction temperatures cause excessive tar formation. On the other hand, too short a reaction time results in too low a conversion per pass; hence for a given amount of end product, a larger throughput of sulfur and a higher ratio of hydrocarbon recycle must be used, which detracts from the economics of the process. Runs 2 and 3 (Table III) represent examples of such unfavorable process conditions.

An increase in pressure on the reaction lowers the yield (runs 6 and 7, Table III); a threefold increase in pressure almost halves the yield of thiophene from *n*-butane. The reaction, therefore, is best run at atmospheric pressure or with enough pressure to give the desired flow through the reactor and auxiliary system.

PRODUCT DISTRIBUTION

In general, the more unsaturated the charge material, the lower the temperature necessary to achieve a given yield of thiophene per pass at a fixed reaction time and constant ratio of sulfur to hydrocarbon (Table I) or, at a fixed temperature and

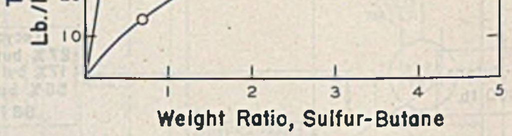

Figure 7. Effect of Varying Ratio of Sulfur to Hydrocarbon on Yield of Thiophene from *n*-Butane

Reaction time 0.07 second; reaction temperature 677° C.

Table II. Variation of Reaction Time with Reaction Temperature[a] for Optimum Yield of Thiophene from *n*-Butane

Reaction Time, Sec.	Reaction Temp., ° C.	Thiophene Yield, Lb./100 Lb. Butane Charged	
		Per pass	Ultimate (calcd.)
0.07	704	18.4	71.6
0.37	594	18.8	68.6
1.23	538	19.9	71.2
5.66	482	19.4	70.4

[a] Ratio of sulfur to hydrocarbon held constant at 1.0.

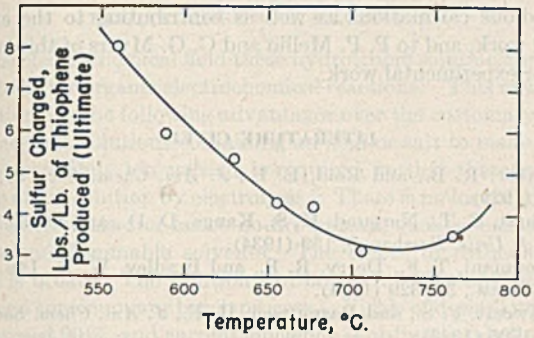

Figure 8. Sulfur Consumption as a Function of Temperature in Production of Thiophene from n-Butane

Reaction time 0.07 second; ratio of sulfur to hydrocarbon 1.0

reaction time, the lower the ratio of sulfur to hydrocarbon for a constant yield of thiophene. The optimum conversion per pass is somewhat higher for butene and for mixtures of butadiene and butane than for butane alone. Ultimate yields, too, are somewhat higher, about 80 pounds of thiophene per 100 pounds of n-butene as compared to 70 pounds of thiophene per 100 pounds of n-butane (Figures 7 and 9). It is also possible to obtain much higher yields of butadiene from butylene than from butane. Figure 9 shows the distribution of products for the reaction of 2-butene with sulfur at 600° C. and 0.07 second.

The nature of the thiophene obtained from the processing of n-butane is of unusual interest. Figure 10 shows the distillation curve using a fifteen-theoretical-plate column for a typical sample of the stabilized crude. Only three components are found in the overhead in addition to a small amount of C_4 coming off initially—carbon disulfide, thiophene, and methylthiophene. Mass spectrographic analysis of the thiophene cut shows the presence of trace amounts of benzene (0.1 to 0.5 mol %), in addition to bordering components. No other impurity has been detected. Thus on a batch distillation using a fifteen-plate column with a 15 to 1 reflux on transitions and a 5 to 1 reflux on plateaus, 99+% thiophene can readily be obtained. The physical properties of a typical sample of constant-boiling thiophene from such a distillation are: Cottrell boiling point (760 mm.) 84.0° C., d_4^{20} 1.0644, n_D^{20} 1.5289, freezing point −38.6° C. The corresponding reported values (*4*) for 99.9+% thiophene are: Cottrell boiling point (760 mm.) 84.12° C., d_4^{20} 1.0644, n_D^{20} 1.5287, freezing point −38.30° C.

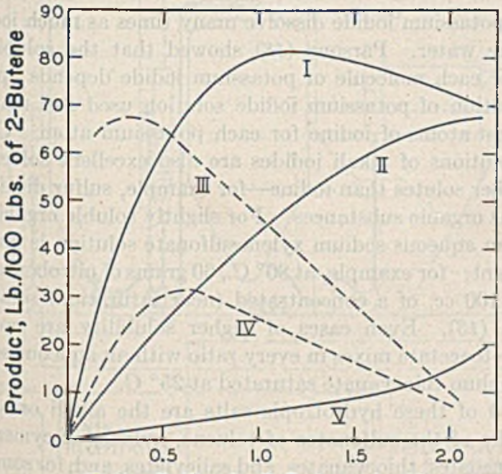

Figure 9. Distribution of Products from Reaction of 2-Butene with Sulfur at 650° C. for 0.07 Second

I. Ultimate thiophene yield with recycling of butadiene and unreacted butene (calculated from single-pass data)
II. Thiophene yield per pass
III. Ultimate butadiene yield with recycling of butene (calculated from single-pass data)
IV. Butadiene yield per pass
V. Carbon disulfide yield per pass

Table III. Effect of Varying Process Conditions on Yield of Thiophene from n-Butane and Sulfur

Run No.	Reaction Temp., ° C.	Preheat Temp. of S, ° C.	Reaction Time, Sec.	Wt. Ratio, S to Hydrocarbon in Charge	Reaction Pressure, Lb./Sq. In. Gage	Thiophene Yield, Lb./100 Lb. Butane Charged: Per pass	Thiophene Yield, Lb./100 Lb. Butane Charged: Ultimate (calcd.)
1	594	677	0.4	1.0	Atm.	18.8	68.6
2	538	675	0.4	1.1	Atm.	12.3	67.2
3	538	677	2.2	1.0	Atm.	24.6	52.1
4	567	706	0.3	1.0	Atm.	22.2	69.3
5	540	540	0.4	0.9	Atm.	17.0	70.1
6	562	683	1.0	1.0	1.2	19.9	69.0
7	562	683	1.0	1.0	30.0	9.5	40.9

Hydrocarbons lighter than C_4 yielded only the corresponding olefins and carbon disulfide. In general, the lighter the hydrocarbon homolog, the higher the reaction temperature necessary to achieve dehydrogenation, other things being constant. The dehydrogenation of ethane to ethylene required a temperature of about 760° C. for a reaction time of 0.1 second and a sulfur ratio of 2 to 1 by weight to give a 15% yield. The reaction temperature under similar conditions and for similar yield of propylene from propane was 704° C. A charge consisting of ethylene or propylene and sulfur gave only carbon disulfide as the main product. Table I gives examples of results obtained in charging lighter than C_4 hydrocarbons to the process.

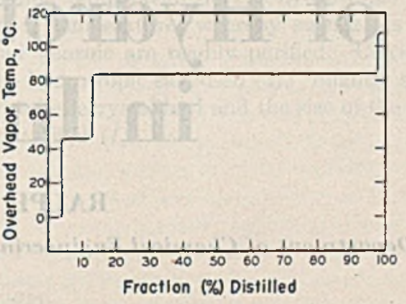

Figure 10. Distillation Curve for Stabilized Crude Thiophene at 760 Mm. on a Fifteen-Plate Column, Using 15–1 Reflux on Transitions and 5–1 Reflux on Plateaus

Higher hydrocarbon homologs than C_4 give the homologous olefin-diolefin-alkylthiophene reaction. The reaction of degradation competes more strongly, however, the higher the molecular weight of hydrocarbon charge. On the other hand, the higher the molecular weight, the more readily is dehydrogenation with sulfur achieved but also the more complicated is the reaction in that complex sulfur compounds are formed in larger amounts. Pentane and hexane have both been successfully used as charge materials in the process to yield methylthiophene and dimethyl- or ethylthiophene, respectively, as well as the corresponding olefins and diolefins. The process where these materials are charged in minor proportions, along with n-butane, to yield a mixture of products which can then be separated by fractionation has also been successfully carried out. Further work on hydrocarbons higher than C_4 is being conducted in this laboratory.

CORROSION PROBLEMS

The superheating of sulfur vapor to temperatures in the vicinity of 700° C. as well as the handling of high concentrations of hydrogen sulfide at elevated temperatures have presented severe corrosion problems. Extensive tests were conducted to find corrosion-resistant alloys for the conditions used. Of the conventional stainless steels, the high chromium type was found to be superior to the chromium-nickel types. For this reason 27% chromium steel (low carbon, no nickel) was used extensively since it is available in tubing of all sizes and can readily be machined. High silicon steels, such as Duriron, were found to be superior to high chromium steels, but they can only be cast and are nonmachinable. A possible solution to the problem is aluminum-coated or calorized steels, or aluminum-containing steel alloys, perhaps also coated with aluminum. An alloy containing 20% chromium and 2% aluminum was found to be superior to 27% chromium steel. Aluminum-coated or calorized steels (both carbon steels and alloys) were found to be more corrosion resistant than any of the alloys just mentioned. The problem in connection with the calorized or aluminum-coated steels is to obtain a coating free of surface imperfections such as slag or oxide inclusions or pinholes. If such defects are present, they invariably cause localized failures. Many failures of aluminum-coated or calorized installations have been reported in connection with other projects, probably largely traceable to surface defects. Recent improvements in the method of applying the aluminum coat may decrease the frequency of such failures. The corrosion resistance of aluminum-coated articles is probably due to a protective coating of aluminum sulfide initially laid down on the aluminum-rich alloy, which is present on the calorized article or which soon forms from the aluminum-coated article as a result of diffusion of the aluminum into the parent metal when the specimen is heated.

ACKNOWLEDGMENT

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Use of Hydrotropic Solutions in Industry

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Hydrotropic solutions are better solvents than is commonly appreciated for slightly water-soluble inorganic and organic solutes. They offer a new basis for organic electrochemical reactions without the handicaps of volatile organic solvents. Other reactions of strictly chemical character proceed better than when ordinary solvents are used; for example, a new process for paper pulp manufacture using a neutral sodium xylenesulfonate solution gives excellent results.

HYDROTROPIC solutions are those aqueous salt solutions which effect decidedly greater solubility of slightly soluble substances than does pure water at the same temperature (*4*). This phenomenon is the reverse of the common salting-out effect following the addition of many electrolytes to aqueous solutions of numerous solutes. These phenomena of increased solubility were first noted by Neuberg (*17*) in 1916. This salting-in, as opposed to salting-out, effect is shown best by concentrated aqueous solutions of very soluble neutral salts of organic acids, with organic substances as solutes which have a low solubility in water. The phenomenon, however, is not confined to the field of aqueous solutions of organic salts and organic solutes, but is found in the inorganic field as well. It is largely independent of pH and seems to be best explained by the theory of mixed solvents (*2*).

An example with which most are familiar is that strong solutions of potassium iodide dissolve many times as much iodine as does pure water. Parsons (*18*) showed that the solubility of iodine for each molecule of potassium iodide depends upon the concentration of potassium iodide solution used and may even reach eight atoms of iodine for each potassium atom. Concentrated solutions of alkali iodides are also excellent solvents for many other solutes than iodine—for example, sulfur dioxide and numerous organic substances. For slightly soluble organic compounds an aqueous sodium xylenesulfonate solution is an excellent solvent; for example, at 80° C., 60 grams of nitrobenzene dissolve in 100 cc. of a concentrated (near saturation) solution of this salt (*13*). Even cases of higher solubility are not rare. Ethyl acetoacetate mixes in every ratio with an aqueous solution of ammonium thiocyanate saturated at 25° C.

Typical of these hydrotropic salts are the alkali or alkaline earth salts of the sulfonates of toluene, xylene, or cymene, the alkali benzoates, thiocyanates, and salicylates, and, for some compounds (particularly inorganic), even such common salts as the alkali bicarbonates, oxalates, and thiocyanates (*8*). The most generally useful of these is sodium xylenesulfonate, because it is both inexpensive and effective as a solvent.

Most hydrotropic solutions precipitate the solute on dilution with water; i.e., generally they show hydrotropic phenomena only when the hydrotropic salt is present in a ratio greater than one part in about three of water. Industrially this fact permits the ready recovery of the hydrotropic solvent for re-use.

ELECTROCHEMICAL REACTIONS

In the electrochemical field these hydrotropic solutions provide a new basis for organic electrochemical reactions. This new type of solution has the following advantages over the customary alcohol or acetone solutions containing an acid or salt to make them conductors: Only low voltage is required, so that there is little heating of the solution by electrolysis. There is no loss of solvent during electrolysis and hence no fire hazard, such as exists with volatile and flammable solvents. The choice of cathodes and anodes is broad. The solution can be operated at any pH and as either a continuous or batch process. Yields of desired product often exceed 90%, and current efficiency is ordinarily about 90%. The solution can be used for either oxidation or reduction without the formation of tars (*3, 12, 13, 14*).

ORGANIC REACTIONS

Many organic reactions, the rates of which are greatly limited by their two-phase nature, can be made to proceed rapidly by the use of such hydrotropic solvents. Typical reactions follow.

1. In Cannizzaro's reaction benzaldehyde is emulsified with caustic soda (5.6 grams in 100 cc. of water) which, after standing for a day at 30° C., gives 4.9% of the theoretical yield of benzoic acid. When a saturated sodium cymenesulfonate solution is substituted for most of the water, the yield is 72.5% (*15*).

2. Amyl chlorides are commercially hydrolyzed at 170° C. with strong caustic soda solution and soap to give an emulsion. If 10% caustic soda in a strong sodium xylenesulfonate solution is used, a temperature of 130° C. serves equally well in the same time period (*1, 11*).

3. When sodium cymenesulfonate is dissolved in aqueous ammonia in which it is readily soluble, benzyl chloride is added, and the whole is kept at 40° C. for a few hours, crystals of tribenzylamine separate. Yield after 2 days is 76% of theoretical, the balance being recovered, on dilution with water, as dibenzylamine (*1*).

4. In coupling for the production of certain common dyes, as Metanil Yellow or Orange IV, a slightly soluble reactant such as diphenylamine is required. Ordinarily this is dissolved in strong sulfuric acid, and later this objectionable and deleterious solvent has to be removed by neutralization. If diphenylamine is dissolved in a hydrotropic salt solvent and the diazotized metanilic acid and caustic soda are added to it, brilliant yellow crystals of Metanil Yellow separate in excellent yield (*1*). If sulfanilic acid is used instead of metanilic acid, Orange IV is likewise obtained in good yield (*1*).

Many substances which boil in a narrow range can be separated by extraction with a hydrotropic salt solution in which one constituent is more soluble than the other. Examples of such extractions follow.

1. When equal volumes of aniline and dimethylaniline are shaken with a calcium cymenesulfonate solution, the top layer contains dimethylaniline free from aniline, and the lower aqueous layer contains the aniline, the hydrotropic salt, and about 5% dimethylaniline. When this lower layer is used for a new extraction, no additional quantity of dimethylaniline dissolves (*4*).

2. The tar acids can be extracted by hydrotropic solutions from tars obtained by low and high temperature distillation of coal and can be readily recovered; thus the use and expense of caustic soda and its neutralization are avoided (*6, 7*).

Purification of many organic substances only slightly soluble in water can readily be accomplished, without expensive or flammable organic solvents, by the use of aqueous solutions of hydrotropic salts. Examples are the preparation of solutions near boiling temperature in the hydrotropic solvent and cooling to room temperature, whereby such acids as sulfanilic, salicylic, and benzoic are readily purified. Calcium cymenesulfonate is the hydrotropic salt used (*4*). Slightly soluble amines can likewise be recrystallized and the size of the crystals simultaneously controlled (*1*).

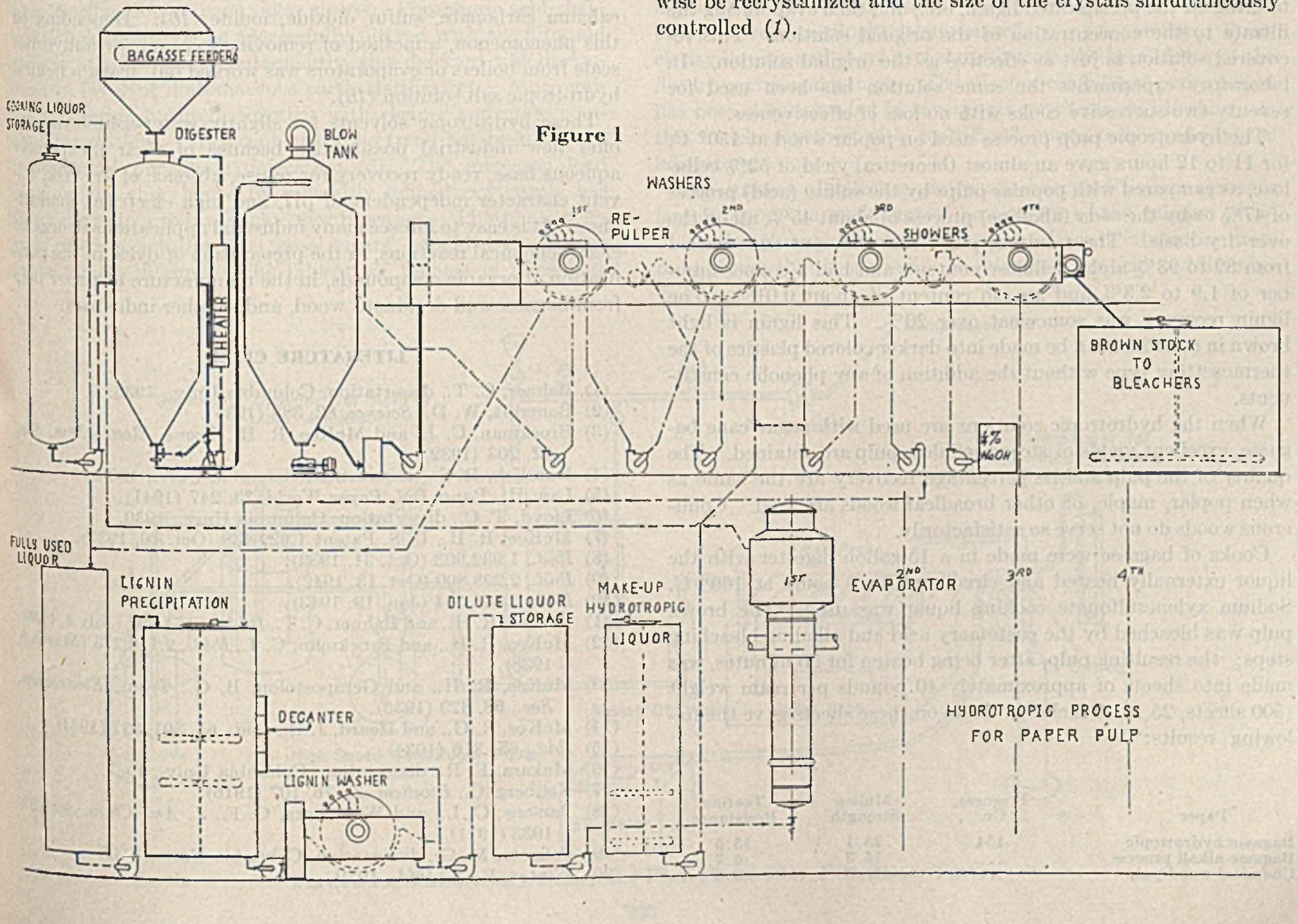

Figure 1

PULP PROCESS

The lignin and pentosans of wood are more soluble in solvents than is the cellulose. A new and potentially less costly method has been developed for making paper pulp by cooking wood, bagasse, bamboo, etc., with hydrotropic solutions (*5*, *10*, *19*). The most useful hydrotropic salts were found to be the alkali salts of xylenesulfonic, cymenesulfonic, and benzoic acids. Of these, sodium xylenesulfonate is the best and also the least expensive.

Since the solution used in the hydrotropic pulp process is neutral, there is little or no degradation of the cellulose, and a high yield as well as a high alpha-cellulose content of the pulp is obtained. The lignin is also recoverable in a form essentially unchanged from that in which it was present in the cellulosic material (wood or bagasse) used.

In comparison, in the sulfite pulp process the action of the acid cooking solution degrades a part of the cellulose and hydrolyzes another part (about 10%) to sugar; the lignin removed is in the form of a nearly useless calcium sulfonate salt and so is normally discarded to the river. In the alkaline processes (soda and kraft) the cellulose is even more degraded, and accordingly the percentage of alpha-cellulose is the lowest of any of the chemically made pulps. The lignin, under the conditions of cooking with alkali, is largely transformed into the sodium salts of useless organic acids. These are generally burned for their fuel value and to recover sodium carbonate for re-use in the plant.

Most of the work in the laboratory and pilot plant stages of this process (Figure 1) was carried out with approximately neutral 30 or 40% solutions of sodium xylenesulfonate. When wood or bagasse is cooked with this solution, the same solution can be used for six or seven cooks before being reworked or recovered for re-use. The limit to the re-use is when saturation with lignin is approached (about 350 grams per liter of solution).

The recovery consists simply in adding water to reduce the concentration of the hydrotropic salt from 30 or 40% to 10%, filtering off the precipitated lignin, etc., and then evaporating the filtrate to the concentration of the original solution. This recovered solution is just as effective as the original solution. In laboratory experiments the same solution has been used for seventy-two successive cooks with no loss of effectiveness.

The hydrotropic pulp process used on poplar wood at 150° C. for 11 to 12 hours gave an almost theoretical yield of 52% cellulose, as compared with popular pulps by the sulfite (acid) process of 47% or by the soda (alkaline) process of about 45%, all on the over-dry basis. The resulting pulp from different runs varied from 89 to 93% alpha-cellulose content, and had a copper number of 1.9 to 2.3% and an ash content of about 0.01%. The lignin recovery was somewhat over 20%. This lignin is light brown in color and can be made into darker colored plastics of the thermosetting type without the addition of any phenolic constituents.

When the hydrotropic solutions are used with sugar cane bagasse, excellent yields of strong cellulose pulp are obtained. The quality of the pulp and its percentage recovery are the same as when poplar, maple, or other broadleaf woods are used. Coniferous woods do not serve so satisfactorily.

Cooks of bagasse were made in a 15-gallon digester with the liquor externally heated and circulated for 3 hours at 160° C. Sodium xylenesulfonate cooking liquor was used. The brown pulp was bleached by the customary acid and alkaline bleaching steps; the resulting pulp, after being beaten for 50 minutes, was made into sheets of approximately 40 pounds per ream weight (500 sheets, 25 × 40 inches). Tests on these sheets gave the following results:

Paper	Freeness, Cc.	Mullen Strength	Tearing Resistance
Bagasse hydrotropic	154	25.1	15.5
Bagasse alkali process	...	15.3	6.7
Chemical wood pulp	...	11.5	8.0

For comparison, data are given for a wood pulp paper, utilized by many magazines, and for an extra-strength bagasse paper made by the alkali process and advocated for corrugated board, all on the basis of 40 pounds per ream.

The yield of bagasse unbleached pulp is about 48%. Bleaching reduces this to about 42%. This is a lower yield of bleached pulp than is now obtained by chemical processes from wood. It is much higher than has hitherto been obtained from whole bagasse, and is to be compared with 30% given by the alkali processes and with 7% obtained by the nitric acid–alkali process. The alpha-cellulose content of the bleached bagasse pulp is about 85%.

The hydrotropic process for making pulp from cellulosic materials is similar to the customary alkaline processes, but only about one third as much evaporation is required. There are no furnace or causticizing steps and there are many other minor advantages. The only losses of chemical solution are mechanical losses such as pulp leaks and in wash water, whereas furnace losses alone in mills using either of the alkali processes normally exceed 10% of the chemicals used per cycle. Mechanical losses in these mills approximate 1 to 2%. As a result of the steps omitted, the mill installation cost will be about one third less than for a soda or kraft mill of the same daily tonnage.

INORGANIC REACTIONS

The use of hydrotropic solutions is not limited to the organic field, although their greatest use will probably be in the organic industries. Beryllium oxide or hydroxide is readily soluble in a number of hydrotropic solutions—e.g., sodium salicylate, beryllium sulfate or nitrate, sodium bicarbonate, or ammonium oxalate. A new method, which depends on the use of hydrotropic solutions, has been developed for the extraction of beryllium oxide from beryl ore (*9*, *20*).

The solubilities of many slightly soluble inorganic compounds are increased ten to a thousand times when an aqueous hydrotropic salt solution is used instead of water—e.g., calcium sulfate, calcium carbonate, sulfur dioxide, iodine (*16*). Depending on this phenomenon, a method of removing gypsum (or anhydrite) scale from boilers or evaporators was worked out, using a neutral hydrotropic salt solution (*16*).

These hydrotropic solvents for slightly water-soluble solutes offer new industrial possibilities because of their inexpensive aqueous base, ready recovery for re-use, absence of fire risk, solvent character independent of pH, and high electrical conductance. It is easy to foresee many industrial applications in organic electrochemical reactions, in the preparation of dyes, in the purification of organic compounds, in the manufacture of paper pulp from bagasse and deciduous wood, and in other industries.

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Defecation of Refinery Sirups

PHOSPHORIC ACID AND LIME AS PIPE LINE DEFECANTS

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Pressure filtration of phosphoric acid–lime defecated refinery sirups using diatomaceous filter aids is now possible with pipe line defecation. Acid and lime are introduced in the pipe line between the pump and filter, and thus form the floc beyond the point where it would be damaged. Addition of phosphoric acid first, followed by the lime slurry, shows best results on cycle lengths, clarity of filtrate, color, and lime salt removal. Previously pressure filtration of the phosphate floc has met with little success owing to the comminution of the floc by centrifugal pump action. Poor-clarity liquor and decreased flow rates have been indicated by refinery and laboratory tests where the floc passes through the pump. Selection of filter aid for percentage of defecant is discussed. Past and recent investigations on phosphate defecation have shown the desirability of using this treatment; however, in the modern refinery this has been accomplished only by considerable initial outlay of equipment. The method described requires little change in filter station layout.

THE introduction in 1914–15 of diatomaceous filter aids and pressure filters replaced the bag filter and opened a new era in the clarification of cane sugar sirups. Phosphoric acid-defecated sirups could not be successfully filtered with the filter aid available at that time; consequently, this defecant was discontinued in favor of diatomaceous earth clarification. More uniform processing resulted, together with cleaner and more compact filter stations. In recent years the trend has been toward the return of phosphate defecation (*5*). The increased load placed on the char house by difficultly refined raw sugars has caused the refiner to investigate new processes. Phosphate defecation offers a solution for these sugars, provided the liquors can be readily filtered. The interest of refiners in phosphate defecation has been prompted by the scarcity and high cost of bone char plus the increasing prevalence of difficulty in refining raw sugars.

Progress in the use of phosphate defecation has been made—for example, the use of Dicalite Speedex in combination with phosphoric acid and lime on pressure filters and the Williamson and Jacobs clarifying systems. The advantages and disadvantages have been shown by Brown and Bemis (*1*). Other methods which have been reported successful are filtration of the phosphate floc (*4*) at low pressures (5–7 pounds) and filtration with cord filters operated by vacuum (*8*).

Many investigators have shown the advantages of the phosphoric acid–lime treatment in the removal of coloring matter and the elimination of gums, albumins, and other colloids. Spencer (*6, 7*) states: "Experience has shown that between 20 and 40 per cent of the total color of the melt liquor is removed by phosphoric acid, which means that the boneblack required for decolorization will be from 40–60 per cent less than with untreated liquors." Phosphoric acid–lime treatment removes up to 40% coloring material and 25% of the ash constituents (*1*).

Use of diatomaceous filter aids in conjunction with phosphoric acid and lime has been proposed (*3, 4*) and used with varying degrees of success. Laboratory tests using air pressure as the driving force give excellent results; however, high-speed centrifugal pumps have exceedingly deleterious effects upon the floc. Poor-clarity liquors and short cycles result from the breakdown of the floc by centrifugal pumps. The effect of centrifugal pump action has been demonstrated in several refinery tests and is shown in this article together with centrifugal pump tests made in the laboratory.

The success of filtering phosphate-defecated liquors depends largely upon the avoidance of breakdown of the calcium phosphate floc through mechanical action. Recent laboratory tests have shown that it is possible to introduce the acid and lime be-

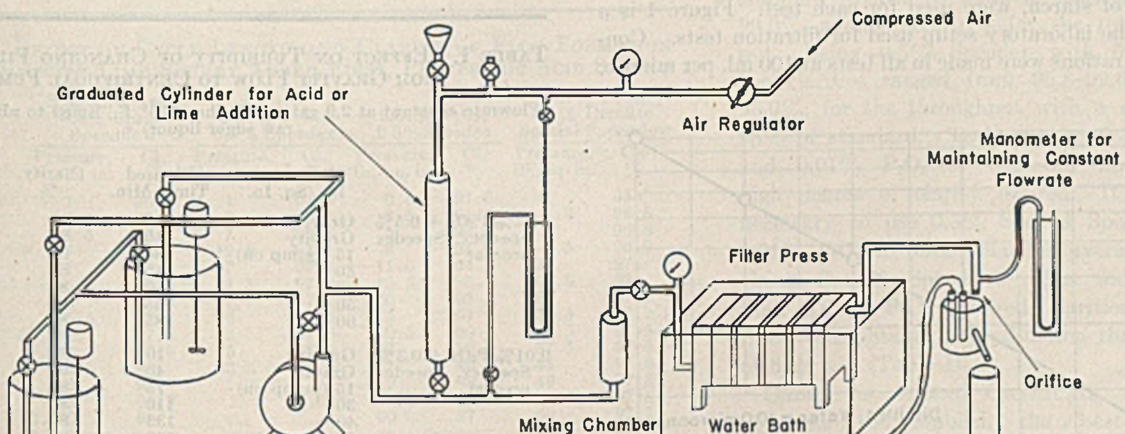

Figure 1. Laboratory Setup for Phosphate Floc Filtration Tests

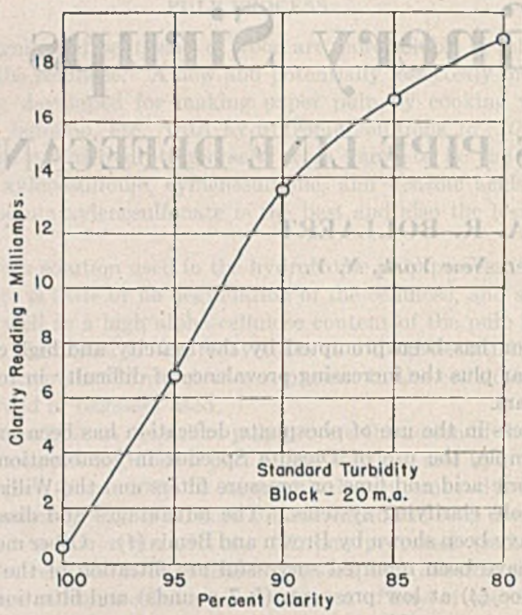

Figure 2. Clarity Curve for Washed Raw Sugar 281

yond the pump and thus defecate in the pipe line in which the unfiltered liquor flows to the presses. The availability of several types of metering and proportioning devices and also pH control systems make it possible for the refiner to install this method of treatment with little change in press room layout.

FILTRATION STUDIES

A stainless steel plate-and-frame filter press was used which had a filtering area of 77.8 square inches. Lime or acid was added in the line after the pump, or the floc was pumped through the pump, depending upon the tests being run. The contact time between chemical treatment and actual filtration was 7 minutes for all tests, since this time period is comparable to refinery operation. Earlier laboratory tests had shown that the color removal is practically instantaneous. There was no observed difference in color removal over a wide range of contact time (10 seconds to 240 minutes). In all tests washed raw sugar liquor (60° Brix) was used. Precoats of 10 pounds per 100 square feet were applied at 1.0 pound per square inch pressure. The filtration temperature was maintained at 176° F. for all tests. New filter cloths (Filter Media Corporation, No. 074-OD), previously washed free of starch, were used for each test. Figure 1 is a diagram of the laboratory setup used for filtration tests. Constant rate filtrations were made in all tests at 100 ml. per minute, equivalent to 2.94 gallons per square foot per hour. The cycle length when 60 pounds pressure was reached was the criterion for rating the performance. For comparison, cycle lengths and clarity determinations were made on the washed raw sugar liquor using 0.3% Speedflow based on the solids and a Dicalite Superaid precoat of 10 pounds per 100 square feet. The Beckman Industrial Model pH meter was used with the hot electrodes; pH determinations were made at 176° F., and the liquor was controlled at 6.8–7.0 for filtration tests.

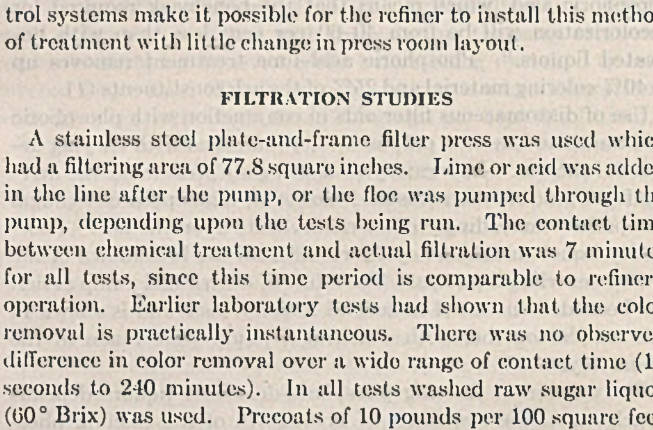

Figure 3. Color Removal Curve for Washed Raw Sugar 281

Turbidity and color removal determinations were made in the Holven-Gillett phototyndallmeter. Clarity determinations were made on each 10-minute increment of flow. The percentage of clarity reported represents the amount of turbidity removed from the unfiltered sugar liquor.

Clarity standards were prepared by mixing 100% with 0% clarity liquor in definite percentages. The 100% clarity liquor is prepared by clarifying with Dicalite laboratory filter aid the 60° Brix, washed, raw sugar liquor to the lowest attainable instrument reading. The 0% clarity liquor is the same sugar liquor strained through an 80-mesh screen, which eliminates only fibers and other coarse material. Figure 2 is a plot of instrument readings against clarity on the standard clarity samples for sugar 281.

Color removal standards were made by mixing 100% clarified, 60° Brix, washed raw sugar and 60° Brix, white refined sugar showing the same degree of transmission as distilled water. Figure 3 is a bleach or color removal curve for sugar 281.

It is well recognized that turbidity interferes with color determinations and color interferes with turbidity determinations. A curve (Figure 4) on sugar 281 allows the interpolation of color removal to 100% clarity and the clarity to 0% color removal so as to have both readings on a comparative basis. Similar curves were used for the other sugars tested.

Lime salts were determined by the soap method (2) to give an indication of the percentage removal of these constituents.

REFINERY TESTS WITH FLOC THROUGH PUMP

During the past two years refinery tests have been conducted with diatomaceous filter aids in conjunction with phosphoric acid–lime defecation. In every case the liquor showed poor clarity when the filter press was changed from gravity flow to the centrifugal pump. Tests using 0.02% P_2O_5 and 0.5% Speedex gave the excellent color removal of 50% and the exceptional clarity of 99% while on gravity feed. The clarity of the liquor immediately dropped to 84–82% after passing through the

Table I. Effect on Turbidity of Changing Filter Press from Gravity Flow to Centrifugal Pump

(Flowrate constant at 2.9 gal./sq. ft./hr., 176° F., limed to pH 7.1, washed raw sugar liquor)

	Pressure, Lb./Sq. In.	Elapsed Time, Min.	Clarity, %	Color Removal, %
0.02% P_2O_5 + 0.5% Speedex, Speedex precoat	Gravity	10	99	50
	Gravity	40	99	
	15 (pump on)	80	99	
	30	140	86	
	40	150	84	
	50	165	84	
	60	185	82	
0.01% P_2O_5 + 0.3% Speedex, Speedex precoat	Gravity	10	89	30
	Gravity	40	97	
	15 (pump on)	75	86	
	30	110	86	
	40	135	82.5	
	50	140	82.5	
0.5% Speedflow, superaid precoat; plant operation at time of tests	Gravity	10	96	None
	Gravity	40	96	
	15 (pump on)	70	97.5	
	30	125	97	
	40	145	97	
	50	170	97.5	
	60	195	98	

Table II. Effect of Place and Order of Adding Chemicals on Cycle Length and Clarity of Washed Raw Sugar 281

Elapsed Time, Minutes	Standard Test, 0.3% Speedflow: Pressure, lb./sq. in.	Standard Test, 0.3% Speedflow: Cl, %	0.02% P_2O_5, 0.5% Speedex: Pressure, lb./sq. in.	0.02% P_2O_5, 0.5% Speedex: Cl, %	0.01% P_2O_5, 0.3% Speedex: Pressure, lb./sq. in.	0.01% P_2O_5, 0.3% Speedex: Cl, %	0.01% P_2O_5, 0.5% Special Speedflow: Pressure, lb./sq. in.	0.01% P_2O_5, 0.5% Special Speedflow: Cl, %	0.0075% P_2O_5, 0.3% Special Speedflow: Pressure, lb./sq. in.	0.0075% P_2O_5, 0.3% Special Speedflow: Cl, %
A. Floc Passed through Pump										
10	1	96.1	2	98.3	0.5	94.0	1.5	97.0	1.0	96.3
20	2.5	97.0	7	98.7	1.0	94.5	4.0	98.0	4.5	96.5
30	4.5	97.2	13	98.8	3.0	92.3	7.0	96.0	7.5	96.9
40	7.0	97.5	20	94.0	4.5	91.1	11.5	96.6	12.0	96.9
50	11.0	97.5	27.5	90.2	6.5	90.4	18.0	96.6	18.0	97.0
60	15.5	97.6	37.0	90	9.5	88.6	24.5	94.6	25.0	95.2
70	20.0	97.6	46.5	89.2	12.5	88.7	32.0	94.5	33.0	94.7
80	25.5	97.6	55.5	87.3	16.0	88.6	40.0	93.3	42.0	92.8
90	31.5	97.8	60.0	85.4	20.5	88.4	49.5	93.0	52.5	92.5
100	37.5	97.9	..	..	25.0	87.2	60	92.0	60.0	91.4
110	43.5	98.0	..	..	30.0	87.2	..	..	..	..
120	50	98.0	..	..	36.0	86.8	..	..	..	..
130	57	98.3	..	..	42.5	86.5	..	..	..	..
140	60	99.0	..	..	49	84.3	..	..	..	..
150	..	..	..	..	57.5	84.1	..	..	..	..
160	..	..	..	..	60.0	84.1	..	..	..	..
Cycle length, min.	135		85		152		100		96	
Flow, % of standard	100		63		112		74		71	
Av. % clarity	97.6		92.4		88.6		95.2		95.0	
% color removal	None		46		35		35		28	
pH	6.8		6.8–7.0		6.8–7.0		6.8–7.0		6.8–7.0	
Precoat, 10 lb./100 sq. ft.	Superaid		Speedex		Speedex		Special Speedflow		Special Speedflow	
B. Length Floc Formed beyond Pump; Phosphoric Acid Added First, Lime Slurry Second										
10	1	96.1	1	95.8	1.0	96.0	0.5	96.0	1.0	96.1
20	2.5	97.0	2.5	97.5	2.5	97.1	1.0	98.5	2.5	98.3
30	4.5	97.2	5.0	98.5	5.0	99.2	1.5	99.4	4.5	99.4
40	7.0	97.5	8.0	98.9	8.0	99.5	3.5	99.4	7.0	99.5
50	11.0	97.5	12.5	99.4	11.5	99.8	6.0	99.5	11.0	99.4
60	15.5	97.6	17.5	99.5	15.5	98.6	9.0	99.5	15.5	99.4
70	20.0	97.6	22.0	99.4	20.0	98.6	13.0	99.4	20.0	99.2
80	25.5	97.6	27.0	99.4	25.0	98.6	18.0	99.3	25.5	99.3
90	31.5	97.8	33.5	99.4	31.0	97.0	23.0	99.4	32.0	99.4
100	37.5	97.9	39.0	99.6	36.5	96.4	27.0	99.5	38.0	99.5
110	43.5	98.0	45.5	99.5	42.5	96.0	33.0	99.5	44.5	99.5
120	50.0	98.0	52.5	99.4	49.0	95.2	39.0	99.6	51.0	99.2
130	57.0	98.3	57.0	99.4	56.0	93.5	45.0	99.7	58.0	99.2
140	60.0	99.0	60.0	99.3	60.0	93.2	52.0	99.5	60.0	99.2
150	..	..	..	..	..	..	60.0	99.5	..	..
Cycle length, min.	135		132		137		150		134	
Flow, % of standard	100		98		101		111		99	
Av. % clarity	97.6		98.9		97.0		99.2		99.0	
% color removal	None		46		35		35		28	
pH	6.8		6.8–7.0		6.8–7.0		6.8–7.0		6.8–7.0	
Precoat, 10 lb./100 sq. ft.	Superaid		Speedex		Speedex		Special Speedflow		Special Speedflow	

centrifugal pump. The same effects were apparent with 0.01% P_2O_5 and 0.3% Speedex. Table I gives results of the tests.

Since the refiner was unable to use phosphate treatment as a result of the poor clarification and short cycles obtained when the floc passed through the pump, this study was made to determine (*a*) filterability of floc when formed in the line between pump and filter, (*b*) effect of the order of chemical addition, and (*c*) choice of filter aid for percentage of P_2O_5 used.

PHOSPHATE FLOC TESTS

Floc through Pump. Tests were first made to establish whether the laboratory equipment gave results comparable to those in the refinery. Laboratory tests (Table II-*A*) on 0.5% Speedex and 0.02% P_2O_5 show the drop in clarity as the pressure increases. This is more pronounced when 0.01% P_2O_5 is used with 0.3% Speedex. Tests were also made using Special Speedflow which has a higher clarifying capacity and a flow rate 40% of Speedex.

Formation of Floc in Line between Pump and Filter. The plant tests suggested that satisfactory results could be obtained if the calcium phosphate floc was not subjected to pump action. By adding both chemicals after the pump, the floc would not be broken down and filtration would, in effect, be comparable to the conditions found with gravity flow. Results on forming the floc in the line between the pump and filter, adding phosphoric acid first and then lime, on washed sugar 281 gave excellent clarities and cycle lengths approximating the standard treatment when the correct grade of filter aid was used.

Table III. Effect on Cycle Length and Clarity of Floc Formation Beyond Pump with Lime Slurry Added First, Phosphoric Acid Second

Elapsed Time, Minutes	Standard Test, 0.3% Speed Speedflow: Pressure, lb./sq in.	Standard Test, 0.3% Speed Speedflow: Cl, %	0.02% P_2O_5, 0.5% Speedex: Pressure, lb./sq. in.	0.02% P_2O_5, 0.5% Speedex: Cl, %	0.01% P_2O_5, 0.3% Speedex: Pressure, lb./sq. in.	0.01% P_2O_5, 0.3% Speedex: Cl, %	0.01% P_2O_5, 0.5% Dicalite Special Speedflow: Pressure, lb./sq. in.	0.01% P_2O_5, 0.5% Dicalite Special Speedflow: Cl, %
10	1	96.1	1	94.9	0.5	91.5	1	95
20	2.5	97	3	96.3	2.5	94.6	2.5	96.8
30	4.5	97.2	7	96.7	5	94.6	5	96.8
40	7	97.5	12.5	97.1	8	94.6	7.5	96.9
50	11	97.5	17	97.2	11.5	94	11	97
60	15.5	97.6	24.5	97.4	15.5	93.7	15.5	97
70	20	97.6	27	97.4	20	93	20	97.2
80	25.5	97.6	36	97.4	24	91	25.5	97.2
90	31.5	97.8	42	97.6	30.5	90	31.5	97.4
100	37.5	97.9	49	97.5	37	89.2	37.5	97.5
110	43.5	98	55.5	97.5	43	89	43	97.6
120	50	98	..	..	49	88.7	49	97.8
130	57	98.3	..	..	54.5	87.5	55	97.8
140	60	99	..	..	60	87	60	97.7
Cycle length, min.	135		117		140		139	
Flow, % of standard	100		87		104		103	
Av. % clarity	97.6		97.0		91.3		97.1	
% color removal	None		42		32		32	
pH	6.8		6.8–7.0		6.8–7.0		6.8–7.0	
Precoat, 10 lb./100 sq. ft.	Superaid		Speedex		Speedex		Special Speedflow	

The filtration of this sugar liquor by the standard treatment showed clarities of 96.1–99.0%, averaging 97.6% for the total throughput. Using 0.5% Speedex with 0.02% P_2O_5, the clarities ranged from 95.8–99.6, averaging 98.9%, for the throughput with a cycle length 98% of standard. Tests run on 0.3% Speedex and 0.01% P_2O_5 or less did not give the high degree of clarity desired. It was found necessary to use 0.5% Special Speedflow with 0.01% P_2O_5 to obtain clarities averaging 99.0%. Using Special Speedflow filter aid with less than 0.01% P_2O_5, desired clarities and flow rates were obtained by adjusting the percentage of filter aid (Table II-*B*).

Order of Adding Chemicals. In a series of tests to establish the best order of chemical addition, lime was added first to the sugar liquor followed by acid. The results (Table III) show poorer filtration rates and slightly lower clarities than when acid is added first.

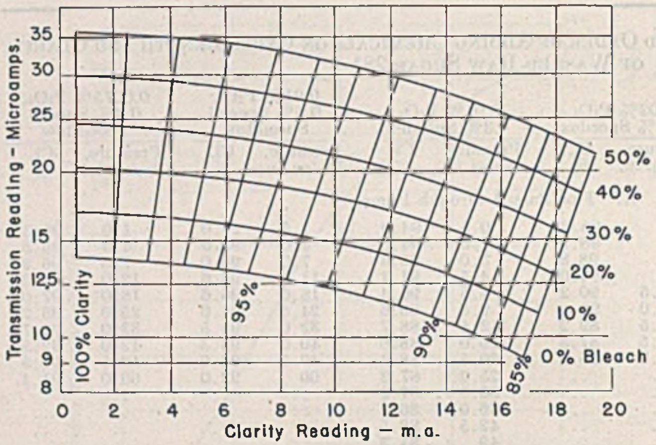

Figure 4. Clarity-Color Relation for Washed Raw Sugar 281

The following data indicate the effect of pH on color at several pH levels (compared to original 100% clarified sugar at pH 6.8):

	% Color Removal	
pH	H_3PO_4 first, $Ca(OH)_2$ second	$Ca(OH)_2$ first, H_3PO_4 second
6.8	46	41
7.3	40	35
7.7	36	34

The results of these tests on the order of chemical addition indicate the desirability of adding the acid first from the color removal standpoint.

Lime salts determined by the soap method (*2*) on the filtrates also show that the addition of acid followed by lime gives best results:

	% Lime Salts as CaO
Filtered sugar, no P_2O_5	0.198
0.02% P_2O_5 first, $Ca(OH)_2$ second	0.148
$Ca(OH)_2$ first, 0.02% P_2O_5 second	0.175

This study demonstrated that longer cycles, better clarities, higher color removal, and lower lime salts are obtained by adding the acid first and then the lime slurry.

CHOICE OF FILTER AID

It was discovered in the early part of this investigation that poor clarities were obtained when Speedex was used with less than 0.02% P_2O_5. Repeated tests have shown that positive clarification is not obtained if the balance between the amount of phosphate defecant and the grade or type of filter aid is incorrect. The tests listed in Table IV were run by adding the acid first and lime last to form the floc beyond the pump. The results show that Speedex gives unsatisfactory performance with less than 0.02% P_2O_5. These tests indicate further that the clarities of the liquor are inferior to those obtained by standard filtration with Speedflow, or with 0.02% P_2O_5 plus 0.5% Speedex. The clarities on these liquors would not be acceptable for refinery operations. With Special Speedflow and lower percentages of P_2O_5, excellent clarities are obtained and the cycle lengths are acceptable. An earlier investigation (*3*) with a filter aid similar to Speedex indicated that this type can handle P_2O_5 percentages of 0.002–0.01%. These results were not substantiated in this laboratory.

Filter aids of the Speedex type have a different surface condition and, since they are also more efficient than Special Speedflow, do not retain the floc unless there is a sufficient quantity of floc present. For percentages of P_2O_5 less than 0.02%, Special Speedflow is recommended.

COMPARISON OF WASHED RAW SUGARS

Table V summarizes tests on two different washed sugars. The results on No. 279, a more easily filtered but darker sugar than No. 281, show cycle lengths 78% of the standard, using 0.5% Speedex and 0.02% P_2O_5 with 40% color removal. With 0.01% P_2O_5 and 0.5% Special Speedflow, the cycle length is 91% of the standard, with 28% color removal. The clarities on both these tests are better than the standard.

Tests on No. 298, an easily filtered, light colored, washed raw sugar, show 72% cycle length of the standard with 0.5% Speedex and 0.02% P_2O_5. The color removal was 52%. A cycle length 83% of the standard with 39% color removal was obtained, using 0.5% Special Speedflow and 0.01% P_2O_5.

These tests indicate that the length of the filtration cycle as compared to the standard depends on the filterability of the washed raw sugar. For example, on difficultly filtered sugar 281, the cycle length for the standard was 135 minutes, and with 0.5% Speedex and 0.02% P_2O_5 the cycle length was 132 minutes, or 98% of the standard. With the more easily filtered sugar 279, the cycle length was 193 minutes for the standard, and for the 0.5% Speedex-0.02% P_2O_5 treatment the cycle length was 150 minutes or 78% of standard.

In the laboratory tests the acid or lime was added on the suction side of the pump, and the floc was formed by addition of lime or acid (depending on the order of chemical addition) on the discharge side of the pump. It would be more feasible for the refinery to add both chemicals, acid first, on the discharge side of the pump. If the pump was made of suitable material to resist the acid condition, the acid could be added on the suction side.

Refinery tests are now in progress on this method of defecation; the results are not complete, but show considerable promise and substantiate the laboratory findings. Tests have also been run on affination sirups with excellent results.

Table IV. Performance Effect of Speedex and Special Speedflow at Various Percentages of P_2O_5 on Sugar 281

P_2O_5, %	Precoat Filter Aid	% Liquor Filter Aid	Cycle Length, Min.	Flow % of Standard	Av. % Clarity
None	Superaid	0.3 Speedflow	135	100	97.6
0.02	Speedex	0.5 Speedex	132	98	98.9
0.015	Speedex	0.5 Speedex	146	108	97.2
0.01	Speedex	0.5 Speedex	182	140	97.0
0.01	Speedex	0.3 Speedex	137	101	97.0
0.0075	Speedex	0.3 Speedex	168	125	94.3
0.1	Special Speedflow	0.5 Special Speedflow	150	111	99.2
0.0075	Special Speedflow	0.3 Special Speedflow	134	99	99.0

Table V. Comparison Tests on Sugars 279 and 298 (Floc Formed beyond Pump, Acid First, Lime Second)

	Sugar 279				Sugar 298			
Treatment	Cycle length, min.	Flow, % of standard	Av. % Clarity	Color removal, %	Cycle length, min.	Flow, % of standard	Av. % clarity	Color removal, %
0.3% Speedflow; superaid precoat	193	100	97.9	None	325	100	97.7	None
0.02% P_2O_5, 0.5% Speedex; Speedex precoat	150	78	99.3	40	235	72	99.2	52
0.01% P_2O_5, 0.5% Special Speedflow; Special Speedflow precoat	175	91	99.4	28	270	83	99.4	39

ACKNOWLEDGMENT

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Vapor-Liquid Equilibria in Three Hydrogen-Paraffin Systems

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The solubilities of hydrogen in isobutane were determined for temperatures from 100° to 250° F. and pressures from 500 to 3000 pounds per square inch. Solubilities in 2,2,4-trimethylpentane were found for temperatures from 100° to 302.5° and in a mixture of isomeric dodecanes for 200° and 300° F. with pressures ranging from 500 to 5000 pounds per square inch. The compositions of the equilibrium vapor phases were also determined. The solubility of hydrogen increases with temperature and pressure but decreases as the solvent molecular weight increases. The solubility of hydrogen follows Henry's law only in isobutane at 150° F. and lower. The hydrogen solubilities in the two heavier hydrocarbons increase more rapidly with pressure at low pressures than at high pressures. Correlation with literature data shows that hydrogen is more soluble in paraffins than in aromatics of similar molecular weight. Vaporization equilibrium constants are computed from the data for both solvent and solute. The constants vary widely with pressure and to a lesser extent with temperature. The constant for hydrogen increases with an increase in solvent molecular weight.

THE solubility of hydrogen at high pressures in several pure hydrocarbons was reported by Frolich (*2*) for 77° F. and up to 100 atmospheres, by Ipatieff (*3*) at higher temperatures for several petroleum fractions, and by Ipatieff (*4*) in several pure aromatic hydrocarbons. More recently solubilities to 106 atmospheres in *n*-butane were reported by Nelson (*7*). In none of these investigations was a comprehensive study of the composition of the equilibrium vapor phase made. Nelson, however, did present some data on the vapor phase.

The purpose of this work was to determine the solubility of hydrogen in a narrow-boiling mixture of isomeric dodecanes and in two relatively pure hydrocarbons—isobutane and 2,2,4-trimethylpentane—for a range of temperature and pressure. In addition, the compositions of the equilibrium vapor phases were to be found, and a study made of the vaporization equilibrium constants of the components and the effect of temperature and pressure on these values.

The hydrogen used was the commercial electrolytic water-pumped grade. The impurity, oxygen, was less than 0.2%. Water vapor was removed by contacting with anhydrous calcium sulfate. The isobutane, with a tested purity of 99.5%, was obtained from the Phillips Petroleum Company. The major portion of the impurity was *n*-butane. The iso-octane, obtained from Rohm & Haas Company, was considered to be essentially pure 2,2,4-trimethylpentane. The physical properties were determined by the National Bureau of Standards:

	Boiling Point, ° F.	Sp. Gr., d_4^{20}	Refractive Index, n_D^{20}	Mol. Weight
2,2,4-Trimethylpentane	210.5[a]	0.6919[a]	1.3915[a]	114.22[b]
Isomeric dodecane mixt.	350–2[c]	0.756[c]	1.4227[c]	170[c]

[a] Determined by National Bureau of Standards.
[b] Calculated. [c] Experimental.

The mixture of isomeric dodecanes was specially prepared for this work by polymerizing isobutylene, hydrogenating the resulting product, and fractionating in a $^1/_2$-inch i.d. column, 36 inches long and packed with $^1/_4$-inch glass helices. A cut boiling between 350° and 352° F. was collected for use in this work. The particular combination of polymerization and fractionation was believed to have yielded a product which was a mixture of isomeric dodecanes. This final product will be referred to as dodecanes. The determined physical properties of the dodecanes are also listed in the table. The molecular weight was obtained by a method utilizing the principle of the freezing-point lowering of benzene.

Vapor pressures of the hydrocarbons are useful in the correlations of experimental data. The vapor pressures of isobutane and 2,2,4-trimethylpentane were determined up to their critical temperatures by Sage (*8*) and Smith (*9*), respectively. Since comparable data for the dodecanes were lacking, the vapor pressure curve was determined to 300° F. The apparatus used was based on the principle of balancing a column of mercury against the vapor pressure of the air-free hydrocarbon confined in a U-tube over mercury. The technique was developed by measuring the vapor pressure of our iso-octane and comparing results with values by Smith. Bridgeman (*1*) described this type of apparatus in detail.

The dodecanes vapor pressures are believed to be in error by no more than ±0.02 pound per square inch at the higher temperatures and less at the lower temperatures:

Temp., ° F.	Vapor Pressure, Lb./Sq. In. Abs.	Temp., ° F.	Vapor Pressure, Lb./Sq. In. Abs.
32.0	0.04	228.7	2.00
77.0	0.11	233.6	2.15
173.7	0.67	297.1	6.49
200.0	1.04	300.0	6.52

APPARATUS

The experimental work on the hydrogen-isobutane system was carried out in the apparatus described by Katz (*5*). Some difficulty was experienced with that style of equilibrium cell due to the difficulty of making a seal for the lead-in wire to the electric stirring motor which would hold hydrogen at high pressures and temperatures. In addition, the nonlubricating atmosphere in which the motor had to operate made its proper lubrication impossible. The consequent low operating speeds resulted in extreme time requirements for obtaining equilibrium between the vapor and liquid phases.

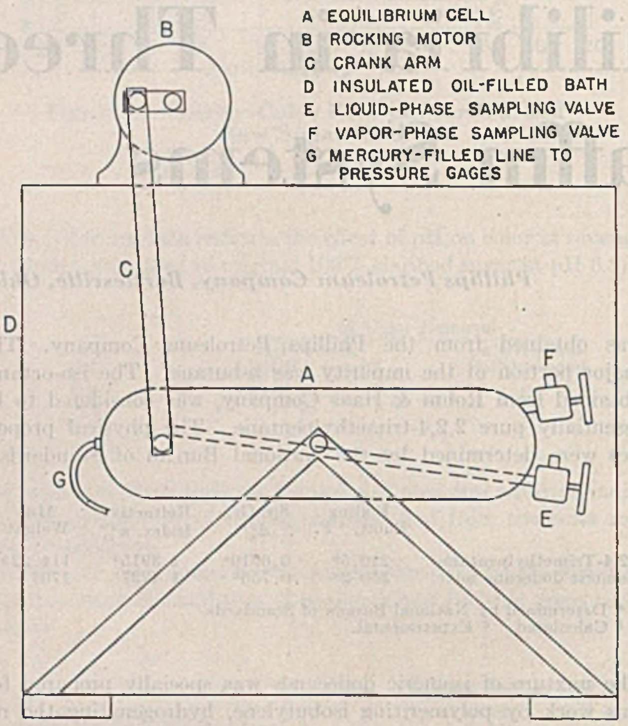

Figure 1. Diagram of Equilibrium Apparatus

The hydrogen–iso-octane and hydrogen-dodecanes systems were tested in an equilibrium cell mounted in an oil-filled bath in which it was rocked at 30 cycles a minute. Figure 1 is a diagram of the cell and bath. The cell was circular in cross section with hemispherical ends and approximately 700 ml. in capacity. A coil of $^1/_8$-inch steel tubing was connected into the bottom of the cell and led to pressure gages through a manifold. At the upper end of the cell one valve was attached with an induction tube for withdrawing liquid-phase samples. Another valve was provided for taking vapor-phase samples. The cell was rocked by a crank arm powered by an electric motor. The crank arm linkage was designed to cause the cell to rock to an angle 30° above and below the horizontal. The crank arm was detachable from the motor in order that the cell could be placed in a vertical position for sampling the phases. The rocking equilibrium cell allowed equilibrium of the phases to be attained quickly.

The two gages were Bourdon-tube type of 1000 and 5000 pound capacities and graduated in divisions of 1% of the capacity, and the pressures were read to 0.2% of capacity. The gages were calibrated with a dead-weight tester before work was begun and at intervals during the work. In recording the pressure in the equilibrium cell, appropriate correction was made for the head of mercury to the gage.

The volume of the cell was adjusted as required by the introduction or withdrawal of mercury through the steel tubing with a hand-operated piston pump. The temperature of the oil bath was measured with mercury-in-glass thermometers with 0.2° F. divisions and calibrated against thermometers of the same type having a Bureau of Standards certificate. Bath temperatures were held constant to ±0.2° F.

Special glass traps and calibrated glass balloons were provided for handling and analyzing the phase samples. In the work on the hydrogen-isobutane system a Podbielniak-type low-temperature fractionating column was also used, together with the usual Orsat apparatus for hydrogen analysis.

PROCEDURE

The first step in preparing for an experiment was to evacuate the equilibrium cell with a vacuum pump to a pressure less than 1 mm. mercury. Three to four hundred milliliters of the desired hydrocarbon were pressured in. Sufficient hydrogen was then pressured in until the pressure in the cell was somewhat higher than the planned equilibrium pressure for the experiment. Agitation of the contents was begun, either by stirring if the stationary cell were used, or by rocking the cell in the case of the second unit. The temperature was adjusted to the desired value and agitation of the cell contents continued until the pressure became constant. Since the pressure was higher than desired, portions of the vapor phase were bled off until the equilibrium pressure was lowered to the desired value. When no further pressure change took place with continued agitation of the cell contents, the vapor and liquid phases were considered to be in equilibrium. In the case of the rocking cell, tests showed that 10 minutes of rocking at constant pressure and temperature would attain equilibrium. The sampling and analysis of the phases were combined into what was essentially a single operation. The analysis of the samples consisted of the physical separation of the hydrogen from the hydrocarbon by freezing out the hydrocarbon from the sample as it was withdrawn from the cell.

In sampling the liquid phase of the isobutane system, a portion was conducted from the equilibrium cell through an unheated steel line terminating in a needle valve to the sampling connection of a Podbielniak-type low-temperature fractional

Table I. Experimental Data for Hydrogen-Isobutane System

Pressure, Lb./Sq. In. Abs.	Composition, Mole %				$K = y/x$		H_2 Soly.[a], Cc. Gas/ G. Solvent
	Liquid phase		Vapor phase				
	H_2	C_4H_{10}	H_2	C_4H_{10}	H_2	C_4H_{10}	
Temperature 100° F.							
3000	17.9	82.1	95.51	4.49	5.34	0.0547	92
2500	14.2	85.8	95.71	4.29	6.74	0.0500	70
2000	11.12	88.88	95.21	4.79	8.56	0.0539	52.6
1500	8.79	91.21	94.23	5.77	10.7	0.0633	40.6
1000	5.92	94.08	91.91	8.09	15.5	0.0860	26.5
500	2.75	97.25	86.31	13.69	31.4	0.141	11.9
Temperature 150° F.							
3000	19.7	80.3	90.18	9.82	4.58	0.122	103
2500	16.9	83.1	87.9	12.1	5.20	0.146	86
2000	12.9	87.1	88.7	11.3	6.88	0.130	62
1500	8.47	91.53	86.7	13.3	10.2	0.145	38.9
1000	6.76	93.24	82.4	17.6	12.2	0.189	30.5
500	2.74	97.26	69.7	30.3	25.4	0.312	11.9
Temperature 200° F.							
3000	24.7	75.3	56.5	43.5	2.29	0.578	138
2500	19.2	80.8	75.8	24.2	3.95	0.299	100
2000	15.6	84.4	75.8	24.2	4.8	0.287	7
1500	10.9	89.1	71.9	28.1	6.60	0.315	51
1000	7.09	92.91	61.5	38.5	8.67	0.414	32.1
500	2.25	97.75	40.7	59.3	18.1	0.607	9.7
Temperature 250° F.							
2000[b]	24.4	75.6	24.8	75.2	1.02	0.995	136
1500	16.2	83.8	42.4	57.6	2.62	0.687	81
1250	11.7	88.3	40.6	59.4	3.47	0.673	56
1000	8.20	91.8	37.0	63.0	4.51	0.686	38

[a] Hydrogen gas at 77° F. and 1 atmosphere.
[b] In the single-phase region.

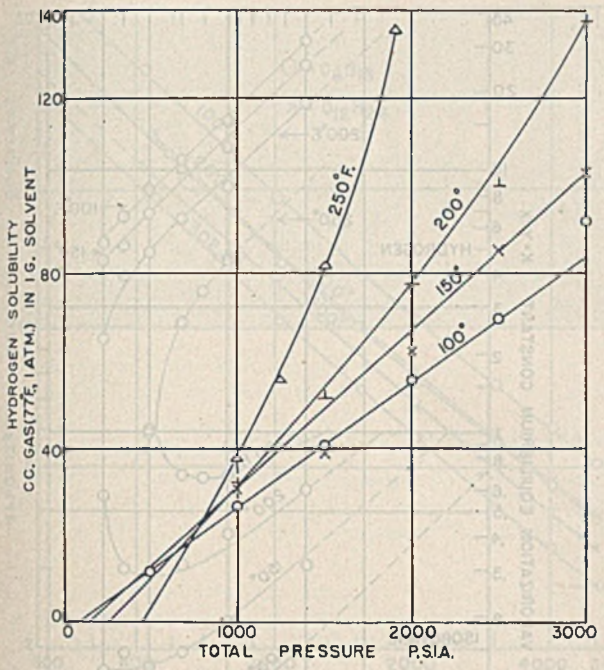

Figure 2. Solubility of Hydrogen in Isobutane

distillation column. The liquid was kept at equilibrium pressure up to the needle valve, and then the sample was flashed into the kettle of the column. The kettle, immersed in liquid nitrogen, acted as a trap and froze out the greater part of the isobutane. The effluent hydrogen gas containing a small concentration of isobutane was collected in glass balloons for measurement. A significant volume of hydrogen remaining in the frozen isobutane was collected by boiling the isobutane in the closed off column, then freezing it again. The undissolved hydrogen was collected and combined with the rest. This operation was repeated until the pressure of the kettle contents was less than 2 mm. mercury at liquid nitrogen temperature. The vapor volume of the hydrogen-free isobutane was found by vaporizing into the calibrated balloons. The isobutane in the effluent gas was determined by passing a known volume of the mixture over copper oxide at 300° C. in the usual Orsat apparatus to convert the hydrogen to water. The gas volume remaining was assumed to be isobutane. The isobutane in the vapor-phase sample was separated from the hydrogen by passing the gas stream through a specially designed trap immersed in liquid nitrogen where most of the isobutane was frozen out. The effluent gas was then passed into the liquid-nitrogen-immersed kettle of the fractionating column where the remainder of the isobutane was frozen out. The isobutane-free hydrogen effluent was collected and measured in the calibrated balloons. After sufficient sample had been taken, the isobutane in the trap was vaporized into the kettle of the column where it was denuded of hydrogen in the same manner as in the liquid-phase analysis. The hydrogen-free isobutane was then vaporized into the balloons and its volume measured. Tests proved that this method separated the components almost completely.

Table II. Experimental Data for Hydrogen–2,2,4-Trimethylpentane System

Pressure, Lb./Sq. In. Abs.	Composition, Mole %				$K = y/x$		H_2 Soly.[a], Cc. Gas/ G. Solvent
	Liquid phase		Vapor phase				
	H_2	C_8H_{18}	H_2	C_8H_{18}	H_2	C_8H_{18}	
	Temperature 100° F.						
5025	19.8	80.2	99.832	0.168	5.04	0.00209	52.9
4010	16.6	83.4	99.840	0.160	6.01	0.00192	42.6
3025	13.2	86.8	99.838	0.162	7.56	0.00187	32.6
2020	9.71	90.29	99.831	0.169	10.3	0.00185	23.0
1020	5.17	94.83	99.764	0.236	19.3	0.00249	11.7
525	2.72	97.28	99.602	0.398	36.6	0.00409	6.0
175	0.90	99.10	98.950	1.050	110	0.0106	1.9
	Temperature 200° F.						
5055	25.8	74.2	99.36	0.64	3.85	0.0086	74
4010	21.8	78.2	99.30	0.70	4.56	0.0090	60
3025	17.4	82.6	99.22	0.78	5.70	0.0094	45.1
2070	13.0	87.0	99.10	0.90	7.62	0.0103	32.0
1520	9.74	90.26	98.88	1.12	10.2	0.0121	23.1
1035	7.10	92.90	98.55	1.45	13.9	0.0156	16.4
583	4.04	95.96	97.65	2.35	24.0	0.0245	9.0
248	1.65	98.35	94.90	5.10	57.5	0.0519	3.6
	Temperature 302.5° F.						
5065	35.5	64.5	97.48	2.52	2.75	0.0391	118
3990	29.2	70.8	97.25	2.75	3.33	0.0388	88
3025	23.8	76.2	96.76	3.24	4.07	0.0425	67
2045	16.7	83.3	96.01	3.99	5.75	0.0479	42.9
1540	12.9	87.1	95.11	4.89	7.37	0.0561	31.7
1020	9.10	90.90	93.34	6.66	10.3	0.0733	21.4
550	4.68	95.32	89.69	10.31	19.2	0.108	10.5
185	1.22	98.78	68.97	31.03	56.5	0.314	2.6

[a] Hydrogen gas at 77° F. and 1 atmosphere.

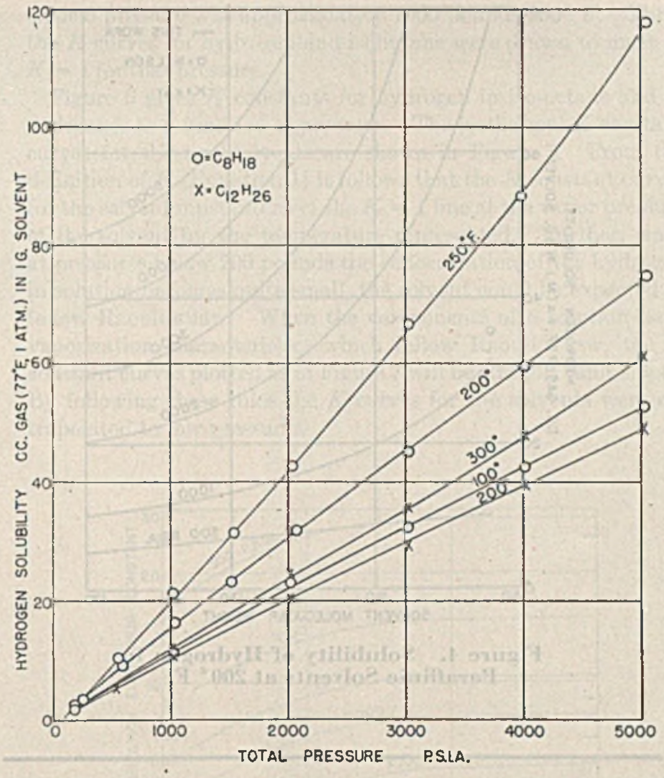

Figure 3. Solubility of Hydrogen in 2,2,4-Trimethylpentane and in a Mixture of Isomeric Dodecanes

Some changes in the method of sampling and separating the components of the hydrogen–iso-octane system were found advantageous. The liquid-phase sample was flashed into a glass trap at atmospheric temperature. The effluent vapors were then passed into a second trap immersed in liquid nitrogen where the remainder of the iso-octane was frozen out. The effluent gas, iso-octane-free hydrogen, was conducted into the balloons for measurement. The steel line connecting the cell with the first trap was heated to drive all the iso-octane into the trap. Both traps were removed, and the weight of iso-octane was found. The separation of the hydrogen and iso-octane in the vapor-phase sample was effected in the same manner as for the liquid phase.

The procedure used in sampling the phases of the hydrogen-dodecanes system and the manner of separating the components were identical with those in the iso-octane system except that a pentane–dry ice mixture was used as the cooling medium instead of liquid nitrogen. With liquid nitrogen the dodecanes had a tendency to freeze into minute particles and entrain in the effluent hydrogen stream.

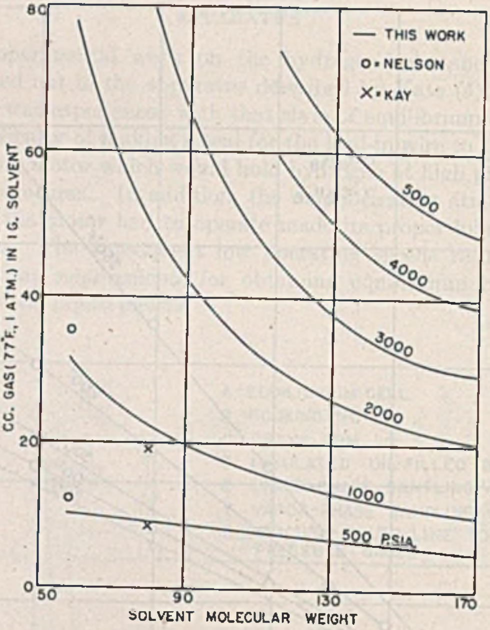

Figure 4. Solubility of Hydrogen in Paraffinic Solvents at 200° F.

Table III. Experimental Data for Hydrogen-Isomeric Dodecane System

Pressure, Lb./Sq. In. Abs.	Composition, Mole %: Liquid phase H_2	Liquid phase $C_{12}H_{26}$[a]	Vapor phase H_2	Vapor phase $C_{12}H_{26}$[a]	$K = y/x$: H_2	$C_{12}H_{26}$[a]	H_2 Soly.[b], Cc. Gas/G. Solven
			Temperature 200° F.				
5035	25.4	74.6	99.930	0.070	3.93	0.00094	49.0
4030	21.5	78.5	99.930	0.070	4.65	0.00089	39.4
3035	16.9	83.1	99.932	0.068	5.91	0.00082	29.3
2025	12.4	87.6	99.929	0.071	8.06	0.00081	20.4
1020	6.84	93.16	99.900	0.100	14.6	0.00107	10.6
525	3.73	96.27	99.831	0.169	26.8	0.00176	5.6
			Temperature 300° F.				
5035	29.9	70.1	99.652	0.348	3.33	0.00496	61.4
4030	25.0	75.0	99.633	0.367	3.99	0.00489	48.0
3035	20.0	80.0	99.602	0.398	4.98	0.00498	36.0
2025	14.7	85.3	99.520	0.480	6.77	0.00563	24.8
1020	7.89	92.11	99.227	0.773	12.6	0.00839	12.3
525	4.42	95.58	98.68	1.32	22.3	0.0138	6.7

[a] A mixture of isomeric dodecanes.
[b] Hydrogen gas at 77° F. and 1 atmosphere.

Mercury was pumped into the bottom of the cell while the phase samples were being withdrawn to maintain a constant pressure.

DATA FOR THREE SYSTEMS

The experimental data consist of the determined compositions of equilibrium vapor and liquid phases and the associated conditions of pressure and temperature. A convenient way to express the vaporization characteristics of the components of a mixture is the vaporization equilibrium constant K, defined as

$$K = y/x \tag{1}$$

where y = mole fraction of component in vapor phase
x = mole fraction of same component in liquid phase

The K constants were calculated by Equation 1 from the experimental data and are included in Tables I, II, and III.

Figure 2 shows the solubility of hydrogen in isobutane at various temperatures. It is noteworthy that the solubility is a straight line-function of the total pressure up to 150° F.; at 200° F., however, the solubility tends to increase more rapidly with pressure than would be indicated by a straight line originating at the lower pressures.

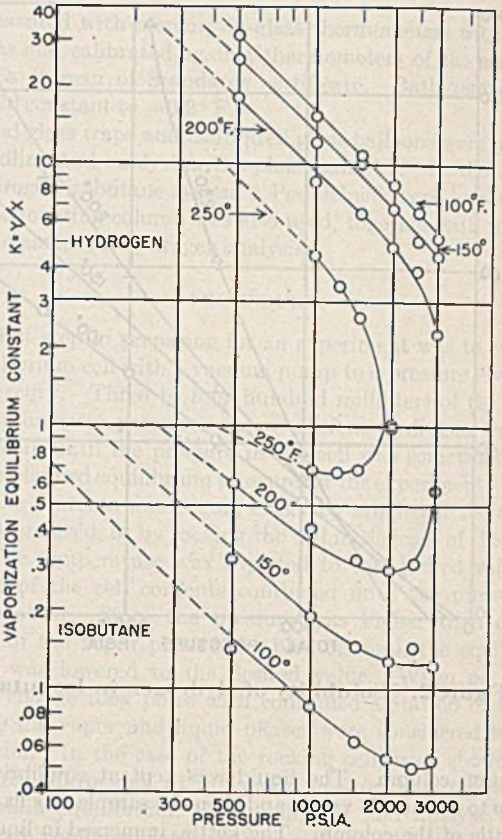

Figure 5. *K* Constants for Hydrogen-Isobutane System

The solubility of hydrogen in 2,2,4-trimethylpentane and in dodecanes (Figure 3) is somewhat different. At the lower pressures and temperatures the hydrogen solubility increases more rapidly with pressure than at the higher temperatures and pressures. Frolich (*2*) reported a similar effect with nitrogen as well as hydrogen in various types of solvents to show the limitation in the use of Henry's law.

The solubility of hydrogen in the three solvents at 200° F. and at various total pressures is plotted against molecular weight in Figure 4 to show the effect of the solvent molecular weight on the solubility. It is apparent that the solubility decreases with increasing molecular weight. Hydrogen solubilities in *n*-butane determined by Nelson (*7*) and in a petroleum naphtha by Kay (*6*) are also plotted.

Kay reported the naphtha to be composed almost entirely of pentanes and hexanes; the composition data showed that the sum of the concentrations of all the normal type components was essentially equal to the sum of the concentrations of all the isomeric types.

Since the data of Kay are in reasonable agreement with the curves of Figure 4, the curves could be useful for estimating the solubility of hydrogen in narrow-boiling mixtures of isomeric paraffin hydrocarbons. On this basis the solubility of hydrogen in an isomeric paraffin mixture of 95 average molecular weight can be compared with solubilities in a gasoline (average molecular weight 99.5) by cross-plotting work by Ipatieff (*3*) and in toluene (molecular weight 92.1) by Ipatieff (*4*). The comparison shows that the solubility of hydrogen in a solvent is a function of the molecular structure of the solvent molecules as well as of the temperature and pressure:

Pressure, Lb./Sq. In. Abs.	Cc. H_2 at 77° F. and 1 Atm. in 1 G. of Solvent: Paraffinic mixtures	Gasoline (*3*)	Toluene (*4*)
500	8	7	4
1000	19	15	8
3000	59	45	26

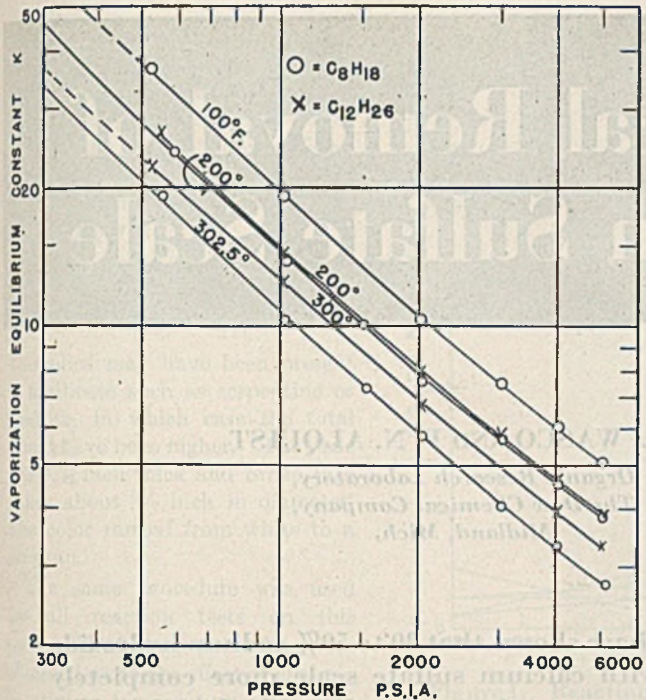

Figure 6. *K* **Constants for Hydrogen in 2,2,4-Trimethylpentane and in a Mixture of Isomeric Dodecanes**

The *K* constants for the hydrogen-isobutane system were plotted as in Figure 5 to show the effect of pressure on *K*. The determination made at 250° F. and 2000 pounds per square inch absolute (Table I) showed that the system was in the critical region. The fact that the pressure was 2000 pounds indicates only that the critical pressure is equal to or below that pressure. Other correlations of the data not shown here showed that the critical pressure was approximately 1900 pounds 250° F. Thus, the *K* curves for hydrogen and isobutane were drawn to meet at *K* = 1 for that pressure.

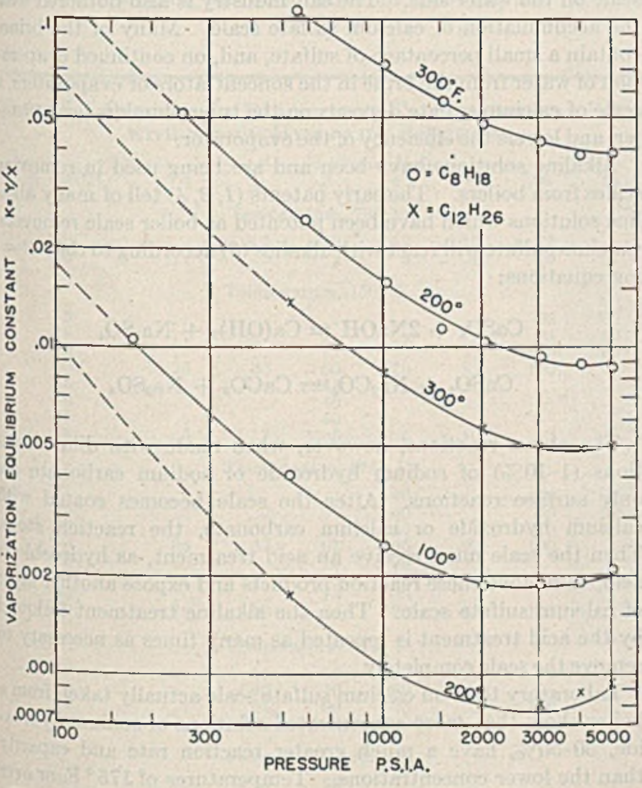

Figure 7. *K* **Constants for 2,2,4-Trimethylpentane and for the Isomeric Dodecane Mixture**

Figure 6 gives *K* constants for hydrogen in iso-octane and in dodecanes as a function of pressure. The isothermal *K* constant curves for the two solvents are shown in Figure 7. From the definition of *K* (Equation 1) it follows that the *K* constant curves for the solvent must intersect the *K* = 1 line at the vapor pressure of the solvent for the temperature represented. Further, since at pressures below 200 pounds the concentration of the hydrogen in solution becomes quite small, the solvent could be expected to follow Raoult's law. When the components of a solution have vaporization characteristics which follow Raoult's law, the *K* constant curves plotted as in Figure 7 will be straight (unit slope). By following these rules the *K* curves for the solvents were extrapolated to low pressures.

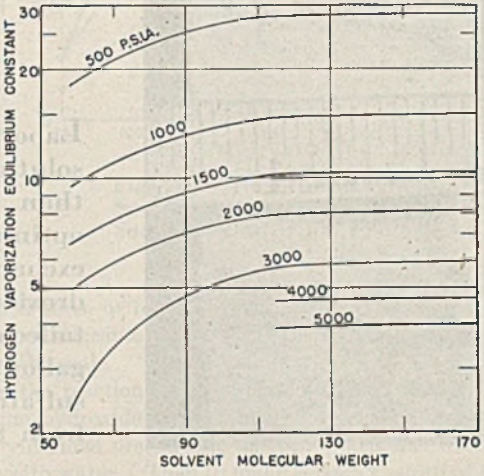

Figure 8. *K* **Constants for Hydrogen in Paraffinic Solvents of Various Molecular Weights at 200° F.**

The effect of the solvent molecular weight on *K* for hydrogen is demonstrated for 200° F. by plotting the hydrogen *K* constant against solvent molecular weight as in Figure 8, which shows that *K* increases with an increase in solvent molecular weight. The plot is useful for estimating *K* constants for hydrogen at 200° F. dissolved in a solvent composed of a single highly branched paraffin and might be used with caution for estimating *K* constants for hydrogen dissolved in a solvent composed of two or more isomeric paraffin hydrocarbons.

ACKNOWLEDGMENT

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Chemical Removal of Calcium Sulfate Scale

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Laboratory tests have shown that 30 to 50% sodium hydroxide solutions react with calcium sulfate scale more completely than do lower concentrations of sodium hydroxide. The optimum temperatures are above 175° F. Commercial heat exchange units have been treated with 30 to 50% sodium hydroxide solutions to remove the calcium sulfate scale. A detailed description is included here for the treatment of a 50,000-gallon brine evaporator from which 100,000 pounds of calcium sulfate scale have been removed. . . . A piece of scale chipped from the evaporator is shown in the photograph at the left.

MOST boilers and other heat exchange equipment become fouled during operation as a result of the deposition on the heat exchange surfaces of various salts which are present in the water. This fouling may be minimized by the treatment of water to reduce the total solids content of the incoming water and by blowing down boilers to reduce the total solids of water in the boiler. With all of these precautions, some sludge or scale accumulates in boilers. Mechanical means were and are still used to rid the boilers of this accumulation. A turbine tool is used on water tube boilers; fire tube boilers are dismantled, and the scale and accumulation are hammered off the outside of the tubes.

More recently, chemical means of descaling heat-exchangers have been introduced. This method consists of introducing into the equipment an aqueous solution of a chemical which will react with the deposits to form soluble reaction products. The common mineral acids, such as hydrochloric, sulfuric and phosphoric, are the most widely used because of their good performance, ease of inhibition, availability, and low cost. Hydrochloric acid will react with many of the scales relatively insoluble in water and change them over to readily soluble compounds: iron oxides are converted to iron chlorides, calcium hydroxy phosphate to calcium chloride and phosphoric acid, calcium carbonate to calcium chloride and carbon dioxide.

Among the compounds frequently found in heat exchange equipment is calcium sulfate. This compound is only slightly soluble in dilute mineral acid solutions and does not lend itself very well to chemical treatment. Calcium sulfate is commonly found in boilers and heat exchange equipment that are forced to use untreated or only partly treated water. Boilers in schools, theaters, and laundries often use untreated water because these units are too small to support a water treating system. Since railroad boilers and marine boilers are part of a mobile unit, they cannot receive treated water at all times. Therefore, any boiler that uses an untreated sulfate water will accumulate a calcium sulfate scale on the water side. The salt industry is also bothered with the accumulation of calcium sulfate scale. Many of the brines contain a small percentage of sulfate, and, on continued evaporation of water from the brine in the concentrators or evaporators, a scale of calcium sulfate deposits on the tubes, hinders heat transfer, and lowers the efficiency of the evaporator.

Alkaline solutions have been and are being used in removing scales from boilers. The early patents (*1*, *2*, *4*) tell of many alkaline solutions which have been patented as boiler scale removers. Calcium sulfate will react with alkalies (*3*) according to the following equations:

$$CaSO_4 + 2NaOH \rightleftarrows Ca(OH)_2 + Na_2SO_4$$

$$CaSO_4 + Na_2CO_3 \leftrightarrows CaCO_3 + Na_2SO_4$$

The above reactions, however, when made with dilute solutions (1–10%) of sodium hydroxide or sodium carbonate are only surface reactions. After the scale becomes coated with calcium hydroxide or calcium carbonate, the reaction stops. Then the scale must receive an acid treatment, as hydrochloric acid, to remove these reaction products and expose another layer of calcium sulfate scale. Then the alkaline treatment followed by the acid treatment is repeated as many times as necessary to remove the scale completely.

Laboratory tests on calcium sulfate scale actually taken from a boiler show that more concentrated solutions of sodium hydroxide, 30–50%, have a much greater reaction rate and capacity than the lower concentrations. Temperatures of 175° F. or over are necessary for the reaction. The rate of reaction is directly proportional to the rise in temperature.

SCALE TESTS

Most of the laboratory work was carried out on a scale turbined from a raw water boiler of a large power plant in the eastern states. X-ray analysis showed it to be 100% calcium sulfate. The chemical analysis showed:

$67.1\%\ SO_4 = 95.2\%\ CaSO_4$
$0.2\%\ Fe = 0.3\%\ Fe_2O_3$
$3.3\%\ SiO_2 = 3.3\%\ SiO_2$
Total 98.8%

The silica may have been present as a silicate such as serpentine or analcite, in which case the total would have been higher. The scale was $^1/_{32}$ inch thick and broke into flakes about $^1/_2$ inch in diameter. The color ranged from white to a pink tan.

The same procedure was used for all reaction tests on this scale. Thus, comparable data were obtained as to the effect of changes in time, temperature, or concentration of sodium hydroxide solutions on the extent of the reaction. The time of the tests varied from $^1/_2$ to 24 hours, temperature from 75° to 230° F., and sodium hydroxide concentration from 5 to 50%. For each test 100 ml. of sodium hydroxide solution (regardless of concentration) were used. It was contained in an 8-ounce wide-mouth bottle and preheated at the desired temperature for 30 minutes; 2.0 ± 0.05 grams of calcium sulfate scale were then added to the sodium hydroxide solution. Only actual pieces of scale were used; any powdery scale was discarded.

After the duration of the test at the desired temperature, most of the solution was decanted from the scale, and the scale was washed three or four times with 100-cc. portions of water. The water was decanted in each case with extreme caution to retain all of the scale.

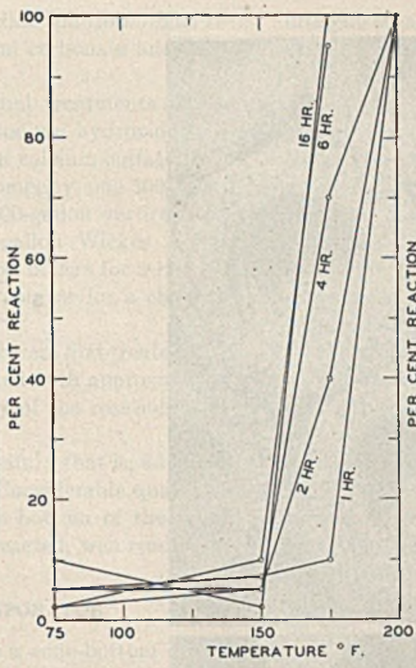

Figure 1. Reaction of Calcium Sulfate Scale with a 50% Sodium Hydroxide Solution

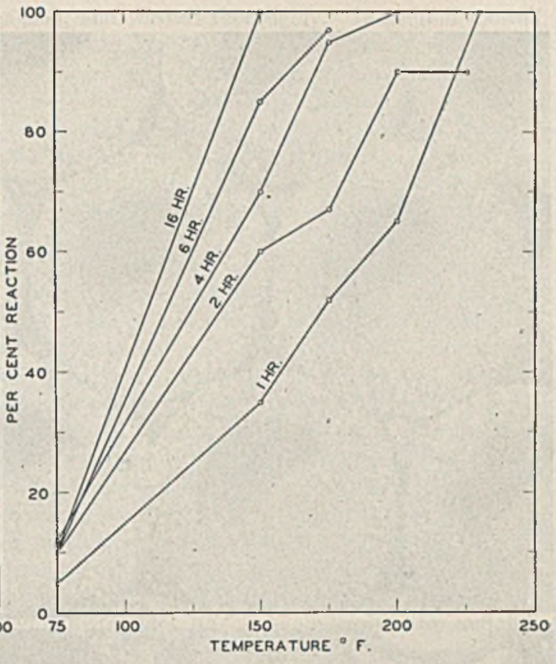

Figure 2. Reaction of Calcium Sulfate Scale with a 30% Sodium Hydroxide Solution

Table I. Percentage Reaction of Calcium Sulfate Scale with Sodium Hydroxide Solutions

% NaOH	Time, Hours $^1/_2$	1	2	4	6	16	24
			Temperature, 70° F.				
30	..	5	10	12	10	7	..
50	..	5	2	5	2	10	..
			Temperature, 150° F.				
5	..	..	..	..	..	58	60
10	..	..	..	..	..	65	60
20	..	..	..	..	..	80	80
30	25	35	60	70	85	100	..
35	..	..	45	..	..	..	..
40	..	..	40	..	..	..	..
45	..	..	40	..	..	..	..
50	5	7	5	5	10	2	..
			Temperature, 175° F.				
5	..	..	..	40	..	60	60
10	..	..	..	50	..	60	52
20	..	..	..	85	..	70	85
30	35	52	67	95	97	100	..
35	..	..	70	98	..	..	..
40	..	..	70	98	..	..	..
45	..	..	75	98	..	..	..
50	10	10	40	70	95	100	..
			Temperature, 200° F.				
10	..	55	55	60	..	70	..
20	..	40	40	60	..	95	..
30	..	65	90	95	..	100	..
50	..	100	100	100	..	..	..
			Temperature, 230° F.				
10	..	45	55	..	..	..	..
20	..	40	50	..	..	..	..
30	..	100	90	..	..	..	..

During the reaction of caustic solutions on calcium sulfate, the calcium hydroxide and sodium sulfate formed were present as a finely divided precipitate, most of which was washed from the scale with water. Then to make certain that all of the reaction products were separated from the unreacted scale, a quick 1% hydrochloric acid rinse was given the scale followed by another water wash. The scale was transferred to a watch glass, dried at 225° F. for an hour, and then reweighed.

In a few cases the finely divided precipitate which was washed away from the scale was analyzed by x-ray diffraction to determine whether any unreacted calcium sulfate was being washed away. The analyses revealed that the precipitates consisted mostly of calcium hydroxide, some sodium sulfate, and a triple salt of sodium hydroxide, calcium sulfate, and sodium sulfate. No calcium sulfate was detected. The tests indicated that no unreacted calcium sulfate scale was decanted from the bottles.

The results of the laboratory tests (Table I) indicate the following conclusions: (*a*) At 70° F. the amount of reaction with 30 or 50% sodium hydroxide is very low regardless of the time of the test. (*b*) At 150° F. 30% sodium hydroxide seems to be the most active, while 50% has very little effect on calcium sulfate. (*c*) At 150° F. the percentage reaction with 30% sodium hydroxide is directly proportional to the time. (*d*) At 175° F. the amount of reaction obtained with 5 and 10% sodium hydroxide is about the same as at 150° F., but the percentage reaction with 20–50% sodium hydroxide shows a definite increase. The 50% caustic which has been quite unreactive at lower temperatures has become reactive at 175° F. (*e*) At 200° F. 50% sodium hydroxide gives the greatest increase in percentage reaction. (*f*) At 230° F. 10 and 20% sodium hydroxide show the same reaction as at 200° F., whereas 30% caustic gives an increase.

