INDUSTRIAL
AND
NGINEERING CHEMISTRY

Process-Adapted FLUID AGITATORS

AT SIZE AND TYPE DO YOU NEED?

TOP ENTERING MIXERS:—A wide range of sizes for large or small tanks—¼ to 50 H.P. for vertical use on pressure or vacuum vessels. Integral mounting, turbine and propeller types.

PORTABLE MIXERS:—⅛ to 10 H.P. for rim attachments to open tanks. Gear and direct drives. Many exclusive conveniences. Off-center positioning. Extended bearing sealed against oil and grease leaks.

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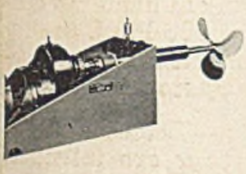

Do you need a Propeller or Turbine Type?
Do you need 1/40th or 50 H.P.?

There is one size and model of mixer which will best answer the requirements of each individual mixing job. "*LIGHTNIN*" and MIXCO Mixers and Agitators are available in sizes ranging from 1/40th H.P. laboratory models to 50 H.P. agitators. Each size and model has a wide range of applications, but each also has definite limitations.

Perhaps you need a turbine type instead of propeller. If that is the case, Mixing Equipment Company have available a variety of turbines to meet every agitation requirement. The right type will greatly increase the efficiency of the process.

That is why it is advisable to have Mixing Equipment Company engineers recommend the equipment for your particular purpose. In some cases they have recommended doubling the size of the mixer with the result of cutting both mixing time and power consumption in half! Or it is possible to use a smaller mixer and thereby reduce installed H.P. and initial cost for simple blending.

You can depend upon Mixing Equipment Company engineers to recommend the right mixer for your job because all types are manufactured. Twenty-three years of experience has resulted in an organization, research facilities and skill which qualify Mixing Equipment Company as a leading authority in the whole broad field of agitation.

Mixing Equipment Company offers its services in the solution of any problem involving controlled recirculation of liquids to produce physical and chemical changes, as included in the table herewith.

Blending Miscible Liquids	Mixing Immiscible Liquids	Crystal Size Control	Gas Absorption & Dispersion	Suspension of Solids	Heat Transfer
Simple Mixing of soluble liquids as in reducing concentration.	Washing of Liquids Extraction Contacting Caustic Treating Emulsions	Precipitation Evaporation Systems	Hydrogenation Aeration Gas Scrubbing Chlorination Gas Washing	Slurries Slaking Lime Suspension of: filter aid, activated carbon, Fullers Earth, Crystals while dissolving.	Stills Evaporators Reactor Vessels Heating Cooling

Bring your mixing problems with you to

BOOTH No. 613

at the 19th Chemical Exposition, Dec. 6
to 11th, where Mixing Equipment's Fa
tory Engineers will be glad to discu
them with you.

There is a process adapted agitator for every size and shape of tank and every operation; for batch or continuous operation. Because Mixing Equipment Co. products include *all* types of fluid agitators, you can obtain from them an impartial recommendation for the most economical solution of any problem involving fluid agitation. Mixing Equipment Co. engineers will gladly assist you in solving your particular agitation problem.

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Answer your questions
ABOUT GLASS-LINED STEEL

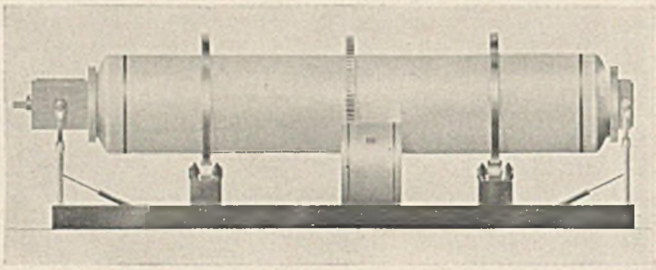
at Booth No. 502 . . . Exposition of Chemical Industries

"At the Chemical Show, we will exhibit the latest developments in glass-lined steel and stainless steel process equipment, some of which are described below. If you can be in attendance, we suggest that you examine these units carefully to see how they can be most helpful to you. If you cannot be there, please write us. We shall be glad to send you our latest catalogs or other technical information required."

GEORGE F. KROHA
Vice-President

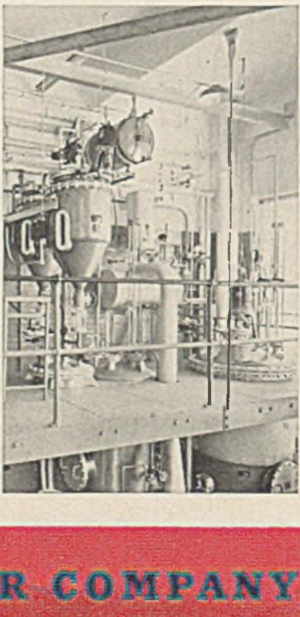
New or improved Pfaudler process equipment includes:

GLASS-LINED ROTARY DRYERS — One of the newest developments in glass-lined steel equipment is Rotary Dryer Shells fully equipped with porcelain flights inside with traction rings and gearing on the outside. This scale model duplicates larger production equipment which is already in successful operation. Units of this type are intended for the drying or crystallization of solids and semi-solids. The anti-friction properties of the glass-lining facilitate movement of the product and corrosion resistance is also improved.



Varying degrees of dryness can be accomplished by the application of proper drying apparatus.

STAINLESS STEEL REACTORS — Representative of a new line of standard stainless steel reactors will be a 200-gallon jacketed closed unit equipped with motor-driven agitator. It is built with an all-welded stainless steel liner with carbon steel jacket. Equipped with ample flanged openings in top head to permit wide range of processing.



HIGH PRESSURE GLASS-LINED REACTORS—This new Pfaudler line is meeting difficult service conditions successfully in many phases of war production. A 500-gallon unit will be displayed, fully equipped with glass-covered impeller agitator and adjustable baffles suitable for incorporating gas into a liquid, mixing products of heavy viscosity, or incorporating solids into a liquid. Built for maximum internal pressure of 125 P.S.I. coincident with jacket pressure of 90 P.S.I. See it in operation!

GLASS-LINED JACKETED PIPE HEAT EXCHANGER — Developed for the polymerization of concentrated sulphuric acid, low-boiling hydrocarbons and tertiary butyl alcohol in the manufacture of butadiene. Units of varying capacity can be built to meet your requirements; maximum lengths, 10 feet.

GLASS-LINED ISOMERIZATION TOWERS — A section of an actual glass-lined tower built for internal pressure of 300 P.S.I. will be on exhibit to permit your inspection of a new type of forged flange as well as means of supporting bubble-cap plates. Intended for the isomerization of butane and pentane, general reaction work and gas absorption. Glass-lining is fully resistant to fluid acid accelerators.

GLASS-LINED CHEMICAL VALVES — This new line embraces glass-lined flush, in-the-line, and relief valves. Flush valves are equipped with porcelain seats and are tested up to 90 P.S.I.

GLASS-LINED LABORATORY AUTOCLAVE — Intended for experimental and pilot plant work in handling corrosives where pressures as high as 500 P.S.I. are involved. Equipped with motor-driven anchor type glass-covered agitator. Built for high temperature heating.

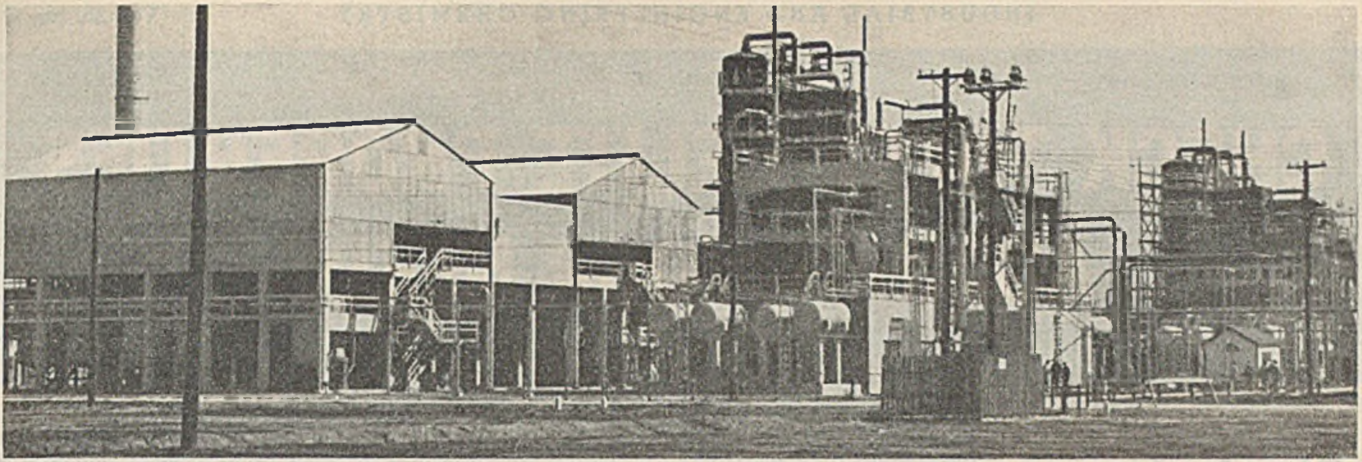
GLASS-LINED EVAPORATING PANS — These standard, jacketed glass-lined evaporating pans are intended for the crystallization of CP salts and provide maximum protection against impurities. A 12-gallon unit will be displayed; also made in 60- and 150-gallon capacity.

A staff of Pfaudler Sales Engineers will be in attendance throughout the show who will be glad to go over your immediate problems and show you what can be accomplished with Pfaudler-built process equipment today.

THE PFAUDLER COMPANY, ROCHESTER 4, NEW YORK

ENGINEERED GLASS-LINED AND STAINLESS STEEL EQUIPMENT

B



INDUSTRIAL AND ENGINEERING CHEMISTRY · INDUSTRIAL EDITION

29,300 copies of this issue printed

Reactor building (left) and recovery structure of butadiene and styrene are shown in the photograph above. They are part of the new plant operated by Firestone Tire and Rubber Company for making GR-S synthetic rubber at Lake Charles, La.

ISSUED DECEMBER 4, 1943 ● VOL. 35, NO. 12 ● CONSECUTIVE NO. 23

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Physical Characteristics of 6 Typical CELITE FILLERS*

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

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

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IF YOU HAVE A PROBLEM with regular or wartime formulae—the chances are good that Celite Filler can provide the solution you have been searching for. That's because of the unique characteristics of these inert, diatomaceous silica fillers. Celite Fillers provide high absorption, light weight, large surface area, low refractive index, and superior suspension.

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Whatever you make—paint, paper, asphalt products, household cleansers, catalysts—you should consider Celite Mineral Fillers in your formulae. Johns-Manville will be glad to recommend the right Celite Filler for your particular requirements. Write Johns-Manville, 22 E. 40 St., New York 16, N. Y.

