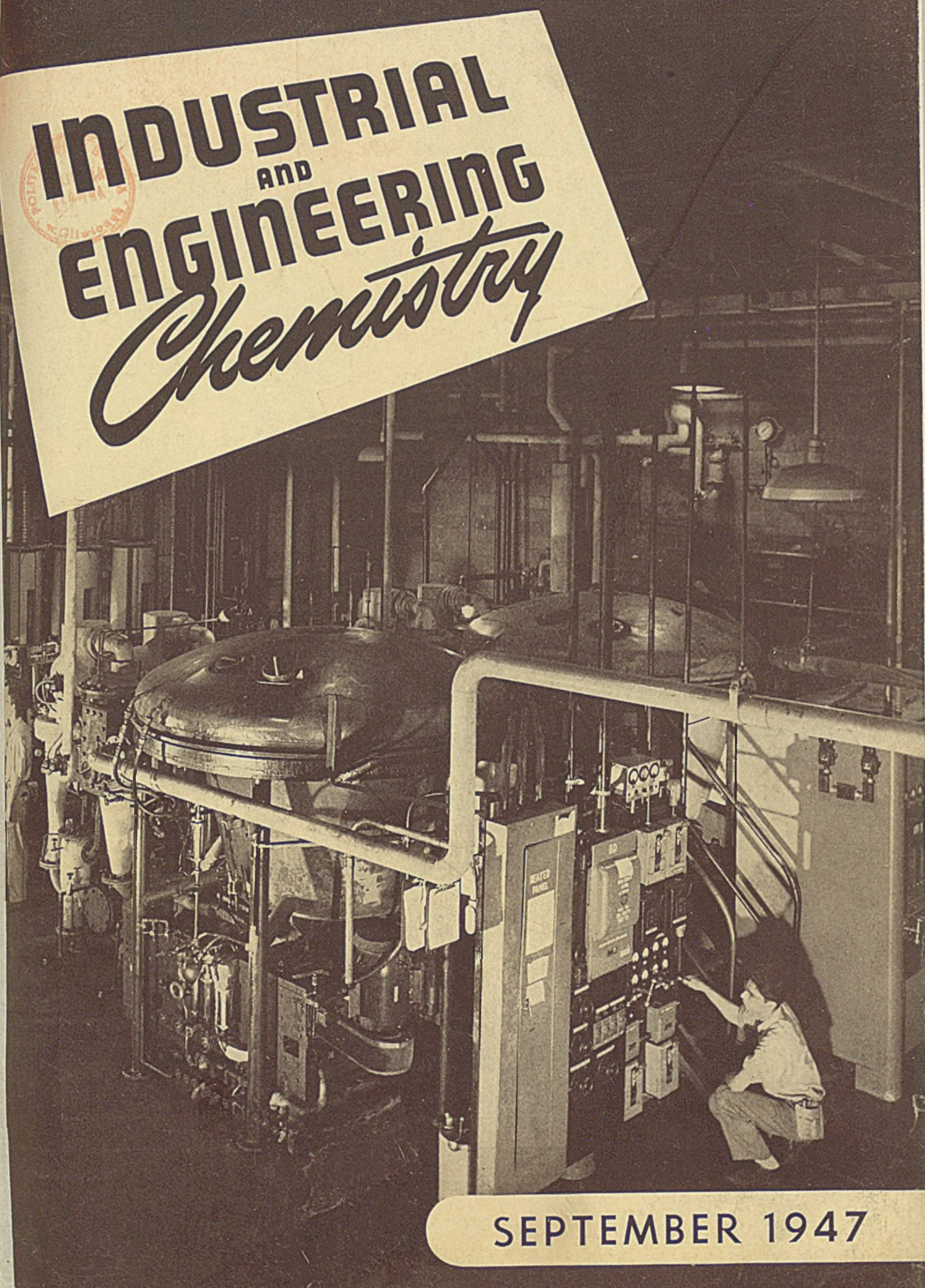
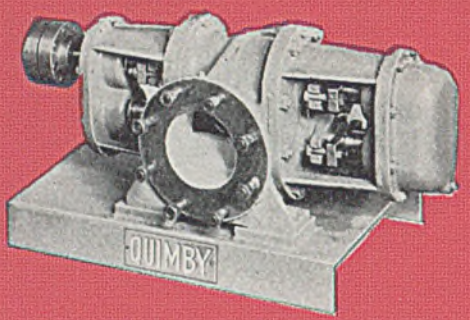
INDUSTRIAL AND ENGINEERING *Chemistry*

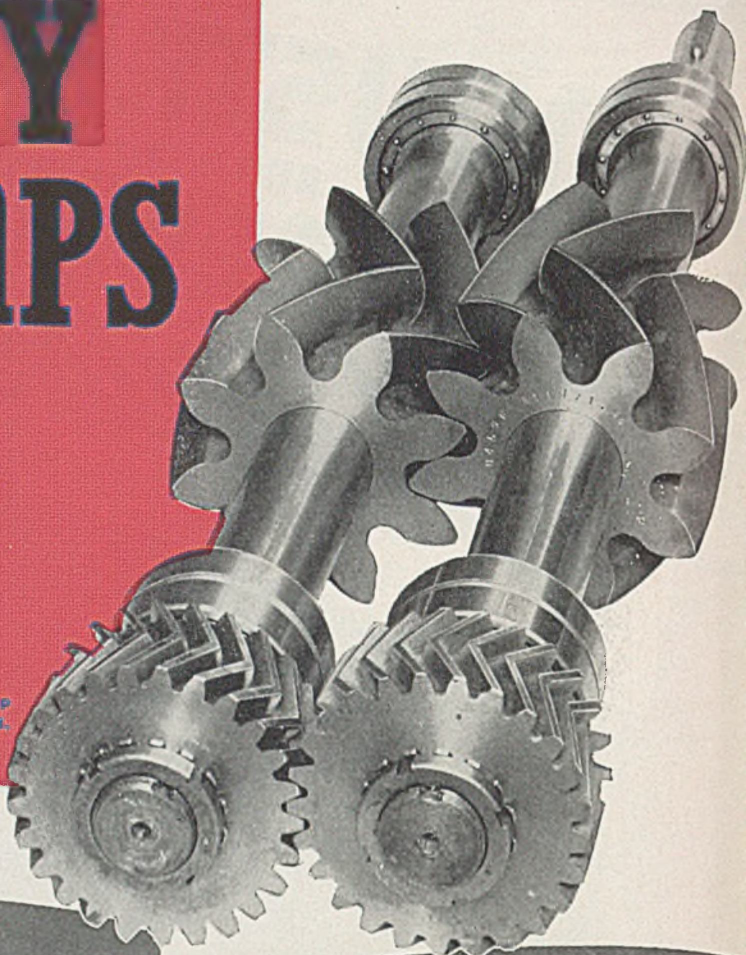


SEPTEMBER 1947

QUIMBY *ROTEX* PUMPS



Horizontal external gear and bearing type ROTEX Pump with accessible driving gears mounted at outboard end.



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Only QUIMBY can make a ROTEX pump. If it's a genuine Rotex, it has these seven advantages:

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7. Every Quimby Rotex is thoroughly engineered for each job application and service-tested at the factory.

***REMEMBER,* THERE IS NO SUBSTITUTE FOR A QUIMBY**

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Quimby has been making *pumps exclusively* since 1894.

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INDUSTRIAL and ENGINEERING *Chemistry*

SEPTEMBER
1947

VOLUME 39 NUMBER 9
ISSUED SEPTEMBER 13, 1947
40,600 COPIES OF THIS ISSUE PRINTED

Industrial Edition, I&EC
Consecutive Number 17

Cover shows distillation of fish liver oils below 10 microns for vitamin A concentrate. It relates to the first article in this issue, which discusses high vacuum technology. Photo courtesy Distillation Products, Inc., Rochester, N. Y.

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4. Carbon, Sulfur, Silver
5. Silt or clay, floc and algae
6. Cysts of Endamoeba Histolytica
7. Nickel and other catalysts
8. Yeast and Trub, Argols (Tartar)
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Filtering them with CELITE Has proved the surest, fastest, most economical method

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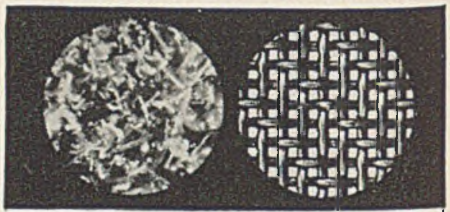


THE CAKE not the cloth DOES THE WORK

These two photomicrographs show that a Celite filter cake has smaller openings than the finest filter cloth—It is the Celite cake that does the work of removing the suspended impurities.

Johns-Manville Celite Filter Aids and Fillers

INDUSTRIAL and ENGINEERING CHEMISTRY.... *Reports* ON THE CHEMICAL WORLD TODAY

FISH TALE

The liver is an important organ in any animal; but that of a shark is especially important to fishermen around the mouth of the Columbia River in the Pacific Northwest. The livers of two species of sharks, soup fin (*Galeorhinus zyopterus*) and dogfish (*Squalus suckleyi*), are rich sources of vitamin A.

Before World War II about 75% of the liver oil consumed in the United States was imported from Norway and Japan. When war came, the disruption was severe. Imports of cod liver oil alone from all sources fell from 29 trillion units in 1939 to about 4 trillion units in 1940, 3.5 trillion of which were used for poultry and fur animal feeds.

When need developed for a domestic supply, the Seafoods Laboratory of the Oregon Agricultural Experimental Station in Astoria, Ore., looked for rich sources of vitamin A in native fish. It was found that rock fish, soles, and flounders could be used at certain times of the year, depending on seasonal abundance and potency values. The viscera of these fish are also processed to recover vitamin-containing oils. The laboratory did not hit the jackpot, however, until they tested the dogfish and the sharks.

Six or seven years ago dogfish livers sold for $0.01 a pound and those of soup-fin sharks for $0.015 a pound. At present all fish livers are sold on a potency basis. Dogfish livers now sell for about $1.00 a pound; soup-fin shark livers, $9.00 a pound. The liver of the soup-fin shark represents about 15% of the total body weight. It contains 62% vitamin A-rich oil, the average potency of which is 100,000 International Units per gram. The liver of the more common dogfish comprises about 72% oil, with a potency of 14,000 I.U. per gram. Many of the low potency oils from the Northwest are now being processed by molecular distillation in eastern plants. A molecular distillation unit being used for such a purpose is shown on this month's cover.

The shark population has suffered distinctly under this onslaught, but the extent of depletion is difficult to estimate. Indications can be judged only by decreased catches and smaller size of individual fish caught. There is considerable evidence of this nature to support the pessimistic forecast of an early extinction of sharks in the waters off northwest Oregon.

On a quantity basis, the principal fish caught and processed in northwest Oregon are tuna, salmon, and rock fish. These are filleted, canned, or frozen for wide distribution. Tuna livers are being used for their vitamin D content; however, the synthetic product has largely displaced the marine extract. Salmon livers are not used at present for vitamin extraction because the total oil and vitamin A contents are low. In filleting operations, two thirds of the fish is considered waste which is selling for $3.00 a ton. Several firms in the area purchase this waste, press it, remove the oil, and grind, dry, and sell it for cattle feed. A premium grade animal feed is made by putting back into the ground fish substance some of the "stick water"—the liquor pressed out of the fish waste. This increases the vitamin and protein content of the feed. At present several companies are vitally interested in stick water concentration and utilization. The fish body oil contains some vitamin A but not enough to make recovery economical; its sale as a technical oil brings a much better price. In this form it is used for making soaps, detergents, linoleum, etc.

Fish waste represents a large, readily available, and cheap source of amino acids. These are chemical building blocks which are important in the growth and regenerative processes of animal bodies. Much work is being done by a few companies—for example, The Borden Company, Van Camp Laboratories—in hydrolyzing fish proteins to amino acids. Arginine is an important one produced.

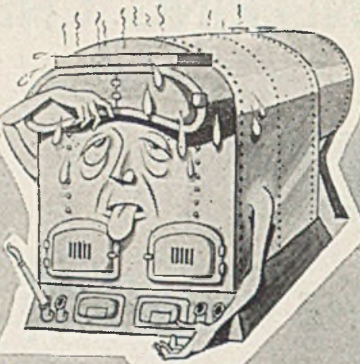
The low cost of the amino acids is assured by the fact that the raw material fish waste (80% water) sells for $3 a ton. Fish meal (about 60% protein) sells for $130 a ton. Other competing sources, such as meat waste and casein, are much more expensive. For example, casein costs $0.40 a pound.

Fish proteins afford superior growth to casein in weaning rats when fed at levels which give suboptimal growth with casein. (Casein is generally used as the basic standard in testing proteins.) The superiority of fish protein is further attested by the fact that it causes greater recovery in weight and a more pronounced stimulation in hemoglobin regeneration than casein in rats rendered hypoproteinemic. It has been suggested that the amino

(*Continued on page 8 A*)

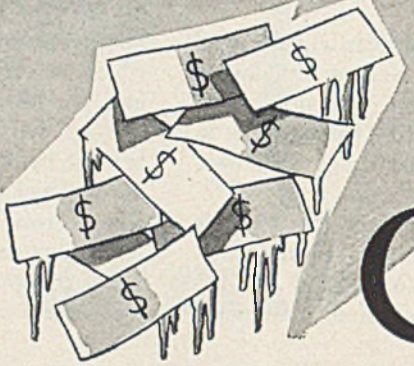
An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries

hot



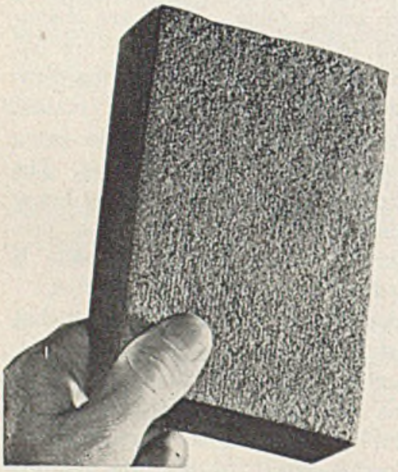
spots

pay off in



cold cash

when you insulate with B-H Mono-Block



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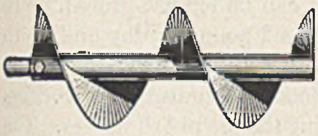
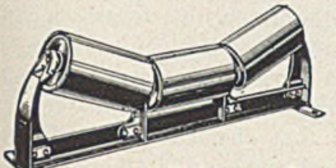
Move Bulk Materials cheaper the LINK-BELT way

. . . by Screw Conveyor — — —



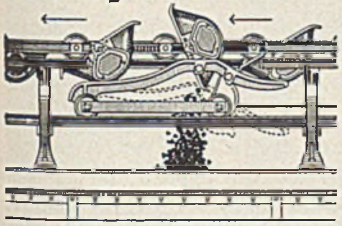
Link-Belt manufactures Helicoid, the original continuous flight screw conveyor. Other Link-Belt screw conveyor equipment includes sectional-flight, ribbon and paddle conveyors, as well as a complete line of accessories, such as collars, couplings, hangers, troughs, box ends, flanges, thrusts and drives.

. . . by Belt Conveyor — — —



Link-Belt makes all types of troughing, flat-roll, return and self-aligning idlers, including all accessories, such as trippers, belts, pulleys, bearings, take-ups, etc., for handling a wide range of materials, for light, medium and heavy-duty service.

. . . by Bucket Carrier — — —



There is a type of Link-Belt bucket carrier and bucket elevator for every service—horizontal, vertical or inclined—for handling all kinds of materials at desired capacities. Illustrated is the Peck Overlapping Pivoted Bucket Carrier.

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Conveyors and elevators are called upon to do an endless variety of tasks. Each presents its own problems . . . each requires its own solution. From the design to the erection of your conveyor system . . . Link-Belt offer experience, backed by thousands of installations and foresight that has established their reputation as pioneers in the field of continuous movement of materials.

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makes conveyors for every purpose —

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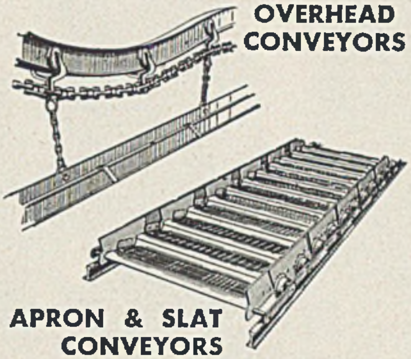
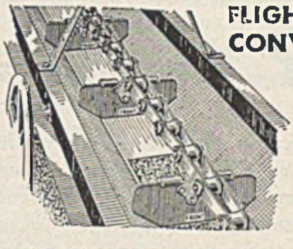
. . . for conveying parts into machines for processing —



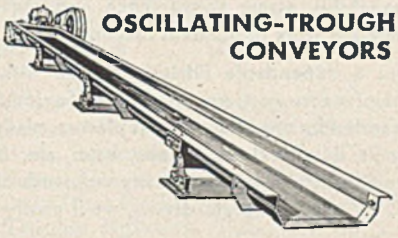
OVERHEAD CONVEYORS

APRON & SLAT CONVEYORS

BUCKET ELEVATORS



FLIGHT CONVEYORS

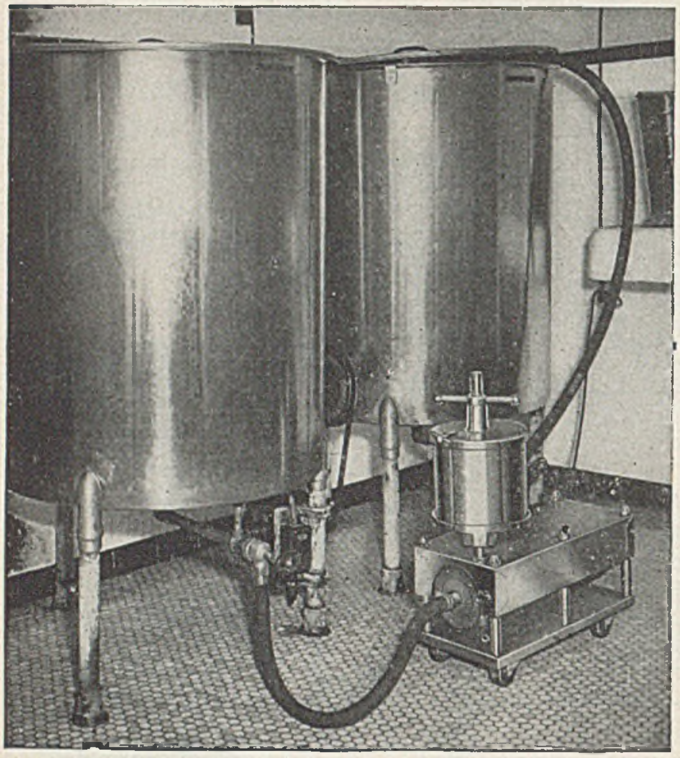


OSCILLATING-TROUGH CONVEYORS

LINK-BELT

Conveyors

A TYPE FOR EVERY KIND OF MATERIALS HANDLING



acid distribution in fish may be responsible for the high biological value of this product.

The appetite of cows is largely governed by sense of smell. They will not eat a feed which contains a high content of fish protein. Hogs and chickens which have been fed too much of it will produce meat and eggs, respectively, with a fishy taste. To eliminate these conditions and to get optimum food value, it has been found that chickens can be fed fish protein up to 10% of the ration; for cattle, 1 to 2 pounds a day and up to 3 to 5 pounds for each 1000 pounds of body weight.

Research workers at the Seafoods Laboratory are working on several other projects involving the use of fish wastes. The value of fish as a natural resource which must be conserved is being realized more and more. F.G.S.

PROFITABLE IMPALPABLE

Machine shop steel scrap has long been considered the most useless form of metal salvage. The war-born scrap shortage forced some steel makers to attempt to use it, but they found, as they had always suspected, that when charged into a furnace most of it went up the stack and annoyed the neighbors. However, a Tacoma metallurgical engineer, Jacob Schoder, has recently brought into production a process whereby this type of waste can be converted into high purity powdered iron, suitable for use in powdered metal molding. With a 36,000-ton annual scrap supply in the Puget Sound area and cheap Bonneville power at its disposal, this new plant promises to become a substantial supplier of this heretofore short raw material.

In the Schoder process scrap steel is dissolved in an acid solution of ferric chloride held between pH 1.5 and 2.0 in a series of concrete tanks arranged stepwise, so that the solution cascades from tank to tank and is finally drawn off at the last step. The solution process is continuous, additional scrap being added into the open tops of the tanks as the initial charge is eroded. The discharged solution is in a reduced state and has the characteristic brilliant green color of ferrous solutions.

The ferrous solution is conveyed through wooden pipes to a bank of forty wooden electrolytic cells equipped with copper anodes and stainless steel cathodes. An electrolyzing current of four volts e.m.f. drop for each cell, obtained by rectifying municipal current with mercury arc rectifiers, is applied for 4 hours to deposit a flaky coat of pure iron on the cathodes. There is no observable erosion on the anodes, so that presumably the copper plates initially installed will last indefinitely. The alloying metals present in the scrap fall to the bottom of the cell in the form of a sludge and are carried away when the electrolyte is discharged from the cell. This sludge has been allowed to accumulate in the bottoms of the dissolving tanks. However, as soon as an acidproof filter can be obtained, it will be installed to remove the solid material from the solution in the normal course of the cycle. Preliminary data now available indicate that 5 kilowatt-hours are expended in reducing 1 pound of iron and that the present installation will produce about 10 to 12 tons of the metal a day.

The solution discharged from

(Continued on page 10 A)

what **HYDROGEN** process is best for your purpose?

THIS BOOK WILL HELP YOU COME UP WITH THE ANSWER

HERE is a book you will want to keep handy for reference. It is the only book in which all the commercially important hydrogen processes are reviewed in concise and readable form for easy comparison. The 32 pages of the book give you factual information supported by photographs, flow diagrams, tables and graphs about all of the following subjects concerning hydrogen production and purification:

- The Water Gas Process
- The Steam-Iron Process
- The Methanol-Steam Process
- The Electrolytic Process
- The Hydrocarbon-Steam Process
- Carbon Monoxide Removal by Conversion to Hydrogen and Carbon Dioxide
- Carbon Monoxide Removal by Methanation
- Carbon Monoxide Removal by Cuprous Salt Solutions
- Carbon Dioxide Removal by the Girbotol Process
- Carbon Dioxide Removal by Soda Solutions
- Carbon Dioxide Removal by Water Scrubbing
- Dehydration of Hydrogen
- Deoxidation of Electrolytic Hydrogen
- Liquefication of Hydrogen for Purification
- Special Gas Mixtures Containing Hydrogen
- Special Catalysts for the Production and Purification of Hydrogen
- Analysis of Hydrogen
- Properties of Hydrogen

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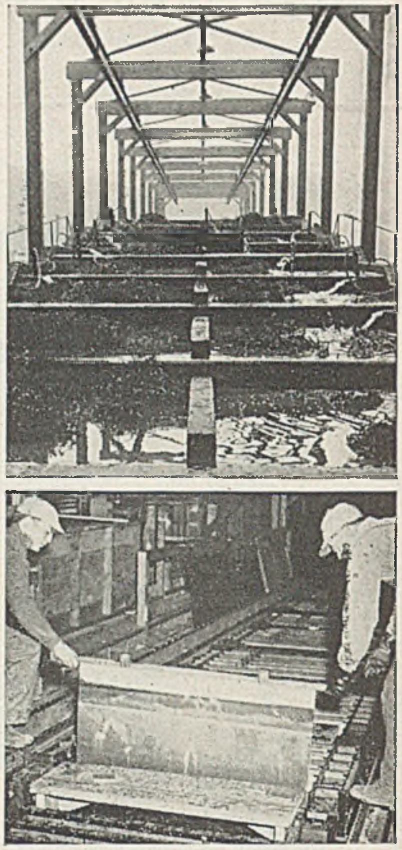
the cells is again in the oxidized state and has a brown color which is due to the presence of the insoluble sludge. Commercial strength hydrochloric acid is added in the amount of about one half pound per pound of iron removed, to bring the pH down to the specified value, and the solution is reintroduced into the dissolving vats to repeat the cycle.

The stainless steel cathodes are removed from the cells by a specially designed machine which strips off the nonadhesive iron deposit with rotary wire brushes and conducts it to a continuous belt conveyer for transfer to washing and drying machinery. The dry powder is fed to a conventional ball mill and then to a hammer mill which operate continuously, discharging particles of a predetermined size by means of an air blast of controlled intensity that carries them to holding bins.



Leach Tanks (*above*)
Cathodes (*below*)

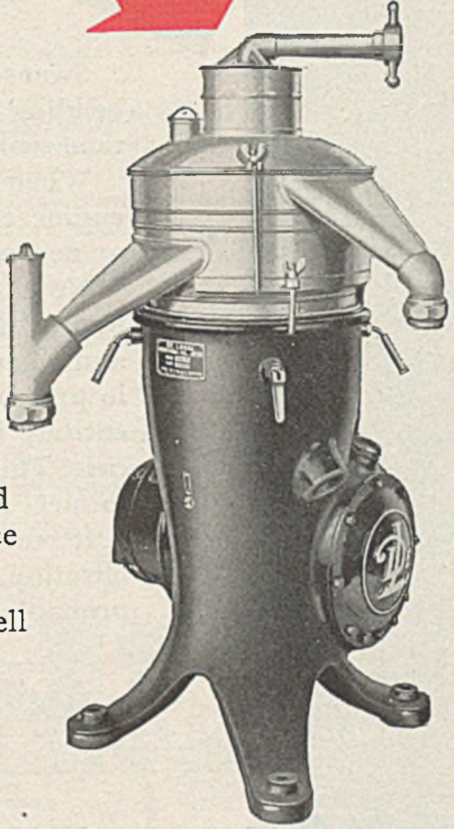
In the final step of the process the fine powder is placed in a continuous electric furnace in an atmosphere of hydrogen at 1700° to 1800° F. The material is retained in the reducing atmosphere during both the heating and cooling stages of the reduction, the entire cycle requiring about 7 hours. Four to five per cent of the reducing atmosphere is reacted with the powder during this cycle. The final product is shipped in air-tight containers to metal powder molders.

The producer of this powdered iron reports that it is consistently superior in purity to the 99+% iron obtained by other electrolytic processes. The only iron of greater purity is carbonyl iron which runs from 99.6 to 99.8% Fe. Ordinary reduced iron made from foundry scale averages only slightly over 96% iron. Although the plant is still running on an experimental basis, low operating costs are expected to enable it to compete with the $0.35 to $0.37 per pound f.o.b. charged by eastern manufacturers, even with the shipping cost to eastern markets included. It is possible that the superior purity of this product will also make it suitable for substitution in some cases for the expensive carbonyl iron which is now selling between $0.90 and $1.75 per pound. M.L.K.

(*Continued on page 14 A*)

HOW CENTRIFUGAL FORCE helps a Ball Pen Write Better

Why the turtle? The story is in De Laval Centrifugal Review No. 2. Write for your copy.



De Laval Centrifugal Clarifiers are used to remove unwanted solid particles from the ink supplied for Eversharp Capillary Action ball pens. Centrifugal force keeps this ink perfectly clean and thus prevents clogging the ball "points" of these famous pens.

This is just another specific instance of how De Laval centrifugal machines speed up a process by making it continuous. Frequently the application is for a much more difficult separation, but a wide range of types and sizes of De Laval centrifugals assures the correct machine for the job.

The De Laval "Nozzle-Matic", for example, separates two liquids continuously, and at the same time removes and continuously discharges solids present in quantities once thought impossible for centrifugal separators.

Write for additional information. It may pay you well and it puts you under no obligation whatsoever.

THE DE LAVAL SEPARATOR COMPANY
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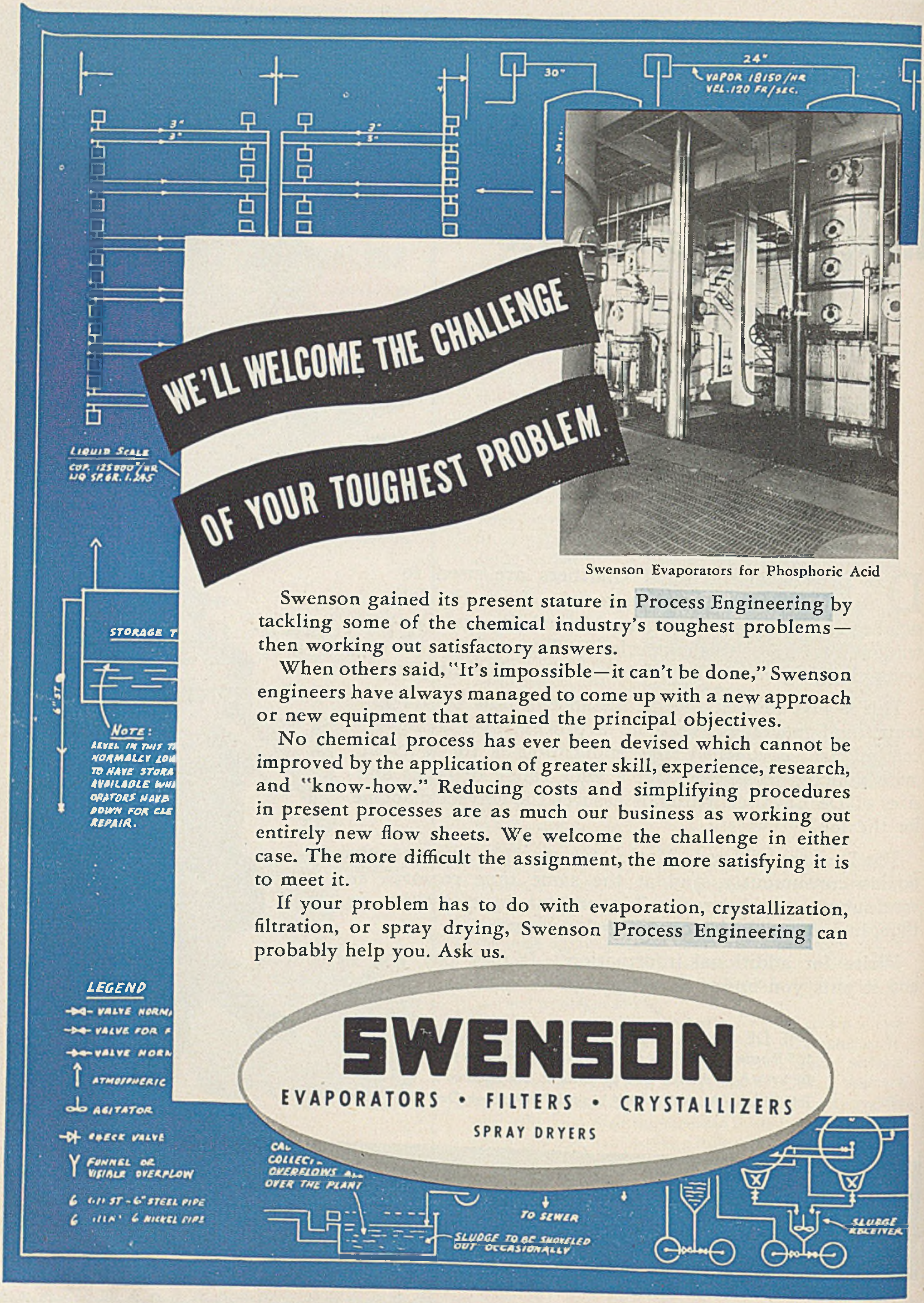
De Laval Centrifugal Machines

FOR PROCESSING SYSTEMS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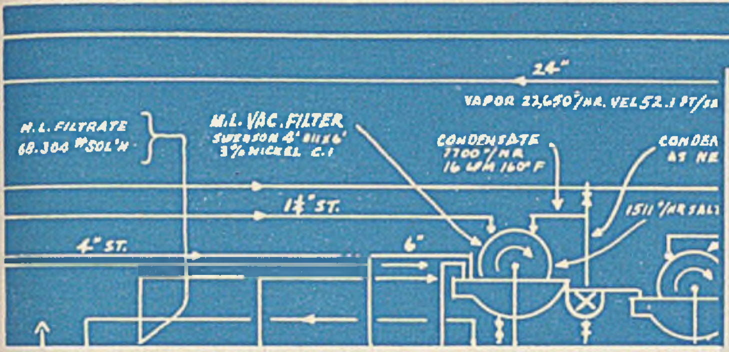
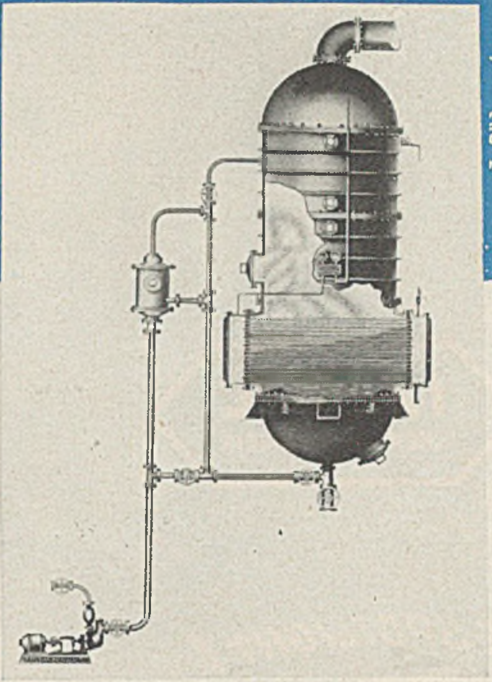
6" NI - 6" NICKEL PIPE
COLLECT
OVERFLOWS ALL OVER THE PLANT
TO SEWER
SLUDGE TO BE SHOVELED OUT OCCASIONALLY
SLUDGE RECEIVER



How Swenson solved evaporation problems of CORROSION, SUBLIMATION, and SCALING in the wet process production of Phosphoric Acid



Sectional Drawing of Swenson Horizontal Tube Cast Lead Evaporator

Phosphoric acid for use in detergents, rustproofing compounds, fertilizers, and similar products can be produced at lowest cost by the wet process, which consists of digesting phosphate rock with sulfuric acid. The dilute phosphoric acid thus obtained is concentrated to commercial strength by evaporation—a process which is beset with special difficulties.

First is the highly corrosive nature of the acid solution itself, which contains numerous impurities, including fluorides.

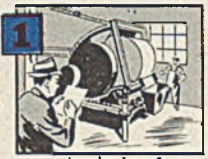
Second is the relatively large amount of gypsum. The inverse solubility curve of gypsum makes it a notoriously bad scaling agent!

A third difficulty, not quite so important, is the sublimation which occurs inside evaporator equipment.

Swenson Process Engineering was called upon to recommend evaporators which would best meet these difficulties. The answer—Swenson Cast Lead Evaporators of the submerged tube type. They were furnished with a special feed arrangement and hook-up which could be recommended only as the result of "know-how" gained from experience in handling many different kinds of rock—minerals indigenous to numerous foreign countries as well as the United States.

The phosphoric acid evaporators which Swenson furnished have been in service for many years with eminent success.

SWENSON EVAPORATOR COMPANY
15671 Lathrop Ave. *Division of Whiting Corporation* Harvey, Illinois
Export Department: 30 Church Street, New York 7, N. Y.

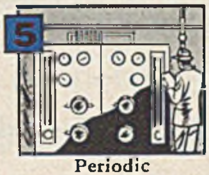


Analysis of Requirements

Design and Layout

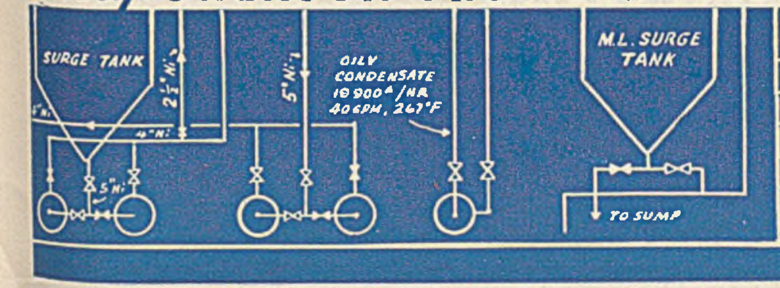
Manufacture of Equipment

Test Operation



Periodic Check-Ups

Only SWENSON PROVIDES THIS FIVE-WAY SERVICE



SWENSON EVAPORATOR CO
HARVEY, ILL., U.S.A.

Req.	Title · FLOW SHEET &
	MATERIAL BALANCE
Ch'd FM	Capacity
Scale ½" = ONE FT.	For
Appr.	D-2265
Appr	

i&ec *reports*

OUR REAL WEALTH

That exhaustive statistical and editorial volume on the Nation's mineral resources, the Minerals Yearbook, issued once a year by the U. S. Department of the Interior, does not appear to support arguments for or against stringent conservation of our underground wealth. The country's mineral production is shown to be declining, but as the data in this study cover the situation in 1945, a year of severe labor shortages and retarded postwar transition, the over-all output loss of 3.3% may not have real significance.

United States' mineral production receded to $8,143,000,000 in value, but it was 47% above the World War I record of $5,540,708,000 attained in 1918. The loss from the preceding year was due to a 15.6% decline in metallic minerals output. The production of fuels was actually 0.66% higher, and that of nonmetallics 6.10% higher. Data for 1946 and 1947, when finally completed, probably will show total production gains.

Business men and scientific workers, however, want to know just how long these mineral reserves are going to last, and the answer cannot be given with any assurance. A New York bank last year found that the United States still has abundant resources of most minerals, even after meeting the tremendous demands of two wars. For materials essential to national security a program of stockpiling and imports was urged.

In this connection it is interesting to compare our mineral reserves from a table compiled by E. W. Pehrson of the U. S. Bureau of Mines on the basis of remaining percentages during 1944:

	Approx. % Remaining		Approx. % Remaining
Magnesium	100[a]	Antimony	45
Nitrogen	100[a]	Petroleum	42[b]
Bituminous coal	98	Copper	40
Salt	98	Zinc	34
Phosphate rock	94	Tungsten	30
Potash	93	Manganese	30
Molybdenum	92	Bauxite (prewar grade)	29
Iron ore	69	Vanadium	29
Natural gas	66	Chromium	23
Anthracite	66	Gold	22
Sulfur	60	Lead	15
Fluorspar	55	Silver	15
		Mercury	3

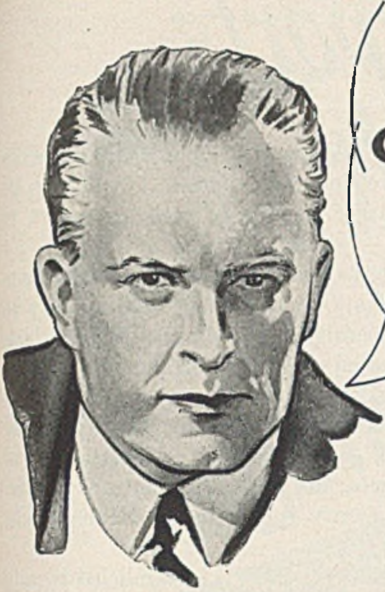
[a] Inexhaustible.
[b] Proved reserves only.

The six most ample resources, nitrogen, magnesium, soft coal, salt, phosphate, and potash, are essential to various forms of chemical manufacture. Two others vital to chemical processing, sulfur and fluorspar, are not yet at the half-way point. Petroleum reserves are less than one half.

Compilations of this kind are valuable for making comparisons, but their percentages should not be taken too literally. In the preparation of such a table some reserves were actually measured, some were indicated, and others were inferred. New discoveries change the picture. In petroleum the proved reserves increased from 20,064,000,000 barrels in 1944 to 20,827,000,000 barrels in 1946. Also, consuming rates vary. The domestic demand for all oils in 1946 had gained 44% since the prewar year of 1939. The rate may increase further.

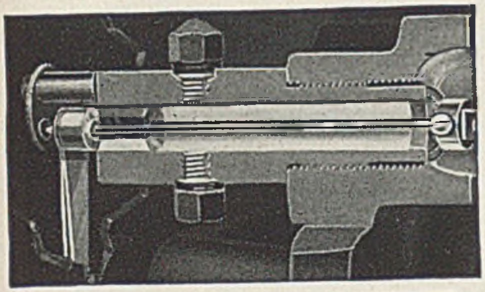
Comparatively small reserves remain for such metallic minerals as copper, lead, zinc, tungsten, and manganese, but domestic production of these necessary items was never sufficient. We have been importing them for many years. The future may find the

(*Continued on page 16 A*)



Look Twice. . . .

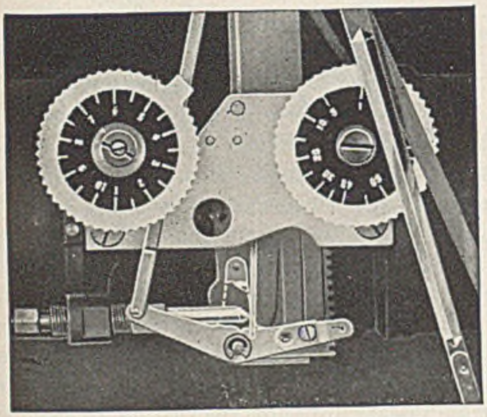
CONTINUOUS PROCESSES *Require Both* ACCURATE MEASUREMENT *and* POSITIVE CONTROL



CONTRIBUTING TO PRECISION MEASUREMENT

PRESSURE-TIGHT BEARING AND SHAFT

The connection between float and lever assembly, a Chrome-Vanadium steel shaft is lapped to clearance of .00005" at bearing surfaces. No stuffing box or packing required. Bearing is filled with suitable grease for the particular service and pressure.



CONTRIBUTING TO POSITIVE CONTROL

STATIONARY NOZZLE

Fixed nozzle eliminates swivel type air connections and additional bellows. Extreme stability of control unit makes this simplified construction possible.
Simple means provided to change controller from direct to reverse-acting or vice versa.

CONTINUOUS operation of chemical and refining processes has imposed a need for positive control, if higher yields, lower costs and unvarying quality of product are to be realized. To accomplish these results a flow controller must first measure precisely—for precise measurement is the *sine qua non* of positive control.

The Brown *Air-o-Line* Flow Controller is an instrument in which advanced design, precision craftsmanship and painstaking assembly of component parts all contribute to optimum sensitivity. This precision measurement, co-ordinated with the full automatic control of the Brown *Air-o-Line* unit, results in a degree of operating excellence not otherwise possible.

Look twice . . . look at the measuring features . . . look at the control features of Brown *Air-o-Line* Flow Controllers. . . . Remember, positive control begins with precision measurement. Write for the Brown Flow Control Catalog No. 2221.

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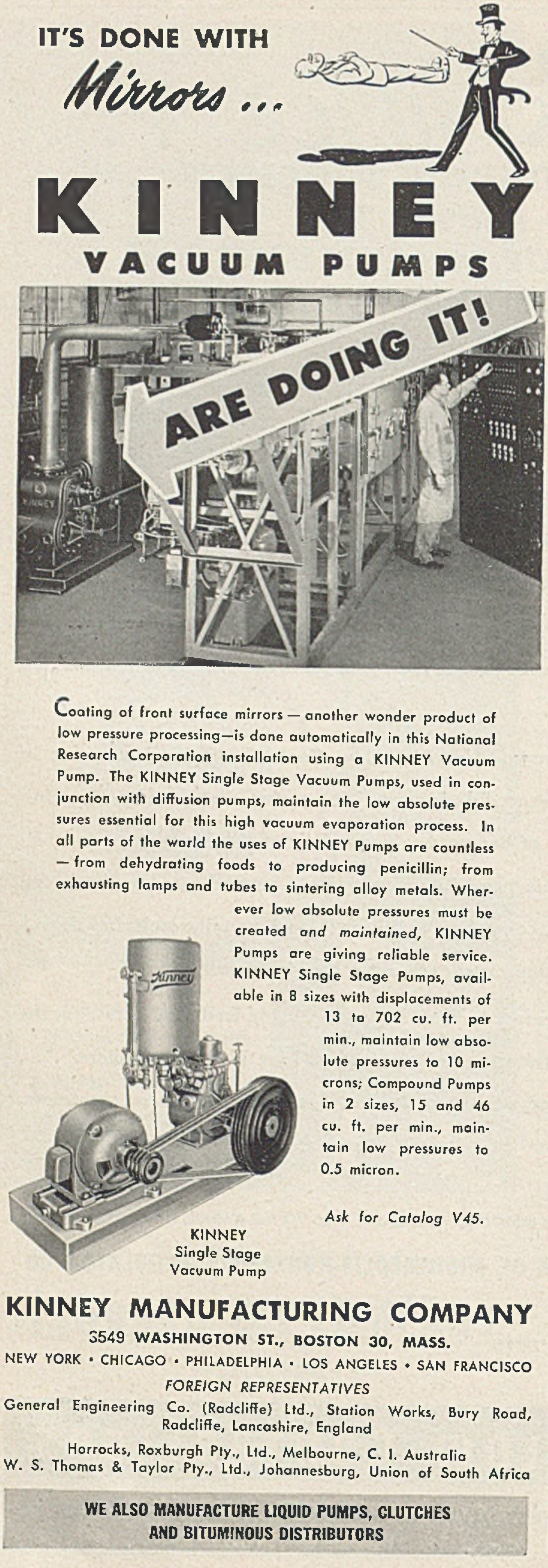
BROWN *Air-o-Line* **FLOW CONTROLLERS**

Air-o-Line—THE COMMON DENOMINATOR OF PROCESS CONTROL



United States increasingly dependent upon other countries for metals, and, with growing consumption, it will also be necessary to bring in larger imports of fuels, or resort to natural gas or oil shales.

Our mineral reserves have been increased through technological advances. The Nation's real wealth is its ability to utilize materials most efficiently. According to R. T. Haslam, the belief that we are endowed with abundant natural resources is a widespread misconception. Only 6% of the world's population is within the United States. We have but 5% of the potential water power for generating electric current, 7% of the world's forest products, and little or no natural rubber, tin, nickel, manganese, mercury, cobalt, industrial diamonds, or quartz crystal.

Still our use of the world's products is unparalleled by any other nation. We use 75% of all automobiles, 50% of all radios, and 54% of all refrigerators. We never thought much of the boast that we have the most bathtubs, but it is no small consideration that America consumes one third of all soap made, more than half of the rubber, and 35% of all leather tanned. The industrial economy that underlies our high standard of living probably could not succeed without the indispensables of coal and iron, but with them we have experienced little difficulty in obtaining other materials not available here that are also required.

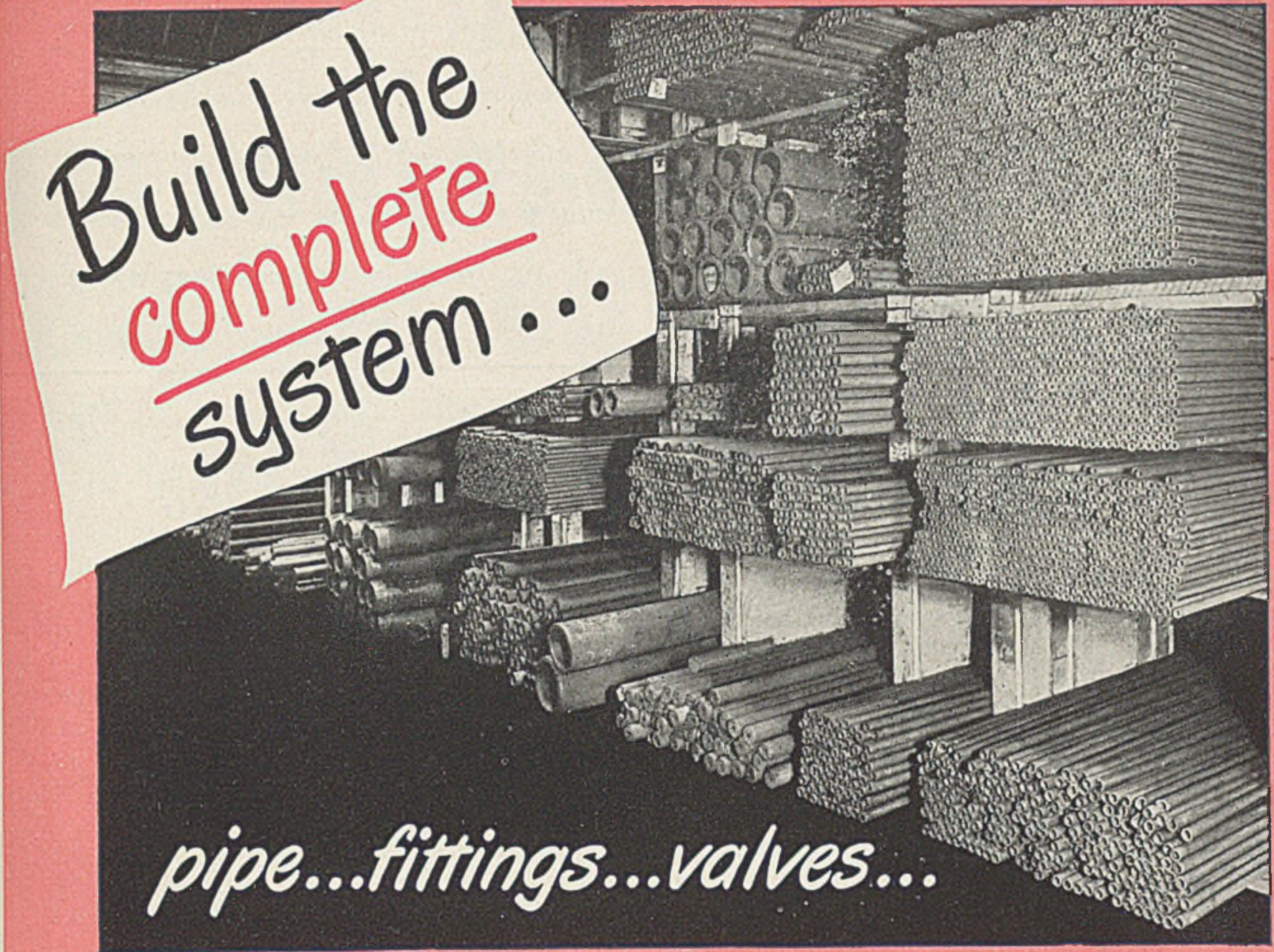
For a country that is strictly a have-not nation in so many things, minerals included, the United States is doing very well, thanks to an energetic and progressive technology. H.S.

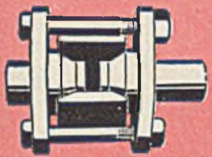
A PIPE WITHIN A PIPE

Quite a few years ago a western sewer construction company decided that what this country needed was a better sewer pipe. The concrete pipe used at that time disintegrated under the action of hydrogen sulfide released from the sewage. This disintegration often attained the rate of two inches a year. This phenomenon introduced a recurrent character into their business but generated no good will whatsoever; consequently an acidproof paint was developed to coat the inside of the pipe. It worked—but not quite perfectly. In due time a better formulation replaced it, and then a better one yet. Other types of pipe were coated. Synthetic resins were introduced into the formulas and the coatings became thicker. They kept getting thicker until now the coating for steel pipe is extruded in the form of a tube, slipped into the pipe, and bonded in place.

This new coating is actually a polyvinyl chloride thermoplastic extruded as a tube slightly smaller than the pipe to be protected and having a wall 0.06 inch thick. The liner is coated with a solution of vinyl resin–type adhesive which is allowed to dry before the tube is inserted in the pipe. Once assembled, an induction coil heats the pipe and resoftens the adhesive, and air pressure expands the liner to effect a uniform bond. The liner is actually enlarged by this process. Thus, there are no strains in the final product. To ensure that the contents of the pipe do not come in contact with metal at any point, the flange faces are covered with a specially formulated vinyl resin composition having the properties of a synthetic rubber gasket. At the same

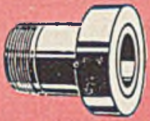
(Continued on page 22 A)




Type FC flexible coupling


"Karbate" valve


Type V flanged connection


Type V nipple


Cross


45° elbow

OF "KARBATE" IMPERVIOUS GRAPHITE

FOR CONVEYING, processing, and storage of corrosive fluids, whole systems are now built 100% of "Karbate" impervious graphite. Complete equipment is available—the pipe itself, fittings, valves, pumps, heat exchangers, towers—for processing HF, HCl, H_2SO_4, and many other chemicals.

This lightweight equipment is easy to install. The pipe is readily cut and fitted in the field.

Standard "Karbate" pipe sizes range from 1″ to 10″ i.d. A full assortment of fittings can be shipped for each size. All parts made of "Karbate" impervious graphite are strong . . . immune to thermal shock . . . and offer the highest resistance to corrosion of any practical high heat-transfer material.

For additional information on "Karbate" impervious graphite for handling corrosive fluids, write to National Carbon Company, Inc., Dept. IE.

The term "Karbate" is a registered trade-mark of

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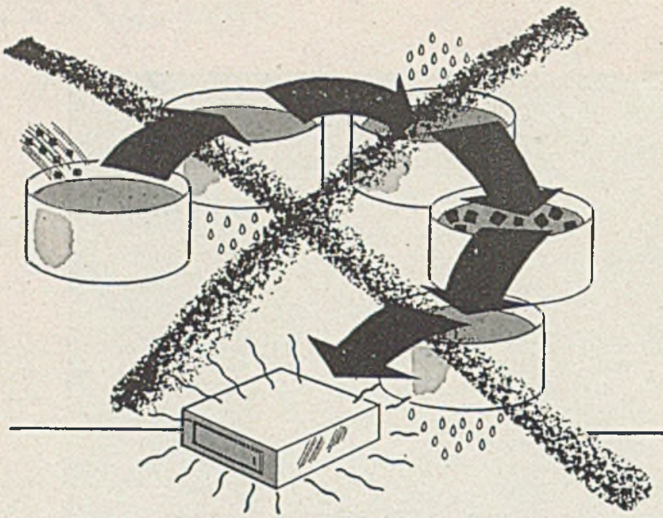
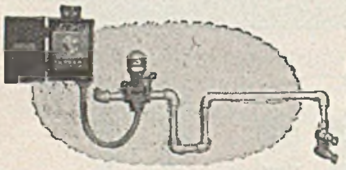


How to simplify a complicated six-step sequence of washing and drying a cellular metal "sponge", so porous that it floats in water — was the problem faced by this well-known firm.

AGAIN . . . *the answer is CENTRIFUGING*

This case study, one of many in our files, offers convincing evidence that AT&M centrifuging saves time, space and money in chemical processing. A cost comparison between your present methods and centrifuging involves neither expense nor obligation. It will pay you to make use of this confidential service of AT&M's experienced engineers. In the meanwhile, for the latest information about AT&M Centrifugals and the savings their unique features bring you, mail the coupon below today. AMERICAN TOOL & MACHINE COMPANY, 1421 Hyde Park Avenue, Boston 36, Mass., 30C Church Street, New York 7, New York.



AN AT&M PLUS

One reason for AT&M Centrifugal superiority is the Automatic Sprayer element . . . which is precisely engineered to function at pre-determined time and pressure . . . assuring exact measurement of liquid at all times.

SAVE TIME, SPACE AND COSTS WITH

A.T. *and* M.

CENTRIFUGING

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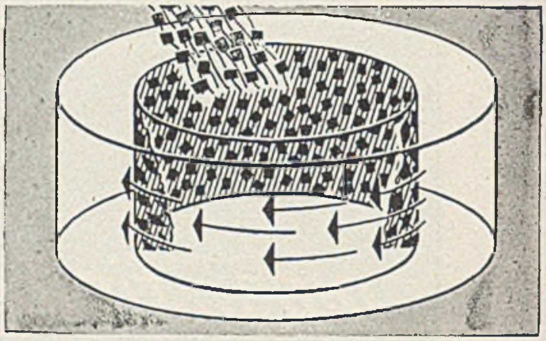
Please send information on centrifuging applied to the following processes:
☐ Extraction ☐ Filtration ☐ Dehydration ☐ Coating ☐ Precipitation
☐ Sedimentation ☐ Impregnation

Write here any other process..

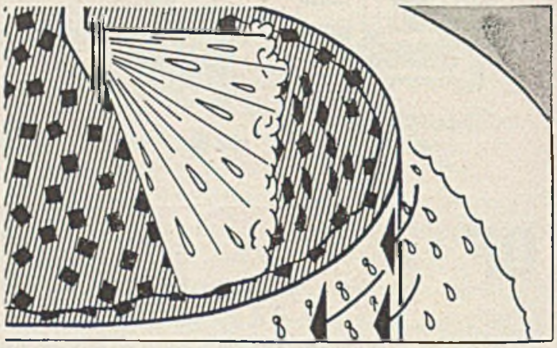
Name..

Company..

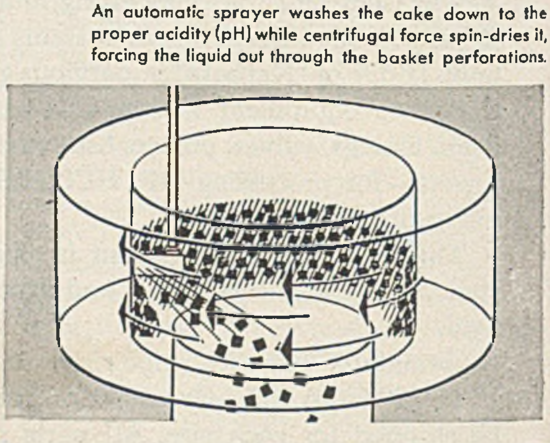
Address..



To handle the cadmium, AT&M installed a centrifugal with a large, thin-walled perforate basket and a specific loading speed to build up a thin, even cake.



An automatic sprayer washes the cake down to the proper acidity (pH) while centrifugal force spin-dries it, forcing the liquid out through the basket perforations.



At a positive unloading speed, and with a special discharger, the load is plowed out through the bottom of the basket.

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

U.S.I. CHEMICAL NEWS

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

USI CONTRACTS FOR TOTAL CHEMICAL OUTPUT OF FIRST FISCHER-TROPSCH PLANTS

Large Quantities of Alcohols, Ketones, Acids, Aldehydes And Esters Will Benefit the Entire Chemical Industry

An event of the utmost importance to all chemical consuming industries was the recent announcement of a long-term contract between Stanolind Oil & Gas Company and U. S. Industrial Chemicals, Inc., for the sale of all of the water soluble oxygenated chemicals that will be produced at the first two synthetic gasoline and oil plants using the much publicized Fischer-Tropsch process. The plants are being undertaken by the Stanolind Oil & Gas Company (subsidiary of the Standard Oil Co. of Indiana) and Carthage Hydrocol Corporation. The plans also call for the erection of U.S.I. plants at the two locations for the production of other products using some of the Fischer-Tropsch chemicals as raw materials.

Expect at Least 300,000,000 Pounds of Chemicals Annually

It is estimated that the chemicals produced from these Fischer-Tropsch plants may exceed a total of 300,000,000 pounds annually, and include ethyl alcohol, methyl alcohol, normal propyl alcohol, normal butyl alcohol, normal amyl alcohol, acetone, methyl ethyl ketone, acetic acid, propionic acid, butyric acid, acetaldehyde, propionaldehyde and butyraldehyde. In addition, U.S.I. will produce esters, higher alcohols and other chemicals from some of the primary products which will add substantially to the number of products made available by this development.

The effect on the chemical industry of large quantities of these important organic chemicals from this new basic process is obvious.

It will mean a dependable new source of much needed chemicals at prices competitive with those from any other synthetic or fermentation process. It will open up new fields by making available for the first time, large quantities of such products as normal propyl alcohol, normal amyl alcohol, propionic acid, and butyric acid and it will stimulate development of new solvents, plasticizers, pharmaceuticals, plastics and a host of other chemical products.

It is important to note that all of the alcohols, acids, ketones and aldehydes produced by this process are the normal compounds. These normal compounds are generally preferred but heretofore only the lower members of the series have been available in quantity at reasonable prices.

A 'Natural' for U.S.I.

U.S.I. is in a particularly favorable position to handle these products from the Fischer-Tropsch process. With its many years of experience in serving the industries using these chemicals, its strategically located, nation-wide distribution facilities, its highly trained technical personnel and well developed production techniques, it will offer very valuable service to all users.

Important contributions will also be made by the use of processes developed by U.S.I. for the conversion of some of the primary products into other chemicals.

During the time the plants are being completed, which it is estimated will be approximately two years, U.S.I. will supply all possible technical assistance to users of these chemicals, particularly the new products, so that adequate data will be obtained in sufficient time to take full advantage of their availability.

ADVERTISEMENT—This entire page is a paid advertisement

September ★ **U.S.I. CHEMICAL NEWS** ★ 1947

High-Purity Caustic Made By New-Type Mercury Cell

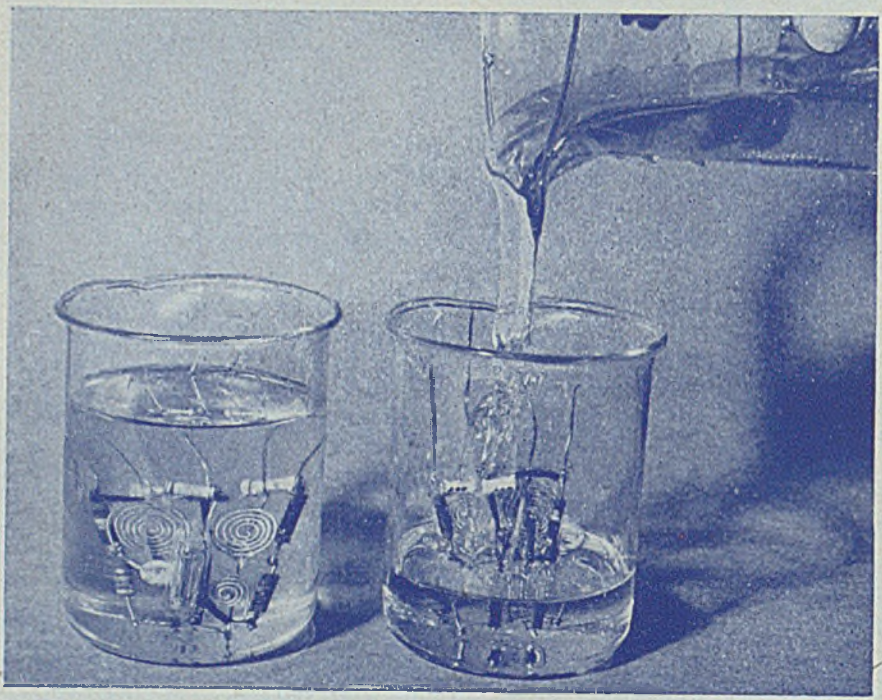
A stationary mercury cell which produces caustic soda of high purity and offers certain operating economies is now ready for licensing, it was announced recently. High-purity caustic is essential to the manufacture of rayon.

The new apparatus is said to produce 50 per cent liquor directly at the cell, a much more concentrated solution than is ordinarily obtained.

Develops Rapid Method For Water Assay of Paints

An accurate, speedy method for determining the volume of water in paints and varnishes has been announced by a government bureau. The method, said to require only small samples, is claimed to determine water content to a tenth of one percent within one hour. It may also be used for water determination in oils, fats, waxes, glues, plasticizers, paper, dry foods, and many other substances, according to government scientists.

ELECTRONIC CIRCUITS "POTTED" BY NEW RESIN



Electronic circuits or even complete plug-in sub-assemblies may be easily embedded or "potted" in a new casting resin developed recently. To "pot" an electronic circuit, it is only necessary to pour the resin into a suitable mold, and then "cure" for a few days until it has solidified.

The resin is said to provide excellent electrical insulation as well as protection against rough handling and deteriorating atmospheric conditions. It should be especially useful in high-impedance control devices in heavy industry to provide adequate protection against vibration, acid fumes, high humidity, and salt spray.

TECHNICAL DEVELOPMENTS

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

To provide termite- and rot-protection, a new product has been marketed which is claimed to protect any wood which comes in contact with the soil. A quart of the preservative is said to cover about 200 square feet of wood surface. **(No. 234)**

USI

To mark glass, cellophane, metal and wood, a new pencil has been developed which is stated to dry instantly. **(No. 235)**

USI

A new inorganic plastic, is said to be unaffected by oil, sunlight, alkali, age, and temperature up to 900 degrees F. The makers claim it is useful in molding articles for the electrical, architectural, general industrial, and consumer goods fields. **(No. 236)**

USI

A new high-speed mill, designed for grinding, emulsifying, homogenizing, mixing, dispersing, disintegrating, and many other uses, is now available. Made of stainless steel, it is said to be useful in the processing of foods, corrosive chemicals, and other materials. **(No. 237)**

USI

To secure labels permanently, a new bottle-labeling adhesive has been developed which is claimed to be highly resistant to water and humidity. **(No. 238)**

USI

A new principle of color-matching panels has been developed which is said to compensate for the error caused by the fact that in most people the right eye is stronger than the left which makes panels on the right seem deeper and darker. **(No. 239)**

USI

A new gum from South America is announced which is designed to increase the bulk of liquid arabic gum glue. **(No. 240)**

USI

A new cure for motion sickness, described as a mixture of three drugs, allays the apprehension and excitement which contribute to sea and air sickness, the makers state. **(No. 241)**

USI

A new temperature measuring system, for measurement and control of gas temperature up to 5,000 degrees Reamur, has been announced. It is said to be accurate to ± 1 per cent to 2,500 degrees R., and ± 2 per cent from 2,500 to 5,000 degrees R. **(No. 242)**

USI

Unusual fatty acids form a sweet-odored, pasty, pale cream compound, suitable for creme shampoos and other products in the sanitary chemicals field. **(No. 243)**

USI

A waterproofing membrane, consisting of an open-mesh fabric, can be used on roofing applications and many waterproofing operations in the construction industry. **(No. 244)**

U.S. INDUSTRIAL CHEMICALS, INC.

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

ALCOHOLS
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- Fusel Oil—Refined

Ethanol (Ethyl Alcohol)
- Specially Denatured—all regular and anhydrous formulas
- Completely Denatured—all regular and anhydrous formulas
- Pure—190 proof, C.P. 96% Absolute
- *Super Pyro Anti-freeze
- *Solox proprietary Solvent

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

*Registered Trade Mark

ACETIC ESTERS
- Amyl Acetate
- Butyl Acetate
- Ethyl Acetate

OXALIC ESTERS
- Dibutyl Oxalate
- Diethyl Oxalate

PHTHALIC ESTERS
- Diamyl Phthalate
- Dibutyl Phthalate
- Diethyl Phthalate

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

INTERMEDIATES
- Acetoacetanilide
- Acetoacet-ortho-anisidide
- Acetoacet-ortho-chloranilide
- Acetoacet-ortho-toluidide
- Acetoacet-para-chloranilide
- Alpha-acetylbutyrolactone
- 5-Chloro-2-pentanone
- 5-Diethylamino-2-pentanone
- Ethyl Acetoacetate
- Ethyl Benzoylacetate
- Ethyl Alpha-Oxalpropionate
- Ethyl Sodium Oxalacetate
- Methyl Cyclopropyl Ketone

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

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

ACETONE
- Chemically Pure

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

OTHER PRODUCTS
- Collodions
- Ethylene Glycol
- Nitrocellulose Solutions
- Ethylene
- Urethan
- *dl*-Methionine

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the RIGHT *horsepower*

Available in sizes from 1/10 to 100 horsepower.

the RIGHT *shaft speed*

Gear reduction ratios range up to 432 to 1.

and RIGHT *where you want it*

Don't put up with make-shift assemblies for your power drives. Master Gearmotors, available in millions on millions of combinations of types and ratings, permit you to use a power drive on each job that's just right . . . a power drive that will add greatly to the compactness, appearance, and economy of each of your applications.

Use Master Gearmotors to increase the salability of your motor-driven products . . . improve the economy, safety, and productivity of your plant equipment. They're the horsesense way to use horsepower.

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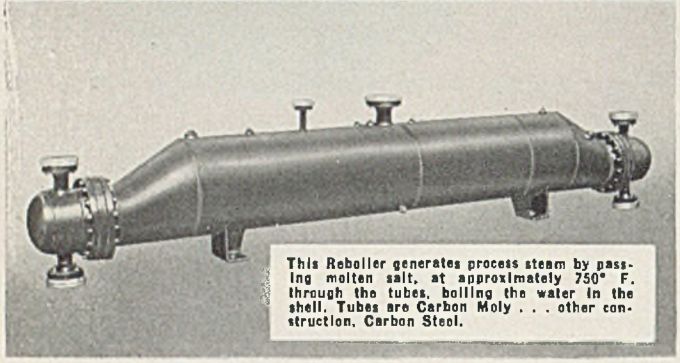
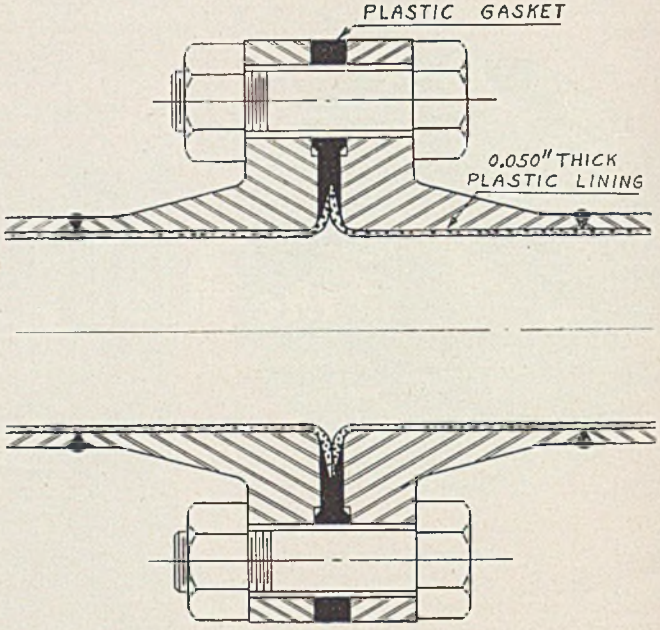


time the liner is molded around the turn of the flange, and blended with the gasket material under heat and pressure, as shown in the accompanying sketch, to form a continuous corrosion-resistant surface throughout the joint. This procedure necessitates plant processing, as it is not feasible to cut and flange this type of pipe in the field.



The lining material is stable to water at 200° F. Tests lasting 90 days at room temperature indicate that it is not affected by any of a long list of industrial liquids, including concentrated and dilute acids, organic acids and solvents. petroleum and vegetable oils, soaps, and alkali solutions. Strong caustic solutions tend to embrittle the material slightly, but, for special installations where continued resistance to such solutions is required, formulations containing different plasticizers can be made which will be caustic stable, according to the producers.

An electrical conductivity method is used to detect possible pinholes in the liner before it is inserted in the pipe. After the bonding operation each completed section of the pipe is plugged at one end, filled with 10% hydrochloric acid, and checked for resistance to electric current from the solution to the pipe to ensure that the coating is continuous.

Initial production of the pipe will be in sizes between 2 and 4 inches. However, eventually all sizes of common welded-steel pipe will be available with this lining. There are as yet insufficient data to determine the exact projected selling price of the material. However, the American Pipe and Construction Company, Los Angeles, Calif., the producers, say that it will compare with rubber pipe now selling at around $1.50 a foot in the 2-inch-diameter size. In the same size, Saran is priced at $3.50 a foot, and Pyrex is about $1.40. The outstanding advantage claimed for the lined product is its steel-imparted strength. Essentially the same resistance to chemical attack offered with the plastic-lined pipe may be given almost any metal or concrete surface by direct application of a fluid preparation that may be applied with a brush or spray gun.

M.L.K

MAGNESIUM PLANT

WINGDALE, NEW YORK

. . . available 4 ways . . .

This large, fully-equipped plant was designed for magnesium metals production from dolomite by the Ferro Silicon Process. Furnaces, kilns and processing equipment are in place, ready now for full-scale production. Its own raw material (dolomite) quarry site lies two miles S. E. of the plant. An overhead tram is installed which operates on a right-of-way between the plant and quarry. A self-contained unit, it's complete to the last detail.

The buildings and structures of this plant are readily adaptable for use in a variety of light metal manufacturing purposes. Reductions of such light metals as calcium and barium can be made by the thermal vacuum method, the smelting process of this plant.

LOCATION: The 203-acre plant site and its 105-acre dolomite quarry are strategically located within 100 miles of such distribution points as: New York City (60 miles); Hartford, Conn. (50 miles); Bridgeport, Conn. (45 miles); Poughkeepsie (20 miles). Most northern New Jersey cities are within 60 or 70 miles. The plant is served by three branch sidings of the New York Central Railroad; inner plant roads connect with New York State Highway No. 22. All utilities are available.

BUILDINGS: At the plant site are 20 buildings and structures, largest of which is the Retort Furnace Building, a 2-story, fully fireproof structure of reinforced concrete construction, with cinder block walls, steel truss roof framing and corrugated asbestos roof. It has 10′ to 14′ headroom on 1st floor and 23′ clearance to truss on 2nd floor. The second floor consists of two 50′ bays with a designed floor load of 120 lbs. per sq. ft. It is provided with 4 one-ton overhead traveling cranes and all necessary utilities. Other structures include office, laboratory, shops, shipping and miscellaneous process space. Total floor area all buildings—approximately 220,000 sq. ft. At quarry site are the following structures: storage, crusher building, shops, pumphouse, compressor house, field office.

EQUIPMENT: Quarrying, lime calcining, thermal reduction, melting and alloying functional items, crushers, grinders, pulverizers, rotary lime kilns, 20 retort reduction furnaces, 6 melting and alloying furnaces, 3 briquetting machines, 5 gas producers, vacuum pumps, various belt and bucket elevators and conveyors, and one 2-mile overhead tram. Also included are various maintenance machine tools, stationary and portable; laboratory and office furniture and fixtures.

SEALED BIDS: Your sealed bids, on the Standard Bid Forms provided, must be received not later than 3:00 P.M., E.S.T., October 1, 1947. Bids are to be addressed: War Assets Administration, Office of Real Property Disposal, P. O. Box 225, Wall Street Station, New York 5, New York. Credit terms will be given qualifying small business.

Standard Bid Forms and complete property descriptions are available. Write:

WAR ASSETS ADMINISTRATION
OFFICE OF REAL PROPERTY DISPOSAL

1311-T

67 BROAD STREET, 10th FLOOR • NEW YORK 4, NEW YORK

1

BUY OR LEASE
entire plant—land, buildings, equipment

2

BUY OR LEASE
entire plant—land, buildings without equipment

3

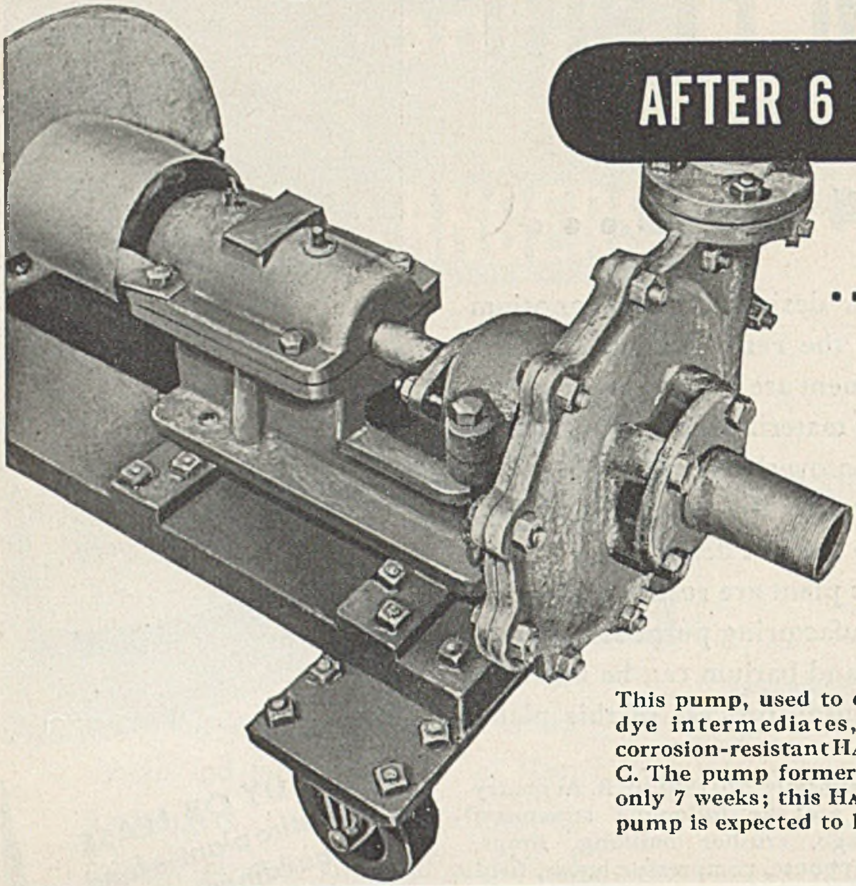
BUY
complete machinery and equipment for off-site use

4

BUY
functional units of machinery and equipment for off-site use

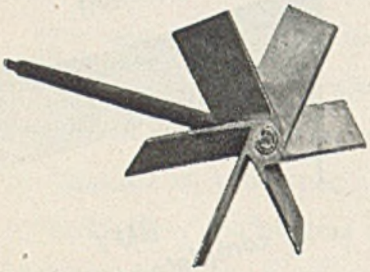
STILL in GOOD SHAPE–

AFTER 6 YEARS OF SERVICE

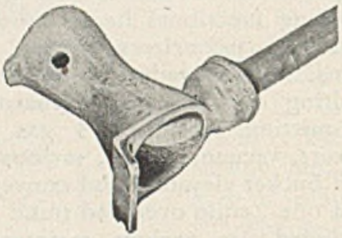


...HASTELLOY Alloy C Parts Resist Corrosive Action of Dye Intermediates

This pump, used to empty vats of dye intermediates, is made of corrosion-resistant HASTELLOY alloy C. The pump formerly used lasted only 7 weeks; this HASTELLOY alloy pump is expected to last 10 years.



HASTELLOY alloy C agitator shaft and blades are used in a reaction vat. Whip and unbalance in the agitated fluid often places considerable stress on the shaft; high-strength HASTELLOY alloy is not affected by this stress.



This steam jet of cast HASTELLOY alloy C is also used in a reaction vat. After 6 years service in acids, alkalies, and strong oxidizing agents, the jet is still in good operating condition.

Write for the booklet "HASTELLOY High-Strength Nickel-Base Corrosion-Resistant Alloys" for information on available forms and methods of fabrication.

HASTELLOY
TRADE-MARK

Haynes Stellite Company
Unit of Union Carbide and Carbon Corporation
UCC
General Offices and Works, Kokomo, Indiana
Chicago—Cleveland—Detroit—Houston—Los Angeles—
New York—San Francisco—Tulsa

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

A struggle on the 30 YARD LINE!

If these two largest fighters in the world had fought it out on a football field, the struggle could have been staged inside one of the two largest thickeners in the world.

Their bones now mingle with those of millions of marine animals to make up the almost inexhaustible deposit of pebble phosphate in the "Billion Dollar Valley of Bones" in Florida.

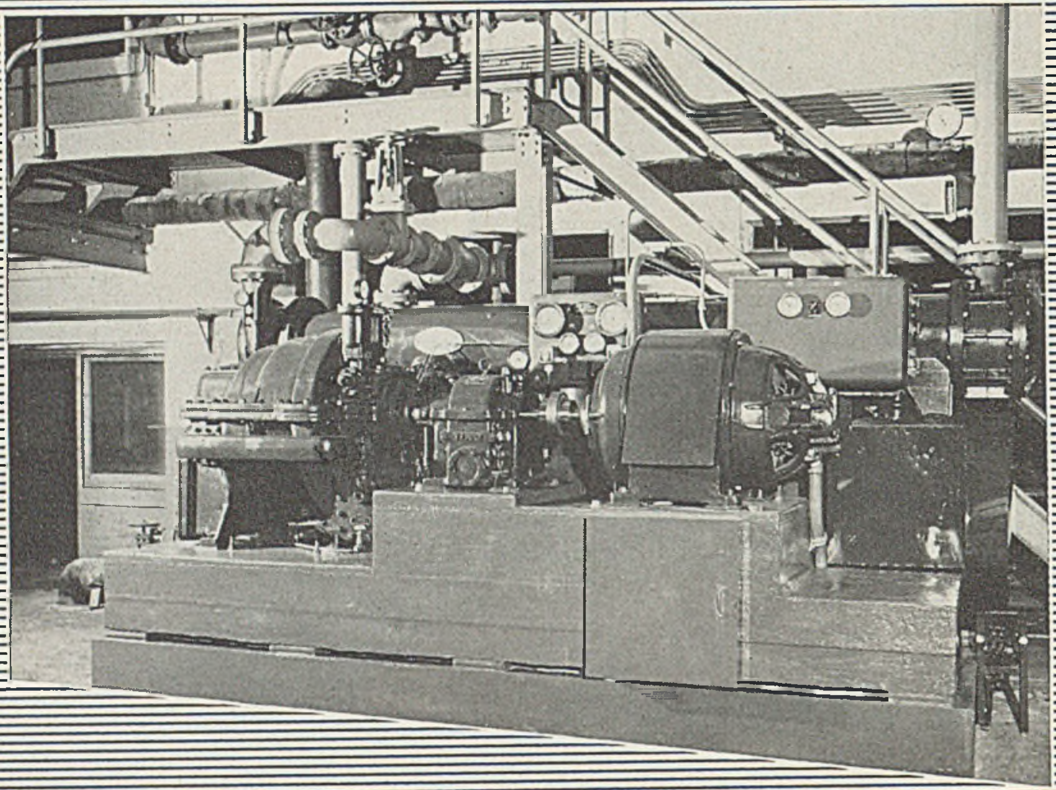
Two General American Thickeners, 383 feet in diameter, in addition to eleven other General American Thickener and Hydroseparator Units, will form an integral part of the equipment installed to assist International Minerals and Chemicals Corporation to increase their production of high grade phosphates for industry and agriculture.

OTHER GENERAL AMERICAN PRODUCTS

Dryers
Filters
Kilns
Tanks
Turbo-Mixers
Evaporators
Pressure Vessels
Towers

General American
TRANSPORTATION CORPORATION
process equipment • steel and alloy plate fabrication

SALES OFFICE: 10 East 49th St., Dept. 800a, New York 17, N. Y.
WORKS: Sharon, Pa., East Chicago, Ind.
OFFICES: Chicago, Sharon, Louisville, Orlando, Washington, D. C.
Pittsburgh, St. Louis, Salt Lake City, Cleveland.



centrifugal speeds chlorine condensing

Refrigeration supplied by a Carrier centrifugal compressor enables The Pennsylvania Salt Manufacturing Company to condense 65 tons of chlorine gas every 24 hours. The gas is led directly from a fractionating tower to the centrifugal unit. Here it is liquefied in a shell and tube cooler by the evaporating refrigerant, inert to the chemically active chlorine. This method gives Pennsylvania Salt 95 per cent chlorine recovery.

Carrier centrifugal refrigerating units are used today in many different industries for economical and efficient condensing of vapors at low temperatures. They take less space than reciprocating machines of equal capacity . . . operate at lower cost . . . do the job better.

The centrifugal refrigerating machine was developed by Carrier . . . and more Carrier-designed units are in use today than any other kind. They offer such dollar-saving features as "Lo-Fin" tubing to reduce size and increase efficiency . . . an economizer to reduce horsepower . . . *and the exclusive Carrier shaft seal to minimize refrigerant loss.*

They're available in sizes from 100 to 1200 tons—using many types of refrigerants. Carrier engineers will be glad to study your refrigeration or gas compression needs. Carrier Corporation, Syracuse, New York.

Carrier

air conditioning

refrigeration

industrial heating

"CORROSION MOST FREQUENT VALVE FAILURE

—REPORT ONE OUT OF TWO ENGINEERS

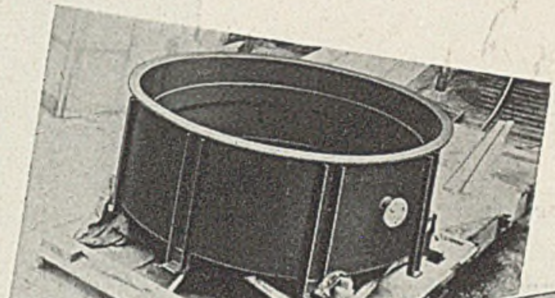
PUMP FAILURES COST $125 AVERAGE"

—CONCLUDES A RECENT SURVEY

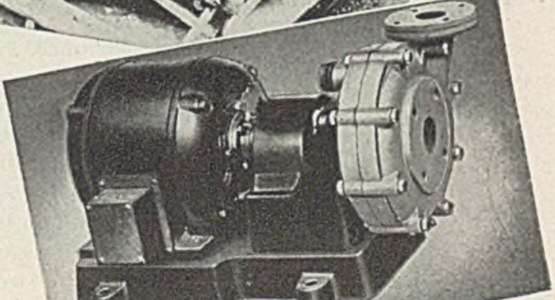
STOP STOPPAGES with ACE Hard Rubber

There's plenty of proof—it's just not safe to guess about corrosion. But there is no guesswork when you specify ACE hard rubber protection for your equipment.

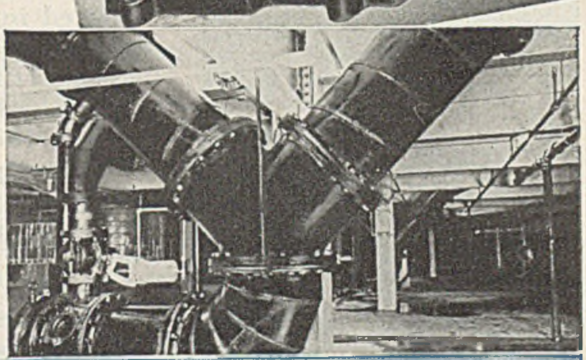
That's because our conservative recommendations and modern techniques are based on 75 years of experience in storage, circulation and processing applications—many of them similar to your problems. We apply natural or synthetic rubber, hard or soft, or Saran plastics to best advantage, for chemical resistance, heat resistance, and mechanical strength that meet job requirements. Let us show you now where ACE equipment can safeguard the vital spots in your plant. Send for Catalog 300-6.



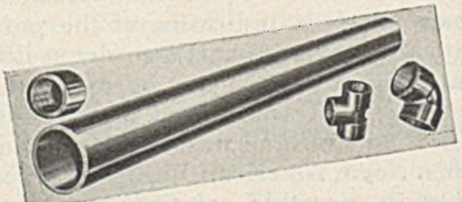
Rubber-protected storage and processing tanks of all descriptions



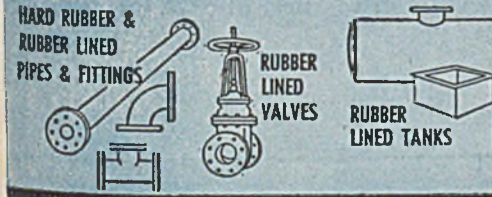
ACE hard rubber pumps, centrifugal and gear, single or double acting



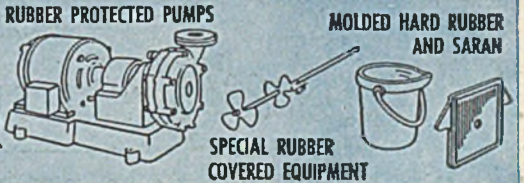
All-rubber or rubber-lined pipe, valves, fittings, molded parts



ACE Saran tubing, pipe, fittings and molded parts



ACE HARD RUBBER AND SARAN

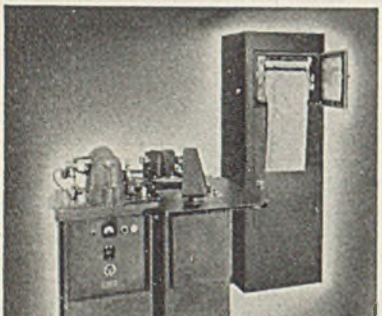


AMERICAN HARD RUBBER COMPANY · 11 MERCER STREET · NEW YORK 13, N.Y.

How Stanford University uses the Norelco X-ray Spectrometer

The NORELCO Spectrometer in use in the Department of Chemistry Stanford University

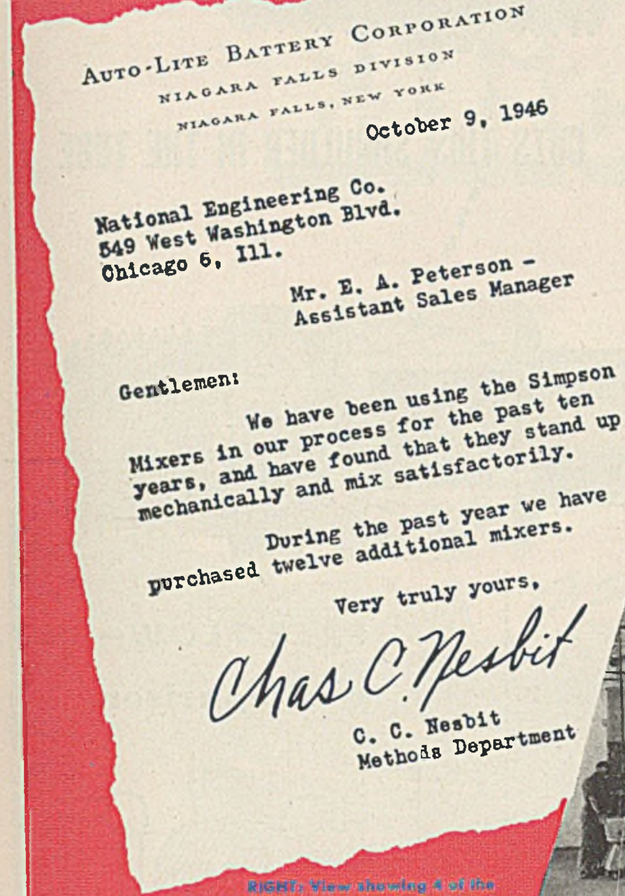
The NORELCO Geiger Counter X-ray Spectrometer is used in the Department of Chemistry, Stanford University, in attacking problems relating to a special class of organic compounds and fatty acid derivatives. • They advise that, "The special virtues of the NORELCO instrument (as contrasted with conventional photographic techniques) in these studies are: (1) that it gives the *shape* as well as the position and intensities of diffraction maxima; (2) the spectrum itself is much more quickly obtainable; and (3) a great deal of the arithmetic involved in interpretation of photographs is done away with." • They have also found it useful to employ the Spectrometer to study diffraction maxima at Bragg angles as low as 0.5°. In addition, it shows promise of usefulness in the Hanawalt method of qualitative analysis. Good results have been achieved from very small amounts of material lodged in the pores of filter paper, which is indicative of the potential of this apparatus. • Equipped with an automatic chart recorder as illustrated at left, the NORELCO Geiger Counter Spectrometer can be used for many phases of product control and analysis. Research and institutional laboratories everywhere are finding new and unique ways to adapt the NORELCO Spectrometer to their problems. North American Philips will accept one of your problems and determine its possible solution by spectrometric technique in its application laboratories. In addition, facilities are offered in training personnel. Write today for full data.



Norelco
Reg. U. S. Pat. Off
ELECTRONIC PRODUCTS

NORTH AMERICAN PHILIPS COMPANY, INC.
DEPT. I-9, 100 EAST 42ND STREET
NEW YORK 17, N. Y.
IN CANADA: PHILIPS INDUSTRIES LTD., 1203 PHILIPS SQUARE, MONTREAL

repeat order for 12 mixers



Auto-Lite Battery Corporation
Niagara Falls Division
Niagara Falls, New York

October 9, 1946

National Engineering Co.
549 West Washington Blvd.
Chicago 6, Ill.

Mr. E. A. Peterson -
Assistant Sales Manager

Gentlemen:

We have been using the Simpson Mixers in our process for the past ten years, and have found that they stand up mechanically and mix satisfactorily.

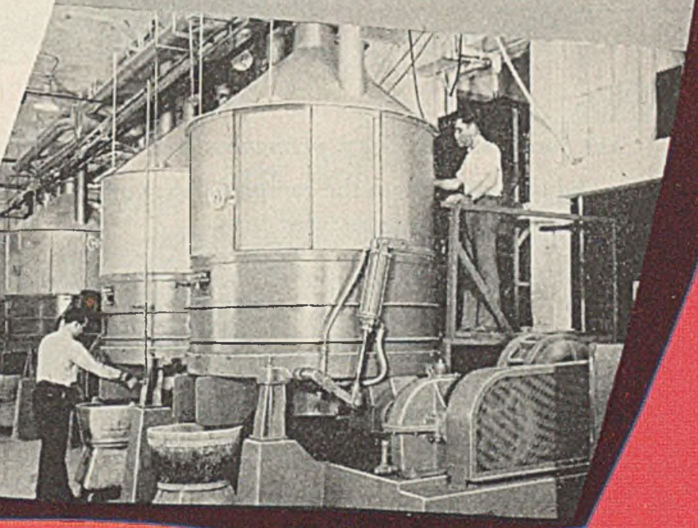
During the past year we have purchased twelve additional mixers.

Very truly yours,

Chas C. Nesbit

C. C. Nesbit
Methods Department

...further proof of SIMPSON Intensive MIXER performance



RIGHT: View showing 4 of the Simpson Mixers referred to in the letter, above, used for storage battery plate paste mixing at an Auto-Lite plant.

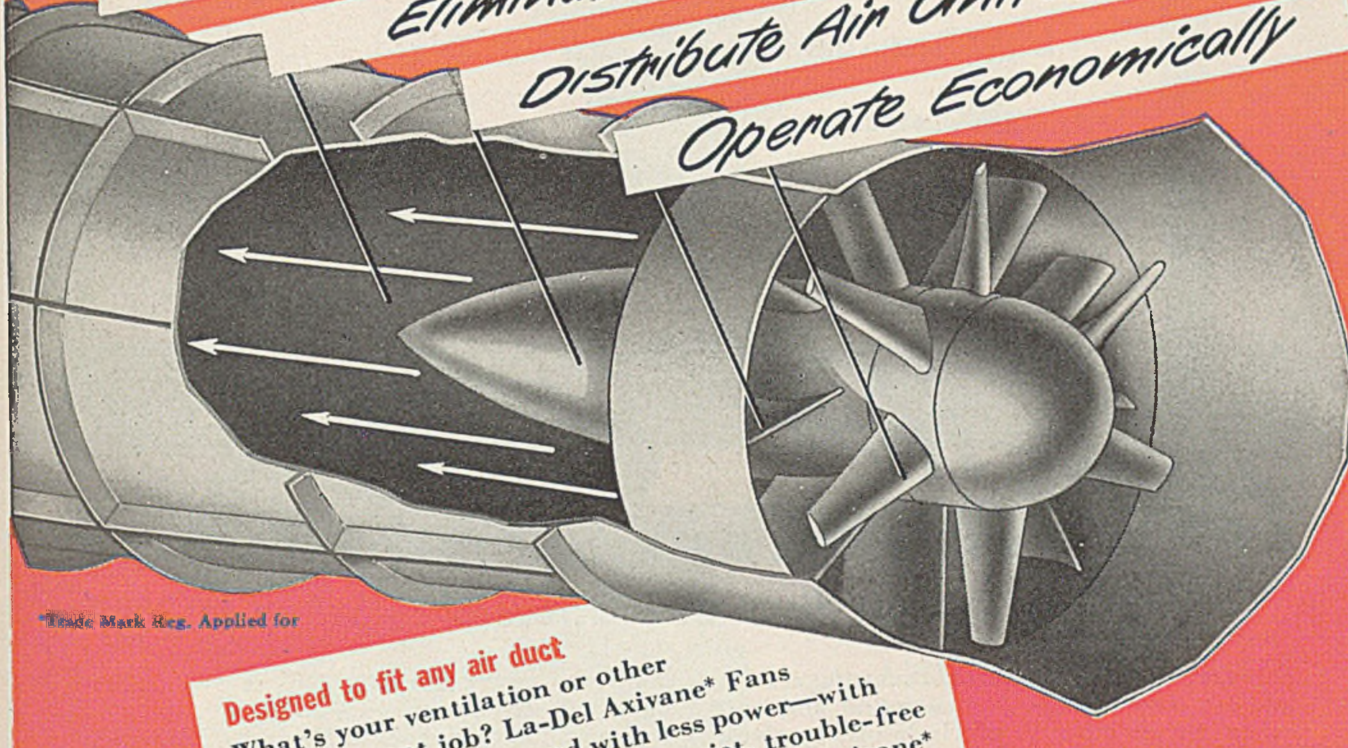
Repeat orders based on performance mean *one* thing . . . *complete satisfaction!* In the case of Simpson Intensive Mixers, increasing product acceptance stems from the fact that users are *assured* of better, faster, *controlled* mixing at less cost . . . with definite improvement in product quality . . . on all types of dry, semi-dry and plastic materials.

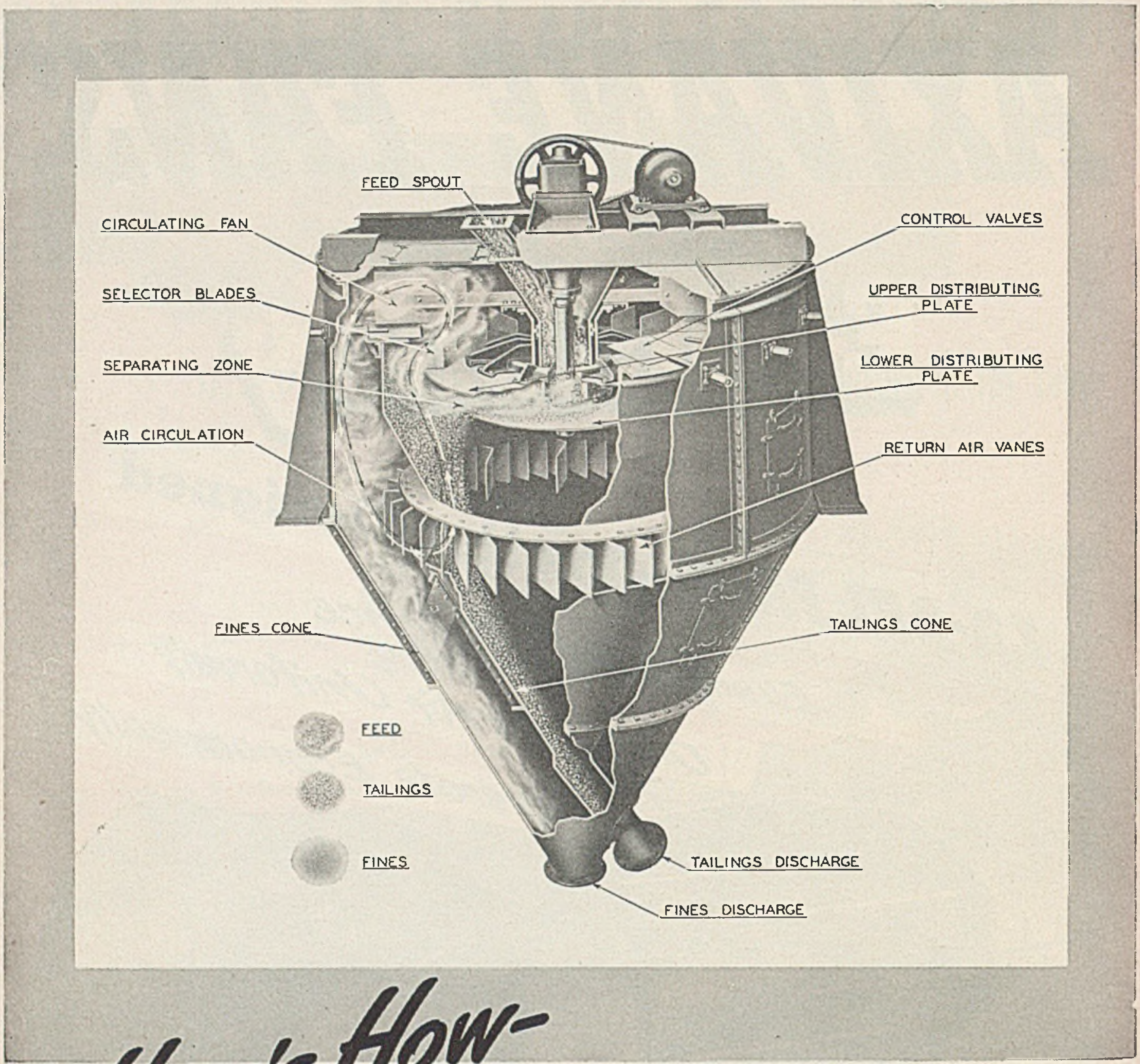
Put National's wide experience with chemical process mixing operations to work in *your* plant or laboratory . . . ask to have a National Engineer outline all the advantages offered with SIMPSON Intensive MIXERS.

SIMPSON Intensive Mixers

NATIONAL ENGINEERING COMPANY
609 Machinery Hall Bldg. • Chicago 6, Ill.

Manufacturers and Selling Agents for Continental European Countries—The George Fischer Steel & Iron Works, Schaffhausen, Switzerland. For the British Possessions, Excluding Canada and Australia—August's Limited, Halifax, England. For Canada—Dominion Engineering Co., Ltd., Montreal, Canada. For Australia and New Zealand—Gibson, Battle & Co., Pty., Ltd., Sydney, Australia





Here's How—

STURTEVANT AIR SEPARATORS

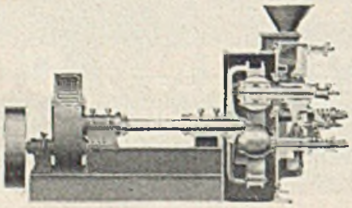
Produce accurate fines with increased output up to 300%

Exact regulation and control of centrifugal forces and air currents, one counteracting and overbalancing the other so precisely that by simple adjustments a product of almost any desired fineness is selected and collected, while coarser sizes are rejected . . . that's the principle of operation of Sturtevant Air Separators.

The benefits you derive from this separator are—increased output by as much as 25% to 300% . . . lower power costs by 10% to 50% . . . reduced maintenance.

A typical on-the-job example is as follows—a 16 ft. separator takes a feed of 750 tons per hour containing only a small percentage of the desired product and delivers 30 tons of material 90%, minus 200 mesh.

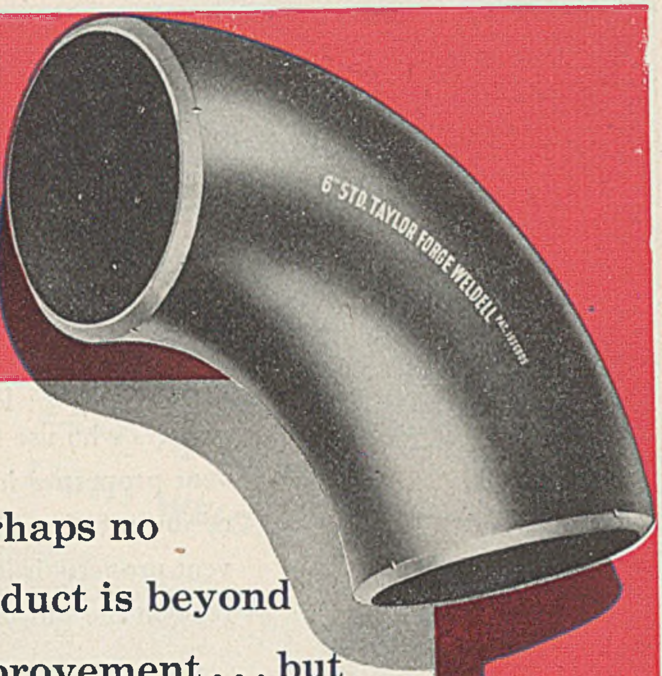
Investigate Sturtevant Air Separators today. Write for information and bulletin.

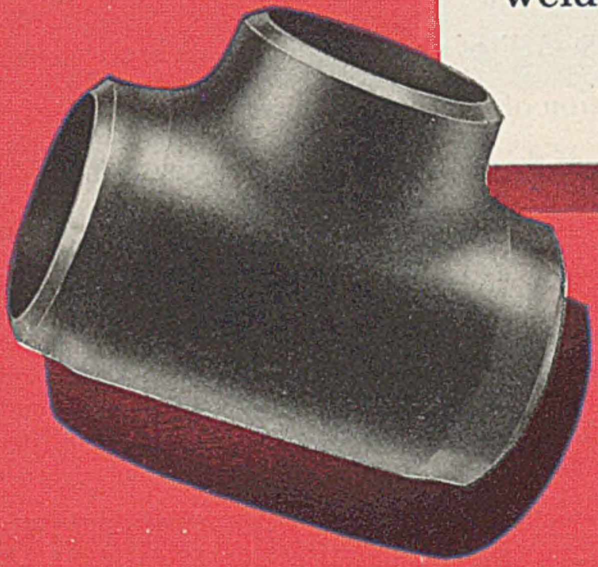


RING ROLL MILL

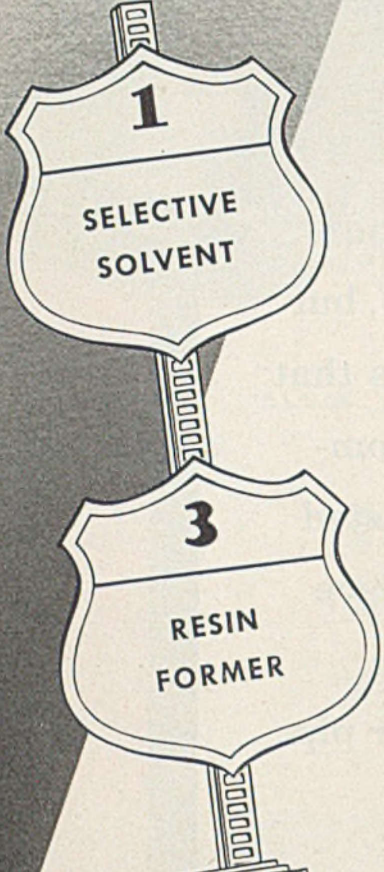
Capacities from 12 to 18 tons per hour. Range 10 to 200 mesh. Use this mill in closed circuit with Sturtevant Air Separators.

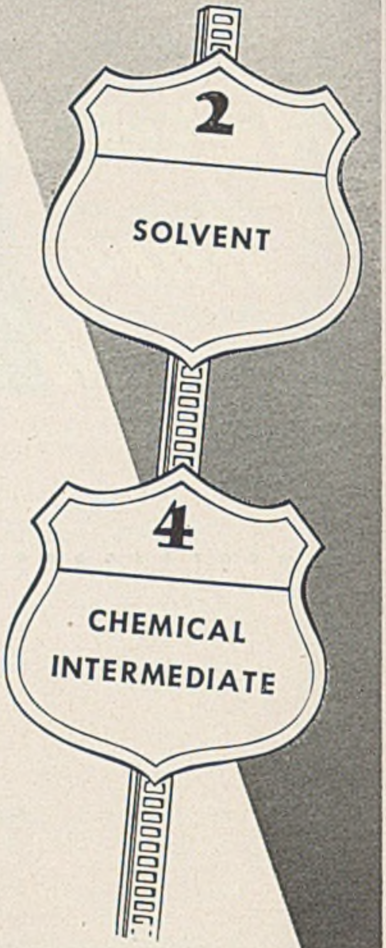
STURTEVANT
MILL COMPANY
105 Clayton Street, Boston 22, Massachusetts
Designers and Manufacturers of
CRUSHERS • GRINDERS • SEPARATORS • CONVEYORS
MECHANICAL DENS and EXCAVATORS • ELEVATORS • MIXERS


6" STD. TAYLOR FORGE WELDELL



TRAVEL THE *Furfural* HIGHWAY





Going by way of furfural to reach their destination has paid off for petroleum refiners who use furfural's selective solvent properties in producing lubricants of improved quality. This selective solvent property is likewise a well traveled road in the purification of butadiene.

Resinoid-bonded grinding wheels roll off production lines that utilize furfural's solvent and wetting properties.

Furfural-phenolic resins as well as resinous products from furfural with urea, casein, lignin or amines are of interest.

And now nylon will soon be traveling the furfural highway by way of adiponitrile using furfural's properties as a versatile chemical intermediate.

THESE ARE SOME of the uses that have brought furfural to a position of paramount importance in industry. The versatility of this compound, the cheapest pure aldehyde today, indicates other uses along many different paths. We suggest that you investigate the possibilities along lines in which you are interested. Write for Bulletin 204 describing the uses of furfural.

VERSATILE CHEMICAL FOR INDUSTRY

Furfural

ITS CURRENT USES

BULLETIN 204

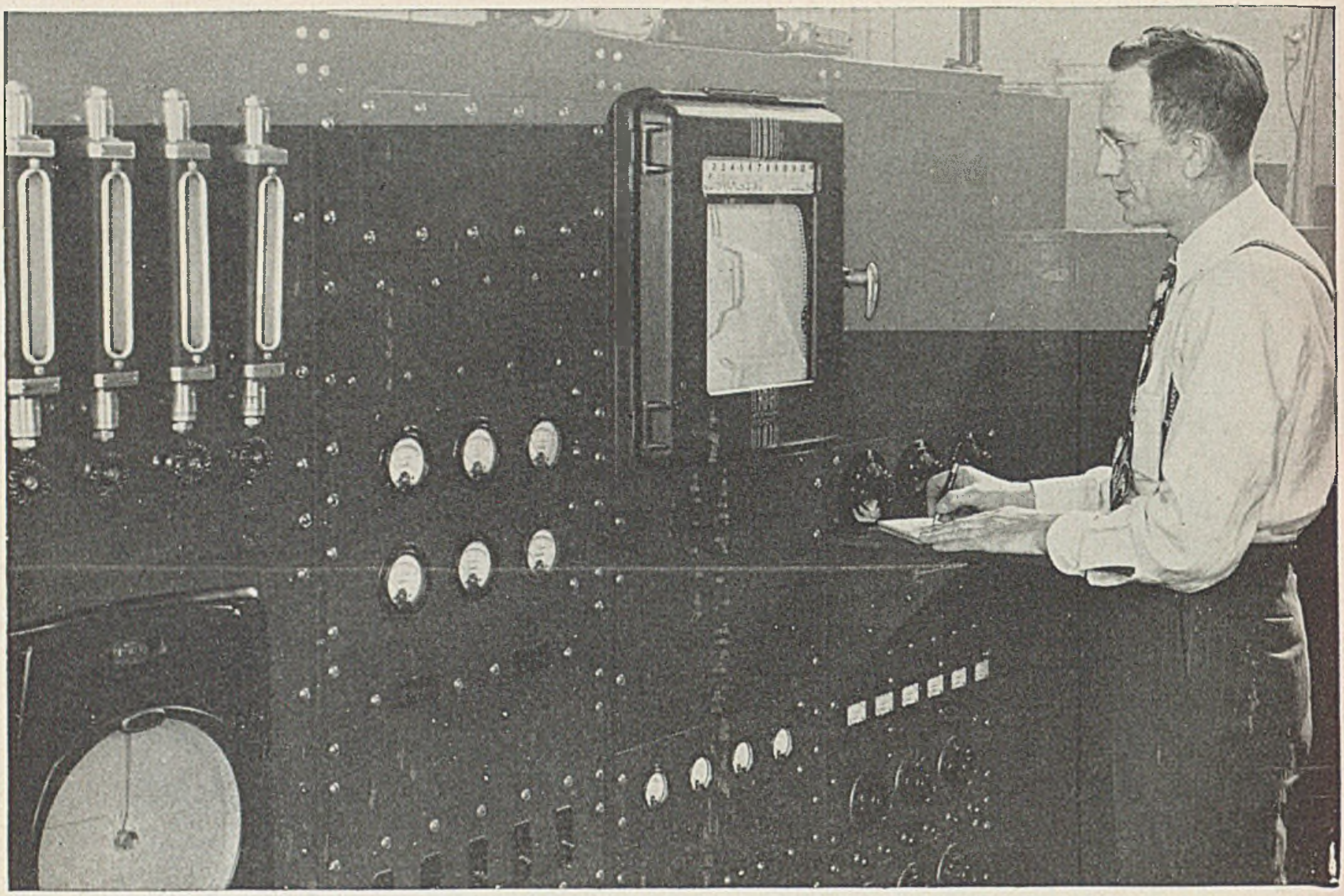
The Quaker Oats Company CHEMICALS DEPT.

The Quaker Oats Company CHEMICALS DEPT.

1910 BOARD OF TRADE BLDG.
141 W. JACKSON BLVD., CHICAGO 4, ILLINOIS

In the United Kingdom, Quaker Oats Ltd., Southall, Middlesex, England
In Europe, Quaker Oats-Graanproducten N. V., Rotterdam, The Netherlands
In Australia, Swift & Company, Pty. Ltd., Sydney

FURFURAL • FURFURYL ALCOHOL (FA) • FUROIC ACID • TETRAHYDROFURFURYL ALCOHOL (THFA)



Photos Courtesy Gulf Research & Development Co

Pilot Plant Uses Speedomax Pyrometer For Ultra-Prompt Records of Temperature

To help satisfy its need for temperature data, Gulf Research & Development Co. is using a several-couples per-minute Speedomax Recorder for the Pilot-plant Control Panel shown above.

This high-pressure unit is liberally studded with thermocouples, in order to detect temperatures at all points needed for the design of petro-chemicals and of processing equipment. Speedomax has several features which make it ideal for measuring and recording these important facts:

Because it is fully sensitive and accurate at both short and low ranges, Speedomax can collect both high and low temperatures on one chart. In photo above, for example, iron-constantan couples are being recorded from 50 F to 575 F.

Speedomax uses many of the time-tested parts used in Micromax Pyrometers, and standardizes itself automatically. Its performance is highly dependable.

Speedomax is fully reliable when its couples are subject to the conditions found in electrically-heated furnaces or towers.

When you need Speedomax performance, there is no substitute!

SPEEDOMAX
TYPE G
PYROMETERS
FOR MEASUREMENT AND CONTROL

LEEDS & NORTHRUP COMPANY

SEE THIS CATALOG

Compressed into 16 pages are the facts you'll need to know about the Speedomax Model G Pyrometer. How it works—what it looks like—its size and the panels available for it—the various types of control for which it's available—all are here. A copy will be sent free on request.

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

LEEDS & NORTHRUP

MEASURING INSTRUMENTS · TELEMETERS · AUTOMATIC CONTROLS · HEAT-TREATING FURNACES

Jrl. Ad N-33A-702(64)

Lithium Salts and Soaps Proving Economically Better Than Traditional Chemicals

The intensive industrial research of the current decade has served to establish lithium salts and soaps as commercial tonnage products. This research, with increased efficiency and economy as its goal, has led to the use of lithium salts in direct competition with the traditional chemical giants . . . for example, winning preference over sulphuric acid or calcium chloride in the dehydration and purification of gases and over sodium, potassium and lead salts in the glass and ceramics industry.

Lithium salts were established in these and other uses as a result of exhaustive tests and research, emphasizing the fact that lithium chemicals are extremely effective industrial raw materials.

The following are a few of the newest results of research work on lithium salts and soaps:

PLASTICS — Lithium Hydroxide (LiOH) and Lithium Carbonate (Li_2CO_3) are used as catalysts in esterification of certain plastics, rendering them crystal clear without filtering.
Lithium Stearate is a heat stabilizer and lubricant used in the production of sheet elastomers. Its stable non-toxic nature is of particular interest here.

COSMETICS — Lithium Stearate helps produce a smoother, fluffier composition with free flowing characteristics and improved adhesion. Thin films can be applied, resulting in better appearance. Because of high moisture and oil absorption qualities, these films are more effective and have increased life.

POWDER METALLURGY — Lithium Stearate serves as a lubricant. Allows the removal of breakdown products in sintering to give a high strength compact, with controlled porosity and negligible refractory oxide content — which other metal stearate-type lubricants leave.

INSECTICIDES — Lithium Stearate used as a gelling agent gives paste form to liquid insecticides for special applications where adhesion and increased life are desirable.
Lithium Stearate can be used as a flowing agent and auxiliary sticker in dust type insecticides.

Lithium chemicals are available for prompt shipment in commercial quantities.
These include:

Benzoate
Borate
Bromide
Carbonate
Chloride
Citrate
Fluoride
Hydroxide
Naphthenate
Nitrate
Oxalate
Phosphate
Stearate
Sulphate
Tartrate

Let Foote research and developmental engineers show you how lithium chemistry might fit in your process or product. Write, wire or phone for further information today!

Foote
MINERAL COMPANY
A Step Ahead in Industrial Ores and Chemicals

Chemicals • Ores • Metals • Alloys

Home Office: 516 GERMANTOWN TRUST COMPANY BLDG., PHILA. 44, PA.
West Coast Representative: Griffin Chemical Co., San Francisco, Cal.

5 Types of Reactions you can carry out with Sulfuryl Chloride

1. Chlorination of aromatic compounds
2. Chlorination of aliphatic compounds
3. Sulfonation of aliphatic compounds
4. Sulfonation of aromatic compounds
5. Acylation (preparation of esters, acid chlorides, anhydrides, etc.)

Chlorination

Sulfuryl Chloride offers certain advantages as a chlorinating agent that are quite universally recognized. They are principally:

1. The heat of chlorination is far less than that using elementary chlorine.
2. It is possible by using different catalysts, reacting at different temperatures and by carefully controlling proportions of reactants, to chlorinate selectively.

Sulfonation

The availability of sulfur in the compound makes it equally valuable in the sulfonation of aromatics and aliphatics. Sulfonyl chloride derivatives may be obtained by the addition of small quantities of aluminum chloride to a cooled reaction mixture of sulfuryl chloride and aromatic hydrocarbons.

Formation of alkyl sulfonyl chlorides with yields as high as 70% are reported in the sulfonation of paraffin hydrocarbons in the presence of light and a catalyst.

Acylation

Alkyl chlorsulfonates are the products of reactions of sulfuryl chloride with many alipathic alcohols. A number of interesting acylated products may be produced through the reaction of this versatile chemical with aliphatic and aromatic amines.

* * *

You who are interested in the synthesis of organic chemicals will find Sulfuryl Chloride a valuable reagent. With Hooker Sulfuryl Chloride you will be working with a particularly pure product that tends to increase yield and eliminate side reactions.

For more information on Sulfuryl Chloride as a chlorinating agent write on your letterhead for Bulletin 328A. It also includes data on other Hooker chlorinating agents. For information concerning other reactions of Sulfuryl Chloride send for Bulletin 330, a reprint of an article on "Sulfuryl Chloride in Organic Chemistry." Technical Data Sheet 717 contains typical properties and specifications of Hooker Sulfuryl Chloride.


Chlorinating Agents

HOOKER CHEMICALS


Sulfuryl Chloride in Organic Chemistry

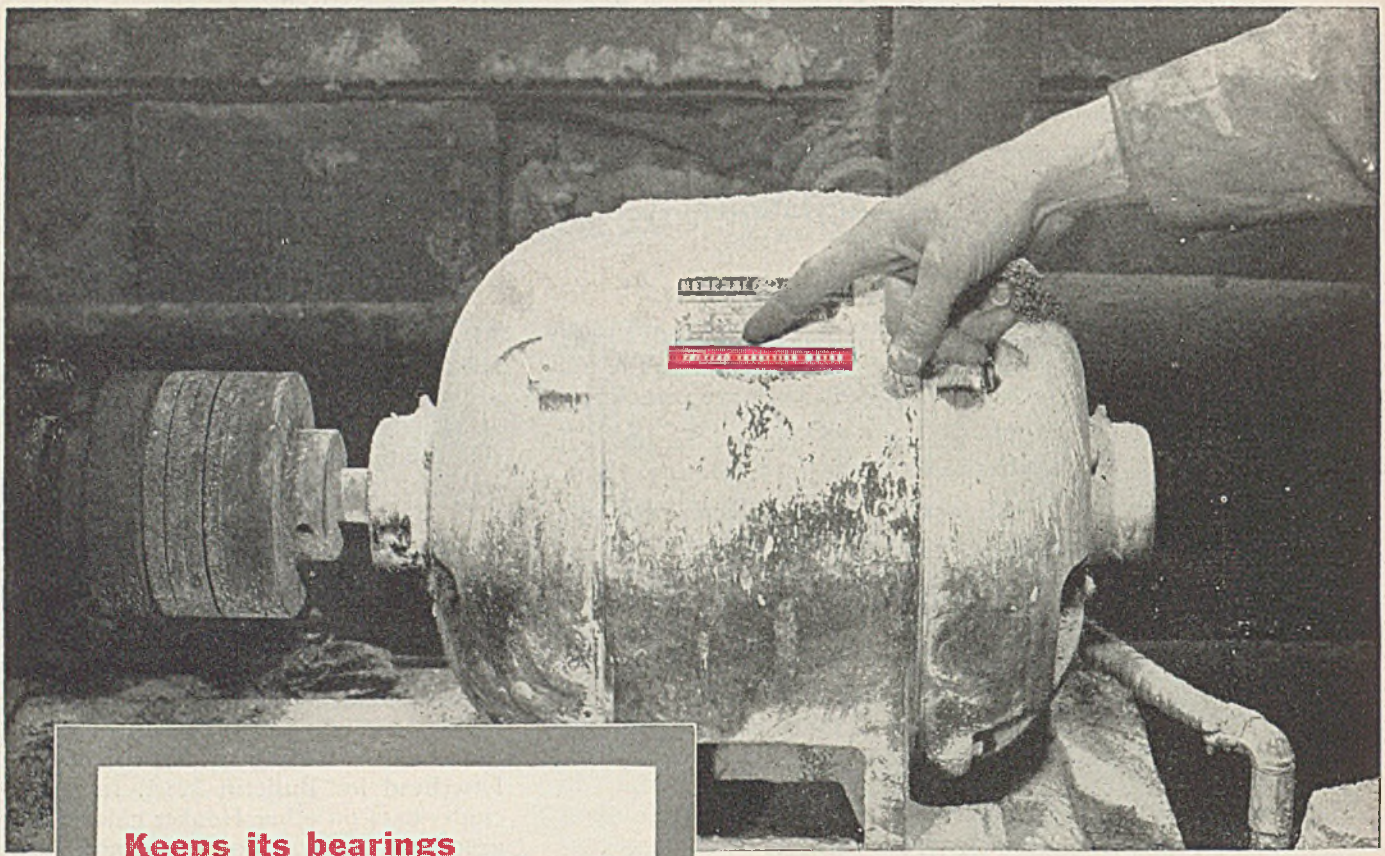
7-358

HOOKER ELECTROCHEMICAL COMPANY

9 Forty-Seventh St., Niagara Falls, N. Y.
New York, N. Y. Wilmington, Calif. Tacoma, Wash.

HOOKER CHEMICALS

ON 1,220,000



Keeps its bearings *in a "dust bowl"*

Ordinarily, we wouldn't recommend that you use an open motor on a job like this. This Tri-Clad motor drives a boiler-feed pump in the National Gypsum Company plant at Clarence Center, N. Y. The air surrounding the motor is constantly filled with gypsum dust which must be kept out of the bearings. And it *has* been kept out of the bearings of this Tri-Clad motor, thanks to its specially designed bearing housing and seals. We believe that the Tri-Clad motor you see here proves that even where dust, moisture, or some other hazard is extremely severe for open-motor applications, the extra protection afforded by Tri-Clad motor construction results in longer motor life and lower upkeep.

and now—THE TOUGHEST TRI/CLAD YET

REG. U.S. PAT. OFF.

Newest addition to the Tri-Clad motor family is the Tri-Clad totally enclosed, fan-cooled motor. It is designed for use in adverse atmospheres—in iron dust, out-of-doors, in hazardous areas, and chemical atmospheres. Available in both standard and explosion-proof types, this Tri-Clad motor gives you these important construction features:

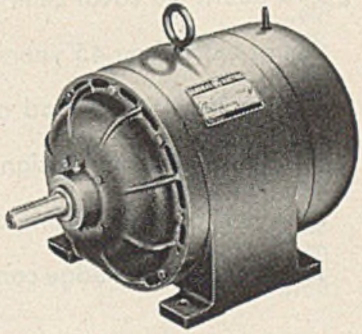
- A cast-iron, double-wall frame which completely encloses and protects the windings and punchings.
- A nonshrinking compound around motor leads which protects motor interior from dust and moisture.
- A rotating labyrinth seal which further protects the motor interior from damage by foreign matter.

MOTORS

TRI/CLAD

THE SYMBOL OF

EXTRA PROTECTION



Announcement of the Tri-Clad motor, back in 1940, ushered in a new concept of general-purpose motor design. Substantially increased horsepower-per-frame-size, was one feature. Smarter appearance was another. But what really sold more than a million Tri-Clad motors is the *extra protection* we built into them.

Often operating under conditions no general-purpose motor should be asked to meet, Tri-Clad motors built up an enviable record of war-time service. Today, with the "family" including dripproof motors, vertical motors, gear-motors, capacitor-motors, and totally enclosed motors, the Tri-Clad motor is, more than ever, the motor that means basic protection, dependable performance, and minimum upkeep. *Apparatus Dept., General Electric Company, Schenectady 5, N. Y.*

EXTRA PROTECTION... AGAINST PHYSICAL DAMAGE!

Rigid cast-iron frame and end shields protect vital motor parts from external abuse and prevent resonance. Because they're not at the mercy of a coat of paint, they strongly resist chemical attack and dampness. Cast iron also gives you tight, *metal-to-metal* fits between end shields and frame.

EXTRA PROTECTION... AGAINST ELECTRICAL BREAKDOWN!

Motor windings of Formex* wire, together with improved insulating materials, reduce the chances of electrical failure. Heat is dissipated quickly — motor stays young for years and years!

EXTRA PROTECTION... AGAINST OPERATING WEAR AND TEAR!

Bearing design affords longer life, greater capacity, improved lubrication features. Bearing seals retain lubricant, keep out dirt. One-piece, cast-aluminum rotor is practically indestructible.

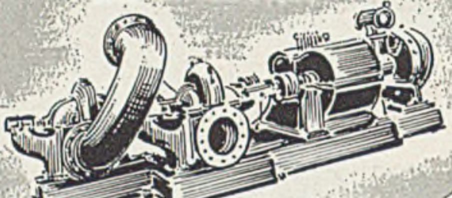
**Trade-mark reg. U. S. Pat. Off.*

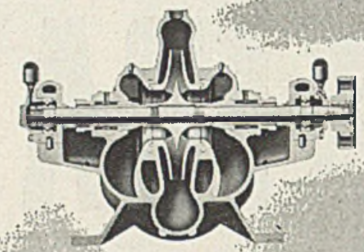
TRI/CLAD
REG. U.S. PAT. OFF.
MOTORS

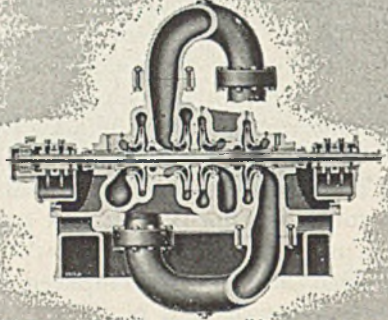
- OPEN (DRIPPROOF)
- TOTALLY ENCLOSED
- EXPLOSION-PROOF

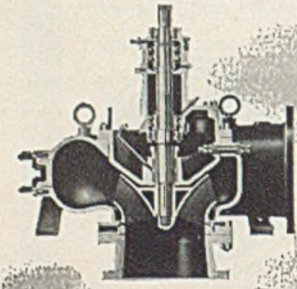
GENERAL ELECTRIC

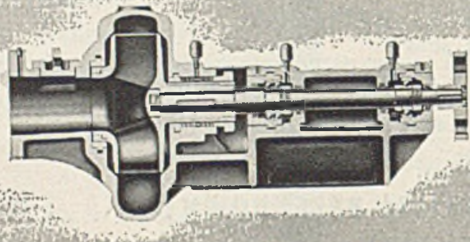
750—285

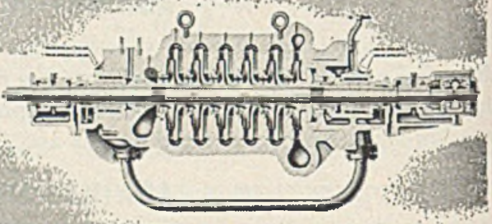


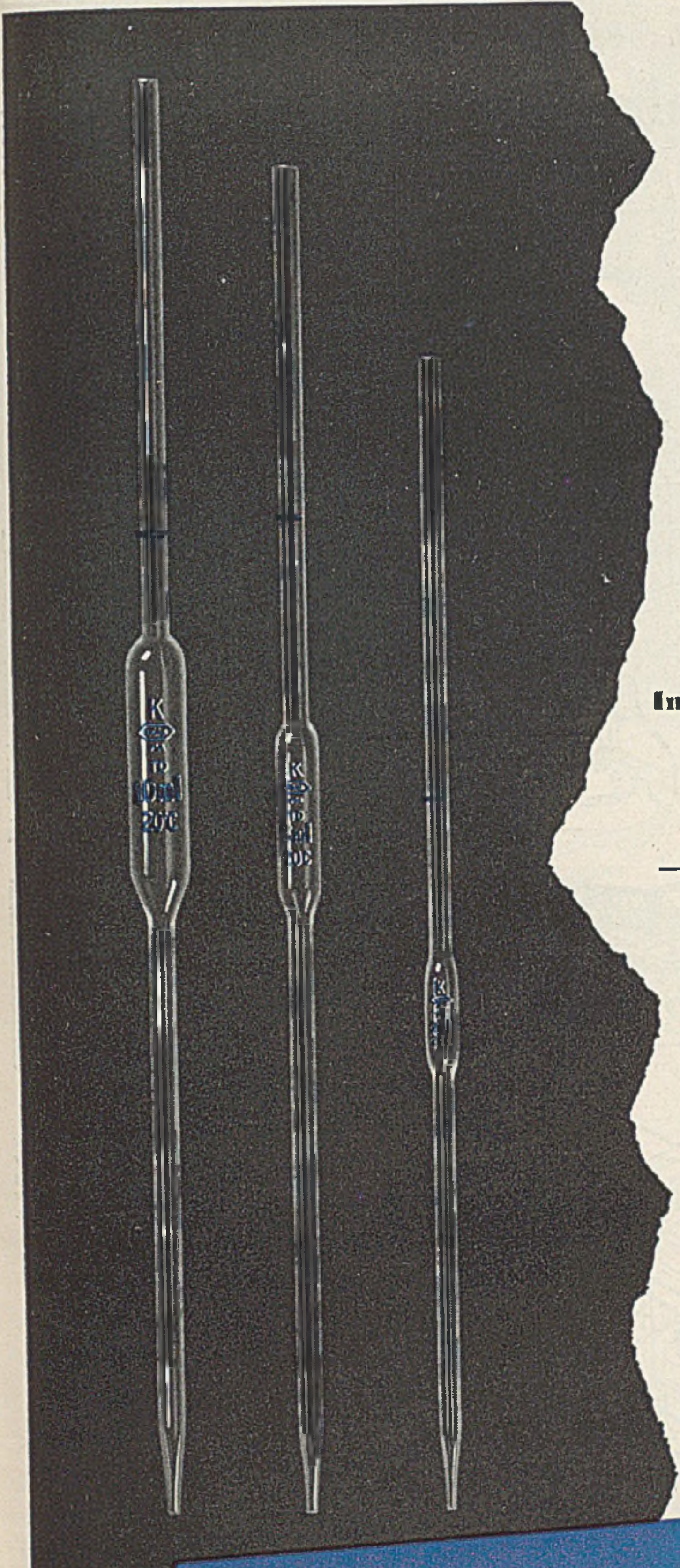












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Blue Line ⟨EXAX⟩ Retested

VOLUMETRIC PIPETTES

Made from automatic-machine-drawn extra heavy tubing.

Expertly annealed for greatest sturdiness.

Individually RETESTED to assure accuracy.

37000 VOLUMETRIC OR TRANSFER PIPETTE

Capacity ml	Price, Each
1	$0.44
2	.44
3	.50
4	.52
5	.52
10	.56
15	.66
20	.70
25	.70
50	1.00
100	1.40
200	3.00

Leading Laboratory Supply houses throughout the United States and Canada will be glad to quote quantity prices and further details.

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KIMBLE (K) GLASS

• • • *The Visible Guarantee of Invisible Quality* • • •

Vineland, New Jersey

DIVISION OF OWENS-ILLINOIS GLASS COMPANY

One order to CRANE fills all your piping equipment needs

Having Crane supply everything means much more than just simplified specifying and buying. It means that every step of the job will go smoothly... from design to erection to maintenance.

Take the case of this synthetic dye and color plant, for instance. Here you'll find not only the common fluids to be controlled, but also the tough problems of handling liquids and gases of corrosive, volatile, or toxic nature. In an operation like this, standardization on the widest possible scale is desirable.

So it's no wonder that this plant, like many others, relies on Crane for piping materials. Because standardizing on Crane offers this 3-way advantage:

ONE SOURCE OF SUPPLY offers you the world's most complete selection of brass, iron, steel, and alloy piping materials—for all power, process, and general services.

ONE RESPONSIBILITY helps you to get the best installation and to avoid needless delays.

OUTSTANDING QUALITY of every item assures uniform excellence and dependable performance in every part of piping systems.

CRANE CO., 836 S. Michigan Ave., Chicago 5, Ill.
Branches and Wholesalers Serving All Industrial Areas

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SOURCE OF SUPPLY
RESPONSIBILITY
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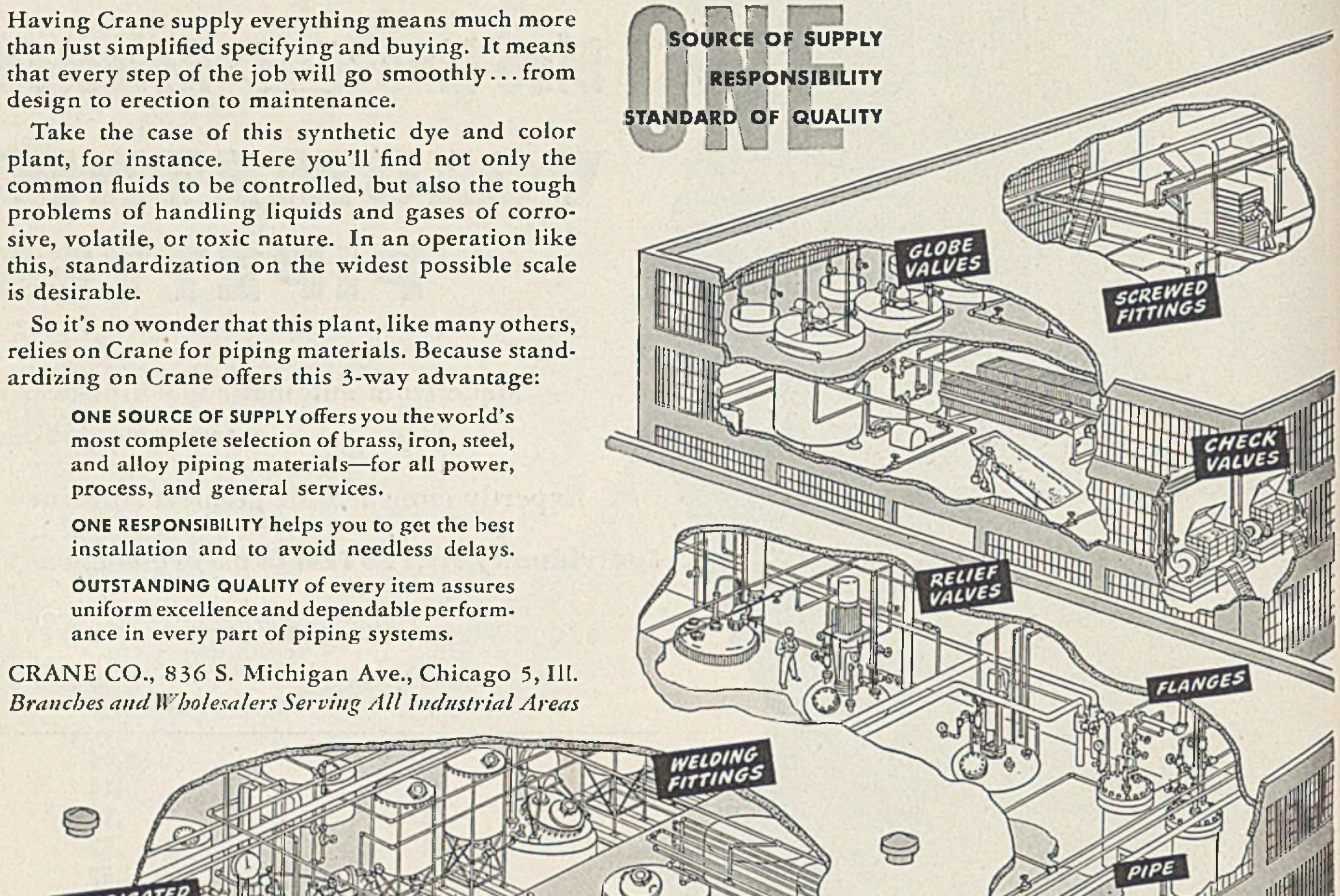
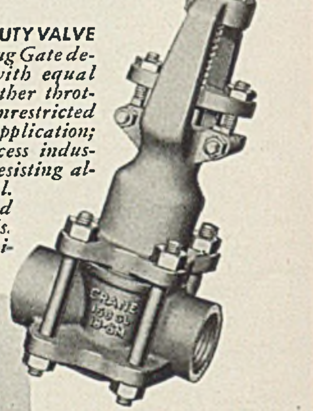


Synthetic dye and color plant... piping materials from the complete Crane line.

NEW DOUBLE-DUTY VALVE
Crane Alloy Plug Gate design. Works with equal efficiency in either throttling service or in providing unrestricted flow. Eliminates valve misapplication; easily repaired; ideal for process industries. Made in two corrosion-resisting alloys—18-8 Mo or Monel Metal. Bolted bonnet, outside screw and yoke; flanged or screwed ends. Sizes ½ to 2 in. Complete specifications on request.



EVERYTHING FROM ...

CRANE

FOR EVERY PIPING SYSTEM

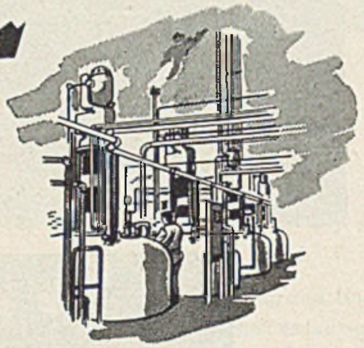
VALVES • FITTINGS
PIPE • PLUMBING
AND HEATING


Do Summer Temperatures have you in HOT WATER?
45° F.
WATER VAPOR REFRIGERATION


WILL
~~DOES~~ PULSATION PLAY TRICKS IN YOUR NEW PLANT?

Guard Against PRODUCT CONTAMINATION

WITH ELECTRUNITE STAINLESS STEEL TUBING



Before specifying tubing for new equipment that comes in contact with delicate, easily contaminated chemical products, consider the many cost-saving advantages of ELECTRUNITE Tubing—made of Republic ENDURO Stainless Steel.

For more than 25 years, ENDURO Stainless Steel has proved itself inherently clean, sanitary and easy to keep clean. It resists corrosion . . . does not contaminate metallically . . . is strong and long lasting because it is *solid* stainless steel throughout.

Add the fabricating economies of all tubing made by the ELECTRUNITE Process of electric resistance welding—*uniform wall thickness, diameter and concentricity*—and you will see why it pays *always* to specify ELECTRUNITE Stainless Steel Tubing.

For further information—including an up-to-date list of sizes, gauges, finishes and analyses—write *today* to:

REPUBLIC STEEL CORPORATION
STEEL AND TUBES DIVISION • CLEVELAND 8, OHIO
Export Department: Chrysler Building, New York 17, N. Y.

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Republic
ELECTRUNITE
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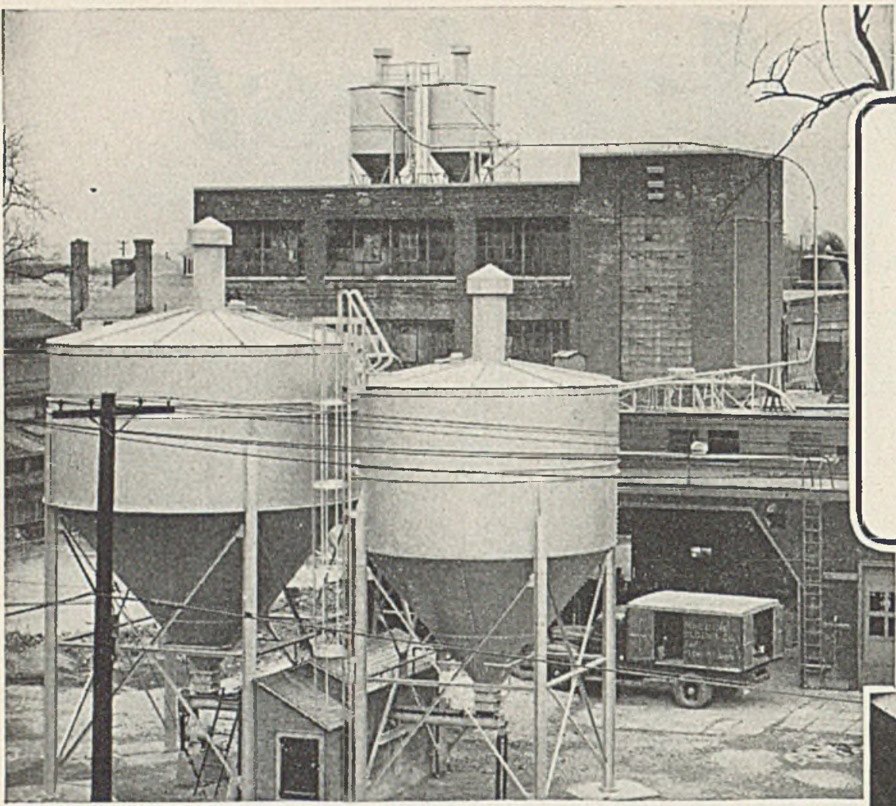
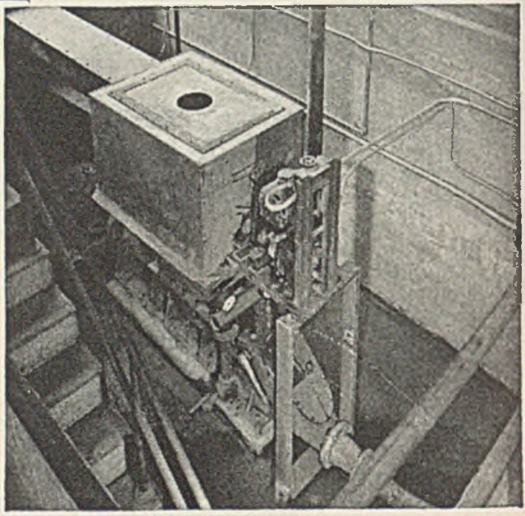
STAINLESS STEEL TUBING



UNLOADING
AND
CONVEYING
TO
STORAGE
AND
PROCESS

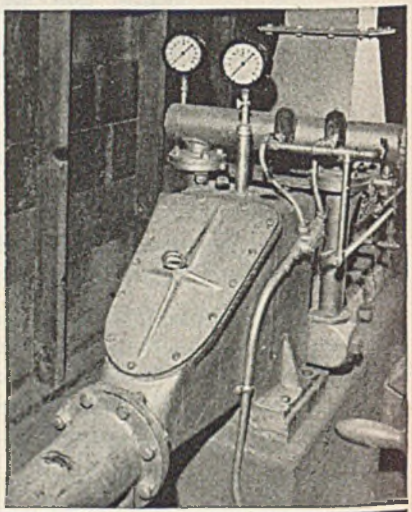


FULLER-KINYON SYSTEMS INSTALLED TO MEET CONDITIONS OF PLANT LAYOUT

The Fuller-Kinyon System illustrated is used for unloading and conveying cement and precipitator dust for the manufacture of asbestos shingles. The system was purchased and installed after the plant had been erected, and, therefore, had to be engineered and built to fit in with the existing building layout.

There are really two systems installed. One system unloads materials from hopper-bottom cars, upper photo right, and conveys materials to the two storage bins, foreground upper photo, or through the use of a two-way valve in the conveying line, direct to process bins shown on building. Materials are also conveyed from storage bins to process bins by another Fuller-Kinyon Pump, housed in the building underneath the storage bins. This pump is shown in photo, lower right.

A very flexible and simple system, economically possible only with a Fuller-Kinyon System. When your problem is conveying of dry pulverized materials, get in touch with us. Our engineering department is at your service.



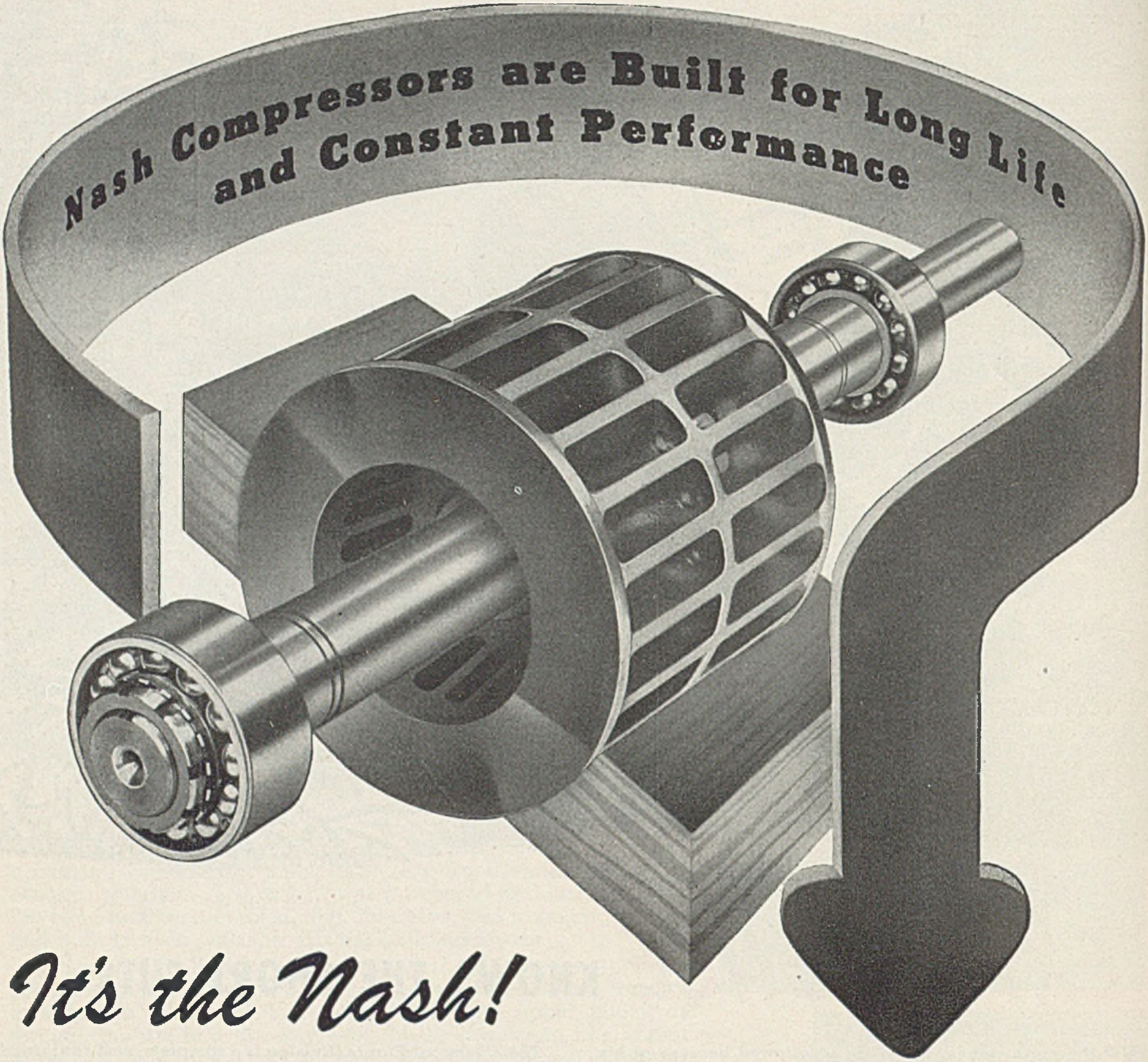
FULLER COMPANY
CATASAUQUA—PENNSYLVANIA

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

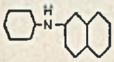
FULLER COMPANY

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

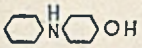
P-87


Nash Compressors are Built for Long Life and Constant Performance

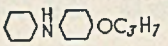
Secondary Aromatic Amines



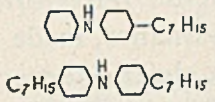
Phenyl B-Naphthylamine



p-Hydroxy Diphenylamine



p-Isopropoxy Diphenylamine

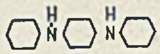


Mixed Mono and Diheptyl Diphenylamines

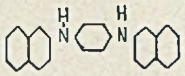
These amines are suggested for use as stabilizers, antioxidants, polymerization inhibitors, and for organic synthesis. It is believed that they will find wide usage in the following industries: Dyes, explosives, plastics, petroleum, photographic, drug, medicinal, and soap.