The data of Table I were plotted to point out certain characteristics of the reaction between calcium sulfate and sodium hydroxide. Figure 1 presents the importance of temperature when reacting calcium sulfate with 50% caustic. At 150° F. all of the tests show a low percentage reaction; at 200° F. all of the tests show complete reaction.

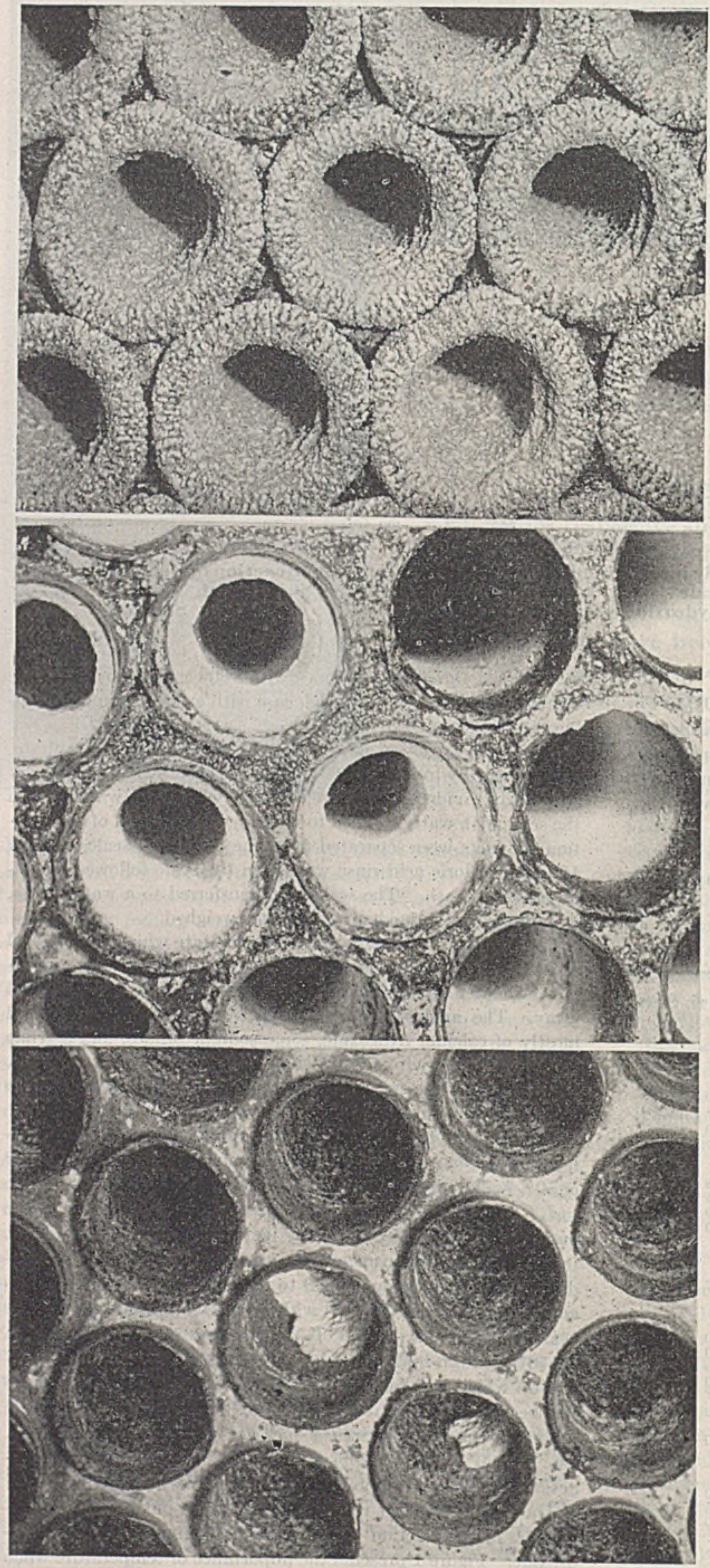

Figure 4. Close-up View of Tubes in Brine Evaporator

Top, before treatment; *center*, after first stage of 45–50% sodium hydroxide treatment; *bottom*, after second stage of 45–50% sodium hydroxide treatment.

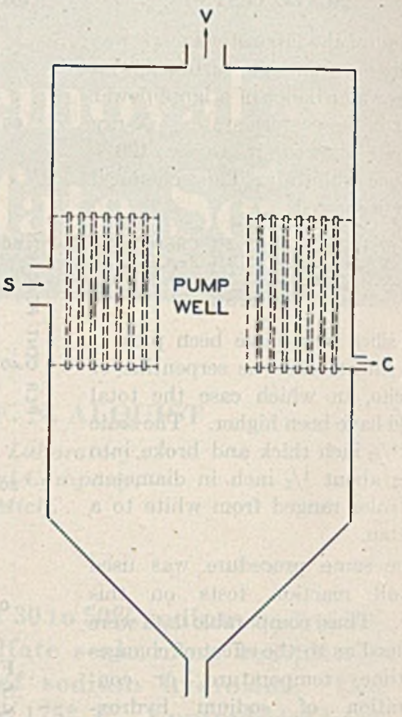

Figure 3. Sketch of a Typical Cone-Type Brine Evaporator

S, steam inlet; *V*, vapor; *C*, condensate

Figure 2 presents data on 30% caustic. The reaction rate is directly proportional to rise in temperature and increase in time of test.

SOLUBILITY OF REACTION PRODUCTS IN CAUSTIC SOLUTIONS

The reaction products of calcium sulfate with sodium hydroxide are calcium hydroxide and sodium sulfate. Only a small portion of the reaction products are soluble in the sodium hydroxide solutions. When 2 grams of calcium sulfate scale are reacted with 100 cc. of sodium hydroxide solution for 16 hours at 200° F., the percentage of calcium remains constant as the caustic is varied; the sulfate content decreases definitely as the caustic is increased from 10 to 50%:

% NaOH	% Ca	% SO_4
10	0.003	0.93
30	0.002	0.27
50	0.002	0.04

After this comparative data on the one scale had been accumulated, tests were made on scales containing calcium sulfate from other boilers and from a brine evaporator. Most of the scales were considerably thicker than 1/32 inch and contained other ingredients besides calcium sulfate.

The laboratory tests on these other scales showed the following results: (*a*) Thicker scales need more severe conditions of treatment—i.e., higher temperatures and longer times. (*b*) Porosity affects the rate of reaction. The more porous the scale is, the more easily it will react. (*c*) Removing scale which is in place on a tube is more difficult than completely reacting a loose piece of a similar scale. (*d*) Scales containing as low as 50% calcium sulfate were disintegrated completely by their reaction with 30–50% sodium hydroxide solution. The remainder of the scales consisted of calcium carbonate and magnesium hydroxide.

These laboratory data led to the actual treatments of the following nine heat exchange units with sodium hydroxide solutions in order to remove the scale high in calcium sulfate: one 1500-gallon locomotive boiler for a steel company, one 500-gallon crane boiler for a steel company, one 6000-gallon vertical tube boiler for a tool company, three 6000-gallon Wickes A-type boilers for a sugar refinery, two 6000-gallon boilers for a coal tar refinery, and one 50,000-gallon brine evaporator for a chemical company.

All the units except the brine evaporator were first treated with 30–50% sodium hydroxide and then treated with approximately 5% hydrochloric acid to help dissolve any of the reaction products.

All the treatments were 85–100% successful; that is, 85–100% of the scale in the boiler was removed. Considerable quantities of the scale disintegrated and fell to the bottom of the units, however, and, although not completely reacted, was readily removed.

TREATMENT OF BRINE EVAPORATOR

The 50,000-gallon brine evaporator was a cone-bottom evaporator (Figure 3) consisting of a steel shell and containing 4100 10-foot copper tubes (2 inches i.d.) rolled into steel tube sheets (Figure 4). Its capacity was 7000 cubic feet or approximately 50,000 gallons. Analysis of four samples of scale showed 100% calcium sulfate, from $^3/_8$ to $^1/_2$ inch thick. The amount of scale was estimated to be 100,000 pounds.

Turbining this evaporator had never been very satisfactory. The hard scale and the relatively soft copper tubes were not the best combination. The scale had a tendency to divert the turbine tool off its course through the side of the tube.

METHOD OF TREATING. The evaporator was filled to its operating level with 48–50% sodium hydroxide and kept at 230° F. (110° C.) for a total of 5 days with constant circulation. The first stage of the treatment lasted 3 days. During this time the caustic concentration dropped from 49.6 to 47.6%. The sodium hydroxide was drained from the evaporator and pumped into settling tanks. The evaporator was then filled with water, brought to a boil, and washed thoroughly. Inspection showed that the scale was approximately half gone (Figure 4).

The evaporator was refilled with 46.0% sodium hydroxide and kept at 230° F. for another two days. During this stage the caustic concentration had dropped to 45.4%; it was then increased to 48.2% by evaporating under vacuum some of the water from the solution and replenishing with 50% sodium hydroxide. The 48.2% caustic dropped to 46.9% at the end of the treatment.

The second stage was stopped 6 hours before its scheduled 2-day run because of the following observations: A large increase occurred in the amount of sludge in the samples. The amperage on the circulating pump increased from 170 to 270 amperes due to the heavier liquid being pumped. A temperature difference was noticed above and below the tubes. This difference was due to poor circulation. On inspection the evaporator was pronounced 90% clean (Figure 4).

During the first stage the solids in the sodium hydroxide solution had increased from 0 to 15.1% by weight. During the second stage they had increased from 6.9 to 20.9%, or 14.0%.

The scale from the evaporator at the end of first stage was 100% calcium sulfate; at the end of the second stage, it was made up of 85% calcium hydroxide, 10% calcium carbonate, and 5% sodium sulfate.

CALCULATIONS. The amount of solids in the drain solutions was 98,500 pounds in the first stage and 92,000 in the second, or a total of 190,500 pounds of solids formed. Since calcium sulfate formed about twice its weight of insoluble reaction products, about 95,000 pounds of calcium sulfate were removed from this evaporator. Therefore it was found that the efficiency of the evaporator increased 40–45%, and the rate of steam condensation increased from 55,000–60,000 to 85,000 pounds of condensate per hour.

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Multicomponent Tray Calculations

Based on Equilibrium Curve of Key Components

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A PREVIOUS paper (*10*) presented an equation for calculating the minimum reflux ratio in multicomponent distillation. In the design of fractionating towers to effect a given separation, it is then necessary to carry out a set of tray calculations to determine the total trays and the feed tray location at a reflux ratio greater than the minimum.

The first rigorous method of multicomponent tray calculations involved a matching of the components at the feed tray by a trial-and-error process. Jenny (*7*) proposed a method whereby this trial and error can be eliminated. The method consists of estimating a feed tray temperature and determining the liquid and vapor compositions at this temperature. The calculations can then be made down the column until the bottom product composition is matched and up the column until the overhead composition is obtained. This method is more direct in that all the heavier components become negligible several trays above the feed and all the lighter components become negligible several trays below the feed. Thus, the trial-and-error method of matching is eliminated. The uncertainty in the method lies in the choice of the feed tray temperature since, if the temperature is too high or too low, a larger number of trays will be required. At reflux ratios close to the minimum, a feed tray temperature must be estimated very accurately, but at reflux ratios generally used in practice, the effect of feed tray temperature on the number of trays is quite small, and little difficulty will be encountered if the temperature is estimated according to the empirical method described by Jenny (*7*).

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A graphical method is presented for tray calculations on multicomponent systems. The method is based on a pseudo reflux ratio which gives the same number of trays for the binary system of the key components as the actual multicomponent calculations. This pseudo reflux ratio is calculated from a general correlation of the results of a large number of tray calculations. This method is simpler to apply than previous methods in that it requires only the equilibrium curve for the key components, and the graphical tray calculations are made by the McCabe-Thiele method. The total trays by this method agree with the rigorous tray calculations with an accuracy of about 5%, and the feed tray is located with an accuracy satisfactory for all practical purposes.

Smith (*11*) described a shorter but more approximate method for determining the number of trays required for a multicomponent distillation. The method is based on assuming average vaporization equilibrium constants for the fractionating and stripping sections of the column. These constants were chosen at a calculated average temperature; however, all the components do not have their average equilibrium constants at the same temperature, and, therefore, the method is not completely accurate.

Another method for making tray calculations, somewhat similar to the method of Jenny, was applied by Hummel (*6*) to the case of a separation in the presence of a component with a volatility intermediate between the key components.

Recently another simplified method (*8*) was proposed for estimating the number of trays required at any reflux ratio when a set of calculations are available at another reflux ratio. The method is based on a two-component equilibrium curve, combining all components lighter than the light key with the light key and all components heavier than the heavy key with the heavy key. To apply this method, a set of tray calculations must first be made.

Several correlations (*2*, *5*) have been proposed for estimating the total number of trays required at given reflux ratios based on the minimum reflux ratio and trays at total reflux. In the course of the present work, about one hundred sets of tray calculations were studied and a general correlation similar to that of Gilliland (*5*) was attempted. The same function of the total trays was used; however, a somewhat better correlation was obtained when a slight correction was made for the composition and condition of the feed. The function of reflux ratio that gave the best results was:

$$(R - R_m)/(R + x_i)$$

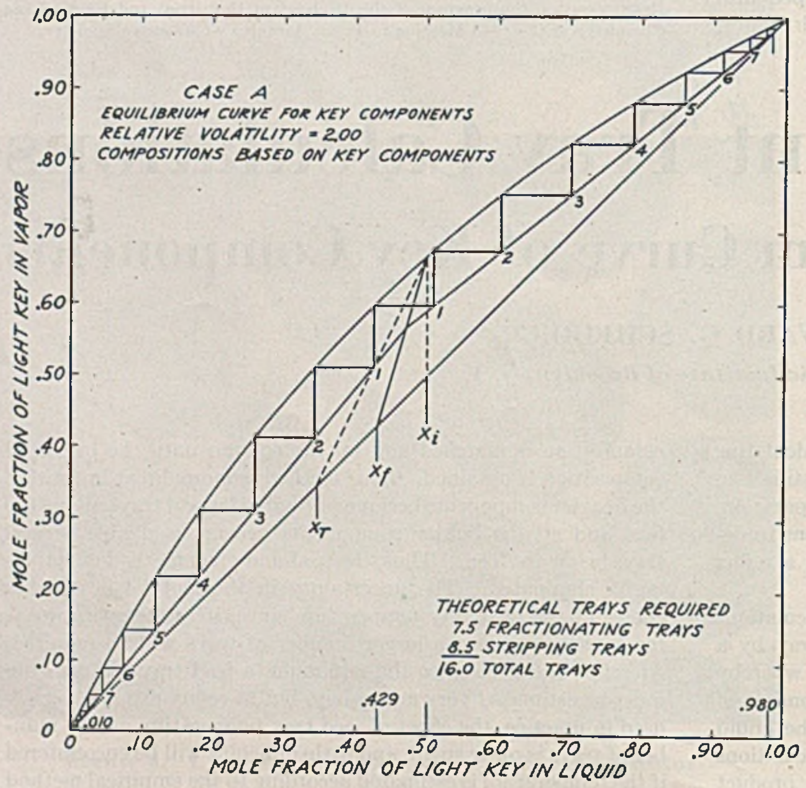

Figure 1

The general correlations give only the total trays required in the column and do not provide any clue as to the feed tray location. This is of equal importance because improper location of this tray will essentially neutralize the effect of some of the trays and make the separation appear more difficult.

THE previous paper (*10*) introduced the concept of a pseudo minimum reflux as a basis for determining the minimum reflux ratio for a multicomponent distillation. It is possible to consider a pseudo reflux ratio as that reflux ratio which gives the same number of total trays on a binary distillation curve as determined by the tray calculations at a given reflux ratio on the actual multicomponent system. It can be seen from the Fenske equation (*4*) at total reflux that the number of trays required in the multicomponent separation is the same as in a binary system when the overhead and bottom compositions are based on the key components alone.

The empirical correlation of the tray calculations indicates that the relation between the pseudo reflux ratio and the actual reflux ratio is given by the following relation:

$$\frac{R - R_m}{R + x_i} = f\left(\frac{N - N_m}{N + 1}\right) = \frac{R' - R'_m}{R' + x_i}$$

where R' = pseudo reflux ratio
R = actual reflux ratio
R'_m = pseudo minimum reflux ratio
R_m = actual minimum reflux ratio
x_i = intersection of operating lines at pseudo minimum reflux
N = trays required in actual multicomponent calculations = trays required at pseudo reflux ratio on binary system
N_m = trays required at total reflux in multicomponent systems = trays required at total reflux in binary system

By solving this expression for the pseudo reflux ratio, the following relation is obtained:

$$R' + x_i = (R + x_i)\frac{R'_m + x_i}{R_m + x_i}$$

When the operating lines, corresponding to the pseudo reflux ratio thus calculated, have been drawn on the binary equilibrium curve for the keys, the stripping and fractionating trays are accurately determined as well as the total trays. The agreement in some cases is within the accuracy of the graphical construction.

It has been found by accurate tray calculations that the optimum feed tray in any distillation is that which properly straddles

TABLE I. DESCRIPTION OF ILLUSTRATIVE CASES

Case No.	Feed Composition				Relative Volatilities				Product Composition Based on Keys	
	X_A	X_B	X_C	X_D	α_A	α_B	α_C	α_D	Overhead	Bottoms
A	0.30	0.30	0.40	..	4	2	1	..	0.980	0.010
B	0.72	0.12	0.16	..	4	2	1	..	0.985	0.010
C	..	0.30	0.40	0.30	..	2	1	0.5	0.990	0.017
D	..	0.30	0.40	0.30	..	2	1	0.5	0.985	0.070
E	..	0.12	0.16	0.72	..	2	1	0.5	0.991	0.054
F[a]	..	0.30	0.40	0.30	..	2	1	0.5	0.990	0.017
G	0.30	0.20	0.20	0.30	4	2	1	0.5	0.975	0.025

[a] Case F is based on vapor feed at the feed plate temperature, and the balance of the cases are based on liquid feed at the feed plate temperature.

TABLE II. COMPARISON OF GRAPHICAL METHOD WITH ACTUAL TRAY CALCULATIONS

Case No.	x_i	R_m	R'_m	R	R'	No. of Theoretical Trays: Fractionating Calcd.	Fractionating Graph.	Stripping Calcd.	Stripping Graph.	Total Calcd.	Total Graph.
A	0.500	1.127	1.88	3.00	4.40	7.3	7.5	8.9	8.5	16.2	16.0
B	0.726	0.500	1.25	0.74	1.68	8.8	9.4	10.7	11.0	19.5	20.4
C	0.429	2.51	2.28	4.00	3.66	10.1	10.4	9.3	8.3	19.4	18.7
D	0.429	2.48	2.25	3.50	3.19	10.2	10.2	6.4	6.2	16.6	16.4
E	0.429	4.05	2.28	5.85	3.37	9.9	11.0	6.8	6.7	16.7	17.7
F	0.225	4.60	4.37	7.38	6.82	9.2	9.5	7.2	6.8	16.4	16.3
G	0.610	0.913	1.47	1.78	1.66	7.0	7.1	7.3	8.6	14.3	15.7

TABLE III. COMPARISON OF GRAPHICAL SOLUTION WITH TRAY CALCULATIONS OF ROBINSON AND GILLILAND (*9*)

Problem	Page No. (*9*)	x_i	R_m	R'_m	R	R'	No. of Theoretical Trays: Fractionating Calcd.	Fractionating Graph.	Stripping Calcd.	Stripping Graph.	Total Calcd.	Total Graph.
Benzene-toluene, etc.	139	0.667	0.975	0.990	2.0	1.974	7	7.0	9	9.5	16	16.5
Phenol-cresol, etc.	158	0.700	4.69	5.35	10.0	9.17	13	13.5	13	12.8	26	26.3
	167	...	...	...	7.0	6.40	16	17.3	18	17.3	34	34.6
Gasoline stabilizer	175	0.695	0.886	0.822	2.0	2.20	3	3.3	8	8.7	11	12.0

the intersection of the operating lines. At total reflux the optimum feed tray liquid would be one half tray below the feed composition and the vapor would be one half tray above the feed composition. The concept is based on 100% tray efficiency, and this value is frequently approached in petroleum fractionating towers. Only at small tray efficiencies does the optimum feed tray liquid at total reflux approach the feed composition. Thus the optimum feed tray composition at total reflux, assuming 100% tray efficiency, is calculated as follows:

$$\frac{x_f}{1 - x_f} = \sqrt{\alpha_B}\,\frac{x_T}{1 - x_T}$$

$$x_T = \frac{x_f}{x_f + (1 - x_f)\sqrt{\alpha_B}}$$

where x_f = concentration of light key based on keys
$= X_B/(X_B + X_C)$
x_T = concentration of light key in optimum feed tray at total reflux
X_B = concentration of light key in feed
X_C = concentration of heavy key in feed
α_B = relative volatility of key components

The only feed tray possible at minimum reflux occurs at the intersection of the operating lines; thus the optimum feed tray must vary between this point and the calculated point at total reflux. It can be found by very accurate calculations on binary systems that the optimum feed tray variation is linear on the conventional McCabe-Thiele diagram (*1*). In Figure 1, which represents the graphical tray calculations for case A in Table I, the locus of the optimum feed tray is given by the heavy dashed line between x_i and x_T. The operating lines are determined from the calculated pseudo reflux ratio, and the trays are stepped off by the conventional McCabe-Thiele method (*1*) starting at the optimum feed tray. The trays determined graphically above and below this feed tray were found to agree very well with those determined by the analytical method of tray calculations.

Tables I and II give the comparison between the fractionating trays and stripping trays determined by actual tray calculations and by the graphical method. The illustrative cases in Table I are based on total liquid feed at the feed tray temperature, with the exception of case F which is total vapor feed at the feed tray temperature. In Table I the feed composition was varied to contain up to 72% of a third composition. Numerous other cases with components of different relative volatilities were also checked with reliable results. The agreement between the total trays required is generally within 5%, and the feed tray location determined graphically will function as well in the tower as that determined by the rigorous method of calculation.

Table III shows the agreement between the graphical method given in this paper with the results of tray calculations on different systems reported in the literature (*9*). In the calculations the feed tray was determined to the nearest tray, and no attempt was made to establish the exact optimum point for introduction of the feed. There is no doubt that the feed tray location determined graphically will function equally well with that given in the actual tray calculations. The last case in Table III involved a split key, and in calculating the minimum reflux ratio the original assumption of Robinson and Gilliland that 20% of this key would pass overhead was employed as described in the previous article. This case also involved subcooled liquid feed, and the agreement between the calculated and graphically determined trays demonstrates the broad application of this method.

In Table III the total trays and the feed tray location determined graphically agree with the actual tray calculations to within a theoretical tray in almost all cases. The time required for application of the graphical method is only a small fraction of the time required to carry out the actual tray calculations, and the results are sufficiently reliable for all practical engineering purposes.

For cases where the differences in latent heats over the column are sufficient to produce appreciable curvature of the operating line, the same technique of locating the pseudo operating lines for the McCabe-Thiele method may be applied to the Ponchon method with equally reliable results.

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Ethylation of Benzene in Presence of Solid Phosphoric Acid

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Phosphoric acid on kieselguhr (the so-called solid phosphoric acid) is an excellent catalyst for the alkylation of benzene with ethylene in continuous-flow operation. The yield of ethylbenzene increases with increase in temperature and pressure; 80% conversion of ethylene in a single pass (at benzene space velocity of 2 cc./hr./cc. of catalyst) is obtained at about 325° C. and 600 pounds per square inch or at about 280° C. and 900 pounds pressure. The ratio of monoethylbenzene to polyethylbenzenes increases markedly with increase in benzene-ethylene ratio; it is thus readily possible to obtain an alkylation product, over 90% of which is the desired styrene intermediate. The life of the catalyst is very satisfactory.

A PAPER (*4*) on the catalytic alkylation of benzene with ethylene showed that with phosphoric acid on kieselguhr (*1*) as catalyst, only 13–15% of the ethylene was converted to ethylbenzene at 239° C. and 100 pounds per square inch pressure. It was stated that "since pressure has been found to have such a pronounced effect on the reaction when the sodium chloride–aluminum chloride–pumice catalyst was used, this phosphoric acid–kieselguhr catalyst would probably give satisfactory conversions at pressures of 300–400 pounds per square inch". Our earlier investigation had already shown that solid phosphoric acid is an excellent catalyst for the preparation of ethylbenzene and has many advantages over aluminum chloride and other catalysts. However, secrecy orders from the United States Patent Office forbade publication of the results. These orders have now been rescinded, and a brief summary of results is presented here.

MATERIALS AND APPARATUS

Merck's thiophene-free C.P. benzene and ethylene (98%), obtained from The Ohio Chemical and Manufacturing Company, were used. The catalyst was standard U.O.P. solid phosphoric acid (*1*). It consisted of a phosphoric acid–kieselguhr composite containing 62–63% of the acid calculated as P_2O_5. The commercial extruded pellets were broken up into 10–12 mesh pieces for the experiments described here.

Alkylations were carried out in an 18–8 stainless steel tube ($^9/_{16}$ inch i.d., $^3/_4$ inch o.d.) which was heated in a vertical furnace. The latter consisted of an insulated, electrically heated, 24-inch aluminum-bronze block; the temperature was controlled within ±3° C. The reaction tube was fitted with a $^1/_8$-inch stainless steel thermocouple well which extended to the bottom of the catalyst bed and thus permitted the determination of temperature at various points in the bed; the temperatures in the tables are averages of the center of the bed. The catalyst (40 cc.) was held in place by a stainless steel rod of such length that the catalyst bed (about 11 inches long) was in the middle of the heated zone. The space above the catalyst was occupied by a similar rod (having a longitudinal hole to fit over the thermocouple well) in which a $^1/_8$-inch spiral groove had been cut. This served as a preheater for the hydrocarbon charge.

TABLE I. SUMMARY OF DATA ON ALKYLATION OF BENZENE WITH ETHYLENE

	Temp., ° C.		Pressure, Lb. per Sq. In.	Charge		Products, Grams per Hr.				Ethylene Converted, %			
Run No.[a]	Catalyst	Furnace		Benzene. g./hr.[b]	Mole ratio C_6H_6/C_2H_4	EtC_6H_5	$Et_2C_6H_4$	Higher[c]	Mono/poly	To EtC_6H_5	To $Et_2C_6H_4$	To higher	Total
1	350	350	50	64	1.8	..	..	2.0[d]	..	..	..	..	..
2	201	201	300	37	1.9	0.6	..	0.3[d]	..	..	..	..	..
3	254	250	300	35	1.8	3.6	..	0.8	..	..	..	..	..
4	312	300	300	37	1.9	10	2.5	1.3	2.6	38	15	10	63
5	366	350	300	35	1.8	13	4.2	1.1	2.5	49	26	8	83
6-5	202	204	600	40	2.0	1.6	..	0.9[d]	..	..	..	..	..
6-9	264	253	600	35	1.9	10	3.6	1.1	2.1	37	21	8	66
6-13	327	302	600	33	1.7	16	6.1	1.5	2.0	60	36	11	107
6-17	373	351	600	34	1.7	15	5.5	1.4	2.2	57	33	10	100
6-20	410	398	600	38	1.9	15	4.9	1.5	2.3	57	29	11	97
7	350	350	50	64	1.8	..	..	2.5[d]	..	..	..	..	..
8-2	201	201	600	75	2.1	..	..	1.1[d]	..	..	..	..	..
8-7	266	254	600	75	2.1	4.4	..	1.4	..	..	..	..	..
8-15	326	299	600	73	2.0	25	6.1	1.9	3.1	51	20	8	79
8-19	364	347	600	74	2.0	25	6.5	2.5	2.8	51	20	10	82
8-23	424	403	600	74	2.0	28	5.7	2.7	3.3	57	18	.11	86
9-7	202	202	900	71	1.7	..	..	2.9	..	..	..	..	..
9-11	278	250	900	71	1.7	27	7.6	2.6	2.6	48	21	9	78
9-14	344	300	900	71	1.7	31	13	3.3	1.9	55	36	11	102
9-18	399	352	900	71	1.7	33	12	3.2	2.2	58	33	11	102
10-5	255	251	900	106	1.7	17	..	4.9	3.5	20	..	..	..
10-10	365	302	900	106	1.7	46	17	4.0	2.2	55	32	9	96
10	416	350	900	102	1.7	44	14	4.3	2.4	53	27	10	90
11-6	346	306	600	75	1.0	38	21	6.0	1.4	38	34	12	84
12-6	376	352	600	76	1.0	40	18	4.8	1.8	41	29	10	80
13-7	310	301	600	75	4.1	14	0.7	0.5	11.7	57	5	5	67

[a] The first number is the experiment; the second is the number of periods since the beginning of the run. The periods were one hour, except for run 6 in which they were 2 hours.
[b] Since 40 cc. of catalyst were used, a charge of 35 grams/hr. of benzene represents an hourly liquid space velocity (H.L.S.V.) of 1.0.
[c] Residue from distillation. In runs for which no diethylbenzene yield is given, the values in this column include diethylbenzene as well as higher-boiling material.
[d] Includes mono- and polyethylbenzenes.

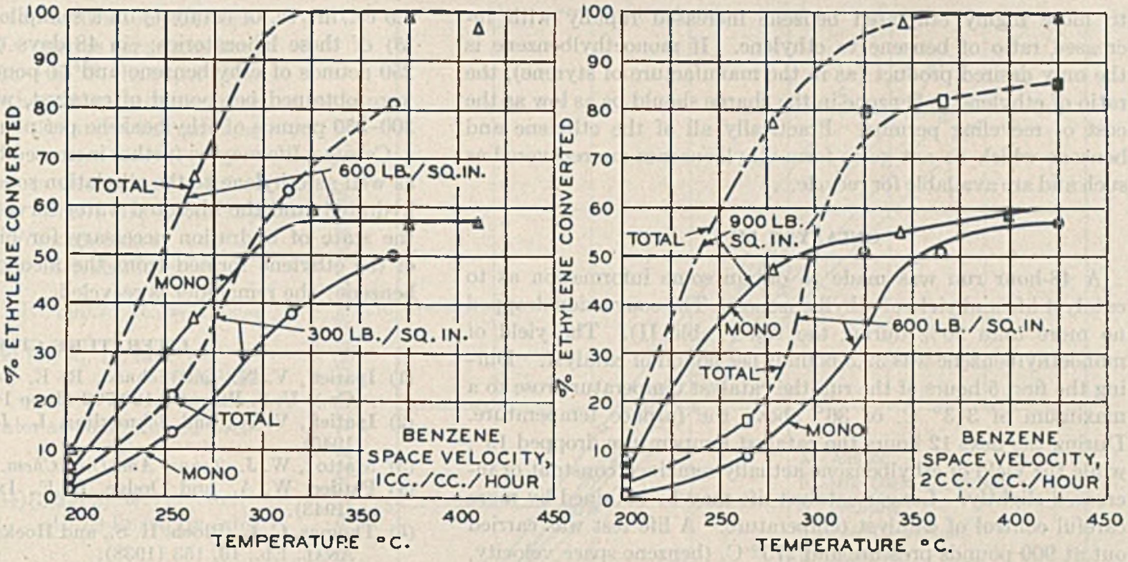

Figure 1. Effect of Temperature and Pressure on Conversion to Ethylbenzenes at a Benzene-Ethylene Mole Ratio of 2

The benzene was pumped from a graduated glass cylinder by a differential-piston-type pump. The ethylene was charged directly from the commercial steel cylinder through a needle valve, its rate being measured by a rotameter. The desired pressure was obtained at the beginning of each experiment with nitrogen.

The products from the reaction tube were released to atmospheric pressure by a Taylor pressure regulator; the liquid product was collected in a glass receiver, and the gaseous product passed through a trap immersed in ice water and then through a wet test meter. The composition of the product was determined by direct distillation (without washing) through a 14-inch total-reflux column (*5*).

The effect of temperature was studied in many of the runs by keeping the pressure and charging rates constant and raising the furnace temperature in 50° C. increments. The product obtained while the temperature was changing was discarded. The results during the latter part of some of these runs may not have been identical with those which would have been obtained with fresh catalyst. However, since the catalyst life is good, it was felt that the results would be sufficiently accurate for the purpose of a rapid survey.

The alkylation was highly exothermic, the maximum rise in catalyst temperature occurring at about 300–350° C. The difference in temperature between catalyst bed and furnace, together with gas exit rate, furnished an excellent means of following the progress of the experiment.

EFFECT OF VARIABLES

Table I summarizes the results obtained at catalyst temperatures of 201° to 424° C., at pressures from 50 to 900 pounds per square inch, and at benzene space velocities of approximately 1, 2, and 3 cc./hr./cc. of catalyst. Figure 1 gives typical curves relating temperature and pressure to conversion.

Increasing the pressure resulted in an increase in the conversion and a decrease in the temperature required to obtain a given yield of ethylbenzene. The use of the higher pressures is essential for satisfactory operation because lower temperatures may then be employed; loss of catalyst activity owing to dehydration and to carbon formation is thus avoided.

Table II. Data from 48-Hour Run

(40 cc. or 33.1 grams solid phosphoric acid; pressure, 600 pounds per square inch gage; benzene H.L.S.V., 2.1; mole ratio benzene/ethylene, 2.0)

Time, Hr.	Temp., ° C.		Composition of Product[a], Wt. %			
	Catalyst	Furnace	Mono	Di	Residue	Mono/ higher
1	335	304	24	3.4	3.5	3.5
2	341	306	35	9.7	4.	2.4
4	343	307	36	8.3	3.0	3.2
11	333	307	37	8.0	3.0	3.4
23	318	306	34	7.7	2.8	3.2
29	315	305	31	8.4	2.5	2.8
34	314	305	31	9.3	2.7	2.6
40	312	304	29	5.4	2.9	3.5
48	310	304	28	7.8	3.6	2.5

[a] The total product (3960 grams) contained 1312 grams of monoethylbenzene, 328 of diethylbenzene, and 119 of distillation residue (about half of which was diethylbenzene). The yields per pound of catalyst are: monoethylbenzene 39.5 pounds, diethylbenzene 10, residue 3.5.

The lower temperature limit was between 200° and 250° C., depending on contact time. For a contact time of 150 seconds (namely, at 600 pounds pressure and a benzene space velocity of 1 cc./hr./cc. of catalyst), about 5% of the theoretical yield of monoethylbenzene based on the ethylene was obtained at 202° C. (run 6–5). At the same pressure but with twice the space velocity, a temperature of 266° was required to give a 7% yield of monoethylated product (run 8–7). On the other hand, conversion of more than 75% of the ethylene could be obtained at 278° and at the higher space velocity by raising the pressure to 900 pounds per square inch (run 9–11).

In all but three cases the feed to the catalyst bed was in the vapor phase under the reaction conditions. Some liquid phase was present in the three runs, which were carried out at about 200° and a pressure of 600 pounds or higher (runs 6–5, 8–2, and 9–7).

The effect of changes in ratio of benzene to ethylene is shown in runs 8, 11, and 13, and Figure 2. The ratio of monoethylated

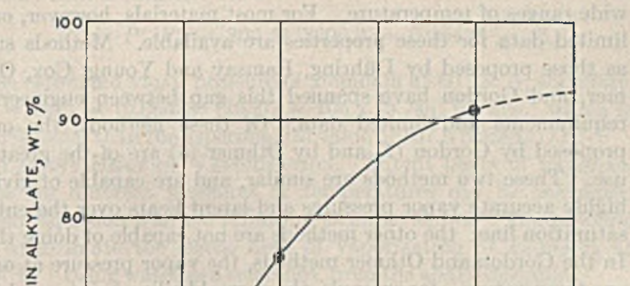

Figure 2. Effect of Benzene-Ethylene Ratio on Composition of Alkylate

to more highly ethylated benzene increased rapidly with increased ratio of benzene to ethylene. If monoethylbenzene is the only desired product (as in the manufacture of styrene), the ratio of ethylene to benzene in the charge should be as low as the cost of recycling permits. Practically all of the ethylene and benzene which do not go to form ethylbenzenes are recovered as such and are available for recycle.

CATALYST LIFE

A 48-hour run was made to obtain some information as to catalyst life and yield of ethylbenzenes. The conversion dropped no more than 20% during the run (Table II). The yield of monoethylbenzene was 39.5 pounds per pound of catalyst. During the first 5 hours of the run the catalyst temperature rose to a maximum of 343° C. or 36° above the furnace temperature. During the next 12 hours the catalyst temperature dropped 19°, while the yield of ethylbenzene actually remained constant or increased slightly. Longer catalyst life may be obtained by more careful control of catalyst temperature. A life test was carried out at 900 pounds pressure and 275° C. (benzene space velocity, 1.5 cc./hr./cc. of catalyst) on a semipilot plant scale by Mattox (*3*) of these laboratories; in 48 days of continuous operation, 250 pounds of ethylbenzene and 41 pounds of polyethylbenzene were obtained per pound of catalyst, with a life expectancy of 300-350 pounds of ethylbenzene per pound of catalyst.

Catalyst life may be further increased by charging ethyl alcohol as well as ethylene to the alkylation zone (*2*). The alcohol is dehydrated, and the liberated water serves to keep the catalyst in the state of hydration necessary for highest activity. A part of the ethylene formed from the alcohol reacts to yield ethylbenzene; the remainder is recycled.

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Correlating Vapor Pressure and Latent Heat Data

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A new method for calculating saturation temperatures, vapor pressures, and latent heats of vaporization is based on comparing these properties for any given material with the same properties of another material whose properties are known. This method permits the calculation of saturation temperatures within ±0.5%, of vapor pressure within ±4%, and of latent heats of vaporization within ±5% along the entire saturation line.

MANY engineering problems require the knowledge of vapor pressures and latent heats of vaporization over rather wide ranges of temperature. For most materials, however, only limited data for these properties are available. Methods such as those proposed by Dühring, Ramsay and Young, Cox, Othmer, and Gordon have spanned this gap between engineering requirements and limited data. Of these methods, the ones proposed by Gordon (*1*) and by Othmer (*5*) are of the greatest use. These two methods are similar, and are capable of giving highly accurate vapor pressures and latent heats over the entire saturation line; the other methods are not capable of doing this. In the Gordon and Othmer methods, the vapor pressure at only one temperature—for example, the normal boiling point—and the critical temperature and pressure are required. The critical constants can be obtained either from existing data or from the known methods for estimating them; these methods are reviewed by Herzog (*2*) and by Meissner and Redding (*4*). The method proposed in this paper is a modification of the Gordon and Othmer methods but is simpler to handle because it involves the use of simple arithmetic calculations only, whereas they are based on logarithmic calculations. The accuracy of the three methods is the same.

The method presented in this paper is derived by starting with the Clapeyron-Clausius equation for two substances. One of these is the unknown whose vapor-liquid equilibrium properties are to be determined. The other substance is the reference whose vapor-liquid equilibrium properties are completely and accurately known. By equating the reduced pressures of the unknown and the reference, substituting T_cT_r for T, and rearranging, the following is obtained:

$$\frac{dT_r}{dT_r'} = \frac{L'T_cT_r^2}{LT_c'T_r'^2} \qquad (1)$$

This equation holds for equal reduced pressures of the unknown and the reference. To integrate Equation 1, it was assumed that L/L', where both latent heats are taken at the same reduced pressure, is constant over the entire saturation line. This assumption introduces only small errors as shown by the application of the integrated equation to actual data. Then, integration of Equation 1, with the condition at the critical point, $T_r = T_r' = 1$ and $P_r = P_r' = 1$, gives the following equation, holding for equal reduced pressures of the unknown and the reference:

$$\frac{1}{T_r} - 1 = \frac{L'T_c}{LT_c'}\left[\frac{1}{T_c'} - 1\right] \qquad (2)$$

This equation is the basis of the proposed method for correlating the vapor data of two different materials.

ANALYTICAL METHOD

SATURATION TEMPERATURE AT A GIVEN PRESSURE. Saturation temperatures for different vapor pressures can be calculated from Equation 2. These calculations can be used either to extend experimental data beyond the range of temperature covered or to smooth out dubious experimental data. The calculations involved can best be illustrated by an example. Consider the

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problem of estimating the saturation temperature of ammonia at 107.6 pounds per square inch absolute, knowing that at −60° F. the vapor pressure is 5.55 and that the critical temperature and pressure are 271.5° F. and 1650 pounds, respectively (*11*).

As an example, water is chosen as the reference, accurate data for which are given by Keenan and Keyes (*3*). For ammonia at −60° F. and 5.55 pounds per square inch absolute:

$$1/T_r = T_c/T = 731.2° \text{ R.}/399.7° \text{ R.} = 1.8294$$

$$P_r = P/P_c = 5.55/1650 \text{ lb./sq. in. abs.} = 0.003364$$

The vapor pressure of water at this reduced pressure is:

$$P' = P'_r P'_c = (0.003364)(3206.2) = 10.79 \text{ lb./sq. in. abs.}$$

The saturation temperature of water at 10.79 pounds is 196.75° F. or 656.44° R. and

$$1/T'_r = T'_c/T' = 1165.09° \text{ R.}/656.44° \text{ R.} = 1.7749$$

From Equation 2,

$$\frac{L'T_c}{LT'_c} = \frac{1/T_r - 1}{1/T'_r - 1} = \frac{0.8294}{0.7749} = 1.0703$$

$$\frac{1}{T_r} - 1 = 1.0703\left[\frac{1}{T'_r} - 1\right] \qquad (3)$$

for ammonia as the unknown and water as the reference.

At a vapor pressure of ammonia of 107.6 pounds per square inch absolute,

$$P_r = P/P_c = 107.6/1650 = 0.06521 \text{ lb./sq. in. abs.} = P'_r$$

Then

$$P' = P'_r P'_c = (0.06521)(3206.2) = 209.1 \text{ lb./sq. in. abs.}$$

The saturation temperature of water at 209.1 pounds is 385.51° F. or 845.20° R., and

$$1/T'_r = T'_c/T' = 1165.09° \text{ R.}/845.2° \text{ R.} = 1.3785$$

From Equation 3,

$$\frac{1}{T_r} - 1 = (1.0703)(1.3785 - 1) = 0.4051$$

$$1/T_r = 1.4051$$

The estimated saturation temperature for ammonia at 10.76 pounds per square inch abolute is, therefore,

$$T = T_c T_r = 731.2° \text{ R.}/1.4051 = 520.4° \text{ R.}$$

which is 0.1% higher than the experimental value of 519.7° R. or 60° F. (*11*).

Vapor Pressure at a Given Temperature. Almost the same procedure is used for estimating the vapor pressure at a given temperature from Equation 2 as for estimating the saturation temperature at a given pressure. This is illustrated by estimating the vapor pressure of ammonia at 60° F. Using water again as a reference, Equation 3 can be similarly applied to this problem.

At 60° F. the reciprocal of the reduced temperature of ammonia is

$$1/T_r = 731.2° \text{ R.}/519.7° \text{ R.} = 1.4070$$

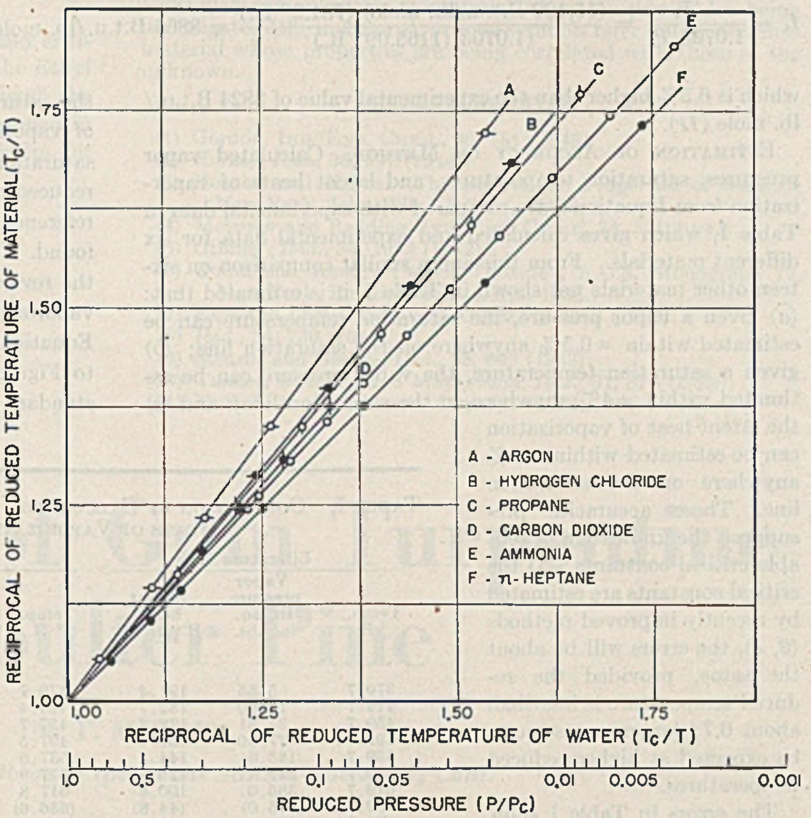

Figure 1. Reciprocal Plot of Reduced Saturation Temperatures of Several Materials against Reduced Saturation Temperature of Water, Always at the Same Reduced Pressure

Then by Equation 3,

$$\frac{1}{T'_r} - 1 = \frac{1}{1.0703}\left[\frac{1}{T_r} - 1\right] = \frac{1}{1.0703}(0.4070) = 0.3803$$

The reduced temperature for water at a reduced pressure equal to the reduced pressure of ammonia at 60° F. is, therefore,

$$T'_r = \frac{1}{1.3803} = 0.7245$$

$$T' = T'_r T'_c = (0.7245)(1165.09° \text{ R.}) = 844.11° \text{ R. or } 384.42° \text{ F.}$$

The vapor pressure of water at 384.42° F. is 206.41 pounds per square inch absolute. Then,

$$P'_r = P'/P'_c = 206.41/3206.2 = 0.06438 = P_r$$

The estimated vapor pressure of ammonia at 60° F. is, therefore, $P = P_r P_c = (0.06438)(1650) = 106.2$ lb./sq. in. abs., which is 1.3% lower than the experimental value of 107.6 pounds (*11*).

Latent Heat of Vaporization. Latent heats of vaporization for different pressures or temperatures can be calculated from Equation 2 as the following example shows. The problem is to estimate the latent heat of vaporization of ammonia at 60° F. Using water as a reference, from the above examples,

$$L'T_c/LT'_c = 1.0703$$

where the molal latent heats of vaporization, L and L', are taken at the same reduced pressure. In this example the reduced pressure of ammonia corresponding to 60° F. is:

$$P_r = 107.6/1650 \text{ lb./sq. in. abs.} = 0.06521 = P'_r$$

$$P' = P'_r P'_c = (0.06521)(3206.2) = 209.1 \text{ lb./sq. in. abs.}$$

The molal latent heat of vaporization of water at 209.1 pounds is 15,120 B.t.u./lb. mole. The estimated molal latent heat of vaporization of ammonia at 60° F. is, therefore,

$$L = \frac{L'T_c}{1.0703\ T_c'} = \frac{(15{,}120 \text{ B.t.u./lb. mole})\ (731.2° \text{ R.})}{(1.0703)(1165.09° \text{ R.})} = 8866 \text{ B.t.u./lb. mole}$$

which is 0.5% higher than the experimental value of 8824 B.t.u./lb. mole (*11*).

ESTIMATION OF ACCURACY OF METHOD. Calculated vapor pressures, saturation temperatures, and latent heats of vaporization from Equation 2 are compared with experimental data in Table I, which gives calculated and experimental data for six different materials. From this and a similar comparison on sixteen other materials not shown in Table I, it is estimated that: (*a*) given a vapor pressure, the saturation temperature can be estimated within ±0.5% anywhere on the saturation line; (*b*) given a saturation temperature, the vapor pressure can be estimated within ±4% anywhere on the saturation line; and (*c*) the latent heat of vaporization can be estimated within ±5% anywhere on the saturation line. These accuracies presuppose the knowledge of reliable critical constants. If the critical constants are estimated by recently improved methods (*2*, *4*), the errors will be about the same, provided the reduced temperature is less than about 0.7; larger errors are to be expected at higher reduced temperatures.

The errors in Table I show a definite trend with increasing reduced temperature, an indication that the coefficient $L'T_c/LT_c'$ in Equation 2 is not actually constant. The same phenomenon occurs when the Gordon and Othmer methods (*1*, *5*) are used.

GRAPHICAL METHODS

Estimation of saturation temperatures, vapor pressures, and latent heats of vaporization can be made easily and with almost the same accuracy by graphical methods as by the analytical method. This is illustrated in Figure 1, a plot of the reciprocal of reduced temperatures for several different materials against the reciprocal of the reduced temperature of water as reference; each point is taken where the reduced pressures for the unknown and the reference are equal. The reciprocal of the reduced temperatures is used in accordance with the form of Equation 2. The plot of $1/T_r$ against $1/T_r'$ is always a straight line going through the point $1/T_r = 1$, $1/T_r' = 1$, which corresponds to the critical point. If the critical point is known or estimated, and the normal boiling point, for example, is known, a second point on a plot like Figure 1 can be located. Drawing a straight line through this point and the 1,1 point gives a line from which the saturation temperatures, vapor pressures, and latent heats of vaporization can be estimated as follows: To estimate the saturation temperature at a given pressure and, hence at a given reduced pressure, $1/T_r'$ is located on a plot like Figure 1 for the reference at this reduced pressure, and the corresponding $1/T_r$ is found. To estimate the vapor pressure at a given temperature, the reverse procedure is used. To estimate the latent heats of vaporization, it is necessary to know the value of $L'T_c/LT_c'$ in Equation 2. This value is the slope of the line in a plot similar to Figure 1 and, therefore, can be determined graphically by standard methods.

TABLE I. COMPARISON OF CALCULATED SATURATION TEMPERATURES, VAPOR PRESSURES[a], AND HEATS OF VAPORIZATION WITH DATA IN THE LITERATURE

Literature			Calculated			% Error		
Temp., ° R.	Vapor pressure, lb./sq. in. abs.	Latent heat, B.t.u./lb.	Temp., ° R.	Vapor pressure, lb./sq. in. abs.	Latent heat, B.t.u./lb.	Temp.	Vapor pressure	Latent heat
			Propane (*9*)					
379.7	5.65	191.4	379.7	5.65	190.1	0	0	−0.7
419.7	16.00	182.7	419.4	16.53	180.9	−0.3	+0.3	−1.0
459.7	37.81	172.2	457.7	39.35	170.3	−0.4	+4.1	−1.1
499.7	77.80	159.6	497.5	80.68	157.8	−0.4	+3.7	−1.1
539.7	143.6	144.5	537.6	147.8	142.6	−0.4	+2.9	−1.3
579.7	243.4	125.8	577.9	248.9	123.7	−0.3	+2.3	−1.7
619.7	385.0	100.4	617.8	393.0	98.6	−0.3	+2.1	−1.8
(659.7)[b]	(575.0)	(44.8)	(656.6)	(592.8)	(59.3)	(−0.5)	(+3.1)	(+32.4)
571.9[c]	668.1[c]	0[c]	671.9[c]	668.1[c]	0[c]	0[c]	0[c]	....
			Methyl Chloride (*10*)					
419.7	6.878	190.66	419.7	6.878	189.1	0	0	−0.8
459.7	18 90	181.85	459.8	18.84	180.7	+0.02	−0.3	−0.6
499.7	43.25	172.00	499.8	43.15	171.5	+0.02	−0.2	−0.3
539.7	86.26	160.91	539.5	86.48	160.9	−0.04	+0.3	0
579.7	154.2	148.46	578.6	156.4	148.9	−0.2	+1.4	+0.3
619.7	253.5	134.66	617.2	261.3	134.7	−0.4	+3.1	+0.03
629.7	283.9	130.96	626.7	294.0	130.8	−0.5	+3.6	−0.1
749.3[c]	968[c]	0[c]	749.3[c]	986[c]	0[c]	0[c]	0[c]	....
			Ammonia (*11*)					
399.7	5.55	610.8	399.7	5.55	608.6	0	0	−0.4
419.7	10.41	597.6	419.8	10.37	596.0	+0.02	−0.4	−0.3
439.7	18.30	583.6	440.0	18.17	582.9	+0.07	−0.7	−0.1
459.7	30.42	568.9	460.1	30.14	569.0	+0.09	−0.9	+0.02
479.7	48.21	553.1	480.2	47.70	554.3	+0.10	−1.1	+0.2
499.7	73.32	536.2	500.3	72.46	538.3	+0.12	−1.2	+0.4
519.7	107.6	518.1	520.4	106.2	520.5	+0.13	−1.3	+0.5
539.7	153.0	498.7	540.4	151.1	502.9	+0.13	−1.2	+0.8
559.7	211.9	477.8	560.6	209.0	482.7	+0.16	−1.4	+1.0
579.7	286.4	455.0	580.6	282.6	461.6	+0.16	−1.3	+1.5
587.7	321.2	445.2	588.7	316.9	450.4	+0.17	−1.3	+1.2
731.2[c]	1650[c]	0[c]	731.2[c]	1650[c]	0[c]	0[c]	0[c]	....
			n-Pentane (*8*)					
559.7	15.69	153.42	559.7	15.69	148.9	0	0	−2.9
619.7	42.48	140.6	620.3	42.09	136.9	+0.1	−0.9	−2.6
679.7	94.91	125.60	680.8	93.68	121.9	+0.2	−1.3	−2.9
739.7	185.55	106.21	741.3	182.6	101.9	+0.2	−1.6	−4.1
799.7	329.16	75.79	801.6	323.5	72.1	+0.2	−1.7	−4.9
846.7[c]	485.4[c]	0[c]	846.7[c]	485.4[c]	0[c]	0[c]	0[c]	....
			Isobutane (*7*)					
529.7	44.97	143.4	529.7	44.97	143.8	0	0	+0.3
559.7	71.91	135.5	559.1	72.64	135.7	−0.1	+1.0	+0.1
589.7	109.80	126.0	588.9	111.5	126.3	−0.1	+1.5	+0.2
619.7	161.10	114.8	618.3	163.9	115.5	−0.2	+1.7	+0.6
649.7	229.3	101.7	648.3	232.8	102.2	−0.2	+1.5	+0.5
679.7	313.7	84.0	677.4	321.4	86.1	−0.3	+2.5	+2.5
(709.7)[b]	(419.7)	(57.5)	(706.3)	(433.8)	(63.9)	(−0.5)	(+3.4)	(+11.1)
733[c]	542[c]	0[c]	733[c]	542[c]	0[c]	0[c]	0[c]	....
			Carbon Dioxide (*6*)					
399.7	94.7	145.8	399.7	94.7	142.3	0	0	−2.4
419.7	145.8	137.8	420.0	145.0	134.8	+0.07	−0.5	−2.2
439.7	214.9	129.4	440.1	213.2	126.2	+0.09	−0.8	−2.5
459.7	305.5	120.1	460.2	302.9	116.4	+0.11	−0.9	−3.1
479.7	421.8	108.9	480.3	418.0	104.9	+0.13	−0.9	−3.7
499.7	567.8	95.0	500.3	563.1	90.8	+0.12	−0.8	−4.4
519.7	748.6	76.6	520.2	743.6	72.6	+0.10	−0.7	−5.2
539.7	968.7	44.8	539.8	967.5	44.1	+0.02	−0.1	−1.6
547.5[c]	1069.4[c]	0[c]	547.5[c]	1069.4[c]	0[c]	0[c]	0[c]	....

[a] Saturation temperatures calculated at experimental vapor pressures, vapor pressures calculated at experimental saturation temperatures. Water used as reference material in all calculated values.

[b] Parentheses indicate dubious experimental accuracy; the errors between calculated and experimental values for these cases were not used in estimating the reliability of the calculations.

[c] Critical points, based on a compilation by R. Herzog, Ethyl Corporation.

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NOMENCLATURE

L = molal latent heat of vaporization, B.t.u./lb. mole
P = vapor pressure, lb./sq. in. abs.
P_c = critical pressure, lb./sq. in. abs.
P_r = reduced pressure, P/P_c.
T = saturation temperature, ° R.
T_c = critical temperature, ° R.
T = reduced temperature, T/T_c.

Unprimed symbols refer to material whose properties are being investigated (the unknown), primed symbols refer to the reference material whose properties are being correlated with those of the unknown.

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Composition of Gum Turpentine of Coulter Pine

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Analysis showed that the turpentine of a rare Coulter pine growing in California consists of two terpenes: *l*-α-pinene and *l*-β-phellandrene with an admixture of two paraffin hydrocarbons, *n*-heptane and *n*-undecane. The presence of paraffins in Coulter pine turpentine shows once more that turpentine as obtained from pine oleoresins is not always a mixture of terpenes alone. Probably an admixture of paraffin hydrocarbons to the terpenes is more common than earlier investigations had indicated.

THE oleoresin composition of only about twenty of the seventy or more species of pines has been investigated. Each new study of a species is a contribution to our knowledge of oleoresins and may help to explain the processes of formation of oleoresin in the living tissue of trees. This is of fundamental importance to the naval stores industry. Although only a few pine species are now used for commercial gum turpentine production, the future may see many more pressed into service with consequent adjustment of turpentine specifications.

The oleoresins of pines are important not only from an industrial point of view; a study of the biochemistry of the genus *Pinus* promises to be of far-reaching importance in various other ways, such as in breeding studies. Coulter pine (*Pinus coulteri* D. Don) has been used in several breeding experiments at the Institute of Forest Genetics, a branch of the California Forest and Range Experiment Station. To facilitate these experiments, an investigation was made of the biochemical characteristics of Coulter pine oleoresin, especially the volatile part. Previous work with the oleoresin of the various pines showed that its specific peculiarities could be used to advantage in differentiating species and identifying hybrids (*9*).

Oleoresin was obtained by standard turpentining methods from 18-year-old planted trees growing in the Eddy Arboretum at the Institute of Forest Genetics, Placerville, Calif. The trees represent almost the whole range of Coulter pine. (Coulter is a rare pine that grows singly, never forming pure stands, in the coastal ranges of California as far north as the latitude of San Francisco; it also occurs sporadically in Lower California.) Fifteen trees were tapped once a week from May 20 to August 12, 1944. The total amount of oleoresin obtained was 8674 grams, about 48 grams per cup per streak. The oleoresin was of a sugary crystalline nature; after prolonged standing a more liquid part separated on the top. It was kept in friction-top cans until analyzed in November, 1944.

The oleoresin was distilled with steam at atmospheric pressure, the temperature not being allowed to rise above 145° C. Batches of about 1000 grams each of the oleoresin were distilled in a round-bottom 2-liter flask. A Kjeldahl connecting bulb was placed between the flask and the condenser to prevent particles of rosin from being carried over mechanically. Eight batches were distilled, and 1443 grams of volatile oil (turpentine) were obtained. The average yield of the eight distillations was as follows: turpentine, 16.92%; rosin, 83.00%; impurities, 0.08%; total, 100.00%.

From the fact that the rosin was not perfectly soluble in 95% alcohol, it appeared that partial polymerization of some ingredients of the volatile oil had taken place at the temperatures of the steam distillation. The volatile oil was dried over calcium chloride and kept in airtight bottles in cold storage until used.

The volatile oil had the following characteristics: specific gravity d_{15}, 0.8505; index of refraction n^{25}_{D}, 1.4767; specific rotation $[\alpha]_D$, -15.21. The oil tended to polymerize much more readily than commercial turpentine.

A sample of 500 grams of the oil was distilled at atmospheric pressure with a 12-inch Hempel column. The results of this distillation (Table I) show the presence of a component boiling below the turpentine range and possessing an index of refraction lower than the indices of terpenes, a decrease in the index of refraction of the last three fractions, and a relatively high percentage (15) of polymerized residue.

Another 500-gram batch of Coulter pine turpentine was distilled with a 12-inch Hempel column under 20 mm. of pressure. Figure 1 shows the results of distillation under atmospheric and

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[1] Maintained by the Forest Service, U. S. Department of Agriculture, in cooperation with the University of California.

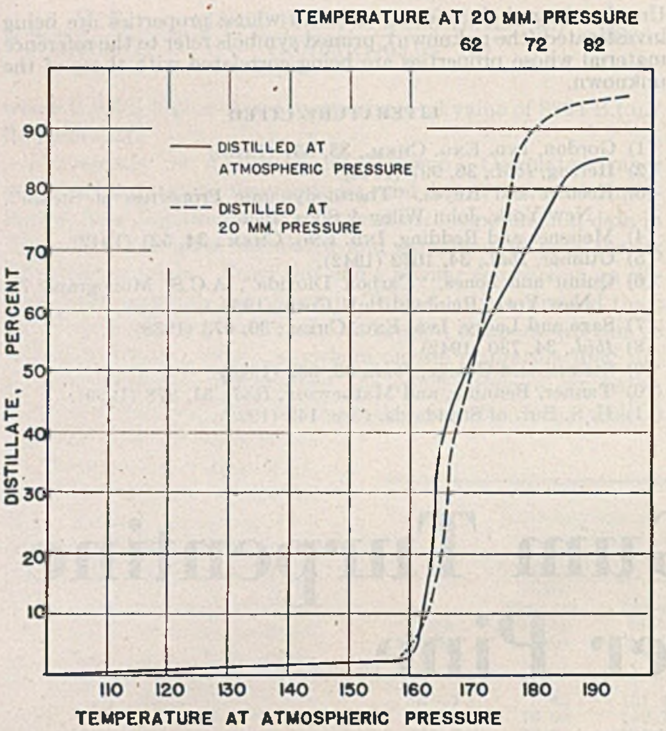

Figure 1. Boiling Point Curves for the Volatile Oil of Coulter Pine Oleoresin

reduced pressure. Specific gravity, index of refraction, and specific rotation were determined for each fraction of the distillation under reduced pressure; the results (Table II and Figure 2) show that the component having the low boiling point was partly lost when the turpentine was distilled under reduced pressure. Nevertheless the constants of fraction 1 indicated the presence of a nonterpene substance. The characteristics of the last two fractions also indicated a nonterpene component.

Only 5% of the residue was left in the flask after distillation under reduced pressure, and this included some of the oil that trickled back to the flask from the column after distillation was completed. It is obvious that polymerization of the volatile oil was greatly reduced by distillation at reduced pressure. The degree of polymerization of the volatile oil is apparent in Figure 1. The values of the physical constants of different fractions (Table II) are, in general, decidedly lower than they should be for terpenes. Apparently the 12-inch Hempel column, which had been used successfully by previous workers (*11*, page 10) for fractional distillation of terpenes, was not efficient enough in the fractionation of Coulter pine oil, which has nonterpene fractions boiling below and above the distillation range of terpenes. In fact, fractionation with this apparatus was very poor.

IDENTIFICATION OF COMPONENTS

It appears from the physical characteristics of Coulter pine turpentine that it contains a readily polymerized terpene and two nonterpene components—one with a boiling point much lower than that of α-pinene, and the other boiling above the boiling range of the terpenes.

n-HEPTANE. The specific gravity and the index of refraction of the first two fractions (Table I) suggested the presence of a paraffin hydrocarbon. These fractions, combined with fraction 1 of Table II, were shaken once with concentrated sulfuric acid and redistilled. The product was so volatile as to make collection and estimation extremely difficult. It possessed a peculiar odor characteristic of purified heptane obtained from *Pinus jeffreyi* and *P. sabiniana*. A sample of 10 cc. of the product was redistilled over sodium. It boiled between 98° and 99° C., and was not affected by the concentrated sulfuric acid. The specific gravity determined in a 5-cc. pycnometer was d^{20}_{20} 0.690, index of refraction was 1.3871 at 23° C., and molecular weight determined cryoscopically in benzene was 101.85. It is concluded that the low-boiling fraction of the oil contains a paraffin, *n*-heptane (C_7H_{16}). Probably about 5% of heptane is present in the volatile oil.

l-α-PINENE. Fractions 2 to 15 of Table II were redistilled four times under 20 mm. of pressure. Two main fractions were obtained. One fraction, amounting to 147 grams or about 30% of the original oil, had the following properties: boiling range, 55° to 59° C. at 20 mm. pressure and 154° to 158° C. at atmospheric pressure; specific gravity, 0.8530 at 15° C.; index of refraction, 1.4690. *l*-α-Pinene was identified in this fraction by preparation of the nitrosochloride. A copious precipitate of pinene nitrosochloride was obtained when 14 cc. of the oil were dissolved in 30 cc. of glacial acetic acid mixed with 20 cc. of ethyl nitrite, cooled with ice, and treated with a mixture of 11 cc. of hydrochloric acid and 11 cc. of glacial acetic acid (*5*). After five recrystallizations from chloroform by methanol, the nitrosochloride melted at 104° C.

l-β-PHELLANDRENE. The other large fraction mentioned in the preceding paragraph, after being redistilled five times under 20 mm. of pressure, amounted to 173 grams or about 35% of the original oil. It had the following properties: boiling point, 69° to 75° C. at 20 mm. pressure; specific gravity, 0.8400 at 15° C.; index of refraction, 1.4701. This fraction had a tendency to poly-

TABLE I. FRACTIONAL DISTILLATION OF COULTER PINE TURPENTINE AT ATMOSPHERIC PRESSURE (756.2 MM.)

Fraction No.	Temp. Cor., ° C.	Cumulative Dist., %	Refractive Index (15° C.)
1	90 –110	0.3	1.4020
2	110 –157	1.1	1.4561
3	157 –161	3.4	1.4691
4	161 –162	5.5	1.4710
5	162 –163	7.8	1.4722
6	163 –164	16.6	1.4730
7	164 –164.8	25.5	1.4742
8	164.8–166	36.8	1.4748
9	166 –170	47.4	1.4778
10	170 –172	53.9	1.4795
11	172 –174.5	59.9	1.4811
12	174.5–177	64.7	1.4821
13	177 –180	69.6	1.4841
14	180 –183	74.7	1.4851
15	183 –186	79.6	1.4825
16	186 –190	83.1	1.4755
17	190 –195	84.9	1.4645
Residue	Above 195	100.0	1.5103

TABLE II. FRACTIONAL DISTILLATION OF COULTER PINE TURPENTINE AT 20 MM. PRESSURE

Fraction No.	Boiling Point, ° C.	Distillate			Specific Gravity at 15° C.	Refractive Index at 15° C.	Specific Rotation at 20° C.
		Quantity, Grams	Obsvd., %	Cumulative, %			
1	To 53	10.3	2.4	2.4	0.8103	1.4596	– 8.94
2	53–55	20.3	4.9	7.3	0.8480	1.4698	–10.10
3	55–57	27.5	6.7	14.0	0.8499	1.4702	–11.01
4	57–58	26.9	6.5	20.5	0.8487	1.4712	–11.23
5	58–59	57.8	13.9	34.4	0.8483	1.4724	–11.84
6	59–60	23.1	5.6	40.0	0.8453	1.4736	–13.10
7	60–62	24.5	5.9	45.9	0.8444	1.4744	–13.54
8	62–63	21.9	5.3	51.2	0.8414	1.4762	–14.33
9	63–64	19.4	4.7	55.9	0.8393	1.4776	–15.48
10	64–66	22.6	5.5	61.4	0.8367	1.4792	–16.51
11	66–67	22.7	5.5	66.9	0.8355	1.4808	–17.84
12	67–68	22.6	5.5	72.4	0.8348	1.4824	–18.88
13	68–69	25.2	6.1	78.5	0.8337	1.4838	–19.42
14	69–70	23.7	5.7	84.2	0.8349	1.4842	–20.12
15	70–73	21.7	5.2	89.4	0 8338	1.4818	–19.86
16	73–87	18.8	4.6	94.0	0.8013	1.4541	–11.21
17	87–89	4.1	1.0	95.0	0.7973	1.4364	– 8.70
Residue	Above 89	20.5	5.0	100	0.9341	1.4971	+24.57

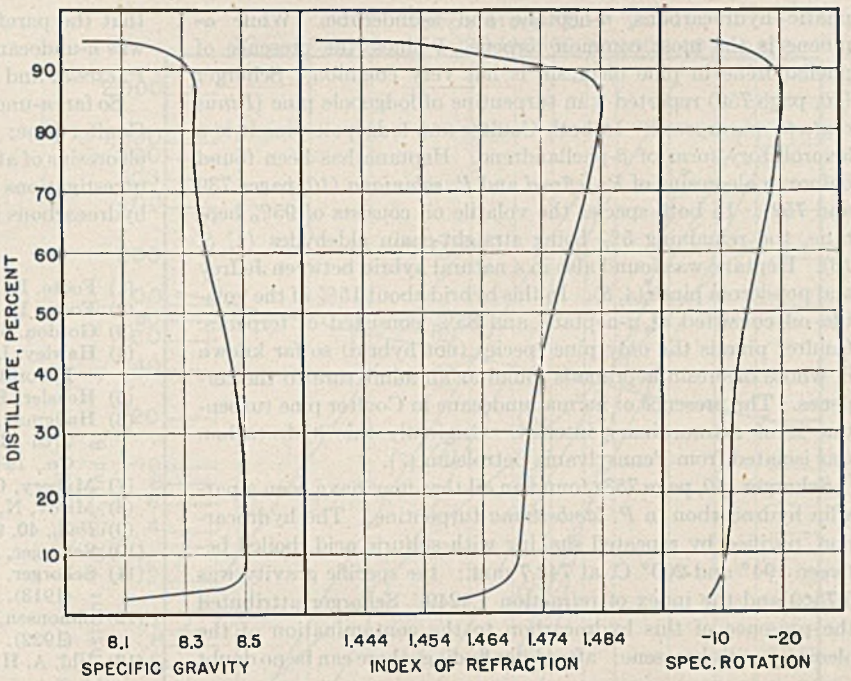

Figure 2. Specific Gravity, Index of Refraction, and Specific Rotation Curves for the Volatile Oil of Coulter Pine Oleoresin

merize when attempts were made to distill it under atmospheric pressure.

This tendency to ready polymerization was noticeable in Coulter pine turpentine in every phase of the work. The incomplete solubility of the rosin in 95% alcohol, the large amount of sirupy residue left in the flask after the fractionating of the oil under atmospheric pressure, the fuming during redistillation, the rapid polymerization of the turpentine when exposed to the air, and the physical properties, all pointed to the presence of one of the least stable terpenes, phellandrene.

Phellandrene nitrosite was obtained in abundance in the fraction by the following method: 5 cc. of the oil were dissolved in 10 cc. of petroleum ether and added to a solution of 5 grams of sodium nitrite in 8 cc. of water; then 5 cc. of glacial acetic acid were added slowly while the solution was stirred constantly and cooled with ice. The nitrosite was filtered, dissolved in a small quantity of chloroform, and precipitated with cold methanol. It melted at 103° C. Further purifications resulted in a product that melted at about 90° C. (*11*, page 27). The instability of phellandrene nitrosite mentioned by other workers (*11*) who prepared it from sugar pine turpentine also occurred in this experiment.

A copious precipitate of phellandrene nitrosite was obtained also when 1 cc. of the crude Coulter pine turpentine was placed in a test tube with 2 cc. of glacial acetic acid, 5 cc. of petroleum ether, and 2 cc. of concentrated solution of sodium nitrite.

Other Terpenes. The fractions boiling between 161° and 170° C. and between 170° and 180° C. (Table I) were redistilled repeatedly. The first group of fractions was tested for the presence of β-pinene and the second group for the presence of limonene and dipentene.

Ten grams of the oil were oxidized with 24 grams of potassium permanganate in 600 cc. of water to which 5 grams of sodium hydroxide were added. The mixture was shaken for 20 minutes, the unreacted oil was removed by steam distillation, and the manganese sludge was filtered off. The filtrate was evaporated to 200 cc. under reduced pressure while a continuous stream of carbon dioxide was passed through the solution. No sodium nopinate was obtained after cooling. Therefore it was concluded that β-pinene was not present in the oil.

In the redistilled fraction boiling between 170° and 180° C. no crystalline tetrabromide or hydrochloride was obtained; this test eliminated the possibility of the presence of limonene or dipentene.

Table III. Physical Characteristics of Coulter Pine Undecane

Constants	Hydrocarbon from Coulter Pine	*n*-Undecane (*6*)
Molecular weight	155.0	156.30
Index of refraction	1.4200 (23.5° C.)	1.4184 (20° C.)
Specific gravity	0.7465 (15/15° C.)	0.741 (20/4° C.)
Boiling point, ° C.	194–194.5	195.84

Table IV. Fractional Distillation of Residues under Reduced Pressure (20 Mm.)

Fraction No.	Temp. Cor., ° C.	Dist., %	Sp. Gr. (22° C.)	Refractive Index (23° C.)
1	66– 68	12.85	0.8388	1.4774
2	68– 70	8.75	0.8310	1.4770
3	70– 73	10.85	0.8289	1.4742
4	73– 84	8.75	0.8180	1.4654
5	84–102	4.40	0.8114	1.4472
6	102–114	4.35	0.9300	1.4852
7	114–128	8.70	0.9340	1.4930
Residue	.....	41.04	Very viscous, dark amber colored	

n-Undecane. The last two fractions (Table II) combined with all collected residues were redistilled with a 12-inch Hempel column, and the portion boiling between 190° and 200° C. was repeatedly shaken with concentrated sulfuric acid until no coloration occurred. It was extremely difficult to get rid of the impurities (probably polymers of phellandrene). Finally about 25 cc. of colorless oil were obtained. After washing with sodium carbonate, the oil was dried for 2 days over metallic sodium. A 15-cc. sample of the oil was distilled in a 30-cc. distilling flask. Ninety per cent of the hydrocarbon boiled between 194° and 194.5° C. (corrected). Molecular weight was determined cryoscopically in benzene. Table III gives the physical characteristics of the hydrocarbon, compared with those for *n*-undecane.

This hydrocarbon was found to be optically inactive. Accordingly, the second paraffin hydrocarbon found in the Coulter pine turpentine was identified as *n*-undecane.

Residue. The residues boiling above 200° C. were fractionated at reduced pressure (20 mm.) with a 12-inch Hempel column. The results are shown in Table IV. *n*-Undecane was found in all fractions.

About half of fraction 4 was found to consist of *n*-undecane. All attempts to obtain a crystalline dihydrochloride from fractions 6 and 7 were futile. No color reactions characteristic of cadinene or aromadendrene could be produced. When 5 drops of oil were dissolved in 1 cc. of acetic anhydride, a pinkish-brown color developed which gradually turned dark brown. It appears that the residues boiling above 200° C. consisted chiefly of polymerized phellandrene, with an admixture of *n*-undecane and possibly a small amount of some unidentified sesquiterpenes.

Summarizing, the turpentine obtained from Coulter pine oleoresin consisted of: *n*-heptane, about 5%; *l*-α-pinene 30–35%; *l*-β-phellandrene 35–45%; *n*-undecane, about 10%; and possibly a small amount of sesquiterpenes.

DISCUSSION

The volatile oil obtained from Coulter pine oleoresin has rather unusual composition. It consists mostly of two terpenes: *l*-α-pinene and *l*-β-phellandrene with an admixture of two aliphatic hydrocarbons, *n*-heptane and *n*-undecane. While α-pinene is the most common terpene of pines, the presence of phellandrene in pine oleoresin is not very common. Schorger (*10*, page 756) reported it in turpentine of lodgepole pine (*Pinus contorta murrayana*). In both Coulter and lodgepole pine it is a levorotatory form of β-phellandrene. Heptane has been found before in oleoresins of *P. jeffreyi* and *P. sabiniana* (*10*, pages 739 and 752). In both species the volatile oil consists of 95% heptane, the remaining 5% being straight-chain aldehydes (*1*, *3*, *13*). Heptane was found also in a natural hybrid between Jeffrey and ponderosa pines (*4*, *8*). In this hybrid about 15% of the volatile oil consisted of *n*-heptane and 85% consisted of terpenes. Coulter pine is the only pine species (not hybrid) so far known in whose oleoresin heptane is found as an admixture to the terpenes. The presence of normal undecane in Coulter pine turpentine is of extraordinary interest. Originally this hydrocarbon was isolated from Pennsylvania petroleum (*7*).

Schorger (*10*, page 753) found an oil that may have been a paraffin hydrocarbon in *P. lambertiana* turpentine. The hydrocarbon, purified by repeated shaking with sulfuric acid, boiled between 194° and 200° C. at 742.7 mm.; the specific gravity was 0.7549 and the index of refraction 1.4249. Schorger attributed the presence of this hydrocarbon to the contamination of the oleoresin with kerosene; after later findings there can be no doubt that the paraffin found by Schorger in the sugar pine oleoresin was *n*-undecane. Later, *n*-undecane was found in turpentines of *P. excelsa* and *P. monticola* (*2*, *12*).

So far, *n*-undecane has been found in four pine species, including Coulter pine; *n*-heptane, in two species. Thus, at present the oleoresins of at least six pines contain paraffins. Probably further investigations in this direction will reveal the presence of paraffin hydrocarbons in other pines.

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CORRELATING EQUILIBRIUM CONSTANTS

Chemical Reactions and Heats of Reaction

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A TOOL which has been found useful in correlating many properties of gases, of liquids, and of solutions is a graph on which some property is plotted on logarithmic paper against the vapor pressure of a reference substance at the same temperature. Such a graph was first used to correlate vapor pressure data (*7*).

The vapor pressures of some standard substance are indicated on the horizontal scale of an ordinary sheet of log paper, and the corresponding points of temperature are indicated. Ordinates for these points are erected, and on these temperature ordinates are plotted values of the vapor pressures of the desired substances to give straight lines. The slopes of these lines are the ratios of the molar latent heat of the substance to the molar latent heat of the reference at every temperature. Besides vapor pressure, many other properties of gases and solutions have been found to give straight lines on the same type of plot, such as gas solubilities and partial pressure (*12*), the pressure of adsorbed materials from adsorbents (*10*), vapor compositions and related properties of solutions (*9*), viscosities (*8*), etc.

REACTION CONSTANT

This method of correlation, giving straight lines, allows the ready checking of experimental data and the possibility, by extrapolation or interpolation from a relatively few experimental points, of obtaining data throughout a complete range. Figure 1 shows the plot of the recent data of Kelley (*5*) on the dissociation pressures as a function of temperature for various reactions (curves 1, 3, 4, 6, 7) and the equilibrium constants against the same temperature functions for other reactions (curves 2, 5, 8).

The latter three straight lines were obtained by extending the field of application of the method of plotting; the thermodynamic background will be indicated later. Reaction rate constants, ionization constants, equilibrium constants, and solubility product constants may all be correlated by the use of Figure 1. In each case the slopes of the resulting straight lines are the ratios of the heats of reaction for the particular system to the latent heat of the reference substance.

All of these plots may be constructed in the same way as the previous correlations on log paper. The Y axis is calibrated in units for the appropriate rate or equilibrium constant; the X axis is calibrated, first in units for the vapor pressure of a suitable reference substance, and then in corresponding temperatures, as indicated above. On the vapor pressure scale of the X axis the temperature lines are erected at the corresponding vapor pressure values, and then the rate or equilibrium constants are plotted on these temperature ordinates.

For equilibrium constants (Figures 2, 3), reaction rate constants (Figures 4, 5, 6), and solubility product constants (Figure 8),

Reaction rate constants, equilibrium constants, solubility product constants, and ionization constants give straight line plots on logarithmic paper against the vapor pressure of a reference substance at the same temperature, using the method of plotting developed for vapor pressures (*7*) and many other physical properties of gases and liquids. The slopes of the lines give the heats involved in the reactions. This method may be conveniently used to correlate the limited amount of experimental data available upon the change of the various types of equilibrium constants with temperature. A minimum of two experimental values is needed to fix the straight line obtained over a wide temperature range. In addition, the slope of the line may be used to obtain the heat of reaction at any temperature for any particular system. The heat evolved in the change in the polymetric structure of water, as indicated by the break in the ionization constant lines, is the same quantity of heat obtained for a similar break in the correlation for viscosity (*8*).

straight lines are obtained by the use of this method of plotting. For ionization constants (Figure 7) straight lines with breaks at about 25° C. are obtained. The abrupt break is probably due to a change in the molecular structure of the solvent water, as noted in plotting other physical properties (*8*, *11*).

In the first three cases only two values of the constant or one value and the value of the heat of reaction are needed to obtain the entire straight-line plot. For the case where the line breaks, two values of the constant are needed for each straight section of the plot.

EQUILIBRIUM CONSTANT

The van't Hoff isochore is:

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2} \tag{1}$$

The Clausius-Clapeyron equation may be written for some reference material:

$$\frac{1}{L}\frac{dP}{P} = \frac{dT}{RT^2} \tag{2}$$

$$\text{or } \frac{1}{L}\, d \ln P = \frac{dT}{RT^2} \tag{3}$$

Combining Equations 1 and 3 and integrating:

$$\ln K_p = \frac{\Delta H}{L} \ln P + C \tag{4}$$

The equilibrium constant may also be expressed in terms of concentration as well as partial pressure; for such a case Equation 4 becomes

$$\ln K_c = \frac{\Delta E}{L} \ln P + C \tag{5}$$

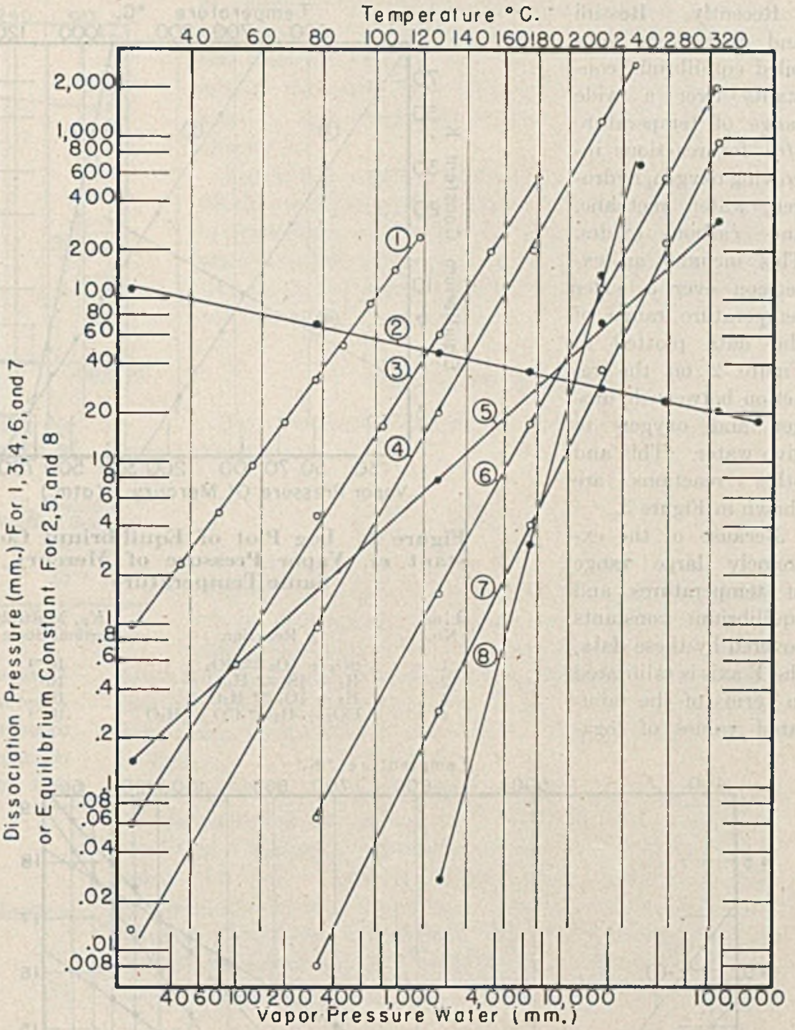

Figure 1. Log Plot of Dissociation Pressure *vs.* Vapor Pressure of Water at Same Temperature

The corresponding temperatures are indicated by the ordinates and the scale at the top

1. $MgCl_2.6H_2O \rightarrow MgCl_2.4H_2O + 2H_2O$
3. $MgCl_2.4H_2O \rightarrow MgCl_2.2H_2O + 2H_2O$
4. $MgCl_2.2H_2O \rightarrow MgCl_2.H_2O + H_2O$
6. $MgCl_2.H_2O \rightarrow MgOHCl + HCl$
7. $MgCl_2.H_2O \rightarrow MgCl_2 + H_2O$

Log plot of equilibrium constant for following reactions on same coordinates

2. $MgCl_2 + H_2O \rightarrow MgOHCl + HCl$
5. $MgCl_2 + \frac{1}{2}O_2 \rightarrow MgO + Cl_2$
8. $MgCl_2.2H_2O \rightarrow MgOHCl + HCl + H_2O$

where the relation between the two different equilibrium constants is:

$$K_p = K_c\,(RT)^{\Delta n} \tag{6}$$

It can be seen that K_p is equal to K_c when Δn is zero.

Another demonstration of the correctness of Equations 4 and 5 follows from the similar equation developed for activities (*9*). Since the log of the equilibrium constant is equal to the difference of the sums of the logs of the activities of the reactants and of the products, these equations for the activities and the respective heat terms may be combined to give Equations 4 and 5.

Figure 2 shows the result of a plot of K_p against the vapor pressure of mercury for several reactions. The slopes of the lines are the ratios of the heat of reaction to the latent heat of mercury at the same temperature. A positive slope to these lines indicates an endothermic reaction; a negative slope indicates an exothermic reaction.

For the reaction between hydrogen and oxygen to form water, the heat of formation at 0° C., as given in the literature from calometric determinations, is −68,310 calories per mole, and that calculated from the slope extrapolated down to 0° C. is −68,600 calories per mole.

Recently, Rossini and co-workers compiled equilibrium constants over a wide range of temperature (*16*) for reactions involving oxygen, hydrogen, water, methane, and carbon oxides. This includes an extension over a wider temperature range of the data plotted in Figure 2 on the reaction between hydrogen and oxygen to give water. This and other reactions are shown in Figure 3.

Because of the extremely large range of temperatures and equilibrium constants covered by these data, the *Y* axis is calibrated in terms of the tabulated values of loga-

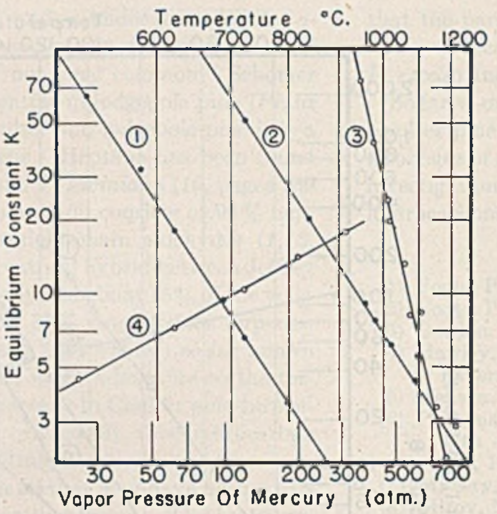

Figure 2. Log Plot of Equilibrium Constant *vs.* Vapor Pressure of Mercury at Same Temperature

Line No.	Reaction	K_p, Multiply Vertical Scale by
1	$SO_2 + \frac{1}{2}O_2 \rightleftarrows SO_3$	10^{-1}
2	$H_2 + \frac{1}{2}S_2 \rightleftarrows H_2S$	10^{1}
3	$H_2 + \frac{1}{2}O_2 \rightleftarrows H_2O$	10^{5}
4	$CO_2 + H_2 \rightleftarrows CO + H_2O$	10^{-1}

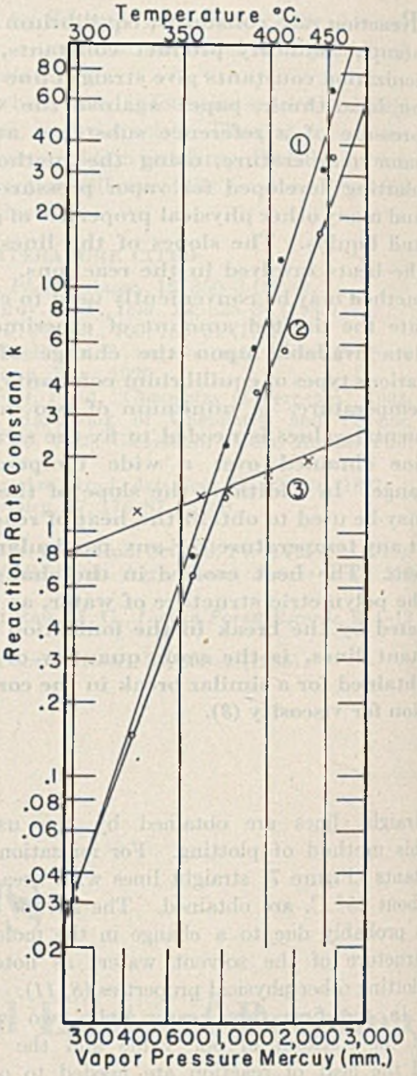

Figure 4. Log Plot of Reaction Rate Constant *vs.* Vapor Pressure of Mercury at Same Temperature

Line No.	Reaction	Constant Plotted	k, Multiply Vertical Scale by
1	$2HI \rightarrow H_2 + I_2$	k_1	10^{-4}
2	$I_2 + H_2 \rightarrow 2HI$	k_2	10^{-2}
3	$2HI \rightleftarrows H_2 + I_2$	$K_c = k_1/k_2$	10^{-2}

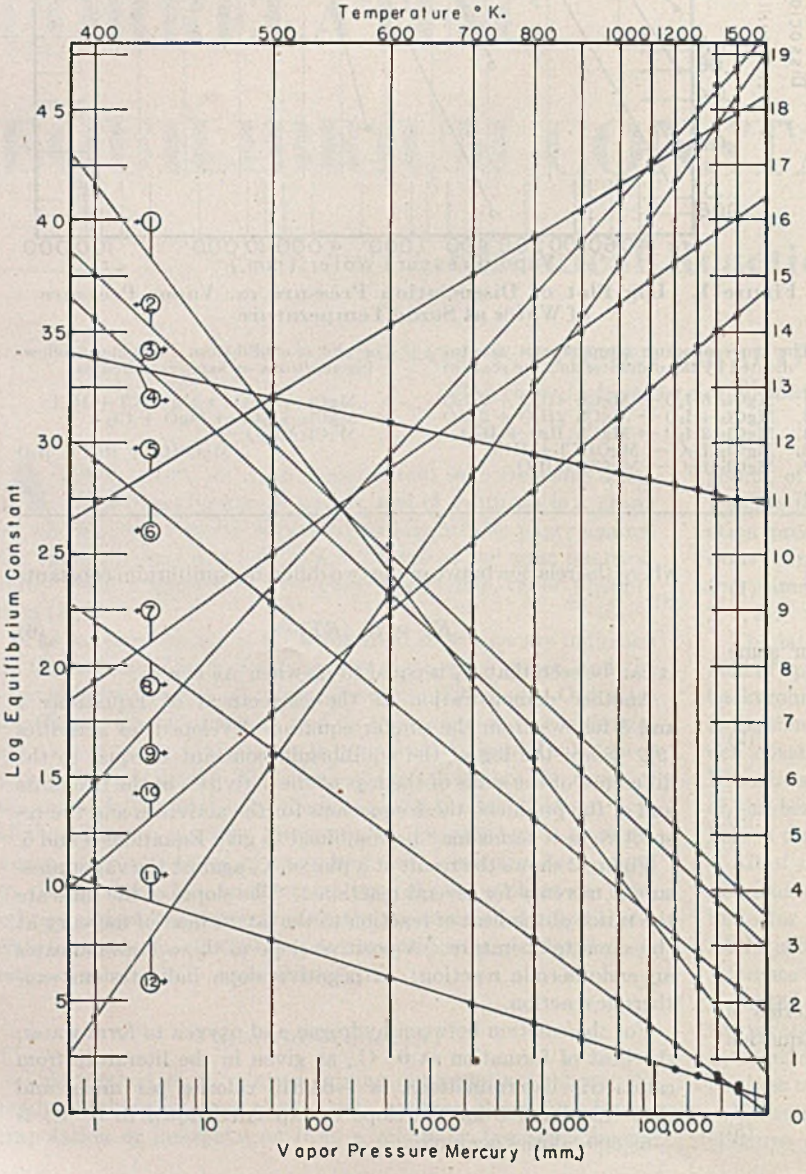

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Figure 3. Plot of Logarithm of Equilibrium Constant *vs.* Vapor Pressure of Mercury at Same Temperature

Arrows indicate whether left- or right-hand scale is to be used for log of equilibrium constant. Because of the wide range of values of *K* encountered (over 10^{40} times) it is necessary to add the indicated number to the respective scale reading to give log *K*.