*Amorphous, diatomaceous, opaline silica

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JOHNS-MANVILLE **CELITE MINERAL FILLERS**

INDUSTRIAL AND ENGINEERING CHEMISTRY
REPORTS
ON THE CHEMICAL WORLD TODAY

Technology

Penicillin Progress. Still topping the list in production priorities, penicillin rapidly approaches the stage of substantial output. Not that this vital drug can be expected in satisfactory output for many months yet, but at least progress has been accelerated to a striking degree. For month after month the output of the drug has increased at a rate approaching 100% each 30 days. That trend must continue into the future before the extraordinary demand created by premature news of its miraculous power can be met with reasonably adequate supplies. Two conclusions are obvious. Production was minuscule when the public generally first learned of it, and expansion of production facilities has proceeded with the utmost speed.

Developments in this field tumble over one another in such rapid succession that no adequate estimate of the entire situation is possible now. Rather the best available at present are no more than snapshots of continuing action likely to change at any moment. Here are a few facts gleaned by I. & E. C. Editors from reliable sources and believed accurate at the time of writing.

Projects of eighteen companies for the production of penicillin have received approval and the necessary high priorities from WPB covering equipment. These projects are in the various stages of completion. Present expectations are that full production by the units now under construction will be reached by late spring of 1944. Then, or soon thereafter, penicillin may be expected to be available in sufficient quantities to permit its use by the civilian medical profession.

Meanwhile no effort is spared to improve the productivity of equipment in terms of potent drug. Conditions for growing the mold are under constant, continuing scrutiny with a view to promoting its optimum growth. Unremitting studies of strains of the mold and related organisms seek to select the best from the point of view of output of potent penicillin. Three methods of growing mold are in use: surface culture, typified by the bottle technique; bran culture, in which the mold is grown on bran moistened by nutrient medium; and submerged culture, where the mold is grown in aerated medium contained in commercial fermenters. Each of these methods has its advocates.

The preferred culture medium is corn steep liquor to which other required nutrients are added. No difficulty is anticipated in securing supplies of medium since the corn processing industry is cooperating fully with penicillin producers.

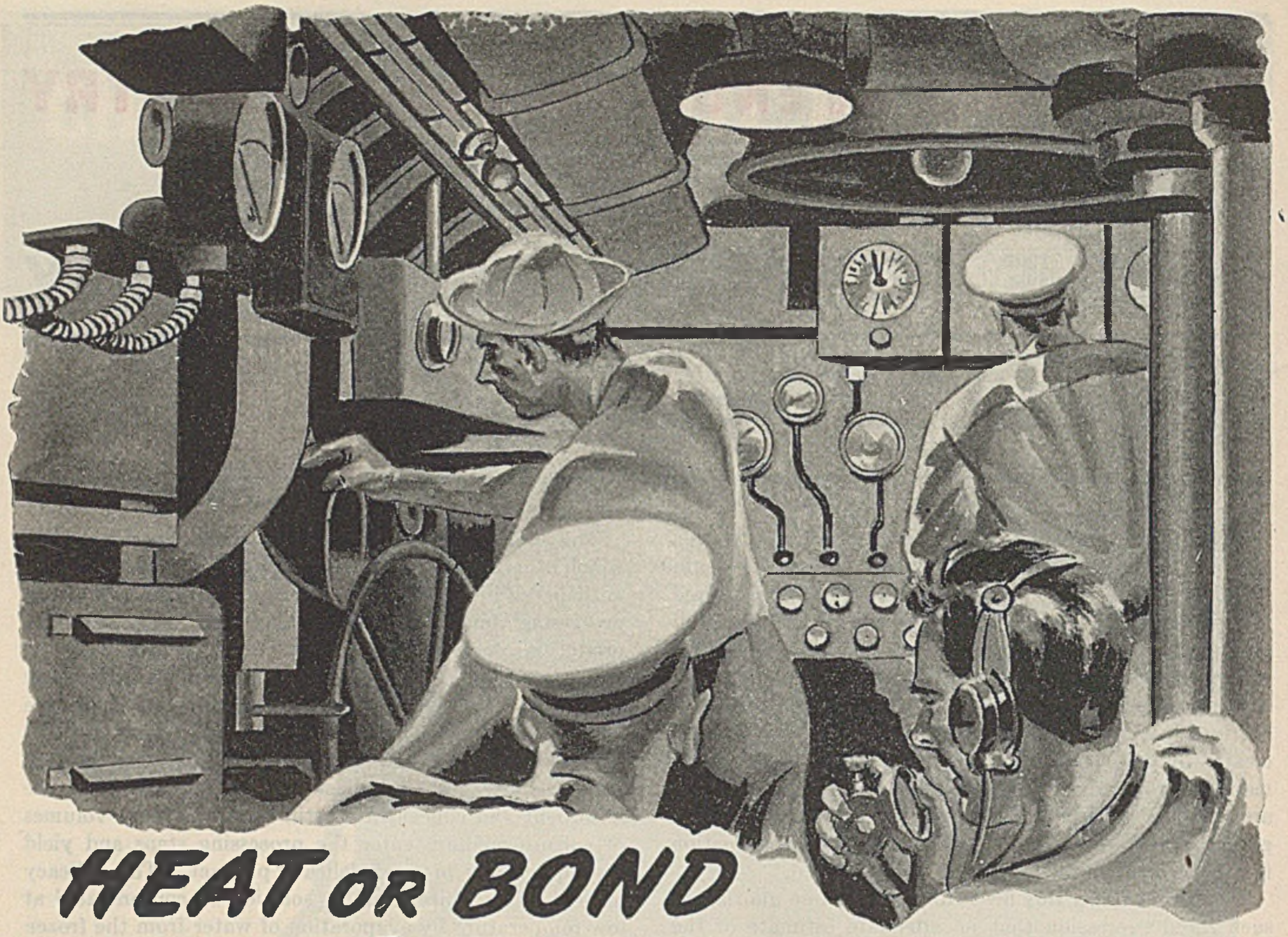
After the mold has grown to its optimum extent, the problem is to separate the potent principle from the culture medium and to concentrate the product. Adsorptive processes are employed in the first concentration step, and the penicillin must then be removed from the adsorbent and concentrated still further. Huge volumes of culture medium enter the processing steps and yield tiny quantities of final delicate product. The delicacy of penicillin requires that its solution be concentrated at low temperature by evaporation of water from the frozen state. The technique employed is somewhat similar to that of drying blood plasma. Like blood plasma, penicillin can be stored without deterioration only when completely dry. Recent improvements in the capacities and efficiencies of diffusion pumps to operate at extremely high vacuum and handle huge volumes of vapor are contributing to this industry.

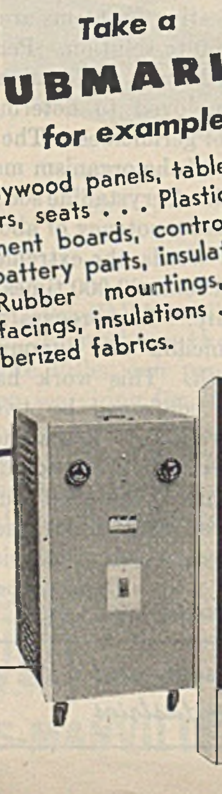
The concentrating and desiccating problems are serious because the mold produces a dilute solution. Penicillin's potency is expressed in Oxford units, determined by a technique resembling that employed to determine the accustomed phenol coefficient of germicides. The culture medium after optimum growth of the organism may have 100 or more Oxford units per ml. A crystalline sodium salt of penicillin is reported to possess a potency of about 2000 Oxford units per mg. In other words, the extremely delicate drug must be concentrated some 20,000 times.

Synthesis is yet in the future. The preparation of a crystalline sodium salt of penicillin was announced by Squibb within the past month. This work has been independently duplicated and confirmed by two other laboratories, and hence seems reliable. Researches looking to the elaboration of its structure are proceeding but under a certain handicap because of the small quantities of material that can be spared for research purposes. Obviously the importance of any successful synthesis of the

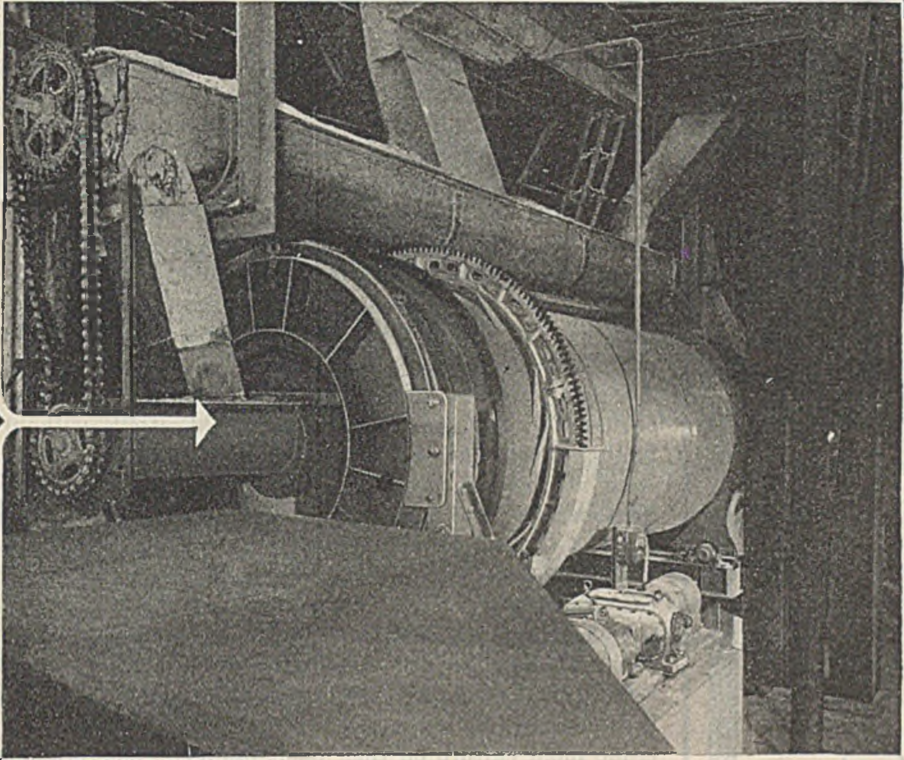
(Continued on page 8)