Other organic chemicals

Di-secondary Aromatic Amines



Diphenyl p-Phenylenediamine



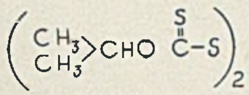
Di B-Naphthyl p-Phenylenediamine

Ethers of Hydroquinone

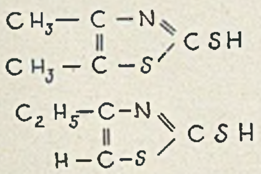
Monobenzyl Ether of Hydroquinone

Dibenzyl Ether of Hydroquinone

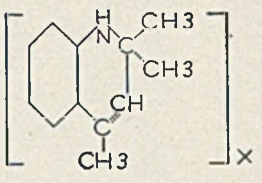
Miscellaneous



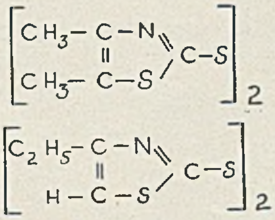
Di-Isopropyl Dixanthogen



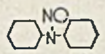
Mixed Ethyl and Dimethyl Mercaptothiazoles



Trimethyl Dihydro Quinoline Polymer



Mixed Aliphatic Thiazyl Disulfides



N-Nitroso Diphenylamine

All materials listed here are available in commercial quantities. Prices and technical information are available on request. Please write Dept. CC-9, B. F. Goodrich Chemical Company, Rose Building, Cleveland 15, Ohio.

B. F. Goodrich Chemical Company

A DIVISION OF
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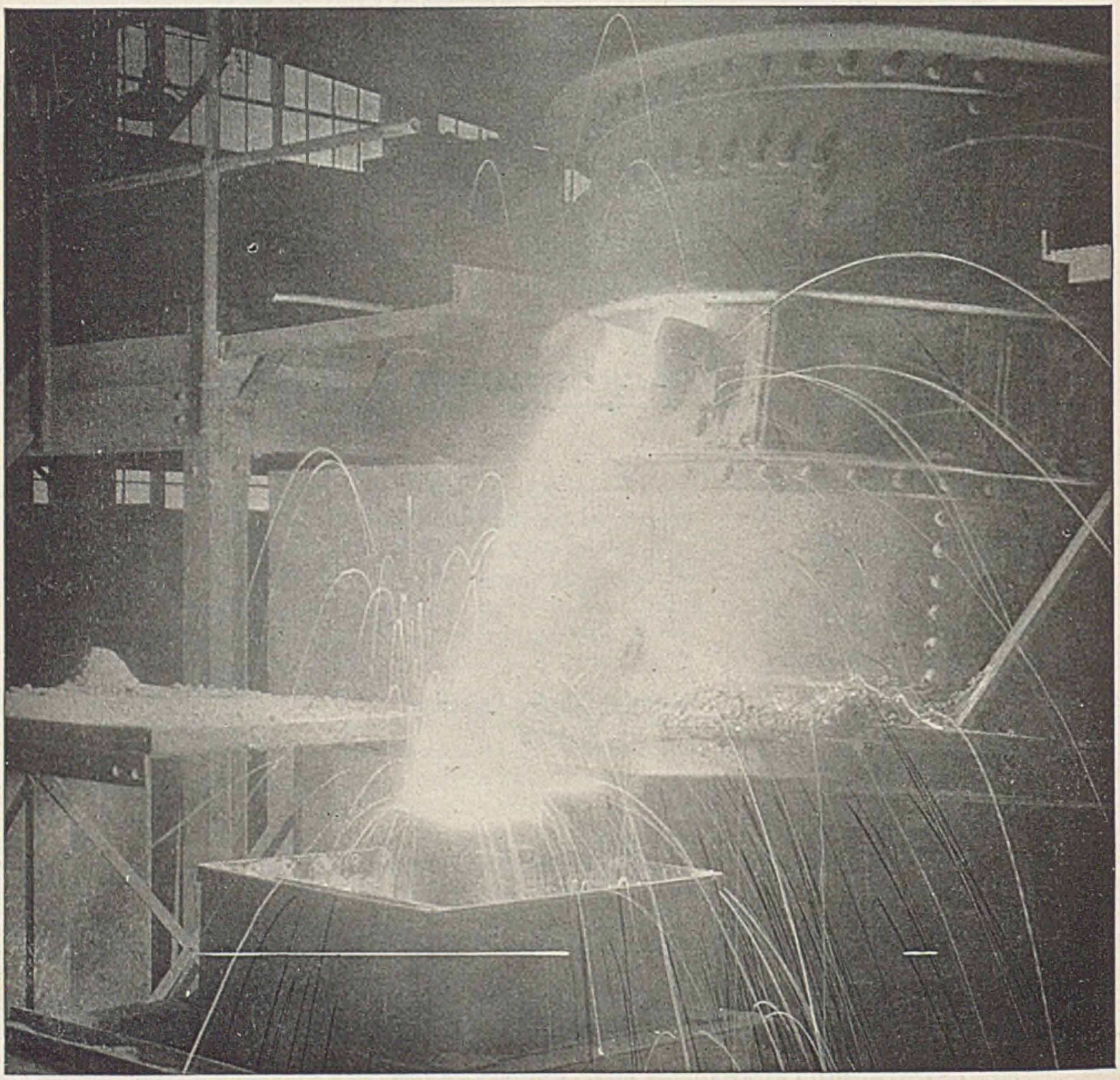
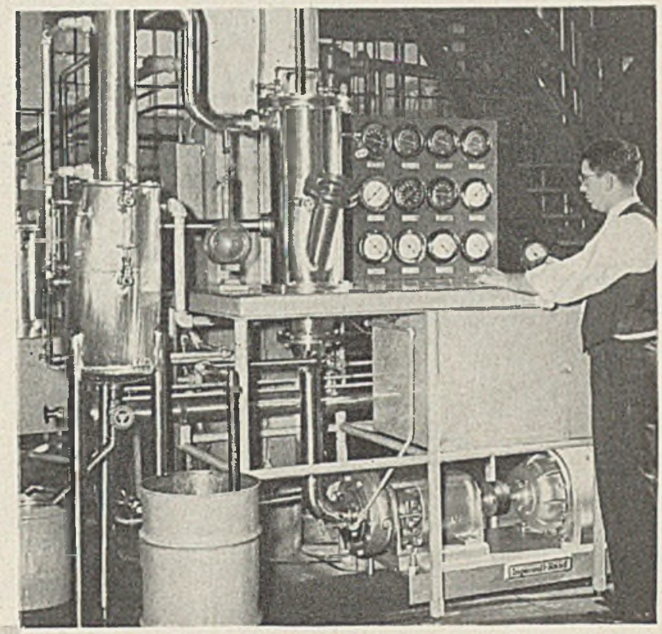
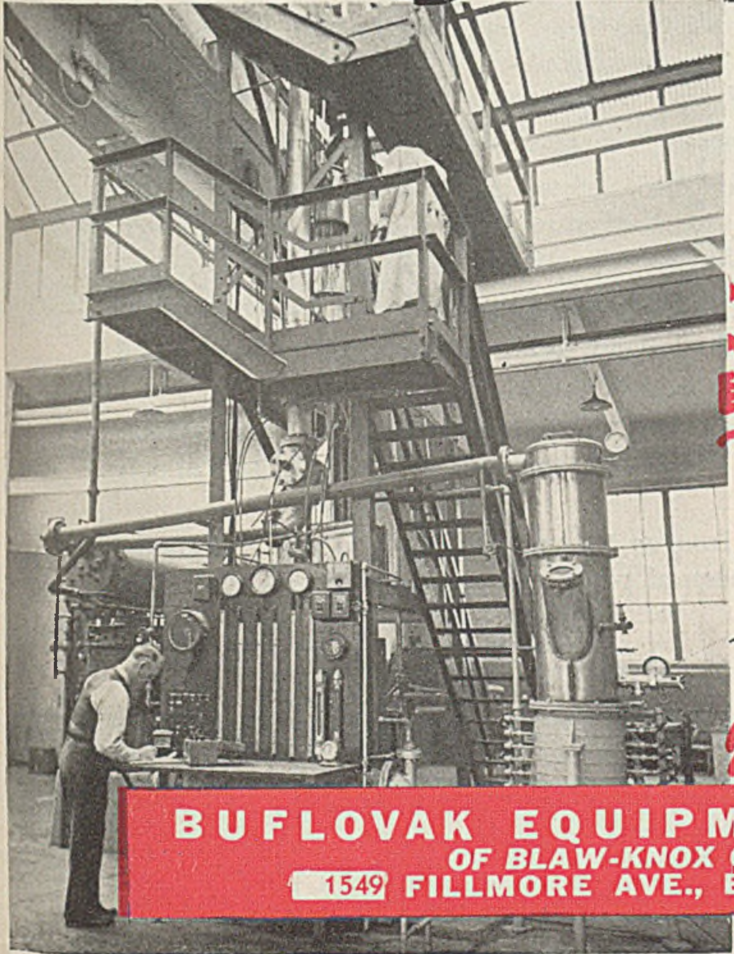
GEON polyvinyl materials • HYCAR American rubber • KRISTON thermosetting resins • GOOD-RITE chemicals



Learn...at the start... If your contemplated process has... *commercial possibilities*

In BUFLOVAK'S Research and Testing laboratories you can learn the commercial possibilities of your contemplated process, with data on production cost, capacity, and the characteristics of the finished product. BUFLOVAK'S Research and Testing Plant embodies the latest and most advanced design to solve processing problems, involving drying, evaporation, extraction, impregnation, solvent recovery, crystallization and food processing.





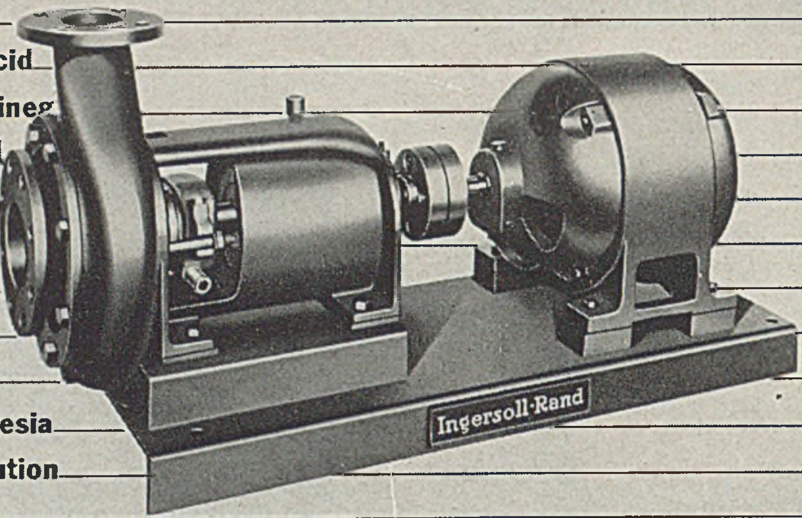
Over 5,000 research processing problems have been studied and completed in the past 30 years. With this background of experience, the highly specialized staff offer their mature counsel, without obligation. Your technicians are at liberty to work with our staff, and the results are held in strictest confidence.

Buflovak's long line of processing equipment for the chemical industry includes EVAPORATORS, ATMOSPHERIC AND VACUUM DRYERS, SOLVENT RECOVERY AND DISTILLATION EQUIPMENT, CASTINGS, CRYSTALLIZERS, AND CHEMICAL PLANT EQUIPMENT.

BUFLOVAK EQUIPMENT DIVISION
OF BLAW-KNOX COMPANY
1549 FILLMORE AVE., BUFFALO 11, N.Y.

DOCTOR OF pH

pH	Water solution	H ion conc. g-mol/l
0	hydrochloric acid	1.0
1	sulfuric acid	.1
2	phosphoric acid	.01
3	acetic acid (vineg	.001
4	carbonic acid	.0001
5	boric acid (ey	.00001
6	milk	.000001
7	pure water	.0000001
8	baking soda	.00000001
9	borax	.000000001
10	milk of magnesia	.0000000001
11	ammonia solution	.00000000001
12	lime	.000000000001
13	washing soda	.0000000000001
14	caustic soda (lye)	.00000000000001



Degrees come the hard way in the corrosive field. They mean years of lab research and more years of field testing. I-R chemical pumps have plenty of both behind them. They have what it takes to run the whole pH scale with distinction in any chemical plant.

These features contribute to the success of I-R chemical pumps:—

"IRCAMET", a special corrosion-resistant alloy, containing high chromium and nickel with molybdenum and low carbon, that has proved itself on a long list of corrosives. (Other materials available for special services.)

HYDRAULIC DESIGN that results in the utmost in economy and power savings.

"LEAKOLLECTOR", the new I-R patented gland, collects all stuffing-box leakage and leads it to a convenient point.

"CAMERON SHAFT-SEAL"— I-R pumps may be equipped with this modern solution to stuffing-box problems that is the talk of the pump world. It is the mechanical seal that *really* performs its function.

Learn more about I-R chemical pumps from an I-R engineer near you who will gladly help you with your problems. Ask for chemical pump catalog No. 7095 and Shaft Seal bulletin No. 7100.

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TURBO BLOWERS • CONDENSERS
CENTRIFUGAL PUMPS • OIL AND GAS ENGINES

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CAMERON PUMP DIVISION

10-931

Fantastic as it seems, the effective *ad*sorbent surfaces of a pound of activated carbon are actually equal in area to about 125 acres.

We don't pretend to know how this can be possible, but our research men, who understand such things, have figured it out scientifically. We like to think of *what* it does rather than *how* it does it.

For example, when used to isolate streptomycin from the mold liquor in which it is produced, a *Pittsburgh* activated carbon, tailor-made for this purpose and with greater adsorptive capacity, assisted materially in the rapid development of a process with a capacity sufficient to permit removal of the "wonder drug" from the government's critical list. Soon streptomycin may be as available as penicillin.

Less dramatically, but like the producer of streptomycin, a manufacturer of water purification systems for homes, institutions, and industries tested every available adsorbent and then selected a *Pittsburgh* activated carbon which was specifically designed to meet the exacting requirements of his purification systems.

If your "problem" involves the use of an adsorbent, in gas or liquid phase, for purification, solvent recovery, decolorization, deodorization, fractionation, isolation, catalysis or air conditioning, you should investigate the adaptability of activated carbon to your processes. *Pittsburgh* activated carbon is produced in the types and grades usually required, or a special type can be developed for your specific need. Your inquiries are invited. Write for latest price list.

P C&C C

PITTSBURGH COKE & CHEMICAL COMPANY

Grant Building · Pittsburgh 30, Pa.

New

Better

Greater Economy

CALCIUM STEARATE

Calcium Stearate Impalpable Powder Grade A

* BULK—*6 lbs. per cubic foot*

† FINENESS—*99½% through 325 mesh*

¶ HEAVY METALS—*Meets food standards*

⁋ WATER SOLUBLE SALTS—*Less than 0.1% as chloride*

* When packed, 11.5 lbs. per cubic foot. Easily fluffed back to 6 lbs. per cubic foot.

† This means that all aggregates will pass the finest commercially used screen. Actually the ultimate particles are of the order of 3 to 5 microns in size. This insures smoothness and freedom from grit.

¶ This means that the excellent properties of the new material can be applied to food and pharmaceutical uses.

⁋ This means that, with the use of this lubricant, electrical parts can be molded without affecting electrical resistance. It also means that emulsions are easily made and permanent when this compound is used in them.

A refinement of manufacturing techniques—backed by 80 years of experience—gives industry a new and better *Calcium Stearate Impalpable Powder Grade A,* with enhanced use values at greater economy than ever before. Other stearates are also improved correspondingly. For further information ask your nearest Mallinckrodt office.

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Eriez PROTECTION

For automatic tramp iron removal from your materials . . . The Eriez Non-Electric Magnetic Pulley.

ERIEZ NON-ELECTRIC *Permanent* MAGNETS *Protect Coal Pulverizers from Tramp Iron*

HERE is an Eriez Permanent Non-Electric Magnetic Separator removing spark producing tramp iron in a coal processing line at the General Electric Company, Erie, Penna.

Installed on the hoppers ahead of Raymond Coal Pulverizers in an area where no electrical connections or outlets are permitted due to extreme danger of explosions —these Eriez Magnets protect machinery, property and working personnel.

Saving many times their initial cost, Eriez Magnetic Separators pull all tramp iron from materials being processed. The economy and dependability of Eriez protection is known throughout industry . . . no current, wiring or attendant electrical equipment needed, and they cost nothing to maintain . . . They are powered by giant Alnico magnets produced under General Electric Patents.

Leading industrial plants specify Eriez because they want safe, reliable Permanent Magnetic Protection. Clip and mail the coupon today for full details.

CLIP AND MAIL TODAY
Dear Sir: We are interested in removing tramp iron or ferrous particles from the following materials: ______________________
We would like to know more about installation of ERIEZ on: IEC-9
☐ Gravity Conveyors ☐ Mechanical Conveyors ☐ Pneumatic Conveyors
☐ Liquid Pipelines Magnetic Trap ☐ Equipment or Processing Machines
Name ______________________
Address ______________ City ______________ State ________

● *When It's Magnetic Protection . . . See Eriez First*

SEE OUR EXHIBIT
PACIFIC CHEMICAL
EXPOSITION
SAN FRANCISCO CIVIC AUDITORIUM
OCTOBER 21 - 26 INC. 1947

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ERIEZ MANUFACTURING CO.
116 EAST 12th ST. ERIE, PENNA.

How's this for GOOD DIGESTION?

TCC UNIT CHARGES 8 DIFFERENT STOCKS ON 8 SUCCESSIVE DAYS!

The remarkable flexibility of the TCC process is well illustrated by the following record from the daily log sheets of a TCC plant:

Date	CHARGE TO TCC PLANT CONTAINED:			
	Full Crude	Reduced Crude	Virgin Gas Oil	Kerosene
June 7	—	—	100%	—
8	—	—	75%	25%
9	—	—	—	100%
10	25%	50%	25%	—
11	70%	—	30%	—
12	50%	—	30%	20%
13	50%	30%	—	20%
14	50%	50%	—	—

Only a Houdry-licensed catalytic cracking unit could possibly accommodate such frequent changes of charge stock without shutdown and consequent considerable (and costly) loss of production. In the case of the TCC unit reported above, no major reduction in throughput, or in output of catalytic gasoline, resulted from the daily and drastic variations in feed charge.

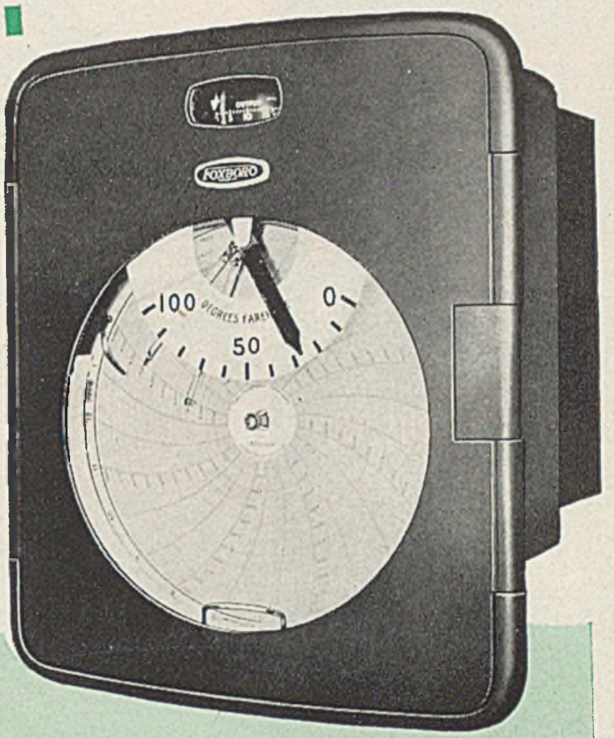
HOUDRY PROCESS CORPORATION

25 Broad Street, New York 4, N. Y.

HOUDRY CATALYTIC PROCESSES

Simplicity...

TO THE Nth DEGREE in Electronic Controllers for Thermocouples



● THE GREATER accuracy, sensitivity, and speed of the new Foxboro DYNALOG Controller are made even more impressive by the utter simplicity of its design. Such a combination is getting enthusiastic approval everywhere, from operating men as well as process engineers.

The heart of the instrument, illustrated at right, is typical of its simplified construction. In one gearless, rugged unit are all moving parts . . . the STEPLESS balancing capacitor, the powerful Dynapoise Drive, the short, patented ball linkage. There is practically no chance of this unit getting out of order . . . and its very simplicity assures longer life.

THE NEW DYNALOG CONTROLLER

the Marvel of Maintenance Men

NO *SLIDEWIRE*—complete slidewire mechanism is replaced by simple balancing capacitor.

NO *MOVING CONTACTS*—slidewire contact is eliminated by positive-connected capacitor.

NO *GEARS*—only simple, direct linkage.

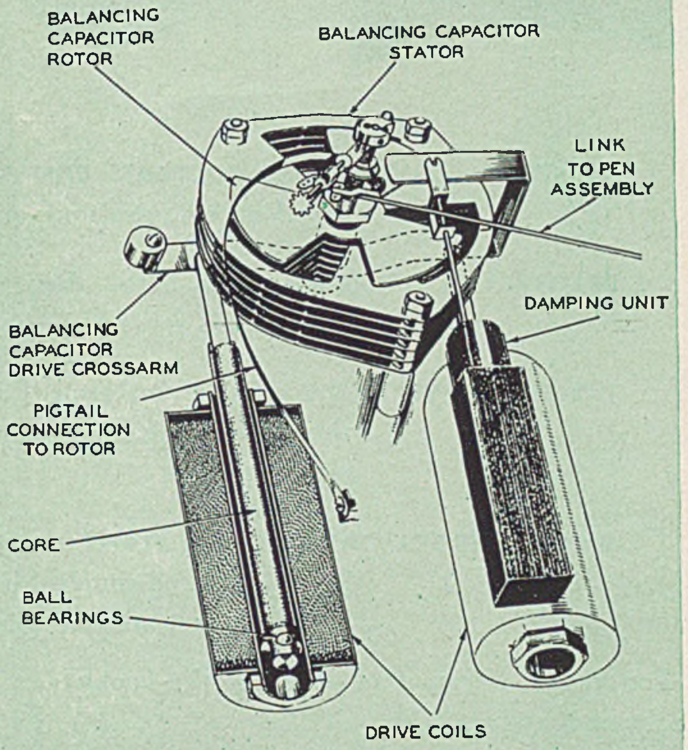
NO *ROTARY MOTORS*—balancing drive motor is simple push-pull, magnetic type. No brushes, commutator or bearings.

NO *GALVANOMETER*—not affected by vibration.

NO *BATTERIES*—no standardizing. Measured voltage is compared directly to standard cell.

NO *SERVICING*—except simple replacement of standard, widely-used type vacuum tubes.

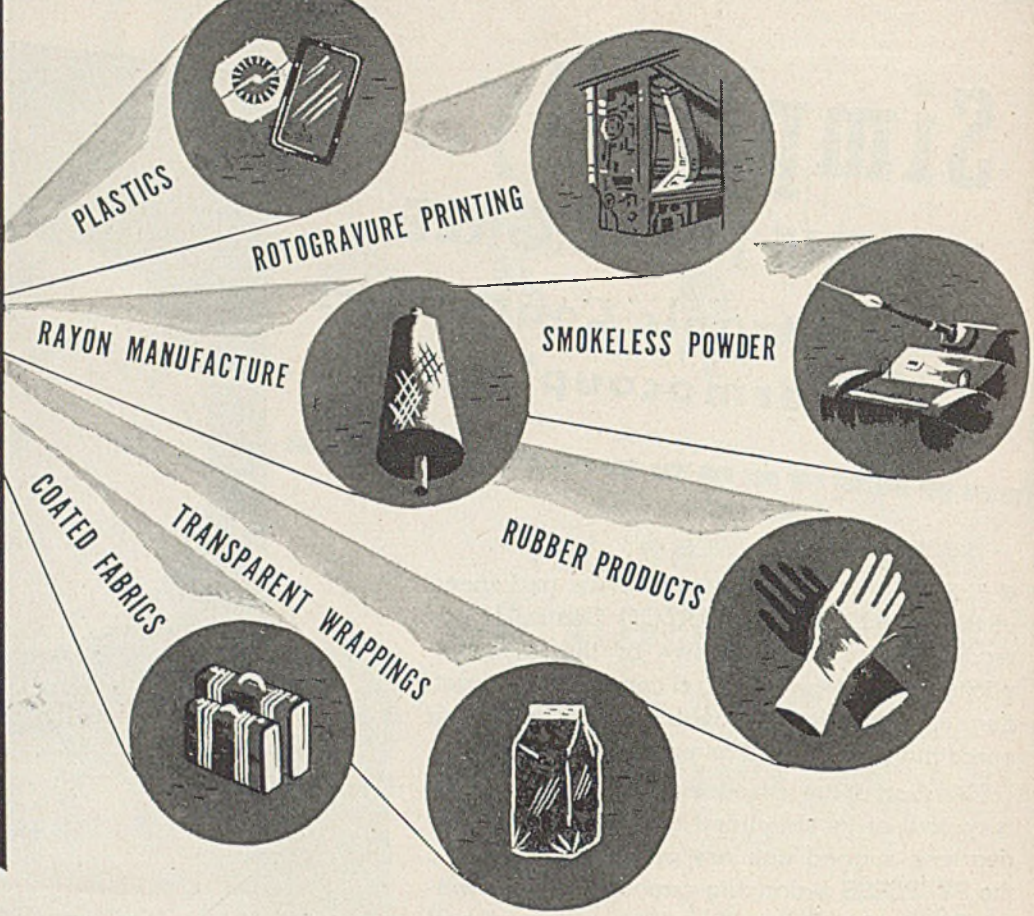
Write for Bulletin 397 containing full details of DYNALOG Controllers in air-operated (Model 40) and electric (Rotax) types. The Foxboro Co., 40 Neponset Avenue, Foxboro, Mass., U. S. A.



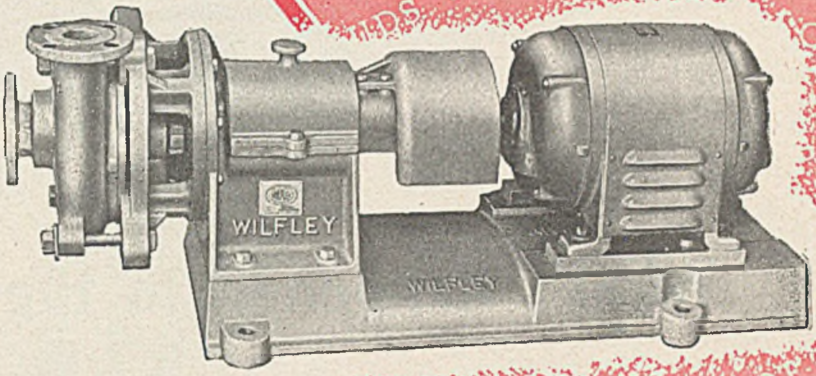
The heart of all Dynalog Instruments is the exclusive Dynapoise Drive shown here. The balancing capacitor eliminates contact and cleaning problems. No lubrication or maintenance of any kind needed.

FOXBORO
REG. U. S. PAT. OFF.

ELECTRONIC INSTRUMENTS


PLASTICS
ROTOGRAVURE PRINTING
RAYON MANUFACTURE
SMOKELESS POWDER
COATED FABRICS
TRANSPARENT WRAPPINGS
RUBBER PRODUCTS

for Acids



Efficient, cost-saving handling of acids, corrosives, hot liquids and mild abrasives is characteristic of WILFLEY Acid Pumps. This is the trouble-free pump that delivers full production on a 24-hour schedule without attention—on intermittent as well as continuous operations. 10- to 2,000-G.P.M. capacities; 15- to 150-ft. heads and higher. It's a companion to the well-known WILFLEY Sand Pump. Both pumps are famous cost savers. Individual engineering on every application. Write or wire for complete details.

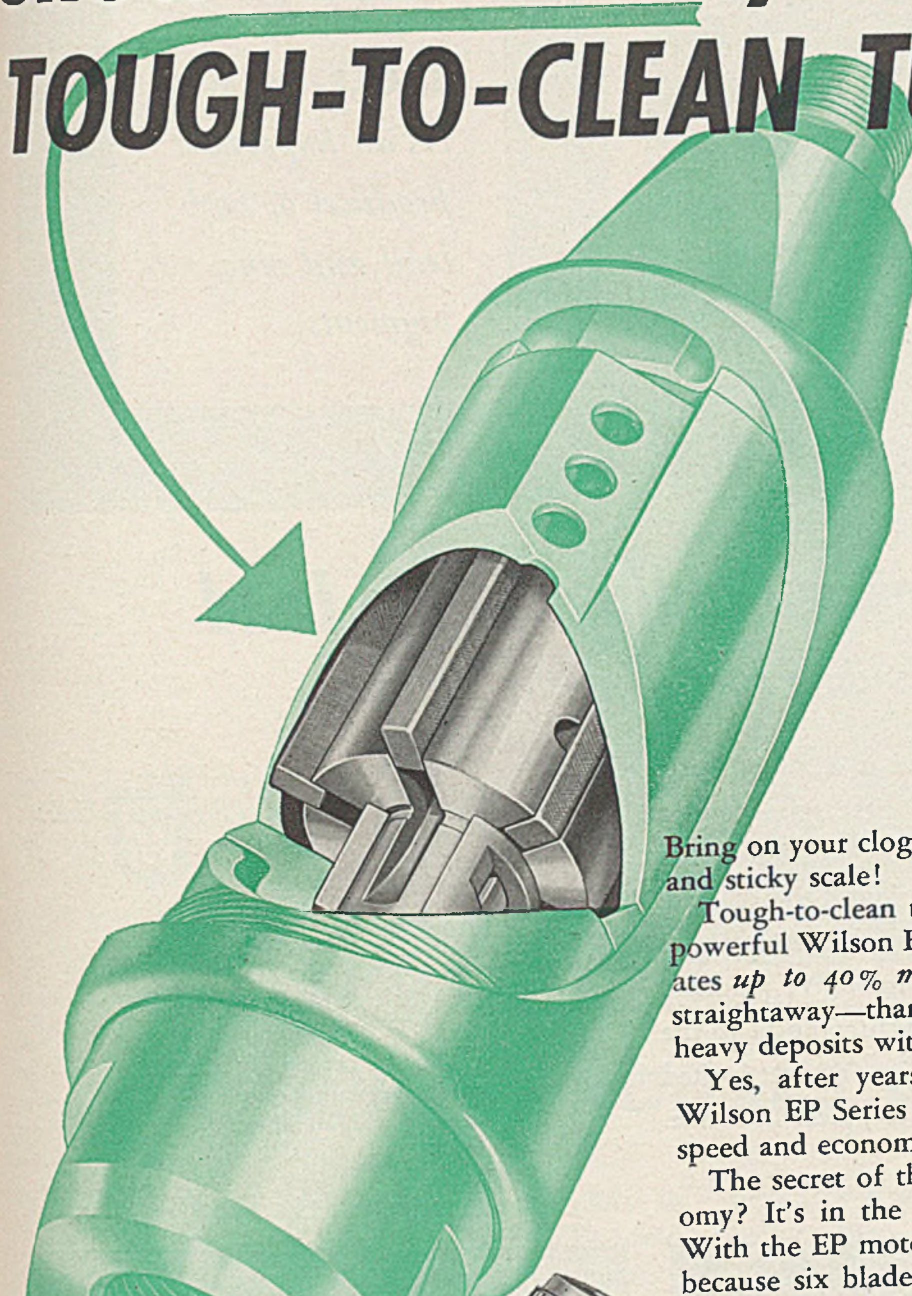
WILFLEY

centrifugal PUMPS

A. R. WILFLEY & SONS, INC., DENVER, COLORADO, U.S.A.
NEW YORK OFFICE: 1775 BROADWAY, NEW YORK CITY


PEPPERMINT LOZENGES
LICORICE
1¢
1¢

Show this motor your TOUGH-TO-CLEAN TUBES

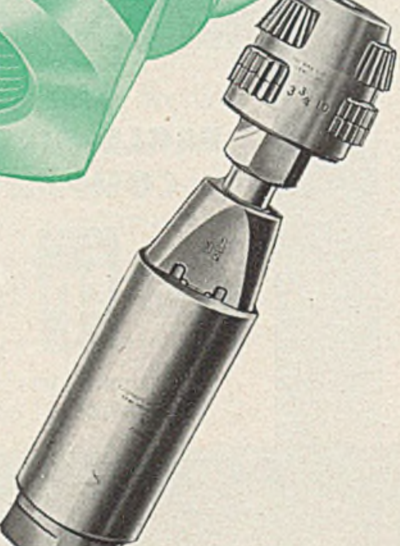


Bring on your clogged up tubes with the heavy deposits and sticky scale!

Tough-to-clean tubes are "duck soup" for this extra powerful Wilson EP Series motor. Size for size, it generates *up to 40% more power*—on the curves or in the straightaway—than ordinary motors. It drives through heavy deposits without stalling or slipping.

Yes, after years of proven performance, this same Wilson EP Series motor still leads the field for power, speed and economy.

The secret of these extras in power, speed and economy? It's in the six-bladed, light-bladed construction. With the EP motor you get higher torque at any speed because six blades produce a smoother flow of power . . . 12 powerful impulses per revolution. Light blades eliminate the need for expensive cylinder replacement. Automatic valving of operating air means less air-consumption . . . a minimum of back pressure. Its six blades eliminate "dead" center . . . make it easy to start—hard to stall. Why not see your local Wilson Representative about cost cutting EP Motors today?



Wilson EP Series Air Motor with Model F Cutter Head.

THOMAS C. WILSON, INC.
21-11 44th Avenue, Long Island City 1, N. Y.
Cable Address: "TUBECLEAN", New York

WILSON
TUBE CLEANERS

Tw.730

EAGLE-PICHER
. . . an important producer of both lead and zinc pigments

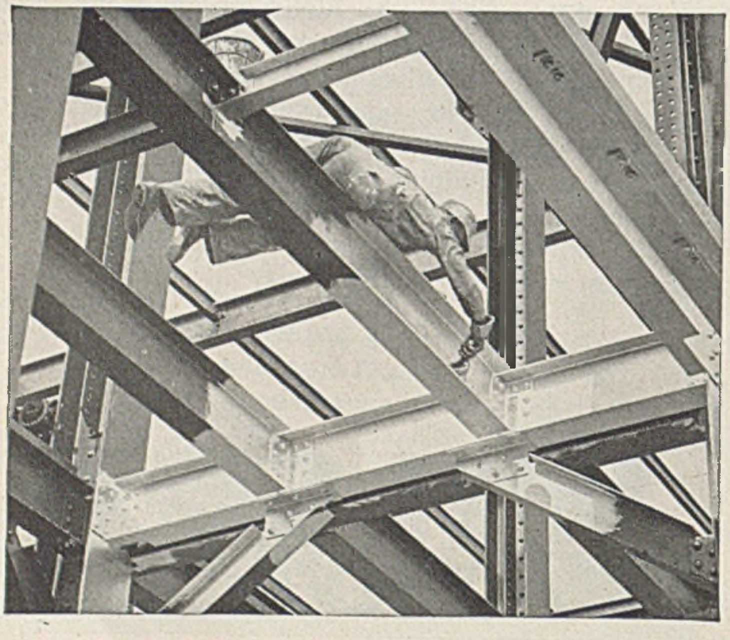
Eagle-Picher Sublimed Blue Lead

. . . an outstanding rust-inhibitive pigment

Eagle-Picher Sublimed Blue Lead is a fumed basic lead sulfate manufactured as a prime product in a specially designed lead ore smelting furnace. It has been extensively specified by various Federal, State and Municipal Governments for use on structural steel because it is an outstanding rust-inhibitive pigment. Three grades are made, all of which conform to the A. S. T. M. and all other specifications. You are invited to write us for free samples and complete literature.

Other Eagle-Picher Industrial Pigments include:

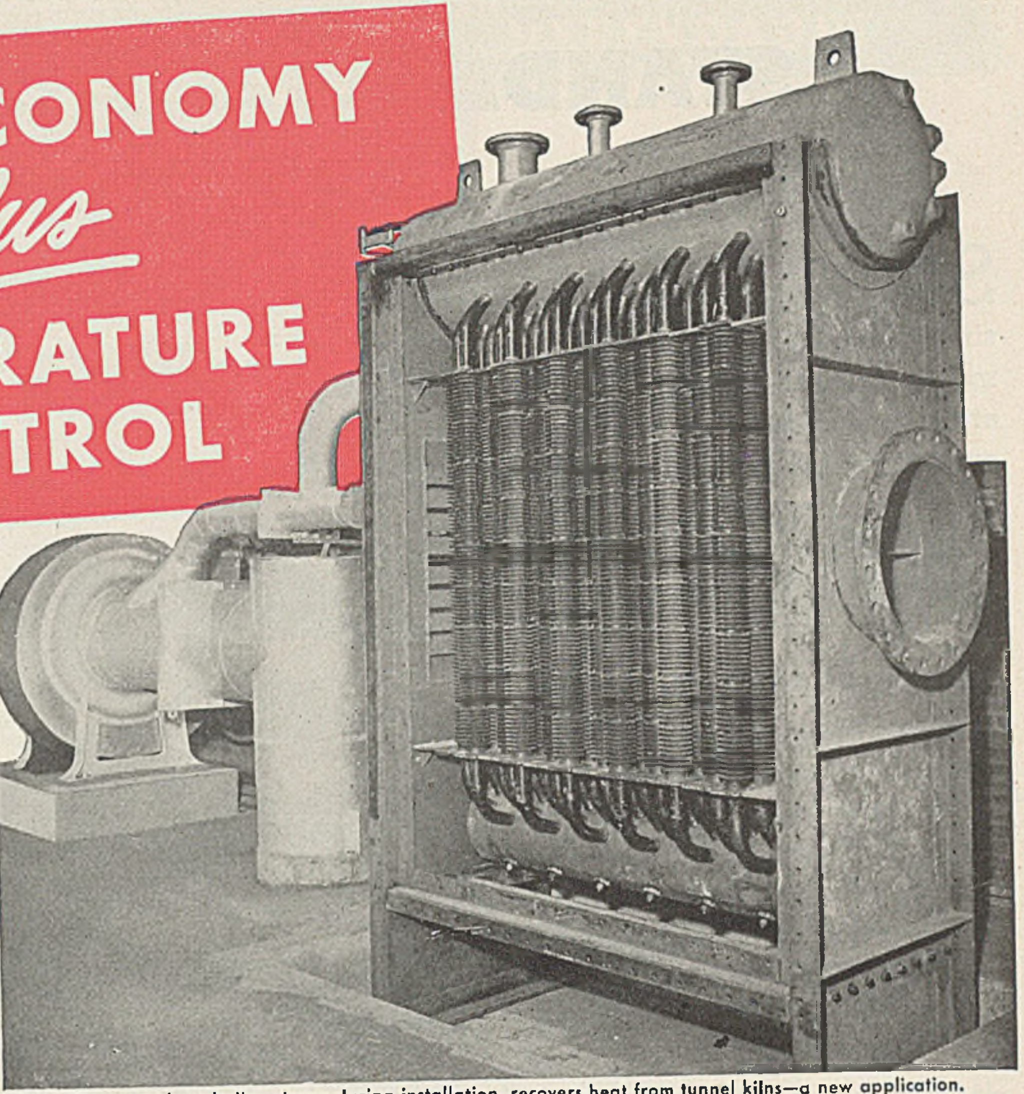
Red Lead
Litharge
Sublimed Litharge
Orange Mineral
White Lead Carbonate
Sublimed White Lead
Zinc Oxide
Leaded Zinc Oxides
Lithopone
Lead Silicate



THE EAGLE-PICHER COMPANY

EAGLE EP PICHER
Since 1843

GENERAL OFFICES
CINCINNATI (1), OHIO

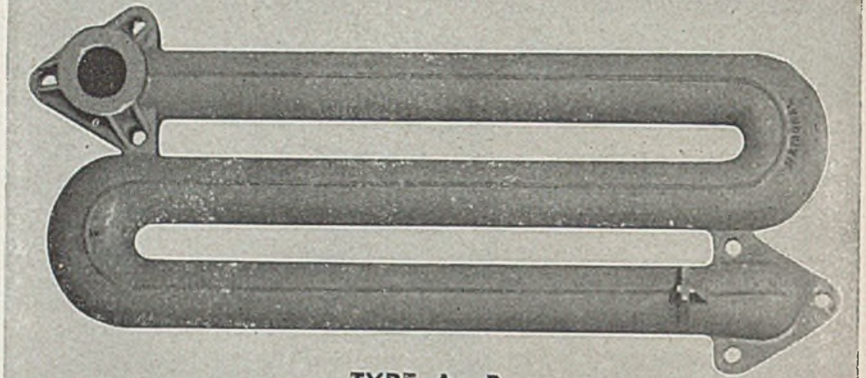


STANDARDIZE with NATIONAL SECTIONS

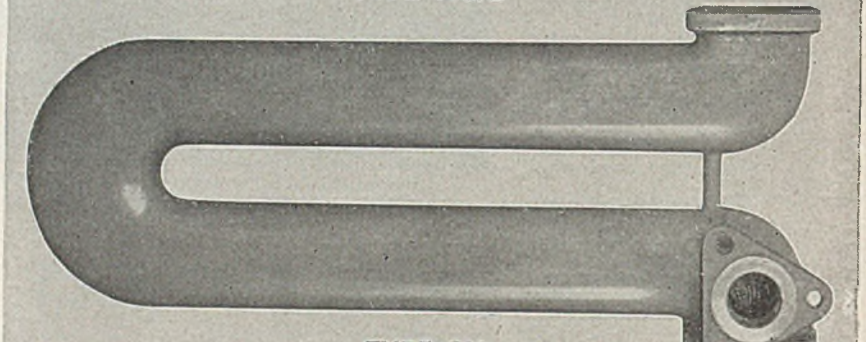
STANDARDIZATION through simplification is the keynote of modern process design and operation. Successful plant executives, engineers and purchasing agents know by experience the advantages and economies to be gained by reduction in the number of sizes and types of process equipment.

National CAST IRON Condensing and Cooling Sections are manufactured in only four basic types. Many of the world's foremost companies in the petroleum, chemical and by-product coke industries now specify and use National CAST IRON Condensing and Cooling Sections, thereby reducing their inventories of spare or replacement parts to a minimum.

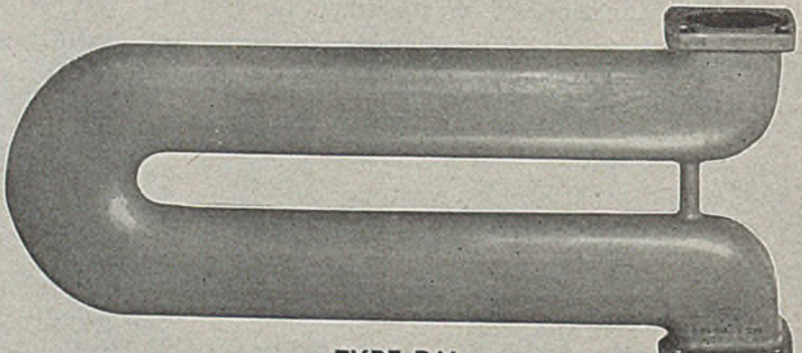
We suggest that you investigate the economies of National CAST IRON Condensing and Cooling Sections. Learn how this standardized process equipment can help solve **your** cooling and condensing problems. National industrial engineers will be glad to consult with you at any time, and without obligation. WRITE FOR CATALOG CP-16.



TYPE A or B



TYPE CM



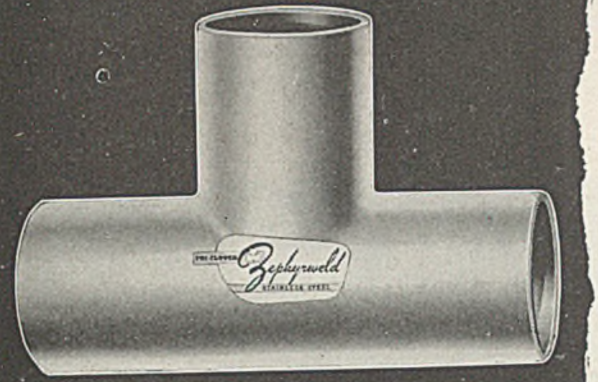
TYPE DM

INDUSTRIAL DIVISION

The National Radiator Company

221 CENTRAL AVENUE . . . JOHNSTOWN, PENNSYLVANIA

TRI-CLOVER OFFERS 3 DEPENDABLE

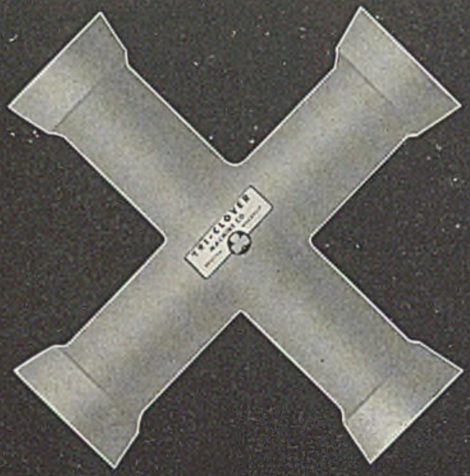


1

Zephyrweld WELDING FITTINGS

. . . in sizes from 1″ thru 18″ O. D., fabricated in gauges from 16 to 10, for use with stainless steel light gauge O.D. tubing, under broad corrosive conditions requiring semi-permanent or permanent welded line installation . . . available in a complete line of ells, tees, crosses, adapters, etc., in stainless steel types 304, 316, 347.

STAINLESS STEEL FITTING TYPES . . .

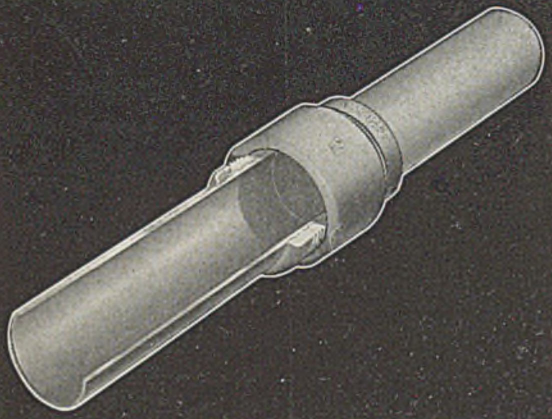


2

FLANGED TYPE Conical End FITTINGS

. . . fabricated from stainless steel type 316 for use with commercial tolerance light gauge tubing having outside diameters from 1″ thru 10.″ Easily assembled with light weight, high strength couplings, which provide an extremely compact, flush, leak-tight union for working pressures up to 250 psi. Complete line of ells, tees, crosses, adapters, etc.

FOR CORROSION-RESISTANT CONVEYING LINES



3

THE WALLACE PIPE UNION*

. . . . fabricated from stainless steel type 316, permits the use of thin wall stainless steel tubing in connection with standard threaded iron pipe size fittings of all kinds . . . saving from 25% to 45% in material without any loss of effectiveness.

*Patent No. 1953665

SEND FOR COMPLETE FACTUAL CATALOGS

All 3 types of TRI-CLOVER fittings are fully described and illustrated in individual catalogs, just off the press. Send for your copies today, mentioning in which of the types you are interested.

Tri-Clover
MACHINE CO.
Kenosha, Wisconsin

TRI-CLOVER

TRIALLOY AND STAINLESS STEEL SANITARY FITTINGS, VALVES, PUMPS, TUBING, SPECIALTIES

FABRICATED STAINLESS STEEL INDUSTRIAL FITTINGS AND INDUSTRIAL PUMPS

THE *Complete* LINE

FOR YOUR INFORMATION

Extremely high detergency under adverse operating conditions

SANTOMERSE No 1

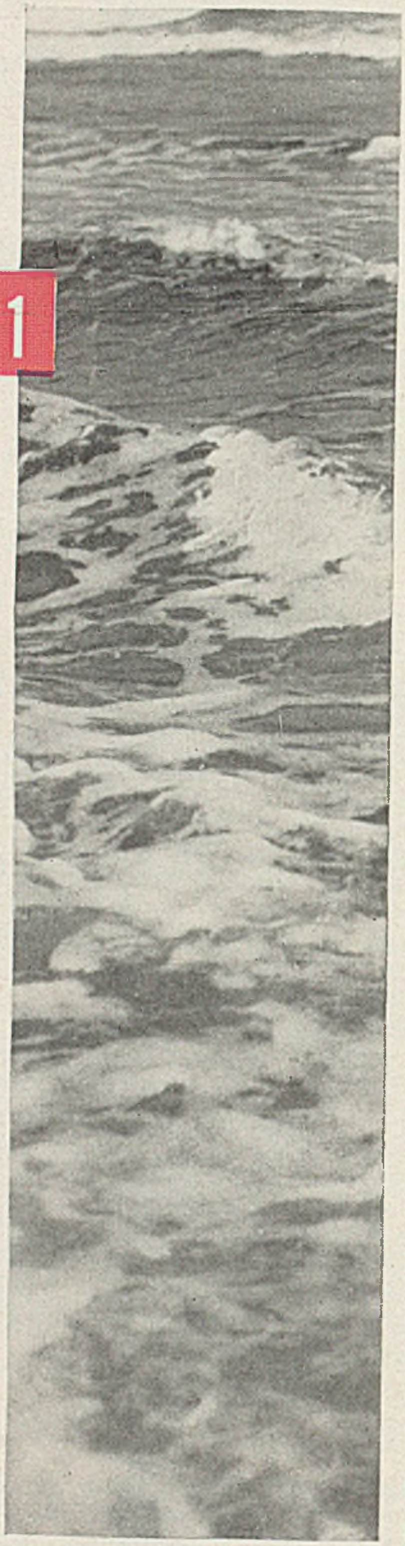
in bead or flake form now readily available

In all cleansing, scouring and washing operations, Santomerse No. 1 — is immediately active in penetrating and loosening soil deposits. As these deposits are freed, they are maintained in suspension, so that subsequent action and rinsing remove soil without redeposition. This multiple detergent action is only one of the many properties of Santomerse No. 1 that makes it the truly modern, all-purpose synthetic detergent and wetting agent.

A prominent characteristic of Santomerse No. 1 is its detersive action in extremely hard water. It is outstandingly effective at any pH in hot or cold solutions.

The washing, wetting, dispersing and emulsifying properties of Santomerse No. 1 — and their superiorities in industrial and household applications — are fully discussed in Monsanto's new Application Data Bulletin No. P-118. Send for your copy — also request additional copies for others in your organization who may be interested . . . Contact the nearest Monsanto District Sales Office, or write to MONSANTO CHEMICAL COMPANY, Phosphate Division, 1705 South Second Street, St. Louis 4, Missouri.

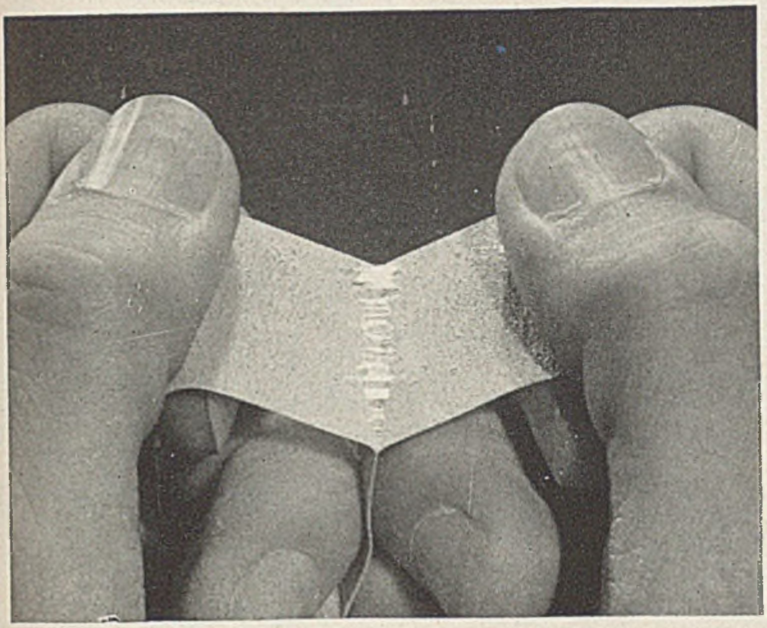
Santomerse: Reg. U. S. Pat. Off.



Check list of a few applications of Santomerse No. 1

- Fruit and vegetable washing
- Automobile cleaning
- Dairy equipment cleaning
- Dishwashing
- Dry cleaning
- Glass cleaning
- Household cleaners
- Commercial laundries
- Household laundries
- Milk bottle cleaning
- Painted surface cleaning
- Railroad car cleaning
- Rug cleaner
- Wall cleaner
- Bubble bath preparations
- Fur processing
- Leather processing
- Metal cleaning
- Cold water paint manufacture
- Paper manufacture
- Paper stock de-inking
- Cotton dyeing, bleaching and finishing
- Rayon dyeing, bleaching and finishing
- Silk dyeing, bleaching and finishing
- Nylon dyeing, bleaching and finishing
- Jute, straw, hair and feather processing
- Wool processing
- Wallpaper remover

News of Monsanto Chemicals and Plastics for the Process Industries..September, 1947



IMPROVED ADHESION

Monsanto Toluene Sulfonamid-Type Plasticizers and Resins

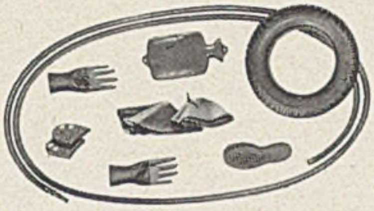
If you are looking for plasticizers to increase the adhesion of your coating or to make adhesives of the solvent or heat-sealing type, you should consider Monsanto's sulfonamide plasticizers and resins. They offer improved adhesion in combination with a large variety of resins. In addition, they give excellent plasticizing value.

One of the unique properties of these sulfonamids is their compatibility with thermo-setting resins. In addition, they are compatible with proteins such as casein, zein, soybean protein, hide and bone glue—synthetic rubbers such as butadiene and acrylo nitrile—cellulose derivatives, polyvinyl acetate and polyamids.

While some Monsanto plasticizers are not yet commercially plentiful, others are becoming more available. In any case, it is quite possible that Monsanto can offer valuable suggestions on different phases of your present or contemplated plasticizer and resin applications. Contact the nearest Monsanto Office, or address Organic Chemicals Division, MONSANTO CHEMICAL COMPANY, 1705 South Second Street, St. Louis 4, Missouri.

SEND FOR SAMPLES OF THESE MONSANTO PLASTICIZERS

Santicizer* 3, Santicizer 8, Santicizer 9, Santolite* MS (80%), Santolite MHP, Santolite K5H, Aroclors,* Dibutyl Phthalate, Diethyl Phthalate, Dimethyl Phthalate, Diphenyl Phthalate, HB-40, Ortho-Nitrobiphenyl, Santicizer 1-H, Santicizer B-16, Santicizer E-15, Santicizer M-17, Santicizer 140, Triphenyl Phosphate, Tricresyl Phosphate.



Monsanto Rubber Chemicals

At Akron, Ohio, Monsanto maintains its Rubber Service Laboratories, the scene of continuing experiments to determine improved techniques for the application of the following Monsanto chemicals widely used in natural, synthetic and reclaimed rubber stocks:

ACCELERATORS
Santocure*
El-Sixty*
Ureka*
Ureka C
Ureka Blend B
Thiotax (2-Mercapto benzo thiazole)
Thiofide* (2,2' dithio-bis benzo thiazole)
A-10
A-19*
A-32
A-77*
A-100
Diphenylguanidine (D.P.G.)
Guantal*
R-2 crystals
Pip-Pip
Thiurad* (Tetra methyl thiuram disulfide)
Ethyl Thiurad (Tetra ethyl thiuram disulfide)
Mono Thiurad* (Tetra methyl thiuram mono sulfide)
Methasan* (Zinc salt of dimethyl dithiocarbamic acid)
Ethasan* (Zinc salt of diethyl dithiocarbamic acid)
Butasan* (Zinc salt of dibutyl dithiocarbamic acid)

ANTIOXIDANTS
Flectol* H
Santoflex* B
Santoflex BX
Perflectol*
Santowhite*
Santovar* A

MISCELLANEOUS MATERIALS
Thiocarbanilide ("A-1")
Insoluble Sulfur "60"

WETTING AGENTS

STABILIZERS

COLORS

REODORANTS

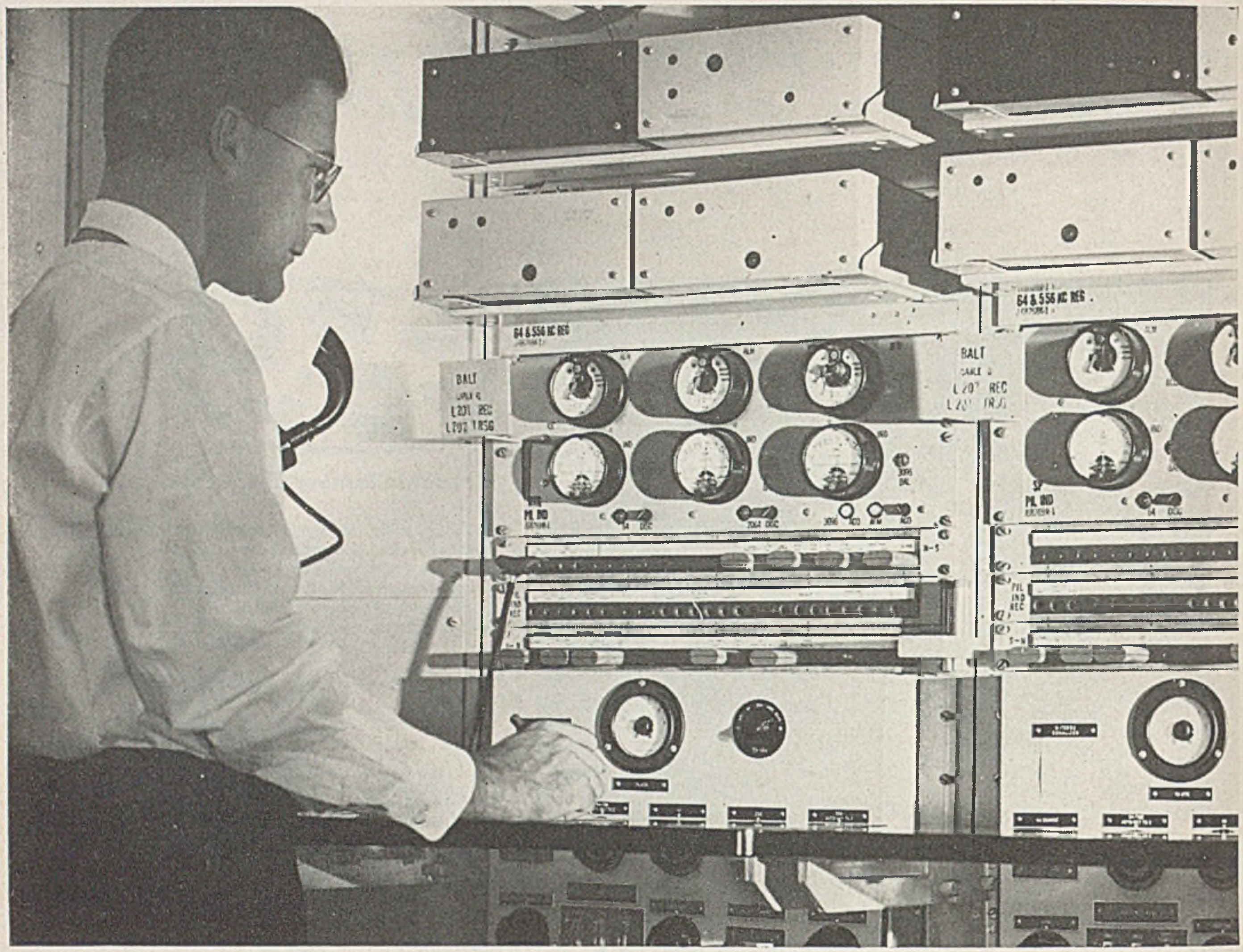
For complete information on any of these Monsanto products, or experienced assistance in your particular rubber chemical problems, address: MONSANTO CHEMICAL COMPANY, Rubber Service Dept., Second National Bldg., Akron 8, Ohio.

*Reg. U. S. Pat. Off.

MONSANTO
CHEMICALS AND PLASTICS

SERVING INDUSTRY ... WHICH SERVES MANKIND

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



At Philadelphia, a testboard man answers as an electronic watchman calls attention to conditions on one of the coaxial systems to Baltimore and Washington.

"Send Help to Manhole 83"

Strung out along every Bell System coaxial cable, electronic watchmen constantly mount guard over your voice. Some are in manholes under city streets; some are in little huts on the desert. Most situations they can deal with; if things threaten to get out of hand, they signal the nearest testboard.

Principal care of the electronic watchman is the transmission level. Sun-warmed cables use up more energy than cold ones, so a transcontinental call may take a millionfold more energy to carry it by day than by night. Each watchman — an electronic regulator — checks the transmission level and adjusts the amplification which sends your voice along to the next point. Many hundreds of regulators may be at work on a single long distance call.

Without automatic regulation, the precise control of energy in the Bell System's long distance circuits would be a superhuman task. So Bell Laboratories, which in 1913 developed the first high vacuum electronic amplifier, went on to devise the means to make them self-regulating in telephone systems. This is one reason why your long distance call goes through clearly, summer or winter.

BELL TELEPHONE LABORATORIES

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

PLASTICS are what you make 'em! There are plastics like leather, like rubber, like metal and like silk, that are better than nature's own materials for their specific purposes. Many of these plastics are made with basic coal-tar chemicals for which Barrett is a key source of supply.

This advertisement in The Saturday Evening Post features Barrett plasticizers and shows how the plastics industry contributes increasingly to the comforts and conveniences of life in America.

HOW BARRETT SERVES THE PLASTICS INDUSTRY: Barrett is a key source of supply for Dibutyl Phthalate and other plasticizers used in the manufacture of plastics for raincoats, luggage, handbags, umbrellas, shoes, chair, floor and wall coverings, and hundreds of other products from motor parts to costume jewelry. Barrett also supplies the Plastics Industry with Phenols, Cresols, Phthalic Anhydride, Cumar* resin and other chemicals widely used in plastics of many varied types. These and other important Barrett products establish Barrett as **ONE OF AMERICA'S GREAT BASIC BUSINESSES.**

Barrett

THE BARRETT DIVISION
ALLIED CHEMICAL & DYE CORPORATION
40 Rector Street, New York 6, N. Y.

BARRETT CHEMICALS FOR INDUSTRY

Phenols
Cresols
Cresylic Acids
Chlorinated Tar Acids
Xylenols
Pickling Inhibitors
Benzol

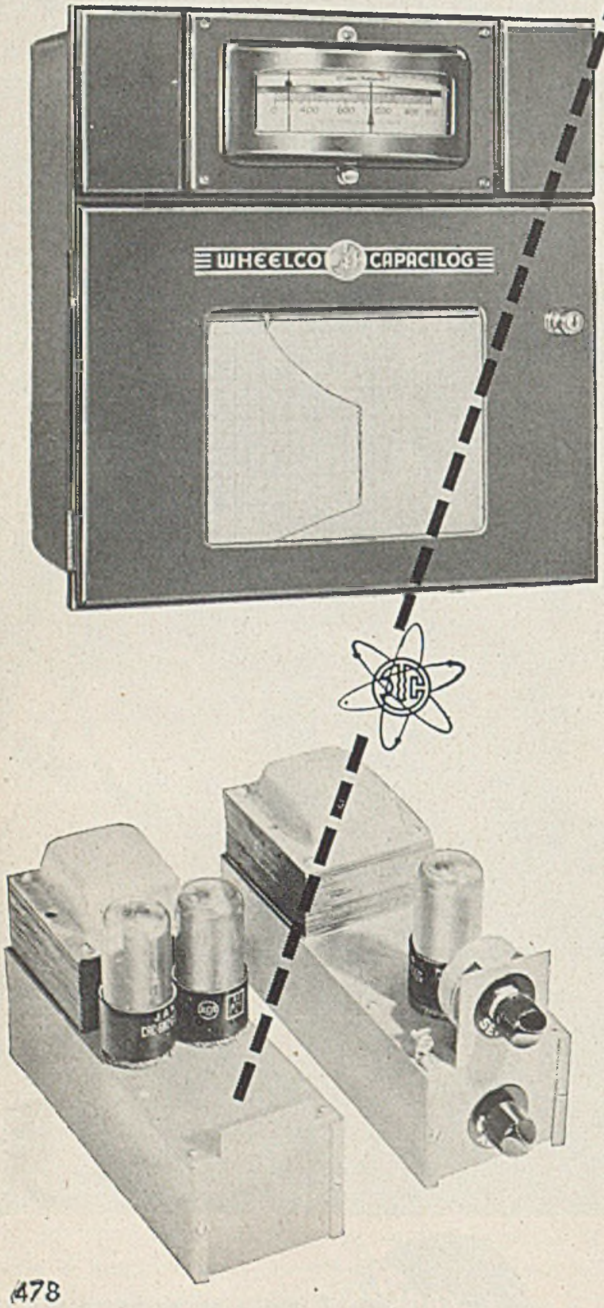
Toluol
Xylol
Naphthalene
Hi-Flash Solvent
Phthalic Anhydride
Dibutyl Phthalate
Dicyclohexyl Phthalate

Plasticizer 50 B
Niacin (Nicotinic Acid)
Pyridines
Picolines
Quinoline
Tar Acid Oils
Neutral Coal-Tar Oils

Creosote Oil
Cumar* Paracoumarone-Indene Resin
Carbonex* Rubber Compounding Material
Bardol* Rubber Compounding Material

Cyclohexanol
Flotation Agents
Anhydrous Ammonia
Ammonia Liquor
Sulphate of Ammonia
Ammonium Nitrate
Arcadian* The *American* Nitrate of Soda

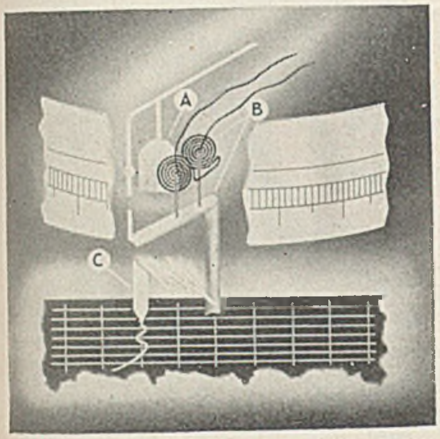
* Reg. U. S. Pat Off.


WHEELCO CAPACILOG

for *Simplified* Recording of Industrial Processes

In the CAPACILOG Wheelco adds the *Recording function* with a positive POWER DRIVEN PEN to the **"Electronic Link"** between Measurement and Control.

No Amplification, Physical Contact or Disturbance in Measuring Circuit—No Converters—No Relays result in Accurate Simple and Instantaneous Response.



Simplicity of Operation

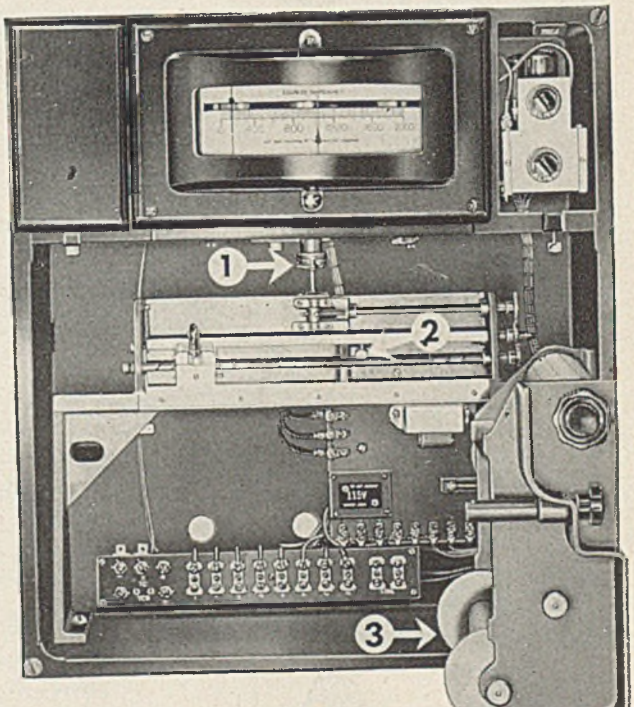
A. Metal Vane, mounted on Indicating Pointer of Measuring System, remains within the field of oscillating current flowing between

B. Two Coils, mounted on Follow-up Arm, driven by a Motor, which also operates double worm gear drive, to cause

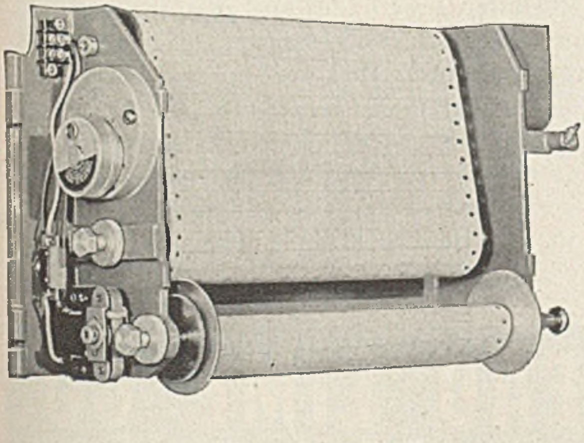
C. Pen to write the permanent record without loss of motion between Measuring and Scribing Systems.

Simplicity of Design

1. Unique coupling allows quick separation of Vertical Shaft for removal of the Plug-in Measuring System.
2. Single Motor drives Scriber mechanism and Vertical Shaft simultaneously, preventing backlash.
3. Swing-out Chart Assembly is hinged to the stand of the Scriber Assembly with two removable stainless steel pins.



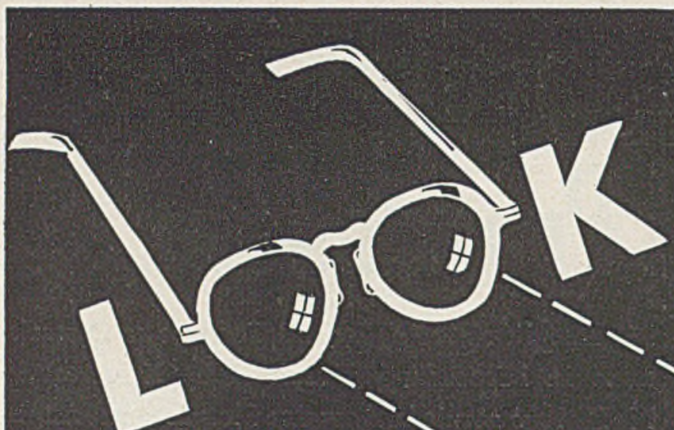
Open View of Capacilog Illustrates Design Simplicity



Backview of Chart Assembly Shows Chart and Reroll Motors

WHEELCO INSTRUMENTS COMPANY EC
847 W. Harrison Street, Chicago 7, Ill.
Please send your literature on the CAPACILOG.

NAME__________ TITLE__________
COMPANY__________
STREET__________
CITY__________ ZONE______ STATE______



at the ANALYSIS for HIGH CALCIUM-LOW IMPURITIES!

CHEMICAL ANALYSIS OF MARBLEHEAD CHEMICAL LIME

	LUMP LIME	"CHEMICALLY PURE" HYDRATED LIME
Calcium as Ca (OH_2)		98.20
Calcium as CaO	97.90	74.40
Silica	.43	.40
Iron and Aluminum Oxides	.45	.44
Sulphur	Nil	Nil
Magnesium Oxide	.52	.35
Ignition Loss	.66	24.34

IT'S the high calcium percentage in Marblehead Chemical Lime that speeds up lime using processes and assures constant, thorough and uniform reaction. But what *isn't* present is equally important. Marblehead is notably low in the impurities that impair quality and slam the brakes on production.

For example, *silica* is harmful in metallurgy and wire drawing. *Sulphur* may show detrimental effects when only 1% is present. *Iron oxide* causes discoloration in the manufacture of glass, leather, paint and varnish. *Alumina* is undesirable in calcium carbide, insecticides and disinfectants. *Magnesia* impairs paper and pulp processes, soap and grease manufacture, water treatment and softening.

Note that Marblehead is relatively free from pernicious substances. It is kept that way by rigid inspections and daily laboratory tests. That's why Marblehead, in any of its four convenient forms, is consistently safe, sure and dependable wherever pure, high quality chemical lime is required.

FOUR FORMS

TRY A CAR NOW IN YOUR OWN PLANT

POWDERED QUICK LIME

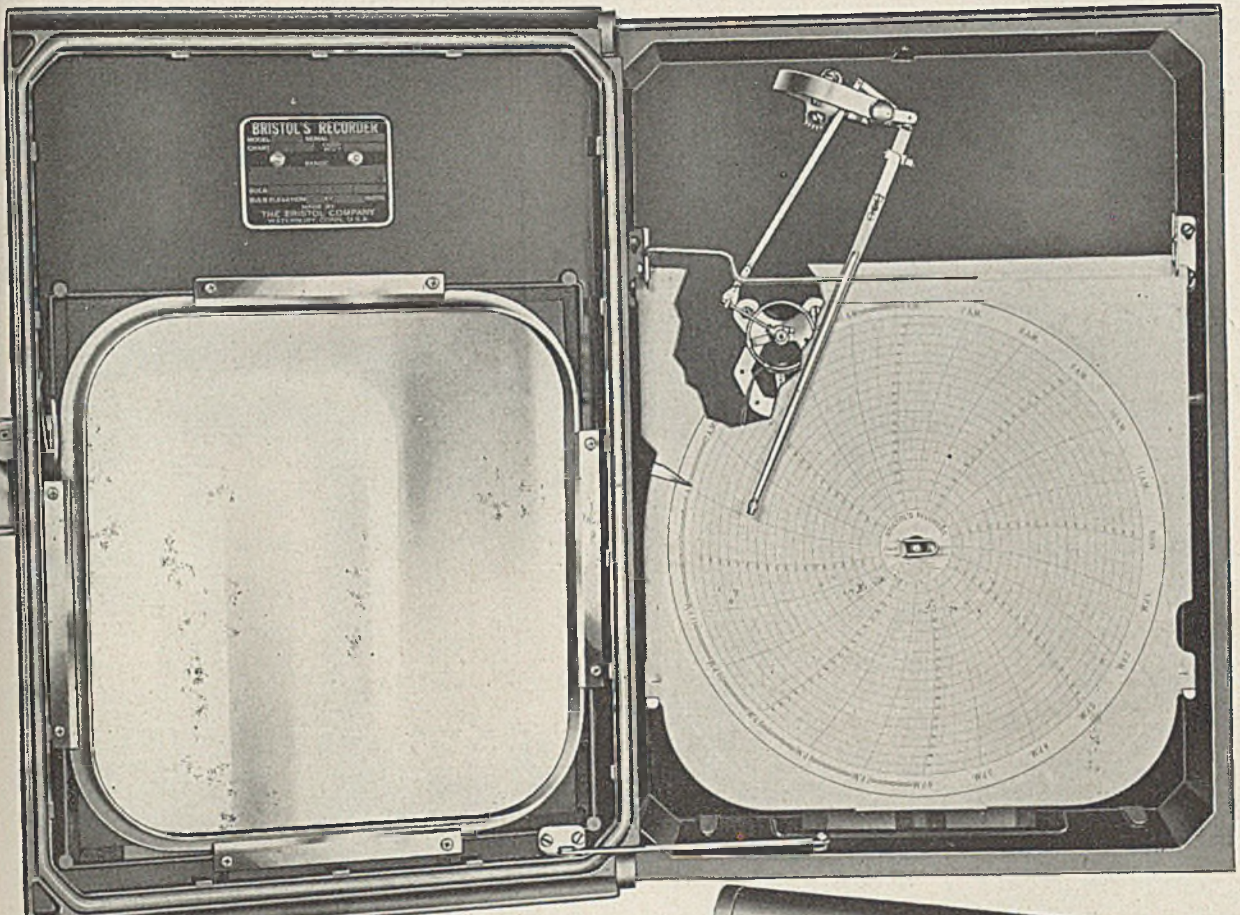
PEBBLE LIME

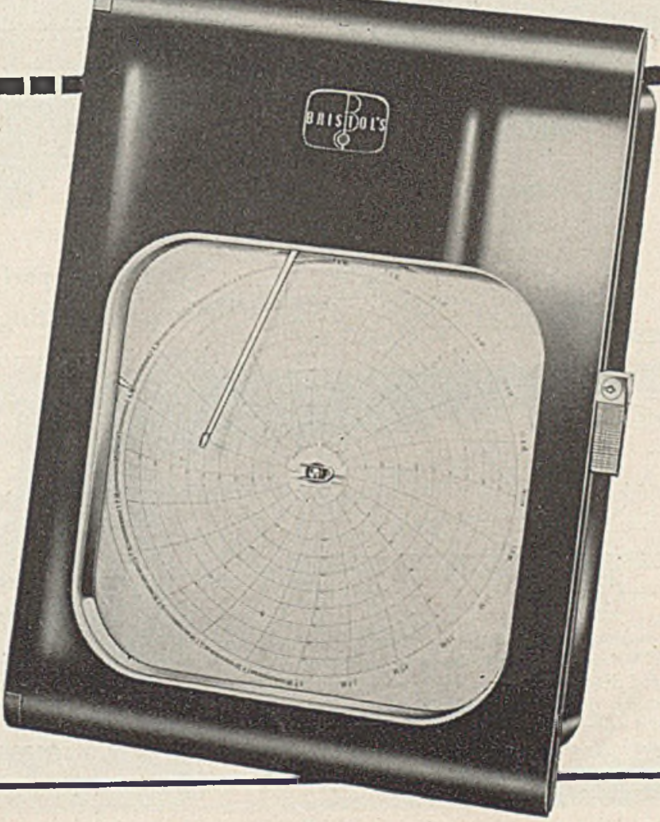
HYDRATED LIME

LUMP LIME

MARBLEHEAD LIME CO.

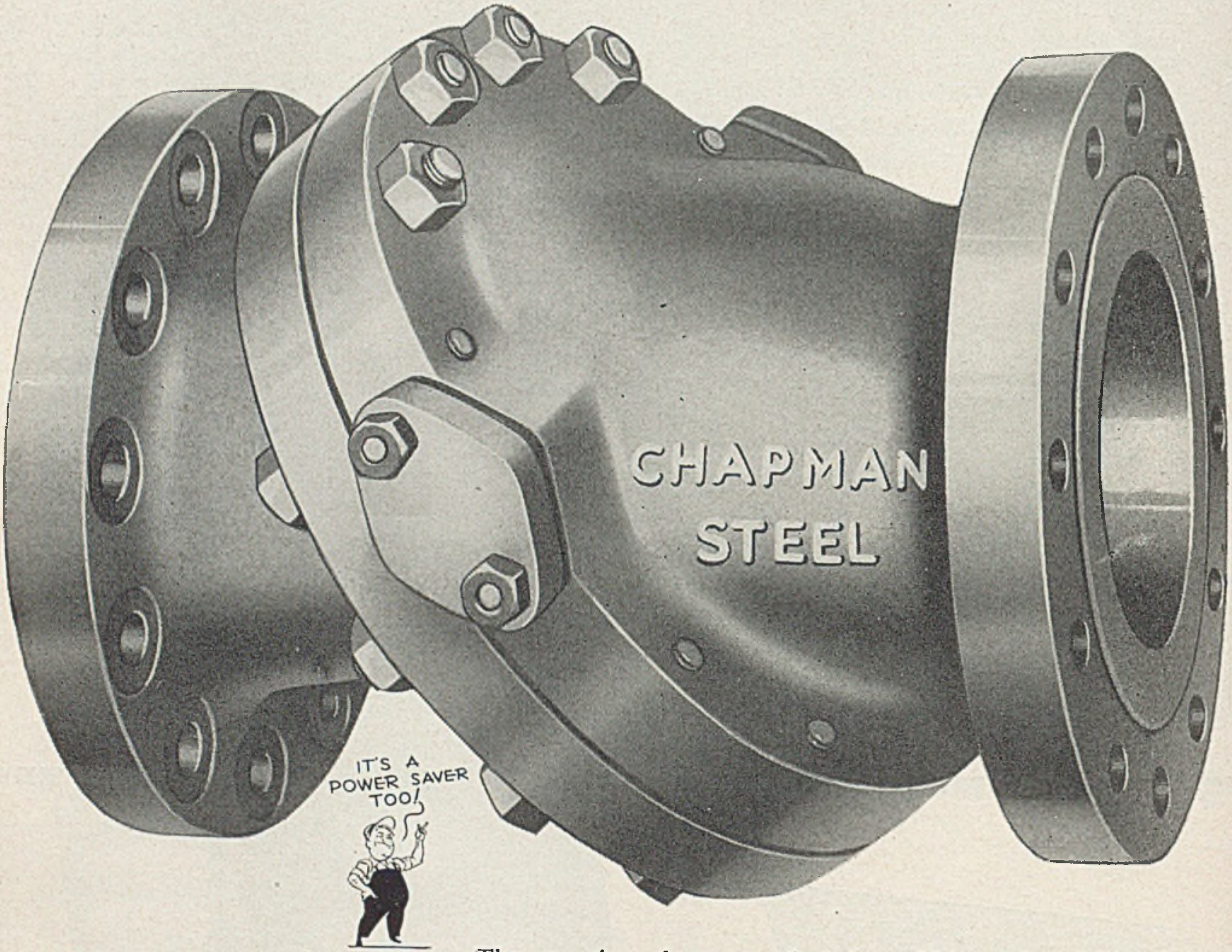
59 EAST MADISON ST. • CHICAGO 2, ILL.

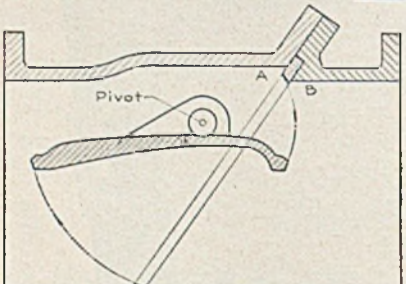

BRISTOL'S RECORDER
THE BRISTOL COMPANY


BRISTOL'S


BRISTOL


TILTING DISC


CHAPMAN STEEL
IT'S A POWER SAVER TOO!


Pivot
A
B


Chapman
CHECK VALVES

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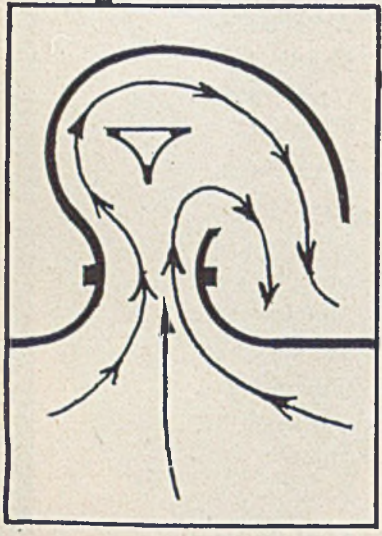
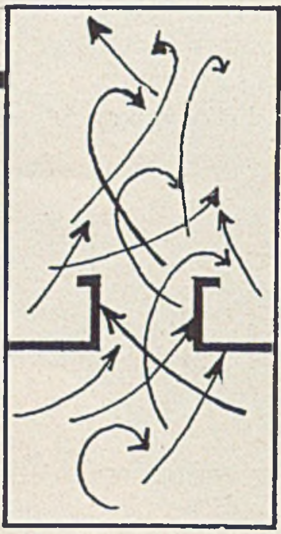
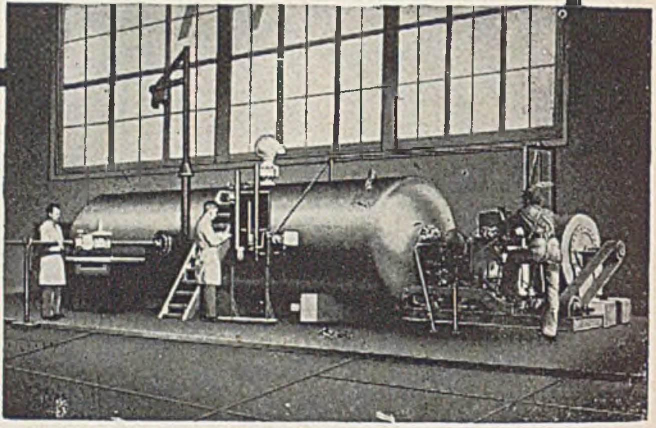
A PERFECTLY DESIGNED TANK VENT VALVE IN FULL OPEN POSITION **WILL FLOW MORE** THAN AN OPEN NIPPLE



Good design channels the flow to smooth streamlined exit.



Excess turbulence friction and back pressure are present due to angularity of design.



"Varec" Testing Laboratory includes what we believe to be one of the largest and most up-to-date capacity finding apparatus in existence. It accurately determines pressure loss and flow capacities up to 500,000 cu. ft. of air per hour. It is here where great engineering studies have been made.

TROUBLE WITH TURBULENCE? Theoretical argument or calculation to the contrary, a perfectly designed tank vent valve, when installed on an open nipple, will ease the exit conditions of flow of the nipple so as to increase its actual flow capacity. Scientific flow tests have proved that the combination of such a valve and nipple will flow *more than the open nipple alone*. By installing a venturi type nozzle instead of a nipple, entrance conditions of flow to such a valve will be greatly eased. Under these conditions the flow capacity of the valve is further increased.

Additional engineering data and other pertinent information about vent valves, tank fittings, etc., will be found in Varec's new P-7 Catalog, a 200 page volume packed full of practical experience and sound technical knowledge.

It is the sincere belief of the Vapor Recovery Systems Company that "Varec" approved Streamlined Tank Vent Valves with expanding passageways and patented hyperbolic inner valves more nearly approach this degree of turbulent-free perfection than other possible designs. Illustrated here is the "Varec" approved Pressure Relief and Vacuum Breaker Valve with Flame Arrester.

Fig. No. 58C

THE VAPOR RECOVERY SYSTEMS COMPANY
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NEW YORK CITY — CHICAGO, ILL. — CLEVELAND, OHIO — HOUSTON, TEXAS — TULSA, OKLA.
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Reprints of this ad for department discussion may be obtained "Varec," Compton, California.

PROVED! More Flow, Less Pressure Loss *with*

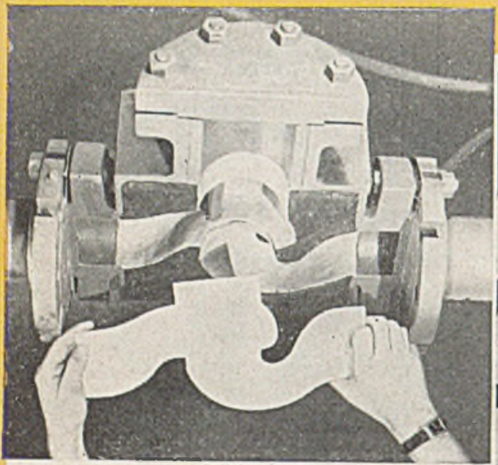
NEW *Edward* STEEL VALVE DESIGNS

To be *sure* that Edward engineers were on the right track in their efforts to cut pressure loss and wear-producing turbulence and to increase flow in new steel valve designs, the Edward laboratories set up an entire new set of research procedures and developed a whole range of new test equipment, much of it not duplicated anywhere.

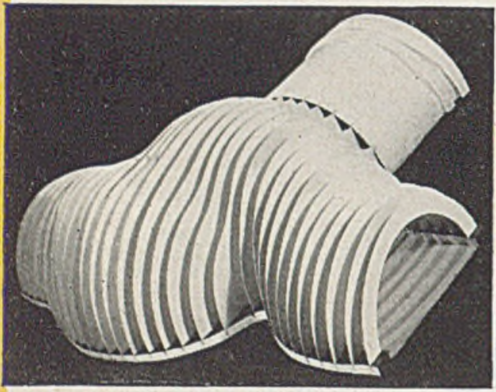
So there's no guessing in the statement that you get up to 30 per cent more flow through new Edward steel valve designs. There's proof aplenty—the evidence of actual field operation and cross-checked laboratory tests . . . the cold facts of pure mathematics, and even the convincing testimony of visual pre-testing.

Here you see plaster casts shaped by half-section plastic valve models. Each model, molded in a steel box and frozen hard, has been flow-tested to develop ideal flow contours. To compute flow test results Edward technicians even developed completely new slide rules, like the one shown. The plaster casts serve as masters from which sectional models and then the actual patterns for Edward valve castings are developed.

No valve series has ever been designed with more extensive flow research . . on no other valves is there more proven flow data.



Half section super-streamlined Edward globe valve of plastic is used in flow tests. After ideal contours for high volume and minimum turbulence are established, casts are made of flow passages.



From actual plaster casts, checked against mass of flow data, model cross section templates are built. These guide design of patterns for Edward steel valve body castings.

Edward Valves, Inc.

SUBSIDIARY OF ROCKWELL MANUFACTURING CO.
EAST CHICAGO, INDIANA

As We See It . . .

Much Ado about Next to Nothing. And no slight intended! For high vacuum operations present problems worthy of the best talent. In our first article Morse reviews recent developments; he convincingly supports the confident statement that "high vacuum is now at the state of advancement where the problems of vacuum per se are usually secondary to other questions of the process. No longer need the engineer assume that a process is economically or technically unsound merely because it involves the use of free air pressures below 100 microns, even in conjunction with valves and vacuum-tight shafts, or temperatures ranging from −100° to +1000° C." Morse refers to some of the vacuum requirements of the atomic energy program, discusses vacuum distillation and metallurgy, and describes several industrial scale applications of high vacuum for drying operations in penicillin manufacture and orange powder production. Numerous photographs and charts accompany the article.

Morse's paper should prove a good background to indicate the scope of a 2-day symposium scheduled for October 30 and 31 to be held in Cambridge, Mass. The symposium, sponsored jointly by the National Research Corporation and the A.C.S. Division of Industrial and Engineering Chemistry, is divided into the following five sections: Scientific Aspects of High Vacuum, High Vacuum Engineering, Vacuum Distillation, Vacuum Metallurgy, and Vacuum Dehydration. Objective of the symposium is to stimulate discussion among technical people concerned with industrial applications of high vacuum, and attendance is limited to this group.

Acid from Apples. In 1945 Buck and Mottern told us how malic acid could be separated from apple juice by adsorption on an anion exchanger, a desirable procedure in the manufacture of bland apple sirup. On page 1087 of this issue they describe a method for its recovery from the exchanger. The by-product can be used as a food acidulant for preparations where its presence is appreciated more than in apple sirup.

Low Flow Know-How. Piret, James, and Stacy tell how water velocities as low as 0.02 foot per second can be measured to an accuracy of about 2%. A fine wire, electrically heated, is the sensitive element in the rig. The experimental work was initially inspired by the desire to develop a device more suited than the Pitot tube for measurement of low velocities; however, by the time the investigation had been resolved into the article presented here, our reviewers considered that its greatest value lay in the fundamental contributions the authors had made to our knowledge of heat transmission. Results are compared with those of previous investigations, and equations are developed.

Plastics Dope. What sulfonamide plasticizers do to resins is reported by Bergen and Craver starting on page 1082. The effect on a number of resins is measured in such terms as tensile strength, elongation, water permeability, and flexibility. Our reviewers rate the contribution as containing many useful data on a subject of timely interest.

Tall Drink. The lengths to which investigators will go to trap a fact is aptly illustrated by Mair, Gaboriault, and Rossini (page 1072). They start in a laboratory penthouse and finish in a basement four stories below with experiments on a 52-foot adsorption column $^3/_4$ inch in diameter and filled with silica gel. Adsorption has been utilized for hydrocarbon analysis in previous work. The report given here is an investigation of the fractionating capabilities of the system on hydrocarbon mixtures as a potential process for large scale production. A number of conclusions are stated about the capabilities and limitations of the method, and the relative adsorbability of various hydrocarbons. This paper will be of substantial interest to the petroleum technologist and those interested in the unit operation of adsorption.

Alum By Alcohol. Our second offering in the new pilot plant section is an article by Gee, Cunningham, and Heindl for a process of removing iron from crude alum. The process exploits the fact that pure alum can be precipitated from a solution also containing ferrous sulfate by addition of ethyl alcohol. The 2-ton-per-day continuous pilot plant described here was used in experiments to see how low the critical factor of alcohol loss could be brought in engineering scale operations. Losses of less than 0.5% were attained, but even this was too much to make the process economically feasible under present conditions. Operating data and cost estimates are included.

High pressure valves that are mechanically operated claim the spotlight in Brown's column this month. He first describes motor-driven and hydraulic regulating valves; then he takes up a recent design for pressures up to 6000 pounds per square inch, actuated by the fluid under pressure. The design is limited to nonregulating valves—that is, those either fully open or completely shut. He voices the need for a similar simple high pressure valve with regulating characteristics.

The instrument man, Munch points out, constitutes the reason why instrumentation can benefit a chemical operation. Munch urges members of management not to underestimate the vital assistance which a well-qualified instrument man can give in recommending suitable instrumentation for a new plant, in checking to see that instruments are most efficiently utilized when the plant first begins to function, and in maintaining or improving the instruments when the plant has settled into the routine of day-to-day operation.

Passivation of metals is a phenomenon important to understand in combating corrosion successfully. Fontana describes recent work to indicate that physically adsorbed gas may account for the phenomenon. He also questions the value of "passivating" stainless steel equipment with dilute warm nitric acid, believing that the only effect of this treatment is removal of iron particles embedded in the surface during fabrication.

Pamphlets on management, published by the American Management Association, are recommended by von Pechmann as excellent background material for the chemical executive. He discusses in some detail the contents of pamphlets dealing with labor productivity, the foreman, and suggestion systems.

D. O. Myatt

Progress Report on a new Industrial Chemical

GLYOXAL

1856 GLYOXAL FIRST SYNTHESIZED by H. Debus.

1940 NEW PROCESS for the synthesis of glyoxal developed in research laboratories of Carbide and Carbon Chemicals Corporation.

1942 PILOT PLANT QUANTITIES – Sodium bisulfite addition product used as intermediate in synthesis of pyrazine 2, 3-dicarboxylic acid, important wartime anti-pellagra pharmaceutical.

1946 NEW CARBIDE PLANT for the production of glyoxal. Carload shipments made as result of demand created by development of "Sanforset" process for dimensional stabilization of rayon. Fabrios of viscose rayon are made permanently resistant to shrinkage through treatment with glyoxal.

1947 SEPTEMBER – Glyoxal used in increasing number of commercial applications, including insolubilization of binders in printing inks; match heads; and paper sizes. Glyoxal shows promise for many new uses: – in leather tanning; insolubilization of starch; shrinkproofing of cottons; and increasing the wet strength of paper in combination with "Cellosize" hydroxyethyl cellulose.

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Unit of Union Carbide and Carbon Corporation

30 East 42nd Street New York 17, N. Y.

Offices in Principal Cities

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MORE INFORMATION: If you would like technical data on glyoxal––write for Form 5654––please address Department H-9.

"Cellosize" is a registered trade-mark of Carbide and Carbon Chemicals Corporation

September 1947

INDUSTRIAL and ENGINEERING Chemistry

WALTER J. MURPHY, **Editor**

The World Outlook for Scientific Publications

WHEN two or more scientists meet nowadays, the conversation is very likely to turn to the subject of the status of scientific publications. No problem received greater attention at the recent meetings in London of the International Congress of Pure and Applied Chemistry and the International Union of Chemistry. In and out of committee rooms chemists discussed formally and informally the outlook for chemical publications during the next few years. Many suggestions were made, some of which were of a most practical nature; others regretfully must be cataloged as mere wishful thinking.

Chemists the world over correctly feel that research is seriously handicapped at present by a lack of definite knowledge concerning the revival of chemical journals in Europe, particularly in Germany and those countries which were under Axis domination prior to and during World War II. Furthermore, stringent currency and exchange regulations which now prevail in many countries make it difficult, if not wholly impossible, for scientists to obtain anything like an adequate selection of important journals. Science cannot flourish under such adverse conditions.

The July 18 issue of *Science* contains two excellent summaries of conditions of publications in Europe which we strongly recommend to our readers. James S. Thompson, executive chairman of the Board of Directors of the McGraw-Hill Book Company, has written his impressions of the technical book publishing field following visits to eleven countries in Europe and considerable correspondence with informed individuals in several others. Charles H. Brown, associate director of the Iowa State College Library, has reviewed in quite some detail the present status of scientific journals in most of the European countries.

Both writers agree that interest in scientific publications in Europe is at a new high. In war-ravished countries intensive efforts are being made to revive old established journals and many new ones have been started, but insufficient supplies of paper and inadequate production facilities are serious handicaps which will not be eliminated for some time. Not only is paper scarce in Germany and much of that nation's printing equipment destroyed, but the fact that technically Germany is still at war multiplies the difficulties. In addition, the obvious lack of cooperation and coordination between activities in the American and British zones on the one hand, and in the Russian zone on the other, is leading to duplication in a number of instances.

The German picture is not all black by any means. At the meetings in London it was indicated that work on both Beilstein and Gmelin is progressing in a reasonably satisfactory manner when existing conditions are considered. However, it was quite apparent that any hope of English language editions is entirely out of the question for a variety of practical reasons, any one of which would be sufficient to postpone indefinitely plans in this direction. Certain other important chemical compendia are being continued by permission of the occupation forces. It is essential that some degree of supervision of the scientific aspects of this work be provided by a qualified international group of chemists. Fortunately there is now every reason to expect that such direction will be provided. Also, it appears that adequate provision will be made for full consideration of a more modern approach to such problems as nomenclature.

One must be realistic in approaching the question of reviving scientific publications in Europe. No immediate panacea is in the offing. There are those who feel that some international body, for example, UNESCO, should provide the necessary funds. Those who think so do not have any tangible ideas concerning such matters as costs, to say nothing of the operational problems involved in obtaining sufficient quantities of paper and production. This is just one of the many penalties the world is paying and will continue to pay, for years to come; further proof that everyone loses when nations unsheath the sword.

One can easily become very pessimistic concerning the outlook for scientific literature during the next decade. Even in the United States, we are woefully short of paper and production facilities. At this moment, most scientific publications face discouraging delays in publishing current scientific developments. Add to these factors rapidly mounting costs and the fact that the international political outlook is uncertain to say the least, and the picture is a most discouraging one.

Internationally the situation is much worse than it is in this country. In discussing scientific matters with scientists in at least six countries in Europe this summer, the question of paper supplies was raised again and again. Occasionally pleas were made that the United States allocate a portion of its paper for use abroad in publishing scientific data. Whether or not such a plan is feasible is beyond the scope of this discussion. It does indicate, though, the desperate straits in which publishers of scientific literature abroad find themselves.

A certain amount of delay, perhaps several years, in restoring the scientific literature of the world to anything like prewar levels is inevitable. But even this objective is inadequate, because research today is being carried on in the United States and elsewhere at a rate far in excess of that which existed prior to 1939. One need but look at the respective print orders for American Chemical Society journals in 1939 and 1947 and also to note the increase in the number of papers being presented now at Society meetings as compared to 1939, to understand the demands that now exist on the paper supplies and production facilities of the American Chemical Society.

A limited world capacity for publication is perhaps the greatest barrier to the rapid strides in science in the near future. What, if anything, can be done to meet this situation in this country and the even more desperate one which hangs like an ominous black cloud over scientific Europe at the present time? Scientists cannot continue indefinitely to operate successfully in a partial vacuum. Our success in restoring the normal, healthy, international exchange of scientific knowledge is now limited by such prosaic but tangible restrictions as paper supplies, printing facilities, artificial currency exchange barriers, and an unfavorable international political outlook. Surmount them, and the spirit of international cooperation that has always existed among investigators can be counted upon to supply the lifeblood of data to keep the body of world scientific knowledge vigorous and growing.

HIGH VACUUM TECHNOLOGY

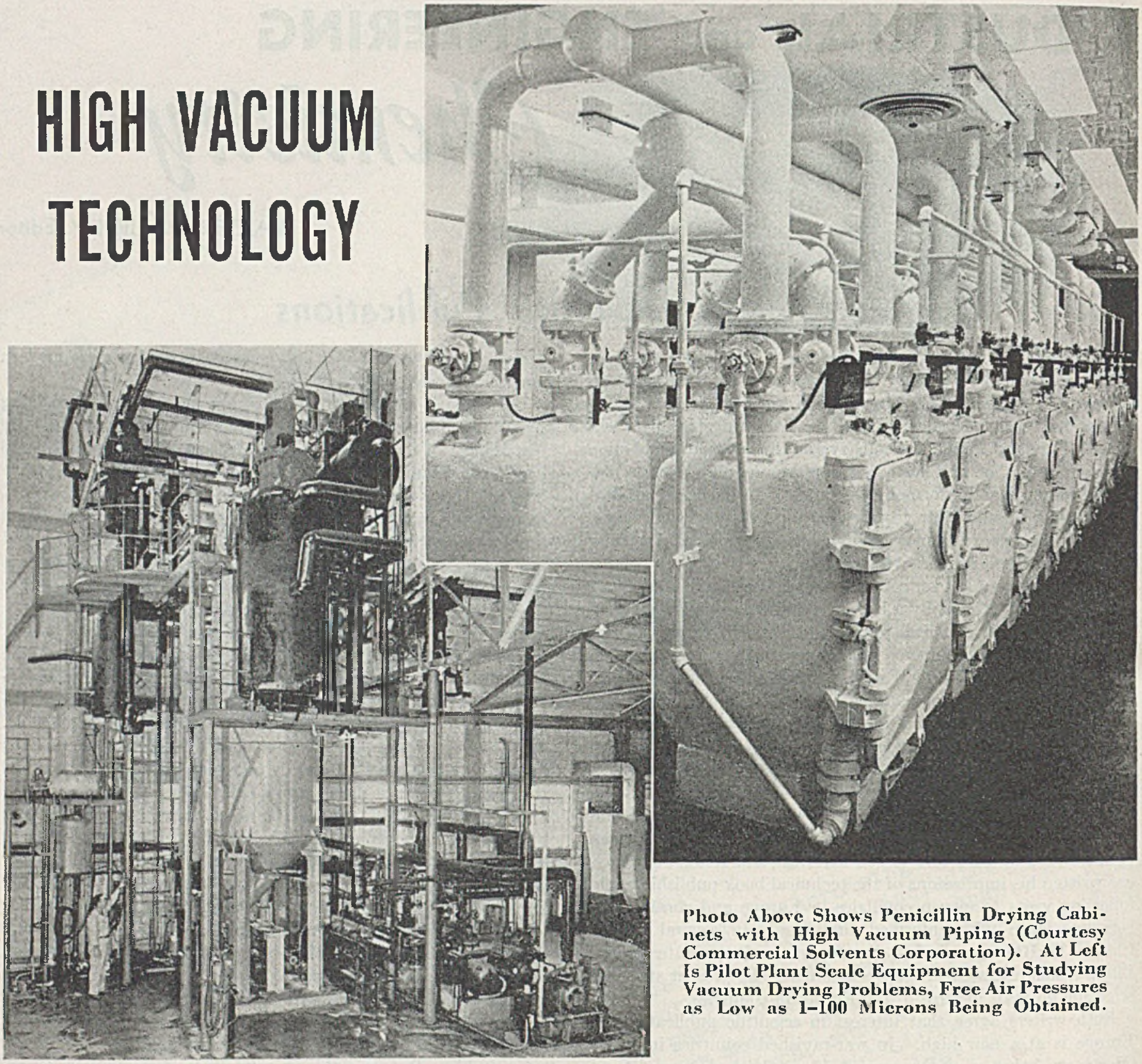


Photo Above Shows Penicillin Drying Cabinets with High Vacuum Piping (Courtesy Commercial Solvents Corporation). At Left Is Pilot Plant Scale Equipment for Studying Vacuum Drying Problems, Free Air Pressures as Low as 1–100 Microns Being Obtained.

RICHARD S. MORSE

NATIONAL RESEARCH CORPORATION, CAMBRIDGE 42, MASS.

PRIOR to 1940, high vacuum (that is, the use of pressures below 0.1 mm. of mercury) was with minor exceptions limited to laboratory use. The electronics industry commonly exhausted various tubes to 10^{-7} mm., but the volumes involved were small and only noncondensable gases were usually pumped. In the chemical industry the distillation of fatty acids was common at slightly higher pressures. The vacuum distillation of fats and oils was done experimentally in Europe (*4*, *23*) and no doubt reached its greatest development on a commercial scale in this country under Hickman (*10, 11*) and associates, who demonstrated the commercial possibility of producing vitamin concentrates from fish oils by distillation in the micron range of pressures (1 micron or $1\mu = 10^{-3}$ mm.).

During the war, high vacuum techniques were developed to a remarkable degree. Many processes have been commercialized, and it is fair to state that high vacuum is now at the state of advancement where the problems of vacuum per se are usually secondary to other questions of the process. No longer need the engineer assume that a process is economically or technically unsound merely because it involves the use of free air pressures below 100 microns, even in conjunction with valves and vacuum-tight shafts, or temperatures ranging from −100° to +1000° C.

The most recent factor in the advancement of modern vacuum technology has been the atomic energy program. The design and construction of both the gas diffusion and electromagnetic separation process plants for the preparation of U^{235} were achieved in spite of vacuum engineering problems of great magnitude (*21*). In the former, although actual operation was not undertaken at extremely low pressures, air leakage specifications were of fantastic rigidity. The original plant design required that the air leakage to the process stream be maintained less than 0.01 cubic foot at 760 mm. per 1000 cubic feet of plant volume—i.e., an 8-micron-

The present status of high vacuum technology is reviewed, with pictures of recently developed equipment and process plants which employ pressures in the micron range. Discussion is limited to industrial applications of vacuum techniques at 10^{-5} to 10^{-1} mm. in such fields as dehydration, metallurgy, distillation, metal evaporation, etc. Operating data on large diffusion pumps, gages, and steam ejectors are given with respective limitations. Large scale operations are mentioned from the point of view of design and construction to illustrate the fact that, in so far as technical problems of high vacuum per se are concerned, operations of any scale are now feasible.

per-hour rise in pressure at high vacuum. Through the use of the leak detection techniques developed, a pressure build-up in the plant of 2 microns per hour was actually achieved (*14*).

CONSTRUCTION OF EQUIPMENT

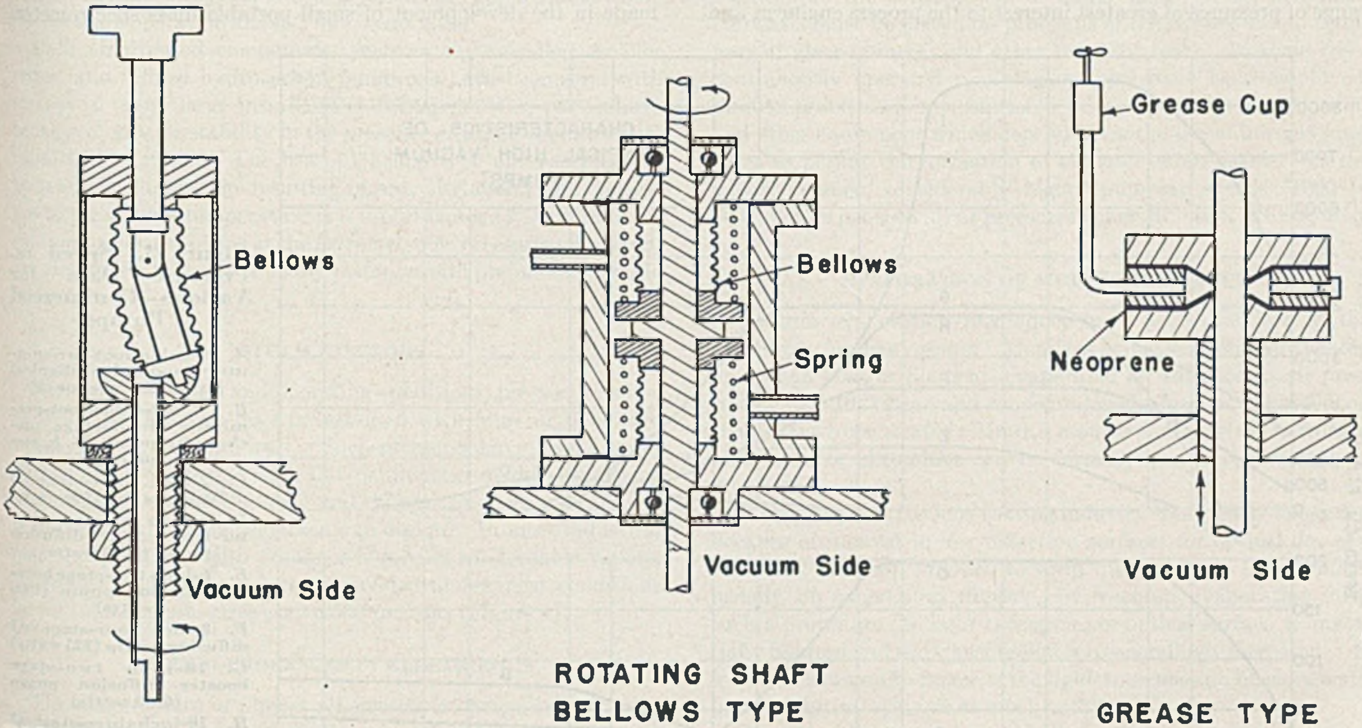
Design problems of the vacuum engineer are many and vary greatly, depending on the process and pressures involved. With present day methods of construction and with pumping speeds available for both condensable and noncondensable gases, there appears to be no limit to the size of vacuum systems which can now be constructed.

Leakage problems usually fall in two categories: (*a*) Small sealed-off systems are common in the electronics industry where pressures below 10^{-7} mm. must be maintained for years. If any leakage or degassing occurs, some form of "pump" in the guise of a "getter" (barium, magnesium, etc.) must be included in the evacuated space to react with and remove any subsequently evolved gases. (*b*) In most processes a certain amount of noncondensable gas leakage, outgassing, or gas or vapor formation may be tolerated, if adequate pumping speed is provided. Leakage may be expressed as a rate of leak or rise in pressure—i.e., in micron cubic feet per hour or microns per hour—for a given apparatus. In studying materials of construction, furnace bricks, etc., from the point of view of outgassing, it is sometimes more convenient to compare products in terms of the time constant for a known rise in pressure after closing off the system.

Special valves are usually required at pressures below 1.0 mm. because of leakage problems. At the lower pressures so-called packless valves are commonly used, the stem movement being incased in a flexible bellows. A somewhat simpler design involves the use of sliding-type stem gaskets (*24*). Considerable attention must also be paid to the design of valve seats; the impedance introduced to gas flow must be kept at a minimum.

Rotating shafts may be introduced into a vacuum system in numerous ways (Figure 1). The use of flexible bellows, for example, offers an interesting means of transmitting limited motion with zero leakage. Various methods for designing self-pumping and externally pumped shaft seals have been developed for use at high speed, which permit transmission of even large amounts of power into any vacuum system, regardless of the pressure or leakage specifications.

The flow of gases and vapors at pressures below 1 mm. must be given special consideration (*15*). Adequate engineering data are now available (*3*) to permit the design of any size equipment, but to date the chemical industry has in many instances failed to realize the fundamental problems involved. It is common practice to employ a combination of the Fanning equation (*16*) and friction graph for Reynolds numbers above 2100, or Poiseuille's law for Reynolds numbers below about 1000. In the micron range, however, Poiseuille's law does not apply, and the effective viscosity may be less than 1% of the gas viscosity as given in the handbooks.



ROTARY BELLOWS SEAL

ROTATING SHAFT BELLOWS TYPE VACUUM SEAL

GREASE TYPE SLIDING SEAL

Figure 1. Three Basic Methods Which May Be Used in the Design of Vacuum-Tight Shafts

GAGES

The problems of measuring gas pressures below 1 mm. are not always simple; in general it is safe to assume that no one has the pressure that he either thinks he has or brags about. True gas pressure as measured is always influenced by one or more of the following factors: the mixture of gases, presence of condensable vapors, point of measurement, temperature of the gage, and type of gage (Figure 2).

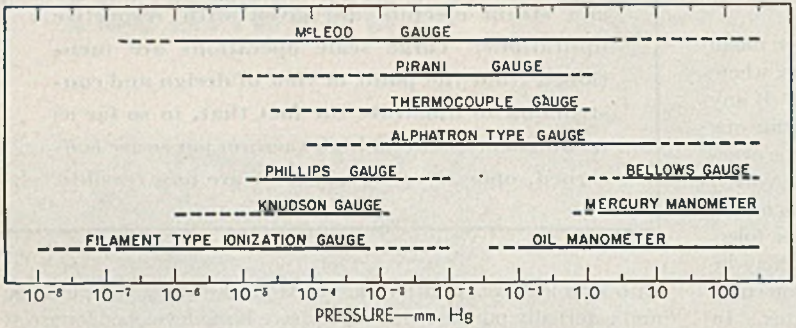


Figure 2. Useful Pressure Ranges for Various Types of Vacuum Gages

The McLeod gage continues to be commonly used as a laboratory standard, and the portable tilt type instrument is convenient for industrial uses. Accurate readings are impossible in the presence of condensable gases, and neither rapid reading nor indicating type instruments appear practical.

Both Pirani and thermocouple type gages are very useful as indicating or recording instruments in the micron range. They are relatively economical, but have minor limitations with respect to accuracy, temperature effects, and aging.

The recently developed Alphatron gage operates similarly to an ionization gage, but the ions are formed by alpha particles, and all problems of filament burn-out, temperature effects, etc., are thereby eliminated (*7*). This instrument is capable of covering the range of pressures of greatest interest to the process engineer, and it is not affected by the presence of vapors. It has the limitations inherent to the sensitive direct current amplifier which is essential to indicate ion current.

The ionization gage indicates pressure as a function of the number of positive ions formed in a three-electrode type of tube. Such instruments are common for the measurement of pressures below 10^{-3} mm. and under special conditions are considered reliable, or at least consistent, for pressures as low as 10^{-7} mm.

Phillips type gages have long been used in Europe and have recently been developed here (*19*) for measurement in the micron range. Pressures are indicated as a function of the resulting current during gas discharge, under applied voltage, and the control circuits involved are relatively simple.

LEAK DETECTION

As larger equipment has been developed for uses below 1 mm. pressure, improved leak detection techniques have been of prime importance. The following methods are most commonly employed.

High Voltage Discharge. In the case of glass apparatus, a high voltage corona discharge is applied near the suspected surface, and small pinholes are easily detected by a change in color of the glow discharge within the system.

Acetone Spray Technique. The system, either glass or metal, is exhausted to 1 mm. or lower, and readings are observed on a thermocouple or Pirani gage. Acetone, ether, or other solvent is sprayed on suspected surfaces, and an apparent change in pressure will be noted, either to a higher or lower value, depending on the solvent's action at the individual leaks. Comparable results may be obtained with helium or hydrogen. At lower pressures (10^{-5} to 10^{-3} mm.) an ionization gage may be used in a similar manner, and an Alphatron permits such an operation throughout both the micron and millimeter ranges of pressure.

Mass Spectrometer. During the war, primarily because of vacuum testing problems at Oak Ridge, Tenn., great strides were made in the development of small portable mass spectrometers

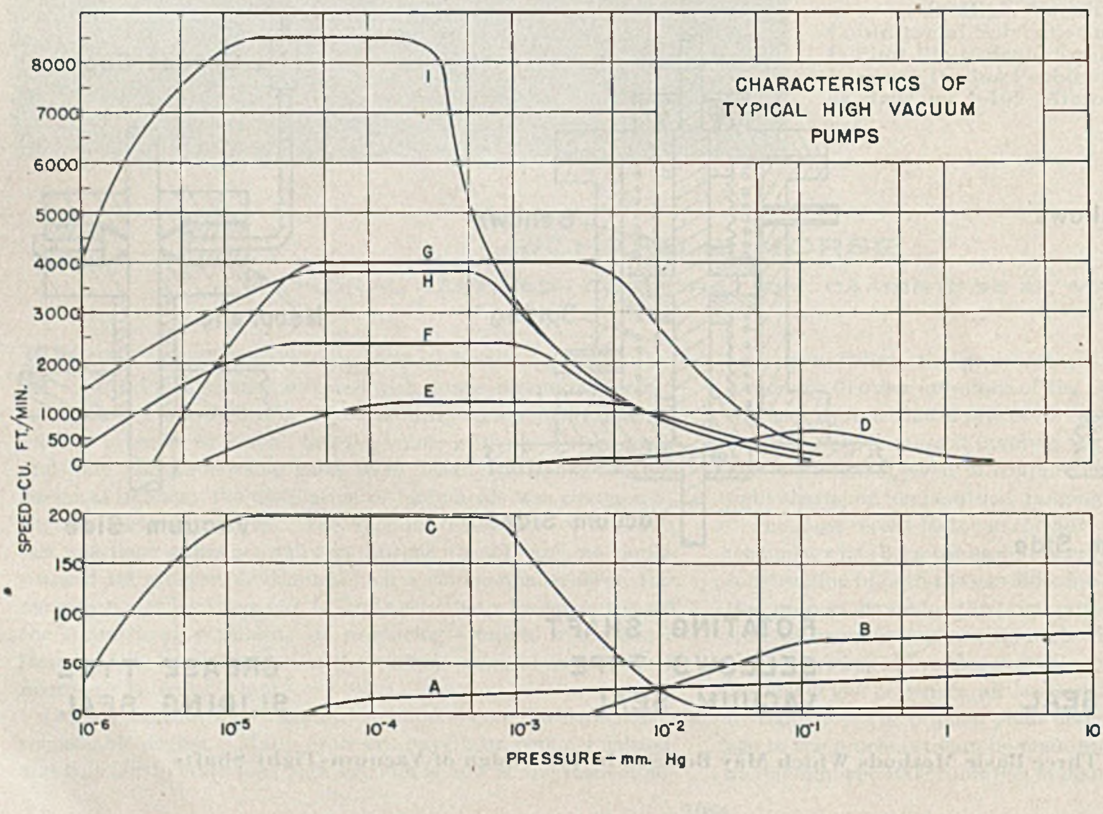


Figure 3. Speed *vs.* Pressure Data for Various Commercial Pumps

A. 50-cubic-foot-per-minute compound mechanical pump (2 horsepower)

B. 100-cubic-foot-per-minute single-stage mechanical pump (5 horsepower)

C. 2-inch three-stage oil diffusion pump (200 watts)

D. 6-inch one-stage ejector-type oil diffusion pump (6000 watts)

E. 6-inch two-stage booster diffusion pump (4000 watts)

F. 8-inch four-stage oil diffusion pump (225 watts)

G. 10-inch two-stage booster diffusion pump (6000 watts)

H. 10-inch three-stage oil diffusion pump (2250 watts)

I. 16-inch three-stage oil diffusion pump (2250 watts)

(*18*). A portion of the gas within the system under test is passed through a mass spectrometer tube designed for maximum response to helium. As a helium probe is passed over the leaking portion of the equipment, extremely sensitive and rapid response is obtained in the output amplifier of the spectrometer tube. This is the most sensitive leak detection method now known, indicating the presence of 1 part of helium in 250,000 of gas at 10^{-4} mm.

DIFFUSION PUMPS

With the exception of molecular drag pumps which are used in some foreign laboratories, diffusion pumps are now universally employed for the attainment of pressures below 10^{-3} mm. on a large scale. Recent trends have demonstrated the possibility of improving the forepressure characteristics of pumps through the use of high boiler pressures and improved jet design. It is now apparent that the limit on gas handling capacity of a diffusion pump below 10^{-4} mm. is in reality only a function of the "pumping speed" of the entrance to the mouth of the pump (Figure 3).

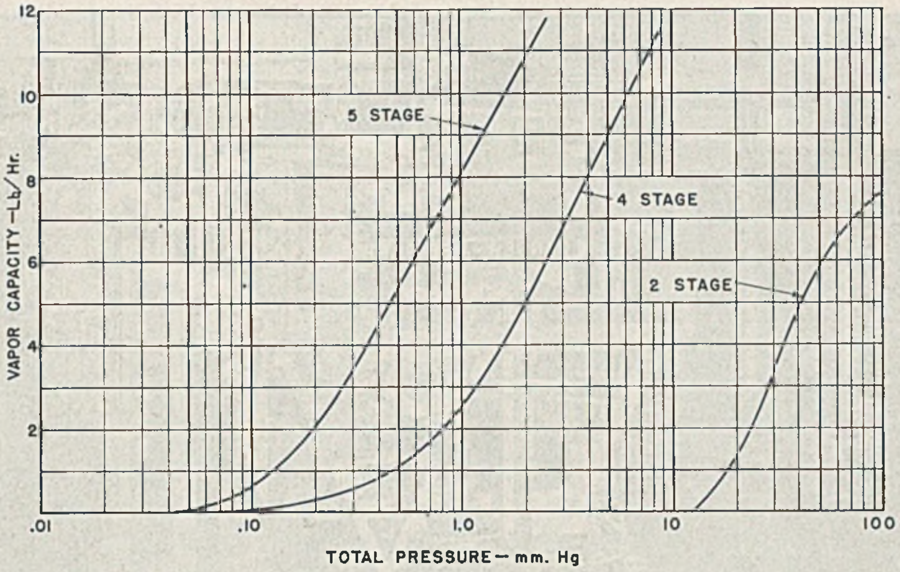


Figure 4. Speed *vs.* Pressure Data for Three Representative Commercial Steam Ejectors

Oil diffusion pumps, 32 inches in diameter with a capacity of over 30,000 cubic feet per minute at 10^{-5} mm., have been built in great numbers. Although this is a large volume at the pressures involved, the actual efficiency in terms of power consumption or investment is ridiculous when one considers that less than 0.0004 cubic foot per minute of gas is being handled at atmospheric conditions.

With newer ejector type oil-diffusion pumps (*13*) greater speeds are now possible in the higher micron range. With minor exceptions the use of mercury in diffusion pumps in this country is now limited to laboratory apparatus or electronic applications where forepressure operation above 1 mm. is essential.

Both chlorinated compounds, such as the so-called Aroclor series, and refined hydrocarbon pump oils have been used with success in many large installations during the war, particularly because of greater stability in the presence of water vapor and because of lower cost. The use of silicone type oils has recently been advanced, and the resulting improved stability after exposure to air at high temperature is a useful factor (*2*). Because of contamination problems at the extremely low pressures employed, the electronics industry in many instances still prefers the organic esters.

STEAM EJECTORS

With proper design and operating conditions, pressures as low as 10 to 100 microns may be attained with four- or five-stage steam ejectors under no load. Such pressures have been accomplished by careful installation and maintenance of ideal conditions with respect to steam quality and diffuser temperatures, rather than by any unique developments in design. In most industrial plants, particularly with processes involving condensable vapors, steam ejector systems are recommended under most conditions for all total gas pressures above 500 microns (Figure 4).

VACUUM PROCESSES IN ELECTRONICS

The manufacture of almost all electronic devices—photocells, rectifiers, radio tubes, x-ray tubes, etc.—involves operations at very low pressures (i.e., less than 10^{-7} mm.) to prevent ionization. Pressures above 1 micron are used on a large scale for the production of light bulbs, fluorescent lights, neon lights, small receiving tubes, etc. Developments in vacuum technique by the electronics industry have not been radical but have centered about the development of automatic machinery for mass production. For pressures below 1 micron, small oil-diffusion pumps without cold traps are now commonly employed except where the extremely good stability of mercury as a pumping medium is a necessity because of the exhaust cycle.

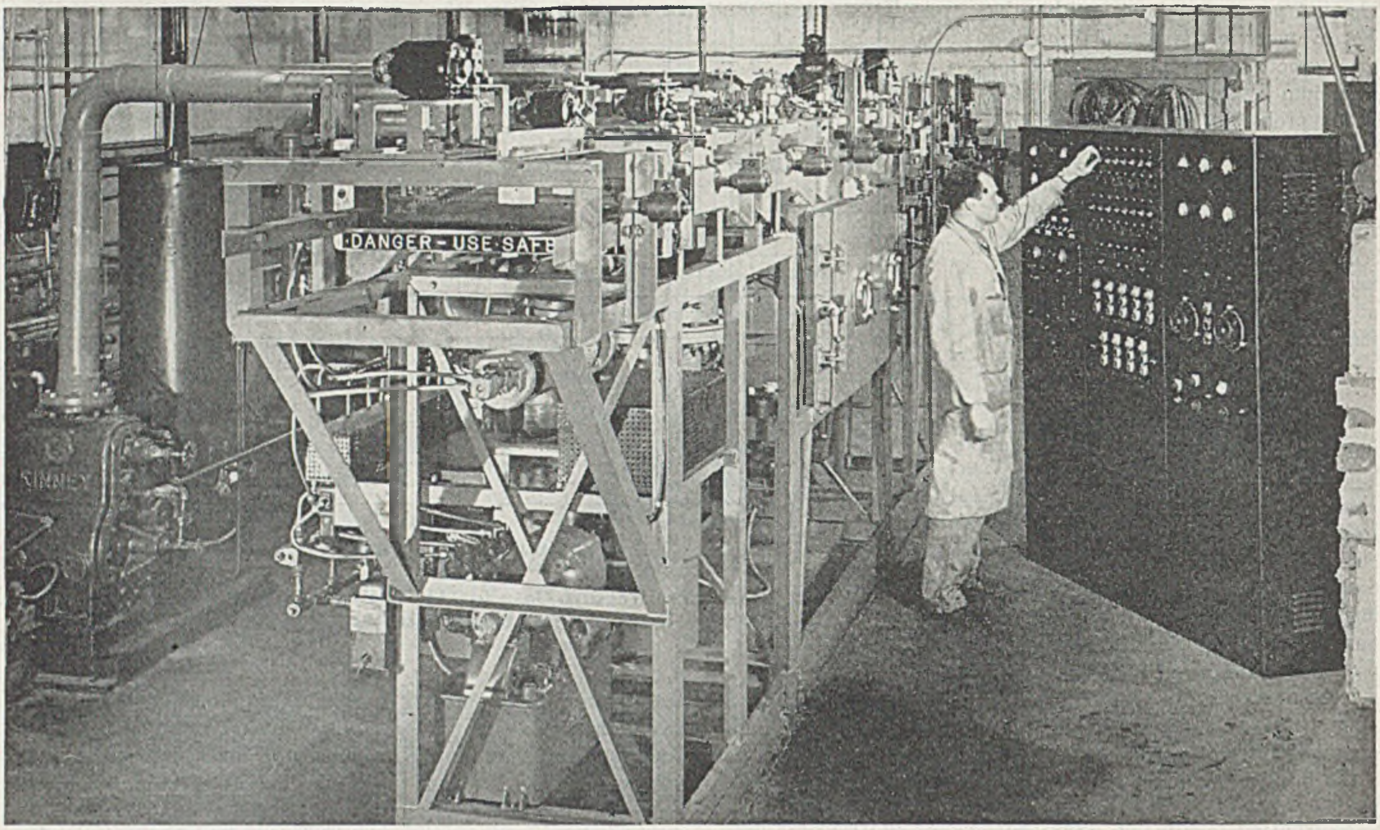
The development of large magnetrons and other high frequency tubes posed new problems for the vacuum engineer. The new high values of voltage and power which have been reached place new requirements on materials of construction to ensure maintenance of high vacuum over a period of time and under adverse operating conditions. Oxygen- or gas-free copper has proved essential to the construction of larger metal tubes, and great emphasis must be placed on problems of outgassing and of tightness of glass-to-metal and other forms of seals. In some cases continuously operated pumping systems have been employed. Similar problems are encountered in the operation of cyclotrons and other equipment which depend upon the use of low gas pressures to permit the formation of electron or ion beams. In the latter instance, considerably higher pumping speeds (1000 to 10,000 liters per second) at pressures below 10^{-5} mm. are common.

EVAPORATION OF METALS AND SALTS

Vacuum evaporation techniques have been practiced in the laboratory for many years. Metals or salts are electrically heated in a small boat or filament, evaporated or sublimed at air pressures below 10^{-4} mm., and condensed in the form of a thin film on the surface to be treated. In this manner front surface mirrors of aluminum or chromium can be formed, quartz replicas made, etc. (*22*).

During the war the lens coating industry was greatly expanded because of interest in low reflection surfaces for optical devices. It is now common practice to form quarter wave length films, usually of magnesium fluoride, by vacuum evaporation. By such a procedure the light reflection per optical surface is materially reduced and the transmission correspondingly increased. It is not uncommon to increase the light transmission of more complicated optical systems as much as 200%.

Considerable interest has recently been shown in the coating of plastic parts with various decorative metals such as gold, aluminum, copper, etc. Larger scale equipment has been developed for such work on a production scale (*1*).



Machine for Producing Vacuum-Evaporated Coatings on Large Surfaces by a Continuous Automatic Process

One of the largest demands for evaporated front surface mirrors may come from the television industry where both front surface plane and spherical mirrors are required for the Schmidt type optical system. Equipment has recently been developed whereby surfaces to be treated (lenses, mirrors, etc.) may be continuously introduced and removed from the high vacuum zone where coating takes place, without the usual loss in pressure. The products are placed on jigs which are automatically moved through successive zones of decreasing pressure, ranging from atmospheric to 10^{-4} mm. Either a metal or salt is evaporated from a continuous type source of vapor, and the jigs then proceed through zones of increasing pressure until removed to the air.

The continuous large scale coating of metals on cloth, paper, and sheet plastics has been known, at least by sputtering techniques, for some time. Gold leaf, for example, is produced on a commercial scale by such a procedure both here and in England. Recently considerable interest has been shown in processes for continuously evaporating zinc and aluminum on paper for electrical condensers, at pressures in the micron range. Improvement in weight, size, and voltage breakdown can be achieved as compared with the usual laminated foil condenser, and products made in this manner have recently been introduced in this country (*8*).

VACUUM METALLURGY

Prior to 1940, with the exception of work by Heraeus in Germany (*9*), large scale applications of vacuum metallurgy were virtually unknown. This situation was largely the result of a lack of adequate vacuum equipment. Vacuum may be applied in the field of metallurgy as follows: (*a*) A high vacuum is a truly inert atmosphere, and by its use metals may be protected during processing. (*b*) At reduced pressures the boiling points of metals are reduced sometimes as much as 1000° C. This phenomenon makes it possible to purify metals by distillation. (*c*) Operation in vacuum tends to favor any reaction in which a gas or volatile metal is produced from nonvolatile materials. As a result it is possible to reduce reaction temperatures markedly. (*d*) When metals are melted in vacuum, dissolved gases such as hydrogen and sometimes oxygen, nitrogen, and carbon monoxide may be removed with improvement in the mechanical, physical, and electrical properties of the cast products.

The large scale application of high vacuum to the magnesium industry during the war was, in a sense, the first demonstration that pressures in the micron range could be employed economically by the process industries (*20*). In the process, dolomite, and ferrosilicon are mixed, briquetted, and charged into evacuated alloy steel retorts maintained at 1175° C. The following reaction occurs:

$$2(\mathrm{MgO,\ CaO}) + 1/6\ \mathrm{FeSi_6} \xrightarrow[100\mu]{1175^\circ\ \mathrm{C.}} 2\mathrm{Mg}\nearrow + 1/6\ \mathrm{Fe} + 2\mathrm{CaO.SiO_2}$$

Table I. Properties of Vacuum-Melted Copper (*17*)

	Vacuum-Melted	Oxygen-Free Commercial
Gas content, %		
Hydrogen	0.00001	0.00012
Oxygen	0.00039	0.00045
Other gases	0.00002	0.00040
Sulfur	0.00006	0.00230
Physical properties		
Density, cast, grams/cc.	8.930	8.922
Tensile strength, drawn (64% cold reduct), lb. /sq. in.	54,500	54,500
Elongation, drawn, %	20.3	17.3
Reduction in area, drawn, %	88	76
Electrical conductivity, cast, % I.A.C.[a]	100.3	99.4
Thermal conductivity, cast, B.t.u./(hr.) (sq.ft.)(in.)/°F.	2430	2340

[a] International annealed copper standard.

The reduced pressure serves two functions in this reaction: It prevents oxidation of the magnesium formed, and it lowers the boiling point of magnesium so that the metal may be removed as rapidly as formed. Finally, the removal of magnesium by distillation forces reduction to proceed at almost 500° C. below the temperature required for reduction at atmospheric pressure.

This general type of vacuum reaction can be applied to the preparation of the other alkali and alkaline earth metals. The production of certain metals from their salts or by direct reduction of ores appears to be competitive with present electrolytic methods. Some of the reactions which have been investigated are:

$$4LiOH + 6CaO + 1/3\ FeSi_6 \xrightarrow[5\mu]{1000^\circ\ C.} 4Li\nearrow + 2(3CaO.SiO_2) + 1/3\ Fe + 2H_2\nearrow$$

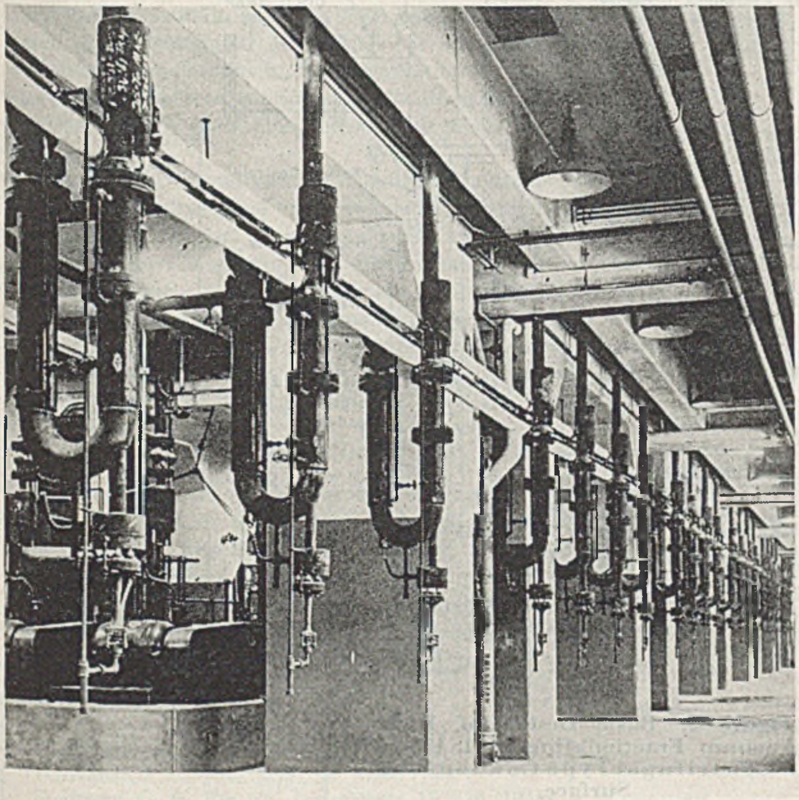
$$6CaO + 2Al \xrightarrow[10\mu]{1100^\circ\ C.} 3Ca\nearrow + 3CaO.Al_2O_3$$

$$2NaCl + CaC_2 \xrightarrow[10\mu]{800^\circ\ C.} 2Na\nearrow + CaCl_2 + 2C$$

$$Fe_2O_3 + 3C \xrightarrow[100\mu]{800^\circ\ C.} 2Fe + 3CO\nearrow$$

All commercial metals are contaminated with dissolved and combined gases. In many cases minute quantities of gas are capable of greatly reducing the ductility and toughness of metals, as well as the electrical and thermal conductivities. Dissolved gases are also released in solidifying metal; this accounts for porosity in castings under some conditions.

In many cases gases may be removed from metal by simply melting under reduced pressure. Hydrogen can almost always be removed by such treatment. Nitrogen can be removed in many cases and occasionally oxygen may be eliminated. Oxygen removal is difficult since this gas is generally present as an oxide of the metal being processed, and the decomposition pressure of a small amount of dissolved oxide is extremely low. If carbon is added, oxygen will be removed as carbon monoxide. This reaction can be carried out at atmospheric pressure, but under such conditions the equilibrium oxygen content of the melt will be fairly high, and vacuum tends to drive the reaction reducing the oxygen content to a negligible value. Oxygen content of many metals may also be reduced to a very low value by hydrogen treatment, but in the process the melt becomes contaminated with hydrogen which must be removed by vacuum treatment in order to produce sound ingots of superior mechanical properties.



COURTESY FORD MOTOR COMPANY

Battery of Gas-Fired Diffusion Pumps in a Large Magnesium Plant

Though the merits of degassing metals by vacuum melting and casting have been known for a long time, there had been no effort to apply these techniques on a commercial scale in this country until recently. However, within the last five years vacuum furnaces have been developed which will melt and cast common metals at ton rates per day, and there is no reason why this production cannot be extended to a much larger scale (*17*).

The properties of metals produced in vacuum furnaces are now being studied in detail, and results of these investigations will be published in the near future. It has been established that vacuum-cast metals have increased ductility and also electrical and thermal conductivity. Ingots are exceptionally sound. Analysis both in elemental materials and alloys may be duplicated with great accuracy, since the danger of atmospheric contamination is removed. Totally gas-free metals (such as copper) now being produced on a pilot plant scale are of particular interest to the electronics field (Table I).

There are also applications for fine wire, deep drawing operation, precision alloys, thermocouple, and resistance wire, etc.

VACUUM DISTILLATION

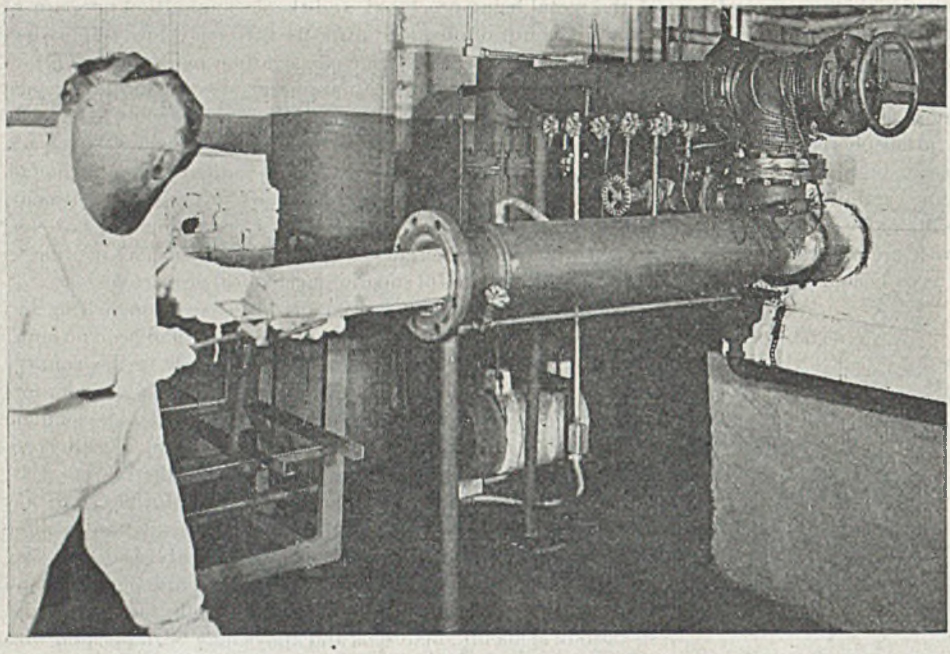
Low free air pressures have long been used by the chemical industry as a means of lowering distillation temperatures. Pressures in the micron range have to date been essentially limited on a commercial scale to the concentration of vitamin fractions in fish liver oils and distillation of high-molecular-weight organic materials. At free air pressures below 10 microns the effect of residual gases on the rate of distillation has been substantially removed. If, in addition, a low impedance path is maintained between the evaporating and condensing surfaces, a wide variety of high-molecular-weight substances may be distilled.

For most efficient operation with minimum decomposition, it is further essential that the distilling surface be constantly renewed and the time of exposure reduced to a minimum. Pot type stills have been largely replaced, therefore, by the falling film type. Only by such a technique, for example, may the common fats and oils such as triglycerides be handled.

Hickman recently described several centrifugal type stills in which extremely short distilland exposure times are made possible with film thicknesses as low as 0.001 to 0.005 mm. (*10, 12*).

All high vacuum stills have severe limitations with respect to fractionating ability—i.e., something less than one theoretical plate. Packed columns as conventionally employed are automatically ruled out because of the pressure drops introduced. Multiple distillations are possible, and various systems for operation of stills in series have been used.

Under conditions of high vacuum distillation, one is not concerned with boiling points but



Laboratory Gas-Fired Furnace, Useful in Studying Vacuum Thermal Reduction Processes or in Vacuum Melting 50–100 Pounds of Metal at 1–100 Microns and 700–1100° C.

rather with the rate of distillation as given by the following equation:

$$n = PA\sqrt{\frac{1}{2\pi MRT}}$$

where n = distillation rate, moles/second
P = vapor pressure, dynes/sq. cm.
A = distilling area, sq. cm.
M = molecular weight
R = gas constant
T = temperature, ° K.

In an effort to solve the intriguing problem of fractionation at low pressures without introducing serious impedance, Bowman *et al.* (6) described a fractionating still of unique design which may prove to be one of the most fundamental contributions in this field to date.

A wetted-wall or falling-film type still is employed with an internal rotating, cooled, concentric condenser. Condensation then takes place in the liquid phase, and the condensate is returned to the hot evaporating surface by centrifugal force (Figure 5). By this procedure an extremely large number of theoretical plates are achieved at any free air pressure, and the same fractionating ability is attained at air pressures in the micron range as is possible with the best conventional packed columns at atmospheric pressure. Power efficiency is admittedly low for such a system, and the period of thermal exposure is of necessity high. As a new tool for the chemical industry, however, this idea seems to offer interesting possibilities.

VACUUM DEHYDRATION

Low temperature dehydration with free air pressures in the micron range was studied shortly after the development of diffusion pumps. In general, high vacuum dehydration or so-called freeze drying is applied to heat-sensitive materials for one or more of the following reasons: (*a*) Thermal decomposition is reduced; (*b*) low moisture contents can be attained; (*c*) a lyophilic structure can be produced.

In the earliest forms of dehydration equipment, noncondensable gases were pumped from a closed system, and moisture rapidly removed from the product by condensing the evolved vapor in cooled concentrated sulfuric acid, or on a refrigerated surface or trap in the form of ice. The cold trap has many advantages and, with the use of improved vacuum equipment and low temperature mechanical refrigeration systems, has been adopted for both laboratory and small scale commercial uses. Larger static traps have been used in the drying of plasma and penicillin where capacities of several pounds of water per

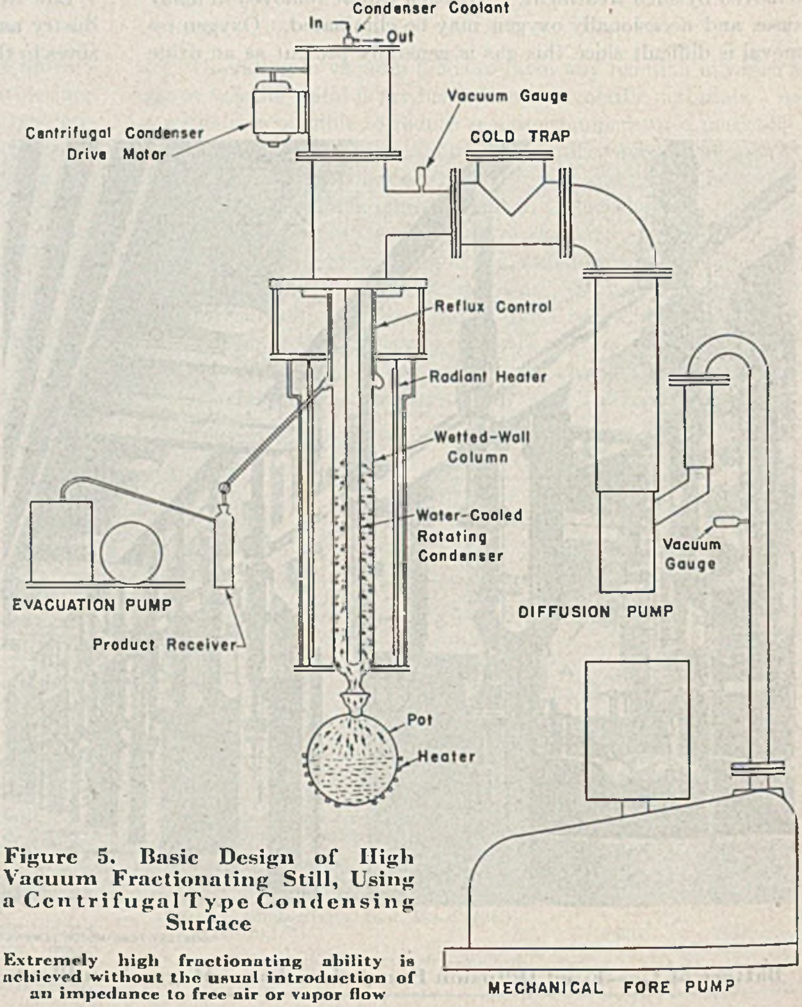


Figure 5. Basic Design of High Vacuum Fractionating Still, Using a Centrifugal Type Condensing Surface

Extremely high fractionating ability is achieved without the usual introduction of an impedance to free air or vapor flow

hour have been encountered, but operating problems to date have precluded their use in the largest installations.

War-stimulated production of penicillin created the first demand for the removal of water from a product maintained at temperatures well below 0° C. and free air pressures in the micron range. Substantially all of the large plants here and abroad originally adopted a water vapor pumping system employing a so-called rotary condenser. By such a technique ice is continuously removed from the cold surface and leaves an efficient condensing area. With this procedure the problem of designing an extremely large cold condensing surface capable of being alternately cooled and then heated to remove the ice layer is eliminated (Figure 6).

The recently completed plant of Vacuum Foods Corporation at Plymouth, Fla., designed for the production of orange juice powder and concentrate, probably represents the largest commercial application of high vacuum drying techniques (*5*). This plant has a juice input capacity in excess of 60,000 gallons per day, a concentrate of 50% solids being first produced by vacuum evaporation at the more moderate pressure of 8 mm. Final drying of a portion of this yield takes place in ten large vertical dryers which operate in pairs with five 25-inch-diameter rotary condensers. Each of these units has a maximum capacity of 50 pounds per hour of water vapor at 100 microns, or 100 pounds per hour at 250 microns. One interesting feature of this installation is the use of ice ejectors which permit continuous and automatic removal of the condensed ice to the atmosphere without loss of vacuum in the system.