Line No.	Reaction	Add to Vertical Scale
1	$C + O_2 \rightarrow CO_2$	+10, left
2	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	− 5, left
3	$C + \frac{1}{2}O_2 \rightarrow CO$	+ 5, right
4	$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$	.....
5	$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	−40, left
6	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	.....
7	$CH_4 + H_2O \rightarrow CO + 3H_2$	−35, left
8	$C + 2H_2 \rightarrow CH_4$	− 3, right
9	$C + H_2O \rightarrow CO + H_2$	−16, right
10	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	−30, left
11	$CO + H_2O \rightarrow CO_2 + H_2$	− 1, right
12	$C + CO_2 \rightarrow 2CO$	−15, right

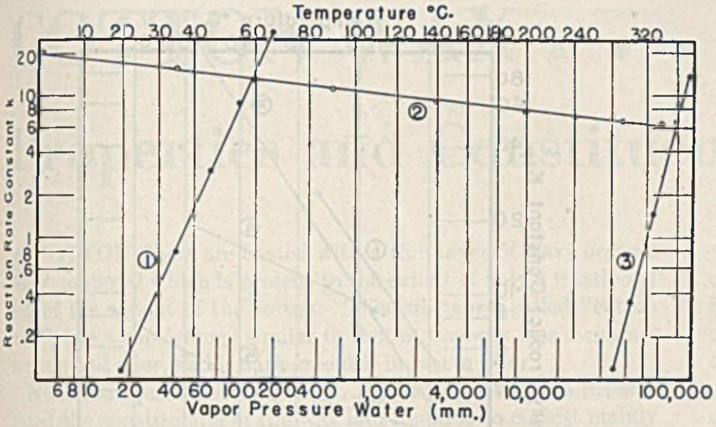

Figure 5. Log Plot of Reaction Rate Constant for Reactions of Different Orders *vs.* Vapor Pressure of Water at Same Temperature

Line No.	Order of Reaction	Reaction	*k*, Multiply Vertical Scale by
1	First	$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$	10^{-2}
2	Third	$O_2 + 2NO \rightarrow 2NO_2$	10^{-6}
3	Second	$H_2 + I_2 \rightarrow 2HI$	10^{-3}

rithms of equilibrium constants. Values plotted are against the temperatures corresponding to the vapor pressure of mercury but do not go below the temperature where the vapor pressure of mercury is 1 mm. Figure 3 shows the excellent correlation obtained in this simple method of plotting even over this tremendous range.

REACTION RATE CONSTANT

Equilibrium constants for a reaction are actually a combination of two reaction rate constants. By definition,

$$K_c = k_1/k_2 \tag{7}$$

Tolman (*15*) showed that the reaction rate constants may be expressed, according to the van't Hoff equation, as follows:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \tag{8}$$

This may be combined with the Clausius-Clapeyron equation to give:

$$\ln k = \frac{\overline{E}}{L} \ln P + C \tag{9}$$

Figure 4 shows the plot of reaction rate constant k_1 for the decomposition of hydrogen iodide, reaction rate constant k_2 for the formation of hydrogen iodide from hydrogen and iodine, and equilibrium constant calculated from the ratio of k_1 and k_2. Line 3 was obtained by dividing k_1 by k_2 and plotting the values so obtained. The points for the plotting are not shown since this line is derived from the other two; crosses indicate the values of Dushman (*2*) who compiled the best work of other experimenters. Correlation of the plotted line with the crosses is good. This type of plot is independent of the order of a chemical reaction, since first-, second-, and third-order reactions give straight lines (Figure 5).

Table I. Heat Change at Break in Curves of Figure 7

Weak Electrolyte	Heat of Ionization, Calories/Mole Below break	Above break	Change due to break
Water	13,600	12,600	1000
m-Nitrobenzoic acid	4,230	3,010	1220
Methyl cyanonitroacetate	732	−91	823
Ammonium hydroxide	2,150	1,110	1040
Toluic acid	−732	−1,660	928
m-Hydroxybenzoic acid	732	−548	1280
		Average	1060

Figure 6 is a plot of reaction rate constants for the alkaline hydrolysis of several different esters. The slopes of these lines are nearly the same, and indicate that the activation energies and, hence, the heats of esterification are about constant for these several different alcohols when esterified with acetic acid.

IONIZATION CONSTANT

For ionization constants Equation 4 may be written:

$$\ln K_i = \frac{\Delta E_i}{L} \ln P + C \tag{10}$$

Figure 7 is a plot of ionization constants for several weak electrolytes. As mentioned before, these lines break at about 25° C. The heat change shown by this break may be calculated by determining the slope of the straight line just below and just above the break. By subtraction, the heat change at the break is determined. These values are given in Table I.

Since all of the ionization constants were calculated from the concentrations of the ions in gram moles per liter of solution, the heats of ionization obtained from the slopes are expressed in calories per mole. Table I indicates that the change in the heat of ionization shown by the breaks in the lines is approximately the same for all cases represented. This seems to show that the change was not due to the electrolyte but rather to the solvent, which was water in all cases. There is probably some change in

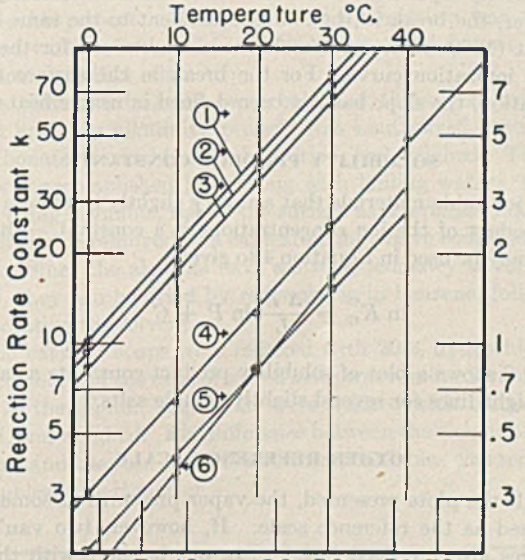

Figure 6. Log Plot of Reaction Rate Constant for Alkaline Hydrolysis of Esters *vs.* Vapor Pressure of Water at Same Temperature

1. Propyl acetate
2. Butyl acetate
3. Isobutyl acetate
4. Isobutyl acetate
5. *sec*-Butyl acetate
6. *tert*-Butyl acetate

Arrows indicate whether the left- or right-hand scale is to be used for *k*.

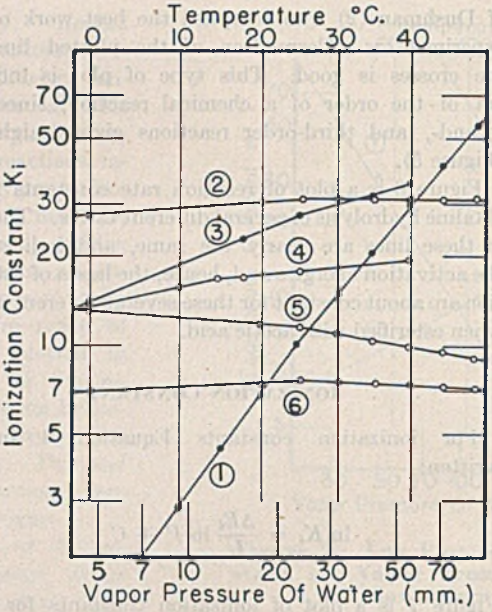

Figure 7. Log Plot of Ionization Constant for Weak Electrolytes *vs.* Vapor Pressure of Water at Same Temperature

Line No.	Weak Electrolyte	K_i, Multiply Vertical Scale by
1	Water	10^{-1}
2	*m*-Nitrobenzoic acid	10^{-5}
3	Methyl cyanonitrosoacetate	10^{-6}
4	Ammonium hydroxide	10^{-6}
5	Toluic acid	10^{-5}
6	*m*-Hydroxybenzoic acid	10^{-5}

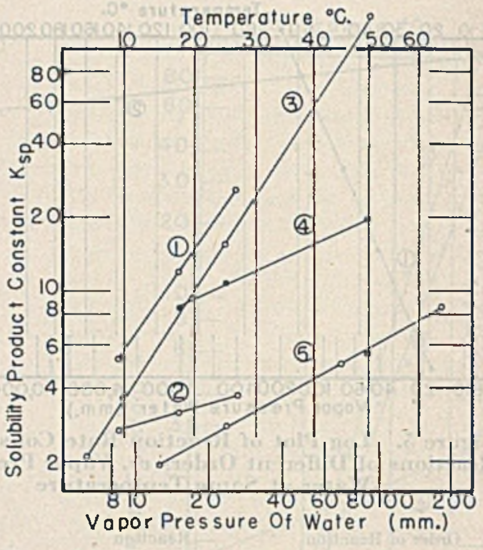

Figure 8. Log Plot of Solubility Product Constant *vs.* Vapor Pressure of Water at Same Temperature

Line No.	Salt	K_{sp}, Multiply Vertical Scale by
1	Lead iodate	10^{-14}
2	Lead fluoride	10^{-8}
3	Silver chloride	10^{-11}
4	Barium sulfate	10^{-11}
5	Calcium oxylate	10^{-9}

state of the water at the point where the curves break. The conversion from one polymeric state to another which occurs for pure water not far from this temperature (*1*) is the most likely explanation for the breaks.

A similar break in the straight lines was obtained in correlations for viscosity (*8*) and surface tension (*11*). For the viscosity curve of water, the break in the line is equivalent to the same change in heat (1090 calories per mole) as was obtained for the break in the ionization curve. For the break in the surface tension correlation, the slope has not been defined in usable heat values.

SOLUBILITY PRODUCT CONSTANT

For ionizable materials that are very slightly soluble in water, the product of the ion concentrations is a constant. This constant may be used in Equation 4 to give:

$$\ln K_{sp} = \frac{\Delta E_i}{L} \ln P + C \qquad (11)$$

Figure 8 shows a plot of solubility product constants as a group of straight lines for several slightly soluble salts.

OTHER REFERENCE SCALE

In all the plots presented, the vapor pressures of some liquid was used as the reference scale. If, however, two van't Hoff isochores are combined rather than one isochore with the Clapeyron equation, the reference scale may be that of the equilibrium constant of the reference substance; the slope of the line will be the ratio of heats of reaction:

$$\ln K_c = \frac{\Delta E}{\Delta E'} \ln K_c' + C \qquad (12)$$

Any of the four types of equilibrium constants may be used as the reference scale, but in the usual case the method using vapor pressures will be found to be the simpler.

NOMENCLATURE

C = constant of integration
$\bar{E}$ = energy of activation
ΔE = increase in total internal energy
ΔE_i = heat of ionization
ΔH = change in heat content for reaction
k_1 = specific rate constant of forward reaction
k_2 = specific rate constant of reverse reaction
K_c = equilibrium constant expressed in concentrations
K_i = ionization constant
K_p = equilibrium constant expressed in partial pressures
K_{sp} = solubility product constant
L = latent heat of reference substance
Δn = change in number of moles during a reaction
P = vapor pressure of reference substance
R = gas constant
T = temperature

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COTTON WAX . . .

Properties and Constituents

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COTTON fibers are coated with a thin layer of waxy organic material which is present to the extent of only a fraction of 1% of the weight of the cotton. This substance, called "cotton wax", has a consistency similar to that of beeswax, has a characteristic bad odor, and is dark greenish-brown in color.

Numerous research workers (*1*, *2*, *4–9*, *14*, *19*) have investigated the constituents of the wax and found it to consist mainly of gossypol and montanyl alcohols, small amounts of other alcohols, glycols, glycerol, sitosterol, α- and β-amyrin, lupeol, hydrocarbons, palmitic, stearic, and carnaubic acids, small amounts of gossypic, montanic, and oleic acids, and unidentified resinous substances. Palmitic, stearic, oleic, and melissic acids occur as esters only; palmitic, stearic, and oleic acids are also present as glycerides. Carnaubic and montanic acids, in the light of more recent terminology, are actually mixtures of several acids.

Previous investigators were handicapped by the small amount of wax present on the bulky cotton and, consequently, had difficulty in working with large quantities of cotton to obtain workable quantities of cotton wax. Samples of 330 and 750 grams, respectively, have been investigated (*6*, *9*). Because of the nature of the wax and the difficulties encountered, previous analytical work has included only qualitative reports on the individual constituents present and incomplete data on the characterizing constants.

The wax for this investigation was obtained as a by-product of a pilot plant operation in which 100-pound batches of Texas cotton fiber were extracted with hot benzene. The wax is present to the extent of 0.2 to 0.7% of the weight of the fiber, so that approximately 25 pounds of wax were recovered from the 10 bales of cotton extracted in the pilot plant.

The benzene solution of the crude wax was filtered through a wire mesh screen to remove stray fibers, leaf particles, stems, hull fragments, and sand, and was blended with the wax solutions from other extractions. The solvent was then evaporated to obtain a homogeneous representative sample of wax which was used for all investigations. The wax had a dark greenish-brown color and a characteristic disagreeable odor.

To ensure complete removal of the wax from the fiber, the use of numerous solvents was studied, such as diethyl ether, benzene, toluene, xylene, petroleum hydrocarbon solvents (Skelly solvents), chloroform, and carbon tetrachloride. All gave complete removal of the wax from the fiber.

PHYSICAL CONSTANTS

The physical constants determined on cotton wax include those customarily reported for waxes and are listed in Table I. The melting point of the wax was determined according to the following procedure: The lower 12 mm. of a 5-cm. glass tube, 7 mm. in diameter, was filled with molten wax which was then allowed to cool and solidify. The tube was attached with a rubber band to a calibrated thermometer and placed in an agitated water bath so that the lower part of tube extended to a depth of 4 cm. below the surface of the liquid. The water was heated and, after thermometer corrections had been applied, the temperature at which the wax plug moved up in the tube was recorded as the melting point.

Specific gravity was determined by the conventional manner of weighing the wax sample in air and in distilled water at 15° C.

The saponification value was found by the standard procedure on 3-gram samples dissolved in 10 ml. of toluene and refluxed for 8 hours with 0.5 N potassium hydroxide. A blank was run, and corrections were made accordingly in calculating the saponification value. If n-propanol is used as solvent for potassium hydroxide instead of ethanol, the saponification time can be reduced from 8 to 2 hours with no loss in accuracy.

The acid value was determined on triplicate samples of cotton wax, which were dissolved in 50-ml. portions of hot isoamyl alcohol and titrated with 0.5 N alcoholic potassium hydroxide using phenolphthalein as the indicator. A blank was also necessary.

The ester value is the numerical difference between the saponification and acid values. It indicates the degree to which the fatty acids present are combined as esters.

The iodine number is a measure of unsaturation and is expressed in terms of grams of I_2° per gram of wax. Hubl's method (*17*) was followed.

The acetyl value is a measure of the alcoholic hydroxylic groupings of one gram of wax. It is expressed as the number of milligrams of potassium hydroxide required to neutralize the acetic acid liberated from the hydrolysis of one gram of acetylated fat or wax. The procedure given Hilditch (*12*) was followed.

The percentage of unsaponifiable matter and mixed fatty acids was determined in the same analysis. Twenty grams of wax were dissolved in 100 ml. of benzene and saponified with 750 ml. of 0.5 N potassium hydroxide. After refluxing 12 hours, 350 ml. of alcoholic calcium chloride (40 grams per 500 ml. of ethanol) were added, and refluxing was continued for another 2 hours. Completeness of the reaction was checked by adding a drop of sodium oxalate solution to test for excess calcium chloride which should be present. The insoluble soap mixture was then extracted with hot ethanol in a Soxhlet extractor followed by hot acetone and ethyl ether.

The solvent extractables were collected, the solvent was evaporated and any alkalinity present was neutralized with sodium bicarbonate, washed thoroughly, dried, and weighed. The washing was accomplished by heating with boiling water; the alcohols, being insoluble, rise to the surface as a separate liquid layer which can be removed as a cake after they have cooled and hardened. Since the alcohols have a strong tendency to form emulsions, they can be dried by redissolving in benzene, followed by evaporating the solvent.

The calcium soaps were refluxed with 20% hydrochloric acid and cooled, and the cake of mixed acids was removed from the surface of the liquid. The acids were washed with boiling water, dried, and weighed. The difference between the weight of original sample and the sum of acids and unsaponifiables was reported as insolubles or inert matter.

TABLE I. PROPERTIES OF COTTON WAX

Melting point, ° C.	68–71
Specific gravity, 15/15° C.	0.959
Saponification value, mg. KOH/gram	70.6
Acid value, mg. KOH/gram	32.0
Ester value, mg. KOH/gram	38.6
Acetyl value, mg. KOH/gram	73.1
Iodine number, grams I_2°/100 grams	24.5
Fatty acids, %	25
Unsaponifiables, %	69
Hehner value, %	100
Reichert-Meissl value, ml.	0

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The Hehner value was obtained by the commercial method described by Hilditch (*11*).

The Reichert-Meissl value was determined by the usual distillation procedure (*16*).

CHEMICAL ANALYSIS

The wax was saponified with alcoholic potassium hydroxide. The acids were precipitated as calcium salts, extracted, etc., by a method similar to that described for determining fatty acids and unsaponifiables. The difference was that 200-gram samples in triplicate were employed, and the amounts of all reagents were increased proportionally.

The fatty acids, which were recovered from their calcium salts by treatment with 20% hydrochloric acid, were collected on the surface as a liquid, cooled, removed, washed, dried, and weighed. The cake was black in color and very hard and brittle in texture. The melting point, acid value, saponification value, and mean molecular weight (calculated by dividing 56.1 by the grams of potassium hydroxide required to neutralize 1 gram of fatty acid mixture) of the fraction were determined to gather some knowledge as to the properties and constitution of the fatty acids and to the completeness of separation.

The acids were separated into saturated and unsaturated fractions by taking advantage of the difference in solubility of metal-salts of fatty acids in organic solvents (*10*). The mixed fatty acids were converted to the lead salts according to the method given by Hilditch (*13, 18*) and extracted with slightly warm diethyl ether. The ether solution was evaporated, and the acid was recovered by regeneration with 20% hydrochloric acid, dried, and weighed. The insoluble lead salts were treated similarly.

The unsaponifiable extract, consisting mainly of alcohols, sterols, and hydrocarbons, was separated into two portions. One contained the hydrocarbons, which were isolated and weighed according to Leys' method (*15*) employing isoamyl alcohol and fuming hydrochloric acid. The other, the alcohol and sterol portion, was further separated by the method described by Cochenhausen (*3*) to give a quantitative measure of the amounts of sterols and alcohols present. This procedure employs concentrated sulfuric acid and extraction with petroleum ether and absolute ethyl alcohol to separate the sterols and alcohols via alkyl sulfate formation of the alcohol portion. The unaccounted for portion of the wax is recorded as insolubles or inert matter; it includes any water-soluble glycols and glycerol obtained in the saponification and also the inherent experimental errors accompanying an analysis of this type.

Table II gives the proximate analysis of the wax, and Table III shows the properties of the individual components separated.

DECOLORIZATION

The dark color of cotton wax, which makes it unsuitable for some industrial purposes, can be reduced and in some instances completely removed. The resulting decolorized wax ranged in color from a faint yellow through lemon yellow to a light orange, depending on the method employed.

Among the substances which removed the objectionable dark color were activated carbon, fuller's earth, and combinations of the two. The wax can be treated either in the molten state at elevated temperature or in solvent solution; the latter gives better results. The degree of decolorization was proportional, but not linearly, to the amount of agent used. Several successive small dosage treatments were much more efficient than a single large dose and gave a final product of better color. The length of contact time for the agent and the wax was not critical. Absorption was almost instantaneous so that the detention period required was only a few minutes. The degree of decolorization finally obtained at equilibrium conditions increased with temperature.

TABLE II. COMPOSITION OF COTTON WAX

Fatty acids		25%
Saturated	24%	
Unsaturated	1	
Unsaponifiable matter		69
Alcohols	52	
Sterols	10	
Hydrocarbons	7	
Inert matter		6
		100%

TABLE III. PROPERTIES OF ACIDS, ALCOHOLS, AND HYDROCARBONS IN COTTON WAX

	Melting Point, ° C.	Boiling Point, ° C.	Mg. KOH/Gram		Mean Mol. Weight
			Acid value	Saponification value	
Fatty acids	84	.....	132.0	132.0	425
Alcohols	61	.....	0	0	...
Hydrocarbons	68	264–340	0	0	...

In removing the color, activated carbon and fuller's earth removed some of the fatty acids, as shown by lower acid and saponification values for the decolorized wax (14.9 and 40.1 mg. potassium hydroxide per gram of wax, respectively); but no change of melting point (70° C.) occurred. The highest efficiency in color removal obtained in any case was 97.5%.

Numerous chemicals have been used to bleach waxes; among them are chlorine, hydrogen peroxide, sodium metal, calcium hypochlorite, nitric acid, sodium chromate, potassium permanganate, benzoyl peroxide, sodium peroxide, and magnanese dioxide. All of these were tried in concentrations varying from 1 to 20%, with the wax at temperatures varying from room to 100° C.; however, only calcium hypochlorite, chlorine, and hydrogen peroxide provided any bleaching action. Basic bleaching agents such as sodium peroxide could not be used because they saponified the wax. Powerful oxidizing agents like potassium dichromate in dilute acid or acidified potassium permangante, when used in concentrations in excess of 5%, carbonized the wax. Combinations of bleaching and treatment with activated carbon also gave decolorization. None of these treatments alter the melting point of the wax.

SUMMARY

Cotton wax is medium high melting, compared to other vegetable waxes. It differs from most commercial waxes in that it is not predominantly an ester, but contains smaller amounts of fatty acids and larger amounts of free alchols as shown by high acetyl value and percentage unsaponifiables. The wax is not hard and brittle at room temperature but has a consistency comparable to that of beeswax; its dark color and obnoxious odor can be removed by decolorizing and bleaching agents. The mean molecular weight of the fatty acids portion indicates that the preponderance of acids present may be cerotic and melissic.

The wax blends well with other natural waxes and resins and has been formulated into pastes and emulsion polishes, lubricants, leather dressings, waterproof preparations, crayons, paints, paper auxiliaries, adhesives, etc., individually and as blends with other waxes.

Whenever requirements demand a wax of medium-high melting point, qualifications generally filled by a vegetable wax, cotton wax should be satisfactory.

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Solubility in Common Solvents

THE solubility of cotton wax was studied by Fargher with reference to complete removal of the wax from the fiber (*1*), but because of the limited quantities of wax available, no attempt was made to obtain solubility curves. Pickett (*2*) suggested that solubility-temperature curves be determined by dissolving weighed amounts of wax in 100 grams of solvent, heating to dissolve wax, cooling, and recording the cloud point as the saturation temperature. This method allows the least soluble constituents to dictate the cloud point, and it is impossible to observe accurately the cloud points of dark colored solutions like those of cotton wax.

A wide range of representative solvents were chosen, including those commonly employed industrially as wax solvents: benzene, toluene, xylene, turpentine, chloroform, carbon tetrachloride, carbon disulfide, Skelly solvent C, methyl, ethyl, *n*-propyl, *n*-butyl alcohol, *tert*-butyl, and isoamyl alcohols, acetone, diethyl ether, ethyl acetate, and glacial acetic acid. All were reagent grade.

Cotton wax was placed in 250-ml. flasks with 200 grams of solvent. The flask was put into a thermostatically controlled water bath at the desired temperature, and agitated or shaken until equilibrium was reached between the solvent and the wax (generally 2-4 hours). This time was increased to 8 hours in order to ensure complete penetration of the solvent into the granulated wax. Care was taken that a large excess of wax is present at all times. Then samples were siphoned off into closed, tared weighing bottles and weighed, the solvent was evaporated at 105° C., and the remaining wax was weighed.

The temperature range of the bath, which had both heating elements and cooling coils, was controllable from 0° to 95° C. However, since most of the boiling points of the solvents were considerably lower than 95° C., the upper limit of the bath was no handicap. No solubility values were determined above 70° C., the melting point of cotton wax. A minimum of ten temperatures at which the solubility of the wax was experimentally measured were chosen for each solvent between 0° and 70° C.; thus, there were always ten points from which to plot the curve. The solubility is expressed as grams of wax per 100 grams of solvent.

The solvents can be broken down into two general groups. In one (Figure 1) the cotton wax was readily soluble (more than

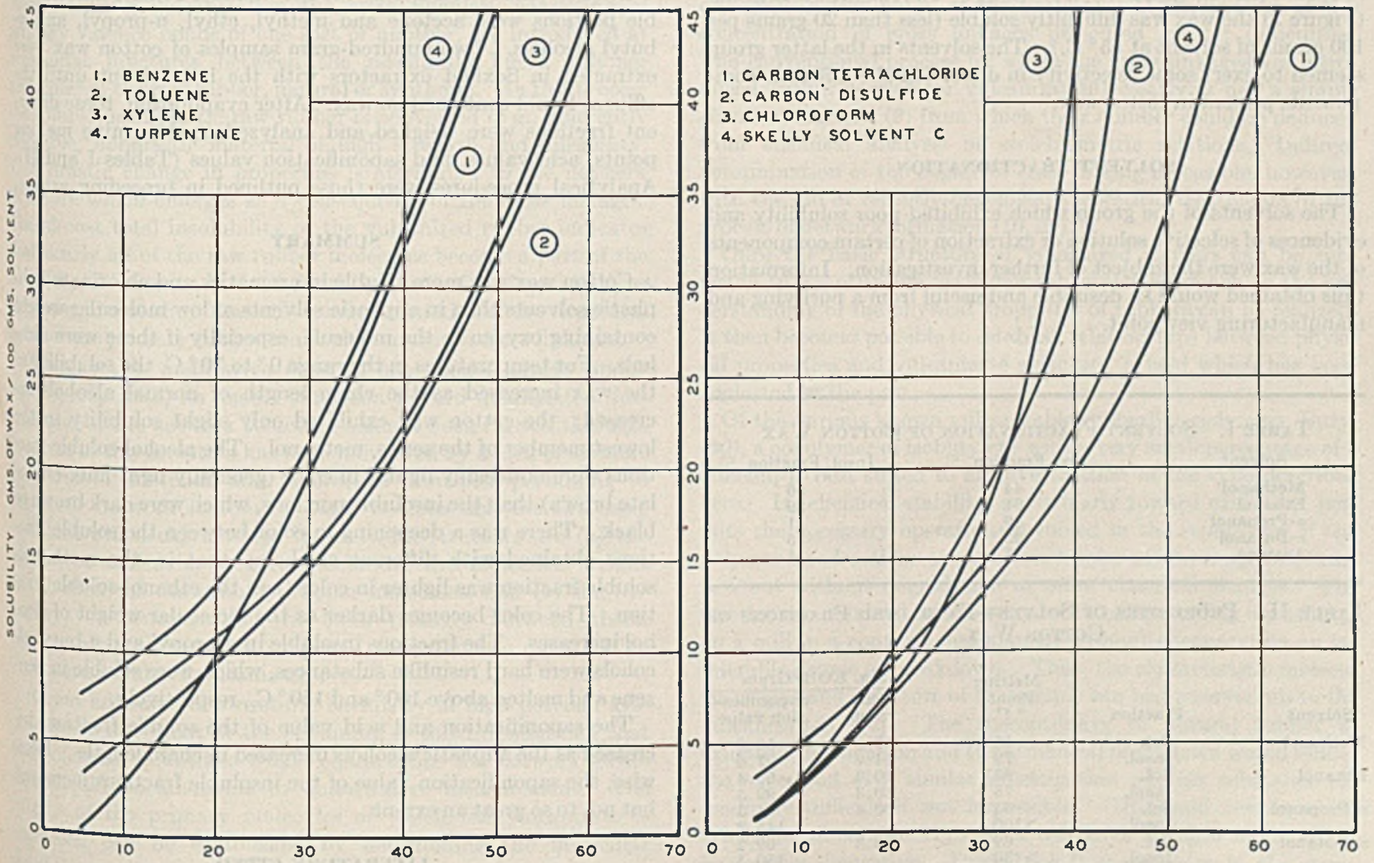

Figure 1. Curves for Solvents in Which Cotton Wax Is Readily Soluble

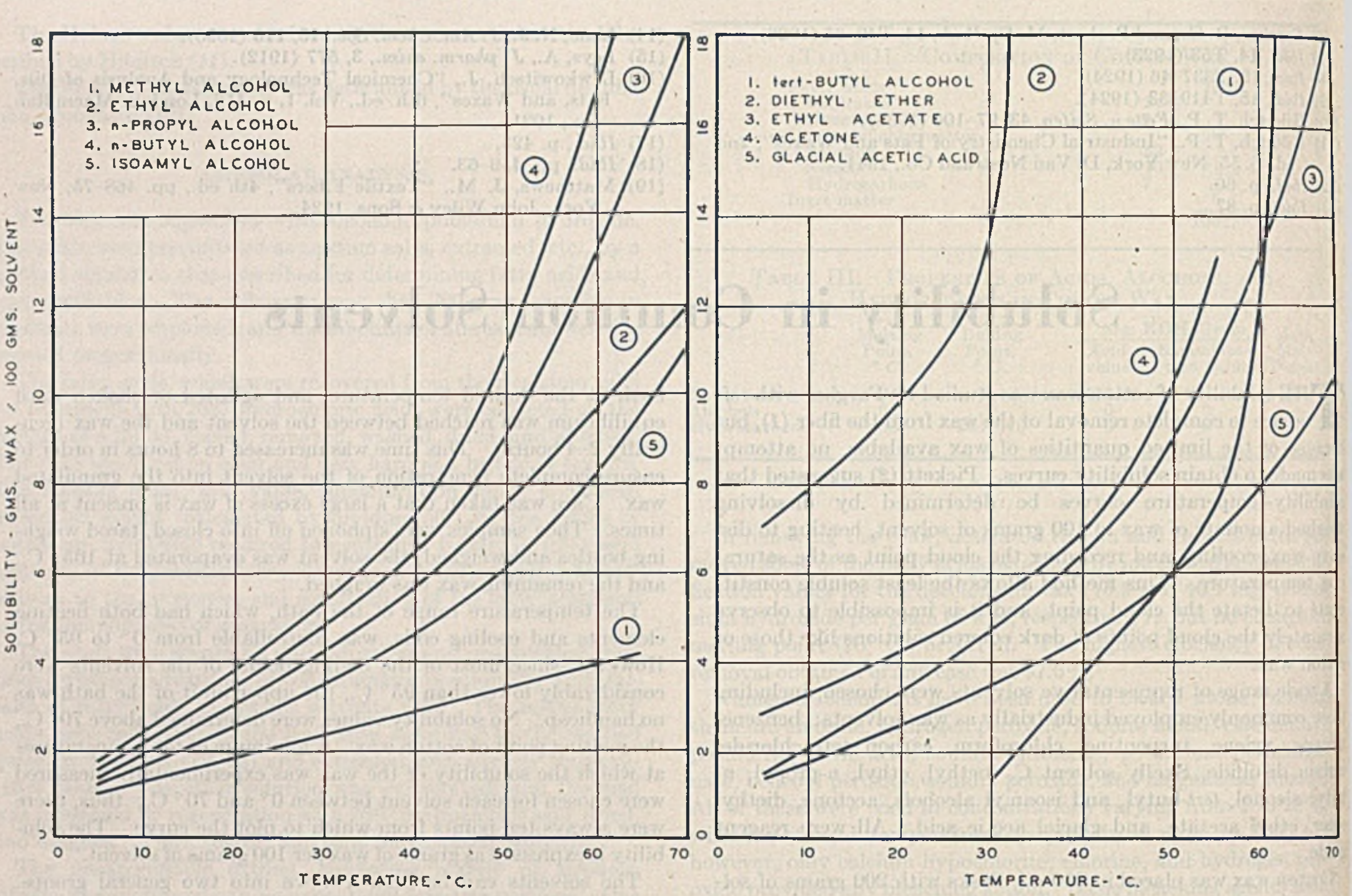

Figure 2. Curves for Solvents in Which Cotton Wax Is Difficultly Soluble

20 grams per 100 grams of solvent at 55° C.); in the other group (Figure 2) the wax was difficultly soluble (less than 20 grams per 100 grams of solvent at 55° C.). The solvents in the latter group seemed to exert some selectivity in dissolving the different components present in cotton wax.

SOLVENT FRACTIONATION

The solvents of the group which exhibited poor solubility and evidences of selective solution or extraction of certain components of the wax were the subject of further investigation. Information thus obtained would be desirable and useful from a purifying and manufacturing viewpoint.

TABLE I. SOLVENT FRACTIONATION OF COTTON WAX

Solvent	Sol. Fraction, %	Insol. Fraction, %
Methanol	44	56
Ethanol	61	39
n-Propanol	89	11
n-Butanol	95	5
Acetone	55	45

TABLE II. PROPERTIES OF SOLVENT-EXTRACTED FRACTIONS OF COTTON WAX

Solvent	Fraction	Melting Point, ° C.	Mg. KOH/Gram Acid value	Mg. KOH/Gram Saponification value
Methanol	Sol.	65	16.5	50.0
	Insol.	79	44.9	97.0
Ethanol	Sol.	63	20.3	60.4
	Insol.	75	30.3	99.3
n-Propanol	Sol.	63	20.4	64.3
	Insol.	>100	..	145.3
n-Butanol	Sol.	69	26.3	69.2
	Insol.	>130	..	150.5
Acetone	Sol.	62	21.7	62.1
	Insol.	60	53.0	63.3

The solvents selected to divide the wax into soluble and insoluble portions were acetone and methyl, ethyl, *n*-propyl, and *n*-butyl alcohols. Two-hundred-gram samples of cotton wax were extracted in Soxhlet extractors with the hot solvent until the effluent liquid contained no wax. After evaporation, these different fractions were weighed and analyzed to determine melting points, acid values, and saponification values (Tables I and II). Analytical procedures were those outlined in preceding article.

SUMMARY

Cotton wax was more soluble in aromatics and chlorinated aliphatic solvents than in aliphatic solvents of low molecular weight containing oxygen in the molecule, especially if these were alcohols. For temperatures in the range 0° to 70° C. the solubility of the wax increased as the chain length of normal alcohols increased; the cotton wax exhibited only slight solubility in the lowest member of the series, methanol. The alcohol-soluble fractions were noticeably lighter in color (generally light milk-chocolate brown) than the insoluble portions, which were dark brown or black. There was a deepening in color between the soluble fractions obtained with different alcohols; that is, the methanol-soluble fraction was lighter in color than the ethanol-soluble fraction. The color becomes darker as the molecular weight of alcohol increases. The fractions insoluble in *n*-propyl and *n*-butyl alcohols were hard resinlike substances, which were soluble in benzene and melted above 100° and 150° C., respectively.

The saponification and acid value of the soluble fractions increased as the aliphatic alcohols increased in chain lengths. Likewise, the saponification value of the insoluble fractions increased but not to so great an extent.

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Effects of Molecular Structure on Physical Properties of Butyl Rubber

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The investigation here described was undertaken in an attempt to establish the fundamental connections which must exist between physical properties of a typical vulcanized rubberlike polymer and its chemical structure. The structural variables to be considered are the molecular weight of the "primary molecules" entering the vulcanizate, their molecular weight distribution, and the concentration (or frequency) of cross linkages introduced during vulcanization. The molecular weights of the Butyl rubbers were determined by previously established procedures; effects of molecular weight heterogeneity were suppressed by careful fractionation from very dilute solution. An indirect method, based on the theory of gelation and on the observation of critical molecular weight for incipient gelation (partial insolubility) in "vulcanizates" formed when the cross-linking capacity is fixed, has been employed to determine the frequency of occurrence of cross-linked units—a quantity not hitherto evaluated in a vulcanized rubber. In representative pure-gum vulcanizates of Butyl the molecular weight per cross-linked unit ranges from about 35,000 to 20,000, depending (inversely) on the diolefin content of the raw rubber. Micro compounding and testing procedures have been devised for evaluating the necessarily small samples obtained in fractionation. Complete evaluation of tensile strength, stress-strain characteristics, swelling in solvents, and creep rate can be obtained with as little as 3 grams of rubber. Results are no less reproducible than those obtained with conventional procedures requiring 50 grams or more. A number of relationships between vulcanizate structure and physical properties have been established. The feasibility of a rational approach to the interpretation of properties of rubber vulcanizates in terms of molecular structure has been demonstrated.

IT IS now generally agreed that vulcanized rubber possesses a network structure made up of cross-linked long-chain molecules. During vulcanization the cross linkages, consisting of primary valence bonds of one sort or another, are introduced at occasional junctures between the essentially linear polymer molecules of the raw rubber, natural or synthetic. In this process the soluble, semiplastic raw rubber is converted to an inherently insoluble, nonplastic material of high strength and durability. This drastic change in properties is attributed to the network structure which emerges as a consequence of the cross linkages. The almost total insolubility of the vulcanized rubber indicates that nearly all of the raw rubber molecules become a part of the network, which extends throughout the piece of rubber. Various lines of evidence show that only a minute fraction of the structural units of the primary rubber molecules enter into cross linkages.

Whereas this qualitative concept has gained almost undisputed acceptance, its logical extension toward quantitative formulation of the network structure has not been carried through. Progress in this direction has been hampered by a lack of suitable experimental methods and theoretical principles pertaining to polymeric network structures. It is obvious that the two basic variables which characterize the network structure are (*a*) the lengths or molecular weights (including the molecular weight distribution) of the primary rubber molecules, and (*b*) the frequency, or concentration, of cross linkages between them. Neither of these has been subjected to systematic quantitative evaluation in rubber valcanizates.

Recent advances in structural chemistry of high polymer systems made it evident at the beginning of this investigation that both of these quantities which characterize the network structure should be amenable to quantitative measurement. The lengths of the primary molecules of which the vulcanizate is composed can be established by determining the molecular weight immediately preceding vulcanization. Methods for the measurement of molecular weights of high polymers have been developed within the past few years which obviate any serious difficulty in this phase of the problem. Determination of the concentration of cross linkages presented greater difficulties. The conventional process by which the cross linkages are introduced (sulfur-accelerator vulcanization) clearly is not a simple chemical reaction (*2*) from which their number could be deduced from chemical analysis or stoichiometric relations. Indirect determination of the degree of cross linking is feasible, however, with the aid of recently developed theoretical treatments of the process of network formation (*10, 29*).

Once the basic structure of vulcanized rubbers can be subjected to quantitative measurement, a new approach to the understanding of the physical properties of rubbers can be realized. It then becomes possible to establish relationships between physical properties and vulcanizate structure, a field which has been neglected in the past.

Of the various known vulcanizable rubberlike polymers, Butyl (*30*), a copolymer of isobutylene with a very small percentage of a diolefin, is best suited to an investigation of the type described here. Its chemical stability, particularly toward oxidation, permits the necessary operations involved in the separation of the polymer into fractions of narrow molecular weight range to be carried out without degradation or other chemical changes. The fractions so obtained can be mixed with compounding ingredients on a mill in a conventional manner without encountering an intolerable degree of breakdown. Thus, the characteristic molecular weight and structure of the sample can be preserved up to the vulcanization step. The susceptibility of natural rubber to oxidative degradation and to mechanical breakdown would render the execution of a similar investigation on this substance exceedingly difficult if not impossible. GR-S and certain other synthetic rubbers undergo other oxidative changes which might be equally disruptive. Deviations from linearity in the structures of their primary molecules adds a further complication not encountered with Butyl rubber.

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A further merit of Butyl for the purposes of the present investigation is the facility with which the degree of cross linking can be controlled by manipulating the amount of diolefin introduced into the polymer during synthesis. Finally, it possesses many of the physical properties of natural rubber, concerning which there is a greater background of fundamental information than for any other rubberlike material. Such properties include (*30*) high tensile strength, both with or without carbon black, the ability to become highly crystalline when stretched, and a simple linear chain structure.

MICRO COMPOUNDING AND TESTING

In order to eliminate the effects of molecular weight heterogeneity, or at least to suppress them sufficiently, it was necessary to employ carefully fractionated samples of Butyl rubber in most of the work. Effective fractionation requires the use of very dilute solutions (*6, 11*); hence, the size of the individual fractions obtained is limited by the volume of solution which can be handled. Conventional compounding and testing methods require a minimum of 50 grams of rubber, a quantity considerably beyond the range of laboratory fractionation. It was necessary, therefore, to devise compounding and testing procedures applicable to fractions of the maximum size which it was practical to prepare by laboratory fractionation—i.e., about 10 grams.

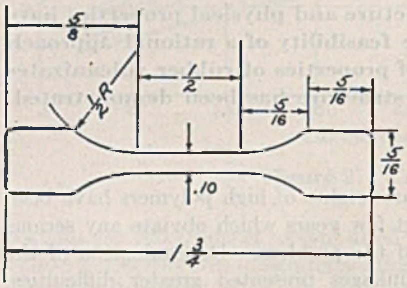


Figure 1. Dimensions of Tensile Dumbbell (in Inches)

These micro compounding and testing procedures are essentially adaptations of the conventional methods employed with larger samples. [In this connection, the small scale evaluation procedures described by Garvey (*16*) are intermediate between our micro methods and those usually employed.] Within the range of the experience gained in the present work, no significant disadvantages in the micro methods have become apparent; furthermore, less space is required and the equipment is less expensive than that for the standard procedures. Tests on equivalent vulcanizates demonstrate that the micro procedures for compounding, curing, and testing of tensile strength and modulus are at least as accurate and reproducible as the conventional methods; the results obtained by the two procedures are approximately the same.

Compounding. All ingredients were weighed on an analytical balance and mixed on a 3 × 8 inch laboratory mill equipped with a movable center guide (*16*). This guide was placed at a distance from the end guide, depending on the size of the sample, such as would assure a small bank at a mill roll setting of 0.010 to 0.015 inch. By placing the center guide only 0.5 inch from the end, less than 2 grams of rubber could be compounded. Compounding ingredients were added immediately to the rubber after banding on the mill. The batch was cut six times from each side during a 10-minute milling period; then it was sheeted off and reweighed.

The mill rolls were maintained at about 130° F. during compounding of the high-molecular-weight fractions (above about 200,000). At low temperatures breakdown becomes excessive. Fractions of lower molecular weight which were too plastic to handle on warm rolls, could be milled at 70° F. without breakdown. Below a molecular weight of about 70,000 the material was too plastic to be handled even on cold mill rolls. Such fractions were mixed by hand in a polished iron mortar, which was heated to about 170° F.

The marked effect of temperature on breakdown of Butyl appears to be due to crystallization under the intense shearing conditions encountered on the mill. Crystallization renders the rubber much less plastic and thereby increases greatly the shearing stresses, which become sufficient to cause rupture of the chains. Elevation of the temperature eliminates the tendency of the rubber to crystallize under deformation, and breakdown is diminished.

Vulcanization. Micro tensile sheets were cured in molds, 2.5 inches long and 0.025 inch thick, and either 1 or 1.75 inches wide. The former required a minimum of about 1.6 cc., and the latter about 2.5 cc. of stock, allowing for overflow. Dumbbells having the dimensions shown in Figure 1 were cut from the sheets. Three could be cut from one of the former, and six from one of the latter. Rings suitable for stress-strain measurements were molded 1.025 inches in outside diameter, 0.050 inch thick, and either 0.10 or 0.25 inch wide. Thus, from as little as 3.5 cc. of rubber, two cures could be obtained, each to furnish three test dumbbells. An additional gram was required for two rings for stress-strain measurements.

Recipes. The following recipe was employed in all pure gum compounds:

Butyl	100 parts
Sulfur	1.5
Zinc oxide	1.0
Tetramethylthiuram disulfide	1.0

The recipe for the compounds containing 50 parts of carbon black was as follows:

Butyl	100	Zinc oxide	5.0
Channel black	50	Tetramethylthiuram disulfide	1.0
Sulfur	2.0		
Stearic acid	3.0		

These recipes were chosen somewhat arbitrarily. They are not necessarily the best from the standpoint of optimum tensile strength or maximum modulus.

Polymers having different degrees of unsaturation were cured with the same proportions of ingredients. A rather large amount of evidence (to be shown later) indicates that, for a given recipe, the percentage utilization of unsaturation in the formation of cross linkages is almost independent of the degree of unsaturation over a wide range. Doubling the proportions of sulfur, zinc oxide, and accelerator in the pure gum recipe affects the moduli and swelling ratios of rubbers of different unsaturations (cured 60 minutes) by factors which are about the same:

Approx. Mole % Diolefin	Recipe	Modulus at 300%, Lb./Sq. In.	Swelling Ratio
0.5	Standard	78	8.05
	Double	99	7.13
	Ratio	1.27	1.13
1.0	Standard	116	6.45
	Double	149	5.50
	Ratio	1.28	1.17

Hence, the influence of diolefin content per se is obtained with the least ambiguity by fixing the curing recipe.

This recipe was selected rather than one containing a greater proportion of curing ingredients because of the lower sensitivity to time of cure. An effort was made to cure (at 307° F.) for times which yield approximately the maximum degree of cross linking as judged by modulus or swelling. For the low-unsaturation Butyl rubbers this stage is reached at about 60 minutes; from 30 to 40 minutes are required for the high-unsaturation Butyls. Excessive times of cure lead to gradual "reversion" which we presume to be due to a competing degradative process.

Physical Testing. Tensile strengths were measured on a Scott X-5 pendulum-type tester equipped with hinged roll clamps; the rolls were 0.25 inch in diameter. Through the use of different weights on the pendulum, any one of four scale ranges, from 0 to 2, 5, 10, or 20 pounds, could be employed. The rate of extension was about 6 inches per minute. This is less than the A.S.T.M. specification of 20 inches per minute, but the greater part of this difference is justified by the difference in length of our dumbbell as compared with that recommended by the A.S.T.M. Elongations were estimated from the distance between marks, initially 0.50 inch apart, as measured with a ruler.

Stress-strain curves were determined on the same instrument, equipped with ring test spools 0.25 inch in diameter and a scale for indicating the distance of separation of the spools. Both spools were mounted in roller bearings, the lower one being rotated by a chain and sprocket in order to ensure even distribution of strain over the rubber ring. The rate of separation corresponded to about 300% elongation per minute. A spark recording of the tension scale reading was taken at regular elongation intervals.

Swelling Measurements. A modification of the method employed by Whitby, Evans, and Pasternack (*35*) was used. Fragments from the tensile sheets or rings amounting to about 0.2 gram, weighed to ±0.2 mg., were placed with 50 cc. of C.P. cyclohexane containing 0.01% phenyl-β-naphthylamine in a glass-stoppered weighing bottle. After standing 48 hours in the dark at room temperature, the swollen sample was placed in a weighing bottle containing filter paper to blot off excess solvent. The bottle and contents were weighed, the sample was removed, the stopper was replaced, and the bottle and moist filter paper were reweighed. The difference represents the weight of swollen polymer. The percentage of soluble components was determined by evaporating the cyclohexane solution to dryness and weighing the residue. The weight of phenyl-β-naphthylamine was deducted. The weight of rubber in the swollen vulcanizate was taken as the difference between the original sample weight and the weight of the extractable material.

The volumes of rubber and solvent in the swollen sample were calculated from their respective weights and their densities at 25° C. (0.93 for the pure-gum Butyl compounds). The swelling ratio is expressed as the ratio of the total volume of swollen sample to the volume of dry (insoluble) rubber it contains.

Creep Measurements. Square-end dumbbells, 0.100 inch wide over a 1.5-inch length, were cut with a die from the tensile sheets (T-50 test specimen). The sample was suspended at one end, and a weight was attached to the other. Reference points for measuring relative lengths were provided by piercing the sample with short wires 0.015 cm. in diameter at points about 3.5 cm. apart within the uniform section of the test piece. The distance between the upper edges of these wires was determined with a measuring microscope equipped with a scale reading to ±0.001 cm. All tests were run in a constant-temperature room regulated at 25.0° ± 0.3° C.

Fractionation. Details concerning the fractional precipitation procedure for the isolation of samples of narrowed molecular weight range were described previously (*11*). One hundred grams (in a few cases, 50 grams) of the crude Butyl rubber were dissolved in 10 liters of thiophene-free benzene. Sufficient acetone to precipitate the first fraction at 25.0° C. was added, and the solution was warmed sufficiently to reach homogeneity. Precipitation was allowed to occur while cooling slowly to 25.0° C. with mild agitation. After the precipitated phase had settled, the liquor was poured off and set aside. The precipitate was redissolved in 6 liters of benzene and reprecipitated as before, using the same proportion of acetone to benzene. After separating the liquor, this precipitate was coagulated and dried in vacuum at 70° C. The liquors were combined, evaporated to remove acetone, made up to 10 liters with benzene, and a slightly larger quantity of acetone was added to obtain the second fraction, which was reprecipitated in the manner mentioned above. After most of the polymer had been separated in the form of fractions, the volumes of benzene used in each step were reduced. Proceeding in this way, a series of some ten fractions of progressively smaller molecular weights was obtained from each polymer. To assure good fractional separations (*6*), polymer concentrations not exceeding 1.0% were used in the first precipitation of each fraction, and around 0.3% in the reprecipitation of high-molecular-weight fractions.

CHARACTERIZATION OF POLYMERS AND FRACTIONS

Raw Polymers. The Butyl polymers were prepared by copolymerization of isobutylene with small proportions of isoprene at low temperature (*30*). Their intrinsic viscosities (Table I) were computed from the viscosities of their dilute solutions in diisobutylene at 20° C. "Intrinsic viscosity" as here employed is defined by the equation (*20*):

$$[\eta] = (\ln \eta_r)/c$$

where η_r is the relative viscosity of a solution of concentration c (in grams per 100 cc.) such that η_r is less than about 1.4, but greater than about 1.15 in order to assure sufficient precision in the value of intrinsic viscosity. The molecular weights were calculated from the intrinsic viscosities by means of Equation 1.

The mole percentages of diolefin units, or percentage unsaturation values (last column of Table I) were obtained by the ozonolysis method of Rehner (*25*). These figures are accurate to about 10%.

It was necessary to include two or more polymers of about the same unsaturation value but differing in average molecular weight in order to obtain sufficiently large fractions covering the desired range of molecular weights. Selection of polymers of exactly the same molecular weight was not feasible, owing to the fact that the more accurate ozonolysis method was not established until much of the experimental work had been completed. However, except for minor variations, the polymers which had been selected fell into two classifications. The first includes polymers I, II, and III (Table I) which contained about 0.5 mole % of diolefin units; those of the second group, consisting of polymers IV and V, possessed slightly over 1.0 mole % of diolefin. These will be referred to merely as the low- and high-unsaturation polymers, respectively. These terms are relative; the so-called high-unsaturation polymers contained only a little over 1% of the unsaturation occurring in natural rubber and most of the other synthetics.

TABLE I. CHARACTERISTICS OF CRUDE BUTYL POLYMERS FROM WHICH FRACTIONS WERE SEPARATED

Polymer Designation	Intrinsic Viscosity $[\eta]$	"$\overline{M}_v$" × 10^{-3}	Mole % Diolefin Units Detd. by Ozone Degradation[a]
I	2.20	820	0.43
II	1.32	370	0.54
II-A	1.45	425	0.53
III	0.67	130	0.48
IV	0.73	145	1.05
V	1.18	310	1.2

[a] These figures divided by 100 represent the ratios of diolefin to isobutylene units in the polymer.

Molecular Weights of Fractions. The fractions employed in this investigation are listed in Table II. The Roman numerals included with the identifying designation in the first column refer to the raw polymer (Table I) from which the fraction was prepared. The fractions from a given raw polymer are arranged approximately in the order of decreasing molecular weight. The second column shows the proportions of precipitant (acetone) used in separating the fraction from preceding and succeeding fractions. For example, polymer I-2 was obtained by precipitating with 3.5 cc. of acetone per 100 cc. of benzene, the preceding fraction having been removed by 3.0 cc. of acetone per 100 cc. of benzene.

Owing to faulty compounding and curing procedures in the preliminary stages of the investigation, much fractionated polymer was wasted in the preparation of vulcanizates which had to be discarded. Consequently in most cases two or more batches of the same raw polymer were fractionated, which explains the overlapping and duplicate fractions from the same polymer (Table II). Two fractions obtained between the same precipitant range are not, of course, identical, owing to the slight irreproducibility of fractionation.

A few of the fractions contained a larger percentage (column 3, Table II) of the raw polymer than was intended. The somewhat broader molecular weight distribution in these fractions, most of which were of high molecular weight, is not believed to have introduced noteworthy errors into the results.

The molecular weights of the fractions (column 5) were calculated from their intrinsic viscosities in diisobutylene, measured as described above and in reference (*11*), using the equation,

$$\log M = 5.378 + 1.56 \log[\eta] \qquad (1)$$

This equation, previously established for polyisobutylene (*11*), was found to be equally applicable to Butyl polymers (*12*), as would be expected.

The polymer fractions were by no means strictly homogeneous. They are believed to have been sufficiently so, however, that the various average molecular weights differed only slightly. These differences between the averages should not be totally disregarded, and for this reason a brief discussion is included of the interrelation of different average molecular weights.

The number, weight, and viscosity average molecular weights are defined, respectively, as follows:

$$\overline{M}_n = \sum_i N_i M_i / \sum_i N_i \qquad (2)$$

$$\overline{M}_w = \sum_i N_i M_i^2 / \sum_i N_i M_i \qquad (3)$$

$$\overline{M}_v = [\sum_i N_i M_i^{a+1} / \sum_i N_i M_i]^{1/a} \qquad (4)$$

TABLE II. MOLECULAR WEIGHTS OF FRACTIONS

Polymer Fraction Designation	Precipitant Range	% of Original Polymer in Fraction	Intrinsic Viscosity [η]	$M \times 10^{-3}$	After Compounding (Pure-Gum Recipe)[a] [η]	After Compounding (Pure-Gum Recipe)[a] $M \times 10^{-3}$
I-1	2.5 – 3	6.9	2.80	1200	2.63	1080
I-2	3 – 3.5	7.4	2.30	875	2.05	730
I-3	2.5 – 3.25	36.3	2.18	805	1.98	690
I-4	3.25– 4	12.3	2.02	715	1.90	650
I-5	3.5 – 4	15.2	1.98	690	1.72	555
I-6	3.75– 4.5	..	1.77	580	...	...
II-1	4 – 4.5	..	1.87	635	...	...
II-2	4.5 – 5	18.4	1.41	410	1.37	390
II-3	5 – 5.5	10.7	1.19	310	1.19	310
II-4	5 – 5.5	13.0	1.27	345	1.12	285
II-5	5.5 – 6	8.7	1.12	285	1.02	245
II-6	5 – 6	22.9	1.12	285	...	...
II-7	6 – 7	9.8	0.89	200	0.90	202
II-8	6 – 7.5	18.5	0.81	172	0.81	172
II-9	7 – 8.5	14.2	0.75	152	0.75	152
II-10	7 – 8.5	12.0	0.72	143	0.75	152
II-11	8.5 –11	..	0.67	127	...	...
II-12	8.5 –11	6.4	0.61	110	0.61	110
II-13	8.5 –11	5.5	0.60	108	0.60	108
III-1	5 – 6	17.0	...	...	1.02	245
III-2	5 – 6	10.5	1.07	265	...	...
III-3	6 – 7	4.0	0.93	213	0.92	210
III-4	6 – 7	13.1	0.85	185	...	(185)
III-5	6 – 7.5	28.8	0.80	168	...	...
III-6	7 – 8	19.6	0.73	146	0.72	143
III-7	7.5 –10	19.3	0.63	116	...	...
III-8	8 –10	16.3	0.58	102	0.60	108
III-9	10 –12	5.1	0.55	94	...	...
III-10	10 –12	15.9	0.515	85	0.515	85
III-11	10 –12	10.3	0.50	81	...	(81)
III-12	12 –15	13.5	0.40	57	...	...
III-13	12 –15	5.4	0.42	62	...	(62)
III-14	15 –20	9.5	0.36	48.5	...	(48.5)
III-15	15 –20	5.6	0.33	42.5	...	...
III-16	20 –30	5.7	0.284	33.5	...	(33.5)
III-17	20 –30	..	0.265	30.0	...	...
III-18	25 –35	4.0	0.24	25.8	...	...
III-19	30 –50	..	0.186	17.3	...	(17.3)
IV-1	5 – 6	13.6	1.20	410	1.23	330
IV-2	6 – 7	20.6	0.98	230	1.04	250
IV-3	7 – 8	10.5	0.79	165	0.82	175
IV-4	8 –10	..	...	...	0.67	127
IV-5	9 –10	6.0	0.66	125	0.65	122
IV-6	12 –15	10.0	0.43	64	...	(64)
IV-7	15 –20	6.0	0.35	46.5	...	(46.5)
IV-8	20 –30	7.0	0.258	28.8	...	...
IV-9	30 –50	3.5	0.185	17.1	...	...
V-1	0 – 5	18.6	1.85	620	1.77	580
V-2	5 – 5.5	15.0	1.57	480	1.57	480
V-3	5.5 – 6	6.2	1.36	385	1.40	400
V-4	6 – 7	11.1	1.09	270	1.11	280
V-5	7 – 8	5.2	0.99	235	1.02	245
V-6	8 –10	18.8	0.76	155	...	(155)
V-7	12 –15	5.5	0.41	60	...	(60)
V-8	15 –20	3.8	0.36	48.5	...	(48.5)

[a] Since the lower fractions undergo no appreciable breakdown during compounding, their viscosities after mixing usually were not determined. Wherever the compounded (uncured) molecular weight has been assumed in the discussion to be the same as the molecular weight before mixing, that molecular weight is included in parentheses in the last column.

where N_i is the number of molecules of molecular weight M_i, and the summations extend over all species in the mixture. The quantity a in the formula for the viscosity average molecular weight (*11*) is the exponent in the alternate form of the intrinsic viscosity–molecular weight formula 1:

$$[\eta] = K\overline{M}_v^a \tag{1A}$$

That is, $a = 1/1.56 = 0.64$ for polyisobutylene or Butyl rubber in diisobutylene. For a heterogeneous polymer $\overline{M}_w$ necessarily exceeds $\overline{M}_n$; their ratio is greater than unity by an amount dependent upon the breadth of the molecular weight distribution. For this value of a, $\overline{M}_v$ lies between $\overline{M}_n$ and $\overline{M}_w$, but much nearer the latter. The intrinsic viscosity relates directly to this average, regardless of molecular weight distribution.

Equation 1 is based on an empirical comparison (*11*) of the intrinsic viscosities (in diisobutylene) of fractions which were prepared essentially as were those of Table II with their absolute number-average molecular weights determined by the osmotic pressure method. Since the degree of heterogeneity in the fractions employed here was therefore similar to those used in establishing Equation 1, it is clear that the M values in column 5, Table II, represent number averages of the relatively homogeneous fractions to a good approximation.

According to the theory of fractionation, in so far as it has been developed (*6*), we estimate that the heterogeneity of the fractions was such that $\overline{M}_w$ in general exceeds $\overline{M}_n$ by some 10 to 15%; the viscosity-average molecular weights of the fractions probably run about 10% higher than the M values in column 5 of Table II. Likewise, when Equation 1 is applied to unfractionated polymers, the average molecular weight obtained is about 10% below the true viscosity average ($\overline{M}_n$ being half or less of $\overline{M}_v$, depending on the heterogeneity). The molecular weights for the unfractionated polymers of Table I have not been corrected by this rather uncertain factor; hence, they are lower than the true viscosity averages by some 10%.

When the higher fractions were compounded on the mill, some breakdown inevitably occurred in spite of the precautions discussed in the preceding section. The degree of degradation was not large, however. This is shown by the intrinsic viscosities of the fractions after compounding (column 6, Table II), which were determined by dissolving weighed samples of the compounded rubber (pure-gum recipe) in diisobutylene, correction being made for the weight of compounding ingredients. Independent experiments established that these did not alter the viscosity.

In the degradation of polymers under the influence of mechanical working of this sort it is known that larger species are degraded preferentially. In consideration of this fact and the relatively small changes which occurred, it is unlikely that the heterogeneity was appreciably increased by milling. The molecular weights based on intrinsic viscosities of the compounded rubbers undoubtedly approximate number averages closely, in so far as heterogeneity is a factor in the samples.

Fractions of lower molecular weight survive milling without measurable degradation. For this reason intrinsic viscosities of many of the low-molecular-weight fractions were not redetermined after compounding. Some of the high-unsaturation fractions intermediate in molecular weight showed increases in intrinsic viscosity after compounding. The onset of the vulcanization reaction to a minute extent during milling may have been responsible for this change, which in any event was too small to warrant further consideration.

Diolefin Content of Individual Fractions. Rehner (*24*) showed that the isoprene units in Butyl rubber are distributed more or less at random along the polymer chains. From this fact and the nature of the polymerization process it is to be expected that the proportion of diolefin units in high and in low-molecular-weight fractions from the same raw polymer should be very nearly

TABLE III. PERCENTAGE UNSATURATION DISTRIBUTION AMONG POLYMER FRACTIONS

Polymer Fraction	Before Ozonolysis $M \times 10^{-3}$	Before Ozonolysis $10^6/M$	After Ozonolysis [η]	After Ozonolysis "$\overline{M}_v$" × 10^{-3}	After Ozonolysis $10^6/\overline{M}_v$	Mole % Diolefin
II-4	345	2.9	0.179	16.3[b]	102	0.56
II-5	285	3.5	0.181	16.6[b]	100	0.54
II-7	200	5.0	0.182	16.8[b]	99	0.53
II-11	127	7.9	0.179	16.4[b]	101	0.52
III(0–5)[a]	370	2.7	0.191	18.1[b]	92	0.50
III-6	146	6.8	0.195	18.7[b]	89	0.46
III-12	57	17.6	0.179	16.4[b]	101	0.47
III-16	33.5	29.9	0.165	14.4[b]	115	0.48

[a] This sample, representing a first fraction from a fractionation of polymer III, is not included in Table II.

[b] The absolute viscosity-average molecular weights are slightly larger than the figures given in this column (see text).

TABLE IV. MIXTURES OF FRACTIONS

Mixt. Designation	% of Polymer of Lower Mol. Wt.	$[\eta]$ Calcd.[a]	$[\eta]$ Obsvd. after Compounding	$\overline{M}_n \times 10^{-3}$ Calcd.[b]	"$\overline{M}_v$" $\times 10^{-3}$ Calcd. from $[\eta]$ after Compounding	$\overline{M}_w$ Calcd.[b]
			Series A			
I-3	0	(2.18)	1.98	805	690	805
A-1	10	2.01	1.92	435	660	735
A-2	20	1.84	1.76	300	575	660
A-3	40	1.51	1.43	183	415	520
A-4	65	1.09	1.02	124	245	335
III-10	100	(0.515)	0.515	85	85	85
			Series B			
II-2	0	(1.41)	1.37	410	390	410
B-1	25	1.24	1.24	280	335	345
B-2	50	1.065	1.07	210	265	275
B-3	75	0.89	0.86	171	188	210
II-10	100	(0.72)	0.75	143	152	143
			Series C			
II-1	0	(1.87)	...	635	...	635
C-1	10	1.71	1.53	210	465	575
C-2	20	1.55		126	...	515
C-3	35	1.31	1.31	79	365	420
III-17	100	(0.265)	...	30	30	30
			Series D			
I-6	0	(1.77)	...	580	...	580
D-1	40	1.32	1.21	240	320	400
D-2	65	1.05	1.03	175	250	285
II-11	100	(0.67)	...	127	...	127

[a] Observed intrinsic viscosities of uncompounded individual fractions shown in parentheses; intrinsic viscosities of their mixtures calculated from Equation 5.

[b] Number- and weight-average molecular weights calculated from molecular weights of individual fractions before compounding.

the same. To confirm this expectation, the percentage unsaturation in several of the fractions was measured by the ozonolysis method (*25*).

This method is based on the knowledge that all, or nearly all, of the isoprene units occur in the 1,4-configuration within the main chain (*24*). When the solution of polymer in carbon tetrachloride is ozonized, these units are split. As Rehner showed, the degradation proceeds to a limit corresponding to complete reaction of the diolefin units, beyond which further ozonization produces little change. The percentage of diolefin units, consequently, is proportional to the increase in the number of molecules during ozonization. Specifically,

$$\text{mole \% diolefin} = (1/\overline{M}_n - 1/\overline{M}_{n,0}) \times 56 \times 100$$

$\overline{M}_{n,0}$ and $\overline{M}_n$ are the number-average molecular weights before and after ozonization, and 56 is the molecular weight per structural unit, the diolefin units being present in extreme minority.

Table III gives typical experimental results on Butyl fractions. $\overline{M}_{n,0}$ is equal to M of Table II, calculated from the initial intrinsic viscosity of the fraction. The molecular weights in the fifth column of Table III were computed from the intrinsic viscosity after ozonization using Equation 1. In accordance with the previous discussion, it is somewhat less than the actual viscosity-average molecular weight. Owing to the (assumed) random distribution of diolefin units in the samples and the fact that, in general, each molecule is split at a number of points, the distribution of molecular weights in the ozonized products will approximate the most probable distribution (*8*), represented by equation:

$$N_i = Np^{i-1}(1 - p) \tag{5}$$

where N_i = number of molecules composed of i structural units
N = total number of molecules
$1 - p$ = degree of degradation or ratio of molecules to structural units in the sample

$$\overline{M}_n = 1/(1 - p) \tag{6}$$

When Equation 5 is substituted into Equation 4, it is found that for this molecular weight distribution,

$$\overline{M}_v/\overline{M}_n = 1.83$$

(The derivation of this factor was published by Rehner, *25*.) Allowing that the actual viscosity-average molecular weights are about 10% greater than the uncorrected values in column 5 of Table III,

$$\overline{M}_n = \text{"}\overline{M}_v\text{"}/1.66$$

By means of this equation the reciprocal $\overline{M}_n$ values in column 6 were computed. The diolefin percentages in the last column were calculated from columns 6 and 3 by the above equation. The variations in these percentages are probably within the experimental error, and there is no significant trend with molecular weight. It is the constancy of the diolefin content, rather than its absolute magnitude, that is of importance for interpretation of the results which follow.

Mixtures of Fractions. All rubbers, natural and synthetic, as normally employed are composed of molecular species covering a wide range of sizes. It is important, therefore, to ascertain the effects of molecular weight distribution on various physical properties. For this purpose heterogeneous polymers of known distribution were required. These were conveniently obtained by mixing pairs of fractions in various proportions as shown in Table IV. Data pertaining to the individual fractions from which each series of mixtures was prepared are included with each set; these are taken from Table II. Intrinsic viscosities in the third column have been calculated for the mixtures by "weight averaging" according to the formula,

$$[\eta]_{mixture} = w_1[\eta]_1 + w_2[\eta]_2 \tag{7}$$

where w_1 and w_2 are the weight fractions of the components present in the mixture, and $[\eta]_1$ and $[\eta]_2$ are their respective intrinsic viscosities (uncompounded). The observed intrinsic viscosities after compounding (column 4) are generally somewhat lower, owing to a small degree of breakdown during milling.

The effects of molecular weight heterogeneity on a given physical property—e.g., on tensile strength—are easily accountable if it can be shown that the property in question depends explicitly on a particular average molecular weight but is otherwise independent of the distribution. A plot of the physical property against this average molecular weight will be the same for various heterogeneous polymers and for homogeneous fractions as well (*9*). Once the specified average has been evaluated for a given polymer, no further consideration need be given the molecular weight heterogeneity. It is not self-evident in advance of experimental verification, however, that an average can be found such that the property in question is specifically defined by the value of that average alone.

In the analysis of the data on physical properties of vulcanizates from fractions and their mixtures, the number, weight, and viscosity averages defined by Equations 2, 3, and 4, respectively, were considered. The first two may be computed from the following expressions applicable to binary mixtures,

$$\overline{M}_n = 1/(w_1/M_1 + w_2/M_2) \tag{2A}$$

$$\overline{M}_w = w_1M_1 + w_2M_2 \tag{3A}$$

which follow from Equations 2 and 3; w_1 and w_2 are the weight fractions, and M_1 and M_2 are the molecular weights of the component polymer fractions. In computing $\overline{M}_n$, M_1 and M_2 should refer to the number averages for the component fractions; in computing $\overline{M}_w$, weight averages should be employed in so far as the heterogeneity of the fractions is to be taken into account.

The number-average molecular weights in column 5 of Table IV were computed using Equation 2 from the M values for the individual fractions before compounding, as given in Table II; as pointed out above, the latter correspond more closely to number averages. Some breakdown generally occurred during compounding, but undoubtedly only the larger component fraction was affected. Minor degradation of these would lower the number averages for the mixtures negligibly. Hence, the $\overline{M}_n$ values for the mixtures in Table IV should correspond closely to their actual number-average molecular weights.

Figure 2. Diagrammatic Representation of a Portion of the Network Structure, Showing Principal Chains *AB* and a Terminal Chain *BC*

In the computation of the weight averages (Table IV), the M_1 and M_2 values inserted into formula 3A should have been increased by some 10 to 15%, according to the estimate quoted above, owing to the residual heterogeneity of the fractions. If this correction were made, assuming all fractions to be equally heterogeneous, the figures in the last column of Table IV would be raised somewhat, but all of them by about the same percentage. Since mixtures and fractions would be equally affected by this correction, any possible empirical correlation of a physical property with the weight average would not be obscured through the use of the uncorrected figures for $\overline{M}_w$ in Table IV.

This average molecular weight, unlike $\overline{M}_n$, is sensitive to the destruction of the larger species during mill breakdown, which occurs to an extent depending on the percentage of low-molecular-weight fraction in the mixture. A more nearly authentic weight average perhaps would be obtained by assuming that the breakdown which occurs is confined to the higher of the two components. However, more accurate values for the weight-average molecular weights are not required for the purposes of the subsequent discussion of physical properties, and this correction has been neglected.

The uncorrected viscosity-average molecular weight, calculated using Equation 1 from intrinsic viscosities after compounding, are also included in Table IV.

In addition to the heterogeneous products obtained by mixing fractions, polymer II-A of Table I was compounded without previous fractionation, and the resulting vulcanizates were subjected to tests. Its molecular weight distribution was determined by careful fractionation on a small scale. According to an analysis of its distribution curve, the ratio of $\overline{M}_v/\overline{M}_n$ was found to be about 2.3 ± 0.2. Its corrected viscosity-average molecular weight should be about 470,000. Hence, $\overline{M}_n$ = 200,000. This value will be employed in subsequent discussions.

STRUCTURE OF BUTYL VULCANIZATES

Theory. The process of cross linking polymer molecules has been analyzed statistically (*10, 29*) with results which are confirmed by widespread experimental observations. As cross linkages are introduced at random between polymeric molecules at accidental points of contact, large structures consisting of many "primary molecules" gradually are built up at the expense of simple molecules consisting of only one primary molecule (not cross linked), or of only a few primary molecules. (The term "primary molecule" throughout this paper refers to the rubber molecules which existed separately before cross linking, or which would exist if all of the cross linkages of the vulcanizate were severed.) According to the statistical theory, "infinite" networks pervading the entire rubber volume suddenly begin to form, owing to interlinking of these large species, when the concentration of cross linkages in the system as a whole exceeds a definite critical limit. If the primary molecules are of uniform length, this occurs when the number of cross linkages exceeds half the number of primary molecules (*10*); if the molecules are nonuniform in length, a somewhat lower degree of cross linking will be required (*10, 29*). These infinite networks are insoluble in all solvents which do not destroy their primary valence structure. Their abrupt appearance at an early stage of the vulcanization process is analogous to the gel point so familiar in the polymerization of thermosetting resins, drying of oils, etc.

As the vulcanization process continues, introduction of additional cross linkages causes more and more of the sol rubber to be converted to gel (infinite networks). Ordinarily the final vulcanizate will consist almost entirely of gel, which is a statistical consequence of the fact that there are, on an average, many cross-linked units per primary molecule.

From a structural point of view, the individual primary molecules to a large extent have lost their identities in the final vulcanizate. The basic element of the structure (Figure 2) is the portion of a molecule reaching from one cross linkage to the next—e.g., the portion of the structure between the cross linkages designated by *A* and *B*. This primary structural element will be referred to as a chain. The cross linkages may be regarded as centers of tetrafunctionality since four chains emanate from each. The network consists of an assemblage of chains attached irregularly to one another through these tetrafunctional centers (*13*).

In addition to chains extending between two cross linkages, there will be chains extending from a cross linkage to the end of a primary molecule; two of these "terminal" chains will occur in the network for each primary molecule. It is apparent that these terminal chains, unlike the principal chains, will not be subjected to permanent orientation when the network is deformed as by stretching. The terminal chains constitute flaws in the network structure. The lower the molecular weight (number average) of the primary molecules, the greater the number of these flaws. Hence, the well known but poorly understood dependence of physical properties upon the molecular weight of the uncured rubber (*5*).

TABLE V. INCIPIENT CURE WITH BUTYL FRACTIONS OF LOW MOLECULAR WEIGHT

Polymer Fraction	Intrinsic Viscosity[a] $[\eta]$	$M \times 10^{-3}$	Time of Cure, Min. at 307° F.	% Soluble	Swelling Ratio[b]	$[\eta]$ after Curing Process
			Fractions from Low-Unsatn. Polymers II and III			
III-6	0.72	143	60	1.6	10.8	...
II-12	0.61	110	60	6.5	11.4	...
III-10	0.515	85	60	10.5	14.6	...
III-13	0.42	62	60	24.6	29.2	...
			120	29.3	35.8	...
III-14	0.36	48.5	30	40	40	...
			60	35	41	...
			120	49	53	...
III-16	0.284	33.5	60	100	..	0.43
			120	100	..	0.34
III-19	0.186	17.3	120	100	..	0.24
			Fractions from High-Unsatn. Polymer IV			
IV-5	0.65	122	40	2.3	..	...
IV-6	0.43	64	40	4.4	..	...
IV-7	0.35	46.5	40	12.6	..	...
			80	13.8	..	...
IV-8	0.258	28.8	40	50	..	...
			80	75	..	...
IV-9	0.185	17.1	40	100	..	0.211
			80	100	..	...

[a] On these low-molecular-weight fractions the intrinsic viscosity is not altered appreciably by milling. In cases where $[\eta]$ has been measured both before and after milling, the latter value has been employed above (Table II).

[b] Swelling ratio = [vol. of swollen vulcanizate]/[vol. of insol. rubber (dry)]. Swelling and solubility determinations were carried out in cyclohexane at room temperature.

The total number of chains will be equal to $\nu_0 + N$, where ν_0 is the number of cross-linked units (the number of cross linkages being equal to $\nu_0/2$), and N is the number of primary molecules in the network. The concentration of primary molecules, expressed in moles per gram, is related to the molecular weight of the primary molecules as follows:

$$N/\rho V = 1/M$$

where ρ is the density and V the volume containing N primary molecules. For a heterogeneous mixture M should be replaced by the number average, $\overline{M}_n$. Similarly, the concentration of cross-linked units is given by

$$\nu_0/\rho V = 1/M_c$$

where M_c is the molecular weight (number average) per cross-linked unit; it will be used extensively as a reciprocal measure of the concentration of cross-linked units.

It follows, then, that the total concentration of chains, in moles per gram, will equal $1/M_c + 1/M$. The molecular weight (number average) per chain, designated by M_c', equals the reciprocal of this quantity:

$$M_c' = MM_c/(M + M_c) \tag{8}$$

When $M >> M_c$,

$$M_c' \cong M_c \tag{8A}$$

Inasmuch as the diolefin units are distributed at random along the polymer chains and vulcanization can safely be assumed to interlink them at random, the lengths of the chains will conform to the most probable distribution expressed by Equation 5. Furthermore, terminal chains and principal network chains will have the same average size. The weight fraction of the network occurring in terminal chains, therefore, will equal the "mole" fraction of terminal chains. Since there will be two terminal chains for each primary molecule, the percentage of nonorienting material in the network structure will be given by

$$\begin{aligned}\%\text{ terminal chains} &= 100 \times (2/M)/(1/M_c') \\ &= 100 \times 2M_c/(M + M_c)\end{aligned} \tag{9}$$

When $M >> M_c$,

$$\%\text{ terminal chains} \cong 100 \times (2M_c/M) \tag{9A}$$

These relationships will be applied in the subsequent treatments of physical properties.

Quantitative Evaluation of Degree of Cross Linking. The preceding discussion makes it clear that the two quantities essential to the quantitative treatment of vulcanizate properties are M and M_c. The former has been determined (Table II) through the application of accepted methods for molecular weight determination. Direct chemical determination of M_c by chemical measurement of the concentration of cross linkages in rubber vulcanizates has not yet proved feasible. Therefore this quantity has been deduced indirectly by locating the critical point for incipient gelation in the manner described below.

It has been assumed that the reactivities of the diolefin units are independent of polymer molecular weight, location of diolefin unit within the polymer molecule, etc. Under this assumption, substantiated by numerous observations on the kinetics of polymer reactions, all polymers of the same diolefin content acquire the same concentration (e.g., in moles per liter) of cross linkages during the vulcanization process, regardless of the molecular weights of the initial polymers; hence, the average number of cross linkages per primary molecule varies inversely as the initial molecular weight. According to the statistical theory of three-dimensional polymers, infinite network formation sets in, with attendant partial insolubility, when an average of one unit per primary molecule (one half cross linkage per molecule) is present (*10*). Hence, a "vulcanizate" which borders on incipient insolubility must contain an average of one cross-linked unit per primary molecule. In other words, at the critical point for incipient gelation $M_c = M$, where M is the molecular weight of the polymer prior to cross linking. This polymer is here considered to be homogeneous. (If the polymer is heterogeneous, then $M_c = \overline{M}_w$ at the critical point, *29*). Once the critical M, and hence M_c, is located, it follows from the above assumption that this M_c value applies to all vulcanizates from fractions containing the same proportion of diolefin units, regardless of molecular weight.

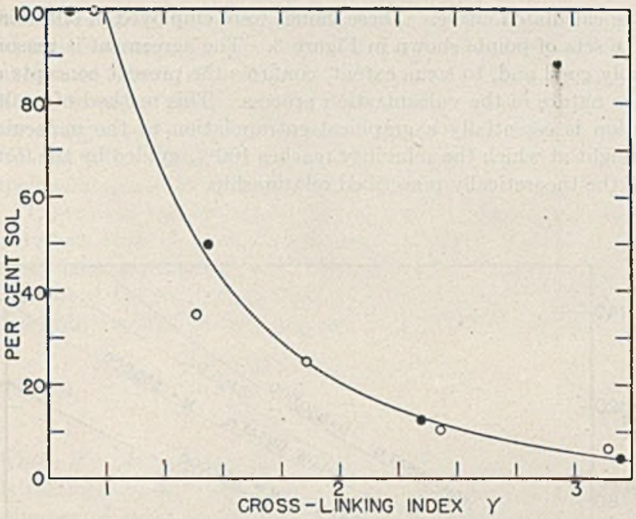


Figure 3. Weight Per Cent of Sol ($100 \times W_s$) *vs.* Cross-Linking Index

Assuming M_c = 35,000 for low-unsaturation polymers ○, and M_c = 20,000 for high-unsaturation polymer IV fractions ●; (i.e., $\gamma = M/M_c$)

Table V lists experimental results for low-molecular-weight fractions compounded according to the pure gum recipe and subjected to "cure" at 307° F. All fractions within each set are assumed to process the same proportion of diolefin units, according to the results previously presented. As the molecular weight was decreased, the percentage of sol (soluble constituents) increased from about 1% or less for fractions of high or medium molecular weight, to complete solubility for the lowest fractions. The latter, which were too low to contain the critical number of cross linkages per molecule required for gelation, nevertheless underwent an increase in intrinsic viscosity as a result of the cross-linking reaction (last column, Table V). Swelling ratios for the gels are also included in Table V.

The molecular weight differences between successive fractions are necessarily rather large. From casual examination of the data, the M_c values can be bracketed only between rather wide limits—33,500 to 48,500 for the low-unsaturation polymers and 17,000 to 28,800 for those of high unsaturation. Further assistance is afforded by the theory of random cross linking (*10*) of chains of uniform length in the form of the equation,

$$(-\ln W_s)/(1 - W_s) = \gamma \tag{10}$$

relating the weight fraction of sol W_s to the "cross-linking index", γ; the latter represents the average number of cross-linked units per primary polymer molecule. In other words,

$$\gamma = M/M_c$$

where M is the molecular weight of the fraction. By arbitrarily choosing M_c values within the required limits, trial sets of γ values are obtained from the known molecular weights of the fractions. These can be compared graphically, as in Figure 3, with the curve calculated from Equation 10. M_c values of 35,000 and 20,000, respectively, appear to give the best fit with the calculated curve. These values were employed in obtaining the sets of points shown in Figure 3. The agreement is reasonably good and, to some extent, confirms the present concepts of the nature of the vulcanization process. This method of evaluation is essentially a graphical entrapolation to the molecular weight at which the solubility reaches 100%, guided by the form of the theoretically prescribed relationship.

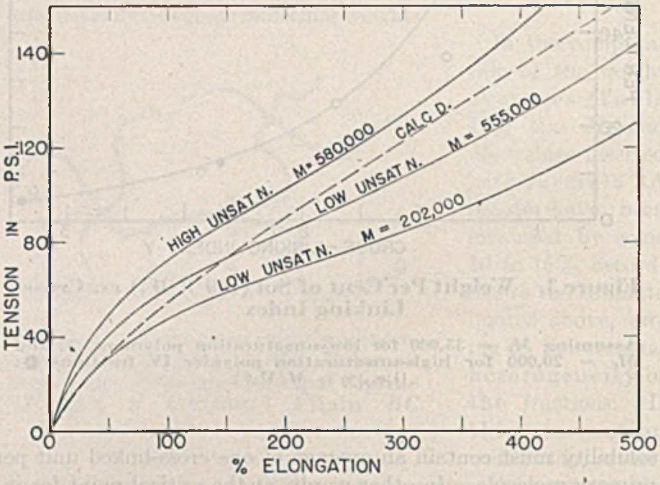


Figure 4. Representative Stress-Strain Curves for Pure-Gum Vulcanizates at Moderate Elongations

The above figures for M_c will be employed in the following discussion of physical properties. Their reciprocals, 2.85×10^{-5} and 5.0×10^{-5} "mole" per gram, respectively, represent the concentrations of cross-linked units in vulcanizates from the low- and high-unsaturation polymers; concentrations of cross linkages are half of these values.

Discussion. In deducing the values for M_c, it has been assumed that the interconnections between molecules are simple cross linkages between two molecules. If three or more molecules were united at the junctions formed during vulcanization, the above procedure would require revision; the critical molecular M would then be less than M_c, the molecular weight per cross-linked unit, by a factor depending on the (average) functionality of the intermolecular linkages. Owing to the low concentration of diolefin units available to the action of the vulcanizing ingredients, it is most unlikely that more than two of them would be linked together, irrespective of the actual nature of the vulcanization reaction. This inference is supported by independent confirmation of the M_c values, obtained in the analysis of the dependences of "modulus" and swelling capacity on molecular weight (to be discussed later in the paper). This agreement would not be observed if the intermolecular connections were of higher functionality.

A 35,000 molecular weight portion of one of the low-unsaturation Butyl polymers includes an average of 3.1 diolefin units, from which we conclude that only about 1 diolefin unit in 3 enters into the formation of cross linkages. Similarly, the 20,000 figure for the molecular weight between cross linkages in polymer IV corresponds to the somewhat lower cross-linking efficiency of 1 in about 3.7. In other experiments not reported here, gelation conditions were explored by varying the degree of unsaturation at constant molecular weight. At a molecular weight level of 350,000, between 0.075 and 0.12 mole % of diolefin units are required for incipient gelation during vulcanization, using the standard recipe. At a molecular weight level of 900,000, a mole percentage of diolefin units between 0.016 and 0.030 is required. These figures represent from 3 to 5 diolefin units per molecule in each case. Thus, the efficiency of utilization of diolefin units in the formation of cross linkages shows a remarkably small variation over a 100 fold range of diolefin concentration.

Doubling the proportions of the compounding ingredients lowers the molecular weight for incipient gelation during vulcanization, as would be expected from results presented in connection with the description of experimental procedures. In the case of fractions from Butyl polymer IV the critical molecular weight (equal to M_c) is lowered to about 15,000. Hence, it is possible to increase the efficiency of utilization of the diolefin units through the use of a greater concentration of compounding ingredients.

By employing nonsulfur vulcanizing agents, it is possible to produce gelation with less than 2 (but more than 1) diolefin units per molecule. Even at molecular weights in the vicinity of 1,000,000, no more than 1 diolefin unit in 10,000 is required for incipient network formation. Polymers containing no diolefin units (i.e., pure polyisobutylene) yield completely soluble products when subjected to the same curing conditions.

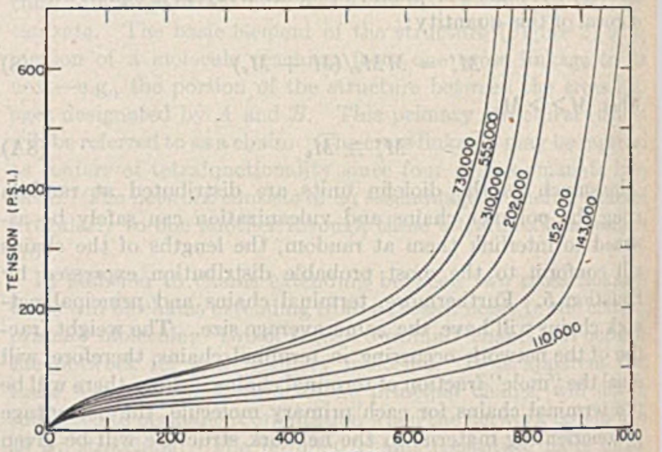


Figure 5. Stress-Strain Curves Extending to High Elongation for Vulcanizates from Low-Unsaturation Fractions of the Molecular Weights Indicated

In this connection, sulfur-accelerator vulcanization of mixtures of polyisobutylene and Butyl yields products from which the polyisobutylene can be removed by extraction. This result provides direct proof that the cross linkages involve 2 diolefin units, and not a diolefin unit in one molecule with an isobutylene unit in the other.

STRESS-STRAIN CHARACTERISTICS

Figure 4 shows stress-strain curves covering the range 0 to 500% elongation, for representative pure gum vulcanized Butyl fractions differing in molecular weight and in unsaturation.

In Figure 5 stress-strain curves extending over virtually the entire elongation region and extending to stresses of 700 pounds per square inch are shown for a series of low-unsaturation Butyl fractions vulcanized according to the pure gum recipe previously given. These cover the molecular weight range 110,000 to 730,000. Progressive changes with molecular weight are particularly great in the region of low molecular weight. They continue, however, even above a molecular weight of 500,000, where there is an average of some fourteen cross-linked units per molecule according to our previous estimate of M_c.

Stress-Strain Curves at Moderate Elongations. Careful analysis of stress-strain curves including others not shown here, reveals a common similarity in shape. If each is transformed simply by altering its tension scale by a suitable factor, all of them may be made to coincide as far as about 400% elongation. Some deviations occur with the vulcanizates from the fractions of low molecu-

Table VI. Stress-Strain and Swelling Characteristics of Low-Unsaturation Butyl Vulcanizates

(Cured 60 minutes at 307° F.)

Polymer Fraction or Mixt.[a]	$M \times 10^{-3}$ (after Compounding)	τ_{300}%[b], Lb./Sq. In.	% Elongation at 500 Lb./Sq. In.	% Soluble	Swelling Ratio[c]
Vulcanizates from Homogeneous Fractions					
I-1	1080	...	...	0	6.13
I-2	730	116	730	0	6.30
I-5	555	108	755	0	6.70
II-3	310	94	790	1.0	7.18
II-5	245	...	...	0.5	7.52
II-7	202	84	825	0.9	7.90
II-9	152	68	905	1.0	9.53
III-6	143	55	955	1.6	10.8
II-12	110	45	...	6.5	11.35
III-10	85	...	...	10.5	14.6
Vulcanizates from Heterogeneous Polymers[d]					
A-1	435	..	...	2.6	6.82
A-2	300	..	...	3.2	7.38
A-3	183	..	...	4.5	8.22
A-4	124	..	...	7.5	10.35
D-2	175	..	...	...	...
II-A	200	78	865	3.5	8.05

[a] See Tables II and IV.

[b] "Modulus" at 300% elongation.

[c] Swelling measurements were carried out in cyclohexane on ring specimens cured simultaneously with those used for stress-strain measurements.

[d] Molecular weights for these mixtures are number averages (Table IV).

lar weight, possibly as a result of high hysteresis. In all other cases, including stress-strain curves for high-unsaturation vulcanizates and vulcanizates from unfractionated polymers, the coincidence is excellent. In other words, essentially all of the stress-strain curves from 0 to 400% elongation can be represented by

$$\tau = G\varphi(\alpha) \tag{11}$$

τ is the tension, in pounds per square inch (initial cross section) at a relative length $\alpha = L/L_0$ [% elongation $= 100 \times (\alpha - 1)$]; $\varphi(\alpha)$ is a function of α which is the same for all of the pure-gum Butyl vulcanizates. G is a parameter which varies from one sample to another; G is dependent on the molecular weight before vulcanization and on the number of cross linkages introduced during vulcanization, but is independent of α.

The separability of structure (G) and elongation [$\varphi(\alpha)$] factors as in Equation 11 is predicted by statistical mechanical theories of the elastic properties of network structures such as exist in vulcanized rubbers. According to these theories (*13*, *17*, *31*, *33*), the dependence of the elastic retractive force on elongation should be represented by

$$\varphi(\alpha) = \alpha - 1/\alpha^2 \tag{12}$$

This expression can be expected to apply only over the elongation region preceding the onset of crystallization. It is further assumed in its derivation that the force of retraction originates entirely from the entropy change on stretching, the change in internal energy with elongation (at constant volume) being negligible. The latter condition is amply fulfilled with natural rubber (*1*, *37*) and GR-S (*36*).

In Figure 4 a stress-strain curve calculated from Equation 12 is included for comparison with the shape of the observed curves over the region of moderate elongations—i.e., up to 400%. The agreement is by no means so good as has been demonstrated for natural rubber (*1*, *32*) and GR-S (*36*). However, the curves observed here, being determined by continuous stretching, are not necessarily representative of the equilibrium curve to which Equation 12 refers. This may account for a large part of the discrepancy. We are less concerned with the particular shape of the stress-strain curve than with the dependence of stress on structure.

In view of the empirically established separability of the structure and elongation factors as expressed in Equation 11, the stress-strain curve for a given Butyl vulcanizate (pure gum cure) can be characterized by a single parameter. Either G or the tension at a given elongation might be used for this purpose. We have chosen to employ the tension developed at 300% elongation. These so-called moduli at 300% elongation, as taken from the stress-strain curves for various samples, are recorded in Tables VI and VII. They are shown graphically as functions of the molecular weight before vulcanization in Figure 6.

Theoretical expositions on the elastic properties of polymeric networks such as exist in vulcanized rubbers in general have dealt only superficially with the influence of the quantitative aspects of the network structure. The "equation of state" for vulcanized rubber has been expressed (*13*, *31*, *33*) in the form

$$\tau = (RT\nu/V)(\alpha - 1/\alpha^2) \tag{13}$$

That is,

$$G = RT\,\nu/V \tag{14}$$

where R is the gas constant, T is the absolute temperature, and ν is the number of "molecules" or, more accurately, the effective number of chain elements in volume V of the network. The effect of the finite molecular weight of the primary molecules is neglected in these formulas, although in one instance (*13*) the assumption that the primary molecules are infinitely long was mentioned specifically. When this is the case, ν will equal the number, ν_0, of cross-linked units or half the number of cross linkages. Equations 13 and 14 have led to the expectation, therefore, that the "modulus" (and G) should be proportional to the degree of cross linking (inversely proportional to M_c), and no particular importance has been attached to the molecular weight M of the primary molecules.

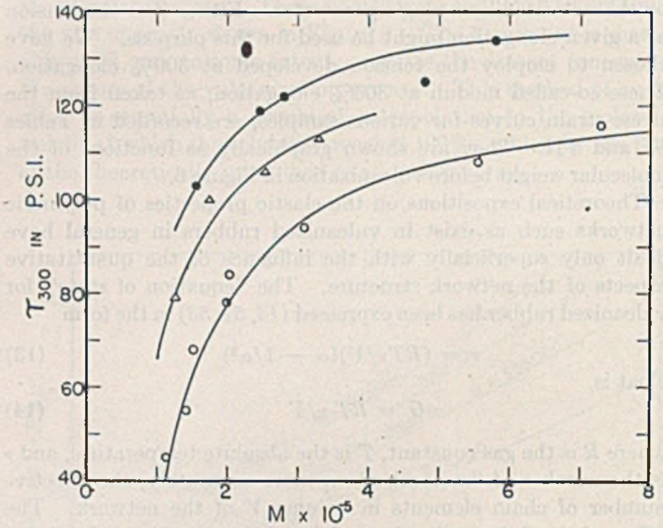
The experimental modulus values in Tables VI and VII and plotted against M in Figure 6 show that molecular weight M is a more critical factor than the degree of cross linking over the range covered by these results. The quantitative effects of these factors will be examined in greater detail in the following sections.

Table VII. Stress-Strain and Swelling Characteristics of High-Unsaturation Butyl Vulcanizates

Polymer Fraction	$M \times 10^{-3}$ (after Compounding)	Cure, Min. at 307° F.	τ_{300}%, Lb./Sq. In.	% Elongation at 500 Lb./Sq. In.	Swelling Ratio[a]
IV-1	330	40	113	700	6.46
IV-2	250	40	106	725	6.57
IV-3	175	40	100	720	7.13
IV-4	127	40	79	...	8.30
IV-5	122	40	...	...	7.94
IV-6	64	40	...	...	11.0
V-1	580	15	...	...	6.14
		30	134	640	6.01
V-2	480	30	125	670	6.10
V-3	400	15	...	...	6.56
		30	...	...	6.11
V-4	280	30	122	...	6.22
V-5	245	30	119	...	6.26
V-6	155	30	103	710	7.19

[a] See footnote [c] of Table VI.