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

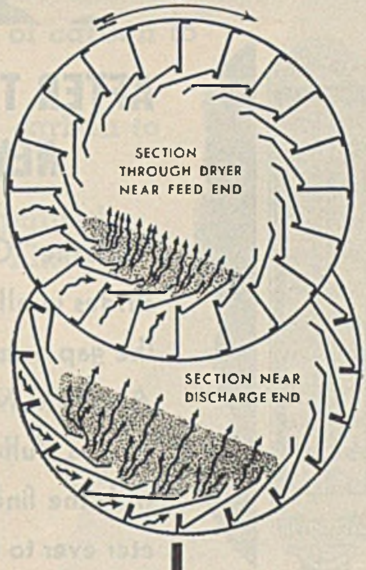




Accurate Uniform Drying... Dehydration With the ROTO-LOUVRE DRYER



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



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

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

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

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

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

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

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

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

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

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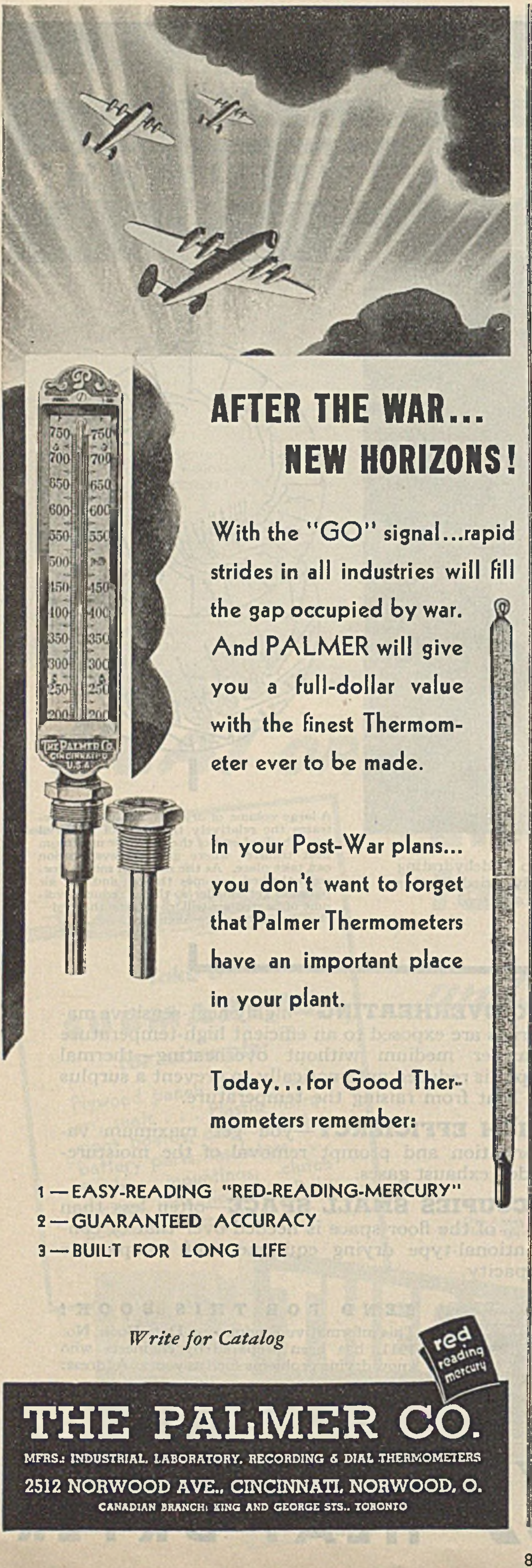
LINK-BELT ROTO-LOUVRE HEAT DRYER



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

Technology

drug will require that details, when known, be at least temporarily witheld from publication. Meanwhile, the action of the story continues.

A Little Knowledge. Seldom has the grave danger of a little knowledge been so clearly demonstrated as in the report, widely headlined in the daily press throughout the country, that penicillin can be grown in the kitchen. The report stems from a statement made by Dr. Julius A. Vogel, plant physician for Jones & Laughlin Steel Corporation, before the Industrial Hygiene Foundation at Mellon Institute in Pittsburgh on November 10.

Dr. Vogel was quoted in news despatches as stating that he had succeeded in growing the penicillin mold in kitchen equipment from a culture obtained from Allegheny General Hospital, using ordinary cornstarch cooked for half an hour. The mold itself without further treatment, he stated, could be used directly on open wounds to destroy surface pyogenic infections. Furthermore, the speaker was reported to have recommended that all physicians use this method of treatment with home-grown mold to avoid scarcity and high cost of the refined drug.

The result of publication of this report has been a titanic furor already headed toward grievous consequences. Several vital points were neglected in thus extending, even by inference, an invitation to all and sundry to slap a crude mold culture on their open wounds. The original audience to whom the suggestion was made consisted of physicians, but laymen, reading of the simplicity of the method, feel fully capable of employing it. Serious difficulties are experienced by expert fermentologists in securing initially pure strains of *Penicillium notatum,* in keeping cultures pure, and in growing it under optimum conditions which encourage it to produce penicillin. These troubles are multiplied a thousand fold if the operation is to be conducted by an inexpert person under the unsterile conditions of an ordinary kitchen. Furthermore, wild molds and sundry bacteria that may become enmeshed in the culture create perils to the patient likely to be far more grievous than those of the wound treated in usual orthodox manner. Death seems invited to visit a patient subjected to such thoughtless treatment.

Water Freshener. Most serious of all problems of mariners from ancient times has been thirst, particularly that of the shipwrecked adrift in open boats. Today's global war and transoceanic air transport magnify the problem and increase the number of its potential victims by subjecting aviators to hazards of the sea. Tales of heroism seldom can omit thirst as the prime peril.

Only now does a partial solution of this ancient problem become possible. The development of ion-exchange substances capable of removing both positive and negative ions of a dissolved salt from solution has finally reached a point of marine utility. Within months the most satis-

(Continued on page 10)

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- Hydrogenation of fats and oils
- Hydrogenation of organic compounds
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- Hydrogenolysis of carbon to carbon bonds
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METAL INDUSTRIES

- Blanketing metals to avoid nitriding and scale
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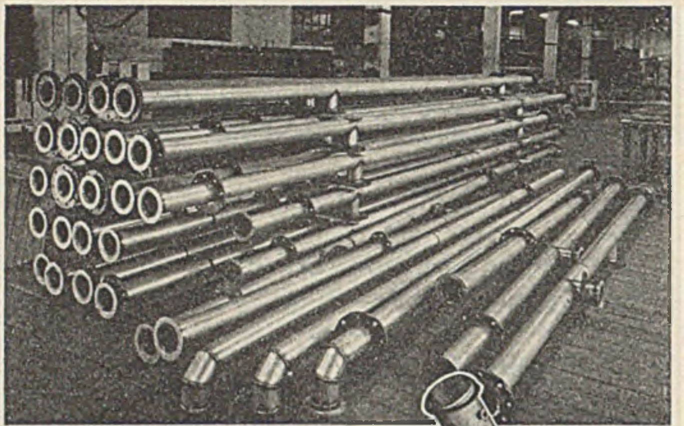
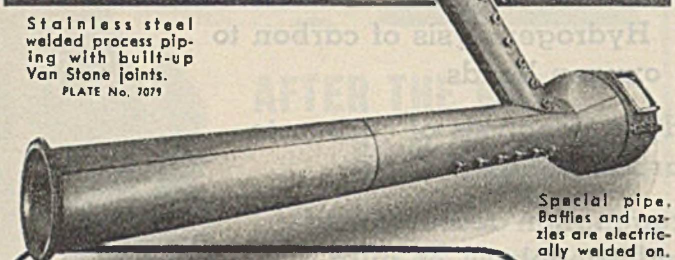




I. & E. C. Report on the Chemical World Today

Technology

factory substances of this class available could produce only the equivalent of their own weight of fresh, potable water from the sea. Thus no advantage could be realized by science and engineering over the time-tried expedient of mariners to carry with them a flask or a keg of water. The intricacy and bulk of distilling equipment, always considered a possible safety measure, confine its use to relatively large vessels if it can be used for rescue at all.

Recently announced ion-exchange agents possess such potency that they are able to extract practically the dissolved salts from four times their weight of sea water without revivification. Thus, a great step has been taken in promising life to those cast adrift at sea.

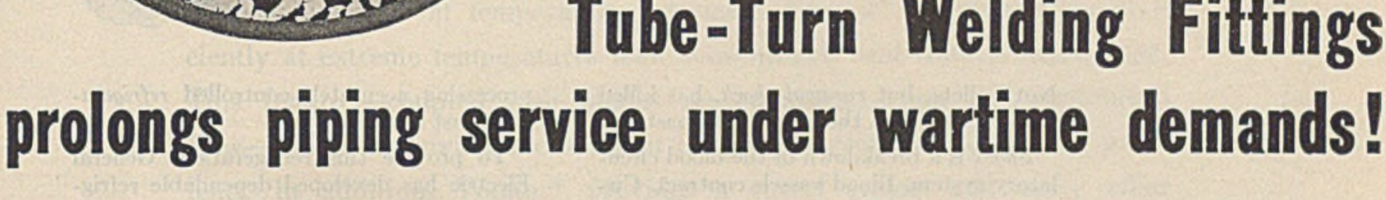
Facts First. When picturing the future, habit and imagination dictate that the sky shall be darkened by fleets of cargo planes carrying all manner of goods to remote points. It is an interesting speculation but scarcely a tenable view. H. W. Prentis, Jr., past president of the National Association of Manufacturers and head of Armstrong Cork Company, stated the facts succinctly and vividly to the American Institute of Chemical Engineers:

> There is nothing at present in the aviation picture to justify such giddy flights of the imagination. The airplane industry is obviously destined for remarkable development. The use of airplanes for passenger travel, mail, and express will be vastly increased, but to envision aircraft as a postwar substitute for steamships, railroads, and motor trucks in the transportation of ordinary freight is to ignore the economic facts of the situation. For example, to transport 100,000 long tons of freight monthly from San Francisco to Australia by steamship would require 44 ships, 3200 men for their crews, and 165,000 barrels of fuel oil. To do the same job by airplane, 10,022 four-engined transport planes, 120,765 men in the flight crews, 8,996,000 barrels of gasoline, and 85 large tank ships to carry the gasoline would be needed. Hence, although we shall see many wonders of industrial and commercial development in the postwar years, the nation should guard itself against fanciful dreams of Aladdin-like advances that will immediately and automatically solve all its employment problems during the years immediately following the cessation of hostilities.

Progress between Wars. If ever there was a sublime example of progress by the chemical industry in the interim between world wars, it is the recent Department of Justice action in indicting four manufacturers of laboratory reagents for conspiracy under the provisions of the antitrust act to fix prices and eliminate competition. We are not commenting on the guilt or innocence of the indicted, but once upon a time, long ago in the first World War, the problem was one of getting reagent chemicals, come high prices, conspiracy, cooperation or any other violations of laws, statutes, and local ordinances. Who knows, next time we may see firms indicted for conspiracy to keep up the prices of synthetic rubber. Progress is wonderful; time levels all things.