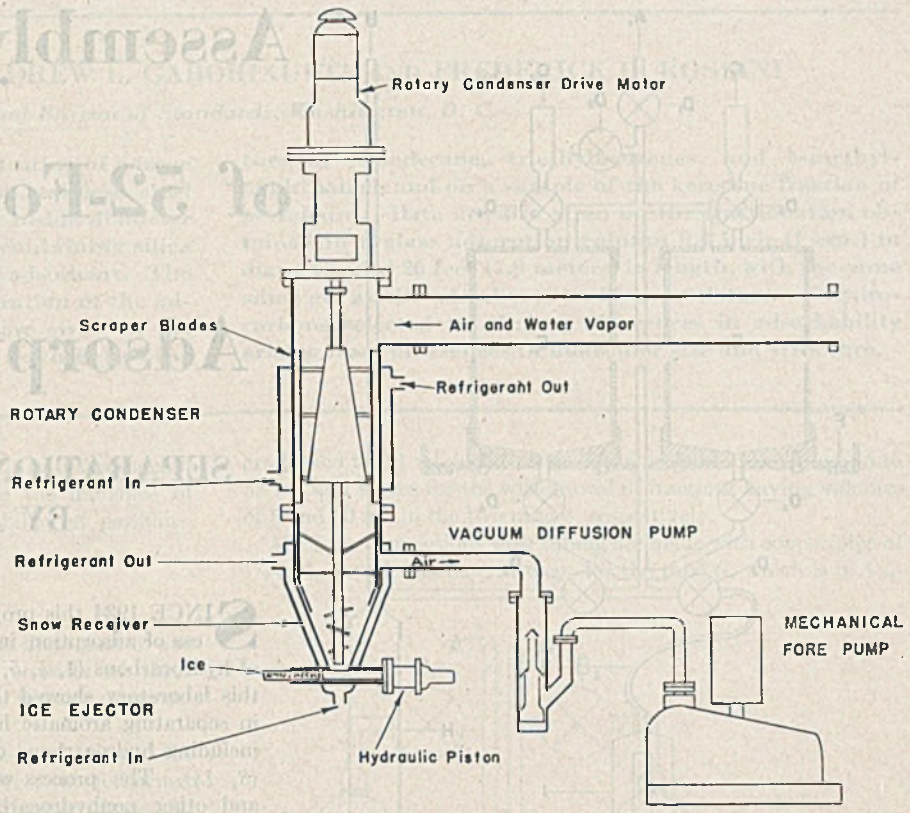


Figure 6. Basic Principle of Large Rotary Condenser Type of Cold Trap

Noncondensable gases are pumped with the diffusion pumps and mechanical unit, vapor being removed as snow from the inner cold wall of the condenser and subsequently ejected as ice to the atmosphere. In smaller installations an ice receiver of 100–250 pounds capacity is used below the scraper blades, and this is periodically emptied

Several experimental vacuum dehydration systems have been developed using chemical absorbers, such as lithium salts. Although little large scale plant experience is available, such a process should prove interesting and efficient because of both lower capital investment and operating costs. For the dehydration of heat-sensitive materials, high vacuum processes appear to be competitive with the conventional spray drying, assuming that low inlet gas temperatures are required in the latter case to preserve the quality of the product.

CONCLUSION

This résumé of the present status of the high vacuum field has of necessity been limited in detail, and each of the subjects presented could lend itself to a more profound technical treatment. High vacuum problems can now be handled by engineering methods, and regardless of whether one is confronted with operating an open hearth furnace at 10^{-4} mm. or developing pressure measuring devices for use in the stratosphere, the present technology is ready for the task.

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Assembly and Testing of 52-Foot Laboratory Adsorption Column

SEPARATION OF HYDROCARBONS BY ADSORPTION

SINCE 1934 this project has made use of the fractionating process of adsorption in its work on the separation and purification of hydrocarbons (*1, 4, 5, 6, 7, 8, 10, 12, 13, 14*). The early work in this laboratory showed the effectiveness of adsorption with silica gel in separating aromatic hydrocarbons from paraffins and naphthenes including hydrocarbons of low (*10, 13*) and of high molecular weight (*8, 14*). The process was also found convenient for removing water and other nonhydrocarbon impurities from purified hydrocarbons. Small but significant fractionation by adsorption was found to occur between paraffins and cycloparaffins and between *n*-paraffins of different molecular weights (*4, 10*). Methods for the analysis of aromatic hydrocarbons in mixtures with paraffins and naphthene hydrocarbons (and some olefins) were developed (*4, 5, 7*) as well as for the quantitative separation of aromatic hydrocarbons on a large laboratory scale (*1, 6, 12*). Current work in this laboratory has been aimed at the extension of the newer analytical method (*4, 7*) to large scale separation and to the investigation of the relations between adsorbability and molecular structure among hydrocarbons having nearly the same adsorbability.

This report describes the assembly and testing of a large laboratory adsorption column having a stainless steel fractionating section $^3/_4$ inch (1.9 cm.) in inside diameter and 52.4 feet (16 meters) in length; this column is capable of separating about 0.5 liter of aromatic hydrocarbons and in it the adsorbent may be regenerated in position. This report also presents the results of experiments performed

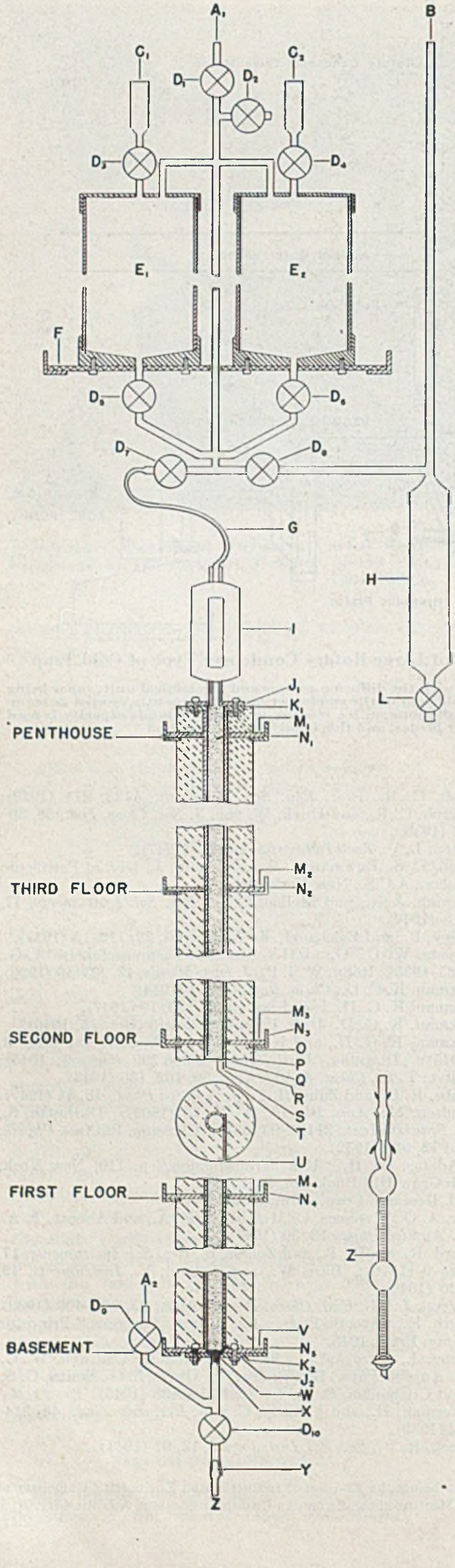

Figure 1. Assembly of 52-Foot Adsorption Column

A_1, A_2. Connections to source of nitrogen under pressure
B. Vent to roof
C_1, C_2. Copper tubes, 1-inch outside diameter, for filling the reservoirs
D_1 to D_{10}. Packless diaphragm line valves with $^1/_2$-inch soldered connections
E_1, E_2. Brass reservoirs 20 inches long and 6 inches in outside diameter, to contain, respectively, hydrocarbon and alcohol
F. Steel plate $^1/_4$ inch thick for supporting reservoirs
G. Copper tubing, $^3/_{16}$-inch outside diameter
H. Receiver of 1-liter capacity for collecting alcohol recovered in regeneration process
I. Prismatic sight glass
J_1, J_2. Flanges at top and bottom of column
K_1, K_2. Gaskets at top and bottom of column
L. Petcock
M_1 to M_4. Transite collars with clearance to permit vertical movement, but to restrict lateral movement, of column
N_1 to N_5. Angle iron supports
O. Aluminum foil
P. Magnesia insulation 1 inch nominal size, $1^3/_4$ inches thick
Q. Nichrome electrical resistance heating wire, asbestos-covered
R. Asbestos coated with resin
S. Column of stainless steel, 1-inch outside diameter, 12 gage, welded to form one section 52.4 feet long, with welds to steel flange at top and stationary steel plate at bottom
T. Adsorbent, silica gel, approximately 60% between 200 and 325 mesh
U. Thermocouple well
V. Steel plate $^5/_{16}$ inch thick bearing entire weight of column
W. Glass wool
X. Brass plug supporting glass wool and adsorbent
Y. Standard taper, $^{12}/_{30}$, glass (male) to copper metal (female) soldered joint (*11*)
Z. Receiver

BEVERIDGE J. MAIR, ANDREW L. GABORIAULT[1], AND FREDERICK D. ROSSINI

National Bureau of Standards, Washington, D. C.

This report describes the assembly and testing of a large laboratory adsorption column having a stainless steel fractionating section $^3/_4$ inch (1.9 cm.) in inside diameter and 52.4 feet (16 meters) in length, and containing silica gel (largely 200 to 325 mesh in size) as the adsorbent. The procedure of operation, including regeneration of the adsorbent in place, is described. Results are given on the separation obtained with this column on a synthetic mixture of *n*-dodecane, triethylbenzenes, and 1-methylnaphthalene and on a sample of the kerosene fraction of petroleum. Data are also given on the fractionation obtained in a glass adsorption column 0.4 inch (1 cm.) in diameter and 26 feet (7.9 meters) in length, with the same silica gel as the adsorbent, on binary mixtures of hydrocarbons selected to disclose differences in adsorbability arising from differences in molecular size and structure.

in a glass adsorption column 0.4 inch (1 cm.) in diameter and 26 feet (7.9 meters) in length to determine the influence of molecular size and structure on the adsorbability of paraffins, cycloparaffins, and alkylbenzenes.

ASSEMBLY OF COLUMN

Figure 1 shows the complete assembly of the main part of one 52-foot adsorption column. The assembly consists of three parts, the head of the adsorption column, the fractionating section, and the receiver.

The head of the adsorption column includes, in addition to the necessary connecting tubing and control valves, the following: receivers E_1 and E_2 for holding the mixture of hydrocarbons and the desorbing liquid, respectively; sight glass I for observing when the mixture of hydrocarbons has all entered the fractionating section; the receiver H for holding the desorbing liquid recovered in the process of regenerating the adsorbent.

The fractionating section proper consists of a stainless steel tube, $^3/_4$ inch in inside diameter and 52.4 feet in length, together with the adsorbent in it. The tube is one inch in outside diameter, has a 12-gage wall, and is welded in one piece. The steel tube is covered with a layer of $^1/_{16}$-inch asbestos paper coated with resin. Electrical resistance wire heating units are wound over the resin-coated asbestos paper. Magnesia "pipe," as insulation $1^3/_4$ inch in thickness, covers the entire fractionating section. The surface of the magnesia insulation is covered with aluminum foil.

The bottom of the stainless steel tube is welded to steel plate N_3, which carries the entire weight of the fractionating section (Figure 1). Transite blocks M provide lateral support for the fractionating section, with sufficient clearance to permit the column to move vertically on expansion or contraction in length with changes in temperature. Connection at the bottom of the column is made through flange J_2, to which the smaller copper pipe is brazed. The solid adsorbent, silica gel, is supported by the plug of glass wool, W, which in turn is held in position by brass plug X. The latter is force-fitted in the copper pipe and is provided with small vertical holes to permit passage of liquid.

Connection to receiver Z is made through the copper-to-glass joint Y, which is sealed with solder (*11*). The glass receiver is graduated to 0.1 ml. in the range 0 to 6 ml. and in the range 45 to 55 ml. and serves for the withdrawal of fractions having volumes of 5 and 50 ml. in the two ranges, respectively.

All of the connections with tubing are made with copper pipe of $^1/_2$-inch outside diameter, except for the tube G, which is of $^3/_{16}$-

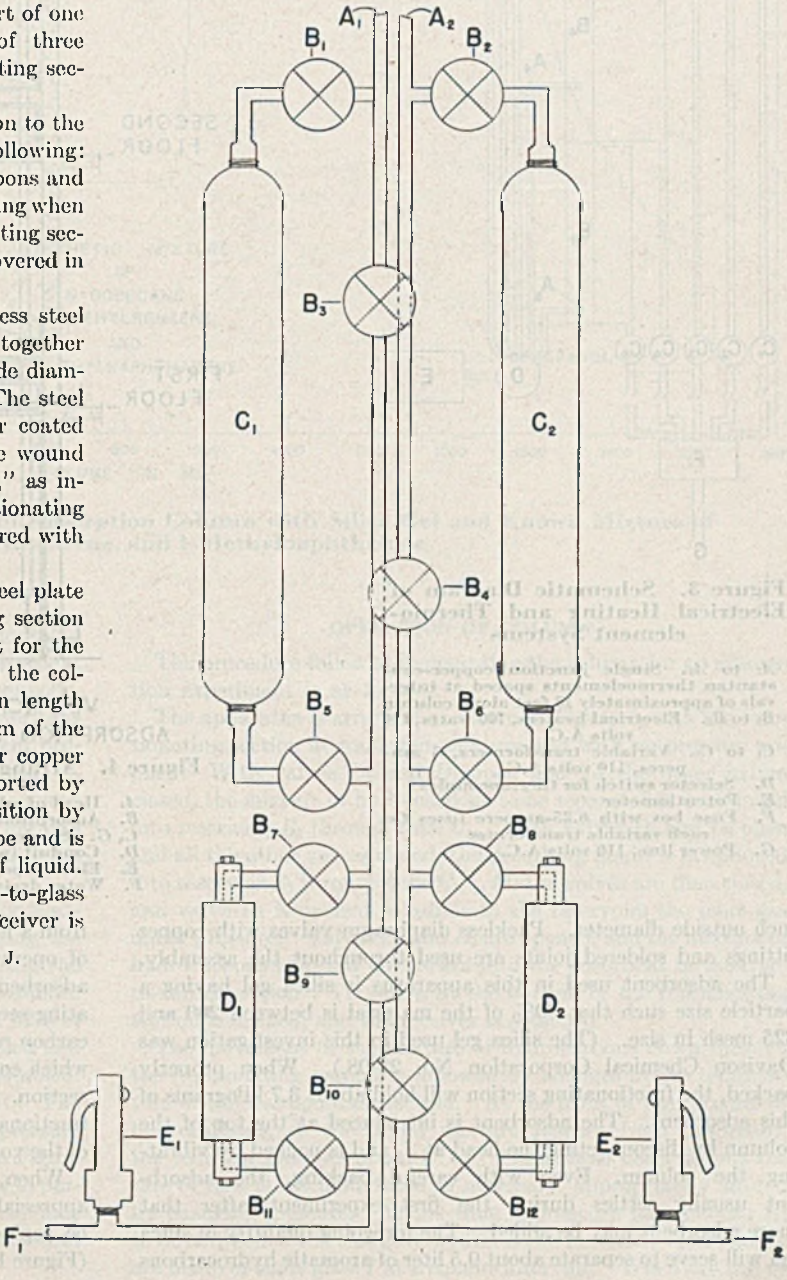

Figure 2. Diagram of Systems Containing Inert Gas under Pressure

- A_1, A_2. Connections to top and bottom of column assembly
- B_1 to B_{12}. Packless diaphragm line valves with $^1/_2$-inch soldered connections
- C_1, C_2. Dehydrators containing silica gel of 28 to 200-mesh size for drying inert gas in regeneration process
- D_1, D_2. Flowmeters (rotameters) with scale reading from 8 to 150 ml. per minute
- E_1, E_2. Relief valves set to release pressures in excess of 120 pounds per square inch
- F_1, F_2. Connections to cylinders of nitrogen, with pressure-regulating valves

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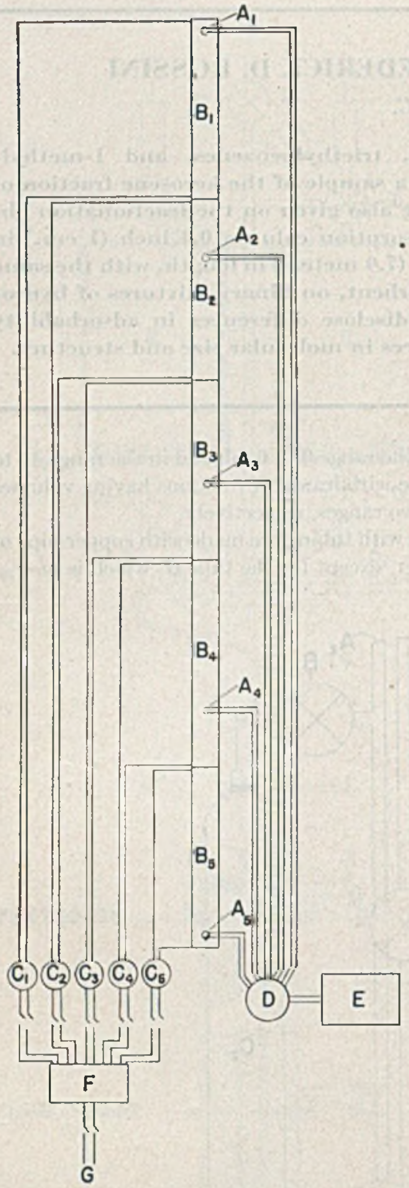


Figure 3. Schematic Diagram of Electrical Heating and Thermoelement Systems

A_1 to A_5. Single junction copper-constantan thermoelements spaced at intervals of approximately 13 feet along column
B_1 to B_5. Electrical heaters, 700 watts, 110 volts A.C.
C_1 to C_5. Variable transformers, 5 amperes, 110 volts A.C.
D. Selector switch for thermocouples
E. Potentiometer
F. Fuse box with 6.25-ampere fuses for each variable transformer
G. Power line, 110 volts A.C.

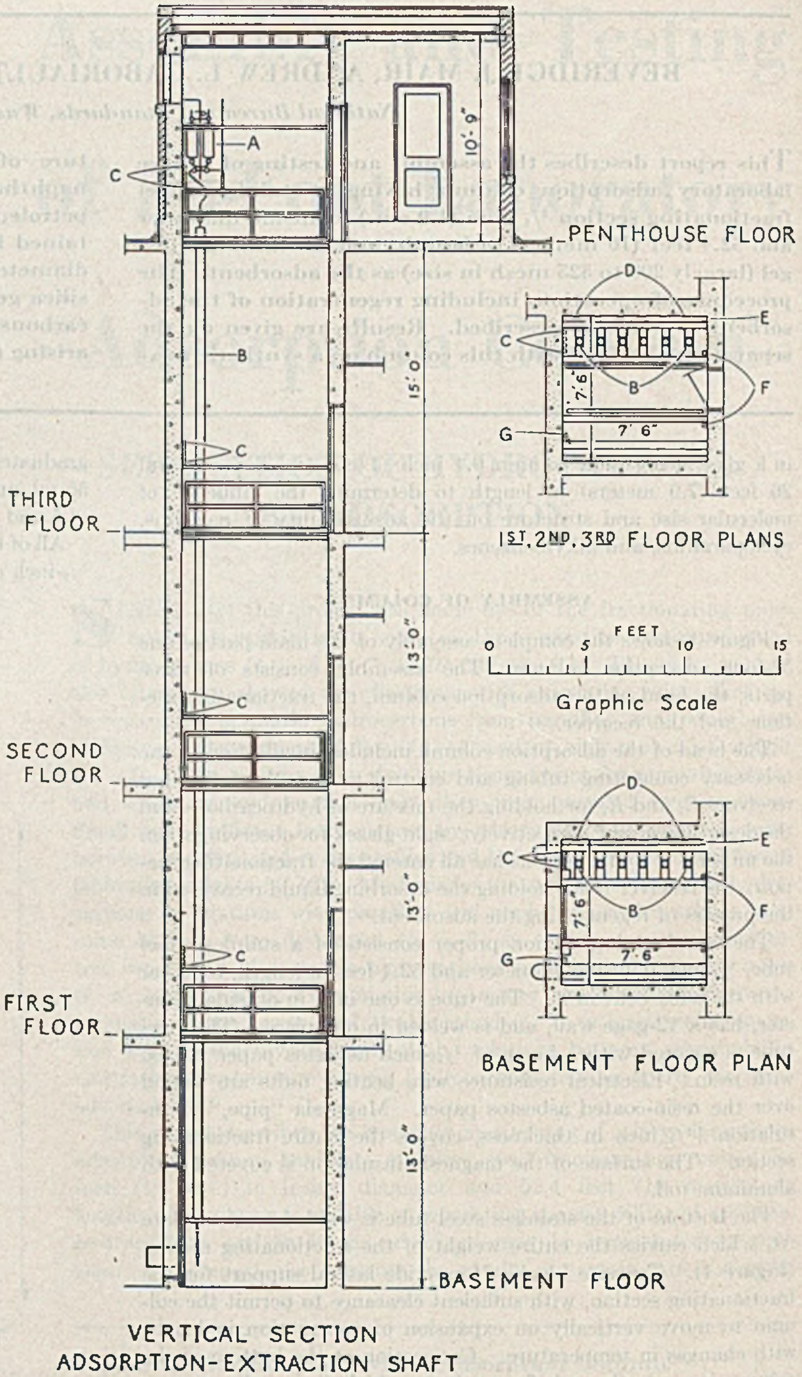


Figure 4. Arrangement of Adsorption Columns in 62-Foot Shaft

A. Head of adsorption column
B. Adsorption columns
C, *G*. Services: gas, air, vacuum, water, refrigerated water
D. Conduit (wire mold) containing electric leads for heating units
E. Electric power line
F. Water drains

inch outside diameter. Packless diaphragm valves with copper fittings and soldered joints are used throughout the assembly.

The adsorbent used in this apparatus is silica gel having a particle size such that 60% of the material is between 200 and 325 mesh in size. (The silica gel used in this investigation was Davison Chemical Corporation No. 22-08.) When properly packed, the fractionating section will hold about 3.7 kilograms of this adsorbent. The adsorbent is introduced at the top of the column by disconnecting the head at J_1 and is packed by vibrating the column. Even with careful packing, the adsorbent usually settles during the first experiment; after that more adsorbent may be added. The foregoing quantity of silica gel will serve to separate about 0.5 liter of aromatic hydrocarbons from a mixture with paraffins and naphthenes, using the method of operation described by Mair (*4*). When fully packed with adsorbent in the manner described, the void space in the fractionating section was obtained by determining the volume of hydrocarbon required to fill this section; it was found to be 3460 ml., which corresponds to 2.17 ml. per cm. length of the fractionating section. The total internal volume of the packed part of the fractionating section is 4520 ml. The void space constitutes 77% of the volume of the packed fractionating section.

When, after repeated regenerations, the adsorbent has lost an appreciable portion of its original adsorptive capacity and must be replaced, the following procedure may be used: Flange J_2 (Figure 1) is removed, and a flexible plastic tube from which water

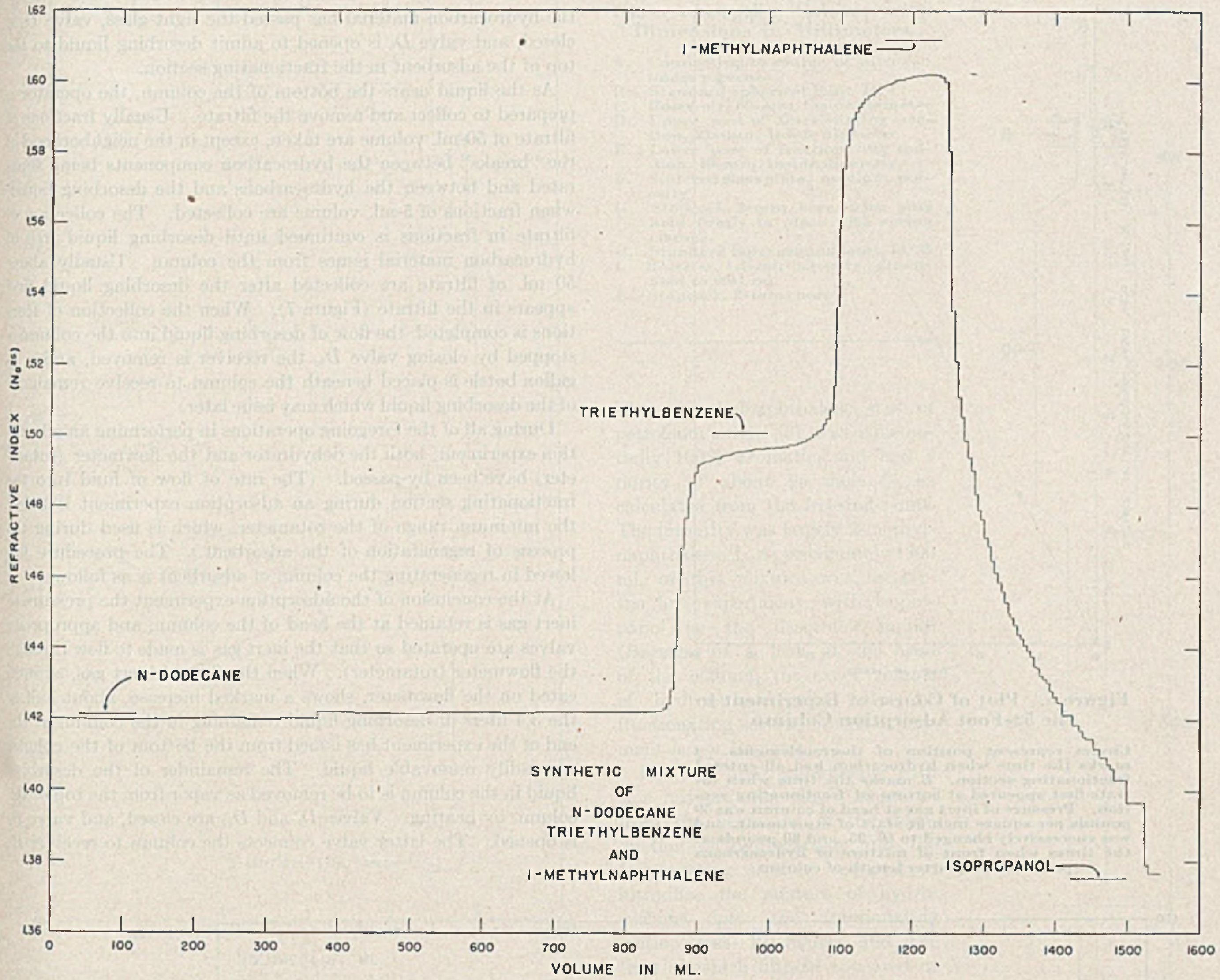


Figure 5. Results of Experiment in 52-Foot Adsorption Column with Silica Gel and Known Mixture of *n*-Dodecane Triethylbenzene, and 1-Methylnaphthalene

is flowing is inserted into and slowly forced up the fractionating section, from which the adsorbent is loosened. The adsorbent then flows out of the bottom with water into a suitable receptacle.

Figure 2 is a diagram of the systems for introducing inert gas under pressure into the fractionating section. One system provides pressure at the head of the column for an adsorption experiment, and the other provides pressure at the bottom of the column for reactivation of the adsorbent. The system of valves permits the inert gas to by-pass either the flowmeters (rotameters), the dehydrators, or both.

Figure 3 is a diagram of the electrical heating system for heating the fractionating section in the process of regenerating the adsorbent, and of the thermoelement system for measuring the temperature at the several indicated places along the column.

Figure 4 is a diagram of the shaft, $7^1/_2$ feet square and 62 feet high, in which the 52-foot adsorption column was assembled and in which five additional similar columns are being assembled. One adsorption column is shown in position in the shaft. The controls for the electric heating, thermoelement, and pressure systems are in an adjoining basement room not shown in Figure 4. With a battery of six adsorption columns, it is planned to perform adsorption experiments simultaneously in three columns while the other three are being regenerated. With this method of operation one head can be made to serve two columns.

OPERATION OF COLUMN

The procedure followed in operating the column for an adsorption experiment is as follows:

The apparatus is arranged as shown in Figure 1, with the fractionating section at room temperature and with no pressure applied. With valves D_2 and D_3 open and all the other valves closed, the mixture of hydrocarbons to be separated is introduced into reservoir, E_1 through tube C_1. With valves D_2 and D_4 open and all the other valves closed, the desorbing liquid is introduced into reservoir E_2 through tube C_2. All the valves are then closed, and valve D_1 is opened to admit to the reservoirs the inert gas under pressure. Valves D_5 and D_7 are opened, and the mixture of hydrocarbons is forced downward into the adsorbent in the fractionating section. Valve D_{10} at the bottom of the fractionating section is opened, and the receiver is attached.

The movement of the mixture of hydrocarbons down through the fractionating section is followed by changes in the temperature of the fractionating section. At the front of the mixture of hydrocarbons, as the liquid mixture reaches fresh adsorbent, the temperature rises about 5° C. From these observations the rate of flow is calculated and, if necessary, appropriately altered by changing pressure. As the time approaches for reservoir E_1 to be emptied of the charge of hydrocarbon material, observations are made of sight glass I at frequent intervals. When the last of

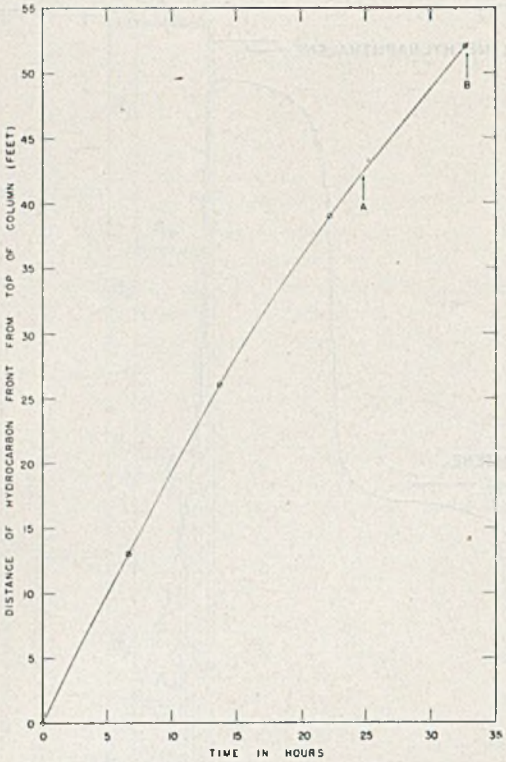


Figure 6. Plot of Course of Experiment in the 52-Foot Adsorption Column

Circles represent position of thermoelements. *A* marks the time when hydrocarbon had all entered fractionating section. *B* marks the time when filtrate first appeared at bottom of fractionating section. Pressure of inert gas at head of column was 30 pounds per square inch at start of experiment, and was successively changed to 60, 85, and 80 pounds at the times when front of mixture of hydrocarbons passed each quarter length of column

the hydrocarbon material has passed the sight glass, valve D_5 is closed, and valve D_6 is opened to admit desorbing liquid to the top of the adsorbent in the fractionating section.

As the liquid nears the bottom of the column, the operator is prepared to collect and remove the filtrate. Usually fractions of filtrate of 50-ml. volume are taken, except in the neighborhood of the "breaks" between the hydrocarbon components being separated and between the hydrocarbons and the desorbing liquid, when fractions of 5-ml. volume are collected. The collection of filtrate in fractions is continued until desorbing liquid free of hydrocarbon material issues from the column Usually about 50 ml. of filtrate are collected after the desorbing liquid first appears in the filtrate (Figure 7). When the collection of fractions is completed, the flow of desorbing liquid into the column is stopped by closing valve D_6, the receiver is removed, and a 1-gallon bottle is placed beneath the column to receive remainder of the desorbing liquid which may issue later.

During all of the foregoing operations in performing an adsorption experiment, both the dehydrator and the flowmeter (rotameter) have been by-passed. (The rate of flow of fluid into the fractionating section during an adsorption experiment is below the minimum range of the rotameter, which is used during the process of regeneration of the adsorbent.) The procedure followed in regenerating the column of adsorbent is as follows:

At the conclusion of the adsorption experiment the pressure of inert gas is retained at the head of the column, and appropriate valves are operated so that the inert gas is made to flow through the flowmeter (rotameter). When the flow of inert gas, as indicated on the flowmeter, shows a marked increase, about half of the 3.4 liters of desorbing liquid remaining in the column at the end of the experiment has issued from the bottom of the column as readily removable liquid. The remainder of the desorbing liquid in the column is to be removed as vapor from the top of the column by heating. Valves D_1 and D_{10} are closed, and valve D_8 is opened. The latter valve connects the column to receiver *H*.

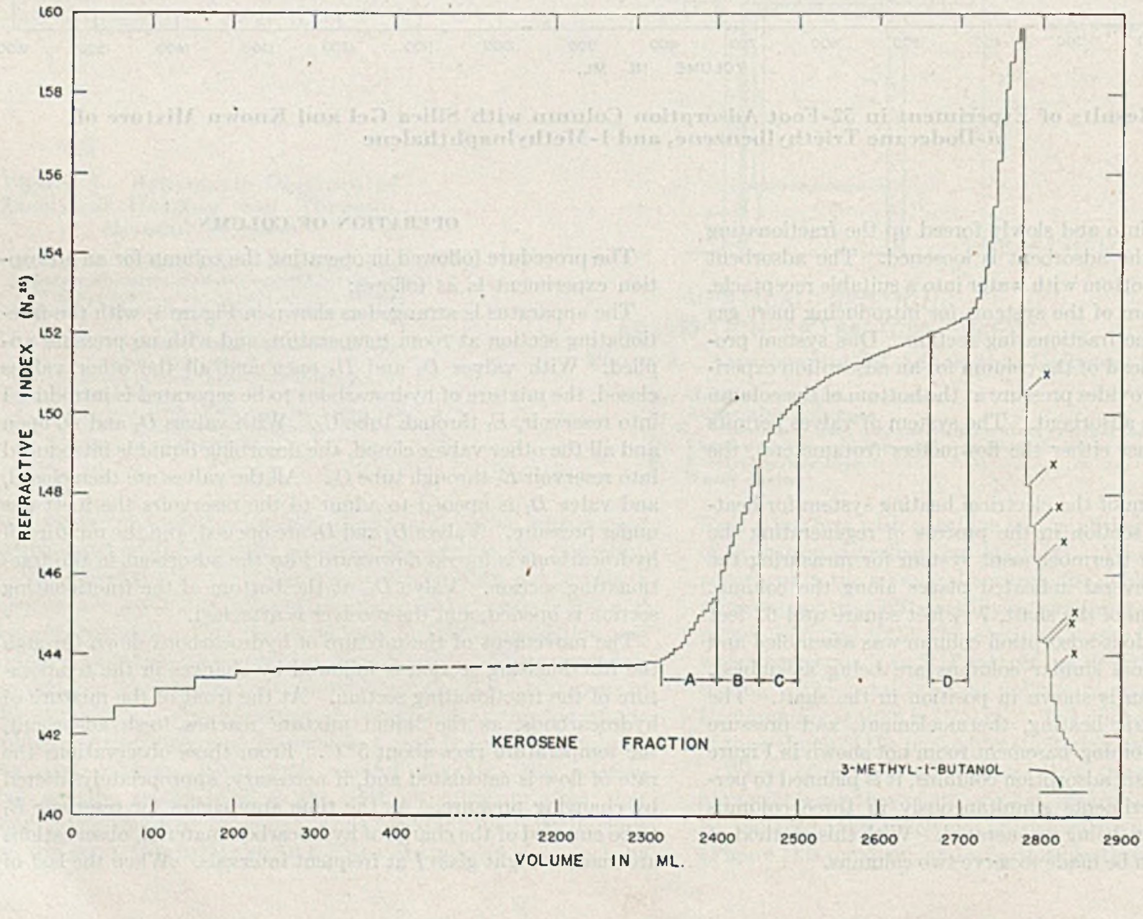


Figure 7. Results of Experiment in 52-Foot Adsorption Column with Silica Gel and a Kerosene Fraction of Petroleum

Fractions designated X showed crystals at room temperature

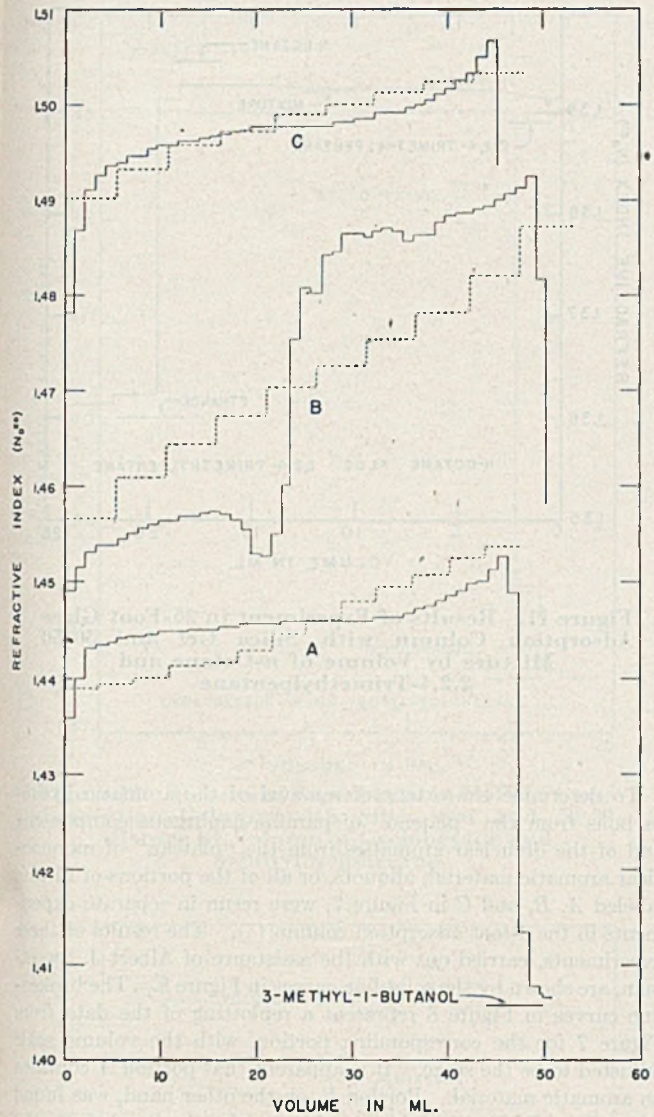


Figure 8. Results of Experiments in 4-Foot Glass Column with Silica Gel and Portions of Filtrate from Kerosene Fraction of Petroleum

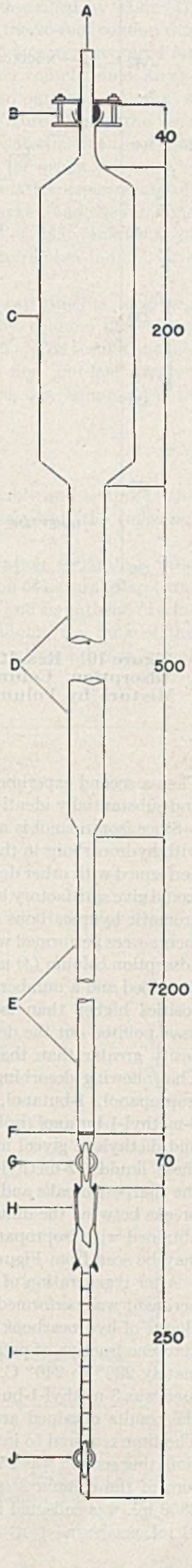
By means of the electrical heating system, the temperature of the fractionating section is raised to about 10° C. above the normal boiling point of the desorbing liquid. When the rate of evolution of desorbing liquid from the top of the column drops, the temperature is raised another 10° C. After the bulk of it has been removed in this fashion, the last traces of desorbing liquid are removed by opening valve D_9, admitting at the bottom of the column a stream of dry nitrogen (which has been passed through the dehydrator) at a rate of 20 to 50 ml. per minute, and maintaining the temperature of the fractionating column at 200° C. This last operation is continued until substantially all the desorbing liquid has been removed from the adsorbent.

TEST EXPERIMENTS

For the first test experiment a mixture was used consisting, by volume, of $66^2/_3$% *n*-dodecane, 20% triethylbenzene and $13^1/_3$% 1-methylnaphthalene. [The *n*-dodecane was of petroleum origin (*9*), was aromatic-free, and had a purity of about 90 mole % as calculated from the freezing point. The impurities were largely cycloparaffins. The triethylbenzene was a middle portion from the distillation of Dow Chemical Company's triethylbenzene. The impurities were believed to be largely isomeric. The 1-methylnaphthalene was of petroleum origin (*9*), was substantially 100% aromatic, and had a purity of about 95 mole % as calculated from the freezing point. The impurity was largely 2-methylnaphthalene.] Approximately 1300 ml. of this mixture was used in the first experiment, with isopropanol as the desorbing liquid. (Because of a leak at the head of the column, the exact volume of hydrocarbon going into the fractionating section in this experiment is not known.)

Figure 9. Assembly of 26-Foot Glass Adsorption Column with Dimensions in Millimeters

A.	Connection to source of nitrogen under pressure
B.	Standard spherical joint 18/9
C.	Reservoir, 60-mm. inside diameter
D.	Upper part of fractionating section, 22-mm. inside diameter
E.	Lower part of fractionating section, 10-mm. inside diameter
F.	Sintered glass plate, medium porosity
G.	Stopcock, 2-mm. bore, with plug held firmly in place with spring clamps
H.	Standard taper ground joint, 14/35
I.	Receiver, 1.1-ml. capacity, graduated to 0.01 ml.
J.	Stopcock, 2-mm. bore



In the first experiment with this mixture, the time (measured from the beginning of the introduction of hydrocarbon into the fractionating section) required to introduce the mixture of hydrocarbons into the fractionating section was 12 hours, and the time at which filtrate appeared at the bottom of the fractionating section was 34 hours. A volume of 1550 ml. of filtrate was collected in $21^1/_2$ hours, which corresponds to a rate of flow of 72 ml. per hour. The pressure of inert gas applied at the head of the column was 15 pounds per square inch at the start and was increased, stepwise, to 90 pounds per square inch at the end of the experiment.

The results of the first experiment, with silica gel as the adsorbent and isopropanol as the desorbing liquid, are shown in Figure 5. The breaks between *n*-dodecane and triethylbenzene and between triethylbenzene and 1-methylnaphthalene are reasonably satisfactory. However, the break between 1-methylnaphthalene and the desorbing liquid is regarded as unsatisfactory.

After the first experiment, the adsorbent in the fractionating section was regenerated as described in the preceding section.

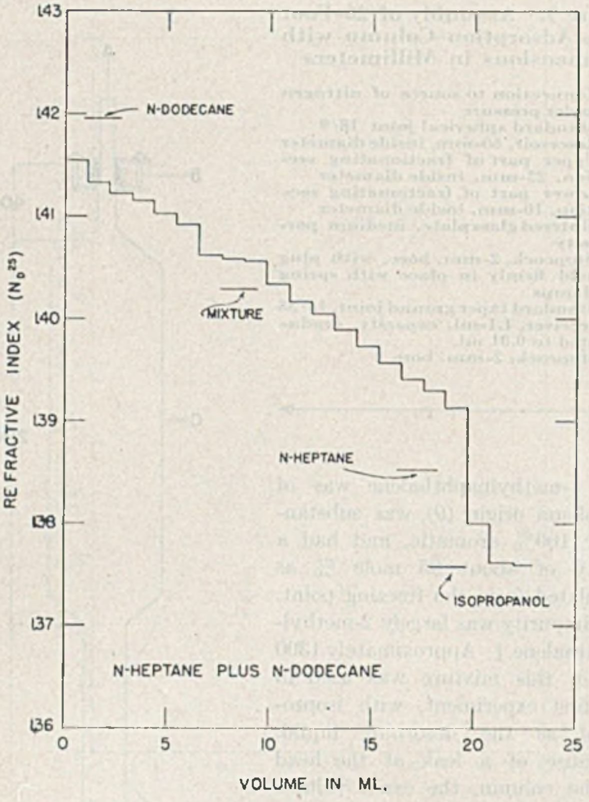


Figure 10. Results of Experiment in 26-Foot Glass Adsorption Column with Silica Gel and 50-50 Mixture by Volume of *n*-Heptane and *n*-Dodecane

Then a second experiment, the same as the first, was performed, and substantially identical results were obtained.

Since isopropanol is not a satisfactory desorbing liquid for use with hydrocarbons in the kerosene region, some experiments were performed with other desorbing liquids to determine which liquids would give satisfactory breaks between the more strongly adsorbed aromatic hydrocarbons and the desorbing liquid. These experiments were performed with the same adsorbent in the 4-foot glass adsorption column (*4*) using the same mixture of hydrocarbons as described and a number of different desorbing liquids having viscosities higher than isopropanol. [Gooding and Hopkins (*2*) have pointed out the desirability of having a desorbent with viscosity greater than that of the hydrocarbons being separated.] The following desorbing liquids were tried in the small column: isopropanol, 1-butanol, 2-methyl-1-butanol (*sec*-butylcarbinol), 3-methyl-1-butanol (isobutylcarbinol), 2-methyl-2, 4-pentanediol, and diethylene glycol monomethyl ether (methyl Carbitol). Of these liquids, 2-methyl-1-butanol and 3-methyl-1-butanol gave the sharpest breaks and were satisfactory. The difference in the breaks between the dinuclear aromatics and the desorbing liquid, obtained with isopropanol and 3-methyl-1-butanol, respectively, may be seen from Figures 5 and 7.

After regeneration of the silica gel adsorbent, another test experiment was performed in the 52-foot adsorption column with a charge of hydrocarbons comprising 2800 ml. of material from the kerosene fraction of petroleum, having a boiling range of approximately 230° to 240° C. at 1 atmosphere. The desorbing liquid used was 3-methyl-1-butanol. The course of this experiment and the results obtained are shown graphically in Figures 6 and 7. The time required to introduce all the hydrocarbon into the fractionating section was 25 hours, with filtrate appearing at the bottom of the column 8 hours after this. A volume of filtrate of 2850 ml. was collected in 70 hours; this corresponds to a rate of 41 ml. per hour.

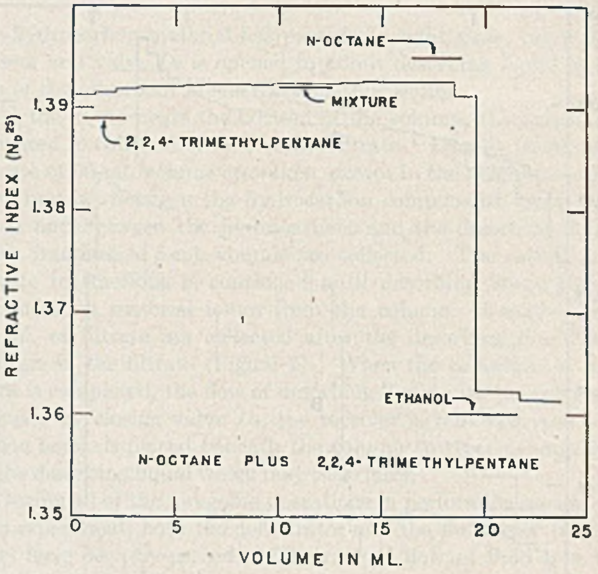


Figure 11. Results of Experiment in 26-Foot Glass Adsorption Column with Silica Gel and 50-50 Mixture by Volume of *n*-Octane and 2,2,4-Trimethylpentane

To determine the extent of removal of the aromatic hydrocarbons from the "plateau" of paraffin-naphthene components and of the dinuclear aromatics from the "plateau" of mononuclear aromatic material, aliquots, or all of the portions of filtrate labeled *A*, *B*, and *C* in Figure 7, were rerun in separate experiments in the 4-foot adsorption column (*4*). The results of these experiments, carried out with the assistance of Albert J. Sweetman, are shown by the solid-line curves in Figure 8. The broken-line curves in Figure 8 represent a replotting of the data from Figure 7 for the corresponding portion, with the volume scale adjusted to be the same. It is apparent that portion *A* contains no aromatic material. Portion *B*, on the other hand, was found to be about 50% aromatic, as evidenced by the break from the paraffin-naphthene material to mononuclear aromatics near half the volume. For portion *C* the results of the rerun experiment are not greatly different from those of the original experiment. The material is all aromatic except for a small amount of nonaromatic material disclosed by the lower refractive index of the first fraction. From these data it is concluded that the transition from paraffin-naphthene material to the mononuclear aromatic material in the kerosene fraction in the 52-foot column occurs sharply within a volume of 50 ml. The portion labeled *D* in Figure 7 was rerun in a similar manner. The results of this experiment (not illustrated) showed that portion *D* consisted almost entirely of mononuclear aromatic hydrocarbons, with no significant amount of dinuclear aromatics. The break from mononuclear aromatics to dinuclear aromatics is reasonably sharp, although the plateau of dinuclear aromatic material still appears to contain some mononuclear aromatics, as evidenced by the refractive index. This experiment also discloses the improvement obtained in using 3-methyl-1-butanol in place of isopropanol as the desorbing liquid, as evidenced by the sharper break between hydrocarbon material and the desorbing liquid.

SEPARATION OF HYDROCARBONS BY ADSORPTION

APPARATUS. The 26-foot glass adsorption column shown in Figure 9 was assembled for experiments on binary mixtures of pure hydrocarbons having nearly the same adsorbability, selected to disclose differences in adsorbability arising from differences in molecular size and structure. This apparatus, which holds ap-

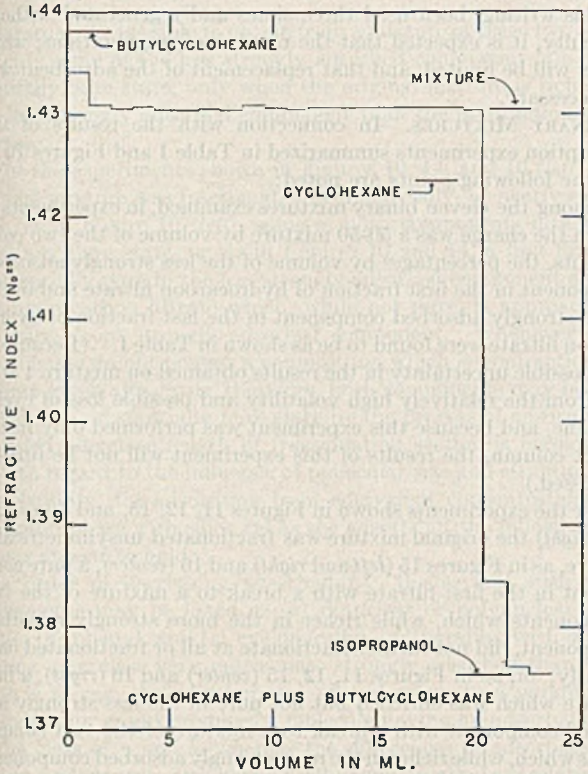


Figure 12. Results of Experiment in 26-Foot Glass Adsorption Column with Silica Gel and 50-50 Mixture by Volume of Cyclohexane and *n*-Butylcyclohexane

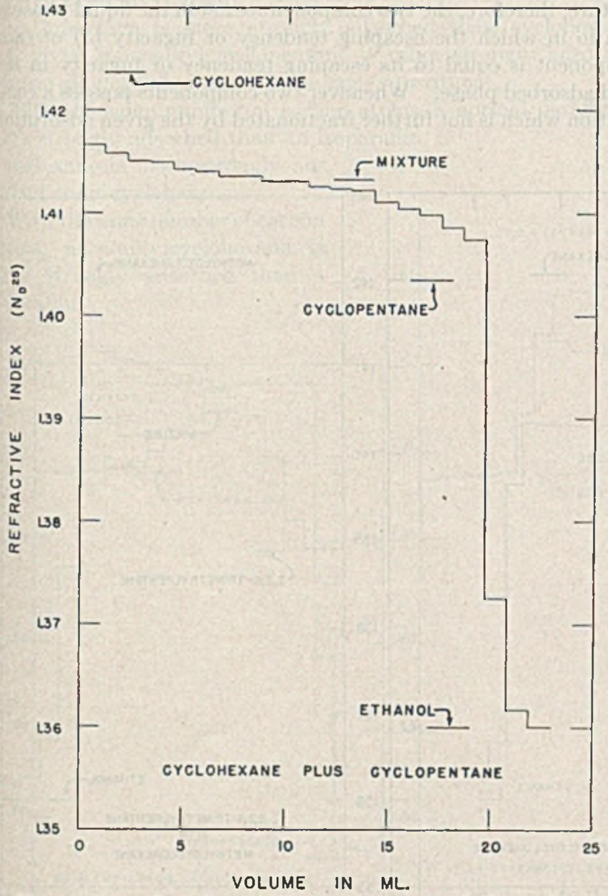


Figure 13. Results of Experiment in 4-Foot Glass Adsorption Column with Silica Gel and a 50-50 Mixture by Volume of Cyclopentane and Cyclohexane

proximately 500 grams of silica gel, was operated in the same manner as the 4-foot adsorption column described by Mair (*4*), except that the time for one experiment in the 26-foot column was about 20 hours, whereas approximately 3 hours were required for one experiment in the 4-foot column. After completion of an experiment in the 26-foot column, the bottom part was cut off at a point above the sintered glass plate (*F*, Figure 9), and the used adsorbent was removed by flushing with water, as for the 4-foot column (*4*). For two of the experiments the 4-foot column was used as previously described (*4*). In the latter experiments refrigerated water was passed through the jacket, and the fractions of filtrate were refrigerated from the time of their removal from the column until the measurements of refractive indices were made.

RESULTS. The results of adsorption experiments made on eleven different binary mixtures (50-50 by volume) of selected hydrocarbons are shown in Figures 10 to 16. The results, including calculation of the composition of the first and last fraction of hydrocarbon filtrate for each mixture, are summarized in Table I.

DISCUSSION

COLUMN. In connection with the assembly and testing of the 52-foot adsorption column previously described, the following points are noted:

The apparatus will, in a one-pass operation, separate a wide boiling gasoline, kerosene, or gas-oil fraction of natural petroleum into (*a*) a portion containing the paraffin and naphthene (cycloparaffin) components, (*b*) a portion containing the bulk of the mononuclear aromatics (free of paraffins and naphthenes and of

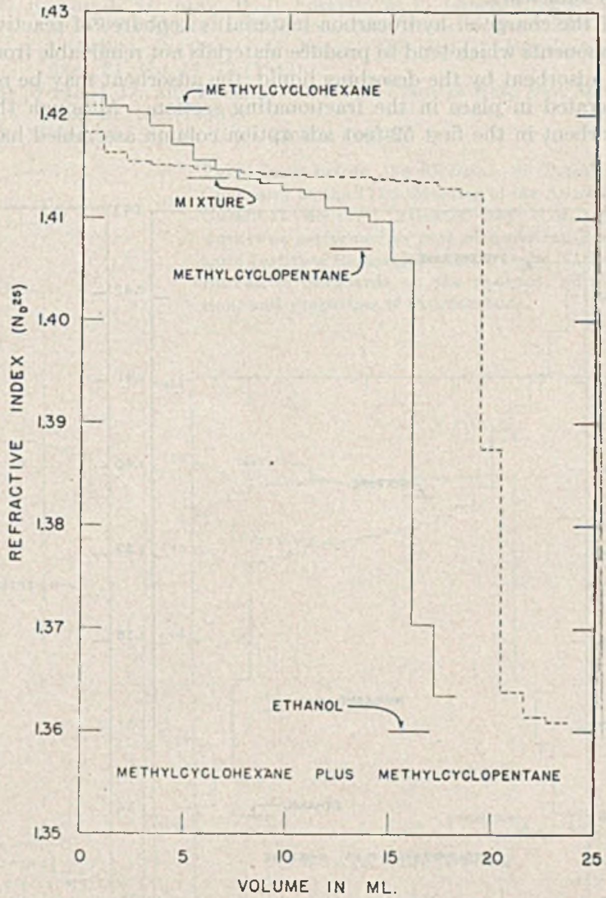


Figure 14. Results of Experiments in 26-Foot (*Solid Lines*) and 4-Foot (*Broken Lines*) Glass Adsorption Columns with Silica Gel and 50-50 Mixture by Volume of Methylcyclopentane and Methylcyclohexane

TABLE I. ADSORPTION EXPERIMENTS WITH SILICA GEL AND ELEVEN DIFFERENT BINARY MIXTURES OF HYDROCARBONS

Mixture No.	Components, 50-50 by Vol.	Approx. Compn.[a] of Hydrocarbon Filtrate, % by Vol. First fraction	Last fraction	Results Plotted in Figure
1	*n*-Dodecane	88	17	10
	n-Heptane	12	83	
2	2,2,4-Trimethylpentane	62	41	11
	n-Octane	38	59	
3	*n*-Butylcyclohexane	58	49	12
	Cyclohexane	42	51	
4	Cyclohexane	65	19	13
	Cyclopentane	35	81	
5	Methylcyclohexane	100	15	14
	Methylcyclopentane	0	85	
6	Cyclohexane	98	33	15 (*left*)
	n-Hexane	2	67	
7	*n*-Heptane	68	48	15 (*center*)
	Methylcyclohexane	32	52	
8	2,2,4-Trimethylpentane	100	25	15 (*right*)
	Methylcyclohexane	0	75	
9	*n*-Butylbenzene	100	0	16 (*left*)
	Benzene	0	100	
10	*n*-Butylbenzene	100	23	16 (*center*)
	1,2,3,4-Tetramethylbenzene	0	77	
11	*p*-Xylene	90	41	16 (*right*)
	o-Xylene	10	59	

[a] Calculated assuming linearity between refractive index and composition in percentage by volume. The uncertainty in the calculated composition is estimated to be ±2% by volume for all the mixtures except No. 2, which is ±5% and No. 9 and 11, which are ±3%.

dinuclear aromatics), (*c*) a portion containing all of the dinuclear aromatic hydrocarbons (contaminated with a small amount of mononuclear aromatics), and (*d*) small intermediate portions between *a* and *b* and between *b* and *c*.

The total amount of hydrocarbon material which may be included in one charge into the apparatus is that quantity which contains about 500 ml. of aromatic hydrocarbons (mononuclear plus dinuclear).

If the charge of hydrocarbon material is kept free of reactive components which tend to produce materials not removable from the adsorbent by the desorbing liquid, the adsorbent may be regenerated in place in the fractionating section. Although the adsorbent in the first 52-foot adsorption column assembled has, at this writing, been used three times and regenerated without difficulty, it is expected that the number of regenerations, while large, will be limited, and that replacement of the adsorbent will be necessary.

BINARY MIXTURES. In connection with the results of the adsorption experiments summarized in Table I and Figures 10 to 16, the following points are noted:

Among the eleven binary mixtures examined, in experiments in which the charge was a 50-50 mixture by volume of the two components, the percentages by volume of the less strongly adsorbed component in the first fraction of hydrocarbon filtrate and of the more strongly adsorbed component in the last fraction of hydrocarbon filtrate were found to be as shown in Table I. (Because of the possible uncertainty in the results obtained on mixture 4 arising from the relatively high volatility and possible loss of cyclopentane, and because this experiment was performed only in the 4-foot column, the results of this experiment will not be further discussed.)

For the experiments shown in Figures 11, 12, 15, and 16 (*center* and *right*) the original mixture was fractionated unsymmetrically to give, as in Figures 15 (*left* and *right*) and 16 (*center*), a pure component in the first filtrate with a break to a mixture of the two components which, while richer in the more strongly adsorbed component, did not further fractionate at all or fractionated only slightly; or, as in Figures 11, 12, 15 (*center*) and 16 (*right*), a first filtrate which was enriched but not pure in the less strongly adsorbed component with a break to a mixture of the two components which, while richer in the more strongly adsorbed component, did not further fractionate at all (or, if so, only slightly). For these seven mixtures and the given fractionating system, more than half of the filtrate (measured from the tail or more strongly adsorbed end of the filtrate) is in each case a mixture which is fractionated very little or not at all. In each unfractionated mixture, therefore, the two components exist in the liquid phase in a ratio in which the escaping tendency or fugacity (*3*) of each component is equal to its escaping tendency or fugacity in the solid adsorbed phase. Whenever two components possess a composition which is not further fractionated by the given adsorption

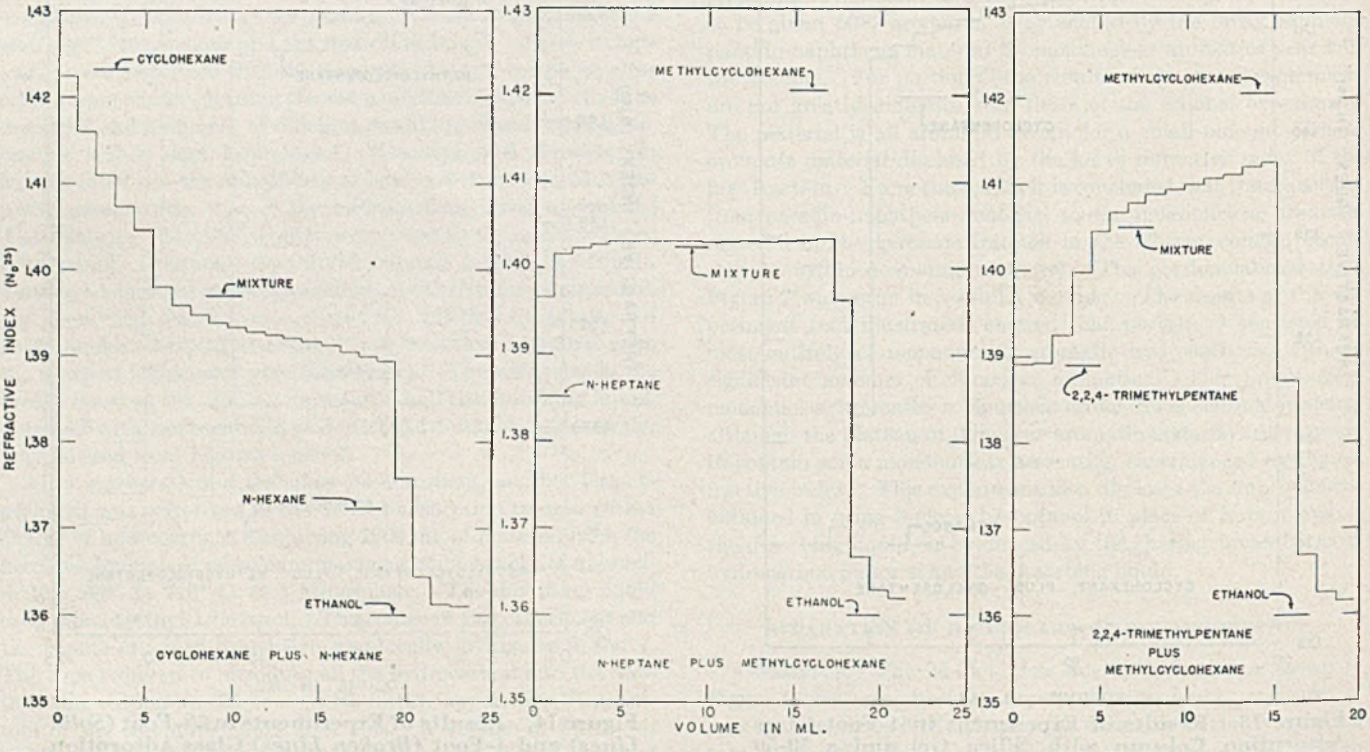


Figure 15. Results of Experiments in 26-Foot Glass Adsorption Column with Silica Gel and 50-50 Mixtures by Volume of Various Components

apparatus, it is possible to obtain from a mixture of these two components some of the less strongly adsorbed component in a substantially pure state, only when the original mixture is richer in the less strongly adsorbed component than the nonfractionating mixture.

For the experiments shown in Figures 10, 14, and 16 (*left*) the original mixture was fractionated symmetrically, or nearly so, to give, as in Figure 16 (*left*), some of both components in a substantially pure state, or, as in Figures 10 and 14, a first filtrate substantially pure in the less strongly adsorbed component and a last hydrocarbon filtrate which, while not pure, is approaching the pure, more strongly adsorbed component. Whenever two components do not possess a composition which is nonfractionating in a given apparatus, therefore, both components may be obtained in a substantially pure state by the process of adsorption, provided adequate length of fractionating section is employed.

With regard to the influence of molecular size and structure on adsorbability, for adsorption from equivalent concentrations in the liquid phase with silica gel as the adsorbent, the following relations appear to hold:

In order of decreasing adsorbability, the several structural components may be listed as (*a*) dinuclear or polynuclear aromatic, (*b*) phenyl, and (*c*) cycloparaffin and paraffin, with *a* and *b* being as a class very much more strongly adsorbed than is *c*. That is to say, the addition of a phenyl group to a paraffin or cycloparaffin group produces a molecule having an adsorbability in the class of *a* and *b*, whereas the differences in adsorbability among cyclopentyl, cyclohexyl, *n*-alkyl, and isoalkyl are relatively small.

Increasing the number of carbon atoms in a *n*-alkyl group decreases the adsorbability. This is true whether the given *n*-alkyl group is already attached to a phenyl, cyclopentyl, cyclohexyl, *n*-alkyl, or isoalkyl group.

Cyclopentane is more strongly adsorbed than cyclohexane. A given monoalkyl cyclopentane is more strongly adsorbed than an alkylcyclohexane with the same substituent.

With the same number of carbon atoms, a normal paraffin is more strongly adsorbed than an isoparaffin.

n-Hexane is more strongly adsorbed than cyclohexane.

With the same number of carbon atoms, a *n*-alkylcyclohexane is more strongly adsorbed than a *n*-paraffin.

With the same number of carbon atoms per molecule a polyalkylbenzene is more strongly adsorbed than a normal alkylbenzene.

For mononuclear aromatics with the same number of carbon atoms per molecule and two alkyl groups attached to the benzene ring, the ortho-substituted compound is more strongly adsorbed than the para-substituted (and presumably more than the meta-substituted).

It is expected that some modification will be made in the details of the foregoing relations between adsorbability and molecular size and structure as additional data become available.

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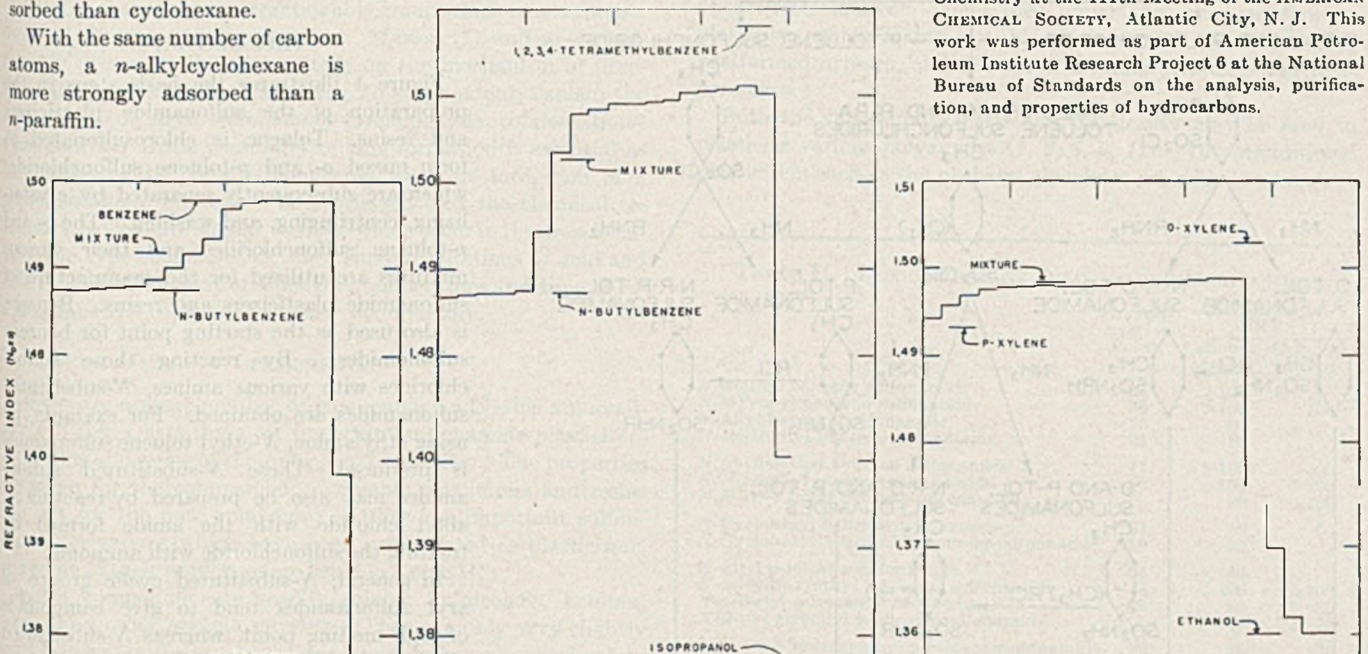

Figure 16. Results of Experiments in 26-Foot Glass Adsorption Column with Silica Gel and 50-50 Mixtures by Volume of Various Alkylbenzenes

SULFONAMIDE PLASTICIZERS AND RESINS

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The sulfonamide plasticizers and resins are compatible with, and impart many desirable characteristics, such as gloss, toughness, and adhesion, to a wide variety of resins, including cellulose nitrate, cellulose acetate, ethylcellulose, nylon, and zein. Physical tests, including tensile strength, elongation, water permeability, and flexibility, were conducted on cellulose nitrate and cellulose acetate films and sheets plasticized with the sulfonamides and using dibutyl phthalate, camphor and dimethyl phthalate, and diethyl phthalate and triacetin as the respective control plasticizers. Tests were also conducted on injection-molded specimens. In cellulose acetate, sulfonamide plasticizers impart greater flexibility and lower water permeability than the control plasticizers. The sulfonamide resins yield films of high tensile strength and extremely low water permeability. In cellulose nitrate the sulfonamides give films of greater tensile strength, elongation, and flexibility than the controls. The sulfonamide resins decrease water permeability, increase solvent resistance, and sharpen the melting point. Some applications of these plasticizers and resins in the paint, varnish, and plastics industry are discussed.

EVER since 1868, when Hyatt successfully plasticized cellulose nitrate with camphor to form celluloid, there has been a desire to utilize other plasticizing materials. Since 1882, when Stevens patented the use of amyl acetate as a solvent for pyroxylin to form a lacquer film, there has been the desire to improve these lacquers and create new types by using various resins and plasticizers. As a result, many different compounds have been investigated; among them are the aryl sulfonamides which have found a secure place industrially as plasticizers and resins.

The first application of the sulfonamides as plasticizers was described in a patent by Schmidt (*10*) in 1904 in which they replaced camphor as a plasticizer for cellulose nitrate. The first application of the sulfonamide resins was described in a patent by Gardner (*3*) in 1925; resins formed by the condensation of aldehydes with toluene sulfonamides are used in film forming compositions in conjunction with cellulose esters and ethers. Since these early times many additional uses of these compounds have been found in coating compositions and molded plastics.

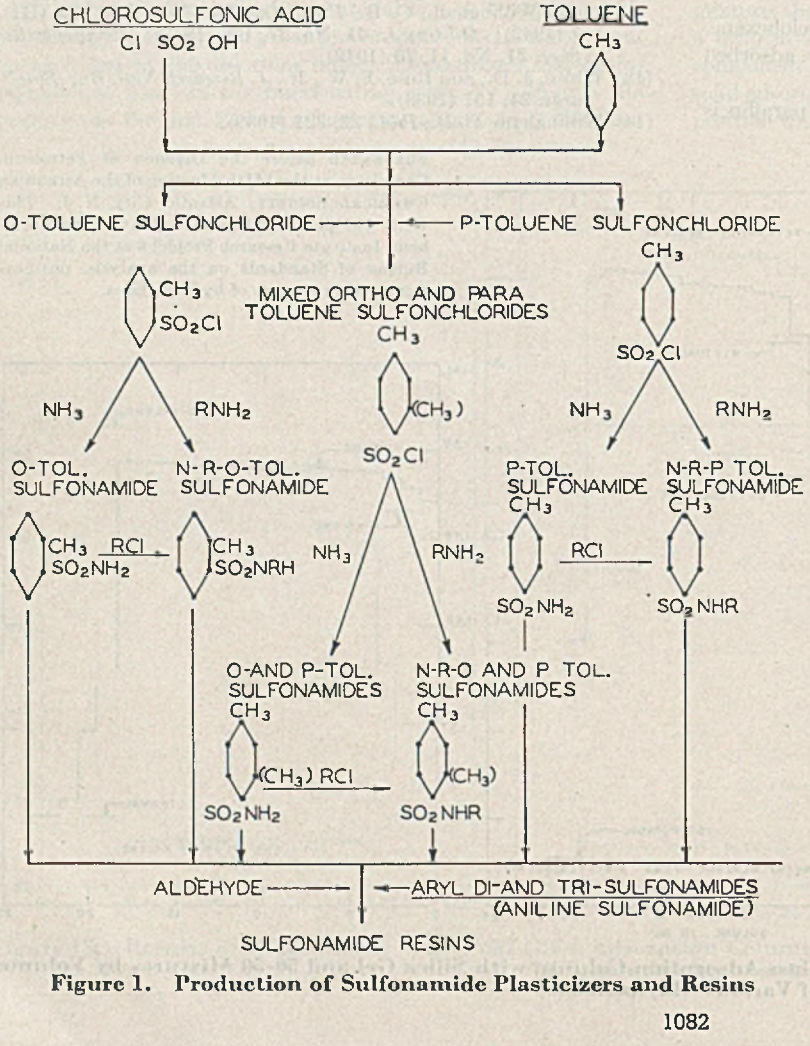


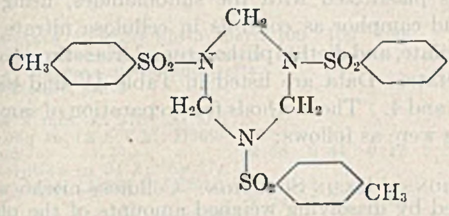
Figure 1. Production of Sulfonamide Plasticizers and Resins

PREPARATION

Figure 1 illustrates the basic steps in the preparation of the sulfonamide plasticizers and resins. Toluene is chlorosulfonated to form mixed *o*- and *p*-toluene sulfonchlorides which are subsequently separated by crystallizing, centrifuging, and washing. The *o*- and *p*-toluene sulfonchlorides and their various mixtures are utilized for the manufacture of sulfonamide plasticizers and resins. Benzene is also used as the starting point for benzene sulfonamides. By reacting those sulfonchlorides with various amines, *N*-substituted sulfonamides are obtained. For example, by using ethylamine, *N*-ethyl toluene sulfonamide is produced. These *N*-substituted sulfonamides may also be prepared by reacting an alkyl chloride with the amide formed by treating the sulfonchloride with ammonia.

In general, *N*-substituted cyclic groups of aryl sulfonamides tend to give compounds of high melting point, whereas *N*-substituted alkyl groups give lower melting points. Di-*N*,*N*-substituted alkyl groups give melting points higher than the mono-*N*-substituted alkyl groups and are generally less compatible with various resins. Increasing the length of the alkyl chain tends to lower the crystallizing point. Alkyl substitution on the aryl group of the sulfonamide causes considerable variation of melting point, and generalities can be drawn only from substituted sulfonamides of the same aryl group.

Resins may be formed by condensing the various sulfonamides with aldehydes such as formaldehyde, furfuraldehyde, and acetaldehyde. Sulfonamide resins of a fusible and soluble type result from the condensation of formaldehyde with aryl monosulfonamides, such as *p*-toluene sulfonamide. In the opinion of various investigators (*6*, *12*) the monoaryl sulfonamide resins may be considered as supercooled melts of mixtures of unchanged sulfonamides and trimeric methylene derivatives having the following structure:



Hard and infusible resins follow the condensation of formaldehyde with di- and trisulfonamides or aniline sulfonamide (sulfanilamide) (*12*). In the latter case the relative positions of the amine groups are important in producing an infusible resin. For example, aniline *o*-sulfonamide with formaldehyde yields a fusible resin (initial softening point 100–118° C. and final softening point 105–157° C.). It is believed that steric hindrance inhibits the primary reaction of the amide with the aldehyde or diminishes the polymerization capacity of the primary condensation product.

On the other hand, aniline *p*- or *m*-sulfonamide condenses with formaldehyde to form an infusible resin. Walter (*12*) views this reaction as proceeding first to a methylene-methylol compound containing more than one reactionable group which reacts further to a polydimensional ring system. Marvel (*7*) and co-workers recently presented their hypothesis on the mechanism of urea-formaldehyde reactions which may, to some extent, explain the mechanism of aryl sulfonamide–formaldehyde condensations. Consideration of the possibility of ring formation is essential as the hardening property is connected with the formation of a polydimensional network. It is believed that the chemical reactions involved are similar to those which occur in the urea-formaldehyde type condensation, since similar variations of acid and alkali catalyst, amount of aldehyde, temperature and time of reaction must be considered in their manufacture.

PROPERTIES

Obviously a great number of compounds and resins are available. Table I lists the more important sulfonamide plasticizers and resins and a few of their physical properties. The properties are given for the commercially available plasticizers and resins and not for the pure compound. Other less important sulfonamide derivatives which have been investigated as plasticizers, and some of their properties are listed in Table II.

These compounds are readily soluble in alcohols, ketones, esters, and other organic solvents. They are only very slightly soluble in water, the greatest water solubility being approximately 1% at 34° C. This solubility generally may be increased in an alkaline solution. However, ammonia in some cases lowers the solubility. The sulfonamides have very low acidity, and vary from colorless liquids, which form a glassy solid at −30° C., to relatively high melting solids and resins.

Table I. Sulfonamide Plasticizers and Resins

Compound	Trade Name	Color and Form	Melting Point, ° C.	Crystallization Point, ° C.
N-Ethyl *p*-toluene sulfonamide	Santicizer 3	White solid	60	..
N-Ethyl *o*- & *p*-toluene sulfonamide	Santicizer 8	Light amber liquid	...	18
o- & *p*-Toluene sulfonamide	Santicizer 9	White solid	105	..
p-Toluene sulfonamide	Santicizer 139	White solid	137	..
N-Ethyl benzene sulfonamide	Santicizer 128	White solid	52	..
N-Butyl benzene sulfonamide	Santicizer 127	Colorless liquid	...	−20
N-Isopropyl benzene sulfonamide	Santicizer 130	Colorless liquid	...	25
Mixed *N*-isopropyl benzene sulfonamide & *N*-isopropyl toluene sulfonamide	Santicizer 131	Colorless liquid	...	−30
Condensation products of aryl sulfonamides and formaldehyde	Santolite H	Colorless, brittle resin	50–58	..
	Santolite MHP	Colorless, brittle resin	45–56	..
A sulfonamide alkyd resin	Santolite K-5	Colorless, viscous resin	...	..

The sulfonamide resins and plasticizers are compatible with and impart many desirable characteristics, such as gloss, toughness, and adhesion, to a wide variety of resins (Table III). In this and subsequent tables the abbreviations N/C, C/Ac, C/AB, and E/C represent cellulose nitrate, cellulose acetate, cellulose acetate butyrate, and ethylcellulose, respectively.

These compatibilities were determined by casting the film from solution, drying, and storing for one week at 95% relative humidity. The maximum compatibility is dependent upon many variables such as the percentage nitration, acetylation, etc., of the base material as the case may be; the environmental conditions at the time of casting (temperature, relative humidity) and of solvent used. Therefore, Table III should serve only as a general indication of the relative compatibilities. Compatibilities above 100 PHR (parts per hundred parts resin) were not tried; however, it is known that in several cases the plasticizers are compatible to 300 PHR.

Although the limits of compatibility are not shown here, it is known that the sulfonamides are compatible with, and in some cases actually enter into, the reaction of various thermosetting plastics such as urea-formaldehyde, melamine formaldehyde, and phenol-formaldehyde. Here they impart an increased flow or plasticity, which makes possible laminated punching stock or postformed articles, and decreased molding pressures and temperatures.

Both the sulfonamide resins and plasticizers may be used to plasticize various polyamides (*1*, *2*, *8*, *9*, *11*). Often additional plasticizers such as the phthalyl glycolates are added to improve

Table II. Less Important Sulfonamide Derivatives

Plasticizer	Crystallization Point, ° C.	Compatibility, PHR[a]	
		Cellulose acetate	Cellulose nitrate
N-Methyl benzene sulfonamide	32	>100	..
N-*n*-Propyl benzene sulfonamide	36	>100	>100
N-Allyl benzene sulfonamide	−25	50	..
N-*sec*-Heptyl benzene sulfonamide	25	50	..
N,*N*-Dimethyl benzene sulfonamide	47	>100	>100
N,*N*-Diethyl benzene sulfonamide	40	>100	>100
N,*N*-Di-*n*-butyl benzene sulfonamide	..	30	>100
N-Cyclohexyl benzene sulfonamide	91	50	50
N-Cyclohexyl-3,4-dichlorobenzenesulfonamide	110	30	..
N-Allyl *p*-toluene sulfonamide	64	< 50	..
N-β-Hydroxyethyl *p*-toluene sulfonamide	−25	>100	>100
N-*n*-Butyl *p*-toluene sulfonamide	−42	80	>100
N-Butyl glycollyl *p*-toluene sulfonamide	..	60	> 75
N,*N*-Di-β-hydroxyethyl *p*-toluene sulfonamide	99	30	30
N,*N*-Di-*n*-butyl *p*-toluene sulfonamide	..	0	>100
N-Cyclohexyl *p*-toluene sulfonamide	86	60	>100
N-Methyl xylene sulfonamide	−25	>100	..
N-cyclohexyl diphenyl sulfonamide	157	0	..
N,*N*-Di-*n*-butyl phenylene disulfonamide	96	60	> 75

[a] Parts per hundred parts of resin.

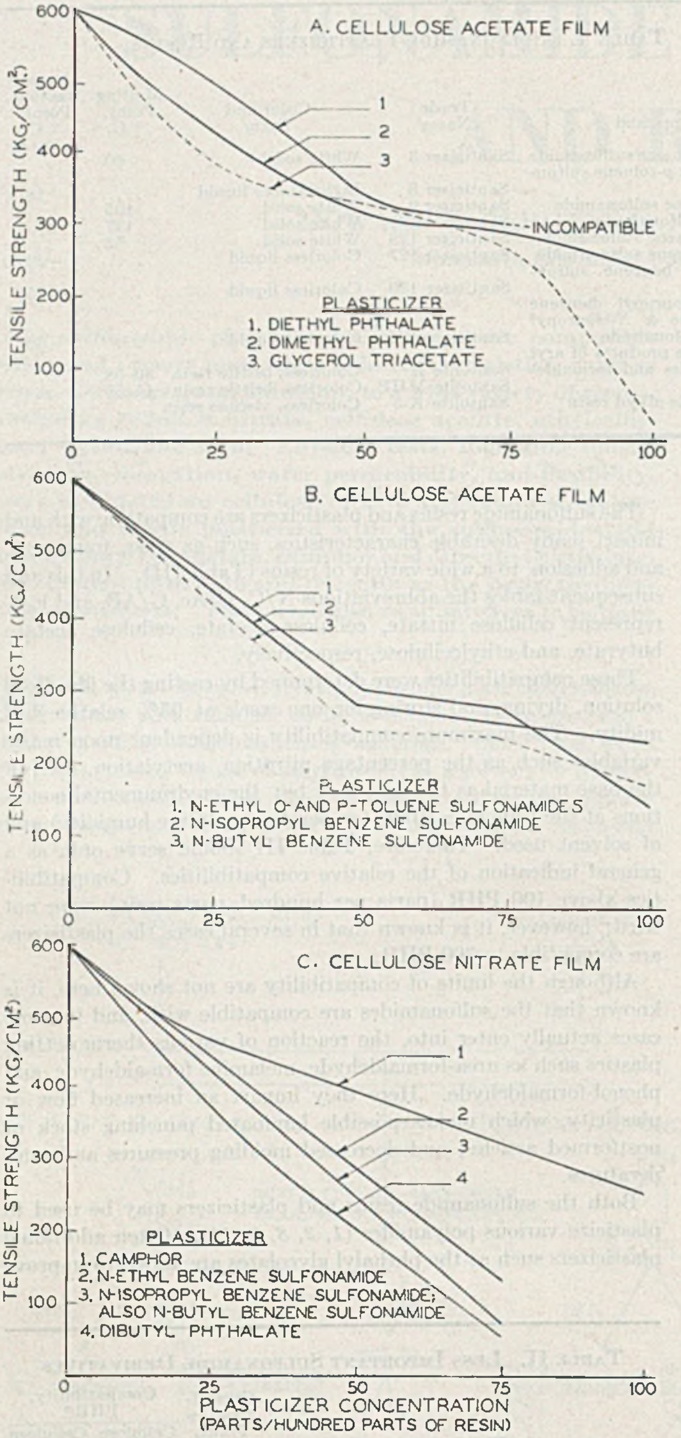


Figure 2. Effect of Plasticizer Concentration on Tensile Strength of Cellulose Acetate and Cellulose Nitrate Film

Table III. Compatibilities of Sulfonamides (Parts per Hundred)

Sulfonamide Derivative	N/C	C/Ac	C/AB	E/C	Zein	Polyvinyl Formal	Polyamide Resins
N-Ethyl *p*-toluene sulfonamide	30[a]	45[a]	40	30	20	45	10
N-Ethyl *o*- & *p*-toluene sulfonamide	100	100	60	80	50	50	30
Mixed toluene sulfonamides	30	30	20	40	20	30	20
p-Toluene sulfonamide	25[a]	30[a]	..	..	..	..	..
N-Ethyl benzene sulfonamide	80	50	50	50	50	50	20
N-Butyl benzene sulfonamide	100	100	60	50	50	50	30
N-Isopropyl benzene sulfonamide	100	100	100	100	60	100	30
Mixed *N*-isopropyl benzene sulfonamide & *N*-isopropyl toluene sulfonamide	100	100	100	100	60	100	30
Santolite H	100	100	100	100	100[a]	..	100
Santolite MHP	100	100	100	100	100[a]	..	100
Santolite K-5	100	100	100	100	100[a]	..	100

[a] Even greater when used in conjunction with additional plasticizers.

low temperature flexibility. The *N*-ethyl *o*- and *p*-toluene sulfonamide and *o*- and *p*-toluene sulfonamide are compatible to the extent of 25 and 50 PHR in shellac, the former exerting a greater softening action. The sulfonamides are compatible with the polyvinyl chloride resins and copolymers; however, they do not impart any outstanding properties.

In general, the sulfonamide plasticizers which are liquids at room temperature are more compatible and exhibit better solvent action than the solid types. However, even at low concentrations the solid sulfonamides are effective in imparting desirable properties which may be more widely enhanced by the use of auxiliary plasticizers such as dibutyl phthalate, the phthalyl glycolates, or tricresyl phosphate.

FILM TESTS

Physical tests were conducted on cellulose nitrate and cellulose acetate films plasticized with the sulfonamides, using dibutyl phthalate and camphor as controls in cellulose nitrate and dimethyl phthalate, and diethyl phthalate and triacetin as controls in cellulose acetate. Data are listed in Table IV and plotted in Figures 2, 3, and 4. The methods for preparation of samples and test methods were as follows:

Preparation of Resin Solution. Cellulose nitrate solutions were prepared by dissolving weighed amounts of the plasticizer in a 15% solution of R.S. $^1/_2$-second cellulose nitrate (12% nitrogen) in a solvent consisting of equal parts by volume of butyl acetate and toluene. Cellulose acetate solutions were prepared by dissolving weighed amounts of the plasticizer in a 11.5% solution of cellulose acetate (38.8% acetyl content) in acetone.

Film Casting. Cellulose nitrate and cellulose acetate films were cast on a spinning plate as described by Gardner and Sward (*5*). The thickness of the film was 0.0010–0.0015 inch for tensile, elongation, and water permeability tests and 0.0025–0.0032 inch for Schopper fold tests.

Conditioning. All samples were dried and conditioned for one week in a constant temperature (25 ± 2° C.) and constant humidity (50–55% relative humidity) room.

Tensile and Elongation. These tests were conducted in a Gardner-Parks tensilemeter.

Fold (Flexibility). Plastic films were tested in a Schopper fold tester in which a tensile load of 1 kg. is applied during the flexibility tests.

Moisture Vapor Permeability. Plastic films, 0.0010–0.0015 inch thick, were sealed over the top of glass bottles containing 10–15 grams of anhydrous calcium chloride so that an area of 10.5 sq. cm. of film was exposed. The bottle was then exposed to an atmosphere of 100% relative humidity for 48 hours and the percentage increase in weight determined. Plasticized films are always compared to a control containing no plasticizer. The gain in weight of the control is taken as 100% permeability, and the percentage permeability of the plasticized films computed from it.

Another series of tests were run in which cellulose acetate, plasticizer, and solvent were mixed, rolled, baked, sheeted, seasoned, and polished to form a sheet approximately 0.010 inch thick. The tests consisted of: tensile strength, using Scott Model S-2 yarn tester; bursting strength, employing a Mullen tester (B. F. Perkins and Son, Inc., Model A); Elmendorf tear test, using Elmendorf paper tearing tester (Thwing-Albert Instrument Company); and water absorption, moisture transfer, and volatility tests.

Table V compares these properties of *N*-ethyl *o*- and *p*-toluene sulfonamide and *o*- and *p*-toluene sulfonamide with dimethyl phthalate, diethyl phthalate, and triacetin in cellulose acetate (38.8% acetyl). The moisture absorption test in this case was determined by keeping the sample over calcium chloride at 25° C. until a constant weight was obtained. The sample was then left over water in a closed container at 25° C. until the weight was again constant. The moisture transfer test was conducted with a setup similar to that used in the previously described water permeability test except the situation was reversed; that is, the water was on the inside to provide 100% relative humidity, and the calcium chloride on the outside for 0% relative humidity. The area of film through which vapor passed was 18.1 sq. cm. The volatility test was conducted in a circulating air oven at 60° C. for 12 days.

For injection molding experiments on isopropyl benzene and toluene sulfonamides, batches of cellulose acetate (38.8% acetyl) plus 40 PHR of plasticizer were prepared by milling at 300° F. Diethyl phthalate was employed as control plasticizer. After milling, the plastic was ground and injection-molded into test samples. The properties of these compounds follow:

Cellulose acetate (Hercules FM-6), parts	100	100	100
N-Isopropyl benzene sulfonamide, parts	40	..	..
N-Isopropyl toluene sulfonamide, parts	..	40	..
Diethyl phthalate, parts	..	..	40
Flow after 2 min. at 275° F. and 1500 lb./sq. in. (A.S.T.M. D569-44T), inch	0.58	0.41	0.17
Water absorption in 24 hr. by 1/8-inch-thick disk (A.S.T.M. D570-42), %	2.24	1.71	2.26
Heat distortion temp. (A.S.T.M. 648-45T), ° C.	64	67.5	69.5
Plasticizer loss, 72 hr. at 82° C., 1/8-inch-thick disk, %	0.57	0.46	1.00

These data, over the various concentration ranges studied, indicate that the sulfonamide plasticizers and resins are compatible to a high degree with cellulose nitrate, cellulose acetate, cellulose acetate butyrate, ethylcellulose, and zein. Their usefulness in polyamides may be inferred from the patents cited.

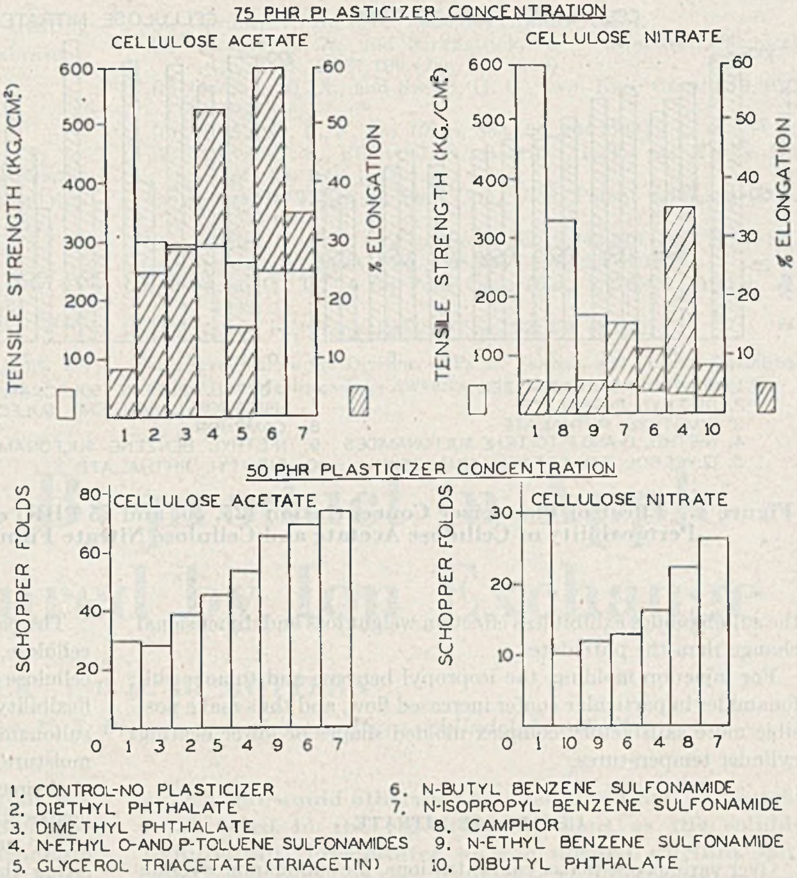


Figure 3. Effect of Plasticizer Concentration on Tensile Strength, Elongation, and Flexibility of Cast Films

Table IV. Effect of Plasticizers on Cast Cellulose Nitrate and Acetate Film

Plasticizer	PHR	Tensile Strength, Kg./Sq. Cm C/Ac	N/C	Elongation, % C/Ac	N/C	Schopper Folds C/Ac	N/C	Water Permeability, % C/Ac	N/C
None	..	600	600	8	6	30	30	100	100
Santolite MHP	25	1050	460	7	2	14	7	67	51
	50	1010	..	7	..	7	..	32	..
	75	565	..	5	..	1	..	22	..
	100	400	..	5	..	0	..	16	..
N-Ethyl *o*- & *p*-toluene sulfonamide	25	455	425	11	7	33	22	50	31
	50	306	165	27	11	55	16	53	63
	75	282	31	53	36	100	..	48	96
o- & *p*-Toluene sulfonamide	25	595	467	9	8	20	27	72	60
	..	..	..	..	..	..	..	..	..
	..	..	..	..	..	..	..	..	..
N-Ethyl benzene sulfonamide	25	310	465	7	11	70	24	67	56
	50	260	195	4	20	67	12	62	98
	75	..	168	..	6	..	..	..	..
N-Butyl benzene sulfonamide	25	425	480	31	4	59	38	67	49
	50	246	175	23	6	70	13	61	57
	75	256	39	59	11	90	..	55	105
N-Isopropyl benzene sulfonamide	25	450	394	6	5	19	27	70	47
	50	280	270	17	5	75	26	47	68
	75	255	46	36	16	159	..	67	87
Glycerol triacetate (triacetin)	25	380	..	8	..	38	..	89	..
	50	330	..	15	..	46	..	84	..
	75	270	..	16	..	66	..	79	..
Dibutyl phthalate	25	..	354	..	5	..	25	..	36
	50	..	185	..	4	..	10	..	65
	75	..	29	..	8	..	3	..	..
Camphor	25	500	460	7	5	26	27	99	89
	50	395	380	16	6	..	22	84	84
	75	..	328	..	4	..	14	..	96
Dimethyl phthalate	25	425	..	6	..	37	..	77	..
	50	310	..	13	..	28	..	71	..
	75	295	..	29	..	28	..	70	..
Diethyl phthalate	25	490	..	24	..	15	..	87	..
	50	330	..	20	..	39	..	77	..
	75	300	..	24	..	49	..	84	..

CELLULOSE ACETATE

Figure 2, *A* and *B*, illustrates the effect of increasing plasticizer concentrations on the tensile strength of cellulose acetate film. The sulfonamide plasticizers are comparable in tensile strength retention to dimethyl phthalate and diethyl phthalate and superior to triacetin. The sulfonamides in cellulose acetate apparently have a certain range of plasticizer concentration (50-75 PHR) in which the elongation increases normally; the tensile strength is only slightly affected (Figure 2*B* and 3). Figure 3 also illustrates the greater flexibility (Schopper folds) obtainable when cellulose acetate is plasticized with sulfonamide plasticizers as compared with dimethyl or diethyl phthalates. Figure 4 indicates percentage water permeability (control taken as 100%) of cellulose acetate films modified with various plasticizers. The sulfonamides show lower water permeability than the reference plasticizers, dimethyl and diethyl phthalates.

The sulfonamide resins are superior in their low water permeability and high tensile strength, and have a unique property of increasing the retentivity of solid plasticizers such as triphenyl phosphate. In cellulose acetate sheets the sulfonamides are better in moisture vapor transfer (Table V) than the phthalates, although the actual moisture absorption is comparable. Further,

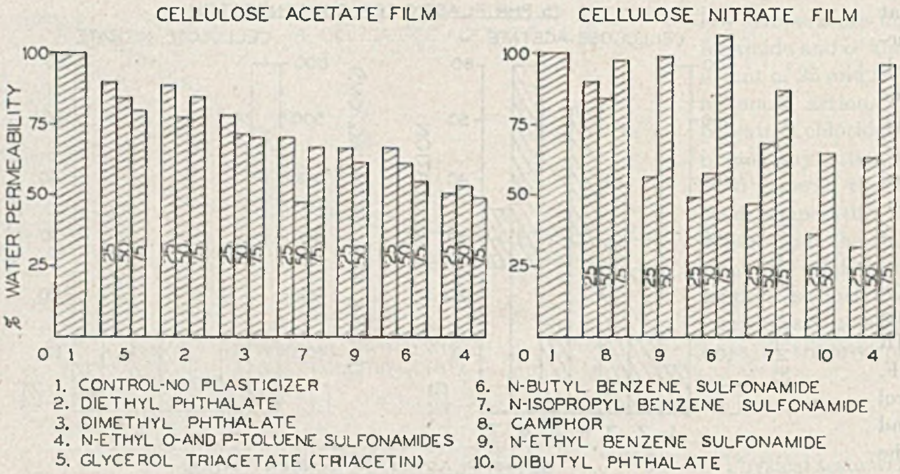


Figure 4. Effect of Plasticizer Concentration (25, 50, and 75 PHR) on Water Permeability of Cellulose Acetate and Cellulose Nitrate Film

the sulfonamides exhibit less effect on weight loss and dimensional change than the phthalates.

For injection molding, the isopropyl benzene and toluene sulfonamides in particular confer increased flow, and thus make possible more satisfactory complex molded shapes or lower heating cylinder temperatures.

CELLULOSE NITRATE

Over various plasticizer concentrations, the sulfonamides retain tensile strength somewhat better than dibutyl phthalate (Figure 2C), yet the elongation at these high plasticizer concentrations is greater than that of dibutyl phthalate (Figure 3). The greatest flexibility (Schopper folds) in cellulose nitrate cast film was obtained on the unplasticized control film, with *N*-isopropyl benzene sulfonamide (Figure 3) giving the next greatest flexibility. Dibutyl phthalate was considerably less flexible than any of the sulfonamides or camphor. The water permeability of plasticizers in cellulose nitrate cast film (Figure 4) varies, depending on the plasticizer concentration. In general, the lowest permeability is obtained around 20-40 PHR of plasticizer. *N*-Ethyl *o*- and *p*-toluene sulfonamide is somewhat better than dibutyl phthalate, and the sulfonamides, in general, are superior to camphor with regard to water permeability. The sulfonamides, when compounded with cellulose nitrate, should not be exposed to temperatures in excess of 80° C. as decomposition occurs, and in molding operations minor explosions may be possible.

The sulfonamide resins are used, generally in conjunction with other plasticizers, in cellulose nitrate surface coatings to lower water permeability and to sharpen the melting point, as in heat-sealing lacquers. They also increase the resistance to gasoline and other aliphatic solvents. Although no quantitative tests have been conducted, the sulfonamide resins and plasticizers generally improve the gloss, clarity, and adhesion of all lacquer films.

APPLICATIONS

Because of these properties, the production of sulfonamides has increased from approximately 1 million pounds in 1939 to approximately 2.5 million in 1945, and many new and varied uses for these materials are being found.

The paint, varnish, and lacquer industries utilize them in nitrocellulose, cellulose acetate, cellulose acetate butyrate, and ethylcellulose resins where films of good clarity, adhesion, durability, flexibility, and gloss and low water permeability are desired. The sulfonamide resins are of value in alkyd resins (*4*) for increasing moisture resistance and compatibility. Typical applications include manicure lacquers, paper and cellophane coatings, adhesives, heat-sealing lacquers, and casein-type paint products.

The sulfonamides are used by the plastics industry for plasticizing thermosetting resins, such as phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, and copolymer-ester-type resins, so that better flow is obtainable and lower temperatures and pressures may be used. Numerous patents refer to the use of sulfonamide plasticizers for plasticizing nylon in order to improve working qualities, durability, flexibility, and moisture resistance of films, sheets, and surface coatings. Reports from Germany indicate that liquid sulfonamide plasticizers were used to plasticize polyamides for making protective gas capes and artificial leathers. It is possible that the sulfonamides may be useful in polyvinylidene chloride films and filaments.

Sulfonamide plasticizers are useful in cellulose acetate, cellulose acetate butyrate, ethylcellulose, and cellulose propionate molded articles because of their good flow characteristics, low volatility and low moisture permeability or transfer characteristics, and good dimensional stability. Sulfonamides are valuable for certain plastic films and lacquers used for packaging because of this low moisture transfer rate.

Table V. Effect of Plasticizers on Rolled and Molded Cellulose Acetate Sheet

Plasticizer	PHR	Tensile Strength, Lb./Sq. In.	Elongation, %	Mullen Bursting Strength, Lb./Sq. M./Mil	Elmendorf Tear Test, G./Mil	Moisture Absorption, %	Moisture Transfer, G./Sq. M./Day/Mil	Volatility (12 Days, 60° C.) % wt. change	Volatility (12 Days, 60° C.) % length change
None (C/Ac, 38.8% acetyl)	..	8924	8.3	22.3	9.3	6.92	2452	1.13	0.32
N-Ethyl *o*- & *p*-toluene sulfonamide	10	7893	11.7	22.9	12.6	4.36	637	0.75	0.51
	25	6640	40.0	22.3	15.9			1.11	0.50
	35	5393	38.8	21.8	20.4			2.59	0.50
o- & *p*-Toluene sulfonamide	10	7710	7.3	25.9	10.9	4.71	549	1.26	0.36
	25	5830	6.0	19.8	15.5			2.02	0.76
	35	4465	19.5	19.4	24.9			2.46	1.10
Dimethyl phthalate	10	8225	3.5	23.9	11.1	4.50	969	0.93	0.24
	25	5160	40.0	20.5	18.0			2.63	0.99
	35	4030	36.5	19.7	19.0			3.60	1.38
Diethyl phthalate	10	7750	3.0	20.9	10.7	4.07	1027	0.90	0.26
	25	5760	40.5	21.1	17.5			2.46	0.88
	35	5360	57.0	17.5	16.5			3.86	1.36
Triacetin	10	7280	5.0	25.2	12.0	4.18	...	1.08	0.18
	25	5730	43.3	20.6	19.2			2.12	0.72
	35	6290	43.8	19.7	20.6			..	..

Some use has been made of the sulfonamide resins in a treating solution for textile fibers to improve dyeing qualities, abrasion, and water resistance of the woven cloth.

ACKNOWLEDGMENT

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l-Malic Acid as By-product in Apple Sirup Manufactured by Ion Exchange

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The *l*-malic acid which is adsorbed on an anion exchanger in the preparation of a bland apple sirup can be recovered from the effluent from the sodium carbonate regeneration of the exchanger. Only a slight modification is necessary in the regular regenerative procedure to recover what would otherwise be waste material. The acid is obtained in the regenerant effluent as the soluble sodium salt, precipitated as the normal calcium salt, and converted to the free acid by double decomposition with sulfuric acid.

A PREVIOUS paper (*4*) described a procedure for the removal of malic acid from apple juice by adsorption on an anion exchanger used in the manufacture of apple sirup. Deacidification results in a lower requirement of lime for the precipitation of pectin than in the original sirup process (*12*), leaves less calcium malate in the juice, and produces a blander sirup. The present paper describes a procedure whereby the malic acid can be obtained as a by-product from the deacidification step in the manufacture of this type of apple sirup. Malic acid can be used as a food acidulant, and the active acid might also have special application in chemistry, where an optically active compound is desired.

It is generally recognized that *l*-malic acid (levorotatory) is the principal organic acid in apples, although the presence of citric acid has been reported (*2, 7, 14*). The absence of other acid simplifies the procedure, since it is not necessary to separate acids. No evidence of an acid other than *l*-malic was found in the apple juice used in the experiments reported herein. Charley *et al.* (*5*) prepared malic acid as a by-product in the manufacture of apple treacle. They neutralized the excess acidity of the juice with calcium carbonate and, on concentrating, obtained a precipitate of neutral calcium malate. Juice of high acidity (0.7%) was used in their work. The present authors were unable to duplicate their results with juices of a lower acidity (0.4%) commonly found in America. Active *l*-malic acid has also been prepared from maple sugar sand (*18*) and mountain ash berries (*20*).

Anion exchangers have been used in the recovery of tartaric acid from grape wastes (*10*). In the present work the anion exchanger is used as an acid adsorber, inasmuch as the main purpose is the reduction of the acidity of apple juice. Regeneration is accomplished with sodium carbonate solution, and the acid is recovered in the regenerant effluent as the soluble sodium salt and is precipitated from the effluent as the insoluble calcium salt.

Free malic acid is very difficult to crystallize. The apple sirup manufacturer would probably prefer to sell the calcium malate to chemical manufacturers, who in turn would prepare the free acid, either in crystalline form or as a concentrated solution.

It was also thought that the distillery waste from apple brandy manufacture might be utilized as another source of malic acid. However, analysis has shown that such wastes contain little, if any, malic acid. Malic acid is partially or completely destroyed during the fermentation process, probably being converted to lactic acid (*8*).

DETERMINATION OF MALIC ACID

Since malic was the only acid in the apple juice used in these studies and since it existed almost entirely in the uncombined condition (*2*), determination of the titratable acidity of apple juice gave its malic acid content. The juice was titrated with standard alkali to a pH value of 8.1 (*3*) rather than to a phenolphthalein end point. The latter is difficult to read because of the color of the juice and because of the appreciable darkening which occurs as the acid is neutralized.

The method generally employed for determination of sodium malate in the regenerant effluent is based on the fact that malic acid with a uranyl salt forms a complex with greatly increased rotatory power (*6, 9, 21*). Many modifications have been described in the literature. The one described here is a simplified A.O.A.C. procedure (*1*), since no other optically active substances are present in appreciable quantities. Analysis has shown that there is no sugar in the regenerant effluent.

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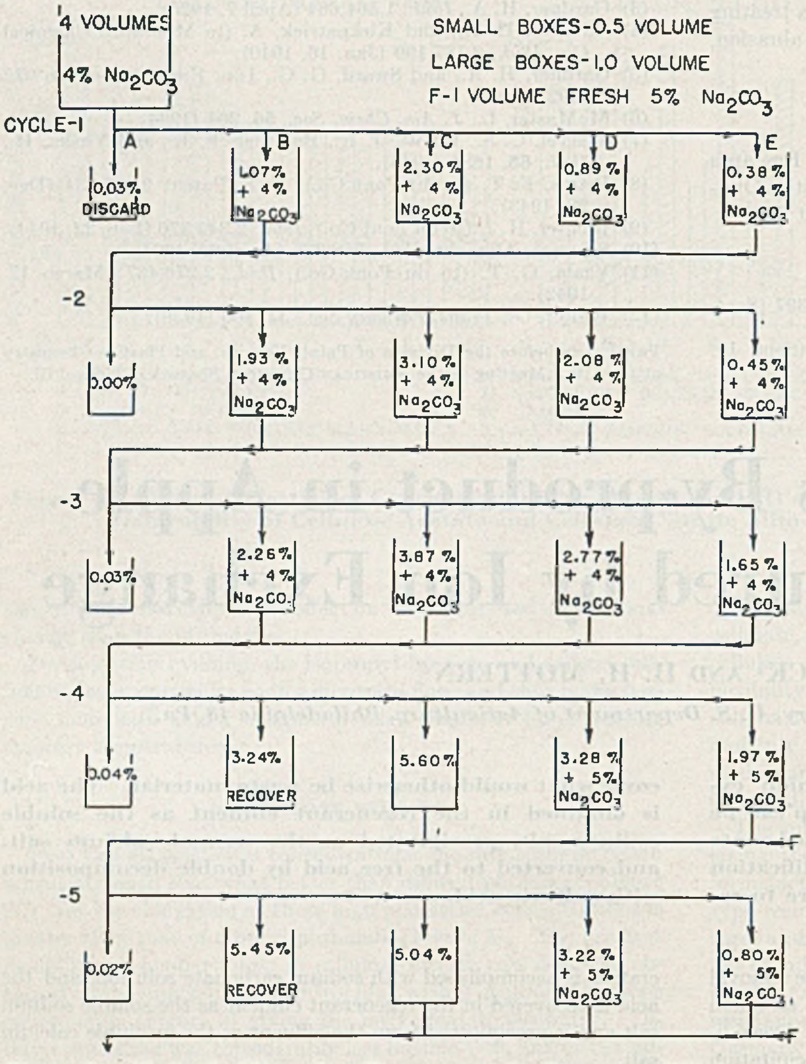

Figure 1. Method of Recycling Regenerant for Recovery of Malic Acid

Upper percentage indicates malate content

The procedure is briefly as follows: Pipet a 25-ml. sample into a 100-ml. volumetric flask; make it just alkaline to a phenolphthalein end point with 1 *N* sulfuric acid or 1 *N* sodium hydroxide; add 2 ml. glacial acetic acid and make to volume; transfer a 20-ml. aliquot to a 25-ml. volumetric flask containing approximately 3.0 grams of uranyl acetate (finely ground); shake vigorously at intervals for 3 hours; make to volume with saturated uranyl acetate solution and filter; polarize in a 200-mm. tube with sodium light. Calculation: degrees angular rotation × 0.519 = grams malic acid per 100 ml. of original solution.

The accuracy of the method varies, but the results are considered sufficiently reliable to estimate the malate content of the regenerant effluent. For determining the purity of the precipitated calcium malate, the authors have relied on calcium and ash determinations. Comparison of the two methods of analysis on samples of calcium malate shows that the polarimetric method gives results which may vary as much as ±5% of those obtained by calcium and ash determinations.

ADSORPTION ON ANION EXCHANGER

General methods for the use of ion exchangers (*13, 15, 16, 19*) and their particular application to the deacidification of apple juice have been described in detail elsewhere (*4*). The screened (200 mesh) juice is passed downflow through an anion exchanger bed until the pH value of the combined effluent juice reaches 5.0; at this point about 80–85% of the malic acid in the juice processed has been adsorbed, and the exchanger is considered exhausted. Exchanger beds of 1- and 4-inch diameters were used.

The capacity of the anion exchanger used is about 15 volumes of juice, of approximately 0.4% malic acid content, per volume of exchanger; this represents an adsorption of about 750 milliequivalents, or approximately 50 grams, of malic acid per liter of exchanger. Variations in capacity from 650 to 850 milliequivalents per liter have been noted for the same exchanger with different juices. The anion exchanger used was De-Acidite (The Permutit Company), although other exchangers will work equally well.

REMOVAL FROM ANION EXCHANGER

After the exhaustion of the exchanger, the bed is backwashed with water to remove residual juice and then regenerated with sodium carbonate solution in preparation for the next cycle. The acid is removed from the exchanger in the regenerant effluent as the soluble sodium salt.

The original regenerant consists of 4 volumes of 4% sodium carbonate solution and is passed downflow through the exchanger bed at a rate of 2 gallons per minute per square foot of cross sectional area of the bed. The volume of regenerant used is expressed in terms of the volume of the bed. As the regenerant passes through the bed, most of the malate is eluted in the first portion of the effluent as shown in Figure 1, in which the percentages indicate the malate concentration in the effluent fractions. The first 0.5 volume of effluent (fraction A) is discarded, since it is largely the water displaced from the bed and contains little, if any, malate.

The regenerant effluent is recycled in order to build up the malate concentration to about 5%, at which point satisfactory precipitation of calcium malate can be obtained. A flow diagram for recycling the regenerant is illustrated in Figure 1. After discarding fraction A, four 1-volume fractions of effluent are collected from each cycle. Water is then passed through the bed to rinse out the excess alkali, and the bed is then ready for the deacidification of apple juice in the next cycle. The regenerant effluent fractions from cycle 1, after fortification with more sodium carbonate, are then passed through the exchanger bed in order as the regenerant for cycle 2. This procedure is repeated until the malate concentration in fraction B has reached the desired value, and B is then removed for recovery. The remainder of the fractions are used as the regenerant for the next cycle with the addition of one volume of fresh 5% sodium carbonate solution as shown in the diagram for cycle 4. From this point on, fraction B, which was fraction C in the preceding cycle, is withdrawn for precipitation.

After cycle 4, fraction C is not fortified with more sodium carbonate, since it already contains an excess, and passage through the exchanger in the next cycle reduces this excess so that there is less carbonate to remove in the precipitation procedure. The slight reduction of malate content from fraction C, cycle 4, to fraction B, cycle 5, is probably due to dilution by water in the exchanger which more than offsets the gain derived from a succeeding elution. The rinse water used after fraction E has been collected may contain small amounts of malate, and the first portion of this rinse water may be used for preparing the fresh sodium carbonate solution.

An excess of sodium carbonate is used to ensure complete removal of the adsorbed acid and to take care of the previously noted variation in the capacity of the exchanger for different juices. Smaller amounts of sodium carbonate did not always give complete recovery. The presence of inorganic anions from the apple juice will increase the requirement of regenerant over that necessary to remove the adsorbed acid. No attempt was made to use an alkali stronger than sodium carbonate as a regenerant.

PRECIPITATION OF CALCIUM MALATE

The portion of the regenerant effluent saved for recovery contains about 5.0% malic acid as the soluble sodium salt in a solution containing an excess of sodium carbonate. The excess carbonate is removed by acidifying with hydrochloric acid. The malate is precipitated from this solution as the relatively insoluble neutral calcium salt.

While neutral calcium malate has limited solubility (20°, 0.82; 57°, 0.57 gram per 100 grams water), it does not precipitate so readily as might be expected. It is not precipitated from alkaline solution, and at too high acidity the more soluble calcium acid malate (20°, 1.5; 57°, 32.2 grams per 100 grams water) is formed, and the yields are lowered appreciably.

The complete procedure for precipitation of the neutral salt is described in detail with a specific example, and the factors affecting the precipitation will be discussed separately: Four liters of regenerant effluent with a pH value of 8.5 and containing 188 grams of malic acid as sodium malate were acidified with hydrochloric acid to a pH of 5.5. This solution was concentrated under vacuum to one fourth the original volume, and the pH value was adjusted to 6.0 with sodium hydroxide. A 40% calcium chloride solution was added slowly with stirring; 10% excess of calcium over the theoretical amount required was used. Usually a grainy precipitate formed immediately. Occasionally it was necessary to seed the supersaturated solution. This was allowed to stand for 24 hours for complete precipitation, and then was filtered by suction and washed with a small amount of hot water. The calcium malate was dried to constant weight at room temperature. The yield was 284 grams of dry product. Calcium determination proved this product to be 97% calcium malate as the trihydrate, and ash determination indicated that it contained 2% ash other than calcium. The yield represented a 90% recovery of the malate from the original regenerant effluent. Drying at 70° C. in a vacuum oven gave a hydrated product containing 1.5 molecules of water.

Figure 2 shows the effect of the malate concentration in the effluent on the yields of calcium malate obtained when precipitated at a pH value of 6.0. The effluent should be concentrated to 15 to 20% malate in order to realize a 90% recovery.

Figure 2 also shows that maximum recovery was obtained when precipitation occurred at an initial pH value of 6.0. Below 5.5 there was an appreciable decrease in yield, probably because of the formation of the more soluble acid salt. The pH value of the mother liquor after the precipitation is decreased to about 4.0. Maintaining the pH value at 6.0 during the precipitation does not increase the yield.

The acid salt can readily be obtained in good yields and with high purity by dissolving the neutral salt in a 10% nitric acid solution until saturated at 57° C., the temperature of maximum solubility. The saturated solution is filtered hot, and, on cooling, a fine white crystalline material separates. The crystalline calcium acid malate is the hexahydrate, and equivalent weight determinations indicate that a product of nearly 100% purity is obtained on the first crystallization.

CONVERSION OF CALCIUM MALATE TO MALIC ACID

The acid or neutral calcium malate can readily be converted to the free acid by treating it with sulfuric acid. The calcium is removed as insoluble sulfate. As might be expected from such a reaction, nearly quantitative yields can be obtained. Crystallization of the free acid from its solution, however, is not so easy.

The finely ground calcium malate is dispersed in about twice its weight of water to form a thick slurry, and 50% sulfuric acid is slowly stirred in. Slightly less than the calculated amount of sulfuric acid required to remove the calcium is used. The mixture is stirred for several hours, allowed to stand overnight, and then filtered on a suction filter. The precipitated calcium sulfate is washed with water, and the filtrate and washings are combined. On concentrating this dilute solution under vacuum, a further slight precipitate of calcium sulfate is formed; this is filtered off, and the filtrate is further concentrated to a thick sirup. For example, 150 grams of calcium malate trihydrate containing 87 grams of malic acid by analysis yielded 84 grams of malic acid as a 67% solution. This represents a 96% recovery of the acid from the calcium salt.

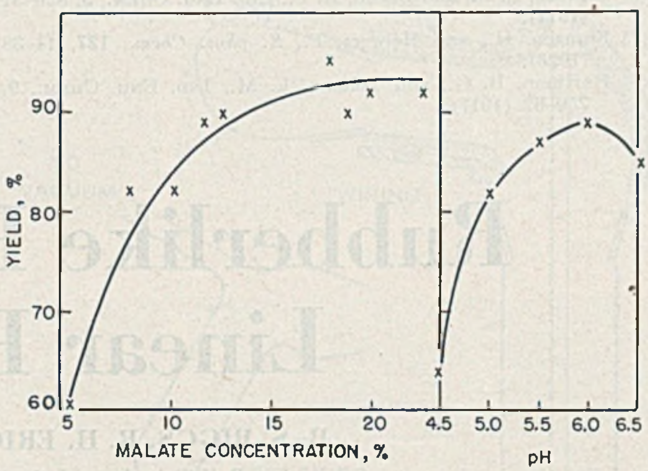

Figure 2. Effect of Malate Concentration and Initial pH of Precipitation on Yields of Calcium Malate

Because of its high solubility, malic acid is difficult to crystallize from its solution. Other workers have stated that crystallization will occur after the acid has been concentrated to a thick sirup and allowed to stand, but we have been unable to obtain a crystalline product. Drying at 70° C. in a vacuum oven does not cause crystallization, and no crystals have been obtained even on holding the thick sirup for long periods of time in a vacuum desiccator. The acid should not be dried at temperatures higher than 70° C. because of the possibility of anhydride formation (*11*).

For identification purposes, a small amount of crystalline *l*-malic acid was prepared by precipitation of the lead salt and subsequent decomposition with hydrogen sulfide to remove the lead. The resulting solution was concentrated in vacuo, and the residual water removed by distillation with absolute ethanol. A crystalline product was obtained, and this was recrystallized from an alcohol-benzene solution, which was evaporated until crystallization occurred. The material melted at 103° C. (corrected), which agrees with that reported by McCall and Guthrie (*9*). The mixed melting point with a known sample of *l*-malic acid was 103° C. The equivalent weight was 67.1 (calculated, 67.0). The melting point of the *p*-bromophenacyl ester was 179° C. (corrected), which agrees with that given by Shriner and Fuson (*17*).

DISCUSSION

l-Malic acid can be produced as a by-product in the manufacture of apple sirup by the ion exchange process. By a slight modification in the regular exchanger regenerative procedure with sodium carbonate, the acid is obtained as the soluble sodium salt in the regenerant effluent in sufficient concentration to permit recovery. The effluent is acidified to pH 5.5 to remove excess carbonate, evaporated to 15–20% malate content, and adjusted to pH 6.0. Calcium chloride is added to precipitate calcium malate trihydrate of about 97% purity and with about a 90% yield. Calcium malate is then converted to the free acid by double decomposition with sulfuric acid with nearly quantitative yields.

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Rubberlike Products from Linear Polyesters

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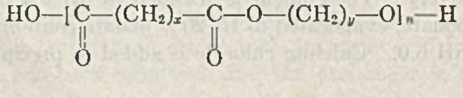
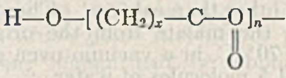
The polymers which result from the condensation of dibasic acids with propylene glycol are viscous gums which can be vulcanized to rubberlike products. In the unpigmented condition these rubbers are quite weak, but when reinforced with suitable pigments their strength and elongation compare favorably with other synthetic rubbers. Because polyesters of known structure and molecular weight can be easily synthesized, these polymers are useful for the study of the relations between structure and properties in rubberlike materials in general. Factors affecting tensile strength, oil resistance, brittle temperature, and stability are discussed.

THE development of rubberlike products from linear polyesters was announced in a short news article more than three years ago (*4*), but a detailed description of their preparation and physical properties has not been published. The object of this paper is to review these properties. However, the paper is written not so much from the viewpoint of offering a synthetic rubber for practical use as from that of applying linear polyesters to the study of the relations between structure and properties of rubberlike substances in general. As has been pointed out in other articles (*3, 8, 15*), the linear polyesters are well suited to serve as models in such a study, since molecules of definitely known constitution and molecular weight distribution can be synthesized by relatively simple methods. Furthermore, the chemical structure of the polyester chain molecules can be varied in a definite and controlled manner by the choice of suitable glycol and dibasic acid or hydroxy acid reactants. The structure of the chains in the case of the former, assuming equal molar proportions, may be represented by the general formula



$$\mathrm{HO{-}[\underset{\underset{O}{\|}}{C}{-}(CH_2)_x{-}\underset{\underset{O}{\|}}{C}{-}O{-}(CH_2)_y{-}O]_n{-}H}$$

where x and y are integers greater than 1 and n is usually above 50 on the average. A polymer from a hydroxy acid has a simpler structure:



$$\mathrm{H{-}O{-}[(CH_2)_x{-}\underset{\underset{O}{\|}}{C}{-}O]_n{-}H}$$

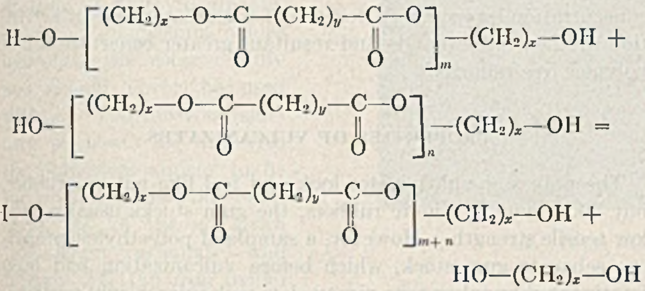
In all cases only linear chains are present, provided strictly bifunctional starting ingredients have been used. Thus many of the ambiguities of structure which complicate diene polymers (such as *cis* and *trans* orientations, 1,2 and 1,4 addition, etc.) are avoided. Finally, because of the known molecular weight distribution, the number average molecular weight, on which the physical properties mainly depend, can be readily determined from viscosity measurements (*3, 8, 12*).

PREPARATION OF POLYESTERS

Polyesters are prepared by condensation of glycols with dibasic acids, or by self-condensation of hydroxy acids. A more diverse series of compounds is possible from the glycol dibasic acid polymers, since the availability of appropriate hydroxy acids is extremely limited; therefore the remainder of this discussion will be confined to the former type of reaction.

The general method of preparation consists of two steps. In the first, a mixture of the dibasic acid and an excess of glycol containing a trace of catalyst—for example, 0.01% zinc chloride—is esterified by being heated at a temperature from 200° to 260° C., depending on the nature of the reactants. Succinic esters darken badly, and adipic esters decompose with formation of cyclopentanone at temperatures above 220° C., whereas sebacic acid can be used satisfactorily at as high as 260° C. or higher. Similarly some glycols decompose at high temperatures. The esterification is carried out under a reflux column heated to such a temperature that water cannot condense and glycol cannot escape. The reaction ingredients are stirred continuously and are kept under an inert atmosphere, preferably of hydrogen. In laboratory runs both results can be accomplished by passage of a rapid stream of dry, oxygen-free hydrogen through the mixture. Esterification may take $^1/_2$ to several hours, depending on the size of the batch and the efficiency of the apparatus, and may be considered complete for practical purposes when a cold surface held against the outlet tube shows no condensation of moisture.

At this point the product consists of low polymer with glycol residues on each end of every chain. The next step consists of a vacuum treatment during which the chain length is built up by ester interchange (*13, 21*) between the small units of polymer with resultant elimination of glycol which distills away. This reaction is illustrated by the following general equation:



$$\mathrm{H{-}O{-}}\left[(\mathrm{CH_2})_x\mathrm{{-}O{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}}(\mathrm{CH_2})_y\mathrm{{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O}\right]_m\mathrm{{-}}(\mathrm{CH_2})_x\mathrm{{-}OH}\ +$$

$$\mathrm{HO{-}}\left[(\mathrm{CH_2})_x\mathrm{{-}O{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}}(\mathrm{CH_2})_y\mathrm{{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O}\right]_n\mathrm{{-}}(\mathrm{CH_2})_x\mathrm{{-}OH}\ =$$

$$\mathrm{H{-}O{-}}\left[(\mathrm{CH_2})_x\mathrm{{-}O{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}}(\mathrm{CH_2})_y\mathrm{{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O}\right]_{m+n}\mathrm{{-}}(\mathrm{CH_2})_x\mathrm{{-}OH}\ +$$

$$\mathrm{HO{-}}(\mathrm{CH_2})_x\mathrm{{-}OH}$$

For this step the reflux column is replaced by a very short distillation head which is wired for heat and is kept at a temperature such that no condensate forms in it. The pressure is reduced slowly to less than 5 mm., the flow of hydrogen being adjusted accordingly, and glycol is distilled off as fast as it is formed. Small amounts of cyclic ester also are found in the distillate. Ester interchange is quite rapid at first while the mixture is limpid, but as the viscosity increases, because of increased molecular weight, the rate of interchange falls off, and a point is finally reached at which the rate is so slow that continuation of the reaction becomes unprofitable. For small laboratory batches (about 50 grams, Figure 1) the time required under favorable circumstances—that is, with reactants which can be run at 250° C.—is about 3 hours. At lower temperature or with larger batches a longer time is required. Efficient stirring is of the greatest importance, particularly after the product becomes viscous, and a powerful and efficient mechanical agitator saves many hours of preparation time on large batches.

At the end of a run the polymer is poured or scraped while hot into large flat pans which have been dusted with talc or whiting.

CONTROL OF MELTING POINT

The high molecular linear polyesters which have received most attention in the literature are microcrystalline waxes. These have been described in the work of Lycan and Adams (*18*), Carothers and co-workers (*6, 7, 8*), and Fuller and co-workers (*3, 16, 17*).

Examples are polyethylene sebacate, melting point 74°, polyethylene succinate, m.p. 100°, polydecamethylene sebacate, m.p. 74°, polyhydroxy decanoate, m.p. 74–76°, etc. All of these materials would be classified as plastics—that is, they are rigid solids at room temperature.

In contrast with them, however, polypropylene sebacate and polypropylene succinate are amorphous balsamlike substances which show no tendency to crystallize at room temperature (*14*). This effect of a lowering of melting point by aliphatic substituents on the chain is common in polymer chemistry—for example, the relation of polyisobutylene to polyethylene, and the methylated polyamides to the unmethylated (*5*)—and it is this effect which makes possible the production of polyester rubbers. Actually polypropylene sebacate crystallizes slowly at lower temperatures and melts at about 10° C. Polypropylene succinate freezes to a glass at about −10° C. The copolyesters formed from the three components ethylene glycol, propylene glycol, and sebacic acid all have melting points between those of polyethylene sebacate and polypropylene sebacate. All ethylene-propylene succinates in which the proportion of propylene residues is more than 50 mole % are completely amorphous at room temperature. Unless otherwise stated, all sebacates in this paper have an ethylene-propylene ratio of 20 to 80 mole %, and all succinates a ratio of 50 to 50 mole %.

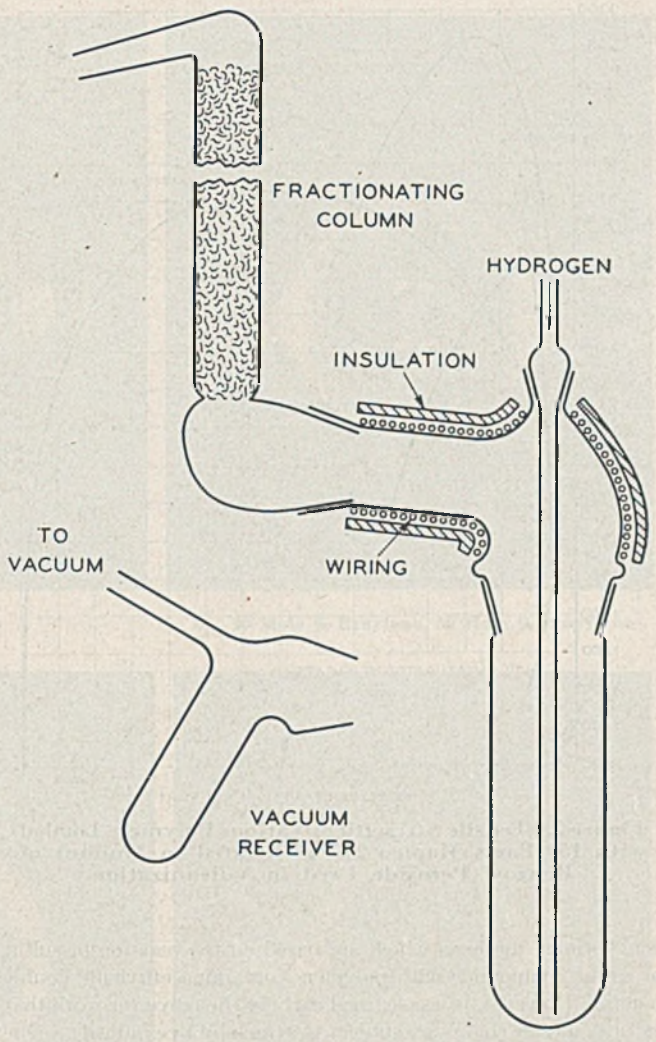


Figure 1. Apparatus for Preparation of Small Laboratory Batches of Polyesters

Another method of controlling the melting point of polyesters for the purpose of making rubbery products is the use of sufficiently complicated mixtures of dibasic acids or glycols without any side chains. When a mixture of several dibasic acids is reacted with ethylene glycol, soft, low melting products may be obtained. The method is of limited application because of the small number of suitable intermediates available, but it makes possible the use of certain acid mixtures resulting from the oxidation of oils, fats, etc. For the purposes of this paper discussion will be confined to ethylene-propylene esters of succinic, adipic, sebacic, phthalic, and maleic acids.

VULCANIZATION

The term vulcanization, as applied to rubber, may be defined as the introduction of primary valence cross links between essentially linear polymer chains. To make the polyester gums useful as rubbers, it was necessary to find some method of introducing cross links in a controlled manner. The esters so far described are completely saturated and hence cannot be vulcanized by the

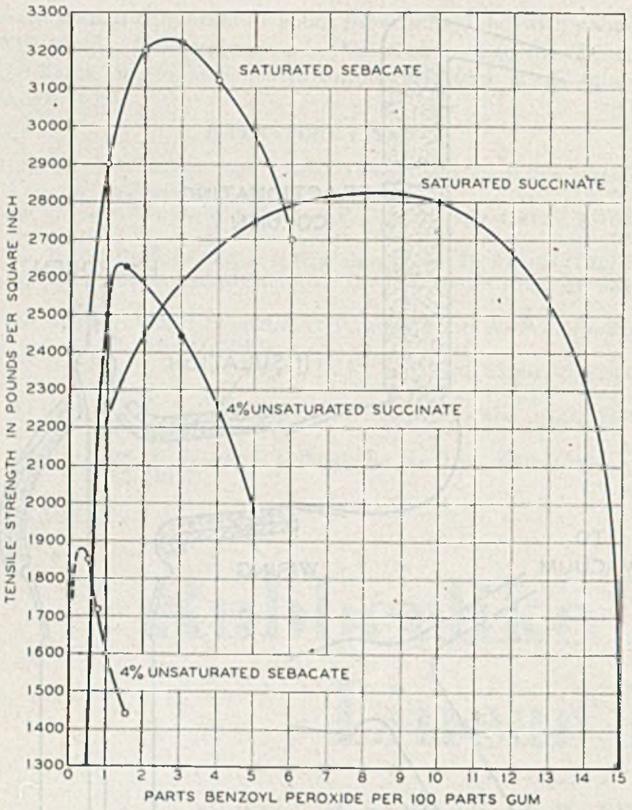


Figure 2. Tensile Strength of Various Polymers Loaded with 150 Parts Mapico 297 as Related to Amount of Benzoyl Peroxide Used in Vulcanization

conventional methods which are based on the reaction of sulfur or sulfur compounds with polymers containing ethylenic double bonds. However, it was learned early in the polyester work that saturated ester chains are subject to attack by free radicals. One of the results of the reaction is the linking of two ester molecules, presumably through the carbon atoms alpha to the carbonyl group. Regardless of the mechanism, which has not been too well investigated, the empirical fact is that attack by free radicals constitutes an admirable method of vulcanizing saturated polyester rubbers.

A convenient source of free radicals for this vulcanization is the decomposition of benzoyl peroxide. A saturated ethylene propylene sebacate polyester requires about 4% of its own weight of benzoyl peroxide for optimum cure. A saturated succinate requires about 10%. In all cases the peroxide is added to the gum on a rubber mill, and the mix is cured in much the same manner as are conventional rubber compounds. The decomposition point of benzoyl peroxide is about 107° C., and any temperature above that is satisfactory for curing polyester rubber. Normally a temperature of 125° to 150° C. is used. The cure is almost instantaneous and is not affected appreciably by time or temperature. Thus the product can be heated for an hour at 150° C. without overcuring, although 10 minutes at 130° C. is adequate. Suitable sources of free radicals other than benzoyl peroxide may also be used—for example, stearoyl peroxide or phenyl azide—but they appear to have no advantage, and in the case of the azides are even dangerous.

Although vulcanization of saturated polyesters can thus be accomplished by the use of 4% or more of benzoyl peroxide, this has the disadvantage that it leaves in the rubber a fairly large amount of benzoic acid, which is one of the by-products of the decomposition. The presence of acidic or alkaline materials materially damages the aging characteristics of esters and hence is undesirable. Efforts were therefore made to lower the amount of peroxide needed for optimum cure. It was soon found that replacement of a few mole per cent of the saturated dibasic acid in the original reaction mixture with an equivalent amount of maleic or other unsaturated acid facilitates markedly the vulcanization of the resulting product. Thus a polyethylene propylene sebacate containing 3 mole % maleic residues is well cured with only 1% of its own weight of benzoyl peroxide. Corresponding succinates require about 2% (Figure 2).

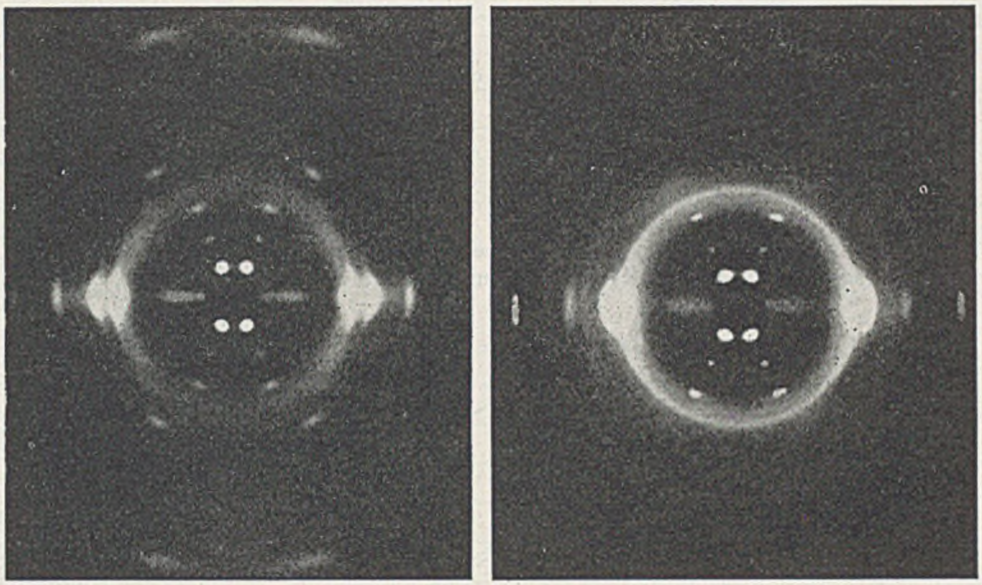
Polyesters containing 3% unsaturation are still not vulcanizable by sulfur, but when the unsaturation is raised to about 15% vulcanization can be obtained with sulfur and the usual organic accelerators. These facts suggest that sulfur vulcanization may require superimposition of double bonds in the adjacent molecules, whereas the peroxide type does not. The peroxide vulcanization of polymers containing unsaturation is effective at low peroxide concentration, presumably because of the greater ease of activation of the double bonds and resultant greater concentration of polymer free radicals.

PROPERTIES OF VULCANIZATES

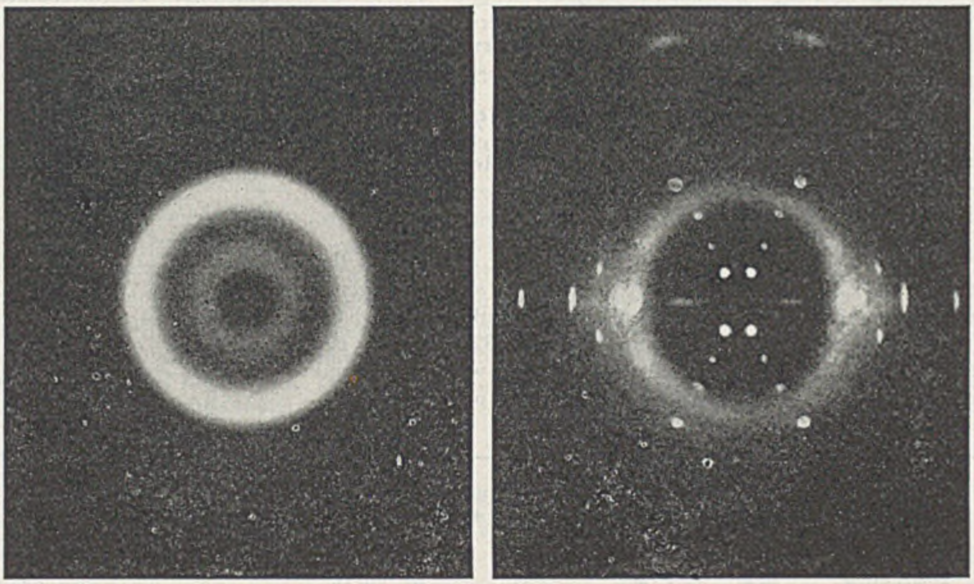
The polyester vulcanizates look and feel like natural rubber, but, like many synthetic rubbers, the gum stocks usually have low tensile strength. However, a sample of polyethylenepropylene sebacate gum stock, which before vulcanization had been fractionated by solvents to remove low molecular weight portions, showed a tensile strength of 1800 pounds per square inch when pulled at the rate of 20 inches per minute. As Figure 3 shows, considerable crystallization occurs during this stretching process. This figure represents x-ray patterns of the unstretched (*C*) and fully stretched (*D*) fractionated polymer which contained 80 mole % propylene and 20 mole % ethylene glycol reacted with sebacic acid (*1*). For comparison, a 50-50 polymer of the same components is shown unstretched in Figure 3*B*, and a fiber pattern of pure polyethylene sebacate is shown in Figure 3*A*. It is evident that, as propylene groups with their appended methyl groups are added, an increased amount of amorphous scattering occurs in the x-ray pattern. Apparently, in the solid, regions of low degree of order are being produced as more methyl is introduced. When still higher percentages are reached (80%) the polymer is entirely amorphous at room temperature. When the sample is cooled to about 35° C. and allowed to stand, even this higher substituted material will crystallize; this shows that the methyl groups lower the melting point of the polymer but do not seriously interfere with the chain packing. When the 80% propylene polymer is vulcanized, its crystallization temperature decreases still further (to approximately 20° C.), as in the case of neoprene. At room temperature (above about 20° C.), therefore, it is necessary to stretch the 80% polymer to induce crystallization. The degree of ordering on stretching is high (Figure 3*B*), and the only effect of the methyl groups on the structure appears to be to expand slightly the dimensions perpendicular to the chains to conform to the greater space requirements. Thus in the pure polyethylene sebacate these dimensions are 4.18 Å. and 3.75 Å., whereas in the 80% propylene copolyester they are 4.20 Å. and 4.00 Å., respectively. There is in addition a decrease in intensity of the original 3.75 Å. reflection. The fiber periods in the two cases are identical (16.9 Å.), as would be expected from the chain structures. When the specimen of Figure 3*B* is relaxed, the pattern of 3*A* is again obtained; this shows that the effect is reversible.

This observed crystalline behavior of the 80% propylene polyester explains the high tensile strength observed in this particular gum stock. The rate of crystallization or ordering on stretch, however, is relatively slow (*1*) compared to natural rubber, so that on a rapid application of force the tensile strength is low. Thus for the best comparison of properties the polyester rubbers should be reinforced with pigments. The remainder of this discussion will deal with pigmented stocks.

The polyesters wet most pigments extremely well and are highly reinforced by those which are finely divided, although the use of certain ones of the available finely divided pigments is undesirable for other reasons. Carbon black, for example, cannot be used with benzoyl peroxide-cured stocks because they catalyze the decomposition of peroxide and prevent its vulcanizing action unless very large amounts are used, in which case the benzoic acid produced causes rapid hydrolysis of the vulcanizate. Zinc and magnesium oxides hydrolyze the ester rapidly and should never be used with it. The most satisfactory pigments for use with the polyesters appear to be the whitings, iron oxides, and clays, and of these Kalvan (a calcium carbonate) and Mapico 297 (an iron oxide) are outstanding. The tensile strength of properly loaded polyester rubbers ranges from 1600 to 3300 pounds per square inch, depending on type, and the elongations average between 300 and 600%. The outstanding characteristic of the vulcanizates is good resistance to oil, ozone, light, and heat. This and other properties of polyester rubbers are functions of composition and structure. Some of these properties have been measured fairly accurately and will be discussed in the following paragraphs.



A. 100% Ethylene *B.* 50 Mole % Ethylene, 50 Mole % Propylene



C. 20 Mole % Ethylene, 80 Mole % Propylene (Unstretched) *D.* 20 Mole % Ethylene, 80 Mole % Propylene (Stretched 600%)

Figure 3. X-Ray Patterns of Sebacic Acid Polyesters at 25° C. with Fiber Axes Vertical

FACTORS AFFECTING TENSILE STRENGTH

Pigment Reinforcement. Figure 4 shows the relation of amount of loading to tensile strength for a 3% unsaturated ethylene-propylene succinate loaded with Mapico 297. The strength rises steeply with increased loading and passes through a maximum. Similar curves are obtained for other pigments, but the maximum tensile strength obtainable varies from one pigment to another and appears to be related to the particle size of the pigment, as might be expected. For the finest pigments maximum tensile strength occurs at a volume loading of 25–30%. The following table gives values of maximum tensile strength for several pigments in different particle sizes at optimum loading in 3% unsaturated ethylene-propylene succinate polyesters:

	Tensile Strength, Lb./Sq. In.
Calcium carbonates	
Whiting A	1200
Kalvan	2550
Iron oxides	
Iron oxide A	1100
Mapico 516	1750
Mapico 297	2400
Talc	
Coarse	900
Reground	1900

Of the two calcium carbonates shown, Kalvan is known to be much more finely divided than Whiting A (*9*), and of the three iron oxides, Mapico 297 is much the finest (*10*). The material designated "reground talc" was obtained by a further grinding operation on the sample called "coarse talc." Although it cannot be said that other factors are not also present, these results show clearly that reinforcement is a function of the particle size of the pigment. This is probably true for all rubbers when the pigment is truly dispersed. It is of interest that Mapico 297 and Kalvan confer almost as high a tensile strength on polyester rubbers as is usually found in carbon black-loaded GR-S stocks, and this suggests that, if they could be properly dispersed in GR-S, equally high tensiles might be obtained (*19*).

Molecular Weight and Molecular Weight Distribution. As with other rubbers, the tensile strength of the polyester rubbers is affected by the molecular weight of the polymer. This point has not been studied systematically, but in the course of the work polymers of different average molecular weights have been examined. Table I presents the tensile values on three saturated ethylene propylene sebacates.

The weight average molecular weights were calculated from solution viscosities with the equation (*3*):

$$\frac{\ln \eta_r}{c} = 0.31 \times 10^{-4} \bar{M}_w + 0.07 \qquad (1)$$

where $c = 0.4$ gram per 100 ml.

The number average molecular weights are assumed to be half the weight average values, in line with Flory's distribution curve (*12*).

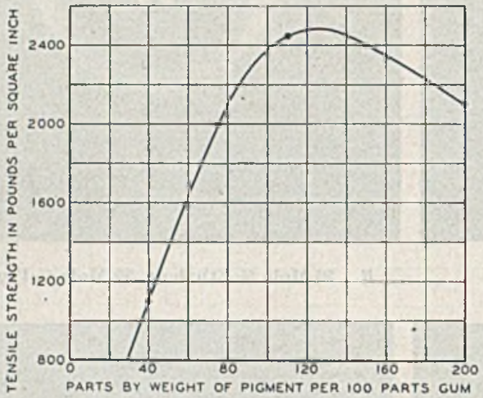


Figure 4. Tensile Strength of 3% Unsaturated Ethylene Propylene Succinate as Affected by Amount of Mapico 297 Incorporated

Further data were obtained by fractionating a sample of the polymer GA 227 (Table I) roughly in halves by suitable solvents and compounding and curing the high molecular weight half. The tensile strength of this vulcanizate was 3200 pounds per square inch. The low molecular weight half was so soft and sticky that it could not be compounded satisfactorily.

TABLE I. EFFECT OF AVERAGE MOLECULAR WEIGHT ON TENSILE STRENGTH OF POLYESTER RUBBERS

Sample Designation	$\frac{\ln \eta_r}{c}$	$\bar{M}_w$	$\bar{M}_n$	Tensile Strength, Lb./Sq. In.
GA 225	0.929	27,700	13,850	3100
GA 226	0.783	23,000	11,500	2915
GA 227	0.698	20,260	10,130	2450

Although the data of Table I are not extensive, they show that variations in molecular weight, at least in the range indicated, have an important effect.