Effect of Molecular Weight on Modulus. If the cross-linking index γ, representing the number of cross-linked units per primary molecule in the vulcanizate, is not very large, the occurrence of terminal chains and related network imperfections or flaws will materially reduce the number of effective chains below ν_0, the number which would be present if M were infinite. This effect of finite molecular weight can be taken into account (*5*) by considering that some of the cross linkages are, in effect, required to combine the N primary molecules into a single ramified molecule devoid of circuitous connections. The number required for this purpose is equal to N. Cross linkages in addition to this number provide internal connections between different parts of the structure, and in this way produce a structure which can be correctly designated as a network. Only cross linkages in excess of the number of primary molecules effectively "fix" the structure so that it responds elastically to deformation. The ef-



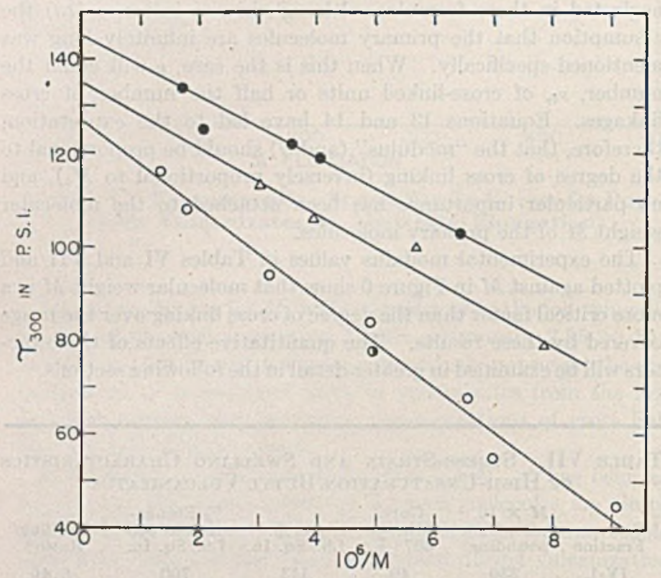


Figure 6 (*Above*). Tension at 300% Elongation ("Modulus" at 300%) *vs.* Molecular Weight M (or $\overline{M}_n$) before Vulcanization

Figure 7 (*Below*). Tension ("Modulus") at 300% Elongation *vs.* Reciprocal of Molecular Weight M (or $\overline{M}_n$)

- ○ Low-unsaturation fractions
- ◐ Unfractionated polymer II-A
- △ High-unsaturation fractions from polymer IV
- ● High-unsaturation fractions from polymer V

fective number of cross linkages is given therefore by $\nu_0/2 - N$. The effective number of chains, ν, will be equal to twice the effective number of cross linkages or number of circuitous connections in the network. (A similar, more detailed treatment of the effects of network imperfections has already been published, *5*.) Hence

$$\nu = \nu_0 - 2N = \nu_0 - 2\rho V/M \qquad (15)$$

where ρ V is the weight of polymer containing N primary molecules. Introducing Equation 15 into 13, the retractive force per unit initial cross-sectional area becomes

$$\begin{aligned} \tau &= (RT/V)(\nu_0 - 2\rho V/M)\varphi(\alpha) \\ &= (RT\rho/M_c)(1 - 2M_c/M)\varphi(\alpha) \qquad (16) \end{aligned}$$

$$G = (RT\rho/M_c)(1 - 2M_c/M) \qquad (17)$$

The above derivation of the simple factor $(1 - 2M_c/M)$ to express the dependence of modulus on M is well founded as long as M is sufficiently greater than M_c to render the residual sol fraction small. This requires that M be at least three times M_c (*10*). Otherwise the disproportionate distribution of cross linkages between sol and gel (*5, 10*) must be taken into account.

In the above analysis of the effect of finite molecular weight on elastic properties, it is the number of primary molecules which enters the equations. Hence, if the polymer is heterogeneous with respect to molecular weight, M is to be replaced by the number average $\overline{M}_n$.

According to Equations 16 and 17, fractions of the same unsaturation but differing in molecular weight should produce vulcanizates the moduli of which vary linearly with the reciprocal of M. In Figure 7 the 300% "modulus" figures of Tables VI and VII are plotted against $1/M$. Results for fractions from polymers I, II, and III are sufficiently concordant, in spite of the minor differences in their unsaturations indicated by the determinations summarized in Table I, to permit them to be considered together without differentiation. They substantiate the predicted linear relationship. The modulus of the unfractionated polymer II-A agrees well with the results for fractions when compared according to its number average.

Results for high-unsaturation fractions from polymers IV and V do not coincide, presumably owing to the difference in their unsaturations (Table I). Separate straight lines are drawn in Figure 7 through these two sets of points. Owing to the limited number of points and the irregularities which occur (probably due principally to poor reproducibility in the curing operation), the straight lines drawn for these polymers are to be considered merely as rough approximations.

The equations of the three straight lines drawn in Figure 7 can be expressed as follows. For the low-unsaturation fractions,

$$\tau_{300\%} = 127\ (1 - 74{,}000/M) \qquad (16A)$$

For the high-unsaturation fractions, polymer IV,

$$\tau_{300\%} = 135\ (1 - 52{,}000/M) \qquad (16B)$$

and for polymer V,

$$\tau_{300\%} = 145\ (1 - 45{,}000/M) \qquad (16C)$$

All are expressed in pounds per square inch. Comparing these with theoretical Equation 16 or 17, M_c values for the respective polymers are 37,000, 26,000, and 22,500. The agreement with the previous independent estimates, 35,000 and 20,000, respectively, for the low (I, II, and III) and high (IV) unsaturation polymers, is good. The differences are within the experimental errors attending either method for determining M_c. Thus the above theoretical explanation for the contribution of initial molecular weight to elastic properties is confirmed and the previous estimates for the M_c's are substantiated.

Effect of Degree of Cross Linking on Modulus. On further examination of empirical Equations 16A, 16B, and 16C it is found that the intercepts for $M = \infty$ (corresponding to the initial numerical factors in these equations) do not agree with theoretical Equation 16, according to which they should equal $(RT\rho/M_c)\ \varphi(\alpha)$. Setting $\alpha = 4$ in $\varphi(\alpha)$, as given by Equation 12, and substituting the M_c values from the above paragraph, these factors are calculated to be 35, 50, and 58 pounds per square inch, compared with the observed 127, 135, and 145, respectively. The differences in magnitude might be excused, in part at least, on the grounds that the statistical mechanical procedure employed in deriving Equation 13, from which Equation 16 was obtained by introducing the above correction for finite molecular weight, is fundamentally only approximate. However, the relatively small change in "modulus" with degree of cross linking cannot be dismissed in this way. The theory predicts explicitly that the modulus for $M = \infty$ should increase proportionally to the abundance of cross linkages (inversely proportional to M_c). High-unsaturation polymer V contains at least 50%

more cross linkages than the low unsaturation polymers, yet its modulus extrapolated to infinite molecular weight is only 14% greater.

It has been suggested (*5*) that these discrepancies are caused by entanglements of chains in the network structure. Two or more chains, though not bonded together at any point, may be looped about one another in such a way that they cannot be disentangled without rupture of a primary valence bond. These entanglements will restrict the number of configurations which the chains are able to assume, and the elastic response of the network to deformation will be augmented by them; they should act in effect like additional cross linkages. In the absence of primary valence cross linkages, however, permanent entanglements could not exist (*5*). (It can be shown readily that these entanglements would not alter the correction factor introduced previously for finite molecular weight; terminal chains cannot become involved in permanent entanglements, *5*).

It would be expected further that the relative contribution of entanglements to the retractive force should be greater, the longer the chains. The increase in modulus with degree of cross linking (decrease in M_c) predicted by Equations 16 and 17 should be partly compensated by a decrease in the entanglement factor, therefore. In other words, the discrepancies between observed and calculated "moduli" should decrease as the degree of cross linking is increased; this is observed to be the case.

Stress-Strain Curves at High Elongations. At elongations of 400 to 700% the stress-strain curves (Figure 5) assume pronounced upward curvature until a steep upward slope has been reached. Thereafter the curves proceed almost linearly to their breaking points; only the onset of these final portions of the curves are included in Figure 5.

Another noteworthy feature of the stress-strain curves in the region of steep ascent is their parallelism to one another; their final slopes above about 500 pounds per square inch are roughly of the same magnitude, independent of initial molecular weight and degree of cross linking. The location along the elongation axis of the steep, linear portion of the stress-strain curve is, of course, displaced for one polymer as compared to another, depending on the vulcanizate structure. As an index of the location of the region where the stress-strain curve assumes steep upward curvature, the elongations at which the tension reaches 500 pounds per square inch are recorded in Tables VI and VII. For samples of about the same tensile strength these figures are directly related to their ultimate elongations, since stress-strain curves for all pure-gum Butyl vulcanizates are approximately parallel and linear from this tension to the breaking point.

The elongations at 500 pounds per square inch do not correlate directly with the 300% modulus over variations in initial molecular weight and in degree of cross linking. For example, a low-unsaturation and a high-unsaturation vulcanizate (the latter from a fraction of much lower molecular weight) which show identical stress-strain curves up to 400% elongation, as indicated by their moduli at 300% in the tables, do not reach 500 pounds per square inch at the same elongation. A lower elongation is required for the latter. Observations such as these are further indications of the fact that the stress-strain curves in general are not rendered superimposable throughout all elongations by adjusting their stress scales by suitable factors. It is apparent that the "modulus" up to 400% elongation and the position of the steep rise in the stress-strain curve depend in different manner on the structure of the vulcanizate.

Butyl, like natural rubber, becomes crystalline on stretching. As would be expected, it shows the same crystal pattern (*12*) with x-rays found for polyisobutylene and analyzed by Fuller and coworkers (*15*). In pure-gum vulcanizates of good-quality unfractionated Butyl the first vestiges of a crystal pattern become apparent in the x-ray diagram at elongations in the neighborhood of 500%. A smaller degree of crystallinity, not detected by x-ray diffraction, may occur at somewhat lower elongations.

Field (*4*) showed that the x-ray diagram acquires the characteristic oriented fiber pattern coincident with the increase in slope in the stress-strain curve of natural rubber gum vulcanizates. The degree of crystallinity which he computed from the x-ray patterns increases rapidly in this region. The percentage of crystalline polymer approaches an asymptotic value (around 80%) which changes little with further elongation over the subsequent fairly linear portion of the stress-strain curve extending to the breaking point. Results of Dart and Guth (*3*) on thermoelastic effects in the fast stretching of Butyl supply further evidence for the rapid acquisition of crystallinity at high elongations. Unfortunately their results did not include suitable stress-strain curves for comparison.

The pronounced upward curvature in the stress-strain curves for Butyl in the region of 400 to 700% elongation, depending on the sample, is doubtless due to the occurrence of crystallization. The final steep ascent of the curve just beyond this region and extending to the breaking point indicates a high degree of crystallinity. In the light of Field's results on natural rubber, we consider that over this almost linear portion of the curve the degree of crystallinity remains almost constant at a value near its asymptotic limit. The similarity in the slopes of the curves in this region suggests roughly similar degrees of crystallinity in different samples. (It is not meant to suggest, however, that they are quantitatively the same regardless of structure.) The elongations at 500 pounds per square inch are considered to represent the points at which about the same (high) degree of crystallinity is developed in different Butyl vulcanizates.

Crystallization would be expected to depend on the average degree of orientation produced by elongation. For chains which exist in more or less random configurations when the network is not deformed, it can be shown that the average degree of alignment produced by a given elongation will be greater, the lower the average length of the chain, M_c. Hence, it is to be expected that, with greater degrees of cross linking, crystallization will set in at lower elongations. The results agree with this deduction. Even when comparison is made between low- and high-unsaturation polymers having molecular weights such that the numbers (γ) of cross-linked units per primary molecule are about the same, the latter are found to undergo crystallization, as indicated by the point at which the tension reaches 500 pounds per square inch, at lower elongations (Tables VI and VII).

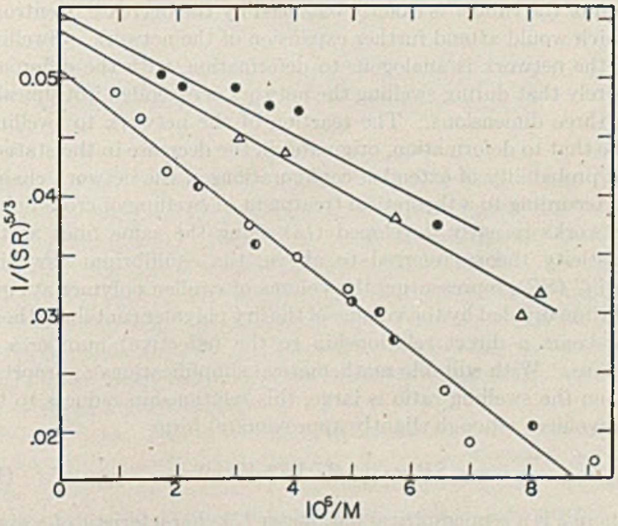


Figure 8. Reciprocal of the 5/3 Power of Swelling Ratio *vs.* Reciprocal of M or $\overline{M}_n$

○ Low unsaturation fractions
◐ Mixtures of low-unsaturation fraction
◑ Unfractionated polymer II-A
△ High-unsaturation fractions from polymer IV
● High-unsaturation fractions from polymer V

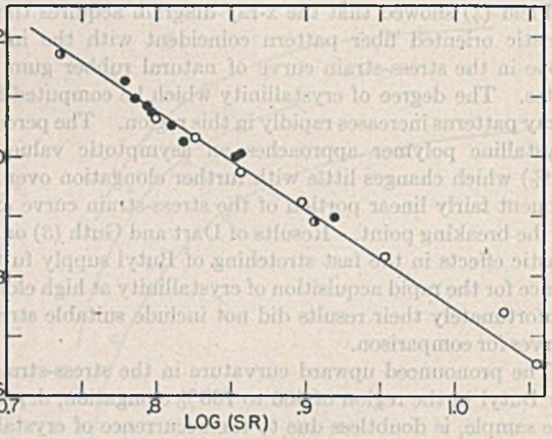


Figure 9. Log-Log Plot of Modulus at 300% Elongation *vs.* Swelling Ratio

○ Low-unsaturation fractions
◑ Unfractionated polymers
● High unsaturation fractions

The increase in the elongation for incipient crystallization with decrease in molecular weight is believed to arise mainly from the concurrent increase in the proportion of terminal chains (Equation 9). These are not subject to permanent orientation when the rubber is stretched; hence, they are not likely to enter into crystallite formation. They can be expected to act like amorphous diluents which not only are themselves reluctant to enter into crystallite formation, but which also repress crystallization of the remainder of the structure. In addition, the average lengths of the elastically effective chain elements of the structure will be increased somewhat, owing to other types of network "flaws" (*5*), as *M* decreases. This factor will also tend to decrease the average orientation at a given elongation, for the reason given in the preceding paragraph.

EQUILIBRIUM SWELLING OF VULCANIZATES

Relationship of Swelling Capacity to Vulcanizate Structure. When a vulcanized rubber is placed in a liquid of similar chemical composition, the former absorbs the latter until a state of equilibrium is reached between swollen rubber and supernatant excess liquid. At this point the gain in entropy afforded by further dilution of the rubber is exactly balanced by the decrease in entropy which would attend further expansion of the network. Swelling of the network is analogous to deformation, with the difference merely that during swelling the network is extended isotropically in three dimensions. The reaction of the network to swelling, like that to deformation, originates in the decrease in the statistical probability of extended configurations of the network chains.

According to a theoretical treatment of swelling of cross-linked networks recently developed (*14*) along the same lines as the elasticity theory referred to above, the equilibrium "swelling ratio" (*SR*), representing the volume of swollen polymer at equilibrium divided by the volume of the dry polymer contained therein, bears a direct relationship to the (effective) number ν of chains. With suitable mathematical simplifications appropriate when the swelling ratio is large, this relationship reduces to the convenient (though slightly approximate) form

$$SR = [(1-2\mu)V/2\nu V_1]^{3/5} \tag{18}$$

where μ is a semiempirical parameter (*7*) characteristic of a given solvent-solute pair, and V_1 is the molar volume of the solvent. Substituting from Equation 15 for the "corrected" number of chains, ν, exactly as was done in deducing Equation 16,

$$(1/SR)^{5/3} = \left[\frac{2\rho V_1}{(1-2\mu)M_c}\right](1 - 2M_c/M) \tag{19}$$

The similarities of this equation to 16 are apparent; taking $(1/SR)^{5/3}$ as the analog of the retractive force of Equation 16, both quantities depend inversely on M_c and directly on the same correction factor for finite molecular weight.

Swelling ratios in cyclohexane at 25° C. for various vulcanized Butyl fractions and mixtures of fractions are included in Tables VI and VII. In Figure 8 $(1/SR)^{5/3}$ is plotted against $1/M$, or $1/\bar{M}_n$ for the heterogeneous polymers. The points for the low-unsaturation polymers describe a straight line, in accordance with Equation 19. The mixtures of fractions, and unfractionated polymer II-A as well, fall on the same line when their number averages are employed, showing that swelling, like modulus, also depends on this average explicitly. The points for high-unsaturation polymers IV and V again are sufficient only for locating approximate lines through them. The equations of the lines drawn in Figure 8 follow: For the low-unsaturation polymers,

$$(1/SR)^{5/3} = 0.0506\ (1 - 78{,}000/M) \tag{19A}$$

For polymer IV,

$$(1/SR)^{5/3} = 0.0540\ (1 - 52{,}000/M) \tag{19B}$$

For polymer V,

$$(1/SR)^{5/3} = 0.0556\ (1 - 47{,}000/M) \tag{19C}$$

The values of M_c indicated by these equations (39,000, 26,000, and 23,500, respectively) are in good agreement with those previously deduced. The first coefficients of these equations, like those of 16A, B, and C, do not agree with theory in that they do not vary in proportion to $1/M_c$. The previous explanation advanced for the similar anomaly in the "modulus" values should be equally applicable here.

Relationship between Modulus and Swelling. Since the "modulus" and the swelling ratio are similarly related to the structure variables M_c and M, they can be related directly to one another. Combining Equations 16 and 19 for this purpose,

$$\tau_\alpha = RT(1 - 2\mu)\varphi(\overline{\alpha})/2V_1(SR)^{5/3} \tag{20}$$

Table VIII. Tensile Strengths of Low-Unsaturation Butyl Fractions (Cured at 307° F.)

Polymer Fraction	$M \times 10^{-3}$ (after Compounding)	Cured 30 Min.[a] Tensile strength, lb./sq. in.	Cured 30 Min.[a] Elongation, %	Cured 60 Min.[a] Tensile strength, lb./sq. in.	Cured 60 Min.[a] Elongation, %
		Pure-Gum Cures			
I-1	1080	4750	950	4400	975
I-2	730	4100	950	4350	975
I-3	690	..	..	4200	1050
I-4	650	4300	1075	4100	1025
I-5	555	4325	1000	4425	975
II-2	390	..	..	4300	1025
II-3	310	3625	1050	3875	1000
II-4	285	3580	1075	3580	1025
II-5	245	2950	1090	..	..
III-1	245	2560	1075	2950	1090
III-3	210	..	..	3150	1000
II-7	202	2850	1050	3200	1050
III-4	185	2200	1150	2850	1100
II-9	152	650	1100	1450	1050
II-10	152	..	..	1700	1050
III-6	143	1650	1100	1700	1025
II-13	108	..	..	89	825
III-8	108	52	770	130	825
III-10	85	..	..	110	950
III-11	81	..	..	50	775
		Fractions Compounded with 50 Parts of Black[b]			
I-4	715[b]	3400	800	3420	775
II-2	410	3340	800	3450	785
II-6	285	2850	900	2900	850
III-2	265	..	..	3000	825
II-8	172	2390	800	2840	800
III-5	168	2300	..	2650	850
III-7	116	850	800	1960	900
III-9	94	..	..	940	700
III-12	57	..	..	145	500
III-15	42.5	..	..	67	400
III-18	25.8	..	..	Uncured (sol.)	

[a] Tensile strengths and ultimate elongations represent mean values obtained with two or more dumbbells from the same cure.

[b] Intrinsic viscosities could not be run on the compounded sample due to partial insolubility resulting from carbon black.

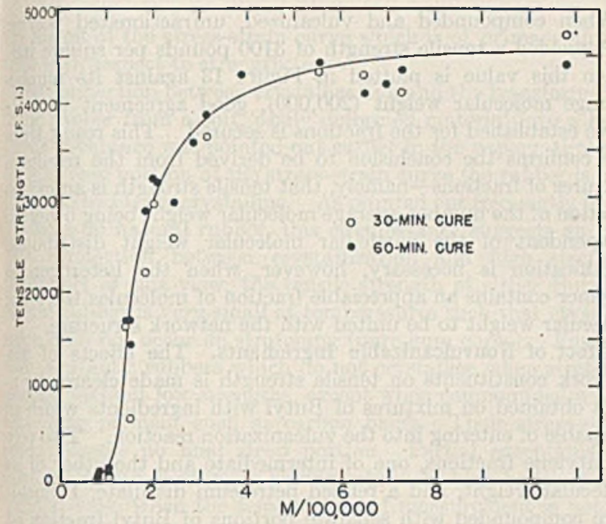


Figure 10. Tensile Strength of Pure-Gum Vulcanizates of Low-Unsaturation Fractions *vs.* Molecular Weight

i.e., the tension at a given elongation is predicted to be inversely proportional to the $^5/_3$ power of the swelling ratio. The existence of some sort of inverse relationship between modulus and swelling capacity has been recognized for some time. Scott (*26*), for example, pointed out that, for a series of cures of natural rubber, the maximum in modulus and the minimum in swelling coincide.

To demonstrate the quantitative significance of Equation 20, the "modulus" at 300% elongation is plotted in Figure 9 against the log of the swelling ratio for various Butyl pure gum vulcanizates. The straight line has been drawn with the theoretical slope $-^5/_3$. The experimental points, which include Butyls differing in unsaturation, molecular weight, and molecular weight heterogeneity, agree satisfactorily with this theoretically predicted relationship.

The irregular deviations which occur are somewhat smaller in general than those in Figures 7 and 8, representing, respectively, the modulus–molecular weight and the swelling ratio–molecular weight relationships. The greatest single source of error in this work is believed to have originated from a certain lack of reproducibility in the curing process. When the one physical property is compared with the other as in Figure 9, errors of this type do not appear—hence, the opportunity for the greater uniformity of results exhibited here.

The experimental confirmation of Equation 20 furnishes proof that the structural factors responsible for the elastic retractive force are quantitatively the same as those which operate in controlling the degree of swelling. Exactly the same cross linkages and entanglements which are operative in elastic deformation are also effective in limiting the equilibrium degree of swelling in the presence of solvent. Hence, their existence cannot depend on van der Waals interactions, which would certainly be overcome by the swelling agent.

By comparing the equation of the line in Figure 9,

$$\log \tau_{300} = 3.41 - 1.67 \log (SR)$$

with theoretical Equation 20, μ is found to be 0.30. This is less than the value 0.42 (*5*, page 72) obtained from osmotic pressure measurements on dilute solutions of polyisobutylene in cyclohexane (*7*, *11*).

TENSILE STRENGTHS

Fractions of Low Unsaturation. Table VIII gives tensile strengths for pure-gum cured fractions from Butyl polymers I, II, and III. The molecular weights in the second column have been computed from the intrinsic viscosities after compounding (Table II). Vulcanizates prepared from fractions below a molecular weight of 75,000 were too fragile to be removed from the molds. At a molecular weight of 100,000 the tensile strength (60-minute cure) is roughly 100 pounds per square inch. Tensile strength increases rapidly with increase in molecular weight immediately above 100,000, reaching 1500 pounds per square inch at about 150,000, and 3000 pounds per square inch at about 200,000 molecular weight. Proceeding to higher molecular weights, the tensile strengths increase more gradually, approaching what appears to be an asymptotic value well above 4000 pounds per square inch at molecular weights beyond 400,000. Figure 10 shows these results.

There is little difference between the 30- and 60-minute cures. In the low-molecular-weight range, tensile strengths of the former fall below those for the longer cure, but at high molecular weights the tensile strengths for the 30- and 60-minute cures are indistinguishable.

Corresponding results for some of the low-unsaturation fractions compounded with 50 parts of carbon black according to the recipe given earlier in the paper are presented in the lower portion of Table VIII and in Figure 11. Above about 30,000 molecular weight the rubber was rendered partially insoluble by vulcanization. Tensile strength is developed at lower molecular weights than for the pure gum vulcanizates, 100 pounds per square inch being reached at a molecular weight of about 50,000 on the 60-minute cure. A tensile strength of 300 pounds is again approached at a molecular weight of about 200,000, but at higher molecular weights the tensile strengths are considerably lower than those obtained with the pure gum recipe.

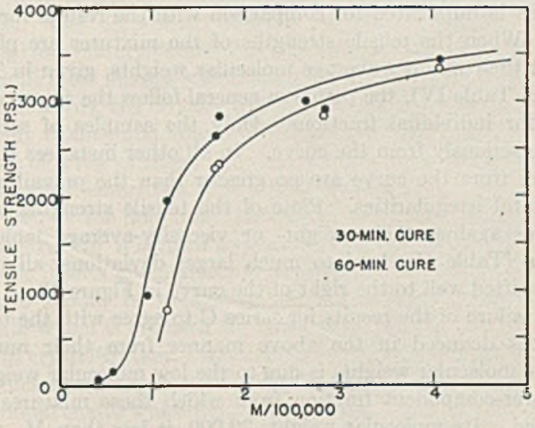


Figure 11. Tensile Strength of Low-Unsaturation Vulcanizates Containing 50 Parts Carbon Black *vs.* Molecular Weight

Fractions of High Unsaturation. Table IX and Figure 12 give tensile strengths and ultimate elongations for cured fractions from polymers IV and V. The onset of measurable tensile strength occurs at a lower molecular weight than for the low-unsaturation Butyls; tensile strengths of 100 pounds per square inch are acquired in the vicinity of 60,000 molecular weight, as compared with 100,000 for the low-unsaturation polymers. The tensile strength curve then rises somewhat less abruptly with increasing molecular weight.

The ultimate tensile strengths attained at high molecular weights are definitely lower than for the low-unsaturation polymers. Results for polymer V fractions point to slightly higher strengths at lower cures in the region of high molecular weights. The deficiency of the tensile strengths of these polymers as compared with the low-unsaturation series cannot, however, be entirely overcome by undercuring. Other experiments not reported here, in which polymers of higher unsaturation than polymer V were included, demonstrate that at the same (high) molecular

TABLE IX. TENSILE STRENGTHS OF HIGH-UNSATURATION FRACTIONS (PURE-GUM CURES)

Polymer Fraction	$M \times 10^{-3}$ (after Compounding)	Time of Cure, Min. at 307° F.	Tensile Strength[a], Lb./Sq. In.	Elongation[a], %
V-1	580	15	3800	925
		30	3500	850
V-2	480	15	3900	925
		30	3400	850
V-3	400	15	3500	960
		30	3450	850
IV-1	330	40	3700	900
V-4	280	30	2970	900
IV-2	250	20	3000	1000
		40	3300	925
V-5	245	15	2200	925
		30	2950	890
IV-3	175	20	2680	990
		40	2800	1000
V-6	155	30	2400	925
IV-5	122	20	1680	1040
		40	1800	925
IV-6	64	20	115	800
		40	150	750
V-7	60	30	200	700
V-8	48.5	30	Very weak vulcanizate[b]	
IV-7	46.5	40	Very weak vulcanizate[b]	

[a] The tensile strength and ultimate elongation figures represent mean values obtained with two or more dumbbells from the same cure.

[b] Vulcanizates too fragile to be removed undamaged from the mold.

weight an increase in diolefin content beyond 1.0% decreases the tensile strength, regardless of degree of cure.

Heterogeneous Mixtures of Fractions. Table X lists tensile strengths and ultimate elongations for mixtures of low-unsaturation fractions, prepared as discussed in connection with Table IV. In Figure 13 the curve previously drawn in Figure 10 to represent the tensile strength–molecular weight relationship for individual fractions is duplicated for comparison with the results for mixtures. When the tensile strengths of the mixtures are plotted against their number-average molecular weights, given in Table X (from Table IV), the points in general follow the course of the curve for individual fractions. Only the samples of series C deviate seriously from the curve. In all other instances the departures from the curve are no greater than the prevailing experimental irregularities. Plots of the tensile strengths of the mixtures against their weight- or viscosity-average molecular weights (Table IV) lead to much larger deviations, all points being shifted well to the right of the curve in Figure 13.

The failure of the results for series C to agree with the tensile strengths deduced in the above manner from their number-average molecular weights is due to the low molecular weight of the lower-component fraction from which these mixtures were prepared. Its molecular weight, 30,000, is less than M_e, which according to the previous estimates is about 37,000 in low-unsaturation vulcanizates. A considerable proportion of these molecules consequently survive the vulcanization process without acquiring any cross linkages. These molecules exist as diluents dispersed in the network structure. It cannot be expected that their influence on physical properties would be equivalent to that of components which "co-vulcanize" with the network structure.

Confirming the predicted partial nonreaction of the low-molecular-weight constituent in these mixtures, the soluble material extractable (with cyclohexane) from vulcanizates C-2 and C-3 was exceptionally high—9.5 and 16.1%, respectively. These figures correspond to 47.5 and 46%, respectively, of the total amounts of the low-polymer constituents in the vulcanizates. Taking M_e as 37,000, the average number, γ, of cross-linked units per primary molecule of the lower constituent becomes 0.81. The fraction of these molecules devoid of cross-linked units will be given, therefore, by $\exp(-0.81)$, or 0.45. Practically all of the cross-linked molecules will be bound to the network, as a consequence of the preponderance of the constituent of higher molecular weight. Hence, the percentage of the lower constituent which remains soluble should be about 45. The observed percentages are in good agreement with this figure.

When compounded and vulcanized, unfractionated polymer II-A yielded a tensile strength of 3100 pounds per square inch. When this value is plotted in Figure 13 against its number-average molecular weight (200,000), good agreement with the curve established for the fractions is secured. This result therefore confirms the conclusion to be derived from the results on mixtures of fractions—namely, that tensile strength is an explicit function of the number-average molecular weight being otherwise independent of the particular molecular weight distribution. Qualification is necessary, however, when the heterogeneous polymer contains an appreciable fraction of molecules too low in molecular weight to be united with the network structure.

Effect of Nonvulcanizable Ingredients. The effects of non-network constituents on tensile strength is made clearer by results obtained on mixtures of Butyl with ingredients which are incapable of entering into the vulcanization reaction. Two polyisobutylene fractions, one of intermediate and the other of low molecular weight, and a refined petroleum distillate, Primol-D, were compounded with separate portions of Butyl fraction I-3. Table XI lists the compositions of these mixtures, their tensile strengths, and ultimate elongations. The nonvulcanizable ingredients were almost quantitatively extractable.

The outstanding result in Table XI is the independence of the tensile strength on the molecular weight of the added nonreactive ingredient; regardless of whether polyisobutylene of 150,000 molecular weight or Primol-D with a molecular weight of only a few hundred is employed, the same tensile strength, within experimental error, is observed for the same weight percentage of nonvulcanizable ingredient. In view of this result it is obviously impossible to include non-network ingredients in the number-averaging rule given earlier.

DISCUSSION OF TENSILE STRENGTH RESULTS

No adequate theory of tensile strength in high polymers exists at present. Proceeding from a phenomenological point of view, it is noteworthy that in Butyl, as in natural rubber, relatively little tension is developed until high elongations are reached, whereupon there is an enormous increase in stiffness, the tension rising rapidly with further elongation. The rubber acquires to a considerable degree the characteristics of a textile fiber. (The tensile strengths of the best fibers of silk and cellulose are in the range 50,000 to 100,000 pounds per square inch. Butyl fractions of high molecular weight register tensile strengths of over 40,000 pounds based on the cross section at break.) Obviously, it is

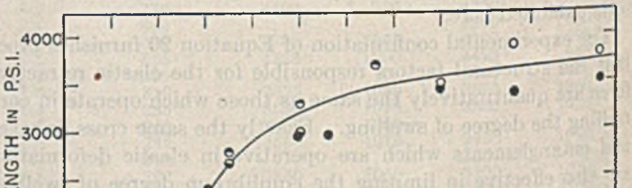


Figure 12. Tensile Strength of Pure-Gum Vulcanizates of High-Unsaturation Fractions vs. Molecular Weight

◒ Polymer IV, 20-min. cures
◓ Polymer IV, 40-min. cures
○ Polymer V, 15-min. cures
● Polymer V, 30-min. cures

this region of the stress-strain curve which is of primary importance with respect to strength.

The connection between crystallization and the transformation of the rubber from a soft, easily deformed material into a hard, fibrous substance was pointed out earlier in the paper; throughout the steep portion of the stress-strain curve the rubber is considered to be highly crystalline. As pointed out frequently in the literature on natural rubber, this circumstance suggests an intimate connection between crystallization and high strength. In support of this view, the tensile strength of either Butyl or natural rubber is very small at temperatures such that crystallization does not occur on stretching (pure gum cures). Furthermore, synthetic rubbers which do not crystallize when stretched generally exhibit low strengths, except when compounded with a reinforcing pigment such as carbon black. Their stress-strain curves possess no final steep portion. Partial exceptions are found in certain elastomers having relatively high brittle points (alternatively, when the temperature of measurement is not far above the brittle temperature); they exhibit intermediate strengths, at the sacrifice, however, of high elongation. Their superiority in strength as compared with other noncrystallizing rubbers may be the result of embrittlement induced by stretching.

On considering the effects of deformation on the structure of the noncrystalline and "fluid" (as opposed to brittle) rubber, it is clear that the chains will easily slip from one configuration to another in whatever manner best alleviates the imposed stresses. Owing to the irregularity of the loose network structure, elongation inevitably induces widely varying degrees of orientation in various elements of the structure, with corresponding inequalities in the distribution of stresses among chains. Only a minute fraction of the chemical bonds in any particular section of the rubber need be broken in order to destroy the continuity of the network structure. Thus, in a given portion of the network structure, where the stresses borne by the chains happen to be excessively above average, breakage of only a few chemical bonds eliminates reaction (of this part of the network) to the applied stress. Thus, in effect, a relatively few bonds withstand the stress.

When elongation induces crystallization, oriented chains are bound together in crystallites. The aggregate lateral van der Waals forces between adjacent chains in the crystallites virtually eliminate longitudinal slippage of a chain relative to its neighbors within the crystallite (*22*, *23*), although there is relatively little resistance to lateral separation of the chains. Thus, crystallization improves orientation of portions of the chains entering the crystallites, and at the same time it impedes longitudinal slippage of the chains. An appreciable fraction of amorphous material remains, and conceivably rupture may eventually originate in these regions. However, many valence bonds must be broken to accomplish the onset of complete failure of the sample. The amorphous regions contain numerous "chains" leading from one crystallite to another, each crystallite functioning as a giant cross linkage which binds together ends of these chains. In other words, the stresses in the amorphous regions are borne by many chains, and failure of the sample cannot occur through rupture of a few of them. An extension of these arguments to a rubber which embrittles on stretching is obvious.

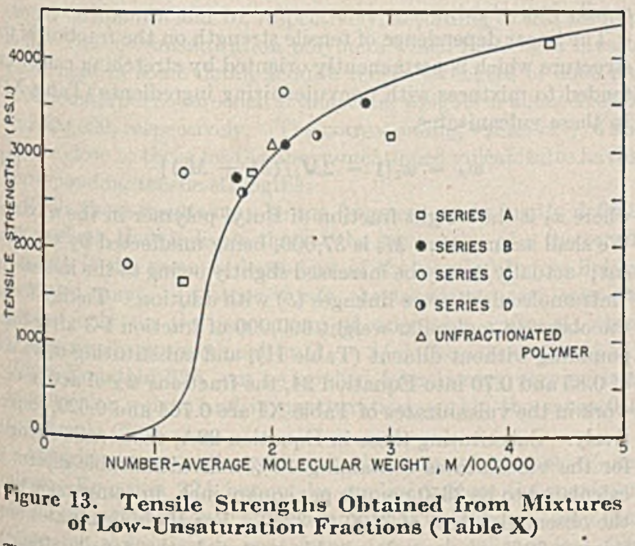


Figure 13. Tensile Strengths Obtained from Mixtures of Low-Unsaturation Fractions (Table X)

The curve is a duplicate of the one for homogeneous fractions in Figure 10.

Table X. Tensile Strengths of Mixtures of Low-Unsaturation Butyl Fractions (Pure-Gum Cures, 60 Minutes at 307° F.)

Designation[a]	% of Polymer of Lower Mol. Wt.	$\bar{M}_n \times 10^{-3}$ Calcd.[b]	Tensile Strength[c], Lb./Sq. In.	Elongation[c], %
I-3	0	805	4200	1050
A-1	10	435	4150	1025
A-2	20	300	3200	1025
A-3	40	183	2800	1075
A-4	65	124	1650	1100
III-10	100	85	110	950
II-2	0	410	4300	1025
B-1	25	280	3540	1025
B-2	50	210	3200	1060
B-3	75	171	2750	1060
II-10	100	143	1700	1050
II-1	0	635	..	..
C-1	10	210	3650	1000
C-2	20	126	2800	1075
C-3	35	79	1830	1100
III-17	100	30	0	..
I-6	0	580	4000	1025
D-1	40	240	3200	1050
D-2	65	175	2600	1100
II-11	100	127	..	..

[a] See Tables II and IV.

[b] Number averages calculated from molecular weights of the individual fractions before compounding. See the discussion of this point in the Experimental part of the paper.

[c] Tensile strengths and ultimate elongations represent mean values obtained with two or more dumbbells of the same cure.

In view of the dominant importance of crystallization in relation to strength, it seemed appropriate in the course of the analysis of the results given above to explore the postulate that tensile strength should be dependent on the proportion of the vulcanizate which is oriented by stretching and, therefore, susceptible to crystallization. According to Equation 9 the fraction of the vulcanizate occurring in principal network chains, exclusive of terminal chains which are not permanently oriented by stretching, is given by

$$w_A = 1 - 2M_c/(M + M_c) \tag{21}$$

If the molecules are heterogeneous in length, M is to be replaced by the number average $\bar{M}_n$ since it is the number of primary molecules which is of concern, as shown in the course of the derivation of Equation 9. The tensile strength could be expected, therefore, to depend explicitly on the number-average molecular weight, in accordance with observation.

If it is postulated further that the tensile strength should increase linearly with the fraction w_A of "active" network, then according to Equation 9 or 21 the tensile strength should decrease linearly with $1/(M + M_c)$, which is about equivalent to $1/M$ except when M is small. In Figure 14 the tensile strengths for the low-unsaturation fractions and their mixtures are plotted against $1/(M + M_c)$, M_c being taken equal to 37,000. The points are in surprisingly good accord with the postulated linear relationship. There is some indication of curvature, but this may not be beyond the experimental error. The equation of the straight line drawn in Figure 14 can be expressed:

$$\text{Tensile strength in pounds per square inch} = 5600\,[1 - 126{,}000/(M + 37{,}000)] \tag{22}$$

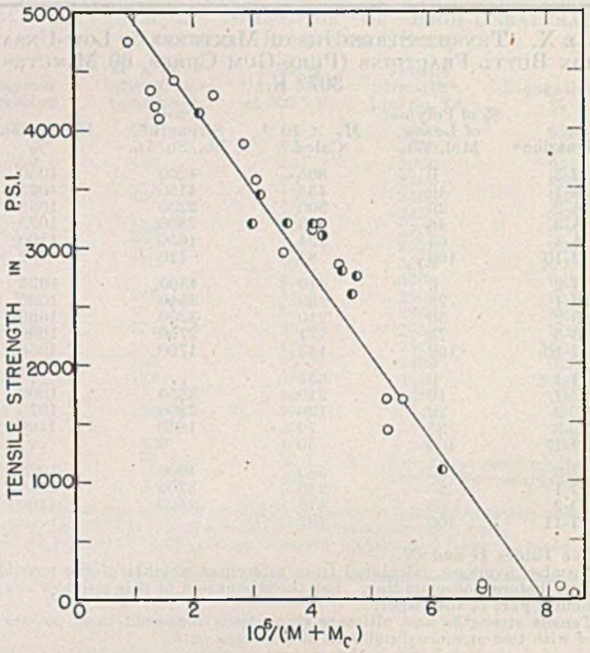


Figure 14. Tensile Strength of Low-Unsaturation Fractions and Mixtures after Pure-Gum Cure *vs.* $1/(M + M_c)$, or $1/(\bar{M}_n + M_c)$

○ **Fractions**
◐ **Mixtures of fractions**
◑ **Unfractionated polymer II-A**

A plot against $1/M$ is about equally satisfactory; i.e., within the limits of experimental errors the tensile strength varies linearly with the reciprocal of M or $\bar{M}_n$ at constant degree of cross linking.

The linear relationship between the fraction w_A of the material which is oriented by stretching is not a direct proportionality. If this were the case, the tensile strength would reach zero at $M = M_c$; the observed linear relationship extrapolates to zero at $M =$ 89,000 (Equation 22). At this molecular weight, according to Equation 21 with $M_c = 37{,}000$, $w_A = 0.41$; i.e., about 41% of the vulcanized polymer is subject to permanent orientation when stretched. If Equation 21 is incorporated into 22, again with $M_c = 37{,}000$, the tensile strength relationship can be expressed in terms of the fraction of orientable material as follows:

$$\text{Tensile strength} = 9540\,(w_A - 0.413) \tag{22A}$$

It is understandable that tensile strength should virtually vanish with decrease in molecular weight well in advance of the disappearance of the orientable fraction of the structure. The unoriented portion of the structure depresses the tendency of the oriented portion to crystallize on stretching. If the former somewhat exceeds the latter, rupture occurs before the material can be induced to crystallize by stretching. In Figure 5, for example, the stress-strain curve for the vulcanizate of 110,000 molecular weight shows no evidence of crystallization (as pointed out in the previous discussion of stress-strain curves at high elongations). Owing to the high proportion $(1 - w_A)$ of terminal chains, an excessive elongation presumably would be required to produce crystallization. Before such elongations are reached, however, sufficient stress is developed within the poorly constructed network to produce rupture. This occurs at an elongation of about 800%. The tensile strength of the material is only of the order of 100 pounds per square inch. For the development of appreciable strength a considerable fraction of the structure must be oriented by stretching.

The present tensile strength relationship should be applied literally only to vulcanizates which exhibit some vestiges, at least, of crystallization before they fail. This follows from the nature of the postulates introduced in the above quasi-theoretical treatment. It is obvious also that it cannot possibly apply in the molecular weight region below about 100,000; at an M of 89,000 the tensile strength is predicted to reach 0, but a polymer of lower molecular weight retains some strength, although it is very low—i.e., less than 100 pounds per square inch. As far as the above relationship is concerned, strengths of this order are negligible.

The numerical coefficients in Equations 22 and 22A doubtless will be altered by a change in temperature. At a lower temperature, for example, it is likely that appreciable tensile strength would be retained to lower molecular weights and, hence, to values of w_A less than 0.4, owing to the increased stability of the crystalline state.

The tensile strengths of cellulose acetate samples are similarly related to their molecular weights. In addition to finding that the tensile strength is an explicit function of the number-average molecular weight, Sookne and Harris (*27*) state that the tensile strength of a mixture of fractions can be deduced by weight averaging over the tensile strengths of the pure fractions; i.e., if $(TS)_1$ and $(TS)_2$ are the tensile strengths of the pure fractions, then the tensile strength of a mixture prepared from weight fractions w_1 and w_2 can be predicted from the equation:

$$(TS)_m = w_1\,(TS)_1 + w_2\,(TS)_2$$

It can be shown (*11B*) that these apparently contradictory statements are reconcilable only if the tensile strength is related to the molecular weight of a pure fraction in accordance with

$$TS = A + B/M \tag{23}$$

where A and B are constants. Equation 23 is equivalent to Equation 22 if $1/(M + M_c)$ is replaced by $1/M$. The tensile strengths of cellulose acetate, according to the results of Sookne and Harris (*27*), should therefore decrease linearly with $1/\bar{M}_n$.

This similarity between the tensile strength–molecular weight dependence for a rubber, on the one hand, and for a cellulose derivative on the other is striking; the one possesses a network structure and is capable of undergoing high elongation, whereas the other contains no primary valence network and elongates relatively little. Spurlin (*28*) suggested that failure in fibers under stress originates from the ends of molecules, which represent points of weakness in the structure. He concluded that tensile strength should depend in some manner on the number-average molecular weight. While the results on cellulose acetate are at least partially accounted for by this explanation, it fails completely if applied to the results on Butyl. Here it is the amount of nonorientable material rather than the number of ends of molecules, or number of terminal chains, which is primarily important.

The linear dependence of tensile strength on the fraction of the structure which is permanently oriented by stretching can be extended to mixtures with nonvulcanizing ingredients (Table XI). In these vulcanizates,

$$w_A = w_1[1 - 2M_c/(M + M_c)] \tag{24}$$

where w_1 is the weight fraction of Butyl polymer in the mixture. We shall assume that M_c is 37,000, being unaffected by the diluent; actually it may be increased slightly owing to the increase in "intramolecular" cross linkages (*5*) with dilution. Taking for M the observed molecular weight 690,000 of fraction I-3 after compounding without diluent (Table II), and substituting w_1 values of 0.85 and 0.70 into Equation 24, the fractions w_A of active network in the vulcanizates of Table XI are 0.764 and 0.629, respectively. Substituting these in Equation 22A, the tensile strength for the vulcanizates containing 15% nonvulcanizable diluent is calculated to be 3350 pounds per square inch, in comparison with the observed values of 3100 to 3250. For the vulcanizates containing 30% of nonvulcanizable material, the tensile strength calculated in this way is 2060, compared with the observed values in the range 2100 to 2250 pounds per square inch. The agreement is all that could be expected.

Evidently the tensile strength is depressed equally (on a weight or volume basis) by terminal chains and by ingredients which are not connected by chemical bonds to the vulcanizate network. These are indistinguishable in so far as their influence on tensile strength is concerned. It now becomes clear why the molecular weight of the nonvulcanizable ingredient exerts no effect on tensile strength.

Table XI. Tensile Strengths of Mixtures of Butyl Fraction I-3 with Polyisobutylenes and Primol-D (Cured 60 Minutes at 307° F.)

Added Constituent: Designation	$[\eta]$	$M \times 10^{-3}$	% of Mixt.	$[\eta]$ of Mixt., Calcd.	$[\eta]$ Obsvd. after Compounding	% Sol.[a] after Vulcanization	Tensile Strength, Lb./Sq. In.	Elongation, %
None added	..	..	..	2.18	1.98	..	4200	1050
Polyisobutylene (8–10)	0.75	150	15	1.96	1.79	15	3250	1050
			30	1.75	1.56	27	2250	1075
Polyisobutylene (18–25)	0.30	37	15	1.90	1.69	11	3100	1100
			30	1.62	1.47	25	2200	1100
Primol-D	..	..	15	1.85	..	..	3200	1100
	..	..	30	1.53	..	32	2100	1150

[a] Extracted 8 days with cyclohexane at room temperature.

Any diluent selected indiscriminately may not necessarily produce the same effect. If an appreciable heat change accompanies the mixing of diluent with network, partial segregation on the one hand, or association on the other, may be expected to modify the tensile strength. Specifically, a diluent which mixes endothermally with the polymer may be expected to reduce the tensile strength somewhat less than would an equal proportion of terminal chains, or of an "athermal" diluent such as one of those selected in Table XI. An exothermic diluent may effect a greater depression in the tensile strength owing to its tendency to associate with, or adhere to, the network chains and thereby suppress crystallization.

The molecular weights at which vulcanizates from the low- and high-unsaturation polymers begin to acquire strength are approximately in inverse proportion to the concentrations of cross linkages which they attain. For example, at molecular weights of 100,000 and 60,000, respectively, their tensile strengths reach 100 pounds per square inch; these figures are about in the ratio of their respective M_c values. In other words, the average number γ of cross-linked units per molecule required for the onset of appreciable strength appears to be about constant.

Other experiments not reported here have shown that a polymer fraction containing about 0.15 mole % of isoprene and for which M = 600,000 yielded a vulcanizate (using the above pure-gum recipe) with a tensile strength of about 3000 pounds per square inch. Another fraction containing 0.30 mole % isoprene and having the same molecular weight produced a vulcanizate with a tensile strength close to 4000 pounds. Assuming that the concentration of cross linkages varies directly as the concentration of diolefin (as indicated by certain results cited in the discussion of the structure of Butyl vulcanizates), the M_c values for these vulcanizates, by comparison with the low-unsaturation vulcanizates, should be about 120,000 and 60,000, respectively. The values of γ ($= M/M_c$) for these vulcanizates should be about 5 and 10, respectively, according to this assumption. The low-unsaturation polymers which have been investigated here in some detail acquire tensile strengths of 3000 and 4000 pounds per square inch at molecular weights of about 210,000 and 400,000, respectively. The corresponding values of γ, 6 and 11, are close to those for the above-mentioned vulcanizates having corresponding tensile strengths.

While these results may be too fragmentary to justify definite conclusions, they indicate that at the same value of γ the tensile strength is the same, independent of the degree of cross linking over this range. In other words, the tensile strength seems to depend only on the percentage of orientable material, which is very nearly proportional to $(1 - 2/\gamma)$ (Equations 9 and 21). Hence Equation 22A can be applied to polymers varying both in molecular weight and in unsaturation, within the range 0.15 to 0.5 mole %.

At higher unsaturations—i.e., in the range of 1.0 mole % and above—Equation 22A cannot be applied. Here the maximum tensile strengths reached at high molecular weights are lower than those for vulcanizates containing fewer diolefin units. The effect is greater in polymers containing 1.5 to 2.0 mole % or more of diolefin. The depression of the tensile strength with increase in the percentage of diolefin cannot be overcome entirely by undercuring; hence it must be attributed to the diolefin units themselves rather than to an excessive concentration of cross linkages. Presumably the failure of the isoprene units to fit into the polyisobutylene crystal lattice is responsible for this effect; i.e., they decrease the degree of crystallinity which can be achieved. It is rather surprising that this effect is noticeable with as little as 1 mole % of isoprene.

Little has been said concerning ultimate elongation values. For a given degree of unsaturation in the polymer, they increase with M to a maximum which occurs at an intermediate tensile strength, then decrease somewhat with further increase in M. If the molecular weight is high, crystallization sets in at a lower elongation, and the ultimate elongation is correspondingly lower. Vulcanizates from polymers of lower molecular weight stretch to high elongations before crystallizing, but rupture before they can be elongated much further. Owing to these competing factors, a maximum occurs in the elongation–molecular weight relationship. The ultimate elongation is decreased by an increase in degree of unsaturation for reasons which are obvious in the light of the earlier discussion of the high-elongation portions of the stress-strain curves.

The effect of carbon black is somewhat obscured by the lack of data bearing on the degree of breakdown which occurs during compounding with carbon black. Solubility data on vulcanizates from low polymers indicate that the degree of cross linking probably is not markedly affected by carbon black. Nevertheless, tensile strength is developed at considerably lower molecular weights in its presence.

Table XII. Creep of Butyl Vulcanizates at Constant Load

Polymer II-5, 21 Lb./Sq. In.		Polymer II-5, 42 Lb./Sq. In.		Polymer V-2, 44 Lb./Sq. In.	
Time, min.	$\alpha = L/L_0$	Time, min.	$\alpha = L/L_0$	Time, min.	$\alpha = L/L_0$
1/2	1.226_5	1/2	1.680	1	1.474_0
1	1.235_2	1	1.711	2	1.482_5
2	1.242_1	2	1.738	4	1.488_3
4	1.246_9	4	1.762	8	1.493_9
8	1.251_6	8	1.784	16	1.499_1
16	1.258_1	16	1.808	39	1.505_0
32	1.263_4	32	1.827	76	1.509_4
60	1.267_0	64	1.846	100	1.511_7
95	1.268_8	100	1.857		

This reinforcing effect disappears, in so far as tensile strength is concerned, as the molecular weight is increased. At the highest molecular weights the tensile strength is reduced, as compared with the pure-gum cures, by an amount which corresponds roughly to the volume percentage of the pigment. In other words, the strength of the black-loaded vulcanizate is about equivalent to the strength of the Butyl rubber in the vulcanizate, the pigment being considered to contribute nothing. There is no enhancement of tensile strength such as occurs when carbon black is in-

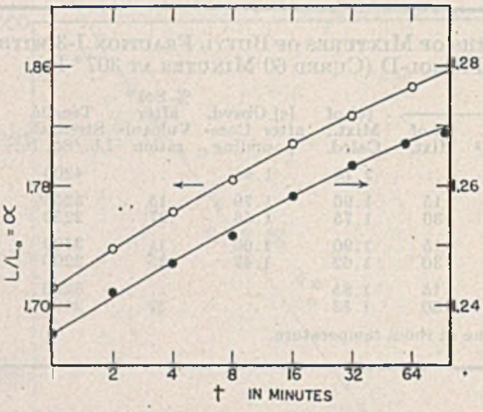


Figure 15. Typical Creep Measurements *vs.* Log of Time

corporated into natural rubber or other synthetic rubbers. Perhaps this situation is due to the low adhesion between polyisobutylene chains and the carbon black surface.

CREEP IN BUTYL VULCANIZATES

Table XII records typical creep measurements under constant load at 25° C. When relative length α is plotted against the log of time t as in Figure 15, the relationship observed is approximately linear, though not exactly so. Approximate linearity in this type of plot is generally found for creep measurements on rubber (*18*, *34*) and other polymeric materials (*19*, *21*). The degree of curvature for other samples and at various loads is about the same as for the examples shown in Figure 15. Inasmuch as the curvature is small and reasonably constant, the slope of this plot at 10 minutes has been chosen to express the creep rate.

The creep rate depends on the applied load in a rather complex manner. A better criterion for characterizing a given rubber is afforded by the relaxation constant, representing the rate of decrease in the tension at constant elongation. This quantity can be deduced from the creep rate as follows: We assume that G of Equation 11 is time dependent, and that φ depends only on α. Then at constant load τ,

$$d\tau = \varphi(\partial G/\partial \ln t)_\alpha \, d \ln t + G(\partial \varphi/\partial \alpha)_t d\alpha = 0$$

which rearranges to

$$(\partial \ln G/\partial \ln t)_\alpha = -(\dot{\varphi}/\varphi)(\partial \alpha/\partial \ln t)_\tau$$

where the derivative of φ with respect to α is written as $\dot{\varphi}$. Assuming φ to be represented approximately by Equation 9, the relaxation "constant" becomes:

$$(\partial \ln G/\partial \ln t)_\alpha = -\left[\frac{\alpha^3 + 2}{\alpha\,(\alpha^3 - 1)}\right](\partial \alpha/\partial \ln t)_\tau \qquad (25)$$

Table XIII presents values of the relaxation constant computed using this equation, from the slope at t = 10 minutes of curves such as those shown in Figure 15 and from α at 10 minutes. For a given sample the relaxation "constant" varies somewhat with initial elongation. It increases with increasing α up to about α = 2, then decreases as the load is further increased. In general, the values are sufficiently uniform to permit characterization of the sample by an interpolated creep constant at about α = 1.5 (last column of Table XIII).

When the network is rapidly deformed, terminal chains will be distorted into nonrandom configurations, much as are the chains bound at both ends to cross linkages. Unlike the latter, however, they are able to relax, owing to the fact that one end of each terminal chain is unattached, and are therefore free to "diffuse" to a new (statistically more probable) location. Hence, with the passage of time they will rearrange to random configurations, and their contribution to the force of retraction eventually will vanish. If observations are made at constant deformation, relaxation of the stress is observed; if at constant load, creep ensues.

The fraction, or number, of terminal chains for a given degree of cross linking is approximately inversely proportional to M, or to $\overline{M}_n$ if the polymer is heterogeneous (Equations 9 and 9A). If, in accordance with the previous discussion, creep in Butyl vulcanizates originates for the most part in terminal chains, the relaxation constant should be expected to increase with $1/M$. In Figure 16 the relaxation constants from the last column of Table XIII are plotted against $1/M$ or $1/\overline{M}_n$ in the case of heterogeneous polymers. The relaxation constant increases about linearly with $1/M$, a plausible result in the light of the previous discussion. In further confirmation of linear dependence of the relaxation constant on the number of terminal chains, heterogeneous polymers fall approximately in line with the results for fractions, number-average molecular weights being employed.

The extrapolated relaxation constants for infinite molecular weight are by no means negligible. Not all of the creep can be attributed to relaxations of terminal chains, of which there are none when M is ∞; some of it evidently arises from rearrangements in the configurations within principal chains.

Although their intercepts are similar, the slope of the curve for the polymers of low unsaturation is about 2.3 times that for the high-unsaturation polymers. If creep depended merely on the proportion of the vulcanizate occurring in terminal chains,

Table XIII. Summary of Creep Results at 25° C. Showing Dependence of Relaxation Constant on Molecular Weight

Polymer Fraction or Mixture	$M \times 10^{-3}$[a]	Ten-Minute Values: Load, Lb./Sq. In.	$\alpha = L/L_0$	$\frac{\alpha^3 + 2}{(\alpha^3 - 1)\alpha}$	$\left(\frac{d\alpha}{d \ln t}\right)_\tau \times 100$	Relaxation constant $\left(\frac{d \ln b}{d \ln t}\right)_\alpha \times 100$	Interpolated relaxation constant for α = 1.5
Low-Unsaturation Vulcanizates (60-Minute Cures)							
I-1	1080	21	1.221	3.82	0.31	1.19	1.25
		42	1.630	1.167	1.09	1.27	
		63	2.40	0.514	2.40	1.23	
I-4	650	20	1.224	3.76	0.39	1.47	1.7
		40	1.662	1.10	1.69	1.86	
		60	2.38	0.521	3.30	1.72	
		80	3.56	0.300	4.65	1.40	
II-3	310	21	1.276	2.96	0.72	2.13	2.20
		42	1.881	0.813	2.74	2.23	
II (5.5-6)[b]	275	21	1.254	3.26	0.77	2.50	2.7
		42	1.792	0.910	3.15	2.85	
II-7	202	20	1.329	2.43	1.39	3.38	3.4
		40	2.050	0.680	5.1	3.45	
A-2	300	..	1.595	1.242	2.37	2.94	2.9
D-1	240	..	1.514	1.462	2.26	3.30	3.3
D-2	175	..	1.375	2.09	1.94	4.05	4.05
II-A (unfractionated	200	20	1.315	2.56	1.17	3.00	3.15
		40	2.033	0.692	4.85	3.36	
High-Unsaturation Vulcanizates (30-Minute Cures)							
V-1	580	22	1.190	4.52	0.22$_6$	1.02	1.05
		44	1.504	1.495	0.70	1.05	
V-2	480	20	1.1925	4.46	0.25$_2$	1.12	1.19
		40	1.496	1.525	0.78	1.19	
V-4	280	22	1.2175	3.89	0.38	1.48	1.52
		44	1.644	1.14	1.36	1.55	
V-6	155	22	1.294	2.76	0.80	2.21	2.2
V-7	60	14	1.327	2.45	1.23	3.0	3.5
		22	1.545	1.37	2.72	3.7	

[a] Number-average molecular weights are given for mixtures of fractions and for the unfractionated polymer II-A.

[b] This particular fraction was not included in Table II.

irrespective of their average lengths, the slopes of these lines should be in the ratio of the respective M_c values—i.e., about as 1.7 is to 1. Apparently the relaxation constant depends also on the lengths of these chains which are free to relax.

SUMMARY AND CONCLUSIONS

In typical vulcanization of Butyl rubber with sulfur, zinc oxide, and thiuram accelerator, only 1 in about 3 of the diolefin units present is cross linked. When the same recipe is employed, this efficiency of utilization of diolefin units shows remarkably little variation over a wide range in diolefin content. The Butyl polymers with which most of the experiments were conducted, referred to as low-unsaturation Butyl, contained about 0.5 mole % of diolefin units. About 1 structural unit in 650 was cross linked during vulcanization of these polymers; the corresponding molecular weight, M_c, per cross-linked unit was about 37,000. Polymers of higher unsaturation (1.0 to 1.2 mole % diolefin) employed in some of the experiments gave vulcanizates in which M_c was 20,000 to 25,000.

Two types of chain elements of the network structure formed by cross linking the primary Butyl polymer molecules during vulcanization must be distinguished—principal or "active" chains, each of which represents the portion of a molecular chain extending from one cross linkage to the next, and terminal or "inactive" chains, extending from the end of a primary molecule to the first cross linkage along its length. The former are permanently oriented by stretching, the latter are not. Hence, only the principal chains contribute to general elastic properties. Likewise, only the principle chains are encouraged to crystallize when the sample is stretched. The unoriented terminal chains, of which there are two for each primary molecule, consequently are detrimental to strength. Physical properties can be quantitatively interpreted on the basis of this elementary concept of the essential structure of a typical rubber vulcanizate.

In accordance with statistical mechanical theories of rubber elasticity, stress-strain curves for various pure-gum Butyl vulcanizates are found to be similar in shape; up to about 400% elongation, one can be superimposed on another merely by altering the stress scale by a suitable factor. The factor of proportionality, G, expressing the force for a given elongation, depends on structure. According to previous theories, which take no account of network imperfections such as arise from the presence of terminal chains, G should be proportional to the number of chain elements—i.e., inversely proportional to M_c. Consideration of the influence of the finite molecular weight M of the primary molecules (in a more rigorous manner than the approach mentioned in the preceding paragraph might indicate) shows that G, and hence the "modulus" (tension) at a given elongation, should be proportional to

$$(1/M_c)\ (1 - 2M_c/M)$$

The latter factor represents the correction for network imperfections. The modulus at 300% elongation has been observed to vary linearly with the reciprocal of M when the degree of cross linking (and hence M_c) is held constant in accordance with this expression. From the slope of this relationship, M_c for the low-unsaturation polymers is estimated to be 37,000, in good agreement with the figure (35,000) estimated from the critical molecular weight for incipient gelation during vulcanization.

While the dependence of modulus on primary molecular weight M (before vulcanization) is in good agreement with theory, the magnitude of the observed modulus is several times greater than that calculated from theory. Furthermore, the modulus extrapolated to $M = \infty$ shows a much smaller change with degree of cross linking than the direct proportionality to $1/M_c$ predicted by theory. These observations are adequately explained by the assumption of network entanglements which impose additional restrictions on chain configurations.

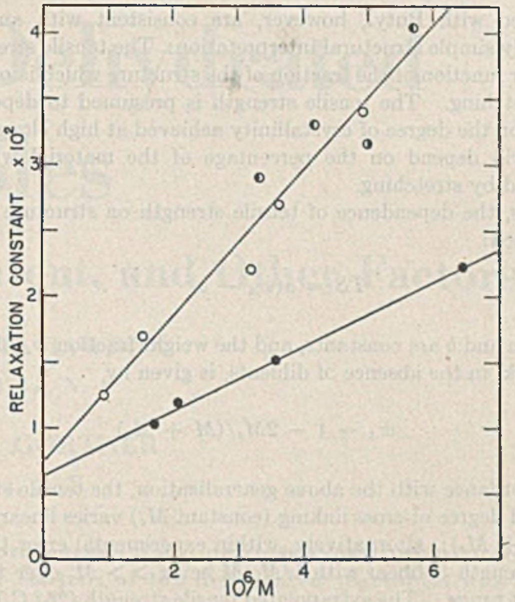


Figure 16. Relaxation Constant vs. Reciprocal of Molecular Weight (Pure-Gum Cures)

○ Low-unsaturation fractions
◐ Mixtures of low-unsaturation fractions
◑ Unfractionated polymer II-A
● High-unsaturation fractions from polymer V

Equilibrium swelling measurements in cyclohexane closely parallel the results on the force of retraction. Taking the swelling ratio SR to be the volume of the swollen vulcanizate divided by the volume of dry rubber before dilution with solvent, theory predicts that $1/(SR)^{5/3}$ should depend on the structure of the vulcanizate in the same manner as the modulus. This quantity, in analogy with the modulus, has been found to vary linearly with $1/M$. From the slope of this relationship an M_c value of 39,000 has been estimated for vulcanizates from the low unsaturation polymers. As further verification of the predicted similar dependences of swelling and modulus on vulcanizate structure, inverse proportionality between the modulus and the 5/3 power of the swelling ratio has been demonstrated for vulcanizates, regardless of primary molecular weight, molecular weight heterogeneity, and degree of cross linking. It is evident that the same cross linkages are effective, both in the response of the rubber to deformation and in its reaction to swelling. van der Waals forces, therefore, play no part in contributing to the effective degree of cross linking, and the same entanglements are operative in the swollen rubber as in the elongated, unswollen material.

At elongations above 400%, the precise region depending on the vulcanizate structure, the slope of the stress-strain curve increases rapidly, reaching a high value. Thereafter the curve continues with approximately constant (high) slope to the breaking point. It is in this part of the stress-strain curve that high tension is developed, and hence the ultimate strength is determined by the character of the rubber in this region.

The fairly abrupt rise in the stress-strain curve is believed to coincide with the occurrence of crystallization; over the final steep portion of the stress-strain curve the rubber is considered to be predominantly crystalline. An increase in degree of cross linking (decrease in M_c) causes crystallization to set in at a lower elongation, presumably owing to the greater alignment of the chains for a given elongation. A decrease in molecular weight M postpones the onset of crystallization toward higher elongations, owing to the increase in the proportion of nonoriented terminal chains which act as a diluent on the remainder of the structure.

Tensile strength ordinarily has been considered to be a most intractable property from a theoretical viewpoint. The results obtained with Butyl, however, are consistent with an unexpectedly simple structural interpretation: The tensile strength is a linear function of the fraction of the structure which is oriented by stretching. The tensile strength is presumed to depend directly on the degree of crystallinity achieved at high elongations. This will depend on the percentage of the material which is oriented by stretching.

Thus, the dependence of tensile strength on structure can be expressed:

$$TS = a(w_A - b) \tag{26}$$

where a and b are constants, and the weight fraction w_A of active network, in the absence of diluents, is given by

$$w_A = 1 - 2M_c/(M + M_c)$$

In accordance with the above generalization, the tensile strength at fixed degree of cross linking (constant M_c) varies linearly with $1/(M + M_c)$; alternatively, within experimental error the tensile strength is linear with $1/M$, M being $>> M_c$ over the significant range. The extrapolated tensile strength (25° C.) for infinite molecular weight ($w_A = 1$) is about 5600 pounds per square inch. The linear relationship with w_A extrapolates to zero strength when w_A is 0.4, although it is actually invalid below about 100 pounds per square inch; vulcanizates with such low strengths show no evidence of crystallization on stretching (before they fail), and presumably rupture occurs by a different mechanism.

The same linear relationship between TS and w_A appears to hold when M_c is varied by altering the proportion of diolefin in the polymer, provided it is not too high. The onset of appreciable tensile strength occurs when there are an average of about 3 cross-linked units per molecule, regardless of the lengths of the molecules. If the percentage of diolefin units is greater than about 1.0, the tensile strength when the molecular weight is large is depressed, owing, apparently, to the inability of the diolefin unit to fit into the polyisobutylene crystal lattice.

As further evidence for the generality of Equation 26, it is found to apply (with the same values of a and b) to vulcanizates which contain inert diluents not connected to the network, such as polyisobutylene or mineral oil; it is necessary in this case merely to let w_A represent the weight fraction of active network in the composition consisting of vulcanized Butyl and diluent. In other words, the diluent and terminal chains are quantitatively equivalent in their effects on tensile strength.

Relaxation rate constants have been computed from creep measurements on the Butyl vulcanizates. These also are approximately linear functions of $1/M$ when M_c is constant. The results extrapolate to appreciable, though small, relaxation rates for $M = \infty$. It has been concluded that most, but not all, of the relaxation (or creep) originates in rearrangements in the configurations of the terminal chains.

Heterogeneous polymers exhibit properties which in all cases coincide with those of a fraction for which M is equal to the number-average molecular weight $\overline{M}_n$ of the heterogeneous polymer. In other words, in each of the various relationships derived from experiments on vulcanized fractions it is necessary merely to replace M with $\overline{M}_n$ when dealing with heterogeneous polymers. This explicit dependence on number-average molecular weight agrees with expectations based on theoretical considerations, according to which each of the various properties depends on the number of terminal chains or on the number of primary molecules.

Although the experiments reported here have been confined to Butyl rubber, it is felt that similar relationships pertaining to "modulus", swelling capacity, and creep can be expected to apply to other vulcanized rubberlike materials. The tensile strength of Butyl, on the other hand, appears to be intimately related to the development of a high degree of crystallinity on stretching. In rubbers such as GR-S which do not possess this characteristic, there is no reason to anticipate that the tensile strength will vary linearly with w_A. A similar linear relationship probably would be expected to apply to natural rubber, however.

Finally it should be admitted that many of the measurements conducted in this investigation leave much to be desired from the standpoint of accuracy. With the application of more refined techniques, deviations from some of the relationships suggested by the present results probably will be observed. Some of these relationships may be presumed to represent first approximations only. At any rate, the results which have been secured justify the view that properties of rubberlike materials can be interpreted rationally and simply in terms of their structures.

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Commercially Dehydrated Vegetables

Oxidative Enzymes, Vitamin Content, and Other Factors

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Commercially dehydrated cabbage, Irish potatoes, and sweet potatoes were stored for one year under controlled conditions of temperature, moisture, and atmosphere. The fresh, blanched, and dehydrated samples were assayed for vitamin, oxidative enzyme, available iron, total copper, and moisture content. Similar analyses on the dehydrated samples were made several times during the storage period. The dehydrated cabbage and potato deteriorated rapidly as evidenced by loss of ascorbic acid, discoloration, and development of off-odor when stored above 70–80° F. and at moisture levels above 7% in the case of the white potato. At lower storage temperatures the products were more stable. No correlation between this deterioration and the oxidative enzyme content or iron and copper content of the dehydrated vegetables was found. All the vitamins assayed except ascorbic acid were fairly stable during storage. The use of sulfite in the blanch reduced the ascorbic acid losses in dehydrated cabbage during storage. However, thiamine was destroyed by the sulfite. There was no evidence of any significant amount of oxidative enzyme regeneration during the storage period. The data do not support the view that the storage deterioration of commercially dehydrated cabbage and potatoes may be due to the action of oxidative enzymes whose presence might arise from inadequate blanching or regeneration during storage.

DURING the past three or four years large quantities of dehydrated vegetables have been produced for the armed forces and for Lend-Lease distribution. In many cases these products deteriorated rapidly under the prevailing transport and storage conditions. There has been a marked tendency to attribute the deterioration to enzymatic activity remaining in the product after processing or to regeneration of the activity during the period of storage (*2*, *4*, *5*). This view was reflected in the fact that the army specifications for dehydrated vegetables called for a negative test for certain oxidative enzymes—i.e., peroxidase and catalase. However, little or no data are available which show a correlation between the deterioration of a dehydrated vegetable and the presence of a specific enzyme system. Because of the suspected oxidative nature of the changes observed in dehydrated vegetables, it was decided to investigate several oxidative enzyme systems rather than just peroxidase and catalase.

Deterioration in dehydrated vegetables is evidenced in several ways—e.g., a change in color, odor, taste, and vitamin content. Of these factors, vitamin content was chosen as a measure of deterioration because of its importance and capability of accurate measurement. In general, only the vitamins present in nutritionally important quantities in the raw vegetable were investigated.

The specific objectives of this joint investigation were, therefore, to determine if a correlation existed between enzyme content and nutritional deterioration, discoloration, and off-odor development observed during storage, and to investigate the possibility of enzyme regeneration during the storage period.

Samples were collected during actual commercial production at various dehydrating plants. The fresh and blanched material was collected in friction-top lacquered cans and quick-frozen by means of dry ice. The dehydrated product was collected in the containers used in commercial production. Cabbage was packed under nitrogen gas. Duplicate samples of each collection were packed in dry ice at the plant and immediately shipped to Columbia University for enzyme studies. Quick freezing of the fresh product was found to be highly unsatisfactory for protecting against vitamin losses during transportation from the manufacturing plant to the laboratory at Cornell University, where the vitamin assays were made. As a result, extracts of all fresh and blanched materials were prepared for vitamin analyses at the plant.

VITAMIN DETERMINATIONS

Reduced Ascorbic Acid. Suspensions of the fresh and blanched vegetables were prepared at the plant by blending with 6% metaphosphoric acid solution in a Waring Blendor. These suspensions could be transported to the laboratory for analysis as the ascorbic acid content was found to be stable for several days. Suitable aliquots of this mixture were diluted with water to make a 3% metaphosphoric acid concentration and filtered. In the case of the dehydrated product, it was first ground through a 20-mesh screen in a micro Wiley mill, extracted with 3% metaphosphoric acid, and filtered. The reduced ascorbic acid concentration of the filtered extracts was measured by a modified xylene method (*17*, *22*).

Riboflavin, Niacin, and Thiamine. Suspensions of the fresh and blanched vegetables were prepared at the processing plant by blending with 0.5 *N* hydrochloric acid in a Waring Blendor. The suspensions were transported to the laboratory and, the following day, were autoclaved for 15 minutes at 15 pounds pressure. The cooled mixtures were adjusted to pH 4.0–4.5 with sodium hydroxide; 4 ml. of a suspension containing 160 mg. each of takadiastase and papain were added, and the mixture was incubated for 12 hours at 37° C. The mixtures were filtered and made to volume, and aliquots taken for vitamin analyses. In the case of riboflavin and niacin the extracts were adjusted to a pH of 6.6–6.8.

Riboflavin was determined by the microbiological method of Snell and Strong (*20*). Niacin was determined by the method of Snell and Wright (*21*), as modified by Krehl *et al.* (*13*). Thi-

Table I. Manufacturers' Data on Samples

	Cabbage 1	Cabbage 2	White Potato	Sweet Potato
ty	Domestic	Mixed	Katahdin	Puerto Rican
Storage	None	None	Cellar	Sheds
Peeling	None	None	Contour steam	Caustic
Form of cut	Shredded	Shredded	Diced	Diced
Blanching				
Type	Hot SO_2 dip[a]	Steam	Steam	Steam
Time	30 sec.	3 min.	5 min.	5 min.
Drying				
Type	Cabinet	Tunnel	Tunnel	Tunnel
Time, hr.	5[b]	6	6[c]	6.5
Temp., ° F.				
Initial	....	170	210	240
Finishing	....	130	150	165
Final moisture, %	4.08	3.15	7.19[d]	5.57
Pack	CO_2	CO_2	Air	Air

[a] 0.5% sodium sulfite solution heated to boiling temperature.

[b] Conditioned in fiber drum for about 1 week, then redried to final moisture in cabinet dryer.

[c] Plus 24–48 hours in bin at 105° F. in the case of the potato sample with 7.19% moisture.

[d] 13.02% moisture after 6-hour tunnel drying.

amine was determined as the hydrochloride by the thiochrome method (*11*).

Carotene. The determination was carried out essentially as outlined by Moore (*16*). However, it was found necessary to rehydrate the ground sweet potatoes with water before extracting with alcohol; the ratio of water to ground dehydrated material was 4 to 1. Extracting the original material with 95% alcohol gave only about half the carotene value obtained when the material was first rehydrated with water.

ENZYME ASSAY

Preparation of Extracts. Cabbage samples were hand-ground in a mortar with water, pH 7.0 citrate-phosphate buffer (McIlvaine), and Berkshire sand. The mixture was then centrifuged, and the extract decanted and used immediately for enzyme assay. White potato and sweet potato extracts were prepared in McIlvaine buffer (pH 7.0) with a Waring Blendor since the dehydrated potatoes were extremely difficult to grind by hand. They were centrifuged and used immediately for enzyme assay. However, it was judged inadvisable to grind cabbage with the Blendor because the violent intermixing of air inactivated most of the ascorbic acid oxidase. To estimate the reproducibility of the extraction process, in addition to the quantitative activity values, an aliquot of the extract was dialyzed and the undialyzable solids were determined by evaporation to dryness at 80° C.

Qualitative Tests. Tests were made for peroxidase, catalase, catecholase, cresolase, and laccase activity prior to each complete enzyme assay, which included also ascorbic acid oxidase and lipoxidase. These qualitative tests in most cases were capable of detecting smaller amounts of enzyme activity than could be assayed quantitatively. Small specimens of the fresh, blanched, or rehydrated vegetable were placed in systems consisting of about 10 ml. of water, 1 ml. of McIlvaine pH 7.0 buffer, and 1 ml. of a 1% solution of the particular substrate in question. For peroxidase the substrates were benzidine, guaiacol, and catechol in the presence of about 0.01 *N* hydrogen peroxide. For catecholase, cresolase, and laccase the substrates were catechol, *p*-cresol, and hydroquinone, respectively. The detection of catalase was based on the evolution of bubbles of oxygen from the surface of the sample suspended in about 0.01 *N* hydrogen peroxide. With the exception of catalase, the presence of enzyme was detected by the development of colored reaction products at room temperature. Because of the susceptibility of the substrates to slow aerobic oxidation, colors appearing on the vegetable sample after standing for an hour were not considered positive tests.

Quantitative Tests. Peroxidase activity was estimated by a modification of the method of Balls and Hale (*3*). A reaction volume of 55 ml. was employed at 25° C. with atmospheric oxygen excluded by means of a continuous stream of nitrogen through the system, as used by Balls and Hale, but without the mineral oil layer. Aliquots for titration of hydrogen peroxide were withdrawn at varying intervals by a pipet which was filled by pressure of nitrogen on the surface of the reaction mixture.

Catalase was assayed manometrically by following the rate of evolution of oxygen from hydrogen peroxide at 25° C. and pH 7.0, in a volume of 8.0 ml. The less sensitive titrimetric method of von Euler and Josephson (*8*) was employed in a supplementary manner where relatively large amounts of the enzyme were found.

Ascorbic acid oxidase activity was estimated by the manometric method described by Lovett-Janison and Nelson (*14*); the use of gelatin was found to be unnecessary with the crude extracts. Laccase was determined by the manometric method of Gregg and Miller (*9*), and the cresolase activity of tyrosinase was assayed by the manometric method of Gregg and Nelson (*10*). The catecholase activity of tyrosinase was estimated according to the manometric method of Adams and Nelson (*1*). Although there are fundamental objections to the latter (*15*) as applied to purified tyrosinase, it is particularly suited to crude extracts containing small amounts of enzyme.

Lipoxidase assays were made by Sumner's colorimetric method (*23*), employing linoleic acid as substrate. Serious difficulty was encountered in the turbidity of the final solutions, particularly with extracts from dehydrated potatoes. This led to the development of a manometric method based on the oxygen absorbed during the enzymatic oxidation of linoleic acid. Details of this manometric method will be published later.

All enzyme assays were corrected for nonenzymatic catalysis by comparison with "boiled" controls. In no case was there significant nonenzymatic action in the controls.

Table II. Color and Odor Key

Color: Appearance	Symbol	Odor: Predominant	Symbol
Normal	0	Normal	0
Slight darkening	+	Haylike or sweetish	+
Definite darkening	++	Slightly toasted	++
Dark	+++	Toasted	+++
Very dark or black	++++	Burned	++++

The oxidative enzyme contents in the tables for the various vegetable samples are expressed in units of enzyme activity. The activity units are in each case proportional to the rate of the enzymatic reaction observed with specific substrates. In the case of peroxidase, the activity unit is based on the first-order rate constant during the peroxidase-catalyzed reaction between pyrogallol and hydrogen peroxide. For all of the manometric methods employed, the unit of activity corresponds to that amount of enzyme causing a rate of reaction of 10 cu. mm. of oxygen per minute. Because of the different enzyme-substrate systems and reactions involved, the use of a common manometric unit (i.e., 10 cu. mm. of oxygen per minute) does not necessarily indicate an equivalent amount of enzyme in each case. It should be particularly emphasized that the defined units of peroxidase, colorimetric lipoxidase, and the various manometrically measured activities differ by large factors in relative size; cross comparisons, therefore, generally cannot be made. All enzyme activities in the tables are expressed as units per 100 grams of sample calculated to a dry basis.

IRON, COPPER, AND MOISTURE

Chemically available iron was determined by the dipyridyl method of Hill (*12*) as modified by Elvehjem *et al.* (*7*), Shackleton and McCance (*19*), and Thierault and Fellers (*24*). In connection with the analytical methods for iron, one of the greatest sources of error was found to be in opening the cans. Most conventional can openers caused a flaking off of small particles of metal from the can which contaminated the contents. No single opener was found to be entirely satisfactory. The most successful for cans containing solid material is an opener that cuts a circular line along the side instead of from the top. In this manner the particles sheared from the can tend to fall outside instead of into the contents. This point should always be given consideration when mineral analyses are to be run on material stored in sealed cans.

The colorimetric diethyl dithiocarbamate method of Parks *et al.* (*18*) was used to estimate copper, after incorporating a number of modifications suggested by Ellis (*6*), including a dry ash at temperatures not exceeding 400° C. in the presence of magnesium nitrate. Because of the minute amounts of copper present and the experimental error involved in the total copper measurement, it did not seem advisable to attempt to differentiate total copper from so-called available copper.

Moisture was determined by the vacuum oven method of the Association of Official Agricultural Chemists, at a temperature of 70° C. and a time of 6 hours.

CABBAGE

The processing data obtained during the dehydration of the various vegetables are given in Table I. Table II is a key to the color and odor record.

The two series of cabbage samples were processed at different times; after collection both were stored at Cornell University in No. 1 cans under an atmosphere of carbon dioxide at various temperatures. These two cabbage series differed not only in the methods of blanching and dehydrating but also in the final moisture level of the dried product (Table I). The significance of the difference in variety cannot be evaluated from the data at hand.

Judging from the time of blanch and the moisture level of the dried product, cabbage series 2 might be expected to show the longer storage life if the deterioration during storage were largely due to enzymatic processes. It must be kept in mind that, at the time these studies were initiated, such enzymatic processes were thought to play a prominent part in the storage deterioration of dehydrated vegetables. However, cabbage 1 proved to have a longer storage life than cabbage 2. This conclusion is based on a comparison of the rates of deterioration of the two series as shown by the ascorbic acid data and color and odor record of Table III.

The enzyme data in Table III reveal that significant amounts of peroxidase, catalase, and tyrosinase (catecholase and cresolase) were initially present in both series; but after blanching, dehydration, and storage, only peroxidase remained in both series in measurably significant quantity. Values of less than 10 units of activity per 100 grams of dry matter are not experimentally significant in the cases of catalase, ascorbic acid oxidase, catecholase, cresolase, and laccase, all of which were measured manometrically. These data, coupled with the fact that the amounts of peroxidase present in the stored samples of both series were approximately equal, makes it clear that the noticeable type of storage deterioration in cabbage series 2 is not due primarily to oxidative enzymatic action. If one assumes that peroxidase action is the fundamental cause of deterioration, then the storage life of both cabbage series should have been about the same.

As a result of studies in numerous laboratories on the effect of gases in storage containers, an important role in the deterioration of dehydrated vegetables during storage has been ascribed to oxygen. For this reason it seemed possible that catalytic oxidations induced by metallic ions might be important, consequently chemically available iron and total copper contents were investigated. However, the available iron data were approximately the same in both cabbage series (Table III) and thus the longer storage life of cabbage 1 cannot be explained in terms of the iron content. Cabbage series 1, having the longer storage life, contained considerably more copper than did cabbage 2.

TABLE III. ANALYTICAL DATA ON FRESH AND COMMERCIALLY DEHYDRATED CABBAGE

Description of Sample	Moisture, %	Available Iron, Mg./100 G. Dry Matter	Vitamins, Mg./100 G. of Dry Matter: Riboflavin	Thiamine	Niacin	Ascorbic acid	Enzymes[a], Units/100 G. of Dry Matter: Peroxidase	Catalase	Ascorbic acid oxidase	Catecholase	Cresolase	Laccase	Physical Characteristics: Color	Odor
Sulfite-Blanched Cabbage, Series 1[b]														
Fresh	92.41	..	0.50	0.69	3.09	[c]	6.6	250	43	190	100	0	0	0
Blanched	94.29	10.6	0.32	0.33	2.43	345	..	50	0	70	20	0	0	0
Dehydrated	3.42	7.1	0.41	0.05	3.30	250	6.0	13	0	5	4	0	0	+
Dehydrated[d]	4.08	7.6	0.40	0.12	3.23	307	4.1	10	0	13	7	0	0	+
Stored 70–80° F.														
6 weeks	4.34	7.3	0.41	0.07	2.92	275	0.05	0	0	0	0	0	0	+
15 weeks	4.20	8.0	0.40	0.04	2.71	201	0.02	6	0	0	6	0	+	+
23 weeks	4.68	7.8	..	..	..	282	0.02	0	0	2	5	0	+	+
27 weeks	5.26	..	..	..	..	255	0.02	0	2	0	0	0	++	+
Stored 95–105° F.														
6 weeks	4.94	7.7	0.39	0.04	2.79	238	0.02	0	0	5	0	0	++	++
15 weeks	4.80	8.0	0.41	0.03	2.66	122	0.02	0	0	0	2	2	++	++
23 weeks	5.58	7.8	..	..	..	40	0.02	2	0	0	0	0	++++	+++
Steam-Blanched Cabbage, Series 2[e]														
Fresh	92.30	13.0	0.61	0.74	4.43	477	6.4	18,000	0	80	50	40	0	0
Blanched	93.00	5.8	0.48	0.63	4.20	380	0.02	50	0	40	30	50	0	0
Dehydrated	3.15	5.2	0.45	0.55	3.86	266	0.02	0	0	20	9	20	+	+
Stored 40–50° F.														
9 weeks	3.83	8.3	0.44	0.70	3.53	228	0.02	0	0	2	0	2	0	+
17 weeks	3.60	9.3	..	..	..	228	0.02	0	0	0	0	0	0	+
21 weeks	4.14	8.8	..	..	..	229	0.03	0	0	0	0	0	0	+
28 weeks	3.35	9.7	..	..	..	221	..	...	..	...	..	..		
46 weeks	3.69	10.2	..	..	..	250	0.03	5	0	2	2	0	+	+
Stored 70–80° F.														
9 weeks	3.48	10.7	0.41	0.66	3.73	235	0.02	0	0	7	0	0	++	++
17 weeks	3.94	7.8	..	..	..	223	0.03	0	0	2	2	0	++	++
21 weeks	4.53	7.2	..	..	..	228	0.03	0	0	0	0	0	+++	++
28 weeks	3.88	7.0	..	..	..	182	..	...	..	...	...	..		
46 weeks	4.10	8.0	..	..	..	205	0.01	0	0	2	0	0	+++	+++
Stored 95–105° F.														
9 weeks	3.79	11.6	0.46	0.69	3.67	131	0.02	0	0	0	0	0	++++	+++
17 weeks	4.53	8.3	..	..	..	50	0.01	0	0	0	2	0	++++	++++

[a] Lipoxidase also determined on all samples; values on the fresh material were so low as to be considered insignificant. Size of unit varies from enzyme to enzyme, cross comparisons are not valid.

[b] Total copper was also determined; values for all samples were of the order of 1 mg./100 grams dry matter.

[c] Sample was quick-frozen at plant and had an ascorbic acid value of only 59 mg./100 grams dry matter when analyzed 18 hours later.

[d] Sample taken from storage at plant, and studies continued on this sample. (Table I, footnote[b].)

[e] Total copper values for all samples were of the order of 0.3 mg./100 grams dry matter.

Table IV. Analytical Data on Fresh and Commercially Dehydrated Irish Potatoes (Steam-Blanched)

Description of Sample	Moisture, %	Mg./100 G. Dry Matter: Available iron[a]	Mg./100 G. Dry Matter: Ascorbic acid	Enzymes, Units/100 Grams of Dry Matter[b]: Peroxidase	Catalase	Ascorbic acid oxidase	Catecholase	Cresolase	Laccase	Lipoxidase	Physical Characteristics: Color	Physical Characteristics: Odor
Fresh	80.6	3.5	103	0.094	5100	17	490	850	47	5300	0	0
Blanched	80.1	3.5	51	0.000	2	0	0	2	0	0	0	0
Dehydrated												
A	20.7	...	25	0.000	0	0	0	2	2	0	0	0
B	13.0	3.8	20	0.000	0	0	0	2	2	0	0	0
C	7.2	2.9	18	0.000	1	3	1	1	1	6	0	0
B, stored 40–50° F.												
6 weeks	13.1	2.8	19	0.000	0	3	3	0	1	0	0	0
12 weeks	12.7	3.9	19	...	...	...	...	...	...	...		
30 weeks	14.1	3.1	14	0.000	1	1	1	0	0	0	+	0
B, stored 70–80° F.												
6 weeks	13.3	2.6	13	0.000	0	0	3	0	1	7	0	0
12 weeks	12.5	2.7	8	...	...	...	...	...	...	...		
30 weeks	14.0	3.1	5	0.000	0	2	0	0	0	0	++	+
B, stored 95–105° F.												
6 weeks	13.7	2.9	5	0.000	0	0	0	0	0	0	+++	++
12 weeks	13.1	4.4	7	...	...	...	...	...	...	...		
30 weeks	14.3	3.0	7	0.000	4	0	0	0	0	0	++++	+++
C, stored 40–50° F.												
6 weeks	7.2	2.7	13	0.000	0	4	1	1	0	0	0	0
12 weeks	6.2	3.2	12	...	...	...	...	...	...	...		
30 weeks	6.6	2.7	13	0.000	3	0	0	0	0	0	0	0
C, stored 70–80° F.												
6 weeks	7.1	2.6	12	0.000	0	10	0	4	0	0	0	0
12 weeks	6.2	3.4	14	...	...	...	...	...	...	...		
30 weeks	6.7	2.8	11	0.000	0	0	0	1	0	0	+	0
C, stored 95–105° F.												
6 weeks	7.0	2.6	11	0.000	0	4	3	0	1	3	+	0
12 weeks	6.2	5.8	13	...	...	...	...	...	...	...		
30 weeks	7.0	2.6	15	0.000	0	3	0	0	0	0	+++	+

[a] Total copper values for all samples were of the order of 0.9 mg./100 grams dry matter.
[b] Size of unit varies from enzyme to enzyme; cross comparisons are not valid.

Thus as with iron, the deterioration during storage probably cannot be ascribed to the action of copper.

Although there was a slight decrease in the riboflavin content of cabbage during the processing, there was no further loss in the dried product during storage up to about 4 months, even at 95–105° F. In the steam-blanched cabbage 2 there was likewise no significant loss of thiamine during storage. However, the use of sulfite during the blanching of cabbage in series 1 almost completely destroyed thiamine. Although there appears to be a tendency toward loss of niacin in dehydrated cabbage during storage, the data offer no evidence that this trend is associated with storage temperature.

Of most interest are the ascorbic acid data, which were used as an index of the rate of deterioration. As a matter of fact, the ascorbic acid content was the only nutritive, enzymatic, or metallic factor measured which correlated with storage deterioration as qualitatively indicated by the record of abnormal color and odor development. The effect of temperature on storage deterioration is clearly shown by the vitamin C data for both cabbage series; the higher the storage temperature, the more rapid the loss of ascorbic acid. However, in the sulfite-blanched cabbage the loss in ascorbic acid and the development of abnormal color and odor were less pronounced during storage at 95–105° F. than in cabbage 2, receiving a more drastic blanch. In series 2 almost 50% of the ascorbic acid content of the cabbage was lost during the blanch and dehydration process, but on storage at low temperature (40–50° F.) the vitamin C content remained constant for nearly a year.

WHITE POTATO

Table IV contains data on the storage of commercially dehydrated Irish potatoes. They had been in cool storage for about 5 months prior to dehydration. They were steam-blanched for 5 minutes and dehydrated to two different moisture levels, about 7 and 13%. One lot of potatoes, which was not stored, was dehydrated to 20.7%.

The fresh vegetable contained experimentally significant amounts of all enzymes, with the possible exception of ascorbic acid oxidase. After the 5-minute steam blanch, none of the enzymes (not even peroxidase) could be detected by qualitative tests. Of the quantitative enzyme data in Table IV, only those values recorded for the fresh vegetable are experimentally significant.

The available iron and total copper data are of no aid in fixing the cause of the deterioration noted during the storage periods. However, the total copper content of the potato samples was about the same as in the samples of cabbage 1, and the available iron content of the potato was much less.

About 50% of the ascorbic acid was lost during the blanch, and 50% of the remainder was lost during the dehydration process. In low-moisture series C the remaining ascorbic acid was considerably more stable during storage than in medium-moisture series B. Thus, when stored at 95–105° F., the 7% moisture sample became inedible in about 7 months, whereas the 13% moisture sample stored at the same temperature was undesirable as a food in a little over 1 month. The effect of storage temperature on the retention of ascorbic acid and the development of off-color and odor is particularly noticeable in medium-moisture series B. It seems likely that the low and practically constant values for ascorbic acid recorded for series B during the 30-week storage period at 95–105° F. may be largely due to the development of pigments having a dichlorobenzenone-indophenol titer.

SWEET POTATO

None of the dehydrated sweet potato samples tested (Table V) showed an experimentally significant quantity of enzymes, and no positive qualitative test was obtained in any case. The fresh and blanched vegetables were not available for assay, and the dehydrated samples were not placed under controlled storage until several months after they had been processed. Here, as in the case of the white potato, no definite conclusions can be drawn from the available iron and total copper content data.

Except for a slight difference in moisture level, the data in Table V reveal no significant difference between the two series even though series J was processed about 3 months before series A. The effect of storage temperature on deterioration is again evident from the ascorbic acid data; storage at 95–105° F. for about 4 months caused a 60% loss in ascorbic acid in both the A and J series. The same general effect of storage temperature is noted also in the carotene content, except that the carotene losses are much smaller than the ascorbic acid losses.