(*Continued on page 14*)


NO. 11 OF A SERIES
HOW TUBE-TURN WELDING FITTINGS BENEFIT WAR INDUSTRY
The FIRST SEAMLESS WELDING FITTINGS 1ST AND STILL THE BEST
TUBE TURNS STEEL BEFORE FORGING
TUBE TURNS STEEL AFTER FORGING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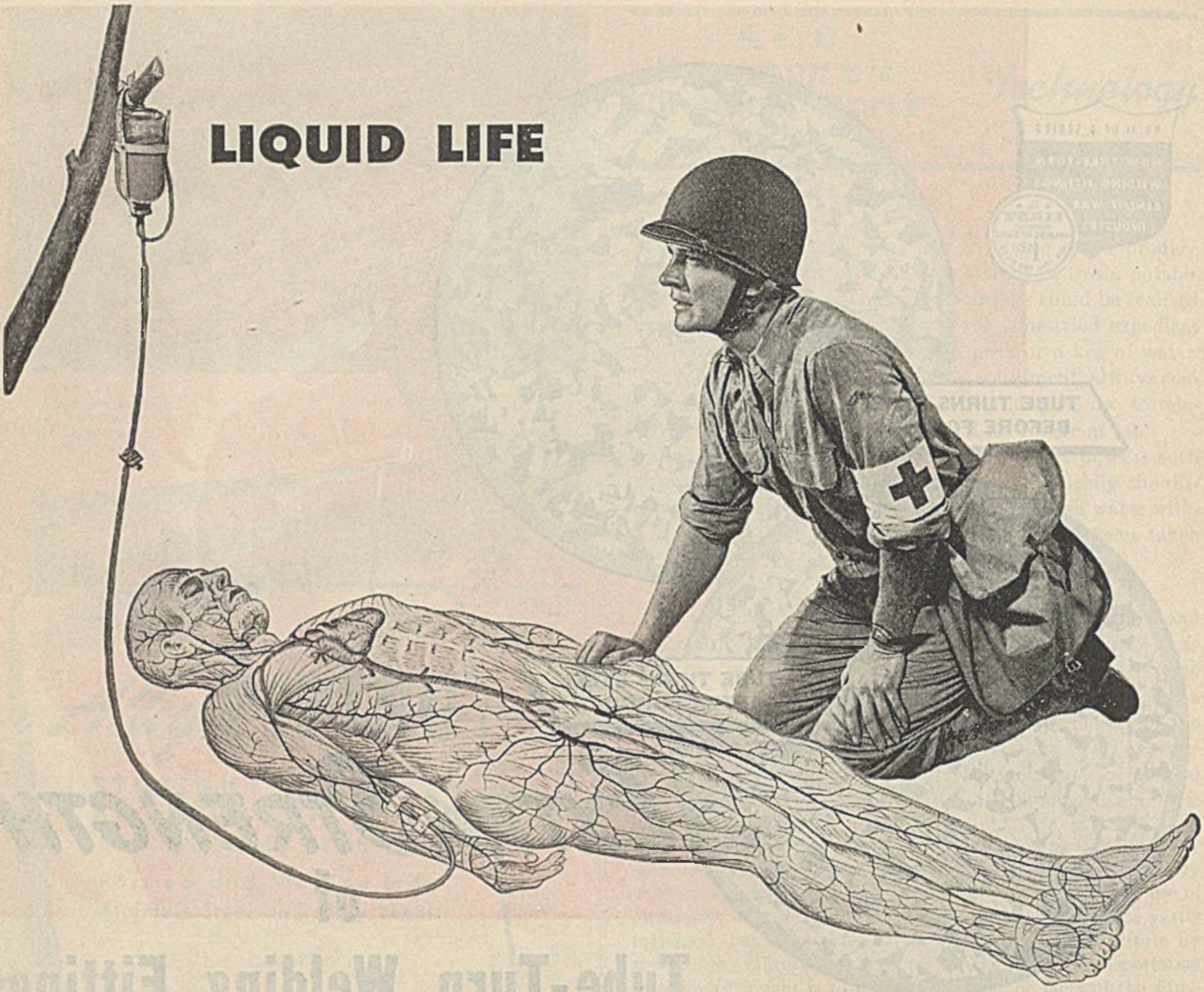

LIQUID LIFE

Not bullets, but *surgical shock*, has killed many a soldier in the wars of the past.

Shock is a breakdown of the blood circulatory system. Blood vessels contract. Circulation slows down, almost stops. If shock is too severe, death results.

Today, when a soldier is wounded, blood *plasma* is injected into his circulatory system. The plasma acts as a sort of pump primer . . . fills up the collapsed veins and arteries . . . starts the system working again. By thus counteracting shock, plasma saves lives and reduces suffering.

The whole blood you give at a Red Cross blood donor station goes through much processing before it gets to the front as plasma. At many points throughout the processing accurately-controlled *refrigeration* must be used.

To provide this refrigeration, General Electric has developed dependable refrigerating equipment that is more efficient, more compact and more flexible—to meet difficult war conditions.

This is only one of the many ways General Electric Refrigeration and Air Conditioning are helping to make a better world.

☆ BUY WAR BONDS ☆

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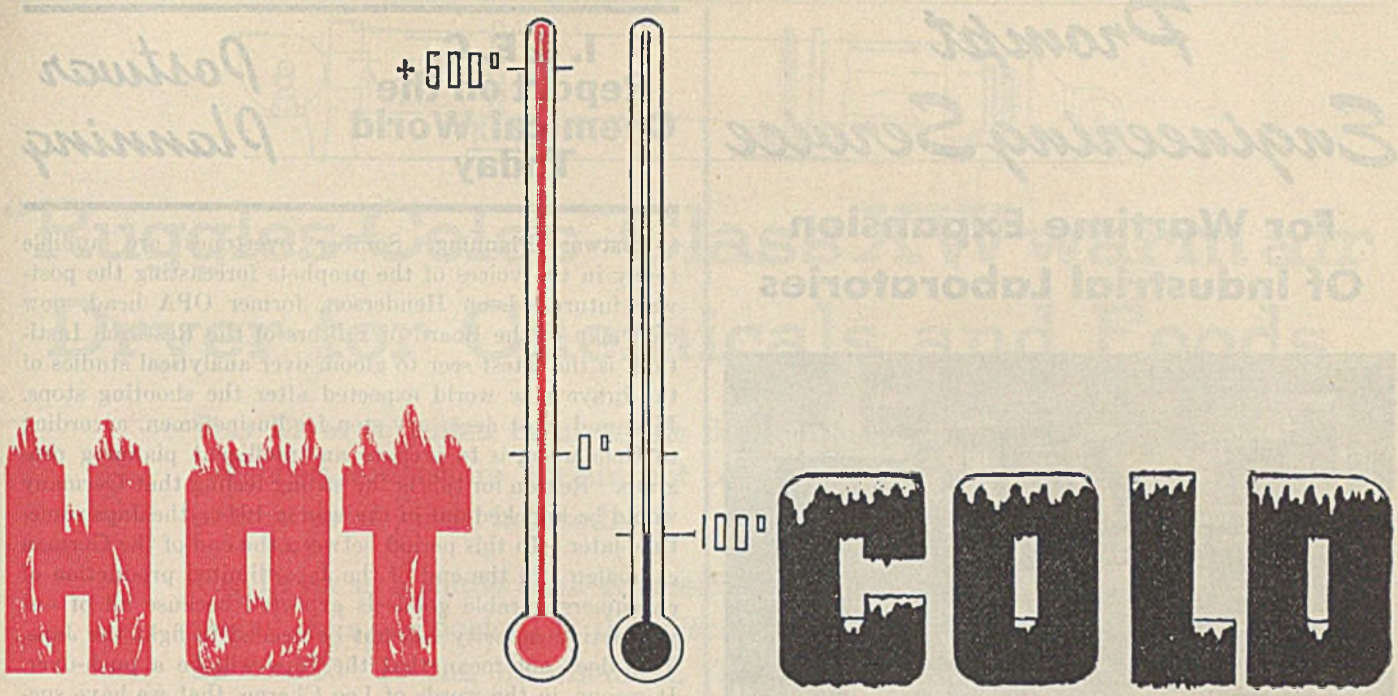

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Investigate Votator* at once if you require heat transfer of liquids or viscous materials at temperature extremes. Votator* operates more efficiently at extreme temperatures than conventional heat transfer equipment. This feature—coupled with almost instantaneous action and continuous flow—offers an invaluable solution to many urgent war processing problems. In addition, Votator* provides a closed system and many other operating advantages available in no other equipment. Let us send you our data questionnaire. Your answers will enable us to furnish specific information that may be a revelation to you.

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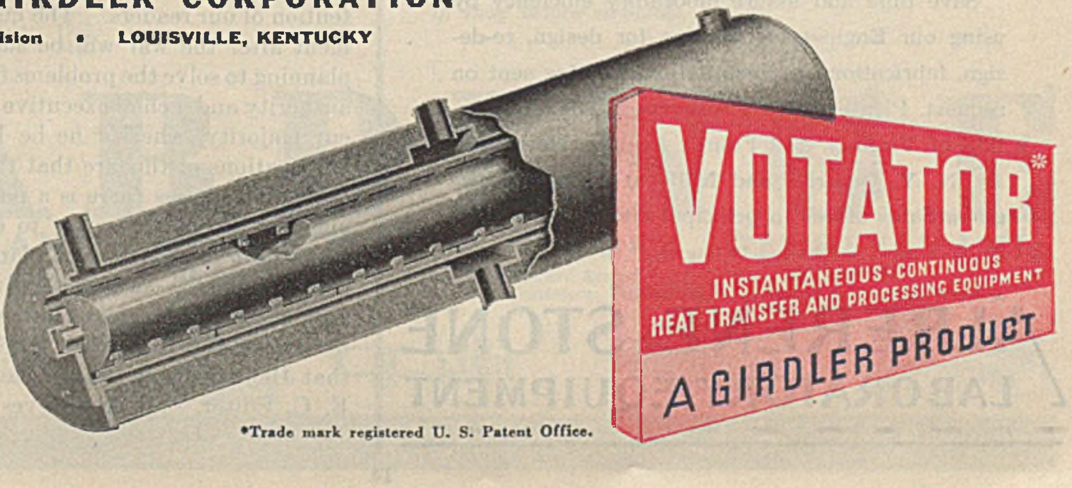
NOTE: *Votator operates efficiently at the high temperatures required for greases, resins and varnishes . . . and at the low temperatures required for crystallization of hydrocarbons.*



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

Postwar Planning

Postwar Planning. Somber overtones are audible today in the voices of the prophets forecasting the postwar future. Leon Henderson, former OPA head, now chairman of the Board of Editors of the Research Institute, is the latest seer to gloom over analytical studies of the brave new world expected after the shooting stops. First and most necessary step for businessmen, according to Henderson, is to prepare an intelligent planning program. Reason for this is the strong feeling that Germany would be knocked out of the war in 1944; the Japs sometime later. In this period between the end of the German campaign and the end of the Japs, limited production of consumers durable goods is expected because all of our productive capacity will not be needed to fight the Japs. This does not mean that the Japs will be a push-over. It means, in the words of Leo Cherne, that we have succeeded in building a war economy on top of our regular civilian economy. The economists considered this impossible; it is, in reality, a dangerous obstacle to full employment after the war. The annual income in America is now approaching the rate of 150 billion, with spending also topping records at the rate of 92 billion dollars. Expected too, in the peace, is a major unemployment crisis which may reach the total of 12 million idle. The institute expects a depression and deflation instead of a boom.

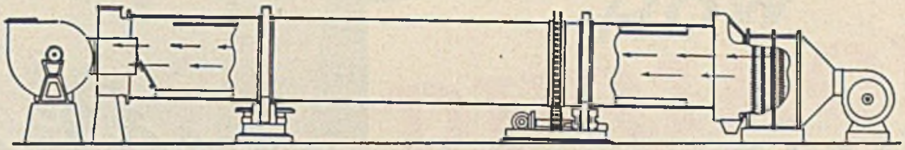
Reasons: Social and psychological fear may keep the public from spending its war savings. The decrease in government spending and termination of contracts may be so rapid that business will be unable to siphon off savings quickly enough to make up the difference in national income.