ORDERLINESS OF CHAIN STRUCTURE. The high tensile strength of crystalline polyesters is to a large extent a result of the attractive forces between the polar groups. When rubbery polyesters are stretched to high elongations they crystallize like natural rubber, provided the orderly occurrence of repeating units has not been disturbed. The highest degree of order obtainable in a polyester rubber of the ethylene-propylene series is that in which a single dibasic acid is involved, such as the saturated sebacate or succinate. These polymers, when properly compounded and cured, have tensile strengths ranging from 2800 to 3200 pounds per square inch. When the orderly repetition of the units is disrupted by inclusion of another reactant as in copolymers, the polar groups in adjacent chains fail to coordinate, and tensile strength falls (Figures 5, 6, 7). This behavior is analogous to that of the linear copolyamides (*2*). Examples of co-reactants which lower the tensile strength of sebacates are succinic and maleic acids. These, being four-carbon acids, alter the spacings of the polar groups along the chain. The effect of succinic and maleic, furthermore, is not the same, that of maleic being much the larger, as a comparison of Figure 8 with Figures 5, 6, and 7 shows. This difference probably reflects a concomitant lowering of chain length, which is a result of the reactivity of the double bond of the maleic residue. This reactivity inevitably introduces some cross linking during the period of preparation of the polymer, so that the limiting melt viscosity is reached at a lower average chain length. This, together with the disrupting effect of the cross links, leads to lower tensile strength.

The effect of small proportions of maleate residues on succinate polymers is less pronounced, presumably because they are both four-carbon units, but it becomes quite large as the maleate content increases. This is demonstrated in Figure 9, which shows a plot of maximum tensile strength at optimum cure against increasing maleate content. The strength is seen to fall off rapidly beyond about 4% maleate, probably because of the decrease in effective chain length and cross linking mentioned. Figure 8, in addition to the sebacate-maleate and succinate-maleate (the 4% unsaturation is from maleate), also presents data on a sebacate-succinate-maleate copolymer and on a mixture obtained by adding sebacate-maleate polymer to succinate-maleate polymer in equal amounts. The mechanical mixing of the two polymers lowers the tensile strength below that of either pure component but still does not have so pronounced an effect as copolymerizing the same intermediates.

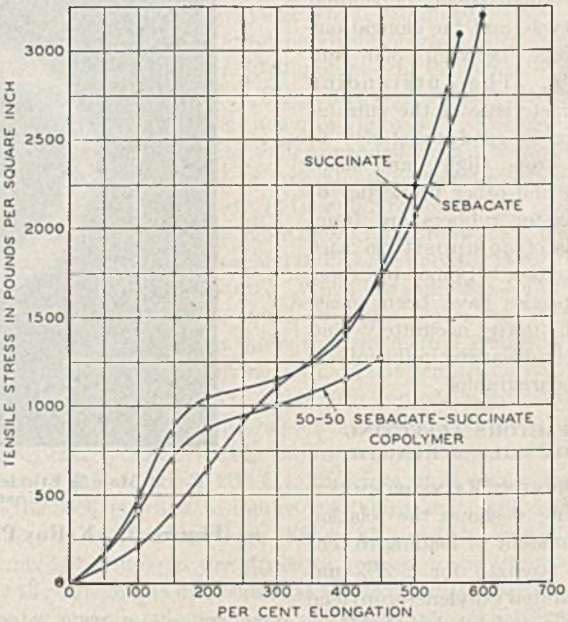


Figure 5. Stress-Strain Curves at Optimum Cure for Various Saturated Polymers Loaded with 150 Parts Mapico 297

STATE OF CURE. It was pointed out earlier that polyesters do not overcure with time or heat, but that degree of cure is controlled by the amount of unsaturation and amount of peroxide used. Figure 2, which was cited in the discussion of vulcanization, illustrates clearly the effect of state of cure on tensile strength. Overcuring lowers tensile rapidly, particularly in unsaturated polymers. This is characteristic of most rubbers and is probably the result of the hampering effect of cross links on chain orientation. The chains in a highly cross-linked sample—that is, in an overcure—are not able to reach the high elongations which permit good chain alignment (and result in wider distribution of the applied stress) and therefore are more easily broken.

BRITTLE TEMPERATURE

Other rubbery systems, such as copolymers of butadiene with styrene, butadiene with acrylonitrile, and butadiene with dichlorostyrene, have given ample evidence that the brittle temperature of the finished polymer is a function of the concentration of polar groups present in it. The work with polyester rubbers adds to the weight of this evidence and furthermore indicates that orderliness of structure, at least in the amorphous state, is not important with regard to this property.

The brittle temperature of ethylene propylene sebecate is about −47° C., that of the succinate is about −12° C., and sebacate-succinate copolymers have intermediate values lying on a curve which is only slightly concave upward (Figure 10). Furthermore the adipate containing two carbonyl groups in a repeating unit of 186 has almost exactly the same brittle temperature as a sebacate-succinate containing the same number of carbonyl groups per unit weight (this polymer results from two moles of succinic acid and one mole of sebacic acid), although the orderliness of structure is far greater in the adipate than in the sebacate-succinate copolymer. The brittle temperature of ethylene propylene phthalate is above room temperature, and the phthalate-sebacate copolymers fall on a smooth curve, which again is only slightly concave upward and shows no significant effect of the greater disorder of the copolymer.

OIL RESISTANCE

The resistance of a rubber to the swelling action of various hydrocarbon oils and solvents has been shown by experience on the Buna N type rubbers of varying acrylonitrile content to be a function of the concentration of the polar nitrile groups in the polymer. Thus a rubber which is 40% acrylonitrile is much more resistant than one containing 18%. The same rules hold for the polyester rubbers, in which the polar group is carbonyl. Succinate polymers are extremely resistant to the swelling action of hydrocarbon oils and gasoline, and even pure toluene produces a linear expansion of only about 10%. Adipates and sebacates are affected proportionately more in toluene or in aromatic gasoline, but are not attacked by mineral oils. As with brittle points the property appears to be a function of composition alone and is not related to orderliness of structure. Thus, as with the brittle point, the adipate is swollen by a given type of gasoline to the same extent as is a succinate-sebacate copolymer which has the same number of carbonyl groups per unit length.

TABLE II. OIL RESISTANCE OF POLYESTER RUBBERS

Polyester Composition		% Change in Length after 48 Hr. in	
Polymer	Pigment or filler, parts	100 octane gasoline	40% aromatic gasoline
Succinate	Clay, 50	0.0	0.7
Adipate	Clay, 50	1.5	6.0
Sebacate	Clay, 50	6.0	20.0
Succinate	Iron oxide, 150	0.0	0.0
Sebacate-phthalate, 70-30	Iron oxide, 150	3.0	6.0
Succinate	Carbon black[a], 60	−1.5	0.0
Succinate	Iron oxide[a], 150	−1.5	−1.5
Sebacate-succinate, 20-80	Clay, 50	0.0	3.0
Sebacate-succinate, 30-70	Iron oxide, 150	0.7	7.0

[a] Cured with 9 parts benzoyl peroxide.

Table II gives the per cent change in length of strips of various compounds after 48 hours immersion in gasoline. The original dimensions of the strips were 1/16 × 1/4 × 2 inches. Change in the 2-inch dimension was used as the criterion of relative swell. Unless otherwise noted, the compounds consisted of 100 parts polymer, the stated amounts of pigment, and 1.5 parts benzoyl peroxide.

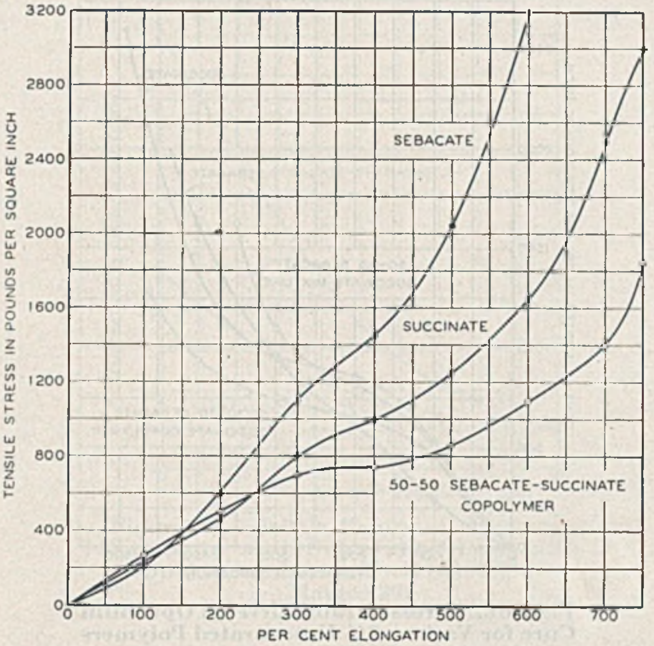


Figure 6. Stress-Strain Curves at Optimum Cure for Various Saturated Polymers Loaded with 75 Parts Kalvan

DIELECTRIC PROPERTIES

The electrical properties of solid linear polyesters have been reported by Yager and Baker (*22*). The present rubberlike polyesters having similar chemical composition exhibit somewhat analogous behavior. The lower intermolecular forces, particularly the reduced polar coordination as a consequence of substitution with its attendant steric disorder, however, result in dielectric constants and power factors, at the same temperature and frequency, which are higher than those shown by the solid linear polyesters. Also the effect of water absorption is greater. Typical dielectric properties are shown in the following table for clay-filled compounds.

	Days in Water at 25° C.	Power Factor, %	Dielectric Constant	D. C. Resistivity, Ohm-Cm. (400 Volts)
Succinate	0	1.30	8.20	5×10^{13}
	7	17.2	25.1	2×10^{9}
Sebacate	0	0.536	5.72	9.8×10^{12}
	7	3.8	10.7	6.5×10^{11}

The better electrical behavior of the more hydrocarbonlike sebacate polyester is evident.

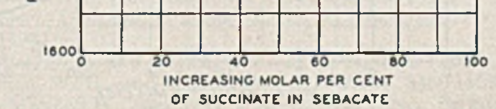


Figure 7. Maximum Tensile Strength at Optimum Cure of Saturated Sebacate-Succinate Copolymers Loaded with 75 Parts Kalvan

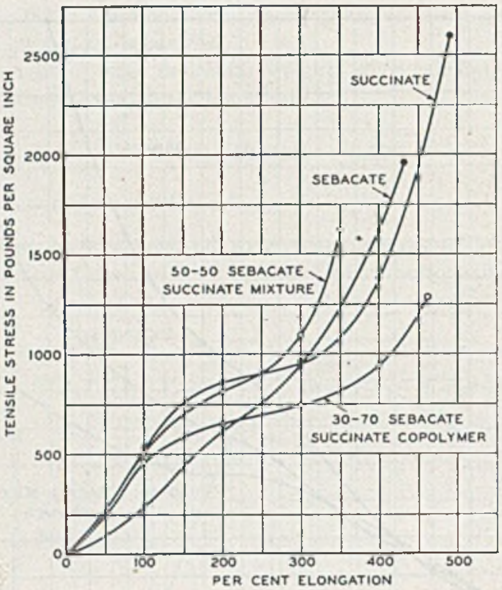


Figure 8. Stress-Strain Curves at Optimum Cure for Various 3% Unsaturated Polymers Loaded with 150 Parts Mapico 297

FACTORS AFFECTING USEFUL LIFE

The properties discussed so far are the original properties characteristic of new samples. It is appropriate now to see what factors act to degrade these properties with time. The atmospheric agents which are known to deteriorate natural rubber rapidly are ozone and oxygen, the attack of the latter being accelerated by heat and light (*11, 20*). It is recognized that the chief action of ozone is attack of double bonds, and since vulcanized polyesters are substantially saturated these rubbers are quite resistant to ozone, as would be expected. In this regard they rank with Butyl rubber, Thiokol, and neoprene. The other enemies of natural rubber, however, also act on polyesters, and in addition the latter are subject to hydrolysis, which is not directly a factor with natural rubber.

Oxidation Accelerated by Heat. The deterioration of natural and most synthetic rubbers with heat (short of pyrolysis) is largely an oxidative effect. This is evident from the fact that the action proceeds from the outside and gradually works to the center of a test piece. Thermal oxidation tests which have been run on polyester rubbers include the standard oxygen bomb aging at 70° C. and air oven aging at 100° C. Data obtained in these tests on compound M 165 (a sebacate–3% maleate polymer) are shown in Table III.

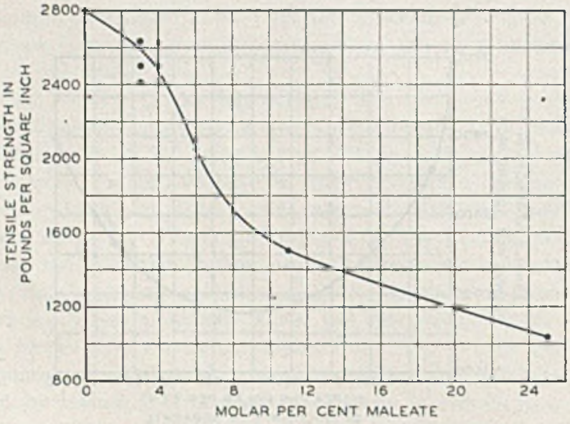


Figure 9. Maximum Tensile Strength at Optimum Cure of Succinates Loaded with 150 Parts Mapico 297 as Affected by Increasing Unsaturation

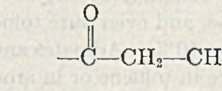
Table III. Aging of Sebacate-Maleate Polyester Rubber Cured 10 Minutes at 150° C.

	Air Oven at 100° C.			
	0	7 days	14 days	28 days
Shore A hardness	66	....	63	63
Tensile strength, lb./sq. in.	1735	1585	1620	1435
Elongation, %	380	330	330	315
	Oxygen Bomb at 70° C. and 300 Lb./Sq. In.			
	0	2 days	4 days	10 days
Tensile strength, lb./sq. in.	1735	1655	1640	1625
Elongation, %	380	355	350	365

Composition of M 165	
Ethylene propylene sebacate maleate (20-80-97-3)	100
Kalvan	75
Luperco A[a]	4.35
Total	179.35

[a] Luperco A is a suspension of benzoyl peroxide on calcium sulfate. Peroxide content is about 23%.

One of the most significant aspects of these results is the fact that hardness does not increase with heat aging. This again reflects the low unsaturation of these rubbers. The usual ultimate effect of thermal oxidation on polyester rubbers is to bring about reversion. Hardness and brittleness result only in polymers containing about 10% or more unsaturation or in sebacates subjected to high temperature (150° C.). In spite of their stability at 100° C. the sebacates deteriorate rapidly at 150° in air. The succinates, however, are quite resistant to oxidation even at 150°, and some samples have been found to retain a high proportion of their original tensile strength, with no increase in hardness, after 30 days at this temperature. This phenomenal resistance to oxidation of succinates as compared to sebacates and adipates suggests that there is special merit in the grouping:


$$-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-$$

and that if polymers could be built with this structure and without the ester link (the great weakness of polyesters) they would have superior stability. The tests reported here are on materials which do not have the protection of antioxidants (since antioxidants inhibit peroxide vulcanization), a fact which makes this stability seem even more remarkable. By external application of antioxidants, such as by diffusion from solutions, it is possible to improve the behavior of both the sebacate and succinate compounds. The sebacate gains considerably by this treatment.

Table IV. Aging of Polyester Rubbers Containing Different Fillers

	White[a]		Red	
	T.S.[b]	E.[c]	T.S.	E.
3% unsaturated succinate				
Original	2600	500	2560	480
After 3³/₄ years outdoors	1075	400	1775	530
4% unsaturated sebacate				
Original	1450	390	1650	400
After 3³/₄ years outdoors	425	210	1100	400

[a] The white samples all contain 75 parts Kalvan and the red samples 150 parts Mapico 297. All samples were given optimum cure.

[b] T.S. = tensile strength, pounds per square inch.

[c] E. = elongation, %.

Oxidation Accelerated by Light. With regard to outdoor exposure, a serious degradative influence for polyester rubbers is light-activated oxidation, which causes surface checking on light colored samples. This action is stopped to a large extent by shutting off the light with a pigment of high opacity such as iron oxide, and the uniformly better outdoor aging of samples containing iron oxide as compared with those containing calcium carbonate

Table V. Effect of Aging Succinate-Maleates of Varying Unsaturation

	0% Unsatn.		3% Unsatn.		6% Unsatn.		8% Unsatn.		11% Unsatn.	
	T.S.[a]	E.[b]	T.S.	E.	T.S.	E.	T.S.	E.	T.S.	E.
Original	2750	540	2560	480	2000	400	1600	340	1650	325
After 3¾ years outdoors	Disintegrated		1775	530	1675	430	1400	380	1150	330

[a] T.S. = tensile strength, pounds per square inch.
[b] E = elongation, %.

is evidence of this. This difference in aging between white and red samples in identical polymers is illustrated in Table IV.

It is to be expected that samples of different structures may vary in their resistance to oxidation. The most striking examples of this encountered in the polyester work are in polymers containing diethylene or dipropylene glycol as a component. These polymers are oxidized much more rapidly than are similar polymers made of ethylene or propylene glycols and testify to the ease of attack on the ether linkage in such structures. This is true both in oven aging and in outdoor exposures. It should be emphasized that these polymers are without benefit of antioxidant.

Hydrolysis. Susceptibility to hydrolysis is a serious defect of polyester rubbers. Polyesters are not resistant to acid or alkali or to hot water or steam, and, as a matter of fact, immersion in water at 60°, 80°, or 100° C. is a convenient accelerated test for studying the effects of various factors on rate of hydrolysis. Samples of 3% unsaturated sebacates lose their shape after about 72 hours of continuous immersion in boiling water, and succinates, being more hydrophilic, break down similarly in about 24 hours. Immersion in water at 60° is a slower and more discriminating test for succinates, and 80° water is convenient for sebacates. Hydrolysis of vulcanized polyester rubbers invariably manifests itself in a lowering of modulus and an increase in elongation; in other words, it has the effect of devulcanization or reversion. Therefore the progress of hydrolysis is easily followed by use of a simple test which measures the elongation of samples of standard size and length under a given fixed load. A reading is taken 10 seconds after the load is applied, and the sample is then released and can be used in further tests. From the hot water tests several facts stand out.

1. Sebacates, presumably because of their more hydrocarbon nature, are markedly more resistant to hydrolysis than succinates; samples of the one, for example, are better after 13 days in water at 80° C. than corresponding samples of the other after 4 days.
2. Other things being equal, the greater the original per cent unsaturation (and therefore presumably the more highly cross-linked after vulcanization) the more resistant is the polymer to hydrolysis. For example, a 4% unsaturated sebacate after 13 days in 80° water is equal to a saturated sebacate containing the same loading after about 4 days. Similarly a 14% unsaturated succinate after 27 days in 60° water is better than a 3% unsaturated succinate of the same loading after 18 days.
3. Pigments which are able to neutralize acid (such as calcium carbonate) confer the greatest resistance to hydrolysis.

Although hot water thus rapidly hydrolyzes polyesters, neutral water at room temperature is not a serious hazard, and outdoor exposure to rain is really beneficial since it tends to leach out and wash away the benzoic acid left from vulcanization. It is interesting in this connection that, whereas iron oxide is the best pigment for outdoor use because of its opacity, polymer samples kept indoors retain their properties much better if they are loaded with calcium carbonate. It follows, then, that for general uses samples should contain both calcium carbonate and iron oxide. When properly compounded, polyester rubbers are far less seriously damaged by atmospheric moisture than are unsaturated hydrocarbon rubbers by atmospheric ozone. Table V gives original and aged tensile strength and elongation measurements on samples of succinate-maleates of varying unsaturation, all loaded with 150 parts of Mapico 297 iron oxide and each given optimum cure.

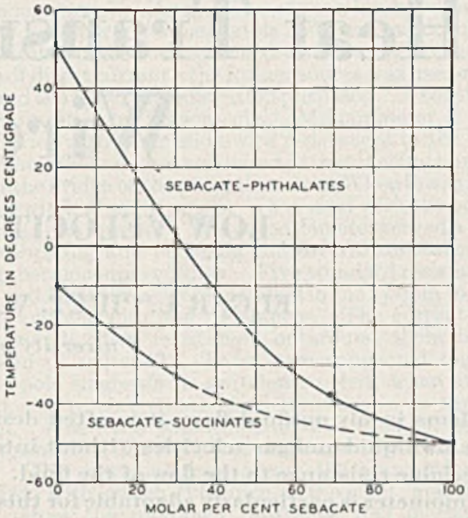


Figure 10. Brittle Points of Sebacate-Succinate and Sebacate-Phthalate Copolymers Loaded with 150 Parts Mapico 297

These changes in properties include the combined effects of oxidation and hydrolysis, and demonstrate the superior aging of unsaturated samples.

All the available test data indicate that, for uses where hydrolysis is expected to be the most serious degradative factor, an unsaturated sebacate would be expected to give the best results, and where oxidative influences predominate, unsaturated succinates would be chosen. Tables IV and V appear to indicate that sebacates and succinates in outdoor exposure degrade at about the same rate, and this presumably means that in these conditions oxidation and hydrolysis are of about equal importance.

ACKNOWLEDGMENT

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Heat Transmission from Fine Wires to Water

LOW VELOCITY DATA AND CORRELATION

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In problems involving fluid flow, it is often desirable to measure low liquid and gas velocities without introducing an appreciable resistance to the flow of the fluid. The hot wire anemometer is particularly adaptable for this purpose because of its small size and its ability to measure velocities well below the practical range of the Pitot tube. Unfortunately relatively few data are available on the characteristics of fine wires at low water velocities. This paper presents heat transfer data obtained on fine platinum and nickel wires at water velocities lower than previously reported, and for a relatively wide range of water temperatures and temperature differences. These data have been correlated by means of dimensionless groups and also by more readily solved empirical relations.

UP TO THE present time, Davis has been the only worker to investigate more or less comprehensively the rate of heat transfer from electrically heated wires to water under forced convection. Such work is significant in the development of our knowledge of heat transfer phenomena. Furthermore, fine, electrically heated wires are useful as hot wire anemometers to measure very low fluid velocities. Ower (*10*) reported in detail methods of using them in the measurement of air flow and Dryden (*3*) described some interesting applications to the measurement of turbulency.

Worthington and Malone (*13*) made some measurements on a vertical wire, 7.9 inches long and 0.010 inch in diameter, which they rotated in a tank of water. Their results were erratic at velocities below 0.2 foot per second as a result of the eddy currents set up by the wire and its holder. The maximum velocity they obtained was 0.5 foot per second. Taking the data of Worthington and Malone, Davis showed that the Nusselt numbers could be correlated as a function of Reynolds and Prandtl numbers (*1*).

In 1924 Davis published the most comprehensive data yet taken with fine wires in liquids (*2*). He used distilled water, paraffin oils, and three transformer oils. Single wires, 0.00803, 0.00598, and 0.00401 inch in diameter and held in a vertical position, were passed at velocities ranging from 0.33 to 2.3 feet per second through the liquids placed in a circular trough. For the water experiments he employed temperature differences of 14°, 36°, and 63° F., and a wire 0.00803 inch in diameter.

Ulsamer (*12*) in 1932 used the data for air of various investigators and the data of Davis for liquids. He arrived at a correlation of the form

$$\mathrm{Nu}_F/(\mathrm{Pr}_F)^{0.3} = a(\mathrm{Re}_F)^n$$

in which the physical properties of the liquids are evaluated at the arithmetic average film temperature. He found that, in general, laws applying to wires will apply to cylinders, and that, on the basis of the work done with gases, the results can be extended to include liquids. Hilpert (*4*) extended the data available on air, and improved the correlation by introducing the additional group, T_w/T_a, and evaluating the physical properties at an integrated mean film value. Mueller (*9*) obtained data on heat transfer from wires to air in parallel flow and found heat transfer rates of only 40% of the normal flow coefficients. Recently Kramers (*6*) published new data on heat transfer from small spheres and also developed a generalized correlation based on literature data for heat transfer from fine wires to various flowing media.

In the present investigation water was caused to flow past the wire placed in a horizontal position just following a rounded-approach nozzle. It was therefore possible to obtain low undisturbed velocities easily and to secure uniform velocities across the entire length of the wire. Anemometer traverses made with a short wire were used to determine the actual velocity distribution across the nozzle opening (Figure 4). The volumetric flow as determined by calibrated orifices was then converted to the actual linear velocity past the wire at the nozzle. The length of the wire was always made about 0.5 inch less than the diameter of the nozzle so as to have a uniform velocity along its length.

Data were obtained for water velocities ranging from 0.01 to 0.5 foot per second past the wire. A velocity of only 8 inches per minute is, indeed, well below the practical range of the Pitot tube. By using distilled water it was found possible to operate without having gas bubbles appear on the wire even at relatively high wire and water temperatures. If ordinary tap water were used, bubbles appeared on the wire when its temperature was about 80° to 100° F. It was also found that the current loss from the holder by conduction through the water was negligibly small, the error being about 0.01% of the operating current. This was determined by breaking off the wire and then measuring the current still flowing through the bridge at normal voltage drop across the wire leads.

The temperature of the water was varied from 78° to 125° F. and was measured by a fine thermocouple placed 0.5 inch below the wire and in the water stream coming from the nozzle. The wire temperature, calculated from the electrical resistance of the wire, was varied from 90° to 230° F. Under conditions of natural convection, wire temperatures as high as 288° F. were attained. At the higher temperatures, gas bubbles would at times appear on the wire. The bubbles and any lint, etc., collecting on the wire could easily be seen through the glass windows by means of a telescopic sight. This and the fact that the current readings were unsteady and erratic made it possible to detect these undesirable conditions and to avoid taking erroneous data.

Two types of wire were used, a 0.001-inch platinum wire and a 0.0028-inch nickel wire. These two wires were useful as a check on the method of correlation and apparatus employed in making the measurements. For a given water temperature, velocity, and temperature difference, the smaller wire gave higher coefficients than the larger, but the results for both were correlated by the usual dimensionless groups.

An experimental method was adopted to determine the importance of the heat loss by conduction through the ends of the hot wire. A 0.75-inch length of wire was used, and the total heat loss determined at constant water velocity. The measurement was repeated with a wire whose length was 35% greater. As closely as could be determined, the results were the same and the conclusion can be drawn that the water conducts the heat away from the wire so rapidly that the end effects are not important. Davis also found this to be true.

APPARATUS

The experimental apparatus can be divided into two distinct parts—the water system and the electrical system. The distilled water, conducted by $^3/_4$-inch pipe, passed through a main control valve, then through two valves in parallel to ensure better control and finer adjustment of water velocity. To cover the velocity range of some fifty fold, two orifices, arranged in parallel, and overlapping in range, were employed. The flow through either of these orifices was controlled by two valves, each located fifty pipe diameters before each orifice. The water then passed through a steam heater that was used only during the hot water runs and then to a tank. The tank was 2 feet long, 15 inches high, and 10 inches wide. A center section divided the tank into two parts. An elliptical approach nozzle, designed according to specifications (*8*), with a 1.5-inch throat diameter, was used to obtain a water velocity of uniform wave front past the wire. This nozzle was bolted on a 7-inch-diameter opening cut in the center section. Figure 1 is a photograph of the nozzle, wire holder, and thermocouple, as taken through the window in the side of the experimental tank. The first half of the tank contained a filter cloth to remove lint, dirt, etc., and, more important, to assure a uniform, noneddying flow of water before it reached the rounded-approach nozzle. The second half of the tank was constructed with plate glass window sides to permit observation of all visible phenomena. The water flowed through the nozzle, past the hot wire, and out of the tank, and was then discarded. Occasional fine particles suspended in the water made it possible to observe that the stream lines flowing from the nozzle were smooth and undisturbed. Davis used an annular trough and moved the wire through the water. Consequently the wire holder was also in the water stream, and the impact of the water against the holder set up undesirable eddy currents. An additional correction for the water slippage in the trough was also avoided by using the present construction.

The electrical system consisted of a Kelvin double bridge (including the hot wire), a thermocouple, a set of standard resistances, and a potentiometer. Figure 2 is a diagram of the electrical system, showing its relation to the tank (water system). The function of the bridge was to control and measure the resistance of the hot wire. The principal reason that this bridge, rather than the Wheatstone bridge, was employed is that it is more sensitive when the resistances to be compared are of low values. *C* (Figure 2) was the known resistance, and the hot wire was the unknown resistance. There were two sets of ratio coils, A_1, B_1, and A_2, B_2. Each set of ratio coils contained a dial resistance box, B_1 and B_2, that permitted great flexibility in the use of the instrument. The values of A_1 and A_2 were 50 ohms at first and later increased to 500 ohms. To ensure a constant resistance with variations in temperature, all of the fixed resistances were constructed with manganin wire. The points of contact (1, 2, 3, etc.) consisted of binding posts arranged in compact rows, to which the lead wires from the various resistances were soldered. The connection between 2 and 3 consisted of a copper bar of negligible resistance sunk in mercury wells. Switch *R* made connections to either a high or a low voltage source of direct current; the former source was used when taking data, and the latter for calibration purposes. A constant voltage was maintained by Edison cells. Milliammeter *A* was connected in series with three slide-wire resistances to the source of current. The galvanometer was wired so that it could be employed with either the bridge or the potentiometer. When it was used with the bridge, switch *D* was opened; when used with the potentiometer, switch *U* was opened. The potentiometer served a dual purpose of calibrating and checking the several resistances and of measuring thermocouple voltage. Five standard resistances (0.1, 1, 10, 100, and 1000 ohms) were installed in the system to facilitate calibrating and checking the resistances. The current could be directed through these resistances or around them by proper manipulation of switch *T*. They were connected together by five double-pole single-throw switches so that, when any switch was closed, the respective standard resistance was thrown into the system. When the potentiometer was used for calibration purposes, open wires *X* were connected across the resistance to be measured. The potential drop across the standard resistance was measured with switch *P* thrown to the right, and the potential drop across the unknown resistance was measured with switch *P* thrown to the left. The calculation of the unknown resistance was based upon Ohm's law. When the potentiometer was used for thermocouple potential measurements, switch *P* was opened and switch *Z* was closed. During all these operations extreme care was exercised in seeing that only the proper switches were used in order that no extraneous currents could flow through the galvanometer and give pseudo null points.

The wire was held horizontally in the flow stream, directly in front of the 1.5-inch-diameter nozzle throat, by a Bakelite wire holder bolted to the nozzle (Figures 1 and 3). The current leads

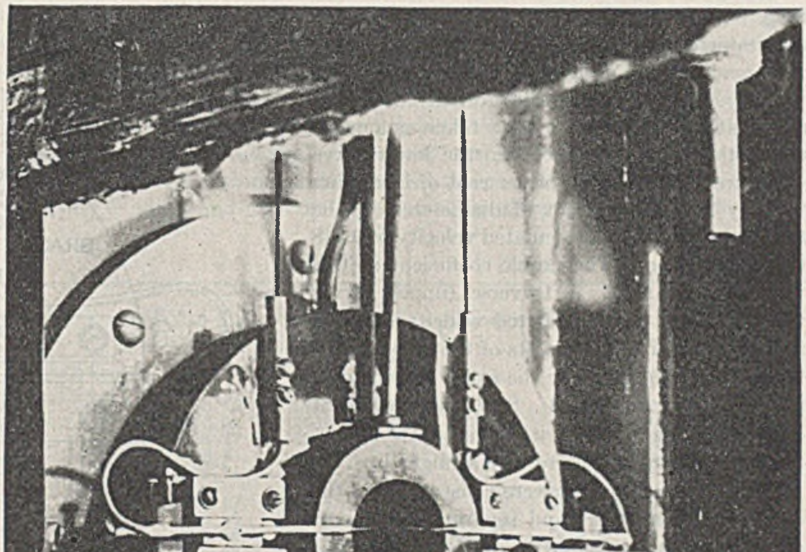

Figure 1. Fine Horizontal Wire in Water Stream Flowing from Nozzle

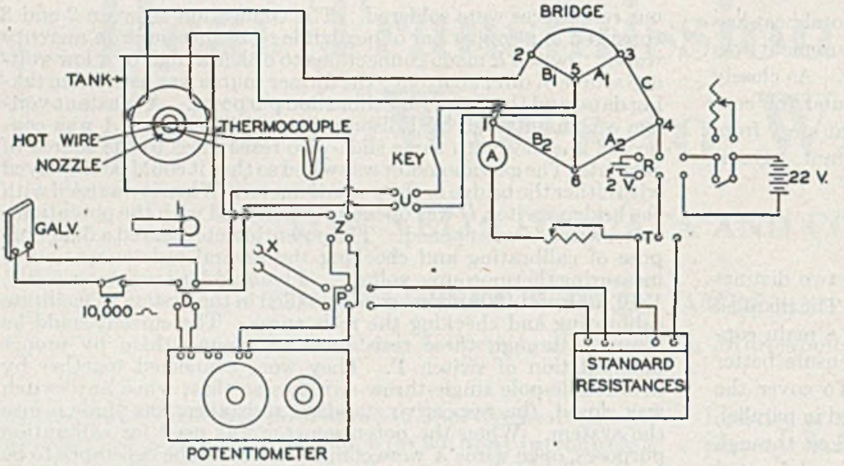

Figure 2. Electrical Measurement Circuit

and wire holder were electrically insulated from the tank and nozzle. The hot wire itself was welded with an electric arc to the heavier, tapered platinum wire leads whose distance apart could be readily adjusted. Minor adjustments in tightening the wire had no appreciable effect on the readings.

CALIBRATIONS

The velocity distribution across the nozzle throat was determined by making traverses with a hot wire anemometer, 0.5 inch long. These traverses were also necessary to determine the nozzle coefficient. Two traverses were made, one at a high, and one at a low water velocity. The maximum flow of current (maximum rate of heat transfer) was taken as a measure of the maximum velocity; the lower curve of Figure 4 shows a plot of per cent of maximum velocity against per cent of diameter from the top of the throat at a calculated velocity of 0.548 foot per second. The nozzle coefficient at this velocity was 1.006. A traverse (upper curve) was also made at a calculated velocity of 0.062 foot per second. The results of the velocity distribution were practically the same, and the nozzle coefficient was 1.018. Since the coefficient changed very gradually with velocity, the correction curve was assumed to be a straight line.

The two water orifices were constructed in the conventional manner, and separate differential pressure gages were used for each orifice. The orifices were calibrated in place by weighing the discharge over an interval of time, measured with a 0.1-second stop watch, at a constant difference of mercury levels. For low differences of pressure, the mercury gage readings were taken with a cathetometer that read to hundredths of a centimeter. The velocity through the nozzle, calculated by volume displacement, was corrected to the actual velocity by the nozzle coefficient, and very smooth linear plots resulted for the two orifices when the square roots of the differential gage readings were plotted against the corrected velocities through the nozzle.

Although pure nickel wire, 0.0028 inch in diameter, was used for several runs, the more important wire used in the present work was platinum wire, 0.001 inch in diameter and of the highest available purity. The principal reason for using such a fine wire was that only small amounts of current were necessary to operate it at any desired temperature. It was important that the coefficient of the change of resistance of the hot wire with temperature be accurately known. The temperature coefficient of electrical resistance, in the interval 0° to 100° C. $(R_{100}-R_0)/100\ R_0$, for a sample of this 0.001-inch platinum wire was found by the National Bureau of Standards to be 0.00387_4. Several sections of the wire were also calibrated in our laboratory and found to agree well with the above value. The Callendar equation was used in calculating the data:

$$t = \frac{R_t - R_0}{\alpha R_0} + 1.5\ (t/100 - 1)\ t/100$$

where $\alpha = \dfrac{R_{100} - R_0}{100 R_0} = 0.00387_4$

$t =$ true temperature, ° C.

$$t_p = \text{platinum temperature} = \frac{R_t - R_0}{\alpha R_0}$$

The diameter of the wire, as given by the company from whom it was purchased, was 0.001 ± 0.00001 inch. This value was checked by an optical method employing the principle of interference bands, and a value of 0.00105 inch was obtained. The value as given by the manufacturer, however, was used in all the calculations because of the greater experience and better equipment they have in measuring such fine diameters.

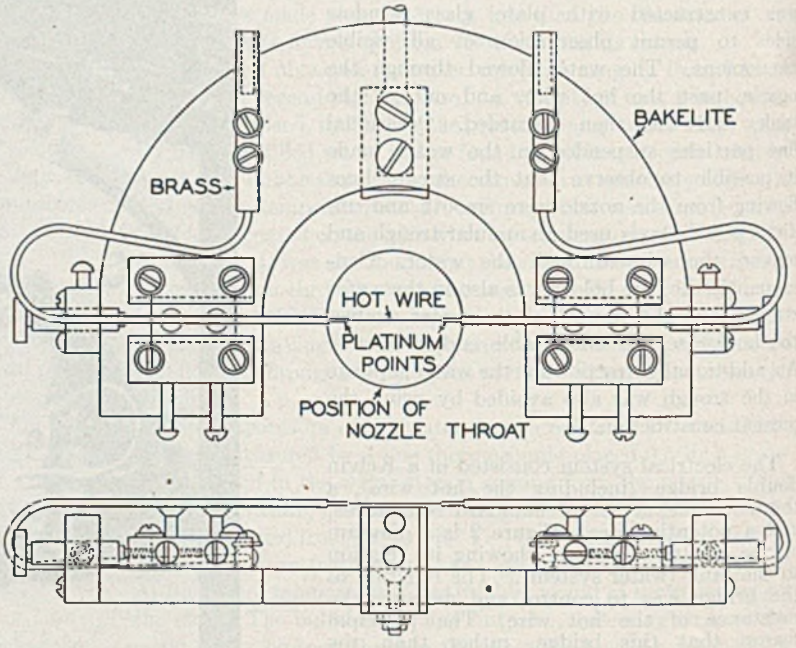

Figure 3. Wire Support

The nickel wire was calibrated by Clyde Berg at the University of Minnesota for use as a nickel thermometer and he obtained the equation

$$\log_{10} (1/2 + R/2R_0) = 0.00102t$$

where R_0 = resistance of wire at 0° C., ohms

t = temperature, ° C.

The nickel wire was used for only two runs. The diameter of the nickel wire was determined by weighing several accurately measured lengths of the wire and found to be 0.00280 inch. This value was checked with a micrometer. The experimental results obtained with the nickel wire were found to agree with those obtained with the platinum wire.

The thermocouple used to determine water temperatures was constructed from copper-constantan wires and was carefully calibrated. The milliammeter was calibrated by connecting it in series with a standard resistance and measuring the potential drop across the standard with the potentiometer at different values of current. The milliammeter readings were accurate to within 1%.

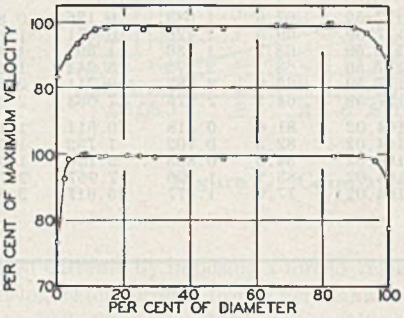

Figure 4. Velocity Distribution at Wire Position Following Nozzle

Davis found that the internal heat distribution of small diameter wires could be assumed to be uniform without involving any appreciable error (*2*). In the present work the wires were even finer in diameter than those used by Davis, so this assumption could be made with greater confidence.

The resistance of the wire leads and hot wire holder was determined by assembling them in a manner identical to that used when making a run except that the hot wire was removed and the opened ends were immersed in a pool of mercury. The measurements were repeated several times, and the resistance of the leads and holder was found to be 0.105 ohm. This value was subtracted from the total resistance to find the resistance of the hot wire itself.

PROCEDURE

At the beginning of a run the pipe lines and tank were flushed out with distilled water until the water in the tank became clear. Any air that may have accumulated in the system was removed through several petcocks located at the high points of the system. Before a new hot wire was used, it was always annealed at red heat for several hours. The wire holder was bolted to the nozzle, and the resistance of the leads and hot wire was determined either by balancing the bridge or by comparing them to a standard resistance. Periodically both methods were used as checks. In either case the amount of current flowing through the hot wire did not exceed 0.003 ampere, and the temperature of the wire during this determination was assumed to be that of the water in which it was immersed. When the comparison method was employed, the bridge was broken at post 6 (Figure 2), and the copper bar lifted from mercury wells 2 and 3. The removal of the bar threw additional external resistances B_1 and A_1 into the circuit. This left a one-loop circuit, and the potential drop was measured across posts 1 and 2 and then across the standard resistance. The measurements were repeated several times, and the amount of current flowing was changed slightly between each pair of measurements by changing the external resistance. If, at any time, it was suspected that this resistance had changed, it was redetermined at a known water temperature. After each set of potential measurements or after balancing of the bridge, the temperature of the water was measured with the thermocouple.

During the experimental runs the external resistance was adjusted until the bridge balanced, an indication that the current flowing through the hot wire had heated it to the resistance determined by the dial box settings. The readings of the several instruments were recorded; then either the dial box resistances or the water velocity past the hot wire was changed, and the bridge rebalanced.

During the hot water runs the temperature of the water sometimes changed appreciably between the milliammeter and thermocouple readings. To correct for this condition, a helper, equipped with a stop watch, recorded the current and thermocouple readings and also the times at which they were given. Plots were

Table I. Constant Velocity Data for Wire 8.33 × 10^{-5} Foot in Diameter

Run No.	V	L	R_0	R	i	T_l	T_w	ΔT	h	$Q/A\theta$	Re_F	Nu_F	$\frac{Nu_F}{(Pr_F)^{0.3}}$
A-1	0.020	0.0808	4.5181	5.1477	0.2893	79.7	96.12	16.4	1.176	19.31	0.197	1.003	0.608
				5.2434	0.3600	79.7	105.93	26.2	1.161	30.45	0.208	0.984	0.608
				5.5249	0.5123	79.6	134.87	55.3	1.176	65.0	0.246	0.976	0.634
				5.8992	0.664	79.6	173.41	94.0	1.240	116.5	0.290	1.004	0.695
				6.2755	0.788	79.5	212.74	133.2	1.311	174.6	0.341	1.037	0.753
A-2	0.0088	0.0808	4.5181	5.5249	0.4556	81.3	134.87	53.6	0.959	51.4	0.108	0.795	0.519
				5.7125	0.524	81.3	153.25	73.0	0,963	70.3	0.118	0.788	0.531
				5.8992	0.584	81.3	173.58	92.3	0.981	90.5	0.129	0.793	0.550
				6.0879	0.640	81.3	193.18	111.9	0.999	111.7	0.140	0.798	0.569
				6.2755	0.691	81.3	212.74	131.4	1.022	134.3	0.151	0.806	0.591
A-3	0.041	0.0808	4.15181	5.0745	0.2603	78.6	88.63	10.0	1.535	15.40	0.384	1.317	0.784
				5.2434	0.412	78.6	105.93	27.3	1.459	39.87	0.424	1.237	0.763
				5.5248	0.576	78.8	134.88	56.1	1.460	82.10	0.494	1.216	0.790
				5.8992	0.734	78.8	173.58	94.8	1.502	142.4	0.593	1.216	0.840
				6.2755	0.862	78.8	212.74	133.9	1.577	211.2	0.697	1.246	0.911
B-2	0.0986	0.08466	4.9754	5.6000	0.276	79.7	89.73	10.0	1.819	18.24	0.953	1.555	0.936
				5.7125	0.391	79.7	100.19	20.5	1.823	37.34	0.991	1.550	0.946
				6.2755	0.721	79.5	152.75	73.3	1.905	139.5	1.302	1.561	1.045
				6.6519	0.862	79.2	188.25	109.1	1.981	216.0	1.521	1.590	1.122
B-3	0.0365	0.08466	4.9754	5.7125	0.338	80.00	100.19	20.2	1.382	27.90	0.367	1.175	0.717
				5.9002	0.456	79.84	117.69	37.9	1.386	52.46	0.405	1.165	0.735
				6.2755	0.620	79.70	152.81	73.1	1.411	103.1	0.482	1.155	0.774
				6.6519	0.763	79.52	188.25	108.7	1.523	165.6	0.564	1.223	0.866
				6.8385	0.824	79.16	205.89	126.7	1.567	198.5	0.605	1.243	0.901
C 1	0.101	0.08466	5.0349	6.2005	0.3114	125.2	138.92	13.7	1.881	25.71	1.536	1.513	1.063
				6.2755	0.3776	125.6	145.86	20.3	1.879	38.06	1.584	1.504	1.069
				6.4632	0.5048	125.8	163.27	37.4	1.881	70.4	1.701	1.489	1.084
				6.6500	0.6110	126.3	180.67	54.4	1.953	106.2	1.822	1.527	1.139
				7.0250	0.7690	126.0	215.71	89.8	1.979	177.6	2.059	1.513	1.168
D-1	0.202	0.08125	4.5551	5.3372	0.4650	89.00	111.11	22.1	2.326	51.43	2.271	1.951	1.238
				5.5249	0.6265	88.83	130.25	41.4	2.333	96.6	2.501	1.930	1.264
				5.7125	0.7520	88.79	149.44	60.7	2.373	144.0	2.738	1.936	1.308
				5.9002	0.8580	88.63	168.71	80.1	2.417	193.6	2.983	1.952	1.357
				6.0879	0.9460	88.63	188.04	99.4	2.442	242.8	3.238	1.949	1.395

Table II. Variable Velocity Data

Run No.	R	R_0	L	D	V	i	T_l	T_w	ΔT	h	Re_F	Nu_F	$\frac{Nu_F}{(Pr_F)^{0.3}}$
I-2	4.142	3.5794	0.0625	8.33×10^{-5}	0.01080	0.3659	77.2	104.37	27.2	1.197	0.110	1.017	0.623
					0.03673	0.4104	77.2	104.37	27.2	1.505	0.373	1.279	0.784
					0.0797	0.4519	77.3	104.36	27.1	1.832	0.811	1.556	0.954
					0.2056	0.5120	77.3	104.37	27.1	2.352	2.091	1.997	1.224
					0.3960	0.5430	77.5	104.37	26.9	2.665	4.031	2.263	1.388
					0.5000	0.5460	78.2	104.37	26.2	2.766	5.110	2.348	1.438
II-5	6.196	4.6633	0.0814	8.33×10^{-5}	0.01133	0.642	82.0	184.37	102.4	1.110	0.174	0.891	0.629
					0.03972	0.757	79.9	184.37	104.5	1.512	0.604	1.216	0.855
					0.08005	0.854	78.4	184.37	106.0	1.897	1.210	1.528	1.071
					0.1019	0.877	77.1	184.37	107.3	1.977	1.532	1.593	1.115
III-3	6.210	4.7252	0.0820	8.33×10^{-5}	0.01056	0.518	109.7	177.59	67.9	1.083	0.176	0.859	0.623
					0.0465	0.600	108.1	177.59	69.5	1.420	0.771	1.126	0.816
					0.0838	0.669	108.9	177.59	68.7	1.786	1.397	1.416	1.027
					0.1942	0.756	109.5	177.59	68.1	2.272	3.244	1.801	1.308
					0.3740	0.816	112.0	177.59	65.6	2.782	6.311	2.202	1.605
					0.4515	0.834	113.5	177.59	64.1	2.975	7.663	2.352	1.717
IV-2[a]	0.721	0.5243	0.0814	2.33×10^{-4}	0.0155	1.922	82.4	164.02	81.6	0.518	0.611	1.178	0.807
					0.0441	2.250	81.5	164.02	82.5	0.702	1.732	1.598	1.094
					0.0804	2.520	80.0	164.02	84.0	0.865	3.134	1.971	1.347
					0.2034	2.947	80.9	164.02	83.1	1.196	7.967	2.723	1.861
					0.3895	3.172	86.1	164.02	77.9	1.477	15.617	3.355	2.311

[a] Nickel wire.

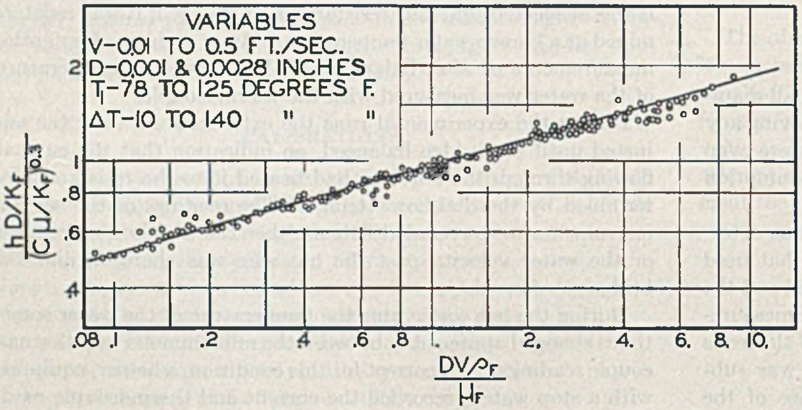

Figure 5. Correlation of Heat Transfer Data for Fine Wires

made of time against the current and thermocouple readings, and the thermocouple reading corresponding to the time of the current reading was taken as the true measure of the water temperature.

ANALYSIS OF DATA

The experimental data were calculated in terms of dimensionless groups and are plotted in Figure 5. The data do not show an appreciable curvature over the experimental range. The equation of the line is:

$$\frac{hD/k_F}{(C\mu_F/k_F)^{0.3}} = 0.965\left(\frac{DV\rho_F}{\mu_F}\right)^{0.28} \tag{1}$$

All of the terms involved are in consistent units, and the thermal conductivities (*7*), densities (*11*), and viscosities (*11*) are taken at the arithmetic mean film temperature. For brevity the data for only every fifth experimental point are given in Tables I and II.

Equation 1 is somewhat cumbersome to use, and can be presented in a simpler form for water by grouping the density, thermal conductivity, and viscosity factors and plotting the value of this product against the average film temperatures ranging from 77° to 180° F. This function can then be substituted and Equation 1 reduced to:

$$h = (0.28\ T_F + 386) \times 10^{-5}\ \frac{V^{0.28}}{D^{0.72}} \tag{2}$$

The probable error of estimating h about this equation is ± 3.4%. A better correlation was arrived at by plotting the values of h against ΔT at a series of constant velocities. From this and similar direct plots of the experimental variables above ΔT of 15° F. and for velocities above 0.02 foot per second the following simple equation for 0.001-inch wire was obtained:

$$h = 2.98\ (V)^{0.28}\ (\Delta T)^{0.065} \tag{3}$$

The probable error of h about this relation is only ± 1.7%. Thus it appears that the data are quite precise and correlate well. By cross plotting the data, Figure 6 was prepared to facilitate the use and interpretation of the results of this investigation for anemometry.

To compare the results of this work with those of previous investigators, the equations proposed by McAdams (*7*) and by Kramers (*6*) were plotted in Figure 7 together with the line of the present data. McAdams' equation in this range is based on King's data (*5*) for air down to a Reynolds number of 0.2 and is recommended for any gas. Kramers recommends that his general correlation for various fluids be limited to the range of the Nusselt number from 20 down to about 2. This approximately corresponds to a range of Reynolds number of 400 to 2. The present data fall between the two correlations.

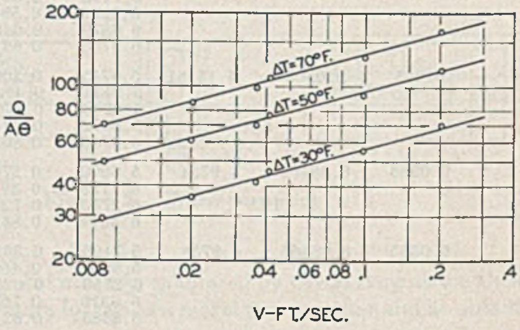

Figure 6. Heat Loss Plot for 0.001-Inch Wire

By plotting the total heat transferred per unit area (Figure 8), a series of nearly parallel lines are obtained except at zero velocity. The slope of the zero velocity curve can be explained as being due to a rapidly increasing effect of the convection currents as the temperature difference increases. Davis determined the velocity

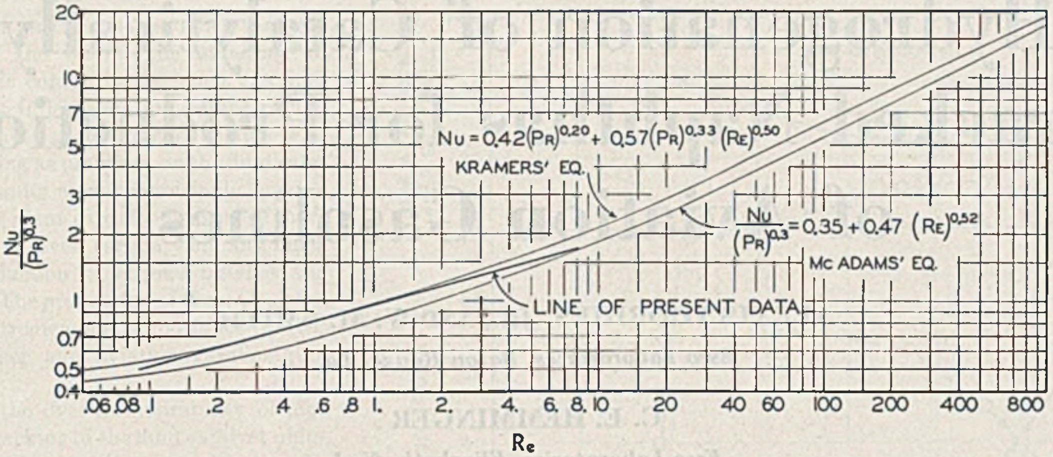

Figure 7. Comparison of Present Work with Available Equations

of the convection currents by imposing a forced velocity at right angles to the rising water currents from a vertical wire and noting the velocity at which the angle of the stream lines became 45°. He assumed that at this point the natural and forced currents are of equal magnitude, and calculated a value of 0.00018 foot/second (° F.). Figure 8 shows that the zero velocity line intersects the line of 0.0088 foot per second at approximately 180° F. Assuming that at this temperature difference the effective velocity of the natural currents is 0.0088 foot per second a value of approximately 0.00005 foot/(second)(° F.) is obtained for a horizontal wire.

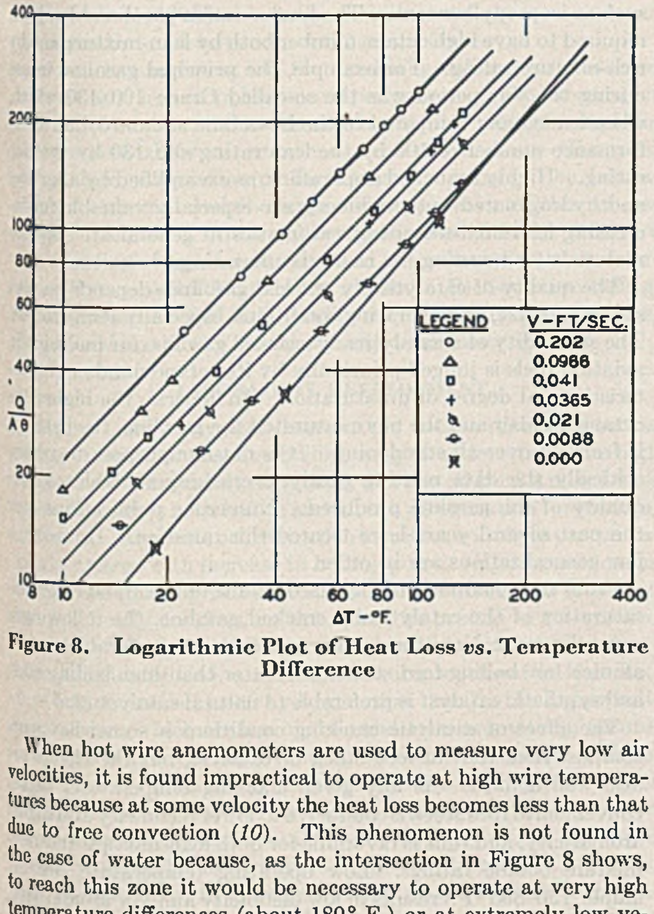

Figure 8. Logarithmic Plot of Heat Loss *vs.* Temperature Difference

When hot wire anemometers are used to measure very low air velocities, it is found impractical to operate at high wire temperatures because at some velocity the heat loss becomes less than that due to free convection (*10*). This phenomenon is not found in the case of water because, as the intersection in Figure 8 shows, to reach this zone it would be necessary to operate at very high temperature differences (about 180° F.) or at extremely low velocities below 0.01 foot per second. Thus no dip is observed when the current is plotted against the water velocity even for the wide range of temperatures and velocities covered in this investigation.

NOMENCLATURE

Any set of consistent units can be used in Equation 1 since it is dimensionless.

T = temperature, ° F.
ΔT = temperature difference between the wire and the main body of water, ° F.
h = heat transfer coefficient, B.t.u./(sec.)(sq. ft.)(° F.)
D = wire diameter, feet
$Q/A\theta$ = rate of heat transfer, B.t.u./(sec.)(sq. ft.)
L = length of wire, feet
i = current, amperes
R = resistance, ohms
V = velocity, feet/second
Re_F = Reynolds number, $DV\rho_F/\mu_F$, calculated at arithmetic average film temperature
Nu_F = Nusselt number, hD/k_F, calculated at arithmetic average film temperature
Pr_F = Prandtl number, $C\mu_F/k_F$, calculated at arithmetic average film temperature
ρ = density
C = specific heat
μ = viscosity
k = thermal conductivity
a = constant

Subscripts

F = film conditions taken at arithmetic average of wire and water temperatures
l = liquid
w = wire

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Hydrogenation of Catalytically Cracked Naphthas for Production of Aviation Gasolines

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Hydrogenation of the olefinic constituents of catalytically cracked aviation gasolines to the corresponding paraffins without hydrogenation of aromatic constituents to naphthenes results in a gasoline of improved stability and lean-mixture octane number after addition of lead, with no sacrifice in rich-mixture rating. Commercial operation of the hydrogenation process for the improvement of fluid-catalyst-cracked aviation gasolines has been successfully carried out both at 150 and at 3000 pounds per square inch pressure using rugged sulfur-resistant catalysts of satisfactory activity and life.

CATALYTIC hydrogenation has been used in several ways in the production of aviation gasoline. Some of these applications have already been described. For example, the use of high pressure destructive hydrogenation to produce high grade aviation fuels from kerosenes and light gas oils was reported by Murphree, Brown, and Gohr (*3, 4*). They also described the simple hydrogenation of selective dimers of isobutylene and normal butylenes to produce iso-octanes for blending into premium aviation gasoline (*3, 4*). The present paper deals with another application of hydrogenation for aviation gasoline production—namely, the hydrogenation of catalytically cracked naphthas. This paper is concerned mainly with the effect of possible changes in product composition on the resulting product quality and not with the details of the methods by which these changes are brought about.

There is considerable similarity between hydrogenation of selective butene dimers and hydrogenation of catalytically cracked aviation naphtha. Both are examples of simple hydrogenation, where conditions are adjusted to prevent splitting of the molecules; both processes are amenable to high pressure or low pressure operation with sulfur-resistant catalysts; both were extensively employed during the war period to augment the supplies of 100-octane aviation gasoline. Reference to the application of hydrogenation in the production of catalytically cracked naphthas has already been made in the literature (*1*); the purpose of this paper is to describe another aspect of this process, as employed on a large scale in the high-pressure hydrogenation plant of the Standard Oil Company of New Jersey (Louisiana Division) at Baton Rouge, and in a low pressure hydrogenation plant operated for Defense Plants Corporation by the Humble Oil and Refining Company at Baytown, Tex.

GENERAL CONDITIONS

The so-called 100-octane aviation gasoline produced in the United States during the war was the mainstay of the air forces of this country and our allies. This 100-octane gasoline consisted of high grade base stocks and blending agents of very high octane number. The base stocks used were selected virgin naphthas or their equivalent produced by destructive hydrogenation, and catalytically cracked naphthas. The blending agents employed were iso-octane from hydrogenation of butene dimers, alkylates of isobutane and C_3–C_5 olefins, and certain low boiling aromatics such as isopropylbenzene. The final aviation gasoline blend was required to have high octane number both by lean-mixture and by rich-mixture rating. For example, the principal gasoline in use during the war period was the so-called Grade 100/130 which, when leaded and compared to the iso-octane standard, had a performance number of 100 by the lean rating and 130 by the rich rating. Highly branched isoparaffins, as exemplified by alkylates and hydrogenated butene dimers, are especially valuable for increasing lean-mixture rating; aromatics in general are superior materials for boosting the rich-mixture rating.

The quality of catalytically cracked gasolines depends on feed stock, catalyst, and operating conditions, especially temperature. The suitability of a catalytically cracked gasoline for inclusion in aviation fuels is judged principally by its octane number characteristics and degree of unsaturation. In general, the higher the octane number and the more saturated the gasoline, the better it is from an over-all standpoint. It is not our purpose to review critically the data relating catalytic cracking variables to the quality of the gasoline produced. Numerous publications over the past several years have treated this question. However, a few generalizations are in order.

From the standpoint of increased octane number and lower unsaturation of the catalytically cracked gasoline, the following is generally true: Naphthenic charge stocks are preferable to paraffinic; low boiling feed stocks are better than high boiling ones; and synthetic catalyst is preferable to natural catalyst (*2, 5*).

The effect of catalytic cracking conditions is somewhat more complex than that of feed stock or catalyst, but the effects are also well defined. At any given cracking temperature, higher conversion of feed stock is conducive to lower olefinicity and higher aromaticity, and thus is favorable for both lean-mixture and rich-mixture octane ratings. Low operating temperature (for example, 750–800° F.) results in low olefinicity and low aromaticity. The low olefinicity is favorable to high lean-mixture octane number, but the low aromaticity tends to give poor rich mixture ratings. High operating temperature (for example, 950–

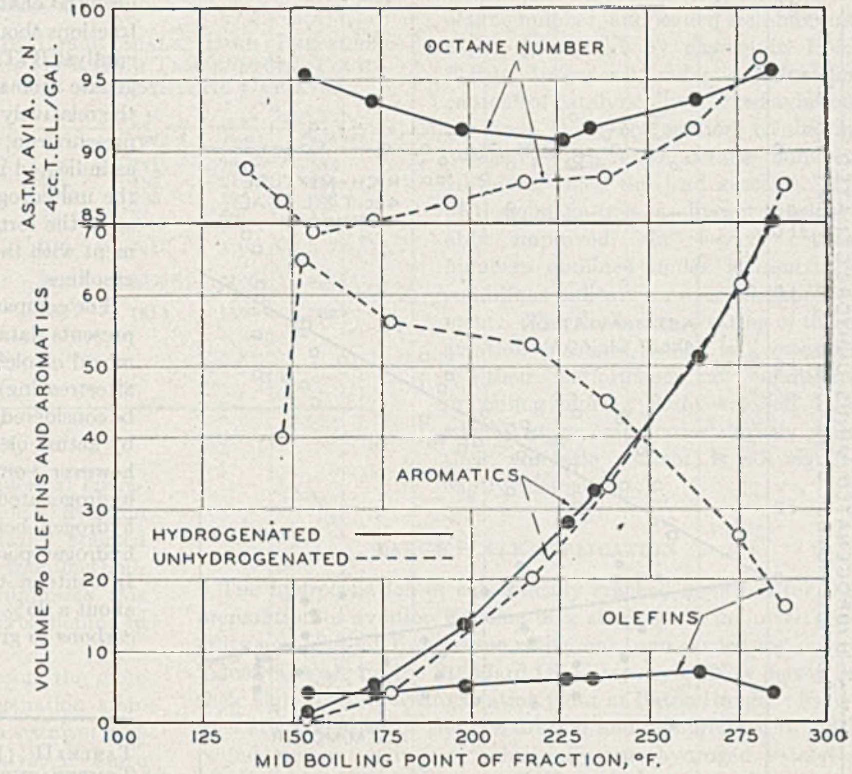

Figure 1. Effect of High Pressure Hydrogenation on Octane Number, Olefin Content, and Aromatic Content of Aviation Gasoline Fractions from High Temperature, Fluid Catalyst Cracking of Tinsley Gas Oil with Synthetic Catalyst

975° F.) results in cracked gasolines that are very olefinic; and despite the advantage of higher aromatic concentration, such gasolines may be too low in lean-mixture octane rating. However, the over-all advantages of high temperature cracking as practiced on the fluid catalyst cracking units were convincingly great—namely, higher plant capacity because of more conversion for a given carbon yield and much increased production of normal butenes and isobutylene. The production of these C_4 olefins has been of tremendous importance to the synthetic rubber and aviation gasoline programs.

In view of the over-all desirability of high temperature cracking in the fluid catalyst units, the problem resolved itself to one of finding the best method for improving the lean-mixture octane rating of the aviation gasoline without detriment to rich-mixture performance. The retreating of catalytic gasoline by a second pass over the cracking catalyst was one answer to this problem. However, in the case of highly olefinic gasolines produced at elevated cracking temperatures, a considerable loss of product was involved. As an alternate it appeared that simple hydrogenation of the catalytically cracked gasoline might be a desirable process if conditions were used to saturate the olefins without hydrogenation of the aromatics. As will be pointed out, this type of hydrogenation process proved both feasible and desirable, since it gave about 100% volumetric yield of saturated product. A large improvement in lean-mixture octane rating of the leaded gasoline was obtained without any loss in rich-mixture performance. The reason for this improvement is that the olefins in the catalytic naphtha are predominantly of branched structure and are thus converted into isoparaffins of high octane number. The laboratory development and the large scale application of this process are discussed later. In the following discussion the lean-mixture octane rating of gasolines is expressed as the octane number determined by the A.S.T.M. aviation method. Rich-mixture ratings are expressed as I.M.E.P. (indicated mean effective pressure) determined on the C.F.R. supercharged aviation engine.

LABORATORY DEVELOPMENT

Figure 1 shows typical data on the composition and octane rating of aviation gasoline boiling range fractions from the high temperature fluid catalyst cracking of a gas oil from a mixed base crude (Tinsley), both before and after hydrogenation for removal of olefins. Aromatic concentration increases and olefin concentration decreases with increase in boiling point. Hydrogenation, as carried out in this process for almost complete removal of olefins, has practically no effect on the aromatics present in the cracked material. The lower boiling fractions of high olefin content show, after addition of lead, a much greater improvement in lean-mixture octane number upon hydrogenation than do the higher boiling fractions which are less olefinic and more aromatic in nature.

Since the greatest improvement, based on octane rating alone, is obtained by the hydrogenation of the light naphtha, the higher boiling fractions may be by-passed around the hydrogenation stage with little loss in total product quality. The improved stability, which is characteristic of fully hydrogenated products, may be maintained in this case by acid treatment of the high boiling by-passed fractions. Table I demonstrates the improvement in stability of high boiling, catalytically cracked fractions following acid treatment. Only low treating losses occur by this procedure since the fraction to be acid-treated is initially low in olefin content. If hydrogenation capacity is limiting, this procedure allows a more efficient utilization of given hydrogenation facilities and a greater over-all production of aviation gasoline. Another advantage for acid treatment of the high boiling aromatic fractions lies in the improved rich-mixture rating which in general has not been found to occur upon hydrogenation.

TABLE I. ACID TREATMENT OF 250–325° F. FRACTION OF AVIATION GASOLINE FROM HIGH TEMPERATURE, FLUID CATALYST CRACKING OF COASTAL GAS OIL WITH SYNTHETIC CATALYST

Acid treat, lb. 98% acid/barrel	0	10
Yield, volume %	100	92
Bromine number, cg./gram	9	2
Copper-dish gum, mg./100 ml.	22	6
5-hour army gum, mg./100 ml.	19	8
Modified 16-hour army gum, mg./100 ml.	37	9

In contrast to the highly olefinic catalytically cracked fractions which boil above the pentane cut and which show, upon hydrogenation, a large improvement in leaded lean-mixture octane number, the cracked pentane fraction has no appreciably better leaded lean-mixture octane number blending value after hydrogenation than before. More advantageously, this cracked material may be alkylated with isobutane to produce a blending agent of high octane number. Where alkylation capacity or isobutane supply is limiting, however, the cracked pentane fraction without alkylation or hydrogenation may be utilized directly in aviation gasoline to the extent allowable by vapor pressure limitations, since the stability of the finished aviation gasoline does not appear to be detrimentally affected by the inclusion of this cracked material.

The advantages of hydrogenation of the highly olefinic, catalytically cracked, aviation gasoline fractions boiling above the pentane cut are rather well defined. The question of whether to alkylate, hydrogenate, or use as such the cracked pentane fraction

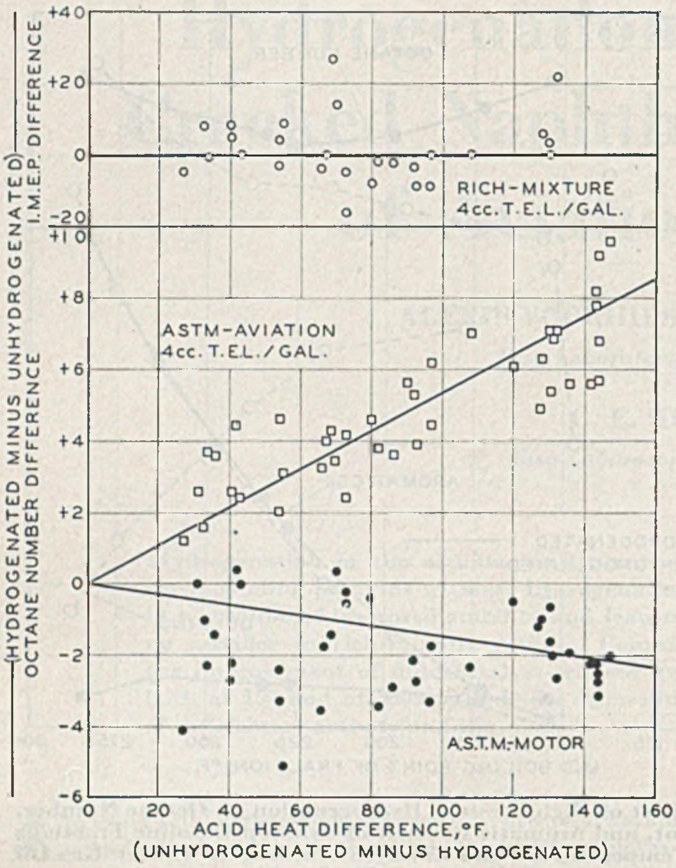

Figure 2. Relation between Change in Olefin Content by Hydrogenation and Change in Octane Ratings for Aviation Gasolines (7 Pounds per Square Inch Reid Vapor Pressure) from Fluid Catalyst Cracking with Synthetic Catalyst

and the question of whether to hydrogenate or acid treat the more aromatic aviation gasoline fractions boiling above 200–250° F. depend upon the current refinery alkylation, hydrogenation, and acid treating capacities and upon the effect of each of those methods of treatment on product yield, stability, and quality.

The continuous type of small pilot unit used for the hydrogenation of various catalytically cracked gasolines has been described (*1*). This type of laboratory unit is suitable for use at pressures up to 3000 pounds per square inch. For operation at any given pressure within this range, the only change necessary is in the type of catalyst required; that is, catalysts which may be used at 150 pounds pressure may not be suitable for use at 3000 pounds, and vice versa. As exemplified in previous publications (*1*, *3*, *4*), the catalysts used are sulfur resistant and maintain their activity in the presence of sulfur-containing feed stocks. In some cases involving the use of a high sulfur feed stock, a substantial sulfur elimination as hydrogen sulfide is effected with the production of materials of lower sulfur content.

Table II compares the properties of a gasoline from a high temperature fluid catalyst cracked Tinsley gas oil (cracking condition different from those used for product in Figure 1), before and after hydrogenation at high and low pressures. Hydrogenation removes olefinic material (characterized by reduction in bromine number and acid heat) and increases the stability (characterized by lower copper-dish gum). The resulting aviation gasolines are poorer in clear octane number but superior in lean-mixture octane number after addition of lead. No significant change in rich-mixture rating upon hydrogenation is noted. This is not surprising for the case of high pressure hydrogenation with catalyst A, since the rich-mixture rating is known to be largely dependent upon the content of aromatics, and Figure 1 indicates that no essential change in the aromatic content of the aviation gasoline fractions should occur upon hydrogenation. On the other hand, catalyst B (Table II), being of higher activity, is known to hydrogenate aromatic materials to naphthenes at high pressures. At the relatively mild hydrogenation conditions employed in the low pressure run, however, no hydrogenation of aromatics took place, as indicated by the identical toluene and C_8 aromatic contents of the unhydrogenated and hydrogenated products. In this case, as in the former, the unchanged rich-mixture rating is in agreement with the unchanged aromatic content of the hydrogenated gasolines.

For comparison with the hydrogenation process, Table II also presents data on the unhydrogenated aviation gasoline after removal of olefins by selective catalytic recracking (retreating or aftertreating). As is the case with acid treating, retreating may be considered to reduce olefin content and increase stability mainly by actual olefin removal. In contradistinction to acid treating, however, some branched-chain olefins are also considered to be hydrogenated under the conditions of the process, the necessary hydrogen being produced concurrently with the deposition of hydrogen-poor carbonaceous residues on the cracking catalyst. In contrast to the hydrogenation process, retreating results in about a 25% loss in yield with concentration of aromatic hydrocarbons to give a more aromatic aviation gasoline (lower aniline

Table II. Properties of Aviation Gasolines from High Temperature, Fluid Catalyst Cracking of Tinsley Gas Oil with Synthetic Catalyst

	Unhydrogenated	Hydrogenated		Retreated
Hydrogenation				
Catalyst	..	A	B	..
Pressure, lb./sq. in.	..	3000	150	..
Aviation gasoline				
Gravity, °A.P.I.	60.2	61.6	62.0	56.6
Dist. + loss at 167° F., %	35	30	35	32
Dist. + loss at 221° F., %	67	68	66	56
90% over, ° F.	292	274	283	293
Final b.p., ° F.	338	307	324	324
Color (Saybolt)	+19	+20	+25	+25
Aniline point, ° F.	66	99	96	64
Bromine No., cg./gram	63	1	3	13
Acid heat, ° F.	135	5	7	27
Copper-dish gum, mg./100 ml.	17	4	4	4
Reid vapor pressure, lb./sq. in.	7.0	7.1	6.9	7.0
Octane No.				
A.S.T.M. Motor	80.5	79.9	79.4	83.1
A.S.T.M. Aviation, 4 cc. T.E.L./gal.	90.6	97.7	96.1	96.0
Rich-mixt. rating (I.M.E.P.), 4 cc. T.E.L./gal.	174	174	177	206
Toluene, vol. %	6		6	
C_8 aromatics, vol. %	15		15	

Table III. Properties of Aviation Gasolines from Low Temperature, Fluid Catalyst Cracking of Tinsley Gas Oil with Synthetic Catalyst

	Unhydrogenated	Hydrogenated	Light Ends Hydrogenated, Heavy Ends By-passed
Hydrogenation			
Catalyst	..	C	C
Pressure, lb./sq. in.	..	3000	3000
Aviation gasoline			
By-passed 200–325° F., vol. %		0	40
Gravity, °A.P.I.	66.1	66.6	65.6
Dist. + loss at 167° F., %	40	39	38
Dist. + loss at 221° F., %	66	67	62
90% over, ° F.	285	293	295
Final b. p., ° F.	310	320	325
Color (Saybolt)	+30	+30	+20
Aniline point, ° F.	119	122	117
Bromine No., cg./gram	23	1	5
Acid heat, ° F.	43	7	12
Reid vapor pressure, lb./sq. in.	7.0	7.1	7.1
Octane No.			
A.S.T.M. Motor	78.3	76.9	78.3
A.S.T.M. Aviation, 4 cc. T.E.L./gal.	92.2	95.8	94.8

Table IV. Typical Data from Baton Rouge Large Scale, High Pressure Hydrogenation of Aviation Gasoline Fractions from High Temperature, Fluid Catalyst Cracking of Paraffinic Type Gas Oils with Syntetic Catalyst

	C_5, 220° F.		C_6, 250° F.		C_5, 315° F.		C_6, 325° F.	
	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Initial b.p., ° F.	90	97	118	113	108	111	131	135
50% over, ° F.	130	126	162	165	176	185	214	219
90% over, ° F.	195	187	208	208	278	285	295	303
Bromine No., cg./gram	105	10	103	6	70	2	60	11
Reid vapor pressure, lb./sq. in.	15.2	12.5	7.0	6.9	7.9	7.1	4.9	3.7
Octane No., A.S.T.M. Aviation[a]	87.0	98.5	86.7	94.7	88.5[b]	96.9[b]	91.0[b]	93.5[b]
Rich-mixt. rating (I.M.E.P.)[a]	171	169	159	162	163[b]	181[b]	155[b]	169[b]

[a] 4 cc. tetraethyllead per gallon.
[b] 4.6 cc. tetraethyllead per gallon.

point) of improved rich-mixture rating. In commercial operation, retreating is usually applied, not to the fraction of aviation gasoline boiling range alone, but to a catalytically cracked gasoline fraction of higher end point with recycle of fractions boiling above aviation gasoline. This procedure minimizes this relatively large loss in yield at the expense of material boiling in the approximate range 325–450° F.

Table III presents data on the effect of by-passing the more aromatic heavy-end fractions around the hydrogenation step. In this case another high pressure hydrogenation catalyst was used with results similar to those obtained with catalyst A. Since the gasoline in this run was produced from low temperature cracking, the olefin and aromatic contents were relatively low, as indicated by the low bromine number and acid heat and the high aniline point of the unhydrogenated aviation gasoline. However, even in this case the leaded lean-mixture rating of the unhydrogenated product was improved by hydrogenation. By-passing the last 40% (high boiling components) of the aviation gasoline resulted in a potential increase of hydrogenation plant capacity of about 66% while still obtaining an improvement in leaded lean-mixture rating of 2.6 octane numbers out of a possible 3.6 for hydrogenation of the total aviation gasoline fraction.

Product yields for the hydrogenation process are virtually 100% with little loss due to light end formation. Hydrogen consumed in the process corresponds practically to that required stoichiometrically for saturation of the olefins reacted plus an additional quantity which is removed from the system by solubility in the product under pressure and which varies directly with the operating pressure for a given product.

Table V. Typical Data from Baytown Large Scale, Low Pressure Hydrogenation of Aviation Gasoline Fractions from High Temperature, Fluid Catalyst Cracking of Paraffinic Type Gas Oils with Synthetic Catalyst

	C_6, 210° F.	
	Feed	Product
Initial b.p., ° F.	140	144
50% over, ° F.	166	164
95% over, ° F.	201	207
Bromine No., cg./gram	94	1
Reid vapor pressure, lb./sq. in.	4.9	4.6
Octane No., A.S.T.M. Aviation + 4.6 cc. T.E.L./gal.	88.5	96.6

Figure 2 correlates the effect of hydrogenation upon change in octane rating for a number of fluid-catalyst-cracked aviation gasolines produced from various types of gas oils under a variety of catalytic cracking conditions. As a convenient measure of the change in olefin content upon hydrogenation, the difference between the A.S.T.M. acid heats of the unhydrogenated and hydrogenated aviation gasolines is used. This is plotted against the corresponding change in clear octane number, leaded lean-mixture octane number, and leaded rich-mixture rating (expressed by change in I.M.E.P.). In general, reduction of olefin content of catalytically cracked aviation gasolines by hydrogenation results in a decrease in clear octane number. However, since the lead susceptibility of these olefin-free gasolines is considerably improved, the leaded octane numbers obtained under lean-mixture conditions indicate an over-all improvement. The rich-mixture rating of these aviation gasolines, which is a measure of their performance at conditions prevailing during flight take-off and which, in general, varies directly with their aromatic content, is not significantly changed.

LARGE SCALE APPLICATION

The hydrogenation of catalytically cracked naphthas for the preparation of aviation gasoline base stocks with improved stability and lean-mixture octane rating has been carried out on an industrial scale by the Standard Oil Company of New Jersey in their high-pressure hydrogenation plant at Baton Rouge. Facilities are available for the preparation and compression to 3000 pounds per square inch of industrially pure hydrogen, catalytic reaction of this hydrogen with feed stocks at elevated temperatures, and stabilization of the resulting products.

Table IV lists corresponding feed and product characteristics for a variety of feed stocks which have been processed. In general, satisfactory reduction in unsaturation was obtained together with improvement in lean-mixture octane number of the leaded gasolines. With feed stocks of low end point no significant change in rich-mixture rating was obtained, as expected; feed stocks of higher end point have appeared to give, somewhat consistently, products of slightly improved rating. Product yields were in the neighborhood of 100 volume % with little light end formation by cracking. Indicated hydrogen consumptions close to the theoretical were obtained which confirmed laboratory data.

The large scale hydrogenation of catalytically cracked naphthas at low pressure has been carried out by the Humble Oil and Refining Company at Baytown. This plant, converted from idle, low pressure refinery equipment during the war, utilizes low pressure by-product hydrogen available locally from various dehydrogenation processes. The low pressure hydrogenation process differs from the usual high pressure process only in that a more active catalyst is required.

Table V presents a brief summary of data on operating conditions and product quality which are representative of this process. In agreement with laboratory data, satisfactory product saturation and improvement in quality are obtained. As is the case with high pressure hydrogenation, yields of saturated product approximately 100% or greater are obtained with little cracking to low boiling products.

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Low Temperature Characteristics of Elastomers

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The low temperature stiffening of elastomers frequently limits their usefulness. A new laboratory test for measuring their stiffness at low temperatures is described. Strips of the stocks to be tested are mounted around a cylindrical rack in a vertical, cylindrical insulated chamber. The temperature in the chamber is controlled by cooling the base externally with dry ice and by a moderate regulated flow of precooled air through dry ice in the bottom of the chamber. This system gives stable temperatures which are easily controlled. The chamber can be rotated to attach the samples in succession, by means of projecting top grips, to a suitably mounted torsion wire. The stiffness is measured by the angle of twist of the sample when the torsion head is rotated 180°. The relative modulus for any temperature is calculated as the ratio of the modulus at this temperature to that at 25° C. Plots of angle of twist against temperature show a rather sharp break at the low temperature end of the curve. This determines a somewhat subjective "freezing point." Curves are given to illustrate the wide variety of low temperature stiffening characteristics for elastomers. In unplasticized stocks the chemical composition of the monomers is the dominating factor for these properties for various synthetic rubbers. The stiffness of elastomers which are capable of crystallization upon stretching, such as Hevea, neoprene, and Butyl rubber, depends not only on temperature but also on time of exposure. To study these effects, the foregoing apparatus was used in a cold room. A rather long induction period occurs during which the stiffness is essentially constant. It then increases and eventually reaches a larger constant value. Several months may be required to complete these changes. X-ray examination of Hevea and Butyl proved that the increased stiffness on long exposure was due to crystallization. No change was observed in the stiffness of GR-S over the period of 2.5 months at −30° C. Reduction in the speed of retraction is a critical measure of the deterioration of high elasticity at low temperatures. It gives a wide differentiation at moderately low temperatures between Butyl rubber and Hevea or GR-S, whereas a slow modulus test does not.

ELASTOMERS characteristically stiffen and suffer impairment of high elasticity at low temperatures. The practical limitations which this imposes on their respective fields of use has led to the development of many laboratory procedures for testing and evaluating low temperature properties. A comparative discussion of the various published methods was undertaken by Liska (*9*) and Mullins (*10*). A broad line of demarkation exists between two types of tests, brittleness and modulus tests, the theoretical relations for which have been elucidated by Boyer and Spencer (*3*). It appears that the most generally applicable type of test is one which gives a measure of the stiffness over a range of temperatures low enough to include the transition region through which the long-chain molecules lose the ability to unkink or uncoil, so that the rubber becomes essentially an ordinary solid. Such modulus determinations have been made in a wide variety of ways using either stretching, bending, or torsional deformations. The results have much in common as they are obtained for relatively small slow deformations, which are more fundamental conditions than the type of deformation. This paper describes a simple and convenient torsion apparatus, which has been useful in securing this type of information, and illustrates the results obtained.

Mullins (*10*) discussed the difficulties in trying to evaluate low temperature stiffening by a single value of the relative modulus. He suggested reporting the temperatures at which the relative modulus (ratio of modulus at low temperature to the modulus at 20° C.) is two and ten. It seems preferable to report the entire modulus curve whenever possible, so that the rubber compounds can be compared in the temperature range of interest for each particular application. For some purposes it may be sufficient to report the relative modulus at a given temperature or at two temperatures bounding the range of interest.

Although a simple modulus or stiffness test is sufficient in a general way for many purposes and is a useful guide for compound and polymer development, in many cases it leaves large gaps in the information which is desirable for understanding low temperature characteristics of rubber. If the use of the rubber involves circumstances which differ widely from the test conditions, such as rapid deformations, large deformations, or long exposure to low temperatures, which conditions are frequently encountered in service, the modulus and brittleness tests as ordinarily carried out are inadequate. To secure a correct perspective, it is then necessary to modify the test or to set up special test conditions, in order to conform more closely to the service conditions. This work, in addition to giving results from the torsion modulus test, is concerned with some aspects of the low temperature behavior for rapid deformations, free retraction, and long exposures to low temperatures.

LOW TEMPERATURE DEFORMATIONS

The kinetic theory of rubber elasticity explains the temperature dependence of the modulus of rubber on a thermodynamic basis which is generally regarded as being satisfactory. According to this theory the modulus decreases linearly with the absolute temperature. The experimental tests of the theory are usually carried out by relaxing the specimen to establish reversible conditions, stretching it at room temperature or higher, and then determining the modulus as the temperature is varied in steps (*12*).

In contrast to these results, modulus measurements as ordinarily made and which are discussed here show increased stiffness at lower temperatures. The apparent contradiction is due to the different experimental procedures used. The theory applies to equilibrium conditions which are readily obtained by stretching the rubber and changing the temperature. In the usual type of measurement, on the other hand, the rubber is brought to the low temperature and then deformed. In another alternative the rubber may be deformed at the higher temperature and cooled so that it shows the normal Joule effect, but subsequent small deformations at low temperature will indicate an increase in the modulus over that measured at the high temperature.

The theoretical explanation of these effects lies in the large influence of the time factor for low temperature deformations. The time for a rubber deformation to occur depends upon molecular relaxation times which, in simple theory, depend exponentially on the temperature. For the usual type of measurement this effect more than counteracts the relatively small linear dependence on absolute temperature explained by the kinetic theory.

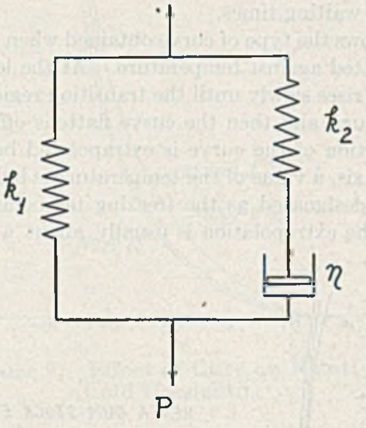

Figure 1. Mechanical Model

The situation can be better understood by reference to the mechanical model shown in Figure 1, which idealizes the rubber structure as a system of linear springs and dashpots. The mathematical solution for this model (*2*, *8*) gives the deformation due to a constant load at time t after load application as

$$D(t) = \frac{P}{k_1 + k_2}\left[1 + \frac{k_2}{k_1}\left(1 - e^{-\frac{t}{\tau}}\right)\right] \tag{1}$$

$$\tau = \eta \frac{k_1 + k_2}{k_1 k_2} \tag{2}$$

where k_1, k_2 = spring stiffnesses
η = viscosity of dashpot

The instantaneous deformation, $t = 0$, is given by the first term of Equation 1. The second term, which has a limiting value secured by making $t = \infty$, represents the contribution of high elasticity to the deformation. To extend the mechanical analogy to rubber, the relaxation time τ is considered to be a function of temperature, according to the equation

$$\tau = A\,e^{\frac{U}{kT}} \tag{3}$$

where U = energy of activation
k = Boltzmann's constant (*1*)

Equations 1 and 3 show that longer periods of time will be required to attain a given deformation at lower temperatures. For $t = \infty$, the deformation is P/k_1, and is independent of τ. The kinetic theory deals with the relatively small dependence of k_1 on temperature—that is, equilibrium deformations obtained theoretically at $t = \infty$. The time factor, however, is of predominant importance for most low temperature measurements as carried out in practice because of the effect of the term containing τ. The deformation at a finite experimental time, $D(t)$, is less than $D(\infty)$. This is interpreted as an increase in modulus.

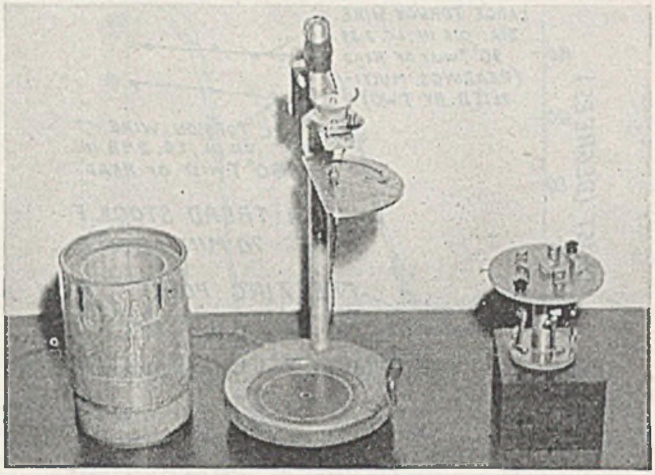

Figure 2. Parts of Torsional Stiffness Tester

This idealized model emphasizes the importance of time as a factor in low temperature measurements for rubber, when the experimental time of measurement is of the same order of magnitude as the relaxation times. It is not to be expected that very good quantitative agreement would be secured with such a simple theory. It is known that an infinite distribution of relaxation times is probably involved in rubber deformations. Furthermore, the elastic and viscous elements may not be linear, and there may be structural effects. It does not seem obvious that the structure achieved in respect to molecular orientation, even after a long period of time in a specimen which is cooled and stretched, would be identical with that in the same specimen which was stretched and then cooled.

LOW TEMPERATURE TORSION TEST

Equipment for measuring torsional stiffness at low temperatures is shown in Figures 2 and 3. The test pieces used are small rubber strips died out from tensile test sheets. The dimensions are 1.625 inches long, 0.125 inch wide, and 0.079 inch thick. Five of these are fastened vertically in the Micarta grips of the cylindrical rack illustrated at the right in Figure 2. The top and bottom disks of the rack are also Micarta. The center post and the external freely turning studs are brass. The insulated chamber used is shown at the left of Figure 2. It is made of an inner aluminum tube 6.5 inches long and 3 inches in inside diameter, and an outer concentric tube of cadmium-plated steel, 4.5 inches in outside diameter. The space between the tubes is filled with insulating material held in place by Micarta rings pressed be-

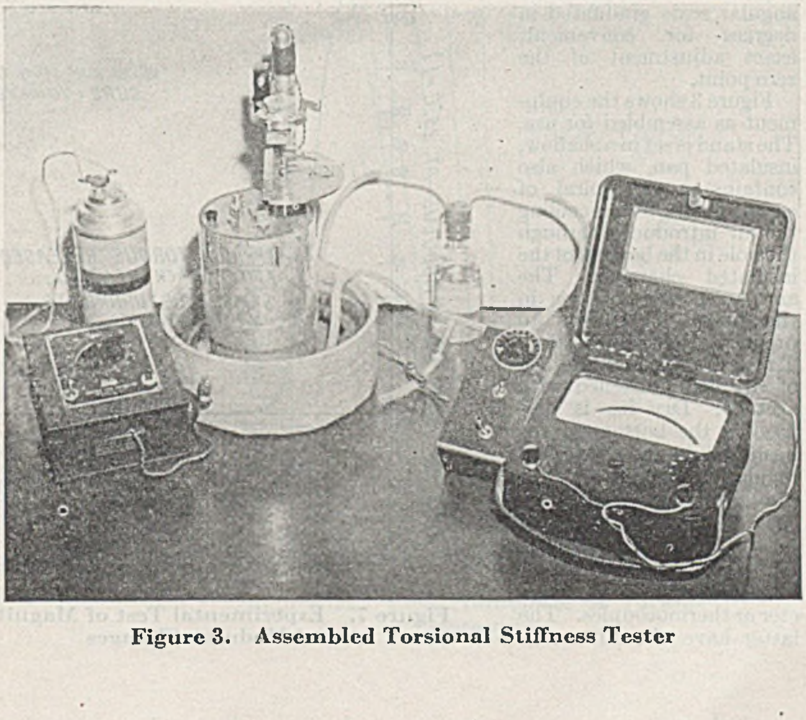

Figure 3. Assembled Torsional Stiffness Tester

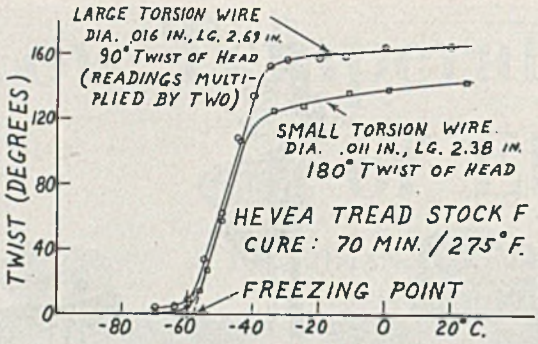

Figure 4. Typical Plot of Twist vs. Temperature

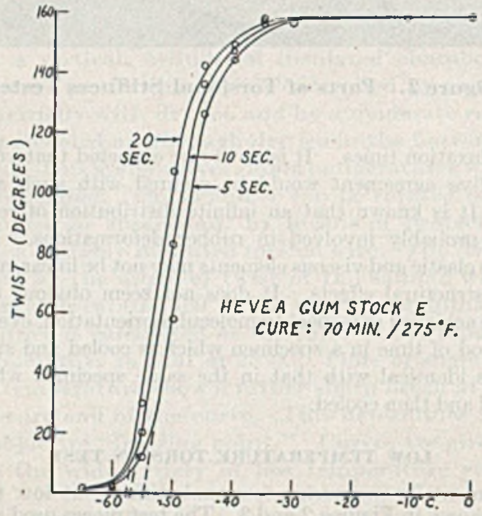

Figure 5. Effect of Time Interval on Experimental Curves

tween the tubes at top and bottom. A Micarta disk having a 0.25-inch hole in the center is pressed in the bottom of the inner tube.

The torsion head and stand are shown at the right in Figure 2 The base includes provision for introducing a stream of air in the bottom of the insulated chamber. The torsion wire is steel of 0.011-inch diameter and 2.38 inches long. A pointer is provided with a movable angular scale graduated in degrees for convenient, exact adjustment of the zero point.

Figure 3 shows the equipment as assembled for use. The stand is set in a shallow, insulated pan, which also contains a flat spiral of copper tubing for precooling the air introduced through the hole in the bottom of the insulated chamber. The air passes over acetone in the bottle as shown, to prevent frost formation. The pan is filled with lumps of dry ice moistened with acetone. Dry ice is also used in the bottom of the insulated chamber. Manual regulation of the air flow provides temperatures in the test chamber down to −90° C. if necessary. The temperature can be determined either by a thermometer or thermocouples. The latter have the advantage of faster response to temperature changes. The specimens are attached in turn to the torsion head by rotation of the chamber and use of a screw connection.

To measure the stiffness, the temperature is held at the desired value for 5 minutes. The scale is then adjusted so that the pointer is at zero. The torsion head is turned exactly 180°, and the pointer reading taken after 10 seconds. Readings are usually secured first at the lowest temperature and then at intervals of 5° or 10° C. as the temperature is raised. An audible timer marks the 10-second waiting times.

Figure 4 shows the type of curve obtained when the twist of the pointer is plotted against temperature. At the low temperature end the curve rises slowly until the transition region is reached, a sharp rise occurs, and then the curve flattens off again. If the transition portion of the curve is extrapolated backward to the temperature axis, a value of the temperature is indicated which is conveniently designated as the freezing temperature. The uncertainty in the extrapolation is usually about a degree; hence

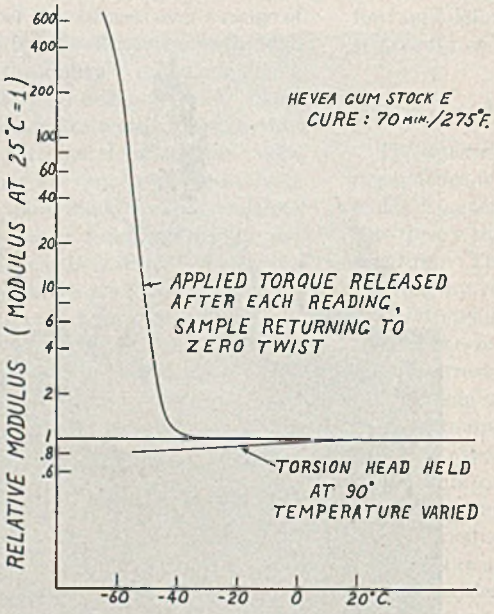

Figure 7. Experimental Test of Magnitude of Modulus Changes

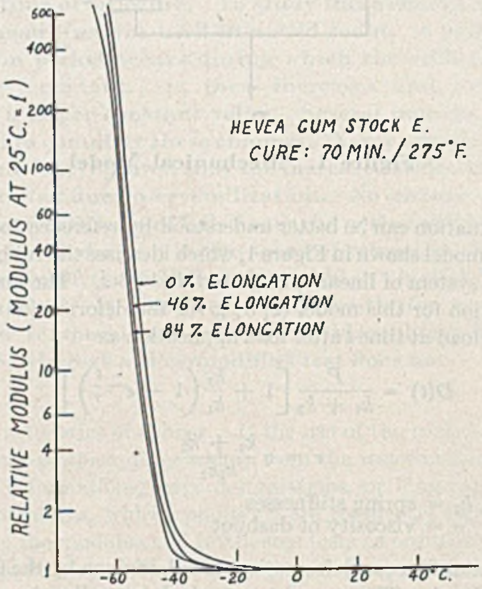

Figure 6. Effect of Elongation on Relative Modulus

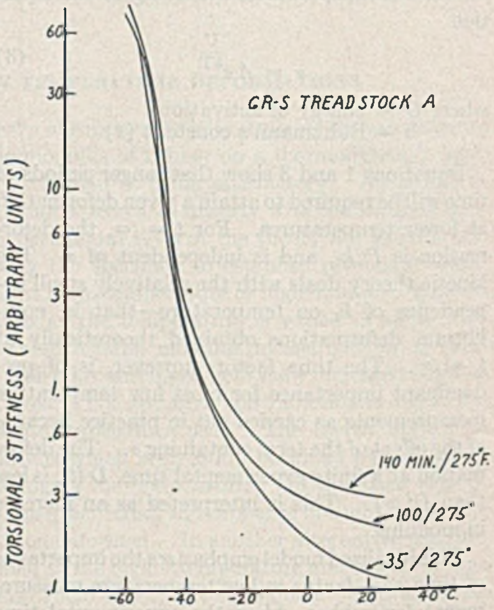

Figure 8. Effect of Cure on Stiffness

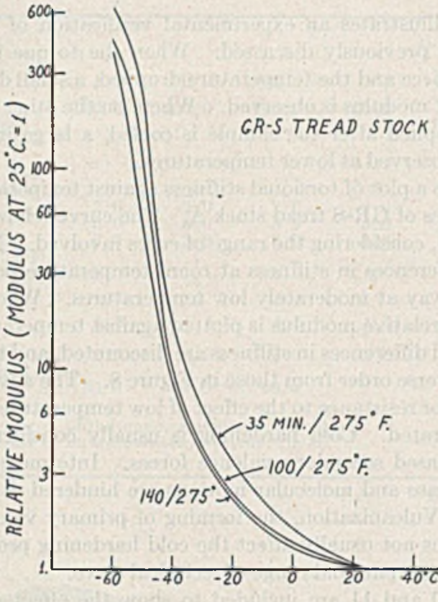

Figure 9. Effect of Cure on Relative Cold Hardening

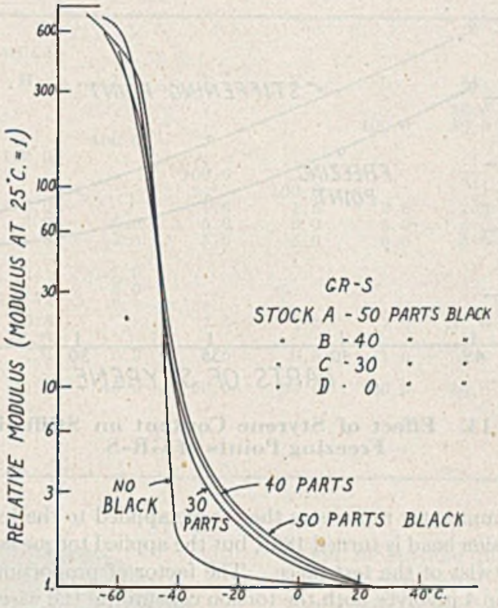

Figure 10. Effect of Carbon Black on Relative Cold Hardening

some subjectivity in the determination must be acknowledged. There may also be some dependence upon the apparatus and testing procedure. Nevertheless, the curves in Figure 4 show that the freezing point is shifted only about 2° C. when the constant of the torsion wire is changed by a factor of about four. Figure 5 shows a very small effect on the freezing point when the time for taking the twist readings after application of the torque is in the range 10 to 20 seconds. The stiffening point defined below is also insensitive in this range, since values for the 5-, 10-, and 20-second intervals are, respectively, −48.7°, −50.5°, and −52° C. At any rate, the freezing temperature serves the purpose of marking the start of the transition region for this torsion test. It does not seem to have any correlation with brittle points which have been reported for stocks similar to those tested here. Freezing points for Hevea and GR-S tread stocks are actually found to be in reverse order from reported brittle temperatures (*9*), which give GR-S as having a lower brittle point than Hevea. This lack of correlation is not surprising in view of the dependence of brittle temperature on the testing conditions (*7*) and the different character of the two determinations. Unless the service for a rubber compound actually includes the possibility of a low temperature brittle failure, the freezing point appears to be a much more significant criterion for evaluating low temperature properties than does the brittle point.

The relative torsional modulus at any temperature is computed as the ratio of the modulus at the low temperature in question to the modulus at 25° C. The temperature for which this ratio is ten is called the stiffening point in this work. In many cases it is preferable to use the temperature corresponding to a lower ratio than ten in order to characterize low temperature stiffening. The modulus is connected with the twist measurement by the relation

$$\text{Modulus} \propto \frac{180^\circ - \text{twist}}{\text{twist}} \tag{4}$$

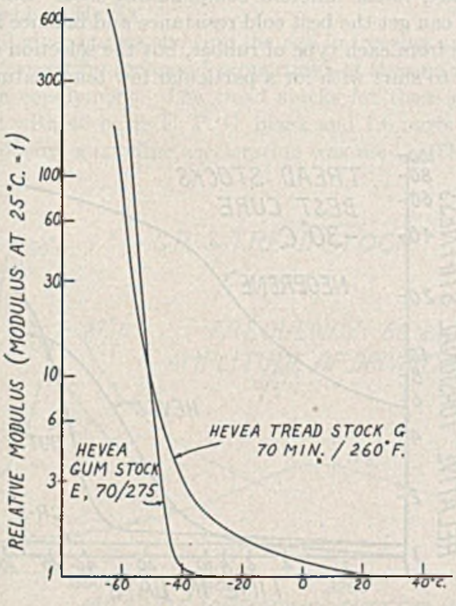

Figure 11. Cold Hardening of Natural Rubber

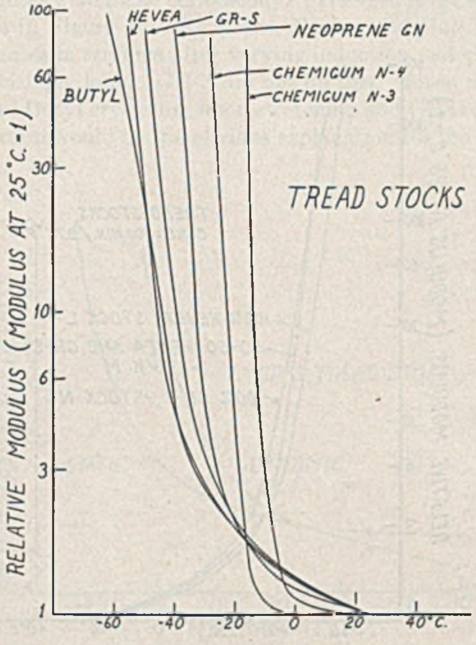

Figure 12. Cold Hardening of Various Elastomers

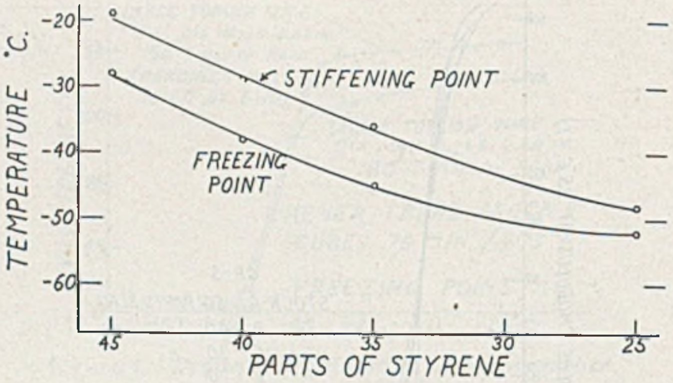

Figure 13. Effect of Styrene Content on Stiffening and Freezing Points of GR-S

The numerator represents the torque applied to the test piece. The torsion head is turned 180°, but the applied torque is reduced by the twist of the test piece The factor of proportionality in Equation 4 involves both the torsion constant of the wire and the geometry of the test piece. Since only relative values of the modulus at different temperatures are of interest in this work, and since a geometrical factor calculated from the theory of elasticity for small deformations would be of doubtful applicability, these factors may be omitted. Values of the twist at various temperatures are taken from twist-temperature curves such as those illustrated in Figure 4. Corresponding values of the fraction (180° − twist/twist are read from a table. The relative modulus can then be readily computed and plotted as a function of temperature. The principal compounds used are given in Table I.

RESULTS OF MODULUS TESTS

Figures 6 to 14 exhibit the type of information which may be secured with the torsion modulus test described. Since the relative modulus curves plotted in the figures are derived from smooth experimental twist curves such as those in Figure 4, which show little scattering of the points from the curves, there would be no object in entering points on the relative modulus curves.

Figure 6 illustrates the small effect of superposed elongations on the test results. Any accidental variation in the tension of the test piece when installed for regular test purposes is negligible.

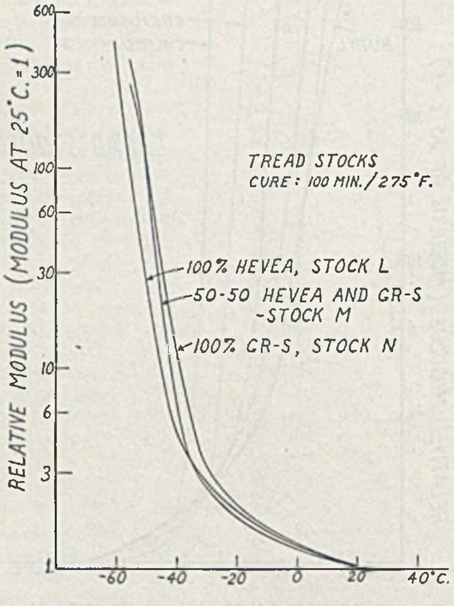

Figure 14. Cold Hardening of a Mixture of GR-S and Hevea

Figure 7 illustrates an experimental verification of the theoretical ideas previously discussed. When the torque is applied to the test piece and the temperature dropped, a small decrease in the apparent modulus is observed. When, on the other hand, the torque is applied after the sample is cooled, a large increase in stiffness is observed at lower temperatures.

Figure 8 is a plot of torsional stiffness against temperature for a series of cures of GR-S tread stock A. The curves show a rather small spread, considering the range of cures involved. Nevertheless, the differences in stiffness at room temperature persist in a systematic way at moderately low temperatures. When, on the other hand, relative modulus is plotted against temperature (Figure 9), initial differences in stiffness are discounted, and the curves lie in the reverse order from those in Figure 8. The advantage of tight cures for resistance to the effect of low temperatures is thereby demonstrated. Cold hardening is usually considered to be due to increased secondary valence forces. Intermolecular distances decrease and molecular motions are hindered at low temperatures. Vulcanization, the forming of primary valence cross linkages, does not usually affect the cold hardening process very greatly in a conventional range of technical cures.

Figures 10 and 11 are included to show the effect of carbon black loadings on the relative modulus at low temperatures. Carbon black increases the relative stiffening appreciably for the most important part of the temperature range and decreases the abruptness of the low temperature transition. These effects are no doubt connected with hindered molecular rotations and segmental movements due to the molecular anchorages at the carbon black particles. The proportional increase in stiffness becomes larger for each molecular segment immobilized as the number of mobile segments is reduced, in the same way that each successive increment of carbon black loading becomes increasingly effective in raising the modulus at room temperature.

Since cold hardening is dominated by secondary valence forces and the hindrance of segmental molecular motions, the chemical composition and chain form of the long-chain molecules are of paramount importance. These have much more influence than other features of the polymer structure, such as molecular weight and the primary valence network structure. This is brought out by the curves of Figure 12, which illustrate the wide range of cold hardening characteristics for a number of technically important elastomers. The Hevea and Butyl curves in Figure 12 are for compounds F and H, respectively. Liska (*9*) showed somewhat more spread between Hevea and Butyl. This may be due, at least in part, to the different compounding used. Suitable compounding can get the best cold resistance and balance in physical properties from each type of rubber, but the selection of the best elastomer to start with for a particular low temperature applica-

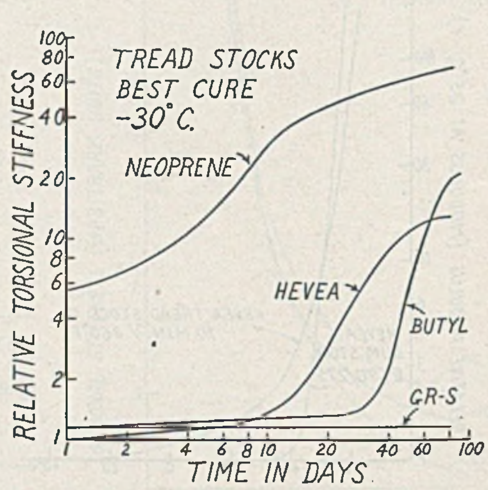

Figure 15. Torsional Stiffness for Long Exposures

TABLE I. COMPUTED FORMULAS

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
GR-S	100.0	100.0	100.0	100.0	...	...	...	...	...	...	...	...	50.0	100.0
Smoked sheet	...	...	...	...	100.0	100.0	100.0	...	...	...	...	100.0	50.0	...
Neoprene GN	...	...	...	...	...	...	...	...	100.0	...	...	...	...	...
Butyl	...	...	...	...	...	...	...	100.0	...	...	...	...	...	...
Chemigum N-3[a]	...	...	...	...	...	...	...	...	...	100.0	...	...	...	...
Chemigum N-4[b]	...	...	...	...	...	...	...	...	...	...	100.0	...	...	...
Sulfur	2.0	2.0	2.0	2.0	3.0	3.0	2.75	2.0	...	1.6	1.6	2.5	2.5	2.5
Zinc oxide	5.0	5.0	5.0	5.0	3.0	3.0	5.0	3.0	5.0	5.0	5.0	5.0	5.0	5.0
Softener	3.0	3.0	3.0	3.0	4.0	4.0	3.0	3.0	3.0	5.0	5.0	6.0	6.0	6.0
Phenylnaphthylamine	...	...	...	...	1.0	...	...	...	1.0	...	...	...	...	...
Magnesia	...	...	...	...	...	...	...	...	4.0	...	...	...	...	...
Santocure	...	...	...	...	...	0.5	...	...	...	...	...	...	...	...
Captax	1.5	1.5	1.5	1.5	1.0	...	1.35	0.5	...	1.5	1.5	1.0	1.0	1.0
Tuads	...	...	...	...	...	...	...	1.0	...	...	...	...	...	...
Stearic acid	2.0	2.0	2.0	2.0	4.0	1.0	3.0	3.0	3.5	0.5	0.5	1.0	1.0	1.0
E.P.C. carbon black	50.0	40.0	30.0	...	...	45.0	50.3	45.0	45.0	50.0	50.0	50.0	50.0	50.0

[a] Copolymer of butadiene-acrylonitrile, 60/40.
[b] Copolymer of butadiene-acrylonitrile, 70/30.

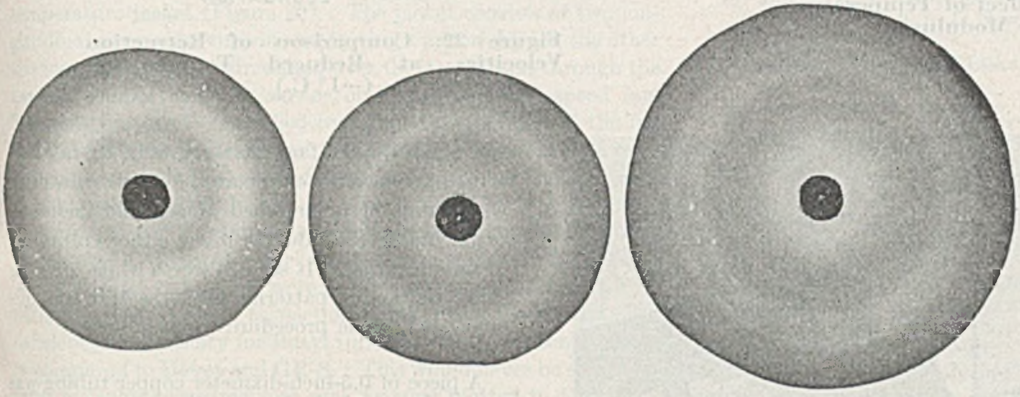
Butyl Rubber, Unfrozen Butyl Rubber, Frozen Hevea, Frozen

Figure 16. X-Ray Diffraction Patterns

tion is very important. In general, when polar molecular groups are present, they tend to increase intermolecular forces. This leads to inferior low temperature properties. Side groups such as occur in the styrene molecules of GR-S can also be effective in hindering the molecular motions requisite for the best low temperature properties of a hydrocarbon polymer. Consequently, the low temperature characteristics of GR-S are not so good as for polybutadiene or Hevea.

Figure 13 gives curves showing the rise in freezing and stiffening points caused by increased proportions of styrene in butadiene-styrene copolymers. The tread stocks for these data were formulated with 45 parts E. P. C. black and 1.6 parts of sulfur. Captax–diphenyl guanidine acceleration was used. The proportion of styrene plotted is the charging ratio. Figure 14 compares the cold hardening of a 50-50 mixture of Hevea and GR-S with that of Hevea and GR-S controls.

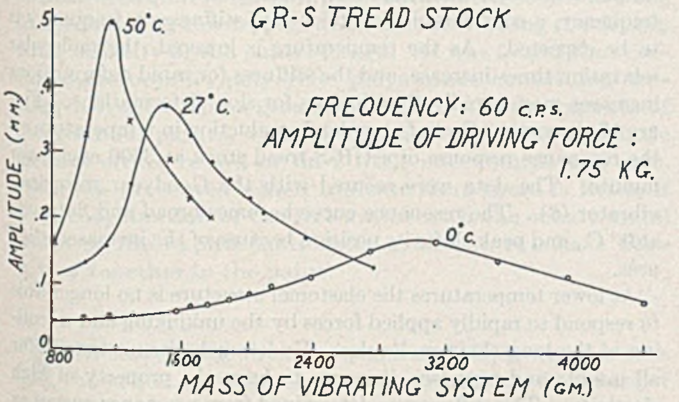

Figure 17. Effect of Temperature on Resonance Curves

LONG EXPOSURE TO LOW TEMPERATURES

It has been previously reported (*4*, *5*, *9*) that vulcanized compounds of Hevea and neoprene crystallize and increase in stiffness upon long exposures to low temperatures. We were particularly interested in determining whether this effect is a contributing factor to the low temperature performance of Butyl rubber. Test pieces of Hevea, Butyl, neoprene, and GR-S tread stocks were therefore mounted in the torsional stiffness tester. This was placed in a cold room at −30° C. Observations of the torsional stiffness were made periodically. The results are shown by the curves in Figure 15. Neoprene, Hevea, and Butyl showed large increases in stiffness after varying induction periods, which were surprisingly long. GR-S did not do this. Since neoprene, Hevea, and Butyl crystallize upon stretching and GR-S does not, crystallization would be the obvious explanation for the observa-

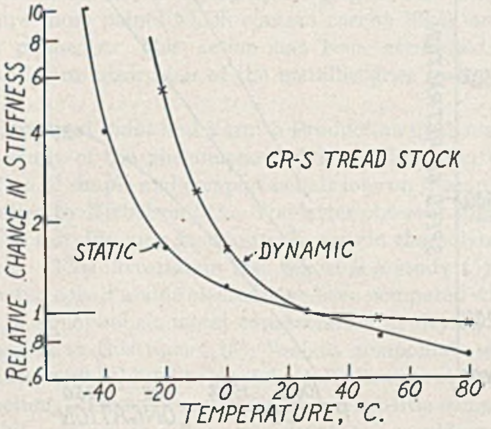

Figure 18. Relative Effect of Temperature on Dynamic and Static Stiffness

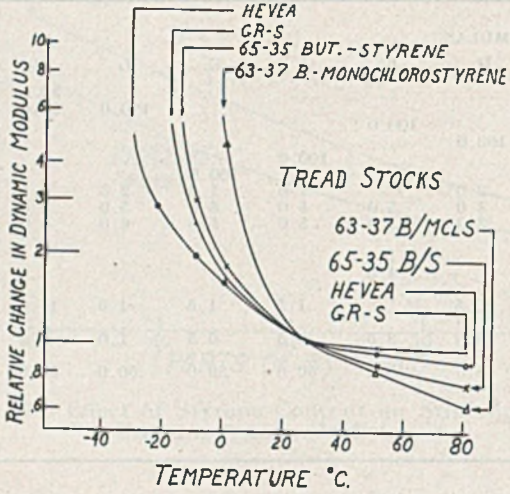

Figure 19. Relative Effect of Temperature on Dynamic Modulus

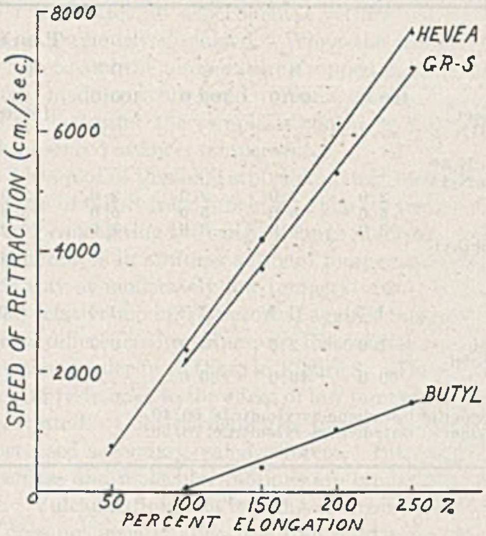

Figure 22. Comparison of Retraction Velocities at Reduced Temperature (−1° C.)

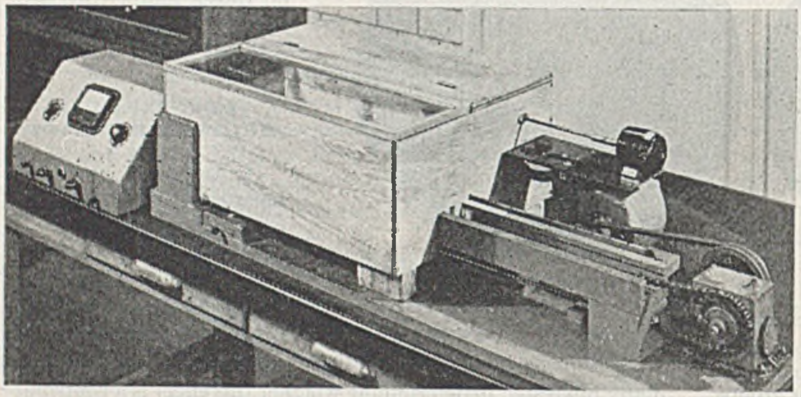

Figure 20. Speed of Retraction Apparatus

tions, despite the fact that crystalline x-ray patterns have never been reported for well vulcanized compounds of unstretched Hevea and neoprene, or for unstretched Butyl rubber, either vulcanized or unvulcanized. It seemed worth while to secure x-ray diffraction patterns when the test was discontinued. The procedure was as follows:

> A piece of 0.5-inch-diameter copper tubing was soldered through the bottom of a quart paint can. Holes were drilled through the tube to serve as windows for the x-ray beam. In the cold room the specimen was mounted in the copper tube between the windows, which were then covered with a very thin film of vulcanized rubber. The can was filled with dry ice moistened with acetone, and the lid put on. The vapors from the dry ice flowed down over the sample and kept it frozen during the x-ray exposure. The diffraction pattern secured for the Hevea and Butyl stocks are reproduced in Figure 16. The Hevea sample was crystallized. The pronounced sharpening of the ring in the Butyl pattern is also considered to be definite evidence of crystallization.

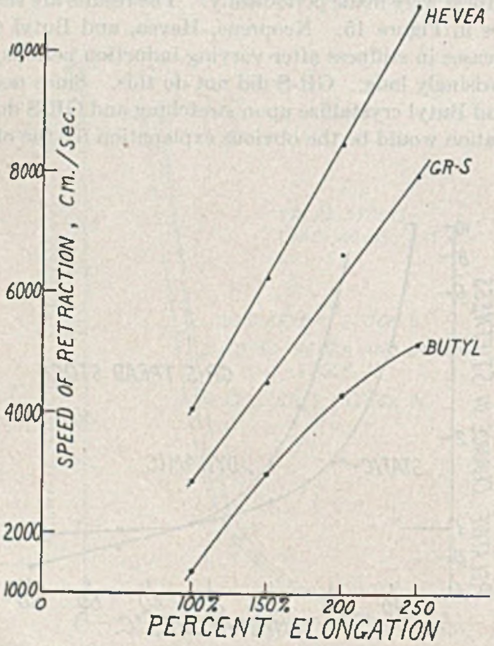

Figure 21. Comparison of Retraction Velocities at Room Temperature (25° C.)

RAPID DEFORMATIONS AT LOW TEMPERATURES

The information secured from a modulus test such as has been described may be inadequate for accurate anticipation of the relative cold hardening for rapid deformations. The theoretical background for this has already been discussed. When the molecular relaxation times reach the same order of magnitude as the frequency, a considerable dependence of stiffness on frequency is to be expected. As the temperature is lowered, the molecular relaxation times increase, and the stiffness for rapid deformations increases more rapidly than it does for slow deformations. Figure 17 shows the effect of a moderate reduction in temperature on the resonance response of a GR-S tread stock at 3600 cycles per minute. The data were secured with the Goodyear resonance vibrator (*6*). The resonance curve becomes broad and flat even at 0° C., and peak shifts its position because of the increased stiffness.

At lower temperatures the elastomer structure is no longer able to respond to rapidly applied forces by the unkinking and uncoiling of the long chain molecules. Under such circumstances, for all intents and purposes, it ceases to have the property of high elasticity. The stiffness, as determined from resonance curves as broad as the one shown in Figure 17 at 0° C., is of limited accuracy and significance, but values are plotted for what they are worth in Figures 18 and 19. Figure 18 compares the relative changes in stiffness as measured by the vibration test and the torsional modulus test. Figure 19 compares the effect of temperature on the dynamic modulus for several synthetic polymers and for Hevea. It is possible that the ordinary type of static modulus test might be generally satisfactory for rating polymers in the correct order for low temperature dynamic service, but any specific value of the modulus thus determined would depart rather widely from the dynamic values, even at moderately low temperatures.

One of the most sensitive measures for the effect of low temperatures on elasticity is the speed of free retraction when the sample is released after stretching. The velocity of retraction depends both upon the modulus and the internal friction. The apparent modulus is higher at lower temperatures, as has been explained, but the dependence of this increased modulus on increased internal friction is indicated by reduced velocities of retraction. Equipment for measuring the speed of free retraction has been already described in detail (*11*). The apparatus was provided with a low temperature jacket (Figure 20). The jacket consists of two longitudinal compartments, one containing a pan of dry ice, the other the test piece. Air is circulated over the dry ice and through the sample compartment by means of a small variable-speed fan. The temperature is controlled by manual adjustment of the fan speed. Suitable baffles to control the air flow in the sample compartment ensure constancy of temperature along the stretched sample to about ±2° F.

Figures 21 and 22 compare speed of retraction results for Butyl, Hevea, and GR-S tread stocks at room temperature, 25° C., and -1° C. The test pieces were cooled, stretched, and held for 1 minute before release. Inspection of the curves shows a startling deficiency in elasticity for Butyl rubber at the lower temperature as compared to Hevea and GR-S. This would never be suspected from modulus measurements such as were plotted in Figure 12. There Butyl seems to be about on a par with the other two in the persistence of its rubberlike character at low temperatures. The speed of retraction test is more critical and hence should be of considerable value to supplement the more conventional modulus data in the development of better compounds and polymers for low temperature service.

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Effect of Nitrogen-Containing Compounds on Drying of Paints

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The effect of free amines on the drying of oleoresinous paints was studied, and the data indicate that these amines are equal to the complex coordinated cobalt amines in accelerating the drying rate and maintaining the drying time stability of the paints tested. It was found that certain heterocyclic, polycyclic polyamines containing tertiary nitrogen atoms greatly accelerate the drying rate of oleoresinous paints, whereas aliphatic and other aromatic amines either retard or have little effect on drying rate. Data are presented which indicate that there is little, if any, coordination of the free amine with the cobalt metal atom of the naphthenate drier after the two have been mixed together in the paint.

THE study of the drying of pigmented oil systems has been the subject of many research investigations. One phase of such studies has involved the problem of so-called drier adsorption. It has been frequently observed that paints containing certain pigments exhibit loss of drying upon aging (*1*, *2*). Of particular notice are those paints which contain carbon black or titanium dioxide pigments. This action has been attributed, perhaps erroneously, to adsorption of the metallic drier by the pigment (*1*, *2*, *6*).

The Montreal Paint and Varnish Production Club made an extensive study of the phenomenon of drier adsorption (*3*). The adsorption of simple and complex cobalt ions on titanium dioxide was studied by Nicholson (*6*). The latter observer suggested (*4*) that loss of drying may be due to changes in the polymerization processes. This investigator also reported a study (*5*) in which coordinated cobalt amine oleates have been compared with simple oleates of equal cobalt metal concentration as drying catalysts.

According to this report (*5*), "cobalt compounds when fully coordinated and oxidized to the cobaltic state are extremely stable to reduction. Thus, by preparing such a cobaltic compound and using this material as a drier in a paint, one would expect practically no catalytic action by this material since the metal atom, being fully coordinated, would be incapable of coordinating with the unsaturated linkages of the oil, and because coordinated cobaltic cobalt is very stable and resists reduction."

The same study (*5*) using coordinated cobaltous and cobaltic *o*-phenanthroline oleate and the simple compounds indicated very little difference in the rate of oxygen absorption (gain in weight) of the unpigmented oil, when complexed or simple cobaltous oleate of equal metal concentration was used. Both materials greatly reduced the induction period, as compared with controls containing no drier. However, when the oil was pigmented with titanium dioxide, the induction period of the paint was very greatly reduced by the presence of coordinated drier, whereas the simple drier compound has little effect in comparison. This difference was assumed to be due to the fact that a metal atom surrounded by a large neutral group or groups (a complexed drier) would have less tendency to be adsorbed by pigment particles than would a similar "uncoated" metal atom.

Contrary to the results expected, Nicholson found that the cobaltic *o*-phenanthroline oleate had as great an effect as the cobaltous compound in shortening the induction period. Since coordinated cobaltic compounds are known for their resistance to reduction, and the cobalt atoms present were fully coordinated, one would have expected this material to have little effect as a paint drier.

In view of these results, studies were carried out in this laboratory to expand the scope of the above work and to determine, by practical drying tests, the effect of the simple and complexed compounds upon the drying rate and drying time stability of certain oleoresinous paints. Preliminary experiments soon indicated that the addition of free amine, to the previously prepared paint containing simple cobalt oleate, was as effective in reducing the drying rates as was the addition of the complexed coordinated cobalt amine oleates (at equal cobalt and amine concentrations by weight). Therefore, the bulk of the work presented in this paper was carried on utilizing the free amines and simple cobalt oleate in place of the coordinated compounds. Several hundred amines were tested; the results given in this paper represent but a few typical examples.

TEST PROCEDURE

The coordinated compounds were prepared according to the method described by Nicholson (*5*). The following formula illustrates the type of paint employed in this work:

	Pounds	Gallons	
Titanium dioxide[a]	3.00	0.086	
Vehicle[b]	6.96	0.914	
10% Pb Naph. Soln.	0.125	0.016	(0.6% Pb on wt. of oil)
1% Co Oleate Drier Soln.	0.104	0.016	(0.5% Co on wt. of oil)
	10.189	1.032	

[a] Pure, rutile TiO_2.

[b] Vehicle, Amberol M-88 (a modified phenolic resin), Z-bodied linseed oil, and mineral spirits. The oil and resin were heated to 500° F. in 30 minutes, allowed to cool, and thinned at 390° F. The vehicle length was 12.5 gallons; solids by weight, 60%; Gardner-Holdt viscosity, U; and acid number, 12.

The complex (coordinated) compounds were added as 1.0% cobalt metal solutions, and the free amines as 5% solutions in a solvent mixture of 50% toluol and 50% butanol (0.188 pound based on the above formula, giving 0.45% amine on the weight of the oil). Simple cobalt oleate was employed with the free amines.

PRACTICAL DRYING TEST. A modified weighted felt method was developed to determine the drying times of the paints. Two lint-free points were measured, at 10 and at 500 grams per square inch applied pressure. The time of contact of the flannel-covered block (1 inch square) with the film was 5 minutes. This method proved to be accurate under conditions of 50% relative humidity, 70° F., a constant artificial light source, and renewal of the air in the room approximately every 2 minutes. The 500-gram lint-free point for the paint in question proved to be approximately equal to a Sward hardness of 18–20%. At the 10-gram lint-free point the films were dry to touch.

The films were considered to be lint-free if the block (weight, 10 grams) fell off immediately upon inversion of the panel. For the 500-gram lint-free point a 490-gram lead weight was placed on the 10-gram block. The drying tests were made on films applied on polished plate glass panels by means of a 0.004-inch Bird film applicator blade.

DRYING TIME DATA

COMPLEX *vs.* FREE AMINES. A comparison of the drying times of the paints containing the complex (coordinated) or the free (uncoordinated) amines indicates that the latter are approximately equal in drying properties to the complex compounds (Table I).

TABLE I. DRYING PROPERTIES OF PAINTS CONTAINING COORDINATED AND UNCOORDINATED AMINES

Amine	Number Co-N Bonds	Drying Time[a], Hr.
Complex ethylenediamine	6	105
Free ethylenediamine	0	105
Complex pyridine	3	13
Free pyridine	0	14
Complex *o*-phenanthroline	6	7
Free *o*-phenanthroline	0	7.5

[a] At the 500-gram lint-free point.

It is also apparent that the size of the complex compound, as indicated by the number of coordinated linkages (degree of coordination), has little influence on the drying rate (Table I).

ALIPHATIC AMINES AS DRYING AGENTS. Short-chain secondary monoamines exhibit faster drying rates than do the longer-chain compounds, but both fail to accelerate the drying of the paint (Table II). Aliphatic primary diamines prolong the drying rate of the paint to a considerable extent, chain length having little effect upon the drying properties of the compound (Table II).

TABLE II. EFFECT OF CHAIN LENGTH ON DRYING

Amine	Drying Time, Hr.	Amine	Drying Time, Hr.
Control	17	Dipropylamine	17
Acrylic nitrile	18	Diamylamine	22
Succinic nitrile	18	Ethylenediamine	105
		Propylenediamine	105

Tertiary aliphatic mono- and dinitrogen-containing compounds, such as acrylic and succinic nitrile, respectively, have little effect on the drying rate of the paint. Here again, chain length has little influence, and the number of nitrogen atoms present does not affect the drying properties of the compound (Table II).

DRYING PROPERTIES OF AROMATIC AMINES. The bulk of the work reported in this paper was carried out with aromatic monoamines and diamines. Observations of the drying properties of representative compounds are given in Table III.

Cyclic tertiary diamines, such as *o*-phenanthroline and α, α'-dipyridyl, accelerate the drying rate to a definite degree. This acceleration of drying is accomplished without altering other paint and paint-film properties. Brittle films are not produced, film hardness being increased by only a few per cent (Sward hardness).

Cyclic tertiary monoamines, in general, prolong the drying rate to a considerable extent. Pyridine, an exception, slightly accelerates the drying of the paint.

Pyridine, *o*-aminopyridine, aniline, and *o*-phenylenediamine reveal some interesting information regarding the nitrogen atom system which produces good drying. Pyridine (a monoamine) has one tertiary amine grouping and accelerates the drying rate to a slight degree; *o*-aminopyridine (a diamine), containing one tertiary and one primary amine grouping, prolongs the drying considerably. A compound such as aniline, containing a single primary amine group, gives slightly better drying than *o*-aminopyridine, whereas the presence of two primary amine groupings, as in *o*-phenylenediamine, is extremely detrimental to the drying rate. The action of *o*-aminopyridine is typical of cyclic diamines containing at least one primary amine group.

Replacement of the primary amine group of *o*-aminopyridine by a vinyl radical to give *o*-vinylpyridine improves the drying properties of the compound to a considerable extent but fails to accelerate the drying of the paint.

AROMATIC AMIDES, NITRILES, AND ISOCYANATES. A comparison of aniline and *o*-toluidine (Tables III and IV, respectively) indicates that a methyl group attached to the benzene nucleus has little or no effect upon the drying properties of an amine. A tertiary amine group (as in *o*-tolunitrile) does not give any improvement in drying rate.

Isocyanates vary in drying properties. *o*-Tolyl- and naphthylisocyanate do not alter the drying time of the paint to any great extent, but the latter gives slightly faster drying than the control. Phenyl isocyanate prolongs the drying of the paint to some extent.

CONDENSED BENZENE AND/OR FIVE-MEMBERED HETEROCYCLIC RINGS. Pyrrole accelerates the drying rate to a slight extent; it is similar to pyridine in this respect. Benzimidazole definitely prolongs the drying, and benzotriazole is extremely detrimental to the drying of the paint.

COMPARISON OF ALIPHATIC AND AROMATIC AMINES. Primary diamines, whether straight chain or cyclic, produce poor drying properties. Primary and secondary monoamines, whether aliphatic or aromatic, retard the drying rate of the paint to a slight degree. Tertiary monoamines, whether aliphatic or aromatic, have little or no effect upon the drying rate.

DRYING TIME STABILITY. Only a few of the amines are outstanding from this point of view. These amines are *o*-phenanthroline, α, α′-dipyridyl, and benzimidazole. All three are aromatic heterocyclic diamines; the first two have only tertiary amine groups, and the last has one secondary and one tertiary amine group. In each case the carbon-nitrogen system is conjugated. In *o*-phenanthroline and α, α′-dipyridyl the tertiary amino nitrogen atoms are separated by two carbon atoms. In benzimidazole the secondary and tertiary amino nitrogen atoms are separated by only one carbon atom which has an attached hydrogen atom. These differences may be responsible for the poor initial drying exhibited by benzimidazole.

DISCUSSION OF DATA

Since the free amines give almost exactly the same drying time as the complex coordinated amines, the question arises as to the possibility of the coordination of the free amine with the cobalt metal atom of the cobalt oleate drier, after the two have been mixed together in the paint. The following observations indicate that coordination of the free amine does not take place in the paint vehicle.

Since the presence of a coordinate link in a compound greatly increases its dielectric constant, the dielectric constants of oleoresinous solutions containing equivalent amounts of free and complex amine were determined:

Vehicle Solution	*E*, Initial	*E*, 3 Days	*E*, 28 Days
(1) Varnish + cobaltous oleate	2.90	2.90	3.02
(2) Varnish + cobaltous oleate + *o*-phenanthroline	3.04	3.19	3.19
(3) Varnish + cobaltous *o*-phenanthroline oleate	5.05	5.03	5.01

The high dielectric constant of (3) is due to the coordinate linkages in the complex drier; and although (2) shows a light increase in 3 days, it is not great enough to indicate that any appreciable coordination of the simple amine with the cobaltous oleate has taken place. (Drying times were determined within this 3-day time interval.)

TABLE III. DRYING PROPERTIES OF AROMATIC AMINES

Amine	Drying Time, Hr. Initial	Drying Time, Hr. 36 weeks
Control	17	30
o-Phenanthroline	7.5	9
α,α′-Dipyridyl	10	14
Pyridine	14	28
o-Vinylpyridine	19	48
Aniline	20	40
α-Naphthylamine	20	38
Quinoline	24	52
o-Aminopyridine	24	60
o-Phenylenediamine	72	96

TABLE IV. EFFECTS OF VARIOUS COMPOUNDS ON DRYING RATE

Compound	Type of Amine Group(s)	Drying Time, Hr. Initial	Drying Time, Hr. 36 hr.
Control	....	17	30
o-Toluidine	1 primary	20	35
o-Tolunitrile	1 tertiary	19	36
o-Toluamide	1 primary	19	36
o-Tolyl isocyanate	1 tertiary	18	32
Phenyl isocyanate	1 tertiary	20	35
Naphthyl isocyanate	1 tertiary	16	36
Control	....	17	30
Pyrrole	1 secondary	15	34
Benzimidazole	1 secondary, 1 tertiary	36	40
Benzotriazole	1 secondary, 2 tertiary	84	96

It is quite evident that the amines which accelerate the drying time to any great extent are heterocyclic, polycyclic polyamines containing tertiary nitrogen atoms. The mechanism by which the acceleration of the drying time is obtained is being investigated.

SUMMARY

Free uncoordinated amines are equal to the complex coordinated amines from the standpoint of initial drying time and drying time stability.

There appears to be little, if any, coordination of the free amine with the cobalt metal atom of the naphthenate drier after the two have been mixed together in the paint.

Primary, secondary, and tertiary monoamines, whether aliphatic or aromatic, have little or no effect upon the drying rate of oleoresinous paints.

Certain heterocyclic, polycyclic polyamines containing tertiary nitrogen atoms greatly accelerate the drying rate and maintain the drying time stability of certain oleoresinous paints.

The mechanism by which the acceleration of the drying time is obtained, and the type of oleoresinous system in which it takes place, are problems which are being investigated. An infrared absorption spectra study would be of considerable value toward the solution of the general problem.

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Calculation Method for Complex Mixtures

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A method using simple calculus is presented for the calculation of vapor-liquid equilibria for complex mixtures. The computations are based on the true boiling point curve of the mixture and are performed with a plot of dM/dT_B vs. T_B. The procedures and equations used are similar to those for component mixtures. The results obtained can be made exact within the accuracy of the data. Four illustrative examples are given of calculations involving a single equilibrium.

IN GENERAL the calculation of pressure-temperature-composition relations and distillation conditions involves two types of mixtures. The first of these is the component mixture, for which the composition is commonly expressed as the percentages of the compounds present. Thus a natural gas is said to contain so much methane, ethane, etc. The other type is the complex mixture, which consists of a large number of compounds and for which the composition is commonly expressed by a batch distillation curve. Thus a kerosene is said to boil between 350° and 550° F.

For component mixtures the use of either Raoult's law or vapor-liquid equilibrium constants, K values, is common for the calculation of such vaporization properties as the dew-point temperature (*5, 6, 10, 13, 16*). There is a complete system of equations and procedures for these computations, and the results can be made as accurate as the data used. The basic equations used for these single equilibrium calculations can be written as follows:

VAPOR-LIQUID EQUILIBRIUM

$$y = Kx \tag{1}$$

or

$$Vy = (VK/L)(Lx) \tag{2}$$

OVER-ALL MATERIAL BALANCE

$$F = V + L \tag{3}$$

COMPONENT MATERIAL BALANCE

$$Fz = Vy + Lx \tag{4}$$

COMPOSITIONS SUMMATIONS

$$\Sigma Fz = F \qquad \Sigma Vy = V \qquad \Sigma Lx = L \tag{5}$$

A mathematical system for complex mixtures comparable with the one for component mixtures would seem to be desirable, particularly for refinery process work. In general, this type of mixture is either considered to be divided into artificial compounds having a short boiling range (*3, 6, 8, 9, 17, 18*) or treated empirically by methods based on large amounts of laboratory data (*4, 11, 12, 14*). The use of differential curves for complex mixtures has been frequently proposed (*3, 6, 7, 17*), but the actual details required to make these calculations practical are not commonly known. The present paper gives the simple calculus for one method by which complex mixtures may be handled by equations and procedures similar to those used for component mixtures. The results obtained with this method can be made exact within the accuracy of the data used.

PLOT OF dM/dT_B AGAINST T_B

For component mixtures the fundamental vaporization data are commonly given in terms of the components present. Thus it is said that the K value of n-hexane is 4.5 at 300° F. and 20 pounds per square inch absolute (*2*). But for a complex mixture the number of compounds is large, so that some basis for the vaporization data other than molecular species is necessary. A common and well developed laboratory determination for complex mixtures is the true boiling point curve, or TBP, which is obtained by the batch distillation of the mixture in a multiplate column at a high reflux ratio. This curve is usually given as liquid volume per cent distilled over plotted against column top temperature or boiling point (v against T_B). For the method of this article the vaporization data of a complex mixture will be based on the boiling points as given by a TBP. Thus it will be said that the K value of the component that boils at 156° F. (n-hexane) is 4.5 at 300° F. and 20 pounds per square inch absolute. Values of K based on boiling temperature have been published by White and Brown (*18*).

But a TBP as such cannot be used in the vapor-liquid equilibrium calculations; consequently it must be changed into a form that can. For direct use in the computations by the method of this article, the TBP is put into the form of the differential curve dM/dT_B vs. T_B, where M represents moles and T_B is the boiling temperature. This curve provides the connections between total moles, component moles, and vaporization properties that are required for the calculations. The simple calculus of obtaining this curve from a TBP will be given, and after this the properties and uses of the curve will be described and illustrated.

The basic relation used in obtaining a value of dM/dT_B is the identity

$$\frac{dM}{dT_B} = \frac{dv}{dT_B} \times \frac{dM}{dv} = \frac{dv}{dT_B} \times \frac{D}{mw} \tag{6}$$

where the values of the derivatives are for the infinitesimal fractions of the mixture boiled over at a temperature in a TBP column. Values of dM/dT_B are plotted at the corresponding values of T_B to give the desired curve. As an example a plot of dM/dT_B against T_B will be obtained for the petroleum naphtha of Figure 1. Curve A is the true boiling point curve for this mixture and gives the boiling temperatures of the liquid fractions distilled over. Curves B and C give the molecular weights and the densities of these liquid fractions, respectively. The steps in obtaining a plot of dM/dT_B against T_B from these data are as follows:

STEP 1. Obtain a plot of dv/dT_B for the mixture. The slopes of the TBP, curve A of Figure 1, are measured, and the reciprocals, dv/dT_B, are plotted against T_B. The resultant points are carefully averaged and smoothed. The final values are given by curve A of Figure 2. Thus at 200° F. the measured slope of the TBP is 3.66, and the reciprocal of this, $dv/dT_B = 0.273$, is plotted at $T_B = 200°$. As a convenient check the area under this curve represents liquid volume and should total 100.

STEP 2. Obtain the plot of dM/dT_B against T_B with Equation 6. Values of dv/dT_B, mw, and D, all at the same value of T_B, are substituted in Equation 6 to give a value of dM/dT_B. Points of dM/dT_B against T_B obtained in this way are plotted and smoothed to give curve B of Figure 2. As an example at 200° F., dv/dT_B is 0.273, and, from curves B and C of Figure 1, $mw = 98$ and $D = 5.67$. Then

$$100\,\frac{dM}{dT_B} = 100 \times 0.273 \times (5.67/98) = 1.58 \qquad (6)$$

and this value is plotted on curve B of Figure 2 at $T_B = 200°$ F.

A principle in the solution of vapor-liquid equilibrium problems is that the entire calculation can be based on dimensionless ratios such as L/V and K. Any absolute values can be made to cancel out in the calculations. Thus in the compositions reported for component mixtures it is only necessary that the ratios of moles of compounds to each other be known; the actual numbers of moles are not needed. For the same reason it is permissible to change the decimal point on the values of dM/dT_B from 0.01 to 1.0, and this is done in the remainder of this article. Similarly Equation 6 does not need to be dimensionally correct. The actual scale used for the values of dM/dT_B plotted against T_B is unimportant so long as the shape of the curve is not affected. Other short cuts based on this use of ratios will be given. These save time and are the way the calculations are actually performed.

It may be desired to do the opposite of the operation just described—that is, to obtain a TBP from a plot of dM/dT_B against T_B. This is done by a reversal of the steps given. Values of dM/dT_B and of D and mw are substituted in Equation 6 to obtain values of dv/dT_B, and these are plotted against T_B as in curve A of Figure 2. The area under this curve represents v, liquid volume. The graphical integration of successive sections of the curve with a planimeter gives the TBP.

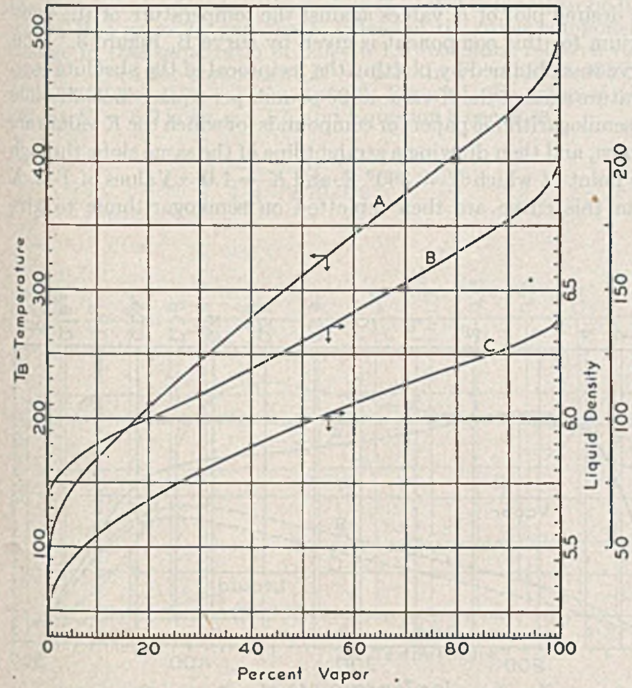

Figure 1. Properties of a Petroleum Naphtha

A = true boiling point curve; B = molecular weight of fractions distilled over; C = liquid density, pounds per gallon, of fractions distilled over

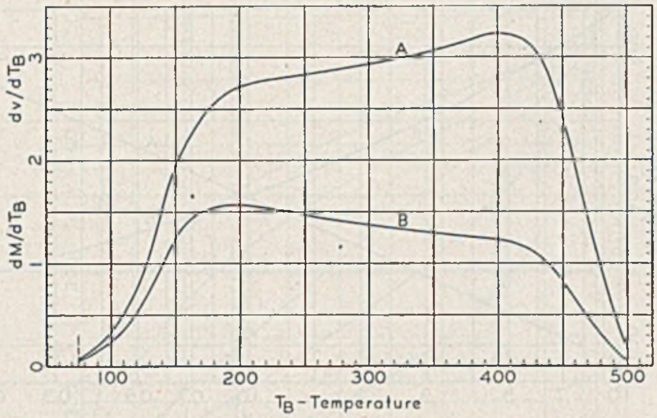

Figure 2. Differential Curves for Petroleum Naphtha Plotted against Boiling Temperature

A = dv/dT_B, reciprocal slope of TBP *vs.* T_B from curve A of Figure 1

In order to use a plot of dM/T_B in the calculations it is first necessary to know the K values at the conditions of the equilibrium as a function of the boiling temperature. This relation for the conditions of 300° F. and 20 pounds per square inch absolute is given by curve A, Figure 3, which is a straight line plot of T_B against K on semilogarithmic paper. This curve was obtained by plotting boiling temperature against the known K values of 300° F. and 20 pounds for the hydrocarbons of lower molecular weight (*2*), and then averaging the resultant points as a straight line extending over the desired temperature range of 75° to 500° F. In using a plot of dM/dT_B it is desirable to be able to read the K values directly from the figure. A convenient way of doing this is to draw vertical lines at values of T_B and label them with the corresponding values of K. A construction of this type is illustrated in Figure 4, where curve A represents the original naphtha and is a copy of curve B, Figure 2. The K values at the boiling temperatures were read from curve A, Figure 3.