TABLE V. ANALYTICAL DATA ON COMMERCIALLY DEHYDRATED SWEET POTATO (STEAM-BLANCHED)

Description of Sample	Moisture, %	Available Iron[a], Mg./100 G. Dry Matter	Vitamins, Mg./100 G. Dry Matter		Enzymes[b], Units/100 Grams Dry Matter					
			Carotene	Ascorbic acid	Peroxidase	Catalase	Ascorbic acid oxidase	Catecholase	Cresolase	Laccase
J[c]	5.96	2.2	15.3	29.7	0.000	3	0	1	1	3
A[d]	5.57	3.4	14.8	28.3	0.000	1	1	0	3	3
J, stored 40–50° F.										
4 weeks	5.73	2.8	15.7	29.2	...	.	.	.	.	.
18 weeks	5.57	2.1	14.3	28.3	0.000	1	0	0	1	1
J, stored 70–80° F.										
4 weeks	5.74	4.7	16.0	25.6	...	.	.	.	.	.
18 weeks	5.74	2.7	12.4	21.4	...	.	.	.	.	.
J, stored 95–105° F.										
4 weeks	5.67	3.0	14.6	25.0	...	.	.	.	.	.
18 weeks	5.70	2.0	11.6	11.8	0.000	1	4	0	0	1
A, stored 40–50° F.										
4 weeks	5.96	2.8	15.7	30.3	...	.	.	.	.	.
18 weeks	5.63	2.1	14.3	28.3	...	.	.	.	.	.
A, stored 70–80° F.										
4 weeks	5.66	2.5	14.5	26.5	...	.	.	.	.	.
18 weeks	5.83	2.1	12.3	20.8	0.000	1	4	1	0	3
A, stored 95–105° F.										
4 weeks	5.76	4.2	14.1	22.2	...	.	.	.	.	.
18 weeks	5.64	2.2	11.1	12.2	0.000	0	0	3	1	0

[a] Total copper values for all samples were of the order of 0.6 mg./100 grams dry matter.
[b] Size of unit varies from enzyme to enzyme; cross comparisons are not valid. Lipoxidase values were so low as to be considered insignificant.
[c] Sample was dehydrated in January, received for storage studies in June.
[d] Sample was dehydrated in April, received for storage studies in June.

If any discoloration of the sweet potato occurred during the storage period of 18 weeks, it was largely masked by the deep orange color natural to the potato. However, after 4-week storage at 95–105° F. a marked haylike odor had developed which became more pronounced after 18 weeks.

ENZYME REGENERATION

No experimentally significant evidence was obtained showing enzyme regeneration during the storage period of any of the dehydrated vegetables. Values of less than 10 units of activity per 100 grams of dry matter are not experimentally significant in the cases of those oxidases measured manometrically. As a further check on the possibility of enzyme regeneration, all cabbage samples after original analysis were placed in storage at two temperatures (room and about −20° F.) and reanalyzed at a later date. These reanalyses were made after storage periods ranging from a few weeks to several months, but in no case was any significant evidence of enzyme regeneration obtained.

The data strongly suggest that, under existing commercial methods of blanching and dehydration, the problem of cabbage and potato deterioration during storage, as evidenced by loss in ascorbic acid and the development of off-color and off-odor, is not fundamentally an enzyme problem. That is, the rate of deterioration during storage was found to bear no relation to the oxidative enzyme content of the dehydrated vegetables. Only in the case of the two cabbage series was a significant amount of an oxidative enzyme (peroxidase) found after the blanch. Dehydrated vegetables containing no detectable amount of oxidative enzyme were found to be as likely to spoil as those containing small amounts of peroxidase. No evidence of enzyme regeneration during the storage period could be obtained. Furthermore the storage deterioration does not appear to be a problem of metal catalysis. The discoloration problem of dehydrated potatoes was particularly important because of the vast quantities processed for the armed forces.

There is no question but that some type of a blanch is required prior to the dehydration of vegetables containing peroxidase and phenolases; it is well known that these enzymes may cause rapid discoloration when the vegetable tissue is cut and exposed to air. The discoloration problem during peeling and dicing is serious with certain vegetables. However, it seems possible that the drastic blanching conditions frequently specified to remove the last trace of peroxidase activity may do more harm than good. Some support for this statement is found in the fact that cabbage series 2 having the more drastic blanch had the shorter storage life. It must be kept in mind, however, that the increased storage life of cabbage 1 was undoubtedly due in part to the presence of sulfite in the blanching solution.

Additional evidence that drastic conditions of blanching may do more harm than good has been obtained in the Columbia University laboratories in connection with work on the discoloration of dehydrated potatoes under contract with the Office of the Quartermaster General. It seems probable that during the blanch and possibly also during the drying process certain hydrolytic reactions are initiated, particularly when the blanch and dehydration are relatively drastic. Reactive chemical groupings thus liberated during processing may then bring about nutrient losses and color and odor changes during storage which are characteristic of deterioration. It seems clear that such chemical reactions during the storage period are not dependent on enzyme activity, at least of the oxidative type; the data in the tables show that the rate of deterioration is markedly dependent on storage temperature and moisture level.

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Molecular Weight–Physical Property Correlation for Petroleum Fractions

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Several correlations of molecular weight with physical properties are presented which cover the ordinary range of petroleum fractions. For fractions of 70–300 molecular weight (gasolines, kerosenes, light lubricating oils) boiling point and gravity are employed; the correlation gives good results for pure hydrocarbons of various types (average deviation 2.4% for 134 compounds) as well as for petroleum cuts. For lubricant fractions of 240–700 molecular weight correlations are described for viscosity with gravity and for viscosity at 100° with viscosity at 210° F.; the former are not, in general, applicable to pure hydrocarbons but give good results for most lubricant fractions, with the exception of Gulf Coast or California distillates above 350 molecular weight. With the use of a correction, the viscosity-gravity correlations give good results for these oils also. The correlation of viscosity at 100° with viscosity at 210° is in approximate agreement with the data for pure hydrocarbons of various types and gives good results for all types of petroleum fractions for which data are available. For petroleum waxes melting point and refractive index at 80° C. are employed; the correlation is in good agreement with the data for the *n*-paraffins as well as for petroleum waxes of various types.

THE experimental determination of molecular weight is time consuming and requires rather highly trained personnel. Therefore, it is desirable to obtain molecular weights for petroleum fractions from correlations with other physical properties which can be more easily and accurately determined.

The correlations presented here are of three types which cover the ordinary range of petroleum fractions: (*a*) molecular weight–boiling point–density for gasolines, kerosenes, and light oils (molecular weight range 70–300); (*b*) molecular weight–viscosity–density and molecular weight–viscosity at 100° F.–viscosity at 210° for oil fractions (molecular weight range 240–680); (*c*) molecular weight–refractive index–melting point for petroleum waxes (molecular weight range 240–560).

MOLECULAR WEIGHT–BOILING POINT–DENSITY

The correlation of molecular weight with specific gravity and boiling point is based on a curve presented by Smith (*27*), which shows the relation between reciprocal absolute boiling point and specific gravity for the various homologous series. Smith's work was primarily concerned with obtaining a constitution index for crude oil fractions. The relation of this graph to molecular weight, however, is quite clear.

Watson (*31*) presented a correlation of boiling point and density with molecular weight, but the derivation and statistical evaluation were not given. The boiling point–density correlation developed in this work is, for the most part, in close agreement with that of Watson. Our correlation, however, is based on true boiling points, and curves are given for correcting observed boiling points obtained in the A.S.T.M. distillation.

In our development of the correlation, pure compound data (*2*, *3*, *29*) were plotted on a graph of the type presented by Smith (Figure 1). Average molecular weight points were spotted and the lines of constant molecular weight were drawn which would agree well for most of the homologous series. The biggest deviation is found with the normal paraffins which always boil considerably higher than the average for any group of paraffin isomers. The molecular weight lines are adjusted to agree with the average paraffin data; therefore the correlation is not quite so good for normal paraffins as for most other compounds.

The above method of spotting constant molecular weight lines was adequate up to 150 molecular weight; however, the reliability of general pure compound data above this molecular weight is somewhat doubtful; therefore the following method

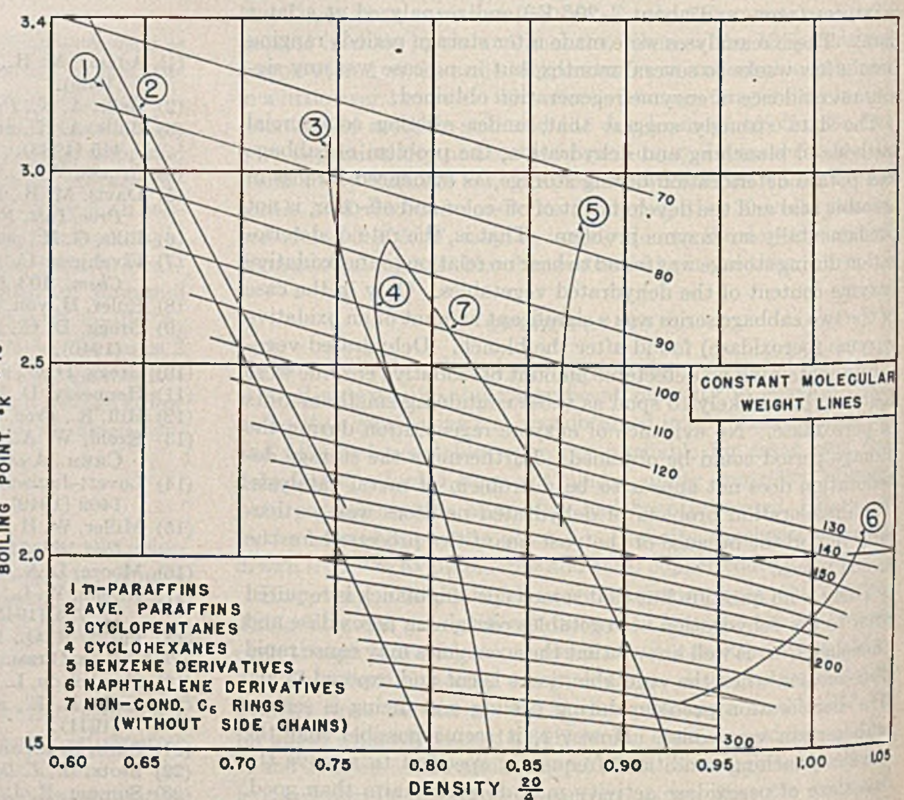

Figure 1. Reciprocal Boiling Point, Density, and Molecular Weight

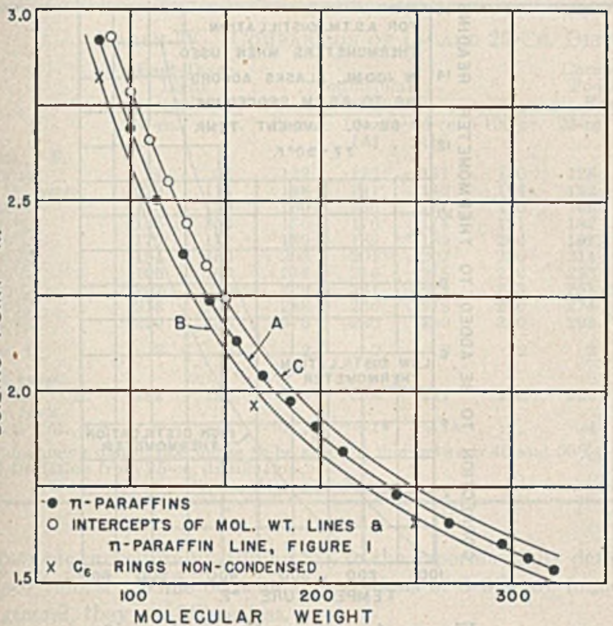

Figure 2. Reciprocal Boiling Point vs. Molecular Weight

was used. The relation presented in Figure 2 shows that, if reciprocal absolute boiling point is plotted against molecular weight for the normal paraffins, a smooth curve is obtained (line *A*). If the data for the noncondensed C_6 ring naphthenes without side chain are plotted, a curve equidistant from that for the *n*-paraffins is obtained (line *B*).

If the intersections between the constant molecular weight lines and the normal paraffin line (from Figure 1) up to 150 molecular weight are plotted on this graph the resulting curve is also equidistant from the actual *n*-paraffin line (curve *C*). It was assumed that the same equidistance would hold above 150 molecular weight, and line *C* was extended on this basis.

Using *B* and *C*, the intercepts of the lines of constant molecular weight with curves 1 and 7 of Figure 1 were established above 150 molecular weight. By using curve *C* (Figure 2) rather than *A* in establishing the lines of constant molecular weight the same deviation is assigned to the *n*-paraffins above and below 150 molecular weight.

The two series of compounds were selected because they are far enough apart in Figure 1 to establish the slope of the constant molecular weight lines, and because their data were considered most reliable in this molecular weight range. The data for the naphthalene series (curve 6, Figure 1) were used to establish the molecular weight lines in the high density range. These data indicated that some curvature had to be applied to the molecular weight lines to fit this series, and they were drawn so that the curvature occurs for the most part beyond curve 7.

Since reciprocal absolute temperature is an awkward term to handle, the graph was shifted over to a boiling point–density plot as shown in Figure 3. Since the correlation is based on pure compound data, the temperature coordinate is true boiling point at 760 mm. In using the correlation, it is therefore necessary to correct boiling points (50% evaporated point) determined with A.S.T.M. distillation equipment (Procedure D86-40). By applying an emergent stem correction to the boiling point, a satisfactory approximation of the true boiling point is obtained where the barometric pressure is in the range 750–770 mm. (Pressure correction should be applied if pressure is above 770 or below 750.) These corrections for A.S.T.M. distillations may be obtained from Figure 4. Both curves are based on a room temperature between 77° and 90° F. and were calculated by the following equation:

$$C = Kn\,(T - t)$$

where C = correction, ° F.
K = 0.00009
n = number of degrees of exposed stem
T = temp. of bulb, ° F.
t = temp. at mid-point of exposed stem

Experimental data for temperature of this mid-point of the exposed stem were found to be in essential agreement with data obtained in another laboratory.

The accuracy of Figure 3 depends somewhat on the law of averages since it is based on the average physical properties for mixtures of isomers. If it is used on a very narrow cut in which there may be a high concentration of one isomer, more variation may be encountered than with mixtures of a considerable number of isomers. This point is illustrated in Table I which gives data for the C_7 paraffins and naphthenes. Table II shows the agreement of Figure 3 for various classes of pure hydrocarbons. The normal paraffins, as previously stated, do not agree particularly well with this correlation, since it was deliberately set to agree with average paraffin data. For the whole group of 134 pure hydrocarbons, the average deviation of the calculated molecular

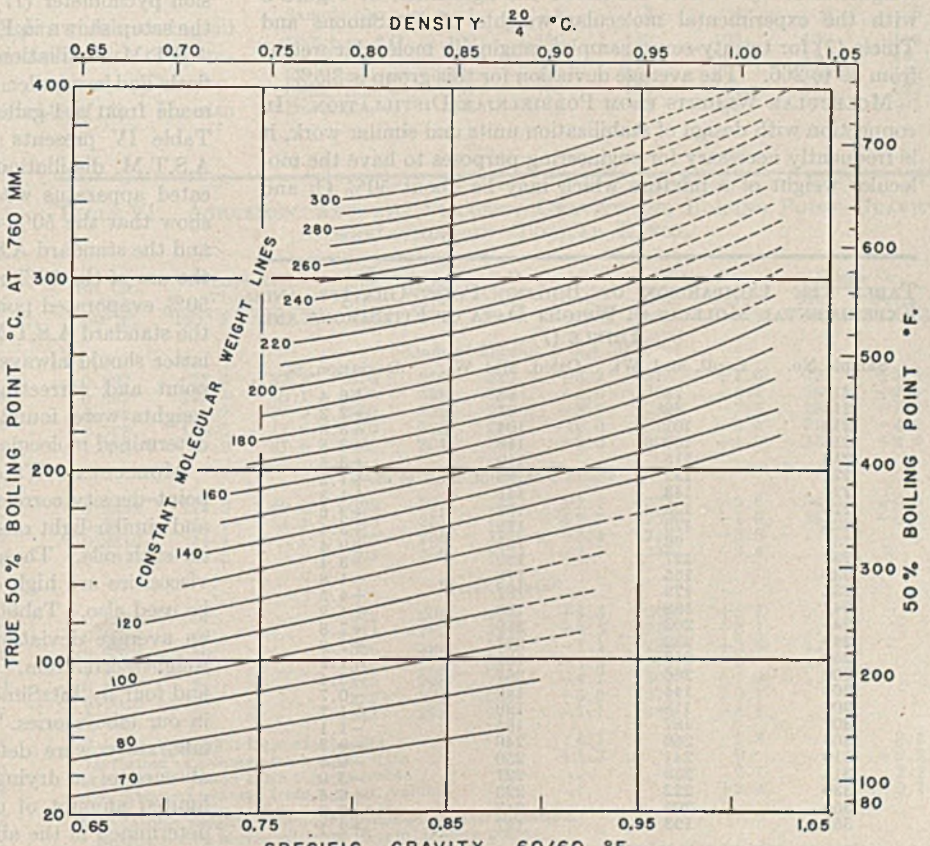

Figure 3. True 50% Boiling Point, Specific Gravity, and Molecular Weight

Table I. Accuracy of Boiling Point–Gravity–Molecular Weight Correlation for C_7 Paraffin and Naphthene Isomers

Compound (Mol. Wt.)	B.P., ° C.	Sp. Gr., d_4^{20}	Calcd. Mol. Wt.	Deviation, %
Paraffins (100)				
2,2-Dimethylpentane	79	0.6736	96	−4
2,4-Dimethylpentane	81	0.6729	97	−3
2,2,3-Trimethylbutane	81	0.6900	95	−5
3,3-Dimethylpentane	86	0.6932	97	−3
2,3-Dimethylpentane	90	0.6951	100	0
2-Methylhexane	90	0.6787	102	+2
3-Methylhexane	92	0.6870	102	+2
3-Ethylpentane	93	0.6984	101	+1
n-Heptane	98	0.6839	107	+7
		Average deviation		3
Naphthene (98)				
1-Methyl-2-isopropylcyclopropane	81	0.7101	92	−6
1,1-Dimethylcyclopentane	87	0.7547	92	−6
1,3-Dimethylcyclopentane	91	0.7479	95	−3
1,2-Dimethylcyclopentane (low boiling)	92	0.7495	96	−2
1,2-Dimethylcyclopentane (high boiling)	99	0.7718	97	−1
Methylcyclohexane	100	0.7707	98	0
Ethylcyclopentane	101	0.7610	99	+1
		Average deviation		2.7

Table II. Accuracy of Boiling Point–Gravity Correlation for Various Hydrocarbon Types

Type Compound	No. of Compounds	Mol. Wt. Range	Av. Deviation, %	Deviation of Av., %
n-Paraffins	14	100–282	5.7	+5.7
Isoparaffins	20	100–184	2.7	−2.1
Monocyclic naphthenes				
Low mol. wt. (C_4, C_5, C_6 rings)	14	98–154	3.3	−2.6
High mol. wt. (C_6 rings)	8	140–252	2.2	+1.9
Alkylbenzenes	12	92–190	4.0	−3.9
Noncondensed dicyclic naphthenes (C_5, C_6 rings)	9	138–236	4.4	−1.9
Naphthalenes	14	128–240	3.3	+1.1
Tetralins	6	132–188	1.2	+1.1
Decalins	8	138–278	2.9	−2.3
Noncyclic mono-olefins	15	98–224	3.1	+1.8
Cyclic mono-olefins	14	96–166	2.6	+1.1
Total	134		2.4	0

weights is 2.4%. Table III shows the agreement of Figure 3 with the experimental molecular weights of FitzSimons and Thiele (*7*) for twenty-seven samples ranging in molecular weight from 89 to 266. The average deviation for this group is 3.5%.

Table III. Comparison of Boiling Point–Gravity and Experimental Molecular Weight Data of FitzSimons and Thiele (*7*)

Sample No.	Exptl. Mol. Wt.	Calcd. Mol. Wt.	Deviation, %
212	78	83	+6.4
213	89	91	+2.2
215	101	104	+3.0
216	106	110	+3.8
218	115	119	+3.5
221	131	133	+1.5
223	143	145	+1.3
225	153	157	+2.6
228	173	179	+3.4
231	96	105	+9.4
232	127	130	+3.4
235	165	173	+4.8
238	179	187	+4.5
242	188	196	+4.2
246	203	219	+7.8
249	232	237	+2.2
250	257	262	+1.9
300	266	257	−3.4
305	141	140	−0.7
306	118	120	+1.7
307	187	185	−1.1
309	266	240	−9.7
310	241	250	−0.4
315	239	227	−5.0
330	222	223	+0.5
350	205	213	+3.9
355	193	197	+2.1
		Average deviation	3.5

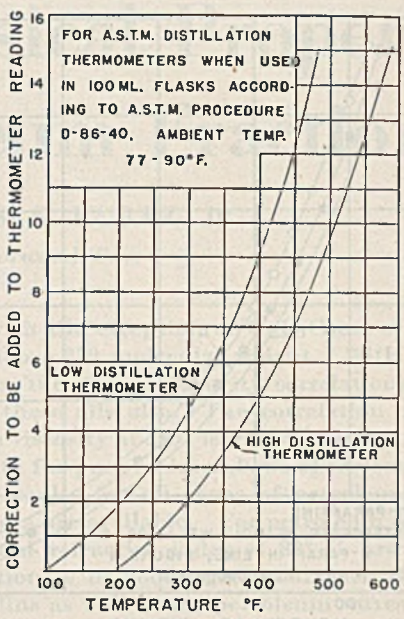

Figure 4. Stem Corrections for A.S.T.M. Low- and High-Distillation Thermometers

Molecular Weights from Podbielniak Distillation. In connection with design of stabilization units and similar work, it is frequently necessary for engineering purposes to have the molecular weight of a mixture which may be about 50% C_4 and lighter and about 50% C_5 and heavier. Materials of this class are too volatile for determination of molecular weight by the methods usually available. With samples of this type a low temperature Podbielniak distillation is always run to obtain the composition of the lower boiling fractions. Usually 20–30 ml. of residue from the Podbielniak distillation can be obtained if a large distilling bulb is used. The molecular weight of the residue can be determined from its boiling point and gravity. Gravity is obtained with a small hydrometer or a Sun Oil Company precision pycnometer (*17*). The boiling point can be obtained with the setup shown in Figure 5. This is similar to the conventional A.S.T.M. distillation apparatus (D-86-40) except that a 50-ml. flask and a smaller condenser are used. The ice bath can be made from a 1-gallon can having a 4 × 6 inch cross section. Table IV presents the agreement between standard 100-ml. A.S.T.M. distillations and distillations carried out in the indicated apparatus with 25-ml. and 15-ml. charges. These data show that the 50% evaporated points of the small distillations and the standard A.S.T.M. distillations agree fairly well. While the use of the 50% recovered point instead of the recommended 50% evaporated point does not cause much error in the case of the standard A.S.T.M. distillation, for the small distillations the latter should always be employed. Using the 50% evaporated point and correcting as usual for emergent stem, molecular weights were found to agree fairly well with experimentally determined molecular weights as indicated in Table V.

Molecular Weight of Transformer Oils. The boiling point–density correlation can also be applied to transformer oils and similar light oils since Engler distillations are normally run on such oils. These oils are of particular interest since their viscosities are high enough for viscosity-density correlations to be used also. Table VI gives data for sixteen light oils showing an average deviation of 4.1% for the boiling point–molecular weight correlation. Five of these were reported by Fenske (*5*) and four by FitzSimons and Thiele (*7*); seven were determined in our laboratories. The molecular weights reported from this laboratory were determined cryoscopically in benzene, in the absence of a drying agent. Subsequently, on the basis of a limited amount of data, it was found that molecular weights determined in the absence of a drying agent averaged 5% lower than those in the presence of a drying agent. Consequently, the data have been corrected for the effect of moisture in the older

Table IV. Comparison of 15- and 25-Cc. Distillations with A.S.T.M. 100-Cc. Distillation (D86-40)

	East Texas Light Gasoline		Podbielniak Residue			Composite of Podbielniak Residues				Gasoline				Heavy Gasoline Fraction		Mineral Spirits	
	100-cc.	25-cc.	25-cc.	15-cc. (A)	15-cc. (B)	100-cc.	25-cc.	15-cc. (A)	15-cc. (B)	100-cc.	25-cc.	15-cc. (A)	15-cc. (B)	100-cc.	25-cc.	100-cc.	25-cc.
Distn., ° F.																	
Initial	94	92	122	122	121	130	128	130	130	90	92	94	94	252	258	302	295
5% over	120	114	148	141	140	164	152	139	154	117	110	109	108	285	282	319	318
10%	133	129	160	156	157	176	166	164	163	132	131	125	127	294	291	324	324
20%	155	153	176	176	174	191	182	181	181	160	160	156	164	304	303	331	330
30%	170	171	189	189	189	206	197	197	200	188	188	191	197	314	312	336	336
40%	184	186	203	201	202	220	214	213	216	211	214	221	221	322	321	343	341
50%	196	197	214	216	215	236	233	234	232	240	240	247	246	327	330	348	349
60%	207	210	229	231	229	253	251	254	248	263	267	277	280	336	339	354	356
70%	218	221	248	250	248	276	274	277	277	288	302	307	310	346	350	361	364
80%	229	238	275	280	280	300	299	303	292	316	332	344	...	358	364	371	375
Loss, %	3	8	2	2	3	2	2	2	2	3	4	5	6	2	2	2	3
50% evapd. point[a], ° F.	192	188	212	213	211	233	229	230	229	231	230	234	230	326	328	347	347
Dev. from A.S.T.M., ° F.	...	−4	...	+1[b]	−1[b]	...	−4	−3	−4	...	−1	+3	−1	...	+2	...	0

[a] Assuming distillation curve to be straight line between 40 and 50%.
[b] Deviation from 25-cc. distillation.

cryoscopic procedure by adding 5% to the experimentally determined values. While occasional deviations of 8–9% are found; in general, they are 5% or less.

In summary, the boiling point–gravity correlation is believed to be satisfactory for determining molecular weight for any petroleum fraction of 70–300 molecular weight for which a good 50% boiling point can be obtained. Obviously, it should not be applied to unusual blends, such as a solution of asphalt in spirits, to cite an extreme example. The crowding of the lines of constant molecular weight as molecular weight is increased, as well as increased difficulty in measuring the boiling point, make other types of correlation more suitable for the fractions of higher molecular weight.

Table VII gives sufficient data for the construction of a graph for the boiling point–gravity correlation.

VISCOSITY-DENSITY AND VISCOSITY SLOPE

Several correlations of the molecular weights of lubricating oil fractions with viscosity slope (change of viscosity with temperature) and viscosity-density data have been proposed. This previous literature has been discussed by Hirschler (*12*). He also proposed (*12*) correlations of kinematic viscosity at 100° and 210° F., density at 25° C., and molecular weight, whereby any two of these four constants could be used to calculate the other two. Molecular weights could thus be calculated from the kinematic viscosities at 100° and 210° F. or from the density and either viscosity.

For the viscosity-density correlations presented in the present paper, Saybolt viscosities and specific gravity (60/60° F.) were employed since inspection tests are still ordinarily given in these latter units. The present viscosity-density correlations are not derived directly from those of Hirschler (*12*) by a simple change in units; the entire correlation was revised, smoothed somewhat, and extended further into the low viscosity region. These modifications have not resulted in any considerable differences from the earlier correlation but are sufficient to require an independent evaluation. Both the present correlations and the earlier ones (*12*) were based primarily on the data of Mair and co-workers (*21*, *22*, *23*).

The greatest difficulty in attempting to correlate molecular weight in the lubricating oil range is the obvious discrepancy in data obtained in laboratories which should be expected to be equally reliable. In this connection, it is well to consider the cooperative molecular weight work carried out by Rall and Smith (*26*). These data are summarized in Table VIII, which also includes later data on the same oils by Hanson and Bowman (*9*). It appears that molecular weights, even when obtained by experienced operators, are subject to considerable error. Thus it is conceivable that any one worker may obtain molecular weight data which are far better in reproducibility than in absolute accuracy. In view of these data, it is also clear that a

Table V. Accuracy of Boiling Point–Gravity Correlation for Podbielniak Residues

Sample No.	1	2	3	4	5	6
50% b.p., ° C.	100	100	140	100	139	149
Gr., ° A.P.I.	59.8	56.8	48.8	59.0	49.6	45.1
Exptl. mol. wt.	98	101	114	99	116	119
Calcd. mol. wt.	101	100	120	101	119	123
Deviation, %	+3	−1	+5	+2	+3	+3

Table VI. Agreement between Viscosity–Gravity and Boiling Point–Gravity Correlations in Overlap Range

Sp. Gr., 60/60° F.	Saybolt Viscosity		Cor. 50% B.P., ° C.	Exptl. Mol. Wt.	B.P.-Gravity		Vis_{100}-Gr.		Vis_{210}-Gr.	
	100° F.	210° F.			Mol. wt.[a]	Deviation, %	Mol. wt.	Deviation, %	Mol. wt.	Deviation, %
Data of Fenske, *et al.*[b] (*5*)										
0.867	77.6	37.3	370	310	320	+3.2	315	+1.6	322	+3.9
0.867	113.4	40.1	395	338	355	+5.0	363	+8.1	360	+6.5
0.932	102.3	37.9	360	305	280	−8.2	282	−7.5	283	−7.2
0.933	188.5	41.8	370	328	295	−10.0	317	−3.4	315	−4.0
0.888	87.0	37.5	365	304	310	+2.0	307	+1.0	310	+2.0
Data of FitzSimons and Thiele (*7*)										
0.8868	113.3	40.2	398	337	345	+2.4	335	−0.6	340	+0.9
0.9191	55.7	34.1	340	257	264	+2.7	252	+1.9	255	−0.8
0.8510	44.4	...	316	266	257	−3.4	258	−3.0	...	
0.8516	44.2	...	303	266	242	−7.3	257	−3.4	...	
Present Data[c]										
0.8877	57	...	332	261	265	+1.5	268	+2.7	...	
0.8751	54	...	321	260	256	−1.5	268	+3.1	...	
0.8529	56	...	336	281	278	−1.1	288	+2.5	...	
0.9147	73	...	340	272	266	−2.2	272	0	...	
0.8883	84	...	349	298	284	−4.7	302	+1.3	...	
0.9018	65	...	327	270	255	+5.6	272	+0.7	...	
0.8649	57	...	338	293	278	−5.1	280	−4.4	...	
Average deviation from exptl. data						4.1		2.8		3.6
Deviation of average from exptl. data						+1.3		0		+0.2
Average deviation from b.p.-gr. value						...		3.7		2.1
Deviation of average from b.p.-gr. value						...		+2.4		+0.7

[a] Molecular weights above 300 obtained by extrapolation.
[b] Boiling points corrected from 10-mm. boiling points.
[c] A 5% correction was applied to experimental molecular weights for reasons given in text.

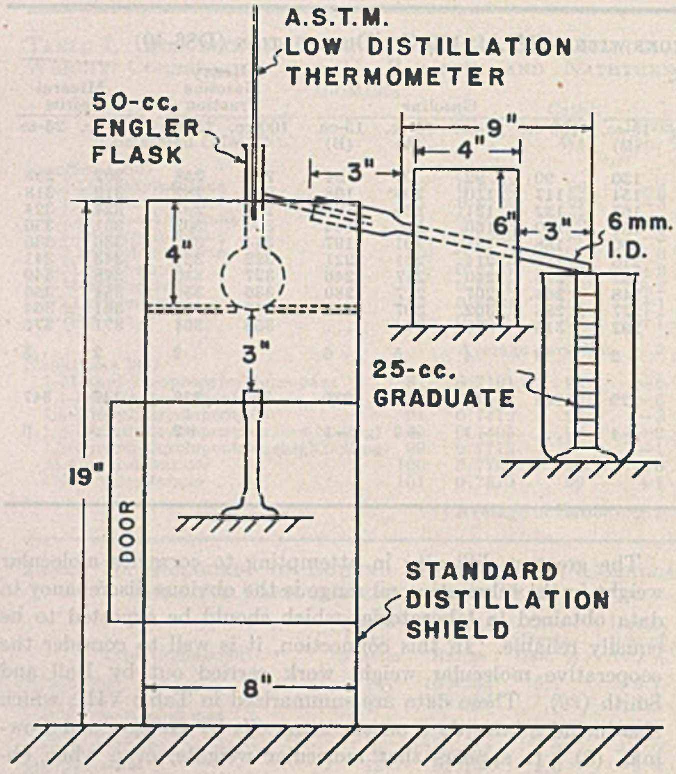

Figure 5. Distillation Equipment for Podbielniak Residues

correlation of molecular weight with physical properties will not necessarily fit equally well the data from different laboratories. It is therefore necessary to decide which data are most reliable as a basis for correlation. The data of Mair and coworkers (*21*, *22*, *23*) were given greatest weight in deriving the correlations presented in this paper.

The data of Mair were obtained by precise ebullioscopic technique. Our experience with the ebullioscopic method, however, does not lead us to recommend it for general use since it is more time consuming than the cryoscopic procedure and has as many, if not more, possibilities for experimental error. However, in the hands of a careful laboratory technician it yields good results.

Table VII. Data for Constructing Correlation of Boiling Point, Density, and Molecular Weight

Mol Wt.	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.02
	Boiling Point in ° C. When Density (20° C.) Is:								
70	28	35	42	50	58	...	...	...	...
80	47	55	63	72	80	...	...	...	...
90	64	74	82	92	101	110	...	...	...
100	..	90	100	110	120	130	...	...	...
110	..	104	116	126	138	148	...	...	...
120	..	121	132	143	154	165	176	...	...
130	..	...	147	158	170	182	195	210	216
140	..	...	162	174	184	196	209	224	232
150	..	...	176	187	198	209	222	239	247
160	..	...	190	200	210	222	236	255	263
170	..	...	203	213	222	234	250	268	278
180	..	...	216	225	236	247	262	282	291
190	..	...	228	238	248	260	275	294	303
200	..	...	...	249	259	272	286	306	315
210	..	...	...	262	271	283	300	320	330
220	..	...	...	272	281	294	310	332	241
230	..	...	...	282	291	303	320	340	350
240	..	...	...	292	301	314	330	352	362
250	..	...	...	301	310	323	340	361	372
260	..	...	...	310	319	332	349	370	380
270	..	...	...	320	328	340	356	378	388
280	..	...	...	328	337	349	366	386	397
290	..	...	...	337	345	357	373	394	404
300	..	...	...	343	351	364	380	401	411

Table VIII. Cooperative Data of Rall and Smith

	Oil 1	Oil 2	Oil 3
Saybolt viscosity, 100° F.	1347	259	105.4
Sp. gr., 60/60° F.	0.879	0.863	0.882
Experimental mol. wt.			
Cryoscopic (Benzene)			
Rall & Smith (*26*)	763	491	333
Hanson & Bowman (*9*)	764	442	358
11 lab., mean	693	447	317
Ebullioscopic (*9*)			
Benzene	671	450	326
Cyclohexane	652	445	312
Mean	661	447	319
Calcd. mol. wt. (vis_{100}–gr.)	690	482	334

In regard to the cryoscopic technique, the previous recommendations (*14*, *26*) that the freezing point depression be determined in the presence of a drying agent are heartily endorsed. At present the 5% difference which we have observed in molecular weights, determined with and without a drying agent, appears to be due to a small trace of moisture picked up at the time the sample is introduced. This 5% difference, if due to this cause, would not be duplicated exactly in other laboratories since details of technique during introduction of sample and the humidity of this atmosphere would be controlling influences.

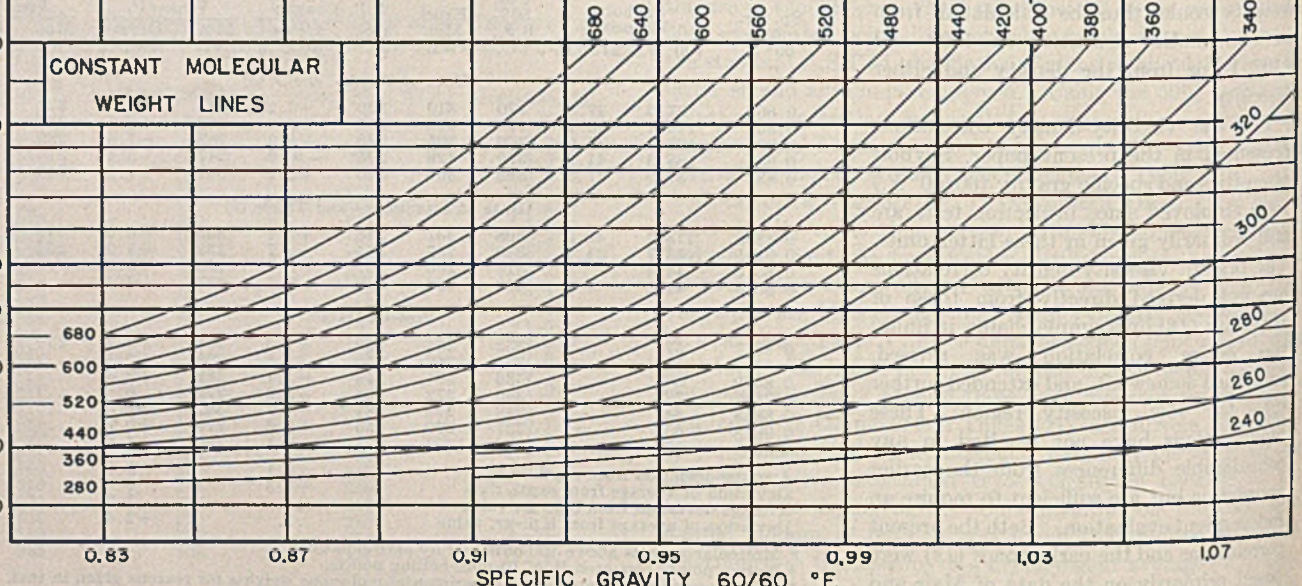

Figure 6. Saybolt Viscosity at 210° F., Specific Gravity, and Molecular Weight

Table IX. Data for Construction of Chart Correlating Molecular Weight with Specific Gravity at 60/60° F. and Saybolt Viscosity at 210° F.

Mol. Wt.	Vis_{210} When $Gr_{60/60}$ Is: 0.84	0.87	0.90	0.93	0.96	0.99	1.02	1.05	1.07	$Gr_{60/60}$ at Vis_{250}
240	31.5	31.9	32.1	32.7	33.5	35.0	36.8	39	41.5	....
260	32.7	33.3	34.2	35.2	36.3	38.5	41.7	46.2	50.0	....
280	33.5	34.8	35.8	37.1	39.4	43.0	48.5	57	65.5	....
300	34.8	36.0	37.3	39.6	43.0	48.8	58.4	78.8	101	....
320	36.0	37.2	39.1	42.3	47.3	55.8	76.0	117	162	....
340	37.0	38.7	41.0	45.1	52.4	67.0	100	170	..	1.0702
360	38.2	40.2	43.2	48.4	58.2	80.5	137	254	..	1.0488
380	39.4	41.9	45.8	52.5	66.2	98.5	177	..	..	1.0358
400	40.8	43.8	48.7	57.5	76.2	124	222	..	..	1.0248
420	42.0	46.0	52.0	63.0	87.2	145	270	..	..	1.0162
440	43.9	48.2	55.7	70.0	101	174	..	..	..	1.0070
460	45.8	51.0	59.5	72.0	115	201	..	..	..	0.9998
480	47.5	53.0	63.5	85.5	134	239	..	..	..	0.9920
500	49.4	56.0	68.5	94	153	..	..	..	..	0.9852
520	51.6	59.0	73.5	106	180	..	..	..	..	0.9767
540	53.9	63.0	79.5	117	204	..	..	..	..	0.9700
560	56.5	66.5	86.0	132	236	..	..	..	..	0.9628
580	59.0	71.0	93.0	148	268	..	..	..	..	0.9568
600	61.8	75.5	102	164	..	..	..	..	..	0.9508
620	65.0	81.0	112	186	..	..	..	..	..	0.9446
640	68.5	87.0	123	210	..	..	..	..	..	0.9388
660	72.2	93.0	135	232	..	..	..	..	..	0.9337
680	75.5	101	150	255	..	..	..	..	..	0.9282

The difficulties in cryoscopic procedure due to mixed crystal formation and solute association have been mentioned in the literature (*10*, *20*). Although we do not claim to have conclusive evidence on this point, a considerable amount of experience with both the boiling point and freezing point technique as applied to naphthenic acids and to lubricating oil fractions lead us to believe that the difficulties due to mixed crystal formation and solute association must be considered; however, details such as presence of moisture, experimental technique, etc., deserve as much consideration. In short, we are inclined to believe that errors due to details of experimental technique are a major source of difficulty and may explain most of the systematic errors which lead to reproducibility, in general, being better than absolute accuracy.

Correlations of molecular weight with vis_{210}–$gr_{60/60}$ and vis_{100}–$gr_{60/60}$ are presented here. Data for the construction of both of these charts are given in Tables IX and X, and Figure 6 illustrates the correlation. Since the correlation of molecular weight with vis_{100}–vis_{210} was presented by Hirschler (*12*), it is not repeated here.

It seems worth while to have available more than one correlation, so that in case of doubt or in the case of an unusual sample, the molecular weight obtained on one graph can be cross-checked with that obtained on the other graphs.

Hirschler (*12*) showed that the vis_{100}–vis_{210} correlation will, in general, fit the various types of pure compounds, particularly the extreme naphthene and aromatic types, with better accuracy than a viscosity-gravity correlation. His data indicate, however, that with normal petroleum fractions the distribution of hydrocarbon types is such that the viscosity-gravity correlation will give a reasonably reliable molecular weight. In the case of the fractions of higher molecular weight derived from Gulf Coast or California crudes, which are highly naphthenic, the molecular weight calculated from our viscosity-gravity correlations are too high. Special viscosity-gravity correlations for Gulf Coast oils have been prepared which give good results for this type of oil. They are described in the next section.

The vis_{100}–vis_{210} correlation is therefore considered most reliable and is recommended when two viscosities are available.

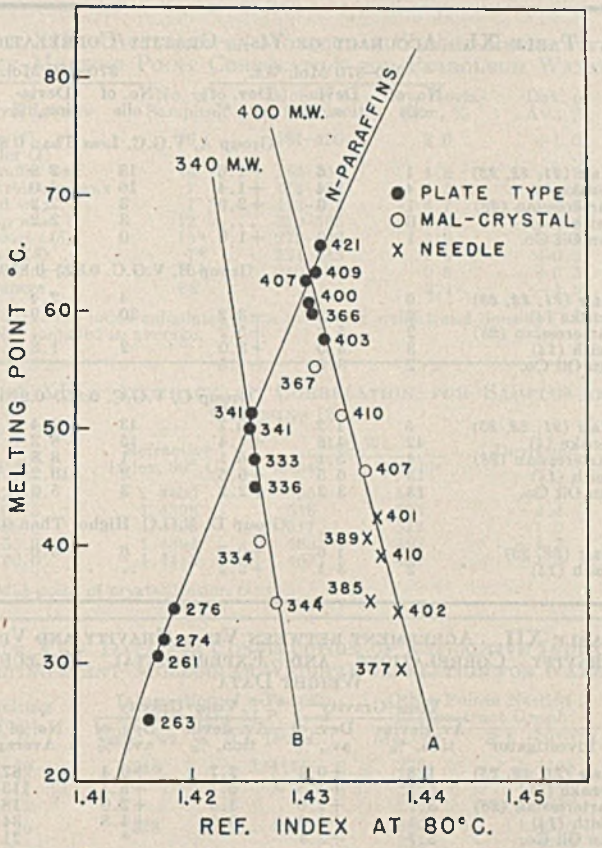

Figure 7. Melting Point *vs.* Refractive Index at 80° C. for Waxes

However, this correlation has a lower viscosity limit of 2.6 centistokes (35 seconds Saybolt) at 210° F. which does not permit its use on certain fractions of low molecular weight; in addition, for many low viscosity cuts, only the 100° F. viscosity is customarily determined. The vis_{100}–gravity correlation may be applied to such fractions down to a molecular weight of 240.

The boiling point–gravity correlation can also be used for oils up to 300 molecular weight; therefore, in this intermediate range it is possible to cross check boiling point–gravity molecular weights against viscosity-gravity values (Table VI). The average deviation between the molecular weights calculated by these two correlations is 3.7% for this group of oils.

The viscosity-gravity correlations may be presented in the

Table X. Data for Construction of Chart Correlating Molecular Weight with Specific Gravity at 60/60° F. and Saybolt Viscosity at 100° F.

Mol. Wt.	Vis_{100} When $Gr_{60/60}$ Is: 0.84	0.87	0.90	0.93	0.96	0.99	1.02	1.05	1.08	$Gr_{60/60}$ at $Vis_{10,000}$
240	...	..	..	49.0	56	72	104	184	392	....
260	...	49.0	56.5	69.5	94	145	273	582	1440	....
280	49.8	58.3	72.0	97.0	150	287	670	1870	6800	1.0880
300	56.5	68.6	90.0	136	242	545	1570	6600	..	1.0568
320	64.9	82.8	114	190	378	970	3660	..	..	1.0375
340	73.5	98.0	143	256	570	1700	7500	..	..	1.0250
360	83.6	116	181	344	810	2750	..	..	..	1.0135
380	94.0	135	225	450	1170	4350	..	..	..	1.0044
400	106.4	162	279	605	1650	6900	..	..	..	0.9964
420	120	189	340	755	2220	10,000	..	..	..	0.9900
440	136	220	408	960	2900	....	..	..	..	0.9837
460	153	252	497	1190	3950	....	..	..	..	0.9780
480	172	293	597	1500	5250	....	..	..	..	0.9725
500	193	335	695	1830	6700	....	..	..	..	0.9675
520	218	385	810	2220	8600	....	..	..	..	0.9627
540	244	435	950	2670	..	....	..	..	..	0.9584
560	272	495	1090	3220	..	....	..	..	..	0.9542
580	304	555	1270	3840	..	....	..	..	..	0.9500
600	333	627	1460	4600	..	....	..	..	..	0.9460
610	370	706	1700	5560	..	....	..	..	..	0.9420
640	402	780	1960	6800	..	....	..	..	..	....
660	440	870	2300	8100	..	....	..	..	..	....
680	479	977	2670	9500	..	....	..	..	..	....

TABLE XI. ACCURACY OF VIS$_{210}$–GRAVITY CORRELATION FOR LUBRICANT FRACTIONS

	240–370 Mol. Wt.			370–450 Mol. Wt.			>450 Mol. Wt.		
	No. of oils	Deviation, %	Dev. of av., %	No. of oils	Deviation, %	Dev. of av., %	No. of oils	Deviation, %	Dev. of av., %
Group A, V.G.C. Less Than 0.825									
Mair (*21, 22, 23*)	1	1.6	+1.6	13	2.9	+2.2	12	1.1	+0.1
Fenske (*4*)	4	1.4	+1.4	16	4.0	+3.8	3	4.3	+4.3
Varteressian (*28*)	1	2.9	+2.9	3	2.2	−1.7	4	1.6	−0.6
Keith (*14*)	0	...	...	3	2.2	−1.7	2	5.0	+5.0
Sun Oil Co.	1	1.0	+1.0	0	...	...	0	...	...
Group B, V.G.C. 0.825–0.850									
Mair (*21, 22, 23*)	0			4	2.4	+2.4	1	0.6	−0.6
Fenske (*4*)	6	4.2	−3.2	20	3.9	+3.2	5	10.1	+10.1
Varteressian (*28*)	2	5.2	+5.2	..	...	...	1	2.1	+2.1
Keith (*14*)	3	3.0	+3.0	2	1.3	+1.3	6	3.9	+1.7
Sun Oil Co.	2	3.5	−1.5	..	...	...	..	...	...
Group C, V.G.C. 0.850–0.920									
Mair (*21, 22, 23*)	5	1.2	−0.7	13	1.4	−0.7	2	1.3	−1.3
Fenske (*4*)	42	4.6	+4.4	15	8.3	+8.3	2	10.0	+10.0
Varteressian (*28*)	4	5.1	+5.1	1	8.8	+8.8	2	4.6	+4.6
Keith (*14*)	13	6.5	+6.5	3	10.2	+10.2	..	...	...
Sun Oil Co.	13	3.3	+2.2	3	5.0	+5.0	2	6.1	+6.1
Group D, V.G.C. Higher Than 0.920									
Mair (*22, 23*)	28	1.6	+0.3	6	3.0	−2.6	2	0.9	−0.8
Keith (*14*)	2	3.1	+2.2	..	...	...	..	...	...

TABLE XII. AGREEMENT BETWEEN VIS$_{210}$–GRAVITY AND VIS$_{100}$–GRAVITY CORRELATIONS AND EXPERIMENTAL MOLECULAR WEIGHT DATA

	Vis$_{210}$–Gravity		Vis$_{100}$–Gravity		
Investigator	Av. deviation, %	Dev. of av., %	Av. deviation, %	Dev. of av., %	No. of Oils Averaged
Mair (*21, 22, 23*)	1.8	+0.2	2.7	+0.4	87
Fenske (*4*)	5.1	+4.5	6.1	+5.1	.113
Varteressian (*28*)	3.7	+2.6	3.4	+2.0	18
Keith (*14*)	5.1	+4.3	5.9	+4.8	34
Sun Oil Co.	3.7	+2.4	[a]	[a]	21

[a] 100° F. viscosity not available.

form of plots of viscosity-gravity constant *vs.* gravity (*11*). An advantage of this type of representation is that the lines of constant molecular weight become almost straight and nearly parallel. These straight lines correspond approximately to the lines of constant boiling point presented by Ward, Kurtz, and Fulweiler (*30*) and to the linear relation between viscosity-gravity constant (V.G.C.) and density for solvent extraction data given by Kurtz (*16*). The disadvantage of this plot is that it is sensitive to small errors in V.G.C. and requires V.G.C. to four significant figures to obtain an accuracy comparable to the viscosity-gravity plots; the nomographs for V.G.C. now available are accurate to about three significant figures (*13*).

EVALUATION OF VISCOSITY-GRAVITY CORRELATIONS

Since the two viscosity-gravity correlations give calculated molecular weights agreeing within 1% average deviation, the statistical evaluation of the correlations is presented only for the vis$_{210}$–gravity plot.

While developing the accuracy of this graph, it was observed that the errors for some published data varied, depending on the molecular weight of the sample and the type of sample—i.e., paraffinic or naphthenic. For this reason the data were grouped as to type, based on V.G.C. and molecular weight, as Table XI shows. The four classifications, groups A to D, are arbitrary but serve as a convenient means of presenting the accuracy of the correlation. Roughly, groups A, B, and C correspond to the conventional type classifications of paraffinic, mid-continent, and Gulf Coast, respectively.

The deviations of the correlation for each laboratory and for each type and molecular weight range are given in Table XI. Table XII summarizes the agreement of the vis$_{210}$ correlation with the vis$_{100}$ plot. In all cases the agreement between the two, as measured by the difference in the average deviations for the data of each investigator, is within 1%, although for some individual samples larger deviations are observed.

Since, as stated previously, the correlation was based primarily on the data of Mair, the agreement shown in Table XI is best for these data. In general, agreement is good for group A samples; only five of sixty-three samples in Table XI have average deviations of 4% or more. The correlation works well for group B oils except for five samples with high molecular weight of Fenske. In the case of group C oils, the correlation agrees well with the data of Mair throughout the molecular weight range; the agreement is fairly good for all investigators in the 240–370 molecular weight range. However, consistently positive deviations of 5% or more are observed for the other investigators above 370 molecular weight. It is possible that to some extent this may be due to systematic errors in the cryoscopic molecular weights for the type of oils present in this group. However, it seems best at present to assign at least the major part of the deviation to a failure of the viscosity-gravity correlations to fit highly naphthenic oils. Hirschler (*12*) showed from pure compound data that a viscosity-gravity correlation tends to give high values for molecular weights of polycyclic naphthenes. Mair's group C oils are extracts from a mid-continent oil; the data of Fenske and of this laboratory were obtained on Gulf Coast and California fractions. Deviations for the latter may be attributed to a larger proportion of polycyclic naphthenes.

To correct for the more naphthenic character of Gulf Coast oils, special viscosity-gravity correlations applicable only to such oils can be constructed. Charts prepared with the limited data available give quite satisfactory agreement. The correlations described in this paper can be used to obtain good results for even Gulf Coast oils if, for fractions between 320 and 470 molecular weight (calcd.), the calculated molecular weight is corrected downward by multiplication with a factor, F, determined by the equation,

$$F = [1000 - 0.7\ (\text{mol. wt.} - 260)] \times 10^{-3}$$

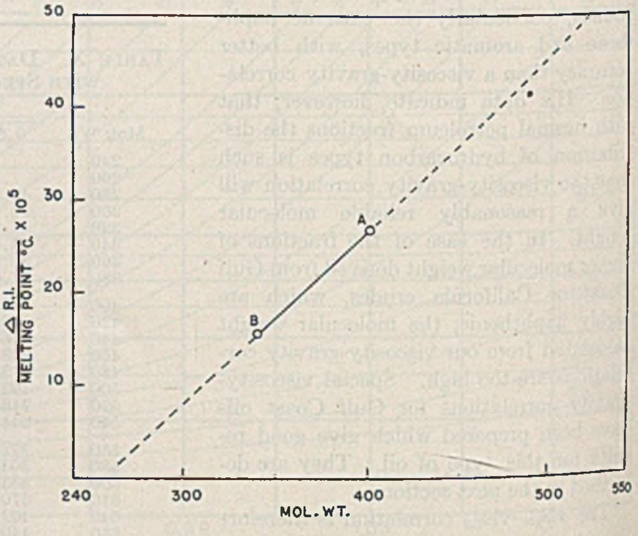

Figure 8. Refractive Index–Melting Point Increment *vs.* Molecular Weight for Waxes

For the fourteen Gulf Coast distillates of Fenske (*4*) in this group, the average deviation of the molecular weights is 1.9%, using the vis$_{210}$–gravity correlation corrected as described; for nine Texas Coastal fractions of Keith and Roess (*14*), it is 1.3%. The same correction factor, applied to the thirteen California cuts of Fenske (*4*) above 300 molecular weight gives values with an average deviation of 3.3%. Applied to the vis$_{100}$–gravity correlation, this correction factor gives results for Gulf Coast oils somewhat better and for the California oils, somewhat worse, than the above.

Data on Gulf Coast oils of high molecular weight are scanty; there is some indication that the correction factor is valid only up to about 430 (actual) molecular weight.

In constructing the two viscosity-gravity correlations, the data in Tables IX and X may be plotted on semilogarithmic paper. If paper of adequate size is not available, the data may be plotted on standard A.S.T.M. viscosity-temperature charts (D341–43), using the nonlinear temperature scale for the gravity coordinate. This method of plotting has several advantages over semilog paper; in particular, the constant molecular weight lines have much less curvature, and the spacing between adjacent lines is more uniform, with the result that their crowding in the region of low gravity is considerably reduced.

CORRELATION FOR WAXES

In considering the physical property relations of the waxes reported by Ferris and co-workers (*6*), it was noticed that, if melting point is plotted against refractive index at 80° C., lines can be drawn connecting points of equal molecular weight (Figure 7). Since only two molecular weight ranges are represented with sufficient samples to establish a means of extrapolation on this chart, an attempt was made to correlate these properties by making use of the slope ΔR.I./M.P.(° C.) of the two lines available. The slopes were plotted against molecular weight and extrapolated as a straight line above and below the available data (Figure 8). (The assumption that such an extrapolation would be useful has been justified by the results obtained.) Then a plot was drawn of molecular weight against refractive index at 80° C. for the *n*-paraffins with data taken from Egloff (*3*), corrected to 80° C. when necessary, as a base line and the values of ΔR.I./M.P.(° C.) from Figure 8. A series of melting point lines (Figure 9) were thus constructed; the 20° and 30° C. lines were slightly curved at the lower end to give better agreement with experimental data. The accuracy of this correlation has been checked against available literature data (Table XIII).

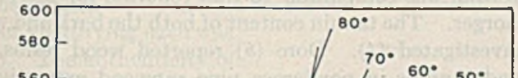

Figure 9. Refractive Index, Melting Point, and Molecular Weight for Waxes

Table XIII. Accuracy of Molecular Weight–Refractive Index–Melting Point Correlation for Petroleum Waxes

Investigators	No. of Samples	Mol. Wt. Range	Av. Deviation, %	Dev. of Av., %
Ferris (*6*)	26	261–420	2.0	+1.0
Buchler (*1*)				
Paraffin wax	14	255–456	1.8	−1.2
Petrolatum wax	7	474–572	4.5	−4.5
Rod wax	7	493–569	4.7	−4.7
Slop wax	12	360–563	4.8	−4.8
Kolvoort (*15*)	15[a]	279–490	3.9	−3.9
Francis (*8*)	7[a]	321–443	1.6	+0.3
n-Paraffins (*3*)	16[b]	240–534	0.8	+0.3
Average	88		3.1	−1.9

[a] Refractive index calculated from molecular weight and density (*18*).
[b] Not included in average.

Table XIV. Accuracy of Correlation for Samples of Ceresins (*24*)

M.P.[a], ° C.	Refractive Index, 80° C.	Mol. Wt. Exptl.	Mol. Wt. Graphic	Deviation, %
74.5	1.4400	586	555	−5.3
69.5	1.4398	546	523	−4.4
66.0	1.4405	517	512	−1.0
55.0	1.4394	483	462	−4.3
50.0	1.4413	467	461	−1.3

[a] Mid-point of crystallization range.

Table XV. Data for Construction of Refractive Index–Melting Point–Molecular Weight Correlation for Waxes

Melting Point, ° C.	Intersection of *n*-Paraffin and Constant M.P. lines		Other Points Needed to Construct Graph	
	Mol. wt.	R.I. (80° C.)	Mol. wt.	R.I. (80° C.)
20	248	1.4144	278	1.4188
			298	1.4220
			384	1.4380
30	268	1.4164	300	1.4216
			328	1.4260
			447	1.4460
40	297	1.4202	495	1.4500
45	312	1.4220	510	1.4500
50	336	1.4248	557	1.4540
55	358	1.4266	579	1.4540
60	381	1.4286	570	1.4500
65	412	1.4308	580	1.4480
70	448	1.4328	590	1.4460
75	494	1.4350	590	1.4428
80	559	1.4378	590	1.4400

For the samples of Ferris *et al.* (*6*), the paraffin waxes of Buchler and Graves (*1*), and the normal paraffins, good agreement was obtained. Less accurate results are observed for the petrolatum, rod, and slop waxes of Buchler and Graves (*1*). No refractive indices were given by Kolvoort *et al.* (*15*) or Francis *et al.* (*8*). They were, however, calculated by Lipkin and Martin (*19*) from density and molecular weight, employing the temperature coefficients of density and refractive index given by Lipkin and Kurtz (*18*). For the samples of Francis *et al.*, the molecular weights as redetermined by Piper and co-workers (*25*) were used. The average deviation for eighty-eight petroleum wax samples is 3.1%[1].

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[1] Recently Moulton and Loop [*Petroleum Refiner*, 24, No. 4, 161 (1945)] published physical property and molecular weight data on forty-three cuts from the wax fraction of a western crude. The molecular weights calculated from Figure 9 are consistently lower than the experimental values, the average being 8.1% low. This deviation is larger than for any other group of data in Table XIII. It is believed that this is due to an error in the molecular weight or refractive index data, since the refractive indices are appreciably lower than those of the corresponding normal paraffins of equal molecular weight. All of the above fractions fall appreciably to the left of the *n*-paraffins line in Figure 9. Further, for a sampling of seven fractions, refractive indices were calculated from density and molecular weight (*19*). The calculated indices were from 0.0027 to 0.0032 larger than the experimental values, which considerably exceeds the probable error of the calculations.

The correlation appears to be applicable to ceresins from ozokerite (Table XIV). The average deviation for the five samples of Muller and Pilat (*24*) is 3.3%. Data for the construction of Figure 9 is given in Table XV.

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CHEMISTRY OF WESTERN PINES

Distribution and Nature of Acetone Soluble Extractives in Ponderosa Pine

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Extractives are not an integral part of wood structure. Preliminary investigations have shown that it is possible to remove all or a portion of the extractives and to dry green lumber simultaneously by means of solvent extraction. If these extractives could be removed and recovered economically, the value of the lumber so treated would be enhanced and a new source of extractive products would become available. This article deals with the distribution and nature of the acetone-soluble materials in ponderosa pine.

The proximate analysis of three commercially important western pines, which include ponderosa (*Pinus ponderosa*), Idaho white (*Pinus monticola*), and sugar (*Pinus lambertiana*) pines revealed that these coniferous trees are relatively rich in extractives (*2*). The extractives form no integral part of wood structure. Their presence degrades the wood for high-grade lumber; their removal enhances the appearance and the finishing properties of lumber. If the extractives could be removed and recovered economically, the lumber would be upgraded, and a new source of commercial products, such as resins, fatty acids, and terpenes, would become available. By choosing the proper solvent, it is possible to recover the extractives and to dry green wood simultaneously.

The composition of the oleoresin from ponderosa pine obtained by wounding the tree was investigated by Schorger (*10*) and reported to consist of 79.5% rosin and 18.5% volatile oil. The rosin was made up of 90% abietic acid, while the volatile portion contained α- and β-pinene and limonene. The turpentine obtained from this conifer was investigated by Adams (*1*), and its composition was comparable to that reported for the volatile oil by Schorger. The tannin content of both the bark and wood was also investigated (*4*). Dore (*5*) reported wood resins, volatile oils, and tannins in ponderosa pine sapwood extractives made with benzene, followed with alcohol. However, neither the distribution nor nature of the extractives in ponderosa pine has been thoroughly studied. The term "extractives" as used here refers to the acetone-soluble material present in the wood and is distinct from the oleoresin. Acetone was chosen as the solvent for this study, since it was found to be one of several good extractants for green wood.

Three mature trees from each of three widely distributed stands of ponderosa pine were used. Stand I, elevation 4950 feet, located in Grant County, near Seneca, Oreg., consists essentially of relatively slow-growing trees taken from an area which is selectively logged. Stand II, elevation 4600 feet, is located in Wallowa County, near Wallowa, Oreg.; these trees likewise represent relatively slow growth, and were in a mixed stand including white fir, Douglas fir, and larch. Stand III, elevation 3200 feet, is located in Eldorado County, near Steeley, Calif. This is a good site, open pure stand, showing rapid growth, particularly during the first sixty years, all dominant.

TREATMENT OF SPECIMENS

As the trees were felled (January to March, 1944), 6-inch cross-sectional disks were cut from three logs from each tree. The butt section was removed from the butt log nearest the stump, from 12 to 18 inches above ground level. The middle disk was

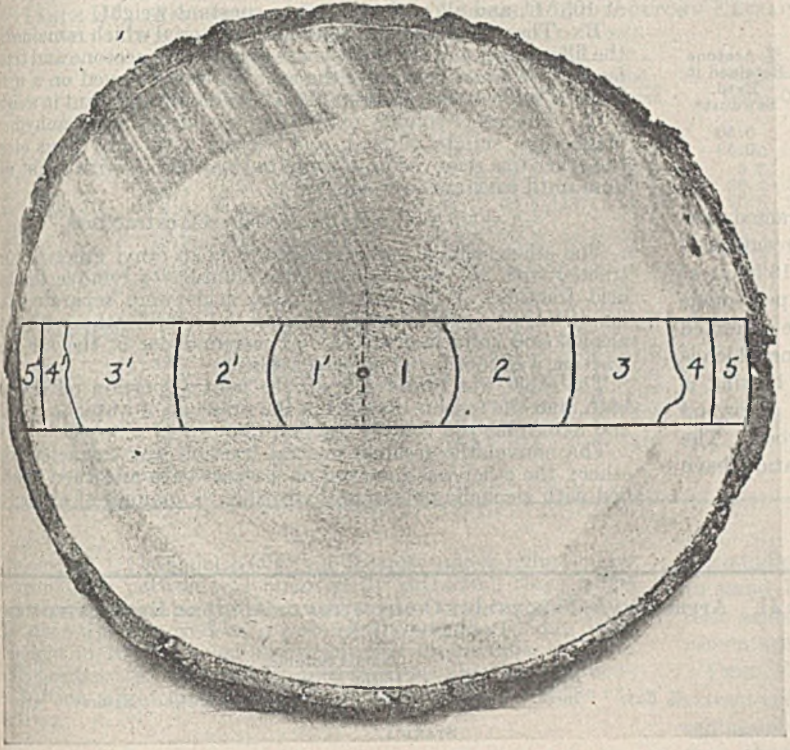

Figure 1. Method of Sampling Disks of Ponderosa Pine

1, 1' = inner heartwood; 2, 2' = intermediate heartwood; 3, 3' = outer heartwood; 4, 4' = inner sapwood; 5, 5' = outer sapwood

cut 32 feet from the butt cut; the third or top section was taken at a point approximately 64 to 65 feet from the stump.

Immediately after removal from the tree, these disks were shipped to the laboratory. Each disk, through its greatest diameter, was separated whenever possible into inner, intermediate, and outer rings in the heartwood as well as in the sapwood areas. Figure 1 illustrates this method of sampling. When it was difficult to distinguish sapwood from heartwood, the benzidine color reaction for identifying each was used (*7*). The authenticity of the tree in all cases was verified by microscopic identification.

If present in the disk, knots and massed pitch areas were removed and discarded before the sample was ground. The segregated wood was chipped and reduced to sawdust to pass a 2-mm. screen in a Wiley mill. The ground samples were kept in sealed glass jars in which most of the air had been displaced with carbon dioxide. This measure was taken to reduce the tendency for the extractives to oxidize and to discourage the growth of certain staining organisms during storage. Kurth (*9*) showed that the chemical constants of the ether-soluble extractive from green slash pine sawdust differs considerably from that of the extractives from seasoned wood.

EXTRACTIONS AND SOLVENT RETENTION

The extractive content was determined, in duplicate, by extracting 4 to 6 grams of green sawdust in Soxhlet extractors, using alundum thimbles with C.P. acetone for 8 hours. The extracted sawdust was dried in an oven for 16 hours at 105° C. and weighed. In this manner the weight of the sample, less moisture and extractives, was obtained. The moisture content of the green sawdust was determined by the toluene method (*13*) rather than by the drying oven procedure. The former method was chosen since some of the samples contain enough volatile oil to cause the oven dry value for moisture to be too high.

Further, a study was undertaken to determine if any acetone was retained by the extracted ponderosa pine sawdust after it was heated for 16 hours at 105° C. If solvent is retained, it lowers the actual extractive content of the wood, if that value is determined by weighing the extracted sawdust (the procedure used in this investigation). As Wiertelak and Garbaczowna (*12*) pointed out, benzene-alcohol is held tenaciously by wood even by prolonged heating at 105° C.

In the case of ponderosa pine sawdust, the percentage of extractives was determined on composite samples of heartwood and of sapwood by weighing the extractives and by the loss in weight of the extracted sawdust after each was dried in an oven for 16 hours at 105° C. In addition, the amount of acetone retained in the oven-dried extracted sawdust was determined by slowly distilling 5 to 10 grams of oven-dried extracted sawdust in the presence of water until the distillate (about 125 ml.) gave a negative test for acetone, as indicated by the well-known salicylaldehyde color test. The total quantity of acetone in the distillate was determined by hydroxylamine hydrochloride according to the method of Krajcinovic (*8*). Oven-dried sawdust, without the solvent, gave a negative test for acetone. A sum-

Table I. Distribution of Acetone Extractives in Ponderosa Pine

Stand	Tree No.	Position in Tree	Approx. Total Ring Count	Diam. Inside Bark, In.	Greatest Radius, In.		Extractives[a], %					
							Heartwood			Sapwood		
					Heart	Sap	Inner	Intermediate	Outer	Inner	Intermediate	Outer
I	1	Top	244	17.7	6.5	3.8	7.0	..	8.1	5.1	..	3.9
		Middle	303	21.0	8.0	2.8	5.7	5.2	6.1	6.0	..	4.5
		Butt	366	23.5	10.5	3.5	6.6	6.9	6.8	5.5	..	4.8
I	2	Top	240	19.6	7.6	2.0	7.9	9.3	6.7	4.4	..	3.0
		Middle	287	21.6	9.7	2.0	5.6	6.8	5.5	3.9	..	2.4
		Butt	355	23.2	10.4	3.3	24.6	20.9	18.6	4.4	..	3.8
I	3	Top	237	17.7	6.1	3.1	4.9	..	7.2	2.5	..	2.3
		Middle	308	20.6	7.5	3.0	5.3	5.6	6.8	4.4	..	3.3
		Butt	348	22.2	9.0	3.0	15.1	8.9	12.2	5.2	..	3.5
II	4	Top	158	11.9	2.6	4.1	6.5	..	..	3.2	..	3.4
		Middle	210	14.7	3.5	4.5	4.2	..	5.2	2.7	..	2.6
		Butt	268	21.7	4.7	8.0	22.2	..	31.4	4.3	3.5	2.4
II	5	Top	107	11.6	2.8	3.7	5.3	..	..	2.8	..	2.7
		Middle	146	14.4	3.7	4.0	3.2	..	3.5	2.4	..	2.7
		Butt	197	23.4	5.1	7.4	19.9	..	15.5	5.6	5.8	3.1
II	6	Top	125	10.4	2.0	4.0	7.6	..	..	2.8	..	2.8
		Middle	231	16.7	7.0	3.0	3.9	3.9	4.5	3.3	..	4.2
		Butt	272	25.6	7.7	7.7	7.5	15.1	17.4	3.7	4.0	3.4
III	7	Top	100	21.7	7.2	4.2	4.5	..	4.5	4.8	..	5.3
		Middle	120	26.3	8.7	5.7	7.6	..	3.6[b]	2.1[c]	..	3.0
		Butt	138	29.7	6.2	9.5	5.2	..	5.1	3.2	3.1	3.6
III	8	Top	59	16.3	2.4	6.1	5.0	..	..	2.6	3.6	3.1
		Middle	69	20.3	4.0	6.7	7.9	..	5.3	4.7	3.6	2.6
		Butt	82	24.9	3.8	9.5	19.8	..	16.8	6.5	4.5	3.7
III	9	Top	54	14.6	1.9	6.5	7.8	..	..	3.2	3.3	2.0
		Middle	70	18.9	2.5	8.0	6.6	..	..	3.0	3.0	2.5
		Butt	83	25.9	3.5	10.4	31.5	..	36.9	9.8	7.6	4.1

[a] Based on moisture- and solvent-free samples.
[b] Massed pitch area, 41.5% extractives.
[c] Massed pitch area, 36.8% extractives.

mary of the average solvent retention and percentage extractives of twenty-four separate determinations follows:

	% Extractives			% Acetone Retained in Extd. Sawdust[a]
	Extractives	Extracted sawdust	Difference	
Heartwood	10.10	9.64	0.46	0.50
Sapwood	4.15	3.58	0.57	0.59

[a] % oven-dry weight of wood (105° C. for 16 hours).

It is shown that acetone is not removed from extracted sawdust even after prolonged heating. Further, the percentage of acetone retained in the solvent-treated sawdust after 16 hours at 105° C. represents approximately the discrepancy in percentage extractives as determined by the loss in weight of the extracted sawdust and by weighing the extractives. The acetone which is held tenaciously in the wood even after prolonged heating is easily removed when heated in the presence of water. Sapwood apparently retains slightly more acetone than heartwood. The percentages of extractives reported in this investigation have been corrected for solvent retention.

Equal quantities of heartwood sawdust from the butt section of each of the trees in stand I were mixed and extracted for 8 hours in large all-glass Soxhlet extractors with C.P. acetone. Sufficient sawdust was treated to give from 7 to 10 grams of extractives. The sapwood sawdust from the butt cut was similarly treated. This procedure was repeated for the middle and top sections and likewise for trees in stands II and III. Table II gives data on the analysis of the various extractives.

In order to determine the nature of the extractives through the cross-sectional growth of the tree, the inner butt heartwood from two trees of stand I was mixed and extracted as previously described. This was repeated with the outer heartwood and inner and outer sapwood of the butt sections. The same procedure was used for the middle and top sections. Two trees from stand III were similarly treated. Table III gives the results.

ANALYSIS OF EXTRACTIVES

The following scheme of analysis was found convenient for separating the various acetone-soluble extractives into their major chemical entities—water- and ether-insoluble, water-soluble, resin acids, free fatty acids, volatile, esters, and unsaponifiable. Hibbert and Phillips (*6*) used similar procedure in their investigation of the benzene- and alcohol-soluble extractives from Jack pine. The modified method used here is described briefly as follows:

The acetone, from an aliquot containing between 7 to 10 grams of extractives, was distilled from a water bath.

A. The extractives and water which remained in the flask were transferred to a separatory funnel with ethyl ether. The water layer was filtered through No. 615 E & D filter paper into a tared evaporating dish. The ether solution was extracted twice with 50 cc. of water and filtered as before. The evaporating dish containing the water solubles was transferred to an oven at 105° C. and allowed to come to constant weight.

B. The water- and ether-insoluble material which remained on the filter paper and in the flask was dissolved in acetone and transferred to a tared flask, and the acetone was removed on a water bath. The flask was put in an 105° C. oven until constant in weight.

C. The ether-soluble extractive was dried over anhydrous magnesium sulfate, filtered, and washed with anhydrous ether; the ether was removed on a water bath at 60° C. with slight vacuum until constant in weight:

$$A + B + C = \text{total acetone-sol. extractives}$$

The ether soluble was again dissolved in ethyl ether and extracted with 3% sodium hydroxide solution to remove the free acid fraction. From this the fatty acids were separated and quantitatively determined by preferential esterification with ethyl alcohol and sulfuric acid (*14*). The remainder of the free acid fraction was considered as resin acids.

The ether was removed from the neutral portion on a water bath, and the residue distilled in the presence of water to remove and determine the volatile fraction (*3*).

The nonvolatile residual neutral fraction was extracted with ether; the ether was removed on a water bath and then saponified with alcoholic potassium hydroxide (6 volumes of alcohol to

TABLE II. APPROXIMATE PERCENTAGE COMPOSITION OF ACETONE EXTRACTIVE FROM PONDEROSA PINE

	% Ext.	H_2O + Ether Insol.	H_2O Sol.	NaOH Soluble: Resin acids	NaOH Soluble: Fatty acids	Volatile	Esters	Unsaponifiable
STAND I								
Top sapwood	3.5	2.4[a] 0.08[b]	13.7 0.48	27.7 0.97	35.7 1.25	1.4 0.05	12.1 0.42	6.8 0.24
Top heartwood	7.3	4.6 0.33	2.2 0.16	36.2 2.64	31.5 2.30	2.6 0.19	11.8 0.86	11.1 0.81
Middle sapwood	3.5	2.8 0.10	16.6 0.58	20.6 0.72	31.9 1.12	1.4 0.05	17.4 0.61	9.0 0.31
Middle heartwood	5.8	5.9 0.34	4.9 0.28	35.2 2.03	27.3 1.58	3.0 0.17	12.2 0.71	11.4 0.66
Butt sapwood	4.5	1.7 0.08	9.3 0.42	22.7 1.02	38.1 1.72	1.9 0.09	16.3 0.73	10.0 0.45
Butt heartwood	13.4	3.5 0.47	2.8 0.37	45.9 6.16	18.2 2.45	5.1 0.68	11.0 1.48	13.5 1.81
Average sapwood[c]	3.8	2.2 0.08	12.9 0.49	23.6 0.90	35.5 1.35	1.6 0.06	15.4 0.58	8.7 0.33
Average heartwood[c]	8.8	4.3 0.38	3.1 0.27	40.9 3.60	23.9 2.10	3.9 0.34	11.5 1.05	12.4 1.09
Average total[c]	6.3	3.7 0.23	6.1 0.38	35.7 2.25	27.4 1.73	3.2 0.20	12.6 0.79	11.3 0.71
STAND II								
Top sapwood	3.0	2.4 0.07	9.9 0.30	24.2 0.73	41.9 1.26	2.1 0.06	10.4 0.31	9.1 0.27
Top heartwood	6.5	2.4 0.16	3.5 0.23	40.4 2.62	26.3 1.71	2.1 0.14	9.2 0.60	15.9 1.03
Middle sapwood	3.0	1.8 0.05	9.6 0.29	24.5 0.73	41.5 1.25	1.7 0.05	9.7 0.29	11.2 0.34
Middle heartwood	4.1	2.9 0.12	5.1 0.21	37.0 1.52	28.8 1.18	1.8 0.07	11.8 0.48	12.6 0.52
Butt sapwood	4.0	2.6 0.10	12.9 0.52	23.2 0.93	42.1 1.68	1.6 0.06	10.5 0.42	7.0 0.28
Butt heartwood	18.4	0.7 0.13	1.5 0.28	46.4 8.54	21.3 3.92	6.7 1.23	8.2 1.51	15.1 2.78
Average sapwood[c]	3.3	2.3 0.08	11.0 0.36	23.9 0.79	41.8 1.38	1.8 0.06	9.7 0.32	8.9 0.29
Average heartwood[c]	9.7	1.4 0.14	2.5 0.24	43.7 4.23	23.5 2.28	5.0 0.49	8.9 0.86	14.9 1.44
Average total[c]	6.5	1.6 0.10	4.7 0.31	38.7 2.52	28.2 1.84	4.2 0.27	9.1 0.59	13.4 0.87
STAND III								
Top sapwood	3.5	5.9 0.21	15.1 0.53	18.4 0.64	41.4 1.45	1.2 0.04	10.4 0.36	7.5 0.26
Top heartwood	5.4	5.0 0.27	1.9 0.10	36.4 1.97	33.3 1.80	1.4 0.08	11.2 0.60	10.6 0.57
Middle sapwood	3.1	1.7 0.05	13.6 0.42	23.0 0.71	41.8 1.30	2.7 0.08	9.0 0.28	8.0 0.25
Middle heartwood	6.2	2.7 0.17	3.7 0.23	40.0 2.48	31.3 1.94	2.2 0.14	10.0 0.62	10.0 0.62
Butt sapwood	5.1	1.5 0.08	7.6 0.39	28.4 1.45	42.4 2.16	1.2 0.06	11.1 0.57	7.6 0.39
Butt heartwood	19.2	0.9 0.17	2.6 0.50	52.0 9.98	19.5 3.74	6.6 1.27	7.1 1.36	11.2 2.15
Average sapwood[c]	3.9	2.9 0.11	11.5 0.45	24.0 0.94	41.9 1.63	1.6 0.06	10.3 0.40	7.7 0.30
Average heartwood[c]	10.3	2.0 0.21	2.7 0.28	46.9 4.83	24.3 2.50	4.8 0.49	8.4 0.87	10.9 1.12
Average total	7.1	2.2 0.16	5.1 0.36	40.6 2.88	29.2 2.07	3.9 0.28	9.0 0.64	10.0 0.71
Middle massed pitch	39.1	0.9 0.35	0.5 0.19	62.2 24.61	4.2 1.64	17.0 6.64	4.5 1.76	10.6 4.14

[a] Upper figure in each case is based on weight of extractives.
[b] Lower figure in each case is based on weight of moisture- and solvent-free wood.
[c] Calculated, based on yield of extractives from each section.

TABLE III. APPROXIMATE PERCENTAGE COMPOSITION OF ACETONE EXTRACTIVE FROM CROSS-SECTIONAL GROWTH OF TREE

	Butt				Middle				Top			
	Heartwood		Sapwood		Heartwood		Sapwood		Heartwood		Sapwood	
	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer
STAND I												
H_2O + ether insol.	3.0	1.7	1.8	4.7	6.7	2.6	3.4	5.7	4.0	2.3	2.2	3.0
H_2O sol.	2.5	1.5	11.6	16.0	7.8	4.1	17.6	18.0	6.2	3.6	16.9	21.6
Resin acids	57.5	45.4	23.2	18.4	35.2	36.7	21.2	20.4	36.2	36.6	19.2	18.0
Fatty acids	9.3	16.6	39.6	36.8	22.7	25.3	33.1	32.4	26.6	29.4	39.7	32.9
Volatile	6.6	4.6	1.0	1.9	2.3	1.9	..	1.6	1.5	2.1	0.6	0.6
Esters	9.7	12.6	12.1	14.3	11.9	15.5	14.4	11.4	12.1	13.4	13.2	14.5
Unsaponifiable	11.3	17.5	10.4	7.5	13.4	13.8	10.0	10.1	13.3	12.5	8.2	9.3
Extract[a]	19.9	13.0	5.3	3.6	5.5	6.1	4.2	2.8	6.6	7.3	4.7	3.5
STAND III												
H_2O + ether insol.	0.9	1.4	2.0	2.1	2.9	4.0	3.1	3.6	..	..	1.9	3.8
H_2O sol.	2.3	1.6	5.8	11.8	4.7	5.5	7.2	15.2	..	..	18.3	21.2
Resin acids	58.2	58.2	33.6	25.9	42.0	31.6	21.3	21.3	..	..	22.9	22.6
Fatty acids	10.7	10.8	38.9	42.5	24.4	31.9	46.3	42.9	..	..	33.9	33.5
Volatile	9.3	8.0	2.8	1.0	4.1	5.0	2.1	..	..	..	1.4	..
Ester	6.4	6.9	7.7	8.7	11.2	11.8	11.1	9.7	..	..	11.2	9.7
Unsaponifiable	11.4	12.9	9.2	8.0	10.6	10.1	8.9	7.3	..	..	10.3	9.1
Extract[a]	18.8	19.6	6.5	3.6	7.8	4.4	3.8	2.6	..	..	2.9	2.5

[a] Based on moisture- and solvent-free wood.

1 volume of 1:1 ethanol:KOH) for 2 hours under reflux. The unsaponifiable portion was removed by extracting three times with ether and washing the ether until neutral to phenolphthalein. The ether was removed on a water bath, and the residue dried overnight in 105° C. oven and weighed as unsaponifiable. The difference between this fraction plus volatiles and the total neutral portion represented the quantity of esters present in the extractives.

DISTRIBUTION OF EXTRACTIVES

While it is hazardous to present definite conclusions relative to the distribution of extractives in wood because of the many factors which affect composition, certain generalizations (with exceptions noted) appear evident. In most cases the results on the trees examined (Table I) seem to indicate the following trends of extractive distribution:

The greatest quantity of extractives occurs at the butt heartwood; the least amount appears at the outer sapwood.

With respect to the vertical distribution of extractables in the heartwood, the maximum is found at the butt and passes through a minimum at the middle of the tree with gradual increase toward the top. Trendelenburg and Schaile (*11*) reported similar distribution for smooth and rough bark pines.

The radial distribution of extractives in the heartwood above the butt appears to be at a maximum at the newly formed heartwood.

Vertically the extractives in the sapwood occur in greatest amount in the butt section; radially they increase inwardly.

At the butt the increase of extractive content from the inner sap to the adjacent heartwood may be quite marked.

The rate of growth does not appear to affect the amount of extractives present.

The extractive content of the tree produced by normal physiological growth increases many fold within an area which comes under the influence of pathological action caused by physical injuries due to fire, bruised, or cut areas.

HEARTWOOD AND SAPWOOD EXTRACTIVES

The majority of the data (Table II) on the composition of the acetone-soluble extractives obtained from ponderosa pine heartwood and sapwood seem to indicate certain trends which may be summarized as follows:

WATER AND ETHER INSOLUBLES. This entity, which appears in minor percentage in the extractives, is uniformly lower in the sapwood, based on wood weight.

WATER SOLUBLES. This constituent is found in much greater percentage in sapwood than in heartwood and is the only sapwood fraction in which the amount exceeds that obtained from heartwood. The water-soluble material is in relatively small proportion in heartwood extractive and its distribution is not uniform. In the sapwood of fast-growing trees (stand III), the percentage of water solubles increases as it approaches the top of the tree; in the slower-growing trees (stands I and II), the distribution in sapwood appears to be irregular.

RESIN ACIDS. The predominating component in heartwood extractives is resin acids. The percentage of resin acids to be found in heartwood appears to be contingent upon the quantity of extractives present. In stands I and II the top heartwood having the larger quantity of extractives contains a higher percentage of resin acids than the middle portion which contains the smaller amount of extract. In stand III this distribution is reversed. The percentage of resin acids in sapwood is approximately 25 to 50% less than the percentage of resin acids that occur in heartwood extract.

FREE FATTY ACIDS. The greatest constituent in sapwood extract is free fatty acids. Generally, in the heartwood the percentage of free fatty acid increases as it approaches the top of the tree; the percentage of this entity is relatively uniform throughout the sapwood region.

VOLATILES. The deposition of this material in the heartwood follows, in general, the same pattern of distribution as indicated for resin acids. In sapwood the percentage of volatile is relatively uniform. This essential oil fraction is found in larger proportions in the heartwood.

ESTERS. At the butt the sapwood extractive contains a greater percentage of esters then the adjoining heartwood. This likewise appears to be true for the sections above the stump level in the slower-growing trees (stands I and II). In the middle and top section of fast-growing trees (stand III), the percentage of esters is higher in the heartwood than in the sapwood.

UNSAPONIFIABLES. Heartwood has the larger percentage of unsaponifiable material than sapwood throughout the bole of the tree.

In some cases physical injury, such as occurred in the middle section of one of the trees in stand III, produced a copious quantity of extractives; a considerable increase in the percentage of resin acids and volatile is also apparent over that produced by normal physiological processes.

The heartwood extractive is a brownish-red semisolid, while the sapwood extract is a transparent yellow viscous liquid. The solid nature of heartwood extract is apparently due to its high resin acid content; the more liquid sapwood extract is due to its high percentage of free fatty acids.

NATURE OF RADIAL EXTRACTIVE

The variation in composition of extractives through the cross-sectional area of the tree (Table III) may be briefly summarized as follows:

WATER AND ETHER INSOLUBLES. This fraction in sapwood appears to decrease in percentage as it approaches the heartwood. In stand I this constituent appears to pass through a minimum in the newly formed heartwood and increases as it approaches the pith. In stand III this percentage distribution in the heartwood is reversed.

WATER SOLUBLES. The outer sapwood has the largest percentage of water solubles, while it appears to pass through a minimum at the newly formed heartwood.

RESIN ACIDS. In sapwood the smallest percentage of resin acids occurs at the outer region and increases as it approaches the heartwood. When the heartwood is reached, a material increase in resin acid is noted, but whether the inner or outer heartwood has the larger or smaller percentage of resin acids is dependent upon their respective extractive contents.

FREE FATTY ACIDS. This constituent increases in per cent as it passes from the newly formed sapwood to the inner sapwood where it reaches a maximum; then the percentage of fatty acids decreases as it approaches the pith.

VOLATILES. This fraction usually increases in per cent as it approaches the pith of the tree.

ESTERS. In heartwood the percentage of esters decreases from the outer heartwood to the pith. In some instances the percentage continues to increase as it approaches the outer sapwood; in others it tends to decrease.

UNSAPONIFIABLES. In general, the percentage of unsaponifiable is the least at the outer sapwood and increases, in some cases, to a maximum in the outer heartwood and then decreases as it approaches the center of the tree.

It is interesting to note that the composition of the outer middle heartwood in stand III indicates that it is apparently in the transition stage from sapwood to heartwood. The relatively low resin acid content, together with the slight increase in unsaponifiable material in this outer heartwood region, suggests that this transitional deposition of extractives was taking place.

APPLICATION OF RESULTS

In seeking means for effectively utilizing the potential chemical products from ponderosa pine, it was found that this wood contained a sufficient quantity of extractives to warrant the possible removal and recovery of these materials from the lumber and from forest and mill wood waste. Preliminary investigations have shown that it is possible to extract all or a large portion of the extractives from lumber; the result is a further improvement in the lumber offered by manufacturers; in addition, a commercial volume of extractive products may become available from this wood. The amount of recoverable extractables is not uniformly distributed throughout the trunk of the tree. The average extractive content in sapwood is usually within the limits 2.0 to 9.8% of the weight of the dry wood, while the heartwood extractables are usually within the limits 3.5 to 31.5% of the weight of the dry wood. The greater quantities of extractives are obtained from the lumber and wood waste originating from the butt portion of the trunk and from that portion of the tree containing massed pitch areas.

The acetone extractives, whether from the heartwood or sapwood, contain, in addition to resin acids and terpenes, free fatty acids, fats, and unsaponifiable material. Thus the extractives differ from gum oleoresin formed by wounding the tree by the presence of these aliphatic and unsaponifiable substances. The percentage of each of these entities is not uniformly distributed throughout the tree but depends from which part of the log the extractives are obtained. In the case of heartwood extractives, the products found in approximate order of quantity present are: resin acids, free fatty acids, unsaponifiable, esters, volatile, water soluble, and water and ether insoluble. In sapwood extractives these entities are found in the following order: free fatty acids, resin acids, water soluble, esters, unsaponifiable, water and ether insoluble, and volatile. Since the commercial value of these extractives is contingent in part upon the quantity and exact nature of its entities, the identification of each of these products is under investigation by this laboratory.

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Dissociation Pressure of Ammonium Carbamate

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TEMPERATURE-pressure relations for the dissociation of solid ammonium carbamate into gaseous ammonia and carbon dioxide have been measured by several investigators. (*1–5*). The reported values are divergent; at a total pressure of 40 atmospheres the divergence is as much as 17 atmospheres. Briggs and Migrdichian (*1*) measured the dissociation pressure of ammonium carbamate over temperature range 10° to 45° C. and obtained very consistent data. They also studied the effect of excess ammonia or carbon dioxide and found excellent agreement with the mass law according to the equation:

$$NH_4CO_2NH_2 \text{ (solid)} = 2NH_3 \text{ (gas)} + CO_2 \text{ (gas)} \qquad (1)$$

The present paper covers a study of the dissociation pressure of solid ammonium carbamate over the temperature range 35° to 83° C. and in the absence of an excess of either gaseous reactant. From the vapor pressure data the free energy of dissociation and the heat of dissociation have been derived.

PREPARATION OF SOLID AMMONIUM CARBAMATE

Solid ammonium carbamate was prepared directly in a 50-cc. sample bulb (Figure 1) which later was connected to the pressure-measuring system. Stoichiometric proportioning of the reactants, as was employed by Briggs and Migrdichian (*1*), proved to be unnecessary. The carbamate was deposited in the bulb from

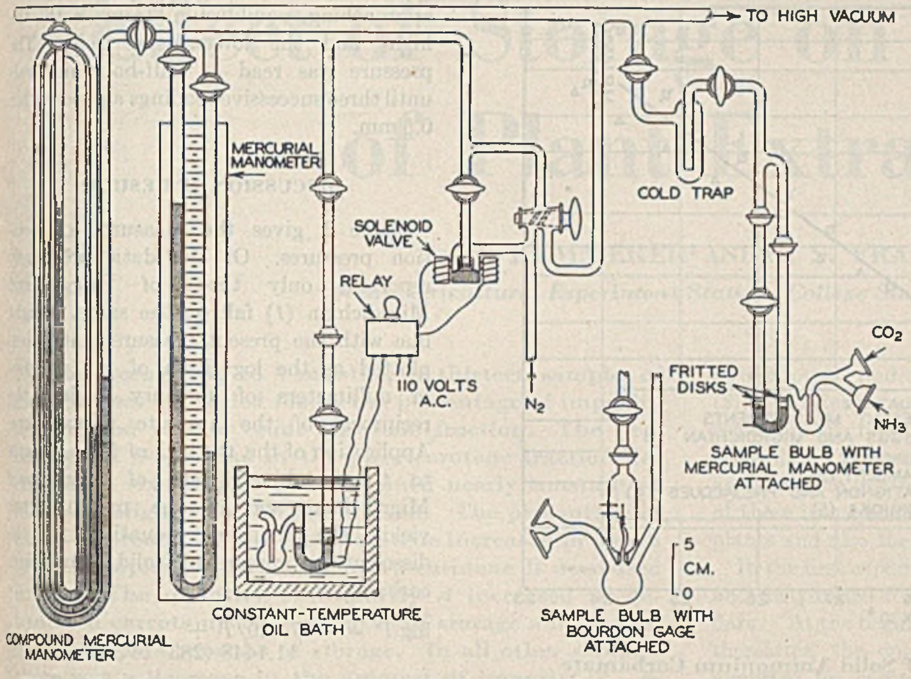

Figure 1. Apparatus for Preparing Ammonium Carbamate and Measuring Its Dissociation Pressure

a roughly equimolar mixture of ammonia and carbon dioxide which was charged at a rate of 1 liter per minute. Deposition of carbamate in the inlet and outlet tubes was prevented by maintaining the temperature of the tubes at 100° C. The gases, which were of commercial grade, were dried thoroughly to prevent the formation of ammonium carbonate and bicarbonate. The carbon dioxide first was washed with acid permanganate and then was dried successively with sulfuric acid and Dehydrite. The ammonia was dried with freshly pulverized fused potassium hydroxide. In preliminary trials in which the sample bulb was cooled with dry ice, expansion of the product on warming to room temperature shattered the bulb. This indicated either a high coefficient of expansion or a phase change in solid ammonium carbamate between −78° C. and room temperature. In subsequent work, therefore, the bulb was cooled in an ice-salt bath.

The ammonium carbamate was purified by alternate partial vaporization and evacuation through a vacuum line that contained a trap cooled with dry ice. The sample was first warmed until the dissociation pressure reached 700 to 800 mm. of mercury, then was cooled with a mixture of dry ice and acetone, and the system was evacuated to 10^{-4} mm. of mercury. After three such cycles of degasification, the sample was assumed to be free of foreign gases. On completion of the purification step, all the tubes joining the sample bulb were sealed off, except a short control manometer. The purified sample was not weighed but was estimated to be 0.2 to 0.4 gram.