Leon Henderson as former head of PWA was responsible for spending large sums of government money for the rehabilitation of unemployed. Therefore, with considerable interest we record here his answer to the question about the future role of government spending in the unemployment crisis. Said he, "Public works is a weak reed to lean upon", because it is not a quick energizer.

Cheerful note: The end of the depression will come sometime in 1946 (assuming the institute's forecast of Jap defeat in 1945 is correct) when the public begins to spend accumulated savings.

Two other important items must be brought to the attention of our readers. The make-up of the U. S. Government after the war will be such as to discourage strong planning to solve the problems that arise. Look for divided authority and a chief executive unable to mainain a clear-cut majority, whether he be Democratic or Republican. Implications of this are that the crisis will bring forth no clear plan, unless there is a popular uprising, such as the one that swept Roosevelt to office. The second item—disposition of government plants, including the synthetic rubber industry—will depend not on economics or necessity of national safety, but solely on the make-up and temper of the Congress. Let it be put into the record that Henderson, in answer to a question from an I. and E. C. Editor, said he believes that the synthetic rubber

(*Continued on page 124*)



"Ruggles-Coles" Class XW warm air Dryer for Chemicals and Foods

This Dryer is suited to materials that must be dried at low temperatures and where hot air, not contaminated with the products of combustion, must be used.

The Dryer is a single shell counterflow type. A casing containing steam coils is located at the discharge end. Air temperatures up to 280° F. can be obtained. The heated air is drawn thru the material showering in the shell by a fan located at the feed end.

Materials such as Ammonium Nitrate, Ammonium Sulphate, Potassium Chloride, Sodium Chloride, Sodium Sulphate and Sugar are being dried in the class "XW" Dryer.

Built in eight sizes to dry from a few pounds to several tons per hour.

Write for Bulletin 16-C

Hardinge Equipment

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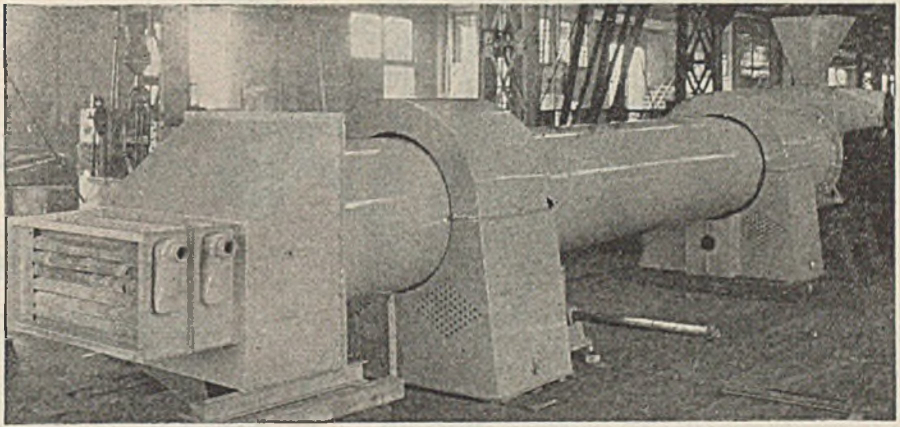

A small class "XW" Dryer assembled in shop before shipment.

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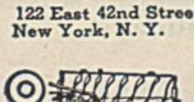
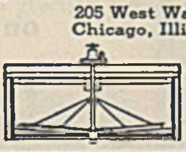
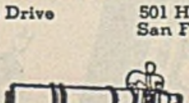
CONICAL MILLS



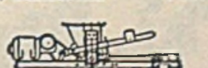
COUNTER CURRENT CLASSIFIERS



THICKENERS CLARIFIERS



RUGGLES-COLES DRYERS

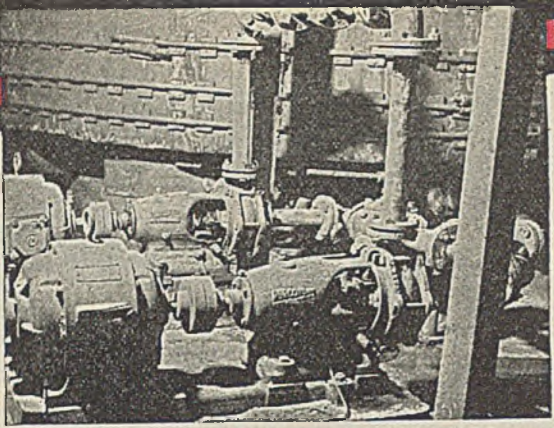


CONSTANT WEIGHT FEEDERS

TUBE ROD AND BATCH MILLS


M.D.

HOW DURIRON HAS HELPED THE RUBBER INDUSTRY



These Durcopumps deliver 1½% sulfuric acid from wood tanks in background to coagulating tanks installed overhead.

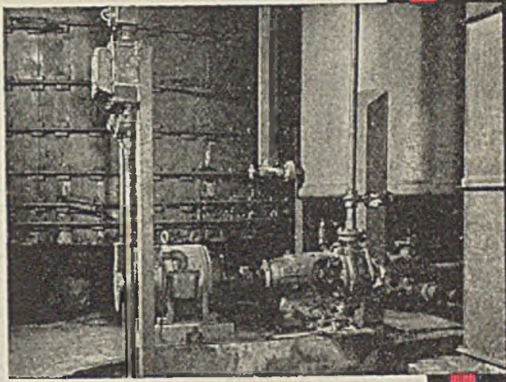
These pictures of Duriron pumps were all taken in just one Goodyear synthetic rubber factory.

In the nation's new rubber industry there are more than 300 Duriron pumps, several thousand valves and jets, as well as long lines of Duriron pipe and fittings.

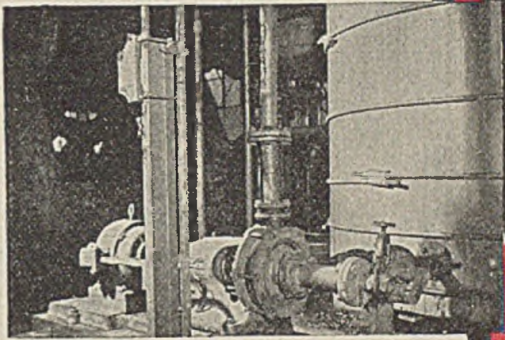
Duriron is a high silicon iron alloy and does not require nickel, chrome or other scarce metals.

These pictures are factual proof, therefore, of critical materials saved for the war without sacrificing the effectiveness of the important rubber development program.

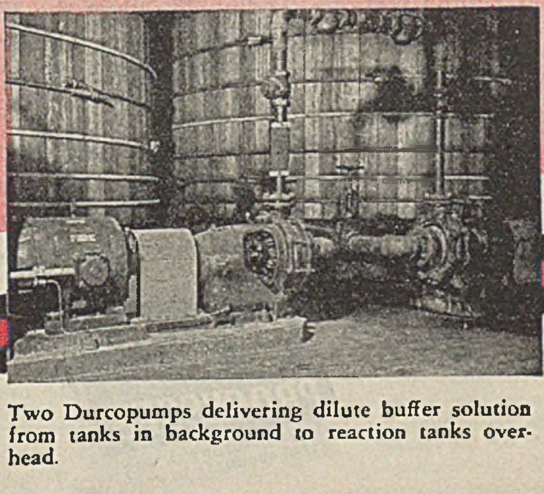
If you are wondering how to meet *your* corrosive problems, consider equipment built of corrosion-resistant Duriron.



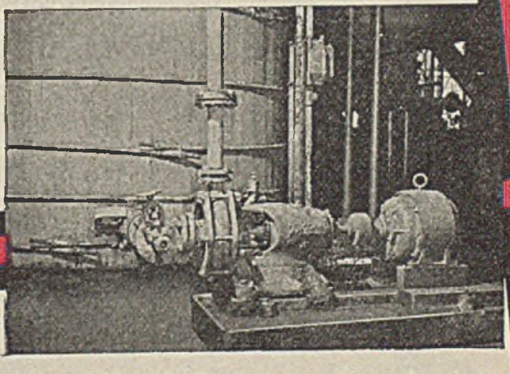
This pump is transferring 66° Be sulfuric acid from the steel tank on right to the large wooden dilute acid tank on left.



This is the filter feed pump handling coagulated latex from holding tank on right to weir box which feeds rotary vacuum filter visible in the upper left corner.



Two Durcopumps delivering dilute buffer solution from tanks in background to reaction tanks overhead.



Another filter feed pump installation handling coagulated latex to weir box.

ARMY NAVY

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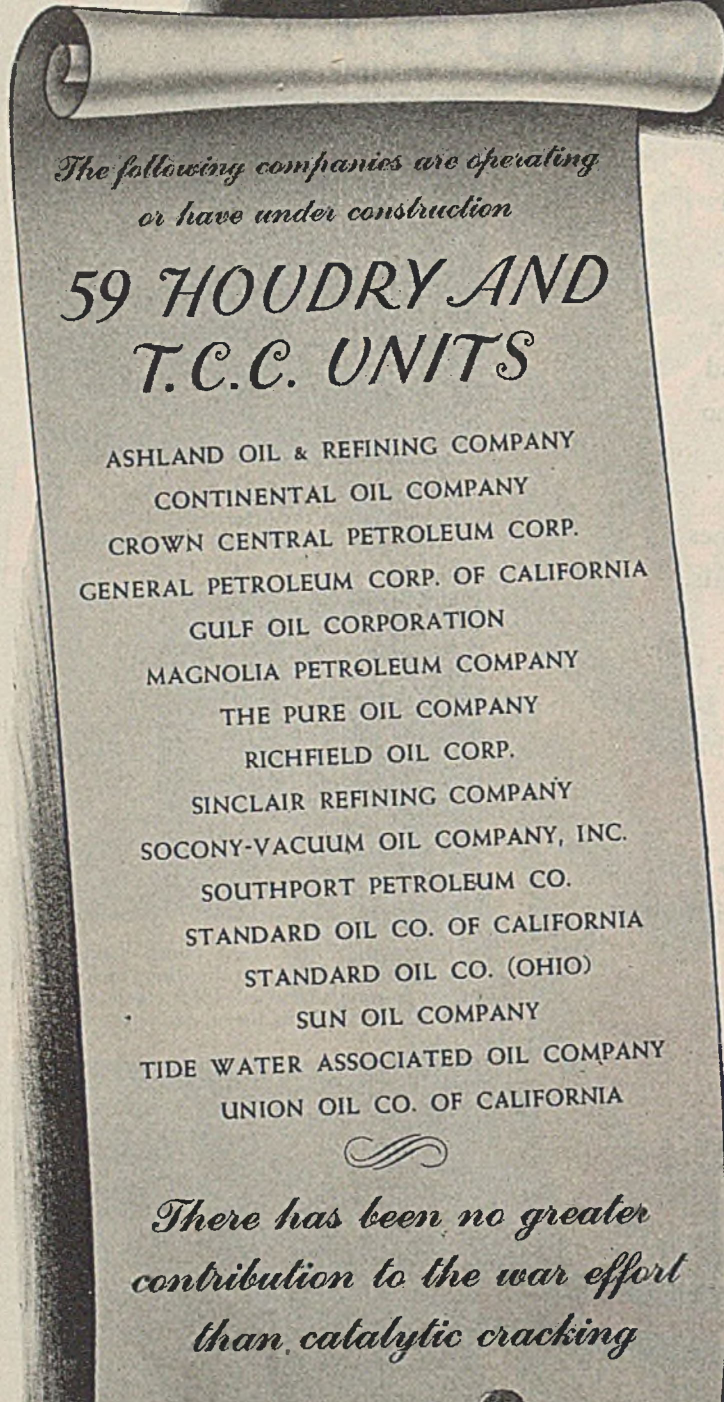

The following companies are operating or have under construction

59 HOUDRY AND T.C.C. UNITS

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There has been no greater contribution to the war effort than catalytic cracking

As we near the second anniversary of America's declaration of war, we may well give due credit to the five leading oil companies which were first to adopt the Houdry Catalytic Cracking Process.