A plot of dM/dT_B against T_B marked off with K lines, such as Figure 4, was chosen for actual use in the complex mixture calculations because of certain very useful properties. First, the area under a plot of dM/dT_B *vs.* T_B represents moles and can be easily and quickly determined with a planimeter. Second, the shape of this curve depends on the mixture and is independent of the conditions of the equilibrium. For new conditions of temperature and pressure new sets of vertical K lines are drawn. Third, the K values for the calculations are read directly from the figure, and the results obtained are plotted on the corresponding K lines. The use of these properties will be illustrated in the example calculations to be given.

ANALOGY WITH COMPONENT MIXTURE CALCULATIONS

A complete mathematical system for the calculation of the vapor-liquid equilibria for complex mixtures could be given independently of the already existing system for component mixtures. However, the calculations are quite similar in many respects, and it is believed that it would be helpful to develop the analogy between them. In order to do this it is necessary that the terms used for component mixtures be defined for complex mixtures in such a way that both can be spoken of with the same words and calculated by the same equations.

For component mixtures the "components" are simply the compounds present, and each has a single distinct set of vaporization properties. For the method given here the fractions of a complex mixture that have distinct vaporization properties are the infinitesimally small increments boiled over in a TBP column. These increments, then, are taken as the components of a complex mixture, and they are designated by one of their vaporization

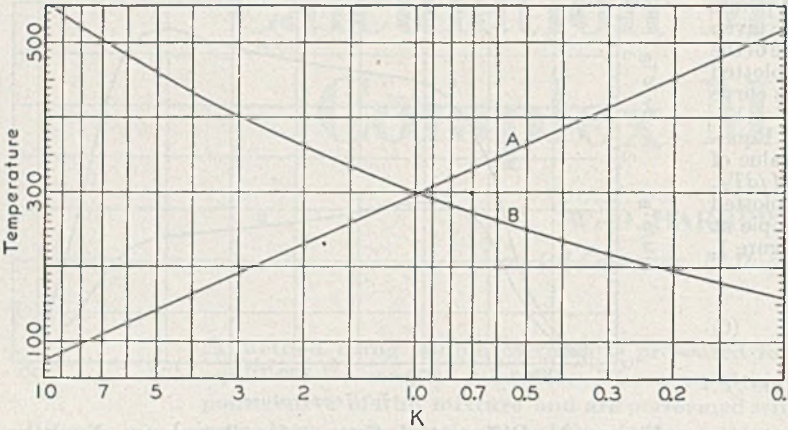

Figure 3. Vaporization Data for Petroleum Naphtha

A = boiling temperature (T_B) *vs.* K at 300° F. and 20 pounds per square inch absolute (straight line on semilogarithmic paper); B = temperature of vapor-liquid equilibrium (T) *vs.* K at 20 pounds for component for which K = 1.0 at 300° F.

properties. Thus for curve A of Figure 1, component $T_B = 200°$ is the infinitesimal fraction of the total naphtha that boils at exactly 200° F. For curve A of Figure 4, component $K = 2.0$ is the infinitesimal fraction boiled over that has a K value of 2.0 at 300° F. and 20 pounds per square inch absolute.

The "composition" of a component mixture gives the finite mole fractions of the components present; but it also can be considered to give the ratios of the amounts of the components to each other. For complex mixtures for the method given here the actual mole fractions of the components are infinitesimally small and are proportional to the values of dM/dT_B. Then a plot that gives values of dM/dT_B at values of T_B gives the ratios of the infinitesimal fractions of the components to each other and so can be considered to be a composition. Thus curve A of Figure 4 gives the molar distribution of the naphtha of Figure 1 along the boiling range and so can be considered to represent the composition of the naphtha.

For component mixtures the terms Fz, Lx, and Vy represent moles of the components and are used to calculate divisions of the total component between vapor and liquid. For complex mixtures, as already stated, the amounts of the components are infinitesimally small and are proportional to values of dM/dT_B. But these values of dM/dT_B can also be used to obtain the division of the components between vapor and liquid. Then for complex mixtures the terms Fz, Lx, and Vy are taken as the corresponding values of dM/dT_B as read from a composition curve. As an example, for the total original naphtha of curve A, Figure 4, the value of dM/dT_B for component $K = 4.0$ is 1.44, and this can be stated simply as $Fz = 1.44$. This definition permits Equations 2 and 4 to be used for complex mixtures exactly as for component mixtures, and this is illustrated in the example calculations to be given later. The terms x, y, and z are not used alone for complex mixtures.

For component mixtures the total mole terms—F, L, and V—are obtained by the summation of the moles of the individual components; but a complex mixture is considered to consist of an infinite number of components, so that an integration rather than a summation is required to obtain total moles. This integral, which corresponds to Equation 5, can be written as

$$\int\left(\frac{dM}{dT_B}\right) dT_B = M \qquad (7)$$

where M represents moles and can be either F, L, or V. In actual use this integral is the area under a composition curve (dM/dT_B *vs.* T_B) and can be easily and quickly determined with a planimeter. As already discussed, it is the ratios of the total mole terms to each other and not their absolute values that are necessary for the calculations. Then in determining moles as areas, no integrating machine factor need be used, provided it is the same for all of the composition curves, as it will cancel out in the calculations. Then as an example, the planimeter reading for the area under curve A, Figure 4, is 18.67, and this can be stated simply as $F = 18.67$.

In summary, then, the infinitesimal components of complex mixtures can be divided between vapor and liquid and summed to obtain total moles exactly as are the finite components. The same equations and procedures can be used for both types of mixtures.

CONSTANT RELATIVE VOLATILITY

A useful assumption that is frequently made for vapor-liquid equilibrium calculations for component mixtures is that of constant relative volatility (*16*). In this it is considered that the ratios of the K values remain constant over a temperature range, however much the K values themselves change. With this assumption the temperature unknown is either eliminated completely from the calculation or its solution is obtained without trial and error. This gives a quicker, more direct calculation. With the use of some care in averaging the K value ratios, the errors due to this assumption can be kept small for regular systems of chemically similar compounds such as the saturated hydrocarbons.

This assumption of constant K value ratios is also useful in the complex mixture calculations. With it the K values at a temperature can be obtained by multiplying the known K values at another temperature by a constant. In order to do this it is first necessary to know the K value-*vs.*-temperature relation for one component. Component $K = 1.0$ is chosen as this reference component for the naphtha composition of curve A, Figure 4, and the desired plot of K values against the temperature of the equilibrium for this component is given by curve B, Figure 3. This curve was obtained by plotting the reciprocal of the absolute temperature against the K value at 20 pounds per square inch absolute on semilogarithmic paper for compounds for which the K values are known, and then drawing a straight line of the same slope through the point at which $T = 300°$ F. and $K = 1.0$. Values of T *vs.* K from this curve are then replotted on semilogarithmic to give

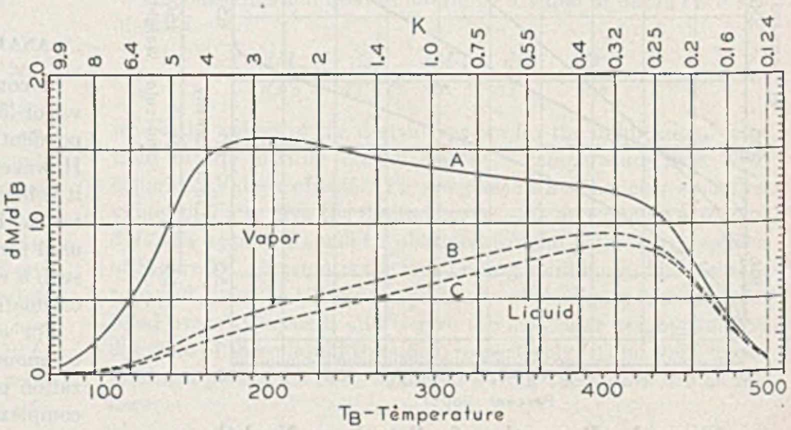

Figure 4. Composition Curves for Example I

A = composition curve for original naphtha; B = division of naphtha into vapor and liquid for first trial; C = division of naphtha into vapor and liquid for final trial curve B, Figure 3. As an example of the use of this curve, the K value of component $K = 4.0$ of curve A, Figure 4, will be found at 260° F. and 20 pounds. From curve B, Figure 3, for reference component $K = 1.0$, the K value at 260° F. is 0.58. Then with the assumption of constant K value ratios, the K value of component $K = 4.0$ at 260° F. is $(4.0/1.0)\ (0.58) = 2.32$. The K values of other components and at other temperatures can be obtained similarly.

The method given here is not dependent on any of the assumptions made for the vaporization data. It is only necessary that the K values be known as a function of the boiling temperature, and any source of these data including direct laboratory determinations can be used. As with component mixtures, the assumption of constant relative volatility is a convenient way of obtaining K values at different conditions, but it is not essential to the method.

EXAMPLE I. EQUILIBRIUM DIVISION INTO VAPOR AND LIQUID

The first calculation is to determine the division of the naphtha of Figure 1 between vapor and liquid at equilibrium for the conditions of 295° F. and 20 pounds per square inch absolute. The principal equation used is

$$(Lx) = \frac{(Fz)}{1 + (VK/L)} \tag{8}$$

which is obtained by combining Equations 2 and 4. The procedure used is to assume a value of L/V for the equilibrium, and, with the Equation 8 and the known K values, to calculate a division of the naphtha into vapor and liquid. From this a new calculated value of L/V is obtained. This step is repeated until the assumed and calculated values of L/V check. Exactly the same procedure is used for component mixtures.

The composition curves required in the calculation are given in Figure 4, and curve A represents the original naphtha. The detailed procedure is as follows:

STEP 1. Assume a reasonable value of L/V, and, with Equation 8 and the K values, calculate a division of the naphtha into vapor and liquid.

The value of L/V assumed for the first trial is 1.0. At 295° F. the K value of reference component $K = 1.0$ is found to be 0.93 (curve B, Figure 3), and the K values of the other components change in this same ratio of 0.93 to 1.0 (constant relative volatility). Then for component $K = 3.0$, the K value at 295° F. is $3.0 \times 0.93 = 2.79$. From curve A, Figure 4, the value of dM/dT_B at $K = 3.0$ is $Fz = 1.57$, and Equation 8 becomes

$$Lx = \frac{1.57}{1 + (2.79/1.0)} = 0.415 \tag{8}$$

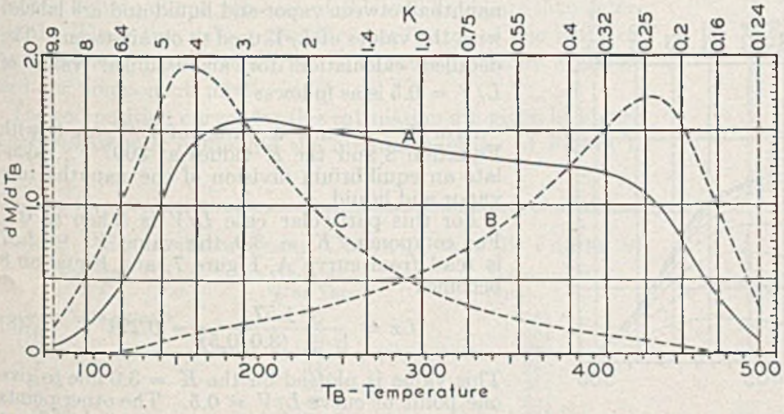

Figure 5. Composition Curves for Example II

A = composition curve for original naphtha; B = composition of liquid in equilibrium with original naphtha as vapor (dew point); C = composition of vapor in equilibrium with original naphtha as liquid (bubble point)

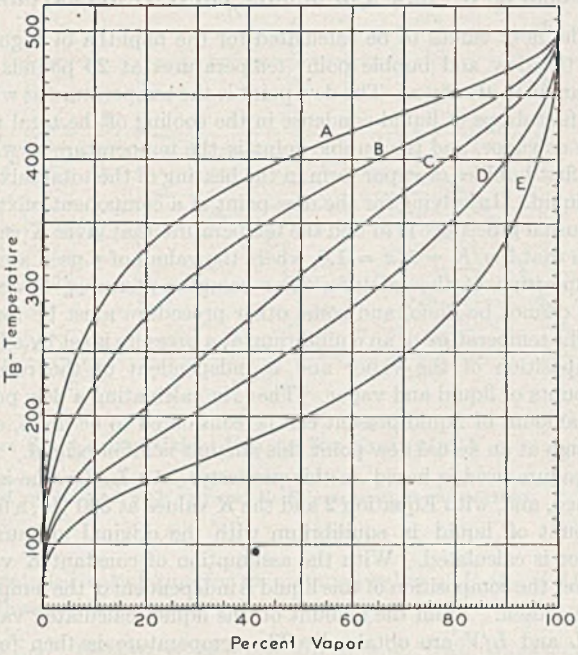

Figure 6. True Boiling Point Curves

A = TPB of liquid in equilibrium with original naphtha as vapor; B = TPB of portion of naphtha that is liquid at 295° F. and 20 pounds per square inch; C = TPB of original naphtha; D = TPB of portion of naphtha that is vapor at 295° F. and 20 pounds per square inch; E = TPB of vapor in equilibrium with original naphtha in liquid

This value of Lx is plotted at $K = 3.0$ to give one point of curve B, Figure 4. The other points at the K values shown were obtained similarly. This curve gives the required division of the original naphtha into liquid and vapor for an assumed L/V of 1.0.

STEP 2. Obtain a new, calculated L/V from the curve of step 1. The moles of liquid present are represented by the area under curve B, Figure 4, and the value is given by the planimeter as $L = 9.07$. The corresponding moles of total mixture is the area under curve A, Figure 4, and has been found to be 18.67. Then by Equation 3, $V = F - L = 18.67 - 9.07 = 9.60$, and the new calculated L/V is $9.09/9.60 = 0.946$. Evidently this is not sufficiently close to the assumed value of $L/V = 1.0$, and a new trial must be made.

STEP 3. Repeat steps 1 and 2 until the assumed and calculated values of L/V check. The third and final assumption was $L/V = 0.72$, and the resultant division of the naphtha is given by curve C, Figure 4. The moles of liquid present are represented by the area under this curve, and the value is found to be $L = 7.84$. Then $V = F - L = 18.67 - 7.84 = 10.83$, and the new calculated L/V is $7.84/10.83 = 0.724$. This is taken as sufficiently close to the assumed value of $L/V = 0.72$, so that no further trials are required. Then curve C, Figure 4, can be considered to represent the final division of the original naphtha into vapor and liquid at 295° F. and 20 pounds per square inch absolute.

STEP 4. Convert the mole fractions obtained in step 3 into liquid volume per cent.

For this a plot of dv/dT_B vs. T_B is prepared for the values of curve C, Figure 4, by means of Equation 6. The area under this curve represents liquid volume and is given as $v = 15.15$ by the planimeter. The corresponding area under curve A, Figure 2, for the total original mixture is $v = 32.79$. Then the liquid naphtha of curve C, Figure 4, is $100 \times (15.15/32.79) = 46.2$ liquid volume per cent of the total.

Then as a final answer the naphtha of Figure 1 is $100 - 46.2 = 53.8\%$ vaporized at 295° F. and 20 pounds. This is a point on the equilibrium flash curve for the mixture (curve B, Figure 9). The TBP values of the liquid and vapor of the equilibrium are given by curves B and D of Figure 6, respectively. These were obtained from curves A and C of Figure 4 by integrating plots of dv/dT_B vs. T_B as already described.

EXAMPLE II. DEW AND BUBBLE POINT TEMPERATURES

The next values to be calculated for the naphtha of Figure 1 are the dew and bubble point temperatures at 20 pounds per square inch absolute. The dew point is the temperature at which the first drops of liquid condense in the cooling of the total mixture as vapor, and the bubble point is the temperature at which the first bubbles of vapor form in the heating of the total mixture as liquid. In solving for the dew point of a component mixture, the usual procedure is to find the temperature that gives K values such that $\Sigma\, y/K = \Sigma\, x = 1.0$, where the values of y used are the composition of the mixture. For complex mixtures, however, this cannot be done, and some other procedure must be found.

The temperature of an equilibrium at a pressure is set by a fixed composition of the vapor and is independent of the relative amounts of liquid and vapor. Then, in calculating a dew point, the amount of liquid present can be considered to be finite, even though at an actual dew point this amount is infinitesimal. The procedure used is based on this property. An L/V value is assumed, and, with Equation 2 and the K values at 300° F., a finite amount of liquid in equilibrium with the original mixture as vapor is calculated. With the assumption of constant K value ratios, the composition of this liquid is independent of the temperature chosen. From the amount of this liquid, calculated values of L and L/V are obtained. The temperature is then found which gives K values such that the assumed and calculated values of L/V check, and this temperature is the dew point. The same procedure could be used for component mixtures.

The composition curves required for the calculation of the dew point are given in Figure 5, where curve A represents the original naphtha. The detailed procedure is as follows:

STEP 1. Consider the original mixture to be all vapor, and calculate a liquid composition in equilibrium with it by means of Equation 2.

It is first necessary that a value of L/V be assumed, and $L/V = 0.40$ is chosen as this gives a conveniently sized composition curve. For component $K = 0.55$ the value of $Vy = Fz = 1.29$ is read from curve A, Figure 5, and Equation 2 becomes

$$Lx = 1.29\ (0.40/0.55) = 0.94 \qquad (2)$$

This value of Lx and others similarly obtained are plotted to give curve B, Figure 5, which is the required composition of the liquid in equilibrium with the original mixture as vapor.

STEP 2. Determine the new calculated values of L and L/V. The moles of the original mixture as vapor are represented by the area under curve A, Figure 5, and the value has been found to be $V = F = 18.67$. The corresponding moles of liquid are shown by the area under curve B, Figure 5, and the value is given by the planimeter as $L = 10.90$. Then the new, calculated value of L/V is $10.90/18.67 = 0.584$, as compared with the assumed value of 0.40 used in step 1.

STEP 3. Find the temperature (dew point) that gives K values such that the assumed and calculated L/V values would check.

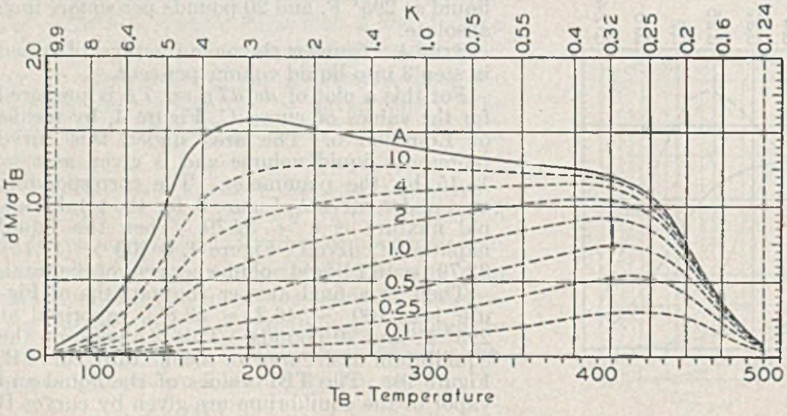

Figure 7. Composition Curves for Example III

A = composition curve for orginal naphtha; broken lines give divisions between vapor and liquid and are labeled with value of L/V assumed in calculation

If the K values at 300° F. used in Equation 2 in step 1 were multiplied by the ratio $(L/V)_c/(L/V)_a$ and the calculation repeated, then the assumed and calculated values of L/V would be the same, and the K values would be at the dew point temperature (constant K value ratios). Then for reference component $K = 1.0$ the value of K at the dew point temperature is

$$K \times (L/V)_c(L/V)_a = 1.0\ (0.584/0.40) = 1.46$$

From the plot of K vs. T for this component (curve B, Figure 3) the temperature corresponding to $K = 1.46$ is 333° F., and this is the dew point temperature for the naphtha at 20 pounds per square inch absolute.

The solution for the bubble point temperature is similar, except that liquid and vapor are interchanged. The original mixture is considered to be all liquid, and a vapor in equilibrium with it is calculated by means of Equation 2. L/V is assumed to be 3.0, and the resulting vapor composition is given by curve C, Figure 5. The moles of vapor are $V = 11.42$, the calculated value of L/V is $18.67/11.42 = 1.63$, and the ratio $(L/V)_c/(L/V)_a$ is $1.63/3.0 = 0.54$. Then the K value of reference component $K = 1.0$ is $1.0 \times 0.54 = 0.54$ at the bubble point, and from curve B, Figure 3, this temperature is 254° F.

These two temperatures, 254° and 333° F., are shown as the end points of the equilibrium flash curve for the mixture (curve B, Figure 9). The calculated TBP of the liquid in equilibrium with the original naphtha as vapor is curve A, Figure 6, and the corresponding TBP for the vapor in equilibrium with the original naphtha as liquid is curve E, Figure 6. These were obtained from curves B and C of Figure 5 by the method already described.

EXAMPLE III. EQUILIBRIUM FLASH CURVE

An important curve in the study of complex mixtures is the equilibrium flash curve, which gives the liquid volume per cent of the mixture that is vaporized against the temperature of the system (T vs. v) for a constant pressure. The present calculation is to obtain the equilibrium flash curve at 20 pounds per square inch absolute for the naphtha of Figure 1. One point on this curve was obtained in example I—namely, at 295° F. and 20 pounds the naphtha is 53.8% vaporized. The calculation of a point on the equilibrium flash curve is quicker than the calculation of example II, as no specific temperature need be set, and consequently the trial and error is eliminated. The general procedure used to find a point on this curve is as follows:

A value of L/V and a temperature are assumed, and an equilibrium division of the total naphtha into vapor and liquid is obtained with Equation 8. The temperature required for this equilibrium (constant K value ratios) and the per cent of the total naphtha that is vapor are then determined. These values are the coordinates of one point on the desired curve. Exactly the same procedure would be used for component mixtures.

The composition curves required for the calculation are given in Figure 7, where curve A represents the original naphtha. The other curves give divisions of the naphtha between vapor and liquid and are labeled with the values of L/V used to obtain them. The detailed calculation for an assumed value of $L/V = 0.5$ is as follows:

STEP 1. Assume a value of L/V, and, with Equation 8 and the K values at 300° F., calculate an equilibrium division of the naphtha into vapor and liquid.

For this particular case L/V is taken as 0.5. For component $K = 3.0$ the value $Fz = 1.57$ is read from curve A, Figure 7, and Equation 8 becomes

$$Lx = \frac{1.57}{1 + (3.0/0.5)} = 0.224 \qquad (8)$$

This value is plotted on the $K = 3.0$ line to give one point of curve $L/V = 0.5$. The other points of the curve and the other curves of this figure were obtained similarly. These curves give equilibrium divisions of the total mixture into vapor and liquid.

Step 2. Determine the temperature required for the equilibrium of step 1.

If the K values at 300° F. used in step 1 were multiplied by the ratio $(L/V)_c(L/V)_a$ and the calculation repeated, then the assumed and calculated values of L/V would check, and the K values would be at the temperature of the equilibrium (constant K value ratios). The planimeter gives the area under curve $L/V = 0.5$ as $L = 6.32$, and the corresponding area under curve A of Figure 7 for the total original naphtha is $F = 18.67$. By Equation 3, $V = F - L = 18.67 - 6.32 = 12.35$, and the new calculated L/V is $6.32/12.35 = 0.51$ as compared with the assumed value of $L/V = 0.50$. Then for reference component $K = 1.0$, the K value at the temperature of the equilibrium is $K \times (L/V)_c/(L/V)_a = 1.0 \times (0.51/0.50) = 1.02$. From curve C, Figure 3, the temperature corresponding to this value of K is 301° F., and this is the temperature of the equilibrium.

Step 3. Determine the liquid volume per cent vaporized in the equilibrium of step 1.

For this a curve of dv/dT_B vs. T_B is prepared for the liquid of curve $L/V = 0.5$ by means of Equation 6. The area under this curve represents liquid volume and is found to be $v = 12.41$. The corresponding area under curve A of Figure 2 for the total mixture is $v = 32.79$. Then the mixture is $100 \times (12.41/32.79) = 37.9$ liquid volume % liquid and 62.1% vapor for the conditions of the equilibrium.

Then the final values obtained for an assumed L/V of 0.5 is 62.1% vaporized at 301° F., and this point is plotted on the equilibrium flash curve of the mixture (curve B, Figure 9). The other points of this curve were obtained similarly and are given in Table I. The end temperatures, the bubble and dew points, are from example II. These points are nearly a straight line. The original naphtha of Figure 1 is a comparatively sharp cut, so that the tails frequently present on flash curves do not occur to an appreciable extent.

EXAMPLE IV. DIFFERENTIAL DISTILLATION CURVE

As an example of a more complicated calculation the differential distillation curve for the naphtha of Figure 1 will be obtained. In a differential distillation the mixture is boiled, and the vapors, which are in equilibrium with the remaining liquid, are removed as fast as formed. The final curve is plotted as boiling temperature against liquid volume per cent distilled over (T vs. v). The basic equation used is the integrated form of the Rayleigh equation (*15*):

$$(A_1/A_2) = (B_1/B_2)^{K_A/K_B} \tag{9}$$

where A is any component and B is the reference component The ratios A_1/A_2 and B_1/B_2 are the reciprocals of the fractions of these components that remain in the still. In order to obtain one point on the differential distillation curve, a value is assumed for B_1/B_2, and the resultant composition of the liquid remaining in the still is found with Equation 9. The boiling temperature and the liquid volume per cent of this still liquid are then determined. These two values give the coordinates of one point on the differential distillation curve. The same procedure would be used for component mixtures.

The composition curves for this calculation are given in Figure 8, where curve A represents the original naphtha of Figure 1.

Table I. Equilibrium Flash Curve (Curve B, Figure 9)

Assumed L/V	v, Liquid Vol. % as Vapor	T, Temp. of Equil., ° F.
α (bubble point)	0	254
10	12.3	264
4	23.1	273
2	34.8	282
1.0	48.5	292
0.5	62.1	301
0.25	74.6	311
0.10	86.8	321
0 (dew point)	100.0	333

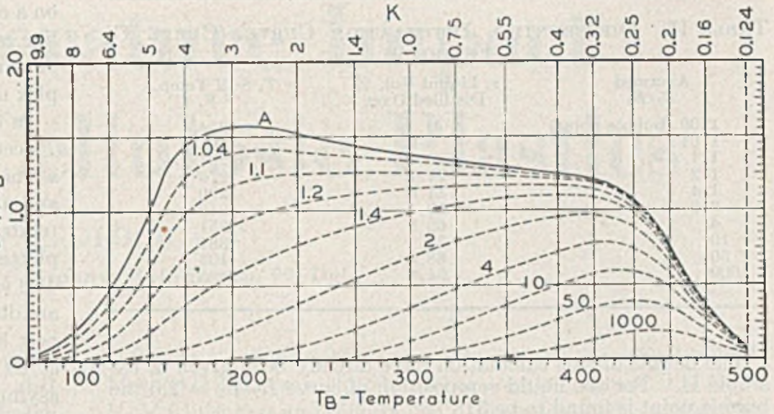

Figure 8. Composition Curves for Example IV

A = composition curve for original naphtha; broken lines give liquids remaining in the still and are labeled with value of B_1/B_2 assumed in calculation

The detailed calculation for an assumed value of B_1/B_2 of 2.0 is as follows:

Step 1. Assume a value of B_1/B_2 and, with Equation 9, calculate a liquid remaining in the still.

The reference component, B, is taken as component $K = 1.0$, and for the present calculation B_1/B_2 is considered to be 2.0—that is, half of component $K = 1.0$ has been distilled over. If A is taken as component $K = 1.4$, then $A_1 = Fz = 1.44$ is given by curve A, Figure 8, and Equation 9 becomes

$$A_2 = \frac{1.44}{2.0^{1.4/1.0}} = 0.56 \tag{9}$$

Then when component $K = 1.0$ is half distilled over, the amount of component $K = 1.4$ remaining in the still liquid is $Lx = 0.56$, and this value is plotted on the $K = 1.4$ line for curve $B_1/B_2 = 2.0$. The other points of this curve and the other curves of this figure were obtained similarly. With the assumption of constant relative volatility the ratio K_A/K_B is independent of the still temperature.

Step 2. Determine the boiling temperature (bubble point) of the liquid composition obtained in step 1.

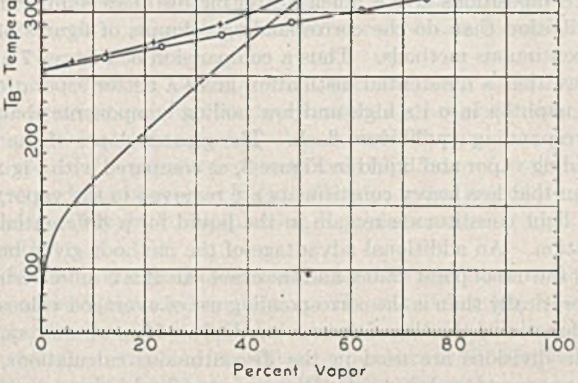

Figure 9. Distillation Curves for Petroleum Naphtha

A = TPB of naphtha; B = equilibrium flash curve from examples II and III; C = differential distillation curve from examples II and IV

TABLE II. DIFFERENTIAL DISTILLATION CURVE (CURVE C, FIGURE 9)

Assumed B_1/B_2	v, Liquid Vol. % Distilled Over	T, Still Temp., ° F.
1.00 (bubble point)	0	254
1.04	5.9	261
1.1	12.5	267
1.2	21.7	276
1.4	34.6	290
2.0	50.1	318
4	66.9	351
10	78.4	381
50	88.0	403
1000	94.8	425

The details of this calculation have already been given in example II. For the liquid composition of curve $B_1/B_2 = 2.0$ the bubble point is found to be 318° F.

STEP 3. Determine the liquid volume per cent of the liquid remaining in the still.

A plot of dv/dT_B against T_B is prepared for the liquid of curve $B_1/B_2 = 2.0$, and the area under this curve represents the liquid volume remaining in the still. The planimeter gives this area as 16.36, as compared with 32.79 for the total original liquid volume as given by the area under curve A of Figure 2. Then $100 \times (16.36/32.79) = 49.9$ liquid volume % of the mixture remains in the still when half of component $K = 1.0$ has been distilled over.

These values, $100 - 49.9 = 50.1\%$ vaporized at 318° F., are plotted as one point on the differential distillation curve for the naphtha, curve C of Figure 9. The other points shown for this curve were obtained similarly. The initial point is the bubble point of the original mixture as obtained from example II. The numerical values obtained for the points are listed in Table II.

A laboratory distillation that roughly approximates differential distillation is the A.S.T.M. (*1*) or Engler, in which the mixture is placed in a flask and boiled off. There is a basic similarity in shape between a typical A.S.T.M. curve and curve C of Figure 9. The low initial temperatures of an A.S.T.M. curve are due partially to the air present in the system at the beginning of the distillation.

DISCUSSION

To a person familiar with the details the methods given here are both direct and quick. They require less time than the corresponding discontinuous methods, in which the complex mixture is divided into artificial components having short boiling ranges. Thus a point on a composition curve can be found as easily as a mole fraction and averaged temperature can be obtained for artificial component. In determining total moles, a planimeter can obtain an area almost as quickly as a column of figures can be added. Values of Lx and Vy can be as easily set down by a point on a curve as by a number in a table. The dew point calculation of example II can be completed in less than ten minutes of comparatively slow work, with seventeen points used to determine the liquid composition in equilibrium with the original mixture as vapor.

Another advantage of the method is that the differential plots of the compositions give a much clearer picture of an equilibrium or distillation than do the corresponding columns of figures of the discontinuous methods. Thus a comparision of Figures 7 and 8 shows that a differential distillation gives a better separation of the naphtha into its high and low boiling components than the corresponding equilibrium flash. The greater slopes of the lines dividing vapor and liquid in Figure 8, as compared with Figure 7, mean that less heavy constituents are removed in the vapor, and less light constituents remain in the liquid for a differential distillation. An additional advantage of the methods given here is that the use of point values and the exact calculus is more desirable theoretically than is the corresponding use of averaged values and arithmetic in the discontinuous methods. If more and smaller finite divisions are used in the discontinuous calculations, the errors are reduced, but, also, the time required is increased.

Pure compounds can easily be combined with complex mixtures in these calculations. A convenient way of doing this is to plot the compound as a vertical line at the correct boiling temperature on a composition curve such as curve A, Figure 4. Length on this line can be considered to represent moles and so is the equivalent of so much area (moles) under the composition curve of the complex mixture.

In the differentiation of a TBP to obtain a plot of dM/dT_B *vs.* T_B certain minor difficulties arise. The TBP should be drawn as a smooth curve that averages the points of the laboratory data, and any plateaus should be either smoothed out or removed and treated as single compounds. The individual values of dv/dT_B plotted against T_B should also be averaged as a smooth curve. The values of dv/dT_B at the low and high boiling ends of the TBP are difficult to measure directly. These portions of the curve are best handled by extending the plot of the measurable values of dv/dT_B in a smooth curve that approaches the T_B axis as an asymptote. Any vapor loss should be added to the low boiling and any residue to the high boiling end of the curve. With reasonable care errors due to these and other causes can be made negligible.

NOMENCLATURE

A = value of Lx for general component in still liquid for example IV and Equation 9
B = value of Lx for reference component (component K = 1.0) in still liquid for example IV and Equation 9
D = liquid density, pounds per gallon
F = total moles of original mixture
Fz = total original amount of a component present (dM/dT_B for complex mixtures)
K = vapor-liquid equilibrium constant, defined by equation $(Vy) = (VK/L)(Lx)$ for complex mixtures
L = total moles of liquid in the equilibrium
Lx = amount of a component present as liquid (dM/dT_B for complex mixtures)
M = number of moles
mw = molecular weight
T = temperature of equilibrium, ° F.
T_B = boiling point temperature, ° F., obtained from TBP for complex mixtures
V = total moles of vapor in the equilibrium
Vy = amount of a component present as vapor (dM/dT_B for complex mixtures)
v = liquid volume per cent of total mixture
x = mole fraction of component in liquid
y = mole fraction of component in vapor
z = mole fraction of component in total original mixture

Subscripts

a = assumed value, on L/V
c = calculated value, on L/V
1 = conditions at beginning of distllation in Equation 9
2 = conditions at any time during distillation in Equation 9

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Low Temperature Impact Strength of Cellulosic Plastics

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Exploration of the effects of plasticizers, degree of substitution, and intrinsic viscosity of ethylcelluloses and cellulose acetates used in plastics showed that both choice of plasticizer and use of a cellulose derivative of high intrinsic viscosity aid in producing materials of improved low temperature impact strength. As to plasticizers, the coefficients of viscosity change with temperature, and the amounts of loosely bound plasticizer seem significant. Use of ethylcellulose with an intrinsic viscosity above 1.3 and of cellulose acetate approaching an intrinsic viscosity of 2 also enhances subzero impact properties.

INTENSIFIED interest in the properties of plastics materials at subzero temperatures developed during the war as a result of the need for aircraft parts and ordnance components which would function properly over a wide temperature range. This interest continues into the present peacetime period as a result of the needs of product designers in the aircraft, automotive, and refrigerator industries in adapting the color and style possibilities of the cellulose plastics to the production of plastic parts which will function properly at low temperatures. Such peacetime uses would be, for example, in aircraft control knobs and windscreens, automotive hardware, steering-wheel covering, and refrigerator breaker strips, trim, and panelling.

The purpose of this article is to show how the basic qualities of cellulose derivatives and formulating ingredients can be chosen to provide the most suitable mechanical properties for plastic compounds entering such uses. As a simple criterion of suitability the impact strength of the plastic materials has been selected, since it is perhaps the best single measure of the toughness which is sought in cellulose plastics and appears to be the most critical mechanical property given in the various A.S.T.M. specifications on rigid cellulosic molding materials, such as D 706, D 707, and D 787. All plasticized thermoplastic compositions show considerable variations in mechanical properties with temperature; the change in impact strength, in addition to showing a large percentage change with temperature, is an easily measured, reproducible indication of these variations. It is known that as the ambient temperature decreases, the impact strengths of the cellulose plastics also decrease (*7*). However, for most civilian uses the lowest temperature to which plastics articles are likely to be exposed will not fall below −40° F. Hence the test work was designed to examine the low temperature impact properties of these plastics at −20° or −40° F.

TEST SAMPLES

Basic raw materials for the tests were commercial grades of cellulose acetate and ethyl cellulose produced by Hercules Powder Company. To extend the range of observation in some of the tests, semiplant batches of these materials, meeting commercial requirements of quality and having unusually high viscosity, also were included. Commercially available plasticizers were used.

Cellulose acetate batches were prepared by a solvent process similar to that used by Gilbert and Gloor (*2*), except that batches of 600-gram weight were made. Test bars called for by A.S.T.M. Method D 256 were molded in a laboratory transfer pot into $^1/_2 \times {}^1/_2 \times 5$ inch bars and conditioned. These tests were repeated on a larger scale, using 7- to 10-pound batches of plastic made by solvent methods with a 4.7-gallon stainless-clad Baker-Perkins mixer with *knaben* blades; later the plastic was rolled to a sheet and granulated, and the granules were dried. Essentially the same results were obtained when these larger batches were injection-molded into $^1/_2 \times {}^1/_2 \times 5$ inch bars, notched, and tested.

Ethyl cellulose batches were prepared in 3.3-pound batches by hot milling the flake and separately premixed plasticizer on a 6 × 16 inch Thropp mill with chrome-plated roll faces. The correct weight of dry ethyl cellulose was weighed into beakers, and weighed portions of plasticizer, stabilizer, and lubricant, heated to 300–340° F., were stirred into the mix by hand. Part of the mix was placed on the turning roll, with surfaces at 280–300° F., and milled into a blanket, and the remainder of the batch was added as the nip was widened. About 25 minutes were required to form a well colloided sheet. This was cooled, granulated, and dried to less than 0.4% volatile material before test bars were injection molded. The standard ethylcellulose test formula was 100 parts ethylcellulose plus plasticizer, 2 parts methylphenol, and 0.75 part calcium stearate.

Formulation of cellulose acetate plastic was carried out using a standard plastics grade of flake material (53.0% combined acetic acid content, 50-second Hercules viscosity, equivalent to 1.25 intrinsic viscosity) with various commercial plasticizers. [Intrinsic viscosity is defined by Kraemer (*3*) as follows:

$$[\eta] = \lim_{C \to 0} \eta_{sp}/C$$

The intrinsic viscosity of materials used in this work was measured as follows: Solutions of 0.1, 0.25, and 0.5 per cent concentrations were prepared, using acetone as the solvent for cellulose acetate and 8:2 toluene:alcohol for ethylcellulose. Viscosity of these solutions was measured at 25° C. using an Ostwald viscometer, and data were extrapolated to zero concentration by using the graph of η_{sp}/C *vs.* concentration. The ratio of cellulose acetate to plasticizer was arranged so that all formulations had the same hardness regardless of the plasticizer used. Thus, the low temperature impact strengths could be compared for formulations with the same hardness.

Data are shown in Table I. This permitted the choice of plasticizers showing optimum low temperature impact properties, and these plasticizers were then used in formulations to explore the effect on low temperature impact caused by flake of varied viscosities and acetylation. Essentially the same procedure was followed for ethylcellulose plastics, formulations being given in Table II.

At the time the plasticizer selection work was done with cellulose acetate, the conditioning procedures and low temperature testing procedures of A.S.T.M. had not been fully standardized. These tests were made by conditioning test bars at 70° F. and 50% relative humidity for 24 hours prior to low temperature conditioning at −20° F. These bars were conditioned at least 2 hours at the low temperature, then put into the Charpy machine which was at 70° F., and tested within 15 seconds. All other tests were

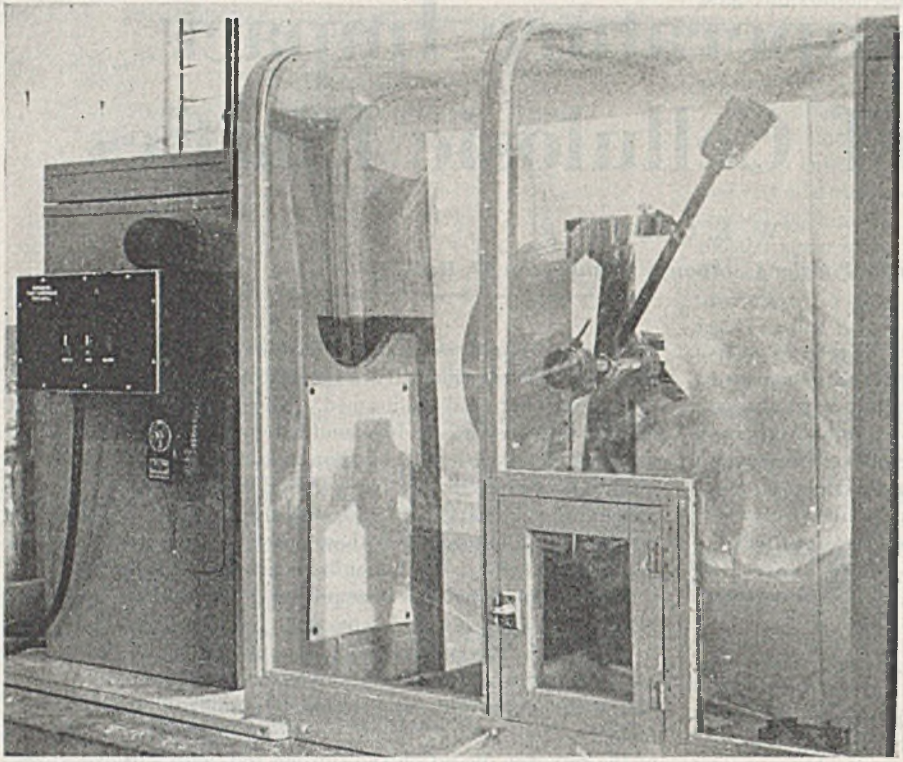

Figure 1. Subzero Test Chamber with Izod Impact Tester and Tenney Conditioning Unit

conducted upon the Izod machine, kept in the subzero atmosphere (Figure 1), and conditioned for at least 4 hours before testing.

IMPACT TESTING PROCEDURE

Figure 1 shows a Tenney conditioning unit, holding about 50 pounds of dry ice, set up to cool the interior of an insulated box built to house a Bell-type 2- and 4-foot-pound impact tester. This box has its top and sides made of three sheets of transparent cellulose acetate sheeting, with half-inch air space between each sheet. The back and sides are made of two plywood walls, with air space of half an inch separating them. The cold air from the Tenney unit is introduced to the far side of the chamber by a duct traversing the rear wall of the box, and is exhausted at a port on a level with the axis of the impact tester on the side of the chamber nearest the conditioning unit. The chamber floor may be detached from the sides and top of the box to permit leveling it or replacing the impact tester with other equipment. The transparent cellulose acetate wall is held in grooves in the side walls and center spar to permit free movement which allows for temperature change. This unit requires about 10 pounds of dry ice per hour to maintain a −40° F. temperature during the summer. Samples are stored on shelves in the chamber to facilitate ready selection for testing. The insulated door is large enough to permit an operator to change samples in the opening. A pull cord leading outside the box enables one to make the test without opening the test chamber. Samples are set in the machine for at least 8 minutes before testing to ensure a low temperature within the box.

The samples were notched prior to conditioning. At first the cellulose acetate materials were notched with a shaped rasp blade; later a motor-driven single-tooth notcher was provided (Figure 2). These devices gave equally significant results on many materials at normal temperatures. At low temperatures the motor notcher gave more consistent values, which were 0.2 foot-pound or more higher in the case of cellulose acetate, as is indicated in Figure 7. All ethylcellulose samples were notched upon the motor-driven notcher.

Impact tests were carried out as called for by A.S.T.M. Method D 256-43T. The preliminary Charpy tests were carried out with a machine using a 100-inch-pound hammer. The Izod tests were carried out using a 2-foot-pound hammer. Although Izod and Charpy methods of measuring impact strength both show up the same trends, the values obtained by each method are not directly comparable.

Rockwell hardness (A.S.T.M. Method D 785-44T) tests were run with a long-stroke machine on compression-molded disks 2 inches in diameter by $^1/_4$ inch thick in the case of cellulose acetate, where the $^1/_4$-inch ball and M scale are reported. For ethylcellulose, injection-molded 2 × $^1/_8$ inch disks were used, the instrument being provided with a $^1/_2$-inch penetrator and results being obtained using the R scale.

Flow temperatures were measured on preformed pellets of molding granules, according to A.S.T.M. Method D 569-44T.

TEST RESULTS

The impact test values at subzero temperatures were chosen as a simple criterion of mechanical properties of the plastics at low temperatures. Hence the work was directed toward finding the effects of different plasticizers, of varying intrinsic viscosities of the cellulose derivatives, and of varying their substitution on

Table I. Plasticizers Tested with Cellulose Acetate[a]

(Cellulose acetate of 53.0% combined acetic acid content, 50-second viscosity—fall time of $^5/_{16}$-inch steel ball through 10 inches of a 20% solution of 9 acetone:1 alcohol in vertical 1-inch tube at 25° C.)

Plasticizer	% Plasticizer in Plastic[b]	Charpy Impact at −20° F., Ft.-Lb./In. Notch
Diethylene glycol dipropionate[c]	23.5	0.57
Diethyl phthalate	31	0.50
Dimethyl phthalate	31.5	0.37
Tripropionin	33	0.35
Triacetin	27	0.32
Triethyl citrate	30	0.26
Dibutyl tartrate	30	0.23
Methyl phthalyl ethyl glycolate[d]	31	0.15

[a] Amount in plastic = 100 − % plasticizer.
[b] To give Rockwell M hardness of 45 at 70° F. and 50% relative humidity.
[c] KP 45, Ohio-Apex, Inc.
[d] Santicizer M-17, Monsanto Chemical Co.

Table II. Plasticizers Tested with Ethylcellulose

(Hercules G-100 type flake; 45.3% ethoxyl, viscosity 97 centipoises in 5% solution in 7 toluene:3 ethanol, intrinsic viscosity = 1.70)

Plasticizer	% Plasticizer[a]	Izod Impact at −40° F., Ft.-Lb./In. Notch
Methyl Cellosolve stearate[b]	9	1.68
Butyl Cellosolve stearate	8	1.76
Tricresyl phosphate[c]	17	1.30
1 tricresyl phosphate:1 methyl Cellosolve stearate	11	1.55
3 dibutyl phthalate:1 Fractol A[d]	12	1.43
1 dibutyl phthalate:1 butyl stearate	9	1.93

[a] To give Rockwell R hardness of 95 at 77° F. and 50% relative humidity.
[b] KP 23, Ohio-Apex, Inc.
[c] Lindol M.P., Celanese Corp.
[d] Stanco., Inc.

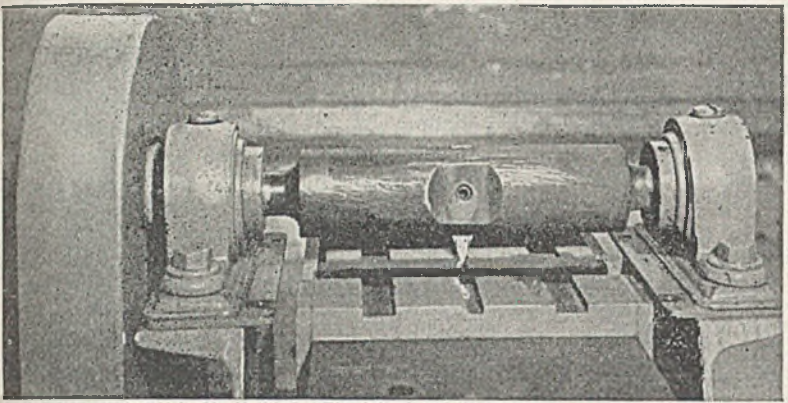

Figure 2. **Motor-Driven Notcher Showing Cutting Tool with Guard Removed and Bar in Notching Holder**

the subzero impact test results. This should enable one to judge how these variables should be controlled to obtain optimum properties at low temperatures.

Low temperature impact test results with the series of ethylcellulose plasticizers summarized in Table II are shown graphically in Figure 3. An effort has been made to correlate the results of these tests with the theory of plasticizer behavior at low temperatures first set forth by Leilich (4). This author stated that, in the polyvinyl chloride plastics, the best low temperature toughness was obtained by using a plasticizer which changed viscosity least with temperature, and further showed that the logarithm of viscosity bore a linear relation with temperature. Kinematic viscosity was used as a criterion of this behavior, since the actual molecular friction uncorrected for liquid density appears to govern. Table III gives the results of kinematic viscosity measurements on the plasticizers used for these tests. There seems to be a relation between the viscosity-temperature coefficient of plasticizers and the low temperature impact properties of plastics made with them (Figure 3). It appears that, of all the plasticizers tested, the methyl Cellosolve stearate is representative of those showing good low temperature properties when used with ethylcellulose, and this plasticizer was selected for use in the rest of the tests made with ethylcellulose.

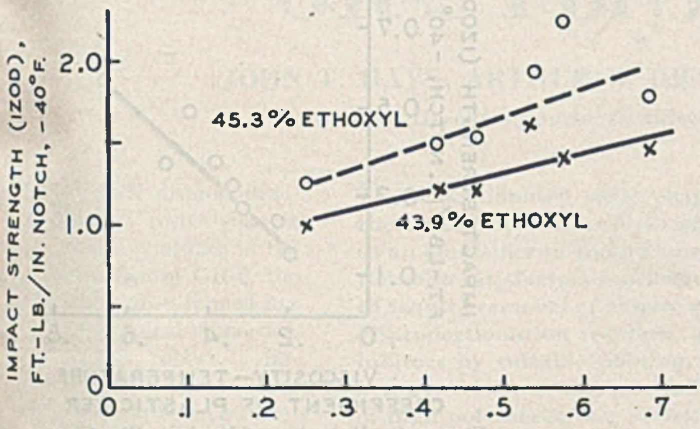

Figure 3. **Effect of Various Plasticizers on Subzero Impact Strength of Ethylcellulose Plastics**

Comparisons made at equal flow (275° F.) or equal hardness Rockwell R scale give nearly identical curves. All ethyl celluloses used had intrinsic viscosity between 1.5 and 1.7

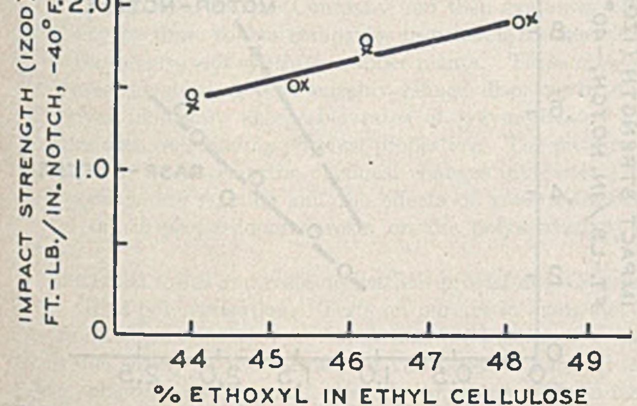

Figure 4. **Effect of Substitution on Subzero Impact Strength of Ethylcellulose Plastics**

Comparisons at flow of 275° F. denoted by circle; at Rockwell R hardness of 95 by cross. Methyl cellosolve stearate used as plasticizer; all ethylcelluloses had intrinsic viscosity between 1.5 and 1.7

The effect of using ethylcellulose of varied ethoxyl content in plastics with methyl Cellosolve stearate plasticizer is shown in Figure 4. This graph indicates the low temperature impact strength of ethylcellulose plastics, at a constant flow temperature and a constant hardness, plotted against the per cent ethoxyl content of the flake used to make the plastic. It appears that the strength of the material at low temperatures rises appreciably with the degree of etherification of the ethylcellulose, with all types showing rather good impact strength at this low temperature.

The effect of viscosity of the ethylcellulose used in a plastic is shown in Figure 5. It appears that, below an intrinsic viscosity of 1.2, the impact strength of molded ethylcellulose plastics at low temperatures falls off, in the G-type material used in making this comparison. Most commercial ethylcellulose plastics, however, are made from material of intrinsic viscosity from 1.3 to 1.7, and in this range the material shows good low temperature impact which increases as the viscosity of the flake increases. Material in the high end of the commercial range (2.7 intrinsic viscosity) gives only slightly better impact strength than material of normal viscosity.

With cellulose acetate, comparison of the plasticizers at a constant hardness level gives the results shown in Table I and Figure 6. Here again a correlation can be found between the temperature coefficient of viscosity change and the low temperature impact strength.

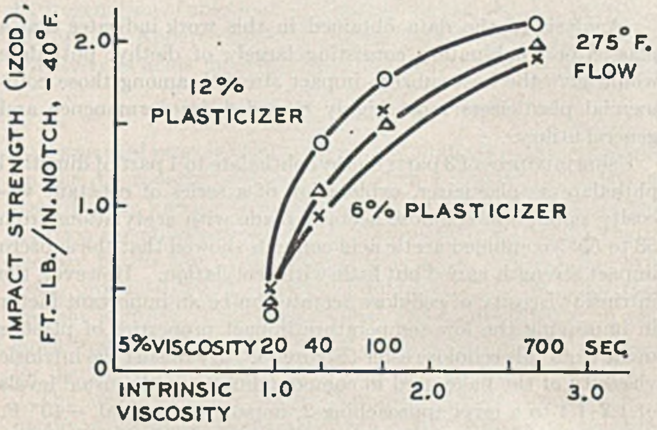

Figure 5. **Effect of Intrinsic Viscosity of Flake on Subzero Impact Strength of Ethylcellulose Plastics**

Plastic compositions contained methyl Cellosolve stearate as plasticizer; all ethylcelluloses were of 44.8 to 45.5%

Table III. Viscosity Data from Plasticizers Used

Material	Ostwald Viscometer A at 25° C., Sec.	Ostwald Viscometer B at 50° C., Sec.	Relative Kinematic Viscosity[a] At 25° C.	Relative Kinematic Viscosity[a] At 50° C.	Viscosity-Temperature Coefficient[b]
Diethylene glycol dipropionate[c]	3.7	7.8	3.46	2.3	0.665
Diethyl phthalate[c]	8.8	12.6	8.2	3.7	0.45
Dimethyl phthalate[c]	10.8	13.3	10.1	3.9	0.39
Tripropionin[c]	7.0	10.8	6.5	3.3	0.50
Triacetin[c]	13.4	14.8	12.5	4.3	0.34
Triethyl citrate[c]	22.7	22.5	21.2	6.6	0.31
Dibutyl tartrate[c]	59.5	44.2	56.5	13.0	0.23
Methyl phthalyl ethyl glycolate[c]	78.6	49.0	73.4	14.4	0.20
Methyl Cellosolve stearate[d]	Solid	16.4	....	....	0.69[e]
Butyl Cellosolve stearate[d]	11.2	17.3	10.5	5.9	0.56
Dibutyl phthalate	14.7	18.5	13.7	5.4	0.39
Mineral oil	81.3	71.8	76.0	21.1	0.28
Butyl stearate	8.8	14.2	8.2	4.9	0.60
3 dibutyl phthalate: 1 mineral oil[d]	20.9	23.8	19.6	8.16	0.41
1 dibutyl phthalate: 1 butyl stearate[d]	9.8	14.6	9.2	5.0	0.55
Tricresyl phosphate (Lindol M.P.)[d]	49.9	39.9	46.6	11.7	0.25
1 tricresyl phosphate:1 methyl Cellosolve stearate[d]	16.2	20.8	15.1	7.1	0.47
Castor oil, AAA grade	695.1	409.5	650[f]	120[f]	0.19

[a] $$\text{Relative kinematic viscosity} = \frac{\text{seconds for liquid flow}}{\text{seconds for castor oil flow}} \times \text{viscosity of castor oil.}$$

[b] $$\text{Viscosity–temperature coefficient} = \frac{\text{relative kinematic viscosity at 50° C.}}{\text{relative kinematic viscosity at 25° C.}}$$

[c] Used with cellulose acetate.
[d] Used with ethylcellulose.
[e] Calculated from mixture data.
[f] Absolute viscosity in centipoises.

Table IV. Comparison of Injection-Molded Plastics from Cellulose Acetate of Usual and High Intrinsic Viscosities

	A	B
Formulations		
Usual cellulose acetate, 53.0% combined acetic acid content, 1.25 intrinsic viscosity	...	72
High viscosity cellulose acetate, 54.0% combined acetic acid content, 1.88 intrinsic viscosity	72	...
Diethyl phthalate	21	21
Dimethyl phthalate	7	7
Properties		
Flow temp., ° C.	167	152
Rockwell hardness, M scale	42	51
Impact strength (rasp-notched)		
Charpy, 77° F., ft.-lb./in. notch	4.36	4.29
Izod, ft.-lb./in. notch		
77° F.	3.29	3.12
−40° F.	0.54	0.25
−70° F.	0.50	0.26
Heat distortion temp., ° F. (A.S.T.M. D648-45T)	158	149
% water absorption, injection-molded disk	2.60	2.94
% soluble loss, same disk (A.S.T.M. C570-42)	0.20	0.23
Molding conditions[a]		
Indicated temp., ° F.		
Front cylinder	450	440
Rear cylinder	450	450
Cycle, total, sec.	33	33
Gage pressure, lb./sq. in.	950	950
Mold temp., °F.	170	170
Duration of high-rate pump impulse, sec.	4.75	4

[a] Reed Prentice 10 A-4-ounce machine 2.75-oz. shot.

Analysis of the data obtained in this work indicates that a plasticizer combination consisting largely of diethyl phthalate would give the best subzero impact strength among those commercial plasticizers most highly regarded for permanence and general utility.

Using mixtures of 3 parts diethyl phthalate to 1 part of dimethyl phthalate as plasticizer, exploration of a series of constant viscosity samples of cellulose acetate, made with acetylations from 53 to 55% combined acetic acid content, showed that the subzero impact strength varied but little with acetylation. However, the intrinsic viscosity of cellulose acetate can be an important factor in improving the low temperature impact properties of plastics made from this cellulose ester (Figure 7). By raising the intrinsic viscosity of the flake used in compounding from the usual levels of 1.2–1.4 to a level approaching 2, impact strength at −40° F. may be improved at [illegible] 50%. Such plastics are readily injection molded and [illegible] other properties well in line with those given by conventional cellulose acetate plastics, as shown by Table IV.

DISCUSSION

Considering the foregoing experimental findings, it appears that choice of the proper plasticizer and a cellulose derivative of intrinsic viscosity above 1.5 will in general give the best mechanical properties to cellulose-derivative hot-molding plastics at low temperatures. The steepness of the viscosity-temperature curve of the plasticizer may be related to the subzero impact strength of the plastic made with it; this finding is in accord with the experience of workers in the vinyl field, such as Reed (*5*) and Leilich (*4*). This should offer a relatively easy way to evaluate new plasticizers which may be suggested for this purpose. However, other criteria may be equally useful in making this selection. For instance, if the data of Fordyce and Meyer (*1*) on the maximum amount of plasticizer held in cellulose acetate films be applied to the plasticizers having viscosity-temperature coefficients shown in Figure 6, it will be found that the smaller the amount of plasticizer which is permanently bound to the flake, the better will be the low temperature impact strength

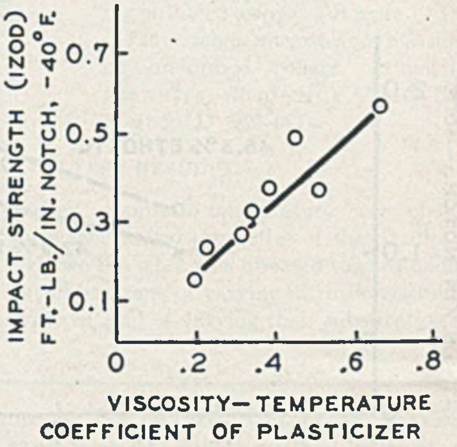

Figure 6. Relation of Various Plasticizers and Subzero Impact Strength of Cellulose Acetate Plastics

Cellulose acetate used had intrinsic viscosity of 1.35 and combined acetic acid content of 53%

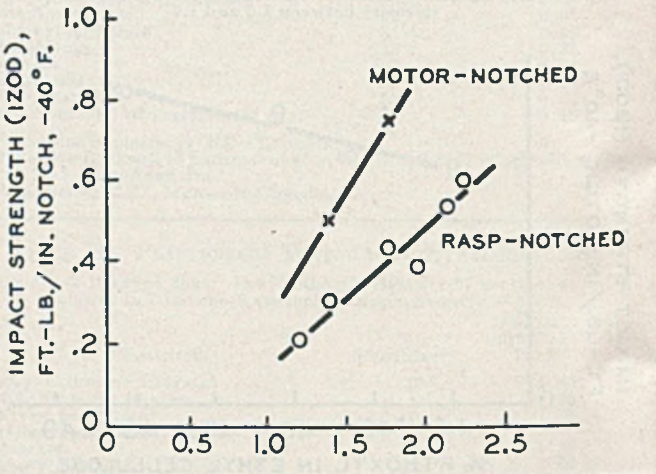

Figure 7. Relation between Intrinsic Viscosity of Cellulose Acetate and Subzero Impact of Plastics

Cellulose acetates used had combined acetic acid contents between 53.0 and 55.0%

of the plastic made using it. This criterion should not be overlooked in the preliminary evaluation of plasticizers for this purpose, particularly since (in the case of ethylcellulose) certain well known plasticizers such as mineral oil, which promote low-temperature impact strength, fall out of line if coefficient of viscosity change is the only criterion applied.

It was found that the use of a cellulose acetate at a high level of intrinsic viscosity will produce a definite improvement in the low temperature impact strength of the resulting plastic; this is also parallel to other experience in the field of high polymers. For instance, Selker (*6*) found that the brittleness temperature of polyisobutylenes decreased—that is, its mechanical properties at subzero temperatures improved—as the degree of polymerization or the intrinsic viscosity of this polymer increased. Since, among other factors, the low temperature impact strength of cellulose acetate plastics has been considered too low for such uses as transparencies for aircraft and certain items of automotive hardware, it is believed that the commercial availability of the varieties of high intrinsic viscosity, not heretofore marketed, may be of interest to plastic manufacturers interested in those applications.

ACKNOWLEDGMENT

The efforts of the writer's co-workers of the Hercules Parlin Plant Plastics Group in obtaining these data, particularly W. O. Bracken, C. A. Borton, Wayne Schrag, and E. Paul, Jr., are gratefully acknowledged. Much credit is due Dean Milliken for design of the low temperature testing cabinet and motor notcher.

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RESENTED before the Division of Paint, Varnish, and Plastics Chemistry at the 110th Meeting of the American Chemical Society, Chicago, Ill.

Disproportionated Rosin Soap in GR-S Polymerization

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Disproportionated rosin soap (Dresinate 731) gives synthetic rubber with excellent physical properties when used as an emulsifier in the polymerization of GR-S. Preparation of a satisfactory emulsifier from wood rosin is shown to require removal of abietic-type acids, preferably by the disproportionation reaction, and removal of phenolic inhibitors by suitable refining. These operations are now being carried out commercially to give a uniform product of high polymerization activity.

WHEN disproportionated rosin[2] soap is used as the emulsifier in the polymerization of GR-S, the synthetic rubber formed has excellent physical properties. This "rosin rubber," designated GR-S-10, is more tacky than GR-S and is therefore superior for tire building (*8*). In addition, improved heat resistance, superior hysteresis properties (*8*), and better reinforcement in low black compounds and nonblack pigment loadings (*1, 3*) combine to make GR-S-10 an outstanding rubber.

In the course of developing a rosin emuslifier which could be used commercially, a large number of samples were prepared and tested by Hercules Powder Company and then evaluated more completely by those rubber companies responsible for the operation of the government synthetic rubber plants. These cooperative studies established that suitably refined disproportionated rosin gives uniformly acceptable rates of polymerization and polymers with outstanding physical properties. The purpose of this paper is to describe the chemical changes involved in the disproportionation reaction and the effects of various constituents of the disproportionated rosin on the polymerization reaction.

Commercial rosins and rosin derivatives proved unsatisfactory in the GR-S polymerization. Tests on pure resin acids and on various fractions isolated from commerical products showed that this is due chiefly to the presence of two types of harmful materials—abietic-type acids and phenolic inhibitors. These must be eliminated by suitable reactions and refining procedures in order to obtain an emulsifier satisfactory for use in GR-S polymerization.

The acids present in wood rosin amount to about 88% of the total and are made up of two groups with different carbon skeletons (Figure 1), the abietic type (I) and the pimaric type (II). Polymerization tests on various pure resin acids (Table I) showed that the abietic type, as exemplified by abietic and levopimaric acids, have a detrimental effect on the polymerization yield, whereas the pimaric type, as indicated by results with isodextropimaric acid (*6*), appear to have no such effect. These data also show that hydrogenation or dehydrogenation of abietic acid converts it to completely satisfactory materials. Apparently the conjugated double-bond system of the abietic-type acids must be destroyed to avoid inhibitory effects.

DISPROPORTIONATION OF ROSIN

A practical process of modifying the conjugated system is based on the disproportionation reaction with a palladium catalyst as described by Fleck and Palkin (*5*) and by Littmann (*9*). In this reaction the abietic-type acids are completely converted to satisfactory hydro acids or dehydroabietic acid. The pimaric-type acids probably also undergo disproportionation, but since they are not harmful, it is apparent that all of the known resin acid constituents of disproportionated rosin form soaps satisfactory for use in polymerization.

The effectiveness of the disproportionation reaction as a means of obtaining a modified rosin satisfactory for polymerization depends on the completeness of removal of the abietic-type acids. The detrimental effect of even small amounts of abietic acid is shown in Figure 2 where addition of 5% of abietic acid to

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[1] Present address, University of Maryland, College Park, Md.

[2] Sometimes termed "dehydrogenated rosin" because of its relatively high dehydroabietic acid content; its soap is designated Dresinate 731.

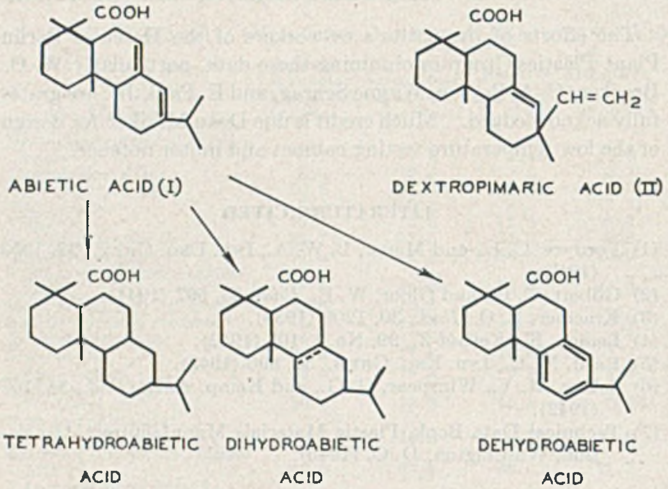

Figure 1. Resin Acid Types

pure dehydroabietic acid leads to a decreased polymer yield by causing an initially slow polymerization rate.

Ultraviolet absorption offers an excellent method for following the progress of the disproportionation reaction on the basis of the characteristic absorptions of abietic acid and dehydroabietic acid (Figure 3). Figure 4 shows the relation between the shape of the absorption curves, the abietic acid content, and the polymerization yield for certain refined disproportionated rosins. Determination of ultraviolet absorption spectra appears to be the most convenient method of following the abietic acid content and is a practical control method. Determination of unsaturation and optical rotation can also be used but cannot be interpreted so readily.

Refining. Even when a sample of wood rosin is disproportionated in such a manner as to be completely free from abietic acid, it usually will not give a satisfactory polymer yield without further refining. Typical results after refining by various methods are as follows:

Refining Method	% Polymer Yield after 14 Hr. at 50° C.
None	40–60
Adsorbent earth	71–80
Distillation	70–80
Crystallization	74–80
Solvent extraction	72–78

The results obtained depend upon the manner in which the refining is carried out and, to some extent, on the individual sample; but these figures show clearly that a refining step is necessary and indicate that the methods cited are applicable. Application of any of these methods can give a product of high polymerization activity, but adoption of any one method would depend on economic factors. As will be brought out later, additional refining removes traces of phenolic materials; therefore, the physical methods listed must also compete with chemical methods suggested by the chemical nature of the inhibitors present.

EFFECT OF NEUTRAL FRACTION

Since it had been shown that the types of acidic materials known to be present in disproportionated rosin were not responsible for the low polymerization yields obtained with soaps of unrefined disproportionated rosin, the neutral fraction was examined. An unrefined disproportionated rosin containing no abietic acid was separated into acidic and neutral fractions. A 10% solution of the rosin in ether was extracted with 2% aqueous sodium hydroxide. Yields of 90 and 8.3%, respectively, of acid and neutral fractions were obtained. A more exhaustive extraction gave values of 88 and 10.6% for the acid and neutral fractions. When the acid fraction was dissolved in petroleum ether, extraction with 5% sodium bicarbonate gave 1.6% of bicarbonate-soluble material (1.3% on the basis of disproportionated rosin). The polymerization results are shown in Table I.

These data demonstrate conclusively that, with the exception of the weakly inhibiting bicarbonate-soluble fraction, the substances responsible for differences between polymerization yields obtained with unrefined disproportionated rosins and pure materials such as dehydroabietic acid are concentrated in the neutral portion of the disproportionated rosin.

Table I. Polymerization Tests

	% Polymer Yield after 14 Hr. at 50° C.
Pure resin acids[a]	
Abietic acid	Trace
Dehydroabietic acid	80
Tetrahydroabietic acid	82
Dihydroabietic acids	71
Disproportionated rosin (refined)	78
10% levopimaric acid + 90% disproportionated rosin	40
10% isodextropimaric acid + 90% dehydroabietic acid	80
Dihydrodextropimaric acid	79
Disproportionated rosin fractions	
Disproportionated rosin	61
Resin acids (after exhaustive extraction), A′	74
10% neutral bodies (after exhaustive extraction) + 90% resin acids A′	60
Resin acids extd. with bicarbonate, A′	77
10% bicarbonate sol. + 90% resin acids A′	70
Inhibitor fractions	
Disproportionated rosin	61
Resin acids[b]	67
Resin acids[b] + 0.01 gram F	58
Resin acids[b] + 0.01 gram E	50

[a] 5 parts (per 100 parts of monomer) of unneutralized resin acid or rosin were used in place of the fatty acid soap usually specified for GR-S polymerizations.

[b] 4.6 parts of the resin acids were used instead of the usual 5 parts to give approximately the same amount of acidic material as in the disproportionated rosin. The resin acids were not extracted so thoroughly as resin acids A′ above, so that the polymerization yield was slightly lower.

Fractionation. The initial neutral fraction, separated as described, was fractionated as indicated in Figure 5. The neutral fraction was dissolved in petroleum ether and repeatedly extracted with aqueous alcoholic potassium hydroxide (20% aqueous potassium hydroxide plus an equal volume of ethanol). When the alkaline solution was diluted with water, extraction with petroleum ether gave 0.11% (based on the disproportionated rosin) of phenolic material of weakly acidic character (E, Figure 5). Acidification of the residual alkaline solution followed by extraction with ether gave 0.17% of slightly stronger phenols (F, Figure 5). Both fractions were dark oils.

POLYMERIZATION INHIBITORS

Polymerization results show that these phenolic materials are very strong inhibitors (Table I). Thus, 0.4% of these phenolic materials is sufficient in each case to account for more than the original inhibiting action of the disproportionated rosin. Inhibiting effects of the same order were indicated by an empirical test based on induction period in the bulk polymerization of styrene. The presence of small amounts of phenols was also determined by an adaptation of a standard method for the examination of water and sewage (*2*) as worked out by E. F. Evans and L. F. McBurney of these laboratories. This is based on the color produced by the reaction of phenols with diazotized sulfanilic acid and offers a very sensitive method of testing for phenols in various fractions.

During the fractionation it was apparent that fractions E and F were different in acid strength, and that the effect of F was not merely due to incomplete removal of E. However, since the separation of this mixture depended on the hydrolysis of one type of phenolate to a greater degree than the other, it would not be expected to be quantitative.

The ultraviolet absorption curves of the two phenolic fractions (Figure 6) are of interest in that they emphasize fundamental differences and are similar to the curves of known phenols. Phenol E, the stronger inhibitor and the weaker acid, gave a curve similar to that of *p*-cresol with maxima at 281 and 287 mμ. The absorption curve of F, the weaker inhibitor and the stronger acid, is similar to that of resorcinol with maxima at 276 and 282 mμ. The same type of absorption is also obtained for thymol, guaiacol, and eugenol. These curves are undoubtedly distorted as a result of the mixture of phenols but serve to indicate the phenolic nature of the constituents. It is also of interest to note that, on the basis of active hydrogen determinations (corrected for resin acids carried through the separation) and Rast molecular weights, one and two hydroxyls are indicated, respectively, for fractions E and F, as might also be inferred from the ultraviolet absorption curves by comparison with *p*-cresol and resorcinol.

METHODS AND MATERIALS

POLYMERIZATION. A small-scale test was used which is similar to and gives results comparable to the Rubber Reserve bottle polymerization test (*10*). In our method 8-ounce bottles were used rather than the 32-ounce bottles. The bottles were rotated at 15 r.p.m. for 14 hours at 50° ± 0.1° C. in a water bath; polymerization yields were obtained by precipitating, washing, and drying the polymer.

The following polymerization formula was used: 75 parts butadiene, 25 styrene, 5 rosin or resin acid, 0.5 DDM (Rubber Reserve mercaptan), 0.3 potassium persulfate, and 180 parts distilled water.

RESIN ACIDS. All rotations were determined in 1% ethanol solution.

Abietic acid, $\alpha_D^{24} = -106°$, melting point = 172–175° C., was obtained by the Harris and Sanderson modification (*7*) of the method of Palkin and Harris (*12*).

Dehydroabietic acid (*4*), $\alpha_D^{24} = +63°$, melting point = 171–173° C.

Tetrahydroabietic acid was obtained by complete hydrogenation of abietic acid with platinum oxide in acetic acid to zero bromine number.

A mixture of dihydroabietic acids was obtained by hydrogenation of abietic acid with palladium-on-charcoal catalyst until slightly more than the theoretical amount of hydrogen was taken up.

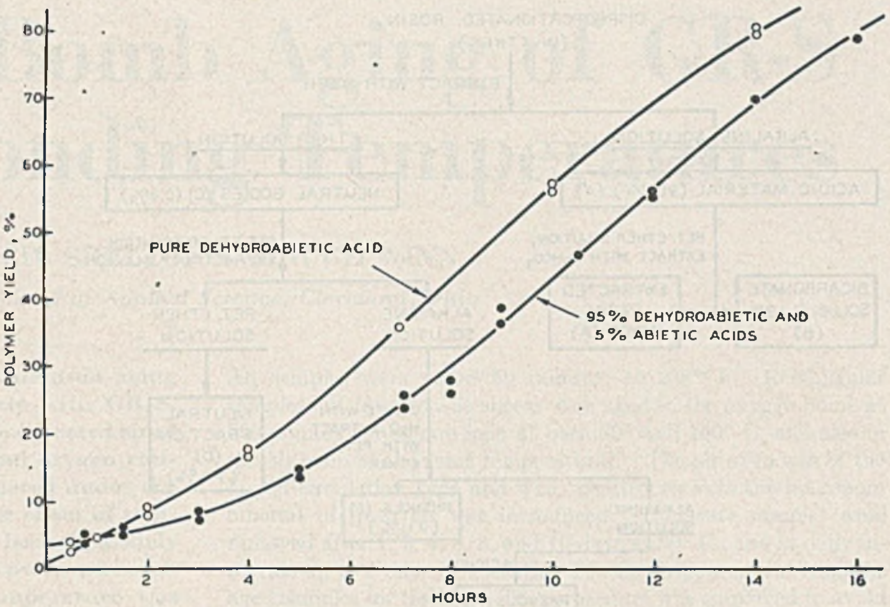

Figure 2. Effect of Abietic Acid on Polymerization

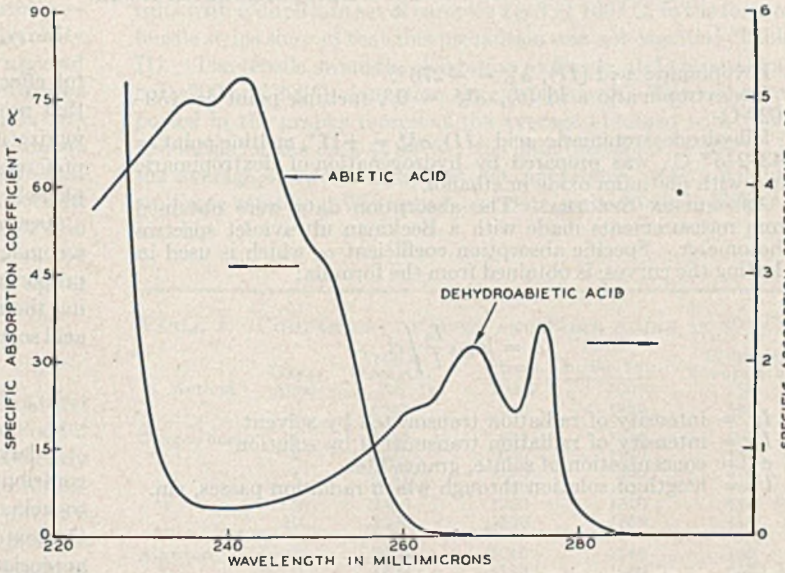

Figure 3. Absorption Spectra of Abietic and Dehydroabietic Acids

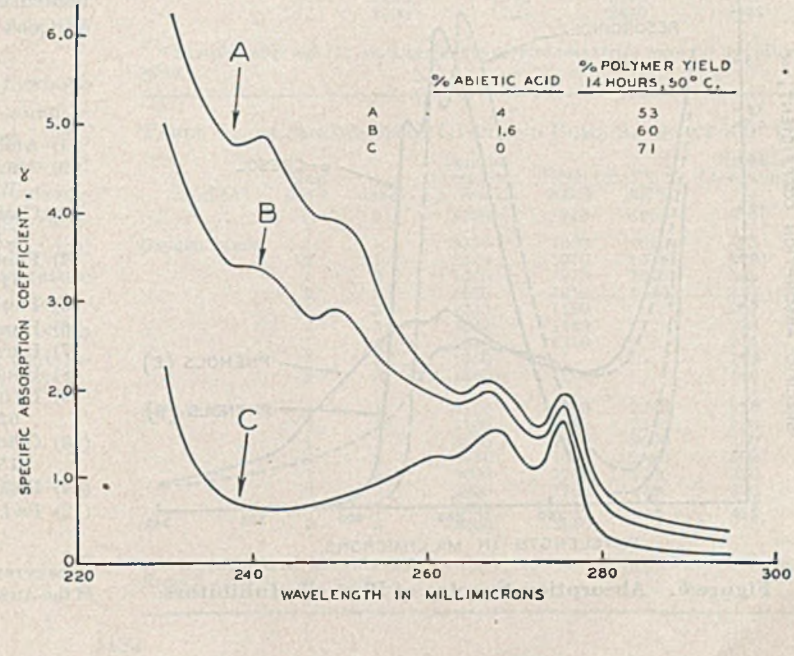

Figure 4. Absorption Spectra of Disproportionated Rosins

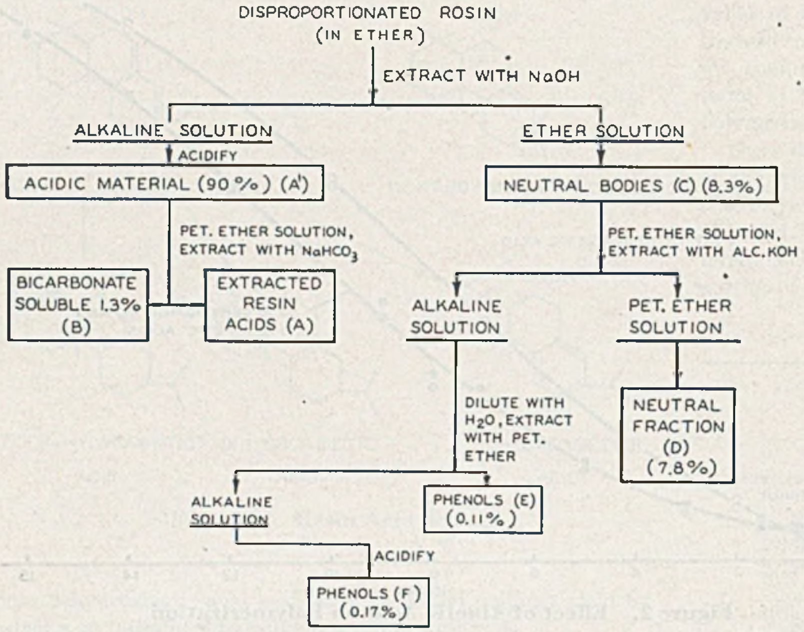

Figure 5. Fractionation of Disproportionated Rosin

Levopimaric acid (*11*), $\alpha_D^{24} = -276°$.

Isodextropimaric acid (*6*), $\alpha_D^{24} = 0°$, melting point = 159–162° C.

Dihydrodextropimaric acid (*11*), $\alpha_D^{24} = +17°$, melting point = 243–245° C., was prepared by hydrogenation of dextropimaric acid with platinum oxide in ethanol.

Absorption Spectra. The absorption data were obtained from measurements made with a Beckman ultraviolet spectrophotometer. Specific absorption coefficient α, which is used in plotting the curves, is obtained from the formula:

$$\alpha = \log_{10} \frac{I_0}{I} \Big/ cl$$

I_0 = intensity of radiation transmitted by solvent
I = intensity of radiation transmitted by solution
c = concentration of solute, grams/liter
l = length of solution through which radiation passes, cm.

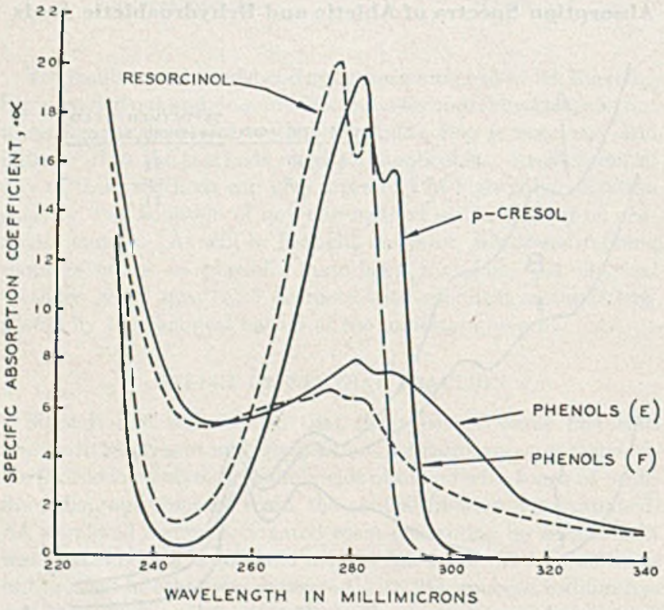

Figure 6. Absorption Spectra of Phenolic Inhibitors

The difference in α at the maximum at 241 mμ and at the inflection point at 248.5 mμ is determined for pure abietic acid. The ratio of this difference for an unknown sample to that for pure abietic acid is a measure of the abietic acid in the unknown.

Analysis of Phenolic Fractions. Crude phenolic fractions E and F were dark oils which could not be crystallized. The following analytical data were obtained:

Fraction	E	F
% OH, (Zerewitinoff)	5.7	8.4
% OCH_3	5.1	4.8
% C	80.1	76.7
% H	10.2	9.6
Mol. weight (Rast)	320	282
Av. No. OH groups per mol.	1.0	1.4 (1.8)[a]
Av. No. OCH_3 groups per mol.	0.5	0.44 (0.88)[a]

[a] The values in parentheses were obtained on the assumption of a 50% resin acid content for F. This value would have been reached if all the resin acids indicated to be present in neutral fraction C (acid number 2) were carried through to F.

CONCLUSIONS

On the basis of the data presented, these powerful inhibitors which have been concentrated and characterized as phenols represent the major portion of the constituents of unrefined disproportionated rosin which have harmful effects on the GR-S polymerization. It is apparent, then, that preparation of a rosin satisfactory for use in emulsion polymerization involves (1) complete removal of abietic-type acids, preferably by the disproportionation reaction, and (2) removal of phenolic inhibitors by suitable refining.

As a result of the application of the conclusions from this work, a commerical plant is now in operation producing a uniform disproportionated rosin soap with polymerization activity approaching the maximum values which can be obtained with pure resin acid soaps.

ACKNOWLEDGMENT

A large number of Hercules personnel have made significant contributions to the research reported here. The authors wish to acknowledge, in particular, those of J. H. Long and P. G. Carpenter in the early phases of the program and to express their appreciation to H. M. Spurlin and D. H. Sheffield for many helpful suggestions and continued encouragement. They are indebted to G. C. Harris for samples of resin acids and to Evelyn V. Cook for all the ultraviolet absorption data cited.

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Oven and Bomb Aging of GR-S at Corresponding Temperatures

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Attempts to correlate oxygen bomb and air oven aging generally prove unsatisfactory, particularly with GR-S. Actually, a direct correlation should not be expected since a simultaneous change in temperature and oxygen concentration is involved when they are compared under the conventional conditions for each test. The effect of temperature and of oxygen concentration have been separately evaluated by comparing the results of both oven and bomb aging at 80° and 100° C. Increased temperature was found to increase the rate of deterioration in both types of aging, but the effect appears to be more marked in the oxygen bomb. Reaction of oxygen with GR-S, which results in hardening (cross linking), appears to be virtually independent of oxygen concentration above that in air and is the predominant reaction in the air oven. Reaction of oxygen with GR-S which leads to chain scission is increased by oxygen concentration and is the predominant reaction in the oxygen bomb. Chain scission is reflected in both tensile breakdown and in a lower modulus than would otherwise be obtained since the shortening of the chains would have a softening effect; this accounts for the smaller modulus increase observed with bomb aging and for the reversion of the modulus observed at 100° C.

ATTEMPTS to correlate the aging characteristics of natural rubber vulcanizates when subjected to standard methods of accelerated aging have generally proved unsuccessful, particularly when the samples differed appreciably in compounding formulations. Neal and Ottenhoff (*2*) compared the resistance of GR-S vulcanizates to the oxygen pressure, air oven, and air pressure heat tests. They reported a complete lack of any correlation of these tests with GR-S, as previously observed with natural rubber. The oxygen bomb at 70° C. and 300 pounds per square inch appeared to be the mildest, followed by the air oven at 121° C; the air bomb at 127° C. and 80 pounds was the most severe.

The absence of a direct correlation between the various methods of accelerated aging is not unexpected, in view of the simultaneous change of temperature and oxygen concentration. The authors previously established that both tensile breakdown and the modulus increase brought about by aging of GR-S vulcanizates is primarily the result of attack by oxygen (*3*), and also demonstrated the effect of temperature in the oxidation reaction (*4*). It appeared desirable, therefore, to study the effect of temperature and of oxygen concentration independently in an attempt to explain the difference in the results obtained in the oxygen bomb and the air oven. For this purpose both types of aging were investigated at the same temperatures—namely, 80° and 100° C.

PROCEDURE

A tread type stock was employed containing the following parts by weight:

GR-S	100.0	Zinc oxide	5.0
Bardol (softener)	5.0	Santocure (accelerator)	1.2
Fatty acid	1.5	Sulfur	2.0
Channel black	50.0		

All samples were cured 50 minutes at 298° F. Rectangular samples cut from tensile sheets were aged in the oxygen bomb at 300 pounds per square inch at both 80° and 100° C. and also in the air oven at the same temperatures. The air oven was of the forced circulation type and was operated so that the maximum amount of fresh air was introduced. Triplicate samples were removed after 1, 2, 4, 6, 8, and 10 days at 80° C., and at daily intervals up to 5 days at 100° C. Tensile strips were cut from the aged samples for testing. This procedure was employed to avoid the possibility of more extensive deterioration along the edges of tensile strips cut before aging. However, comparison of the results with a duplicate set of samples aged at 100° C. in the form of tensile strips showed that this precaution was not essential (Table II). The tensile strength, elongation at break, and the stress at both 200 and 300% elongation were determined. The values reported in the graphs represent the average obtained with three test strips for the data at 80°C.; the data presented for 100° C. is the average of two independent determinations, each involving triplicate samples. The actual test data are recorded in Tables I and II.

TABLE I. COMPARISON OF OVEN AND BOMB AGING AT 80° C.[a]

Method	Days Aged	Tensile Strength, Lb./Sq. In.	Stress, Lb./Sq. In. 200%	300%	Ultimate Elongation, %
....	0	3290	760	1330	590
Oxygen bomb	1	2970	970	1670	500
	2	2930	1090	1770	480
	4	2770	1110	1800	475
	6	2680	1240	1900	440
	8	2520	1200	1820	440
	10	2300	1220	1830	410
Air oven	1	3200	1010	1740	490
	2	3220	1110	1980	450
	4	3190	1320	2170	420
	6	3140	1450.	2400	380
	8	2940	1560	2490	350
	10	3020	1700	2690	345

[a] Samples were aged in rectangular strips, and test strips were cut out after aging.

TABLE II. COMPARISON OF OVEN AND BOMB AGING AT 100° C.

Method	Run No.[a]	Days Aged	Tensile Strength, Lb./Sq. In.	Stress, Lb./Sq. In. 200%	300%	Ultimate Elongation, %
....	..	0	3220	740	1250	625
Oxygen bomb	1	1	2370	1080	1610	475
	2	1	2420	1070	1590	480
	1	2	1570	970	1370	380
	2	2	1530	1010	1400	350
	1	3	1330	1130	..	260
	2	3	1380	1140	..	270
	1	4	1340	1310	..	215
	1	5	1350	..	..	150
	2	5	1300	..	..	140
Air oven	1	1	3150	1400	2290	410
	2	1	3160	1350	2310	410
	1	2	3000	1610	2600	350
	2	2	3070	1600	2590	360
	1	3	3000	1760	2790	330
	2	3	2800	1790	2790	300
	1	5	2880	2010	..	275
	2	5	2860	2060	..	275

[a] Runs 1, aged in rectangular strips; test strips cut out after aging. Runs 2, aged as test strips.

COMPARISON OF AGING DATA

Figure 1 shows the change in ultimate elongation brought about by heating a GR-S vulcanizate at 80° and at 100° C. in both the air oven and oxygen bomb. At the lower temperature the oven is the more severe, but at the higher temperature the oxygen-pressure test produces a greater change after the first day. The temperature coefficients per 10° C. from the data of Figure 1 are 2.09 for the air oven and 2.63 for the oxygen bomb. Thus the effect of temperature upon the rate of change in ultimate elongation is greater at the higher oxygen concentration. Considered together with the effect upon tensile strength and modulus as described below, the more rapid decrease in ultimate elongation produced by oxygen pressure aging at 100° C. may be attributed to an increased rate of chain scission.

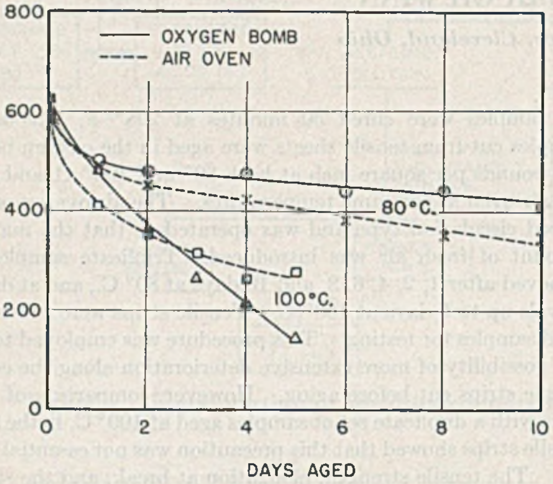

Figure 1. Elongation at Break

The effect of aging upon the tensile strength of a GR-S tread stock is much less drastic in the air oven than in the oxygen bomb, as Figure 2 shows. In fact, the decrease in tensile strength was greater at 80° C. and 300 pounds per square inch oxygen pressure than in air at 100° C. Since the decrease in tensile strength may be regarded as primarily the result of chain scission, it follows that the rate of the chain-scission reaction increases with both oxygen concentration and with temperature. The temperature coefficients per 10° C. increase in temperature, calculated from the data of Figure 2 for tensile breakdown, are 1.97 for the air oven and 3.09 for the oxygen bomb.

The effect of oven and oxygen bomb aging on the stress required to produce a given elongation is shown in Figure 3 for 80° C. and in Figure 4 for 100° C. The air oven is much more drastic than the oxygen bomb in producing hardening as measured by modulus increase. At 80° C. the increase in both the 200 and 300% stress was about the same in oven and bomb during the first day. Thereafter the increase continued in air but leveled off at approximately a constant value in the bomb.

The authors showed previously (*3*) that the increased modulus brought about by aging in the air oven is largely the result of attack by oxygen. Since the increase is actually less in the oxygen bomb at the same temperature, it appears that this reaction is little affected by oxygen concentration above that in air and that the smaller modulus increase is due to the effect of the chain-scission reaction which tends to offset the hardening reaction. The net effect in the oxygen bomb at 80° C. is a balance between the oxygen-induced hardening (which may be presumed to involve cross linking) and the oxidative scission of chains which would have a softening effect.

This interpretation of the results is supported by the behavior of the modulus curve at 100° C., as Figure 4 shows. The stress at both 200 and 300% elongation increased in both bomb and oven during the first day. During the second day the modulus continued to increase in the air oven although at a slower rate. The drastic reduction in tensile strength in the bomb, however, continued through the second day, with the result that the chain-scission reaction predominated over the hardening reaction and the net effect on the modulus was a decrease. Thereafter the tensile curve for the bomb aging leveled off while the hardening reaction, as measured in the oven, continued and the 200% stress once more started to increase in the oxygen bomb. The slope of the curve from this point (second to fourth day of aging) is essentially the same as that of the corresponding curve for the stress at 200% elongation in the oven. Since the effect of chain scission was small during this period, as shown by the tensile curves, this slope represents primarily the hardening reaction and demonstrates that it is virtually independent of oxygen concentration above that in air. It was not possible to observe a similar increase in the curve for the 300% stress since the ultimate elongation was reduced below 300% after 3 days in the bomb at 100° C. The shape of the modulus curves of Figure 4 and the crossover of the elongation curves at 100° C. in Figure 1 show that a comparison of the effectiveness of the two types of aging cannot safely be made with a single aging period since the relative magnitude of the changes taking place varies as aging progresses.

A reversion of the modulus (Figure 4) is quite common with natural rubber but has not been previously reported with GR-S. At first we were inclined merely to regard the data as erratic, and consequently the aging tests were repeated at 100° C. The two sets of experimental points plotted for both the 200 and 300% stress in Figure 4 represent the two independent sets of aging data, and the good agreement clearly shows that the reversion is real and the data are reproducible.

This evidence that reversion of the modulus takes place with GR-S upon aging at the appropriate temperature and oxygen concentration lends support to the idea previously suggested (*4*) that the fundamental reactions involved in the deterioration of both natural rubber and GR-S are the same. These fundamental reactions appear to be (*a*) chain scission, which results in tensile breakdown and a reduction of stress at a given elongation, and (*b*) cross linking, which increases the modulus and produces a general hardening. The difference between the behavior of natural

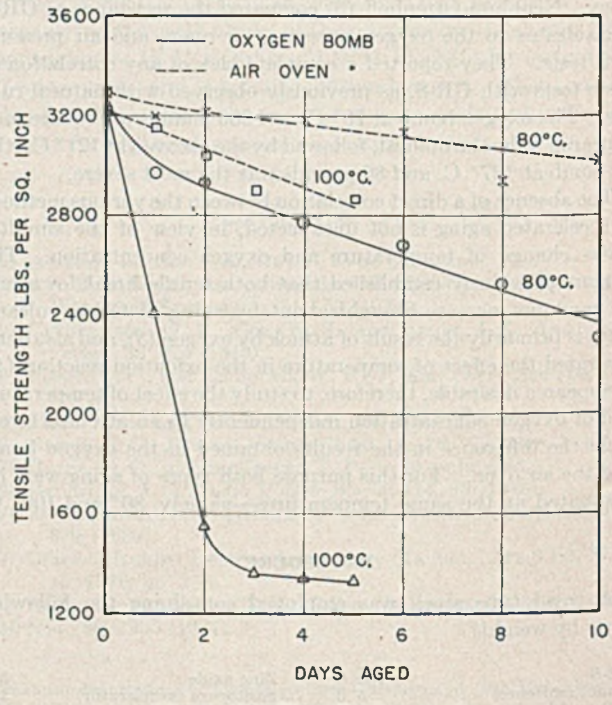

Figure 2. Tensile Strength

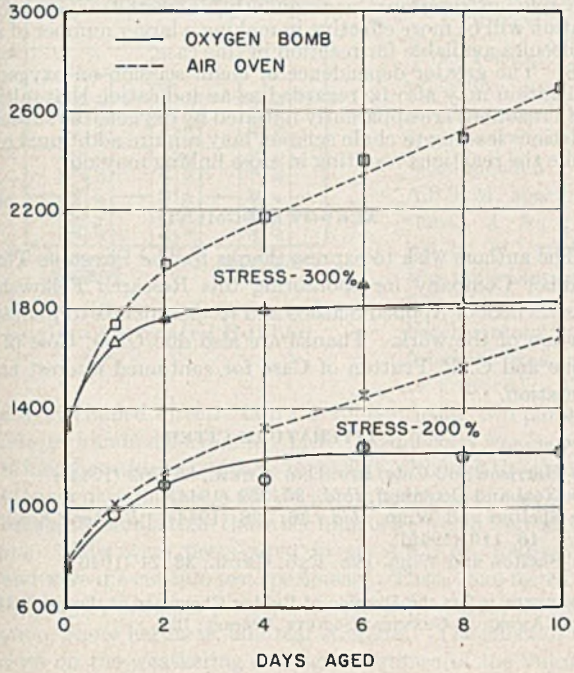

Figure 3. Stress at 200 and 300% Elongation after Aging at 80° C.

rubber and GR-S under a given set of aging conditions may then be attributed to a difference in the relative rates of these two reactions. Likewise the failure to demonstrate a real correlation between the various standard methods of aging appears to be due to the fact that changes in temperature and oxygen concentration alter the ratio of these two reactions and thus change the resultant effect as measured by physical properties.

The temperature coefficient for modulus increase in the air oven, calculated from the time required to produce a given change as shown in Figures 3 and 4, is 2.00 for both the 200 and 300% stress. Coefficients for bomb aging would be meaningless in this case as a result of the reversion which occurred at 100° C. Harrison and Cole (*1*) determined the temperature coefficients for oven aging of GR-S over the range 100° to 132° C. Their values are compared in the following table with those obtained in the present study over the range 80° to 100° C.:

Physical Property	Temperature Coefficient per 10° C. Air oven, 80–100° C.	Air oven, 100–132° C.	Oxygen bomb, 80–100° C.
Stress (200%)	2.00	1.97	..
Stress (300%)	2.00	2.00	..
Tensile strength	1.97	1.95	3.09
Elongation at break	2.09	1.96	2.63

The agreement is sufficiently close to justify extension of the relations which they established to include the lower temperature range.

The higher temperature coefficients for both tensile strength and elongation at break, as observed with oxygen bomb aging, may be attributed to the effect of increased oxygen concentration on the chain-scission reaction, since the cross-linking reaction appears to be little affected by oxygen concentration above that in air. The resultant effect upon tensile strength is greater than on ultimate elongation, as would be expected from consideration of a typical stress-strain curve, since the elongation changes more slowly as the stress approaches the breaking load.

The evidence presented in this paper that the chain-scission reaction increases with oxygen concentration whereas the cross-linking reaction is virtually independent of oxygen concentration above that in air suggests certain possibilities with respect to the mechanisms of these reactions. For example, it may be postulated that, while both reactions are apparently initiated by oxygen, the subsequent reactions resulting in chain scission may require additional oxygen; this is indicated by the dependence of tensile breakdown on oxygen concentration whereas the cross-linking reaction may not require any additional oxygen.

The effect of oxygen concentration upon the temperature coefficients is even more significant. The rate of the hardening reaction, as measured by stress increase in the oven, gives a temperature coefficient of about 2.0, and this value appears to be unchanged by additional oxygen concentration. On the other hand, the temperature coefficient for tensile breakdown increases with oxygen concentration, and since chain scission is shown to be the predominant reaction in the oxygen bomb, the higher value of about 3.1 may be regarded as an approximation of the temperature coefficient for the chain-scission reaction. The energy of activation calculated from this value is 29.7 kg.-cal. for the scission reaction; that of the cross-linking reaction is 18.2 kg.-cal. Apparently a sufficient number of oxygen molecules having sufficient energy at the temperatures involved are present in air to maintain the cross-linking reaction, and thus additional oxygen concentration becomes unimportant. However, there do not appear to be enough oxygen molecules in air with an energy of 29.7 kg.-cal. to support the scission reaction at its maximum rate. In this latter case the higher oxygen concentration in the bomb becomes an important factor.

SUMMARY AND CONCLUSIONS

The relations observed in this comparison of air oven and oxygen bomb aging of GR-S at corresponding temperatures and the interpretations suggested by these relations may be summarized as follows:

1. Comparison of the results of tests in which some samples were aged in the form of tensile test strips while others were cut from rectangular strips after aging indicates that edge effects during aging are negligible and that the former practice is satisfactory.
2. Increased temperature increases the severity of both types of aging, but the effect is greater at the higher oxygen concentration of the bomb.

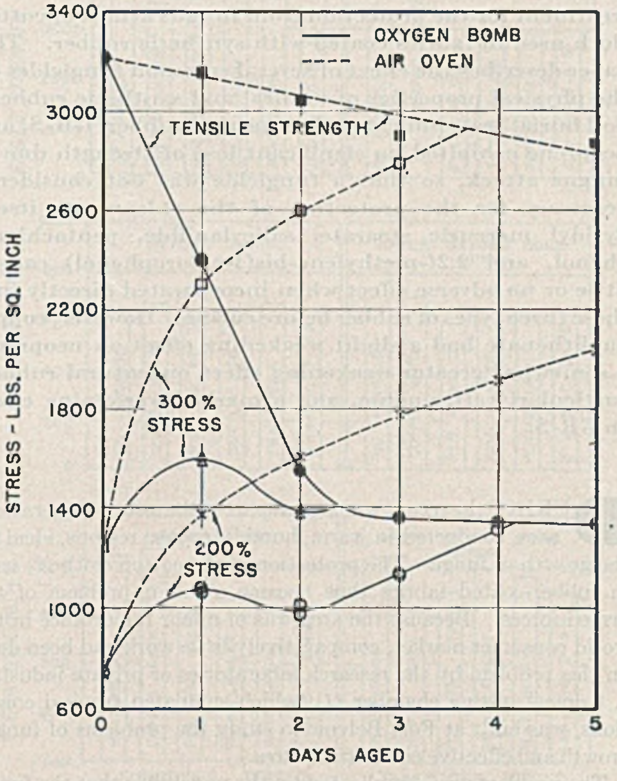

Figure 4. Stress at 200 and 300% Elongation after Aging at 100° C.

3. The hardening reaction, as measured by the increase in modulus, appears to be little affected by increased oxygen concentration above that in air and is the predominant reaction in the air oven.

4. Chain scission, as measured by decrease in tensile strength, increases with oxygen concentration and is the predominant reaction in the oxygen bomb.

5. Chain scission is also reflected in the smaller modulus increase observed with oxygen bomb aging as compared to the air oven, and is responsible for the reversion of the modulus observed at 100° C. and 300 pounds per square inch oxygen pressure.

6. Changes in temperature and in oxygen concentration, therefore, alter the ratio of the fundamental aging reactions of chain scission and cross linking. Since the effect of these two reactions upon physical properties is different, no direct correlation can be expected between methods of aging which differ in both temperature and oxygen concentration.

7. Activation energies calculated from the temperature coefficients observed for tensile breakdown in the oxygen bomb (29.7 kg.-cal.) and for modulus increase in the air oven (18.2 kg.-cal.) may be regarded as approximations of the activation energies required for chain scission and cross linking, respectively. The observation has been made that the latter reaction is virtually independent of oxygen concentration above that in air, whereas the former increases with oxygen concentration. This may be interpreted as indicating that, at the temperatures involved, a relatively large number of oxygen molecules are sufficiently activated to maintain the lower energy reaction, even in air, while a much smaller number have the energy required for the scission reaction; consequently, increased oxygen concentration will be more effective in making a larger number of active molecules available for reaction in this case.

8. The greater dependence of chain scission on oxygen concentration may also be regarded as an indication that, although both reactions are apparently initiated by oxygen, the subsequent reactions leading to chain scission may require additional oxygen while the reactions resulting in cross linking may not.

ACKNOWLEDGMENT

The authors wish to express thanks to The Firestone Tire and Rubber Company for sponsoring this Research Fellowship at Case School of Applied Science and for permission to publish this portion of the work. Thanks are also due O. D. Cole of Firestone and C. F. Prutton of Case for continued interest and cooperation.

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Effect of Fungicides on Natural and Synthetic Rubber

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Military operations in tropical regions necessitate treatment for the protection from fungus attack of cotton cloth used in fabrics coated with synthetic rubber. This paper describes the effect of several common fungicides on the physical properties of natural and synthetic rubbers. Soil burial tests indicated that natural rubber, GR-S, and neoprene exhibited no significant loss of strength due to fungus attack, so that a fungicide was not considered necessary for the protection of the vulcanizate itself. Pyridyl mercuric stearate, salicylanilide, pentachlorophenol, and 2,2′-methylene-bis(4-chlorophenol) caused little or no adverse effect when incorporated directly into these three types of rubber before curing. However, copper naphthenate had a slight weakening effect on neoprene, a somewhat greater weakening effect on natural rubber, particularly after aging, and a marked weakening effect on GR-S.

DURING the recent war a great part of the military operations were conducted in warm, humid, tropical regions, ideal for the growth of fungi. The protection of the cotton cloth (*2*) used in rubber-coated fabrics thus became a major problem of the armed forces. Because the area was of minor importance in the world consumer market, comparatively little work had been done on this problem by the research laboratories of private industry. A tropical testing chamber (*1*), which simulated tropical conditions, was built at Fort Belvoir to study the problems of fungus growth and effective countermeasures.

The problem was complicated by the possibility that the fungicide which had a protective effect on the cloth might have had a destructive effect on the rubber coating. Tests on pentachlorophenol and 2,2′-methylene-bis (4-chlorophenol) by two industrial concerns had indicated that these two fungicides had no adverse effect on either natural rubber or GR-S when used in small concentrations. Tests by another industrial concern had indicated that salicylanilide was satisfactory for use with natural rubber and neoprene. However, because of the meager amount of information available, a study was conducted to determine what fungicides, and in what concentrations, might abnormally deteriorate rubber coatings.

This problem was divided into two parts. The first was to determine the effect of the various fungicides on the physical properties of natural and synthetic rubber when incorporated directly into the rubber compound prior to vulcanizing. The second part was to determine the effect of the fungicides on the adhesion, abrasion, and general wearing qualities of coated fabrics when the fungicide is impregnated into the fabric prior to coating.

The work to date covers five fungicides and three types of rubber. The fungicides tested include copper naphthenate, pyridyl mercuric stearate, salicylanilide, pentachlorophenol, and 2,2′-methylene-bis(4-chlorophenol), sometimes designated as dihydroxydichloro diphenylmethane. (An abbreviated form of the latter designation is used in the figures for simplicity.) These fungicides were selected as representative of the types found most effective in preventing the fungus deterioration of cotton fabrics in a considerable number of tests conducted by The Engineer Board. Table I lists the types of rubber tested and the compounding formulations used. Natural rubber, GR-S, and neoprene are the subject of this report, but other coating materials such as vinyl butyral, the vinyl copolymers, Butyl rubber, and butadiene-acrylonitrile rubber, are to be included in future work.

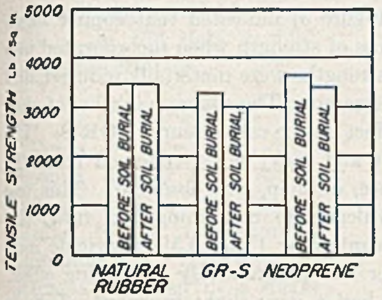

Figure 1. Effect of Exposure to Fungi on Untreated Rubber

MIXING, CURING, TESTING

In general, the procedure used in preparing the test specimens was that recommended by A.S.T.M. specifications. A separate batch of rubber was milled for each fungicide, and a batch containing no fungicide was used as control. The fungicide was milled directly into the rubber, using two parts of fungicide per hundred parts of polymer. No difficulty was encountered in incorporating any of these fungicides, although the concentrated copper naphthenate, a sticky, gummy substance, was somewhat harder to handle than the other fungicides which were all dry powders. Slabs were press-cured in an A.S.T.M. four-cavity mold and were die cut into test specimens. These were tested for tensile strength, ultimate per cent elongation, modulus at 300% elongation, Shore hardness, and tear strength. The effect of the fungicides on the weathering and age resistance of the vulcanizate was investigated by subjecting test specimens to light aging, heat aging, oxygen bomb aging, and soil burial test conditions. However, only the tensile strength, elongation, tear strength, and unaged and oxygen bomb aging test conditions are reported here since they are sufficient to illustrate the observed effects.

The results of the soil burial tests on vulcanizates containing no added fungicide, summarized in Figure 1, indicated that there was no significant loss of strength due to fungus attack. No

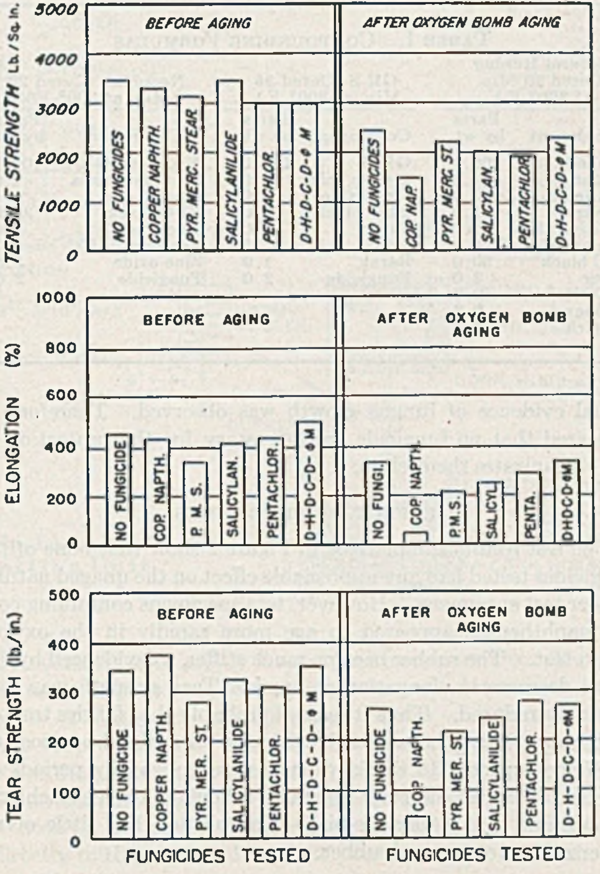

Figure 2. Effect of Fungicides on Natural Rubber

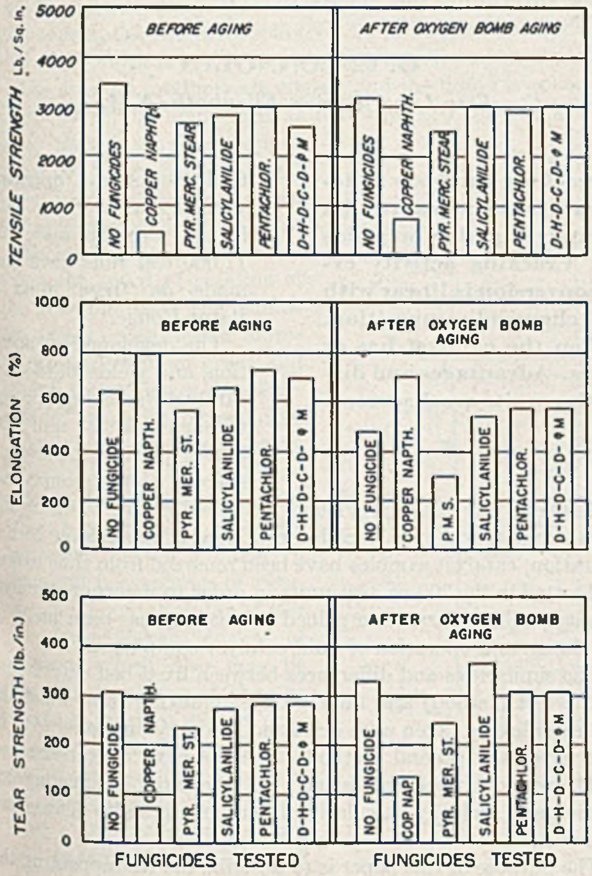

Figure 3. Effect of Fungicides on GR-S

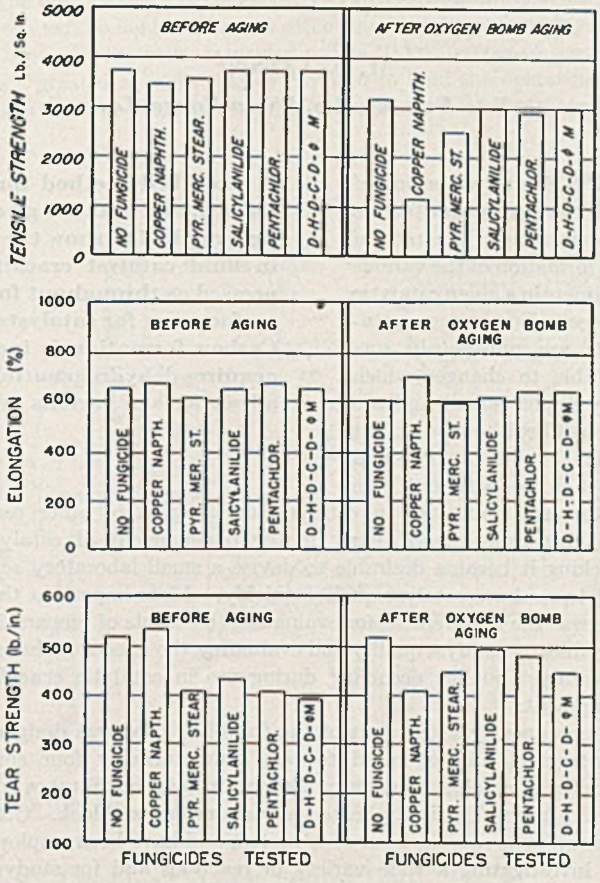

Figure 4. Effect of Fungicides on Neoprene

Table I. Compounding Formulas

Natural Rubber (Cured 20 Min. at 300° F.)		GR-S (Cured 35 Min. at 300° F.)		Neoprene (Cured 20 Min. at 300° F.)	
Component	Parts by wt.	Component	Parts by wt.	Component	Parts by wt.
Smoked sheet	100.0	GR-S	100.0	Neoprene GN-A	100.0
Reogen	2.0	Stearic acid	2.0	XLC magnesia	4.0
Stearic acid	3.0	Zinc oxide	5.0	Stearic acid	0.5
Pine tar	1.0	EPC black	50.0	EPC black	30.0
Neozone D	1.0	Sulfur	2.0	Neozone D	2.0
Zinc oxide	5.0	Altax	0.75	Accelerator 552	0.1
EPC black	50.0	Barak	1.0	Zinc oxide	5.0
Sulfur	3.0	Fungicide	2.0	Fungicide	2.0
Altax	2.0				
Thionex	0.2				
Fungicide	2.0				

visual evidence of fungus growth was observed. Therefore, it appeared that no fungicide was necessary for the protection of the vulcanizates themselves.

EFFECT OF FUNGICIDES

The test results summarized in Figure 2 show that none of the fungicides tested had any appreciable effect on the unaged natural rubber test specimens. However, test specimens containing copper naphthenate appeared to age more rapidly in the oxygen bomb test. The rubber became much stiffer, as evidenced by the sharp decrease in elongation at break. Tear strength was considerably reduced. Thus it seemed probably that fabrics treated with copper naphthenate and having a natural rubber coating might be expected to crack when used after lengthy periods of storage. Pyridyl mercuric stearate, salicylanilide, pentachlorophenol, and 2,2′-methylene-bis(4-chlorophenol) had little or no adverse effect on natural rubber.

The results on GR-S (Figure 3) indicated that copper naphthenate caused a serious loss of strength when incorporated into GR-S. Tensile and tear strengths were materially reduced, and elongation at break was increased. The copper naphthenate had a considerable retarding effect on the rate of cure of GR-S. The vulcanized slabs were soft and tacky when removed from the mold. Very little resilience, or snap, was observed. This test was made on a GR-S vulcanizate containing 2% fungicide. Other tests on specimens containing 1 and 0.5% fungicide indicated a considerably lesser and progressively decreasing effect. Pyridyl mercuric stearate had a very slight injurious effect on GR-S. Salicylanilide, pentachlorophenol, and 2,2′-methylene-bis(4-chlorophenol) had little or no adverse effect on the physical properties of GR-S.

The results of tests on Neoprene (Figure 4) indicated that pyridyl mercuric stearate, salicylanilide, pentachlorophenol, and 2,2′-methylene-bis(4-chlorophenol) caused no measurable loss of tensile strength (within the limits of experimental error), and only a very slight reduction of tear strength. Copper naphthenate caused an appreciable loss of tensile strength after aging, but apparently produced an increase in the ultimate elongation and tearing strength.

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TESTING OF CRACKING CATALYSTS

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A fixed bed method for testing cracking catalysts is described, and data are given to indicate how the test results were applied to show the effect of catalyst quality on yields in fluid catalyst cracking units. Cracking activity expressed as throughput for a given conversion is linear with surface area for catalysts of a given chemical composition. Carbon formation is increased when the catalyst has or acquires dehydrogenating properties. Advantages and disadvantages of various types of testing units are discussed.

The catalyst is one of the paramount factors in determining the rate of the formation of the various products in a given catalytic process. Furthermore catalysts are notoriously susceptible to changes which may appear small and are often difficult to predict, but which have a profound effect on production. These factors are important in catalytic cracking as in other catalytic processes; hence, early in the development of catalytic cracking it became desirable to devise a small laboratory scale test to measure catalyst quality quickly. More important than this was the requirement for evaluating the effects of preparation variables on catalyst quality and evaluating the effects of changes of catalyst quality occurring during use in catalytic cracking equipment.

Consequently a test unit of the fixed-bed type was designed, constructed, and operated to test simultaneously four small samples of catalyst (generally 200 cc.) in four KA_2S tubes supported in an electrically heated aluminum-bronze block. Other such units have since been constructed, and have been employed for investigating a wide variety of reactions and for studying feed stocks and operating variables as well as catalysts. A total of more than 11,000 test runs have been made on these units at Baton Rouge.

The development, operation, and yields for the fluid catalyst cracking process through the 2- and 100-barrels-per-day pilot plant stages to the commercial scale plants have been previously described (*2*, *3*). During this development, and ever since the commercial plants have been in operation, catalyst samples have been removed from time to time and tested in the 200-cc. test units in order to determine catalyst quality. The information gained in this way has been useful in the design and operation of fluid catalyst equipment.

The similarities and differences between fixed-bed cracking (as in the test method) and fluid catalyst cracking from which the test samples are taken were discussed in a previous paper (*5*). In this paper the general methods for expressing conversions and yields were described and defined, and the variables affecting conversion and yields, particularly of carbon, were also defined and discussed.

The purpose of this paper is to describe the test apparatus, the test procedure, the pilling and pretreating of the catalyst samples,

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and to illustrate the application of the test data to fluid catalyst operations.

EQUIPMENT

Figure 1 is a flow sheet showing one of four testing systems which are operated in parallel to test four samples simultaneously. The four reactors are heated in a single aluminum-bronze block (about 90% copper, 10% aluminum), and the equipment is in effect a single unit of four parallel testing systems. Figure 2 shows the dimensions of the reactor tubes and of the electrically heated aluminum-bronze block. The reactors are constructed of KA$_2$S (18-8, chrome-nickel steel) tubing and are inserted and removed from the top of the block. The shoulders of the reactor tubes rest on accommodating offsets in the tube holes and are thus supported.

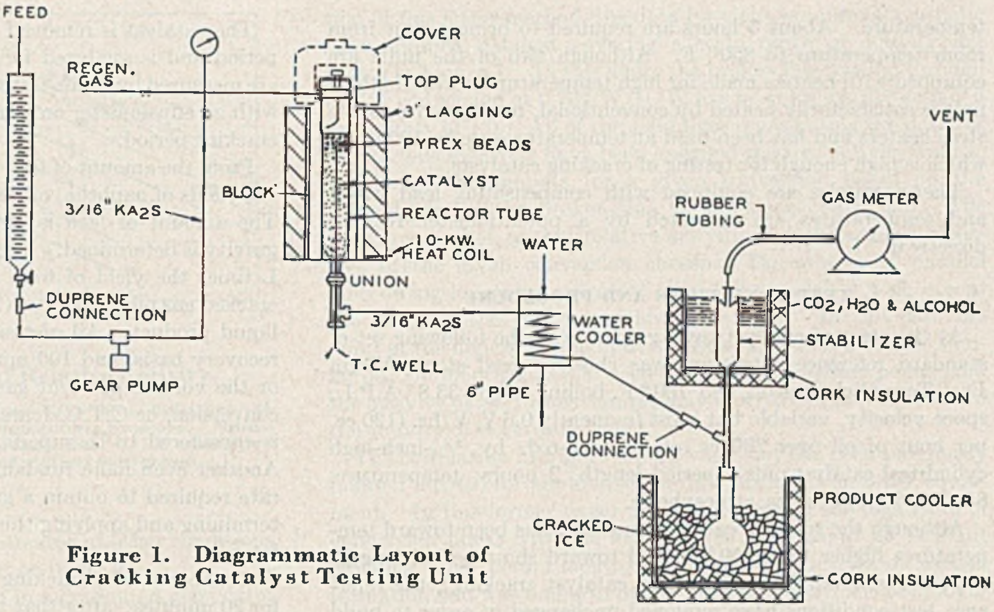
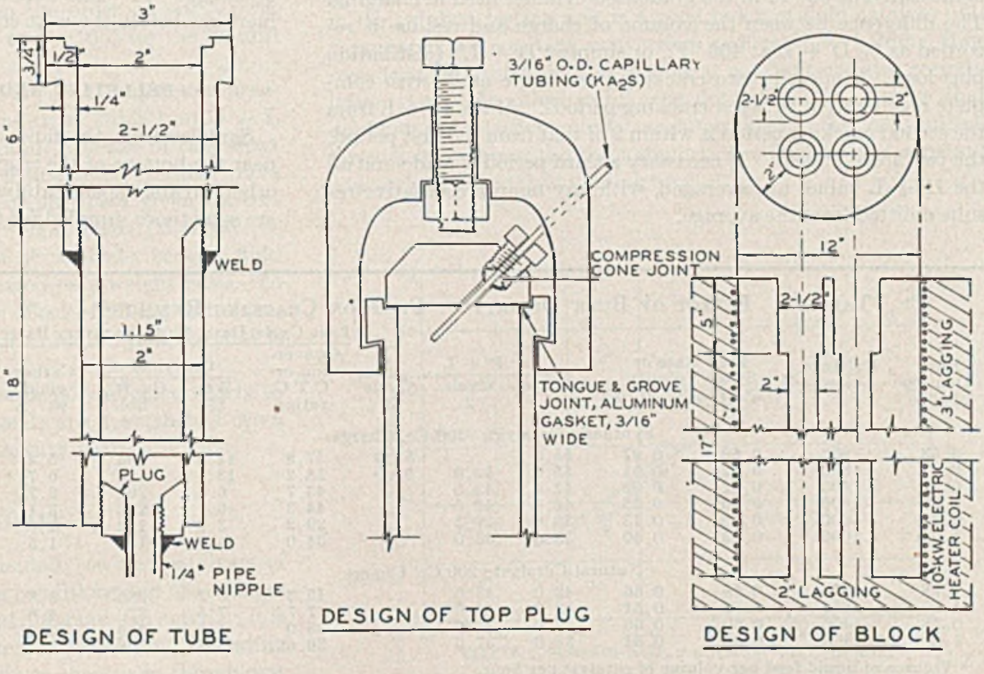


Figure 1. Diagrammatic Layout of Cracking Catalyst Testing Unit

The flow diagram in Figure 1 is that of a conventional fixed-bed process, which is operated in cycles. The cracking period is followed by a regeneration period, during which the catalyst deposit formed during cracking is removed by burning. In the cracking period the feed is pumped from burets into the tops of the reactors by small gear pumps, is vaporized and preheated by glass-chip packing, and is then cracked by the catalyst pellets below the glass packing. The catalyst and glass packing are supported by a perforated KA$_2$S disk (1-inch outside diameter) welded to an axial thermocouple well ($^3/_{16}$-inch KA$_2$S tubing). The thermocouple well runs the length of catalyst bed and is fitted with an iron-constantan thermocouple (No. 24 or 26 glass-covered enameled wire) which is free to be moved up and down in the well.

The cracked products are cooled, and the liquid is collected at about 32° F. by equipment as indicated in Figure 1, while the gases pass through a copper reflux condenser held at -40° to -45° F. and thence through the wet-test meter to the vent.

The oil feed rate is fixed by fixing the speed of rotation of the gear pumps. The pumps are driven by an electric motor through a system of gears, and several sets of gears are available for changing the feed rate. This system is eminently satisfactory; it gives a uniform, steady, trouble-free oil rate which is generally set at 120 cc. per hour, or 0.6 volume of liquid oil per volume of catalyst per hour (V/V/hr.) over the usual 200-cc. charge of catalyst, which also may be varied over a range of 25 cc. or less to as much as 400 cc.



DESIGN OF TUBE

DESIGN OF TOP PLUG

DESIGN OF BLOCK

Figure 2. Cracking Catalyst Testing Unit

The regeneration equipment simply consists of needle valves and pressure gages in the inlet lines. The needle valves control the rate of air and inert gas (an oxygen-free flue gas) which are available from supply lines at moderate pressure. The gases are mixed in proper proportion for the controlled combustion of the coke. The pressure gage (Figure 1) serves to indicate the pressure drop, and hence the rate of flow, through the reactor and KA$_2$S inlet and outlet lines ($^3/_{16}$-inch outside diameter, $^3/_{32}$-inch inside diameter tubing). During regeneration the rubber connection on the outlet of the water cooler (Figure 1) is connected directly to the vent, and thus the product recovery system is bypassed.

The designs of the electrical heaters for the blocks vary among the three units now in operation, but all have a capacity of about 10 kw. and are hand-controlled through variable tap transformers. The heat capacity of the block is so great that a uniform temperature can be held with scant attention from the operator, and no automatic controller is needed. The 10-kw. output of the heater is a great deal more than is required to hold the operating temperature but is useful for rapidly bringing the block to operating temperature. About 3 hours are required to bring a unit from room temperature to 850° F. Although two of the units are equipped with heaters made for high temperature work, the third unit is satisfactorily heated by conventional, readily purchasable strip heaters and has been used at temperatures up to 1000° F., which is high enough for testing of cracking catalysts.

Thermocouples are equipped with compensating lead wires, and temperatures are indicated by a potentiometer reading directly in ° F.

TEST CONDITIONS AND PROCEDURE

At the start of catalyst testing operations the following set of standard reference conditions was chosen: feed stock, Virgin East Texas light gas oil, 485–700° F. boiling range, 33.8° A.P.I.; space velocity, variable but most frequently 0.6 V/V/hr. (120 cc. per hour of oil over 200 cc. of $^3/_{16}$-inch-o.d. by $^3/_{16}$-inch-high cylindrical catalyst pills); period length, 2 hours; temperature, 850–860° F.; pressure, atmospheric.

Although the trend in catalytic cracking has been toward temperatures higher than 850° F. and toward short period lengths (or catalyst holding times in fluid catalyst cracking), the reference test conditions have remained unchanged in order to build up a log of experience on catalyst preparation and usage. A wide variety of conditions (750–975° F., 20-minute to 4-hour period lengths, 0.15–4.0 V/V/hr.) have been employed experimentally from time to time in order to supplement the data at the standard reference conditions. Although atmospheric pressure has usually been used for catalyst testing work, higher pressures have been employed with some modification of the equipment.

Not only is a wide variety of test conditions possible, but also it is possible to work up the cracked products in a number of ways depending on the degree of sharpness of separation of the products, the number of cuts to be taken, and the number of analyses desired. The routine procedure generally used is greatly simplified because it is designed to determine activity and carbon-and-gas-forming tendencies of a large number of catalysts with a minimum of expense. In this procedure the liquid product is weighed, the gravity is determined, and a 100-cc. portion (at 60° F.) is taken in a precooled graduated cylinder for charging into a precooled distillation flask for an A.S.T.M. distillation (Serial D86–38). When the distillation thermometer reaches 400° F., the burner flame is turned off and the residue in the flask is measured at 60° F. in the graduated cylinder used in charging. The difference between the volume of charge and residue is recorded as % D + L at 400° F., or simply "D + L" (distillation plus loss). Generally two cracking periods are made with complete regeneration between cracking periods. If the D + L from the second cracking period is within 2 of that from the first period, the two are averaged. If necessary a third period is made and all the D + L values are averaged, with any nonrepresentative results omitted from the average.

The catalyst is removed unregenerated after the last cracking period and is analyzed for carbon content. The cracked gases are measured by a wet-test meter, and a gravity (air = 1) is taken with an effusiometer on a snap sample of gas at the middle of the cracking period.

From the amount of feed and products it is possible to calculate the yields of naphtha, of uncracked gas oil, of gas, and of carbon. The amount of feed is obtained from buret readings, and the gravity is determined. The yield of naphtha is taken as the D + L times the yield of total liquid product, and the yield of uncracked gas oil is taken as (100 − D + L) times the yield of total liquid product. All of the yields are then adjusted to a 100% recovery basis, and 100 minus the volume per cent gas oil yield or the volume per cent gas oil "disappearance" is taken as the conversion, or C.T.C. (catalyst testing conversion) rating, which is considered to be superior to D + L as an index of activity. Another even more fundamental measure of activity is the feed rate required to obtain a given conversion. The method of determining and applying this measure of activity will be discussed later.

At the end of a cracking period the lines are allowed to drain for 20 minutes; after that the unit is purged with a small flow of inert gas for about an hour or more before the regeneration period is begun. The inert gas flow is then increased, and air is bled in at such a rate that the temperature of the catalyst does not rise much in excess of 1000° F. After the critical period of the regeneration (the passage of the first flame front through the catalyst) is over, the inert gas is shut off, and straight air is introduced. Considerable care must be exercised in introducing air, because at times there is the equivalent of a second flame front. The flame front or "hot spot" is followed down through the bed by adjusting the position of the thermocouple in the axial well. The inert gas is introduced at a rate of 27.5 cubic feet per hour (3900 V/V/hr.), which has been found to correspond to a back pressure of 10 pounds per square inch gage. A small amount of air is then introduced to give a gage pressure of about 10.5 pounds per square inch, which is then increased as rapidly as possible, with the limitation that the catalyst temperature must not greatly exceed 1000° F. After the critical period of the regeneration has passed, the inert gas is cut out, and sufficient air to give a back pressure of 10 pounds is gradually introduced. The full air flow is allowed to continue for about 8 hours while the block temperature is held at about 850° F. The unit is then flushed for a few minutes with inert gas before the next cracking period is started.

PELLETING AND PRETREATING CATALYST

Samples from the fluid catalyst units are usually taken from near the bottom of the regenerated catalyst standpipes, although other streams (spent catalyst, fines collected by the Cottrell, etc.) are sometimes sampled for testing. These powders or those from fresh catalyst, as the case may be, are then compressed into $^3/_{16}$-inch-long by $^3/_{16}$-inch-diameter cylindrical pellets with a rotary tablet machine.

After pilling, the next step is the pretreatment of the pellets before charging to the test unit. Nearly all samples are calcined at 850–900° F. for 3 to 16 hours in KA_2S trays fitted with legs to prevent overheating by direct contact with the floor of the muffle furnace. This calcination completes the pretreatment of used catalyst samples, but, in addition to the 0–900° F. calcina-

Table I. Effect of Bulk Density of Pills on Cracking Results

Bulk Density of Pills	Calcination, ° F.	Feed Rate or Space Velocity		D + L			Last Cycle Data, 100% Recovery Basis			
							Conversion or C.T.C. rating	Gas yield		Carbon yield, wt. %
		V/V/Hr.[a]	W/H/W[b]	Cycle 1	Cycle 2	Cycle 3		Wt. %	Cu. ft./bbl.	
Synthetic Catalyst; 200 Cc. Charge										
0.53	850	0.60	0.97	55.0	..	53.0	57.8	11.4	434	5.4
0.87	850	0.62	0.61	55.0	52.0	52.0	58.2	13.1	489	6.7
0.58	1400	0.62	0.92	42.0	42.5	..	43.7	6.4	261	2.7
0.93	1400	0.60	0.55	42.0	42.0	..	44.3	6.7	268	3.1
0.70	1600	0.60	0.73	30.0	29.5	..	29.2	3.6	152	1.0
1.01	1600	0.59	0.50	33.0	33.0	..	34.0	4.7	192	1.5
Natural Catalyst; 200 Cc. Charge										
0.78	850	0.60	0.66	42.0	43.0	..	45.3	6.7	280	3.3
1.00	850	0.60	0.51	43.0	44.0	..	47.7	7.5	320	4.6
0.78	1400	0.60	0.66	37.0	37.0	..	38.0	4.9	260	2.2
1.00	1400	0.60	0.51	38.0	37.0	..	39.6	5.8	308	3.1

[a] Volume of liquid feed per volume of catalyst per hour.
[b] Weight of liquid feed per weight of catalyst per hour.

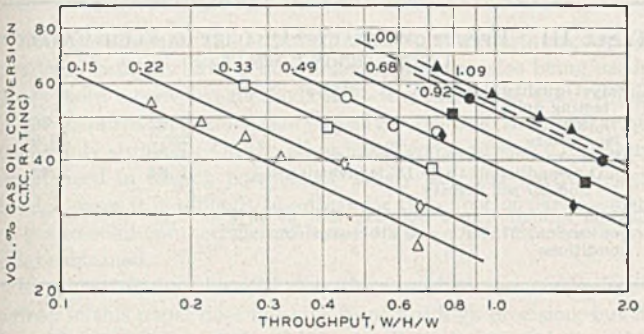


Figure 3. Determination of Relative Activity

Conditions, 200-cc. catalyst testing units; East Texas light gas oil feed; 850–860° F.; 2-hour periods; atmospheric pressure. Numbers are relative activities based on broken line = 1.0 where activity is defined as throughput for a given conversion.

tion, fresh materials are frequently pretreated at other conditions, such as calcination for 3 hours at 1400° or 1600° F.

The pretreated pellets are measured in a graduated glass cylinder (usually 200 cc. in a 250-cc. cylinder) with a standardized tapping technique. The charge is also weighed, and the bulk or pill density is calculated.

The effect of the amount of compression in pilling (as measured by the bulk or pill density) on results from the cracking test was appraised for a sample of synthetic silica-alumina powder and for a sample of natural clay-type powder. Fresh catalysts not exposed to temperatures above 300° F., and therefore much more easily compressible than catalysts exposed to higher temperatures, were used. By this method and by using extreme conditions on the pilling machine the range of densities investigated was made much greater than that encountered in actual practice. The data for the tests made on pilled samples calcined at 850°, 1400°, and 1600° F. at standard conditions (East Texas light gas oil feed at 0.6 V/V/hr. for 2 hours at 850–860° F.) are presented in Table I. The results for the samples calcined at 1600° F. are exceptional in that a large effect of density on % D + L and conversion was indicated. The majority of the data, however, show that D + L did not change with increased pill density, and that carbon and gas formation increased with an accompanying rather small increase in conversion. For example, carbon yields at similar conversion show deviations on the order of ±9% from the average for the synthetic catalyst and ±16% for the natural catalyst.

Because pilling technique does not vary greatly in actual practice, and because of the small effect shown in Table I on D + L or conversion for 0.6 V/V/hr. throughput, the use of this index of activity without adjustment is well justified. Another more fundamental index of activity—throughput for a given conversion—is frequently expressed on a weight basis (W/H/W = weight of oil feed per hour per weight of catalyst), because fluid unit throughputs are invariably expressed on a weight basis. In this case the data of Table I show an effect of pilling technique, but, as mentioned, the effect is small in actual practice and is neglected.

Carbon and gas yields, although not usually affected nearly so much as shown by the data of Table I, are nevertheless often adjusted slightly to a common bulk density basis.

RELATIVE ACTIVITY

Although it is convenient experimentally to test catalysts of all activities at a fixed set of operating conditions and use changes of D + L or conversion as a measure of differences in activity, it is fundamentally more sound to fix the conversion and operating conditions other than throughput and use changes in throughput as a measure of differences in activity. To illustrate the application of this latter method, the data for eight samples of synthetic silica-alumina catalyst covering a wide range of activity are shown in Figure 3. In this figure the broken line passing through 61.5% conversion at 0.734 W/H/W has been arbitrarily assigned an activity of 1.0. All of the solid lines representing the data for the various catalysts have been assigned relative activity values, which are throughputs for a given conversion based on the throughput for the broken line at the same conversion. The lines are parallel, so that relative activities are the same irrespective of the given conversion chosen. The system of parallel lines on log-log paper represent all of the data fairly well, except the data for the catalyst of lowest activity. In this case the point at the highest throughput was established for a sample similar but not identical to that used to establish the other points, and the activity of the former sample may truly be slightly lower than the activity of the latter sample.

The correlation in Figure 3 is not new but has been previously pointed out (*5*) for another set of data obtained on other equipment. In this former paper a relation showing the logarithm of conversion linear with the logarithm of throughput at constant cracking time (period length) was derived from data on carbon formation and was found to fit the measured conversion-throughput data. In fact, the slope of lines established from the data in the earlier paper is the same as those in Figure 3 of this paper, if the conversions for the former are adjusted for differences in fractionation efficiency for the gasoline–gas oil separation.

It will be apparent that the correlation of Figure 3 permits the rapid estimation of relative activity from a single experimental point; the estimation of relative activity has become a standard procedure in this laboratory.

RELATIVE ACTIVITY APPLIED

In fluid catalyst cracking several important variables affect throughput for a given conversion and catalyst holding time; in addition to catalyst activity there are such factors as feed stock quality, temperature, and oil partial pressure. The data of Table II demonstrate how catalyst activity, as determined by the method described, can be applied to fluid catalyst operations—data were selected from the 100-barrels-per-day fluid catalyst cracking unit. In this comparison catalyst activity is the major variable affecting throughput for a given conversion and given catalyst holding time. Relative activity as measured in the catalyst testing unit is a good index of fluid catalyst unit throughput at constant conversion and catalyst holding time (constant catalyst weight in reactor at constant catalyst recirculation rate). In other words, the data of Table II show that doubling the relative activity, as determined in the test unit, allowed a doubling of the throughput in the fluid unit at constant conversion and catalyst holding time.

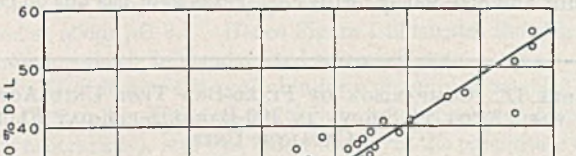


Figure 4. Activity *vs.* Total Reacting Surface

EFFECT OF SURFACE AREA ON ACTIVITY

Surface area was found to be a major factor contributing to the activity of cracking catalysts. In Figure 4 the activities, expressed as throughput for a given D + L, are shown to decrease linearly with decreasing surface area. As it happened in this correlation V/V/hr. for a given D + L was plotted against surface area (sq. m./g.) times bulk density, but W/H/W for a given conversion can be plotted against surface area alone to show the same trend. This is illustrated in Figure 5, which was derived from Figure 4. The activities were measured on the catalyst testing unit by methods already illustrated, and the surface areas were determined by nitrogen adsorption measurements according to the method of Brunauer, Emmett, and Teller (*1*). The catalysts were all made in the same way and had the same chemical composition. The range of activity was obtained by deactivation through use and through calcination at various conditions. If activity is the result of the number and character of the active centers, as has been frequently suggested, then evidently the active centers are destroyed or modified proportionately to the destruction of the total surface during deactivation.

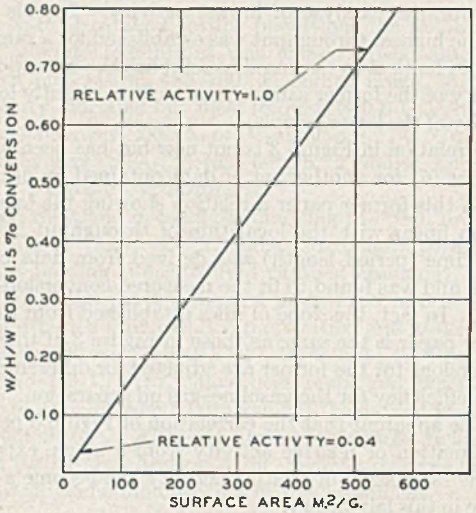


Figure 5. Weight Space Velocity for a Given Conversion *vs.* Surface Area

CATALYST QUALITY FACTORS

The 200-cc. testing unit results may be used to rate catalysts with respect to carbon-and-gas-forming tendencies in addition to the use of these data to determine activity. Table III gives illustrative data showing the effect of carbon-forming tendency of the catalyst (as determined from the standard test at 0.6 V/V/hr., 2 hours, and 850–860° F. with East Texas light gas oil) on carbon formation in a 2-barrel-per-day fluid catalyst unit. In this case two catalysts of similar activity but of widely different carbon-forming tendencies were tested in the fluid catalyst unit at essentially the same conditions, with good regeneration and with substantially complete stripping of spent catalyst. The carbon formation thus represents catalytic carbon affected only by catalyst quality. The poorer quality material gave about 53% more carbon than the better quality catalyst in the fluid catalyst unit; this is in accordance with that predicted from the catalyst quality data obtained in the test unit.

Table II. Comparison of Fixed-Bed Test Unit Activity with Activity Shown in 100-Barrels-per-day Fluid Catalyst Unit

	Synthetic Catalyst A	B	A/B
Fixed-bed test unit			
East Texas gas oil at 850° F. for 2 hr. at 0.6 V/V/hour (0.8 W/H/W)			
% Conversion (C.T.C. rating)	48.5	35.4	..
Relative activity (Figure 3)	0.63	0.31	2.03
100 bbl./day fluid catalyst unit			
Wide cut paraffinic gas oil at 950° F. and 0.45 min. catalyst holding time[a]			
% Conversion	70.5	70.5	..
Throughput (W/H/W)	11.0	5.3	2.07

[a] Catalyst holding time $= \frac{60}{\text{(cat./oil wt. ratio) (W/H/W)}}$.

Table III. Effect of Catalyst Quality on Fluid Catalyst Unit Carbon Formation

Catalyst quality data (200-cc. catalyst testing units)		
Pill density	0.62	0.80
Conversion	28.2	30.0
Wt. % carbon on feed, as measured	1.50	2.70
Above adjusted to 29.1% conversion and 0.7 pill density	1.64	2.48
Carbon formation in 2 bbl./day unit at 60% conversion, 975° F., and otherwise constant conditions	2.8	4.3

In the more general case, where the catalysts under consideration differ widely in activity as well as in carbon-forming tendency, the situation is more complicated. As far as the test data are concerned, it is convenient to establish a correlation of carbon yield *vs.* conversion for a reference material and to express the carbon-forming tendency of the materials being tested as a ratio of their carbon yield to that for the reference material at the same conversion. Gas-forming tendency is handled in a similar manner except that the yields are on a volumetric basis—that is, gas yields in cubic feet per barrel of feed are used.

CARBON FORMATION AS RELATED TO DEHYDROGENATION

Figure 6 shows a trend of increasing carbon-forming tendency with decreasing density of the gas for a series of catalytic materials tested at the usual test unit conditions. This trend has been found to be typical for vapor-phase operation with gas oil feeds and solid catalysts. The change in density is due to a change in gas composition, the low density gas being characterized by a high hydrogen content and a low C_3 and C_4 hydrocarbon content.

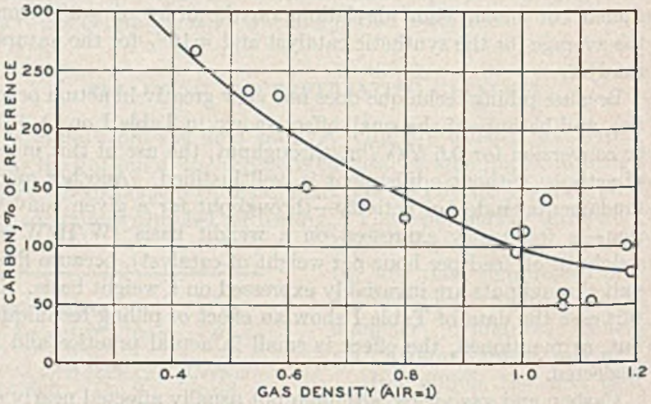


Figure 6. Carbon-Forming Tendency *vs.* Dehydrogenation Tendency (Gas Density)

Apparently catalysts having dehydrogenating and aromatizing tendencies which are high relative to their cracking tendency cause a relatively large proportion of the feed to go to carbon possibly via unsaturates, cyclics, aromatics, condensed-ring aromatics, asphaltenes, carboids, carbon, or some other such route. It is a well known fact, also, that when dehydrogenation is prevented (as in high pressure hydrogenation) carbon formation is substantially eliminated (*4*).

OTHER TYPES OF CRACKING TESTS

With the advent of fluid catalyst cracking other tests employing powdered catalyst have been developed and are also being used. These more recent test methods have the advantage that pilling is not required and that short catalyst holding times may be more easily studied. On the other hand, some difficulty has been experienced in testing powders of widely differing particle size. In such cases it is difficult to adjust for the effect of particle size on gas-to-solid contacting and hence on the conversion (activity index) obtained.

In general it may be said that the fixed-bed test method described in this paper does not give results of high precision, but it has been extremely useful and has contributed a great deal to the development of catalytic cracking. The emphasis has been on rapidity in order to survey a broad and extensive field. The need for improved precision for a more intensive study of certain factors has become a prime consideration in the continuing development of cracking test methods.