The pressure of dissociation of solid ammonium carbamate into gaseous ammonia and carbon dioxide was measured over the temperature range 35° to 83° C. The results, when plotted as log P against $1/T$, fall on the same straight line as the data of Briggs and Migrdichian for the range 10° to 45° C. The combined data of the two studies are represented by the equation:

$$\log P\ (\text{mm. Hg}) = -2741.9/T + 11.1448\ (283° \text{ to } 355° \text{ K.})$$

The slope of the curve defined by this equation indicates that the heat of dissociation of ammonium carbamate, if assumed to be constant over the experimental range of temperature, is 37.6 kg.-cal. per mole. This value agrees with calorimetrically determined values reported previously. The equation is applied also in the derivation of the free energy of dissociation.

Each preparation was checked for quality by comparison of its dissociation pressure at an arbitrarily selected temperature of 34.5° C. with the value interpolated from the data of Briggs and Migrdichian (*1*). About one third of the preparations were discarded because their dissociation pressures exceeded the adopted tolerance of 1 mm. of mercury deviation from the interpolated value of 170 mm. of mercury. None of the preparations yielded a pressure of less than 170 mm. at 34.5° C.

MEASUREMENT OF DISSOCIATION PRESSURE

In the technique used for the pressure measurements, the autogenous dissociation pressure was allowed to come to equilibrium at a given temperature with the gases exposed only to the sample bulb and the short control manometer. The control manometer was a null-point instrument with sealed-in electrical contacts in a circuit that automatically balanced the dissociation pressure with nitrogen pressure. The measuring manometer was in the nitrogen system, as Figure 1 shows.

The control manometer used for pressures above 1000 mm. was a glass Bourdon gage that established electrical contact at the tip of the free end of the elastic element. This gage had the advantage that it presented only glass surface to the products of dissociation, but its sensitivity to temperature introduced a significant correction factor at pressures below 1000 mm. At these lower pressures, therefore, a mercurial control manometer was used. A correction factor representing the pressure required to establish electrical contact was determined for each type of gage and was added algebraically to the observed dissociation pressures.

The balancing pressure was obtained from a nitrogen cylinder through a reducing valve. The dissociation pressure was balanced by continuously bleeding a small amount of nitrogen from the system to a vacuum and intermittently introducing nitrogen under pressure through a solenoid valve that would pass a slow stream of gas under a differential pressure of about 10 cm. The valve consisted of an 8-mm. tube that terminated with a fritted glass disk slightly above a pool of mercury in an integral jacket to which the nitrogen source was connected. A cylindrical iron plunger surrounded the 8-mm. tube and floated on the mercury. A solenoid surrounding the jacket pulled down the plunger and thereby raised the mercury surface sufficiently to seal the fritted disk and prevent the passage of nitrogen. The solenoid was actuated through a vacuum tube relay and the contacts in the null-point manometer. At equilibrium the intermittent action of the solenoid caused fluctuations of less than 0.2 mm. in the level of mercury in the measuring manometer.

Pressures up to 1000 mm. were measured on a mercurial manometer with a 12-mm. bore. One leg of the manometer was evacuated to $< 10^{-4}$ mm., which made the manometer absolute within the accuracy of the readings. To eliminate parallax, a glass mirror scale and a sliding hairline index were employed for

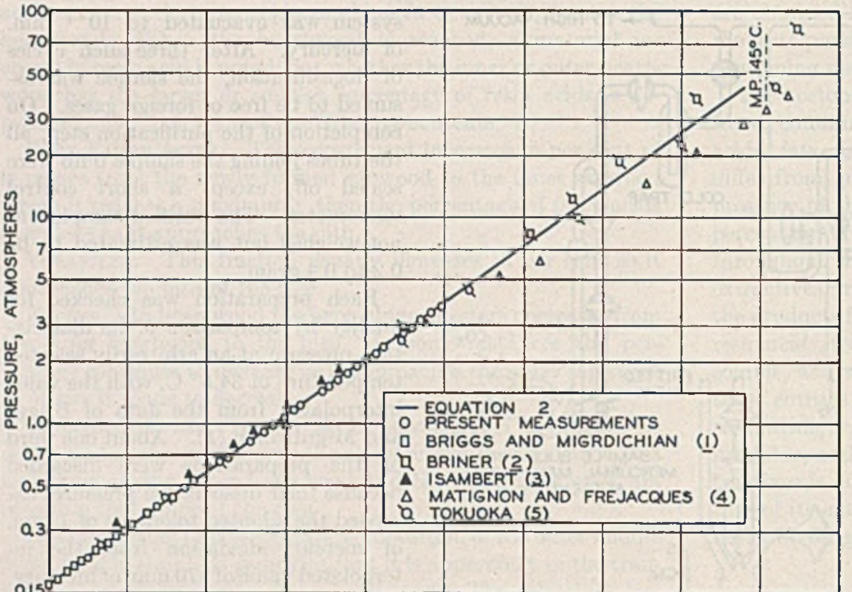

Figure 2. Dissociation Pressure of Solid Ammonium Carbamate

reading the manometer. The pressure readings were corrected to 0° C. for the expansion of glass and mercury.

Pressures above 1000 mm. were read on a three-stage compound mercurial manometer in which the interstage spaces were filled with freshly boiled distilled water. As with the simple manometer, the final leg of the compound manometer was evacuated. The manometer was mounted on a heavy paper scale that differed from the glass scale by less than 1 part in 1000. The pressure differentials in the three stages of the manometer, corrected for the head of water in each stage, were added to give the total pressure. The total pressure was corrected to 0° C. for the expansion of mercury.

The sample was heated in a thermoregulated oil bath. The temperature of the bath was estimated to the nearest 0.01° C. with a calibrated thermometer; the over-all accuracy probably was ±0.1° C. The attainment of equilibrium was ensured by approaching equilibrium from both the high- and the low-pressure sides. The pressure was read at half-hour intervals until three successive readings agreed within 0.5 mm.

Table I. Dissociation Pressure of Ammonium Carbamate

Temp., ° C.	P, Mm. Hg	Temp., ° C.	P, Mm. Hg	Temp., ° C.	P, Mm. Hg
34.49	170.1	56.98	688.7	68.91	1327
34.55	171.2	58.26	743.7	70.43	1459
34.59	170.9	59.31	790.1	71.74	1551
42.99	294.2	59.83	812.5	73.18	1673
43.18	295.1	61.24	881.9	74.40	1805
46.48	366.8	62.09	924.2	76.47	1998
47.53	388.9	62.09	925.7	77.30	2093
50.92	479.2	62.13	927.2	78.82	2264
52.19	517.2	65.20	1096	80.27	2456
54.73	603.2	66.19	1158	81.81	2659
55.00	610.2	67.20	1223	83.33	2856
55.78	641.6	67.56	1248	83.38	2864

Table II. Free Energy of Dissociation of Solid Ammonium Carbamate

Temp., ° C.	P, Atm.	K_p, Atm.[a]	$\Delta F°$, Cal./Mole
0[b]	0.0167	6.90×10^{-7}	7700
20	0.0811	7.90×10^{-5}	5500
40	0.3212	4.91×10^{-3}	3310
60	1.078	1.86×10^{-1}	1110
80	3.153	4.64	−1080
100[b]	8.223	8.23×10	−3270
120[b]	19.45	10.90×10^2	−5460
140[b]	42.33	11.23×10^3	−7660

[a] $K_p = \frac{4}{27}P^3$, where P is dissociation pressure in atmospheres.

[b] Extrapolated.

DISCUSSION OF RESULTS

Table I gives the measured dissociation pressures. Of the data previously reported, only those of Briggs and Migrdichian (*1*) fall on the same straight line with the present measurements when plotted as the logarithm of the pressure in millimeters of mercury against the reciprocal of the absolute temperature. Application of the method of least squares to the combined data of Briggs and Migrdichian and of the present work yields the following equation for the dissociation pressure of solid ammonium carbamate:

$$\log P = -2741.9/T + 11.1448 \quad (283° \text{ to } 355° \text{ K.}) \qquad (2)$$

where P = pressure, mm. of Hg
T = absolute temperature

The average deviation of the present measurements from Equation 2 is ±0.4% and the maximum deviation is 1.4%; the corresponding values for the data of Briggs and Migrdichian are ±0.3 and 1.3%, which are of the same magnitude as for an equation representing Briggs and Migrdichian's data alone. Figure 2 compares calculated and measured dissociation pressures.

If it is assumed that solid ammonium carbamate dissociates according to Equation 1 and that the vapor is a perfect gas system,

$$p_{NH_3} = \left(\frac{2}{3}P\right)^2, \; p_{CO_2} = \frac{1}{3}P$$

$$K_p = \frac{4}{27}P^3$$

Values of the dissociation constant, K_p, as calculated from smoothed dissociation pressures derived from Equation 2, are presented in Table II together with values for the free energy of dissociation as calculated from the relation:

$$\Delta F° = -RT \ln K_p$$

The heat of dissociation corresponding to Equation 1, as calculated from the slope of the vapor pressure line in Figure 2 on the assumption of constancy of the heat of dissociation, is 37.6 kg.-cal. per mole of solid ammonium carbamate. This value agrees with calorimetrically determined values (*3*) but is lower than the heat of dissociation calculated by Krase (*3*) from the dissociation pressure data of Briner (*2*).

In this paper no correction of measured pressure to fugacity has been made. A trial calculation, assuming the absence of mixture effect, indicates that, at the melting point, the fugacity of the mixed gases would be about 10% lower than the pressure, which is within the error introduced by extrapolation.

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Effect of Storage on Carotene of Plant Extracts

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During storage, up to 8 months, of thirteen samples of dried grasses and dried foods, the percentage of impurity *A* increased in the crude carotene fraction. The percentage of β-carotene in the pure carotene fraction decreased in six samples and remained nearly constant or increased slightly in the other seven. The percentage of neo-β-carotene U in the pure carotene increased in eleven of the samples, and that of neo-β-carotene B decreased in ten. The quantity of impurity *A* increased in dehydrated carrots up to 14 months of storage and in beet greens up to 4 months of storage. In all other samples there was a decrease in the amount of impurity *A*. β-Carotene, neo-β-carotene U, and neo-β-carotene B decreased in all the samples except beet greens, in which there was a slight increase in neo-β-carotene B during the second and fourth months of storage.

POLGÁR and Zechmeister (*6*) showed that *trans*-β-carotene can exist in a number of other stereoisomeric forms. Kemmerer and Fraps (*4*) reported that two of these stereoisomeric forms, neo-β-carotene U and neo-β-carotene B, are found in appreciable amounts in carotene extracts of plants. Neo-β-carotene B (*1, 3*) is reported to have one half the vitamin A activity of β-carotene, and neo-β-carotene U, one fourth (*5*) to one third (*2*). Carotene is known to be lost in storage, but no information regarding the relative stability of the several isomers in storage is available. The experiments reported here were conducted to ascertain the relative changes during storage in the percentages of these isomers and other constituents of the crude carotene of plants and also their relative loss during storage.

In the first experiment, samples of freshly dried ground grasses and dehydrated foods were stored at room temperature in the dark. At the beginning of the experiment and from time to time thereafter, the crude carotene fractions of the samples were analyzed for carotenoid constituents by a method previously published (*3*). The sample is treated with alcoholic potassium hydroxide in a Waring Blendor. The crude carotene is extracted with petroleum ether, and the petroleum ether solution purified by shaking with 90% methanol. Since the coloring matter is not entirely carotene, it is termed "crude carotene". All operations are carried out at room temperature. The various carotenoids in the crude carotene solution are finally ascertained by chromatographic analysis on calcium hydroxide (*3*). With this procedure there is less than 10% loss of pigment.

Table I gives the results. Impurity *A* consists of several pigments which do not have vitamin A potency. Pure carotene may be defined as the crude carotene minus impurity *A*, and consists of the vitamin A active pigments neo-β-carotene U, β-carotene, neo-β-carotene B, and, in the case of carrots, α-carotene.

TABLE I. EFFECT OF STORAGE ON PERCENTAGE OF CONSTITUENTS IN CRUDE AND PURE CAROTENE

Sample	Storage Time, Months	Crude Carotene, P.P.M.	Impurity *A* in Crude Carotene, %	Carotenes in Pure Carotene, %		
				Neo-β carotene U	β-Carotene	Neo-β-carotene B
Beet greens	0	517	4.1	8.5	70.3	21.2
	2	322	7.3	15.6	74.6	9.8
	4	270	10.1	20.4	68.3	11.3
	10	167	11.6	21.9	61.5	16.6
Eastern grama grass	0	121.0	11.0	19.3	69.6	11.7
	2	72.0	24.8	15.3	75.7	9.0
	4	52.0	23.8	19.2	65.0	15.8
	10	36.6	27.0	23.0	68.0	9.0
Buffalo grass	0	79.0	13.0	19.4	65.7	14.9
	2	60	23.9	31.4	55.7	12.9
	4	45.0	18.7	20.6	66.4	13.0
	10	28.0	19.6	26.6	67.5	5.9
Bermuda grass	0	94.0	11.2	18.8	69.8	11.4
	2	52.0	17.5	20.7	67.0	12.3
	4	32.0	20.3	24.7	61.5	13.8
	10	17.2	27.8	26.6	68.4	5.0
Dallis grass	0	65.0	14.2	18.6	71.7	9.7
	2	18.5	35.4	22.3	71.3	6.4
	4	9.3	40.3	27.1	60.4	12.5
	10	4.4	57.3	30.9	61.7	7.4
Rhodes grass	0	117.0	11.3	16.6	71.0	12.4
	2	74.0	15.6	15.8	67.7	16.5
	4	51.0	15.7	18.7	70.0	11.3
	10	34.8	20.5	25.5	64.5	10.0
Crab grass	0	90.0	11.2	16.0	72.5	11.5
	2	47.0	23.9	15.9	71.0	13.1
	4	34.0	24.6	21.3	66.6	12.1
	10	18.6	31.0	...	...	...
Dehydrated carrots	0	862	3.0	36.0[a]	64.0	0
	2	765	6.2	34.2[a]	57.5	8.3
	6	650	6.2	28.5[a]	69.0	2.5
	10	650	9.1	32.1[a]	63.0	4.0
	14	675	7.5	32.1[a]	64.9	3.0
Dehydrated alfalfa	0	213	14.9	25.1	57.4	17.5
	2	173	20.0	23.0	61.4	15.6
	6	128	22.1	29.0	56.0	15.0
	10	97	22.5	29.4	56.0	14.6
	14	65	26.1	33.1	55.0	11.9
Dehydrated bur clover	0	290.0	4.5	0.0	84.5	15.5
	2	218.0	6.9	15.0	69.0	16.0
	6	112	10.7	19.5	66.5	14.0
	10	135	12.3	21.2	66.8	12.0
	14	83	15.7	23.1	65.7	11.2
Swiss chard	0	365.0	6.3	10.3	80.9	8.8
	2	...	13.0	18.8	66.7	14.5
	4	15.8	13.0	17.2	63.8	18.8
	10	5.9	17.4	22.6	59.8	17.6
Turnip greens	0	553.0	4.9	13.2	76.4	10.4
	2	...	18.4	21.7	65.7	12.6
	4	78.0	20.0	23.5	64.3	12.2
	10	30.6	24.1	20.0	76.0	4.0
Collards	0	432	23.9	14.7	67.2	18.1
	4	74.0	34.4	19.1	74.2	6.7
	10	28.5	41.9	12.1	77.0	10.9

[a] α-Carotene in carrots.

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Table II. Effect of Storage on Quantity of Carotenoid Constituents

	Quantities of Constituents, γ/Grams					Loss of Constituents, % of Original				
	Crude carotene	Impurity *A*	Neo-β-carotene U	β-Carotene	Neo-β-carotene B	Crude carotene	Impurity *A*	Neo-β-carotene U	β-Carotene	Neo-β-carotene B
Swiss chard	365.0	23.0	35.4	277.0	29.6	...	...	...	...	...
4 mo.	15.8	2.1	2.4	8.7	2.6	96	91	93	97	91
10 mo.	5.9	1.0	1.1	2.9	0.9	98	96	97	99	97
Beet greens	517.0	21.2	42.4	349.4	104.0	...	...	...	...	...
2 mo.	322.0	23.5	46.7	223.0	28.8	38	−11	−10	36	72
4 mo.	270.0	27.2	49.2	166.0	27.6	48	−28	−16	52	73
10 mo.	167.0	19.4	37.4	91.0	24.2	68	8	12	74	77
Turnip greens	533.0	26.1	66.5	387.0	53.4	...	...	...	...	...
4 mo.	78.0	15.6	14.7	40.2	7.5	86	40	78	90	86
10 mo.	30.6	7.4	4.7	17.6	0.9	94	72	93	95	98
Dehydrated carrots	862.0	25.0	300.0[a]	537.0	00.0	...	...	...	...	...
2 mo.	765.0	47.5	244.0	414.0	59.5	11.2	−90	19[a]	23	...
6 mo.	650.0	40.0	174.0	421.0	15.0	24.6	−60	42	22	75
10 mo.	660.0	60.0	190.0	384.0	24.0	23.4	−140	36	28	60
14 mo.	675.0	50.0	201.0	405.0	19.0	21.7	−100	33	24	68
Dallis grass	65.0	9.2	10.4	40.2	5.2	...	...	...	...	...
2 mo.	18.5	6.6	2.7	8.4	0.8	72	28	74	79	85
4 mo.	9.3	3.7	1.5	3.4	0.7	86	60	86	92	87
10 mo.	4.4	2.5	0.6	1.2	0.1	93	73	94	97	98
Bermuda grass	94.0	10.5	15.8	58.3	9.4	...	...	...	...	...
2 mo.	52.0	9.1	8.9	28.7	5.3	45	13	44	51	42
4 mo.	32.0	6.5	6.3	15.7	3.5	66	38	60	73	63
10 mo.	17.2	4.8	3.3	8.4	0.7	82	54	79	86	93
Buffalo grass	79.0	10.2	13.4	45.4	10.0					
2 mo.	60.0	14.3	14.4	25.5	5.8	24	−4	−7	44	42
4 mo.	45.0	8.4	7.5	24.3	4.8	43	18	44	46	52
10 mo.	28.0	5.5	6.0	15.2	1.3	65	46	55	67	87
Rhodes grass	117.0	13.2	17.2	74.0	12.6					
2 mo.	74.0	11.6	9.8	42.3	10.3	38	12	43	43	18
4 mo.	51.0	8.0	8.1	30.0	4.9	56	39	53	60	61
10 mo.	35.0	7.2	7.1	17.9	2.8	70	45	58	77	78
Dehydrated alfalfa	213.0	31.8	45.5	104.0	31.8	...				
2 mo.	173.0	34.6	31.7	85.2	21.5	19	...	30	18	32
6 mo.	128.0	28.1	28.5	56.0	15.3	40	12	37	46	52
10 mo.	97.0	21.8	22.1	42.1	11.0	54	31	51	59	65
14 mo.	65.0	17.0	15.9	26.4	5.7	70	46	65	75	82

[a] α = Carotene in carrots.

The percentage of impurity *A* in the crude carotene increased with the length of the storage period. For example, at the end of 10 months the percentage of impurity *A* had increased from 3.0 to 9.1 in dried carrots, 6.3 to 17.4 in Swiss chard, 4.1 to 11.6 in beet greens, 4.9 to 24.1 in turnip greens, 11.2 to 31.0 in crab grass, and 14.2 to 57.3 in Dallis grass.

In the pure carotene the percentage of β-carotene decreased in six of the samples; it remained nearly constant or exhibited a slight increase in the other seven. The percentage of neo-β-carotene U increased in eleven of the samples, and the percentage of neo-β-carotene B decreased in ten. Apparently neo-β-carotene U is more stable than the other two carotenes. The α-carotene in carrots decreased from 36.0 to 32.1%.

Table III. Effect of Storage and Stirring on Loss of Carotenoid Constituents in Alfalfa

Storage Conditions	Time Stored	Crude Carotene, P.P.M.	Impurity *A* in Crude Carotene, %	Carotenes in Pure Carotene, %		
				Neo-β-carotene U	β-Carotene	Neo-β-carotene B
Refrigerator, 5° C.	0	173	7.8	16.5	71.0	12.5
	1 mo.	170	9.9	18.3	66.3	15.4
	2 mo.	152	...	...	...	...
	3 mo.	160	10.2	15.8	68.8	15.4
	4 mo.	144	11.5	16.3	71.7	12.0
	8 mo.	116	17.0	16.9	62.5	20.6
Incubator, 37° C.	0	173	7.8	16.5	71.0	12.5
	1 wk.	172	12.6	17.3	70.5	12.2
	2 wk.	152	12.4	16.3	74.5	9.2
	4 wk.	114	11.6	18.6	66.3	15.1
	2 mo.	97	15.3	18.7	70.2	11.1
	3 mo.	68	18.5	21.0	61.6	17.4
	4 mo.	57	19.4	23.3	65.2	11.5
	6 mo.	46	22.0	20.5	59.0	20.5
	8 mo.	38	27.3	23.6	62.3	14.1
Incubator, 37° C., stirred	0	173	7.8	16.5	71.0	12.5
	1 wk.	172	9.3	18.3	72.2	9.5
	2 wk.	144	11.3	17.7	71.5	10.8
	4 wk.	100	14.3	17.3	66.7	16.0
	2 mo.	78	20.9	22.6	67.2	10.2
	3 mo.	52	21.9	23.8	63.5	12.7
	4 mo.	43	21.8	24.8	62.6	12.6
	6 mo.	33	23.5	27.2	56.7	16.1
	8 mo.	28	28.3	25.2	58.3	16.5

The data were further examined (Table II) to ascertain if the changes in percentage were due to an increase in the quantities of any of the carotenes or to differences in the rates of loss. The quantity of impurity *A* increased only with dehydrated carrots, and with beet greens after storage for 2 or 4 months. When stored 10 months, there was a loss of impurity *A* from the beet greens. An apparent gain of neo-β-carotene U occurred with the beet greens during 2 and 4 months of storage and with buffalo grass after 2 months of storage. In the other tests there were losses of all pigments in storage. Most of the increase in percentages of impurity *A* in the crude carotene and of neo-β-carotene U were due to greater resistance to destruction than the other pigments possessed, and not to increase in quantities present.

In a second experiment a sample of dehydrated alfalfa leaf meal was divided into three aliquots. One aliquot was stored in a refrigerator at 5° C. and one in an incubator at 37° C.; the third was stored in an incubator at 37° C. and stirred for 5 minutes, twice weekly. After the storage periods designated in Table III, the constituents of the crude carotene in the three aliquots were determined. The percentage of impurity *A* in all three was increased during storage. Lower percentages of impurity *A* were found in the sample stored at 5° C. than in the two samples stored at 37°. The stirred sample did not contain any greater percentages of impurity *A* than the unstirred samples. As in the first experiment, the carotenoid constituents were calculated exclusive of impurity *A*. There was an increase in the percentage of neo-β-carotene U and a decrease in the percentage of β-carotene in the pure carotene fraction of the two samples stored in the incubator. The results on neo-β-carotene B were erratic but indicate no appreciable change in its percentage. Stirring did not affect the percentages of these pigments.

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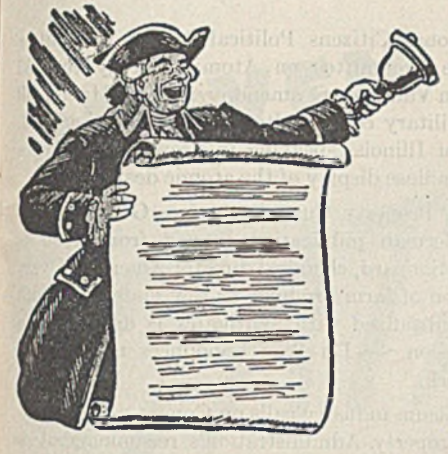

MARCH'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ MARCH 1. Messel Medal of Society of Chemical Industry awarded to Wallace P. Cohoe, former president of the society, New York consultant~~Expansion program for more than doubling manufacture of Geon polyvinyl resins announced by W. S. Richardson, president of B. F. Goodrich Chemical Co.~~Government-owned aluminum sheet mill at McCook, Ill., leased to Reynolds Metals Co.

¶ MARCH 2. Harold C. Urey criticizes Army's Manhattan District Engineer Corp. for insistence that the control of atomic power be vested in the military, and assails Maj. Gen. Groves for recommending press curbs during Bikini atomic bomb experiments.~~Federation of American Scientists receives annual New York Teachers Union award for outstanding leadership in educating America for international control of atomic power.~~Five Jewett Fellowships of $3000 each awarded by Bell Telephone Laboratories for research in physical sciences[1].

¶ MARCH 3. Monsanto Chemical Co. invested $29,000,000 in new manufacturing facilities since 1941, chairman of the board Edgar M. Queeny reports, announcing plan for financing an expansion program.~~War Assets Corp. reports that disposals of surplus capital and producers' goods rise steadily but still lag behind declarations of surplus, while sales of plants show marked acceleration.~~Major changes in Du Pont explosives department announced, including dropping war explosives unit.~~War Department reports that Army Ordnance plants are turning out 4000 tons of anhydrous ammonia monthly to alleviate a critical fertilizer chemical shortage.

¶ MARCH 4. Canadian Royal Commission investigating espionage activities names four involved in leakage of secret information on atom and radar data.~~Rubber Manufacturers Association says synthetic rubber consumption in 1945 hit a record total of 700,000 tons.

¶ MARCH 5. J. R. Oppenheimer, former director of atomic bomb project at Los Alamos, receives 1945 Wedge Award from Georgia Hardwood Lumber Co. for "accomplishments reflected toward the betterment of others".~~Westinghouse Electric awards $11,000 in scholarships to high school winners of talent search.

¶ MARCH 6. W. S. Carpenter, Jr., Du Pont president, says company has set up a three-year plan of expansion.

¶ MARCH 7. Supplementary report of Oil Division, U. S. Strategic Bombing Survey, details what happened to oil, chemical, explosives, and rubber industries in Germany and sees no defense against bombing.~~Corning Glass Works signs consent decree in antimonopoly suit.

¶ MARCH 8. Two hundred German scientists and technicians being brought to Britain to work in advisory capacity with industry, London Board of Trade announces; all volunteers employed by British Government, which will lend them to trade associations and research organizations.~~Infrared eye, known as superconducting bolometer, which can see in the dark 10 to 15 miles, disclosed by Donald H. Andrews, Johns Hopkins University, before American Optical Society meeting in Cleveland.~~Monsanto Chemical Co. says all-wool suits that will be cool in warm weather can be made by using Resloom, a melamine-formaldehyde resin.

¶ MARCH 9. Concentrated arc lamp, using zirconium, invented by W. D. Buckingham and C. R. Deibert, and demonstrated in New York by Western Union Telegraph Co., is expected to open up new researches with the optical microscope and aid photography.~~L. W. Houston, installed as president, Rensselaer Polytechnic Institute, announces expansion plans to meet shortage of engineers and scientists caused by war.

¶ MARCH 10. W. S. Hallanan appointed head of committee of seven by American Petroleum Institute to urge Congress to remove price ceilings on petroleum products.~~W. H. Kenyon, Jr., Patent Survey Committee counsel, Department of Commerce, says private inventor is giving way to corporation research teams.

¶ MARCH 11. James E. Pew, of Sun Oil Co., announces $4,000,000 program to conserve natural gas.~~Camille Dreyfus, chairman of board of Celanese Corp., tells of expansion program to meet demand for rayon.~~Federal Trade Commission recommends that Phosphate Export Association withdraw from cartel agreements with foreign producers of phosphate.~~Strikers permit supervisory, technical, and scientific employees of General Electric Co. to cross picket lines to resume atomic and medical research.~~Melvin Calvin, University of California, announces a new and simplified method of obtaining oxygen from air for industrial use.

¶ MARCH 12. Henry A. Wallace, Secretary of Commerce, officially opens Nuclear Energy Exhibit of the AMERICAN CHEMICAL SOCIETY in Department of Commerce building, Washington, D. C.[2]~~Special Senate Committee on Atomic Energy approves formation of military committee to review measures of Atomic Energy Control Commission proposed in McMahon bill.~~R. G. Gustavson, University of Chicago, urges National Foundation for Infantile Paralysis to set up research approach to close gap between biology and medicine and physics, chemistry, and mathematics.~~Zay Jeffries, testifying in GE antitrust suit, says company spent $27,000,000 to develop electric bulb.~~Edible squash seed, rich in oil and protein announced by L. C. Curtis, University of Connecticut, as possible basis of new industry.~~Alexander Silverman tells ACS Detroit Section glass may provide best defense against A-bomb radiation.

¶ MARCH 13. Department of Commerce says 12 patents owned by Walter Kidde & Co., Inc., Belleville, N. J., and Hercules Powder have been dedicated to U. S. public for free use.~~Hans

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[1] *Chem. Eng. News*, **24**, 815 (March 25, 1946).

[2] *Ibid.*, 770 (March 25, 1946).

Molitor, Merck Institute of Therapeutic Research, in address before Federation of American Societies for Experimental Biology in Atlantic City, says widespread use of penicillin and streptomycin germs may develop resistance to them within the next 5 or 10 years making them ineffective.

¶ March 14. A. E. Lacomble, president Shell Development Co., announces $3,500,000 expansion of Shell's research laboratories at Emeryville, Calif.[3]∼∼Maj. Gen. Leslie R. Groves announces he has authority to release information on atomic energy processes for peacetime purposes "in so far as such use does not impair the national security of the United States".∼∼President Truman renews demand for over-all control by civilians of atomic energy development.

¶ March 15. Kirby F. Mather, Harvard geologist at international convention of YMCA in N. Y., urges collaboration of 10 nations, including the Big Five, which have deposits fairly rich in uranium.∼∼Secretary of War Patterson at special press conference says he approves civilian control of atomic energy development but wants military "participation" in developments for military uses and also in decisions involving security.

¶ March 16. Rollins College Conference for World Government urges that General Assembly be reconstituted as legislative branch of world government and make laws regulating uses of atomic energy.∼∼Special Senate Committee on Atomic Energy adopts provisions affirming President's supreme control over atomic bombs, transferring all atomic energy plants and bombs from Army to a proposed Atomic Energy Control Commission, and prohibiting distribution of fissionable materials to foreign governments.

¶ March 17. Interagency Policy Committee on Rubber urges U. S. to retain nucleus of synthetic rubber industry and produce one third of country's estimated peacetime requirements, resorting to private ownership, continued Government allocation and specific control into 1948, and mandatory use of synthetic rubber.

¶ March 18. President Truman drafts Bernard M. Baruch as U. S. representative on United Nations Atomic Energy Commission. Baruch announces as alternates and co-workers, John Hancock, Wall St. banker; Ferdinand Eberstadt, N. Y. investment banker and lawyer and former vice chairman WPB; Herbert Bayard Swope, publicist and journalist; Fred Searls, N. Y. mining engineer. James B. Conant, Vannevar Bush, and Arthur H. Compton will supply "the necessary scientific guidance", Baruch says.∼∼Supreme Soviet adopts Russia's new Five-Year Plan for extensive research in atomic power.∼∼WAC places four aluminum reduction plants, representing a government investment of almost $73,000,000, on market.∼∼Government sources reveal big gain in penicillin output enables industry to increase by about 2.5 times amount of drug allocated for domestic civilian use in December.

¶ March 19. Libbey-Owens-Ford Glass earmarks $13,458,257 for current and future construction projects, John D. Biggers, president, informs stockholders.

¶ March 20. G. G. Oberfell, vice president in charge of research and development Phillips Petroleum Co., says gasoline from natural gas will not compete with present methods of refining from crude oil until crude is about $1.75 to $2.00 per barrel.∼∼Five scientists, key figures in development of atomic bomb, receive medal of merit, highest award the Government can make to civilians.

¶ March 21. Owens Corning Fiberglas announces purchase from WAC of plant in Huntingdon, Pa., which Fiberglas has operated since 1943.∼∼Representatives of 59 citizens groups in Washington, D. C., start drive to defeat Vandenberg's amendment to give the military control over atomic energy.

¶ March 22. President Truman orders 6 weeks delay in atomic bomb tests at Bikini Atoll.

¶ March 23. National Citizens Political Action Committee urges Special Senate Committee on Atomic Energy to hold full public hearings on Vandenberg amendment to McMahon bill as amendment for military control alters intent of original bill. ∼∼Senator Lucas of Illinois, speaking in Providence, opposes Bikini tests as a "grandiose display of the atomic destruction".

¶ March 24. Alien Property Custodian seizes German copyright interests in German publications issued from 1939 to 1945.∼∼Norman A. Shepard, chemical director American Cyanamid, says exportation of farm products as raw materials which cannot compete unsubsidized with synthetics is dangerous to sound market expansion.∼∼Du Pont announces new foamed plastic lighter than cork.

¶ March 25. Petroleum industry calls on Congress to veto immediately Surplus Property Administration's recommendations for government operation of Big and Little Inch pipe lines.∼∼President Truman announces appointment of five scientists and four members of Congress as his personal committee to evaluate forthcoming atomic bomb tests—Senators Hatch and Saltonstall, Chairman May of House Military Committee, and Representative Andrews to serve with scientists J. Robert Oppenheimer, Karl Compton, Bradley Dewey, Wm. S. Newell, and Fred Searls.∼∼Goodyear announces method of converting Pliofilm into a fabric. ∼∼Myron P. Backus and John F. Stauffer, University of Wisconsin, discover new mold which may double penicillin production.∼∼Truman Administration discloses to Congress plan to vest atomic energy control in international agency of UNO and that plutonium may be denatured.

¶ March 26. U. S. Department of Agriculture issues new rules for use of DDT to prevent food contamination.∼∼Commercial Solvents announces commercial production of sodium penicillin in crystalline form, eliminating refrigeration storage.∼∼Naugatuck Division of U. S. Rubber announces development of a permanent starch in form of resin that lasts the life of a garment.∼∼Members of Special Senate Committee on Atomic Energy ask for practical demonstration on denaturing plutonium.

¶ March 27. Association of British Chemical Manufacturers propose that Germany's dyestuff industry be revived for a time to help relieve world shortages and then be completely eliminated.∼∼GE announces expanded program of atomic power research, with appointment of 14 scientists formerly engaged in wartime atomic radar and similar projects.∼∼W. B. Bell, president American Cyanamid, announces plans of immediate expansion at a minimum of six different locations.

¶ March 28. State Department releases report of Board of Consultants headed by David E. Lilienthal of TVA urging a world-embracing technological monopoly of atomic power under UNO and declaring atomic energy feasible for early use in industry.∼∼Eastman Kodak, according to annual report, budgets $11,000,000 to cover research, development, and process equipment.∼∼Du Pont announces shatter-resistant sheets of Lucite acrylic resin with surface patterns formed as made.

¶ March 29. State Department says U. S. and Britain have signed new agreement on interchange of patent licenses.∼∼Senator Jas. W. Huffman introduces Senate resolution requesting President Truman to abandon atomic bomb experiments on surface targets at Bikini Atoll.

¶ March 30. Representative Hugh De Lacy, addressing Association of Teachers of Social Studies of New York declares military authorities in U. S. have 1500 atomic bombs and are making more.∼∼Republican unofficial Congressional food study committee proposes virtual reorganization of Department of Agriculture in food research bill.

¶ March 31. WAC places on market six carbon black plants, three magnesium properties, a potassium perchlorate plant, two butane plants, and a gasoline refinery.

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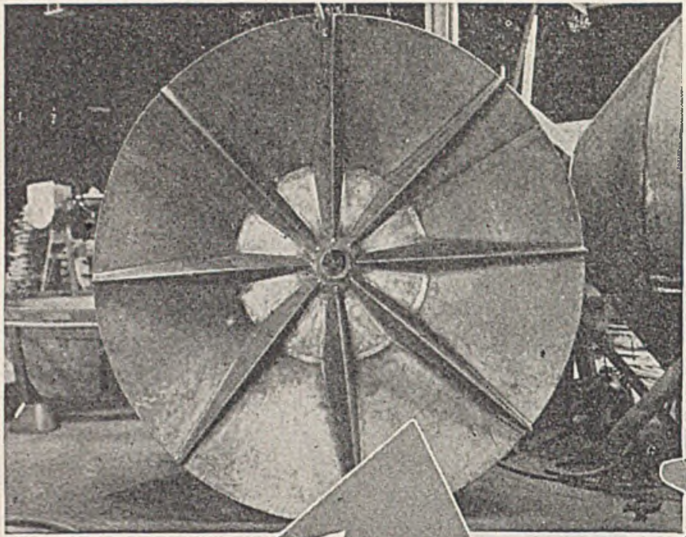
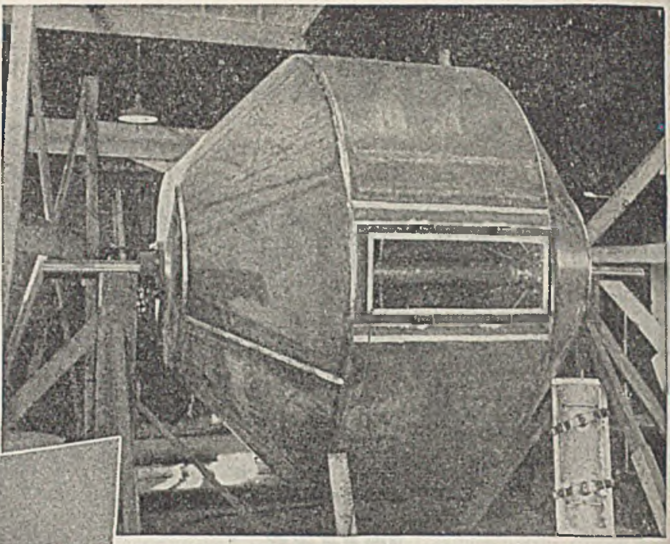
[3] *Chem. Eng. News*, 24, 796 (March 25, 1946).





FOR WORKABLE SHEET MATERIALS
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THESE pictures show plant equipment in special shapes and large sizes, fabricated of Revere sheet copper and sheet Herculoy by the Camden Copper Works, Camden, N. J. They illustrate the amazing versatility of these metals, which skilled coppersmiths the country over fabricate into practically any desired shapes from the flat.

Easy workability of course means faster and more accurate fabrication of apparatus for your plant. It may also mean lower prices from the fabricator, or lower labor costs in your own plant if you make your own equipment. Whether the final form be simple or complicated, the workability of copper and its alloys is a tremendous advantage.

More than this, copper's high heat conductivity may speed up processing, and cut fuel expense.

Copper resists attack by many substances, and thus has a long, sometimes endless life. Often copper pipes and vessels are replaced only because of a change in the plant; then the metal has a high reclaim value.

The Revere Technical Advisory Service will gladly cooperate with you in working out applications of copper, whether plate, sheet, strip or roll, or in other mill forms such as pipe and tube, rod and bar, and extruded shapes. Write Revere or see your Revere Distributor.

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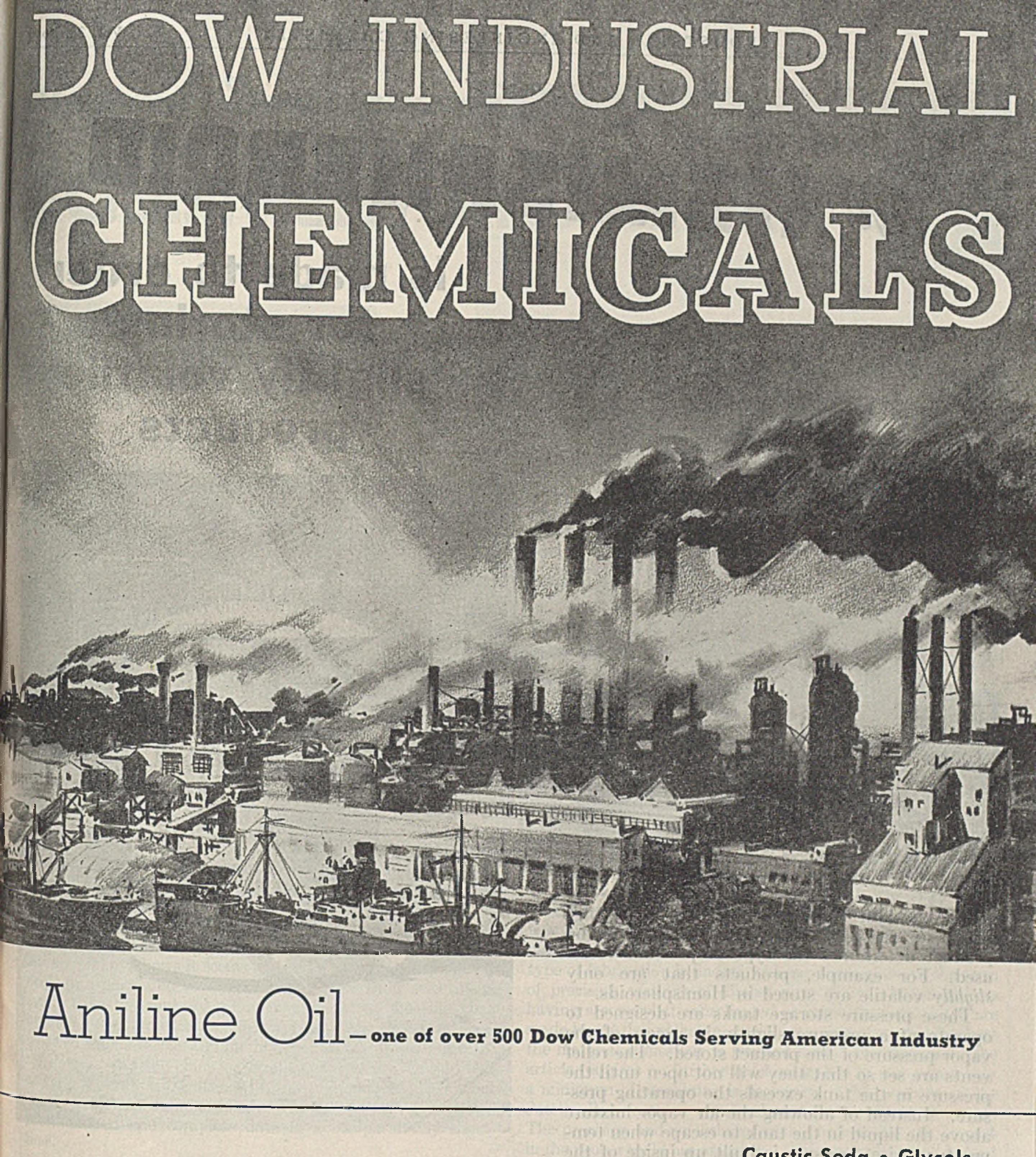
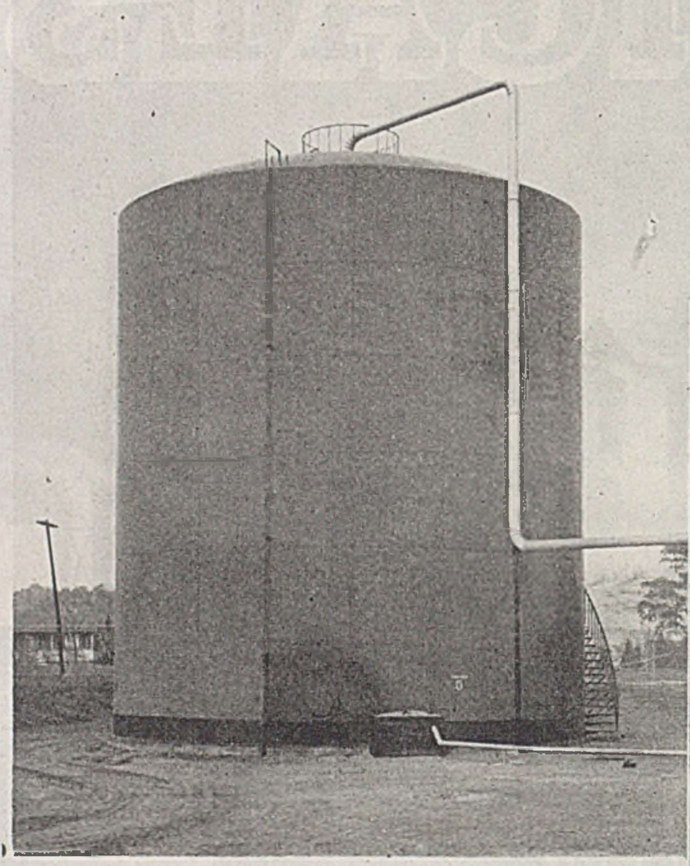
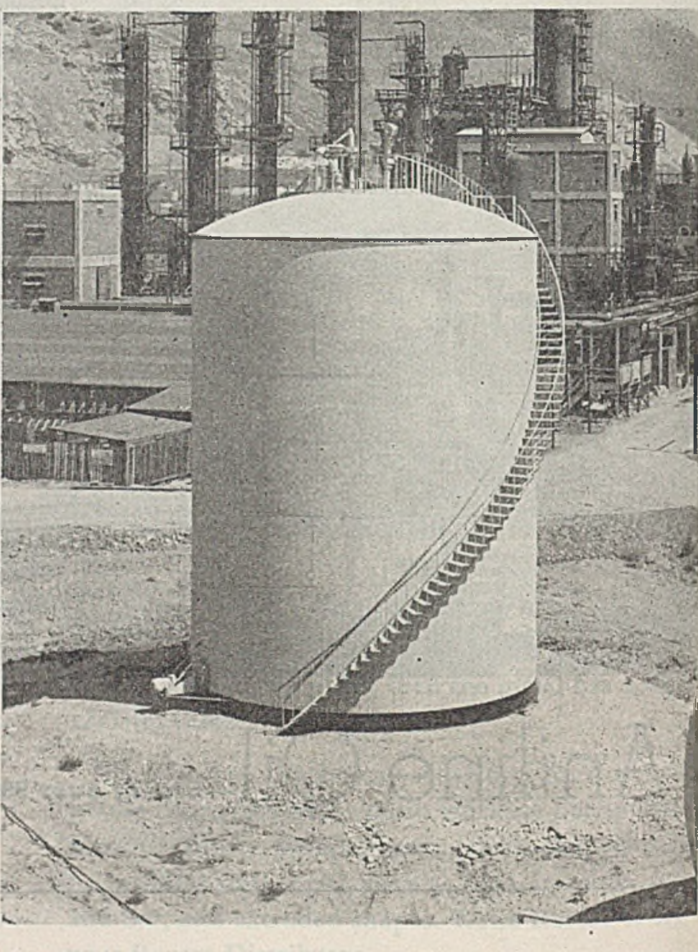


the HEMISPHEROID

is made to order for storing slightly volatile products





The Hemispheroid above holds 5,000 bbls. and is used to store isomate at 5 lbs. per sq. in. The Hemispheroid at the upper left of this page holds 12,500 bbls., is designed for a working pressure of ½ lb. per sq. in. and is used to store aqua ammonia

Liquids with volatile components are usually stored in pressure vessels. The volatility of the product determines the type of pressure vessel used. For example, products that are only *slightly* volatile are stored in Hemispheroids.

These pressure storage tanks are designed to operate at a pressure slightly in excess of the vapor pressure of the product stored. The relief vents are set so that they will not open until the pressure in the tank exceeds the operating pressure. Instead of allowing the air vapor mixture above the liquid in the tank to escape when temperatures rise, pressure is built up inside of the tank. Evaporation loss is prevented as long as the pressure inside of the tank does not exceed the operating pressure for which the tank was designed.

Hemispheroids are built in capacities from 2,500 bbls. to 30,000 bbls. for pressures from $2^1/_2$ to 5 lbs. per sq. in. For pressure storage tanks of larger capacities and higher working pressures Hortonspheroids or Hortonspheres are used.

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Current Developments in

EQUIPMENT AND DESIGN

Nickel and its alloys prevent equipment from wearing out under severe conditions.

Discussed by Charles Owen Brown

The chemical show was held in New York recently after an interruption of several years. As always, this show assembled an excellent collection of equipment and products, both durable and consumer goods. The equipment and products were primarily of interest to chemists—hence the name, Chemical Exposition. It is helpful and efficient to be able to inspect so many different lines, so many different types of equipment, and so many different products in one place. The magnitude of the exhibits offered, however, presents the problem to every chemist of attempting to absorb a reasonable proportion of the scientific data available. It is at least a three-hour job just to walk through the aisles and give a casual glance to each booth. To examine them carefully requires more than a day.

There are two methods by which one may view a show of this size. The popular method is to visit each booth in sequence, starting at the door, to give at least a brief inspection to the display featured, and to try to visualize the particular field of chemistry which the wares of that booth serve. This plan gives a complete but somewhat confused review of the show. The second and perhaps more interesting way is to pick some one line or phase of chemistry and follow this thread to those booths dealing with the subject.

To the young chemist the first method is probably the more profitable for a limited amount of time. However, after one has seen many shows it seems logical to measure the progress made in a particular field by inspecting the show selectively rather than horizontally. For example, after choosing corrosion as an important phase of equipment designing, we followed the materials and methods proposed for dealing with this factor. As the chief material for longer life we selected nickel. Recent applications of this valuable anticorrosion metal were located and studied. We found that this method gave detailed and complete data in a comparatively short time.

Properties of Nickel

The melting point of nickel, just below that of iron, is relatively high, 1452° C. (2646° F.). The tensile strength of annealed bars and sheets (99% Ni) is 62,000 to 75,000 pounds per square inch; it can be heat-treated and cold-worked to give a tensile strength of 150,000 pounds. The elastic limit or yield point is from 20,000 to 35,000 pounds for the annealed and 110,000 to 130,000 pounds for the heat-treated and worked material. It is a valuable metal for the designer and a great factor in preventing destruction of useful equipment.

The first application of nickel to catch our eye was a special concentric wire with a copper core and a pure nickel cover firmly bonded together. The entire outer surface was of pure nickel, but the wire had 73% of the electrical conductivity of pure copper, 137% of the strength of copper, and the resistance of nickel to all corrosion. Great resistance to corrosion at high temperatures led to the design of electrical heaters enclosed in a pure nickel cover, for fusing tanks of sodium nitrate and other pure salts. Nickel is not always used for its resistance to corrosion. It is also tough, hard, and wear resistant. These properties were utilized in making a relatively simple nozzle to direct a stream of water under 1400 pounds per square inch pressure. This water is used for its powerful action in removing scale from metals and bark from pulp logs. The force of this fast-moving stream does a real job of scouring on everything it touches, but the nickel nozzles withstand the wear.

Nickel has reasonably good heat conductivity. It is a valuable metal for heat transfer under corrosive conditions at high temperatures. Nickel tubes are available from stock with finned or extended surface for heat exchange equipment. Seamless drawn tubing and also lap-welded tubing are available in pure nickel with helical-coiled fins or lateral continuous-strip fins.

A rather new application is the development of ball bearings made of 100% nickel. The high tensile and compression strength required of the small parts are well supplied by nickel; in addition, the entire bearing withstands corrosion of salt air, salt water, and oxidation. These useful ball bearings are based on a better understanding of the heat treatment and fabrication of precision nickel parts. An important type of fabrication is finding wide economical use in the form of precision castings of almost pure nickel. Small objects having a somewhat complicated or intricate outer shape are made by casting nickel in special smooth surface molds where the material comes out in finished form. In many cases the article requires no further machining, but in any event only a minimum of machining is necessary. This was one of the outstanding features of nickel metallurgy during the war. The precision and smoothness with which nickel can be cast in the proper mold are amazing. This type of casting is used for the body of globe valves, special cocks, and pump impellers.

A special cast nickel containing 3% beryllium deserves mention. Fortunately the beryllium destroys none of the corrosion resistant properties of nickel, but adds considerably to the mechanical and physical properties. Such beryllium nickel can be hardened up to nearly 600 Brinell hardness number after proper heat treating. Centrifugal cast nickel wearing rings hardened with beryllium are finding useful applications in pump propellers, shafts, thrust bearings, and other pieces of moving equipment where corrosion resistant properties and high wear resistance are required.

Large-Scale Uses

Nickel is not confined to the fabrication of small pieces or decorative coatings. Caustic soda is made in enormous tonnage in the alkali industry,

(Continued on page 70)

Equipment and Design

and the large evaporators required for producing concentrated caustic solution are sometimes made of pure nickel. Since the advent of nickel-clad steel and improved practices in welding nickel so bonded to steel, it has been possible to make these large vessels of 20% nickel and 80% steel. When evaporators and other equipment of this type are finished, only nickel is exposed to contact with the caustic. Although there are serious differences between the physical properties of steel and nickel, the present nickel-clad steel is sufficiently perfected so that these large vessels give satisfactory performance under severe use conditions. A similar application is the manufacture of large rolls for heavy pressures by bonding a nickel outer covering to cast iron or steel cores. This combination permits corrosion-free rolls to have high heat transfer rates and long life.

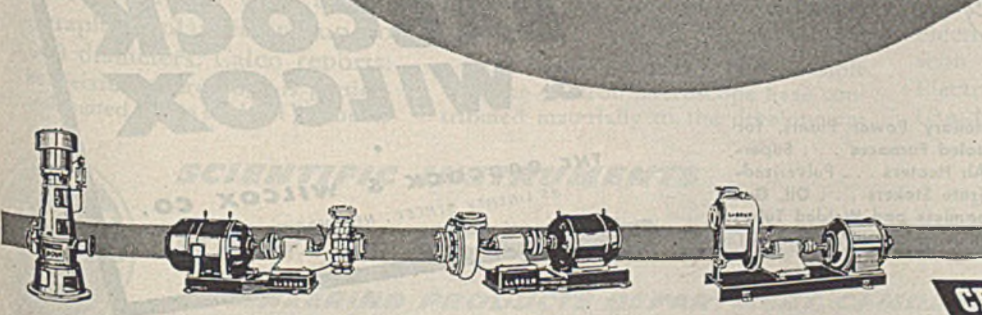
Another alloy widely used in ammonia oxidation equipment is nickel containing 3% silicon. Its duty is twofold: to resist high temperatures of 900° C. (1652° F.) and to furnish an anticatalytic effect on ammonia-air mixtures which inhibits decomposition of the ammonia by heat. The high tensile strength of this nickel alloy permits small thin-wall sections where heat transfer rates can be made rather large.

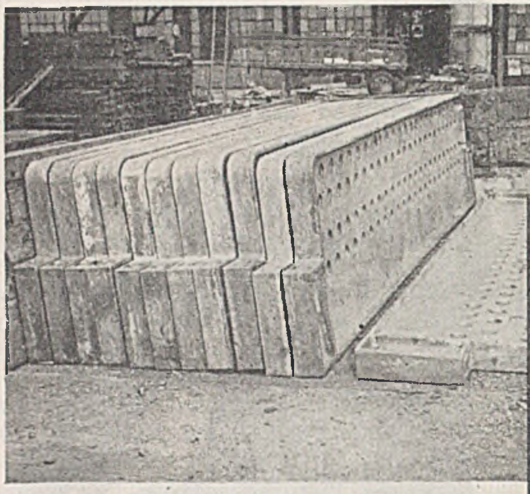
A list of a few unusual chemicals for which nickel or nickel alloys offer satisfactory resistance shows the wide range of useful properties this metal possesses: aluminum chloride, chocolate, cresylic acid, fatty acids, fruit juices, levulinic acid, nitrosyl chloride, phenol, tetraethyllead, urea, and even raw whisky.

An alloy containing 98% nickel and designated "Z nickel" is used for its resistance to fatigue and high temperatures in the manufacture of springs. This alloy can be heat-treated to develop remarkable strength up to 2.5–4 times the strength of structural steel. This alloy can be hardened to a Rockwell C hardness of 30 to 45. Its use in springs results from cold working followed by thermal treatment, which gives this material extreme resistance to fatigue or brittleness by intercrystallization. After the proper heat treatment and hardening, the alloy has a tensile strength of over 220,000 pounds per square inch with a cold reduction in area of 70%. This material is used in heavy-duty coil springs, having a diameter of 10 to 12 inches and using a wire 1.75 inches in diameter. The performance of these springs under many tons of load is exceptional. The full application and usefulness of this material are scarcely known as yet.

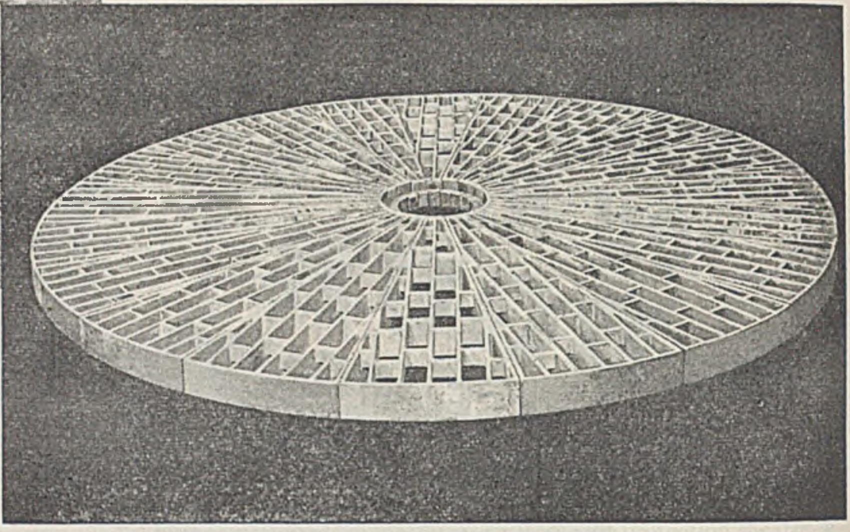
Nickel is used satisfactorily in applications where it is under heavy stress, heavy vibration, and high speed at the same time. It has been found possible to fabricate liners for the interior of Jordan engines from special nickel alloys having a Brinell hardness of 250. In spite of the high abrasion, corrosion, and heavy stresses of this piece of equipment, nickel has given longer life than other alloys because the only wear is from friction without corrosion. The special application of nickel in making wedges, expanded metal, screen cloth, pyrometer and other instrument tubes, and protection sheaths is almost endless.

Space is lacking to report on all of these special applications, but this brief description gives evidence that nickel is an important element in the equipment which supplies the needs of everyday life. Living standards improve because of the availability of nickel. It should be conserved and used sparingly in those purposes where only nickel will serve, and should not be used for mere decorative purposes.





● Alloy Tube Support Castings



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HOW CALCO USES THE RCA ELECTRON MICROSCOPE TO IMPROVE PRODUCT QUALITY

Pictures courtesy of "Textile World"

RCA Type EMC electron microscope used by Calco to speed textile and pigment research.

Disintegrated Cotton Fiber X20,000—Calco uses such micrographs to study fibers and thus determine proper dyeing technique.

Vat Green Dyestuff X20,000—Crystal size and shape are important properties in determining suitable dyeing applications.

The Calco Chemical Division, of the American Cyanamid Company, uses the RCA desk-type electron microscope in developing new and improved dyes, pigments, and textile finishes. This remarkable instrument has proved invaluable in this company's research on the size and structure of particles, surfaces, and fibers.

Magnifications of 500 or 5000 times are obtained with useful photographic enlargement up to 100,000 diameters. Calco reports: "The electron microscope is particularly well suited to the study of pigments and insoluble dyes. For maximum hiding power, tinting strength, and coloring value, the primary particle size of pigments must be well below the dimensions that can be clearly resolved by visual light.

"The electron microscope, utilizing electrons instead of light waves, has a resolving power many times that of the ordinary light microscope, and shows with great clarity the outlines of individual particles. It reveals not only the shape and surface smoothness but frequently the structure of secondary aggregates.

"The studies which have been possible with the electron microscope have contributed materially to the development of pigments with improved properties and performance."

In an impressive number and variety of industries and institutions, the RCA electron microscope is uncovering new knowledge, speeding research, and improving product quality and performance.

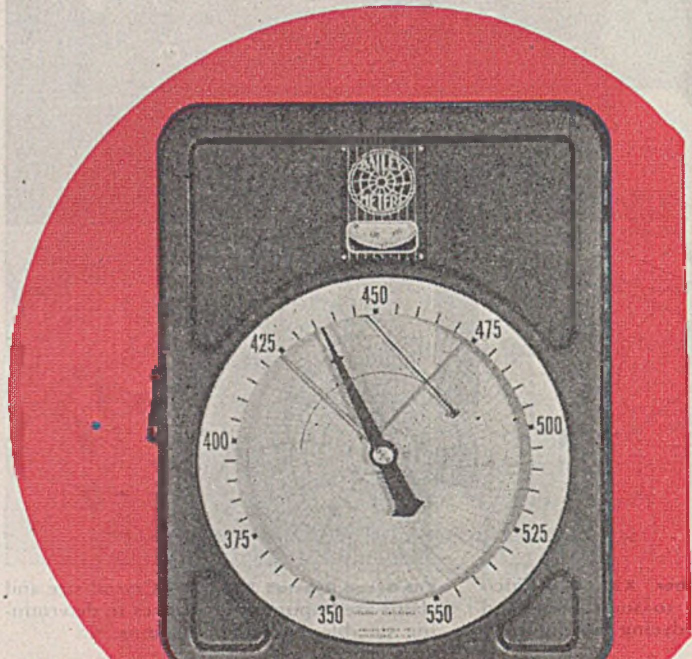
* * *

Our electron-microscope engineers will gladly help you appraise the possibilities of the desk-type or the even more versatile "universal" type RCA electron microscope in connection with your work. Write Dept. 39-D, Electron Microscope Section, RCA, Camden, New Jersey.

SCIENTIFIC INSTRUMENTS

RADIO CORPORATION of AMERICA

ENGINEERING PRODUCTS DEPARTMENT, CAMDEN, N.J.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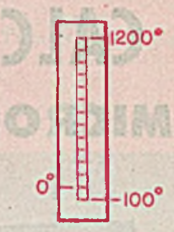
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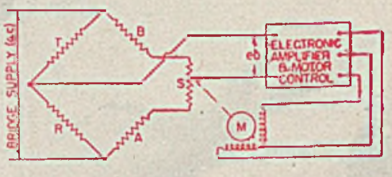
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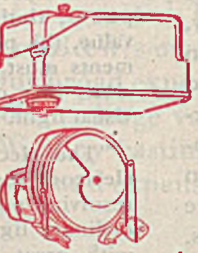

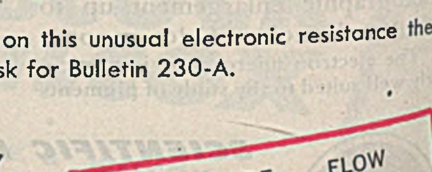

Current Developments in INSTRUMENTATION

The same basic instrument can often be used for many kinds of measurements.

Discussed by Ralph H. Munch

The wide variety of measurement and control problems to which a particular type of instrument can be adapted is one of the aspects which makes instrumentation such a fascinating subject. This is particularly true of certain basic electrical instruments. A good example of the adaptability and usefulness of a unit of this type is the series of instruments announced during the last year and a half by the Bailey Meter Company, Cleveland, Ohio. They are all built around a well designed electronic null-point indicator and balancing motor. The first to be announced was the Pyrotron resistance-thermometer temperature recorder-controller described in this column for January, 1945 (advertising section, page 75). In that case the amplifier and balancing motor were parts of the resistance-thermometer bridge. The second of the series was the combustibles recorder described in January, 1946 (advertising section, page 79). This unit measures the concentration of combustibles in gases by mixing an excess of air with the sample and measuring the temperature attained by a catalytically active filament when the gas is burned at its surface.

A third instrument basically similar to the combustibles recorder has just been announced. It is an automatic continuous analyzer for indicating and recording the oxygen content of gases. To accomplish this, a continuous gas sample is mixed with an excess of vaporized liquid fuel. When this mixture is burned at the surface of a catalytically active filament, the temperature reached by the filament is proportional to the oxygen content of the sample. This temperature is determined, as in the case of the combustibles recorder, by measuring the resistance of the filament. In this fashion the same basic units for resistance thermometer measurement and control of temperature can be used to measure the concentration of combustible gases or of oxygen.

In each of the three instruments mentioned, the variable to be measured was made to produce a resistance change which could be recorded by the instrument. This instrument is not suitable for measuring temperatures when thermocouples are the primary element, since they produce a voltage change instead of a resistance change when subjected to a temperature change. Because of their simplicity and low cost, thermocouples are widely used where temperature measurements of moderate accuracy are required. Therefore, each instrument manufacturer is anxious to include in his line recording potentiometers suitable for use with thermocouples. The Bailey Meter Company has solved this problem in an interesting manner.

The electronic null-point indicator used in the resistance measuring instruments described above is sensitive only to alternating current voltages. To be used as the null-point indicator in a recording potentiometer, it must be made sensitive to direct-current voltages. Other makers have achieved this end by using vibrating reed-type converters or mechanically driven carbon microphones. Figure 1 is a schematic diagram of the device chosen by Bailey Meter Company engineers. Their converter consists of two saturable core reactors and two resistors arranged in an alternating current bridge circuit. The output of the bridge is connected to the same amplifier and balancing motor used in the resistance measuring instruments. The reactors are of special design and use a core material of high permeability so that the impedance of their alternating current windings is very sensitive to minute fields caused by small currents flowing in the direct current windings.

The bridge is supplied from a low voltage, 60-cycle, alternating current source. There are two sets of direct current windings on each reactor, one of which carries a constant bias current, and the other the unbalance from the potentiometer. The direct current windings are connected in such a way that a direct current input of one polarity will set up a magnetomotive force opposing that produced by the bias current in one reactor and aiding that produced by the bias current in the other. With this arrangement the impedances of the alternating current windings of the two reactors vary in opposite directions. The alternating current output voltage of the bridge is proportional to the difference in reactance of the two reactors, and its phase relative to the supply voltage depends on whether reactance *A* is larger or smaller than *B*.

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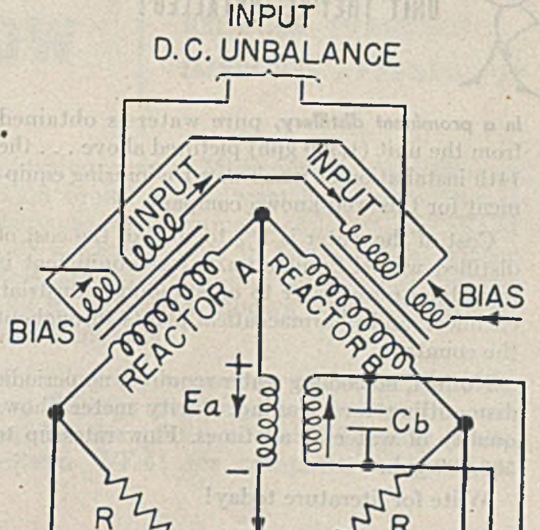
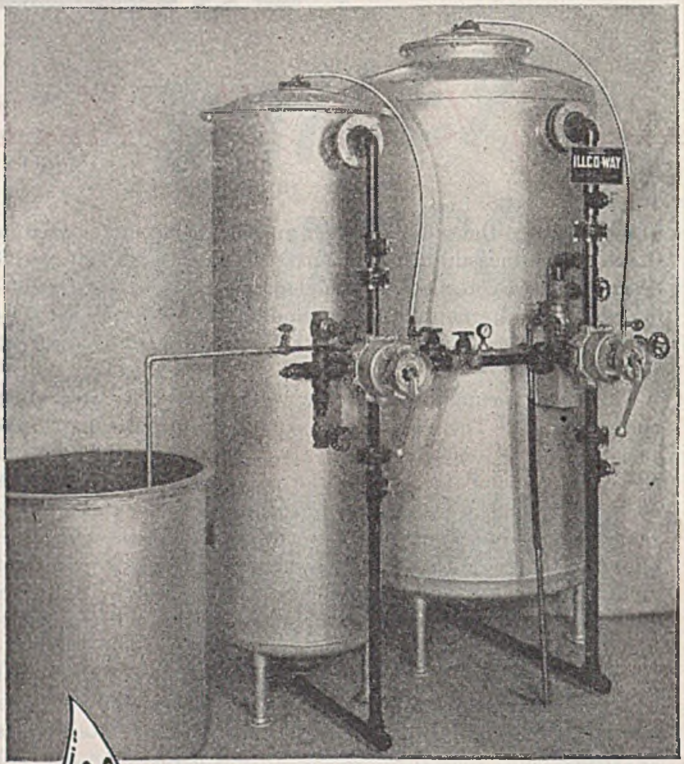
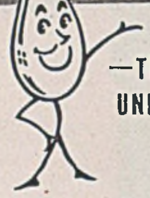


Figure 1. Diagram of Converter





Instrumentation

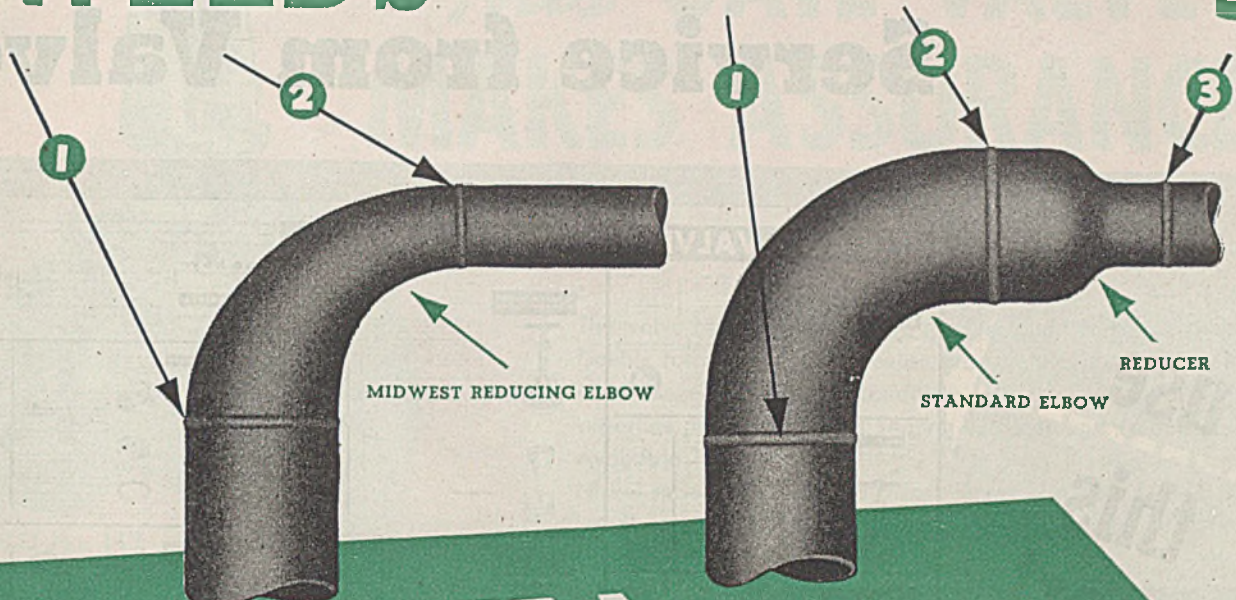
Thus the magnitude and phase of the alternating current output are dependent on the magnitude and polarity of the direct current input. With this converter, the same electronic null-point indicator and balancing motor for resistance measuring instruments can be used in direct current potentiometers. The converter is unique among devices used for this purpose since it has no moving parts or contacts. The standard Pyrotrons can traverse the full scale in 10 seconds. Their minimum scale range is 10 millivolts. The Pyrotron potentiometer may be used with primary elements other than thermocouples for the measurement of speed, smoke density, turbidity, color, and vacuum. Thus the same basic instrument can be applied to a wide range of measurements.

Manufacturers' Publications

Moore Products Company, H and Lycoming Streets, Philadelphia 24, Pa., has recently put on the market the Nullmatic pressure regulator. This instrument is a pilot-operated valve which gives remarkable regulation of gas pressure even with wide variations in supply pressure and load. An increase in flow from 0.5 to 5.5 cubic feet per minute is said to decrease the regulated pressure approximately 1 inch of water when supply pressure is 150 pounds per square inch; a change of 25 pounds per square inch in supply pressure is said to change the regulated pressure about 2 inches of water. A valve of this type should have many applications in the laboratory as well as in the plant. The makers have incorporated it into the Nullmatic remote manual control unit used to give accurate remote operation of air-operated valves, pneumatically loaded rolls and presses, remote setting of control index on automatic controllers, and manual operation of automatic control installations while the process is being started. Bulletins 401 and 402 give complete information on these devices.

Leeds & Northrup Company, 4934 Stenton Avenue, Philadelphia 44, has just issued Bulletin N-96-709C, entitled "For Improved Clarification of Raw Cane Juice". This publication describes the latest form of Micromax pH control which automatically regulates the flow of lime as required. It is claimed that users of this equipment are holding juice so steadily to specified pH that clarification is notably improved, less lime is used, better settling characteristics are obtained, and boiling house operation is improved. The bulletin includes a description of a glass electrode assembly now available for cane sugar applications which is said to hold its calibration and be remarkably free from maintenance requirements.

Volume 2, No. 1, of *Instrumentation*, a quarterly publication of the Brown Instrument Company, Wayne and Roberts Avenue, Philadelphia 44, has recently appeared. The first article in this issue is a résumé of the history and present status of thermoelectric pyrometry by C. A. Vogelsang. All who are seriously interested in automatic control should read the article by D. P. Eckman on "Automatic Control Terminology". For mutual understanding, we must have a consistent and usable set of terms. Another important article in this number is that by S. D. Ross on "Significance of Design in Motorized Control Valves of the Sliding-Stem Type". "Instrumentation of Dough and Proof Rooms" by L. E. Cuckler and R. E. Jones, and "Instrumentation of Annealing Furnaces" by J. P. Vollrath are followed by "Oil Refinery Instrument Maintenance" (Part 2) by Alfred Krieg, of Socony Vacuum Oil Company, Inc. This article gives a great deal of practical information on systematic maintenance of instruments in plant service.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MIDWEST REDUCING ELBOW
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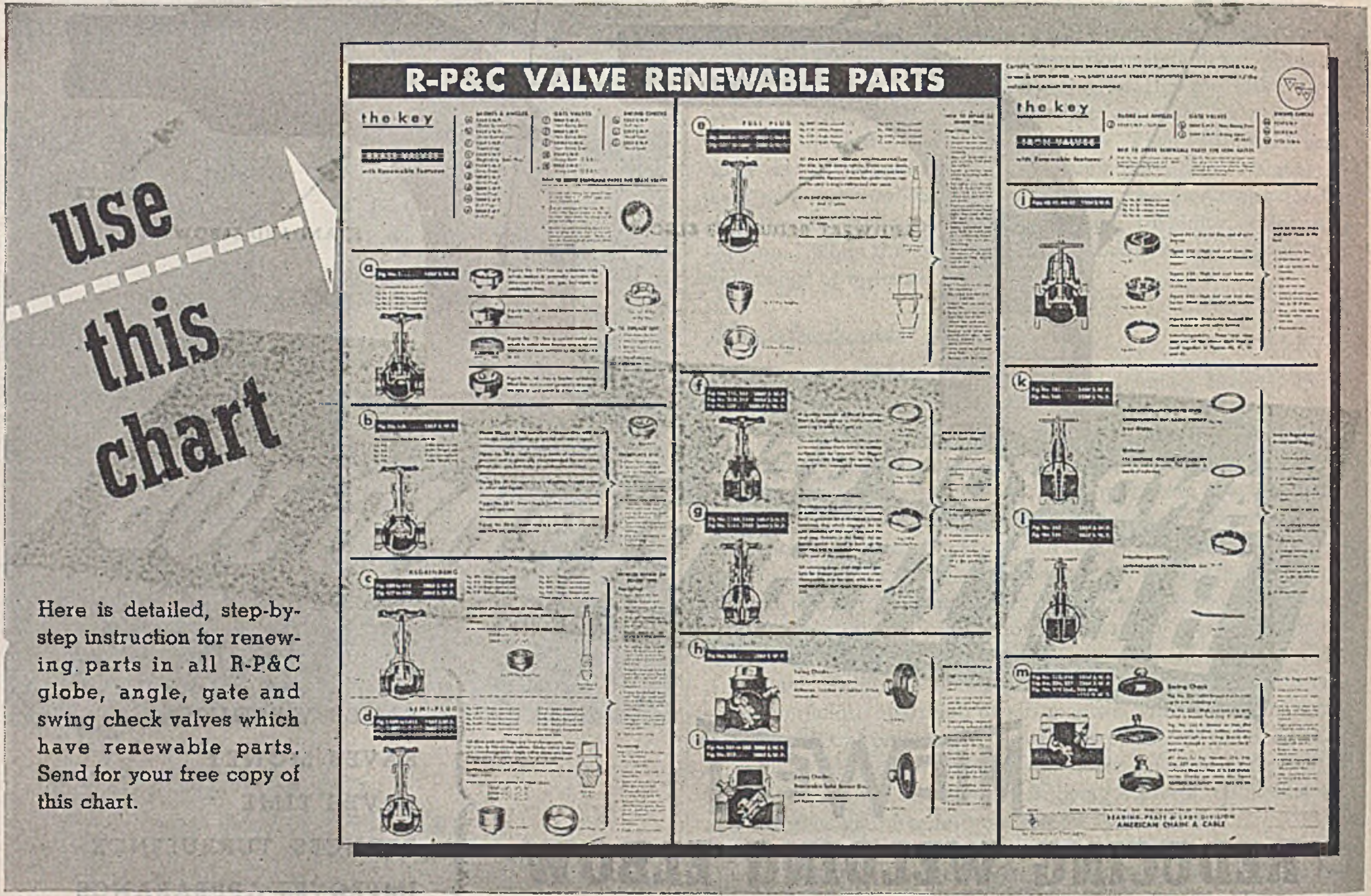
To Get Longer, Better Service from Valves



Here is detailed, step-by-step instruction for renewing parts in all R-P&C globe, angle, gate and swing check valves which have renewable parts. Send for your free copy of this chart.

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With distributors in all principal cities, Reading-Pratt & Cady offers a single responsible source for practically all of your valve requirements. Moreover R-P&C can give you the benefit of long experience toward getting more economical service from your valves.

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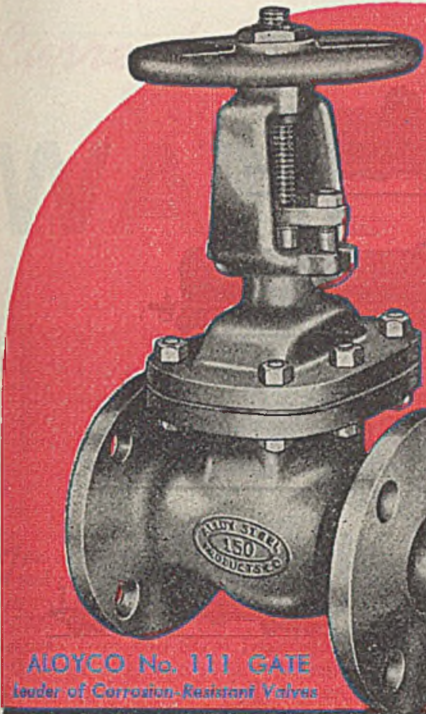
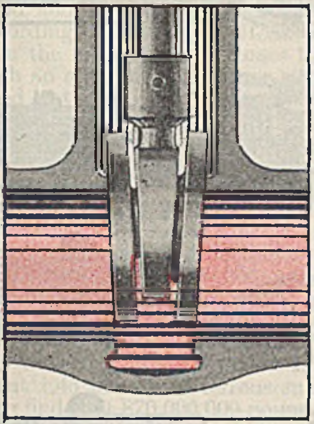
This GATE VALVE MAKES ASSURANCE DOUBLY SURE



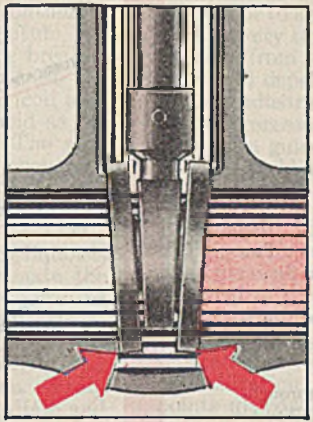
ALOYCO No. 111 GATE
Leader of Corrosion-Resistant Valves

This valve has what it takes to handle tough corrosive solutions. Double rotating wedges provide drop-tight closure and long life under severe operating conditions. Has precision construction, superfine machine finished seating surfaces and unique design. Available in Aloyco 20, 18-8S, 18-8 SMo, the higher Chrome-Nickel series, Worthite, Hastelloy, Monel and pure Nickel. If you handle corrosive fluids or vapors, investigate this valve. Write for circular.



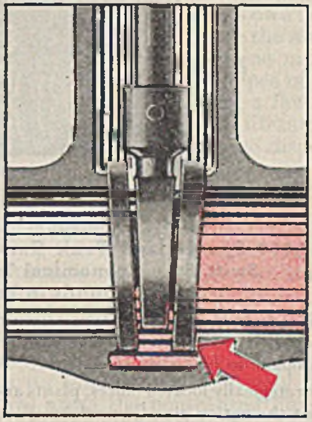
FLOATING DISCS, FREE TO ROTATE WEAR EVENLY

Being free to rotate, the twin discs cut sludges, slurries and viscous solutions. Not held to one point, they wear evenly.



WEDGE—RING FORCES DISCS AGAINST SEATS SEALING THE PORTS

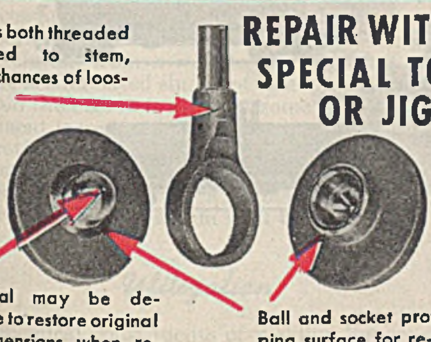
Simple ball and socket construction permits wedge to "take-up" any unevenness and provides better metal-to-metal contact.



DOUBLE VALVE EFFECT! IF ONE DISC LEAKS — OTHER CAN STILL *SEAL*

Should pipe misalignment, shock or scale prevent one disc from seating, the other can still be "drop-tight." Like two valves on one line!

REPAIR WITHOUT SPECIAL TOOLS OR JIGS



Husky ring is both threaded and pinned to stem, minimizing chances of loosening.

Weld metal may be deposited here to restore original contact dimensions when reseating is required.

Ball and socket provide gripping surface for re-seating in lathe.

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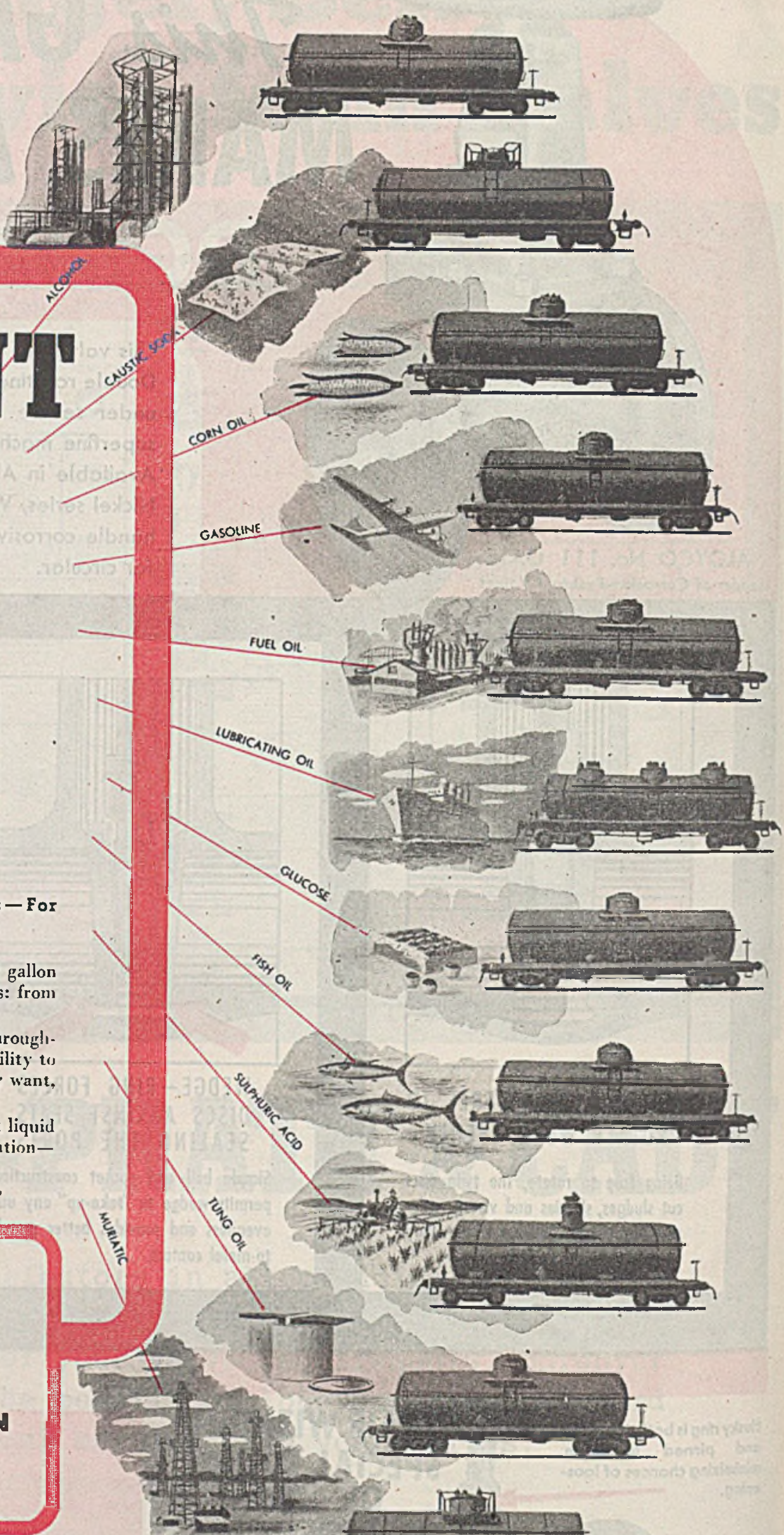
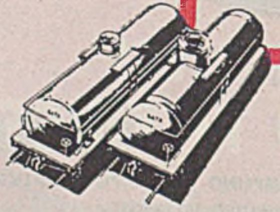

ALCOHOL
CAUSTIC SODA
CORN OIL
GASOLINE
FUEL OIL
LUBRICATING OIL
GLUCOSE
FISH OIL
SULPHURIC ACID
TUNG OIL
MURIATIC



Current Developments in WASTE UTILIZATION

There are many ways for alert manufacturers to utilize spent pickle liquor.

Discussed by Harold R. Murdock

THE disposal of spent pickling liquors has become a serious and difficult waste problem. Extensive investigations have been undertaken in an attempt to utilize this residual substance. In 1938 the Mellon Institute accepted a fellowship from the American Iron and Steel Institute with the purpose of finding methods for the disposal and utilization of spent pickling liquors.

Steel is pickled by both batch and continuous methods, and sulfuric acid is the most common acid used. In the batch process the steel product is immersed in the acid pickling bath from about 10 minutes to an hour, depending on the results desired. The spent liquor from the batch process usually contains from 0.5–2% free acid and 15–22% ferrous sulfate. In the continuous process, according to Richard D. Hoak of Mellon Institute, the steel strip in the form of a coil passes through a scale breaker, then through an automatic welder or stitcher where a fresh coil can be joined to the end of the strip ahead of it. The coil next passes through a series of tanks containing sulfuric acid as the pickling agent and on to rinsing tanks and dryers. The steel strip is finally recoiled. The total immersion time is about one minute per unit of area. The waste pickling liquor from the continuous method averages 4–7% free acid and 14–16% ferrous sulfate.

The average total annual production of spent pickling liquor is reported to be about 600,000,000 gallons. To estimate the probable amount of both sulfuric acid and ferrous sulfate present in this waste from the steel industry, we have assumed a concentration of 6% free sulfuric acid and 15% ferrous sulfate. Such a solution will have a density of about 1.56 specific gravity and contain about 1.45 pounds of ferrous sulfate per gallon. From such data we find that 870,000,000 pounds of ferrous sulfate and 390,000,000 pounds of sulfuric acid are available in the annual production of spent pickling liquor. These figures fully justify the organized attempts to utilize this industrial waste.

Disposal without Utilization

The liberation of spent pickling liquor directly into a stream gives an unnatural color to the receiving water, although the actual pollutional effect is negligible compared to sewage and organic wastes from industry. The free acid in such wastes also aggravates the situation. Treatment of the waste with soda ash or lime to neutralize the free acid is expensive. Prolonged contact with scrap iron will reduce the acidity, but it is desirable to precipitate the total iron content in the spent liquor before purging the solution to the stream. When lime is used for this purpose, it is necessary to retain the treated solution in a lagoon to permit the settling of ferrous precipitate and the overflow of supernatant solution from a weir to the receiving water. The removal of the accumulated sludge of calcium sulfate and ferrous hydroxide from the lagoon is a troublesome operation. The cost of such treatment is reported to be about equal to the cost of the pickling operation itself. Attempts to use limestone in place of lime for economy have not been entirely satisfactory because the coating of calcium sulfate which forms around the limestone particles prevents further reaction with the encased limestone.

Utilization

Since the chemical constituents of pickling liquors are low in economic value, the utilization of this waste is not easy. The situation appears to be complicated by other competitive materials. When specific uses for pickling liquors are found, steel scrap and spent sulfuric acid may also be available as rival materials from other industries. We have mentioned in previous columns that utilization is best found within the plant producing the waste. Steel mills should be constantly watching for such possibilities. The next best chance to find a market is in near-by industries, since transportation costs for the waste material can be kept at a minimum. There is often "gold in your own backyard" for the alert operator. For example, it is reported that iron salts have outstanding coagulating properties for sewage and organic wastes. During the next few years industry and municipalities will be forced to abate the pollution of streams. It would therefore be wise for a steel mill producing spent pickling liquor to keep abreast of developments within its own locality.

Not every steel mill will find it feasible to produce the same byproduct from spent pickling liquor. What each one manufactures will depend upon the local market and the types of neighboring industries. As suggestions we have selected a few of the many processes and products mentioned in the literature to serve as a guide in a survey of local markets for the disposition of spent pickling liquors.

Copperas. The recovery of copperas, $FeSO_4.7H_2O$, from pickling liquor is an established operation for a limited market in this chemical. The process usually consists of neutralizing the free acid in the liquor with scrap iron, settling the liquor to remove suspended solids, and then evaporating and cooling the solution to crystallize the copperas. After the crystals have been separated and dried, the product contains about 45% water of crystallization, which makes its shipment to relatively distant points uneconomical. In local areas the neutralized liquor can be used most economically. Many methods have been proposed for producing the monohydrate which contains 1.5 molecules of water of crystallization. This product contains only about 15% water and, therefore, can be shipped to remote points more economically than can copperas. Several processes have been proposed for direct dehydration of copperas: (1) spray drying of the spent liquor, (2) evaporating the pickle liquor under vacuum until the sulfuric acid content reaches 78% (at which point the monohydrate ferrous sulfate is insoluble), and (3) heating the liquor in an autoclave with live steam to about 350° F. and filtering the precipitated monohydrate without reducing the temperature or pressure.

Mellon Institute reports an ingenious process for recovering copperas which utilizes the property of certain organic solvents of reducing the solubility of ferrous sulfate; acetone was found to be the most practical reagent for the purpose. Equal volumes of spent pickling liquor and acetone precipitate about 95% of the ferrous sulfate content of the liquor as copperas. The acetone is recovered by distillation of mother liquor from the separation of the copperas, and the residue from the distillation contains all the free acid originally present in the spent liquor. When this residue is fortified with enough sulfuric acid to bring it to pickling strength, it is reported to contain less than 2% ferrous sulfate. Comparisons made with this recovered acid solution and fresh acid pickling baths showed no tendency for the impurities to accumulate and interfere with the pickling operation. This process may find practical application when equipment becomes more readily available.

Sulfuric Acid. Because copperas melts in its own water of crystallization, it cannot be used directly in the production of sulfur dioxide for sulfuric acid manufacture. The monohydrate lends itself readily to this purpose. Technically the process appears to be sound, but economically the high cost of equipment and maintenance is a serious

(*Continued on page 82*)

Waste Utilization

obstacle, particularly when no single steel mill produces sufficient pickle liquor to keep the minimum size sulfuric acid plant of 100 tons per day in operation continuously. Cooperative acid plants maintained by several steel mills have been deemed impractical. The re-use of free sulfuric acid, as explained in preceding paragraphs, appears to be the best solution for the recovery of this by-product.

Electrolytic Iron. Many investigators have attempted the economic production of electrolytic iron from ferrous sulfate solutions. Iron tubing of small diameter was produced by this process over twenty-five years ago. The tendency of ferrous ions to oxidize to ferric ions and precipitate basic iron salts is a serious obstacle in electrodeposition. Private communications have indicated that this can be overcome. An acid bath is desirable. Powder metallurgy has overcome the inertia, and the future may show that substantial production of electroplated articles is possible from spent pickling liquor.

Iron Oxide Pigment. This type of pigment is being produced from pickling liquor according to reports from several places. The method used is a carefully guarded secret. A British method is recorded in which scrap iron is added to the spent pickling liquor to neutralize the free acid. The liquor is then continuously spray-dried into a furnace, which reduces ferrous sulfate monohydrate to the oxide. In another process the double salt of ferrous iron and sodium sulfate is roasted to 700° C. (1292° F.) after crystallization. The total production of such pigments is relatively insignificant compared to the vast production of pickle liquor.