Whether by fate or foresight, they were ready. The day the dreadful news of Pearl Harbor broke upon an unsuspecting and unready America, these five companies—Socony-Vacuum, Sun, Magnolia, Tide Water Associated and Standard of California—had 14 Houdry catalytic cracking units in operation and two more nearing completion. Within a few months, most of these facilities had been converted to the manufacture of this war's most critical material, high octane aviation gas.

These pioneers of catalytic cracking soon were joined by other leading petroleum refiners. Sixteen companies are now operating or building Houdry and T. C. C. units. They include many of the industry's best known names and represent more than 50% of total U. S. refining capacity.

During two critical years of a war whose issues have been mainly decided in the air, Houdry licensees have carried almost the entire load of producing catalytically cracked aviation gas for the United Nations. Today, 23 out of the 27 catalytic cracking units in operation are Houdry-licensed units. Thirty-six more Houdry and T. C. C. units are being built.

Houdry Catalytic Processes and the Thermofor Catalytic Cracking Process are available to all American refiners, under license arrangements, subject to approval by the United States Government.

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

U.S.I. CHEMICAL NEWS

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

Diethyl Oxalate Supplements Scarce Lacquer Solvents

Reagent Uses Also Afford Many Possibilities in Synthesis

Although in the past diethyl oxalate has found its greatest use in organic synthesis, it is today being employed in substantial quantities to replace and extend critically short nitrocellulose solvents.

Diethyl oxalate is an excellent solvent for nitrocellulose and has a slow evaporation rate. While its applications have previously been limited to specialized fields, due to its tendency to hydrolize, it is now being used very successfully where special care is taken to eliminate all possible water from the formulation. It is recommended that wherever possible diluents with high aromatic content be used inasmuch as diethyl oxalate has a much higher dilution ratio with aromatic hydrocarbon diluents than it has with petroleum naphthas.

Diethyl oxalate offers many possibilities in chemical synthesis. Here are a few typical examples:

1. **With ethyl acetate in the presence of sodium ethoxide (sodium ethylate) it yields ethyl sodium oxalacetate.**
2. **With acetone in the presence of sodium ethoxide, it yields xanthochelidonic acid ester (acetone dioxalic ester) from which the ethyl ester of chelidonic acid may be obtained. Gamma-pyrone may in turn be obtained from this latter substance.**
3. **With zinc and alkyl iodides, it gives ethyl esters of dialkylglycolic acid.**
4. **With sodium amalgam, the alcoholate of ethyl glyoxylate, ethyl oxomalonate, ethyl racemate, and the ethyl ester of desoxalic acid may be obtained. From this latter acid there may be obtained by reacting with phenylhydraxine, the phenylhydrazone of ethyl glyoxylate.**
5. **Electrolytic reduction gives ethyl glyoxylate.**
6. **With sodium ethoxide and urea, it gives parabanic acid (oxalylurea).**
7. **It is used to manufacture phenobarbital.**
8. **With ortho-nitrotoluene there results an alcohol condensation product containing a third group in the benzene ring.**
9. **By distilling with an alcohol other than ethanol the oxalic ester of the alcohol may be obtained through alcoholysis.**

Patents New Protective Treatment for Textiles

A Canadian Patent has been granted covering the use of trichlorobenzyl phenyl ether dissolved in alcohol or acetone as a mothproofing agent for textiles. It is mixed with salicylanilide as a fungicide or with pyrethrum as an insecticide.

New Anti-Rust Compound Is Announced by U.S.I.

Extensive Use in Automotive and Industrial Cooling Systems Seen for New Powder

Improved protection for radiators and other cooling-system surfaces is made possible by a new anti-rust compound in powder form, recently developed by U.S.I. Orange in color, the powder works equally well with water or any type of anti-freeze solution. Two ounces will protect a five-gallon capacity automobile cooling system.

Use of an inhibitor of this type in automobile cooling systems is particularly advisable this winter where anti-freeze solutions are being re-used, as the rust-inhibiting qualities originally present in the anti-freeze will have been lost.

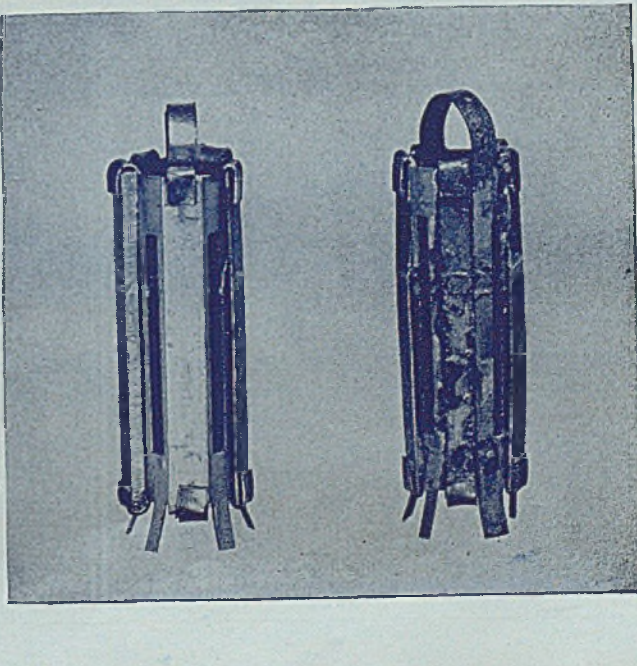
Summer Use Important

In addition to imparting anti-corrosive properties to alcohol or permanent type anti-freeze solutions, the compound is recommended for use for summer radiator protection. Recent reports by government agencies and automotive engineering groups indicate that radiator corrosion is at its peak during the summer, due to the higher temperatures and the fact that ordinary water is so generally used as a coolant.

Protects Many Metals

Extensive tests in U.S.I. laboratories have shown that the new inhibitor will protect surfaces of a wide range of metals, including aluminum, steel, cast iron, copper, brass and solder. By keeping heat transfer surfaces clean, the product helps assure efficient cooling, thus preventing engine overheating and loss of anti-freeze from boil-over.

U.S.I.'s new compound has no effect on rubber, and therefore cannot cause trouble with radiator hoses or other rubber appliances in the cooling system. It is also entirely odorless.



Unretouched photo of test bundles just as they appeared after an accelerated corrosion test simulating the most severe conditions encountered in automotive radiators. Bundles consist of strips of copper, aluminum, solder, brass, and cast iron, all crimped with good electrical contact to a steel frame. Note the corrosion and severe electrolysis which has taken place on the "control" bundle at right, which was exposed to untreated tap water. Note how clean and free from electrolysis the bundle at left is after exposure to similar tap water which had been protected with U.S.I.'s new anti-rust compound.

Tests Possible Solvents For Tung Oil Extraction

Renewed interest in the possibility of increasing the yield of tung oil from domestic fruits is reflected in a recent study of solvents which might be used in an extraction process. Out of a total of 33 solvents studied, ethyl acetate and some 10 others held the most promise, from the standpoints of quality and yield of tung oil produced and from that of economics.

The study, carried on by three Department of Agriculture scientists, points out the necessity of selecting a solvent of sufficiently high boiling point to avoid excessive vapor losses, yet low enough to prevent deterioration of the tung oil quality through exposure to unduly high temperatures.

Alkyd Resin Can Replace Phenolics in Navy Primer

The Navy Department has announced that it will now accept, tentatively, a primer based on Holabird Specification ES-680a, Class 101 for use on all Naval equipment and machinery. This is covered by Specification 52-P-26 Primer, Metal (Brown) dated June 1, 1943, and will replace the original Zinc Chromate Primer 52-P-18 (phenolic) which will be used only for the painting of ships' hulls and com-

(Continued on next page)

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December ★

U.S.I. CHEMICAL NEWS

★ 1943

Resins in Navy Primer

(Continued from preceding page)

partments. Until such time as the Navy can evaluate submitted samples of Specification 52-P-26 and can establish an approved list, those products now having the approval of Holabird Quartermasters Depot will be accepted by them.

Specification 52-P-26 is met completely by Aroplaz 1323-D, a product of U.S.I.'s Stroock & Wittenberg Division, which is already being used extensively in Holabird Specification ES-680a. Although this is one of the lowest priced pure alkyd resins, it is a versatile high-quality product.

Recovery of Free Acid From Pickling Liquors

Acetone has been found superior to solvents previously tried for promoting the crystallization of copperas from pickling liquor. While acetone is not satisfactory for the treatment of continuous-process liquor, batch liquor responds well from the standpoints of ferrous sulfate removal, acid concentration, quality of copperas, and acetone separation.

Reports New Remedy For Skin Ailments

Tetraethylthiuram monosulfide is reported by a British Journal to have proved effective in the treatment of scabies. The liquid preparation used was an emulsifiable oil having the composition:

Tetraethylthiuram monosulfide	25%
Polyglycerol ricinoleate	10%
Industrial methylated alcohol	65%

One part of this oil was added to four parts of water immediately before use.

Influence of Alcohols On Indicators Described

Color change of some titration indicators is reported to be markedly influenced by the lower alcohols.

The change is least pronounced with ethyl and *n*-propyl alcohol, more so with methyl, and most pronounced with iso-propyl alcohol. Impurities in the alcohol also have an appreciable effect, impossible values being obtained in the presence of ethers.

Method for Determining Chlorophyll and Carotene

Of significance to the dehydrated food and other industries is a recently announced method of determining chlorophyll, pheophytin, xanthophyll and carotene — key factors in the taste and nutritional "goodness" of vegetables.

The method involves a combination chromatographic, solvents-partition, and spectrophotometric techniques. Pigment is first extracted with acetone, then transferred to ether and subjected to direct spectrophotometric analysis for chlorophyll and henophytin. Xanthophyll and carotene are subsequently determined by chromatographic analysis.