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Composition of Rosin Size Precipitate

OCCURRENCE OF ALUMINA

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A method for determining alumina in wet rosin size precipitate floc has been developed and applied. Its use showed that a standardized size precipitate contained no appreciable amount of alumina; this demonstrated that the aluminum ion, rather than alumina, was necessary for the formation of an effective rosin size precipitate. It was also shown that any excess alkali introduced into the papermaking system reacted with alum to form alumina, which coprecipitated with the rosin size.

MANY conflicting opinions exist at the present time both in the theory and in the practice of papermaking. One unanswered question of importance in this field concerns the roles of alumina [hydrated Al_2O_3 or $Al(OH)_3$] and the aluminum ion in the formation and performance of an effective size precipitate. An outline of the literature concerning alumina in the sizing system was prepared and briefly discussed by Collins, Davis, and Rowland (*4*) in 1941. To obtain a general view of the present status of opinion, recent conclusions will be listed briefly. Collins *et al.* (*4*), from their study of ranges of complete precipitation of alumina and/or rosin, favor the view that the rosin size precipitate is a coprecipitate of alumina and rosin rather than a precipitate of a compound such as aluminum resinate; this seems also to be the view of Booth (*3*). Miller (*11*) and Redd (*15*), on the other hand, have concluded that the aluminum ion, rather than alumina, is necessary for the formation of an effective size precipitate. Miller and Booth both advocate the use of more, rather than less, alum than is current practice in papermaking; Price and Cameron (*12*), in order to improve sizing, advise reducing the amount of alum used in many cases. [Papermakers' alum, $Al_2(SO_4)_3 . 18H_2O$, is designated as alum throughout the paper.]

The present work shows that alumina, as $Al(OH)_3$, is not a part of a standardized size precipitate (defined in a later section), and that it is therefore the aluminum ion rather than alumina which is necessary for the formation of an effective rosin size precipitate.

This paper represents a portion of a broad program, now in progress, designed to study the physical and chemical phenomena involved in rosin sizing of paper.

ANALYSIS FOR ALUMINA

The first step toward determining the role of alumina in the sizing mechanism consists of developing a method of analyzing the size precipitate for alumina. With such an analytical tool it is then possible to determine whether alumina, as such, is a necessary component of the size precipitate, whether it occurs during some sizing operations, and under what conditions it appears.

An analytical method for determining alumina in size precipitate flocs has been developed and is fully described in a later section. A standardized procedure of preparing the precipitate from rosin size and alum was used to obtain a standardized size precipitate for analysis.

Of greatest importance to the fundamental knowledge of rosin sizing is the fact that the alumina determination showed the absence of alumina in such a standardized size precipitate. Figure 1 shows typical potentiometric curves. While the standardized size precipitate (curve II) required more acid to reach pH 3.5 than did the distilled water adjusted to pH 4.5 with alum (curve I), the form of its curve is quite distinct from that obtained with an alumina suspension (curve III). In contrast to the rapid fall of pH with the addition of acid found for the standardized size precipitate, the alumina suspensions maintained their pH above 4 until practically all the floc had reacted with the acid. The pH then dropped comparatively rapidly; the point of inflection was located at about pH 3.5. Hence Figure 1 illustrates the absence of alumina, as such, in standardized size precipitate.

Curve II of Figure 1 is typical in form not only of emulsions of size A (70% solids, 20% free rosin) but also of solutions of size B (a dry neutral size), and was found whenever the precipitate was prepared in distilled water. Moreover, distilled water, adjusted to pH 4.5 with alum, contained no floc and showed no alumina by electron microscope examination. Since satisfactory sizing can be obtained with these sizes on a neutral pulp with distilled water used as the papermaking water (*14*), it follows both from the analyses and the papermaking that alumina [$Al(OH)_3$] is not a component of standardized size precipitate.

Data to be presented show that sodium carbonate, sodium bicarbonate, and sodium hydroxide added to the size reacted, apparently quantitatively, to form alumina when the size was

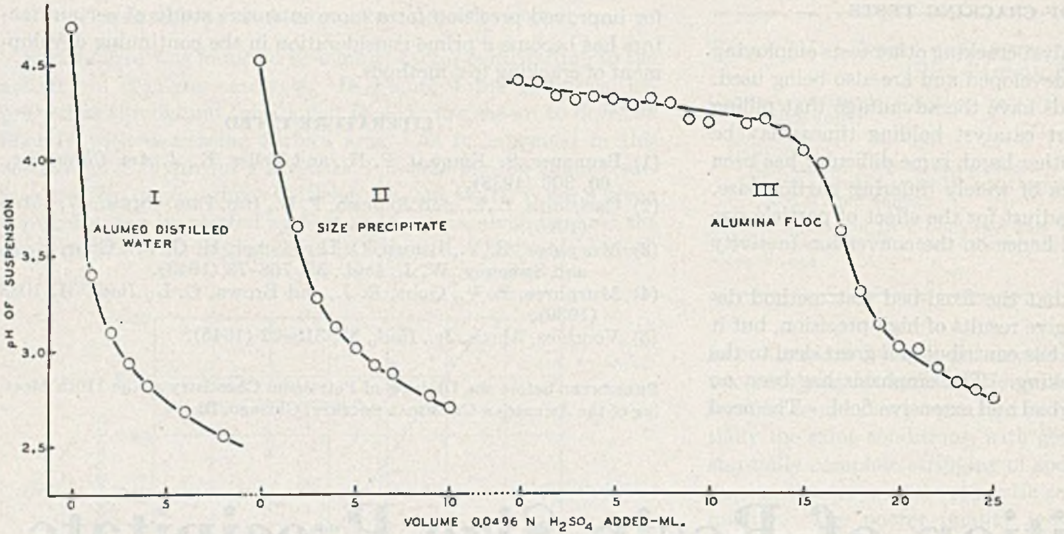

Figure 1. Comparison of Potentiometric Curves for Standardized Size Precipitate and for Alumina

treated with alum to a final pH of 4.5. Hence, it is obvious that excess alkali introduced in the water or in the pulp will cause the formation of alumina, which will coprecipitate with the normal size precipitate.

Another series of precipitates investigated were those made in sodium and calcium bicarbonate waters. They were chosen to parallel conditions of the paper sizing study described in a previous paper (*12*).

Former work on sizing in bicarbonate waters showed that the best sizing was achieved at a pulp slurry pH of about 6.5. Accordingly, precipitates were made in tap water, adjusted to pH 7.0 with sulfuric acid, to which 12.5 ml. of 6.05% sodium carbonate and, in some cases, 4.95 ml. of 10% calcium chloride were added per liter. Throughout this discussion alkaline hard waters refer to a bicarbonate ion concentration equivalent to 450 parts per million of calcium carbonate. Generally an equivalent amount of Ca^{++} ion was also present; the results were the same whether Ca^{++} ion was present or not. After this water was adjusted to pH 6.5 with sulfuric acid, 25 ml. of 3% size A was added per liter, and alum was added to the mixture to obtain a pH of 4.5. The possible change in the tap water composition from day to day was considered the most important uncontrolled variable in this procedure. That this was not generally serious can be seen in the reproducibility of results on different preparations shown in Table I. Three results of the eighteen determinations seem to be obviously in error; they have been omitted from the average. The rest of the data showed an acid requirement of 11.8 ml. of 0.0516 *N* sulfuric acid; the maximum variation from this value was 5%. Hence, size precipitate made under these conditions contained 21.0 ± 1.0% $Al(OH)_3$ based on the size or 17.4 + 0.9% based on the total precipitate. This amount of alumina in papers made in the presence of other alkalies was definitely detrimental to sizing (*14*). The sizing improvement obtained from a pulp slurry pH of 6.5 which was observed for treated bicarbonate waters must, therefore, be due to some other factor.

Table I. Alumina in Size Precipitates from Bicarbonate Water of pH 6.5 and Bicarbonate Content Equivalent to 450 P.P.M. $CaCO_3$

Ppts. in Order of Prepn.	0.0516 *N* H_2SO_4 Required by 100-Ml. Ppt. Suspension, Ml.	Ppts. in Order of Prepn.	0.0516 *N* H_2SO_4 Required by 100-Ml. Ppt. Suspension, Ml.
1	11.9	9	11.8
2	(13.5)[a]	9	11.6
3	(13.8)[a]	10	11.8
4	11.7	10	11.3
5	(10.7)[a]	10	11.4
6	11.6	11	11.7
7	12.0	11	12.0
8	11.5	12	12.1
9	11.9	13	12.4
		Average	11.8

[a] Values in parentheses omitted from average.

A determination of alumina in size precipitate from calcium bicarbonate hard waters with adjusted pH (3.0 to 8.0) was also made; this corresponds to conditions studied by papermaking in a previous paper (*12*). The results are given in Table II and plotted in Figure 2. In order to apply the data from the wet suspension to computing percentage composition of the precipitate, the alumina has been regarded as $Al(OH)_3$ or $Al_2O_3.3H_2O$. The percentages computed on this assumption are plotted (Figure 2) against the pH of the water in which the corresponding precipitates were made. This shows no correlation with the analogous sizing curve of the preceding paper (*13*) for bicarbonate waters.

Conclusions. (*a*) A method of analysis for alumina in rosin size precipitate floc has been developed. (*b*) Use of this method showed that standardized size precipitates contain no alumina. (*c*) Alkali introduced into the papermaking system by water or pulp will react with alum to form alumina which will be coprecipitated with the alum-size precipitate.

DETERMINATION OF ALUMINA

Present opinions of the composition of rosin size precipitate and, therefore, of the roles of alumina and of aluminum ion in sizing are confused because no satisfactory analytical methods have been available for the determination of alumina, aluminum resinates, and free resin acids, as such, in the precipitate which is formed. [Methods reported in the literature for the study of the composition of the precipitate consisted of determinations of total ash and of solvent extractions (*16*). Later work will consider the effect of the presence of cellulose on the size precipitate composition. The existence of such an effect has been emphasized in Bialkowsky's work (*2*) which preceded more recent studies of base exchange capacity of cellulosic material.] The first effort made in this work to determine alumina, as such, in the presence of aluminum resinates and of resin acids was by x-ray studies. Various size precipitates, prepared at beater concentrations of size and of alum were vacuum dried and examined. They were all amorphous, although some exhibited a halo at 5.8 Å. A sample of alumina was then prepared by adding alum to a 0.0133% sodium carbonate solution to a pH of 4.5. (This solution is equivalent in concentration to 3.0% size based on pulp of 2.5% consistency.) The precipitate was filtered off, washed free of sulfate (barium chloride test) with 0.01 *M* ammonium hydroxide, and dried in a vacuum desiccator. This alumina sample was completely amorphous by x-ray examination and showed only one faint line by electron diffraction. It seems quite likely, therefore, that any alumina present in size precipitate will be amorphous and not detectable by these physical means. Refractive indices were equally ineffective for this analysis.

Development of Titration Method. The difficulties of quantitative titration of aluminum salts with alkalies are well known (*6*). Some of the difficulties are introduced by the heterogeneity of the reaction mixture and by the characteristic surface properties of the alumina formed. For a titration of alumina with acid, however, the end point would occur with a homogeneous system. It was therefore decided to attempt a titration of dilute alumina suspensions with dilute standard acids. After each addition of acid the mixture was stirred until the pH was constant; this meant 2 hours in some cases and days in others. A rapid titration was impossible and would give meaningless curves, since the reaction was not complete until an appreciable time after the acid had been added.

Alumina suspensions were prepared by adding alum to an ammonia solution of pH 10 to obtain a pH of 4.5. Standardized size precipitates were prepared by adding 25 ml. of 3% size A (70% total solids, 20% free rosin) to a liter of distilled water and adding alum to pH 4.5. A 100-ml. sample of suspension was used for the titrations, and 0.05 *N* acid was added in 1-ml. portions. The suspension was stirred vigorously throughout the determination, and the steady pH was recorded when it was attained after each acid addition. Not only was the reaction slow, but attainment of equilibrium of the glass electrodes of the Beckman industrial-model pH meter with the suspension required an appreciable length of time; occasionally the electrodes had to be cleaned with acid. Consequently, the curves of Figure 3 portray determinations which extended over a period of days.

Curves III and IV of Figure 3 show that the alumina suspensions maintained their pH above 4 until practically all of the floc had reacted with the acid. The pH then dropped comparatively rapidly; pH 3.5 seemed to be the point of inflection. These curves are quite different from those reported by Datta (*5*) for alumina sols. His curves showed nothing corresponding to the point of inflection at pH 3.5. All the titrations of Figure 3 were carried out with 0.05 *N* sulfuric acid, except for curve IV in which hydrochloric acid was used. Although curve V shows, for a suspension of the amorphous alumina prepared for x-ray examination, a behavior very similar to suspensions in which the alumina has not been dried, subsequent preparations of dried alumina exhibited insolubilized portions of the material. Hence, these determinations have been applied only to wet flocs and to those of less than two weeks' age.

In contrast to the curves of alumina, curve I is the control, a titration of distilled water adjusted with alum to pH 4.5. Curve II is for a standard size precipitate; while it required more acid to reach pH 3.5 than did the control, the form of its curve is quite distinct from that of the alumina curve. Curve VI shows that an artificial mixture of 50% alumina suspension and 50% size precipitate suspension required slightly more than half the acid demanded by an equal amount of alumina suspension. This would be expected from the acid requirements shown by curve II (size precipitate); and by curve III (alumina). Curve VII for a soft tap water adjusted with alum to pH 4.5 shows that this procedure detected small amounts of alumina. Finally, curve VIII illustrates the fact that, when size precipitate was prepared in alkaline water, all of the excess alkali reacted with alum to form alumina, which, in such cases, was coprecipitated with the size. There seems no doubt that this procedure offers a method of determining the relative amount of alumina present in a given size precipitate mixture.

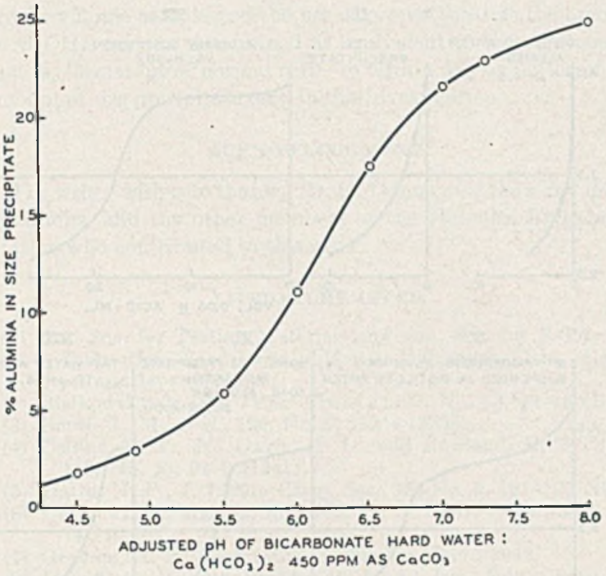

Figure 2. Alumina Formed in Size Precipitates in Alkaline Hard Water

Table II. Alumina in Size Precipitates Made in Alkaline Hard Water of 450 P.P.M. $Ca(HCO_3)_2$ as $CaCO_3$

pH of Water Adjusted with H_2SO_4[a]	0.0516 *N* H_2SO_4 Used by 100-Ml. Size Ppt. Suspension. Ml.	0.0516 *N* H_2SO_4 Required by Alumina in Size Ppt. Suspension, Ml.	$Al(OH)_3$/0.75 G. Size, G.	$Al(OH)_3$ in Total Size Ppt., %	Al from $Al(OH)_3$ in Total Size Ppt., %
3.0	...	...	0[b]	0	0
4.5	4.65	1.05	0.0138	1.81	0.63
4.9	5.32	1.72	0.0227	2.94	1.02
5.0	...	...	....	...	1.19[b]
5.5	7.14	3.54	0.0466	5.85	2.03
6.0	10.65	7.05	0.0928	11.00	3.80
6.5	16.60	12.00	0.158	17.4	6.02
7.0	19.23	15.63	0.206	21.5	7.44
7.3	20.48	16.88	0.222	22.8	7.88
7.5	...	...	....	...	8.15[b]
8.0	22.03	18.43	0.248	24.8	8.58
Control (standardized size ppt.)	3.60	0.0	....	0	0

[a] This adjustment frees CO_2 which is not immediately lost from system; hence adjusted waters are not at equilibrium when used.

[b] Interpolated.

Revised Method. Because these determinations were so tedious, and because of the possibility of errors being introduced during the lengthy procedure, a revison was made to allow greater speed and accuracy. As before, a 100-ml. sample of the dilute alumina suspension was used. An excess of 0.05 *N* acid, generally 25 ml., was added to this. If the approximate amount of alumina is unknown, the excess of acid must be determined. Any amount of acid which produces a solution of pH less than 3.5 after reaction is adequate. In general, an excess to give pH 2.5 or less was used. The mixture was allowed to stand overnight, although a shorter time may be used in most cases, and then back-titrated to pH 3.5 with 0.05 *N* sodium hydroxide. The equivalence of the two methods may be illustrated by the following typical determinations on 100-ml. portions of the same alumina suspension at pH 4.5:

	Original Method	Revised Method
Vol. 0.0494 *N* H_2SO_4 to attain pH 3 5, ml.	19.5	19.4
Vol. control (100 ml. distilled water plus alum, pH 4.5), ml.	0.5	1.0
Vol. acid required by alumina present, ml.	19.0	18.4
Time required by determination, days	19	0.67

The two methods, therefore, agreed within about 3.0%, and much of this difference could have been introduced by extraneous factors such as laboratory fumes, rinsing of electrodes, etc., which would affect the 19-day determination. Hence, the revised method was used for the rest of the work. [This revised method is similar to a procedure used by Graham (*7*) in the analysis of hydrous alumina sols. It differs in the nature of the starting material and in the end point of the back-titration. However, the principle is the same in both cases.]

As had been indicated in the preliminary work, the relative amount of alumina in prepared mixtures of alumina and size precipitate suspensions could readily be found. For such determinations the control used was the standardized size precipitate at pH 4.5 rather than distilled water alumed to pH 4.5. As indicated in Figure 3, the size precipitate consumed, probably byhydrolysis, some of the acid which was added.

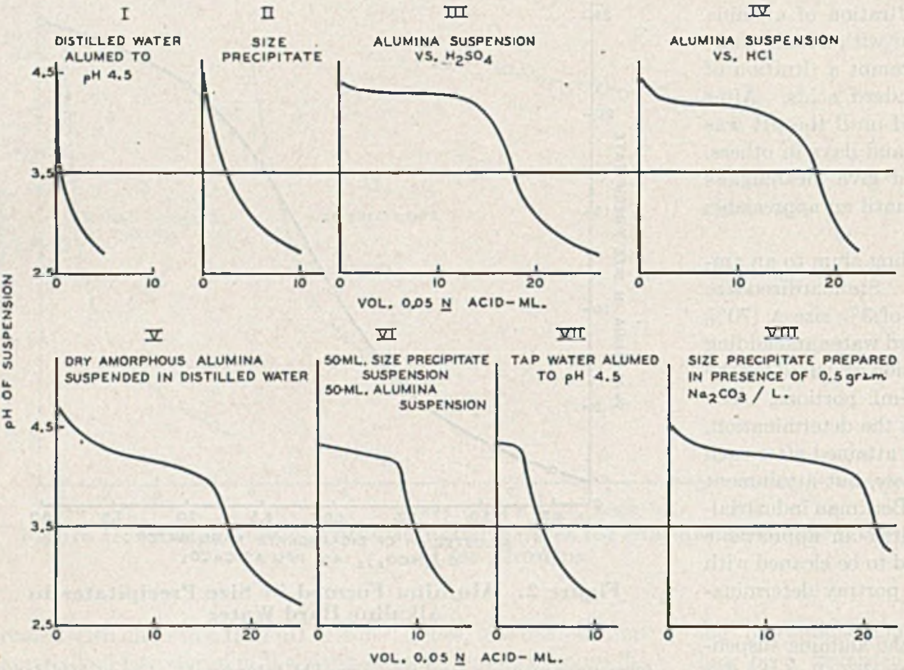

Figure 3. Potentiometric Curves for Various Suspensions

CHEMICAL FORM OF ALUMINA

Although the method just described offers a fairly convenient way of determining relative amounts of alumina present, the absolute quantity cannot be determined until the chemical form of the alumina, and its reaction with acids, is known. Mellor (*10*) lists a multitude of basic aluminum salts which various investigators have reported; both soluble and insoluble sulfates are included. Miller (*11*) believes that the alumina floc at pH 5.4 is the basic salt $5Al_2O_3.3SO_3.4H_2O$, and that $Al(OH)_3$ is formed only at pH 8.7. Weiser *et al.* (*19*) report an insoluble product of the approximate composition $Al_2O_3.SO_3.1.5H_2O$ which loses no SO_3 at 600° C. and decomposes at 700° C. This material was obtained from aluminum sulfate solutions at pH <5.5 and gave an x-ray diffraction pattern different from that of γ-$Al_2O_3.H_2O$. However, Imhoff and Burkhardt (*8*) could not identify the alumina in flocs at pH 4.5 as a basic salt. Alumina prepared at pH 4.5 for this work and examined by x-ray was either amorphous (one sample) or gave the pattern for boehmite, γ-$Al_2O_3.H_2O$ (several samples). Therefore, the floc at pH 4.5 was considered to be essentially $Al(OH)_3$. It is realized, of course, that the aluminum ion is highly hydrated, and that a variety of physicochemical changes occur in the course of aging the floc (*18*). No study was made of this aspect of the subject, but its probable influence was recognized by the specifications given here for the preparation and age of the suspensions.

If $Al(OH)_3$ is the skeletal formula for the initial material, then it reacts with sulfuric acid to form $Al_2(SO_4)_3$ or some soluble basic sulfate at pH 3.5. Mellor (*10*) mentions several such sulfates, and Wilson (*20*) has patented the preparation of $Al_2O_3.2SO_3.9H_2O$. When the titration (preliminary method) of the alumina suspension was stopped at pH 3.5 and the solutes were recovered by evaporating this solution, the solid material was amorphous to x-ray examination. After standing for 10 days, the material gave a faint x-ray diffraction pattern; after heating to 370° or 430° C., its x-ray pattern was definite but did not correspond to any in Hanawalt's catalog (*1*). When the material was heated to 550° C., the x-ray pattern was that of anhydrous $Al_2(SO_4)_3$. A sample of Merck's C.P. $Al_2(SO_4)_3.18H_2O$ showed the x-ray pattern reported by Hanawalt for this hydrate. Upon heating to 200° C., the material became amorphous. Further heating to 430° C. converted it to anhydrous $Al_2(SO_4)_3$. The x-ray evidence is, therefore, inconclusive as to the product of the reaction; the intermediate pattern might be that of a basic sulfate or of a hydrate other than the common one of $Al_2(SO_4)_3$. Many other hydrates have been mentioned, but their x-ray patterns are not available.

An indirect method of determining the reaction product is through the acid requirement of a definite amount of alumina. Thus:

$$2Al(OH)_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 6H_2O \quad (1)$$

$$2Al(OH)_3 + 2H_2SO_4 \longrightarrow 2Al(OH)SO_4 + 4H_2O \quad (2)$$

$$2Al(OH)_3 + H_2SO_4 \longrightarrow Al_2(OH)_4SO_4 + 2H_2O \quad (3)$$

are some possible reactions if the basic sulfates shown are soluble. However, the acid requirements are distinctly different, and all samples titrated indicate that the reaction is according to Equation 1 (Table III).

Another indirect method of establishing the reaction product was used. To determine the amount of alumina present in dilute suspensions as accurately as possible, 1-liter samples of the suspension were used instead of 100-ml. samples. The first suspension was prepared by adding alum to tap water to pH 4.5. A control was prepared by adjusting the pH of tap water to 4.5 with sulfuric acid. The 1-liter samples were first run in duplicate by the revised method. The data obtained were:

Sample		0.0512 *N* H_2SO_4 Required, Ml./Liter
Alumina floc suspension 1		33.24 33.26
	Average	33.25
Control		7.89 7.91
	Average	7.90

One liter of this alumina suspension, therefore, required 25.35 ml. of 0.0512 *N* sulfuric acid to dissolve the floc. If the reaction results in the formation of the normal $Al_2(SO_4)_3$, this amount of acid is equivalent to 11.7 mg. per liter of aluminum in the floc as alumina.

Samples of this same suspension and of its clear supernatant liquor were acidified and analyzed for total aluminum content by the haematoxylin method (*17*). The determination gave:

Sample	Total Al (Haematoxylin Method), Mg./Liter
Alumina floc suspension 1	31, 31
Supernatant liquor	20, 20
Difference, Al in floc	11

By these analyses, the aluminum in the alumina floc amounts to 11 mg. per liter. This is an excellent agreement with the 11.7 mg. per liter found by acid titration, on the assumption of the formation of $Al_2(SO_4)_3$, in view of the limitations of the colorimetric analysis.

SUMMARY OF METHOD

X-ray work has shown that the alumina from a floc at pH 4.5 is aluminum hydroxide rather than a basic sulfate. (The x-ray evidence of boehmite and, therefore, of $Al(OH)_3$ as the initial

TABLE III. ANALYSIS FOR ALUMINA ON VARIOUS FLOCS

Alkali Used to Prepare Alumina at pH 4.5	Alkali/Liter Milliequivalent (Milliequivalent Required by Equation 1[a])	H_2SO_4 Required to Dissolve Alumina, Milliequivalent/Liter	Milliequivalent Required by Equation 2[a]	Size Present
Na_2CO_3	29.8[b]	30.0[c]	19.7	Yes
$NaHCO_3$	9.5[d]	9.7[d]	6.3	No
NaOH	6.8[b]	6.9[d]	4.5	No
NaOH	3.2[b]	3.1[d]	2.1	Yes
NaOH	6.9[b]	6.9[d]	4.6	Yes
NaOH	12.1[b]	12.3[d]	8.0	Yes

[a] Equations: (1) $2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O$; (2) $2Al(OH) + 2H_2SO_4 \rightarrow 2Al(OH)SO_4 + 4H_2O$.

[b] By titration of alkali with standard acid.

[c] By titration of suspension with 0.05 N H_2SO_4, original method.

[d] By titration of solution or suspension with 0.05 N H_2SO_4, revised method.

material does not rule out the possible presence of basic salts amorphous to x-ray examination, in which $Al(OH)_3$ is present as a unit in a larger structure. For example, Kohlschütter (*9*) proposes a basic salt of the composition $AlCl_3.2Al(OH)_3$. Acid would attack such a structure with the removal of the alumina, and the presence of the normal salt would have no effect on the titration. However, the analytical determination of $Al(OH)_3$ as a chemical unit is attained whether the initial material is in the complex or the simple form.) When such a floc has reacted with sulfuric acid and therefore obtained a pH of 3.5, the product in solution is the normal aluminum sulfate. On this basis the revised method of determining alumina in dilute suspensions and in the presence of size precipitate gives the absolute amount of alumina in the sample. It may be used on fresh (aged not more than 2 weeks) wet precipitates (pH 4.5), and consists of adding a known amount of 0.05 N sulfuric acid (in excess of amount required by the alumina present) to the sample, allowing 16 hours for complete reaction, and back titrating to pH 3.5 with 0.05 N sodium hydroxide standardized against the standard sulfuric acid. The presence of materials other than size and alumina does not interfere unless such materials form a complex with alumina or show buffering action between the pH values 4.5 and 3.5. With the proper volume sample and the use of proper controls the amount of $Al(OH)_3$ may be determined as equivalent to the acid used—that is, formation of normal salt—to within 5% or better of the amount of size precipitate used in this investigation.

ACKNOWLEDGMENT

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Molal Refractions of Mononuclear Aromatic Hydrocarbons

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The molal refractions of mononuclear aromatic hydrocarbons are additive in a homologous series, and may be expressed by an equation of the form $R = k + an$, where R is molal refraction, calculated by either the Lorenz-Lorentz formula or the Gladstone-Dale formula, and n is the number of carbon atoms. Constants a and k have been evaluated by the method of least squares for fourteen homologous series of mononuclear aromatic hydrocarbons.

A RECENT collation and critical evaluation of data on physical constants (*3*) has made readily available all recorded values for density and refractive index of mononuclear aromatic hydrocarbons. These data have been used to evaluate the effect of structure on molal refraction, which is both an additive and a constitutional property. It cannot be predicted, therefore, unless the effects of structure are known. Molal refraction depends on refractive index, density, and molecular weight. For comparative studies molal refraction is preferred to refractive index because of the minimization of effects of temperature and density.

Molal refractions of aliphatic hydrocarbons for the sodium D line are additive within a single homologous series. For many series of aliphatic hydrocarbons the effect of adding a CH_2 group is constant (*13*). The effects of structure, such as increments in molal refraction caused by branching and by unsaturation, have been thoroughly investigated and evaluated for aliphatic hydrocarbons (*7, 8, 13*).

Physical constant data for aromatic compounds are not nearly so complete as those for the aliphatics. They are, however, sufficient to permit evaluation of the relation between molal refraction and the number of carbon atoms for fourteen homologous series of mononuclear aromatic hydrocarbons.

CALCULATIONS

Molal refractions have different numercial values, depending on how they are defined. The different systems are internally consistent, but values based on different definitions cannot be compared with one another. A number of different definitions have been proposed. The Lorenz-Lorentz equation was developed from the electromagnetic theory of light and, therefore, has a theoretical basis (*11*, *12*). Most of the other formulas are purely empirical, but their relative ease of calculation has led to their continued use. Two of the more widely employed empirical relations are the Gladstone-Dale (*6*) and the Eykman (*4*) formulas. Molal refractions for the sodium D line, calculated by three equations, were used in the present study:

Lorenz-Lorentz formula,

$$R_L = \frac{M}{\mathrm{d}}\,\frac{(n_{\mathrm{D}}^2 - 1)}{(n_{\mathrm{D}}^2 + 2)} = V\,\frac{(n_{\mathrm{D}}^2 - 1)}{(n_{\mathrm{D}}^2 + 2)} \tag{1}$$

Gladstone-Dale formula,

$$R_G = \frac{M}{\mathrm{d}}\,(n_{\mathrm{D}} - 1) = V\,(n_{\mathrm{D}} - 1) \tag{2}$$

Eykman formula,

$$R_E = \frac{M}{\mathrm{d}}\,\frac{(n_{\mathrm{D}}^2 - 1)}{(n_{\mathrm{D}} + 0.4)} = V\,\frac{(n_{\mathrm{D}}^2 - 1)}{(n_{\mathrm{D}} + 0.4)} \tag{3}$$

where R_L, R_G, and R_E = molal refraction, M = molecular weight, d = density, V = molecular volume, and n_{D} = refractive index.

It has been stated that molal refraction is virtually unaffected by temperature (*1*, *6*). However, later studies show that the effect of temperature on molal refraction is actually significant for R_L and R_G. R_L increases with increasing temperature, whereas R_G decreases with increasing temperature. The Eykman formula was developed empirically for the purpose of minimizing variations caused by temperature, and for many compounds the change in R_E is negligible over a wide range of temperature. The validity of the Eykman formula was confirmed by Gibson and Kincaid (*5*) in their outstanding work on the effect of temperature and pressure on benzene.

The rate of change of molal refraction with temperature depends on the relation of the temperature coefficient of density to that of refractive index. Kurtz and Ward (*10*) showed that this relation is nearly constant for a large number of compounds, and may be expressed by the equation,

$$\Delta n_{\mathrm{D}} = 0.60\ \Delta \mathrm{d} \tag{4}$$

When Equation 4 holds, R_E is affected very little by temperature. However, when the temperature coefficients of both density and refractive index are evaluated from experimental data, their ratio frequently deviates from the theoretical value of 0.60, and R_E is not constant over a range of temperature. The data on aromatic compounds are insufficient to determine whether all the variations are caused by inaccurate experimental values, or whether the value of 0.60 should be modified for some types of compounds. Since the rate of change of molal refraction (R_L, R_G, or R_E) with temperature is dependent on the ratio of the temperature coefficients, it varies for different compounds, so that molal refraction cannot be converted from one temperature to another unless the temperature coefficient is known for the compound in question. Table I gives two examples of the variation of molal refraction with temperature. The values for R_L, R_G, and R_E are calculated from experimental data (*3*) and the temperature coefficients of density and refractive index. In order to eliminate discrepancies owing to temperature, densities and refractive indices at 20° C. were used throughout this study.

Table I. Temperature Variation of Molal Refraction

Temp., ° C.	Toluene			9-p-Tolyloctadecane		
	R_L	R_G	R_E	R_L	R_G	R_E
0	31.00	52.83	69.44	114.50	193.98	255.64
20	31.06	52.75	69.43	114.73	193.91	255.80
40	31.12	52.66	69.43	114.95	193.83	255.94
60	31.17	52.57	69.41	115.14	193.71	256.04
80	31.23	52.45	69.39	115.36	193.62	256.18
100	31.27	52.38	69.37	115.56	193.52	256.32
% change	0.87	0.86	0.10	0.92	0.24	0.27

The relation of molal refraction to the number of carbon atoms may be expressed by an equation of the form,

$$R = k + an \tag{5}$$

where R = molal refraction and n = the number of carbon atoms.

For the aliphatic compounds constant a had the same value for all homologous series studied, except that the first member of a series was often anomalous. Constant k varied from series to series. The value of a as determined by Huggins (*7*) was 7.815 for R_G. The values of a calculated from the density and refractive index data given by Taylor *et al.* (*13*) were 4.640 for R_L, 7.810 for R_G, and 10.314 for R_E.

The constants of Equation 5 were evaluated for fourteen homologous series of aromatic hydrocarbons by the method of least squares. Contrary to the results with aliphatic hydrocarbons, the values for a as well as for k were found to vary in some cases from series to series, as Table II shows. For five series, a is significantly different from the value of a for the 1-phenylalkanes. These series are the 2-phenylalkane, phenylcyclane, 1-cyclopentyl-n-phenylalkane, 1-phenyl-1-alkene, 1-n-diphenylalkane, and 1,1-diphenyl-1-alkene.

DISCUSSION OF RESULTS

Molal refraction of hydrocarbons appears to depend primarily on the bonding electrons (*10*), and numerous attempts have been made to calculate molal refractions by simply adding atomic refractions and/or bond refractions (*1*, *2*, *9*). This method disregards the influence of one part of a molecule on another, and leads to identical refractions for structural isomers. More accurate determinations of molal refractions have shown significant differences between isomers, an indication that structural

Table II. Constants of Molal Refraction Equations at 20° C.

Series	No. of Compounds	Equation 1 (Lorenz-Lorentz)			Equation 2 (Gladstone-Dale)			Equation 3 (Eykman)		
		k	a	Deviation	k	a	Deviation	k	a	Deviation
1-Phenylalkane	11	−1.46	4.653	±0.005	−1.87	7.839	±0.009	−2.69	10.347	±0.011
2-Phenylalkane	12	−1.23	4.618	±0.013	−1.73	7.790	±0.019	−2.48	10.283	±0.032
o-Dialkylbenzene	5	−1.30	4.639	±0.018	−1.64	7.828	±0.035	−2.48	10.333	±0.045
m-Dialkylbenzene	6	−1.25	4.652	±0.018	−1.65	7.845	±0.037	−2.41	10.354	±0.042
p-Dialkylbenzene	16	−1.06	4.643	±0.005	−1.39	7.836	±0.010	−2.07	10.343	±0.015
Phenylcyclane	5	−1.86	4.514	±0.054	−3.25	7.747	±0.104	−4.27	10.157	±0.130
1-Cyclopentyl-n-phenylalkane	5	−0.72	4.448	±0.048	+0.14	7.501	±0.097	−0.57	9.904	±0.108
1-Phenyl-1-alkene	5	+2.74	4.248	±0.051	+6.65	7.097	±0.098	+3.97	9.807	±0.070
1-Phenyl-(n − 1)-alkene	6	−2.12	4.643	±0.019	−2.86	7.839	±0.035	−4.94	10.409	±0.052
2-Phenyl-2-alkene	5	−1.39	4.637	±0.064	−0.83	7.794	±0.140	−1.32	10.254	±0.214
1-Phenyl-1-alkyne	5	−3.71	4.848	±0.122	−5.06	8.201	±0.262	−7.30	10.802	±0.315
1,1-Diphenylalkane	6	−5.06	4.655	±0.012	−4.96	7.820	±0.020	−8.41	10.336	±0.026
1 n-Diphenylalkane	7	−7.66	4.795	±0.087	−6.13	7.890	±0.120	−10.30	10.450	±0.173
1,1-Diphenyl-1-alkene	9	−7.44	4.787	±0.057	−8.03	8.051	±0.099	−12.91	10.635	±0.130

factors have an appreciable effect on refraction. The variations in the value of constant a among the series covered in this study are probably accounted for by structural factors. The differences in constant a are in many cases statistically significant, as indicated by the standard deviations of a shown in Table II.

One of the earliest noted discrepancies between calculated and observed molal refractions was the optical exaltation caused by the presence of conjugated double bonds. This exaltation is a factor in some of the series covered in this study. The benzene ring does not exhibit exaltation, but conjugation of a double bond in a side chain with the double bonds of the benzene ring leads to marked exaltation. This effect is shown by both 1-phenylalkenes and 1,1-diphenylalkenes with the double bond in the 1-position. Compounds with a double bond in the side chain not conjugated with the double bonds in the benzene ring do not exhibit this phenomenon. For example, 1-phenylalkenes with the double bond at the opposite end of the chain from the benzene ring have lower molal refractions than the corresponding phenylalkanes. A triple bond conjugated with the double bonds of the benzene ring does not lead to exaltation, and compounds of the 1-phenyl-1-alkyne series have lower molal refractions than the corresponding phenylalkanes.

Other structural effects may be noted by comparison of some of the series. Greater molal refractions are exhibited by 1-phenylalkanes than by the corresponding 2-phenylalkanes. Change of the substituent on benzene from an alkane to a cyclane decreases the molal refraction, as shown by the fact that phenylcyclanes have lower refractions than the corresponding phenylalkanes. Diphenylalkanes with the phenyl groups at opposite ends of the chain (1-n-diphenylalkanes) have greater molal refractions than the corresponding compounds with both phenyl groups on the first carbon atom (1,1-diphenylalkanes). Among the dialkyl benzenes, the ortho compounds have the smallest refractions. The values for meta and para isomers are practically the same. Meta compounds with fewer than twenty carbon atoms have slightly lower refractions than the corresponding para structures; above $n = 30$ the reverse is true.

An attempt was made to determine the effect of branching and of position and type of unsaturation in side chains on molal refraction, but the data were too few and too inconsistent to permit statistical analysis. In general, the effect of structure on molal refractions appears to be more pronounced among mononuclear aromatics than among the aliphatic hydrocarbons.

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Effect of Humidity on Properties of Plasticized Ethylcellulose

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The purpose of this investigation was to study the effect of varying humidities on the properties of plasticized ethylcellulose, using a typical nonsolvent and a typical solvent modifier. Standard A.S.T.M. procedures were used for such properties as Izod impact, flexural and tensile strengths, as well as Rockwell hardness and heat distortion. Comparison of the effect of humidity with that of plasticizer content shows that the absorbed moisture changes all but one of the properties in the same direction. The similarity in the changes of properties of the two types of modifiers with increasing moisture content is discussed, as the results indicate the necessity for a review of the method for defining plasticizers used in ethylcellulose.

IN MANY plastics the variation in climatic conditions affects the properties of the material to a considerable extent. The quantitative amount is of importance to the engineer and chemist making use of the plastic. It is known that temperature affects the properties of plastics to a considerable extent (*4, 5, 6, 14, 15, 18*). Published information on the effect of humidity on physical properties of cellulosic plastic materials with various plasticizers has only recently appeared (*18, 20*). The purpose of this investigation was to evaluate the effect of humidity on the different properties of ethylcellulose when plasticized with a typical nonsolvent and a typical solvent modifier.

Current theories regarding the function of plasticizers frequently differentiate between two types (*11, 17*)—namely, the solvent types, which are generally considered to have a definite effect on the polymer, and nonsolvent types, which do not show a solvent effect or, at most, only a slight swelling action at elevated temperatures.

Two representative plasticizers were selected—butyl stearate (solvent type) and a mineral oil (nonsolvent type). The method of Fordyce and Meyer (*7*) was used in this evaluation for determining solvent effect on the resin. A 10-gram sample of the polymer is placed in 100 cc. of the test plasticizer and heated for one hour at 180° C. At the end of this period the test tube is removed from the bath and the contents examined. The chemical is considered to be of the solvent type if a completely clear solution is obtained. If large globules or masses of undissolved portions of the plastic remain, the plasticizer is a nonsolvent. Gradations between these two limits are noted and considered as semisolvent type or seminonsolvent in activity. In this test at 180° C. the ethylcellulose is substantially dissolved by the butyl stearate, while the mineral oil does not dissolve any noticeable portion of the polymer.

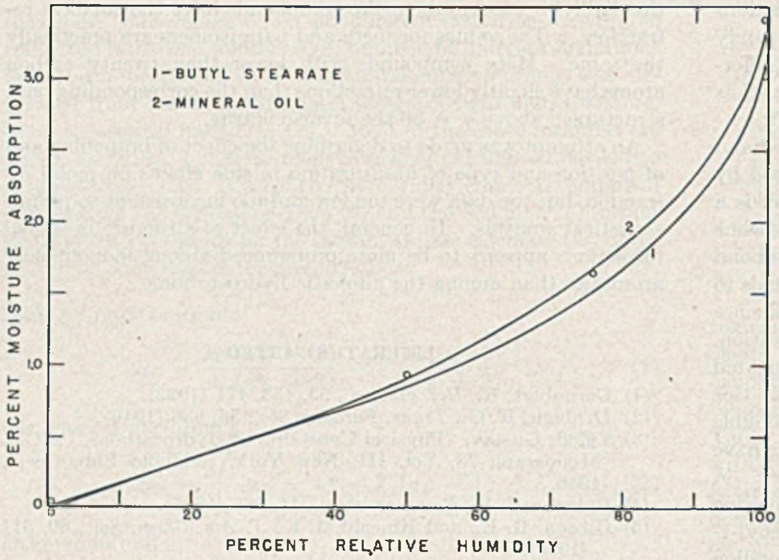

Figure 1

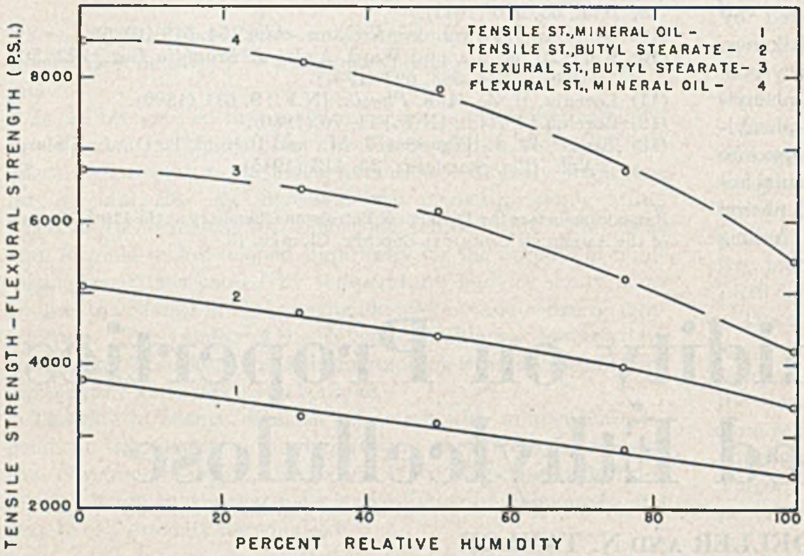

Figure 2

Other methods, such as casting films containing the plasticizer used to evaluate its effect on polymers (*8*), also show the difference in the action of butyl stearate and mineral oil on ethylcellulose.

FORMULATIONS

The experimental compositions were prepared to contain 100 parts (86.2%) ethylcellulose, 15 parts (12.9%) plasticizer, and 1 part (0.9%) stabilizer. The ethylcellulose had an ethoxyl content of 46.3% and a viscosity of 103 centipoises. The viscosity (*8*) was determined by drying the flake for 30 minutes at 100° C. and then making a 5% by weight solution, the solvents being a 70:30 mixture of toluene and ethyl alcohol (95% 2B denatured). The ethoxyl content is obtained by a semimicromethod in a modified Zeisel apparatus (*19*). The plasticizers were of standard commercial quality, the mineral oil being mainly aliphatic in nature and meeting the specifications of 0.860–0.870 specific gravity at 60° F., a Saybolt viscosity at 100° F. of 125–135, and a pour point of 10° F.

The plasticizers with the flake were processed in a small laboratory Banbury mixer. The material, after thorough mastication for 5 minutes at 300° F., was removed from the mixer, sheeted on a small two-roll mill, and ground into powder through a standard rotary grinder, using a screen opening of $^{5}/_{16}$ inch. The plastic materials were dried for 30 minutes under infrared lamps to remove all residual moisture and molded on a 1-ounce injection molding machine into A.S.T.M. test bars. The machine, described by Ball, Leyes, and Melnychuk (*2*), is similar in design to the two-piston hydraulically operated units used in the injection molding industry. The mold contains two test bar cavities of polished steel $5 \times {}^{1}/_{2} \times {}^{1}/_{8}$ inch in size.

In molding the test compositions all variables except the cylinder temperatures were kept constant. The cycle was held at 30 seconds and the mold temperature at 120° F. The piston pressure and speed did not change during the collection of samples. In each composition the lowest injection molding temperature to fill the mold completely with plastic was determined under the above conditions. An operating temperature of 50° F. higher on both the front and back cylinders was then used for producing samples. This procedure gives reproducible operating conditions and is necessary in order to make a valid comparison of the physical properties of plastic compositions of different formulation, according to Ball, Leyes, and Melnychuk (*2*).

The A.S.T.M. tensile test pieces were molded on a 2-ounce injection molding machine (Reed Prentice Corporation, model 10A). A cycle of 45 seconds was used, and all other variables were held constant except temperature. The temperature was determined as above for this machine and a two-cavity tensile bar die. The molding temperature for producing specimens was 50° F. above the lowest value found to give a complete molding. Sufficient samples were molded to obtain all properties at the various conditions tested, and random selection was used in taking pieces for any given test and condition.

TEST METHOD

American Society for Testing Materials methods were used (*1*). The main difference in the evaluation was the use of preconditioning at the various humidities, as explained later.

The impact strength tests were carried out in accordance with A.S.T.M. Standard D256–43 (Method A). The Izod impact specimens are cut 2.5 inches long from the center of the molded bar. The notching is done on a shaper to a depth of 0.100 inch. The flexural strength evaluation was carried out according to A.S.T.M. Standard D650–43T. A bar, $5 \times {}^{1}/_{2} \times {}^{1}/_{8}$ inch, was used. Young's modulus is calculated from the flexural strength test data. The tensile strength procedure is outlined in A.S.T.M. Standard D638–44T. Tests for distortion under heat were carried out in accordance with A.S.T.M. Method D648–45T except that the specimen, instead of being solid bars $5 \times {}^{1}/_{2} \times {}^{1}/_{2}$ inch, was made up by compositing four thinner bars placed in close proximity and held together at their ends by elastic bands. The direction of load application was perpendicular to the shortest dimension of the individual bars. Laboratory tests show that this modification will give reproducible results and can be used for evaluating properties of different plastic materials. The Rockwell hardness was determined on the R scale, using A.S.T.M. Standard D785–44T. This requires a minor load of 10 kg. and a major load of 60 kg. with the use of a half-inch-diameter hardnened steel ball. The specimen was made up of two of the ends of a tensile strength bar, stacked on top of each other to make a block approximately $1 \times 1{}^{1}/_{2} \times {}^{1}/_{4}$ inch in size.

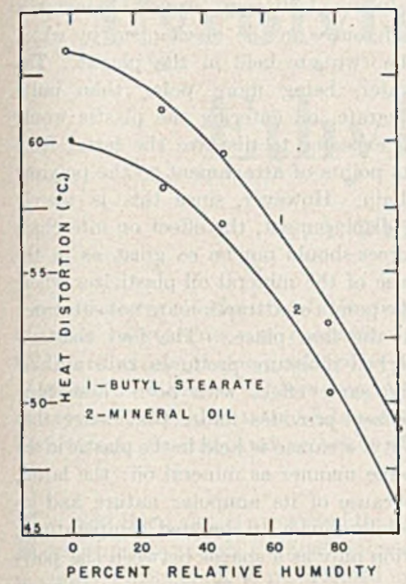

Figure 3

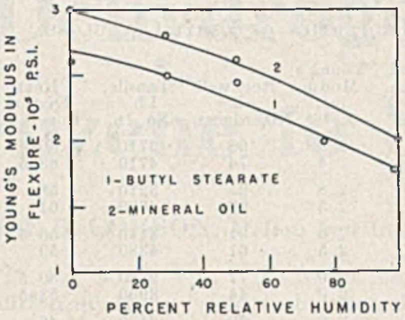

Figure 4

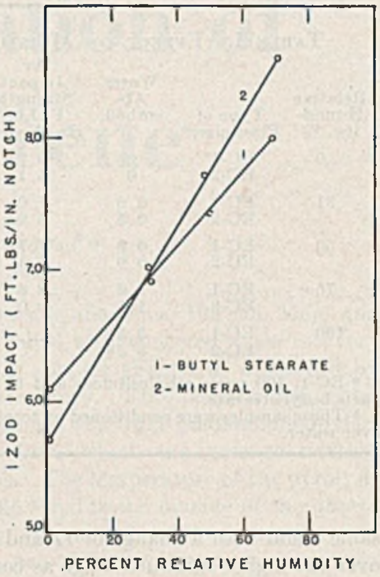

Figure 5

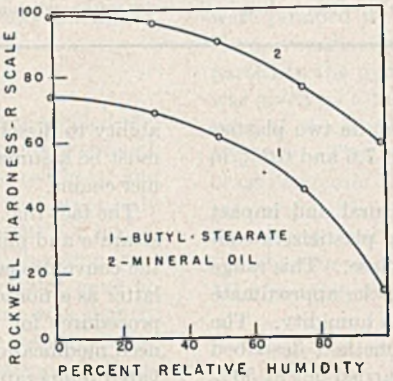

Figure 6

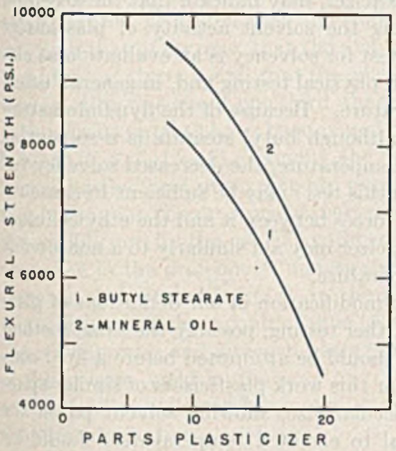

Figure 7

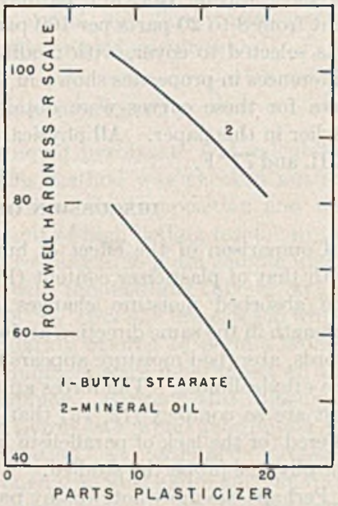

Figure 9

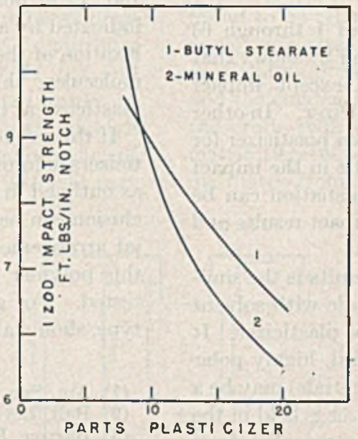

Figure 8

The percentage of water adsorbed was carried out by placing impact bars at 0% relative humidity for 10 days, obtaining their weight, then conditioning specimens at the various humidities for an equal length of time, and again weighing. The difference in weight divided by the original weight was taken as the percentage of water absorbed. The time for a 1/8-inch-thick sample to come to equilibrium had been previously determined to be 7–10 days.

CONDITIONING OF TEST SAMPLES

All samples were conditioned at 77° ± 2° F. (25° ± 1° C.) in the constant temperature test room. The various humidities were obtained by the following procedures: for 0% relative humidity, anhydrous calcium chloride; for 31% R.H., a saturated solution of calcium chloride. The 50% R.H. conditions were obtained in the test room, which is kept at this humidity; the 77% R.H., by conditioning over saturated sodium thiosulfate solution; the 100% R.H., by conditioning the samples over water.

With the exception of 50% R.H., the samples were prepared by separately inserting each bar in a test tube hung in a large, tightly covered jar containing the solution to give the proper humidity. The jars were held in the 77° F. test room, and at the end of 10-day conditioning, each jar was opened, each tube was immediately corked, and the pieces were tested as soon as possible. In all instances the results gave no greater variation from sample to sample than would be expected from the normal distribution of test results under each procedure.

EFFECT OF MOISTURE ABSORPTION

Table I and Figures 1 through 6 reveal that the physical properties of the plastic are substantially affected by absorption of moisture. Only Izod impact strength shows an increase with higher humidities. The change from mean conditions for flexural and tensile strengths, as well as Rockwell hardness, heat distortion, and Young's modulus, is greater in going to the higher than to the lower humidities. There is a change in flexural strength (Figure 2) of 31.2% for butyl stearate and of 31.6% for mineral oil, from 50–100% R.H., whereas the changes from 50 to 0% R.H. are only 9.8% for the solvent plasticizer and 7.6% for the nonsolvent. Similar but not so striking differences are observed in the other properties. The tensile strength (Figure 2) drops 22.6%, regardless of plasticizer, over the humidities of 50–100%, although in going to 0% R.H. the active-modified polymer increases in strength by 12.1% and the inactive-modified plastic by 18.2%. Heat distortion values (Figure 3) follow this

TABLE I. EFFECT OF MOISTURE ON PROPERTIES OF ETHYL CELLULOSE

Relative Humidity, %	Type of Plasticizer[a]	Water Absorbed, %	Av. Impact Strength, Ft.Lb./In. Notch	Flexural Strength, Lb./Sq. In.	Young's Modulus, $\times 10^5$	Rockwell R Hardness	Tensile, Lb./Sq. In.	Heat Distortion, ° C.
0	EC-1	0	5.7	8500	2.9	98	3710	60
	EC-2	0	6.1	6700	2.4	74	4710	63.5
31	EC-1	0.6	7.0	8200	2.8	95	3210	58
	EC-2	0.5	6.9	6400	2.5	67	4690	61
50	EC-1	0.9	7.7	7900	2.6	91	3140	56.5
	EC-2	0.9	7.3	6100	2.5	61	4380	59
76	EC-1	1.6	8.6	6700	2.0	77	2780	50.5
	EC-2	1.5	8.0	5200	2.0	44	3960	53.5
100	EC-1	3.3[b]	...	5400	2.0	59	2430	46
	EC-2	3.2[b]	...	4200	1.8	13	3390	49

[a] EC-1, 100 parts ethylcellulose and 15 parts mineral oil; EC-2, 100 parts ethylcellulose and 15 parts butyl stearate.

[b] These samples were conditioned by total immersion in water; others in this series were conditioned over water.

same trend with a change of 17 and 17.6% for the two plastics over the higher moisture range as compared to 7.6 and 6.2% in the lower range.

Figures 7, 8, and 9 show the effect on flexural and impact strength and on Rockwell hardness of varying plasticizers content from 8 to 20 parts per 100 parts ethylcellulose. This range was selected to cover, with modifier variation, the approximate differences in properties shown in the changes in humidity. The data for these curves were obtained by the method described earlier in this paper. All physical tests were carried out at 50% R.H. and 77° F.

DISCUSSION OF RESULTS

Comparison of the effect of humidity (Figures 1 through 6) with that of plasticizer content (Figures 7, 8, and 9) shows that the absorbed moisture changes all properties except impact strength in the same direction as does added plasticizer. In other words, absorbed moisture appears to be acting as a plasticizer for the ethylcellulose. The forces applied to a plastic in the impact test are so complex (*12, 13*) that no simple explanation can be offered for the lack of parallelism between the impact results and the physical properties studied.

Perhaps the most noteworthy point in these results is the similarity in the effect of moisture on the plastic made with solvent (butyl stearate) and nonsolvent (mineral oil) type plasticizer. It appears that this method of adding water (a third, highly polar component in plastics modified with different materials) may be a method for studying the manner which a plasticizer is held in the polymer.

It is generally accepted that a plasticizer functions by weakening the attractive forces between the polymer chains and thus permitting slippage of chain segments or chains past one another when the plastic is under stress (*16*). However, there has not been agreement on the way in which this was accomplished (*3*). Some investigators (*3, 16, 17*) believe that plasticizers act mechanically through their bulk to hold the chains apart and thus decrease the interchain forces merely by requiring them to act over a greater distance. Others (*10, 17*) have differentiated between polar and nonpolar plasticizers or solvent and nonsolvent plasticizers. In the latter theory it is assumed that the nonsolvent plasticizers act as chain separators or furnish a lubricating action, whereas the solvent types attach themselves to the polar points on the polymer chain (probably hydroxyl groups in the case of ethylcellulose) and thus reduce the interchain forces, both by pushing the chains apart and by saturating some of these forces. On this basis solvent type plasticizers should affect the properties in a different manner from those of the nonsolvent type (*9*).

The similarity in the effect of absorbed water on the physical properties of ethylcellulose plasticized with both solvent and nonsolvent plasticizers argues against any differences in the mechanism by which the two are held in the plastic. The water, being more polar than butyl stearate, on entering the plastic would be expected to displace the latter from its points of attachment to the polymer chain. However, since this is merely a displacement, the effect on interchain forces should not be so great as in the case of the mineral oil plasticizer where the points of attraction are not saturated in the first place. The fact that absorbed moisture produces substantially the same effect with both these plasticizers provides indirect evidence that butyl stearate is held in the plastic in the same manner as mineral oil; the latter, because of its nonpolar nature and inability to dissolve ethylcellulose even at elevated temperatures, must be assumed to function only as a spacer between the polymer chains.

The fact that the data show similarity in the behavior of butyl stearate and mineral oil over the range of humidities, in spite of the conventional classification of the former as a solvent and the latter as a nonsolvent plasticizer, may indicate that the accepted procedures for determining the solvent activity of plasticizers need modification. The test for solvency is an evaluation at elevated temperature, but all physical testing and, in general, usage is at or near room temperature. Because of the dynamic nature of the interchain forces, although butyl stearate is a solvent at 180° C. at normal room temperature, the decreased solvency (as indicated by a hazy gel in this test) may be sufficient to cause relaxation of the attractive forces between it and the ethylcellulose molecules; thus this plasticizer may act similarly to a nonsolvent plasticizer at the test temperature.

If this is the case, some modification in our definitions of plasticizers is in order, but further testing, possibly the same method as outlined in this paper, should be attempted before a final conclusion can be drawn. For this work plasticizers of similar spacial arrangement and molecular size, showing solvent power for this polymer from normal to elevated temperatures, should be tested. For general utility other plastics, probably of the vinyl type, should also be evaluated.

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Pyrolytic Dehydrogenation of Ethylbenzene to Styrene

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The efficiency of the pyrolytic dehydrogenation of ethylbenzene to styrene was determined at 700°, 750°, and 800° C. at atmospheric pressure in the absence and presence of steam as diluent. Operating with a 20% per pass yield of styrene, an ultimate yield of 55–60% was obtained, both in the absence and presence of steam.

IN 1869 Berthelot (*1*) reported that ethylbenzene yielded styrene upon pyrolysis. He passed gaseous ethylbenzene through an empty porcelain tube maintained at moderate red heat, and the conditions were such that the ethylbenzene was practically all decomposed. From the fraction boiling up to 250° C., he isolated benzene, toluene, styrene, and a xylene-ethylbenzene fraction which was mainly *p*-xylene. Although Berthelot gave no actual figures, he stated that the yield of benzene was slightly less than that of styrene, that the yield of toluene was about one third that of styrene, and that the yield of the xylene-ethylbenzene fraction was about one third that of toluene.

Numerous patents have been issued on the pyrolysis of ethylbenzene (*5, 6, 7, 11–15*). Among the various means claimed for increasing the yield of styrene are pyrolysis under reduced pressure (*15*) and in the presence of inert diluents (*12, 13*), disturbing the equilibrium by the use of hydrogen acceptors (*7, 11, 14*), and operation in the presence of undesirable by-products in order to suppress their formation (*14*), in the presence of steam at high temperature and short contact time (*5, 6*), and in the presence of organic chlorides and nitrogen bases (*13*). In this last case part of the styrene yield is due to chlorination followed by dehydrochlorination.

Relatively few studies have been made on the noncatalytic dehydrogenation of ethylbenzene to styrene. There are a few papers on the thermodynamics and mechanism of the reaction (*8, 9*), but most of the information is found in the claims of the patent literature. Berthelot's data (*1*) are only qualitative with respect to temperature and yield, and the two reports by Dobryanskiĭ and coworkers (*3, 4*) cover only the relatively low pyrolytic temperatures of 600° and 650° C.

This paper presents data on the relation of styrene yield to contact time and temperature in the absence and presence of steam. These noncatalytic data were obtained in order to have a measure for evaluating catalysis in the conversion of ethylbenzene to styrene.

APPARATUS AND PROCEDURE

Figure 1 is the flow diagram, and Figure 2 shows the details of the furnace and preheater. The quartz pyrolysis tube (12-mm. inside diameter, 15-mm. outside diameter, 105 cm. long, and packed with 4-mesh quartz chips) was connected to the recovery system by a metal-to-quartz adapter (Figure 3) developed by Robert Johnson of this laboratory. Ethylbenzene and water were pumped by bellows pumps (*2*) from graduated cylinders to a vaporizer-preheater, from which the gaseous mixture passed to the pyrolysis tube. The temperature of the pyrolysis was given by a thermocouple wired to the outside of the quartz tube at the experimentally determined point of average temperature. The pyrolyzate passed through a gas separator (a brass condenser with internal cooling coil), which retained the greater portion of the liquid product. The exit gas from the separator passed through two wet ice traps, a sampling manifold, a bubbler for visual observation of rate, and, finally, a gas meter. All runs were made at essentially atmospheric pressure.

ANALYSIS OF PYROLYZATE

The styrene content of the liquid pyrolyzate was calculated from its bromine number. This method was checked against ethylbenzene-styrene mixtures of known composition and was found to be reliable. The amount of high boiling residue in the pyrolyzate was determined by topping a 25-gram sample under an absolute pressure of 2 mm. with the distilling tube at 30° C. and the condensing tube at −78° C. For the few cases in which the crude pyrolyzate was too darkly colored to permit bromometric titration, the bromine numbers were determined on the distillates from the vacuum topping. Benzene and toluene in the pyrolyzate were determined by distillation at ordinary pressure through a microcolumn, and the fractions boiling up to 85° C. and from 85° to 125° C. were assumed to be benzene and toluene, respectively. Vacuum fractionation of a 2500-cc. composite sample of pyrolyzate had previously shown that these two distillation fractions were essentially (95+%) benzene and toluene,

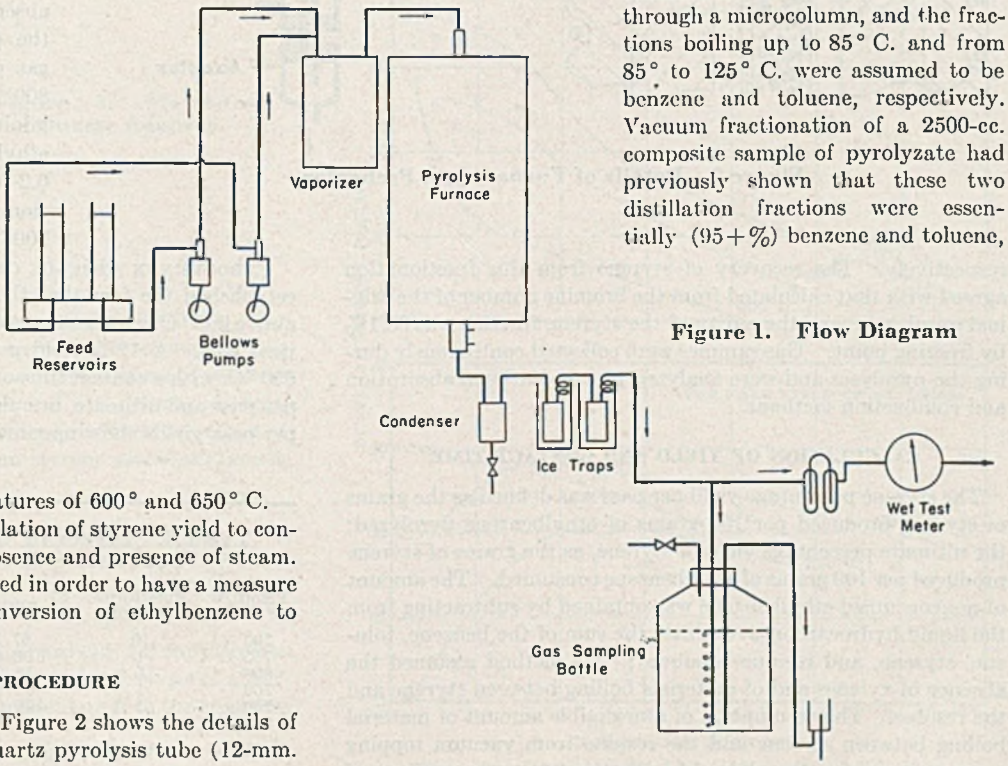

Figure 1. Flow Diagram

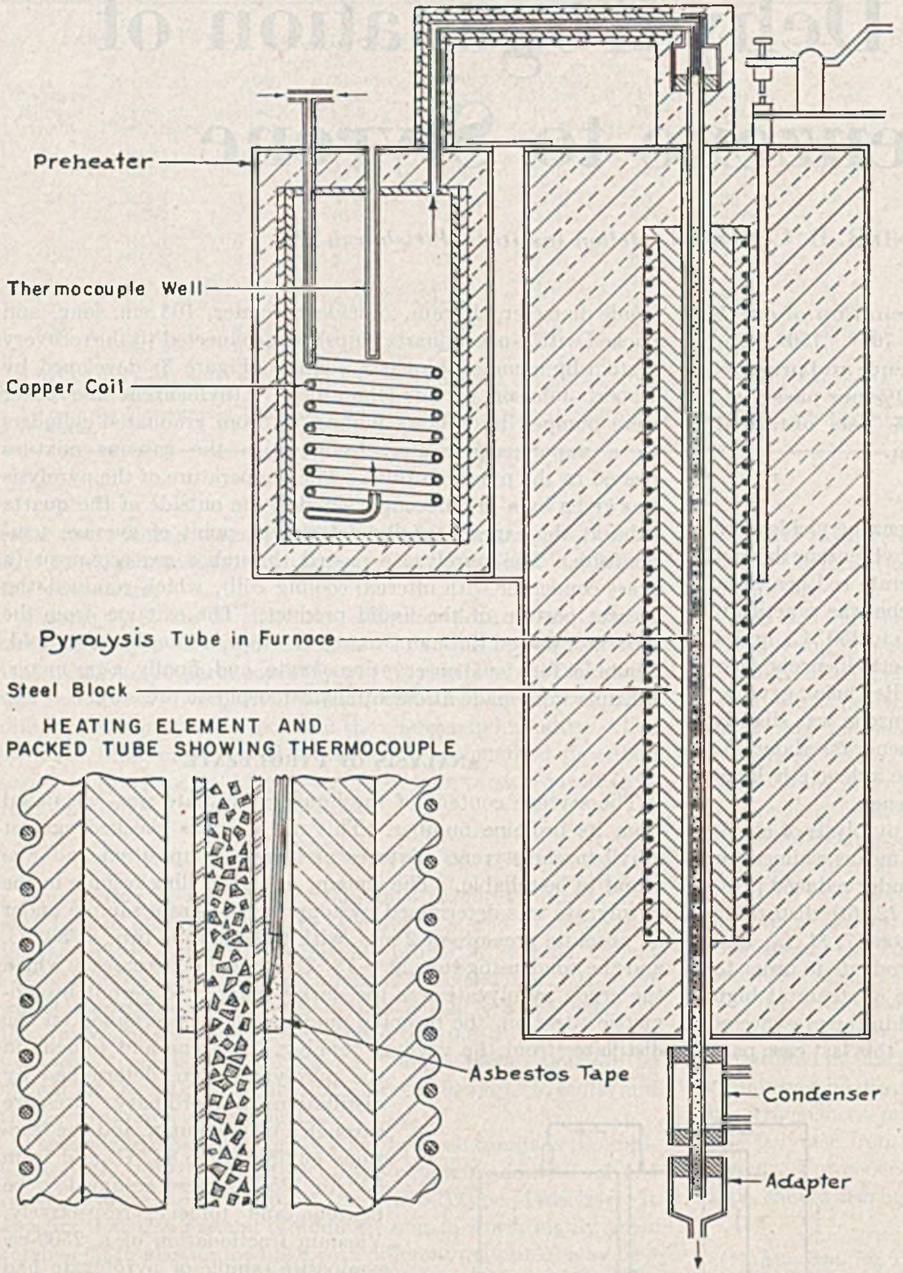

Figure 2. Details of Furnace and Preheater

respectively. The recovery of styrene from this fractionation agreed with that calculated from the bromine number of the original pyrolyzate, and the purity of the styrene fraction was 98.1% by freezing point. Gas samples were collected continuously during the pyrolyses and were analyzed by conventional absorption and combustion methods.

CALCULATION OF YIELD AND CONTACT TIME

The styrene percentage yield per pass was defined as the grams of styrene produced per 100 grams of ethylbenzene pyrolyzed; the ultimate percentage yield of styrene, as the grams of styrene produced per 100 grams of ethylbenzene consumed. The amount of nonconsumed ethylbenzene was obtained by subtracting from the liquid hydrocarbon pyrolyzate the sum of the benzene, toluene, styrene, and residue produced; this method assumed the absence of xylenes and of materials boiling between styrene and the residue. The assumption of a negligible amount of material boiling between styrene and the residue from vacuum topping was confirmed by the close agreement between the amount of bottoms obtained in the vacuum distillation and the amount of residue obtained in vacuum topping.

This method of analysis was employed rather than that of Mavity, Zetterholm, and Hervert (*10*), who assumed the benzene and toluene productions to be stoichiometrically equivalent to the ethylene and methane contents, respectively, of the gas. This assumption is satisfactory for evaluating catalytic dehydrogenation of ethylbenzene where the ultimate yield of styrene is 90% and better, but it was found to be quite inadequate for evaluating the pyrolytic dehydrogenation of ethylbenzene where the ultimate yield is relatively low. In other words, if the reaction is not cleancut, as is the case with pyrolytic dehydrogenation, the stoichiometric relation fails.

The contact time in seconds at the temperature of pyrolysis was calculated as free space (41 cc.) divided by gas rate per second. The gas volume was arbitrarily taken as the gas volume of the total feed.

DISCUSSION OF RESULTS

Gas Composition and Production. The gas consisted of hydrogen, paraffins, and ethylene (Table I). The paraffin index was 1.3–1.4 for operation in the absence of steam and 1.2 for operation in the presence of steam. The presence of steam favored the production of ethylene at the expense of paraffin. The total weight of gas produced at 700° C. was essentially independent of the presence or absence of steam (Figure 5). At 750° C. the presence of steam increased the gas production slightly (Figure 6); at 800° C. the experimental data show a minimum in gas production at a steam-ethylbenzene ratio of 5 (Figure 7). At 0.2-second contact time the gas production ranged approximately from 2% at 700° C. to 9% at 800° C.

Pyrolysis in Absence of Steam. Exploratory experiments established the fact that the temperature of pyrolysis must be above 600° C. in order to produce styrene at a commercially practical rate. A 12% yield per pass of styrene was obtained at 650° C. with a contact time of 2.3 seconds. The yields of styrene, per pass and ultimate, are plotted in Figure 4. The plots of the per pass yields show maxima at 700° C. (1-second contact time)

Table I. Effect of Operating Conditions on Gas Composition at 0.2-Second Contact Time

Temp., ° C.	Mole Ratio, H_2O/EB[a]	Gas Compn., Mole % H_2	Gas Compn., Mole % C_2H_4	Gas Compn., Mole % C_nH_{2n+2}	Paraffin Index
700	0	67.8	14.0	18.2	1.4
750	0	60.6	18.6	20.8	1.3
800	0	58.0	21.1	20.9	1.3
700	5	66.8	20.1	13.1	1.2
750	5	60.5	26.1	13.4	1.2
800	5	56.3	28.1	15.6	1.2

[a] EB = ethylbenzene.

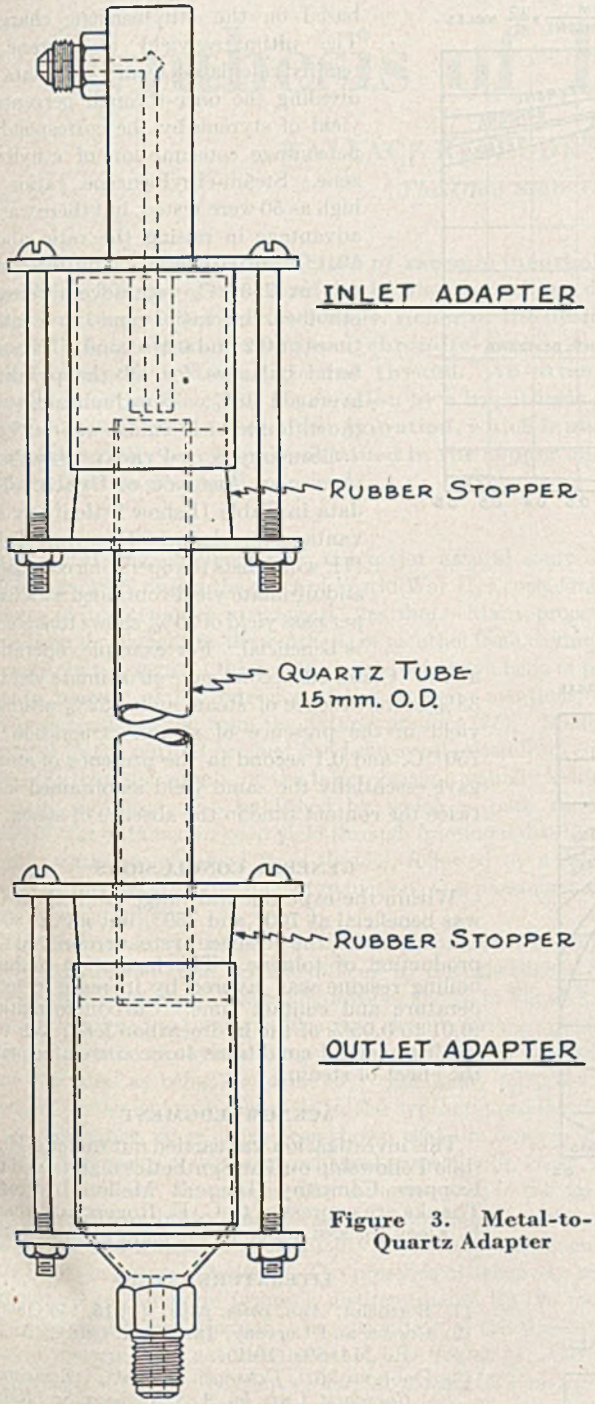

Figure 3. Metal-to-Quartz Adapter

and at 750° C. (0.7-second contact time), but not at 800° C. The maximum at 800° C. presumably occurs at a shorter contact time than the one experimentally employed. The ultimate yield increased with decrease in contact time and with increase in temperature. The following table lists the required contact times at 700°, 750°, and 800° C. for maximum styrene yields per pass in the absence of steam:

Temp., °C.	Contact Time, Sec.	Styrene Yield, % Per pass	Styrene Yield, % Ultimate
700	1.0	21	35
750	0.7	28	48
800	0.1	30	48

According to Ostromislensky and Shepard (*12*, *13*) the ultimate percentage yield of styrene obtainable by the pyrolysis of ethylbenzene in the absence of steam is dependent on K in the equation

$$\frac{0.64\ V/R + T}{633} = K$$

where V = volume, cc. of hot tube
R = ethylbenzene rate, g./min.
T = interior temperature of tube at longitudinal center
K = parameter varying between 0.8 and 1.2, optimum efficiency being attained at $K = 1$

The maximum yield of styrene should therefore be obtained at a temperature below 633° C., which is completely in disagreement with our data.

PYROLYSIS IN PRESENCE OF STEAM. Pyrolysis at 700° C. in the presence of steam was studied at contact times ranging from 0.1 to 0.6 second and pyrolysis at 750° and 800° C. was studied at contact times ranging from 0.1 to 0.4 second. Figures 5, 6, and 7 compare data for pyrolysis in the absence and presence of steam at these three temperatures. These plots include per pass weight yields of gas, benzene, toluene, styrene, and residue,

Table II. Effect of Steam-Ethylbenzene Ratio on Styrene Yield at 750° C.

Contact Time, Sec.	Mole Ratio, H_2O/EB	Styrene Yield, % Per pass	Styrene Yield, % Ultimate
0.2	10	23	53
0.2	7.5	25	52
0.2	5	29	55
0.2	2.5	17	60
0.2	0	20	55
0.1	50	21	52
0.1	10	21	49
0.1	7.5	16	59
0.1	5	20	60
0.1	2.5	14	63
0.1	0	12	58

Table III. Operating Conditions and Ultimate Yields of Styrene at 20% Yield Per Pass

Mole Ratio, H_2O/EB	Temp., ° C.	Contact Time, Sec.	Ultimate Styrene Yield, %
0	700	0.8	38
0	750	0.2	55
5	700	0.8	52
5	750	0.1	60

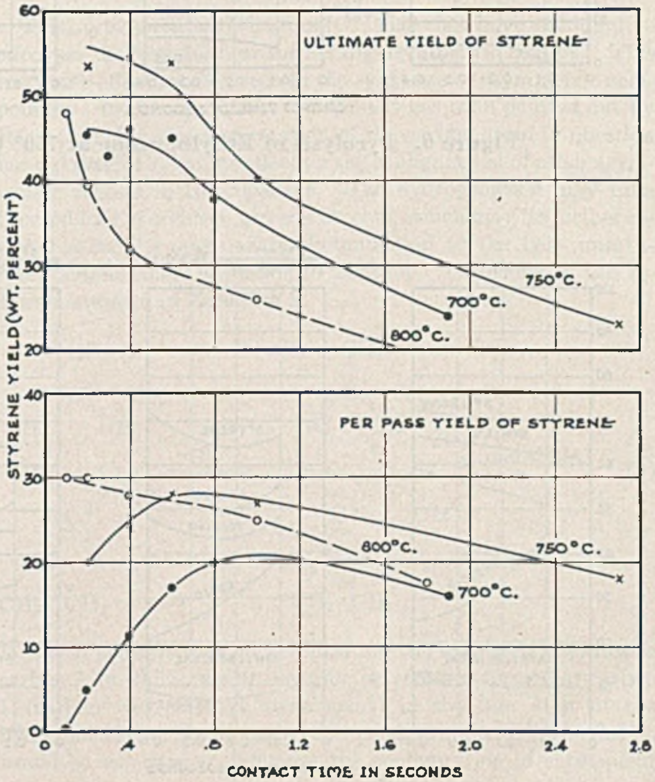

Figure 4. Styrene Yield in Absence of Steam

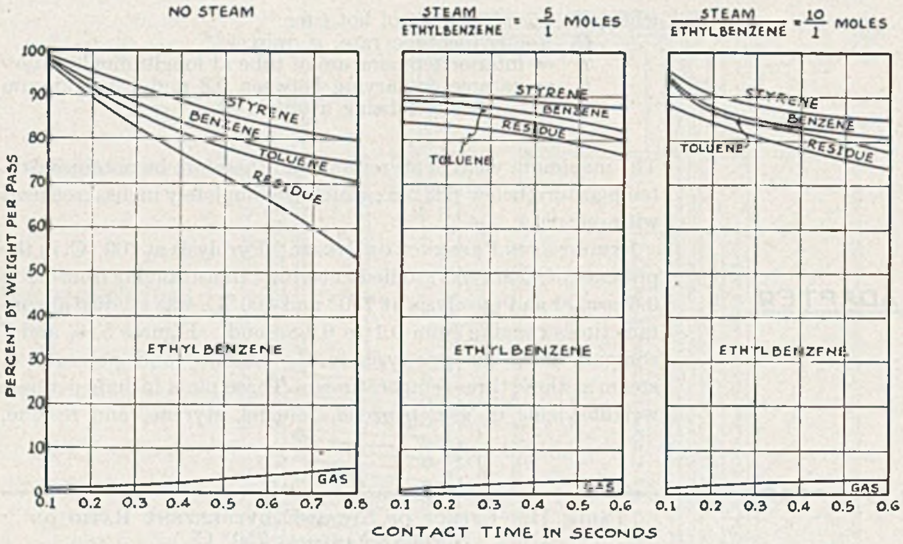

Figure 5. Pyrolysis of Ethylbenzene at 700° C.

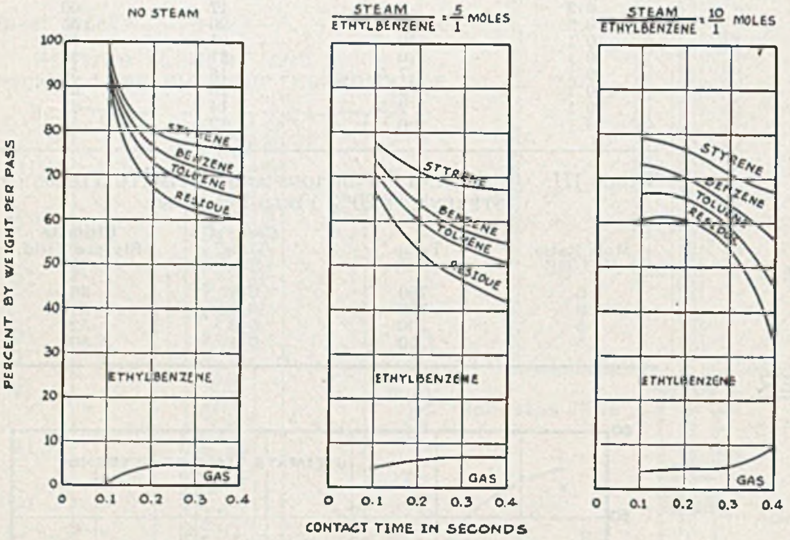

Figure 6. Pyrolysis of Ethylbenzene at 750° C.

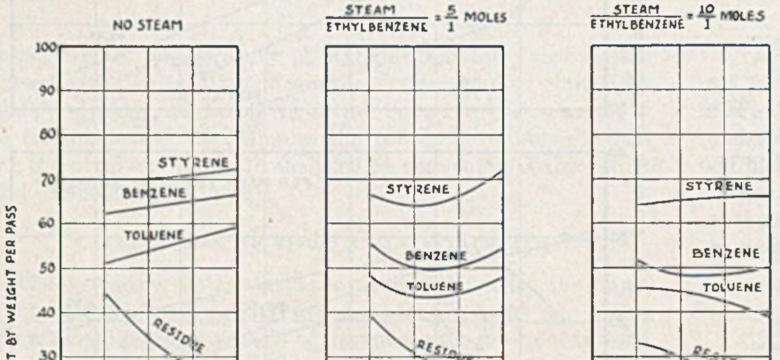

Figure 7. Pyrolysis of Ethylbenzene at 800° C.

based on the ethylbenzene charged. The ultimate yield of styrene is readily calculated from these data by dividing the once-through percentage yield of styrene by the corresponding percentage consumption of ethylbenzene. Steam-ethylbenzene ratios as high as 50 were tested, but there was no advantage in raising the ratio above 10. Table II presents data for pyrolysis at 750° C. with several steam-ethylbenzene ratios and at contact times of 0.2 and 0.1 second. The material balances for all the pyrolyses averaged 98%. The duplicability of the ultimate yield values was ±2%.

Comparison of Pyrolysis in Presence and Absence of Steam. The data in Table II show little if any advantage for steam. However, Table III, which lists the operating conditions and ultimate yields obtained at a fixed per pass yield of 20%, shows that steam is beneficial. For example, operation at 700° C. and 0.8 second gave an ultimate yield of 38% in the absence of steam and a 52% ultimate yield in the presence of steam. Operation at 750° C. and 0.1 second in the presence of steam gave essentially the same yield as obtained with twice the contact time in the absence of steam.

GENERAL CONCLUSIONS

Within the experimental range studied, steam was beneficial at 700° and 750°, but not at 800° C. In general, the presence of steam repressed the production of toluene. The formation of high boiling residue was favored by increase in temperature and contact time. Carbon formation (0.01 to 0.05% of the hydrocarbon feed) was too small under all conditions to be correlated with the effect of steam.

ACKNOWLEDGMENT

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Synthesis of Racemic Menthol

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A new method for the production of racemic menthol is described. The process is based on the discovery that a different mixture of isomeric menthols, richer in the desired *dl*-menthol, is obtained by copper chromite- rather than nickel-catalyzed hydrogenation of thymol. An attempt is made to rationalize this observation by a hypothesis for stereochemical inductance of configuration, which is aided circumstantially by evidence obtained in the copper chromite reduction of *o*- and *m*-cresols.

WITH the elimination of the major natural sources of menthol due to the onset of World War II, a considerable amount of interest arose in synthetic menthol. Many processes have been developed for the synthesis of menthol from thymol or *m*-cresol, but in general the resulting products have been of poor quality because of the presence of the isomeric menthols, different in configuration from the natural product (*21*). Menthol identical to the natural product has been synthesized from citronellal (*8*), but the supply of the latter became equally critical. Recently a process was published by which a pure racemic menthol was obtained in good yield through fractional distillation of the menthones obtained from thymol, followed by a second fractional distillation, after further reduction, to separate menthol from neomenthol (*2*).

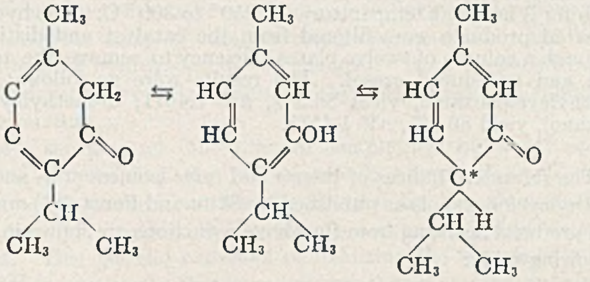
The problem of synthesizing racemic menthol from nonasymmetric starting materials is made difficult by the existence of four racemic modifications. The configurations shown in Figure 1 are generally assigned to these modifications, despite a recent publication in which the methyl and isopropyl groups in natural menthol were indicated as being *cis* forms (*9*). For many purposes the presence of the isomeric menthols in the synthetic product is of little importance, since it has been shown that the isomers differ but little in toxicity or in pharmacological properties (*3*, *11*, *16*, *19*). They are, however, characterized by different, and, in the case of the stereoisomers other than *dl*-menthol, unpleasant tastes and odors (*9*). *dl*-Menthol of good quality is virtually indistinguishable from the natural product. The presence of relatively small amounts of the isomeric forms is distinguishable by the musty odor imparted to the product. In recognition of the similarities between racemic and natural *l*-menthol, the British (*4*), German (*18*), and recently, United States Pharmacopoeias (*20*) have given the former official status.

A mixture of inactive menthols is easily obtainable through the catalytic hydrogenation of thymol, which in turn is available through the condensation of *m*-cresol with isopropylene, isopropyl chloride, or other related compounds. The mixture of stereoisomers as usually obtained is difficultly separable into its components, although the patent literature gives methods for the isolation of *dl*-menthol by such procedures as fractional distillation or crystallization, or recrystallization of ester derivatives. It was felt that a possible solution to the problem lay in changing the proportions of isomeric menthols obtained on catalytic hydrogenation of thymol to a mixture richer in *dl*-menthol, since the more common techniques of separation and purification may often be successfully accomplished if the crude material is sufficiently rich in the desired isomer. Since the catalyst in general use for such hydrogenations is nickel in various forms, it was desirable to attempt the reduction of thymol with a different catalyst, one which was thought to effect hydrogenation through a different mechanism. Such a catalyst is copper chromite.

THEORY OF COPPER CHROMITE REDUCTION

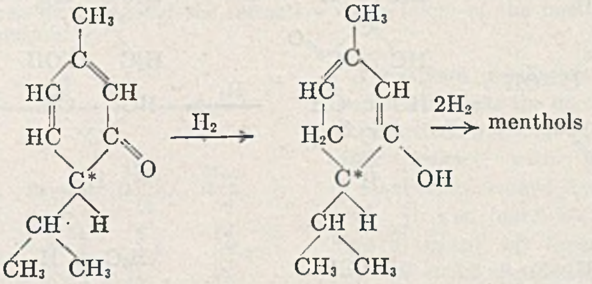
Musser and Adkins (*12*) first noted that copper chromite effects the reduction of β-naphthol and monohydroxy derivatives of biphenyl in the oxygenated rings, leaving the other rings unreduced. Moreover, under the same conditions of reduction they noted that the ethers of these phenolic compounds could not be hydrogenated. This observation, together with the knowledge that nickel catalysis would effect the reduction of phenols and their ethers with essentially equal ease, led the authors to postulate that the reduction of phenolic compounds by means of copper chromite proceeds through the tautomeric ketones. If this theory is applied to the reduction of thymol some interesting conclusions may be drawn.

In the reduction of thymol, formation of the tautomeric ketones may lead to a compound containing an asymmetric carbon atom, as indicated in Equation 1.



(1)

This asymmetric carbon atom (C*) may then have an inductive effect on the formation of succeeding asymmetric centers. This inductive effect is often seen in the synthesis of asymmetric compounds. In the case of the menthols it has been pointed out by Read (*14*) that the configuration of the carbon atom in question has a powerful inductive effect on the configuration of other asymmetric centers in the molecule. The hydrogenation may then proceed by 1:6 addition to yield an enol, which may be further reduced as such or may undergo ketonization to the beta unsaturated ketone before reduction to menthol. The course of this reaction is shown in Equation 2.



(2)

It is also possible that on ketonization the hydrogen migrates to carbon 2, in which case an asymmetric center is formed at carbon 1 (carbon with methyl attachment) in the first step of the hydrogenation. Here again the configuration of this carbon would be expected to influence the configuration of subsequent asymmetric centers, although the effect should not be so pronounced (*14*).

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No menthone could be isolated from the reduction mixtures of thymol even when the reduction was stopped at 50% completion; nor could any partially unsaturated products be isolated from the reduction mixtures. The presence of varying quantities of menthones has been reported in most reduction mixtures following hydrogenation with a nickel catalyst. This discrepancy between the two results would in itself suggest different modes of reduction. The absence of menthone or menthene derivatives might indicate that the reduction proceeds by 1:4 addition to the enol rather than addition after ketonization.

Assuming the inductive stepwise mechanism, an increased yield of one stereoisomer in the reduction mixture could be expected, although one could not forecast with certainty which isomer would predominate. It was found that, by copper chromite reduction, a yield of 81% *trans*-menthols (*dl*-menthol and *dl*-neomenthol) and 60 to 70% *dl*-menthol was obtained. In contrast to this a hydrogenation of thymol using nickel on kieselguhr (Universal Oil Products Company) gave only 56% *trans*-menthols and about 40% *dl*-menthol. The yield of *trans*-menthols is important in the purification, since *dl*-neomenthol may be readily separated from *dl*-menthol in the procedure to be described later. To test further this catalytic specificity of copper chromite catalyst, *o*- and *m*-cresols were reduced with copper chromite. These experiments were as follows:

The cresols used were Coleman and Bell pure grade. Before reduction they were distilled under reduced pressure in an atmosphere of nitrogen and yielded water-white products. The cresols were hydrogenated with 10% of their weight of copper chromite catalyst at pressure of 500 to 2600 pounds per square inch for 3 hours at temperatures of 250° to 300° C. The hydrogenated products were filtered from the catalyst and distilled through a column of twelve plates efficiency to remove the toluene and unreduced cresol. The results were as follows: 2-methylcyclohexanol, yield 86.5%, n_D^{20} 1.4611; 3-methylcyclohexanol, yield 86.4%, n_D^{20} 1.4573.

The refractive indices of the *cis* and *trans* isomers of 2- and 3-methylcyclohexanols as published by Skita and Faust (*17*) and of the products resulting from the above reductions are shown in the following table:

	2-Methyl-cyclohexanol	3-Methyl-cyclohexanol
cis	1.4640	1.4572
trans	1.4611	1.4550
By copper chromite reduction	1.4611	1.4573

The results indicate essentially quantitative yields of *trans*-2-methylcyclohexanol and *cis*-3-methylcyclohexanol. Figure 2 gives an interesting comparison between the configurations of the methylcyclohexanols obtained by copper chromite reduction with that of *dl*-menthol.

REDUCTION OF CRESOLS

The reduction of *o*- and *m*-cresols through a similar inductive mechanism as postulated for the reduction of thymol is shown in Equations 3 and 4.

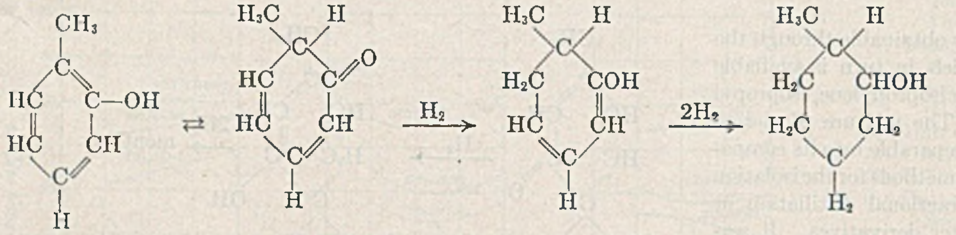
In Equation 3 an asymmetric center may be formed on carbon 2 through ketonization which could then allow for the induction of configuration of carbon 1. In the reduction of *m*-cresol the primary ketonization does not form an asymmetric center. Further reduction of the tautomer, however, does form an asymmetric carbon atom, which can then exert an influence on the configuration of the second asymmetric center. Although only one possibility of reduction is shown in these equations, if the ketonization and subsequent stepwise reduction mechanism is followed, an asymmetric center is formed at some time in the reaction which may then influence the formation of subsequent asymmetric centers.

REGENERATION OF CATALYST

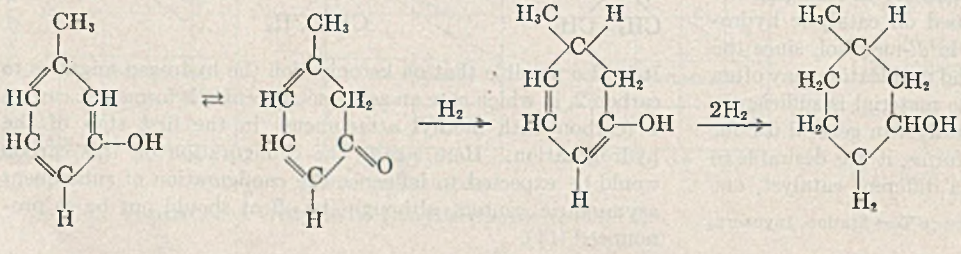
The copper chromite used in carrying out the reductions reported here was prepared by a procedure given by Lazier (*10*). As has been previously described in the literature, different preparations of the catalyst tended to have different activities. These differences in activity are partially accounted for by a lack of uniformity in the preparation of different batches. Calingaert and Edgar described a process whereby a uniform and active copper chromite catalyst can be prepared on a semiplant scale (*5*).

It was of interest to see whether the efficiency of a particular sample of copper chromite decreased with continued use in successive hydrogenations. Copper chromite has a tendency to be reduced, under the conditions of hydrogenation, to an inactive red substance containing copper in the cuprous state. This reduction may possibly be catalyzed by water, usually present in the reduction of thymol through hydrogenolysis of the menthol to menthane. This tendency is, to a certain extent, circumvented by the incorporation of small amounts of barium or other alkaline earth oxides in the catalyst (*6*). In these reductions it was found that the catalyst, under the conditions employed, became less efficient with continued use and after two or three runs had a copper red color. In handling the used catalyst it was noted that the material tended to turn slowly black or dark green on the outside and to evolve a noticeable amount of heat. This led to the development of a method for the regeneration of used copper chromite catalyst.

It was found that if the catalyst, after washing with a solvent such as acetone, is dried and placed in an oven at 100° to 120° C., a decidedly exothermic reaction follows. If too high a temperature was used, the reaction was accompanied by a bright glowing of the catalyst mass, which left a grayish-green material found to be less active. Advantageously the spent catalyst is spread out in a thin layer, and the oven supplied with air when large quantities are to be treated. This gives a product of improved appearance and avoids the production of too much heat by the exothermic reaction. The catalyst thus regenerated is then ready for use without further treatment. Such a catalyst was found to have an equal or possibly greater activity than had the fresh catalyst and was more active than catalysts used for successive hydrogenation without such treatment. One sample of copper chromite was



(3)



(4)

used for five successive reductions of thymol with a regeneration following the third run. By this regeneration the catalyst cost in a process which requires the use of large quantities of catalyst is measurably decreased. Since this work was completed, this method has been independently noted and described by Dunbar and Arnold (7).

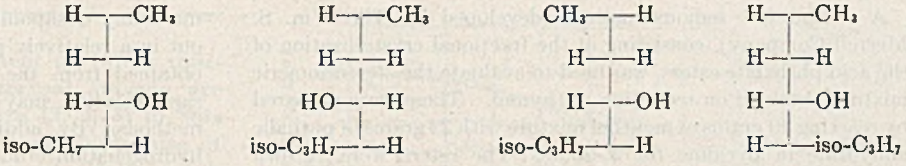

dl-Menthol *dl*-Neomenthol *dl*-Isomenthol *dl*-Neoisomenthol

Figure 1. Configurations Assigned to Four Racemic Modifications of Menthol

HYDROGENATION OF THYMOL WITH COPPER CHROMITE

The reduction of thymol with copper chromite is not so efficient as when nickel is used for the catalysis. However, when a catalyst of sufficient activity is used and efficient mixing of the hydrogen with the thymol is accomplished, the reduction may be carried out within a reasonable length of time. The results of a number of reductions of thymol are listed in Table I.

A typical reduction, as carried out in the laboratory, is as follows:

> The equipment used consisted of a rocking steel autoclave of 3100-cc. capacity (American Instrument Company) which was supplied with a potentiometric thermoregulator (Brown Instrument Company). Hydrogen was supplied to the autoclave at the pressures obtainable from the cylinder. Seven hundred and fifty grams of thymol (U.S.P. quality) and 75 grams of copper chromite catalyst were placed in the autoclave, and air was removed by displacement with hydrogen; then the temperature was raised to 200° C. Hydrogenation was carried on at pressures varying from 800 to 1400 pounds per square inch until the reduction, as indicated by the uptake of hydrogen, was fairly complete. The crude reduction mixture was filtered from the catalyst by means of a basket centrifuge. The product gave the following values: freezing point 9° C., n_D^{20} 1.4460, methane 2%, thymol 0.8%, yield of mixed isomeric menthols (by difference) 97%.

The per cent menthane given here and in the table includes the water formed in the reaction and was determined by distillation through a short column. The amount of menthane formed is, to a considerable extent, dependent upon the temperature of the reaction (Table I). In the reduction carried out at 300° C., 50% of the reaction mixture consisted of menthane while some thymol still remained unreduced. This would indicate that the hydrogenolysis of menthol to menthane runs concurrently with the reduction of thymol to menthol. It was also found that, if the reaction were allowed to continue at 200° after a theoretical conversion to menthol, as determined from the hydrogen uptake, a considerable amount of menthane was produced. It is difficult to correlate the production of menthane with variation in the catalyst used, although there are some indications that a more active catalyst produces less menthane. Adkins *et al.* (1) studied the effects on the ratio of alcohol to hydrocarbon resulting from copper chromite reduction of esters produced by modifications of the catalyst, but could obtain little or no correlation.

An interesting correlation was found between the amount of thymol placed in the autoclave and the length of time necessary for reduction. The greater the amount of thymol placed in the autoclave, the longer the time it took for reduction, other factors being equal. This was probably due to a lack of thoroughness in the mixing of the thymol with the hydrogen or to a lack of solubility of the hydrogen in the thymol. It was also noted that, if the autoclave had been used for a nickel reduction prior to its use for copper chromite reduction, there was a considerable induction period before hydrogenation began. This induction period could be circumvented by the rapid reduction of acetone with copper chromite in the autoclave prior to its use for thymol.

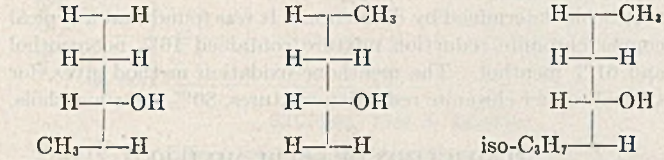

2-Methylcyclohexanol 3-Methylcyclohexanol *dl*-Menthol

Figure 2. Configurations of Methylcyclohexanols and *dl*-Menthol

The table lists the freezing points and the refractive indices of the crude reduction mixtures. These are not of great significance, but illustrate some of the variations encountered when the conditions of hydrogenation are changed. Both properties are largely dependent on the amounts of thymol and menthane found in the mixture.

One of the greatest difficulties in completing this study was that of determining the stereoisomeric composition of the mixture. A method was developed whereby the amounts of *trans*-menthol, as compared to the *cis*-menthol, could be determined. This method consisted of oxidizing the menthols in a distilled sample to the corresponding menthones and determining the ratio of the two menthones by means of the refractive index. This method will be briefly described. The procedure for the oxidation of the mixture to menthone is modified after that of Sandborn (15).

> A stock solution of oxidant was prepared containing 134 grams of potassium dichromate dissolved in 111 grams of concentrated sulfuric acid and 670 cc. of distilled water; 76 cc. of this were sufficient for the oxidation of a 10-gram sample of menthol. The menthol was added to the oxidant and stirred vigorously until the maximum temperature was reached (around 49–50° C.). The reaction mixture was warmed gently until the black complex had decomposed completely, and then the mixture was steam-distilled. The steam distillate was extracted with ether, dried, then distilled, and the refractive index taken of the menthone mixture.

Table I. Hydrogenations of Thymol

Run No.	Thymol, Grams	Catalyst, Grams	Temp., ° C.	Pressure, Lb./Sq. In.	Time, Hr.	n_D^{60}	F.P., ° C.	Thymol, %	Menthane, %	Menthols, %
1	1500	150	200–40	2820–780	23	1.4459	1	1.54	4	94
2	750	75	200	1400–800	13	1.4460	9	0.48	1–2	98
3	750	75[a]	200–40	1600–1000	10	1.4444	−3	0.92	16	83
4	750	75[b]	220	2880–1680	13	1.4554	−21	20.3	10	70
5	400	40[c]	220	3000–1400	6	1.4449	−7	1.58	10	88
6	400	40[d]	220	2900–1340	5	1.4448	−6	1.07	8	91
7	400	40	300	3000–1560	1	1.4394	−20	3.94	50	46
8	500	25[e]	220	2500–660	6	1.4455	1	0.2	4	96

[a] Second consecutive use.
[b] Third consecutive use.
[c] After regeneration.
[d] Second use after regeneration.
[e] From a more active preparation.

The steam distillation was used to eliminate the necessity of repeated washing of the ether extract with water or alkalies to remove residual acid. It was found by running a control on *l*-menthol that the steam distillation did not cause measurable inversion. Although this method is not very accurate, it gives a fair approximation of the ratio of isomers present in the mixture.

A second but tedious method (developed by The Wm. S. Merrell Company), consisting of the fractional crystallization of the acid phthalate esters, was used to evaluate the stereoisomeric mixture obtained on reduction of thymol. These were prepared by reacting 20 grams of menthol mixture with 22 grams of phthalic anhydride in pyridine for 3 hours. The esters were thrown out by adding the reaction mixture to dilute hydrochloric acid, and the stereoisomeric forms were isolated by recrystallization from petroleum ether. By this method only the neomenthol and menthol contents were usually determined, the *cis*-menthol content being determined by difference. It was found that a typical copper chromite reduction mixture contained 16% neomenthol and 61% menthol. The menthone oxidation method gives, for typical copper chromite reduction mixtures, 80% *trans*-menthols.

PURIFICATION OF CRUDE MIXTURE

Even with the increased amount of *dl*-menthol in the crude mixture, purification by such methods as distillation or recrystallization was still unsatisfactory. However, the mixture could be readily purified by means of esterification with phthalic anhydride as originally described by Pickard and Littlebury (*13*). The best conditions found for the purification are as follows:

One hundred grams of crude menthol are mixed with an equal weight of phthalic anhydride and heated under a reflux condenser with stirring at 100–130° C. for 2 hours. At the conclusion of the esterification the melt is allowed to cool to 85–90° C., and 300 cc. of petroleum ether (boiling point 90–95° C.) are added and stirred thoroughly into the melt. When the mixture is allowed to cool, the ester slowly crystallizes out. To avoid the formation of a hard mass of solid in the bottom of the container, the mixture should be stirred gently until crystallization has well begun. This gives a readily filterable slurry. The ester is removed by filtration and washed with 200–300 cc. of the same solvent by resuspension of the solid, stirring, and subsequent filtration. It may then be further purified by recrystallizing from a minimum of hot petroleum ether and filtering hot to remove any difficultly soluble *dl*-neomenthyl acid phthalate. The ester thus obtained is saponified by refluxing 1 hour with 2.2 molar proportions of sodium hydroxide and then steam distilling. The menthol is separated from the aqueous layer and dried by distillation or treatment with a drying agent.

By this method 60% yields of menthol (freezing point 26–28° C.) were obtained, the product having an excellent odor and taste; this indicated the absence of appreciable amounts of the stereoisomeric menthols. The phthalic acid is recovered by acidifying the hot residue from the steam distillation and filtering hot to remove any unsaponified ester. On cooling, the acid crystallized out in a relatively pure condition. The isomeric esters may be obtained from the mother liquors by evaporation and, after saponification, may be isomerized by any of several well known methods. By adding this isomerized mixture to succeeding hydrogenation crudes, the over-all yield of *dl*-menthol may be increased.

ACKNOWLEDGMENT

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Based on a dissertation submitted by Robert W. Van Dolah to the faculty of The Ohio State University in partial fulfillment of the requirements for the degree of doctor of philosophy.

Storage of Commercial Dehydrated Alfalfa Meal

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THIS storage study was undertaken in the hopes of finding a possible postwar means of utilizing the natural cooler storage which was developed as a wartime expedient. The effect of different types of bags for storage of dehydrated alfalfa meal was also a consideration.

The dehydrated alfalfa meal used in this study was placed in a blender and mixed thoroughly. The meal used in the first series was of relatively high carotene content and was placed in regular size plain burlap bags, small plain burlap bags, small waterproofed burlap bags, plain paper bags, and two types of paper bags containing special asphalt-laminated sheets. The regular burlap bags contained 100 pounds of meal, whereas all of the others held approximately 25 pounds. A lower carotene meal was chosen for the second series, but no paper bags were available for samples of this meal.

The plain burlap bags were sewed by hand, and all of the other bags were closed by use of a stapling machine. Precautions were taken to avoid trapping air above the meal in the stapled bags.

The various bags of meal in each series were placed in a single

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The advantages of storing alfalfa meal at lower temperatures than those obtained in normal storage are shown; the results confirm other data (*2, 4, 5*) in this respect. There seems to be no advantage to the use of waterproofed packaging for the storage of alfalfa meal. Results indicate that it may be advantageous, from the standpoint of carotene retention, to have the moisture content somewhat greater than that at which the alfalfa is normally milled.

row, so that each would be subjected to identical conditions. It was possible to put the bags of meal in warehouse storage on a platform approximately 15 feet from the floor, where they remained undisturbed. Those stored in the natural cooler storage were placed on pallets which did not have to be moved.

The natural cooler storage facility at Atchison, Kans., was developed by the War Food Administration as a means of keeping certain surplus foods which require special storage conditions. The administration of this project is now handled by the United States Department of Agriculture.

STORAGE CAVE

An artificial cave, which resulted from removal of limestone used for commercial purposes, was developed into the natural cooler. The limestone had been removed according to specifications of the United States Bureau of Mines. Thus, huge pillars of the original stone were left intact as supports for the overcast. The floor of the cave was leveled, and concrete poured over a bed of crushed rock to make a smooth surface. The height from floor to ceiling is approximately 12 feet, and there are about 14.5 acres of floor space. An estimated 2500 to 3000 carloads of material may be accommodated in the cave.

An ammonia system was installed for cooling the brine, which was circulated through forty-eight refrigeration units placed at suitable locations throughout the cave. The relative humidity and temperature of the cave can be regulated, so that ideal conditions can be maintained for storing a wide variety of products.

Location of the entrance tunnel at a convenient distance from the exit tunnel allows simultaneous two-way traffic. An open area is available in front of the entrances, and this is connected to the long loading dock by a 450-foot ramp. Materials are placed on pallets and transported on trailers, which are drawn by modern electric warehouse tractors. Each tractor has an attached hoist for placing the loaded pallet in the proper place for storage.

The alfalfa meals for warehouse storage were stored in the Kansas City warehouse of The W. J. Small Company. The temperatures and humidities in Table I were taken from records of the Kansas City Weather Bureau, which was located within a mile of the warehouse. Although warehouse conditions would not be identical with those listed in Weather Bureau records, they are likely to be quite similar, since the warehouse was of open construction. Both the temperature and the relative humidity in the natural cooler remained relatively constant throughout the storage period. The temperature varied from 37° to 40° F., and the relative humidity from 80 to 85%.

Table I. Temperature and Humidity Conditions during Warehouse Storage

Month	Temp., ° F.			Relative Humidity, %		
	High	Low	Mean	High	Low	Mean
Sept. 15–30	89	42	65	96	34	78
Oct.	83	32	57	98	25	65
Nov.	81	20	46	96	23	62
Dec.	60	14	26	100	29	73
Jan. 1946	53	7	33	99	25	71
Feb. 1–15	72	17	40	89	35	61

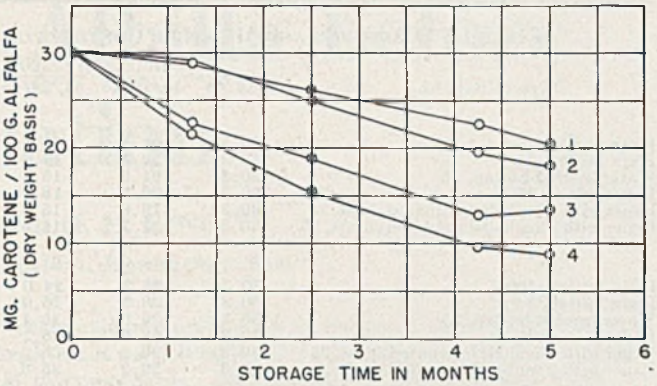

Figure 1. Effect of Storage Conditions and Types of Bags on Carotene Content of Dehydrated Alfalfa Meal (Series 1)

1. Burlap bag, plain, 25 pounds, natural cooler storage
2. Waterproofed burlap bag, 25 pounds, natural cooler storage
3. Burlap bag, plain, 25 pounds, warehouse storage
4. Waterproofed burlap bag, 25 pounds, warehouse storage

Samples of meal were taken on the same day from each type of bag stored either at the warehouse or in the natural cooler. A special sampling tube was used so material could be obtained from the full length of a given bag.

Sufficient bags were placed in storage so that each sample and duplicate analyses were made from separate bags. This permitted sampling with a minimum of disturbance to the material. Care was exercised to secure samples from corresponding sections of the several bags. Four separate samples were taken from each of the 100-pound bags, and eight samples from each of the smaller bags for the composite. All samples from a given bag were carefully mixed and sampled by quartering before the portion used for the different determinations was taken.

PROCEDURES

Moisture determinations were made by placing the weighed sample in a vacuum oven at 100° C. for 2 hours. The low vacuum obtained with a Cenco Hypervac 20 was maintained throughout the period.

The Silker, Schrenk, and King (*3*) method was used for all of the carotene analyses. A 1-gram sample of the dehydrated alfalfa meal was weighed into a 125-ml. Erlenmeyer flask and carefully mixed with 60 ml. of a 2-to-1 mixture of Skellysolve B and acetone. The stoppered flask was then set aside in the dark for 16–18 hours. The extract was next poured onto a Büchner funnel, and the residue washed by decantation with several portions of Skellysolve. After the extract had been transferred to a 600-ml.

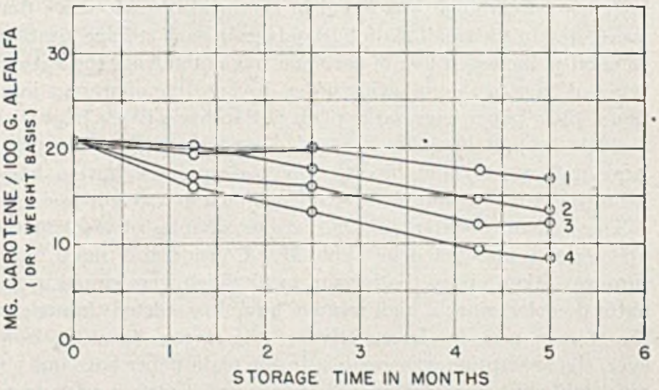

Figure 2. Effect of Storage Conditions and Types of Bags on Carotene Content of Dehydrated Alfalfa Meal (Series 2)

1. Burlap bag, plain, 25 pounds, natural cooler storage
2. Waterproofed burlap bag, 25 pounds, natural cooler storage
3. Burlap bag, plain, 25 pounds, warehouse storage
4. Waterproofed burlap bag, 25 pounds, warehouse storage

TABLE II. CAROTENE AND MOISTURE CONTENTS OF DEHYDRATED ALFALFA MEAL DURING STORAGE (SERIES 1)

	Carotene, Mg./100 G. (Dry Wt.)					Moisture, %				
Type of Bag, Lb.	9/14/45	10/20/45	11/29/45	1/23/46	2/15/46	9/14/45	10/20/45	11/29/45	1/23/46	2/15/46
WAREHOUSE STORAGE										
Plain burlap, 100	30.3	21.5	15.5	12.0	11.2	5.3	6.9	6.6	6.8	7.6
Plain burlap, 25	30.3	22.6	19.0	13.0	13.5	5.3	7.9	8.1	7.9	8.7
Waterproofed burlap, 25	30.3	21.6	15.3	9.6	8.8	5.3	5.7	5.8	5.7	5.8
Paper, plain, 25	30.3	20.5	18.1	12.8	12.9	5.3	7.5	8.0	8.1	9.0
Paper with 1 asphalt-laminated sheet, 25	30.3	19.6	15.4	10.6	8.6	5.3	5.8	5.9	5.5	6.0
Paper with 2 asphalt-laminated sheets, 25	30.3	21.7	14.6	10.0	9.0	5.3	5.8	6.0	5.3	6.2
NATURAL COOLER STORAGE										
Plain burlap, 100	30.3	28.7	24.0	19.3	18.9	5.3	7.4	7.5	8.5	8.8
Plain burlap, 25	30.3	28.9	26.0	22.5	20.4	5.3	8.5	9.1	10.0	10.3
Waterproofed burlap, 25	30.3	29.0	25.1	19.5	18.3	5.3	5.3	5.6	5.6	5.9
Paper, plain, 25	30.3	28.6	25.1	21.6	20.3	5.3	7.8	9.8	10.2	10.9
Paper with 1 asphalt laminated sheet, 25	30.3	29.2	26.2	19.7	18.2	5.3	5.2	5.5	5.8	5.7
Paper with 2 spphalt laminated sheets, 25	30.3	29.2	25.6	19.6	18.3	5.3	5.5	5.4	5.8	6.2

TABLE III. CAROTENE AND MOISTURE CONTENTS OF DEHYDRATED ALFALFA MEAL DURING STORAGE (SERIES 2)

	Carotene, Mg./100 G.					Moisture, %				
Type of Bag, Lb.	9/14/45	10/20/45	11/29/45	1/23/46	2/15/46	9/14/45	10/20/45	11/29/45	1/23/46	2/15/46
WAREHOUSE STORAGE										
Plain burlap, 100	21.2	16.2	15.5	11.7	11.1	5.3	7.2	7.3	7.8	7.8
Plain burlap, 25	21.2	16.7	16.1	12.0	12.2	5.3	7.6	8.3	8.5	9.0
Waterproofed burlap, 25	21.2	16.0	13.3	9.3	8.3	5.3	6.0	5.9	6.0	6.2
NATURAL COOLER STORAGE										
Plain burlap, 100	21.2	19.2	18.5	16.1	15.3	5.3	7.1	7.4	9.1	8.7
Plain burlap, 25	21.2	19.5	20.1	17.8	16.9	5.3	8.8	9.4	9.4	10.2
Waterproofed burlap, 25	21.2	20.1	17.9	14.6	13.4	5.3	5.3	5.7	6.1	6.0

beaker, it was concentrated to a volume of 30–40 ml. on a steam bath and then poured onto a column for separation of the carotenes from the other pigments. A layer of anhydrous sodium sulfate was placed on top of the column, which consisted of two parts of Hyflo Super-Cel and 1 part of magnesia (Micron No. 2641). The chromatogram was developed, and the carotenes eluted with an approximately 5% solution of acetone in Skellysolve B. The eluate was made up to a volume of 250 ml., and the optical density read on a Beckman (*1*) quartz spectrophotometer at 436 mμ.

RESULTS

The carotene content of the dehydrated alfalfa meal at the different time intervals is shown in Table II for the first series. The first half of the table represents the values obtained for the meals which were stored in the warehouse, and the second half records the values for the meals stored in the natural cooler.

Table II shows that considerably less carotene was lost from the meal which was stored in the natural cooler than from the meal stored in corresponding bags in the warehouse. A number of workers (*2*, *4*, *5*) have shown that the stability of carotene in alfalfa decreases as the storage temperature is increased. The least loss of carotene was found in the meal of each series that was stored in the small plain burlap bags in each storage location. Generally, increased loss of carotene was noted from the various types of bags in the following order, irrespective of storage location: plain paper bags, large plain burlap bags, paper bags with a single asphalt laminated sheet, paper bags with two asphalt laminated sheets, and, finally, the waterproofed burlap bags. All of the carotene values are expressed on a dry weight basis.

The moisture content of the various samples of meal in the first series is also listed in Table II. Considerably more moisture was taken up by the bags of meal which were stored in the natural cooler, since a high relative humidity existed throughout the storage period. Irrespective of the storage location, however, the absorption was greatest in the plain paper bags but not much different from that noted for the small plain burlap bags. Somewhat less moisture was absorbed by the meal in the large plain burlap bags, as the exposed area was relatively less. Relatively little moisture was absorbed by the meal stored in the waterproofed burlap bags or the two types of paper bags which contained the special asphalt-laminated sheets.

Generally, the amount of carotene present in the meals which had the higher moisture content was greater than in those which had a lower percentage of moisture.

The data in Table III were obtained on determination of the carotene in the meal of the second series. Table III also contains the data resulting from moisture determinations of the same meal. Comparison of values in these tables will show that the results were analogous to those found for the first series.

The difference in the carotene content of the alfalfa meal stored in particular types of bags in both the warehouse and the natural cooler is represented graphically in Figure 1 for the meal of series 1 and Figure 2 for the meal of series 2. The widest differences due to the different type of bags used in this study are also shown in the figures.

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Handling Fresh Alfalfa before Dehydration

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Dehydrated alfalfa meal obtained from field-chopped alfalfa contained slightly less carotene than did meal produced in the conventional manner from long alfalfa, which was chopped just prior to the dehydration. Slightly more than 4% of the carotene was lost during the normally anticipated time required to load, haul the chopped hay, and feed it into the dehydrator. This loss was countered in some measure, however, by a lower loss of carotene during dehydration of the field-chopped hay than that noted during dehydration of the long hay. On standing for a period of several hours, the field-chopped alfalfa lost about 3% of its carotene per hour. The results indicate that field chopping does not seriously reduce the carotene content of alfalfa meal.

THE usual method of handling green alfalfa for commercial dehydration is to cut the alfalfa with a mower and elevate it directly onto a truck or trailer for transportation to the plant site. It is then pitched, or fed by automatic equipment, onto a conveyor which feeds the alfalfa into a chopper; there it is cut into short lengths before being elevated into the dehydrator.

There has been a trend recently, however, toward use of field equipment whereby the alfalfa is chopped in the field instead of at the plant. Field-chopped alfalfa is produced by one or the other of the following methods: First, a regular mower, having an attachment which causes the alfalfa to fall in windrows similar to those made with a side delivery rake, may be used for mowing. This necessitates a second machine which follows the mower, picks up the alfalfa from the windrow, chops it, and then elevates or blows the chopped material onto a truck or trailer. The second procedure uses a single field machine which mows the alfalfa directly, conveys it to a chopper, and finally elevates or blows the freshly chopped material onto a truck or trailer. An auxiliary power unit which is an integral part of the machine is used to operate the chopper. The second method is superior to the first since only one operation is involved, and the cut material never touches the ground to collect dust and other foreign material.

Several advantages are advanced for using the field chopping procedure. The most important factor to consider is that chopped alfalfa can be fed into the dehydrator at a more uniform rate than is possible when long alfalfa is used and chopped just before going to the drying chamber. An exceptionally good job can be done by using a special automatic feeder, but the work can be done manually with efficiency. A better product is obtained when a uniform rate of operation can be maintained, and a given unit should produce a somewhat greater quantity of product. Some operators state that less help is required in the field when field chopping is done. There is also less loss of material during transportation of chopped alfalfa than of long alfalfa.

Variation in carotene content is of primary importance in any problem involving the production of dehydrated alfalfa meal, but no attempt had been made on the part of plant operators to evaluate the two methods from the standpoint of the carotene content of the final product. Since operators' opinions differed widely regarding the effect of field chopping on alfalfa, and since considerable interest was shown by operators in widely scattered localities, it was felt advisable to carry out the following study on the two procedures. The data were obtained in August and September of 1945.

COLLECTION OF SAMPLES

Field samples were collected as follows: Walking beside the field machine, the collector picked samples of the long alfalfa from the conveyor as it passed from the mower to the chopper; simultaneously, samples of the chopped material were collected as it came from the blower tube. By this procedure samples of both types were obtained from identical parts of the field. The samples were placed in paper bags to minimize evaporation during the short time required to reach the laboratory, which was set up at the plant. Samples of the chopped alfalfa from the different loads at the plant were obtained by taking small handfulls from widely different parts of the load, the storage pile on the dock, or the conveyor as the alfalfa was fed into the dehydrator. All samples of the dehydrated meal were taken directly from the spout at the bagger and stored in a refrigerator in tightly covered glass jars until analyzed.

A portable laboratory, which had been used throughout the summer during a survey of alfalfa dehydrating plants located in the Kaw Valley, was utilized in this study.

PROCEDURE

All samples of fresh material were cut into small pieces—$^1/_8$- to $^1/_4$-inch lengths—mixed well, and carefully sampled by quartering, before weighing out individual samples for determination of carotene or moisture. Five grams of the various samples of fresh alfalfa were extracted in a Waring Blendor for 5 minutes with a foaming mixture of alcohol and Skellysolve B. The method has been described previously (*4*) and is essentially that of Moore and Ely (*3*) as modified by Wall and Kelley (*6*). The total contents of the Blendor were transferred to a 250-ml. Erlenmeyer flask, with Skellysolve B to rinse and wash out particles which did not pour out readily. Sufficient solvent was used so that only enough space remained to accommodate a tight-fitting cork. Charkey and Wilgus (*2*) showed the necessity for protecting alkaline ethanol extracts of alfalfa from the air and the effective manner in which Skellysolve may be used. The completely filled flasks were placed immediately in an ice chest and transported to the laboratory where the analyses were completed on the following day.

The contents of the Erlenmeyer flasks were filtered through a Büchner funnel and the extract transferred to a 500-ml. separatory funnel. Water (100 ml.) was used to wash the extract and to remove most of the alcohol from the mixture. A small portion of anhydrous sodium sulfate was added to prevent the formation of an emulsion. After separation, the aqueous layer was extracted three times with 35-ml. portions of Skellysolve B. The combined extracts were washed by pouring 100 ml. of water through the mixture, and then concentrated to a volume of 30–40 ml. on a steam bath and dried with a small amount of anhydrous sodium sulfate. The concentrate of extract was next drawn through a 2-1 mixture of Hyflo-Super-Cel and magnesia (Micron No. 2641). The chromatogram was developed, and the carotenes eluted with an approximately 5% solution of acetone in Skellysolve B. The eluate was made up to a volume of 250 ml., and the optical density measured at 436 millimicrons with a Beckman (*1*) spectrophotometer.

Carotene determinations on the samples of dehydrated meal were made by a simplified method (*5*) developed in this laboratory. One gram of meal was weighed into a 125-ml. Erlenmeyer

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Table I. Carotene Content of Fresh Alfalfa from Field No. 1

Type of Fresh Sample	Carotene in Fresh Sample, Mg./100 G.	Dry Matter, %	Carotene, Dry Basis, Mg./100 G.	Vitamin A, I.U./Lb.[a]	Loss of Carotene, Unchopped Basis, %
Long alfalfa directly from mower	8.7	29.8	29.2	219,000	..
Chopped alfalfa directly from blower	7.8	26.8	29.1	218,000	..
Long alfalfa after 1 hr. on dock	1st of load, 9.2 Last of load, 8.3	31.3 28.8	29.4 28.8 Av., 29.1	218,000	..
Chopped alfalfa after 0.5 hr. on dock	1st of load, 7.5 Last of load, 7.6	26.8 27.5	28.0 27.7 Av., 27.9	209,000	4.1
Chopped alfalfa after 4.5 hr. on dock	Top of pile, 9.4 Center of pile, 7.0	37.5 27.0	25.1 25.9 Av., 25.5	191,000	12.4

[a] International Units per pound = mg. per 100 grams × 7500.

flask and covered with 60 ml. of a mixture containing one part of acetone and two parts of Skellysolve B. The mixture was shaken, and the tightly stoppered flask then set aside in the dark for 16–18 hours. The extract was then filtered through a Büchner funnel and the residue washed by decantation with several portions of Skellysolve B. It was found advisable to have a total volume of 250–300 ml., as this ensured removal of the acetone during the concentration, which was next carried out on a steam bath. Separation of the carotene from the chlorophylls and xanthophylls was carried out chromatographically as indicated.

Moisture determinations were made by placing the dehydrated meal in a vacuum oven at a temperature of 100° C. for 2 hours at the very low pressure obtained with a Cenco Hypervac 20 pump. Samples of fresh material were predried for approximately 2 hours at 105° C. in an air oven before being placed in the vacuum oven.

RESULTS

Table I presents the data which were obtained on the fresh alfalfa from a field which was exceptionally uniform in stand and growth, and was ideal for a study of this type. The weather was clear and hot. Definite heating occurred in the pile of alfalfa which stood on the dock, and the top of the pile wilted considerably.

The chopped alfalfa which stood on the dock for 0.5 hour contained approximately 4% less carotene than the long alfalfa which had stood for an additional 0.5 hour. The loss in carotene from the chopped material which stood for 4.5 hours amounted to 2.75% per hour during the total elapsed time. However, the rate of loss per hour after the first 0.5 hour was but slightly over 2%.

Table II presents the data on the dehydrated meal produced from the fresh alfalfa listed in Table I. The meals from the fresh chopped material contained less carotene than the meal from the long alfalfa, but the percentage of carotene lost during the process of dehydration was progressively less with material which contained less carotene as fed into the dehydrator. This might indicate that a portion of the carotene present in fresh alfalfa is more easily destroyed than is the remainder. Because of the rapid loss of carotene which occurs when dehydrated alfalfa meal is placed in normal warehouse storage, the differences in the carotene content of the final meals are not so significant as they might appear at first glance.

The losses in carotene during the process of dehydration were considerably less than those ordinarily incurred in commercial dehydration. The operator of this plant was careful in controlling conditions and is responsible for the efficiency which resulted.

The data in Table III were obtained during the third week of September. The alfalfa was taken from a field which had not previously furnished material for dehydration. The surface of the field was irregular; consequently plants were not cut at a uniform height from the ground, and the alfalfa itself was neither uniform in growth nor in stand. Thus it was not possible to obtain samples, particularly of long alfalfa, which were truly representative. Field equipment for cutting and collecting long alfalfa, as in the first part of this study, was not available, and several breakdowns were experienced with the field chopping equipment. The weather conditions were much different from those obtained when the first set of data was collected, since the sky was overcast and the temperature was lower.

However, the loss of carotene suffered by the fresh chopped hay on prolonged standing was of the same order as previously noted. A relatively low loss of carotene was again noted during dehydration of two of the samples. The high loss in the case of the other sample was expected, since the dehydrator had been shut down for some time and operating conditions had not reached

Table II. Carotene Content of Dehydrated Alfalfa Meal from Field No. 1

Origin of Dehydrated Meal	Carotene in Fresh Sample, Mg./100 G.	Dry Matter, %	Carotene, Dry Basis, Mg./100 G.	Vitamin A, I.U./Lb.	% Loss of Carotene during Dehydration	% Less Carotene than in Meal from Long Alfalfa on Dock
Long alfalfa after 1 hr. on dock	1st of load, 26.5 Last of load, 26.9	97.7 96.3	27.1 28.0 Av., 27.6	207,000	5.2	..
Chopped alfalfa after 0.5 hr. on dock	1st of load, 25.1 Last of load, 25.6	97.3 94.4	25.8 27.1 Av., 26.5	199,000	4.8	3.9
Chopped alfalfa after 4.5 hr. on dock	Ist of load, 23.0 Last of load, 23.3	96.8 93.5	23.8 24.9 Av., 24.4	183,000	4.2	11.6

Table III. Carotene Content of Dehydrated Alfalfa Meal from Field No. 1

Type of Fresh Sample	Carotene in Fresh Sample, Mg./100 G.	Dry Matter, %	Carotene, Dry Basis, Mg./100 G.	Vitamin A, I.U./Lb.	Loss of Carotene, % Hr. on Dock
Long alfalfa directly from mower	9.0	25.5	35.3	265,000	..
Chopped alfalfa directly from blower	8.8	23.3	37.8	283,500	..
Chopped alfalfa directly from field	1st of load, 10.9 1/4 load off, 9.9	27.0 27.0	40.4 36.6 Av., 38.5	289,000	..
Chopped alfalfa after 2.5 hr.	Ist of load, 8.8 Last of load, 8.8	25.3 24.3	34.8 36.2 Av., 35.5	266,000	3.2
Chopped alfalfa after 4.5 hr. on dock	Top of pile, 10.7 Center of pile, 8.1	31.3 23.8	34.2 34.0 Av., 34.1	256,000	2.6

Table IV. Carotene Content of Dehydrated Alfalfa Meal from Field No. 2

Origin of Dehydrated Meal	Carotene in Fresh Sample, Mg./100 G.	Dry Matter, %	Carotene, Dry Basis, Mg./100 G.		Vitamin A, I.U./Lb.	Loss of Carotene during Dehydration, %
Chopped alfalfa directly from field	1st of load, 29.3	96.3	30.5	Av., 30.4	228,000	21.1
	¹/₄ load through, 29.7	98.0	30.3			
Chopped alfalfa after 2.5 hr. on truck	1st of load, 32.3	95.2	34.0	Av., 33.5	251,500	5.5
	Last of load, 31.9	96.4	33.1			
Chopped alfalfa after 4.5 hr. on dock	1st of load, 30.6	95.9	31.9	Av., 31.7	237,500	7.2
	Last of load, 30.1	96.0	31.4			

equilibrium. The higher carotene values in Tables III and IV were due to the more succulent material obtained during the cooler weather and later in the growing season.

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Vapor Pressure of Water Adsorbed on Dehydrated Alfalfa

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The vapor pressure of water adsorbed on dehydrated alfalfa was measured in the region of 2.2 to 14.1% moisture and in the temperature range from 17° to 50° C. Adsorption isotherms are the typical S-shaped isotherms of other similar materials. Isosteric plots of the data were made by the method of Othmer and Sawyer (*6*), and the ratios between the heat of adsorption of water by alfalfa meal to the heat of vaporization of water at the same temperature were calculated. This paper shows that protein content, within the range studied, has little effect on the vapor pressure. Blanching the alfalfa meal prior to dehydration does not appear to alter the position or shape of the vapor pressure curves.

A RECENT paper (*7*) indicated that a relation may exist between moisture content and carotene retention in dehydrated alfalfa. Since these data may make it desirable to dehydrate alfalfa to a known moisture content, information regarding vapor pressure equilibrium data becomes necessary, not only for the dehydration process, but also for purposes of determining optimum storage conditions and indicating types of packaging materials which would be desirable.

This paper therefore presents data regarding the vapor pressure of water adsorbed on dehydrated alfalfa and indicates its usefulness to the industry.

Two different commercially dehydrated alfalfa meals and one steam-blanched sample produced in this laboratory were investigated; they contained 20.1, 15.2, and 19.3% protein, respectively. The blanched sample was prepared by placing fresh alfalfa in a steam cabinet through which live steam was passed at atmospheric pressure for 10 minutes before the alfalfa was dehydrated. Moistures were adjusted in the laboratory by means of a vacuum oven for the low values (operated at room temperature) and a temperature-humidity cabinet for the higher levels. Moisture levels approximating 2, 3, 5, 7, 10, and 14%, calculated on a dry weight basis, were obtained.

The moisture contents of the samples were determined by placing the samples in a vacuum oven at 100° C. for 2 hours. Previous measurements had indicated no further loss of weight in this type of material after 2 hours. Vapor pressure measurements are expressed in terms of these determinations.

The equilibrium vapor pressures were determined by the manometric method described by Makower (*3*, *5*). For low pressures (below 30 mm. of mercury) dibutyl phthalate was used in the manometer; for higher pressures mercury was used. For the lower temperatures the flask containing the sample was placed in a constant temperature water bath, and for higher temperatures the entire unit was placed in a constant temperature air cabinet, so that the moisture in the system would not condense. Samples of approximately 10 grams were used. All connections were made by means of ground glass joints and stopcocks.

The techniques of evacuation and making readings were also similar to those described by Makower (*3*, *5*). During evacuation the moisture trap was cooled to −80° C. by means of an acetone-dry ice mixture. Measurements were first made at the low temperatures and then at successively higher temperatures up to 50° C. Pressure readings were continued for several hours, although equilibrium was apparently attained in 30 to 45 minutes. It was found possible to return to lower temperatures after making a reading at a higher temperature and to repeat the previous reading within experimental error. This would indicate the reversibility of the sorption process within the limits of the experiment.

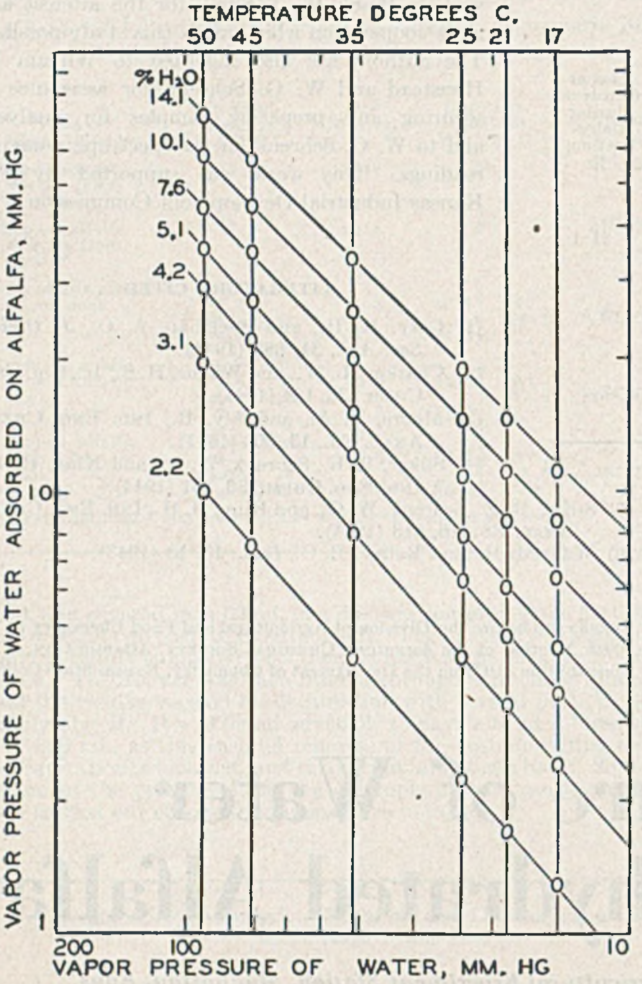

Figure 1. Isosteres of Water Adsorbed on Dehydrated Alfalfa Meal at Moisture Levels between 2.1 and 14.1%

No difficulty with carbon dioxide as mentioned by Makower (*3*) was experienced, although the high temperature (70° C.) at which he worked was not used.

DISCUSSION AND RESULTS

The vapor pressure data obtained are given in Table I. These data were obtained by plotting measured vapor pressure against moisture content. Graphical interpolation then permitted the construction of the table.

If the data are treated by the method described by Othmer and Sawyer (*6*), they may be interpreted graphically as shown in Figure 1 by plotting the vapor pressure of water in equilibrium with the dehydrated alfalfa against the vapor pressure of pure water at the same temperature. This gives a linear plot which permits extrapolation, within reasonable limits, to lower or higher temperatures. The experimental data fit straight lines nicely.

As has been shown for white potatoes (*4*), blanching produces a change in the dehydrated product which is reflected in changes in the vapor pressure data; consequently it was thought advisable to obtain vapor pressure data on steam-blanched alfalfa meal. When this procedure was followed, the type of change in vapor pressure, due to blanching white potatoes, was not observed, and the data obtained were identical with those obtained on unblanched samples. However, commercial dehydration of alfalfa is a rapid process; it occurs at high temperatures and therefore differs considerably from the usual vegetable dehydration procedures. This may account for similarities obtained under the two conditions, since it is possible that alfalfa is almost self-blanched during commercial dehydration. The different levels of protein also seemed to have no effect on the vapor pressure data. The data presented here also show quite close agreement with those of Makower (*3*) on dehydrated egg powder which contained approximately 52% protein.

Table I. Vapor Pressure of Water over Dehydrated Alfalfa at Various Temperatures and Moisture Levels

Moisture Content, %	Vapor Pressure, Mm. Hg at 0° C. 17° C.	21° C.	25° C.	35° C.	45° C.	50° C.
2.2	1.3	1.7	2.2	4.1	7.5	10.0
3.1	2.4	3.3	4.2	7.9	14.5	19.8
4.2	3.5	4.7	6.2	12.0	22.1	29.5
5.1	4.4	6.6	7.8	14.7	26.8	36.5
7.6	6.2	8.5	10.5	20.0	35.1	44.1
10.1	8.4	11.0	14.5	25.5	45.2	58.0
14.1	11.0	14.5	18.8	34.1	57.0	72.1

Table II. Ratio of Heat of Adsorption of Water by Dehydrated Alfalfa to Heat of Vaporization of Water

Moisture, %	E_a/E_L[a]	Moisture, %	E_a/L_L[a]
2.2	1.13	7.6	1.03
3.1	1.12	10.1	1.01
4.2	1.12	14.1	1.01
5.1	1.09		

[a] E_a = heat of adsorption of water vapor on alfalfa; E_L = heat of vaporization of water at the same temperature.

The slopes of the isosteres of Figure 1 may be used to calculate directly the ratio of the heat of adsorption of water by dehydrated alfalfa to the heat of condensation of water vapor at the same temperature. The results of such calculations are shown in Table II. The ratio E_a/E_L slowly increases as the moisture content decreases; this indicates that the heat of vaporization of water from alfalfa increases as the moisture level drops. This agrees with other data of a similar nature (*5*) and should be useful information in the design of dehydration equipment. At moisture levels higher than the 14.1% given here, the ratio closely approaches unity, as is to be expected.

Figure 2 presents the data taken at two different temperatures calculated on the basis of relative humidity, with temperature constant (adsorption isotherms). These data are presented in order to show that the dehydrated alfalfa meal adsorption isotherm is similar to that of many other substances (*4, 9*). The isotherms show the typical S-shape characterized by an inflection point at a moisture content of approximately 5%. This inflection point is considered by Emmett (*2*) and also Stamm and Millett (*8*) to represent the limit of ordinary surface adsorption at

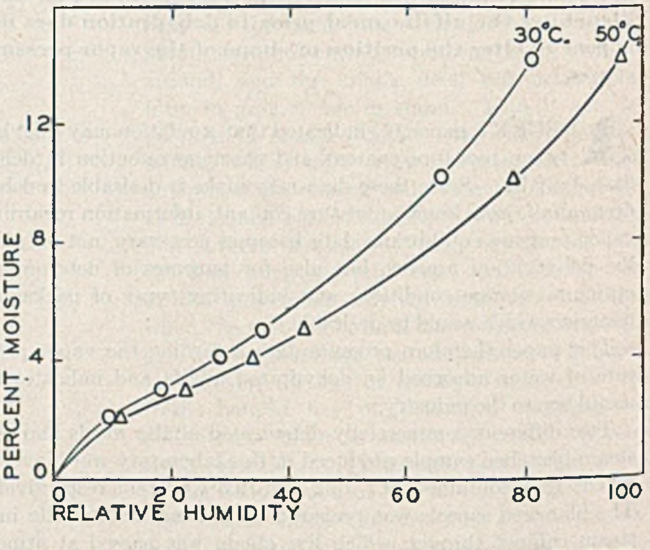

Figure 2. Adsorption Isotherms for Dehydrated Alfalfa Meal at 30° and 50° C.

low humidities and the beginning of multilayer and capillary adsorption.

The isotherms of Figure 2 suggest that the adsorption data should follow the theory of Brunauer, Emmett, and Teller (*1*). Calculations based on their equation were made but are not presented here, because more experimental points would be desirable for proper handling of these data. However, it was noted that, in the region of relative pressure (P/P_0) between approximately 0.2 and 0.5, the data approximated a straight line in accordance with their theory.

ACKNOWLEDGMENT

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Contribution 320 from the Department of Chemistry, Kansas State College.

Industrial Aspects of Browning Reaction

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The browning reaction in foodstuffs is attributed to a reaction between reducing sugars and proteins or other amino bodies. This reaction has steadily achieved increased recognition as a factor in the formation of color and flavor in foodstuffs since Maillard published his paper on the reaction of amino acids with glucose in 1912. The flavor and color effect of the browning reaction may be either desirable, as in the drying of malt and in baking, or undesirable, as in the storage of dried fruits and vegetables. The experience in the General Foods laboratories with desiccated coconut and tomato is summarized. The study of the formation of flavors from the reaction of pure amino acids with reducing sugars resulted in the discovery that aminobutyric acid and others of similar molecular weight give rise to a flavor similar to that of maple.

MAILLARD presented his paper in 1912 on the action of amino acids on sugars to produce what he called melanoidins, dark colored nitrogen compounds of high carbon content (*24*). Lafar (*19*) followed this with his study on foam fermentation in the sugar industry, and Ruckdeschel (*29*) with a consideration of this reaction in kiln malt, whereupon the Maillard reaction took on industrial importance for the first time. Spasmodically, during the early 1920's and in increasing tempo through the 1930's, the information on the Maillard reaction grew, to reach a climax during the recent war years. Today it is the subject of extensive programs in many industrial laboratories and a major effort of a coordinated attack by university, government, industrial, and private laboratories under the sponsorship of the United States Office of the Quartermaster General.

Until the war years the Maillard reaction had been just slightly more than a laboratory curiosity. Then operations in the tropics developed food spoilage problems attributable to the browning reaction and necessitated immediate study to develop a means of control. Actually, the problem was not new, but it now became important. Earlier investigators had recognized the reaction in the sugar industry (*9, 19, 33*), the beer industry (*11, 20*), malting (*21, 22, 23, 29*), and milk (*28*). More recent work has demonstrated like deteriorative effects on dried eggs (*3, 4, 26, 32*), molasses (*7*), dehydrated vegetables (*8, 27*), dried fruit (*15, 30, 31*), dried juices (*16*), breakfast cereal (*17*), coconut (*17*), soups (*17*), and dried fish and meats (*17*). It is undoubtedly a factor in the crumb color of breads and cakes and is suspected of being responsible for off colors developed in canned goods during processing. There is some indication of its occurrence in wines.

One glance at this list is, the authors believe, sufficient justification for the importance now assigned to the Maillard or browning reaction, in so far as the food industry is concerned, and its eventual control assumes great importance in our plans for research today.

The course of the reaction between amino acids and sugars has been studied by carbon dioxide evolution (*1, 2, 5, 14*), color change of reaction products (*23*), decrease in amino nitrogen during the course of the reaction (*2, 6, 18*), decrease in pH which occurred as the free amino groups were used up (*5, 13*), increase in property of reducing methylene blue (*6, 12, 14*), freezing point determination (*12*), and the change in optical rotation (*12, 14, 25*). Euler (*12*) showed that the decrease in free glucose determined by Willstätter-Schudel method coincides with the decrease in amino acid determined according to Van Slyke, and both are in agreement with the results of the freezing point determinations. The velocity of the reaction depends on the nitrogen compound and carbohydrate used, conditions of concentration, temperature, pH and time of heating, and the presence of accelerating and inhibiting agents. More recently, fluorescence has come to the fore as a tool in measuring the course of the reaction, and Dutton and Edwards (*10*) report the colored compounds and the fluorescent compounds as identical. The present work confirmed this to the extent of showing that the color and fluorescence curves are parallel, but with an interesting exception. In the presence of bisulfite the ratio of fluorescence to color was about five times that of an unprotected sample.

BASIC RESEARCH WORK

In our own laboratories we have attacked this general problem in two ways. Our basic research group has proceeded from the premise that a study of the reactions between individual amino acids and individual carbohydrates would ultimately develop a sufficient understanding of the reactions involved, so as to enable this type of change to be controlled much more rationally than at present. In a sense, this may be considered the synthetic approach, inasmuch as the objective of controlling the positive development of flavors is just as important to this program as is the negative control of the reaction to prevent formation of flavors that happen to be regarded as undesirable.