Ammonium Sulfate. Because many steel mills which produce pickling liquor also operate by-product coke ovens which make ammonia, a considerable amount of research has been done to find an economical process for fertilizer-grade ammonium sulfate. Several conditions make this utilization of spent pickling liquor difficult. In the first place ammonia is usually produced in largest amounts when the pickling operation is not running at full rate. Then when the pickling step is in full swing, ammonia is being produced at a lower rate. This lack of coordination makes storage of the materials essential and expensive. Another difficulty is that certain impurities in both the ammonia and pickle liquors are deleterious to plants. These toxic impurities are not easily removed from the reacting materials. A third difficulty is the expense of evaporating the large volumes of water in order to crystallize ammonium sulfate. Possibly new methods can be found to overcome these obstacles, but it should be remembered that the ferrous hydroxide formed is a difficult material to handle and its disposition will require further development.

Miscellaneous Method

The patent literature abounds with proposed processes for utilizing this troublesome waste material. Soluble ferric salts have been prepared as coagulants, and building blocks have been manufactured by treating the spent liquor with milk of lime under carefully controlled conditions and then extruding the filter cake into blocks. Another interesting plan is to substitute copperas for gypsum in the manufacture of cement. This could become a large outlet for ferrous sulfate; however, the color of the resulting cement is cream rather than the normal gray-white, and the specifications for cement and the resistance of contractors would first have to be overcome. Recently it was reported that the combination of copperas with activated silica gives excellent results as a coagulant in sewage and industrial processes; apparently the silica makes oxidation of the copperas unnecessary for efficient coagulation.

Scientific men in other industries should not overlook the possibility of utilizing spent pickling liquor in their operations. The material is available in most of the industrial centers of the United States and provides excellent chances of recovering values of an organic nature.

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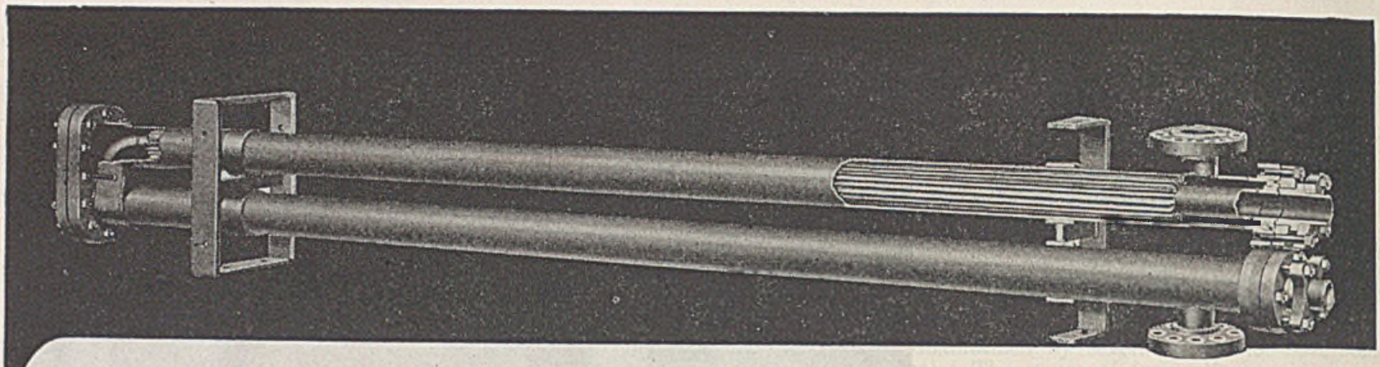

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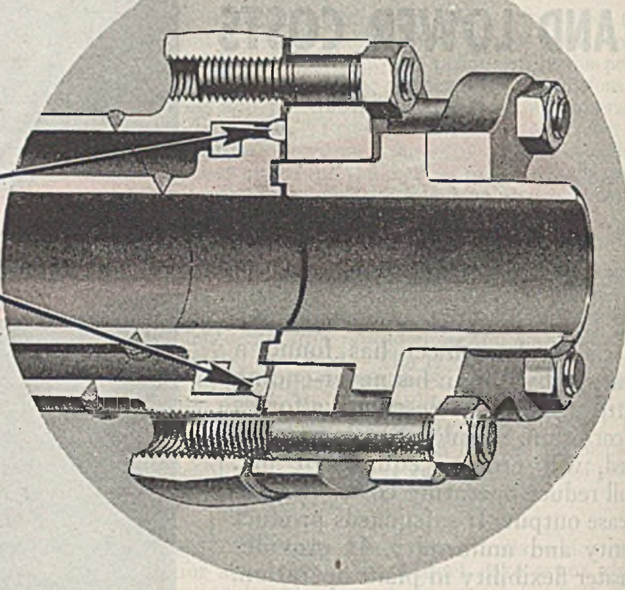

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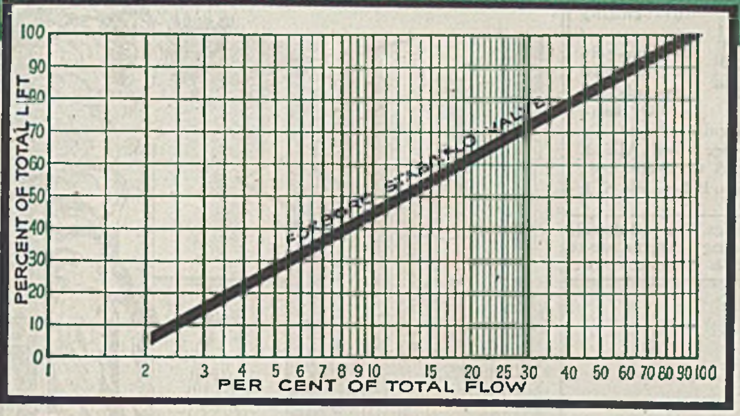
PERCENT OF TOTAL LIFT
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FOXBORO STABILFLO VALVE
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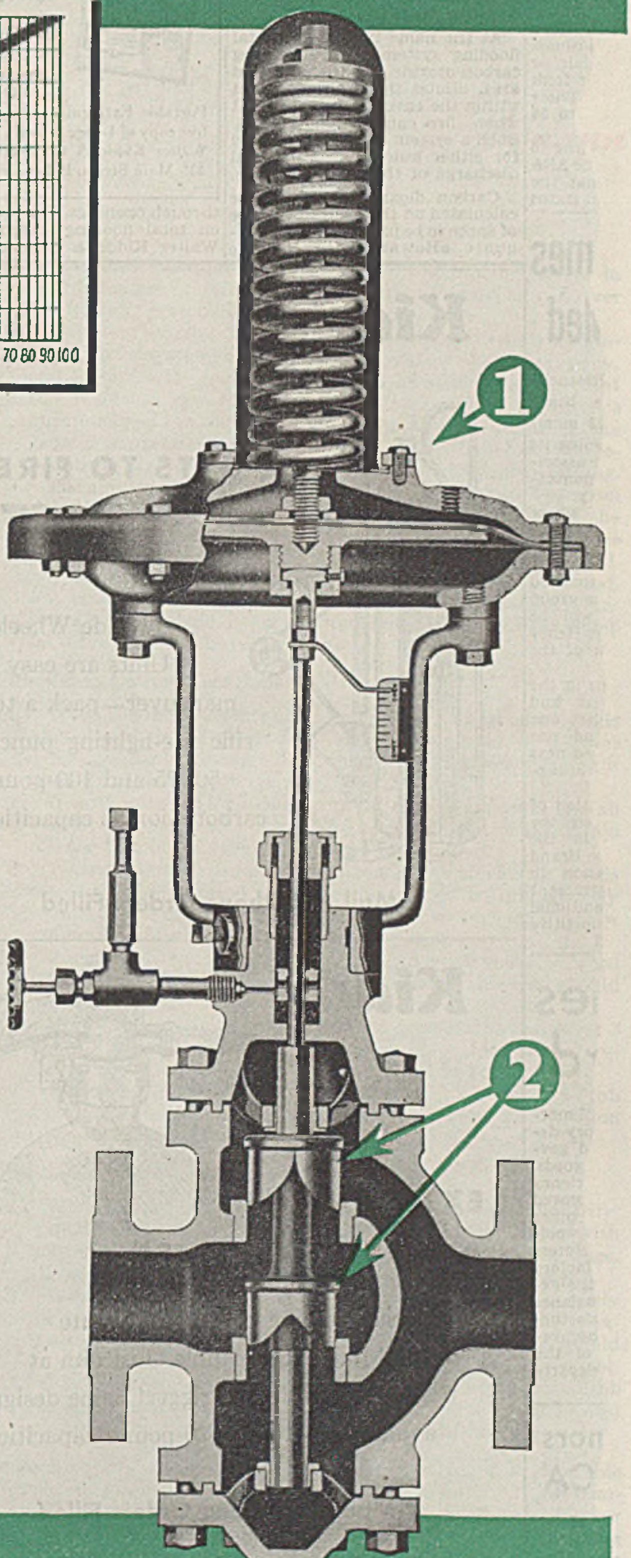
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3,076,011 ... over the previous high of 3,008,750 last October; New Haven 2,521,712 also a new high.

... them ... according to assignment ... will go back to Shanghai. I want to return to China and still work with my company."

... library, auditorium, music room, gymnasium and ... door swimming pool. One complete wing will be devoted to hospital facilities.

... previously ... acknowledged that the separatists were operating in Khamseh, armed with weapons which were distributed by unknown people.

Total Flooding Kills Fires in 20 Seconds

When fire breaks out in a room housing a flammable liquid or electrical equipment hazard, a Kidde total flooding system extinguishes the flames in 20 seconds—or even less.

As the name indicates, a total flooding system, by discharging carbon dioxide into the protected area, dilutes the oxygen content within the entire room to a point where fire can no longer exist. Such a system can be engineered for either automatic or manual discharge of the carbon dioxide.

Carbon dioxide capacities are calculated on the basis of the size of space to be protected, with adequate allowance for leakage through openings. For full details on total flooding systems write Walter Kidde & Company, Inc.

Short Story on TRIGGER CONTROL

For a quick-reading summary of the outstanding advantages of Trigger-grip Control (now standard on all Kidde Hand Portable Extinguishers) write for free copy of 4-page bulletin AD531. Walter Kidde & Company, Inc., 435 Main Street, Belleville 9, N. J.

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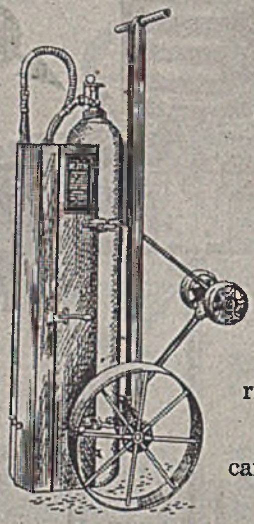

GETS TO FIRES *FAST*

Kidde Wheeled Units are easy to maneuver—pack a terrific fire-fighting punch! 50, 75 and 100-pound carbon dioxide capacities.

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No special training needed to operate the Model 15 Portable. Just aim at the fire and pull the trigger! Same design available in 10 and 20-pound capacities.

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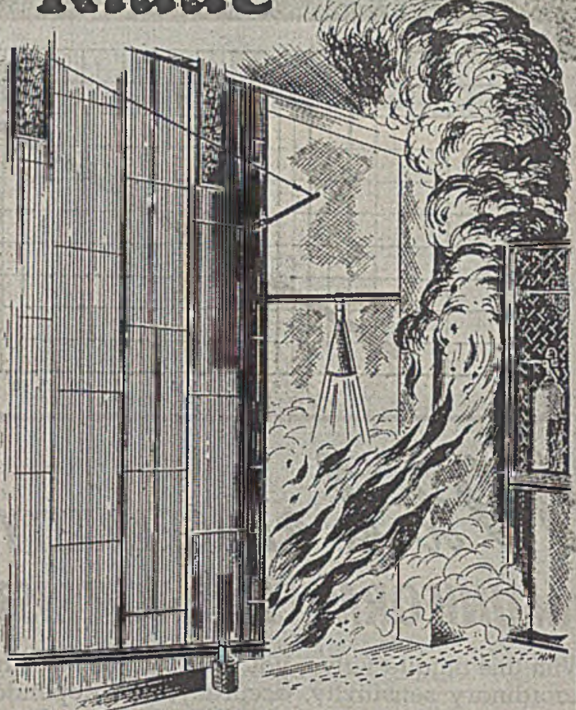

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Process rooms and other hazardous areas can be automatically isolated, if desired, as part of the operation of Kidde built-in systems. Release of the carbon dioxide actuates trips which allow fire doors and windows to close. Time delay mechanisms allow workers plenty of time to leave before doors close.

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Disorders Break Out

General output at factories and mines decreased 4 per cent in October, while in the first half of November output of basic in-... petroleum

Bill May Force

stationed in a little town in France for several months, wooed a French girl by telling her about ...

Current Developments in PLANT MANAGEMENT

The acceptance of job evaluation systems in the chemical industry is recommended.

Discussed by Walter von Pechmann

AGREEMENTS on wage payments are often difficult to reach because there is no measuring stick for gaging the value of different jobs in terms that both management and labor can understand. Although ordinary job-to-job comparison of rates between companies in a given community or industry is still widely used, it does not satisfy labor any more; for upon close examination, the work on presumably similar jobs is usually found to vary. This applies especially to the chemical industry where job titles often embrace a variety of similar tasks, yet disregard the education, mentality, or skill required for efficient performance (kettle operator, chemical mixer, coating man, etc.). Job evaluation, often called "job rating", is, in my opinion, the only accurate method of measuring the relative worth of a job. Large concerns have used this system successfully for many years. It is not universally employed in the chemical industry because of the erroneous belief that it requires the services of an industrial engineer who is specially trained in this field. Some job evaluation programs have been unworkable because management did not first form a sound wage policy or make sufficient provisions for the proper maintenance of the system. Such failures have caused other manufacturers to believe that the system is complicated or not suited to their problems.

The first steps in establishing a sound job evaluation program are the formation of a policy governing future wage payments and the creation of a job evaluation committee. The following description of a wage policy, intended to serve as a guide in working out the program, brings out the factors to be considered.

A. General Policy

1. The company should maintain a general wage level at least equal to that for similar work and conditions in the community.
2. Wages for each job should be established in relation to other jobs in the plant, with due regard for mentality, skill, responsibility, physical demands, working conditions, and hazards.
3. Wage incentive systems, where they may be fairly applied, are considered the fairest method of rewarding individual or group effort.
4. In using incentive systems, a fair standard of performance should be carefully established which can be reasonably and consistently attained. No change in such rates based on these standards should be made unless a substantial change has been made in conditions, materials, methods, or equipment, or unless a general wage level change is required by economic conditions.
5. A job evaluation program should establish the rate to be paid each employee qualifying for a specific position. Wages in excess of the minimum will be established in some departments by incentive systems which will permit average workers to attain a 15 to 20% bonus.
6. The company should raise or lower the general wage scale as economic conditions require. In case of such change, the relation between various job rates will be maintained in accordance with the job evaluation program, and incentive or piecework rates will be modified only in proportion to the general wage level change.

B. Payment of Evaluated Rate

1. New employees, who have no experience in the work for which they are hired, are started at the minimum rate. After 2 months any new employee must qualify for a beginner's job in his department and receive the evaluated rate on that job. In all cases the evaluated rate should be paid when the employee is able to handle the job with only routine supervision. This training period may be shortened somewhat for rapid learners or lengthened for slow ones, but the average should be maintained. Intermediate adjustments may be made either as the employee qualifies for evaluated preliminary jobs or in approximately uniform steps of 5 cents per hour, spread over the learning period in line with progress made.
2. If the new employee is experienced, qualifies through a training period elsewhere or previous employment at this company, and requires only routine supervision, he should be started at the evaluated rate for the job. If the previous training is questionable, the employee should be started at either the general minimum or an intermediate figure, based on the department head's opinion of the value of the previous training.
3. The employee advanced by transfer to a higher rated position should not be paid the evaluated wage for that job until the approximate training period is completed, or until only routine supervision is necessary. In considering the training period, any applicable preliminary job periods should be included. For example, a foreman's position may call for 5 years of training, a considerable portion of which may be in jobs over which he will eventually have jurisdiction.

C. Transfer to Lower Rated Jobs

1. When the requirements of a job decrease and an employee is offered a choice of a layoff in excess of one week or a lower rated job, his wages should be changed to the lower rating if he remains in that job for an extended period.
2. If work runs out for a short period (less than a week) and an employee is assigned a lower rated task instead of being laid off, the rate of his usual job may be maintained.
3. When an employee fails to perform a task efficiently and is assigned a lower rated task, the rate should be immediately reduced to that of the assigned job. The wage in the new range should be based on merit at that task.
4. When, as part of a training program, an employee is assigned a lower rated job even for an extended period, his rate should not be reduced.
5. If an employee fills a lower rated job temporarily (not over 3 weeks) while the regular employee is ill or temporarily reassigned, his wage classification should not be reduced.
6. When an employee is temporarily assigned a lower rated job for demonstration or teaching purposes, his wage classification should not be reduced.

D. Transfer to Higher Rated Jobs

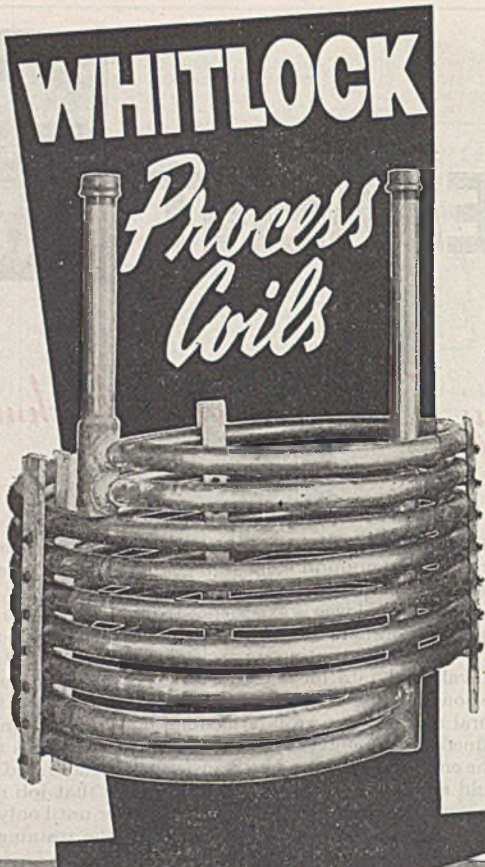
1. When an employee is assigned a higher rated job temporarily, is qualified for it through experience, and handles the job with only normal supervision, he should be given the higher wage. His old wage should be paid when he returns to the old job.
2. When an employee is assigned a higher rated job temporarily for training or any other purpose, is not qualified for it by experience, and requires special supervision, no increase should be made in his wage rate until advanced qualifications are met.
3. When an employee is repeatedly assigned a higher rated job for short intervals, either his job should be redescribed and evaluated, or a new job classification should be set up.

E. Handling of Several Jobs. As far as possible, it is desirable to set up job descriptions and evaluations for normal job combinations. This will include assistants who fill duties of other workers at lunch time, etc. The program provides for paying employees for what they actually do in a proficient manner, not for what they may be capable of doing either proficiently or inadequately.

F. Maintenance of Job Evaluation Program

1. Major changes in job descriptions or assignments should be reported at once. A revised description sheet should be forwarded to the production office.

(Continued on page 88)



Plant Management

2. All job descriptions should be reviewed annually to check for minor but cumulative changes. New descriptions should be made out as required.
3. All wages should adhere to the evaluated rates.
4. All interdepartment assignments of work (not requiring transfer slips) should be made with careful consideration to wage changes in accordance with the evaluation. When such reassignments are permanent, the personnel department should be notified.
5. Although the plan should be explained to any employee upon request, and such comparisons made as are necessary to clarify the relations between jobs, the complete manual of all job data, wage conversion tables, policies, etc., should be regarded by department heads and major assistants as confidential.

G. Procedure When Present Rate Is in Excess of Evaluated Rate

1. Within the ability limits of overpaid employees, an attempt should be made to reassign them to higher paid tasks. However, such procedure should not block the promotion of more capable employees who are not overpaid.
2. When overpaid employees leave the company's service or are transferred from a department, their jobs should be filled at the evaluated rate.
3. A few jobs in the plant are paid in excess of the present evaluated scale as a result of labor conditions. Over a period of years an attempt should be made to bring these rates more nearly in line with the evaluated scale.

Job evaluation committees should include representatives of labor. It is important to acquaint employees with the workings of the new plan in order to show them that job evaluation is a sound measuring stick. Also when the job evaluation committee includes employees, greater cooperation is ensured in the adoption of the new plan. It should be clearly understood by all members of the committee that their function is to determine the relative worth of each job in the plant and not to form wage policies or establish the rate scale.

To measure the relative worth of dissimilar jobs, it is necessary to create a common denominator—the job factor. A job factor need not be considered as a segregated portion of a job, but rather as a certain aspect from which the job is to be viewed. The number and kinds of factors to be used depend on the type of industry where the investigation is made and on the insistence of management upon accuracy. The number of factors to be used will often be a compromise between the greater accuracy effected by a large number of factors and the greater clarity of a few. For example,

Five-Factor Plan	Ten-Factor Plan
Mental effort	Education
Skill	Previous experience
Physical effort	Training time
Responsibility	Physical or mental fatigue
Working conditions	Details
	Quality
	Resourcefulness
	Versatility
	Cooperation and personality
	Responsibility

It is important for the job factors selected to be adequately described. Many an evaluation program has failed because the committee did not issue clear explanations of factors selected.

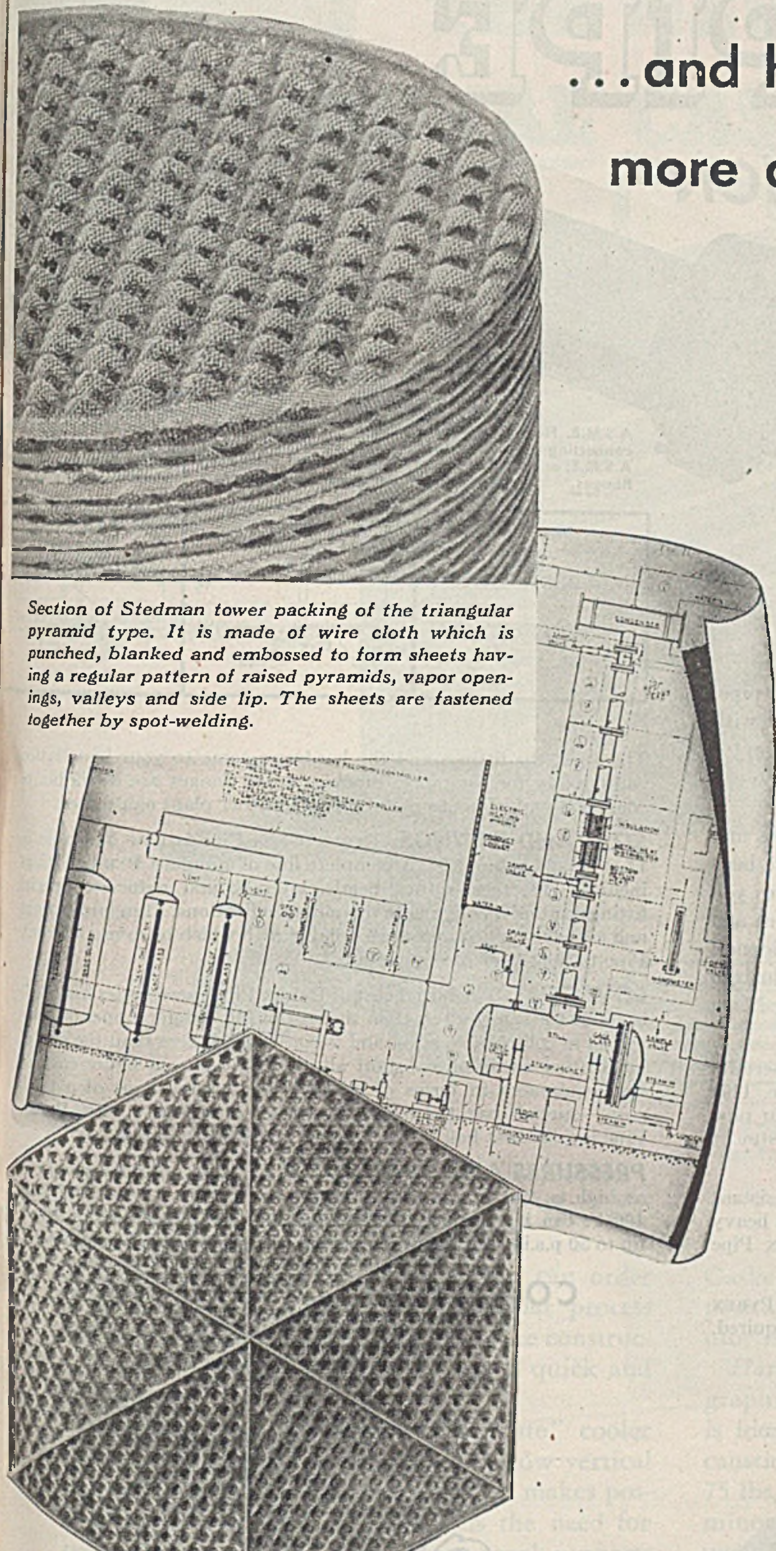
The determination of the relative importance of selected factors is usually a function of the job evaluation committee. A simple way to establish a numerical scale is to set the maximum point rating of factors in such a manner that their combined value adds up to 100. For example, for the five-factor plan: mental effort = 12, skill = 57, physical effort = 6, responsibility = 12, working conditions = 13, total = 100.

The determined maximum points for each factor are now subdivided. For skill: no skill required = 0, little skill required (training time not to exceed 6 months) = 1–4, average skill required (training time not to exceed 3 years) = 5–30, high skill required (training time over 3 years, maximum 5 years) = 31–57.

However, the value of points does not rise in proportion to the measurable element (in this case, time). This is because the value of points must be adjusted so that wages will meet the prevailing community levels. It is good practice to draw the definitions of the various factors and the established point ratings in chart form for quick reference.

WIRE CLOTH TOWER PACKING

...and how it helps to achieve more accurate fractionation



Section of Stedman tower packing of the triangular pyramid type. It is made of wire cloth which is punched, blanked and embossed to form sheets having a regular pattern of raised pyramids, vapor openings, valleys and side lip. The sheets are fastened together by spot-welding.

Arrangement of triangular Stedman packing sections in hexagonal casing as used in larger distillation units. The wire most commonly employed for cloth is 0.009" in diameter, and is woven into a 60 x 40 mesh. Illustrations supplied by Foster Wheeler Corp. For further information, see text.

Stedman tower packing for distillation processes combines ingenious design and construction with the liquid film-forming characteristics of wire cloth.

The packing provides independent paths for the flow of both liquid and vapor, yet assures intimate contact of the two. Liquid continuously follows contours of the wire cloth, forms a film over the open spaces of the screen, and seals mesh openings on both top and bottom surfaces. Vapor rises through openings provided in the packing, and flows over and around these surfaces.

Because of its intricate construction, Stedman packing requires wire cloth of high mechanical strength and exceptional amenability to forming and welding. Corrosion resistance, too, is essential for efficient operation and long life.

Well fitted to meet those specifications are nickel alloys. Monel wire cloth, for example, is strong, readily fabricated, and resistant to a wide range of corrosives. It has the additional advantage of being lowest in cost among wire cloths of comparable qualities.

In achieving fractionation of high accuracy, Stedman packing has been markedly successful. Its ability to separate individual hydrocarbons of 99%-plus purity has been demonstrated. Its other advantages include:

1. **Low frictional loss, vital in vacuum distillation**
2. **Low hold-up**
3. **Increased efficiency through reduction of installation height per theoretical plate equivalent**
4. **Increased yield of closely fractionated products**

Originally a product of Canadian research, Stedman tower packing has been further developed by the laboratories of Foster Wheeler Corporation. Their Bulletin ID-44-2, carrying more information on Stedman columns, may be had by writing them at 165 Broadway, New York 6, N. Y.

And for helpful data concerning the use of INCO Nickel Alloys in the petroleum industry, write to the address below for your copy of *"Monel, Nickel and Inconel in Oil Refining."*

THE INTERNATIONAL NICKEL COMPANY, INC.
67 Wall Street, New York 5, N. Y.

Monel

NICKEL INCO ALLOYS
TRADE MARK

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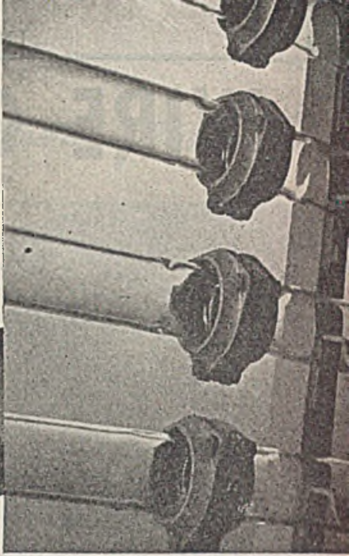
*Reg. U. S. Pat. Off.

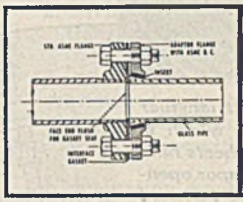
Ready to connect to your present equipment...

GLASS PIPE

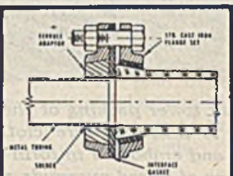
THAT DEFEATS CORROSION—MAINTAINS PRODUCT PURITY



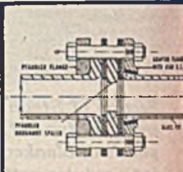
A.S.M.E. Flange Set—for connecting glass pipe to A.S.M.E. or A.S.A. drilled flanges.



Tubing Ferrule Flange Set—for connecting glass pipe to metal tubing or unthreaded metal pipe.



Glass Lined Flange Adap *for Set—for connectin glass pipe to glass line flanges.



CONNECTING PYREX brand Glass Pipe to metal pipe, tanks, valves and other plant equipment is easy with the simple adaptor flanges shown below. With these adaptor fittings you can easily discover where and how PYREX Pipe can be used profitably in your plant.

PYREX Pipe is practical plant equipment. Its sturdiness and serviceability have been proved by installations that have been in operation for many years. It is the only pipe that gives you the combined advantages of visibility, corrosion resistance and purity maintenance. It can be installed and used with confidence.

For complete details on PYREX Pipe, write to the Industrial Sales Department IE-3, Corning Glass Works, Corning, N. Y.

VISIBILITY. The crystal clear transparency of PYREX Pipe permits visual inspection of every foot of your pipe line at any time. This feature serves to forewarn you of unexpected trouble in your pipe lines. In some cases it has saved the entire amount of the investment in PYREX Pipe in a single installation.

MAINTAINING PRODUCT PURITY. PYREX Pipe is resistant to all acids (except H.F.) and moderate alkalis. There is no heavy metal pick-up or danger of metallic contamination. PYREX Pipe lines assure the ultimate in obtaining product purity.

EASE OF INSTALLATION. Your own men can install a PYREX Glass Pipe Line. No special tools or special training are required. The Pipe, the fittings and the hardware come to your installation point ready for assembly. Stock adaptor flanges are available to connect PYREX Pipe to metal pipe and other plant equipment.

SIZES AND FITTINGS. PYREX Glass Pipe is now available in 1″, 1½″, 2″, 3″ and 4″. A complete line of standard PYREX fittings includes ells, tees, return bends, laterals, and reducers. Special fittings can be readily made to your specifications. Standard fittings and adaptor connections are available with which to connect PYREX Pipe to your present equipment.

LOW COST. The initial cost of PYREX Pipe (accessories included) is about the same or less than the cost of full weight copper or brass piping in comparable sizes, and is considerably less than the cost of most other corrosion resistant alloys. Whether you figure costs of new equipment in terms of initial outlay or in terms of over-all costs—spread over the length of service it will give you—PYREX Pipe is your best bet.

PRESSURES AND TEMPERATURES. Operating temperatures as high as 250°F. are not unusual—and temperatures as high as 400°F. can be considered. Most installations operate at pressures up to 50 p.s.i.—but pressures as high as 100 p.s.i. can be considered.

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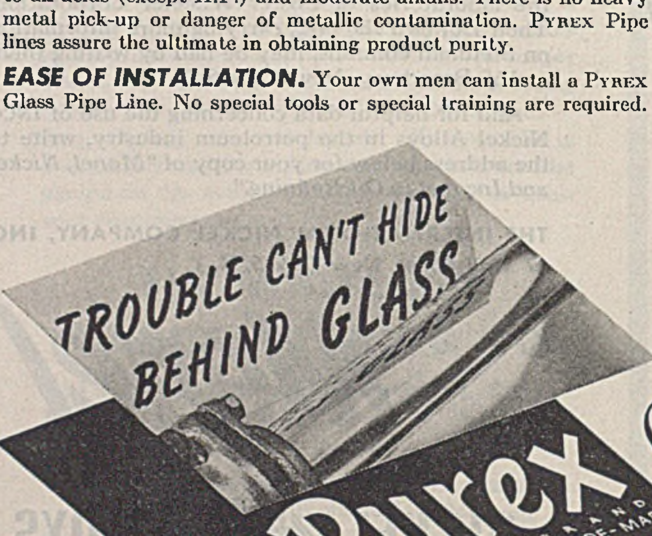
CORNING, NEW YORK



Pyrex BRAND **GLASS PIPE**

"PYREX" IS A REGISTERED TRADE-MARK AND INDICATES MANUFACTURE BY CORNING GLASS WORKS, CORNING, NEW YORK

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Corning Glass Works, Corning, New Yo

Please send me 1A-2 "PYREX Pipe" for the Process Indust

Name...Title..........

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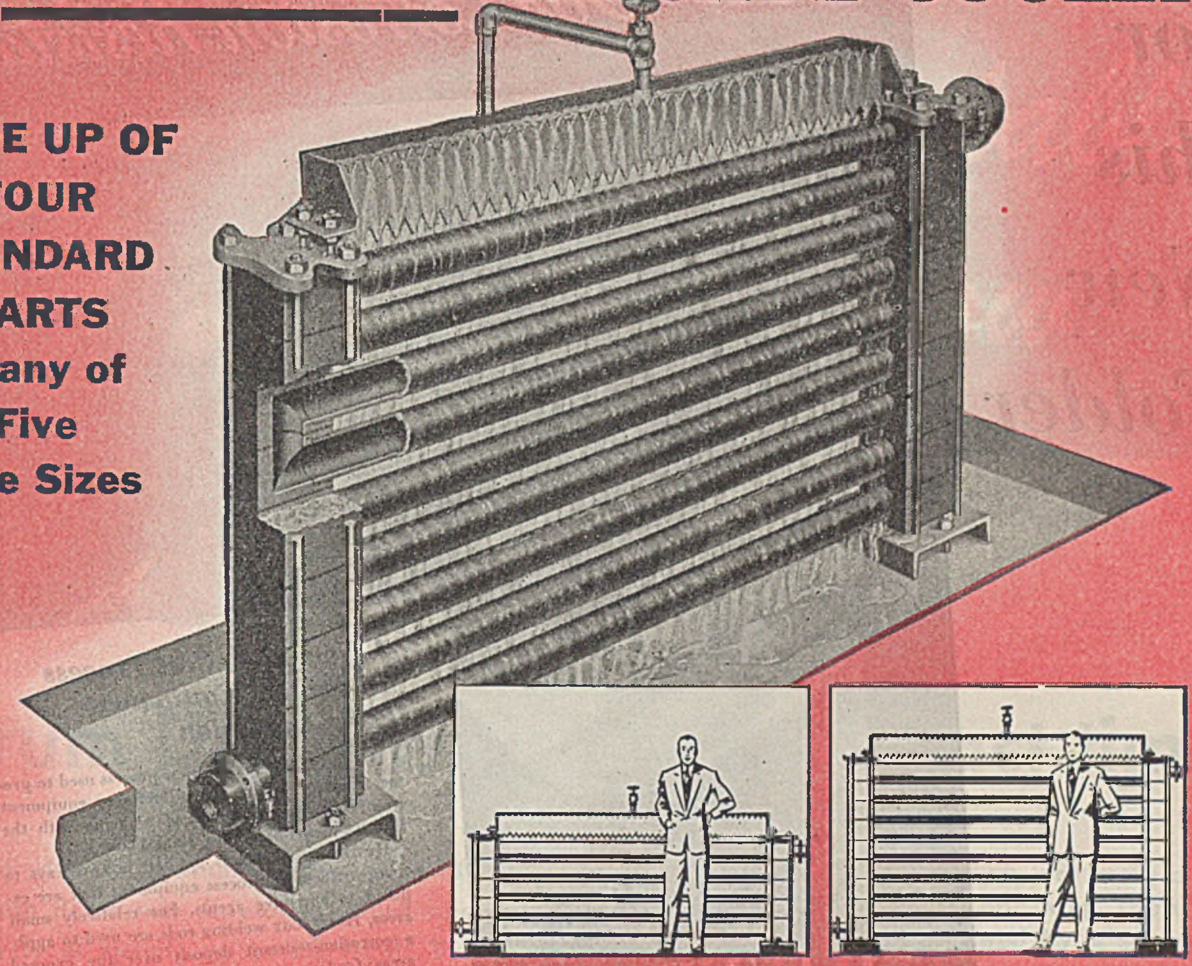
Announcing

THE NEW KARBATE
TRADE MARK
SECTIONAL CASCADE COOLER

MADE UP OF FOUR STANDARD PARTS In any of Five Pipe Sizes



It's quick and easy to increase or decrease the capacity of your "Karbate" Sectional Cascade Cooler.

HERE'S a cascade cooler that you can order from stock to suit your particular process needs. Its interchangeable sections make construction—and additions or subtractions—a quick and easy matter.

Nine-foot-long, single-pipe "Karbate" cooler sections are stacked to form a series flow vertical bank. The compact joint construction makes possible close pipe spacing, and ends the need for redistribution baffles. Also, no external supports are necessary. Maximum effective external areas: about 120 sq. feet in all five pipe sizes in the maximum recommended cooler height of six feet.

Gaskets are of synthetic rubber or of asbestos composition, as desired. A standard steel water distributor is mounted atop the steel tie rod assemblies.

Has many uses! Made of "Karbate" impervious graphite material, the Sectional Cascade Cooler is ideal for efficient cooling of almost all acids, caustics, and organic solvents at pressures up to 75 lbs. p.s.i., and temperatures up to 338° F. With minor changes in applying the cooling water, gases well above this temperature can be handled.

For engineering details on this Sectional "Karbate" Cascade Cooler, ask our nearest Division Office for a copy of Bulletin M-8807.

The words "National" and "Karbate" are registered trade-marks of National Carbon Company, Inc.

NATIONAL CARBON COMPANY, INC.

Unit of Union Carbide and Carbon Corporation

UCC

General Offices: 30 East 42nd Street, New York 17, N. Y.
Division Sales Offices: Atlanta, Chicago, Dallas, Kansas City, New York, Pittsburgh, San Francisco

Send for this New Folder

HASTELLOY Facing

For Corrosion Resistance

HAYNES

TRADE MARK

Alloys

A New Low-Cost Process To Protect Equipment From Corrosion

HASTELLOY Facing is a new process used to protect chemical plant and oil refinery equipment from corrosion by means of a facing with the HAYNES nickel-base alloy HASTELLOY.

HASTELLOY Facing is applied in two ways to those surfaces of process equipment that are exposed to corrosive agents. For relatively small areas, HASTELLOY welding rods are used to apply a corrosion-resistant deposit over the exposed areas; for large areas, such as the interior surfaces of autoclaves or reaction vessels, thin sheets of HASTELLOY are welded in place as a protective lining.

HASTELLOY Facing was developed by Haynes Stellite Company, Unit of Union Carbide and Carbon Corporation, in conjunction with a number of fabricators and operators.

The words "HAYNES" and "HASTELLOY" are registered trade-marks of Haynes Stellite Company.

● This new folder describes new ways to protect equipment from corrosion. It tells you about the corrosive media the HASTELLOY alloys will resist; parts that can be faced with HASTELLOY alloy; and procedures for facing with HASTELLOY sheet, plate, or welding rod.

HAYNES STELLITE COMPANY

Unit of Union Carbide & Carbon Corporation

UCC

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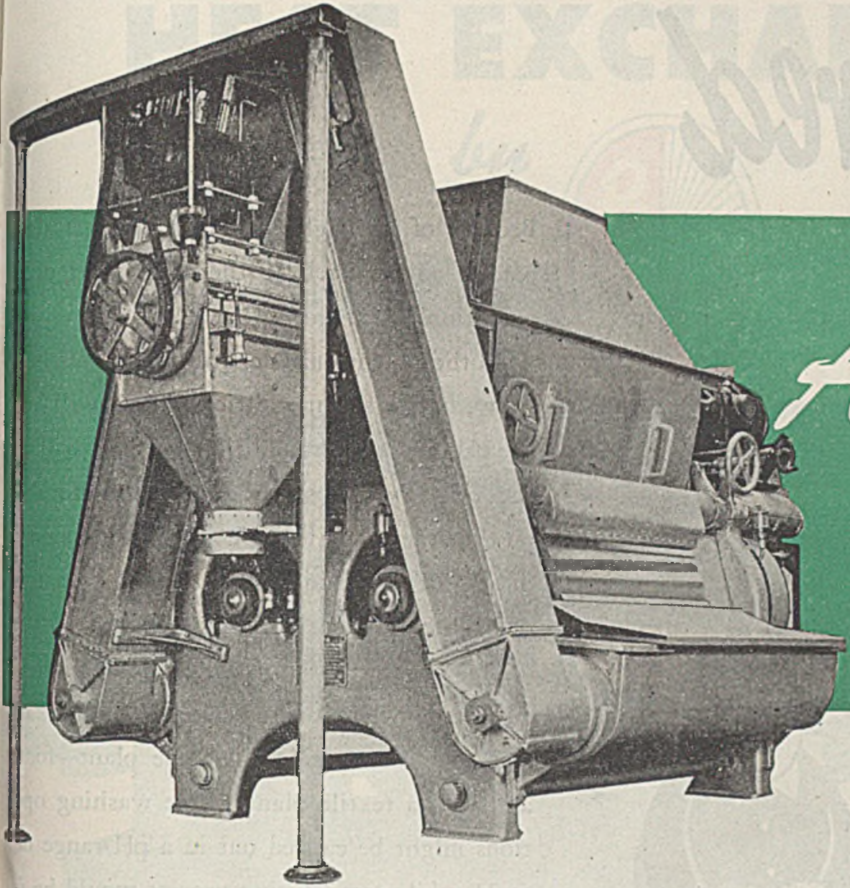

Available Now

A Drum Dryer which cuts contact time

Not satisfied with the ordinary drum speed of 2 RPM, a drum dryer was developed which operates effectively at speeds up to 20 RPM. Thus contact time is far less than with the conventional dryers, output is increased and substantial savings in processing costs result.

This dryer has many unique construction and mechanical features which permit its economical and efficient use on a wide range of materials having different viscosities, and concentrations of solids.

Many materials of liquid consistency are most economically and profitably dried on drum dryers. Also, there are many cases in which fine suspended solids, in slurry form, are more conveniently dried directly in one step than by mechanical dewatering followed by a separate drying operation.

Write today for Bulletin No. 250 which illustrates special construction features, gives range of sizes, etc.

Other General American Products

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GATX

Unbuffered

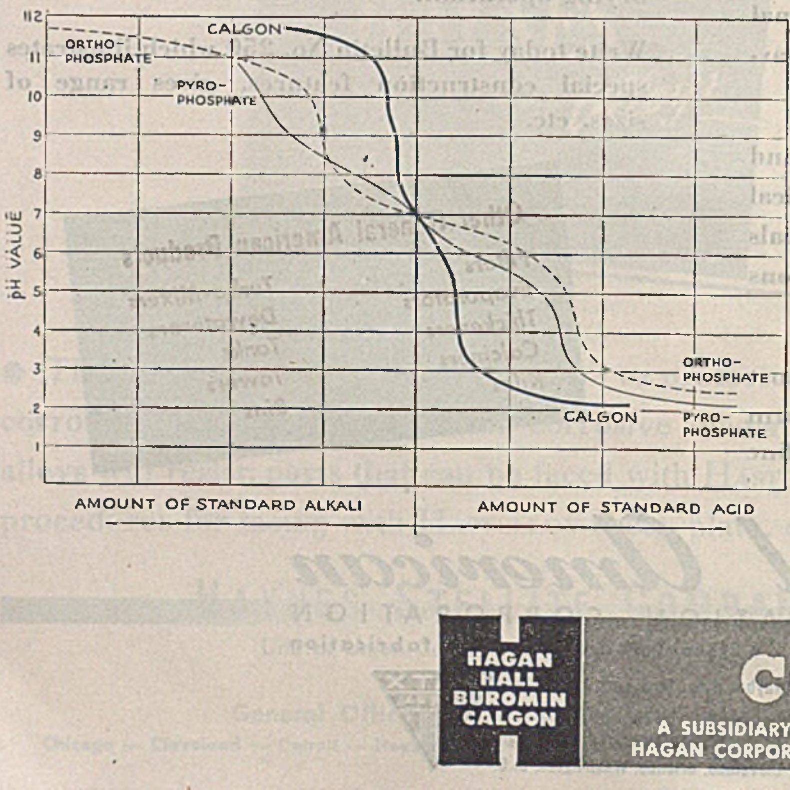
Because of its slight buffering effect, Calgon* readily adapts itself to the desired pH of any operation.

As the potentiometric titration curves below show, only a slight addition of acid will lower the pH, and a slight addition of alkali will raise the pH. Pyrophosphate and orthophosphate, on the other hand, require much larger amounts of acid or alkali to change the pH to a lower or higher value.

This characteristic of Calgon is of particular advantage where it is to be used in both alkaline and acid processes in the same plant—for example in a textile plant where washing operations might be carried out in a pH range of 10 to 11 while some dyeing process would be in a pH range of 3 to 4.

The slight buffering capacity also means that the introduction of Calgon into any existing process requires only minimum changes in the amounts of acid or alkali previously used.

The essentially non-buffering action of Calgon is only one of the properties which distinguish Calgon from the crystalline orthophosphates and pyrophosphates. More detailed information on its properties will be found in the "Calgon Data Book." We will be pleased to send you a copy, and we invite correspondence concerning the relation of Calgon to processes in which you are interested.



* *T. M. Reg. U. S. Pat. Off.*

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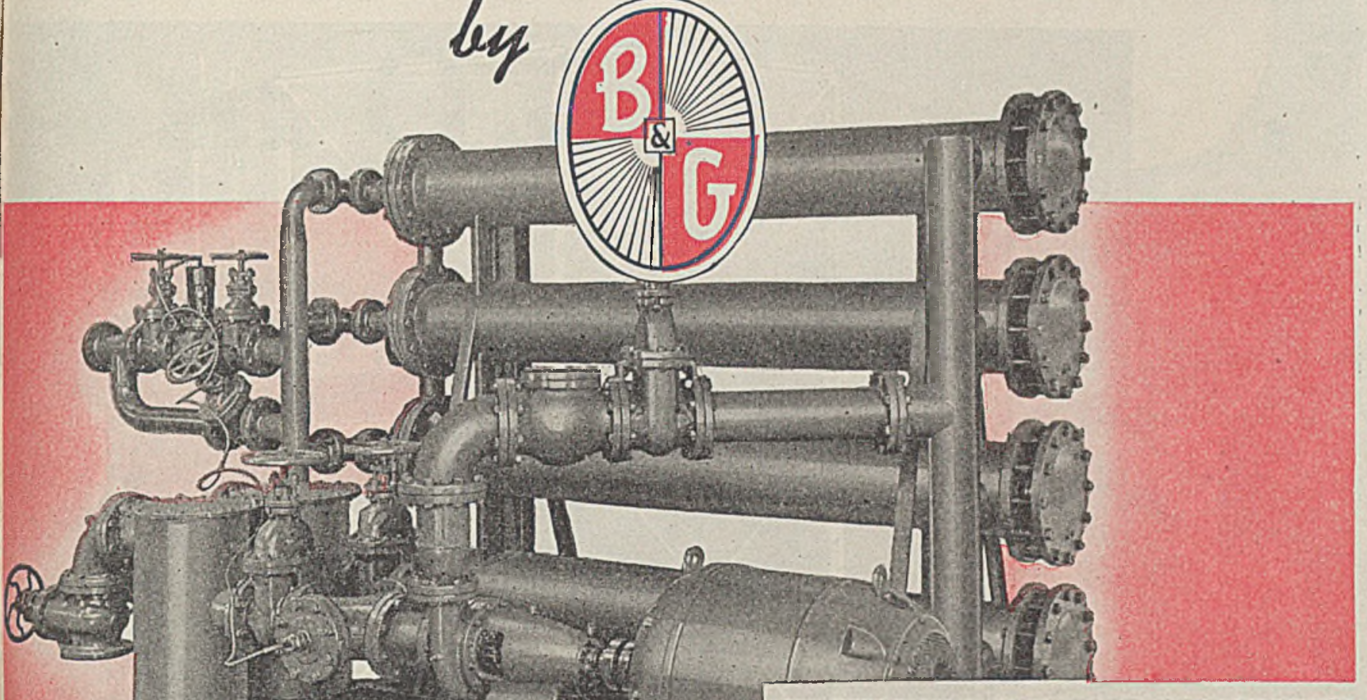
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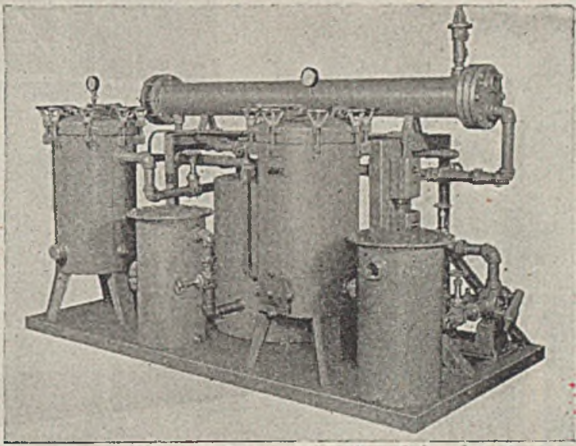
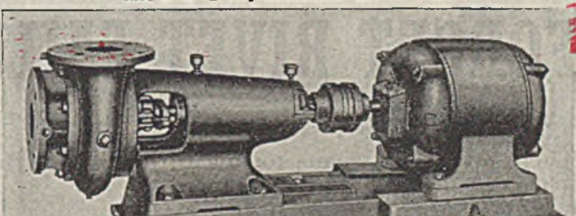
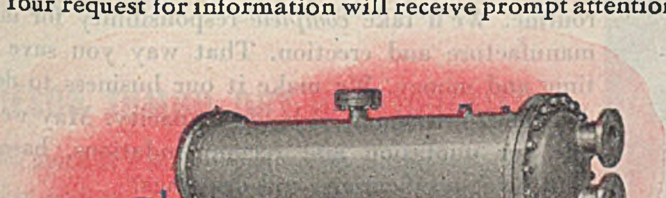
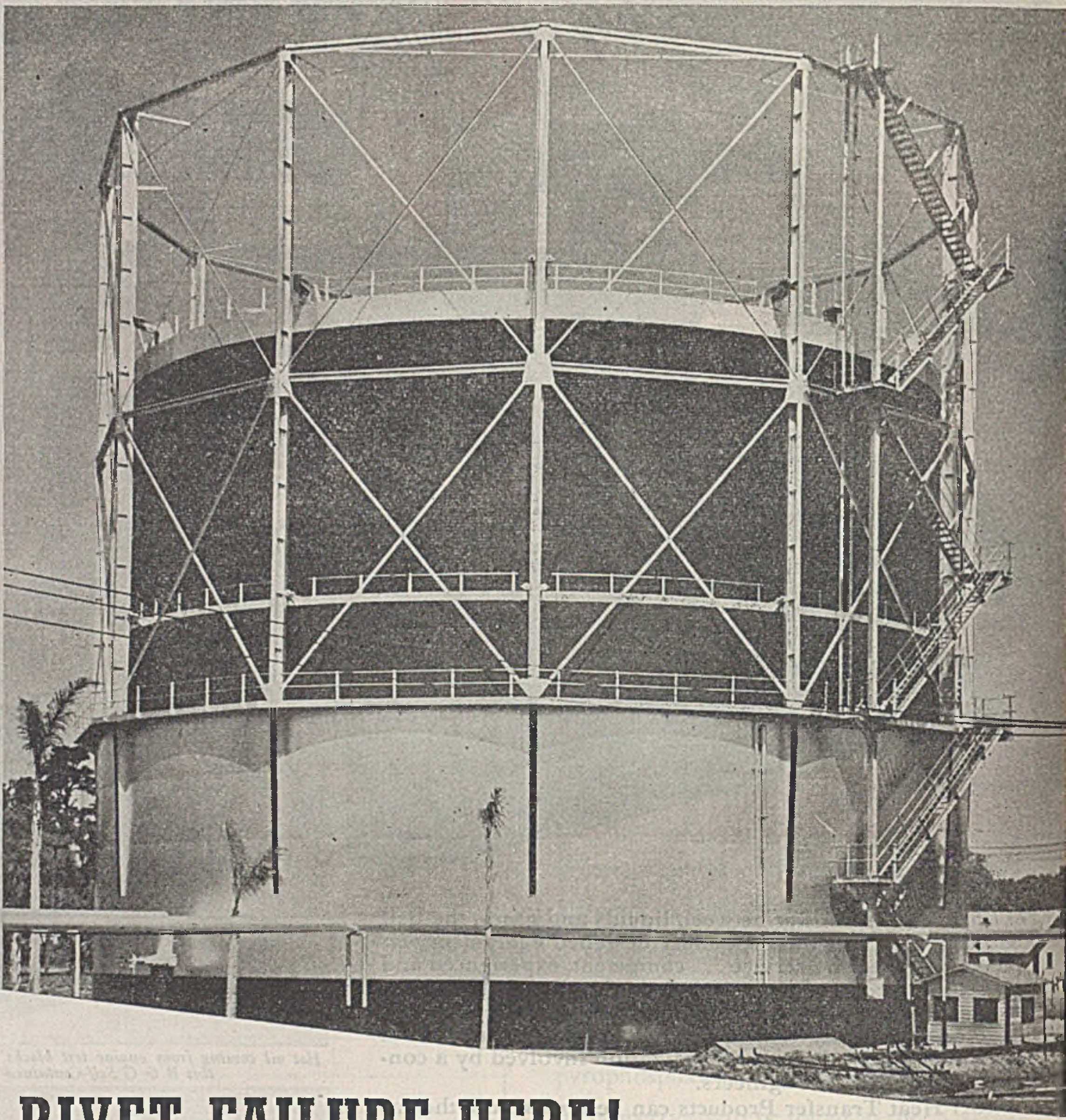








FORGET RIVET FAILURE HERE!

There *aren't* any rivets to fail in this Stacey Brothers All-Welded Panel Type Gas Holder.

That's one important advantage of this type of construction, a Stacey Brothers feature. There are others, too—greater strength, more efficient operation, less maintenance expense.

It's reasons like these that have influenced the choice of Stacey Brothers for tanks. The installation pictured is typical—a 500,000 cu. ft. All-Welded Panel Design Wet Seal Holder.

Our experience includes more than three hundred distinct types of tanks—any practical size or shape—with gas holders ranging in capacities from 100 cu. ft. up to 10,000,000. We fabricate as light as No. 16 gauge sheet metal, and up to three inches thick.

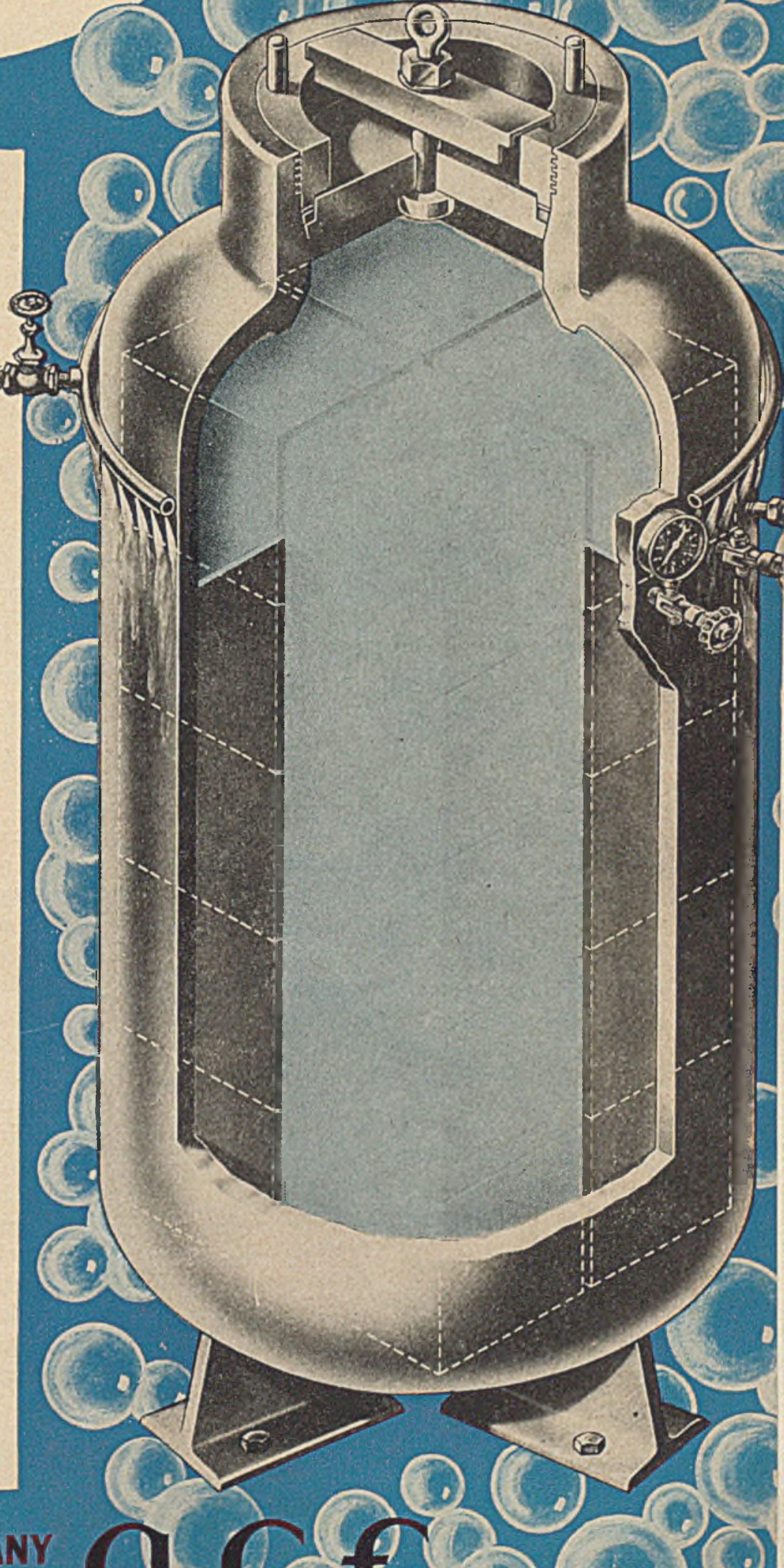
Whether your needs are standard—or unusual—there's a Stacey Brothers Holder, *custom built* to fit your requirements. No problem is too tough for us—or too routine. We'll take *complete* responsibility for design, manufacture and erection. That way you save both time and money. We make it our business to deliver dependable, economical holder capacity. May we submit our quotation and recommendations, based on your own specifications and drawings?

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

Stacey Brothers
TANKS

If it's a TOUGH job . . .

ask a.c.f.



THE PROBLEM: The Mathieson Alkali Works, in order to provide more efficient distribution of Carbon Dioxide, designed a high pressure tank for liquefying dry ice. The process required a pressure vessel designed for a working pressure of 1,200 p.s.i. with a capacity of a thousand pounds of dry ice. A standard nozzle and cover plate would be too slow and difficult to operate in service.

THE SOLUTION: The tank was designed with sufficient diameter and height to obtain the weight of dry ice capacity desired. A special closure assembly design was adopted—not only withstanding the 2,400 pound test pressure required by the A.S.M.E. Code, but completely gas-tight at low pressure. This involved developing a method of welding the closure neck to the tank head with a minimum distortion in the precise threading of the neck. a.c.f. experience and facilities long used in the manufacture of welded tank cars, processing tanks and heavy storage tanks were readily adapted to the construction of this special pressure vessel.

If you are faced with a difficult manufacturing problem in construction of tanks or pressure vessels take advantage of a.c.f. advanced techniques in tank car, processing vessels and storage tank design and manufacture.

MATHIESON JUMBO DRY ICE LIQUEFIER

Taking the place of 7 small liquefiers the Jumbo is the most economical and convenient method of converting dry ice into liquid carbon dioxide. A large capacity of one thousand pounds of dry ice; tank is in accordance with stringent A.S.M.E. specifications and Hartford Inspection. Within ten minutes after ice is deposited the liquefier operates at top efficiency and pressure tight performance is assured.

MERICAN CAR AND FOUNDRY COMPANY

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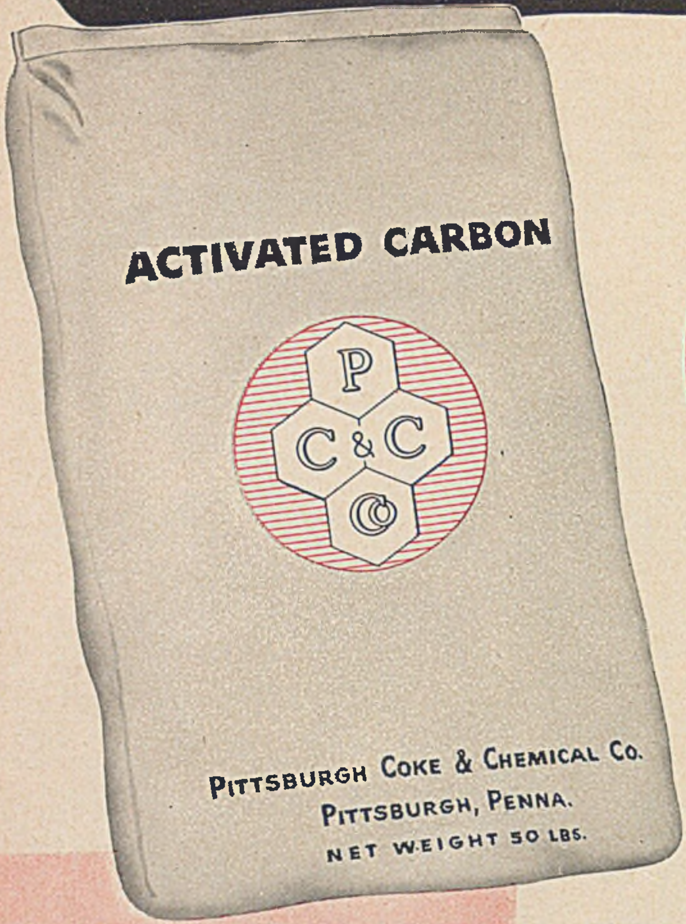
a.c.f.


ACTIVATED CARBON
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C&C
PITTSBURGH COKE & CHEMICAL CO.
PITTSBURGH, PENNA.
NET WEIGHT 50 LBS.

How to "Take the Heat Off" your motor maintenance problems

Excessive time and dollar losses are being avoided in every industry—by *specifying* Fiberglas* *High Safety Factor* Electrical Insulation in new motors and for rewinds.

When scores of plants were operating at full-time war production, Fiberglas Insulation Materials provided "extra" protection to overcome conditions which caused most motor burnouts and failures—heat, moisture, corrosive vapors or acids, overload and the human element. One company was operating twenty-five variable speed motors which were subjected to heavy overloads under conditions of high ambient heat, high humidity. The average life of these motors, ranging from 2½ to 10 hp. had been about four weeks. Fiberglas-Base Insulation Materials were specified—the service life of these motors was lengthened many times—and "the heat was off" the motor maintenance problem in this plant.

Why not try the remedy that has been so successful for other concerns? Get complete information about Fiberglas Electrical Insulation Materials. Write for your copy of the new catalog and ask for the names of the distributors serving your locality. *Owens-Corning Fiberglas Corporation, 1951 Nicholas Building, Toledo 1, Ohio. In Canada, Fiberglas Canada Ltd., Oshawa, Ont.*

ASK FOR FIBERGLAS—IN YOUR NEXT MOTOR—AND ON YOUR NEXT REWIND.

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ELECTRICAL INSULATION MATERIALS

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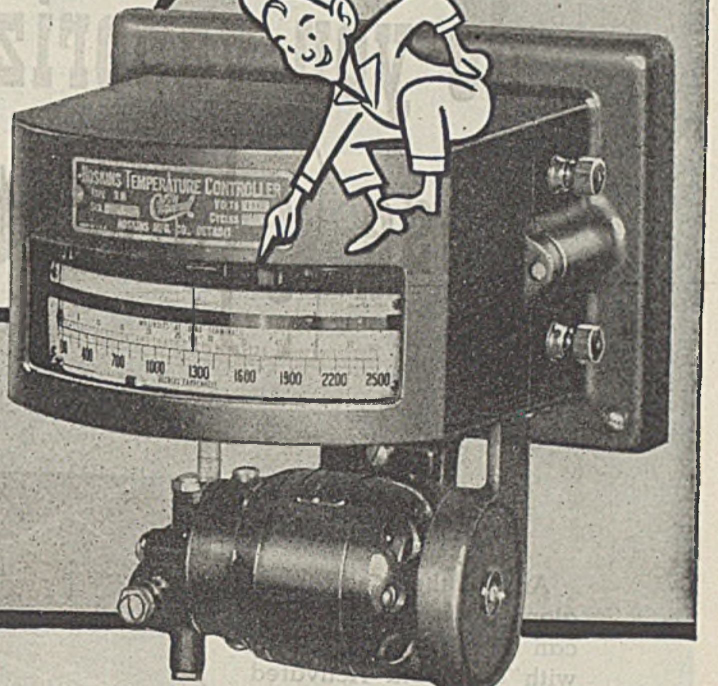
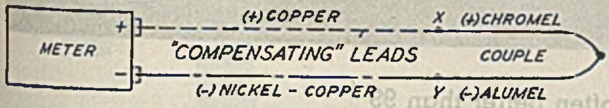
Other Fiberglas Products: Thermal and Acoustical Insulations • Dust-Stop* Air Filters • Yarns, Cloths, Mats and Basic Fibers

COMPENSATING LEADS ON ACCURATE PYROMETERS *MAY FOOL YOU*



HERE'S WHY...

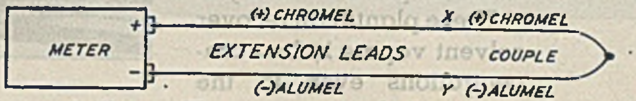
When wires of different composition are placed in contact and heated, an E.M.F. is developed, the value of which depends upon the temperature reached. Thus, by using so-called "compensating" leads with your Chromel-Alumel Thermocouples, you create two sources of erratic E.M.F.'s outside the furnace at points X and Y in the pyrometric diagram below.



DIAGRAM—A

As you know, these outside thermo-electric junctions often become extremely hot and frequently one gets hotter than the other. When this occurs, the opposing E.M.F.'s generated become more and more unequal, the "compensating" leads fail to compensate for these inequalities, and the resulting plus or minus error is registered by your accurate but "misinformed" pyrometer.

How to eliminate this common source of cold-end error? How to take full advantage of the fine accuracy of Chromel-Alumel Couples and modern precision pyrometers? Simply use Chromel-Alumel Extension Leads with your Chromel-Alumel Thermocouples.



DIAGRAM—B

By eliminating the "break" at points X and Y, you eliminate all chance of "cold-end" errors between the hot-end of the couple and the accurate mechanism of your pyrometers.

Remember, where accurate temperature control is important to furnace operation, use Chromel-Alumel Extension Leads with Chromel-Alumel Thermocouples. Ask for folder, "They belong together."

HEATING ELEMENT WIRE
Chromel
NICKEL-CHROMIUM

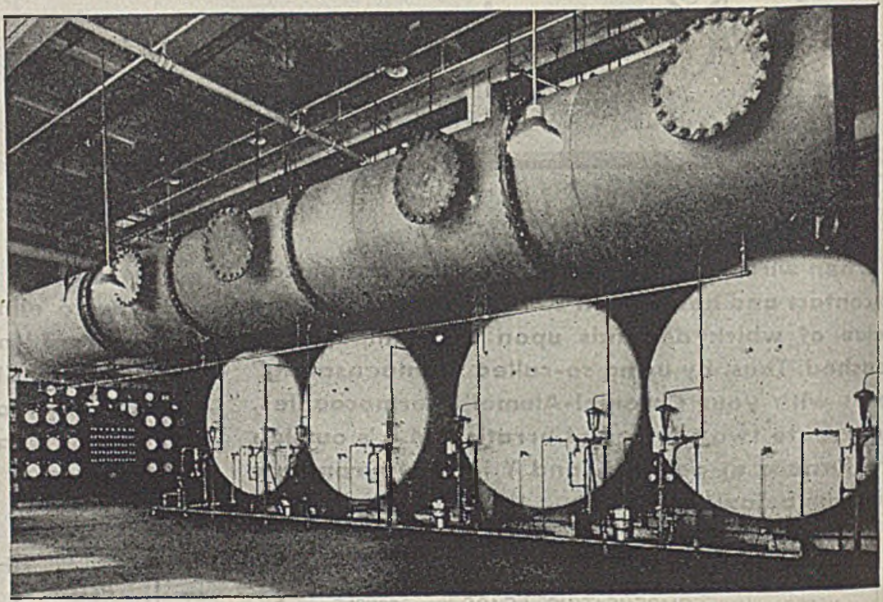
HOSKINS MANUFACTURING CO.

4445 LAWTON, DETROIT 8, MICHIGAN

ELECTRIC HEAT TREATING FURNACES • HEATING ELEMENT ALLOYS • THERMOCOUPLE AND LEAD WIRE • PYROMETERS • WELDING WIRE • HEAT RESISTANT CASTINGS • ENAMELING FIXTURES • SPARK PLUG ELECTRODE WIRE • SPECIAL ALLOYS OF NICKEL • PROTECTION TUBES

do you vaporize these Solvents?

- ALCOHOLS
- CHLORINATED COMPOUNDS
- ESTERS
- ETHERS
- HYDROCARBONS
- KETONES
- CARBON BISULFIDE



Any of these solvents—alone or in combination—can be recovered from air with "Columbia" Activated Carbon.

Carbide and Carbon Chemicals Corporation supplies complete solvent-recovery systems designed and engineered to recover solvents economically with "Columbia" Activated Carbon. A large indoor installation is pictured at right.

These plants can recover solvent vapors in low concentrations even in the presence of water vapor. Their efficiency is high, often better than 99 per cent of the solvent vapor passed to the adsorbers. However, overall recoveries of solvent used vary with the vaporizing operation and the type of vapor-collecting system. These solvent recovery plants can be completely automatic. The investment is moderate, the recovery expense is only a fraction of the cost of replacing the solvents. For further information write for the booklet, "Solvent Recovery by the 'Columbia' Activated Carbon System" (Form 4410).

CARBIDE AND CARBON CHEMICALS CORPORATION
Unit of Union Carbide and Carbon Corporation
UCC
30 East 42nd Street, New York 17, N. Y.

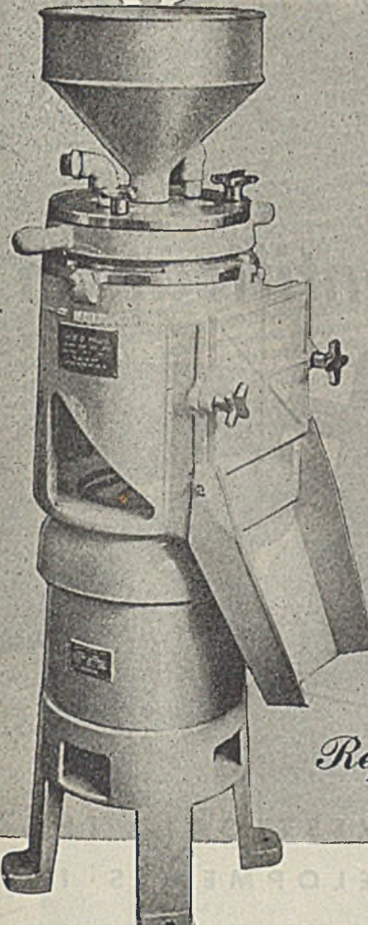
COLUMBIA
TRADE-MARK
Activated Carbon

Life-Saver for Men and Materials

SOLVENT RECOVERY · CATALYSIS · GAS AND AIR PURIFICATION

ONE MOVING PART . . . SIMPLE IN DESIGN . . . SANITARY IN CONSTRUCTION

THE DOOR TO EFFICIENCY



SANITARY
HOMOGENIZING
EMULSIFYING
DISPERSING
GRINDING

Increased Production at Lower Costs
Definite Product Improvements are
Reported by **PREMIER COLLOID MILL** *users*

"Definitely improved both quality and life of our product" . . . "Increased production 15% without added labor" . . . "Greater capacity per HP consumption" . . . "Test samples superior" . . . "We no longer have packing-gland trouble or product contamination" . . . "No internal corrugations to cause unsanitary conditions". These actual quotations are typical of performance reports from users of Premier Colloid Mills.

Whether the work to be done is emulsifying, dispersing or disintegrating . . . whether the material to be processed is liquid, paste or solid, every Premier installation proves itself by giving consistently successful results. Finer particle size is an important factor in finer products. Moreover, compulsory treatment of every particle assures uniform standards of quality. A partial list of fields which benefited from these results:—

Adhesives, sealing compounds; asphalt emulsions; ceramic colors; coating and waterproofing emulsions; cosmetics; foods and beverages; oil emulsions; inks; leather finishes; latex (synthetic and natural); lacquer emulsions; lubricating oils, greases; pigment dispersions; organic chemical dispersions; paints, lacquers, varnishes; paper coatings, fillers, waterproofing; pharmaceuticals; plastics, resins; polishes, waxes; rubber compounds; textile finishes. (Special laboratory models are available for research work.)

Where a new process is involved and performance data desired, a test run may be arranged. Premier Mill Corporation, Factory and Laboratory, Geneva, N. Y.; General Sales Offices, 110 East 42nd Street, New York 17, N. Y.

Descriptive Literature on Request

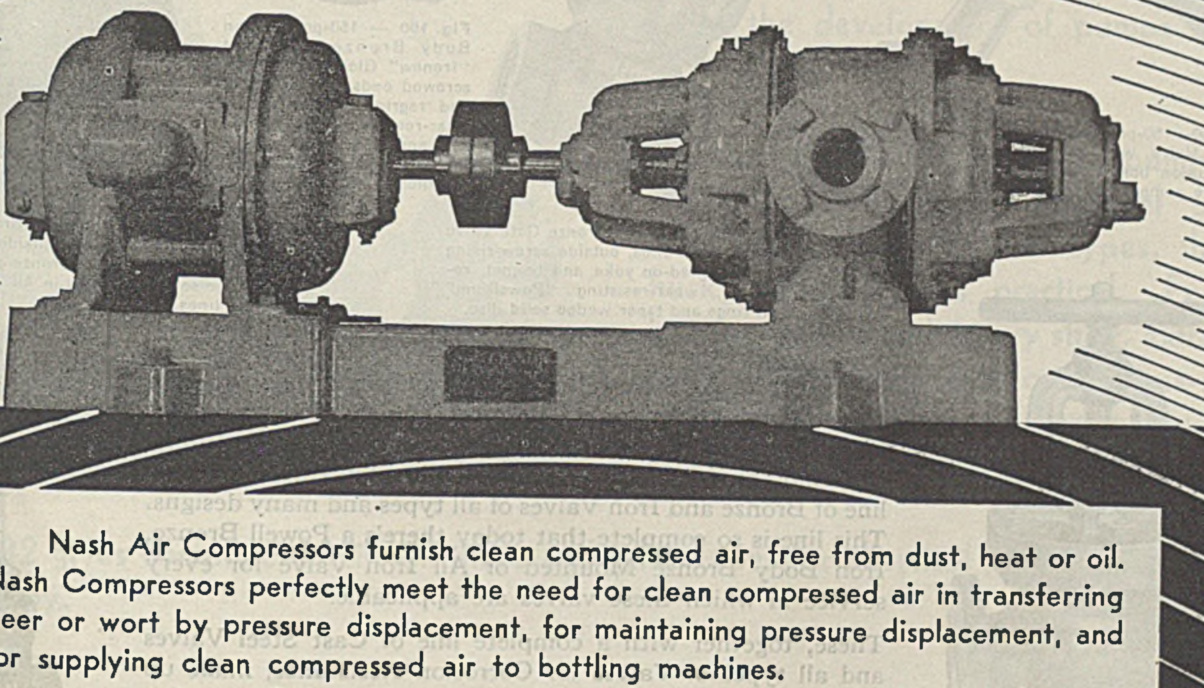
THE PREMIER MILL

Better products more profitably processed


MEYERCORD Decal Selector
HOW TO USE THE SELECTOR
TYPE OF SURFACE
DESIGN
DECAL
FEATURES
LIST OF SURFACES
Without Moving Slide TURN SELECTOR OVER TO DETERMINE CORRECT APPLICATION METHOD.
THE MEYERCORD CO.


• IDENTIFY
• DECORATE
• ADVERTISE
your products
with
MEYERCORD
DECALS

CLEAN COMPRESSED AIR



Nash Air Compressors furnish clean compressed air, free from dust, heat or oil. Nash Compressors perfectly meet the need for clean compressed air in transferring beer or wort by pressure displacement, for maintaining pressure displacement, and for supplying clean compressed air to bottling machines.

Nash Compressors furnish clean air without supplementary filters or air washers. They are simple, efficient and economical. One moving part, rotating on ball bearings. No internal wearing parts in metallic contact, and no internal lubrication. Ask for Bulletin D-236.

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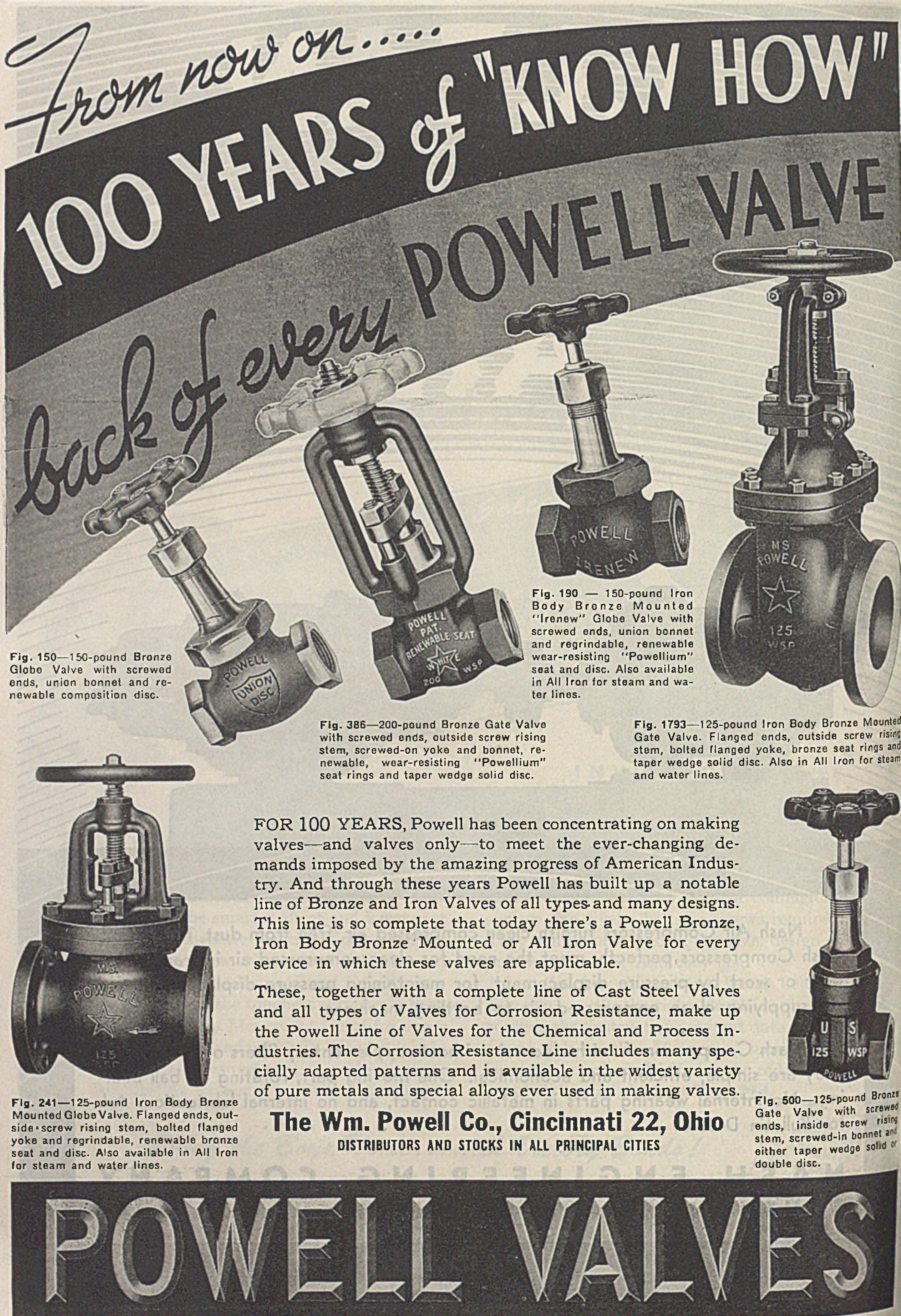
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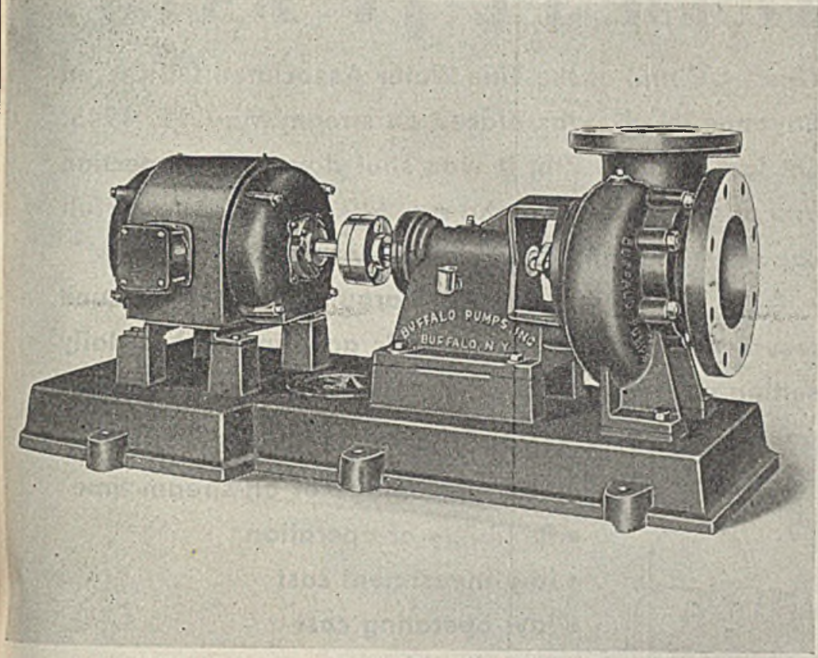

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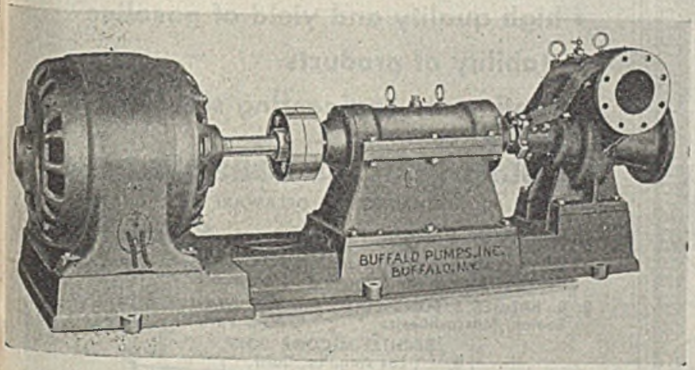

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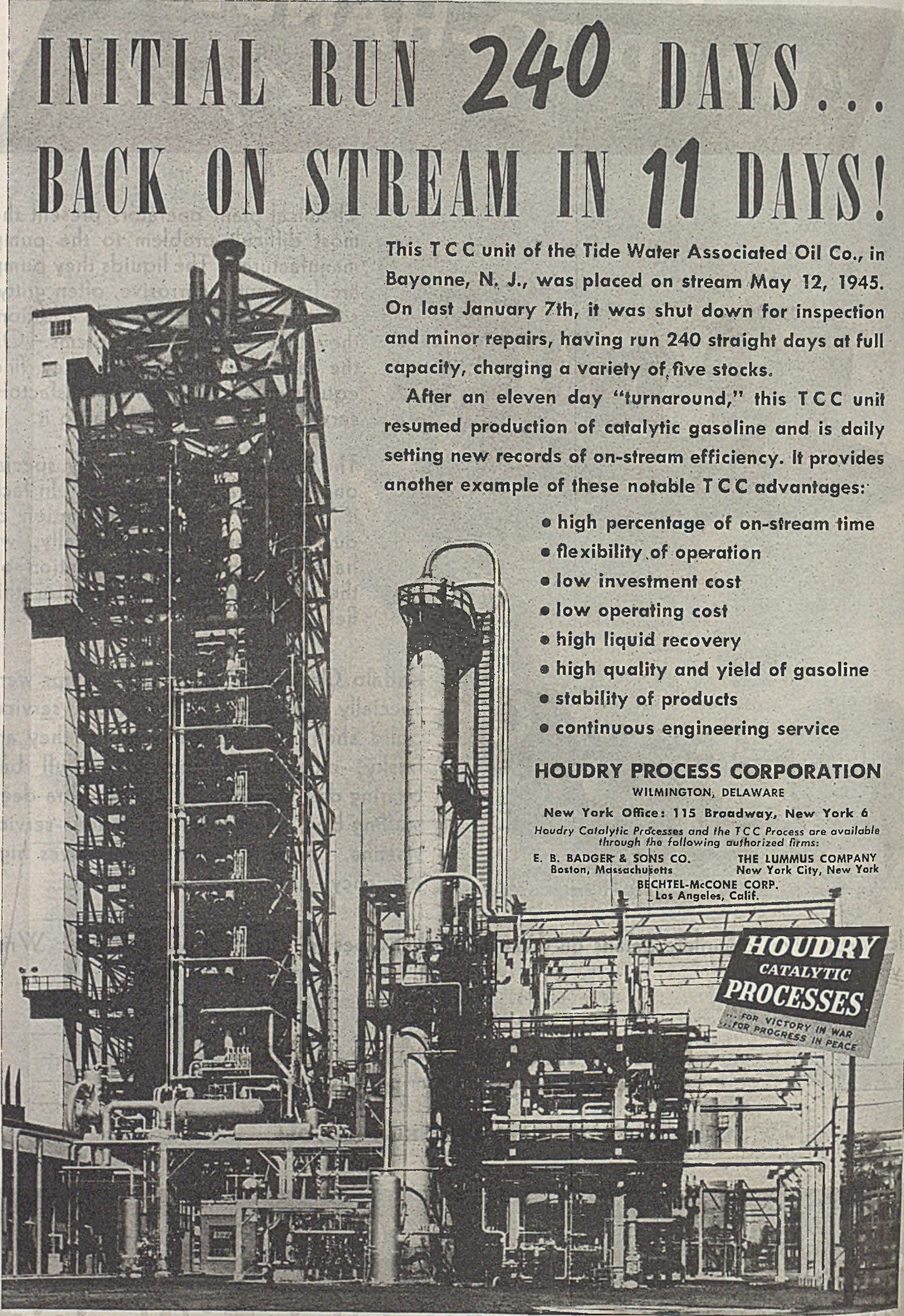

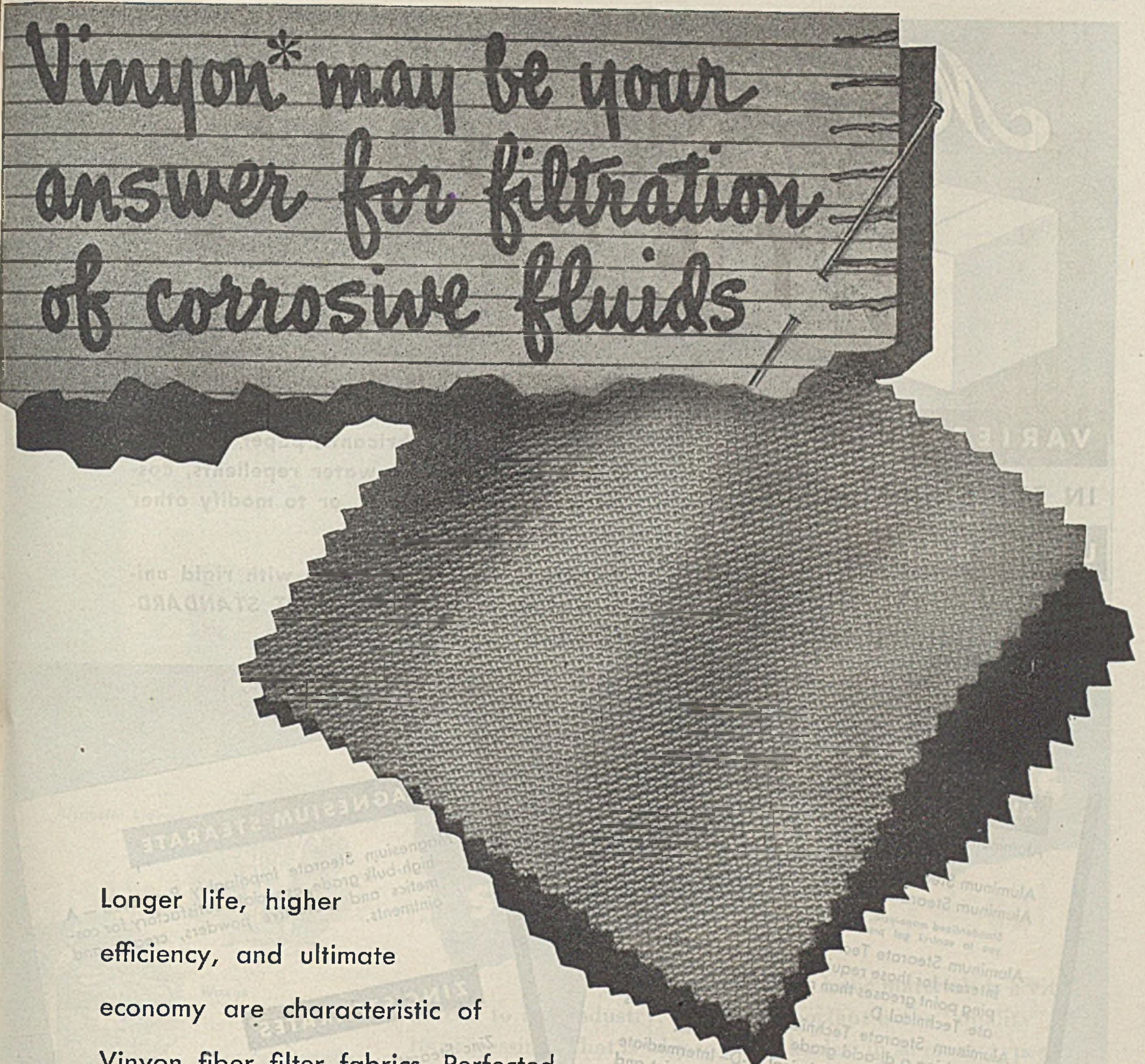
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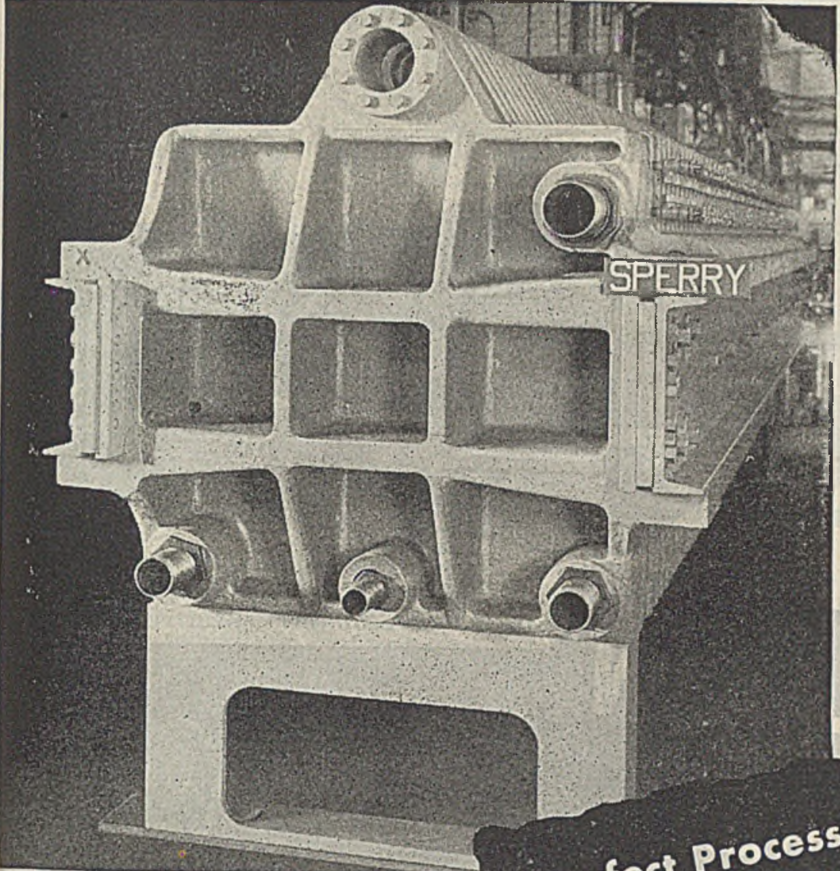
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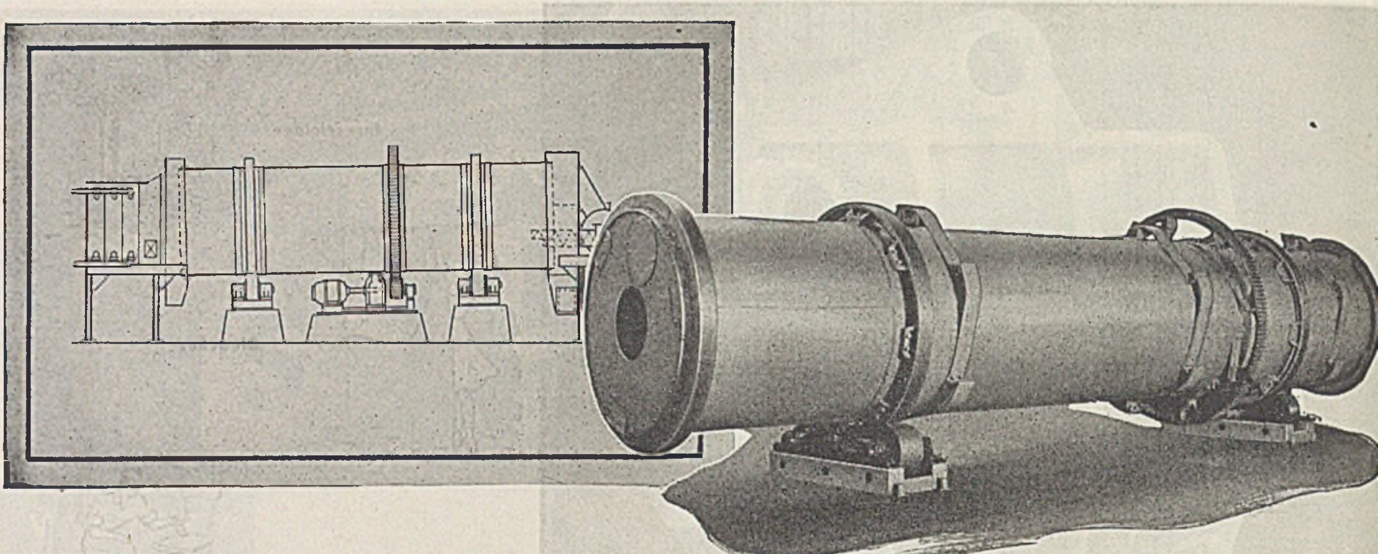