Molasses Extender

Demand for Special Liquid Curbay as an extender for molasses in hog and dairy feed manufacture continues to grow. This U.S.I. product is also finding increased industrial use as a binder, and is said to offer interesting possibilities in the preparation of specialty agricultural products for plants and soils.

Special Liquid Curbay contains approximately 40-45% solids, can be handled just like molasses in storage or mixing equipment, and is available in tank car quantities without allocation limitations.

Determination of Water In High-Proof Ethanol

A mixture of anhydrous ethanol and bicyclohexyl exhibits a critical solution temperature of 23.4°C.; with 1 per cent of water present, this temperature becomes 41.4°, and with 2 per cent water 54.1°. Thus the critical solution temperature can be plotted against the percentage of water present and the resulting curve used for determining the water content of high-proof alcohol.

The procedure recommended is to add 4.0 ml. of bicyclohexyl to 2.0 ml. of the alcohol to be tested and stir with a dry thermometer. Heat until the solution becomes clear and then cool slowly with stirring. Note the temperature at which the mixture becomes slightly opalescent.

TECHNICAL DEVELOPMENTS

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

Two new fatty acids, azelaic and pelargonic, described as straight chain acids containing nine carbon atoms are announced. Now in commercial production, these acids suggest new fields for investigation in textile applications, modifications of resins, plasticizers, etc. (No. 749)

U S I

A paint brush cleaner is offered which the maker claims will swell the bristles and loosen dried paint in 12 to 96 hours. The liquid is non-inflammable, non-fuming and harmless to the hands. It can be re-used after straining. (No. 750)

U S I

Low freezing points and mild odors are the featured points of a new series of plasticizers and softeners now being offered for use in coatings, adhesives, plastics, synthetic resins and rubbers, etc. A chart of the physical properties of these new products is available from the maker. (No. 751)

U S I

A quick-setting, tacky adhesive, developed primarily to cement cork inserts in reconditioned or new crowns, is reported to work especially well in automatic cork inserting machines. The maker states the product is odorless and non-toxic. (No. 752)

U S I

Preventing electrolysis and consequent boiler corrosion is the purpose of a new galvanic cell designed to hang from a tube in the boiler. The cell, it is stated, concentrates electrolytic action at its negative pole, precipitating the mineral matter for removal during blowdown. (No. 753)

U S I

A new plasticizer, claimed to impart striking low temperature flexibility to synthetic rubber products, is being offered to processors of Butaprene, Chemigum, Hycar, Neoprene, Perbunan and Thiokol. (No. 754)

U S I

A new floor cleaner, recommended also as an oil and grease absorbent for reducing fire and slipping hazards, is announced. Said to be non-abrasive, odorless, and non-injurious to skin, clothing or flooring, the product will absorb up to 50% of its weight of oil or grease. (No. 755)

U S I

Stable, uniform oil emulsions are said to be produced at higher speed with the aid of a new group of soluble resinates. Sodium and potassium salts of selected resins, these resinates are useful in the manufacture of cutting oils, polishes, paints, and many other products. (No. 756)

U S I

A new gas mask, approved for use in the presence of acid gases, organic vapors, ammonia, carbon monoxide and toxic smokes, where sufficient oxygen is present to support life, is announced. Shatter-proof lenses, an arrangement to prevent lens-fogging, and a dial which indicates safe remaining service time are incorporated in the design. (No. 757)

U S I

A new paint remover is reported to cut through the toughest film, leaving a clean, neutral surface that requires no after-washing or neutralizing. The product is said to be waxless, involve a minimum of fire and toxic hazards. (No. 758)

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- Ethyl Acetate

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- Diethyl Oxalate

PHTHALIC ESTERS
- Diamyl Phthalate
- Dibutyl Phthalate
- Diethyl Phthalate

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

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- Acetoacet-ortho-anisidide
- Acetoacet-ortho-chloranilide
- Acetoacet-ortho-toluidide
- Acetoacet-para-chloranilide
- Ethyl Acetoacetate
- Ethyl Benzoylacetate
- Ethyl Sodium Oxalocetate

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- Ethyl Ether
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- Synthetic

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- Ethylene Glycol
- *Indalone
- Nitrocellulose Solutions
- Urethan

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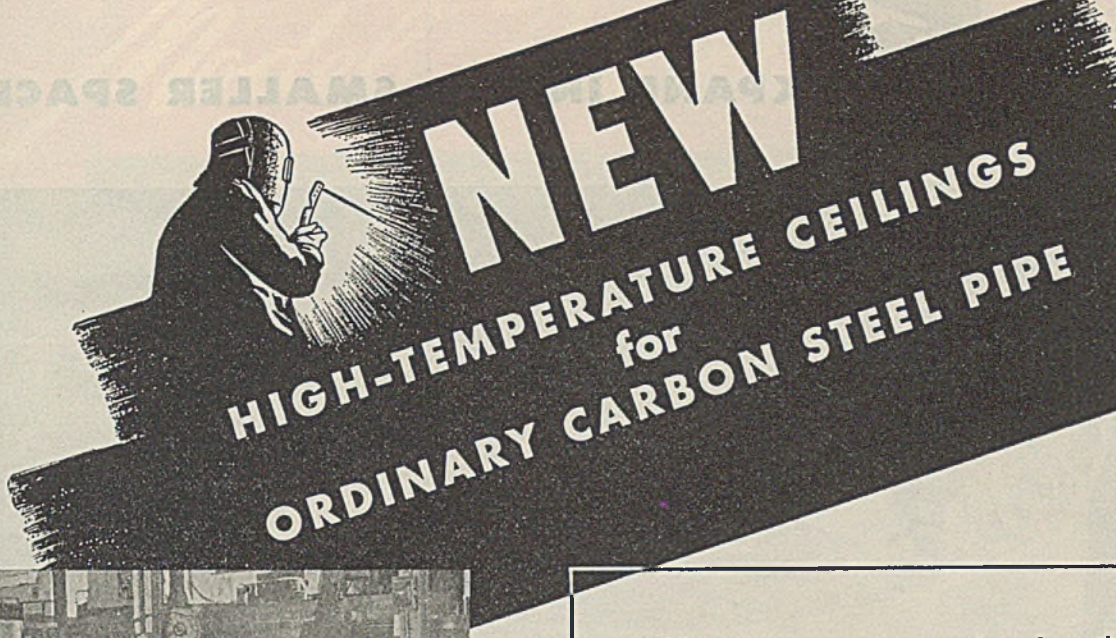
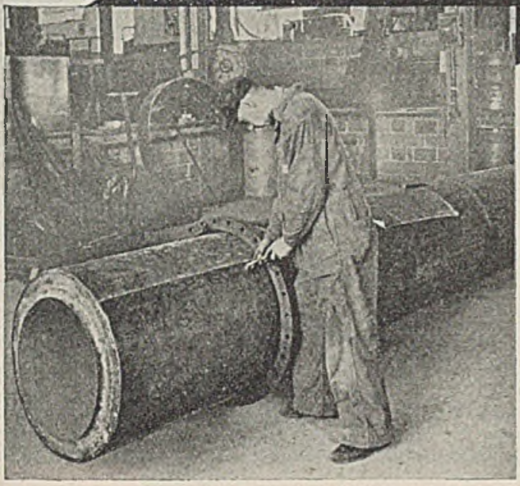
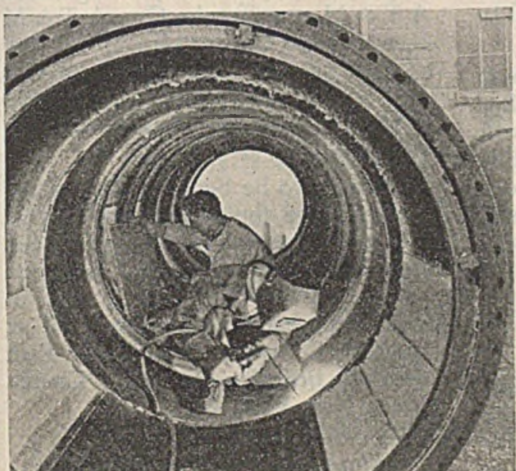


NEW HIGH-TEMPERATURE CEILINGS for ORDINARY CARBON STEEL PIPE



Insidline installations in pipe from 2" I. D. to 36" I. D. are made with a cartridge type of insulation that is built up first and then drawn into the pipe.



In larger diameters from 36" up to over 100", a panel type of Insidline is built up on the inside of the pipe.

Many new processes involve the piping of flue gases, steam, petroleum gases, hydrogen, and fluid catalysts at temperatures up to 1500° F., pressures up to 300 pounds, and velocities up to 500 feet per second.

Insidline, an internal insulation, was developed to enable ordinary carbon-steel pipe, with its comparatively light weight and low cost, to stand up under these conditions. The insulation holds the temperature of the piping to 750° F. or below, where the phenomenon of "creep" does not occur, and the pipe can be operated indefinitely at the usual stress allowances. The use of Insidline simplifies pressure-piping design, too, by reducing the number of expansion joints, bends, and other provisions for pipe expansion.

If you have a high-temperature, pressure-piping problem, it will pay you to investigate Insidline.

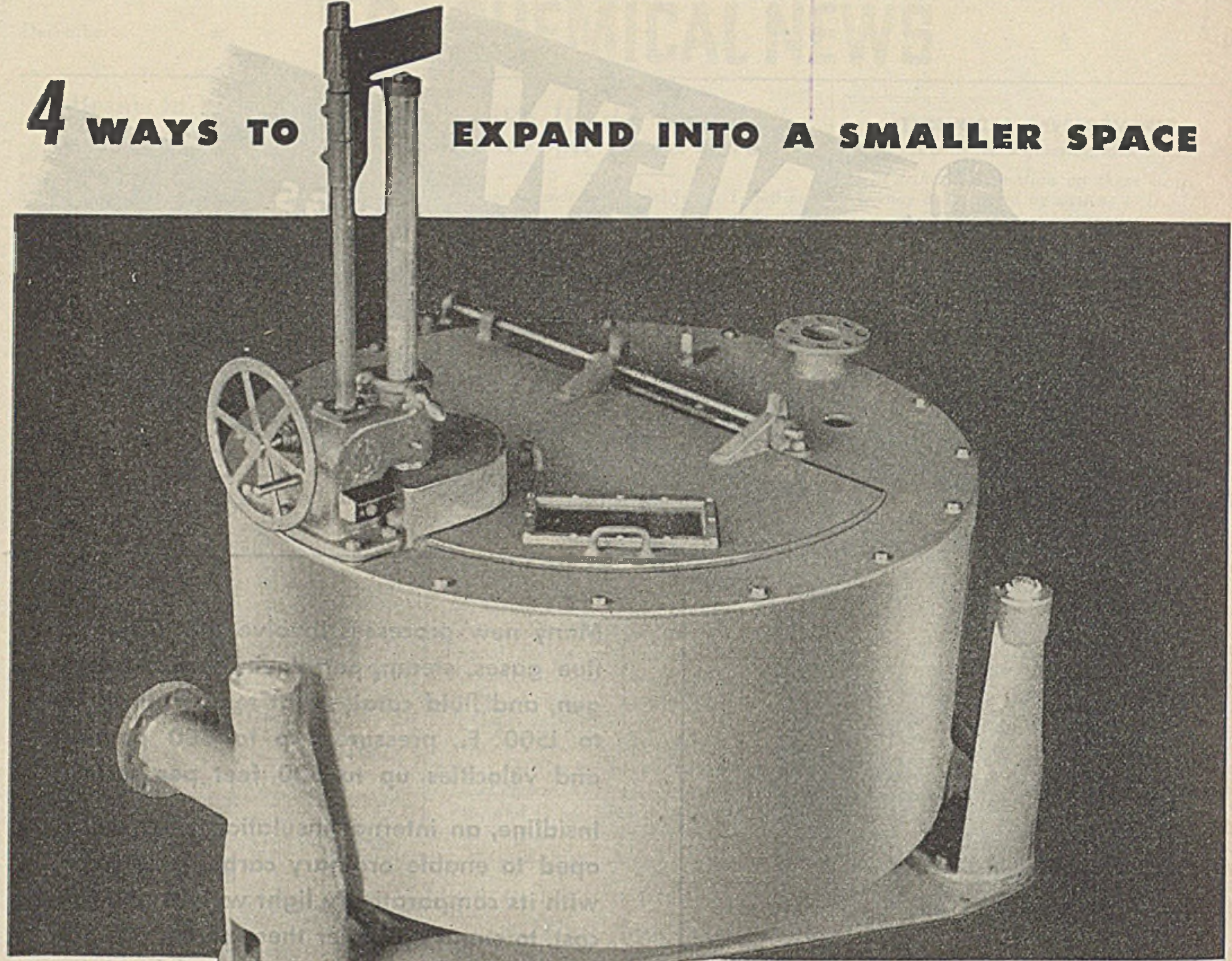
Send for descriptive booklet.