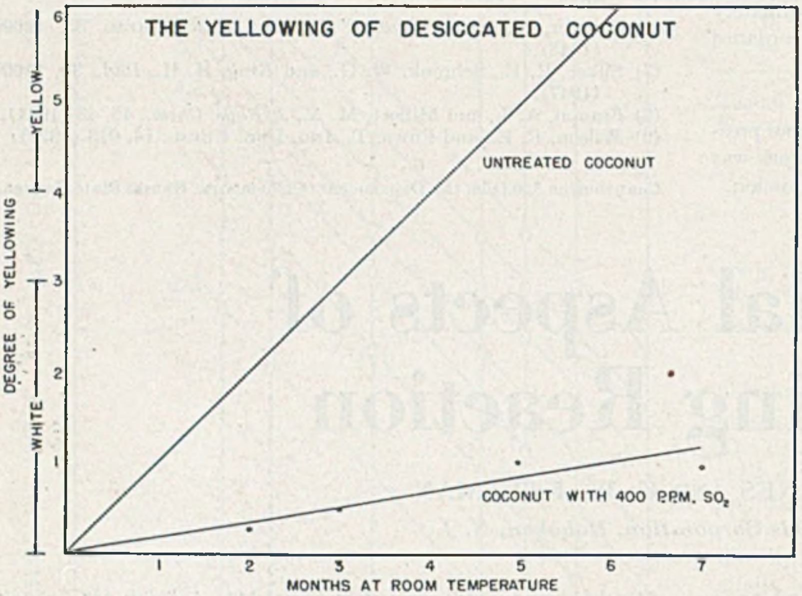


Figure 1

In the course of the basic research program many hundreds of tests were made, each test generally involving only one amino acid and one sugar. In this way most of the simple binary mixtures which are possible between the known amino acids and the known simpler carbohydrates were reacted under at least one set of conditions. The field is still far from covered, so that any conclusions reported here must be regarded as purely tentative. Using dextrose and glycine mixtures in a 50% aqueous solution as the simplest form of the reaction, a technique was developed for the comparison of the rates of color development by means of the half transmission time at 400 millimicrons in a cell of 1.3 centimeters thickness. The factors influencing this development have been studied. pH has been found to be important, the reaction proceeding more rapidly at higher pH values. Apparently the rate of browning is doubled at pH 6 to the rate obtained at pH 4. Temperature is an important factor. Three or four hours at 100° appear to be equivalent to one week at 40° C.; this indicates a two- or threefold increase for each 10° rise in temperature.

General conclusions which have developed from this program to date are as follows:

1. In many instances the development of flavor is rather specifically dependent upon the particular amino acid that participates in the reaction.
2. The reactivity of the sugars generally parallels the reactivity of these compounds in other respects. The aldopentoses, for instance, react more rapidly (or at lower temperature) than do the aldohexoses, and these, in turn, more rapidly than the di-, tri-, and polysaccharides. Carbohydrates having a free aldehyde or ketone group naturally react more rapidly than those that first have to be hydrolyzed or otherwise broken down to release these groups. Xylose and arabinose were so reactive under the conditions used that color development could not be satisfactorily measured even in the presence of sodium bisulfite. Additional work indicated that xylose is about forty times as reactive as dextrose, and arabinose about twenty times as reactive as dextrose.
3. The over-all reaction of the amino acids and sugars appears to be a complex series of stepwise reactions about which very little is known, except that the reaction mixture becomes more acid. Carbon dioxide is evolved under some conditions, and an aldehyde corresponding in structure to the amino acid used is sometimes formed in significant amounts, but it contains one carbon atom less (through loss of carbon dioxide).
4. At elevated temperatures large quantities of water are formed in proportion to the number of amino acid molecules entering into the reaction. In some respects it appears that the amino acid is acting as a catalyst in the dehydration of carbohydrate.
5. There appears to be a high degree of specificity in the kinetics of these reactions. For instance, the reaction characteristics of a given pair of reactants in the dry state cannot be used to predict with assurance the characteristics of the same pair reacted in aqueous solution. Dipeptides also participate in this type of reaction, but their rate of reaction may be either greater or less than that of the component amino acids.
6. Measured by color development, sulfur dioxide is still the best known inhibitor of these reactions.

Most of the present work has been in the area of inhibitors. Approximately 100 different compounds have been tested. Half transmission times have been determined for each of these (Table I) compared to the uninhibited dextrose-glycine mixture. The ratio of glucose, glycine, and water used was 4:1:5 by weight. All results to date tend to confirm the statement given that sulfur dioxide or sulfur-containing compounds are effective to a degree comparable with their ability to liberate sulfur dioxide on hydrolysis. However, hydroxylamine, hydrazine, and semicarbazide were moderately effective.

In general, inhibition produced by sulfur dioxide increased with increasing amounts of inhibitor. At the same time, the sulfur dioxide content decreased markedly during the course of the reaction, and it could be demonstrated that such loss was due to irreversible binding and not to oxidation to sulfate.

TABLE I. HALF TRANSMISSION TIMES AT 400 mμ (1.3-CM. CELL) FOR DEXTROSE-GLYCINE REACTION PLUS INHIBITORS AT A LEVEL OF 0.1%

Inhibitor	Time, Hr.	Inhibitor	Time, Hr.
None	65	Dextrose sodium bisulfite addn. compd.	200
Sodium bisulfite	250	Sodium formaldehyde sulfoxylate	130
Sodium dithionite	160	Hydroxylamine	160
Stannous chloride	180	Hydrazine	150
Sodium sulfide	110	Semicarbazide	100
Glyoxal sodium bisulfite addn. compd.	120		

The basic research groups at this laboratory have developed the conclusion that at the present time sulfur dioxide, properly applied and in limited but adequate quantities, represents the best means of preventing the deteriorative effects of the browning reaction.

TECHNOLOGICAL WORK

The second approach to the general problem was by the technology group who endeavored to find solutions to specific product problems as they arose, utilizing all of the information available from the literature, or from the basic research of this company. It appeared that dehydrated vegetables, coconut, soups, etc., all of interest to the applied group, fell into this reaction class. At least they knew that each of these foods had a characteristic dark color, off-flavor, and off-odor. In desiccated coconut the authors had a problem representing their first acquaintance with this type of reaction. Here the reaction takes the form of producing saffron yellow coconut—an unsalable item.

DESICCATED COCONUT. The applied work on desiccated coconut has just been completed. It is summarized in the following way:

1. A reduction in moisture level retards but does not stop the browning action. This statement should be qualified by a practical limitation—namely, the inability or impracticability of drying below 2% moisture for general purpose use.
2. A shift in pH toward the acid side retards but does not stop the reaction.
3. An increase in either invert sugar, protein, or amino nitrogen accelerates the reaction. It has been established that invert sugar and protein decrease on ripening of the coconut. A correlation between analytical factors, maturity, and rate of browning has been established.
4. Partial removal by leaching, oxidation, fermentation, etc., of either amino nitrogen or invert sugar retards the reaction, but by all techniques used to date has so altered the flavor of the product as to make application impossible.
5. Among all chemical treatments tried, sulfur dioxide in concentrations of less than 300 parts per million prevented the reaction from occurring. This is effectively demonstrated in Figure 1, which shows (*a*) a color change curve actually established by plotting color change occurring in normal (70° F.) storage over a long period of time, and (*b*) the color change in the presence of sulfur dioxide on the same color scale.

Figure 2 shows (*a*) an accelerated change curve made at 175° F., (*b*) an accelerated change curve showing the effect of adding sulfur dioxide as an inhibitor, (*c*) the increased rate of color formation in the presence of sodium acetate, pH 8, (*d*) the decreased rate in the presence of calcium chloride, pH 5, and (*e*) the decreased rate caused by leaching out the water-soluble material.

Dehydrated Tomatoes. As another example of even more complex nature, dehydrated tomatoes were selected for study. It was recognized that two chemical changes were involved in the storage effects noted on this product. In addition to the bitter, dark complex in the serum, this development is preceded or paralleled by the appearance of the hay flavor and odor characteristic of some of the highly pigmented dehydrated vegetables. One reaction is apparently catalyzed by the other, and as a result dehydrated tomatoes have an extremely short shelf life. Because of its delicate nature the product is also extremely heat sensitive, and overheating during drying, with consequent chemical changes, appears to accelerate markedly the off-flavor changes in storage.

Although much of this work is still going on, it may be summarized as follows to date:

1. Good storage life depends upon adequate control of drying to see that the product is not overheated. The critical temperature of this product is extremely low, probably below 150° F.
2. Darkening of the serum is attributable to the amino acid–aldehyde reaction plus a probable true caramelization of the invert sugar by the high acid in the dry final mixture. This caramelization, as well as the Maillard reaction, is extremely susceptible to traces of moisture. Metal ions in trace quantities materially accelerate the rate of deterioration, and trace quantities of copper from equipment are a definite hazard. Cyanides inhibit the reaction. Treating the juice with deaminase, extracted from pig kidneys, had a similar effect.
3. The hay flavor development, paralleling loss of red color, is an oxidative change (of the color fragments present). The authors have been able to isolate the flavor fraction in methanol extracts, which would indicate that it is xanthophyll in character rather than lycopene, carotene, or fat, as originally suspected.
4. Both changes can be controlled by the use of sulfur dioxide in comparatively low levels to give a product that will store adequately as long as the necessary reduction potential of the system is maintained.
5. Proper packaging at low moistures is a necessity to keeping quality.

In summing up all of these practical observations, the authors conclude that these complex amino acid–aldehyde reactions can in general be controlled by the use of sulfur dioxide in quantities of less than 1000 parts per million, so that the eventual consumer obtains a product superior to that which he would otherwise obtain.

FLAVORS FROM AMINO ACIDS

In the course of the fundamental studies, it was noted that the flavors and odors developed were apparently characteristic of the particular amino acid being used. A survey of the literature indicates a similar observation by earlier workers. Lintner (*23*) reported that the aroma, taste, and color of the reaction products of the amino acids and sugars are different with each amino acid used. Ruckdeschel (*29*) reported that glycocoll plus dextrose resembles beer; phenylalanine resembles dead roses; and leucine, fresh bread. Ambler (*2*) noticed that melanoidins caused a tendency to foam. Enders and Lother (*11*) found that melanoidins increased foam and head retention in beer and that they further improved the taste of beer.

The present authors now believe that, in addition to being responsible for many deteriorative changes that occur in food products, the Maillard reaction may also be the contributing factor in the development of many of our characteristic food flavors. Although no evidence is as yet available, there is reason to suspect that the distinctive flavor differences in breakfast foods, the crust of baked bread, roasted coffee, etc., may be attributed to chemical combinations brought about during the heat treatment operation.

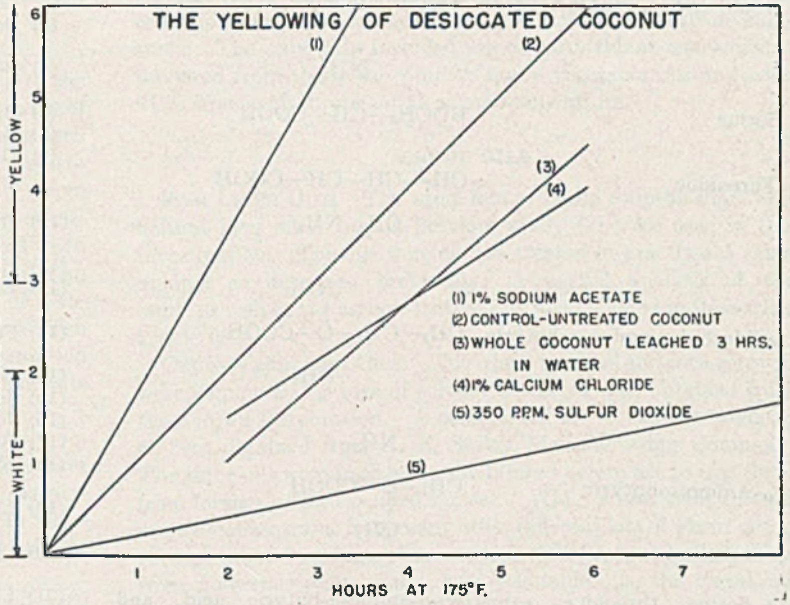
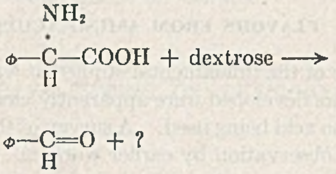


Figure 2

As a specific instance, the applied laboratories of this company have demonstrated that soy flour may be processed with special sugars in a variety of ways to develop distinctly different flavors. The flavor characteristics resulting in the final product appear to be closely correlated with time, temperature, moisture, and pH relations of the baking operation.

MAPLE FLAVOR

In the course of considering the fundamental reactions of amino acids with reducing sugars, the authors went over again some of the same ground that was covered by Maillard thirty-five years ago and covered by many workers since. It was observed that many of the amino acids when heated with glucose or levulose generated odors which were similar to the aldehydes having one less carbon atom than the amino acids. The example of this which is most easily and certainly recognized is the benzaldehyde odor which is formed by the reaction of glucose with α-aminophenylacetic acid.



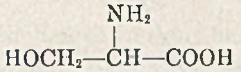
$$\phi\text{—}\underset{H}{\overset{NH_2}{C}}\text{—COOH} + \text{dextrose} \longrightarrow$$

$$\phi\text{—}\underset{H}{C}\text{=O} + ?$$

A large number of amino acids formed aldehyde odors in this manner, the requisite conditions being that the aldehydes be volatile and that they have an appreciable odor intensity. Tyrosine, for example, would not be expected to give a volatile aldehyde, and the acetaldehyde derived from alanine would not be expected to have a high odor effect. The amount of aldehyde formed, however, is quite small. The major course of the reaction leads elsewhere. Sourness and bitterness are the main flavor products. Moreover, the aldehyde does not appear to be the only aromatic body formed. Leucine, for example, gives an odor which undoubtedly contains isovaleraldehyde, but the total odor of the reaction is reminiscent of rye bread. Similarly, α-amino-*n*-butyric acid when heated with glucose yields an odor that is more complex than the expected propionaldehyde. The total odor was strongly suggestive of maple.

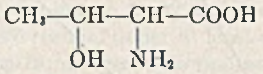
The aminobutyric acid was not the only amino acid which would develop maple flavor on heating with glucose.

Serine



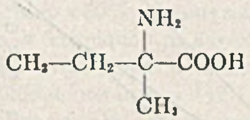
$$HOCH_2\text{—}\overset{NH_2}{CH}\text{—COOH}$$

Threonine



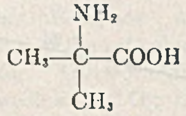
$$CH_3\text{—}\underset{OH}{CH}\text{—}\underset{NH_2}{CH}\text{—COOH}$$

α-Methyl-α-amino-*n*-butyric



$$CH_3\text{—}CH_2\text{—}\underset{CH_3}{\overset{NH_2}{C}}\text{—COOH}$$

α-Aminoisobutyric



$$CH_3\text{—}\underset{CH_3}{\overset{NH_2}{C}}\text{—COOH}$$

Serine, threonine, α-methyl-α-amino-*n*-butyric acid, and α-aminoisobutyric acid were also effective, although in a lesser degree. It was evident that a reducing sugar was necessary for the development of the maple character. As an example of a nonreducing sugar, sucrose was tried. It did not react until much higher temperatures were reached—that is, around 160° C.—and at this point the formation of caramel tended to mask the maple. It is known that the heating of sucrose to about this temperature range causes the formation of reducing sugars, and it is believed that this is a necessary precursor of the formation of a maple flavor.

A few roasts were made under conditions making it possible to catch the gases evolved, and it was found that 1 mole of aminobutyric and 2 moles of glucose formed 0.53 mole of carbon dioxide, 5 moles of water, a trace of propionaldehyde, and insoluble material equal to 14% of the product weight. There was 0.17 mole of amino acid left, judged by formol titration, and 0.30 mole of organic acid formed, judged by straight titration. The pH of the solution of the product was 3.6.

SUMMARY

The Maillard or browning reaction, as it is becoming more commonly known, is responsible for many of the deteriorative changes that take place in our food products, and it is amenable to control by the use of sulfur dioxide in reasonable quantities. At this writing, a less frowned-upon control procedure has not been found. More recently the browning reaction is assuming an added industrial implication, that of being important in the area of developing flavor characteristics common to many of our food products. This area is only now beginning to unfold. Fundamental research on this aspect may provide a means of chemically synthesizing some flavors which will nearly approximate the natural flavors.

ACKNOWLEDGMENT

The authors are indebted to Clair Kennedy of the Organic Research Laboratory for his many contributions to the fundamental work on browning and to A. A. Winston of the Food Technology Laboratory for most of the applied work on desiccated coconut, as well as to a large number of the technical personnel at Central Laboratories, General Foods Corporation.

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Vegetable Oil Concentrates as Antioxidants for Vitamin A in Fish Liver Oils

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Stability data on antioxidant concentrates, prepared from crude wheat germ, corn germ, and soybean oils by solvent extraction and tested in crude and carbon-treated soup-fin shark liver and halibut liver oils, establish that such concentrates are highly effective antioxidants for inhibiting peroxidation and vitamin A destruction in such type oils. In all cases, and for the same percentage of vitamin A destruction, much lower peroxide numbers were observed in the oils containing the vegetable oil antioxidant concentrates than in the blank crude fish liver oils or carbon-treated oils. The crude vegetable oils, when tested under similar conditions, displayed only minor powers to inhibit peroxidation and vitamin A destruction. The solvent-insoluble residual fractions, even though exhibiting no antioxidant activity for inhibiting vitamin A destruction in the carbon-treated halibut liver oil, displayed greater activity for inhibiting peroxidation than the crude vegetable oils themselves.

MUCH work has appeared in the literature relating to the oxidative instability of glyceride-type oils and to the use of synthetic, as well as natural-type antioxidants for inhibiting such undesirable deteriorative changes. No attempt has been made to review all of that work in this report. Previous studies (*1*) from this laboratory established that the antioxidants occurring naturally in crude fish liver oils were either removed or destroyed when the oils were treated with activated carbon in the presence of an organic solvent for the oil. Furthermore, the addition of α-tocopherol or α-tocopherol plus lecithin to such carbon-treated fish liver oils, or to the untreated oils, failed to inhibit peroxidation effectively in such oils, even though that type of antoixidants markedly decreased the rate of vitamin A destruction (*2*).

Attempts to isolate and identify the individual, naturally occurring antioxidant principles of crude vegetable and fish liver oils have been only partially completed. Most natural oils contain more than one active antioxidant component, and in vegetable oils particularly two or more components act synergistically to afford antioxidant protection.

Mattill (*9*) was the first to associate the stability of a fat with the presence of natural antioxidants in it. Since that date (1927) numerous data have been reported to the effect that the stability of crude antioxidant-containing oils is decreased following certain treatments (*1*, *11*). Mattill and co-workers (*13*) showed that the antioxidant substances in certain vegetable oils could be concentrated in the unsaponifiable fractions of such oils and that their activity depended on free hydroxyl groups. Sterols present in the unsaponifiable fractions were found to be devoid of antioxidant activity. Mattill (*10*) first recorded that gossypol present in crude cottonseed oil possessed marked antioxidant activity. Sesamol, a constituent of sesame oil, is an effective inhibitor for preventing oxidation (*12*). Fawcett (*6*) demonstrated that, during the molecular distillation of crude cottonseed oil, the antioxidants are concentrated in both the first distillate and in the residue. Golumbic (*7*) concludes that cottonseed and soybean oils and mixed hydrogenated vegetable oils contain alkali-labile antioxidants other than the tocopherols, probably chroman-5,6-quinones. In a later article Golumbic (*8*) states that the antioxygenic chroman-5,6-quinones which appear during the induction period in vegetable fats, but never during the oxidation of animal fats, retard the accumulation of fat peroxides in vegetable fats after the complete disappearance of the tocopherols. These references are only a few of the many relating to the antioxidant qualities of vegetable oil materials which have appeared in the literature in recent years.

This investigation reports the antioxidant effect of crude vegetable oil materials for inhibiting vitamin A destruction and peroxide formation in samples of crude and carbon-treated soup-fin shark and halibut liver oils. No attempt has been made to include antioxidant effectiveness data on solvent extracts prepared from all types of crude vegetable oils under different experimental conditions, or with all possible types of solvents or solvent mixtures. The only data included are on antioxidant concentrates prepared from the more common crude vegetable oils and with 91% aqueous isopropanol at a low temperature.

CRUDE OILS

FISH LIVER OILS. The same lots of crude soup-fin shark and halibut liver oil A from a previous study (*2*) were used in this investigation. The oils were carbon-treated in exactly the same manner as described previously. A partial analysis of the crude as well as the carbon-treated oils was included in the earlier article (*2*).

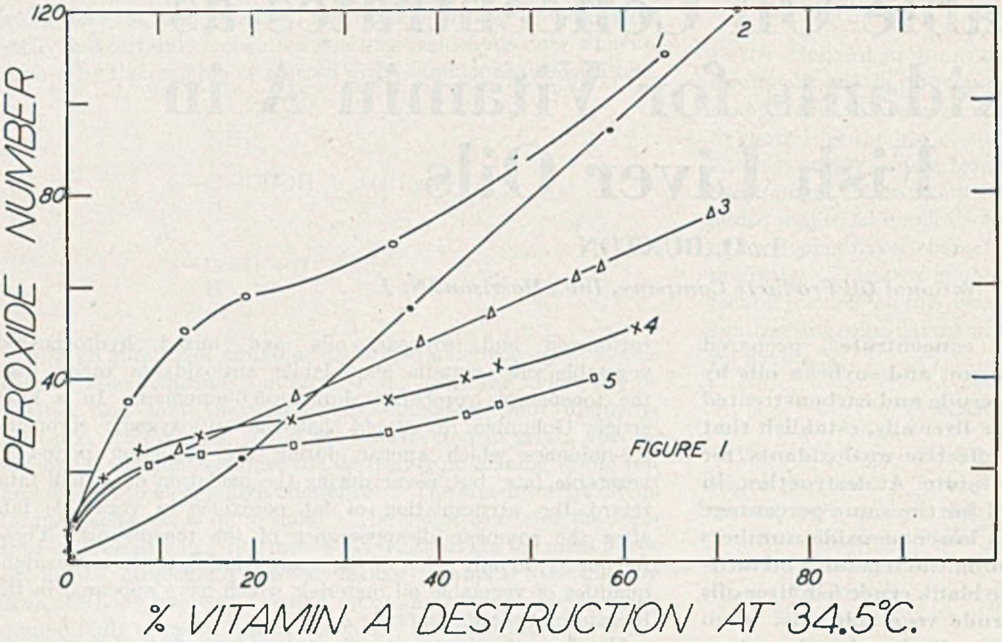
CRUDE VEGETABLE OILS. The wheat germ oil and corn germ oil were commercial grades of solvent-extracted oils, obtained from the VioBin Corporation. A commercial lot of expeller soybean oil was obtained from A. E. Staley Manufacturing Company. The three oils were fresh and were filtered before use to free them from foreign and suspended matter. While antioxidant solvent extract concentrates from many other different lots of wheat germ, corn germ, and soybean oils were also examined, as well as those from numerous other varieties of vegetable oils, the variations were a matter of degree rather than a demonstration of some different effect. A partial analysis of the crude oils used is included in Table I.

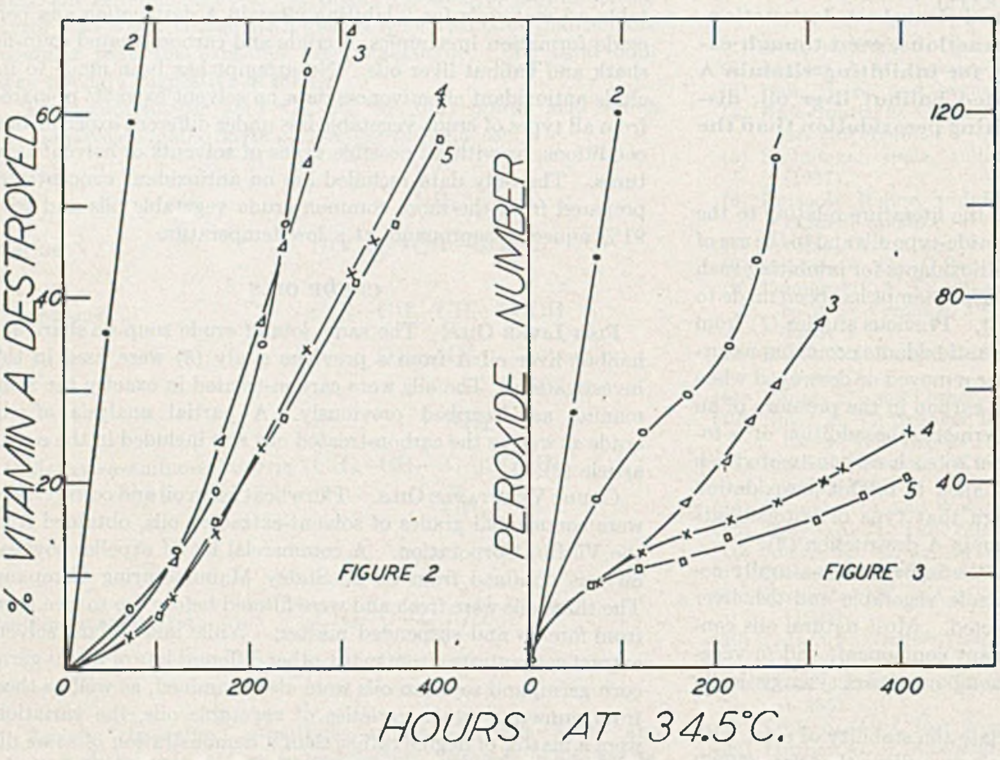
SOLVENTS

In this investigation on the use of solvent extract antioxidant concentrates from crude wheat germ, corn germ, and soybean

TABLE I. COMPARATIVE ANALYSIS OF CRUDE VEGETABLE OILS AND 91% ISOPROPANOL EXTRACT CONCENTRATES FROM THE OILS

	Wheat Germ Oil	Ext. Wheat Germ Oil	Soybean Oil	Ext. Soybean Oil	Corn Germ Oil	Ext. Corn Germ Oil
% free fatty acids	5.6	23.6	1.1	8.4	1.8	35.1
% unsaponifiable	5.3	10.5	1.3	8.4	1.3	9.7
Iodine value	119.1	113.2	121.1	115.0	118.5	108.3
Saponification value	182.5	184.6	193.0	183.3	189.0	169.0





Curve 1. Crude soup-fin shark liver oil

Curve 2. Carbon-treated soup-fin shark liver oil

Curve 3. Carbon-treated soup-fin shark liver oil + 3% of solvent extract antioxidant concentrate from crude soybean oil

Curve 4. Carbon-treated soup-fin shark liver oil + 5% of solvent extract antioxidant concentrate from crude soybean oil

Curve 5. Crude soup-fin shark liver oil + 5% of solvent extract antioxidant concentrate from crude soybean oil

oils as antioxidants for inhibiting peroxidation and vitamin A destruction in fish liver oils, only data on extracts prepared with 91% aqueous isopropanol at a low temperature (−18° C.) are included. While many other types of solvents have been studied in the course of this work, most of them acted similarly, the difference again being a matter of degree. Percentage yield, as well as antioxidant potency of the solvent extract concentrates, depends largely on factors such as the temperature at which the extractions are performed, number of extractions, type of crude oil extracted, and the particular extracting solvent used. For example, solvent extract concentrates prepared from crude soybean, corn, wheat germ, cottonseed oils, etc., by extraction with 85-88% aqueous isopropanol at about +20° C. are slightly less effective as antioxidants in fish liver oils than extracts prepared with 91% aqueous isopropanol at −18° C. The percentage yield obtained with the former type solvents is, however, somewhat greater. Extracts prepared from the same type oils with 91% aqueous isopropanol at about −25° C. or lower are still more potent as antioxidants. The solvent extract concentrates can be processed further in several ways to improve the color, remove free fatty acids, part or all of the phosphatides, and the inactive sterols, and thus further concentrate the active antioxidant principles. However, in this study the crude solvent extract concentrates were used without such further treatments.

The general extraction method used for preparing the antioxidant extract concentrates studied in this report is recorded elsewhere (*3*). This general extraction method is also applicable for concentrating the naturally occurring antioxidants in fish liver oils (*5*). Briefly, the details of the method are as follows:

One hundred grams of the crude vegetable oil to be extracted were weighed into a 1000-ml. Erlenmeyer flask equipped with a nitrogen gas inlet tube, and 400 ml. of 91% aqueous isopropanol were added. While bubbling a brisk supply of nitrogen gas through the oil and solvent mixture, the mass was heated in a water bath to 50° C. After the mixture was thoroughly shaken, the nitrogen supply was cut off, the flask stoppered, and the mass cooled gradually to the low temperature. The three oils were all solvent-extracted at −18° C. The oil and solvent mixture was allowed to remain at the low temperature for about 12 hours before the supernatant extractant solvent layer was decanted. In most instances the said upper solvent layers were clear and the residual oil layers were solid. In this investigation two solvent extractions of each oil were made; the second extraction was similar to the first. The first and second solvent extraction fractions were combined and gravity-filtered at −18° C. The clear solvent extract filtrates were distilled under reduced pressure in a hot water bath (maximum temperature about 50° C.) in the

Table II. Stability of Halibut Liver Oil at 34.5° C.

Antioxidant		0 Days	2 Days	3 Days	4 Days	5 Days	7 Days	8 Days	9 Days	10 Days	11 Days	12 Days	13 Days	16 Days	20 Days
							Crude Halibut Oil								
None	Perox. No.	1.2	..	21.2	..	28.4	52.6	71.3	80.5	...	..	...	..	...	..
	% A destr.	..	..	7.7	..	18.1	53.9	70.0	77.0	...	...	...	..	...	...
3% ext. soybean oil	Perox. No.	1.2	..	..	4.8	..	5.2	..	5.4	...	7.3	...	11.0	12.5	13.8
	% A destr.	..	..	..	4.0	..	11.0	..	14.1	...	17.0	...	21.0	30.0	37.0
							Refined Halibut Oil								
None	Perox. No.	3.0	26.7	39.3	57.4	..	...	..	...	...	...	...	..	...	..
	% A destr.	..	35.4	52.6	68.5	..	..	..	..	...	..	...	..	...	..
3% wheat germ oil	Perox. No.	1.1	..	10.9	19.8	30.8	..	..	..	...	..	...	..	...	..
	% A destr.	..	..	13.8	32.6	55.1	..	..	..	...	..	...	..	...	..
3% ext. wheat germ oil	Perox. No.	2.6	3.0	4.4	..	10.1	11.6	..	12.0	...	13.1	16.2	..	...	..
	% A destr.	..	2.9	3.3	..	9.9	17.0	..	34.6	...	55.2	69.2	..	...	..
3% residue wheat germ oil	Perox. No.	3.3	16.3	19.2	24.6	..	...	..	...	...	..	...	..	..	..
	% A destr.	..	24.6	43.2	61.8	..	..	..	..	...	..	...	..	...	..
3% corn germ oil	Perox. No.	1.8	12.0	23.0	36.4	46.9	..	..	..	...	..	...	..	...	..
	% A destr.	..	23.9	36.7	54.5	69.7	..	..	..	...	..	...	..	...	..
3% ext. corn germ oil	Perox. No.	5.7	..	7.5	..	11.0	..	14.4	..	20.9	22.3	24.4	31.1	...	..
	% A destr.	..	..	5.4	..	13.5	..	20.4	..	38.4	51.8	57.3	68.5	...	..
3% residue corn germ oil	Perox. No.	3.2	20.7	19.1	27.1	..	..	..	..	...	..	...	..	...	..
	% A destr.	..	30.0	45.1	63.7	..	..	...	...	...	...	...	..	...	..
3% soybean oil	Perox. No.	1.8	12.1	21.3	35.8	47.8	..	..	..	...	..	...	..	...	..
	% A destr.	..	19.8	32.4	54.0	69.8	..	..	..	...	..	...	..	...	..
3% ext. soybean oil	Perox. No.	2.4	4.7	..	7.5	..	5.7	..	5.6	...	11.6	...	14.8	16.8	..
	% A destr.	..	2.3	..	5.2	..	13.1	..	18.7	...	28.7	...	40.0	54.5	..
5% ext. soybean oil	Perox. No.	1.7	2.0	..	6.7	..	4.3	..	4.9	...	10.1	...	12.1	11.2	14.8
	% A destr.	..	1.4	..	1.4	..	5.9	..	7.7	...	12.4	...	18.4	28.0	36.1
3% residue soybean oil	Perox. No.	3.2	21.5	21.0	21.9	..	...	..	..	...	..	...	..	...	..
	% A destr.	..	35.5	49.5	65.6	..	..	..	..	...	..	...	..	...	..
0.5% α-tocopherol	Perox. No.	9.8	..	46.1	..	70.1	91.0	..	..	121	..	134	..	154	..
	% A destr.	..	..	1.4	..	4.7	8.4	...	..	14.5	..	20.6	..	58.5	..

presence of nitrogen gas to remove all traces of the solvent. The residual oil fractions insoluble in the solvent at the low temperature were also freed of solvent traces in a similar manner. Both the soluble extract fractions and the solvent-insoluble oil fractions were stored in closed vials at +4° C. until they could be tested. Table I gives comparative analysis of the crude vegetable oils used, as well as of the solvent extract concentrates prepared from these oils.

Samples of the crude soup-fin shark liver and halibut liver oils were carbon-treated in cyclohexane using 20% of activated carbon (Nuchar XXX) exactly as reported previously (*1*). The carbon-treated samples were either used immediately or stored in completely filled closed vials at −18° C. until the studies were conducted.

Portions of the crude soup-fin shark liver and halibut liver oils, the same oils carbon-treated, and the oils containing the various vegetable oil materials to be tested for antioxidant properties, were studied for percentage vitamin A destruction and peroxidation at 34.5° C. by the method outlined in a previous report (*1*). The results on vitamin A and peroxidation for the various oils studied are summarized in Figures 2 and 3 and in Table II. An experiment is shown in Table II in which 0.50% α-tocopherol was added to the carbon-treated halibut liver oil for comparison. The percentage of vegetable oil material added to the fish liver oils and tested for comparative effectiveness, as indicated by rate of peroxide formation and percentage vitamin A destruction, was arrived at somewhat arbitrarily from preliminary studies. One of the aims was to add sufficient of the vegetable oil solvent extract antioxidant concentrates to the samples of carbon-treated oils to produce oils exhibiting approximately the same rate as, or a slower rate of vitamin A destruction than that displayed by the crude fish liver oils. Comparison of curves 1 and 3, Figure 2, shows that when 3% of the solvent extract of crude soybean oil was added to the carbon-treated soup-fin shark liver oil, the resulting oil exhibited about the same vitamin A stability as the crude soup-fin shark liver oil. This type of antioxidant concentrates is also equally effective for inhibiting oxidation of many other types of oxidizable substances (*3*, *4*).

EFFECT OF PEROXIDATION ON VITAMIN A DESTRUCTION

Figure 1 and Table II show the data obtained on the relation between peroxidation and percentage vitamin A destruction in the samples of crude and carbon-treated soup-fin shark liver and halibut liver oils containing the various types of crude vegetable oils and fractions studied. These results indicate that, at a given percentage of vitamin A destruction, the peroxide numbers of the crude fish liver oils containing the solvent extract concentrates and of the carbon-treated oils containing the crude vegetable oils, the solvent-soluble extract concentrates and the solvent-insoluble residue fractions from the crude vegetable oils are considerably lower than the peroxide numbers of the corresponding blank samples. In the carbon-treated oils, the solvent-insoluble residue fractions are more effective in holding down the peroxide numbers at various percentages of vitamin A loss than the crude vegetable oils, even though the crude oils exhibit slightly greater ability to prevent vitamin A destruction. At various percentages of vitamin A destruction, the peroxide numbers of the carbon-treated halibut liver oil containing the solvent extract and residue fractions from the crude vegetable oils are much lower than those of the crude and carbon-treated halibut liver oil. The solvent extract concentrates are greatly superior to the residue fractions in this respect. All of the vegetable oil materials were much more effective than α-tocopherol for holding down the peroxide number at a given percentage of vitamin A destroyed (Table II).

EFFECT OF TIME ON VITAMIN A DESTRUCTION

One of the main objects in fractionating the various crude vegetable oils was to prepare, by relatively simple and practical means, highly active antioxidant concentrates for inhibiting peroxidation and vitamin A destruction in fish liver oils. These oils, particularly when refined, are such easy prey to the influences of oxidation that many commonly used antioxidants, normally active in other types of fats at low percentage concentrations, are of little value in preserving vitamin A and minimizing peroxidation in such oils. Figure 2 and Table II show the percentages of vitamin A destroyed after various hours of standing at 34.5° C. Comparison of curves 1 and 3 shows that 3% of the solvent extract from soybean oil when added to the carbon-treated soup-fin shark liver oil, makes the vitamin A content of the oil as stable as that of the crude soup-fin shark liver oil. Five per cent of the solvent extract (curve 4) makes the vitamin A content of the same oil more stable than that of the crude oil. The carbon-treated soup-fin shark and halibut liver oils display a vitamin A destruction rate directly proportional to the time, which suggests that these oils must have been devoid of active vitamin A antioxidants. The results in Table II on the rate of vitamin A destruction in the carbon-treated halibut liver oil containing the solvent extract antioxidant concentrates from crude wheat germ, corn germ, and soybean oils clearly demonstrate that 3% of the concentrates stabilizes the vitamin A content of the carbon-treated oil to a degree much greater than that displayed by the crude halibut liver oil. When 3% of the solvent extract antioxidant concentrate from soybean oil was added to carbon-treated halibut liver oil, the rate of vitamin A destruction was nearly the same as when 0.50% of synthetic α-tocopherol was added to the same oil (54.5% vitamin A destruction after 16 days as compared to 58.5%, respectively). The remarkable difference was in the respective peroxide numbers, which were 16.8 as against 154. Five per cent of the solvent extract concentrate from soybean oil was considerably more effective for stabilizing the vitamin A content of the carbon-treated halibut liver oil than 3% of the concentrate or 0.50% of α-tocopherol. The results show further that the solvent extract concentrates from soybean oil are more effective for inhibiting vitamin A destruction in the carbon-treated halibut liver oil than similar extracts from wheat germ and corn germ oil. These findings are substantiated by unpublished data on similar type solvent extract antioxidant concentrates from many individual lots of the three types of oils. The percentage yield of antioxidant extract concentrate obtained from the wheat germ oil was considerably greater than that obtained from the soybean oil (10.9% as against 5.5%, respectively). This may account in part for the slightly lower antioxidant potency displayed by the wheat germ oil extract concentrate. From a percentage weight yield standpoint, there is actually more antioxidant in the solvent extract from wheat germ oil than from soybean oil. Results in Table II indicate that at a 3% concentration the three crude vegetable oils possess only minor ability to protect the vitamin A in the carbon-treated halibut liver oil under the conditions employed. The solvent-insoluble residue fractions exhibit no protective action for vitamin A under the same circumstances.

EFFECT OF TIME ON PEROXIDE FORMATION

The inhibition of peroxidation is secondary in importance to the prevention of vitamin A losses in fish liver oils on contact with air. Antioxidants of the type of α-tocopherol or α-tocopherol plus lecithin are ineffective for preventing peroxidation in fish liver oils (*2*). Figure 3 and Table II show the results obtained in this investigation on the peroxidation rate of the various samples studied. Curves 3 and 4, as compared with curve 1, demonstrate clearly that the soybean antioxidant extract fractions at a 3 and 5% level in the carbon-treated soup-fin shark liver oil are extremely potent in peroxide-inhibiting principles. After 125 hours the peroxidation rate of the sample containing 5% was much slower than in the sample containing 3%. The blank carbon-treated soup-fin shark liver oil (curve 2, Figure 3) exhibited a straight line of oxidation, which indicates the absence of active antioxidants. The rate of peroxide formation in the samples of carbon-treated halibut liver oil (Table II) containing the antioxidant extract concentrates from the three crude vegetable oils studied was much slower than in the crude halibut liver oil. For example, after a storage period of 9 days at 34.5° C. the peroxide numbers of the crude halibut liver and the carbon-treated halibut liver oil containing 3% of the antioxidant extract concentrates from wheat germ and soybean oils were 80.5, 12.0, and 5.6, respectively. The antioxidant extract concentrate from crude corn germ oil was slightly less active for inhibiting peroxidation in the carbon-treated halibut liver oil than in the carbon-treated soup-fin shark liver oil. This behavior is undoubtedly due to differences in the degree and type of unsaturation and in the glyceride configuration of the two fish liver oils. Samples of the carbon-treated halibut liver oil containing 3% of the crude vegetable oils and the solvent-insoluble residue fractions from the crude vegetable oils displayed slower peroxidation rates than did the blank carbon-treated oil.

The results indicate that crude wheat germ, corn germ, and soybean oils are valuable sources of antioxidants; from them concentrates very active for inhibiting vitamin A destruction and peroxidation in fish liver oils can be prepared by solvent extraction. Even though the crude vegetable oils, as such, possess only minor powers to inhibit peroxidation and vitamin A destruction, solvent extract concentrates from the said oils are highly effective for both purposes.

The insoluble residue fractions from the crude vegetable oils possess less antioxidant potency toward preventing vitamin A destruction, but somewhat greater activity than the crude vegetable oils themselves for inhibiting peroxide formation in the carbon-treated halibut liver oil. This fact indicates that the peroxide-inhibiting type antioxidants are not removed by the solvent extraction treatment to the same extent as are the vitamin A inhibiting type antioxidants. Certainly the solvent extract concentrates contain large amounts of the active peroxide-inhibiting type antioxidants; otherwise these concentrates, which are known to contain the major proportion of the unesterified tocopherols present in the crude vegetable oils, even though they are effective in inhibiting vitamin A destruction in the carbon-treated oils, would not have so effectively inhibited peroxide formation. Some of the antioxidant activity of the concentrates is the result of the synergistic action between the phosphatides, which are present in large amounts in the extracts, and other antioxidant components also present, such as the tocopherols and chroman-5,6-quinones. Further work is required along these lines before a clear understanding of all the factors involved can be realized.

ACKNOWLEDGMENT

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Composition of Vapors from Boiling Binary Solutions

ACETONITRILE-WATER SYSTEM[1]

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The vapor-liquid compositions for the binary system acetonitrile-water were determined at atmospheric pressure, at 300 mm., and at 150 mm. pressure. It was found that at all of these pressures a minimum-boiling azeotrope was present. Extrapolation showed that at about 10 mm. pressure this azeotrope would have a composition of 95 mole % acetonitrile boiling at approximately −12° C. The data were correlated by the methods of Othmer and Gilmont (*8*) and were further checked by the method of Carlson and Colburn (*1*).

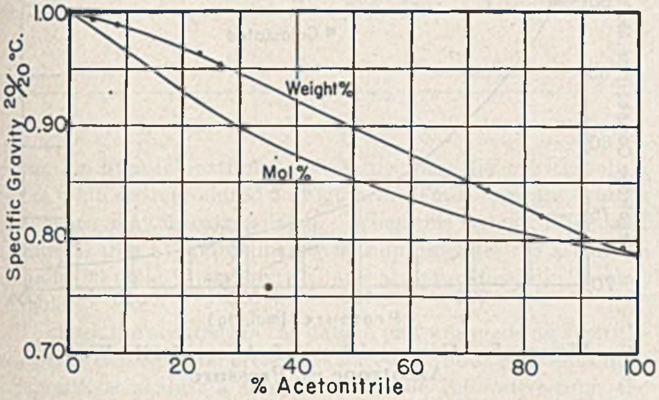

Figure 1. Specific Gravity of Aqueous Solutions of Acetonitrile at 20° C.

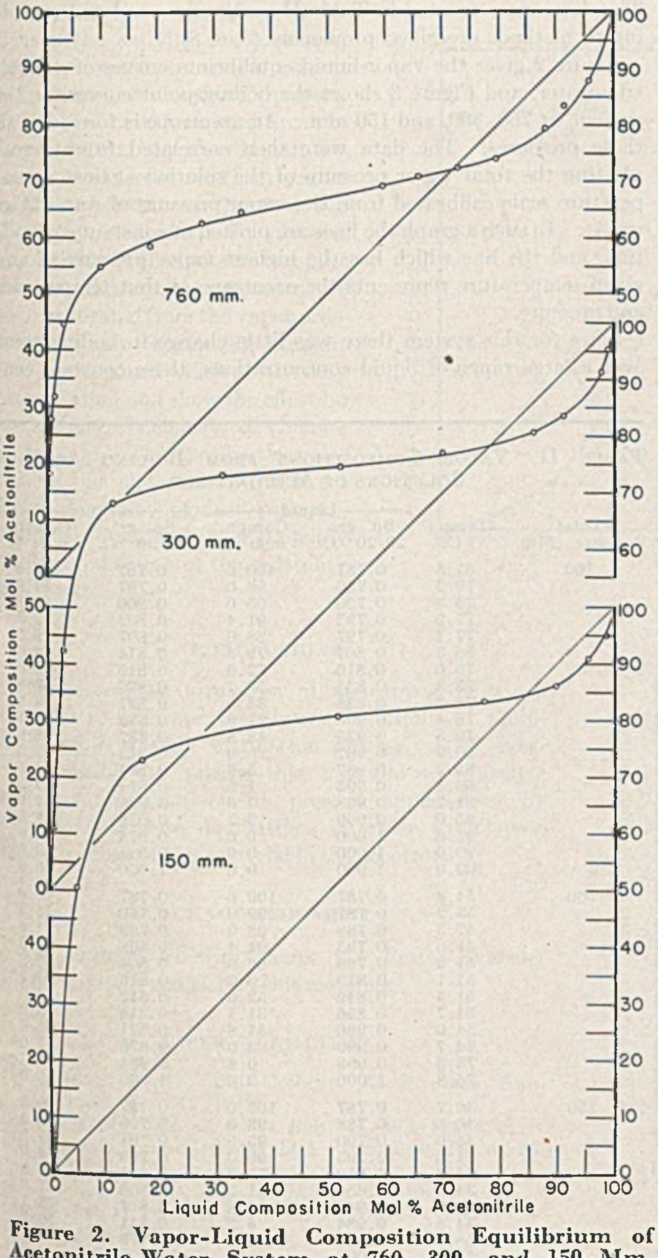

Figure 2. Vapor-Liquid Composition Equilibrium of Acetonitrile-Water System at 760, 300, and 150 Mm. Pressure

THE use of acetonitrile as a solvent and as a starting point in the production of ethylamine, intermediates, and synthetic aromatics has expanded greatly during the last few years. Users of acetonitrile have been confronted with the problem of separating this material, which is completely miscible with water, from its aqueous solutions. The data on this system are sparse indeed. Ewert (*2*) reported some vapor pressures of aqueous solutions of acetonitrile at 20°, 25°, 30°, 35°, and 40° C. In reviewing the vapor pressures of binary solutions, Landsberg (*4*) calculated the composition of aqueous acetonitrile solutions at 30° C. Therefore, the vapor-liquid equilibrium of aqueous solutions of acetonitrile was studied, and the effect of pressure on the azeotrope formed was investigated.

In this investigation C.P. acetonitrile was further purified by drying with calcium chloride and by redistilling. The fraction boiling between 81.5° and 81.7° C. was used for these experiments. The specific gravities of aqueous solutions of acetonitrile were studied by a Westphal balance at 20° C., and are given in Table I and Figure 1. The analysis was made by measuring the specific gravity of solutions and reading off the compositions directly from Figure 1.

The method and apparatus for determining the vapor-liquid equilibria have been described previously (*3*, *7*). The temperature was observed directly with a thermometer calibrated by the National Bureau of Standards within 0.1° C., and the pressure was read and maintained constant by a mercury manometer and constant pressure device (*3*). The liquid and vapor states in equilibrium were determined by gravimetric analysis of samples of the liquid withdrawn from the still and from the distillate

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[1] Previous articles in this series appeared in 1928 (page 743), 1943 (page 614), 1944 (page 1061), 1945 (page 279), and 1946 (page 751); also in ANALYTICAL EDITION, 1932 (page 232).

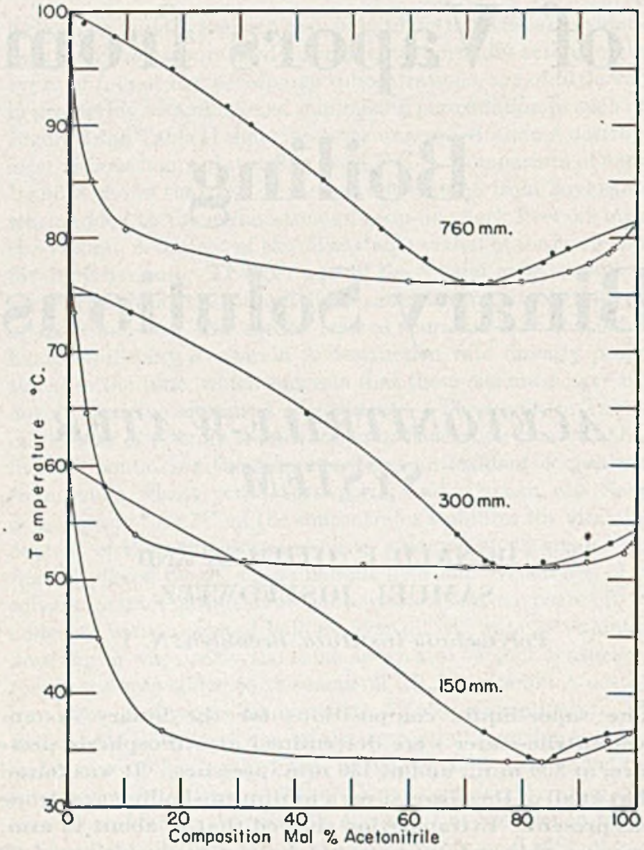

Figure 3. Temperature-Composition Curves for Acetonitrile-Water at 760, 300, and 150 Mm.

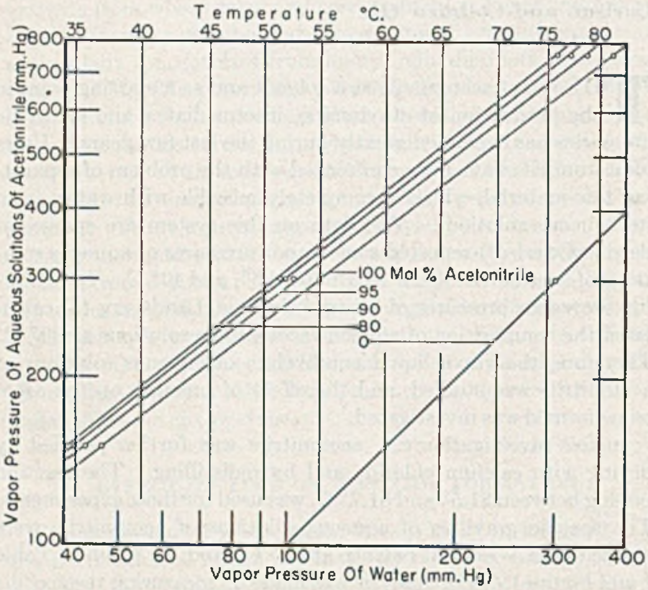

Figure 4. Total Vapor Pressure of Aqueous Solutions of Acetonitrile *vs.* Vapor Pressure of Water at Same Temperature

TABLE I. SPECIFIC GRAVITY (20/20° C.) OF AQUEOUS SOLUTIONS OF ACETONITRILE

Wt. % Acetonitrile	Sp. Gr.	Wt. % Acetonitrile	Sp. Gr.	Wt. % Acetonitrile	Sp. Gr.
100.0	0.787	73.7	0.844	22.8	0.965
97.1	0.794	50.0	0.899	8.1	0.990
90.3	0.804	26.3	0.955	3.7	0.994
83.0	0.822			0.0	1.000

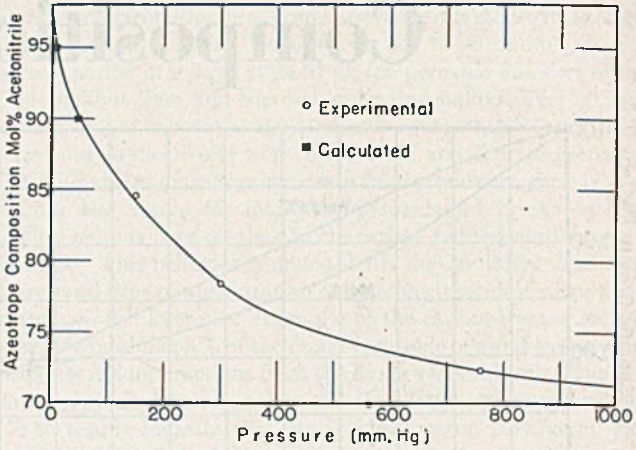

Figure 5. Composition of Acetonitrile-Water Azeotrope *vs.* Pressure

trap, respectively, after the mixtures were allowed to boil for at least 30 minutes after they had reached constant temperature. The data are presented in Table II and were correlated according to methods described previously (*5, 6, 8*).

Figure 2 gives the vapor-liquid equilibrium curves of acetonitrile-water, and Figure 3 shows the boiling point curves for the system, at 760, 300, and 150 mm. An azeotrope is formed at all these pressures. The data were then correlated (*6*) by cross plotting the total vapor pressure of the solution against a temperature scale calibrated from the vapor pressure of water (Figure 4). In such a graph the lines are plotted at constant composition, and the line which has the highest vapor pressure at any given temperature represents the azeotrope at that temperature and pressure.

Since for this system there was little change in boiling point over a large range of liquid concentrations, these constant con-

TABLE II. VAPOR COMPOSITIONS FROM BOILING AQUEOUS SOLUTIONS OF ACETONITRILE

		Liquid		Vapor	
Total Pressure, Mm.	Temp., ° C.	Sp. gr., 20/20° C.	Compn., mole %	Sp. gr., 20/20° C.	Compn., mole %
760	81.5	0.787	100.0	0.787	100.0
	79.2	0.789	96.0	0.797	87.9
	78.8	0.790	95.0	0.800	85.1
	77.9	0.793	91.4	0.802	83.5
	77.1	0.797	88.0	0.807	79.5
	76.3	0.807	79.5	0.814	74.0
	76.0	0.816	72.6	0.816	72.6
	76.3	0.835	59.7	0.820	69.3
	78.2	0.886	34.9	0.827	64.5
	78.4	0.906	27.9	0.830	62.7
	79.3	0.935	18.8	0.837	58.5
	80.9	0.967	9.9	0.843	55.0
	85.2	0.987	3.9	0.864	44.7
	90.1	0.995	1.5	0.894	32.0
	91.7	0.998	0.6	0.906	27.9
	95.0	0.999	0.2	0.938	18.0
	97.8	1.000	0.0	0.974	7.9
	99.0	1.000	0.0	0.991	2.6
	100.0	1.000	0.0	1.000	0.0
300	54.4	0.787	100.0	0.787	100.0
	53.2	0.7875	99.0	0.790	95.3
	52.3	0.788	98.0	0.793	91.4
	51.6	0.793	91.4	0.802	83.5
	51.2	0.799	86.0	0.804	80.8
	51.1	0.819	70.0	0.810	77.2
	51.4	0.849	52.0	0.813	74.6
	51.7	0.896	31.1	0.814	73.2
	54.0	0.960	11.8	0.821	68.6
	64.7	0.990	3.0	0.876	42.0
	73.5	0.998	0.8	0.964	10.7
	75.8	1.000	0.0	1.000	0.0
150	36.7	0.787	100.0	0.787	100.0
	36.6	0.788	98.0	0.790	95.5
	36.0	0.790	95.5	0.794	91.0
	34.6	0.795	90.0	0.799	86.0
	34.1	0.810	77.2	0.802	83.5
	34.5	0.850	51.3	0.806	81.0
	36.7	0.942	16.8	0.814	73.2
	44.8	0.984	5.2	0.851	50.7
	58.7	0.999	0.3	0.979	6.4
	60.2	1.000	0.0	1.000	0.0

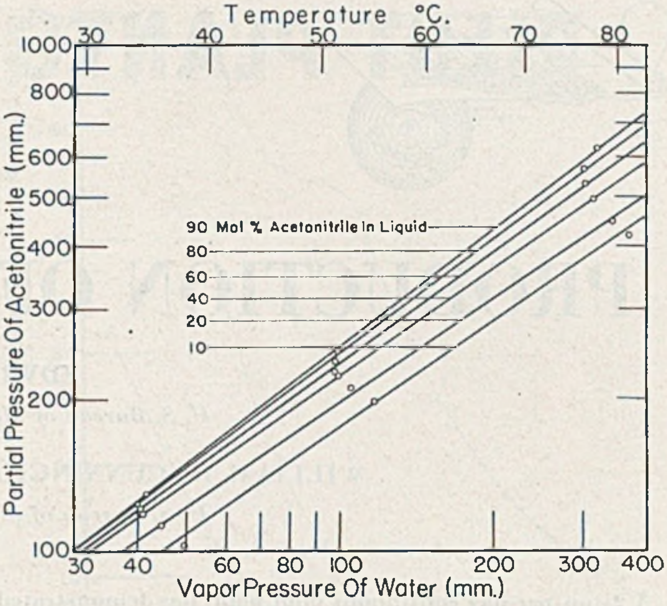

Figure 6 (*Top*). Partial Pressures of Acetonitrile *vs.* Vapor Pressure of Water at Same Temperature

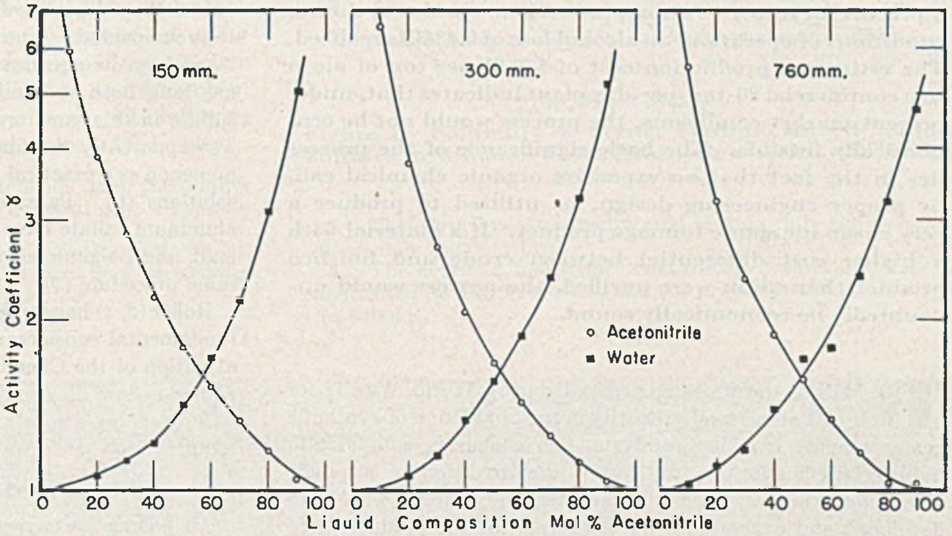

Figure 7 (*Center*). Activity Coefficients of Acetonitrile and Water *vs.* Composition at 760, 300, and 150 Mm.

centration lines fell extremely close together; for clarity only a few of them are reproduced on Figure 4. These lines are straight and, hence, may be extrapolated. When this is done, it is found (Figure 5) that at approximately 50 mm. pressure the azeotrope contains 90 mole % acetonitrile, and at approximately 10 mm., 95 mole %.

To check the accuracy of the data, a plot was made on logarithmic paper of the partial pressures of acetonitrile at constant liquid compositions against a temperature scale calibrated from the vapor pressure of water (Figure 6). The lines obtained were all straight within the accuracy of the experimental data, as pointed out previously (*8*).

Figure 7 shows further correlations of the activity coefficients of both components against liquid composition at constant pressure. Excellent correlations were thus obtained which, as pointed out by Carlson and Colburn (*1*), may give another evaluation of the accuracy of this type of data. By plotting the activity coefficients at constant concentration against a temperature scale calibrated from the vapor pressure of water (Figure 8), straight lines are obtained which permit easy extrapolation and show the effect on the activity coefficients of changes in pressure. The excellent correlation on this plot and on the direct logarithmic plot against pressure, previously described (*8*), is probably the best indication of the reliability of the data.

CONCLUSIONS

Because of the formation of azeotropes, it is not practical to separate the aqueous solutions of acetonitrile by a straight distillation process. It is, however, possible to purify this material to a degree sufficient for most of its present applications by using low pressure distillations in order to increase the percentage of this material in the azeotrope.

ACKNOWLEDGMENT

The authors wish to thank the Foster Wheeler Corporation for sponsoring this research.

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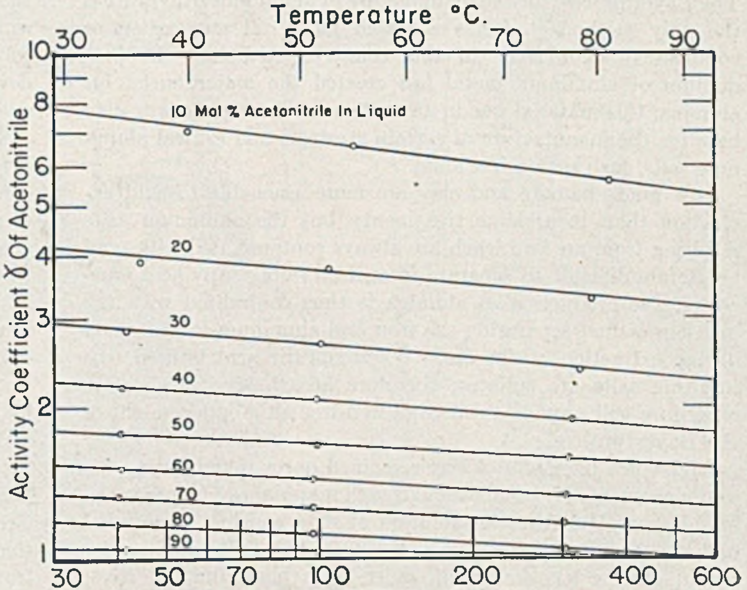
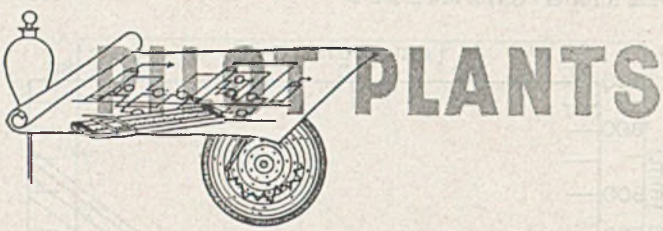


Figure 8. Activity Coefficients of Acetonitrile *vs.* Vapor Pressure of Water at Same Temperature



PRODUCTION OF IRON-FREE ALUM

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A 2-ton-per-day continuous pilot plant has demonstrated conclusively the chemical and mechanical feasibility of a process for iron-free alum production. Under optimum conditions of operation, an alcohol loss of 0.43% is realized. The estimated production cost of $39.91 per ton of alum in a commercial 20-ton-per-day plant indicates that, under present market conditions, the process would not be economically feasible. The basic significance of the process lies in the fact that an expensive organic chemical can, by proper engineering design, be utilized to produce a very cheap inorganic tonnage product. If a material with a higher cost differential between crude and finished product than alum were purified, the process would undoubtedly be economically sound.

TO MEET the growing demand during World War II for iron-free alum, used primarily in the production of synthetic gems, gasoline cracking catalysts, fine chemicals, and certain military applications, and to stop the diversion of strategic aluminum trihydrate for this purpose, the Bureau of Mines developed and evaluated a novel process for the production of alum directly from domestic raw materials of unrestricted supply. The Bayer process for the manufacture of aluminum trihydrate is the only method that has achieved industrial application or commercial significance in this country. Although the production of aluminum metal has created the major outlet for alumina, this material was in great demand during the war as a base for the manufacture of certain strategic and critical aluminum salts, such as iron-free alum.

Low grade bauxite and clay are more amenable to acid extraction than to alkaline treatment; but the aluminum salts resulting from an acid leach are always contaminated with, and heretofore difficult to separate from, iron salts. Any acid process for the production of alumina is thus confronted with the problem of first separating the iron and aluminum salts formed during extraction of the ore. When sulfuric acid is used, the resulting salts are sulfates; therefore an effective purification procedure will provide a source of iron-free alum independent of the Bayer process.

High silica bauxite and clay remained unrestricted during the national emergency, and although such material can be processed in a Bayer plant, the consumption of soda and loss of alumina make production expensive. A successful acid process for manufacturing iron-free alum must, as a minimum objective, achieve an economy that will compare favorably with the alternative of using a premium-priced aluminum trihydrate made from low grade bauxite.

The separation of two water-soluble salts can frequently be achieved by introducing to the system an organic solvent in which one of the salts is insoluble and thus effects selective removal of that component. The fact that aluminum sulfate can be precipitated from its aqueous solution by the addition of ethyl alcohol has long been recognized, and the marked solubility of ferric sulfate in this same organic solvent is well established. Vittorf was apparently the first to propose the application of this phenomenon as a practical method for the purification of crude alum solutions (*6*). Patents covering the use of alcohol to purify aluminum sulfate have been issued in England, France, Switzerland, and Belgium, although the first three presumably cover the same procedure (*2*).

Roller (*3, 4*) has conducted considerable experimentation on the fundamental considerations of the problem, and brought to the attention of the Chemical Engineering Section of the Bureau of Mines a flow diagram utilizing elevated temperatures, the advantage being a substantial reduction in the quantity of alcohol required.

LABORATORY STUDIES

An exhaustive series of laboratory tests demonstrated that, within practical process limits of temperature and concentration, the alcohol does not enter into chemical combination with other components of the system, nor does any appreciable amount of the solvent decompose. A theoretical approach to the problem of developing a process therefore resolved itself primarily into a study of solubility and phase relations.

The solubility of aluminum sulfate in aqueous solutions was determined and plotted as shown in Figure 1. Although the concentration of dissolved salt is at a minimum when the solvent contains approximately 81% alcohol, it was apparent from the change in slope of the curve that an ultimate process concentration of 50 to 55% alcohol would favor the use of less alcohol without appreciable sacrifice in yield of product. As the insolubility of aluminum sulfate in alcohol solutions is significant only as contrasted with the solubility of iron sulfates, these data were determined and are also plotted in Figure 1. To prevent hydrolysis of iron salts, a small quantity of free sulfuric acid was added to the solutions.

It is apparent that both ferrous and ferric sulfates are considerably more soluble in alcohol solutions than is aluminum sulfate. Crude alum normally does not have an Fe_2O_3:Al_2O_3 ratio greater than 0.04; on this basis, if precipitation with alcohol is effected from a saturated solution, the residual solvent mother liquor will be greatly undersaturated with respect to iron sulfates.

Simple mixing of alum and alcohol solutions, however, was found to result in precipitation of a product from which only about 90% of the iron had been extracted. If the crude alum contains Fe_2O_3 equivalent to 3% of the Al_2O_3 content, it is necessary to extract 97 to 98% of the iron in order that the product may meet specifications for iron-free alum. Extensive laboratory studies were conducted to develop processing details that would raise the efficiency of extraction from 90 to 98%.

Quality specifications for iron-free alum depend upon the purchaser's requirements. One large consumer has reported that, before the national emergency, material made from high grade trihydrate had to conform to the following analysis: Al_2O_3, approximately 17.00%; Fe_2O_3, not to exceed 0.003%; Na_2O, not to exceed 0.15%. An inferior but apparently acceptable grade that was available under wartime restrictions had the following composition: Al_2O_3, 17.33%; Fe_2O_3, 0.010%; Na_2O, 0.11%.

Quantitative investigation of the system $Al_2(SO_4)_3$–C_2H_5OH–H_2O (*1*) revealed that a three-phase system of alum hydrate plus alcohol-rich liquid phase plus water-rich liquid phase could be produced under certain conditions of temperature and concentration; further empirical tests demonstrated that consistently high purification could be attained only when the final crystal crop was developed from the foregoing three-phase system.

To minimize the amount of alcohol required for precipitation and attain optimum purification, the following procedure was finally adopted: Alcohol at room temperature was added to hot alum solution to effect an immediate precipitation of impure alum which, upon heating to equilibrium temperature and subsequent cooling, gave the required 97–98% iron removal. The following points were also established during the laboratory development:

1. The quality of the final product depends upon the quality of the raw material; low iron in the crude will give a superior product.
2. In the range 0.1 to 5.0% equivalent Fe_2O_3, no distinction is apparent between extraction of ferrous and ferric iron, an average iron removal of 97–98% being easily obtained.
3. Product yields of 93 to 97% are realized.

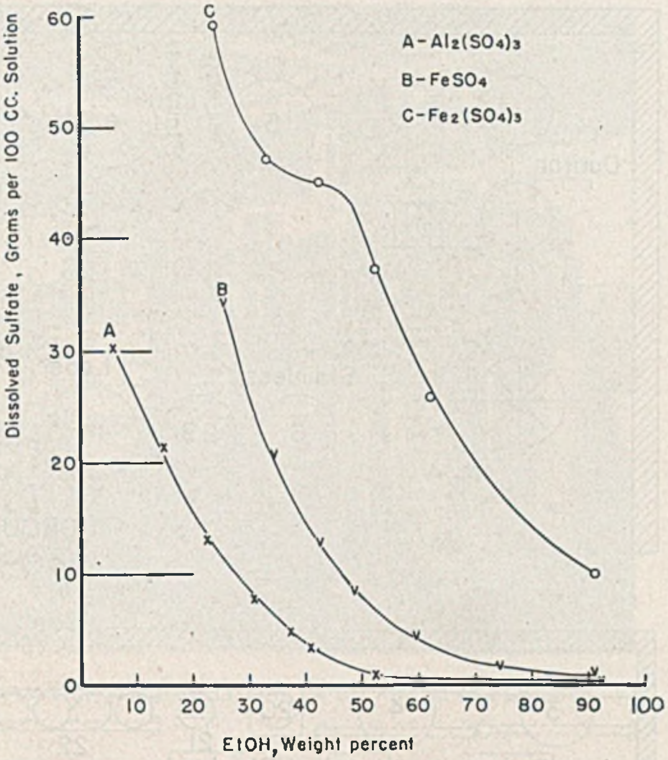


Figure 1. Solubility of Ferric, Ferrous, and Aluminum Sulfates in Ethanol-Water Solutions at 33° C. (1.7% Free Sulfuric Acid)

4. The alum hydrate precipitated is uniformly the hexadeca salt at room temperature.
5. The common industrial denaturant, formula 2B, may be substituted for U.S.P. alcohol, and the process can thus use a tax-free solvent.

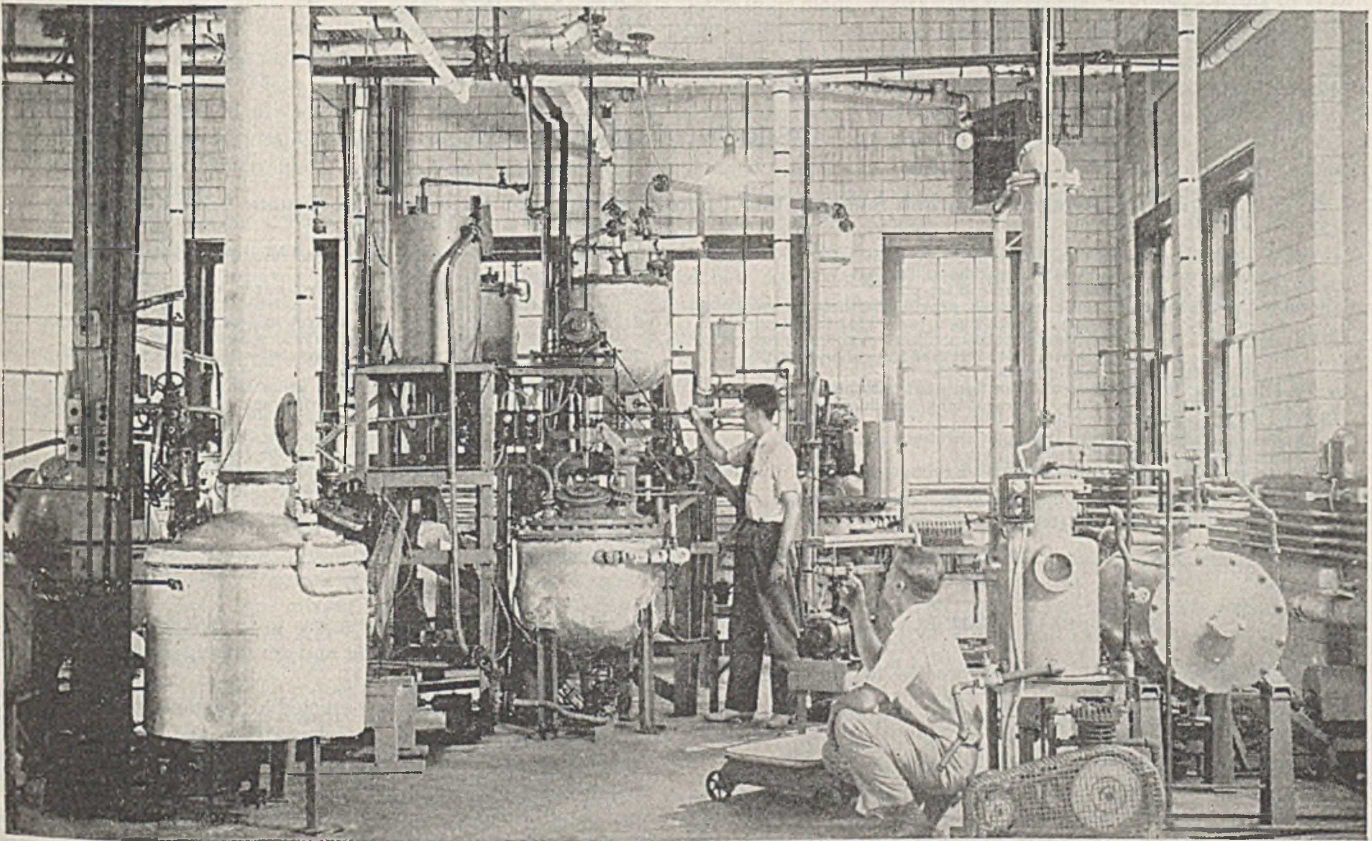


Figure 2. South Elevation of Small Scale Pilot Plant

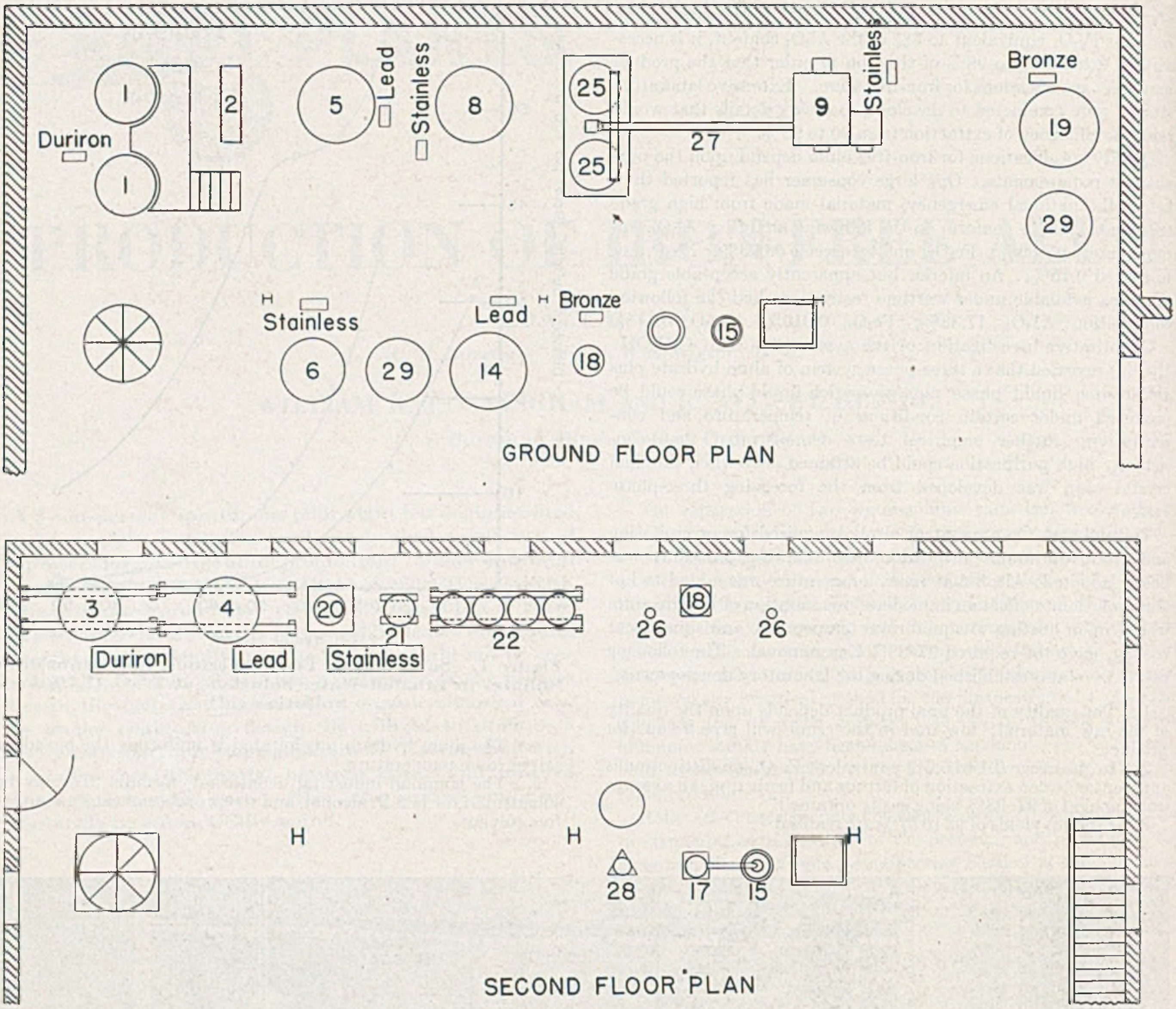


Figure 3. Ground Floor and Second Floor Plans of Equipment Layout in Continuous Pilot Plant

1. Two lead-lined jacketed dissolution tanks for alum, each of 450-gallon capacity, with steam coils and paddle agitators
2. Twelve-inch Shriver plate-and-frame filter press
3. Single, lead-lined, jacketed evaporator, provided with 1-inch lead coils for primary heat transfer; 18-inch flue attached for vapor exhaust
4. Alum storage tank. Identical in construction to evaporator except for steam coils and sight glasses; both items of 530-gallon capacity
5. Lead-lined 840-gallon alcohol storage tank
6. Batch crystallizer (this unit did not figure in continuous operation)
8. Lead-lined 940-gallon slurry storage tank provided with two large paddle agitators
9. Stainless-steel 28-inch Bird solid-bowl continuous centrifugal
14. Filtrate storage tank (identical to item 5)
15. Thirteen-plate, bubble-cap fractionating column, fabricated of stainless steel
17. Copper condenser (6 feet × 16 inches) for vapors from column
18. Primary alcohol receiving tanks, of copper construction and 120-gallon capacity
19. Alcohol blending tank, identical to item 5 with side-entering propeller agitator
20. Eighty-gallon lead-lined, jacketed mixer, equipped with steam coils and turbine agitator
21. Half-inch lead heating coil, 45 feet in length, immersed in a drum of water provided with steam inlet as a heat source
22. Four 25-gallon crystallizers fabricated of stainless steel, with cooling coils and turbine agitators
25. Two duplicate lead-lined alum stills of approximately 230 gallons capacity, jacketed, provided with heat coils and large paddle agitators with supplementary baffles
26. Small copper water-cooled condensers, 3 feet × 6 inches
27. Six-inch stainless-steel screw conveyer for wet cake
28. Constant-heat lead feed tanks of approximately 6 gallons capacity
29. Two supplementary lead-lined alcohol storage units, of approximately 300 gallons capacity each

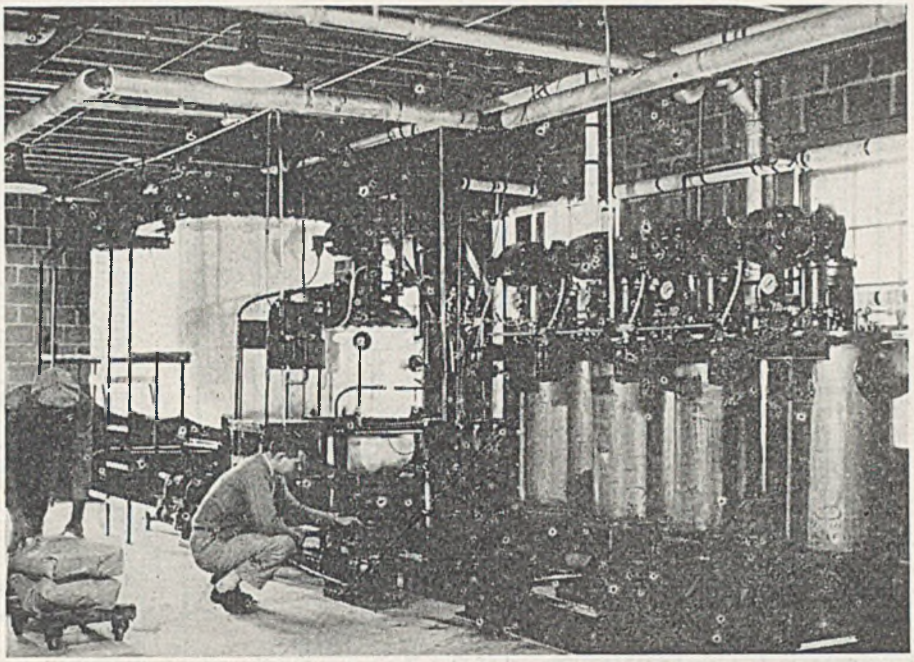
The rectangular blocks represent 1- and $^3/_4$-inch centrifugal pumps with the material of construction printed for each.

SMALL SCALE PILOT PLANT

Superficial consideration of any process for an inexpensive tonnage chemical, using an organic carrier for the product, discloses that solvent losses in the operation must be held very low. For this reason it seemed advisable to pursue a pilot plant development as a two-stage study. First, the fundamental characteristics of the operations were explored in an inexpensive batch plant, and from the data obtained a well designed continuous plant of semicommercial scale was erected. In the continuous unit, investigation was to be directed toward achieving a minimum loss of solvent and developing a detailed economic evaluation of the process.

The small pilot plant was erected at the Southern Experiment Station, Bureau of Mines, Tuscaloosa, Ala., and Figure 2 shows the general arrangement. The majority of tests were made on a batch basis, approximately 40 pounds of alum being processed per batch in equipment units of approximately 35 gallons capacity. The following points were established during the batch pilot plant tests:

1. Pilot plant iron-extraction efficiencies average 97.8%.
2. An average alum yield of 94.6% was attained.
3. No unusual mechanical problems were encountered.
4. Of the alloys tested to meet the abrasive characteristics of the crystal slurry, stainless steel appeared to be the most satisfactory, except where concentrated alum solutions were concerned.
5. Lead was an acceptable material for all stationary equipment and piping requirements.
6. Based on higher recoveries of solvent, simplicity of equipment, and superior heat transfer characteristics, distillation drying was selected as the best system for recovery of the wash alcohol.
7. As expected, the over-all loss of alcohol in this unit was extremely high, amounting to 0.05 gallon of 100% ethanol per pound of product.
8. As it was impossible to relate the foregoing figure to performance that could be anticipated in a well designed, totally enclosed plant, a larger installation was a virtual necessity for evaluating this factor alone.



Mixer, Heating Coil, and Crystallizers (Items 20, 21, and 22 of Figure 3)

CONTINUOUS PILOT PLANT

The foregoing laboratory and semipilot plant studies demonstrated the chemical feasibility of the process, but the operations were not on a scale large enough to permit a reliable evaluation of cost. As stated before, the critical variable that could not be fixed was alcohol recovery, which obviously controlled the commercial possibilities of the development.

The continuous pilot plant was located in the College Park Experiment Station of the Bureau of Mines where 3700 square feet of floor space equally distributed between two floors was allocated to the project. Plant design was based on the foregoing two sections, and Figure 3 shows location of various items.

Process. The initial conception of the continuous process is illustrated by Figure 4 which shows the flow of materials based on primary process piping.

The raw material for the process was crude alum containing varying percentages of iron and insolubles as the principal impurities. The alum, as received in 100-pound paper sacks, was charged to the dissolution tanks by means of chute and hopper from the second floor. Sufficient alum was dissolved in hot water to produce the desired specific gravity, and the solution was acidified by the addition of concentrated sulfuric acid introduced through a lead funnel via the chute. Insolubles present in the solution were removed in the Shriver filter press, and the clarified liquor was pumped to the evaporator, where the final adjustment of concentration (varying from specific gravity 1.20 to 1.44) was made. The adjusted alum solution was then pumped to the alum storage tank, from which it was metered through a rotameter at any desired rate and mixed with a metered stream of alcohol in the mixing tank at about 60° C. with the immediate formation of a slurry of impure alum crystals. By means of the coil heat exchanger the temperature was raised to the invariant point and the requisite three-phase system was attained, temperature varying from 68° to 78° C., depending upon initial conditions. Cooling and concomitant crystallization were accomplished in four successive stages of approximately 10° temperature differential. The cooled alum-alcohol-water mixture was collected in the slurry storage tank, where large-blade agitators prevented premature solids separation. Slurry was subsequently metered to the Bird centrifugal, where the alcoholic mother liquor was separated from the alum crystals, which were then washed with fresh alcohol. The combined filtrates were pumped to storage preparatory to fractionation, and the alum cake was carried alternately by screw conveyer to one of the distillation units, where adhering alcoholic wash liquor was distilled off. Molten alum from this operation was poured into iron pans for solidification and packaging.

Equipment Modification. In view of the limited design data and operating experience that could be gathered from the batch pilot plant, it was anticipated that initial operation of the continuous unit might demonstrate the necessity for some major changes. However, this was not the case, and, except for minor piping revisions and slight adjustments, the basic arrangement of the plant was not altered during the entire development study.

A major difficulty arose in the metering of slurry. It had been planned originally to maintain a constant level of slurry in the alum-alcohol mixing tank by automatic instrumentation actuating a centrifugal pump. Frequent plugging of the elbows resulted from intermittent pump operation, and manual control of flow was attempted with little improvement. The problem was nicely solved by the use of a side overflow on the mixing tank, whereby the slurry was indirectly metered by the incoming streams of alum and alcohol.

A similar problem resulted in attempted metering of slurry from the storage tank to the Bird centrifugal. The special rotameters provided for this purpose failed completely, and it was again necessary to utilize a side overflow to control flow. In this instance rate of flow was regulated by the incoming stream of slurry from the last crystallizer.

Some difficulty was experienced in duplicating the high iron-reduction ratios characteristic of the laboratory. This was attributed to the relatively large temperature drops experienced by the slurry in the crystallizers and the short interval of time at which the reaction mixture was maintained at the invariant point. An additional holding tank, in which the slurry was held for about 15 minutes at its invariant point, was installed between the reheat coil and the crystallizer; this obviated the foregoing variable. Prohibitive delivery schedules mitigated against installation of additional crystallizers, and the slurry storage tank was adapted subsequently as a crystallizer and arranged parallel with the preceding four. This lowered the individual temperature drop to about 7° and had a beneficial effect on purity of

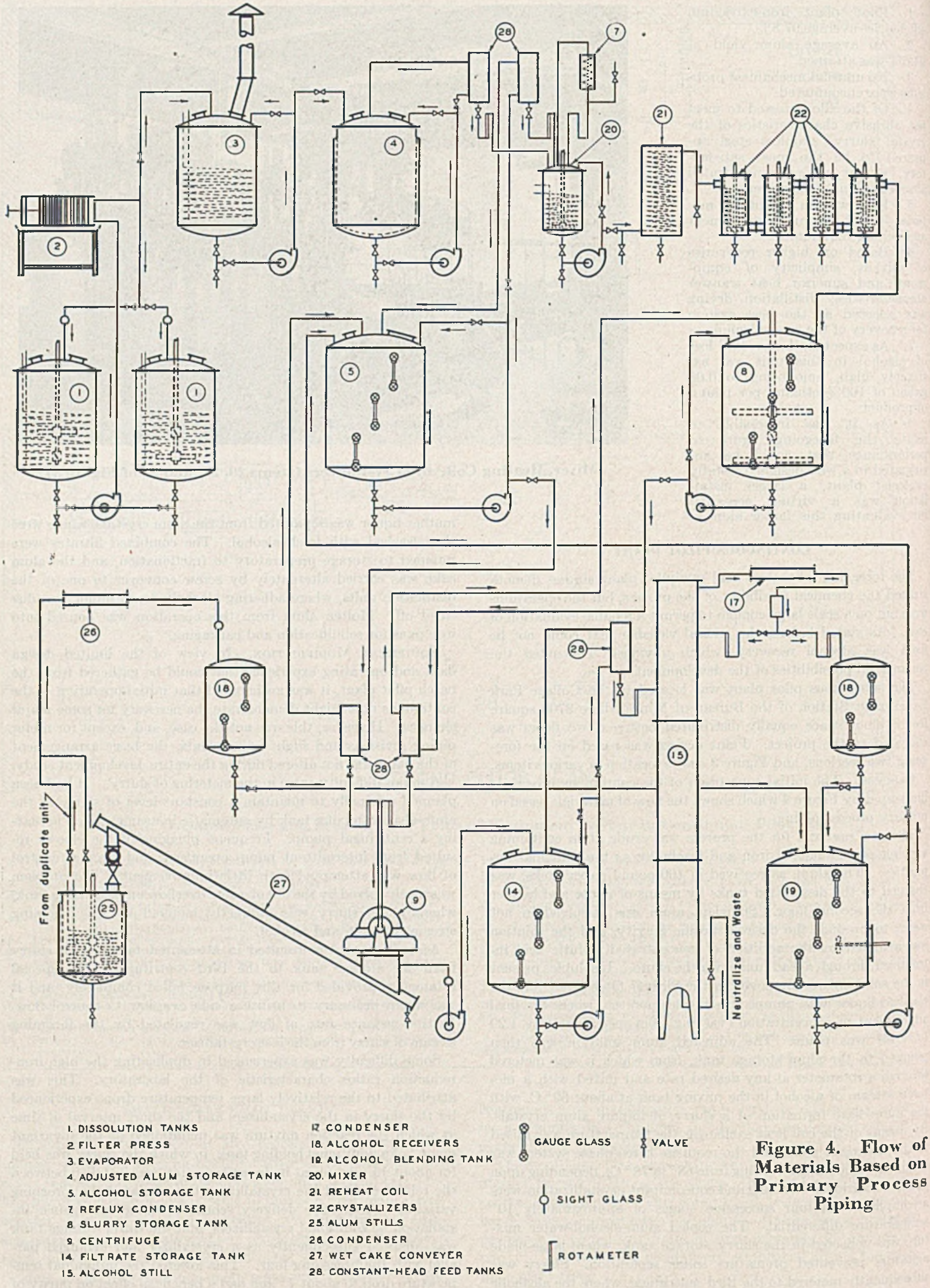


Figure 4. Flow of Materials Based on Primary Process Piping

product. In similar equipment at least eight crystallizers should be utilized, representing a temperature drop of approximately 4° per unit.

The Goslin-Birmingham rotary vacuum filter was tested in lieu of the centrifuge for solid-liquid separation, and some modification of equipment was necessary. However, this was a planned alternative and was not caused by operating exigencies. Figure 5 is a material balance based on the optimum conditions of operation.

Capacity. Originally designed for a production of 2 tons of alum per 24-hour day, the plant proved quite flexible, and satisfactory operating rates of 1 to 2.5 tons per day were achieved. All equipment proved to be of sufficient size and flexibility to operate adequately over this range, with the exception of the Bird centrifugal. This unit did not provide satisfactory washing efficiencies at the higher rates.

The Goslin-Birmingham rotary vacuum filter was oversize at the lower rate, and a portion of the 3 × 1 foot drum was blocked off for continuous operation.

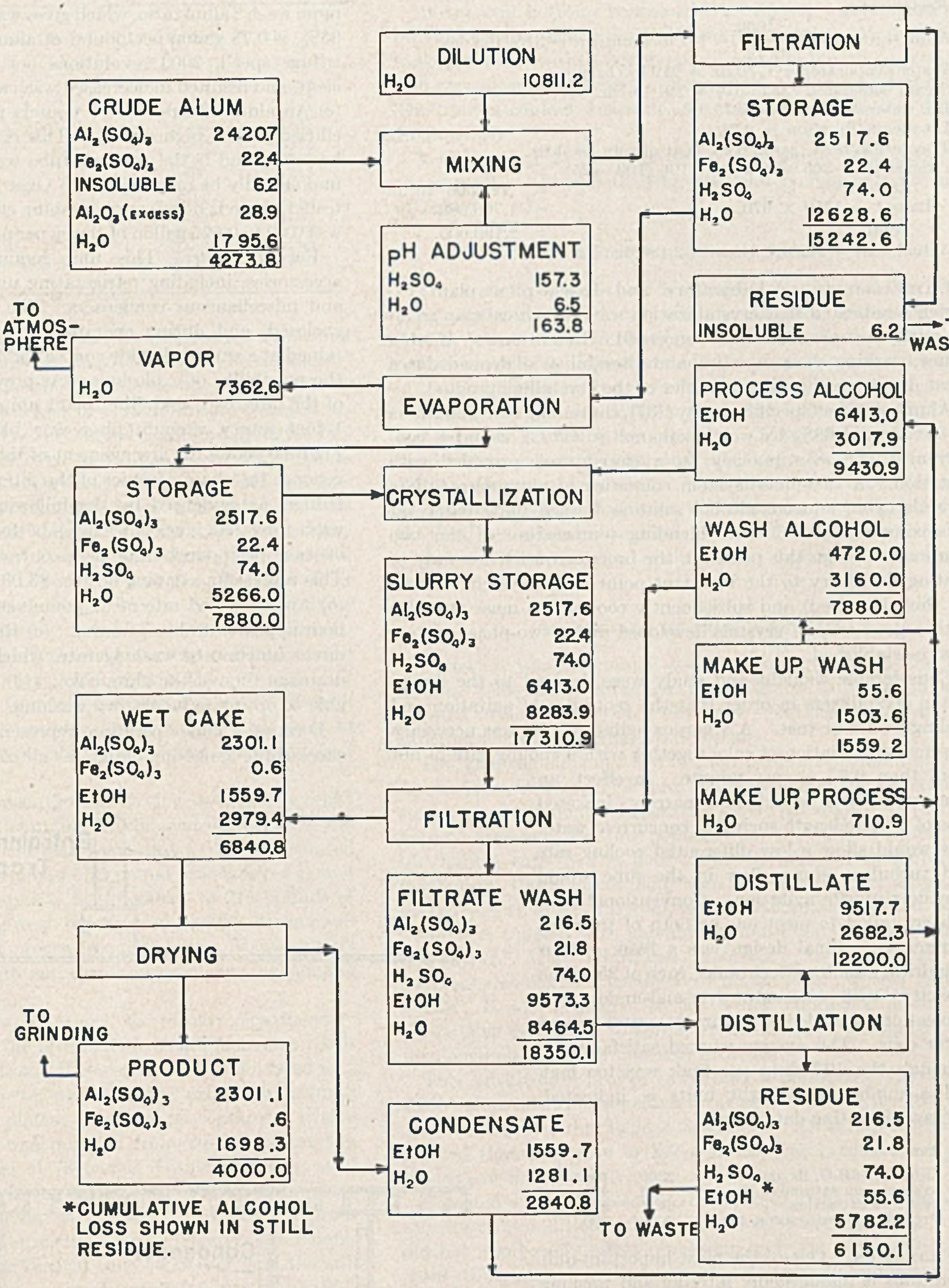


Figure 5. Material Balance in Pounds per Day

UNIT OPERATIONS

Crude Alum Adjustment. Although any industrial application of an alcohol process for producing iron-free alum undoubtedly would be located in a commercial plant producing crude alum, the pilot plant necessarily included facilities for dissolving and concentrating dry ground alum as supplied to the market.

After dissolution in acidified aqueous solution, the crude alum solution was filtered in a Shriver plate-and-frame press, using canvas cloth. Concentration in a steam-heated evaporator preparatory to storage or use was controlled by specific gravity and pH measurements. An operating schedule for this unit follows:

Charge. 635 gallons of solution at specific gravity 1.196 (25° C.); alum content 1000 pounds at 17% Al_2O_3, H_2SO_4 content 35.7 pounds.

Evaporation Time, Hours	Sp. Gr. (80° C.)	Steam Condensate, Lb.
0	...	...
1	...	...
2	1.174	648
3	1.184	936
4	1.217	1324
5	1.252	1602
6	1.280	1862
7	1.316	2100
8	1.378	2325

Product. 155 gallons of solution at specific gravity 1.378 (80° C.); alum content, 1000 pounds at 17% Al_2O_3 = $Al_2(SO_4)_3 \cdot 16H_2O$.

Performance

Alum throughput = $\frac{1050}{8}$ = 131 lb. alum/hr. = 3150 lb./day

Water evaporated = 1750 lb. = 219 lb./hr. av.

Steam condensed (2325 lb.) = 291 lb./hr. av.

Lb. water/lb. steam = 0.75

Lb. steam/lb. alum = 2.21

Theoretical heat (assume sp. heat of soln. = 1.0)

$$\text{Sensible} = \frac{365 \times 8.33 \times 1.196\ (100 - 25)}{1.8 \times 1.0} = 490{,}000\ \text{B.t.u.}$$

$$\text{Latent} = 1750 \times 970 = \underline{1{,}700{,}000}$$

$$\text{Total} \quad 2{,}190{,}000$$

Actual heat = 2325 × 940 = +2,185,000 B.t.u.

Crystallization. Laboratory and batch pilot plant experience indicated that crystallization was the critical step as far as purity of product was concerned. Retention of mother liquor, washing characteristics, and filterability all depended to a great degree on the characteristics of the crystalline product.

Alum solutions (specific gravity 1.37), containing 8.87% alumina at 90° C. and 68% by weight ethanol at 25° C., were fed concurrently and continuously to a closed tank provided with agitation. A two-phase system consisting of aluminum sulfate crystals in an aqueous-alcohol solution formed immediately at approximately 50° C. (the blending temperature of the two solutions). From this point on, the process consisted mainly of heating the slurry to the invariant point of the system (68° C. for this alum feed) and subsequently cooling the mass stepwise until a good crop of crystals developed and a two-phase system was re-established.

Considerable thought and study were devoted to the design of the crystallizers in order that the requisites of agitation and cooling would be met. A vigorous agitation rate was necessary to prevent formation of cake together with a cooling rate of not more than 0.5° C. per minute. In effect, an ideal crystallizer would be a narrow, jacketed pipe of infinite length such that concurrent water flow would allow a low differential cooling rate and turbulent slurry flow in the tube would provide requisite agitation. Conventional crystallizers failed to meet one or both of these requirements. Final design was a bank of four cylindrical stainless-steel tanks, each of 25-gallon capacity, with alternate over-and-under flow connections provided with turbine agitators and water coils. This system worked satisfactorily, although the 10° drop per tank was too high and a minimum of eight units is indicated. Average operating data follow:

Run	A	B
$Al_2(SO_4)_3 \cdot 16H_2O$, lb./day	2300	4600
Average iron extraction, %	97.2	97.1
Best iron extraction, %	97.7	97.2
Over-all processing time, min.	600	300

Filtration. One of the most important unit operations is undoubtedly filtering and washing the purified alum crystals. This step controls the ultimate quality of product and must be conducted in a vapor-tight continuous unit to minimize loss of solvent. Either a continuous centrifugal or a hooded vacuum filter fulfilled these requirements; therefore, both were provided for alternate testing. It was immediately apparent that the smaller the temperature differential between adjacent coolers or crystallizers, the better the filtering and washing characteristics of the resulting alum crystals.

Centrifugal. Mechanically the continuous, 18 × 28 inch, stainless steel centrifuge was the simpler unit, although supplied fume seals failed to provide good solvent recoveries. The following factors were evaluated for this unit: (*a*) The minimum wash : alum ratio, which gives wash efficiencies of better than 95%, is 0.78 gallon per pound of alum. (*b*) The maximum centrifuge speed, 2000 revolutions per minute, proved most efficient, and resulted in decreased wash and mother liquor retention. (*c*) An alum feed rate of 97 pounds per hour gives better wash efficiency than higher rates. This is because of machine design, however, and if the washing tube were enlarged the rate could undoubtedly be increased. (*d*) Over the range of slurry density tested, there is no effect on washing efficiency. The range tested was 0.40 to 0.626 gallon of slurry per pound of alum.

Vacuum Filter. This unit required numerous mechanical accessories, including refrigerating unit, vacuum pump, blower, and miscellaneous condensers. The entire system was totally enclosed, and during operation the vapor system was maintained at a carbon dioxide content of 36% by volume to minimize the possibility of explosions. As previously stated, the capacity of the filter exceeded other plant units, and a portion of the 3 × 1 foot rotary vacuum filter was blocked with canvas strips. Figure 6 shows the arrangement of the filter and accessories. In general, the characteristics of the filter were superior to the centrifuge, as evidenced by the following data: (*a*) The minimum wash rate that gives efficiencies better than 95% is 0.21 gallon of wash per pound of alum in contrast to 0.7 in the centrifuge. This represents a saving of over $3.00 per ton of alum produced. (*b*) An alum feed rate of 64 pounds of alum per square foot per hour appeared to be optimum. (*c*) Retention of wash liquor is a direct function of washing rate, which is attributed to variable drainage time of the alum cake. (*d*) Product purity is comparable to optimum laboratory washing.

Drying. This operation represented a major obstacle to successful engineering design, as all commercially available units

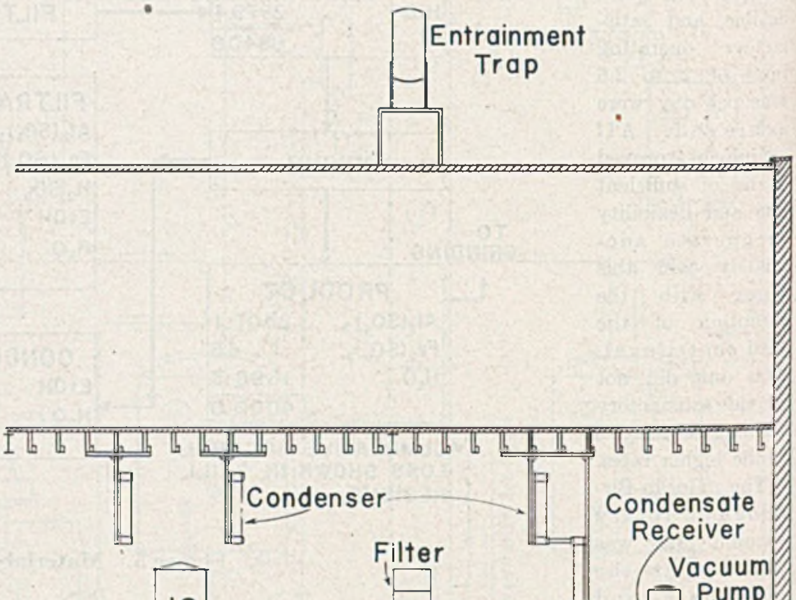


Figure 6. Vacuum Filter Layout

Table I. Still Performance in 5-Hour Runs

	Test 1	Test 2
Total feed, gal.	645	670
Feed rate, gal./hr.	129	134
Alcohol concn. of feed, wt. %	57.0	53.6
Alcoholic content of feed, lb./gal.	4.28	4.06
Total dist., lb.	3340	3415
Alcohol in dist., lb.	2750	2720
Water in dist., lb.	660	745
Alcohol concn. of dist., wt. %	80.6	84.8
Total slop, lb.	3980	3980
Slop from feed, lb.	1425	1605
Slop from steam, lb.	2555	2375
Total steam consumption, lb.	2560	2380
Steam consumption, lb./lb. alcohol	0.93	0.875

were inadequate for various reasons. Since virtually all alcohol must be recovered, a completely enclosed system is mandatory, and continuous operation does not appear feasible.

As alum will melt in its water of crystallization, retained alcoholic mother liquor could be recovered by simple distillation in a semicontinuous unit. Wet cake discharged from the filtration operation was transported to the batch stills by a 6-inch stainless steel screw conveyer. Between the conveyer and each dryer were two 6-inch rising-stem gate valves, separated by an auxiliary horizontal conveyer. After a dryer was three quarters filled, the horizontal conveyer was reversed and the alternate dryer placed in operation. Closing the gate valve on the filled dryer isolated it from the conveyer system, and alcohol could then be recovered by distillation. Temperature measurements of the melted alum provided an index of concentration.

The molten alum, free from alcohol, was discharged through 2-inch drainage valves by gravity into stainless steel pans of 300 pounds capacity. These alum ingots were finally crushed and bagged.

This rather novel semicontinuous drying operation worked smoothly and had no outstanding mechanical or technical defects. The following conclusions were drawn: When operated continuously, the dryers required 0.75 pound of steam per pound of alum. The average capacity is equivalent to 215 pounds of alum per hour. Adhering wash is recovered as 60% ethanol and is suitable for subsequent process requirements. Stainless-steel pans had sufficient strength and corrosion resistance for molding 300-pound alum ingots.

Distillation. It was necessary to recover continuously the alcohol discharged in the filtrate and wash liquors as a result of the solid-liquid separation. The required unit consisted of a 12-foot-high, 20-inch-diameter, stainless steel exhausting column equipped with thirteen plates; each plate contained twelve bubble caps. Still feed was pumped from storage through a preheater, which consisted of 73 feet of $^3/_4$-inch stainless steel tubing inserted in the top of the column, where ascending vapors provided the requisite amount of preheat. The alcoholic product was collected in an intermediate copper receiver after liquification in a $6 \times 1^1/_3$ foot vertical tube condenser, and the still bottoms were discharged to a central sump after partial neutralization.

Instrumentation consisted principally of a series of rotameters, hydrometers, and pressure regulators. Two rotameters provided with stainless steel floats were utilized to meter the still feed and to control the reflux ratio. A Brown recording regulator, actuated by pressure within the still, controlled the flow of steam by means of an automatic valve. Two hydrometers, mounted on the control panel, were used to determine the concentration of alcohol in the distillate and in the vapor over the still bottoms. Two thermometers were inserted in the still body below the first and the tenth plate, respectively, providing an index for the operator of the relative concentration of alcohol in the slop and distillate.

To minimize fluctuation in the still feed and in the rotameter readings, constant-head tanks were installed for both the feed and product rotameters.

As the still bottoms contained free acid, it was necessary to provide partial neutralization before discharge. A lead-lined tank was filled with a 2-foot bed of crushed limestone, and the slop was allowed to percolate through the bed to a central sump. The time of contact was restricted, but the pH was raised from 1.03 to 1.97.

A series of tests was conducted to determine the operating characteristics of the distillation unit, and average data are given in Table I.

RECOVERY OF ALCOHOL

The lowest loss of alcohol in the pilot plant was 0.022 pound per pound of alum produced, with an equivalent average figure of 0.0478. As the former figure was maintained over a 21-hour operating schedule, it is assumed to represent a true evaluation of the over-all solvent recovery efficiency.

Loss of 0.20% of the alcohol processed in the distillation column was good for a unit of this capacity. Filtration represents the largest unit processing loss, and the rotary filter is superior to the centrifuge in this respect. It is believed that modification of design would permit utilization of the mechanical superiority of the Bird centrifugal at equivalent recoveries. Losses of 0.0075 pound of alcohol per pound of alum were experienced in the drying unit.

MATERIALS OF CONSTRUCTION

Corrosion was the major problem encountered in the continuous pilot plant although materials of construction were selected in accordance with extensive small scale tests and the experience of the Tuscaloosa batch plant.

The greatest difficulty lay in the distillation column and the crystallizers, both of which were constructed of Type 304 stainless steel. After one month of operation severe corrosion of the column became apparent, locating primarily on the spiders which held the bubble caps to the plate disk. Because of difficulties in machining, these pieces had been fabricated from Type 303 stainless steel which was completely unacceptable, as low initial resistance, coupled with galvanic action, quickly resulted in its dissolution. After additional laboratory testing, Type 316 stainless was selected as the best material for process requirements. It was necessary to cut 6-inch handholes in the still shell above each plate to permit replacement of the spiders, and then portholes were permanently attached.

This substitution proved to be only a temporary solution, as acidic alum filtrate immediately attacked the Type 304 shell after removal of the Type 303 spiders. At this point it was realized that Type 316 or 317 stainless was mandatory in any subsequent installation.

Fortunately the problem of the existing plant was completely solved by the addition of 0.5% nitric acid to the alum feed. This did not appreciably affect processing and, for all practical purposes, completely inhibited corrosion of the still and other steel units.

Minor difficulties were experienced with pinholes in the lead, which is directly attributable to faulty workmanship. Ballooning of linings on application of heat to faulty tanks was eliminated by providing weep holes in all lead-lined equipment. These should be specified on all such equipment used at atmospheric pressures.

Stainless steel or Duriron pumps were used for crystal slurry, antimony lead for hot alum, and bronze for alcohol, all with satisfactory results. Lead was employed for alum, slurry, and filtrate lines, and copper for transporting all alcohol-water mixtures.

COLLECTION OF DATA

Data were collected on each of the unit operations and are itemized in Table II; Table III gives the sampling schedule.

Table II. Data Schedule

Unit Operation	Measurement	Method	Frequency
Crude alum adjustment	Alum analysis	Chemical	8 hr.
	Alum charged	Weight	8 hr.
	Water charged	Flowmeter	8 hr.
	H_2SO_4 charged	Measurement	8 hr.
	Alum specific gravity	Hydrometer	30 min.
	Free acid	pH meter	30 min.
Crystallization	Alum feed rate	Rotameter	15 min.
	Alcohol feed rate	Rotameter	15 min.
	Alcohol concn.	Hydrometer	3 hr.
	Mixing temp.	Thermometer	15 min.
	Equilibrium temp.	Thermometer	15 min.
	1st cooler temp.	Thermometer	15 min.
	2nd cooler temp.	Thermometer	15 min.
	3rd cooler temp.	Thermometer	15 min.
	4th cooler temp.	Thermometer	15 min.
Filtration (Bird centrifugal)	Slurry temp.	Thermometer	15 min.
	Filtrate temp.	Thermometer	15 min.
	Wash rate	Rotameter	15 min.
	Current consumption	Ammeter	15 min.
	Filtrate vol.	Gage glass	1 hr.
	Filtrate concn.	Distillation	1 hr.
	Wash-liquor retention	Evaporation	30 min.
Filtration (Goslin-Birmingham filter)	Slurry temp.	Thermometer	15 min.
	Filtrate temp.	Thermometer	15 min.
	Drum speed	Stop watch	On adjustment
	Wash rate	Rotameter	15 min.
	Vacuum	Gage	15 min.
	Hood pressure	Gage	15 min.
	Blow pressure, cake discharge	Gage	15 min.
	Vapor temp.	Thermometer	1 hr.
	Condenser temp.	Thermometer	1 hr.
	Filtrate vol.	Gage glass	1 hr.
	Filtrate concn.	Distillation	1 hr.
	Wash-liquor retention	Evaporation	30 min.
Drying	Vol. of charge	Observation	15 min.
	Alum temp.	Thermometer	15 min.
	Dist. vol.	Gage glass	1 hr.
	Alum discharged	Weight	6 hr.
	Alum analysis	Chemical	6 hr.
Distillation	Feed rate	Rotameter	10 min.
	Reflux ratio	Rotameter	10 min.
	Distn. rate	Rotameter	10 min.
	Dist. concn.	Hydrometer	30 min.
	Pressure on bottoms	Automatic recorder	10 min.
	Top-plate temp.	Thermometer	10 min.
	Bottom-plate temp.	Thermometer	10 min.
	Feed vol.	Gage glass	30 min.
	Dist. vol.	Gage glass	30 min.

Table III. Sampling Schedule

Unit Operation	Sample	Frequency
Crude-alum adjustment	Raw alum	3 hr.
Crystallization	Alum feed	1 hr.
Filtration	Slurry to filter	30 min.
	Cake from filter	30 min.
	Filtrate	1 hr.
Drying	Discharged alum	5 hr.

No special problems were encountered in either collection of data or sampling. For purposes of pilot plant control, several analytical control expedients were adopted to facilitate operations.

Analysis of Aluminum Sulfate Solutions. Iron was determined in the crude alum solution by titration with 0.25 *N* potassium dichromate. Diphenylamine was used as indicator after total reduction of the iron with stannous chloride; excess of the latter was destroyed with mercuric chloride.

Alumina was determined in the crude alum liquor by gravimetric precipitation of the R_2O_3 with ammonium hydroxide, using bromocresol purple as indicator. The alumina was then determined by difference, using the iron value obtained above. For rapid pilot plant control this method was unsatisfactory; therefore, specific gravity or density was employed in the pilot plant. Table IV gives data on these constants, which agree in general with those previously reported (*5*). The boiling points provided an additional index of alumina concentration and were of special value in the drying operation.

Considerable difficulty was experienced in determining free acid. The standard potassium fluoride titration is difficult, time consuming, and not applicable to pilot plant operations. To minimize lag in obtaining control data, considerable study was made, and a novel procedure was developed in which pH of diluted aluminum sulfate solutions (specific gravity 1.18) were plotted against concentration of sulfuric acid per 100 grams of alumina. Data were obtained by adding known quantities of sulfuric acid to an acid-free solution of aluminum sulfate, and the pH was determined. By means of such an empirical relation, the net acidity of aluminum sulfate solution can be measured when diluted to the above specific gravity. Figure 7 shows such a curve and the data from which it was plotted.

Analysis of Aluminum Sulfate Hydrates. Iron in the final product was determined colorimetrically, using orthophenanthroline as indicator. In the reduced state, iron produces a red complex with orthophenanthroline, the intensity of which is proportional to the iron concentration. The reagent has several advantages over usual colorimetric methods in stability of color and independence of color intensity from impurities.

An alternate procedure utilizing sodium thiocyanate was employed in preliminary work. A red complex is obtained with iron in the oxidized state which also is proportional to the concentration of iron; however, sulfate solutions have a detrimental effect upon color formation, and numerous precautions are necessary to procure accurate results.

Analysis of Alcohol. The alcohol content of various mixtures was determined by distillation. A unit volume of sample was diluted with two units of water, and a two-unit volume of distillate was collected. The specific gravity, as the index of alcohol concentration, was then determined with a specific gravity balance or pycnometer.

Using these analytical techniques with reference tables and charts prepared for the various unit operations, there was no lag in data reports. Plant technicians made all determinations concomitant with operational duties, and satisfactory results were obtained.

The time required for equilibrium or steady-state conditions was, of course, a function of production rate, varying from 6 hours at 1 ton per day to 3 hours at 2.5 tons per day.

All crystallization conditions are rather critical, feed rates and temperatures being maintained within very narrow limits. The most critical temperature control is that of the heating coil (item 21, Figure 3) in which the slurry is brought to its invariant point, ± 1° C. being the maximum allowable limit. Higher temperatures cause complete solid-phase dissolution, while the converse is true of lower temperature; both, however, result in marked lowering of ultimate purity of product. Crystallizers were maintained by automatic regulators at ± 2° F., but even larger variations did not appreciably affect either purity of product or subsequent operational details.

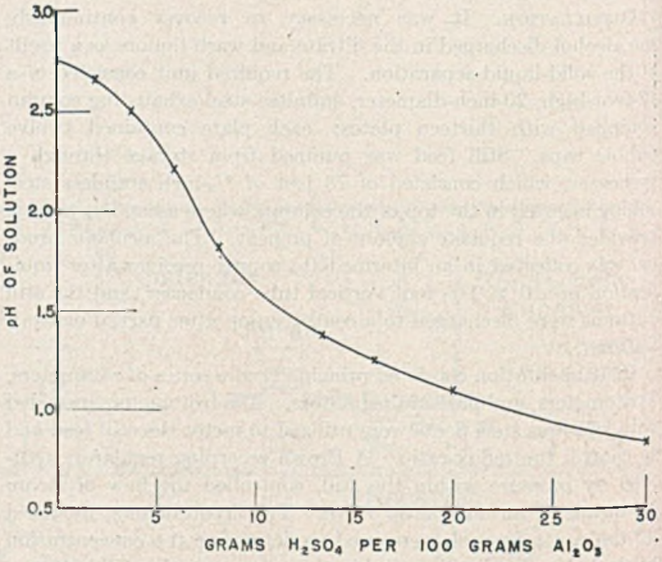


Figure 7. Calibration Curve for pH Measurements of Aluminum Sulfate Solutions (Specific Gravity 1.18, 25° C.)

pH	G. H_2SO_4/100 G. Al_2O_3	pH	G. H_2SO_4/100 G. Al_2O_3
2.72	0.0	1.57	10.0
2.63	2.1	1.38	13.7
2.48	4.2	1.47	16.0
2.31	6.1	1.06	20.0
1.78	7.9	0.84	30.0

TABLE IV. SPECIFIC GRAVITY, DENSITY, AND BOILING POINT OF AQUEOUS ALUMINUM SULFATE SOLUTIONS

Concn., Grams Al_2O_3/100 Ml.	Sp. Gr. (90°/4° C.)	Density (100° C.)	Boiling Point, ° C.
10	1.27	1.26	102.4
12	1.33	1.32	104.0
15	1.40	1.39	106.0
16	1.43	1.42	106.6
17	1.46	1.45	107.2
18	1.48	1.47	107.8

EVALUATION OF PROCESS

The primary objective of the pilot plant development was to evaluate this process with respect to potential commercial application. The preceding discussion of pilot plant data is confined largely to mechanical operation and quality of product obtained. While these studies were being conducted, the optimum operating conditions were being established, and on this basis the material-balance flow chart (Figure 5) was prepared. Data and basis for calculation of the balance are as follows:

Product: 2000 lb. $Al_2(SO_4)_3 \cdot 14H_2O$; 0.035% Fe_2O_3/Al_2O_3.

Crude alum: sp. gr. 1.37 at 100° C.; 1.19% Fe_2O_3/Al_2O_3; pH = 1.0 (21 lb. H_2SO_4/100 lb. Al_2O_3); 352 gal. of solution; 2200 lb. $Al_2(SO_4)_3 \cdot 14H_2O$ = 2360 lb. $Al_2(SO_4)_3 \cdot 16H_2O$.

Alum yield: 90% recovery (from plant experience).

Process alcohol: 68% by wt. (sp. gr. 0.868); 660 gal. (from chart 1.88 gal./gal. alum).

Wash alcohol: 60% by wt.; 550 gal. (from filter data, 0.25 gal./lb. cake).

Wet cake: 35/1 reduction ratio (40/1 in crystallization); 97.3% washing efficiency; 35% wash-liquor retention; 90% product yield.

Dry cake (product): 2000 lb. $Al_2(SO_4)_3 \cdot 14H_2O$.

Filtrate: approx. 54.2% EtOH by wt.; sp. gr. 0.899; approx. 1225 gal.

Distillation: 8680 gal. distillate; 78% EtOH by wt.; sp. gr. 0.844 (plant practice); steam consumption 4900 lb. (from plant run 25) (0.875 lb/lb. C_2H_5OH fed).

Residue: approx. 0.58% acid.

As a starting point for developing the cost estimate of a commercial plant, it is well to review the actual cost of the 2-ton-per-day continuous pilot plant. These data are summarized as follows:

Total major items of equipment	$39,020
Total minor items of equipment (valves, pipes, etc.)	9,820
Total labor (direct)	5,740
Total construction cost (exclusive of buildings, power generation, etc.)	$54,580

This cost can be distributed as follows:

	Major Item Cost, A	% Total Major Items	Prorated Minor Items, B	Prorated Labor, C	Total Cost, A + B + C
Alum dissolution	4,020	10.3	1010	590	5,620
Evapn. & storage	3,130	8.0	785	460	4,375
Alcohol storage	1,500	3.9	385	225	2,110
Crystallization	8,040	20.6	2020	1180	11,240
Filtration (filter only)	11,400	29.2	2870	1675	15,945
Drying	3,150	8.1	795	465	4,410
Distillation	7,780	19.9	1955	1145	10,880
Total	39,020	100.0	9820	5740	54,580

Since the pilot plant was designed for production of 2 tons per day, the foregoing cost represents an investment of approximately $91.00 per annual ton, 54,580/(2 × 300).

The production of iron-free alum by this process can be considered as a series of operations supplementary to standard commercial practice in the manufacture of crude aluminum sulfate. The annual domestic production of crude alum is approximately 400,000 tons, whereas the manufacture of iron-free alum is normally about 25,000 tons per year. In attempting to evaluate the purification process, it has been assumed that a commercial plant would be constructed in conjunction with an existing crude alum plant and that an annual production of 6000 tons could be marketed. Based on 300 operating days per year, the daily capacity of the unit would be 20 tons.

To distribute the anticipated capital investment equitably, process equipment for crude-alum manufacture has been included in the cost estimate, but no investment cost for buildings or power-generating facilities has been charged to the cost of the production unit.

The foregoing breakdown of pilot plant construction cost indicates that the accessory items of the unit cost approximately 25% of the major item cost [(9820/39,070)100 = 25.1%]. Similarly the installation labor amounted to 14.7% [(5740/39,020) × 100] of the major item investment. This labor cost, however, included no supervisory expense, and in a comparable commercial construction it was estimated that labor would comprise about 20% of the major item cost.

With the foregoing ratios in mind and applying a conservative estimate to the cost of necessary major equipment items for a commercial plant, the estimated capital expenditure for a unit to produce 20 tons of iron-free alum per day can be broken down as in Table V. As previously mentioned, the cost of buildings and power-generating facilities has been omitted, since it is assumed that the unit would be erected in an operating crude alum plant.

In the commercial production of crude alum, reaction of bauxite with sulfuric acid is exothermic, and the resultant hot solution is normally discharged to the settling tanks at about 35° Bé. A solution of this strength is suitable for feed to the crystallization

TABLE V. ESTIMATE OF EQUIPMENT COST

	Major Items	Accessories at 25%	Installation Labor at 20%	Total Cost
Crude alum preparation				
Crusher	$1,500	$400	$300	$2,200
Bauxite feeder & conveyer	3,000	800	600	4,400
Acid storage	2,000	500	400	2,900
Digester	2,000	500	400	2,900
Settling tanks (2)	5,000	1200	1000	7,200
Filter	3,000	800	600	4,400
Evaporator	3,000	800	600	4,400
Storage	3,000	800	600	4,400
Pumps (4)	2,000	500	400	2,900
Alcohol storage				
Storage tank	2,000	500	400	2,900
Feed tank	1,000	300	200	1,500
Pumps (2)	1,000	300	200	1,500
Crystallization unit				
Mixer	2,000	500	400	2,900
Heaters	1,000	300	200	1,500
Holding vessels	2,000	500	400	2,900
Coolers (8)	8,000	2000	1500	11,600
Storage	3,000	800	600	4,400
Pumps (4)	3,000	800	600	4,400
Filtration				
Vacuum filter	12,000	3000	2400	17,400
10-inch conveyer	4,000	1000	800	5,800
Wash tank	2,000	500	400	2,900
Filtrate storage	3,000	800	600	4,400
Pumps (3)	2,000	500	400	2,900
Drying unit				
Dryers (2)	8,000	2000	1600	11,600
Condensers	1,000	300	200	1,500
Receivers	1,000	300	200	1,500
Distillation unit				
Feed tank	1,000	300	200	1,500
Still	15,000	4000	3000	22,000
Receiver	1,000	300	200	1,500
Blending tanks (2)	4,000	1000	800	5,800
Pumps (4)	3,000	800	600	4,400
Product handling				
Cooling pans	4,000	1000	800	5,800
Crusher	2,000	500	400	2,900
Dust collector	2,000	500	400	2,900
Bagging machine	3,000	800	600	4,400
Conveyers	4,000	1000	800	5,800
Sewage treatment (neutralizer)	3,000	800	600	4,400
Fire protection	8,000	2000	1600	11,600
Service lines, etc.	6,000	1500	1200	8,700
Subtotal				199,000
Contingencies (20%)				41,000
Total estd. cost				$240.000

process, and although the equipment cost estimate has included an evaporator, it is assumed that this will be required only periodically for minor adjustments of density. Steam consumption in this operation is, therefore, negligible. A detailed calculation of manufacturing cost estimate per ton of product follows:

I. Raw Materials

A. Bauxite at 55% Al_2O_3 and $6.00/ton

$$\overset{102}{Al_2O_3} + \overset{98}{3H_2SO_4} \longrightarrow \underset{2000}{\overset{594}{Al_2(SO_4)_3 \cdot 14H_2O}}$$

$$Al_2O_3 = \frac{102 \times 2000}{594} = 344 \text{ lb.}$$

$$\text{Bauxite} = \frac{344}{0.55 \times 0.90 \times 0.97} = 717 \text{ lb.} = \$2.15$$

B. $$\text{Sulfuric acid} = \frac{3 \times 98 \times 2000}{594} = 990 \text{ lb.}$$

990/0.90 = 1100 lb. digestion

$$(21 \times 3.44)/0.90 = \frac{80 \text{ lb. adjustment}}{1180 \text{ lb. total } H_2SO_4}$$

$$\frac{1180}{0.935} = 1262 \text{ lb. } 66° \text{ Bé. at } 16.50/\text{ton} = 10.42$$

C. Alcohol at 99.5% recovery at $0.30/gal. 95%

660 gal. 68% for ppt. = 660 × 8.33 × 0.868 × 0.68 = 3250 lb.

550 gal. 60% for wash = 550 × 8.33 × 0.860 × 0.60 = 2360 lb.

5610 lb.

5610/(0.785 × 0.95 × 8.33) = 904 gal.

904 × 0.005 × 0.30 = $1.36/ton

II. Labor (process per 8-hr. shift): crushing 2 hr., extraction 4, adjustment 2, crystallization 4, filtration 2, drying 2, crushing 2, packaging 3, distillation 4, alcohol adjustment 3; total 28 hr. + supervision (15%) 4 hr. = 32 hr. at $1.20 hr.

(32 × 3 × 1.20)/20 = $5.75/ton

III. Packages (100-lb. bags estd. at $0.10 each)

20 × $0.10 = $2.00/ton

IV. Power

A. Electricity at $0.03/kw.-hr.

Operation	Estd. Horsepower	Hr./Day	H. P.-Hr.
Crushing	20	2	40
Conveying	10	4	40
Extracting	15	20	300
Mixing	5	24	120
Cooling	24	24	575
Filtering	15	24	360
Drying	10	6	60
Crushing	20	2	40
Conveying	10	4	40
Pumping (gen.)	30	15	450
Lighting	10	16	160
Total			2185

(2185 × 0.745)/20 = 82 kw.-hr./ton

82 × 0.03 = $2.45/ton

B. Steam at $0.35/1000 lb.

1. Crude alum prepn. is exothermic = 0
2. Crude alum evapn. = 0, assuming 35° Bé. soln. from digesters
3. Reheat = negligible
4. Distillation of alcohol (from pilot plant data) = 4900 lb. steam/ton alum
5. Drying (from pilot plant data) = 0.85 lb. steam/lb. alum
   2000 × 0.85 = 1700 lb. steam
6. Miscellaneous (10% of distn. & drying) = 660 lb. steam

Total steam = 4900 + 1700 + 660 = 7260 lb./ton

7260 × $0.35 = $2.54/ton

C. Water at $0.015/1000 gal.

1. Still and dryer condensers (assume 20° F. rise). Heat to be removed is essentially 1000 B.t.u./lb. steam consumed; sensible heat is lost in still bottoms and hot alum:
   $\therefore (4900 + 1700) \times 1000 = 6.60 \times 10^6$ B.t.u.
   $(6.60 \times 10^6)/(20 \times 8.33) = 39{,}500$ gal./ton
2. Cooling slurry (180 B.t.u./lb. alum from batch pilot plant)
   2000 × 180 = 360,000 B.t.u.
   Assume 5° F. rise in water
   360,000/(5 × 8.33) = 8600 gal./ton
3. Miscellaneous water = 10% of foregoing = 4820 gal./ton

Total H_2O = 39,500 + 8600 + 4820 = 52,920 gal./ton

(52,920 × 0.015)/1000 = $0.79/ton

Total power (*A* + *B* + *C*) = $2.45 + $2.54 + $0.79 = $5.78/ton alum

V. Maintenance (estd. 9% of capital investment/year)
(0.09 × 240,000)/6000 = $3.60/ton alum

VI. Depreciation (estd. at 10%)
(0.10 × 240,000)/6000 = $4.00/ton alum

VII. Miscellaneous Minor Cost Items

A. Insurance (2% capital cost)
(240,000 × 0.02)/6000 = $0.80/ton

B. Research (2% gross sales) (iron-free alum at $2.15/100 lb.)
[6000 × (20 × 2.00) × 0.02]/6000 = $0.80/ton

C. Analytical control: one sample/ton estd. at $0.50 = $0.50/ton

D. Management and sales expense (estd. 20% direct labor)
0.20 × 5.75 = $1.15/ton

E. Taxes (estd. 4% capital cost)
(240,000 × 0.04)/6000 = $1.60/ton

SUMMARY OF MFG. COST ESTIMATE PER TON IRON-FREE ALUM

Raw materials (bauxite + acid + alcohol)	$13.93	Depreciation	4.00
Labor	5.75	Insurance	0.80
Packages	2.00	Research	0.80
Power	5.78	Analysis	0.50
Maintenance	3.60	Management	1.15
		Taxes	1.60
		Total	39.91

DISCUSSION

The cost evaluation demonstrates that under current conditions of peacetime economy with an available supply of alumina trihydrate, this process, at a manufacturing cost estimate of $39.91, will not economically compete with comparable market product selling at $40.00 per ton. The entire pilot plant development was carried out at a cost of approximately $100,000 and permitted a technical and economic evaluation of the process.

The significance of the entire development is twofold. It provides a reliable alternate process for the production of iron-free alum from virtually inexhaustible domestic raw materials in time of national emergency. In addition, it clearly demonstrates the economic possibility of utilizing relatively expensive organic solvents for producing cheap-tonnage inorganic products. There are innumerable inorganic salts with phase diagrams similar to aluminum sulfate and ethanol, and further laboratory investigation should be directed along these lines. If a cost differential of over 2 cents per pound between crude and purified product were available, other factors being equal, the process would undoubtedly be justified.

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August's HEADLINES...

Events of Interest to Chemists, Chemical Engineers, and Executives∼∼*Reviewed by the Editors*

¶ August 1. Louis Schmerling, Universal Oil Products Co., Chicago, Ill., selected to receive first Ipatieff Prize in chemistry, honoring achievements in study of catalysis or high pressure, for his contribution to knowledge of catalytic reactions of hydrocarbons, A.C.S. announces[1].

¶ August 2. Report by Isotopes Branch, U. S. Atomic Energy Commission, on first year's use of radioisotopes in medical, biological, industrial, and agricultural research, proves atomic aid to man through more than 1000 shipments to 170 institutions and researchers in 92 localities in country; reveals most important isotopic use as research tool through tracer technique[2].∼∼American Cancer Society announces 22 new grants totaling $133,382 have been recommended by National Research Council to research centers and cancer specialists in 10 states to aid in search for cancer cause and cure.

¶ August 3. Record on bills affecting chemical and allied industries approved or discussed by closing session of Congress include: Congress-approved—National Science Foundation, fats and oils census, allocation extensions on quinine and fertilizers, extension of 1920 Mineral Leasing Act, extension of permission to produce alcohol, sugars, and sirups in industrial alcohol plants; held over—6 bills relating to atomic energy, health legislation, Hatch Bill amending Mineral Leasing Act, Rogers Bill on barbiturates; House-approved—legislation authorizing construction of mining research laboratory; House-discussed—food and drug amendment; Senate-approved—water pollution control, milder enforcement provisions on same; Senate-discussed—national soil fertility policy, technical information centralization.∼∼American oilmen and Dutch civil authorities report only slight damage to Sumatra oil fields by Indonesian conflict; expect full production by fall.∼∼Manufacture of industrial chemicals reaches 4 times 1935–39 production rate.

¶ August 4. Bureau of Mines will conduct 35 explorations in 19 states and Alaska for strategic metals and minerals on nation's scarcity list; lead deposits head group including tin, copper, iron, mercury, beryllium-tantalum, and tungsten.

¶ August 5. Office of Materials Distribution announces amendment of tin conservation order removing restrictions on tin content of solder for list of specified refrigeration and motor uses, and permitting production and unlimited use of tin tetrachloride from low-grade drosses, residues, and scrap metal.∼∼Office of International Trade ends export controls of acetone to all countries but Spain, Spanish possessions, and Korea.∼∼Department of Agriculture authorizes third quarter export quota of 6000 to 7000 metric tons linseed oil.∼∼Soviet Union seizes Austria's largest oil refinery in Russian zone, property of U. S. and British oil interests and controlled by subsidiaries of Shell Oil Co. and Socony-Vacuum Oil Co.; act to be brought before 4-power commission on Austrian peace treaty now meeting in Vienna.∼∼Mojave Desert, Trona, Calif., yields record output of borax expected to exceed 1946 total of 429,798 tons borate minerals; operation produces 95% of world's output and all of U. S. supply.

¶ August 6. President vetoes Science Foundation bill, terming it "so complex and unwieldy" as to "impede rather than promote government's efforts to encourage scientific research"; urges Congress to pass new bill[3].∼∼Frederick H. Osborn states Soviet proposals on atomic control agency are "wholly unacceptable" to U. S.∼∼War Assets Administration announces sale of Morganton, N. C., graphite electrodes plant to Great Lakes Carbon Corp. for $2,000,000; new owner plans to lease plant to National Carbon Co., wartime operator, for production of special graphite for AEC.∼∼India can become self-sufficient in fine chemicals, drugs, and pharmaceuticals in 15 years, report by advisory panel to Indian chemical industry says.

¶ August 7. Investigators at Lederle Laboratories, Pearl River, N. Y., find high vitamin B content in penicillin waste, enabling its use as livestock feed enricher; American Cyanamid Co. converts and markets by-product.∼∼Yale University will double science requirements in "revolutionary" step to meet demands of atomic age, Wm. C. De Vane, dean, discloses[4].

¶ August 8. Great Britain will submit questionnaire to Soviet Union asking further explanations on how Russian atomic control plan would work; general feeling is that attempt to set up control plan has reached deadlock as serious as that of last year.∼∼President vetoes bill to subsidize mining of copper, lead, zinc, and manganese for 2 years.∼∼GE breaks ground at Knolls, near Schenectady, N. Y., for government's fifth nuclear research laboratory, to cost $20,000,000; objective is "utilization of atomic energy for production of power for industry and domestic use."

¶ August 10. Chamber of Commerce condemns proposal that UN control world oil resources, saying it violates free enterprise policy, Earl O. Shreve, president of chamber, declares.∼∼Monsanto Chemical Co. announces completion of $3,000,000 synthetic detergent plant at Monsanto, Ill.

¶ August 11. Ground is broken at Brookhaven, L. I., for government's $10,000,000 peacetime atomic project; staff ultimately expected to reach 2000, including 500 scientists.∼∼Rubber firms ask Government to terminate war agreement pooling all discoveries; claim pact stifles incentive to develop synthetic rubber favorably comparable to natural.∼∼Imperial Chemical Industries restores full soda ash production.∼∼AEC appoints following to administrative and operating positions: R. S. Warner, Jr., director of engineering; J. C. Franklin, manager, Oak Ridge operations office; A. L. Tammaro, acting manager Chicago office; and P. S. Fogg, adviser to Tammaro.∼∼Quaker Chemical Products Corp. begins manufacture of polyethylene glycol esters at Conshohocken, Pa., laboratories.∼∼Coast Guard bans loading or unloading of ammonium nitrate in populated areas except by Army.∼∼Du Pont develops new insecticide, Methoxychlor, which is $^1/_{40}$ as toxic to warm blooded animals as DDT.

¶ August 12. U. S., Britain, and Russia join in successful fight to shelve proposal for UN control of Middle East oil resources.∼∼Sidney P. Colowick, Public Health Research Institute, New York, N. Y., selected to receive Eli Lilly and Co. award in biological chemistry, W. Albert Noyes, Jr., President A.C.S., announces.∼∼Stanolind Oil and Gas Co. contracts to sell entire production of by-product chemicals from its two Fischer-Tropsch synthetic gasoline plants, scheduled for completion in 2 years, to U. S. Industrial Chemicals, Inc.[5]

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[1] *Chem. Eng. News*, 25, 2195 (Aug. 4, 1947).
[2] *Ibid.*, 2202 (Aug. 4, 1947).
[3] *Ibid.*, 2347 (Aug. 18, 1947).
[4] *Ibid.*, 2485 (Sept. 1, 1947).
[5] *Ibid.*, 2436 (Aug. 25, 1947).

¶ August 14. Glidden Co. completes Chicago plant for commercial recovery of soya sterols, Paul E. Sprague, vice president, announces[6].

¶ August 17. Continental Oil Co. announces plans for construction of $8,500,000 refinery on 100-acre tract in Billings, Mont., with daily capacity of 7500 bbl., to manufacture high octane gasoline and full line of burning oils and road asphalts.

¶ August 18. UN Security Council extends membership to Yemen and Pakistan, rejects Albania, Outer Mongolia, Trans-Jordon, Ireland, and Portugal.∼∼Government files criminal complaint accusing Dayton Rubber Co., Firestone Tire and Rubber Co., General Tire and Rubber Co., B. F. Goodrich Co., Goodyear Tire and Rubber Co., Lee Rubber and Tire Corp., Seiberling Rubber Co., and U. S. Rubber Co., 10 company officials, and Rubber Manufacturers Association, Inc., of conspiracy to fix prices of automobile tires and tubes since 1935, and determine other trade practices on uniform basis.∼∼Organon Pharmaceutical Laboratories, The Netherlands, announces first successful synthesis of vitamin A, completely by chemical methods, after 4 years' research by J. F. Arends and D. A. Van Dorp.∼∼Libby-Owens-Ford Glass Co. announces it has received experimental shipment of 500 tons soda ash from Oslo, Norway, for use in pot-casting operations where special type glass is processed. ∼∼Shell Pipe Corp. and Texas Pipe Line Co. announce plans for construction of $22,000,000 common carrier petroleum pipeline from Cushing, Okla., to Wood River and Salem, Ill., with daily capacity of 150,000 bbl., to be completed early in 1949.

¶ August 19. OIT will appeal for reversal of Inter-agency Export Policy Control Board's recent decision to ban issuance of new export licenses for soda ash and caustic soda until Oct. 1.∼∼WAA approves sale of government's $14,000,000 wartime 100-octane gasoline refinery at Duncan-Beckett, Okla., to Sunray Oil Corp., Tulsa, for $5,100,000.∼∼George C. Supplee, president G. C. Supplee Research Corp., selected to receive 1947 Borden Prize for research in chemistry of milk at A.C.S. New York meeting Sept. 15, for first practical methods for commercial irradiation of milk to increase vitamin D content.∼∼E. H. Volwiler, executive vice president Abbott Laboratories, will receive honor scroll of American Institute of Chemists on Oct. 10 for "outstanding work in organization of research programs and active part in furthering work of scientific societies."∼∼Koppers Co., Inc., chemicals division, will begin operation of new Kearny, N. J., chemical plant on Sept. 1, for production of sulfuric acid; hydrogen cyanide and related chemicals will be produced next year[6].

¶ August 20. Chemicals production in zone of Germany now occupied by U. S. continues restrained by shortages of coal, transportation, and skilled labor, but reaches approximately half prewar volume.∼∼Sharp & Dohme, Inc., purchases plant facilities on 72-acre tract near North Wales, Pa., from WAA for $1,750,000; plans eventually to move entire pharmaceutical and biological facilities and shipping and warehouses departments to location.∼∼Westvaco Chlorine Products Corp. discloses mining of 10-foot bed of trona, natural sodium carbonate, near Rock Springs, Wyo.; deposit expected to become important new source of commercial soda ash.

¶ August 21. Russian veto bars Italy, Austria, Rumania, Bulgaria, and Hungary from UN membership on grounds peace treaties of former enemy countries have not been ratified.∼∼OIT places naphthalene, lead arsenate, naphthalene balls and flakes, and tri- or pyro-sodium phosphate on consolidated license basis when exported to any country but Korea, Spain, and Spanish possessions.∼∼Monsanto (Canada) Ltd. forecasts 100% increase in its Canadian plastics production within 2 years.

¶ August 22. J. D. Goodloe, Reconstruction Finance Corp. chairman, discloses federal government made wartime profit of $37,000,000 on Big Inch and Little Big Inch pipelines.∼∼Mid-Continent Pipe Line Co. plans $2,000,000 expansion and modernization program including construction of crude oil line into active development area of McClain and Garvin counties, Okla.

¶ August 26. WAA announces sale of Building 401 at Kentucky Ordnance Plant, Paducah, Ky., to AEC for $315,440; Commission will dismantle electric and steam generating equipment for use elsewhere.∼∼Department of Commerce establishes August streptomycin export quota of 300,000 grams, double July quota, in view of 100% streptomycin production increase.∼∼Government authorizes Research Information Service, Inc., to translate and publish in near future German technical information reports of interest to industry, engineers, and scientists in various fields of research; subjects given priority are: cellulose products, plastics, rayon, compounding formulas for dyestuffs, textile auxiliaries, intermediates, as well as metals and metallurgy, alloys, optical and photographic equipment, color photography, and preparation of emulsions[7].∼∼El Paso Natural Gas Co. applies to Federal Power Commission for authority to construct 470-mile pipeline from San Juan, N. Mex., to Needles, Calif., at estimated cost of $55,000,000; construction to begin in 1951, and be completed in 1952.

¶ August 27. President's Scientific Research Board urges 1% outlay of national annual income for U. S. scientific research and development, double present percentage. Federal program designed to correct present imbalance between basic and applied research through following 6 recommendations: set up National Science Foundation to make grants in support of basic research; assist undergraduate and graduate students in sciences as part of over-all national scholarship and fellowship program; assist universities and colleges in maintaining laboratory facilities and scientific equipment as part of aid-to-education program; set up federal committee to assist in coordinating and developing government's research and development programs; and help reconstruct European laboratories and orient scientists of other countries with wartime scientific research and development gains. Program to be in full effect by 1957; requires $1,000,000,000 in federal funds. Corporate tax laws revisions suggested to encourage continued industrial research at present level of $1,000,000,000, giving total of $2,000,000,000[8].∼∼Canada permits continuation of ammonium nitrate shipments through British Columbia ports; will enforce strict safety regulations.∼∼Major U. S. platinum refiner increases price $10 per ounce; London refiner boosts price $4.

¶ August 28. Justice Department engages in probe to determine whether streptomycin manufacturers are violating antitrust laws.∼∼Commerce Department will discontinue monthly magazine, "Domestic Commerce," after September issue.∼∼Sinclair Refining Co. announces completion of pipeline connecting refineries at East Chicago, Ind., and Marcus Hook, Pa.

¶ August 29. AEC announces undertaking, with National Research Council, of long-range, Truman-ordered study of survivors of Hiroshima and Nagasaki atom-bomb attacks to determine effect of atomic radiation on blood cells, physical growth of children, mechanisms of heredity, and development of various pathological conditions, including formation of massive scar tissue.∼∼Andrei A. Gromyko rejects operational blueprint of Atomic Control Agency, says it would give U. S. virtual monopoly in atomic field.∼∼Farben officials trial discloses transmission of American tire firms' complete records on progress in synthetic rubber experiment to German industry in prewar years.

¶ August 31. AEC announces new atomic power plant at Los Alamos, N. Mex., "has been operated successfully at low power since November 1946"; first to use fast, instead of slow, neutrons, and employ fission of plutonium, instead of uranium.

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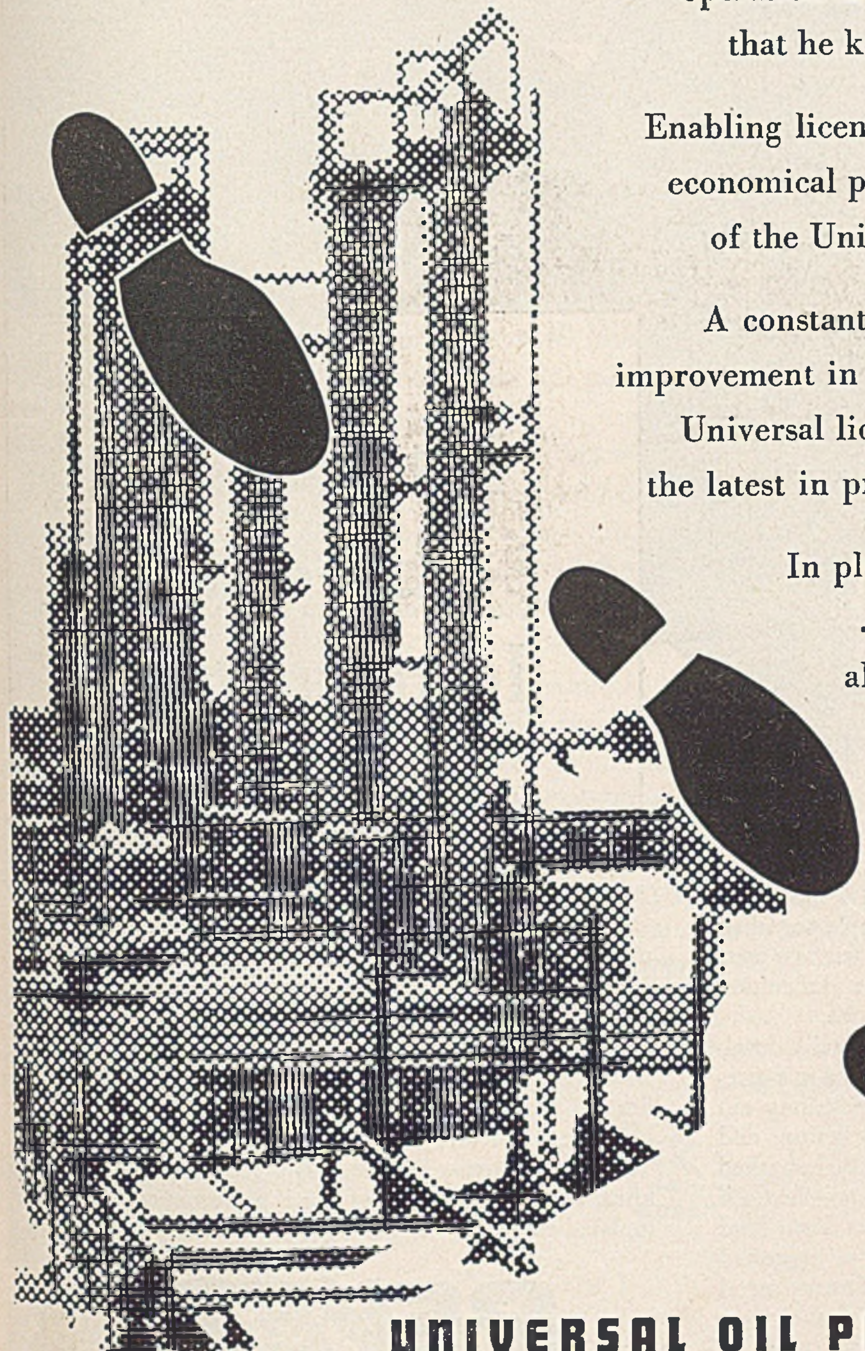
[6] *Chem. Eng. News*, 25, 2568 (Sept. 8, 1947).

[7] *Ibid.*, 2440 (Aug. 25, 1947).

[8] *Ibid.*, 2551 (Sept. 8, 1947).