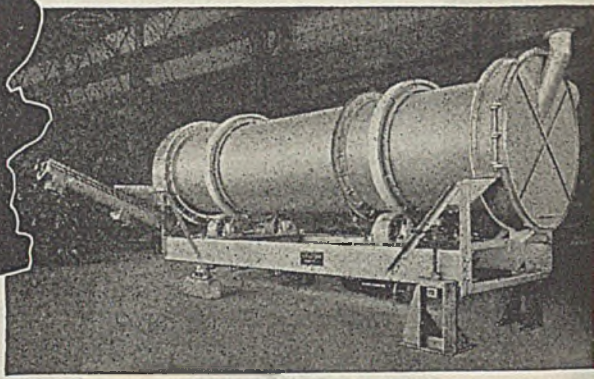

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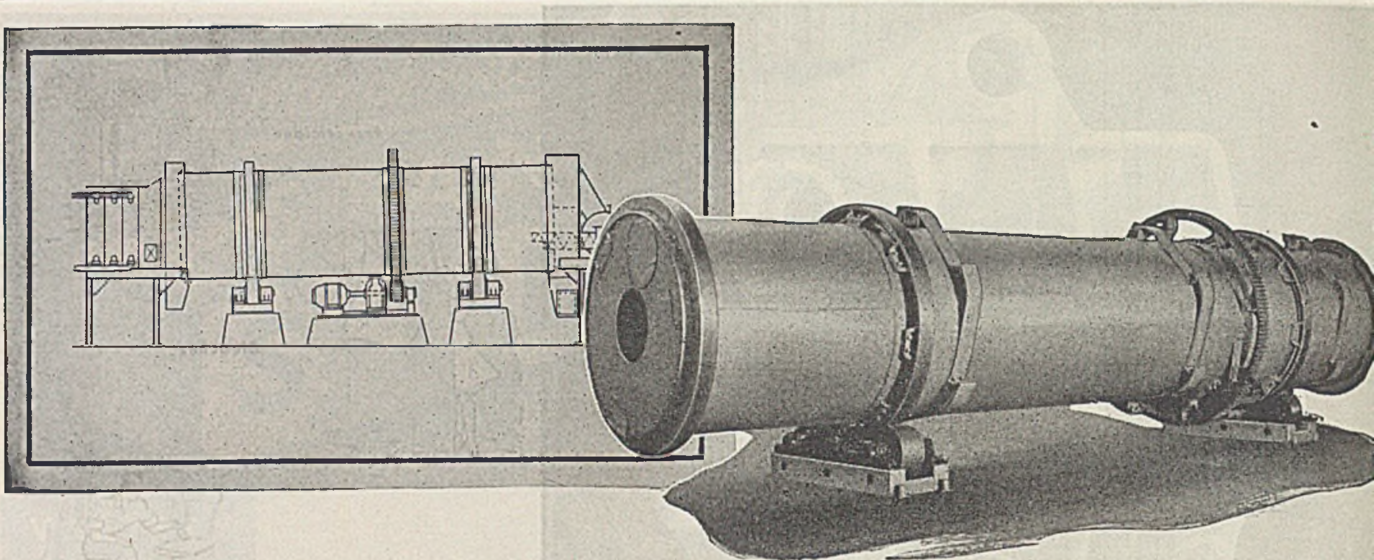

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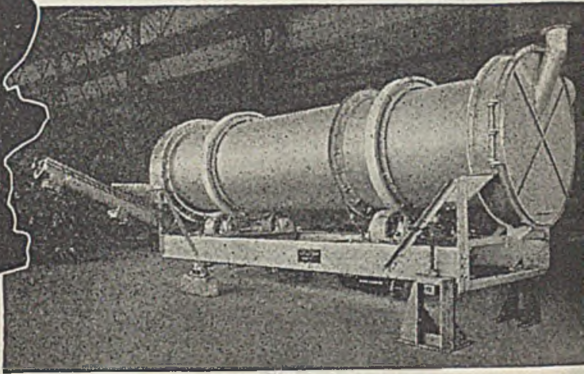

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TABLE OF CONTENTS

General Introduction
Preface
I. Introduction
II. Benzene and Its Aliphatic Derivatives
III. Benzene with Alicyclic Substitutions
IV. Biphenyl and Its Aliphatic Derivatives
V. Two Phenyl Substitutions on Aliphatics
VI. Biphenyl with Alicyclic Substitutions
VII. Two Phenyl Substitutions on Alicyclics or Alicyclicaliphatics and Alicycliphenyl Substitutions on Aliphatics
VIII. Terphenyls and Their Aliphatic Derivatives
IX. Three Phenyl or One Phenyl and One Biphenylyl Substitutions on Aliphatics
X. Terphenyls with Alicyclic Substitutions
XI. Three Phenyl or One Phenyl and One Biphenylyl Substitutions on Alicyclics
XII. Quatraphenyls and Their Aliphatic Derivatives
XIII. Four Phenyl, Two Phenyl and One Biphenylyl, or Two Biphenylyl Substitutions on Aliphatics

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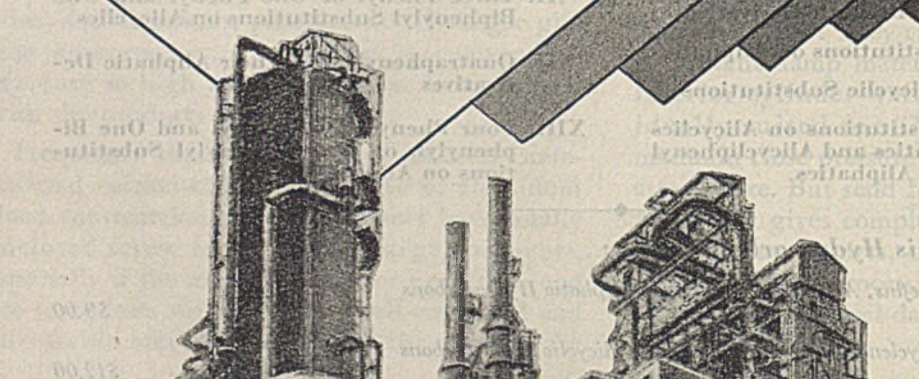

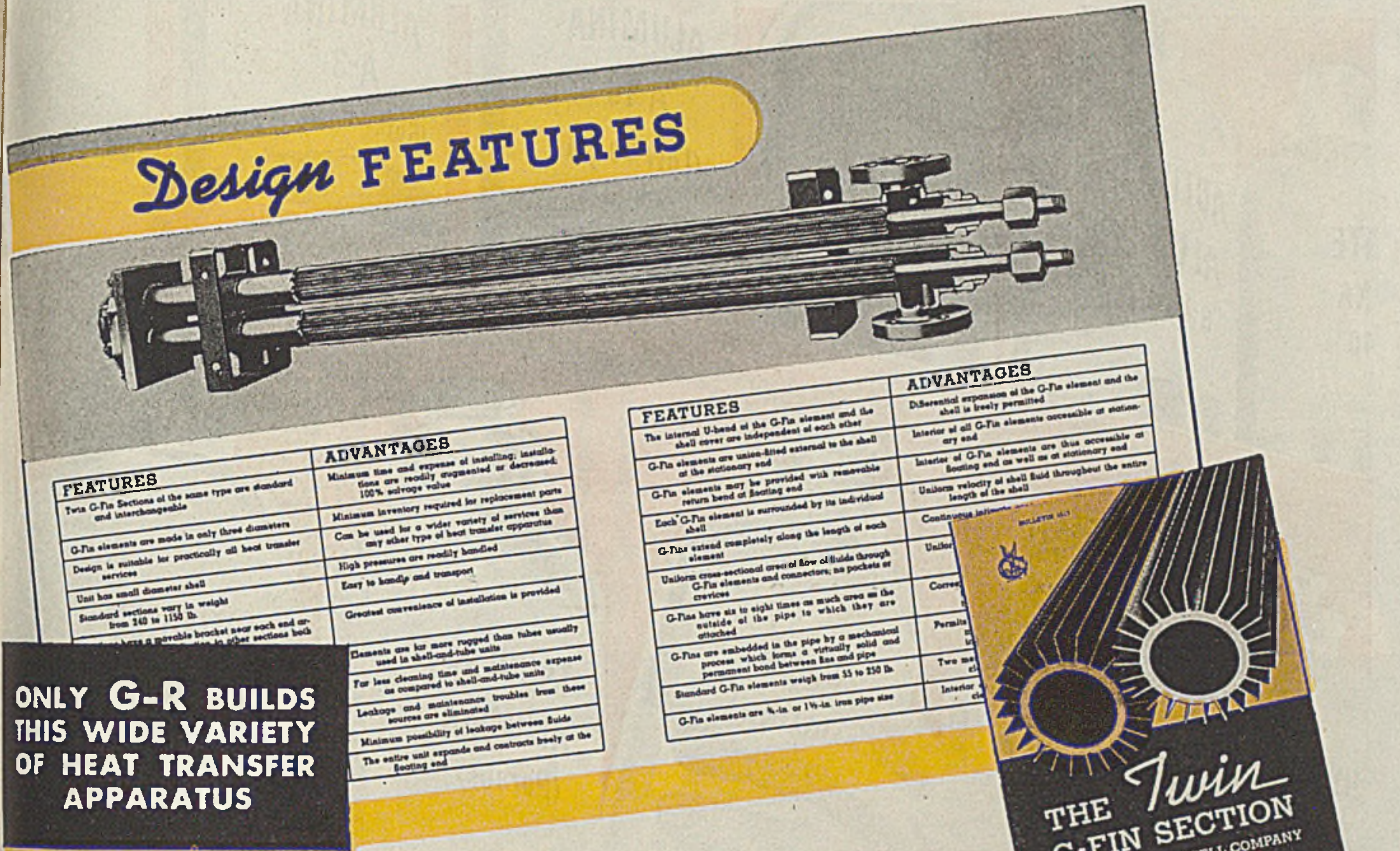

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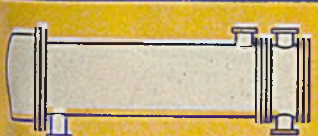

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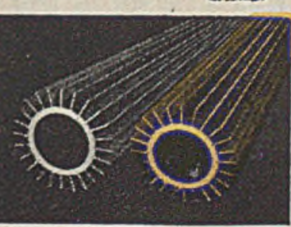


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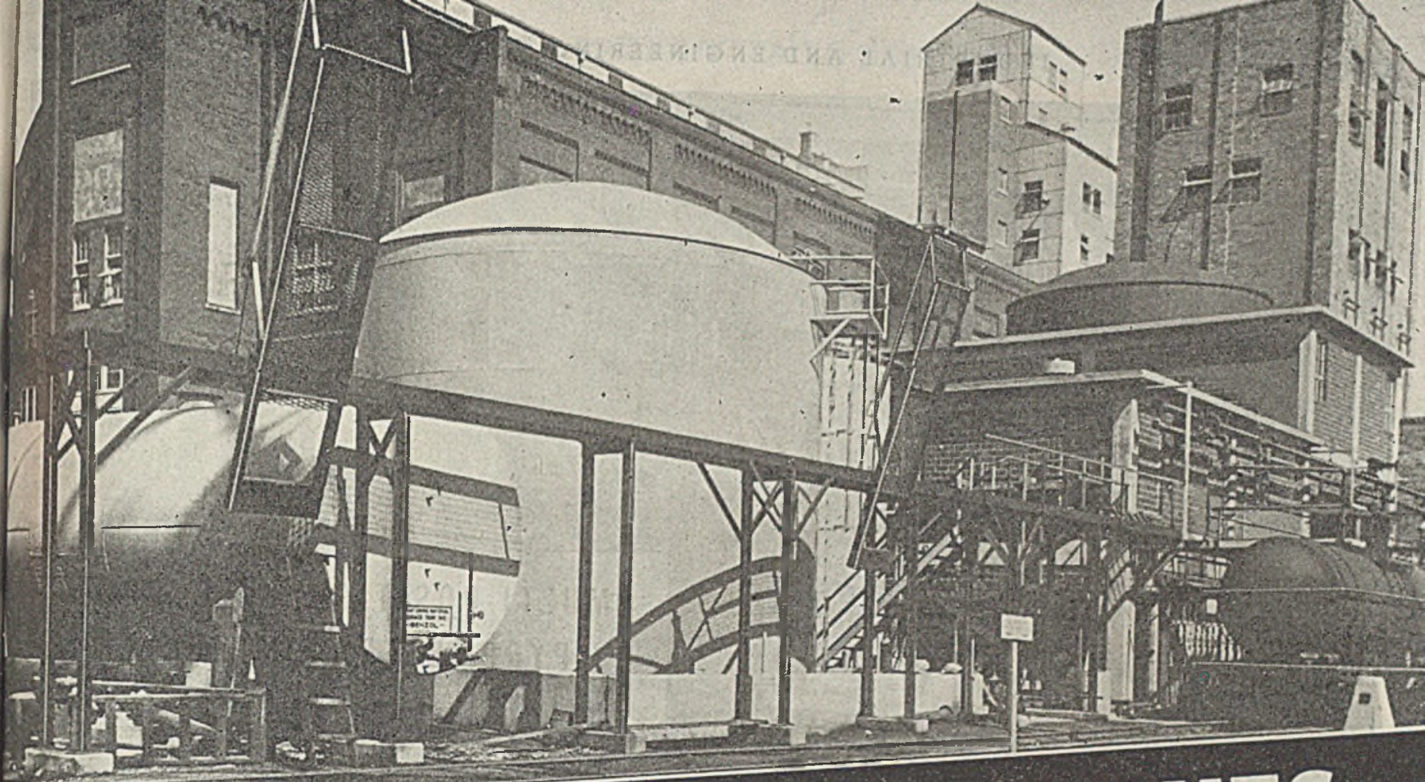

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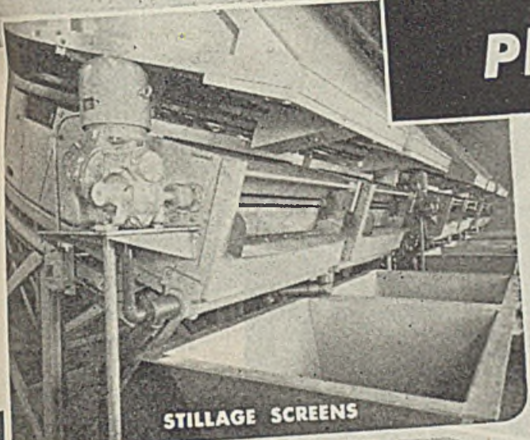

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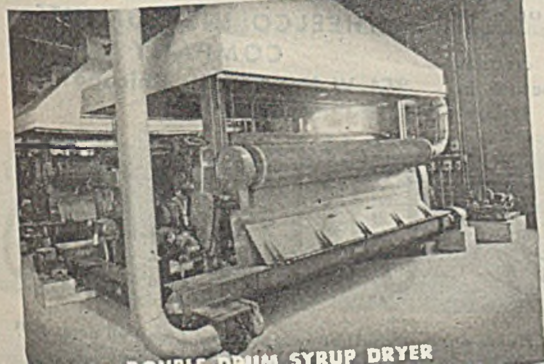

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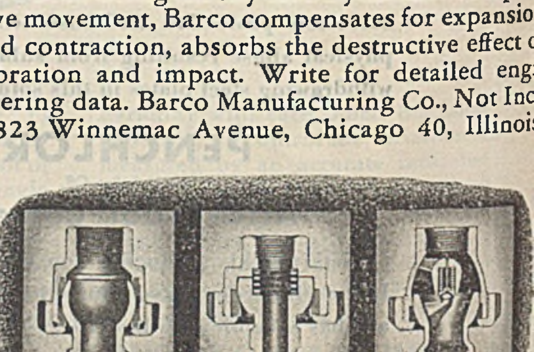

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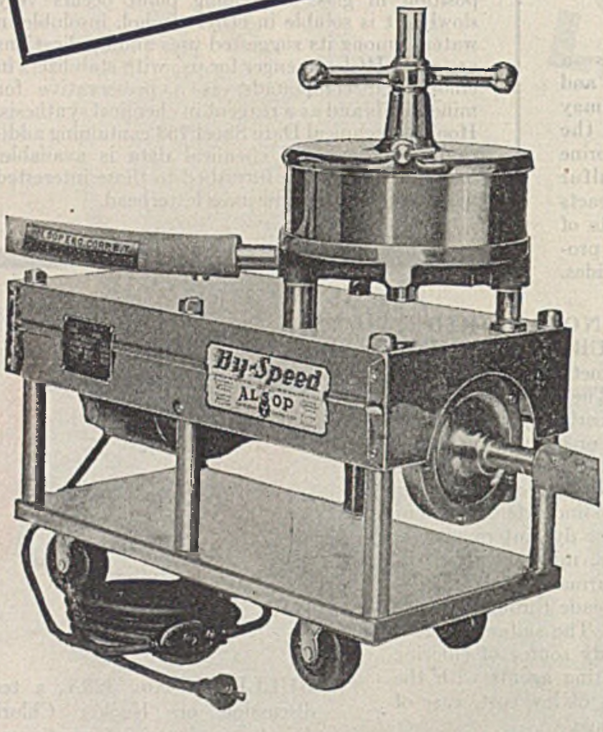

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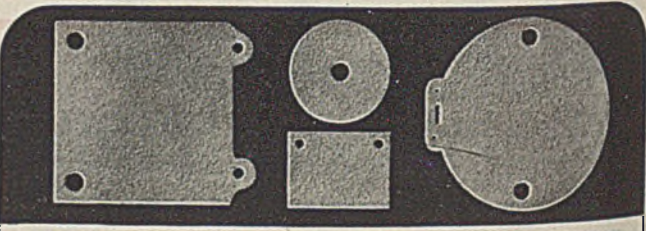
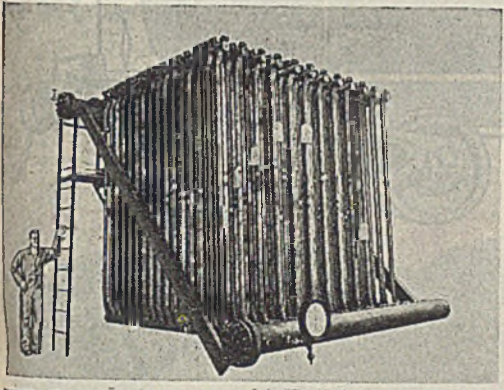
104 BLACK ROAD MILLDALE, CONNECTICUT



In addition to the discs for our own filters, we can supply discs or sheets cut in any shape and size to fit other type filters.

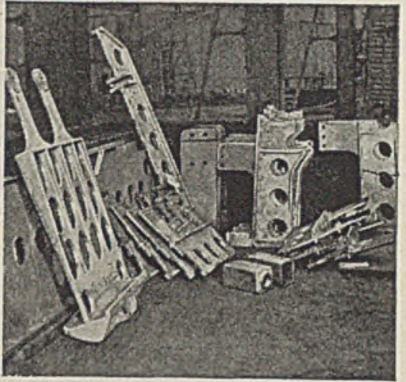
B&W EQUIPMENT for the PROCESS INDUSTRIES

BOILERS. The complete line of B&W boilers and related equipment meets all requirements for dependable, low-cost steam generation in any combination of capacity, pressure, temperature, fuel and space conditions.

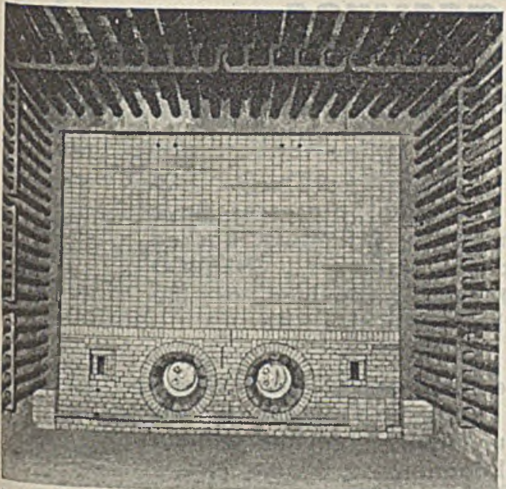


TUBES. Seamless and Welded Tubes are made by B&W in a full range of analyses from low carbons to high alloys, including stainless steels, to meet any service condition in high-temperature, high-pressure applications in chemical processes.

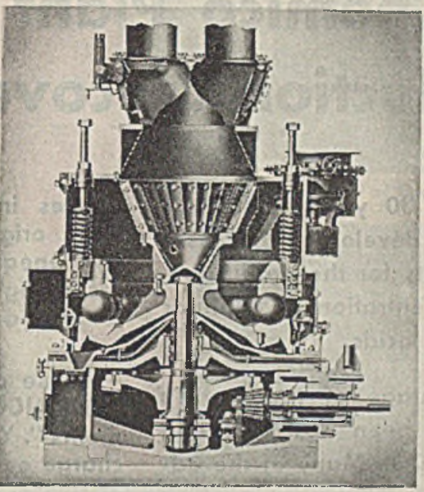
PRESSURE VESSELS. Sizes and shapes of dependable welded construction for any process requirement can be fabricated by B&W from carbon, alloy or clad steels. All vessels are x-ray inspected and stress relieved.



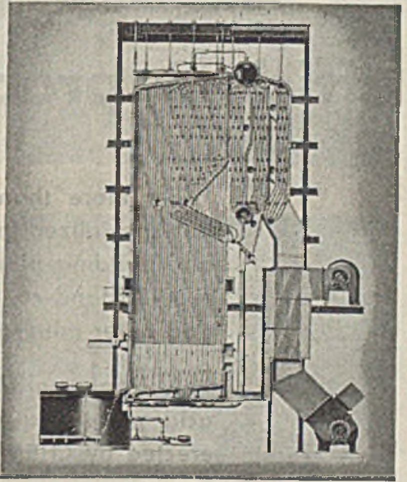
ALLOY CASTINGS. Parts for process equipment requiring high strength, and resistance to abrasion, corrosion and oxidation are made in a wide variety of shapes and analyses in B&W's foundry.



REFRACTORIES. B&W refractories are widely used in chemical process furnaces. Long life, low maintenance, fuel economy and continuous furnace operation account for their extensive use.



PULVERIZERS. For pulverized coal firing of boilers and furnaces, and for raw material grinding, B&W Pulverizers offer many installation, operating and maintenance advantages.



RECOVERY UNITS. High chemical recovery, dependable steam supply and wide operating flexibility are obtained at low operating cost with B&W Tomlinson Recovery Units.

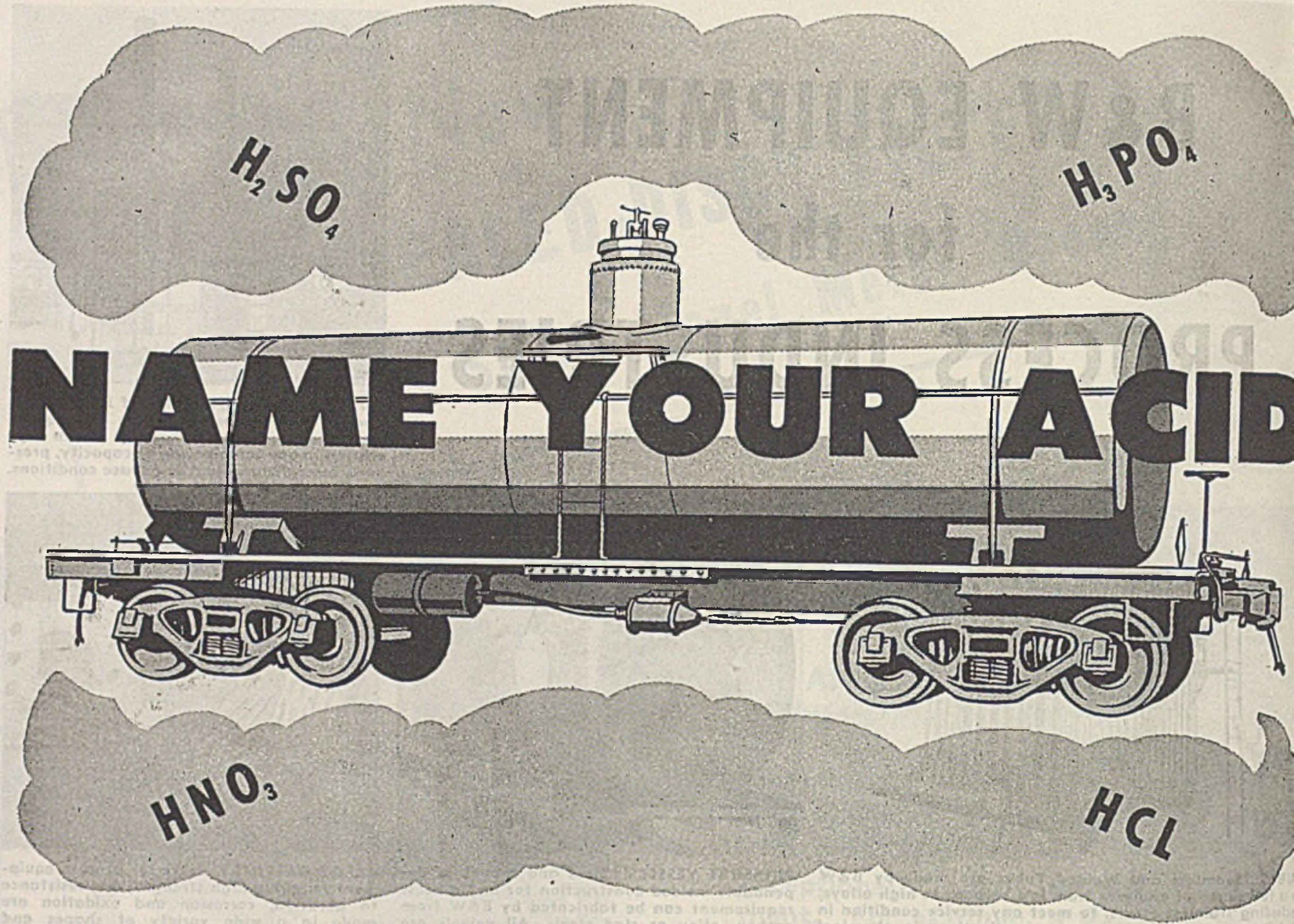
B&W

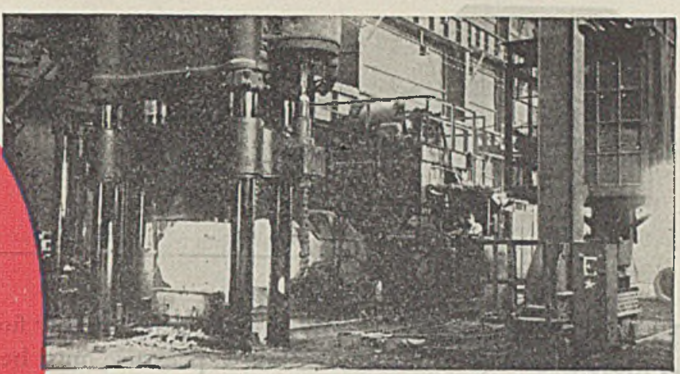
Water-Tube Boilers, for Stationary Power Plants, for Marine Service . . . Water-Cooled Furnaces . . . Superheaters . . . Economizers . . Air Heaters . . . Pulverized-Coal Equipment . . . Chain-Grate Stokers . . . Oil, Gas and Multifuel Burners . . . Seamless and Welded Tubes and Pipe . . . Refractories . . . Process Equipment.

BABCOCK & WILCOX

THE BABCOCK & WILCOX CO.
85 LIBERTY STREET, NEW YORK 6, N.Y.

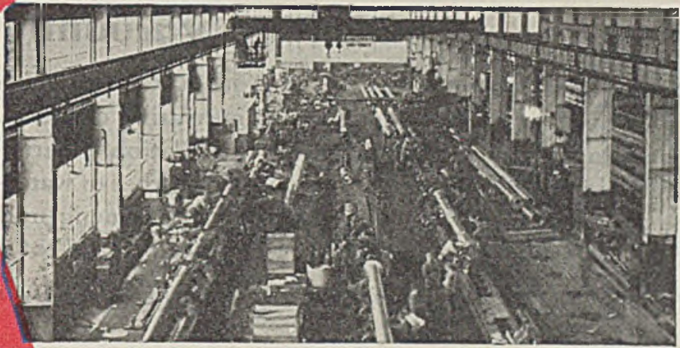
5-68


H_2SO_4
H_3PO_4
NAME YOUR ACID
HNO_3
HCL

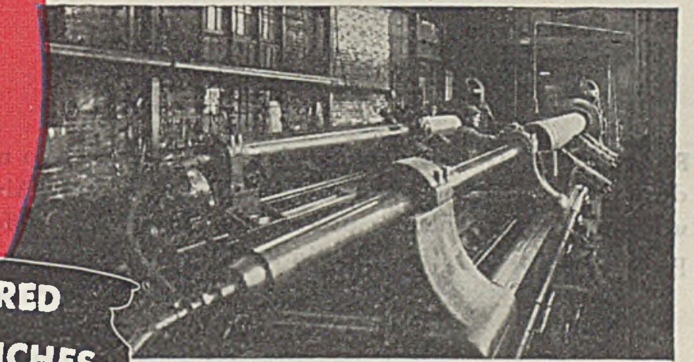


Electrically Operated, 2000 Ton Forming Press

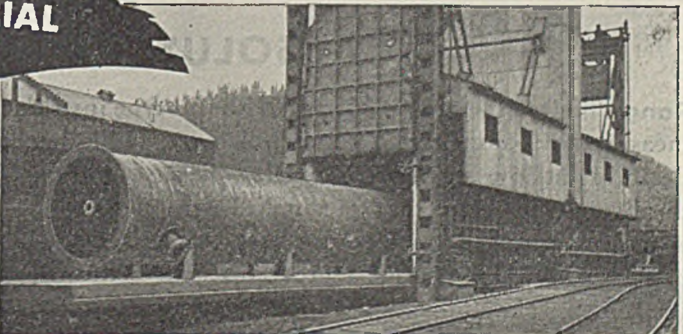
Modern Milling Machinery and Equipment



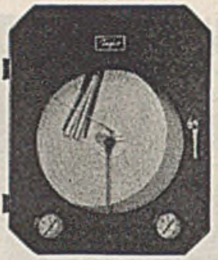
Partial View of One Bay in Our No. 2 Machine Shop



Boring Lathes up to 108 Feet in Length



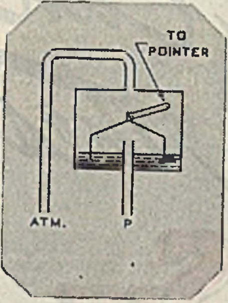
Largest Gas Fired Annealing Furnace of its Kind



Here's what we

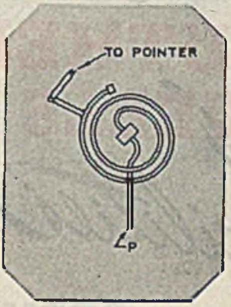
IF YOU have a pressure problem, you can probably find the answer on these two pages. As you well know, pressure must be accurately *measured* before it can be accurately indicated, recorded or controlled. And accurate measurement depends upon proper selection of the measuring element for the operating pressure range, required safety factors, and details of the medium to be measured.

This array of Taylor pressure-measuring elements is the result of our many years of development in serving the process industries. All are standard, proven, high quality Taylor systems. They are available in indicating, recording and controlling instruments, and widely interchangeable. With this complete line to choose from, your Taylor Field Engineer can help you select the exact combination that fits your requirements. Taylor Instrument Companies, Rochester, N. Y., and Toronto, Canada. *Instruments for indicating, recording and controlling temperature, pressure, humidity, flow and liquid level.*



bell manometer

Cast iron, mer cury sealec Range limits for pressure o vacuum from 0- to 0-10″ water or equivalen units of meas urement.



bourdon spring

Standard actua tion for pres sure. Bronze steel or alloy steel. Ranges: 0- 25 to 0-2000 psi.

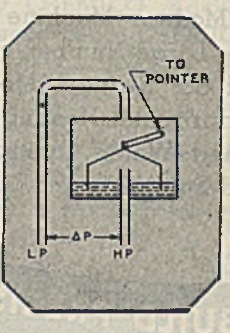
GAGE (and vacuum)

Range limits: 0 to 1″ water to 0 to 10,000 psi. The most common type of pressure instrument. Correct measuring element is determined by operating range and conditions of installation. Charts are usually calibrated in pounds per square inch (psi) or inches of water—but usually can be provided in any suitable units of measurement: millimeters of mercury, atmospheres, etc. Accuracy guaranteed to ½% of scale range.

**Asterisk indicates measuring element is for pressure only, not vacuum.*

DIFFERENTIAL

Range limits. 0-1″ water to 25 psi. Widely used to measure pressure drop between two points . . . over a still, for example. Also used to measure rate of flow when an orifice or other suitable differential-pressure producing device is installed in fluid line. Accuracy guaranteed to 1%.

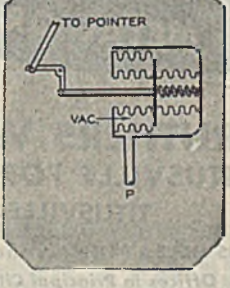


bell manometer

Cast iron, mercury sealed. Ranges: 0-1 to 0-10″ water.

ABSOLUTE

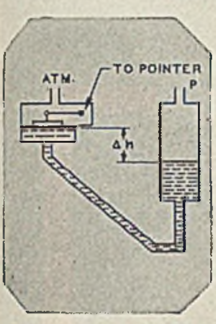
Range limits: 0-5 to 0-25 psi. With this type instrument, pressures are measured by compensated bellows element. (This becomes increasingly desirable at low absolute pressures—because boiling points are related to absolute pressure, not vacuum.) Instruments with absolute pressure actuation are used on low pressure condensers, stills, vacuum pans—in fact wherever absolute temperature correlation is important. These instruments are completely compensated for barometric pressure changes. Accuracy guaranteed to 1% of scale range.



bellows

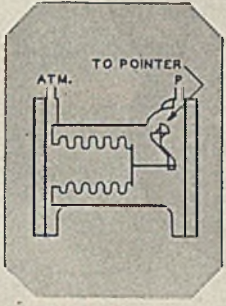
Sealed bellows, no stuffing box. Bellows and housing bronze. Ranges: 0-5 psi absolute (or 0-10″ mercury; or 0-250 mm mercury) to 0-25 psi absolute.

do under Pressure...



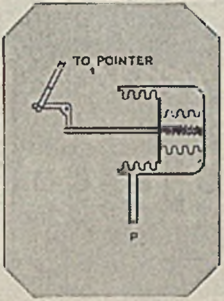
U-tube manometer

Mercury U-tube with float on surface. Cast iron or steel. Range limits: 0-10 to 0-200″ water.



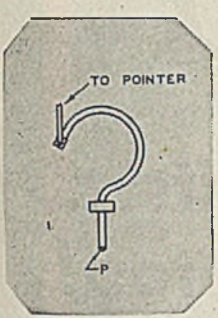
aneroid manometer

Steel body with bellows of bronze or 18-8 alloy. Torque tube, no stuffing box. Ranges: 0-20 to 0-500″ water; 0-20 to 0-100 psi.



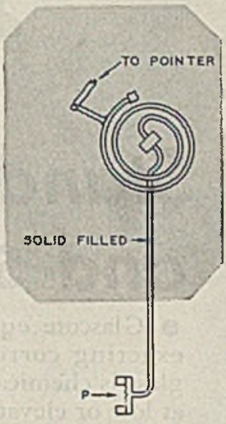
bellows

Sealed bellows, no stuffing box. Bellows and housing bronze. Ranges: 0-3 to 0-25 psi.



C spring*

Variation of multi-coiled bourdon spring. Entirely steel. Ranges: 0-2001 to 0-10,000 psi.

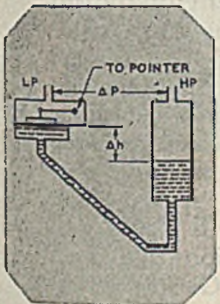


diaphragm*

Self-contained. For measuring sludges, etc. Diaphragm of any material. Maximum length of tubing 50 ft. Ranges: 0-15 to 0-500 psi.

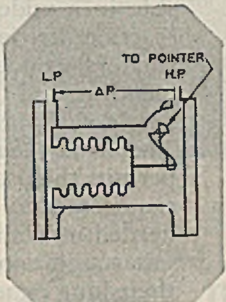
volumetric pressure for liquids*

Steel (silverplated for sanitary services). Compression of bulb actuates spring. Temperature compensation permits tubing up to 35 ft. Range: 0-5000 psi.



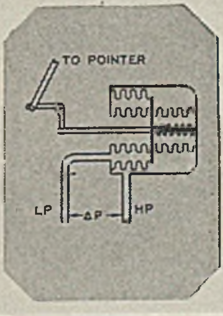
U-tube manometer

Mercury U-tube with float on surface. Cast iron or steel. Ranges: 0-10 to 0-200″ water.



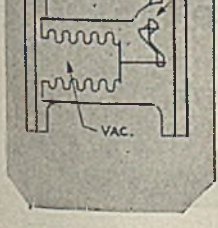
aneroid manometer

Steel body with bellows of bronze or 18-8 alloy. Torque tube, no stuffing box. Ranges: 0-20 to 0-200″ water (0-500″ on order).



bellows

Sealed bellows, no stuffing box. Bellows and housing bronze. Ranges: 0-5 to 0-25 psi.



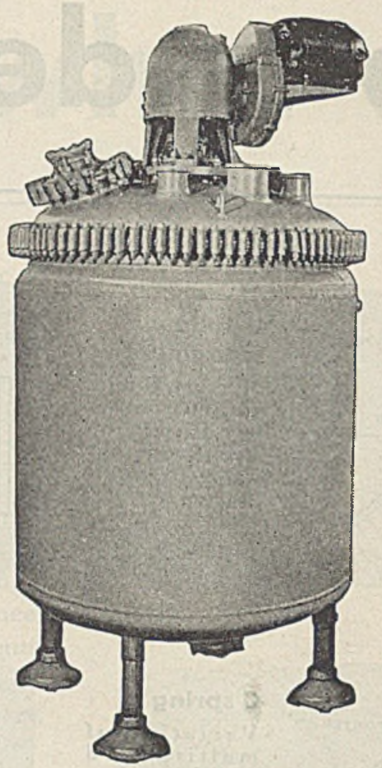
aneroid manometer

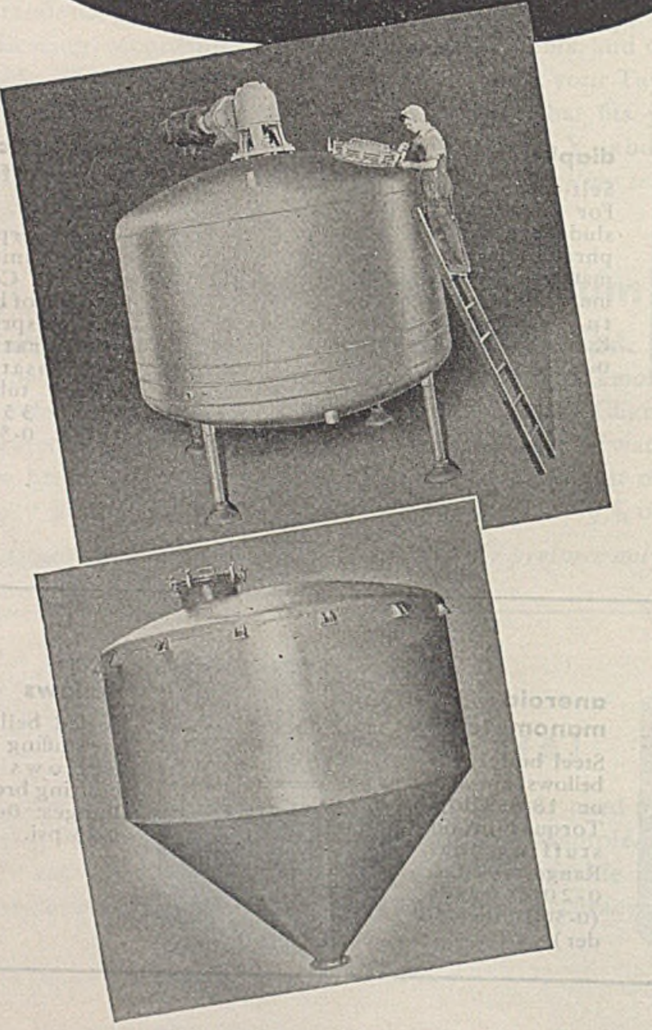
Steel body with bellows of bronze; torque tube of stainless steel; no stuffing box. Ranges: 0 to 20 to 0-500″ water absolute, or equivalent units of measurement.

Taylor Instruments
MEAN
ACCURACY FIRST
IN HOME AND INDUSTRY

THE INERTNESS OF GLASS THE STRENGTH OF STEEL

GLASCOTE
Corrosion Resistant
Equipment



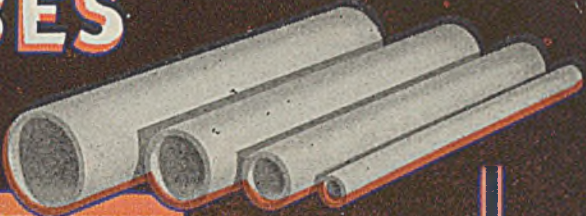


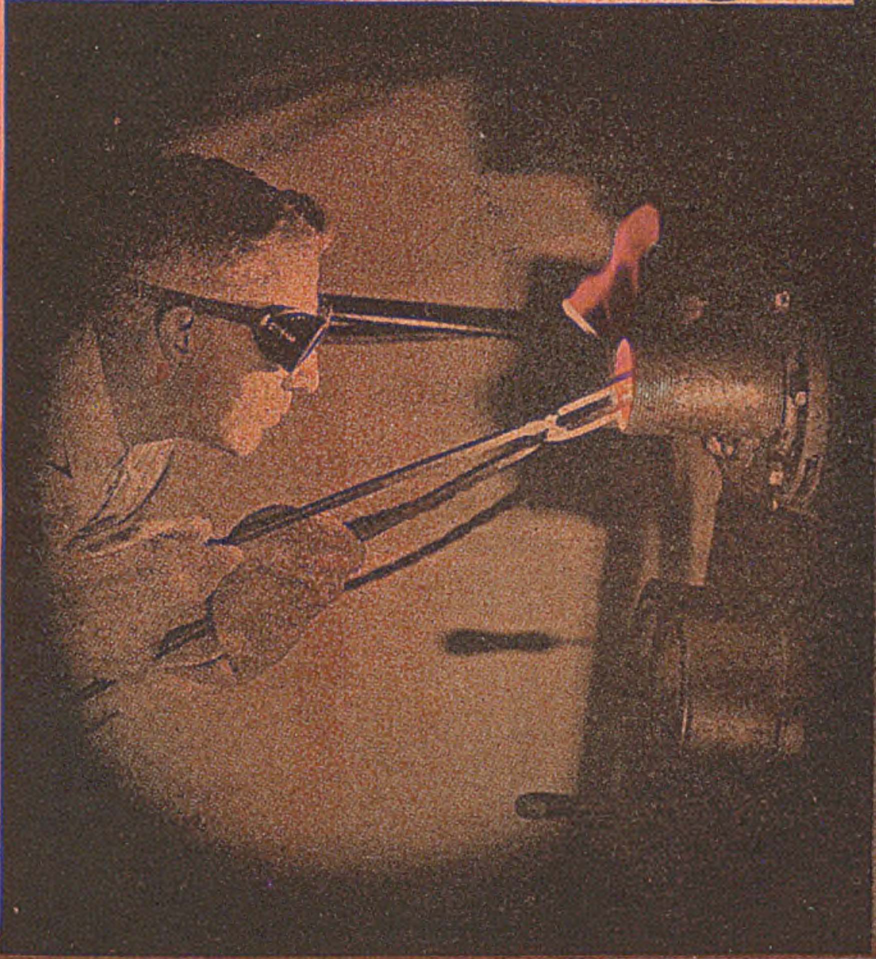
Standard Units...
and "SPECIALS" too!

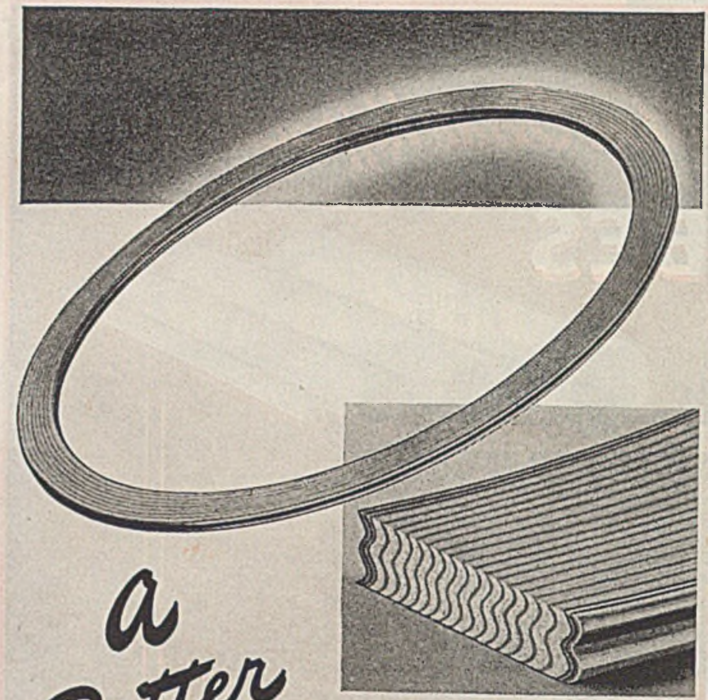
● Glascote equipment meets industry's most exacting corrosion resistant requirements. The glass is chemically inert. It is resistant to all acids at low or elevated temperatures, excepting hydrofluoric and hot concentrated phosphoric,—and has all the properties of laboratory glassware combined with greater strength and elasticity.

This proven glass-on-steel construction is available in a wide range of equipment including reaction kettles, crystallizers, evaporators, chlorinators, condensers, distilling, mixing, storage, blending and other standard units. These include single shell or jacketed, open or closed designs. The wide range of sizes and diameters available permits the use of standard units in meeting most requirements, but in cases where "specials" are needed or desired, our engineers will gladly submit suggestions and recommendations, based on their long experience, using either Glascote glass-on-steel, or Glascote stainless steel or alloy metal construction. Let us quote on your requirements!

GLASCOTE PRODUCTS, *Inc.*
20901 ST. CLAIR AVENUE • CLEVELAND 17, OHIO
ENGINEERING AND SALES REPRESENTATIVES IN THE PRINCIPAL CITIES
CORROSION RESISTANT EQUIPMENT FOR THE PROCESSING INDUSTRIES







a Better gasket

Cross section view of GARLOCK *Guardian* gasket shows three points of resiliency of the metal strips which separate the layers of asbestos. Inner and outer edges of the gasket are reinforced with double thicknesses of metal, electrically welded for added strength.

RESILIENT—EXPANDS AND CONTRACTS WITH CHANGING TEMPERATURES

For a permanently tight joint under changing temperature conditions your gasket should be a GARLOCK *Guardian* gasket. This gasket combines extraordinary resiliency with great strength.

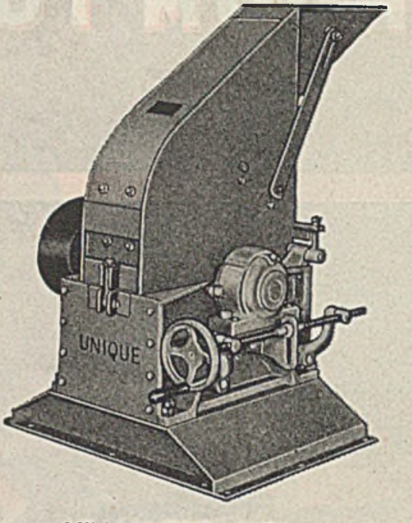
Because of its unique structural design it adjusts itself instantly and repeatedly to expansion and contraction of the pipe line or equipment.

Also *Guardian* gaskets withstand extreme temperatures and pressures and effectively resist the destructive action of gases and liquids.

THE GARLOCK PACKING COMPANY
PALMYRA, NEW YORK
In Canada: The Garlock Packing Company
of Canada, Limited, Montreal, Que.

GARLOCK
Guardian
GASKET

ROBINSON
UNIQUE
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.

HEAVY DUTY TYPE

ROBINSON MANUFACTURING CO.
Plant: Muncy, Pa.
SALES REPRESENTATIVE
MERCER-ROBINSON COMPANY, INC.
30 CHURCH ST., NEW YORK 7, N.Y.

EASILY MARKS ON GLASS

and all other materials!

IDEAL ELECTRIC MARKER

New, dependable tool, built to Industrial Standards, permanently writes on all types of glass—test tubes, beakers, etc.—mark names, formulae, other identification. Light in weight (weighs only 10 oz.) with powerful marking stroke, operating like a small electric hammer, cutting mark that cannot be erased through ordinary usage. Shaped to fit the hand, it is as easy to use as a pencil.

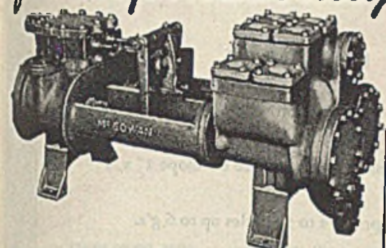
AVAILABLE WITH DIAMOND POINT

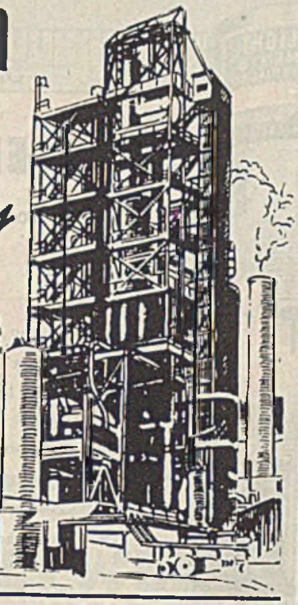
IDEAL has the most complete line of
ETCHERS and MARKERS on the Market

Industrial Products Division
IDEAL INDUSTRIES, Inc.
(Successor to Ideal Commutator Dresser Co.)
1347 PARK AVENUE SYCAMORE, ILLINOIS
Sales offices in all principal cities
1698

McGOWAN PUMPS

for dependability





Dependable Since 1852

DUPLEX SIDE POT

Used in petroleum service where pressures are usually above the average. Can be equipped with water jacketed stuffing boxes for hot oil service and the liquid end is available in cast steel as well as commercial alloys with removable levers.

Write our engineering department for complete data—
Leyman Manufacturing Corp.
McGowan Pump Division
58 Central Ave., Cincinnati 2, Ohio

McGOWAN PUMPS

LEYMAN MANUFACTURING CORP.
The JOHN H. McGOWAN Co. DIVISION
59 CENTRAL AVE., CINCINNATI 2, OHIO

Chemical Engineering to Fit

—we specialize in big-plant efficiency for the smaller process and chemical manufacturer. Your inquiry *(no obligation whatever)* may bring you the practical answer. Don't hesitate to

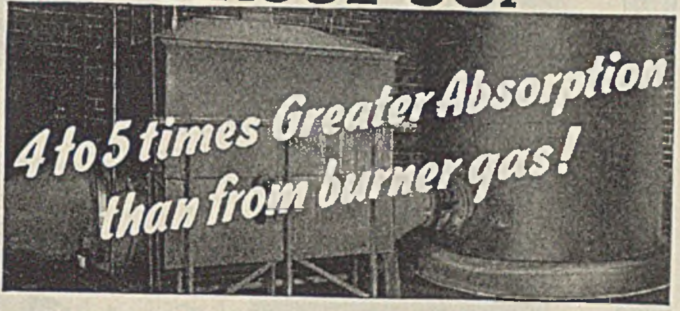
call on Hicks

SINCE 1841

S. D. HICKS & SON COMPANY
1671 HYDE PARK AVE., BOSTON 36, MASS.
NEW YORK OFFICES

GET *maximum absorption*

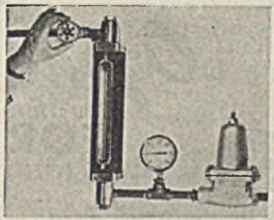
OF SULFUR DIOXIDE IN WATER WITH ANSUL SO_2



EQUILIBRIUM SOLUBILITY OF SO_2 IN WATER AT ONE ATMOSPHERE (Saturated Solution)

Temp. F.	% SO_2 by Weight in Solution			
	From Ansul Liquid SO_2	From Burner Gas Containing:		
		20% SO_2	18% SO_2	16% SO_2
32	18.59%	4.61%	4.15%	3.68%
50.6	13.95%	3.25%	2.93%	2.60%
68	10.14%	2.27%	2.02%	1.82%
77	8.60%	1.89%	1.70%	1.51%
86	7.30%	1.58%	1.42%	1.26%

It's So Easy to Install This Ansul SO_2 System and Get These Proved Advantages:



GREATER SOLUBILITY—As indicated in the table, much more concentrated water solutions of SO_2 may be obtained from 99.9+% Ansul Liquid SO_2 than from the most efficiently produced burner gas.*

HIGHER PURITY—Elimination of impurities inherent in burner gas (Ansul Liquid SO_2 is 99.9+% [by weight] PURE).

FINGER-TIP CONTROL—Easy, positive, finger-tip control providing extreme accuracy for reaction or adjustment of pH.

GREATER ECONOMY—Small investment in equipment, materially reduced operating and maintenance costs, and freeing of valuable floor space.

*This follows the principle described in Henry's law that the concentration of a dissolved gas in solution is in direct proportion to the concentration in the free space above the liquid.

WRITE THE ANSUL TECHNICAL STAFF FOR FURTHER INFORMATION

LIQUID Sulfur Dioxide BY ANSUL*

PHYSICAL PROPERTIES

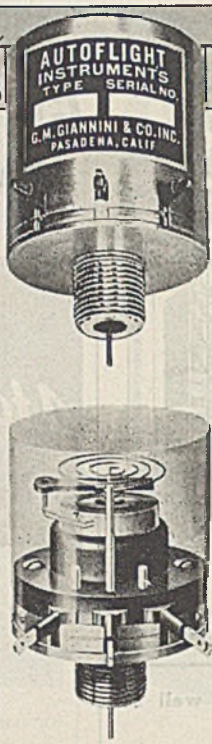
Chemical formula	SO_2
Molecular weight	64.06
Color (gas and liquid)	Colorless
Odor	Characteristic, pungent
Melting point	−103.9° F. (−75.5° C.)
Boiling point	14.0° F. (−10.0° C.)
Density of liquid at 80° F.	(85.03 lbs. per cu. ft.)
Specific gravity at 80° F.	1.363
Density of gas at 0° C. and 760 mm:	2.9267 grams per liter (0.1827 lb. per cu. ft.)
Critical temperature	314.82° F. (157.12° C.)
Critical pressure	1141.5 lbs. per sq. in. abs.
Solubility	Soluble in water
Purity	99.9+% (by wt.) SO_2 (H_2O less than 0.01%)

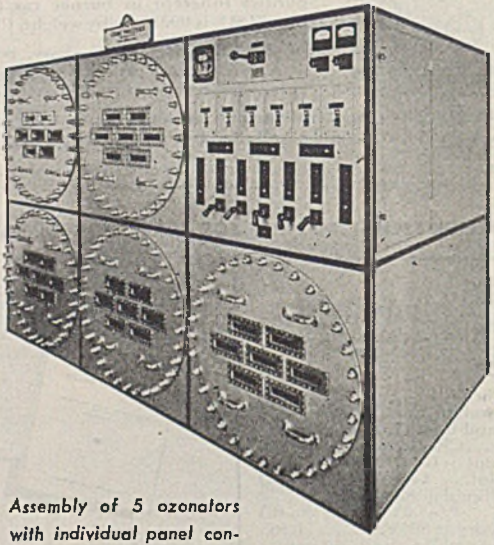
*REG. U. S. PAT. OFF.

Send for Bulletin 020.1, "A Comparison of Ansul SO_2 and Sulfur Burner Gas," and also for your copy of "Liquid Sulfur Dioxide"—a treatise on the properties, characteristics, and industrial uses of Liquid Sulfur Dioxide—written by the Ansul Technical Staff.

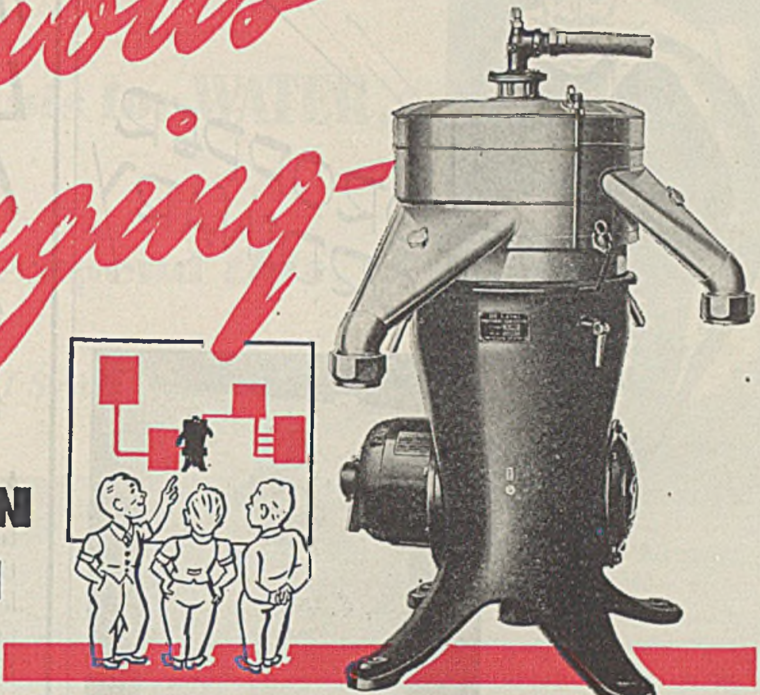
WRITE: Dept. C.

ANSUL CHEMICAL COMPANY
INDUSTRIAL CHEMICALS DIVISION, MARINETTE, WIS.
Eastern Office: 60 E. 42nd St., New York Cit


AUTOFLIGHT
INSTRUMENTS
TYPE SERIAL NO.
G.M.GIANNINI & CO.INC.
PASADENA, CALIF



Continuous Centrifuging—



THE SHORTEST DISTANCE BETWEEN TWO PRODUCTION POINTS

A De Laval Centrifugal enables separation, clarification or concentration to be effected *continuously*, in place of outmoded gravity settling or other obsolete methods. It instantaneously divides liquids into their respective light and heavy phases, continuously discharging both. Simultaneously, solid impurities are removed, in some machines being stored in the bowl outside the zone of separation and in the "Nozzle-Matic" models being discharged continuously with one effluent.

De Laval continuous centrifugals have other advantages besides that of reducing processing time. They save labor. They simplify waste disposal. They conserve material. And usually, if not invariably, they improve the product as well. All of these features add up to this:—a De Laval Centrifugal eliminates the slow-spots in a process line and does it economically and well.

In writing for Bulletin 225, mention whether you are interested in separation, clarification or concentration, and specify the liquids to be handled. No charge, of course.

★

THE DE LAVAL SEPARATOR COMPANY
165 Broadway, New York 6 427 Randolph St., Chicago 6
DE LAVAL PACIFIC CO., 61 Beale St., San Francisco 19
THE DE LAVAL COMPANY, Limited
MONTREAL PETERBOROUGH WINNIPEG VANCOUVER

DE LAVAL CENTRIFUGAL PROCESSING SYSTEMS

For SEPARATION • CLARIFICATION • CONCENTRATION

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THE CHEMISTRY OF LEATHER MANUFACTURE

by **GEORGE D. McLAUGHLIN**

Director, B.D. Eisendrath Memorial Laboratory, Racine, Wisconsin; Formerly Director, Tanners' Council Research Laboratory, University of Cincinnati.

and **EDWIN R. THEIS**

Professor of Chemical Engineering and Director of the Industrial Biochemistry Laboratories at Lehigh University.

A. C. S. MONOGRAPH No. 101

THIS scholarly treatise presents a vast fund of experimental information which is of the first importance not only to leather chemists and technologists, but to a number of other groups of scientists. Because of its extremely detailed reports of all recent research findings on the preservation, pickling, tanning and histology of hides and skins, it will be invaluable to dermatologists, cosmeticians, and colloid chemists, as well as to researchers in the electrochemistry of proteins. Much attention is devoted to acid-base equilibrium and the effect of pH on various phases of operations in the manufacture of leather. The chapters on vegetable and chrome tanning unquestionably constitute the most complete treatment of this subject to be found in the entire literature of leather chemistry.

Prepared as the third volume of the monograph of the same title written by the late John Arthur Wilson, it is a most worthy and notable addition to its predecessors. All the experimental material described is carefully and painstakingly evaluated by the authors in the light of their own extensive work and their profound knowledge of protein chemistry. The result is a body of correlated facts and theories which can be described only by the word "monumental."

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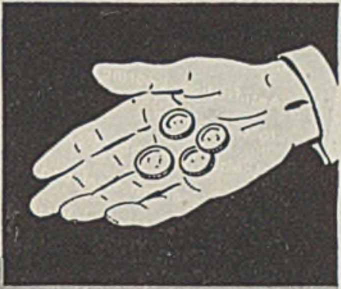

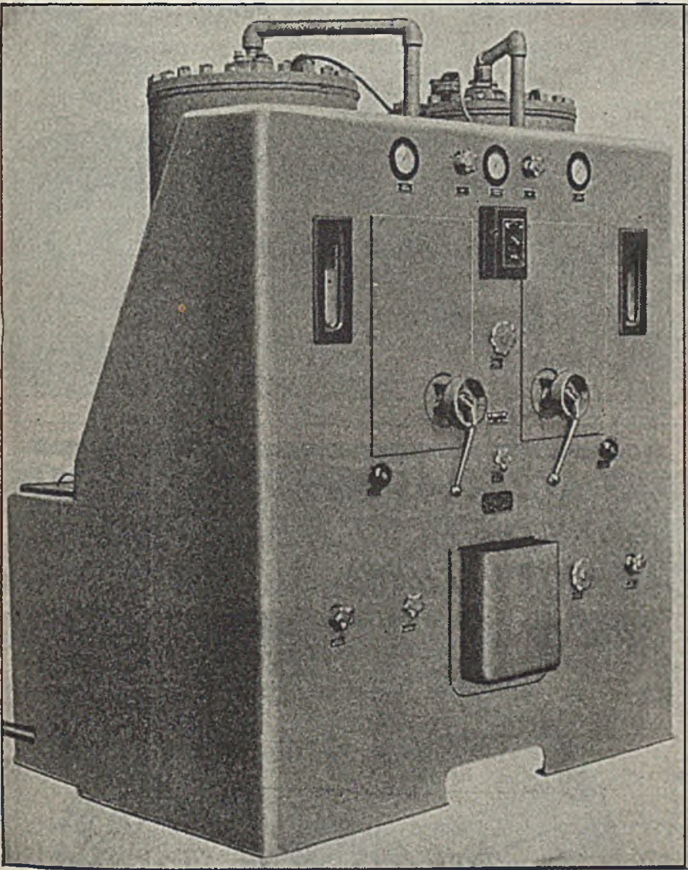

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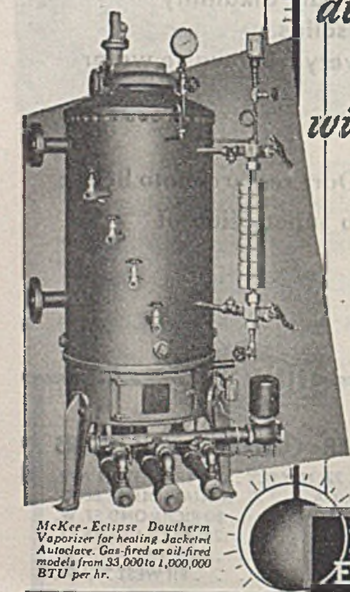

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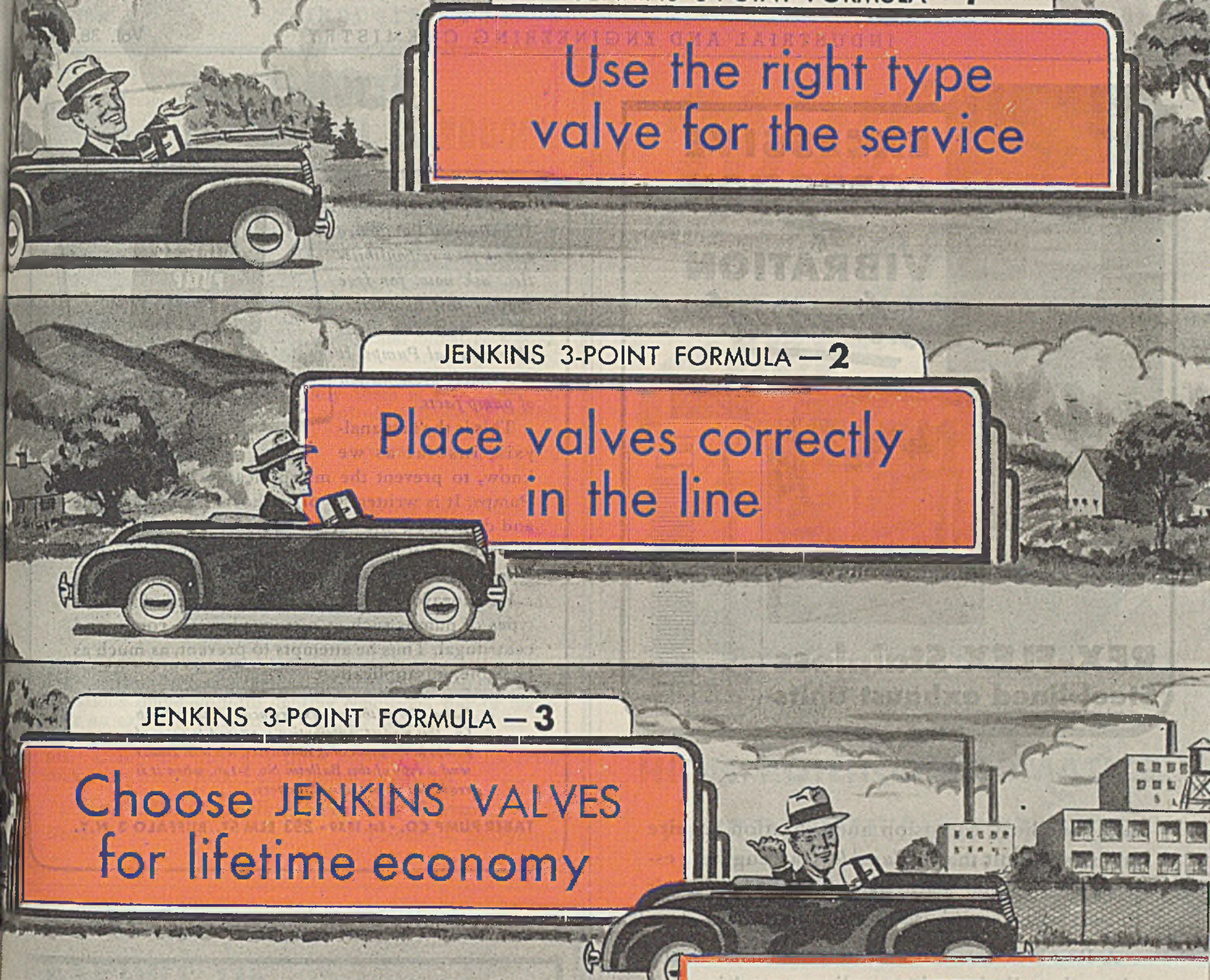

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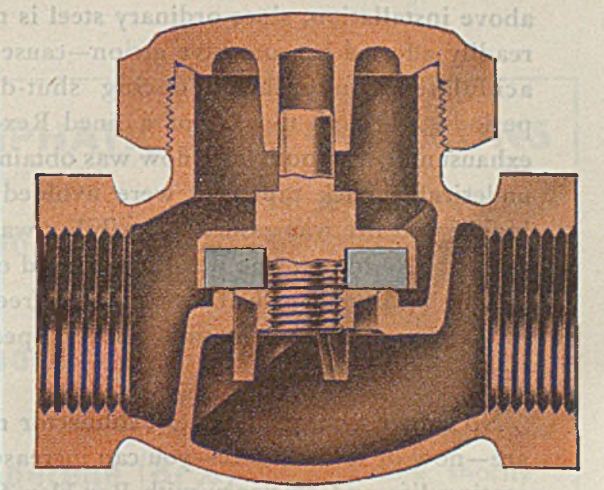

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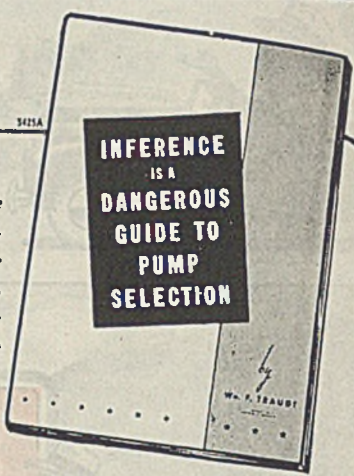
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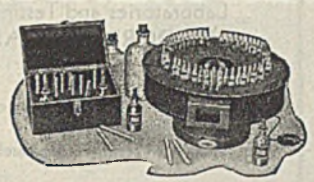

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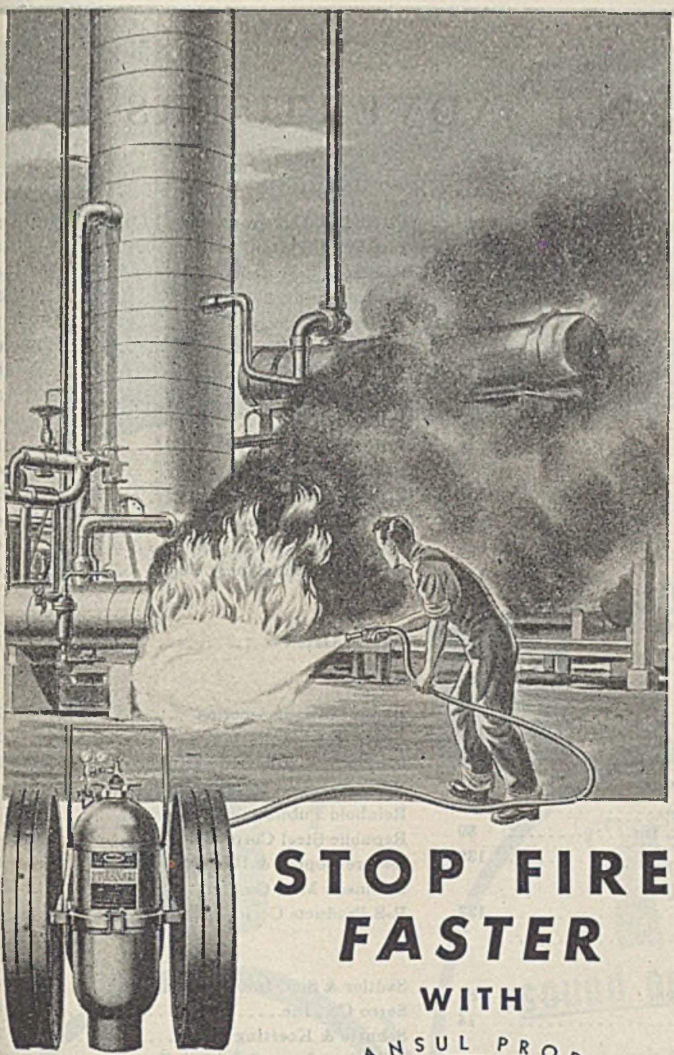

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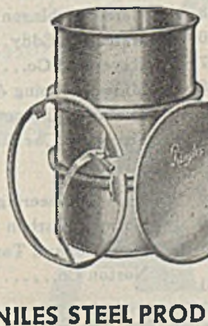

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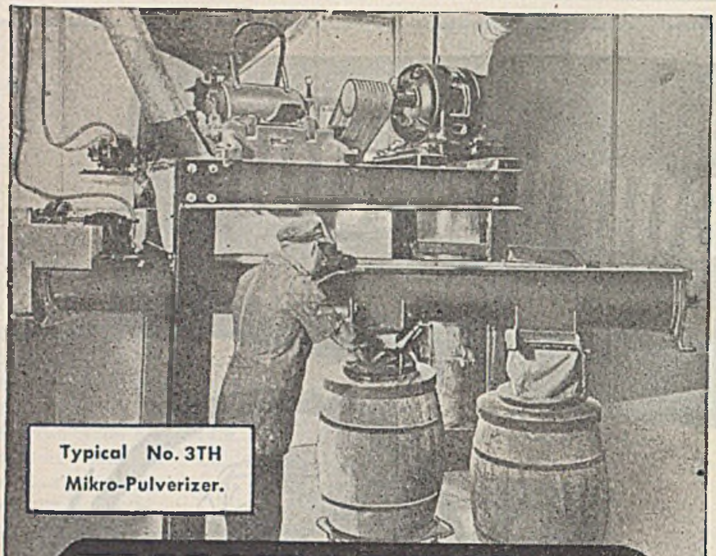

From the Editor's Desk

WAR's threat to the supply of mica stimulated research on delamination equipment, and the National Bureau of Standards succeeded in developing a machine which was fairly adequate for the task of making thin sheets of mica. With the new equipment splits of mica are made four times faster than could be achieved by tedious hand splitting.

★ Since the first postwar import of wood pulp in June of last year, the United States has received over 800,000 short tons. About 40% of this was unbleached sulfite, and 44% was unbleached sulfate.

★ Americans continue to have the highest per capita rate of soap consumption in the world. It is now about 25 pounds a year per person.

★ Tetradiphenylethane is more deadly than DDT in killing mosquito larvae.

★ Sunshine exerts a major influence on the vitamin C content of tomatoes. When test tomato plants were allowed to mature in the sun, the vitamin C level was half again as much as that of shade-ripened fruit. Tomatoes from Fresno, Calif., had nearly three times the vitamin C of Rhode Island tomatoes.

★ Butadiene production from alcohol at the Institute, W. Va., plant has been ordered resumed, despite the comparatively high cost of this method. The resumption was ordered because postwar imports of natural rubber have increased more slowly than original estimates indicated.

★ January production of penicillin was 1.3 billion units, 80% above December, 1945, and nearly one-fifth the total output for 1945. Total monthly manufacture is expected to exceed 2 billion units by April.

★ A gold-germanium alloy, containing 12% of the latter metal, melts at only 673° F. and has desirable wearing and expansion properties. About a ton of germanium is produced annually in the United States as a by-product of cadmium manufacture, but additional quantities could be obtained from zinc production.

★ Carbon black production in the United States approximately doubled during the war years. Estimated demand for 1946 will equal the capacity output of 600,000 long tons because of expanded use in synthetic rubber tires, electrical equipment, and ink, paint, and plastics.

★ A molten zirconium oxide spot only 0.003 inch in diameter is the light source of a new electrical lamp of high brilliancy and efficiency, developed by Western Union. The new lamp is expected to have particular value as a light source in optical systems.

★ Demand for tin in the United States is twice the supply.

★ World-wide demand for oils and fats is 9 billion pounds; only 6 billion pounds are available.

★ Lumber production is still well below the 1942 record of 36 billion board feet, but the estimated 1946 output of 30 billion board feet is 5 billion more than the 1939 supply. Green lumber is no novelty on the black market, but most of the legitimate output of established mills now is properly seasoned.

★ Production of tung nuts in Mississippi has increased more than 9000 tons in the past five years.

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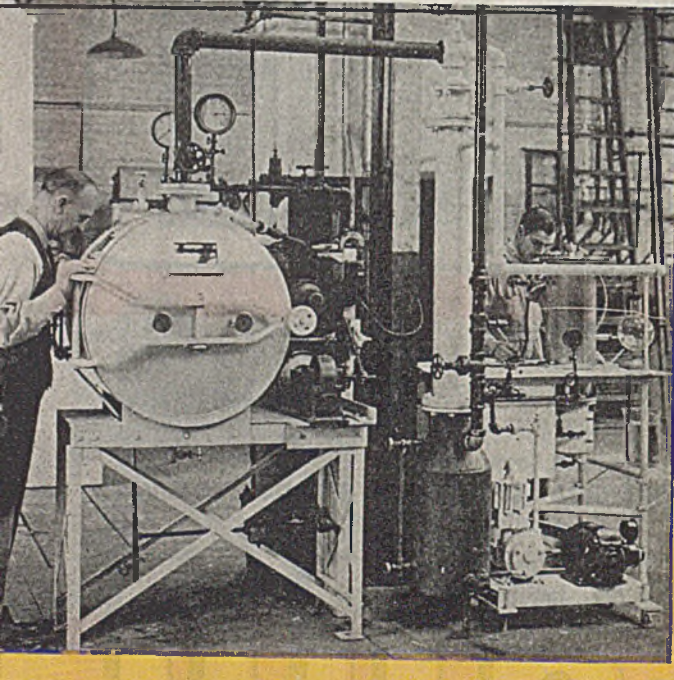

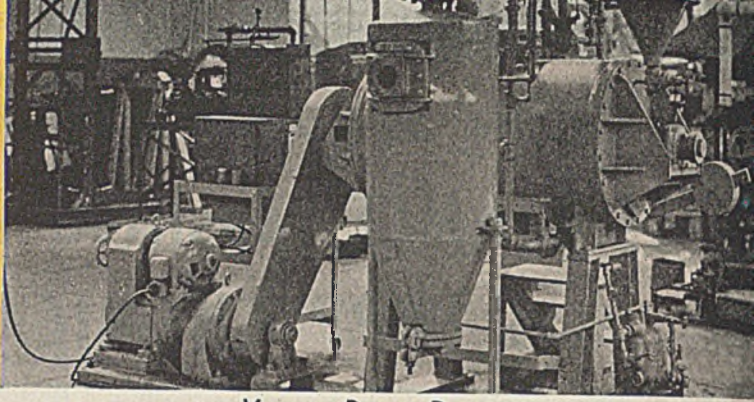

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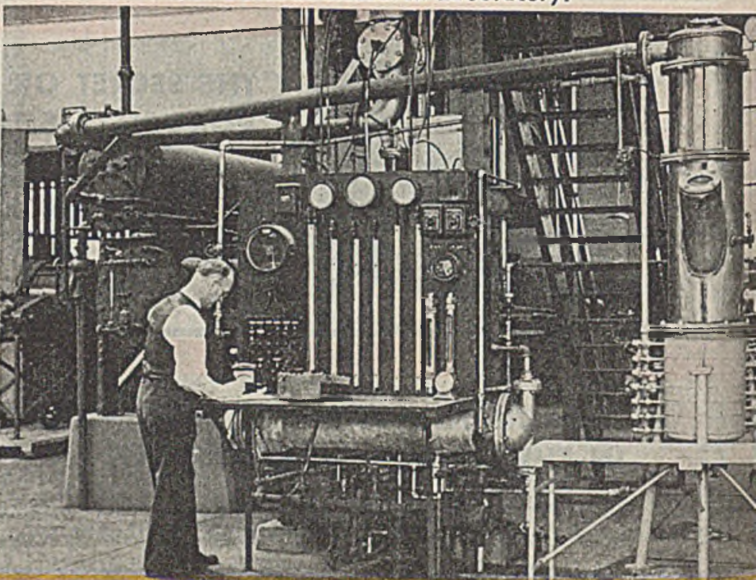

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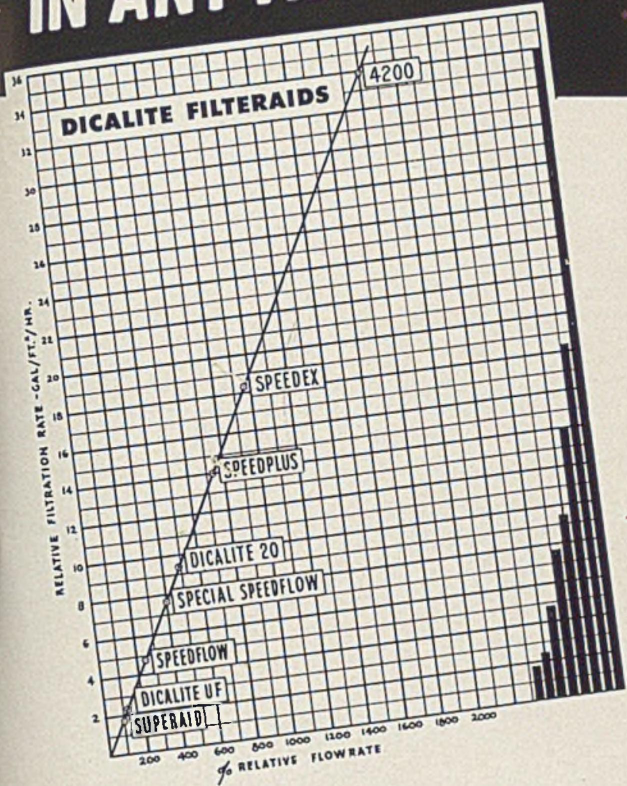
Choosing THE RIGHT FILTERAID is important IN ANY FILTRATION



...a guide to maximum production and operating economy

The relative flowrates and capacities of standard grades of Dicalite filteraids are charted above. They afford desired clarity with a wide range of flowrates. Liquors that are difficult to filter, temporary shortage of filter capacity, liquors containing an unusual percentage of suspended solids from colloidal to coarse in size—these and other conditions may be corrected by selection of the most suitable Dicalite filteraid grade. You thus have at hand a "balancing" factor to insure maximum production at lower cost.

DICALITE FILTERAIDS

... *what they are*
... *what they do*

ORIGIN—Dicalite filteraids are produced from diatomaceous silica, a material deposited several million years ago on the bottoms of oceans and lakes. It is composed of the "skeletons" of aquatic plants called diatoms.

STRUCTURE—Particles of the materials are microscopic in size and "elongated" or "needle-like" in shape, a structure found to make most efficient filtering materials.

USE—The finished Dicalite materials are in powder form and are used in conjunction with filter presses or other equipment in filtration of liquids of all kinds, being added to the liquid before filtering.

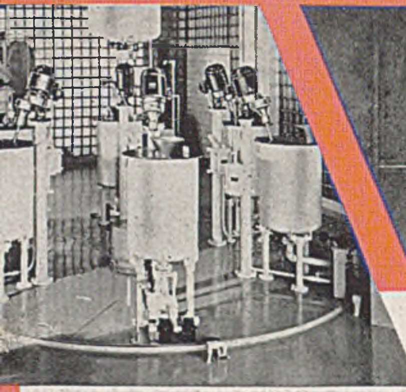
ACTION—As the liquid is pumped through the filter, the particles of Dicalite filteraid collect on the cloths or screens together with the suspended solids being removed. As the filter cake builds up, the filteraid particles interlace and overlay in the fashion of a pile of straws. Thus, millions of extremely fine openings, continually forming, keep the filter cake porous for liquid flow.

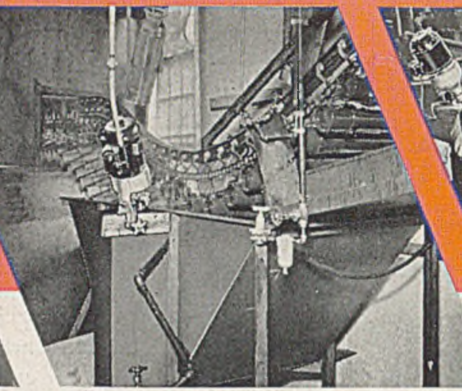
RESULTS—These openings are so small that even the finest solids are trapped and held, to give the liquids brilliant clarity. The openings being so numerous, free flow through the cake gives high flowrates and long filter cycles.

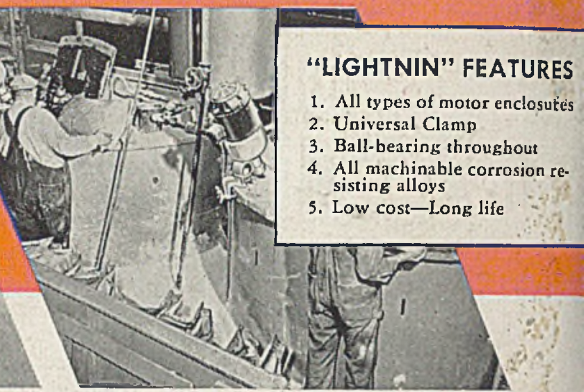
THE DICALITE COMPANY CHICAGO 11 • NEW YORK 5 • LOS ANGELES 14

DICALITE FILTERAIDS

Process Adapted Agitation BROUGHT TO
EVERY PROCESS THROUGH *LIGHTNIN* PORTABLE MIXERS


1. Unusual application of Lightnin Mixers to cyclic, automatic batch operation.


2. Paint dip tank irregular shapes easily handled by Lightnin Mixers.

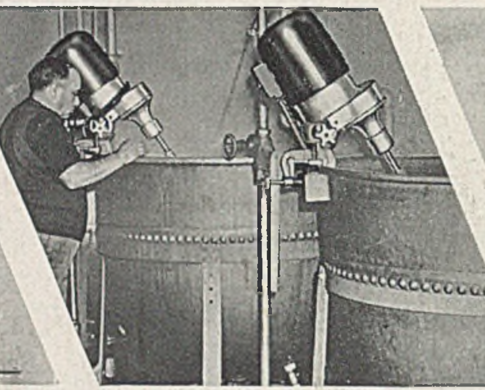


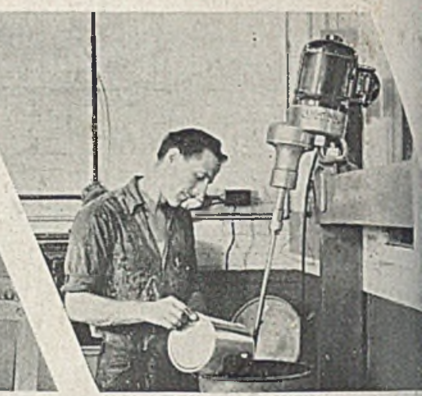
"LIGHTNIN" FEATURES

1. All types of motor enclosures
2. Universal Clamp
3. Ball-bearing throughout
4. All machinable corrosion resisting alloys
5. Low cost—Long life

3. Large capacity tanks are handled with ease.


4. Note Lightnin Mixers ability to fit into odd corners and different shaped tanks.


5. For food processing Lightnin Mixers improve heat transfer and uniformity.


6. Lightnin Mixer supported separately for small containers.

LIGHTNIN PORTABLES ... *HANDY LOW COST AGITATORS ...*

Where to use Portable Mixers

Whether your requirements call for mixers to operate on a wide range of tank capacities and liquid viscosities or for permanent mounting on single tanks, you can adapt "Lightnin" Portable Mixers to solve your problem efficienctly.

Designed primarily for open tanks up to 8 ft., in depth, these mixers give all of the benefits of Process Adapted Agitation. Available in ⅛ to 3 H.P., direct or gear drive for liquids up to 4000 centipoises at mixing temperature.

Watch these factors:

1. The size of the batch does *not* affect the load. You can use a small mixer on a 50 gal. or a 5,000 gal. batch without danger to the motor but mixing action will be reduced to an unusable degree.
2. Watch the effect of viscosity. A mixer specified for water-like material probably operates at 80% full load. Use this on a material like molasses, and you overload and burn out your motor. Specific gravity also affects load on propellers.
3. Don't increase the propeller size. Propeller sizes are selected for specific viscosities. Increasing the propeller size can also overload and burn out motors.
4. Ask Mixing Equipment Co., whether your present mixer is adaptable to a new use or whether a different size mixer will save time and trouble.

The Basis of Our Recommendations

Twenty-five years of experience have resulted in an organization, research facilities and skill which qualify Mixing Equipment Company as a leading authority in the whole broad field of agitation. Mixing Equipment Company offers its services in the solution of any problem involving controlled recirculation of liquids to produce physical and chemical changes. See table.

Mixing Equipment Company Offers

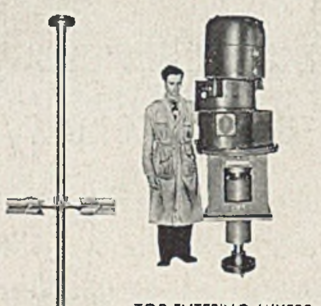
Complete coverage of industrial areas with service for individual user and engineers or equipment manufacturer.

Assumption of responsibility for selection of mixer size, types, performance, characteristics within limits of existing technology.

Blending Miscible Liquids	Mixing Immiscible Liquids	Crystal Size Control	Gas Absorption and Dispersion	Suspension of Solids	Heat Transfer
Simple Mixing of soluble liquids as in reducing concentration	Washing of Liquids Extraction Contacting Caustic Treating Emulsions	Precipitation Evaporation Systems	Hydrogenation Aeration GasScrubbing Chlorination Gas Washing	Slurries Slaking Lime Suspension of: filter aid, activated carbon, Fullers Earth, Crystals while dissolving	Stills Evaporators Reactor Vessels Heating Cooling

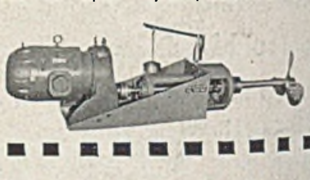
PORTABLE MIXERS: ⅛ to 10 H.P. for rim attachments to open tanks. Gear and direct drives. Many exclusive conveniences. Off-center positioning. Extended bearing sealed against oil and grease leaks.

LAB MIXERS — Little brothers to "Lightnin" Portables. 4 models — Electric and Air Driven. Described in Bulletin B77.



TOP ENTERING MIXERS: —A wide range of sizes for large or small tanks —¼ to 50 H.P. for vertical use on pressure or vacuum vessels. Integral mounting, all Impeller types, Radial Turbines and propellers. Illustration above—for open tanks.

SIDE ENTERING MIXERS—1 to 2 H.P. for horizontal use. Any size tank. Propeller type only. Many models and drives. In use on tanks up to 5,000,000 gallons capacity



MIXING EQUIPMENT CO., INC.
1062 Garson Ave., Rochester 9, N.Y.

Please send me the literature checked:

☐ B-66 and B-76 Side Entering Mixers
☐ B-78—Top Entering Mixers
☐ B-75—Portable Mixers (*Electric and Air Driven*)
☐ B-77—Laboratory Mixers
☐ Mi-11—Operating Data Sheet

Name……………………………………………
Title……………………………………………
Company………………………………………
Address

TOP-ENTERING LIGHTNIN MIXCO PORTA ENTERING

MIXING EQUIPMENT CO., INC.
1062 Garson Avenue ROCHESTER 9, NEW YORK