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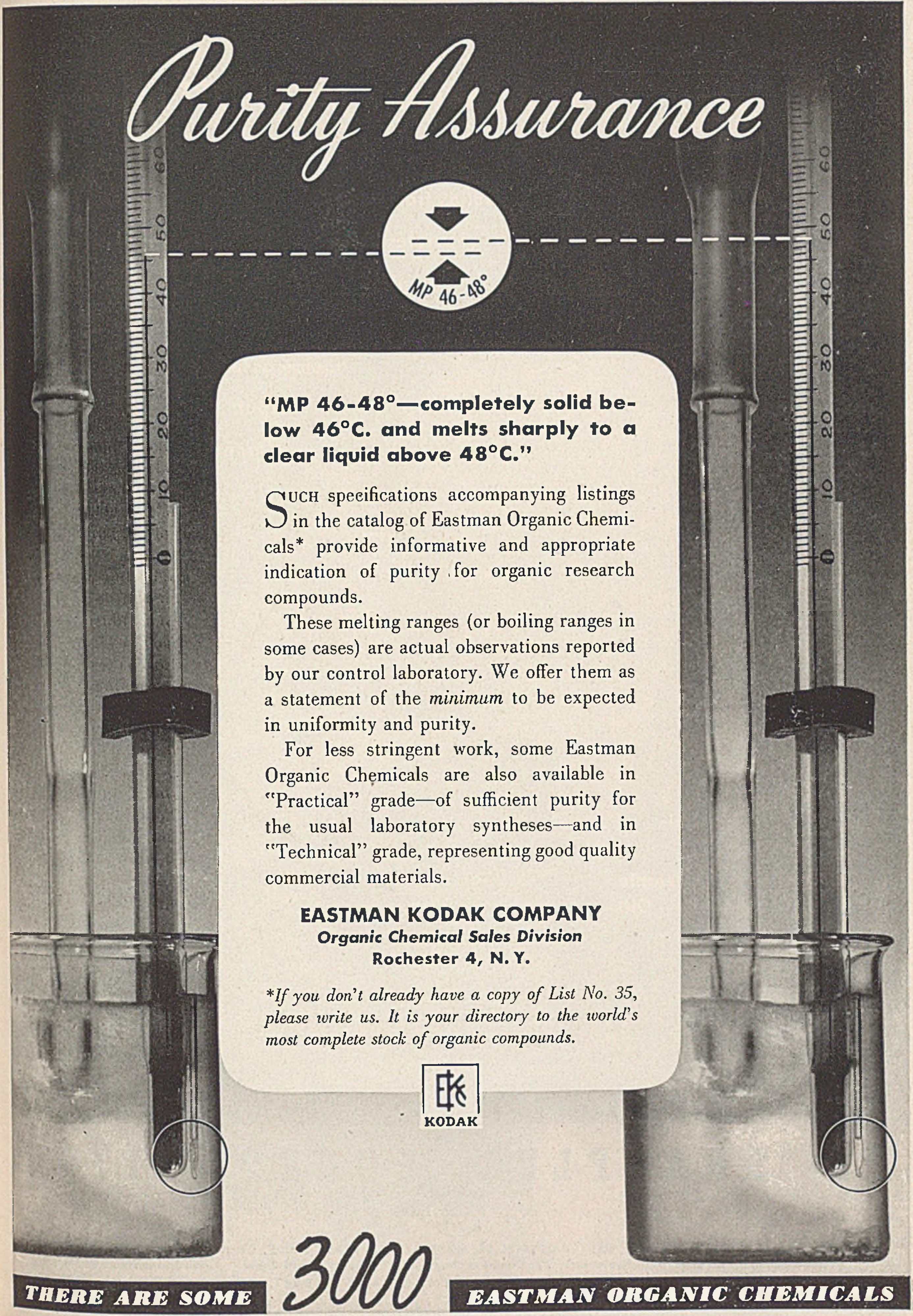

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Equipment and Design

Several reasons are given to show the advantages of operating two types of valves mechanically.

by Charles Owen Brown

There are at least two reasons why valves should be operated mechanically rather than by hand. Materials or fluids are now handled at much higher pressures in the lines containing the valves, and chemical plant operators are often young ladies who are not capable of opening and closing high pressure valves manually. Both trends are modern, and it is desirable that both be encouraged. The need for perfected devices to operate valves mechanically is urgent.

The problem, like the prevailing types of valves, may be divided into two classes. One type should be capable of positioning the valve opening so that the fluid flow may be regulated from full capacity down to a few per cent of capacity, or completely shut off. The second type of control need be only a full-shut or full-open device to correspond with that type of valve.

The first or regulating type is the more difficult to design. Among the many designs that exist to accomplish the controlled regulation of large and small high pressure valves, one is to enlarge the diameter of the stem of a regulating type valve and substitute a motor-driven pinion and worm gear for the hand wheel at the top of the valve stem. The worm gear stops a movement of the valve from internal pressure and has sufficient reduction to change the position of the valve by very minute amounts. This design is widely used, but is expensive because the reversing limited torque motor is a highly developed apparatus and requires costly electrical controls. This valve is many times heavier than the manually operated valve for the same pipe size and pressure.

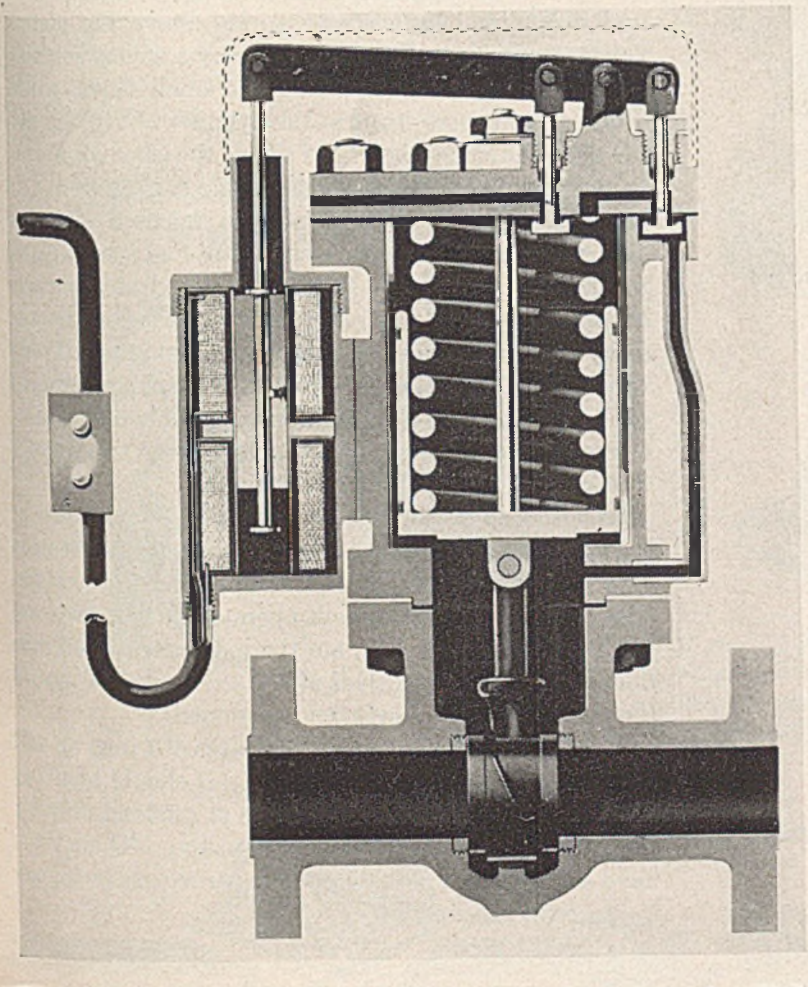
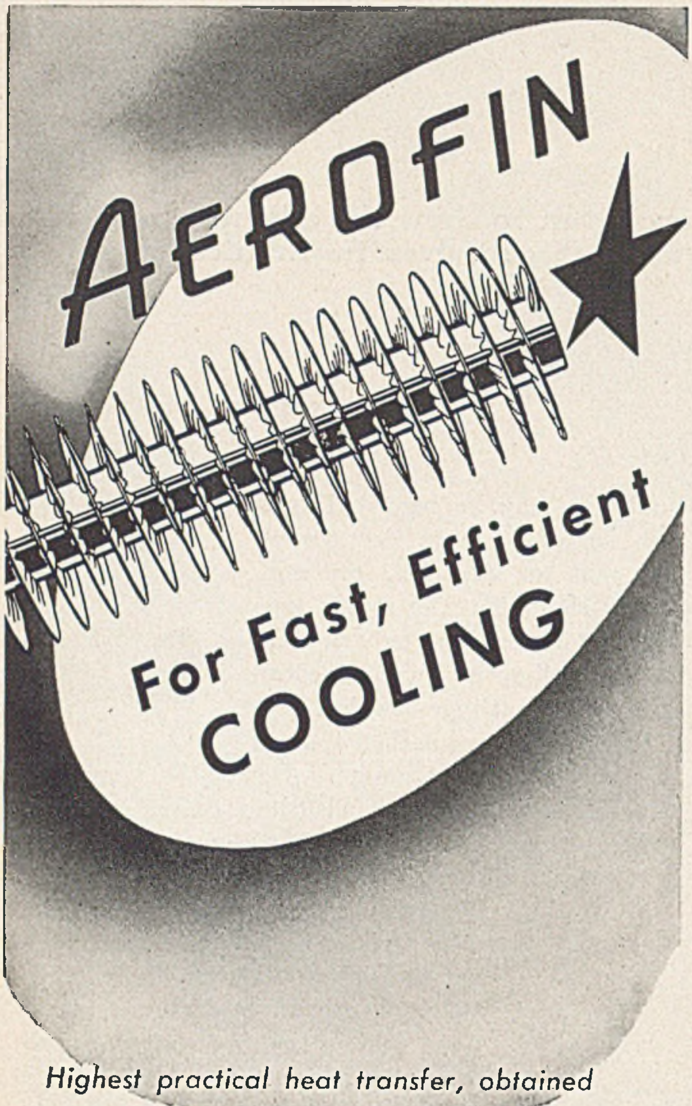


Figure 1. Cut-away Section of Wedge-Type Gate Valve for High Pressure Lines, Actuated by Solenoid Control and a Hydraulic System

Simplicity

A much simpler design has been perfected and used to a limited extent, but in practice the performance has not been nearly so good as the design appeared on paper. This mechanism was hydraulic, simple, and rugged; but in use it either failed or reverted to a control of the second type—either full open or completely closed. This design deserves a brief description. It is a regular high pressure regulating type of valve with a straight packed stem, and the outside yoke is equipped with a cylinder attached to the yoke. The valve stem enters

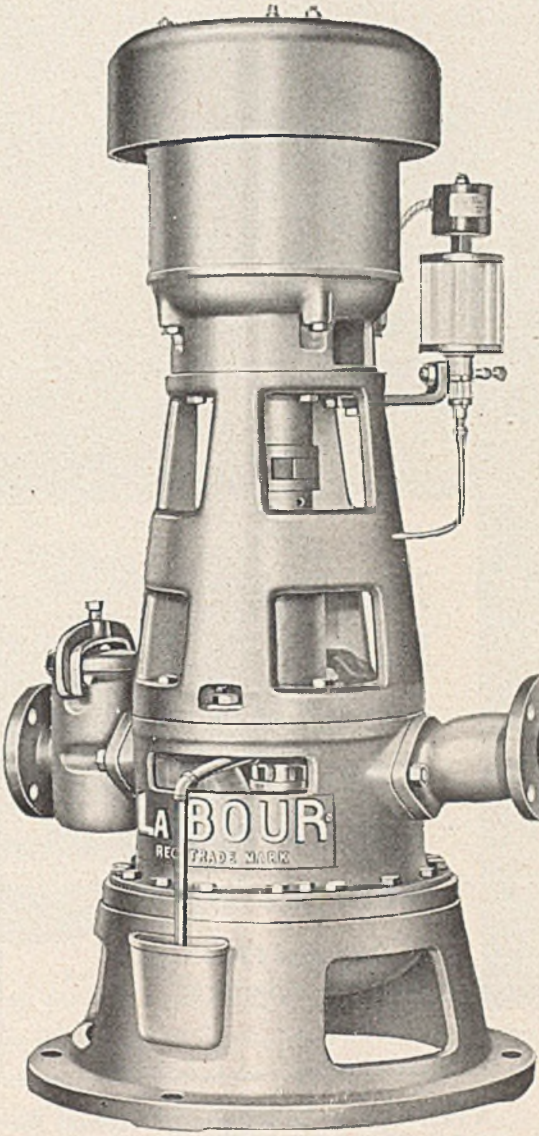


this cylinder and contains a piston equipped with three or four rings attached to the valve stem. The piston usually has twenty times the area of the full valve seat opening; thus when oil at 250 pounds per square inch is pumped into the cylinder above the piston, the valve can be closed against 5000 pounds per square inch, and 300 pounds of oil pressure will provide a seating pressure of 1000 additional pounds. The valve is opened by internal line pressure, and it was assumed that, by regulating the amount of oil released (or sent in above the piston), the valve could be held in any regulated position. The element of time, however, and the large influence of a small seepage of oil past the piston rings proved more disturbing than was anticipated; as a result this simple rugged type of control is not well accepted.

A new design of the simpler second type has recently been perfected by the Shafer Valve Company, Inc., of Mansfield, Ohio. This simple mechanical control is shown in cross section in Figure 1. This device is simply a cylinder with upper head closed, containing a piston connected to the valve stem, all mounted on the bonnet flange of the valve body. The valve is a wedge-type gate without packing, which is opened by pressure of the fluid flowing in the line, acting below a piston; and it is closed by a strong spring above the piston. Operation is controlled electrically by a strong solenoid coil and plunger connected to two small valves which divert the line pressure into the cylinder above the piston or to the atmosphere. Of course the lever connected to the solenoid may be hand-operated, if desired, and requires no more effort than the solenoid supplies. The piston and cylinder are under full-line pressure and in contact with the fluid flow. The electrical circuit actuating the solenoid can be carried to places as remote from the valve as desired, and current is required only while the valve is opening or closing. Constant exhaust of the line fluid has been eliminated, as only one volume of the line fluid is vented to atmosphere as the valve is changed from closed to open position.

This simple device appears excellent for an open or shut valve, but it is also a challenge to urge the creation of a similar sturdy control for regulating-type valves. The electrical circuits which operate the solenoids are less costly to install than are the high pressure oil pipe lines, pumps, and oil valves which are needed to control the hydraulic type of cylinder mentioned.

The Shafer valve is available in sizes of 1 inch up and for pressures of 25 to 6000 pounds. It should be noted that, when open, the line pressure is confined only by the packing rings on the movable piston. These rings have a differential of 6000 pounds per square inch gage to atmospheric pressure.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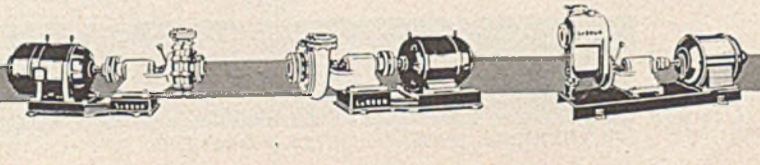


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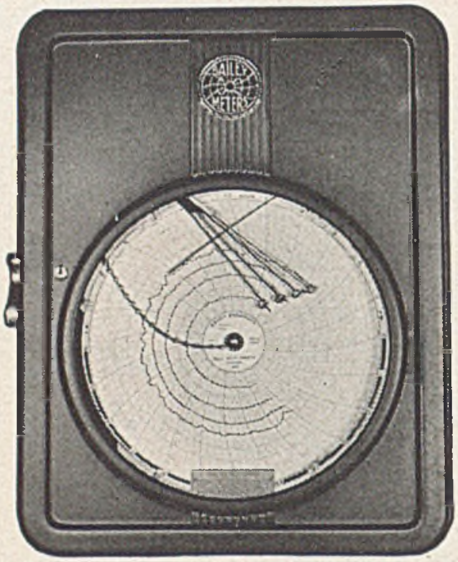

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Instrumentation

Management has recognized the utility of instruments; now it should discover the instrument man.

by Ralph H. Munch

PROCESS industry executives, research workers who devise industrial processes, process plant design engineers, and chemical engineers who operate plants have all come to realize the advantages of proper instrumentation in their plant. Even the plant foremen and the operators, who at first rather resented instruments because they felt that management was using instruments to check up on them, or that instruments would result in workers' losing their jobs, are coming to realize that instruments help them and make their jobs better ones.

Instruments are required to make most processes operable. Even simple batch processes require a certain amount of instrumentation. They may be as elementary as mercury-in-glass thermometers or hydrometers, but usually recorders and controllers will earn a good return on the money invested in them.

In addition to those applications where instruments are necessary before a process can produce, there are other instances where they allow production of more uniform finished goods and eliminate the need for reworking bad lots and blending off goods not quite up to specifications.

Some processes are safe when conditions are maintained within certain limits, but may become exceedingly dangerous to the lives of workers and to the plant equipment if these limits are exceeded. It is much safer to trust instruments to maintain conditions within the safe range and to give warning if safe limits are exceeded than it is to trust human watchfulness. Great care must be used in planning instrument layouts for plants to ensure that failure of an instrument will not produce unsafe conditions.

The advantages mentioned all result in lowered production costs. Also, instruments often make it possible to produce more material in smaller, less expensive equipment, so that costs are still further reduced.

The use of instruments has now become sufficiently widespread so that the cost of instruments and their installation is a very appreciable fraction of the cost of installing a process plant. In an article entitled "Estimation of Instrument Costs," which appeared in the July 1947 issue of *Chemical Engineering*, D. M. Considine of the Brown Instrument Company presents some interesting data on the cost of instrumenting plants for producing various types of chemical and petroleum products. The figures he has compiled indicate that instrumentation costs range from a negligible amount for such industries as superphosphate up to 19% of the plant cost for certain processes in the perfume and cosmetics industry. To some extent the wide variation is an indication of the difference in process complexity from one industry to another. It also indicates that some industries are more progressive than others. Other causes of the variation are the scale of operations in the different industries and the precision with which the quality of the output must be controlled. Considine states that it is not unusual for 50% of the total investment in a pilot plant to be tied up in instrumentation. This is because of the small scale of the operation and the large amount of data desired for design of plant size units.

In addition to the cost of the instruments and their installation must be considered the cost of operation, which includes repairs, maintenance, calibration, chart changing, compressed air, and electricity. This amounts to about $60 per year for an average control instrument. Where hundreds of instruments are used, this becomes an appreciable item.

Because instruments are necessary to make plants operate, to secure uniformity of product, to promote safety of employes and plants, and to secure economy of operation, and because instruments account for an appreciable fraction of the investment in a plant and of plant operating expenses, management is becoming increasingly aware of instruments. Management, however, has not yet become sufficiently aware of the men who are responsible for the results which their organizations get from instruments.

Those who make and sell instruments employ design engineers who are responsible for many of the new developments in the field of instrumentation. Their mathematicians contribute much to the theory of instrument performance, making possible more efficient and widespread use of instruments. The instrument sales and service organizations of manufacturers are available to help select their most suitable instrument for a given job and to help keep it on the job after it is installed. These activities all increase the sale of instruments. Although the user finds these organizations very helpful he cannot rely altogether on the services of instrument manufacturers if he is to make much use of instruments.

As soon as it appears likely that a process under development by a research group may end up as a plant process, someone should be assigned to make a study to find which of the process variables are critical, and

Instrumentation

what means can be used to control them. If these variables are such that they can be controlled by standard commercial instruments, no further work is required at this point. However, it is quite likely that no suitable instrument will be available to control one or more of the critical process variables. In this case a group which specializes in adapting available commercial instruments must be called upon. Savings in time and effort can be effected by carrying out this development while the process is in the laboratory and pilot plant stages.

When plant design is started it becomes exceedingly important to have someone familiar with instrumentation check the design to see that it takes full advantage of the savings available through instrumentation.

During construction of the plant, care in installation of the instruments is well repaid. Before operation is attempted calibration of all instruments should be checked, and each should be shown to be functioning: control instruments should be adjusted to suit the process characteristics. When the plant is in operation, a good preventive maintenance program will help avoid emergency repairs.

The men who fulfill these functions for instrument users should be regarded as valuable assets by their employers. Unfortunately, they cannot be hired already trained. No schools have courses which fit men for these jobs. Men who do instrument work have various backgrounds. Some were trained as mechanical engineers, others as chemical engineers; but too many have had little or no training for the important jobs they are expected to fill. They have merely an interest in gadgets and more or less experience in their jobs.

In this situation instrument users who wish to make the most of the benefits of instrumentation must encourage the instrument men in their employ to improve their knowledge of the subject. The company library should include the standard texts and journals covering the field. Able men should be encouraged to study related subjects such as electronics, mathematics, and chemical engineering in night schools. Some men should be sent to the instrument schools maintained by manufacturers. Other educational opportunities are provided by short courses, such as those presented annually by the Texas Agricultural and Mechanical College. The meetings of the Instrument Society of America include short courses on various types of instruments as well as technical sessions where research papers are presented. Their meetings feature exhibits of instruments by all makers and provide instrument men with an opportunity to learn from one another. Men should be encouraged to present papers on instrumentation before technical societies and in technical journals. Key men have the obligation of training those who work under them. Employers' efforts to improve the training of their instrument men will be repaid by increased benefits from instrumentation.

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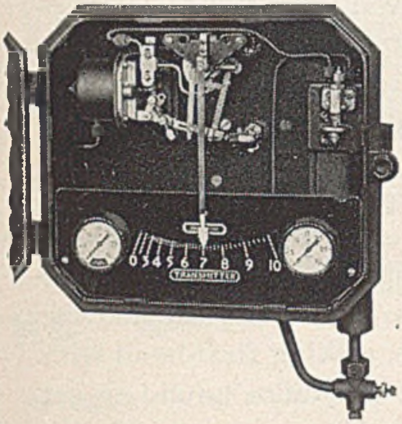

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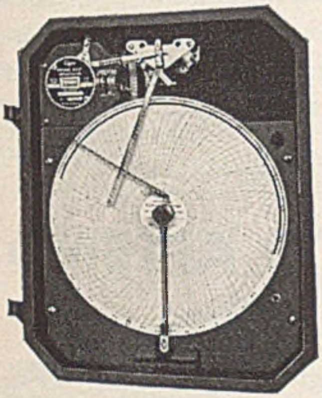

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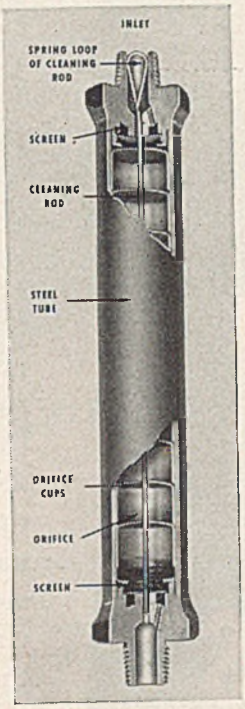

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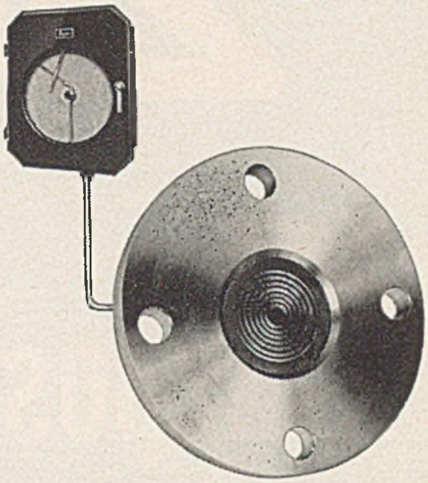

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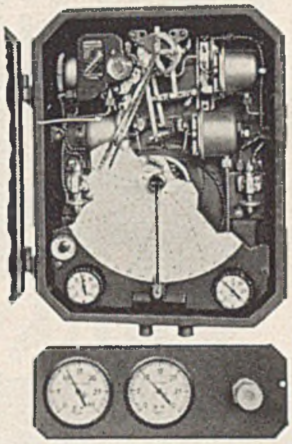

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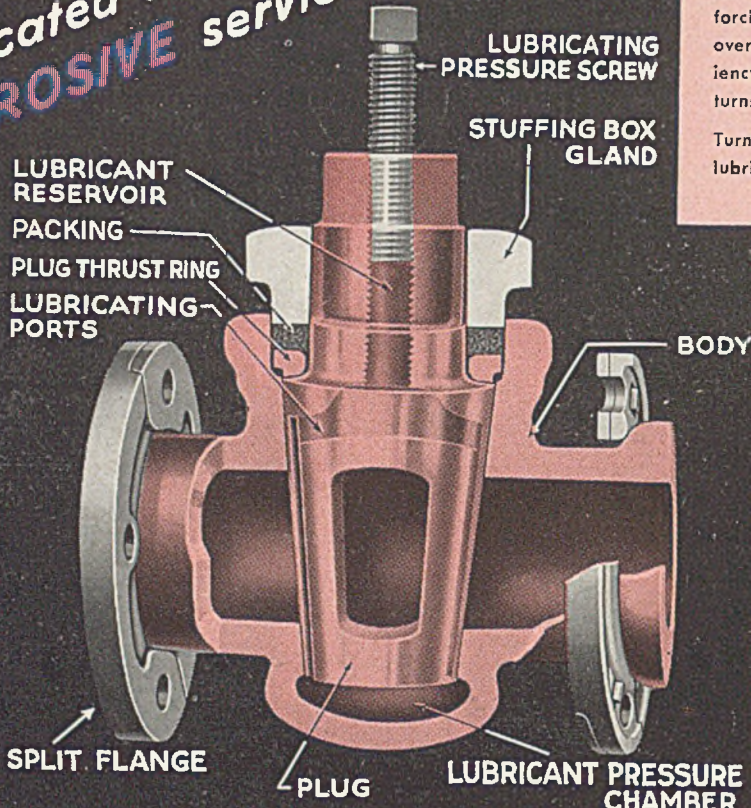

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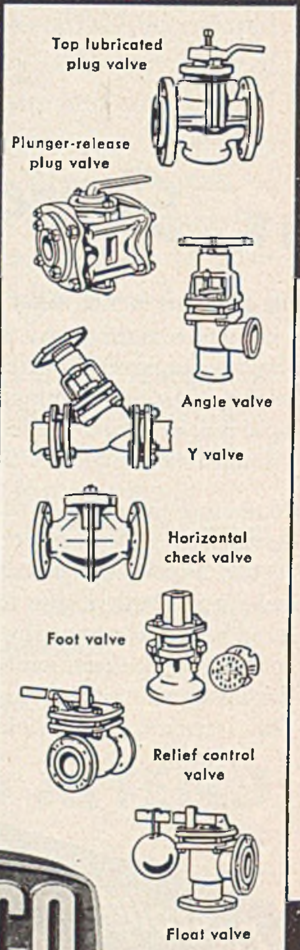

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Corrosion

A new theory for the passivation and corrosion resistance of 18-8S stainless steel is described.

by Mars G. Fontana

The excellent corrosion resistance of the stainless steels is usually attributed to "passivation" of the surfaces of these materials. A "passive" surface is one that exhibits "noble" characteristics or practical immunity to attack by corrosive environments as compared to the substantial corrosion that occurs on an "active" surface. In other words, a passive alloy shows much better corrosion resistance than the electromotive series positions of the constituent elements would indicate. For example, the position of chromium in the e.m.f. series indicates poor corrosion resistance, yet chromium is the major element contributing to the corrosion resistant properties of the stainless steels.

Several explanations have been advanced concerning the nature and mechanism of passivity of stainless steels. (It should be emphasized that passivation is a relative term; an alloy may be passive to one environment, but it may be violently reactive to another corrosive medium.) The most widely accepted theory postulates the formation of an oxide, such as chromium oxide, on the surface of the metal and the protection of the metal by this oxide from corrosion. Another theory assumes that chemically adsorbed oxygen forms a protective layer on the metal surface. However, little or no proof has been found to substantiate and, accordingly, to promote the definite acceptance of these theories.

Physically adsorbed gas

Studies during recent months in the Corrosion Research Laboratory at The Ohio State University, on a fundamental corrosion research project sponsored by the Office of Naval Research, indicates that 18-8S stainless steel becomes passive because of a physically adsorbed gas. At room temperatures specimens of this alloy display passivity upon exposure to air and lose passivity upon exposure to reduced pressure (vacuum). This process is reversible in that the alloy can be passivated, broken down, repassivated, broken down, and so on, by alternate exposure to air, vacuum, air, vacuum, etc. The ready breakdown of the passivity under vacuum at room temperature indicates weak bonds between the gas and the metal, which, in turn, indicates physical adsorption. Oxides or chemisorbed gases would be considerably harder to remove or break down, and this would probably require an elevated temperature.

Treatments and tests

Several passivation treatments were tried during the preliminary phases of this study. The treatment found most effective, based on corrosion tests, is the one which is designated as the sulfuric-air treatment. It consists of exposing a specimen of 18-8S to boiling 10% sulfuric acid for 3 minutes, washing thoroughly in water, and then exposing the specimen to air. Similar results are obtained if hydrochloric instead of sulfuric acid is used. Removal by corrosion of a small amount of metal from the alloy, followed by exposure to air, was found to be an effectve passivation treatment by the writer several years ago. (Incidentally, this situation accounts for many of the apparent inconsistencies in the data resulting from corrosion tests on stainless steels and stainless alloys in sulfuric acid and some other media.)

We arbitrarily prefer to regard the air passivation as the true passivation of stainless steel. This alloy can be protected from corrosion by the formation of surface coatings such as corrosion products, by inhibitors in the corroding medium, and—to take an extreme case—by painting.

Specimens treated in the preferred manner and so passivated are then tested for corrosion resistance by complete immersion in 10% sulfuric acid and in synthetic ocean water at 50° C. (122° F.). Sulfuric acid is selected because it rapidly corrodes an active specimen and is practically harmless if the specimen is passive. In other words, this test is a good yardstick to determine in a short time the performance of the specimen. Another reason for the selection of these media is that the acid results in uniform corrosion or general attack, and the sea water results in the localized or pitting form of corrosion.

In order to clarify the procedures used, it should be emphasized that sulfuric acid is used to treat the specimen prior to exposure to air (passivation), and also to determine the corrosion resistance of the 18-8S after passivation.

Table I shows the breakdown of passivation as a result of exposure to vacuum. Specimens 2 and 3 indicate that passivity is destroyed after 1.5 hours under a pressure of 0.001 mm. Specimens 4 through 11 show that a longer time, or about 4 hours, is required for breakdown at the higher pressure of 0.002 mm. Specimens 12, 13, and 14 also show that the time for breakdown increases as the pressure increases. Perhaps there is a critical pressure above which the passive film would not breakdown.

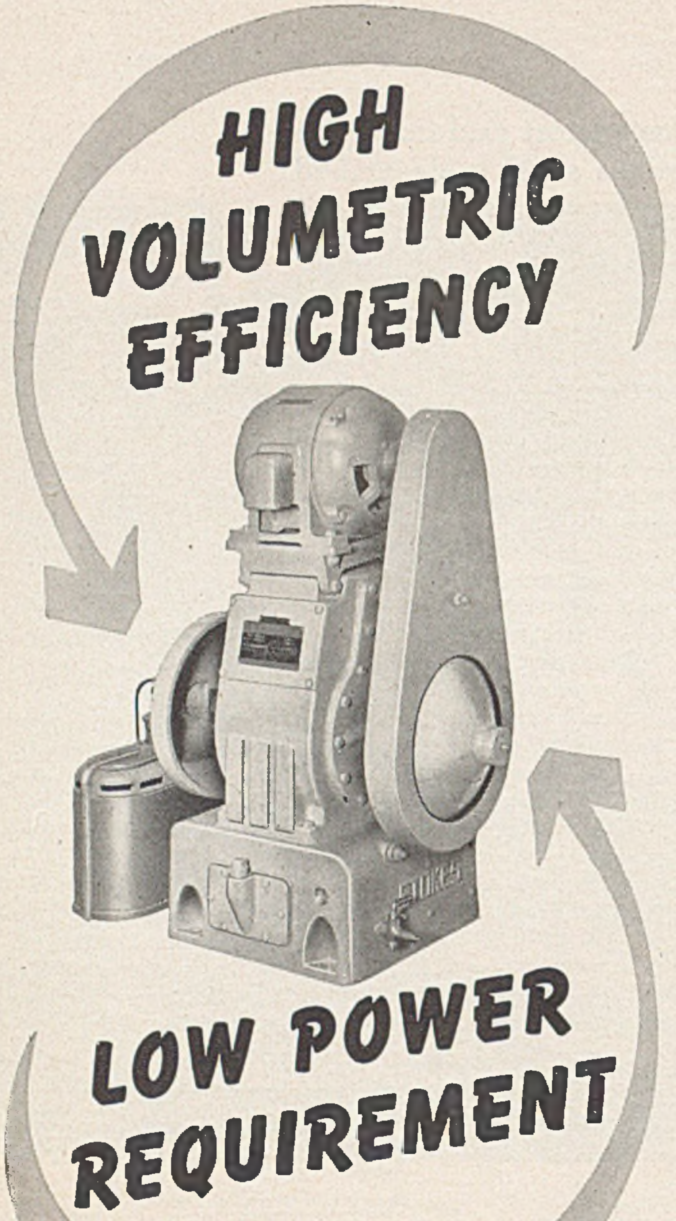
TABLE I. VACUUM BREAKDOWN OF PASSIVATION

(Passivation treatment: boiling 10% H_2SO_4 for 3 minutes, washed, then exposed to air)

Specimen Designation	Pressure, Mm. Hg	Time under Vacuum, Hr.	Behavior in Corrosion Test[a]		Remarks
			Surface	Corrosion rate, mils/year	
1 (many)	None	None	Passive	0	....
2	0.001	1.5	Active	278	....
3	0.001	6.0	Active	280	....
4	0.002	1.8	Passive	0	....
5	0.002	2.0	Passive	0	....
6	0.002	3.2	Passive	0	....
7	0.002	4.5	Active	N.D.[b]	Corrosion started immediately
8	0.002	6.3	Active	N.D.	Corrosion started immediately
9	0.002	7.0	Active	N.D.	Corrosion started immediately
10	0.002	18.0	Active	N.D.	Corrosion started immediately
11	0.002	24.0	Active	N.D.	Corrosion started immediately
12	0.06	6	Passive	0	....
13	0.03	75	Borderline	N.D.	Broke down slowly, then corroded
14	0.2	24	Passive	N.D.	....

[a] 10% H_2SO_4 at 50° C.
[b] Not determined.

Table II gives the results of experiments where the passive film is destroyed by vacuum treatment and then the specimens are again made passive by a subsequent exposure to air. Based on the results in Table I and numerous similar tests, the 6-hour exposure to vacuum assures breakdown of the passive film. With a little experience one can readily tell whether the specimen is active or passive by observing the action on the metal for a few minutes after the acid is bled into the specimen flask. In most runs, however, the specimens are subjected to an actual corrosion test.



Corrosion

TABLE II. RESULTS OF CYCLIC TESTS

(Specimens exposed to air after breakdown of passivation by vacuum treatment)

Specimen Designation	Vacuum Treatment		Time Exposed to Air after Vacuum Treatment	Surface
	Pressure, mm. Hg	Time, hr.		
C-1	<0.0005	6	1 hour	Passive
C-2	0.001	6	5 min.	Passive
C-3	0.001	6	30 min.	Passive
C-4[a]	<0.0005	50	30 min.	Passive
C-5[a]	<0.0005	50	30 min.	[b]
C-5a	<0.0005	6	None	Active

[a] Runs 4 and 5 run simultaneously. Run 4 removed and tested for corrosion resistance, but run 5 again broken down by vacuum treatment (see 5a)

[b] Not subjected to corrosion test but continued as run 5a.

TABLE III. CORROSION OF 18-8S BY SYNTHETIC OCEAN WATER AT 50° C.

(Heavy metals added; pH = 8.2)

Specimen	Passivation Treatment	Pits
S-1	None	Many
S-2	Boiling 3% H_2SO_4, 3 min.; air 1/2 hr.	None
S-3	Fuming HNO_3, 1 hr. at room temp.	Many
S-4	30% HNO_3 + 0.5% $K_2Cr_2O_7$, 1 hr. at 60° C.	Many
S-5	10% $K_2Cr_2O_7$, 1 hr. at 60° C.	Many
S-6	Air at 870° C., 1 hr.	Large

Table III shows the results of tests in synthetic ocean water on 18-8S specimens with different passivation treatments. The sulfuric-air treatment is the only one which prevents pitting of the alloy. In connection with run S-6, it may be of interest to state that numerous corrosion tests were also made in sulfuric acid on 18-8S heated in air at temperatures in the range 225° to 870° C. (430° to 1600° F.) to form oxide coatings. None of these coatings are protective in this acid.

Exposure of active specimens to an atmosphere of purified argon indicates that passivity develops. If passivation by argon could be conclusively demonstrated, it would provide definite and strong support for the new theory involving physically adsorbed gas.

Electron diffraction studies

Passivated 18-8S surfaces were intensively investigated by electron diffraction in an attempt to find crystalline oxides. Electron diffraction patterns gave no evidence of their existence, and these experiments are considered as indirect evidence that passivity is due, rather, to an adsorbed gas.

Electron diffraction did show, however, a diffuse and unidentified pattern which may be a hydrous oxide of nickel or chromium. This material may be of assistance in providing a surface that readily adsorbs gas.

"Passivation" with nitric acid

"Passivation" of stainless steel equipment by exposure to warm dilute nitric acid is quite a common practice in industry. Numerous tests using this "passivation" treatment force the conclusion that this treatment does not passivate stainless steel; it is a fruitless operation and a waste of money as far as passivation benefits are concerned. More and more students of corrosion are adopting this viewpoint. The nitric acid treatment may be of some benefit in removing iron particles that may have been imbedded in the surface of the metal during rolling or other fabrication operations, but this is not a passivation effect; if the metal is pickled after rolling or forming, which is often the procedure, the nitric acid treatment is a superfluous operation. The usual mill operation of pickling should be considerably more effective than the nitric acid treatment by the fabricator or user, as far as passivation is concerned. Pickling doubtless dissolves some of the metal surface, and the pickling operation is normally followed by washing and exposure to air. In other words, a pickling operation in the steel mill is somewhat similar to the sulfuric-air passivation treatment described.

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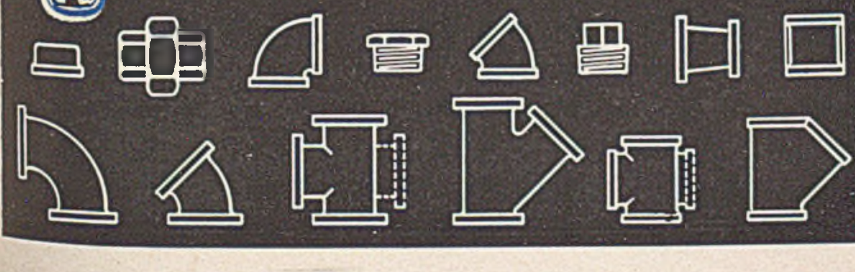
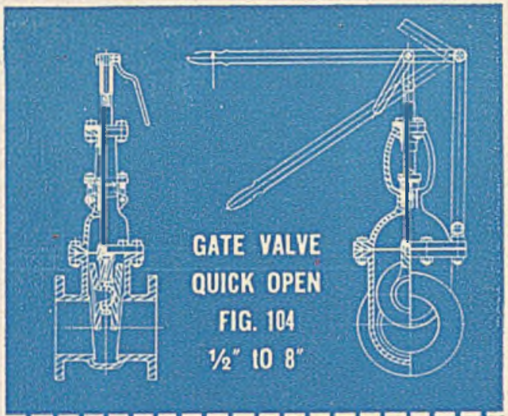
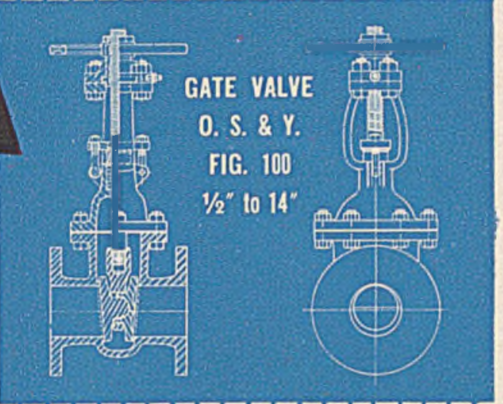
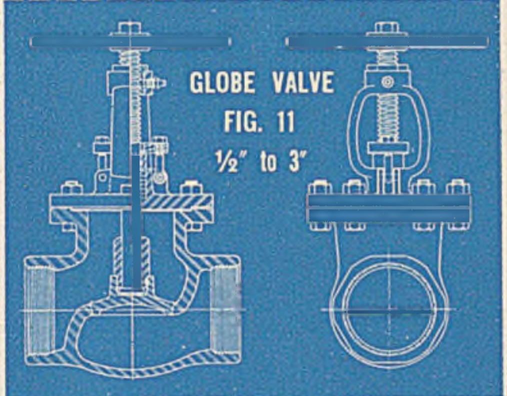
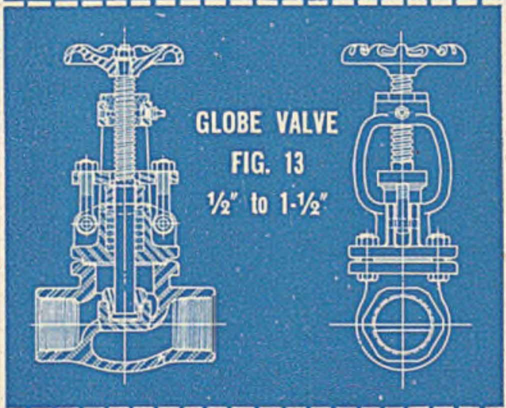
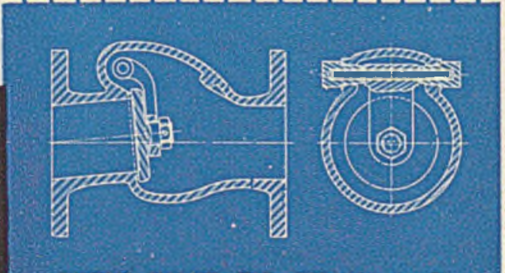


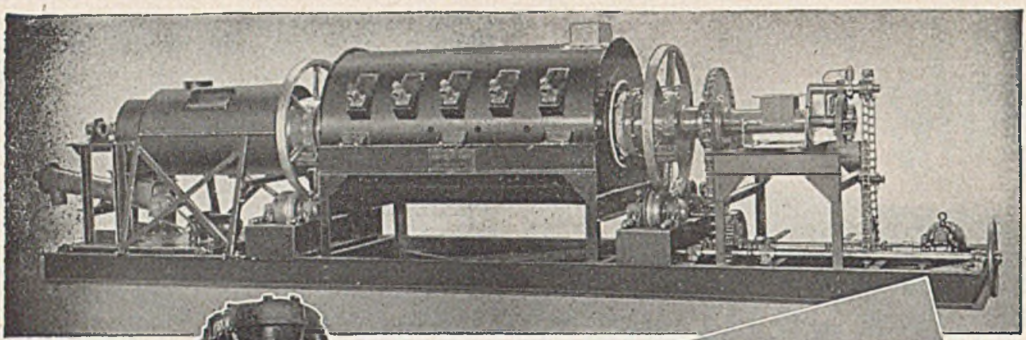

GATE VALVE
QUICK OPEN
FIG. 104
½" to 8"

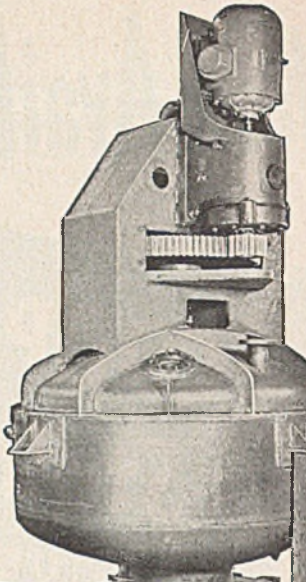

GATE VALVE
O. S. & Y.
FIG. 100
½" to 14"

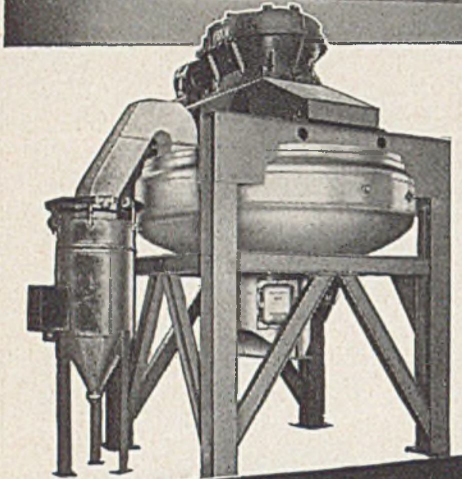

GLOBE VALVE
FIG. 11
½" to 3"

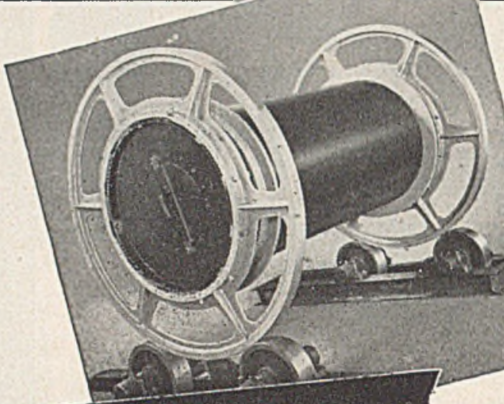

GLOBE VALVE
FIG. 13
½" to 1-½"

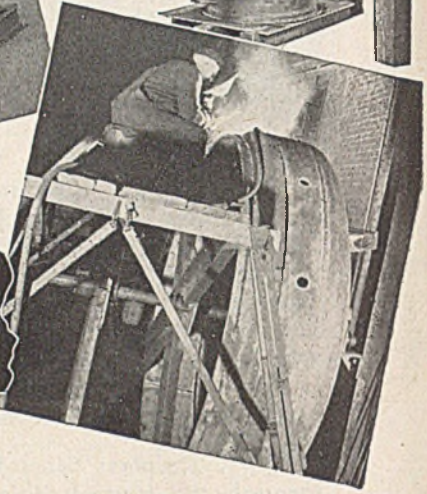

CHECK VALVE FIG. 200 ½" to 6"











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Plant Management

New literature on plant management, published by the American Management Association, is discussed.

by Walter von Pechmann

Every plant executive likes to have at his finger tips specific written information pertaining to problems he occasionally encounters. Information should deal directly with the problem, should be short and concise, and, above all, should suggest practical means for solving the problem.

The American Management Association, 330 West 42nd St., New York 18, N. Y., periodically issues pamphlets which are an excellent source of information for busy production executives in the chemical industry. The following review of some of the articles published recently by the American Management Association is intended to give executives in the chemical industry an outline of the material which is available and to give the highlights of its content. The pamphlets are issued in consecutive numbers and consist of articles written by mechanical and chemical engineers with production experience, top executives well known throughout the industry, and management's consultants and statisticians. The articles usually follow the pattern of problem discussion, a summary, and a record of questions and answers as they took place at panel sessions.

No. 163: MANAGEMENT TECHNIQUES FOR INCREASING LABOR PRODUCTIVITY

A. "Economic Considerations for Production Executives," *by Charles F. Roos.* The writer discusses the subject according to the following groups: perishable goods, consumers' semidurable goods, consumers' durable goods, and capital goods. Three charts are given: Federal Reserve Board production index and components, labor cost and prices, and population, labor force, and its use.

The author points out that the production levels he forecasts will require capacity operations in a vast majority of industries and that the principal problems of the economy during the next several years will be concerned with production. Future output per man-hour, unit labor cost, and wage levels are forecast. The article also deals with employment and supply of materials within the next few years. It is the author's opinion that a manufacturer who would like to protect himself adequately against the ever-present risk of deflation must take steps now to maintain in his plant an output at or above the industry average. He also points out that the various supply situations will force manufacturers to operate with less material and, therefore, where possible, products should be redesigned to use lighter gages and weights or substitutes that are in adequate supply.

B. "Labor Productivity and Technological Advances," *by Albert Ramond.* This article deals with measures for attaining a real productive efficiency of workers, which, according to records, is now substantially lower than it was before the war. The author points out that, in order to achieve real technological progress, one must not only be able to stimulate constructive ingenuity but also make sure that this ingenuity is used to the best advantage. He believes that the time has passed when management could compel acceptance of new ideas without convincing evidence that their adoption will result in more effective operations. Factors of resistance on the part of labor, and corrective and compensating measures, are discussed. Pros and cons of suggestion plans, profit sharing, production incentives, and special incentives are considered. Ramond believes that it is fundamentally necessary to convince labor that it will benefit more than anyone else from increased productivity, and that it is the relation between wages and prices rather than the dollars of take-home pay that regulates material comforts.

C. "What Is a Fair Day's Work?" *A panel session.* This is a record of a panel session which makes interesting reading. Productivity and wage rates, management's failure to sell time study, union time study stewards, wash-up time and rest periods, worker morale, union authority and time study, making time study acceptable, incentive pay, effort rating, and training foremen are discussed. No practical solution is given to all the problems involved. However, some of the specific problems discussed may provide the answer to a certain problem with which a production executive is confronted.

No. 166: THE FOREMAN, THE JOB, AND THE MAN

A. "The Foreman, the Job, and the Man," *by C. F. Mugridge.* This article deals with foremen and their responsibilities. The following questions are answered: Do foremen have unique characteristics that mark them off from other people in industry? Are they truly part of management? What is it that gives them distinction and makes them the subject of endless discussion? What qualifications must one possess to fill adequately the job of foreman?

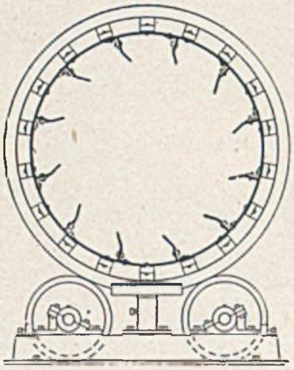
The author especially discusses the effect of foremen unionization, the Case bill, industrial democracy, the need of a new business philosophy, selection of foremen and their salaries, and management training. He believes that an analysis of the present standing of foremen refutes the opinion of those who believe them to be management. Foremen, he says, often perform almost no real executive duties; they are not entrusted with decisions of importance; they are seldom consulted about confidential plans; only in rare cases do they participate in policy making; in fact, they are frequently not so well informed about company matters as are union stewards; literally they function in no greater capacity than lead men, clerks, inspectors, and expeditors. The present author believes that Mugridge generalizes too much about a condition which might exist in some organizations; however, the point is well taken that jurisdiction over technical matters does not make a foreman, and that a real foreman is management in the true sense and, therefore, should function as a member of the management team.

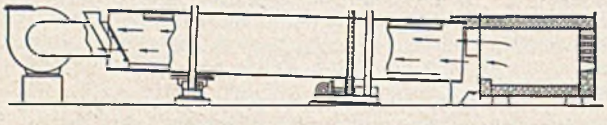
B. "Labor Relations Tools for Foremen," *by C. W. Hodges.* In order to play an effective part in the development and maintenance of good relations between the management and the union, the author calls attention to the foreman's need to be properly coached and adequately equipped with labor relation tools. Simple loose-leaf labor relations manuals called "Your Questions Answered" and "Grievance Digest" are available which contain an account of settled cases of grievances. Attention is called to the fact that labor relations tools are of little value if the right spirit is not behind them. Of special interest is the author's insistence that management make it clear to supervision that the union is a permanent part of the framework in which a company must operate. He also points out that every level of supervision is part of management and, therefore, must include the carrying out of company policies. Finally, he says, supervisors can stand together only if their authority, rights, and responsibilities are clear-cut.

C. "Incentive Compensation for Foremen," *by Charles W. Lytle.* The author realizes the need of strengthening the foreman's position. The true solution to this problem is believed to be an adequate financial award for services rendered and special awards for achievements not usually expected from supervisory personnel below the executive line. Arguments for and against incentives for foremen are discussed. This article should be of considerable interest and help to chemical concerns which intend to install an incentive compensation system for foremen, since this author not only covers the entire subject thoroughly but also describes in detail how to set up a compensation system. Of interest to the reader should be a list of comments from companies which have a foreman bonus plan in operation.

No. 165: GETTING AND USING EMPLOYEES' IDEAS

A. "Why a Suggestion Plan?" *by F. A. Denz.* The article deals first with the reasons why suggestion plans are often not successful. The author encourages the use of suggestion systems, believing that management, employees, and the consumer will benefit by it. He points out that a good suggestion system does not mean fewer jobs and that industrial relations are bettered when employees receive a compensation for suggestions not





considered within the scope of their regular work. The Remington Rand plan is described.

B. "Suggestion Plans—the Value to the Personnel Relations Program," *by Herman W. Seinwerth.* Suggestion programs, says the author, should be looked upon as an aid in improving employee-employer relations but not as panaceas or cure-alls for labor troubles. You must have the proper policy and procedure setup, and you must administer them well. Advantages of a suggestion system are given as follows: (*a*) Cash awards are a primary incentive to constructive thinking; (*b*) there is a personal satisfaction on the part of an employee in contributing an idea and assisting in putting it to use; (*c*) employees feel that they are an integral part of management; (*d*) accepted suggestions make employees feel that they are important and needed; (*e*) employees learn more about the company and its various problems; (*f*) suggestion plans are an excellent means of determining who is most suited for advancement; and (*g*) suggestion plans encourage individuals to make the most of their latent abilities.

Attention is called to the fact that a suggestion plan deals with people and not things. The delicate matter of turning down suggestions is discussed at length. Other paragraphs deal with awards, eligibility, grievances, and the importance of dealing promptly with suggestions submitted.

C. "Suggestion Statistics," *by L. J. Alger.* This interesting article states that 90% of the suggestion systems initiated during the last twenty-five years have failed. Features common to all suggestion systems are used to analyze and compare the various plans now in existence. A survey covering the actual performance of suggestion systems is also included. It deals with participation, percentage of adoptions, and average awards. The author concludes that the economic return which industry as a whole can reasonably expect from the adoption of a suggestion system is considerable; he backs up his statements by figures.

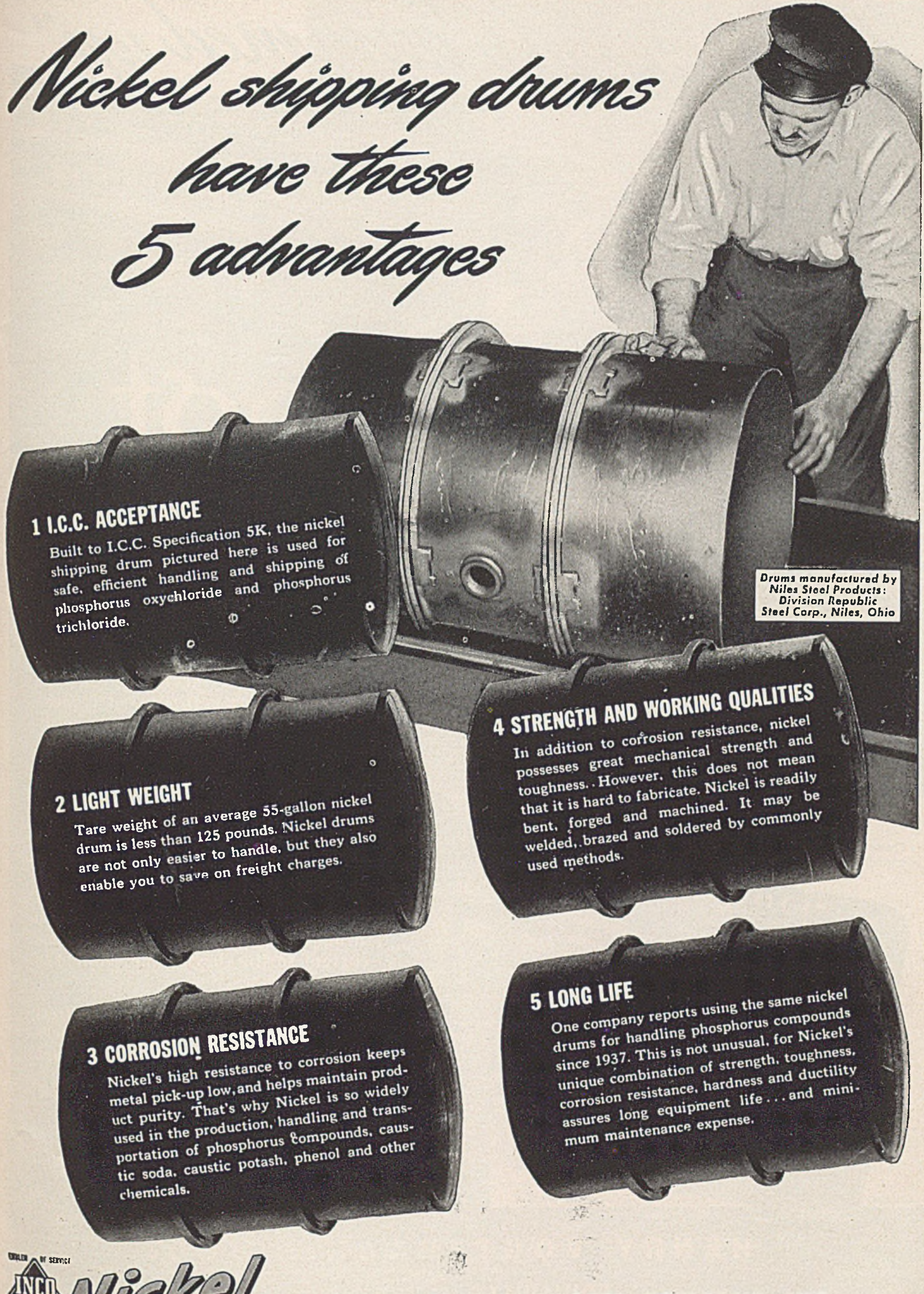
D. "Building a Suggestion Program," *by R. E. Loesges.* This discussion is unique inasmuch as the author considers the suggestion program a buying and selling relation between management and employee. Although it is suggested that ideas submitted should be handled as a pure matter of business, attention is called to the need for considering suggestions as "brain children" of the employees. Special stress is put on the importance of proper executive support. Adequate organization, proper incentive, continued and dramatic publicity and promotion, promptness and thoroughness of investigation, and tactful and complete presentation of the reasons for action by management, are discussed in the order stated. The article concludes with a summary of tangible and intangible advantages of having a suggestion plan in operation.

E. "Training or Educating Imagineers," *by W. E. Byrne.* The following subjects are discussed: support of top management, cooperation of supervision, introducing the plan, publicity, recognition, training classes, personal contact, and awards.

The success of suggestion systems is believed to depend upon giving employees a certain percentage of the savings resulting from their suggestions, with no strings attached. Although the operation of a suggestion system on this basis seems rather unconventional, some companies do operate a suggestion plan successfully in this way. Although the author states that suggestions must be in operation and be proved successful before any payment is made, the reviewer noticed the absence of a formula for determining the savings expressed in dollars and cents. Intangible suggestions submitted can seldom be evaluated; therefore a fixed percentage can scarcely be applied to all suggestions submitted.

F. "The Illinois Central Suggestion System," *by H. C. Marmaduke.* This article will probably be of little help to a production executive in installing a suggestion system as far as the technique is concerned; but, it is one of the most interesting articles on the subject of suggestion systems, since it deals with the subject entirely from the human point of view. The author states that when, in the suggestion business or anything else, we come to the point where we are no longer willing to learn, we are beginning to stand still. He criticizes justly management's attitude of "you do the work and we up here will do the thinking." He believes that the man behind the wheelbarrow or the lathe knows more about his own particular job than anyone else in an organization, and thinks that it is smart for management to recognize this fact and to obtain essential information from the men who have the know-how. Advantages gained by management in the installation of a suggestion system are discussed. It is believed that every production man, every officer, and every supervisor who has anything to do with investigating an employee's suggestion profits from it himself; he is supposed to learn more about the department when he is given an opportunity to see it through the other fellow's eyes and therefore becomes a better boss.

Nickel shipping drums have these 5 advantages



1 I.C.C. ACCEPTANCE

Built to I.C.C. Specification 5K, the nickel shipping drum pictured here is used for safe, efficient handling and shipping of phosphorus oxychloride and phosphorus trichloride.

2 LIGHT WEIGHT

Tare weight of an average 55-gallon nickel drum is less than 125 pounds. Nickel drums are not only easier to handle, but they also enable you to save on freight charges.

3 CORROSION RESISTANCE

Nickel's high resistance to corrosion keeps metal pick-up low, and helps maintain product purity. That's why Nickel is so widely used in the production, handling and transportation of phosphorus compounds, caustic soda, caustic potash, phenol and other chemicals.

4 STRENGTH AND WORKING QUALITIES

In addition to corrosion resistance, nickel possesses great mechanical strength and toughness. However, this does not mean that it is hard to fabricate. Nickel is readily bent, forged and machined. It may be welded, brazed and soldered by commonly used methods.

5 LONG LIFE

One company reports using the same nickel drums for handling phosphorus compounds since 1937. This is not unusual, for Nickel's unique combination of strength, toughness, corrosion resistance, hardness and ductility assures long equipment life . . . and minimum maintenance expense.

Drums manufactured by
Niles Steel Products:
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Nickel

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67 Wall Street, New York 5, N. Y.

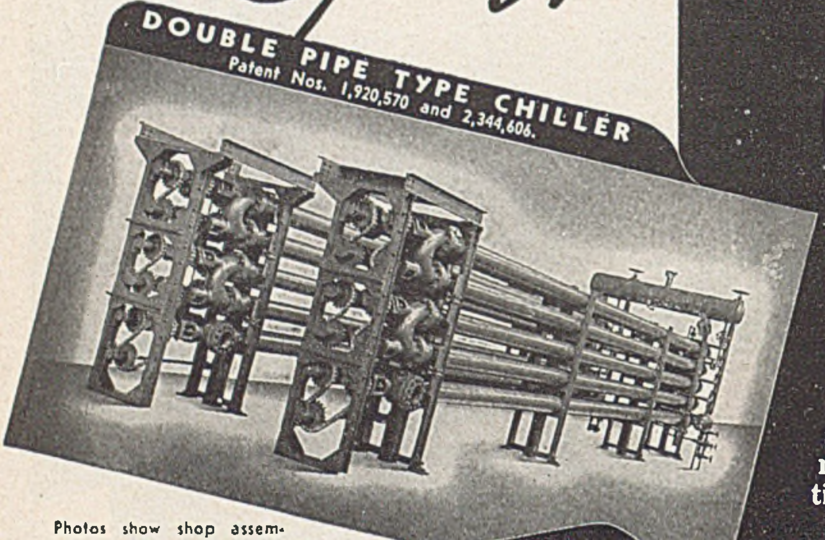
If you're all "gummed up"

in a tough heat transfer problem

Specify..

Vogt Spiral, Spring Type Scraper
Patent No. 2,117,175

Vogt SCRAPER TYPE CHILLERS



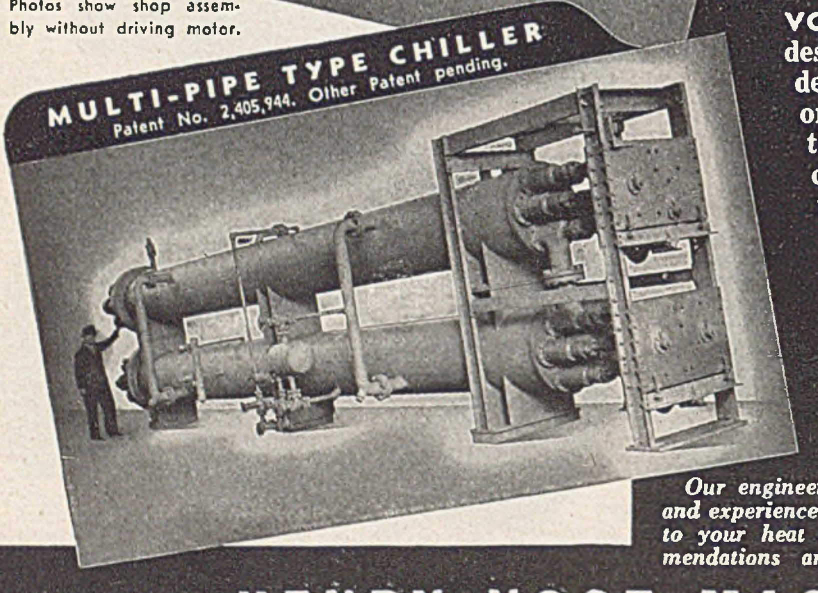
DOUBLE PIPE TYPE CHILLER
Patent Nos. 1,920,570 and 2,344,606.

Photos show shop assembly without driving motor.

Fouling of the inner pipe surfaces of Vogt Chillers is eliminated, because they are swept clean continuously during operation by patented spiral, spring type scrapers. And these clean surfaces achieve the highest possible rate of heat transfer between the solution and the refrigerant.

VOGT DOUBLE PIPE TYPE CHILLERS are designed to use ammonia, brine, or cold dewaxed oil as the cooling medium. Oil or brine, when employed, is circulated through the jacket pipes countercurrent to the flow of the solution in the inner pipes.

MULTI-PIPE TYPE CHILLERS, for direct expansion, have large jacket shells each containing seven inner pipe sections and employ volatile refrigerants such as ammonia, freon, propane, etc.



MULTI-PIPE TYPE CHILLER
Patent No. 2,405,944. Other Patent pending.

Our engineering staff is qualified by training and experience to help you find the right answers to your heat transfer problems. Their recommendations are available without obligation.

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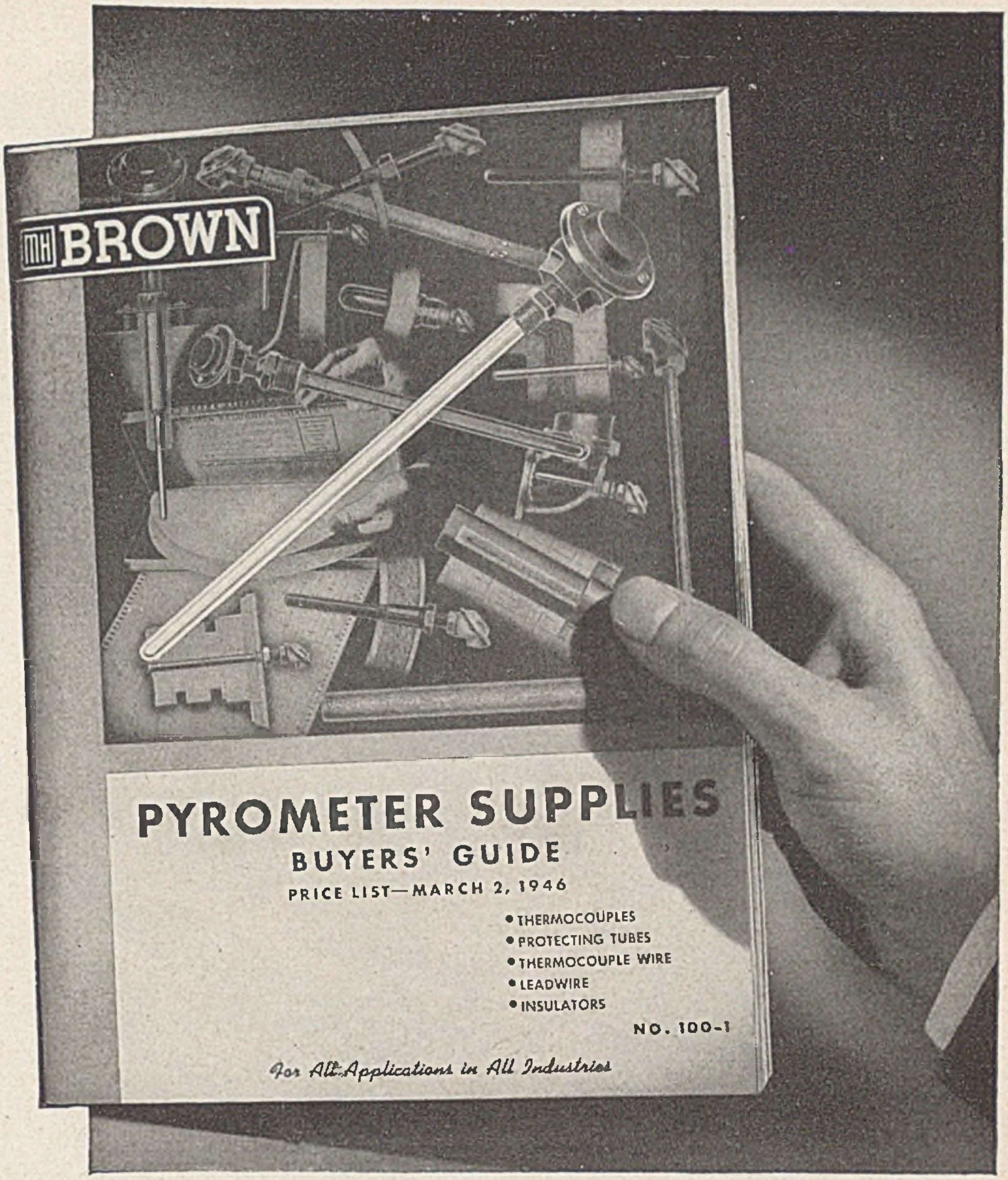
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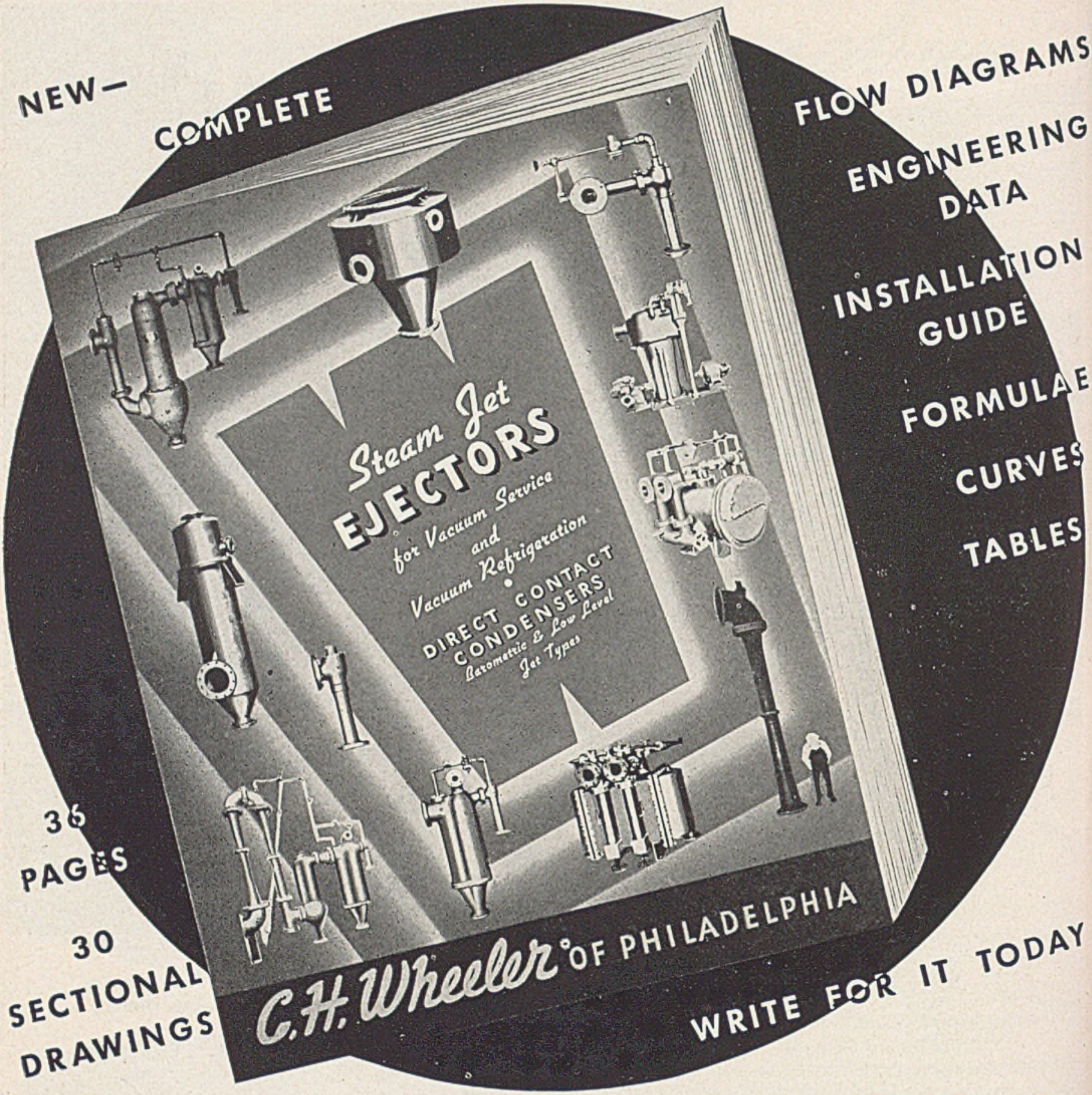
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A. O. SMITH Corporation

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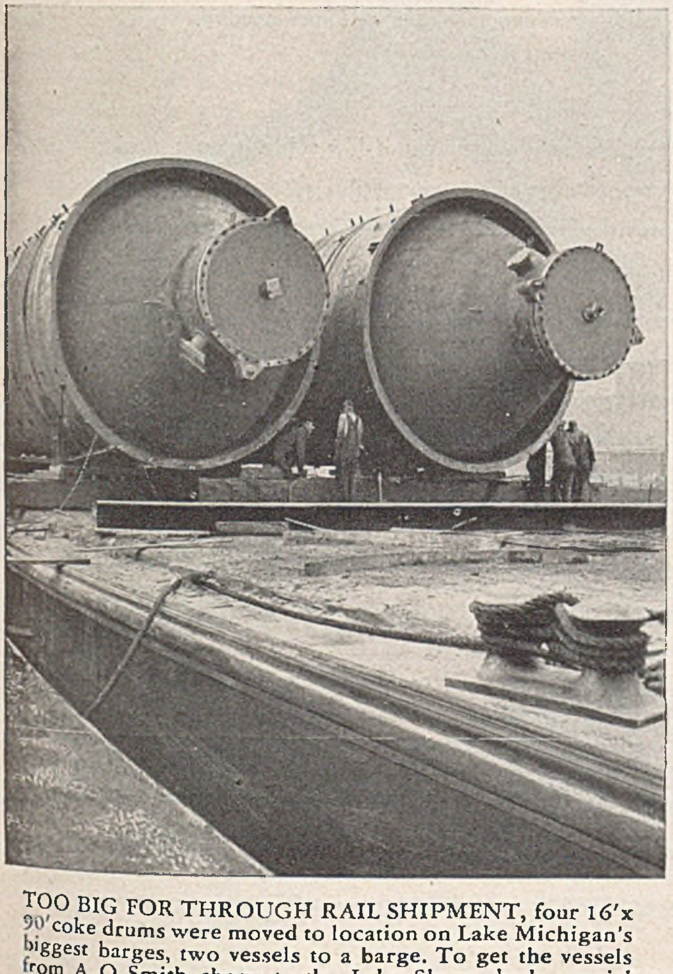
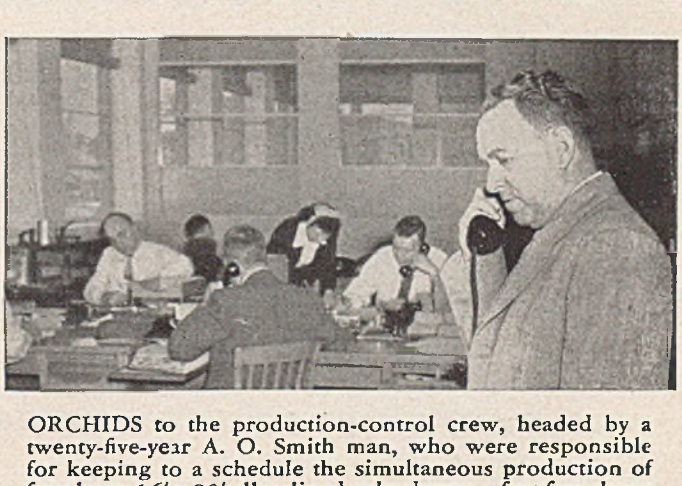
NEW VESSEL DIVISION HEADQUARTERS. Paint is scarcely dry on new air-conditioned building (above, center) which puts administration, sales, engineering, drafting, production control, and inspection immediately adjacent to the A. O. Smith vessel shops, Milwaukee.



TOO BIG FOR THROUGH RAIL SHIPMENT, four 16'x 90' coke drums were moved to location on Lake Michigan's biggest barges, two vessels to a barge. To get the vessels from A. O. Smith shops to the Lake Shore dock, special arrangements had to be made on five miles of railway track.

THESE SULFUR CRACKS are dangerous in welded heavy sections. A. O. Smith metallurgists have figured out a way to avoid them by controlling the residual sulfur in welding wire.



ORCHIDS to the production-control crew, headed by a twenty-five-year A. O. Smith man, who were responsible for keeping to a schedule the simultaneous production of four large 16' x 90' alloy-lined coke drums, a feat few shops in the world could accomplish.

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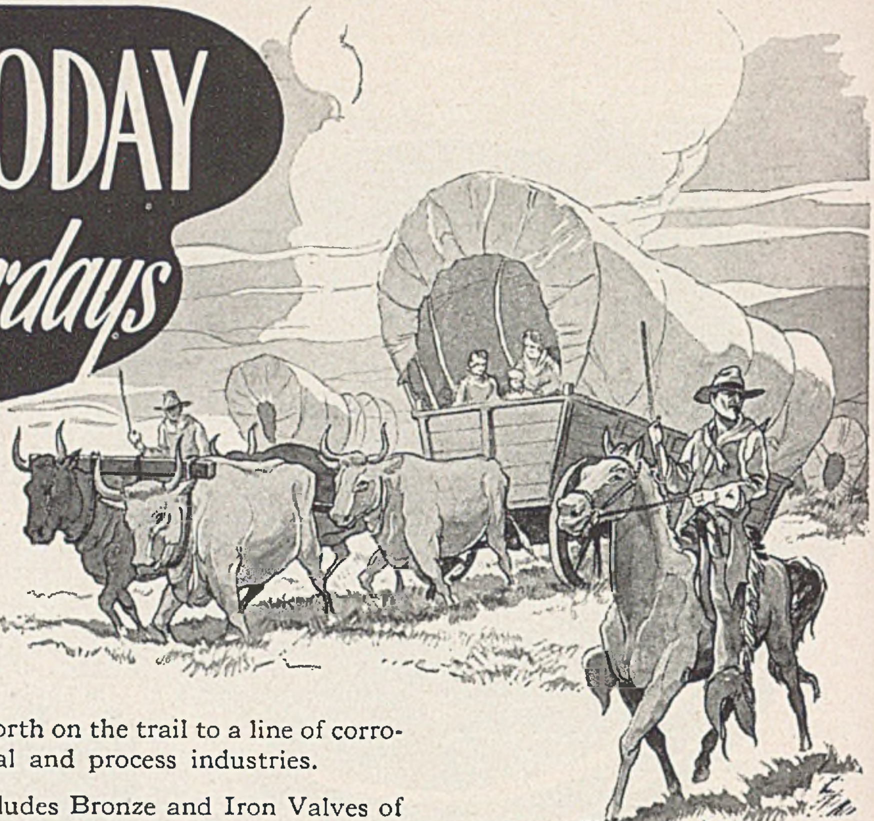
PIONEERS TODAY
as in the yesterdays



More than a century ago Powell started pioneering in the field of industrial valves.

The first bronze regrinding globe valve was a *Powell "first"*

And, twenty-five years ago, with the establishment of the Special Design and Alloy Valve Division, Powell Pioneers were the first to set forth on the trail to a line of corrosion-resistant valves for the chemical and process industries.

Today the complete Powell Line includes Bronze and Iron Valves of every required type, design, size and pressure; Cast Steel Valves of every type, in pressure classes from 150 to 2500 pounds; and, for the chemical and process industries, a complete line of Corrosion-Resistant Valves in many special designs and the widest range of pure metals and alloys ever used in making valves.

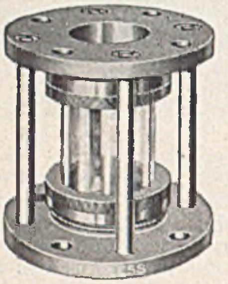


Fig. 2097—Stainless Steel Glass Sight Feed, or Look Box. Available in pipe sizes from ½" to 6", inclusive, in iron, steel, pure metals, special alloys, and rubber lined.

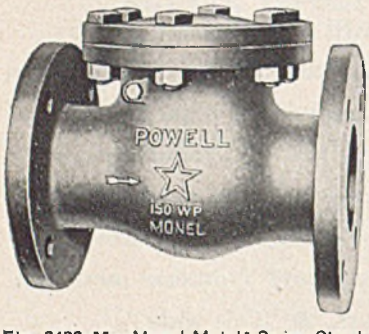


Fig. 2433-M—Monel Metal* Swing Check Valve for 150 pounds W. P. Has flanged ends and bolted flanged cap.

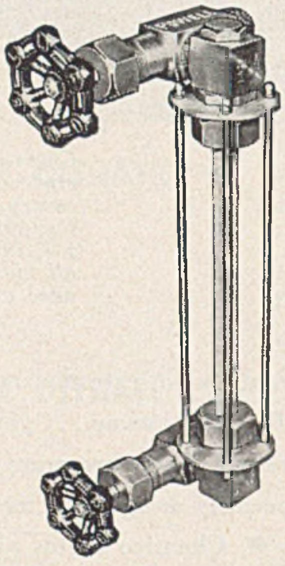


Fig. 1886—Screwed end Liquid Level Gauge for 350 pounds W.W.P. Powell offset pattern. Available in Stainless Steel, Inconel*, Monel Metal*, Pure Nickel, and other metals and alloys for corrosive services.

*A registered trade name of the International Nickel Company, Inc.

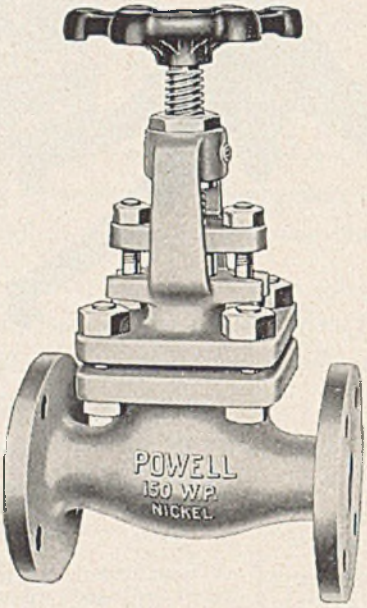


Fig. 1969-NI—Pure Nickel Gate Valve for 150 pounds W. P. Has flanged ends, bolted flanged bonnet, outside screw rising stem, and precision-fitted solid wedge.

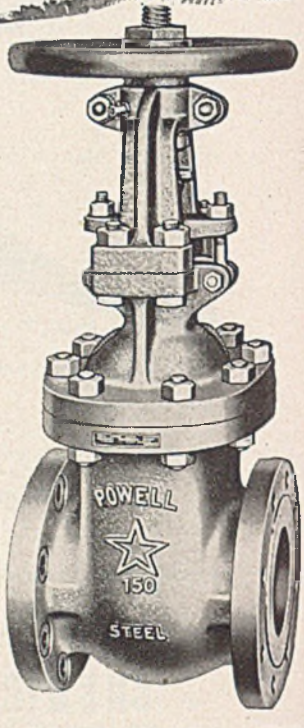


Fig. 1503—Class 150-pound Cast Steel Gate Valve. Has flanged ends, outside screw rising stem, bolted flanged yoke and taper wedge solid disc.

The Wm. Powell Co., Cincinnati 22, Ohio
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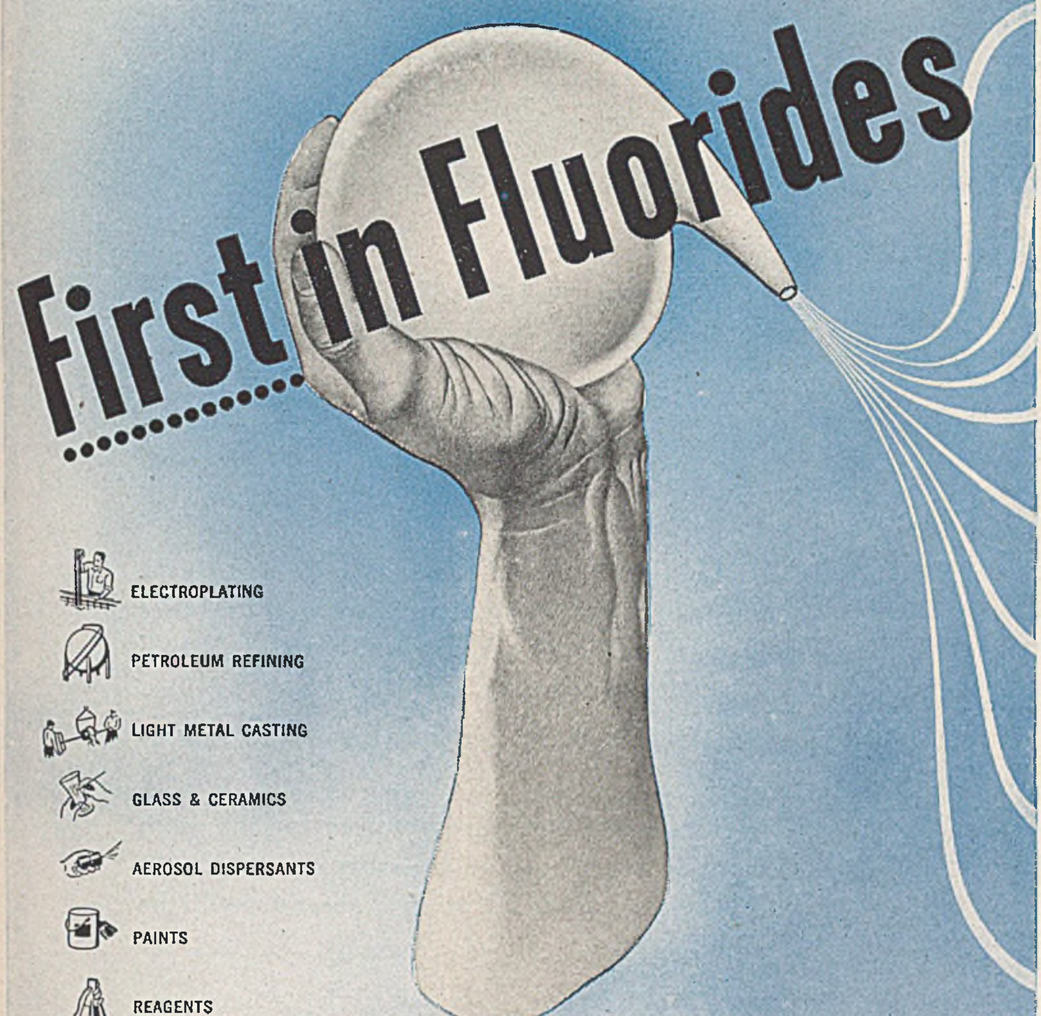
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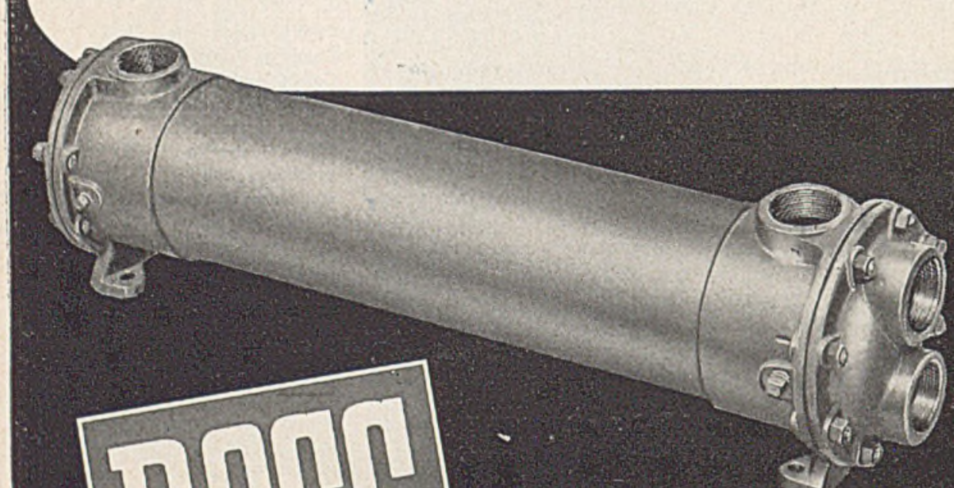
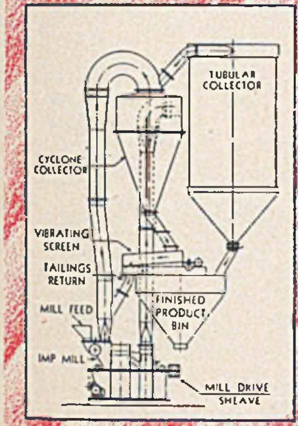
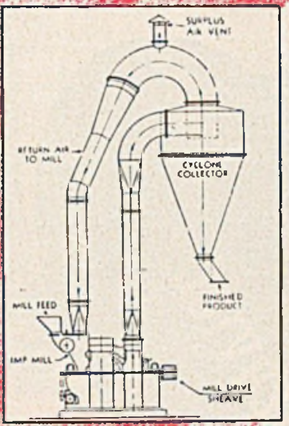


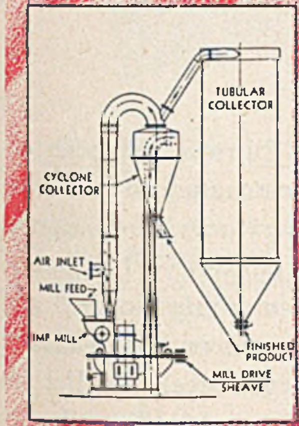
Combinations of the RAYMOND IMP MILL



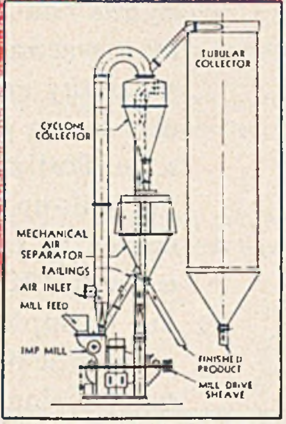
With Screen Classification in Closed Circuit



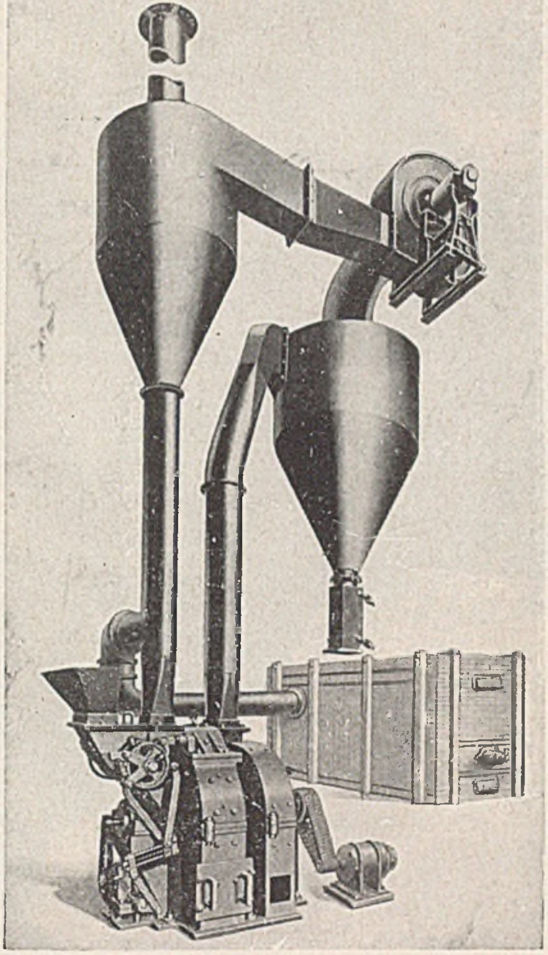
With Cyclone Collector and Piping



With Cyclone and Tubular Collectors



With Mechanical Air Separator Classification in Closed Circuit



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The set-up shown above is widely employed in the chemical and process industries. It consists of the Imp Mill with *air separation* and *flash drying system.* The material is dried, ground, classified and conveyed to the bin in one continuous process, automatic and dustless. The product may also be cooled in the same system for bagging or storage.

At left are alternate arrangements: (a) With screen classification, as in making coarse granular materials; (b) With cyclone collector for standard pulverizing, blending and separating; (c) With tubular collector for recovering superfine dust in grinding special materials; (d) With Mechanical Air Separator in closed circuit for extreme fine classification and uniformity of product.

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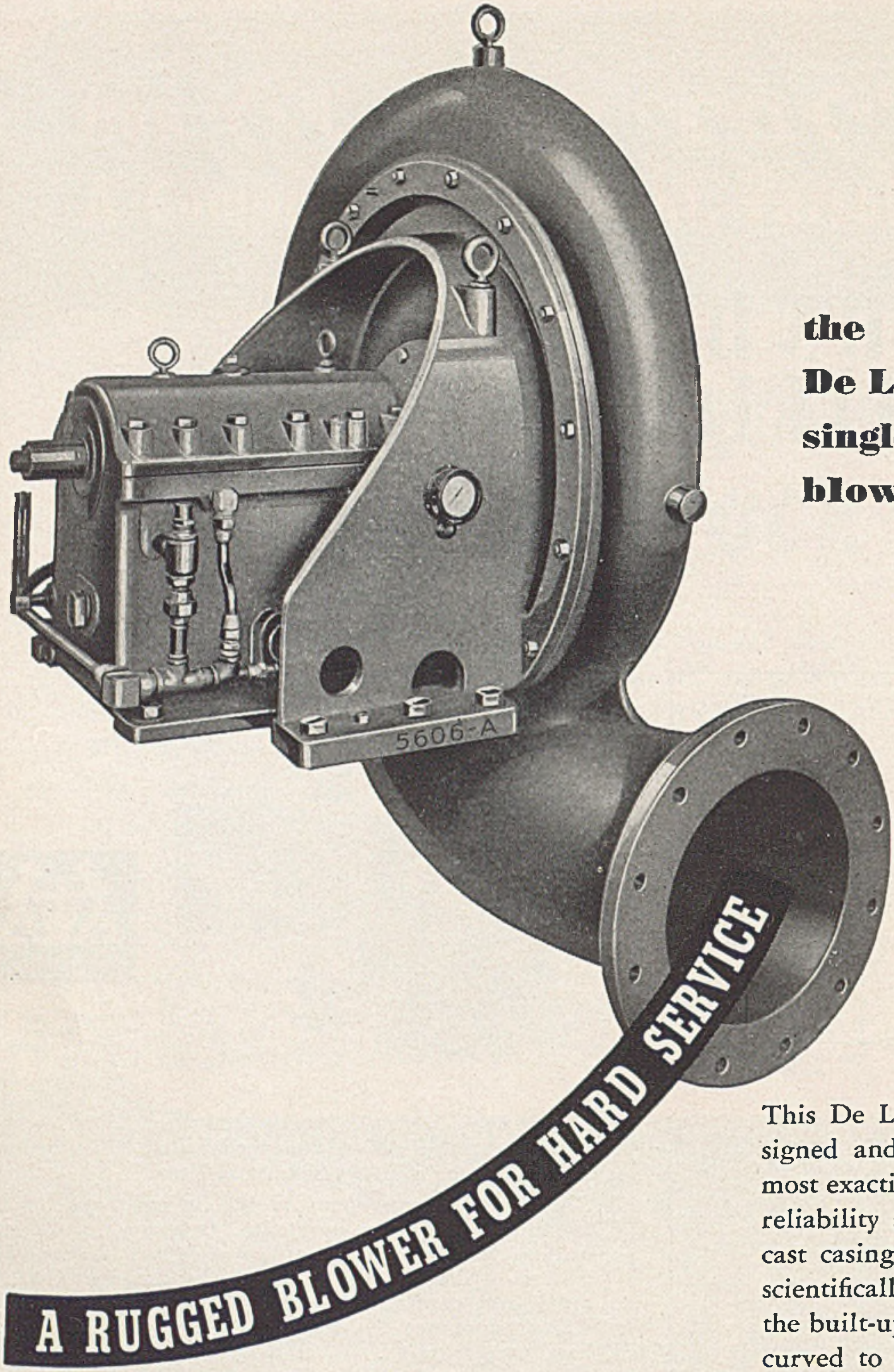

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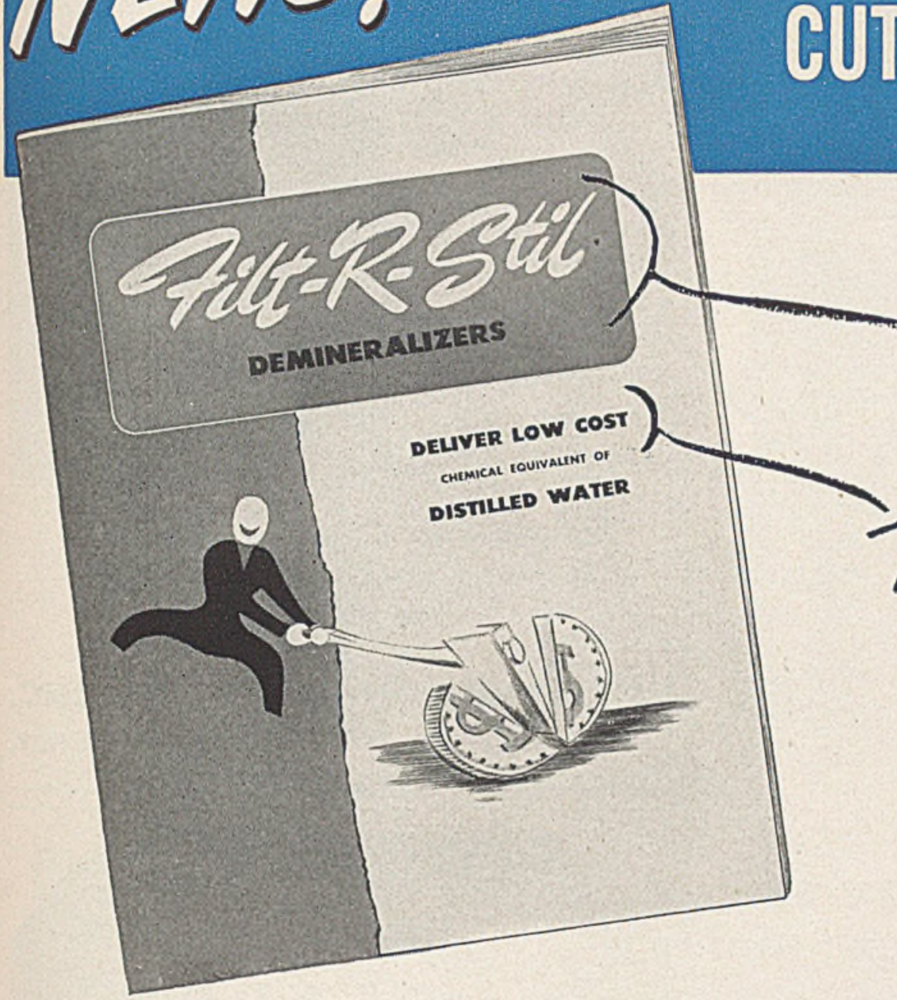

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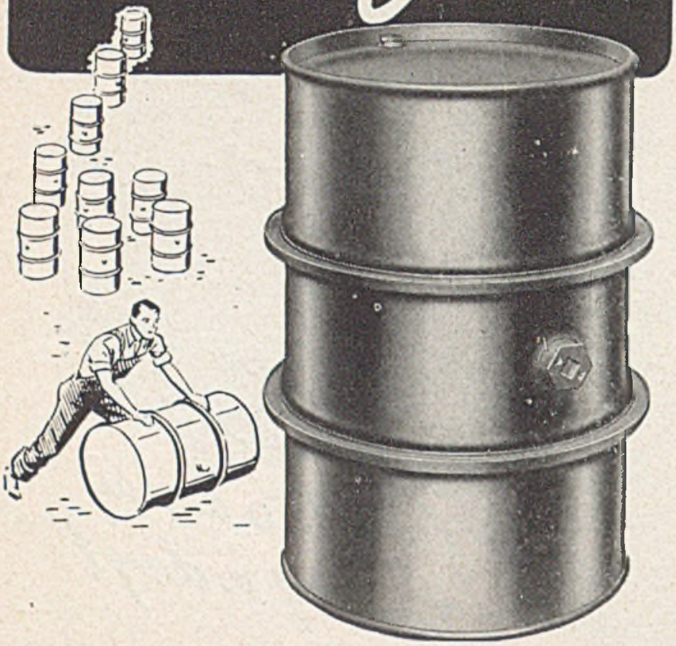

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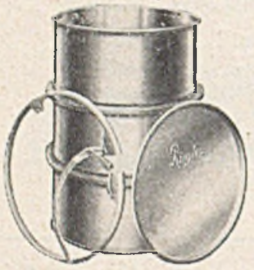

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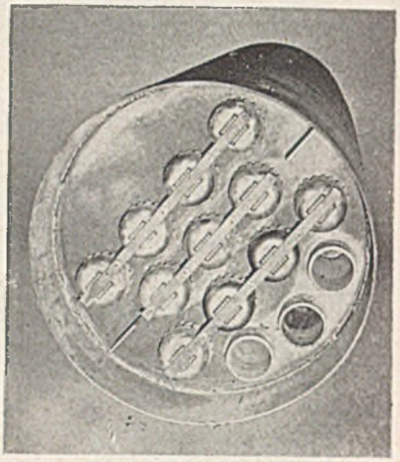

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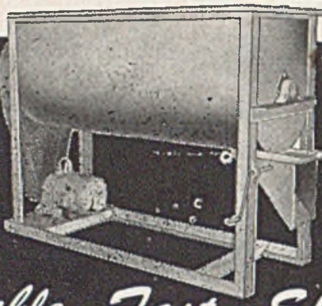

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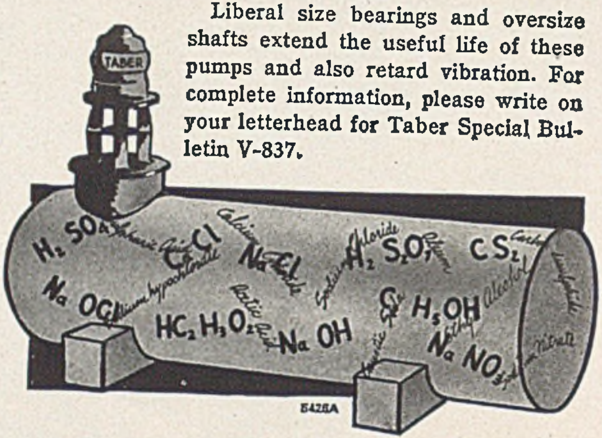

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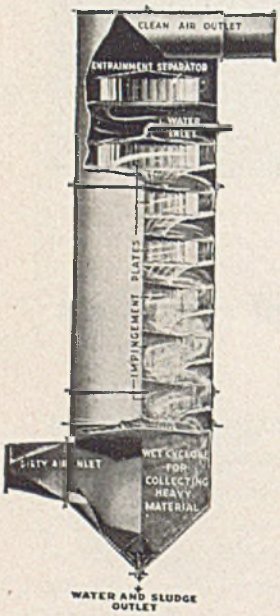

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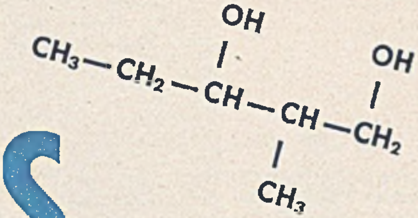

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Containing one primary and one secondary hydroxy group, Celanese* Methyl-Pentanediol has unusual solubility for a wide variety of resins and is miscible with most common organic solvents. Its high boiling point (215°C.) plus limited solubility in water give it a combination of properties not found in any other glycol now in use.

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REFRACTIVE INDEX n_D 20° C.	1.4492
POUR POINT, °C.	minus 4
FLASH POINT, °F. approx.	230
BOILING POINT, °C.	215
SOLUBILITY IN WATER @ 20° C.	10 cc in 100 cc
WATER SOLUBILITY IN @ 20° C.	250 cc in 100 cc

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A Celanese Chemical*

Methylal (dimethoxy-methane) is now available in commercial quantities from Celanese. This chemical promises to be of great value to those industries requiring a low boiling liquid of extremely high solvent power. As a chemical intermediate in organic synthesis it can be used to provide a controlled source of anhydrous formaldehyde and menthanol by hydrolysis under acid conditions. It has relatively high water solubility and is readily salted out of solution. Call on Celanese for technical assistance and information regarding the applications of Methylal in your field.

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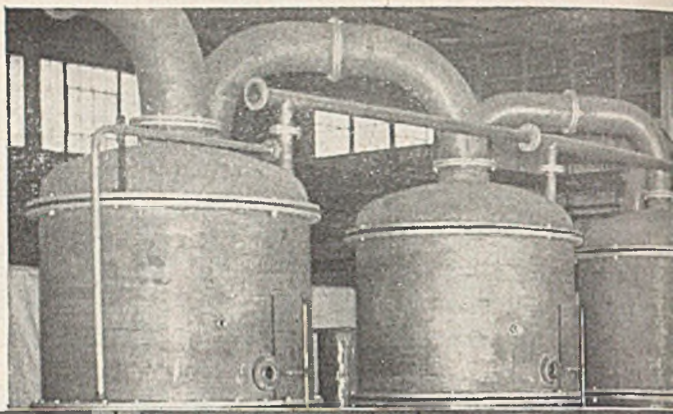
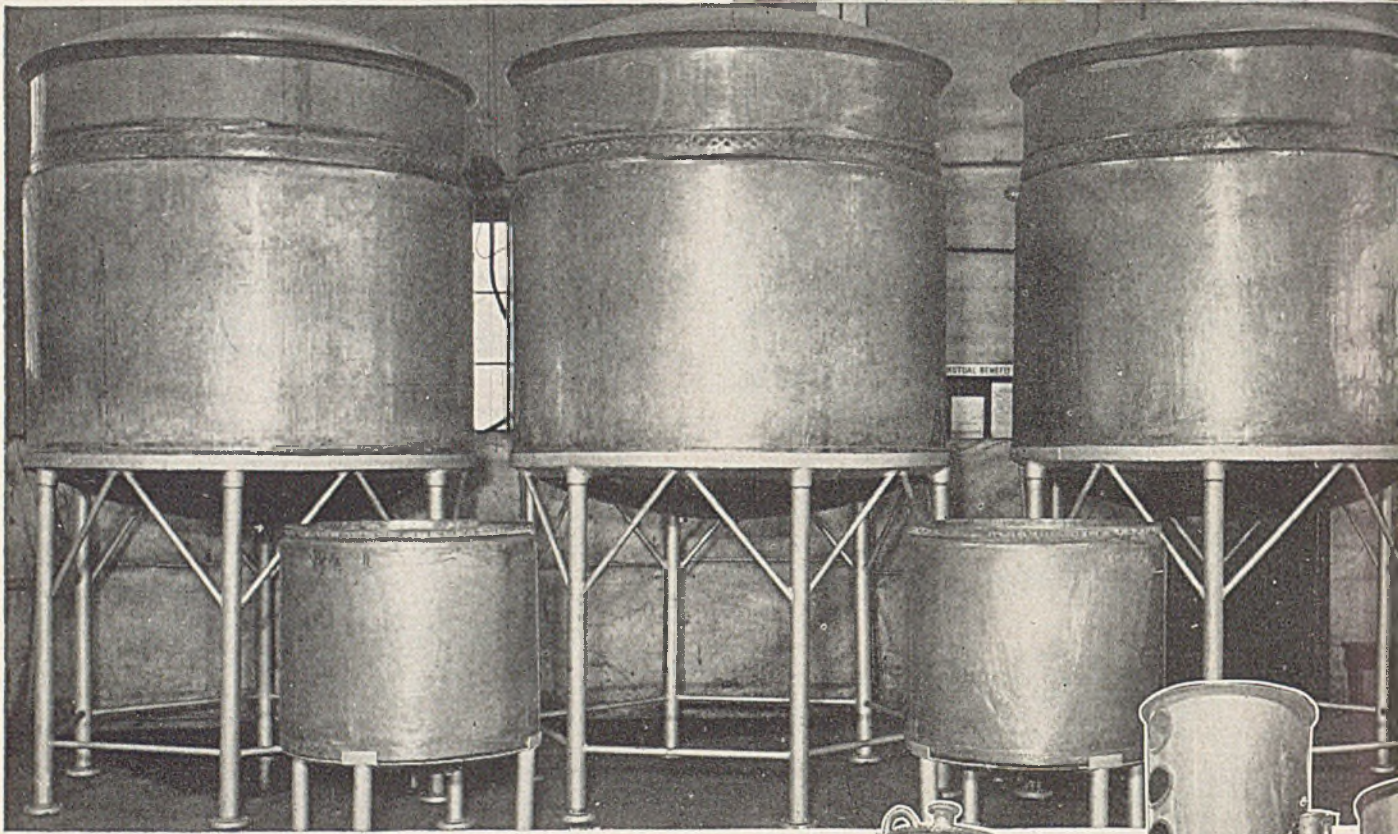
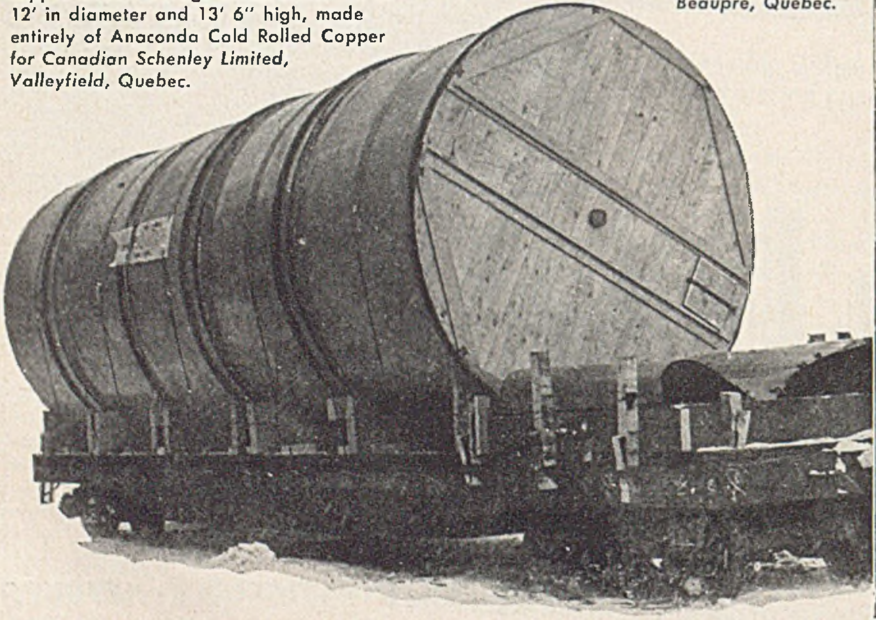


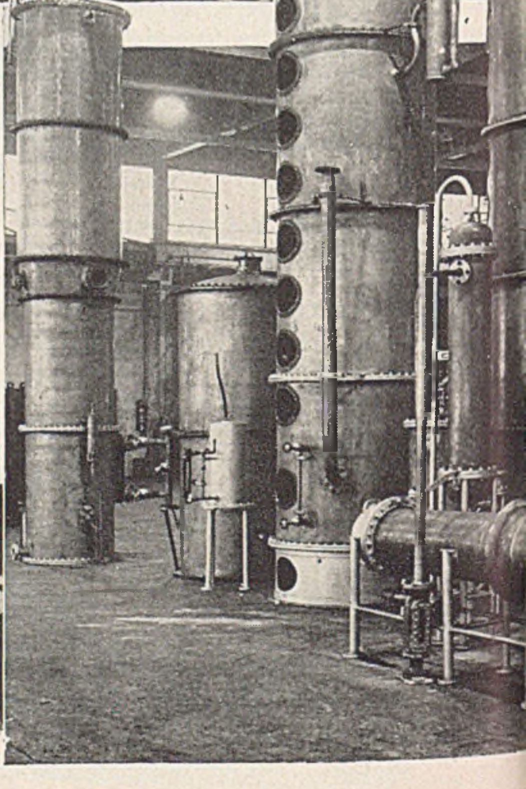
Top and middle sections of 8400 sq. ft. quadruple evaporator. Shells, heads and bottoms (bottoms not shown) are ⅜" Anaconda Copper. *For British Columbia Distillery Company Limited, Vancouver, B.C.*



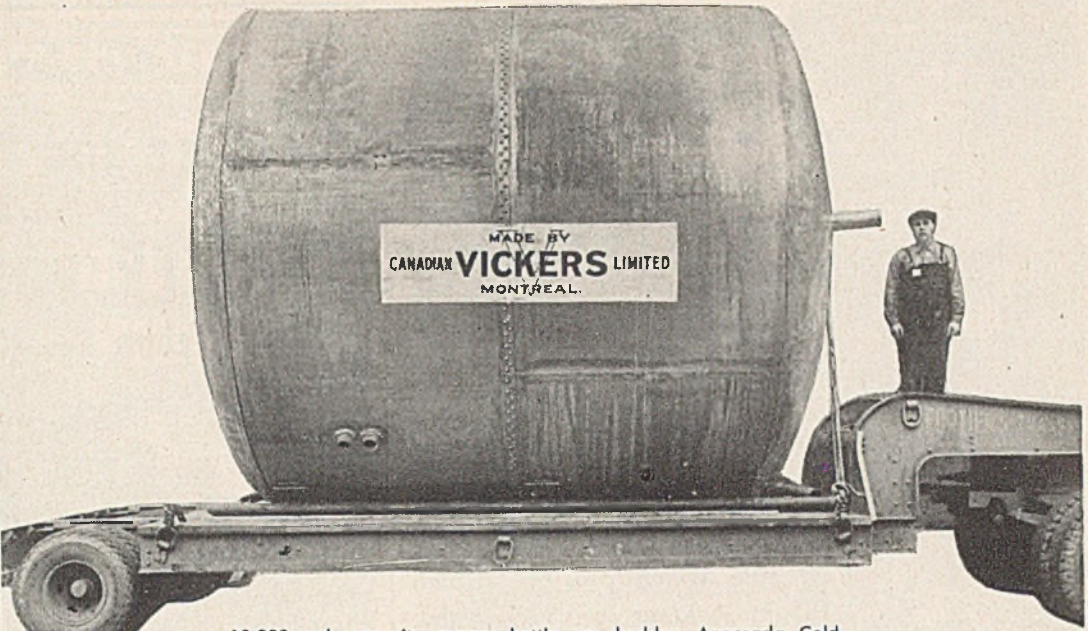
Three copper water jacketed yeast tanks, each of 1600 Imp. Gal. capacity. Cold rolled, 0.109" Anaconda Copper was used for these, and for the two smaller water jacketed Dona tanks. *For Montreal Products Company Limited, Montreal, Quebec.*



Bottom sections for five new 10,000 gal. copper alcohol storage tanks. Tanks will be 12' in diameter and 13' 6" high, made entirely of Anaconda Cold Rolled Copper *for Canadian Schenley Limited, Valleyfield, Quebec.*



This varied distillation equipment—beer still, heads column, condenser and cooler—all fabricated from Anaconda Copper *for Montmorency Distillery, Inc., Beaupre, Quebec.*



10,000 gal. capacity copper kettle, or doubler. Anaconda Cold Rolled Deoxidized Copper was used—shell and head 3/16" thick, bottom ¼" thick. Internal heating unit was made from 3" x 0.134" copper coil, *for Distillers Corporation Limited, Ville LaSalle, Quebec.*

COPPER

A Tradition in Distilling

All of the equipment shown was recently fabricated from Anaconda Copper by Canadian Vickers Limited, Montreal, for several well-known Canadian distilleries. In each distillery, copper tube coils are used by the score, and copper and brass pipe lines are the connecting links between copper equipment which is found at every stage of the distilling process—from mash tubs to bottling rooms.

When copper was first used in distilling has probably been forgotten. But its ease of fabrication, corrosion-resistance, strength, durability and high thermal conductivity have all contributed to the traditional use of copper for distillery equipment.

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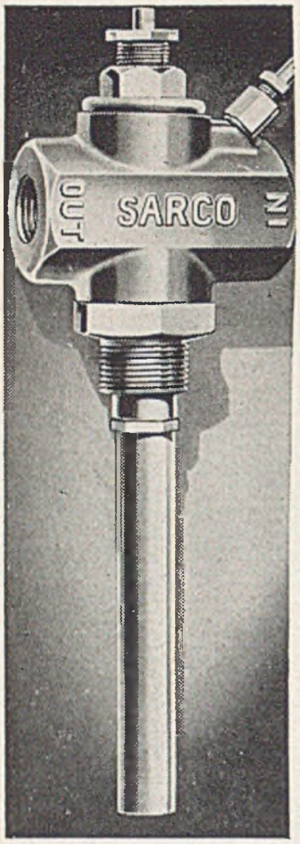
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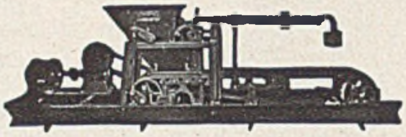

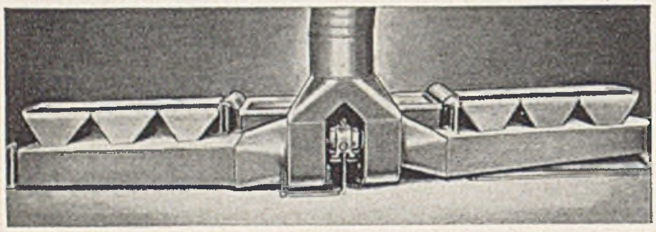


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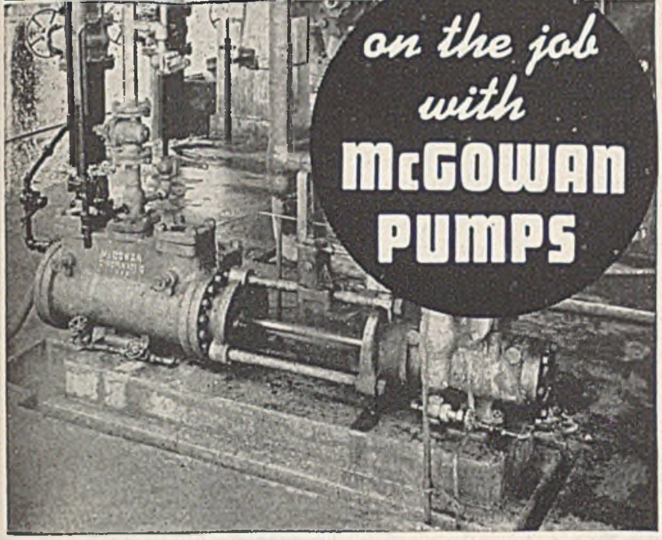
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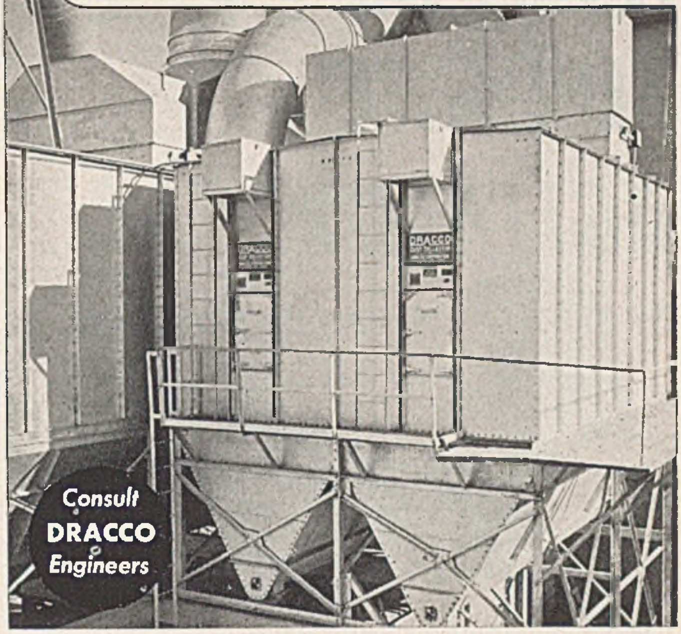
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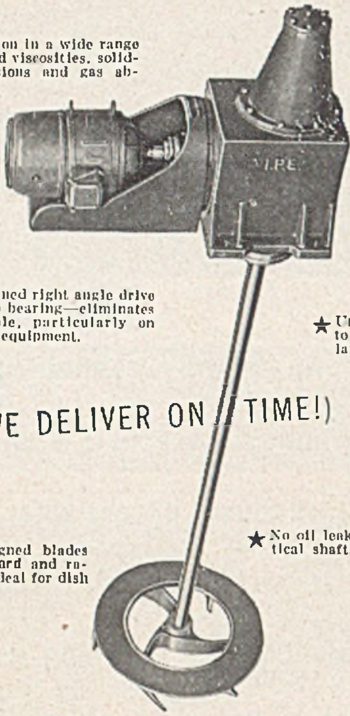

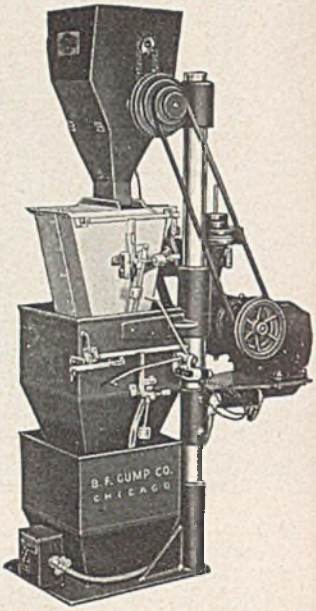
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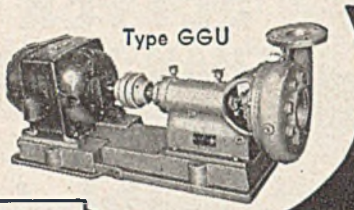
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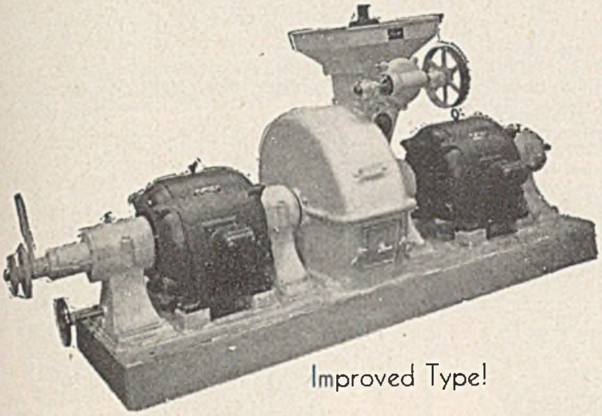

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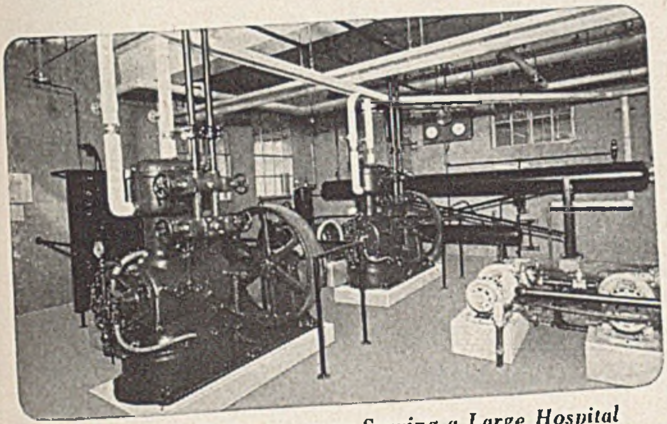

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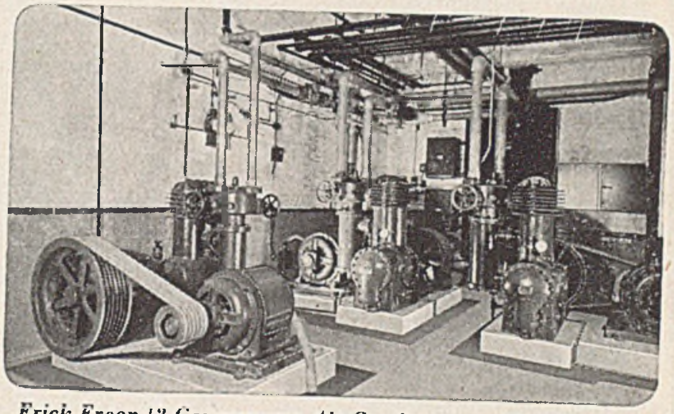

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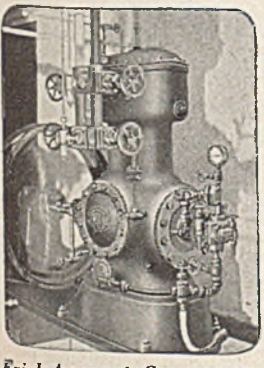

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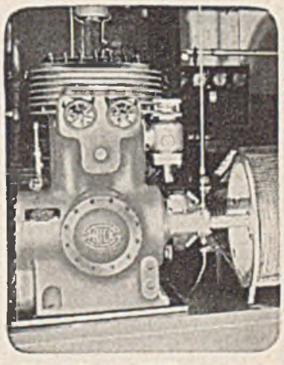

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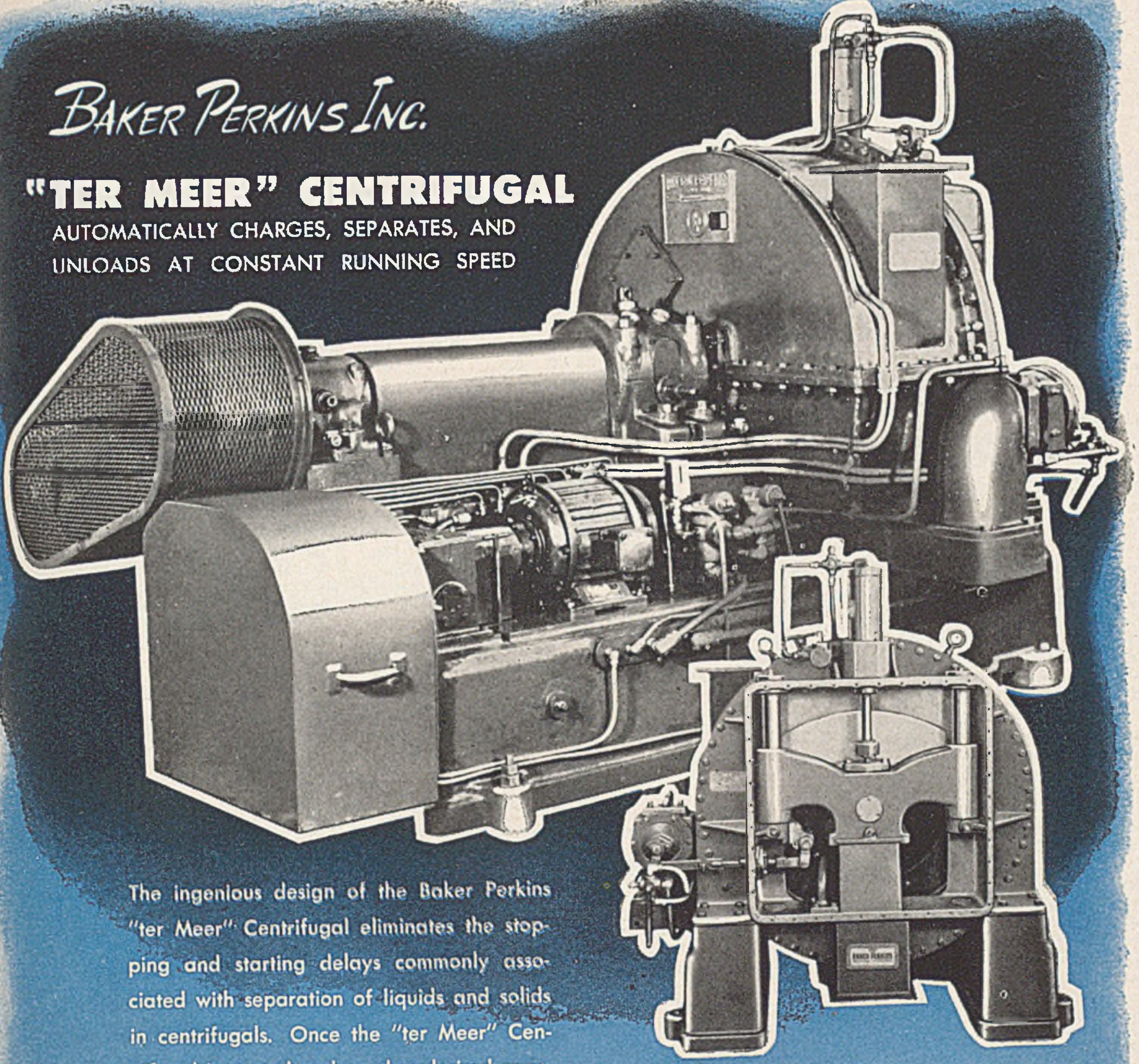

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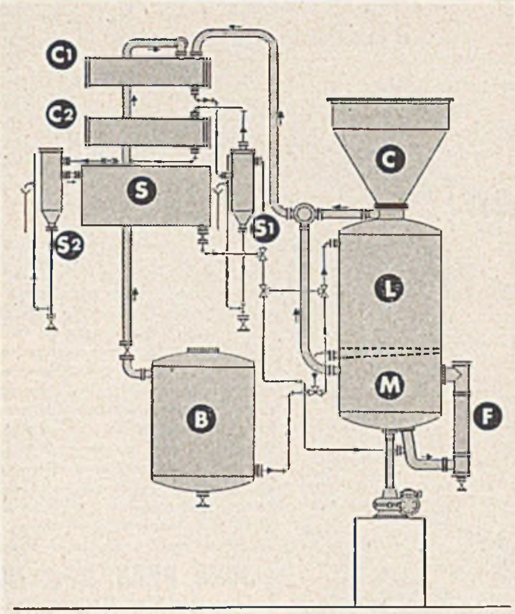

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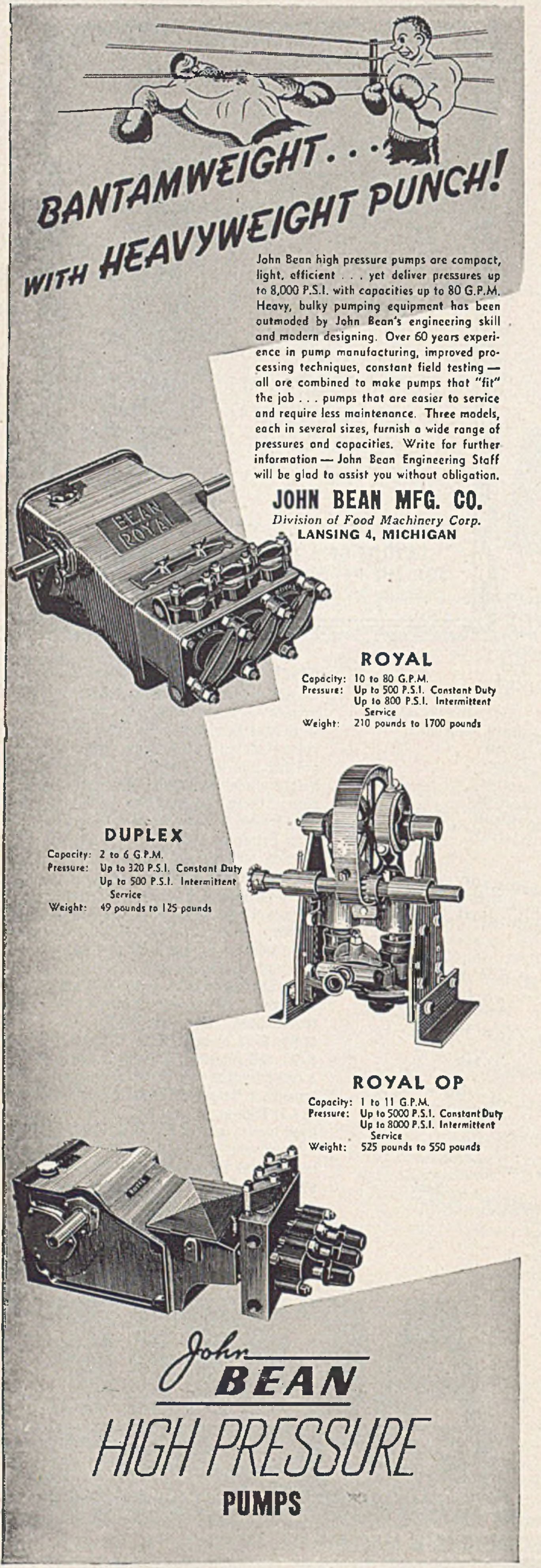

Sidelights and TRENDS

September 1947. Pneumatic rubber tires designed fo use with conventional railroad rails are used on several trains now in successful operation in France. Additional rubber applications are shock absorbers, springs, and flexible couplings between axles and cars. Improved comfort and increased acceleration and deceleration have resulted. Tires are inflated to approximately 125 pounds per square inch and require retreading about every 20,000 miles. [*Rubber Age* (London), p. 156, July 1947]

■ Radioactivity from cosmic ray–induced radiocarbon in the human body is about ten times that of radium present in the human system. Largest source of human body radiation comes from potassium, which emits about twice the number of total disintegrations per minute produced by the carbon. (*Science*, p. 88, July 25, 1947)

■ Transparent methyl methacrylate and polystyrene resins with refractive indices approximating crown and flint glass are used to correct spherical aberrations in some recent television receivers An image 2 to 3 inches in diameter at the fluorescent end of a cathode ray tube is projected through a Schmidt optical system onto a larger screen. The system consists of a deep concave mirror of large aperture and the transparent plastic correction plate of the necessary complex surface. (*Nature*, p. 99, July 19, 1947)

■ A new low in use of Plexiglas may soon be achieved. Two conical-shaped pieces 15.5 inches in outside diameter, 6 inches thick, and nearly 4 inches in inside diameter will be used fo windows in the Bathyscaphe, in which Auguste Piccard hopes to establish a new deep sea exploration record. (North American Newspaper Alliance release, Aug. 7, 1947)

■ Minute quantities of carbon 14 can be measured by conversion to carbon dioxide, which is used as a gaseous filling for a Geiger-Müller counter. Quantities below 10^{-5} gram-moles of radioactive carbon dioxide can be measured with satisfactory accuracy by this method. (*Review of Scientific Instruments*, p. 496, July 1947)

■ Brazil's tung oil output has increased from 20 tons in 1942 to nearly 300 tons in 1946, with 1947 production expected to double the latter figure. Total present plantings are expected to provide an eventual annual output of about 2750 tons. Production of tung oil in China totaled 90,000 tons in 1946, and approximately the same amount is expected this year. (*Chemistry & Industry*, p. 444, July 19, 1947)

■ Production schedules of ceramic floor and wall tile manufacturers increased an estimated 13% in the first quarter of this year, compared to the last quarter of 1946. The industry is expected to produce 95,000,000 square feet of tile this year, 35% over 1946 output and 20,000,000 square feet over that of 1925, the Nation's greatest homebuilding year. (*Domestic Commerce*, p. 72, June 1947)

■ A lack in perception of odors is common in nearly 40% of people tested recently. In the case of potassium cyanide 44% were not conscious of any smell, whereas the rest described the odor of bitter almonds. Hydrogen sulfide, sulfur dioxide, and hydrogen cyanide appear to promote insensitivity by acclimating nasal organs to their odors. (*Chemical Age*, p. 181, Aug. 1947)

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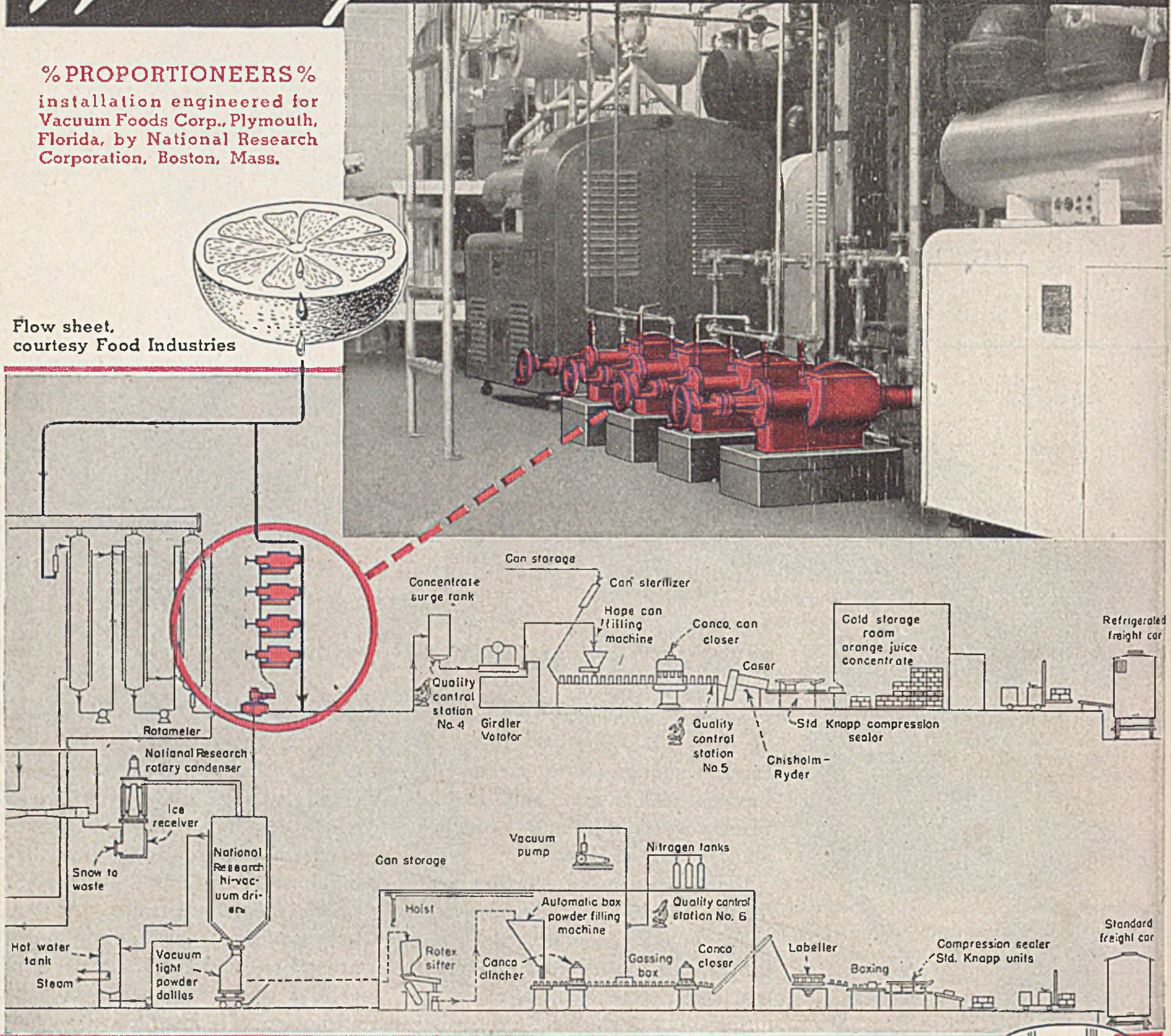
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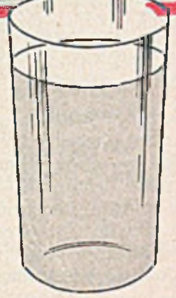

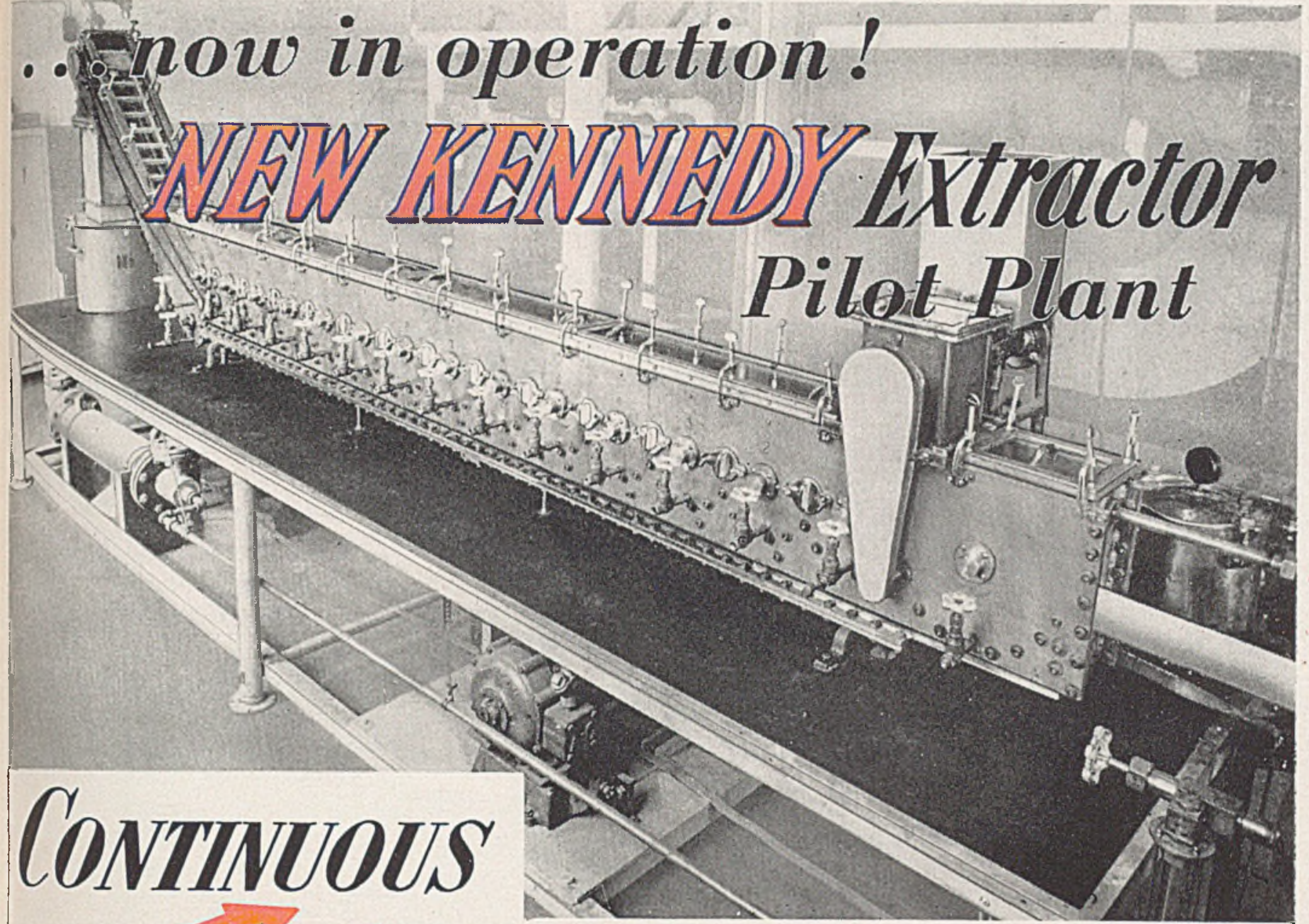

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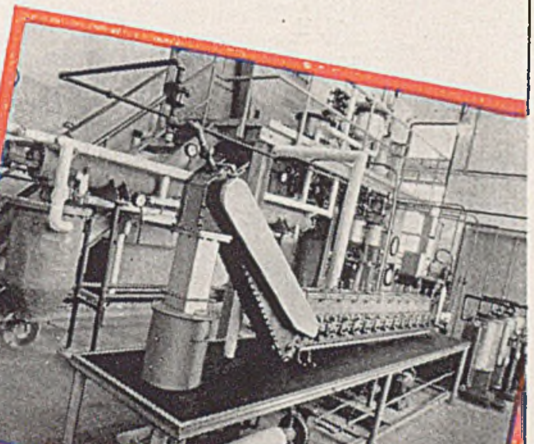
The Kennedy Extraction Division of Vulcan offers complete Solvent Extraction Plants for the economical and efficient recovery of oils, fats and waxes from a variety of vegetable and animal materials.

The Kennedy Continuous Extractor of stainless steel construction is unique in its ability to handle high oil content materials and finely ground products containing excessive "fines". Materials containing as high as 55% oil are readily extracted to less than 1% in a single, continuous operation. This "one step" method of extraction eliminates the costly "fore-pressing" operation. The Kennedy Extractor is also adaptable to many leaching and washing processes.

Complete pilot plant facilities are available for the comprehensive study of special extraction problems. In conjunction with pilot plant operation, the Vulcan laboratories, adequately staffed by chemical engineers and chemists of long experience, are at your service for analytical work. Vulcan design engineers carefully convert pilot plant data to commercial scale design.

Vulcan has the organization to design, fabricate, erect, and initially operate complete plants to successfully overcome all extraction problems.



Complete PILOT PLANT Facilities

VULCAN

DISTILLATION
EVAPORATION PROCESSES
EXTRACTION and EQUIPMENT

KENNEDY EXTRACTION DIVISION FOR

THE VULCAN COPPER AND SUPPLY CO. - CINCINNATI, OHIO

Eliminate THE EXTRA STEP

Cut MIXING COSTS 20% or more

One way to reduce material handling costs is to eliminate the extra step of emptying drums into mixing units.

Wherever mixing can be performed by revolving or tumbling the container, "U. S." Drum Mixing equipment can save you time and money.

"U. S." Drum Mixing equipment permits mixing in your own or supplier's drums . . . avoids the costly delays from emptying and cleaning fixed containers . . . eliminates danger of contamination.

AVAILABLE

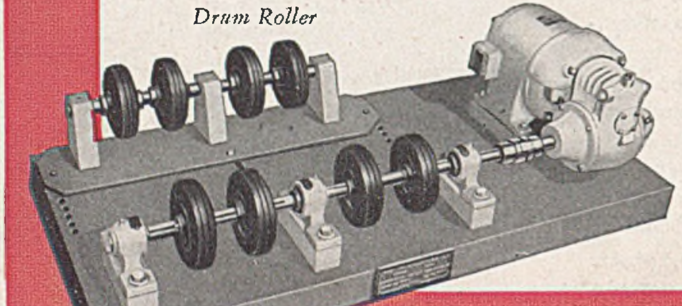
for Quick Shipment

While our present supply of highly scarce motors lasts, we can make prompt shipment of certain size units. Write or wire for details.

DRUM ROLLERS

"U. S." Adjustable Drum Rollers will roll any round container from a one-gallon pail to a 70-gallon drum. Eight heavy-duty rubber wheels are adjustable to provide ample clearance for rolling hoops and bung openings. Powerful, heavy-duty motor will roll loads up to 1,000 lbs. "U. S." Drum Rollers are built in sizes to handle one, two, three, or four drums, constant or variable speed drive.

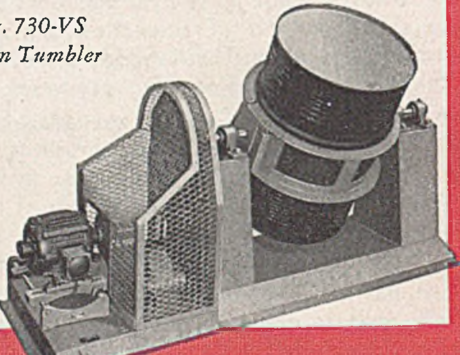
Fig. 745-S
Drum Roller



DRUM TUMBLERS

"U. S." Drum Tumblers are built in two sizes: single and double drum units to handle standard 55-gallon drums. Units to handle 30- or 70-gallon drums are available on special making order. Variable speed drive permits tumbling speeds from 8 to 21 RPM. Powerful, heavy-duty motor will handle loads up to 1,000 lbs. Adjustable yoke opens quickly and easily, locks securely.

Fig. 730-VS
Drum Tumbler



WRITE FOR OUR MIXING EQUIPMENT CATALOG TODAY!

PROCESS EQUIPMENT DIVISION

U. S. STONEWARE
Akron, Ohio