BALDWIN-HILL COMPANY

533 KLAGG AVE., TRENTON 2, N. J.

NEW YORK, N. Y. • CHICAGO, ILL. • KALAMAZOO, MICH. • HUNTINGTON, IND.

4 WAYS TO EXPAND INTO A SMALLER SPACE



Expanding production in less floor space is not exceptional, when A T & M centrifugals are used instead of slower, more costly methods.

1. Centrifugals instead of filters —Perhaps, as in certain cases encountered by A T & M engineers, your filters are slowing down your entire process. Often difficult to clean, they are of course limited to one extractive operation at a time. A T & M centrifugals have removed 2 liquids from a solid in *one* operation . . . combined clarifying and filtering . . . efficiently separated crystals from a *sticky* fluid —and generally in less floor space than the filters required.

2. Centrifugals instead of settling tanks. More immediate precipitation, finer degree of clarity, dryer cake . . . are normal results when centrifugals are used instead of tanks. An A T & M centrifugal has been designed to precipitate an oxide and decant an acid in one swift, space-saving operation.

3. Centrifugals instead of kiers, autoclaves. If you are pressing liquids into solids or semi-solids, you will find standard A T & M centrifugals provide more convenient cell-positioning, more uniform impregnation, easier removal of surplus impregnatory material. Nitrating and final wringing of cotton in manufacture of high explosives is being considerably speeded by A T & M centrifugals.

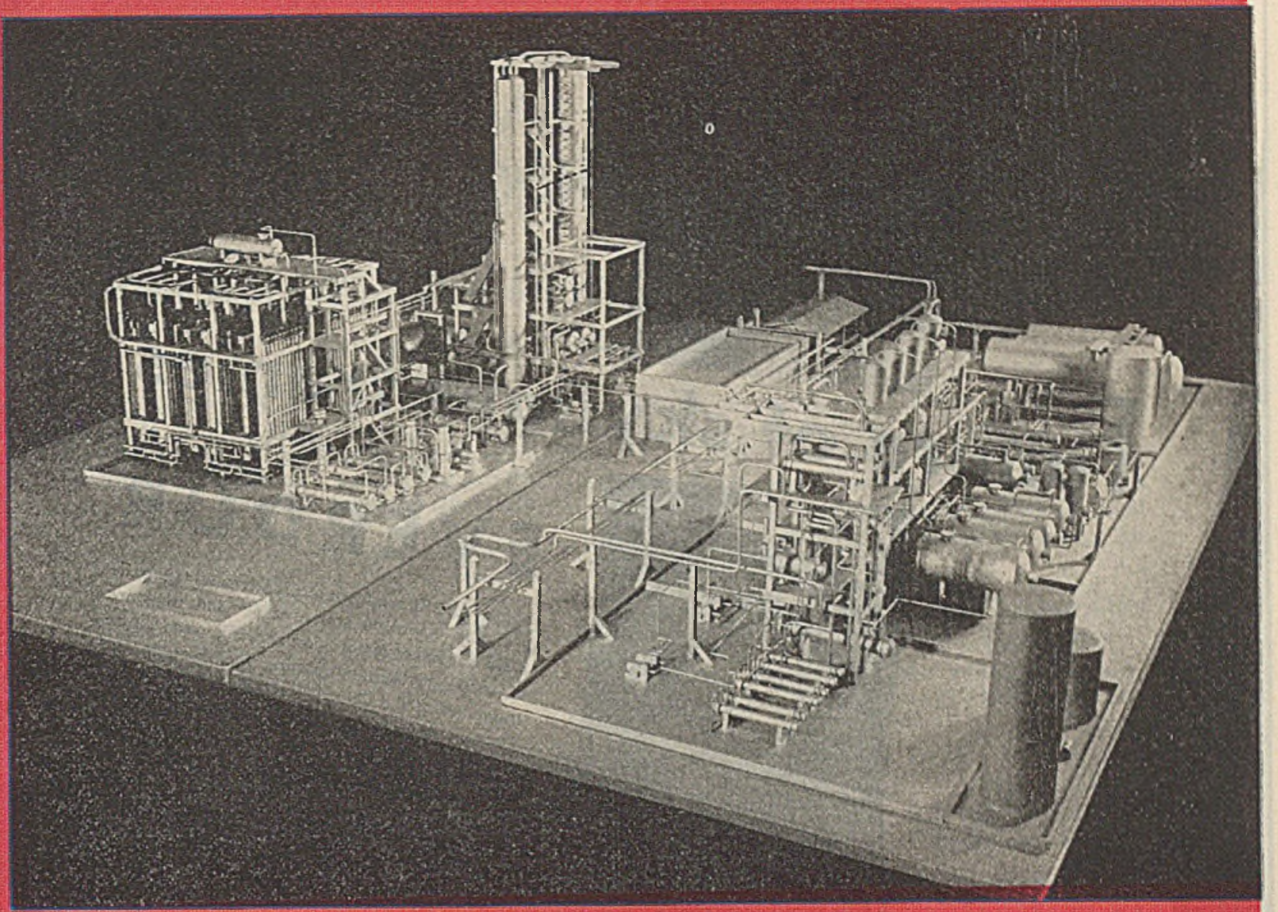
4. Centrifugals instead of drying machines. If you are now using ovens, squeeze rolls, boxes, or special and expensive drying machinery . . . or planning a post-war dehydration process . . . the chances are you can realize tremendous savings in time of process, or power costs, or factory footage, with A T & M centrifugals. One A T & M customer was able to save up to 70% of drying time. Another found that one A T & M centrifugal made available a $35,000 machine formerly tied up with drying.

Plan now to be best and first on the market, once the "Go Ahead" signal is given. As national needs permit, our engineers will gladly consult with you without cost or obligation . . . and in strict confidence. American Tool & Machine Company, 1421 Hyde Park Avenue, Boston — or 30C Church Street, New York, N. Y.

Extraction
Dehydration
Filtration
Precipitation
Impregnation
Coating

A T *and* M

A T & M CENTRIFUGALS SAVE TIME AND SPACE



Failure of skylight frames
checked by
EVERDUR

Smoke and fumes from locomotives added to the naturally corrosive action of air and moisture were important factors contributing to the failure of metal skylight-supporting members in the train shed at the Central Railroad of New Jersey Terminal, Jersey City, N. J. This condition led to two trial installations of Everdur Metal (strengthened copper) in 1928.

Everdur proved so successful that it is now being used for all metal parts in the new skylights. To date, there have been 250 replacements.

Everdur Metal, which combines the strength of steel with immunity to rust and corrosion-resistance actually exceeding that of copper and costing only slightly more than copper, is being utilized for an increasing number of architectural uses. It is readily welded and can be fabricated by the same general methods as steel.

Detailed information on the physical properties and general characteristics of Everdur Metal is contained in Publication E-2, sent on request. The American Brass Company, General Offices, Waterbury, Connecticut.

Skylight installation, C. R. R. of N. J. Terminal, Jersey City, N. J. A. E. Owen, Chief Engineer, E. A. Kunze, Architect, Craig & Brown, Fabricators.

ANACONDA
COPPER • BRASS • BRONZE

This advertisement originally appeared in Architectural Forum, April, 1931. A recent check-up by The American Brass Company, in conjunction with representatives of the Railroad Company, disclosed that the Everdur Metal, installed between 1932 and 1935, is holding up very well under extremely severe conditions of exposure to engine gases, etc.

This isn't a record, of course. It is simply the beginning of a performance story and an example of the durability and dependability of Everdur Metal—appreciated particularly during these recent years, when manpower and material shortage made maintenance problems increasingly difficult.

ANACONDA
from mine to consumer

Everdur Copper-Silicon Alloy

We go afield for an example of Everdur in Service

YOU ASK: *What has corrosion in a railroad terminal to do with processing equipment?*

Just this: The Everdur* Metal that is doing such a satisfactory job "under extremely severe conditions of exposure to engine gases, etc.," is the same metal that has been doing such a stand-out job for so many years in so many different types of service in the process industries.

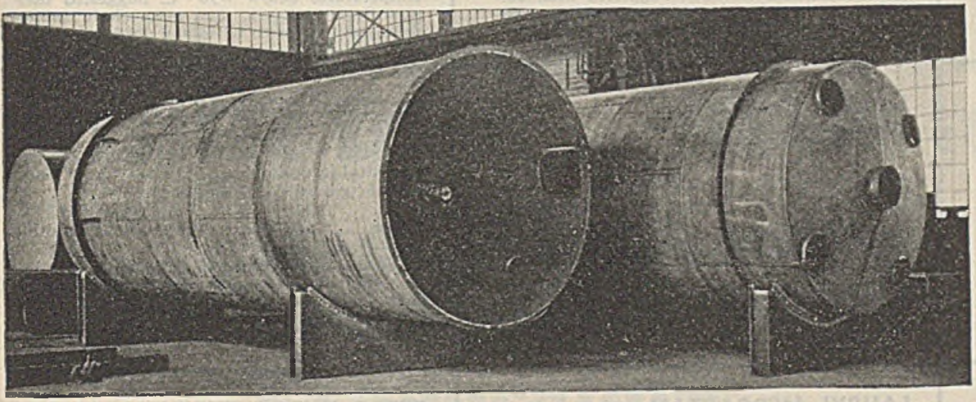
Everdur is a copper-silicon alloy. Its high strength and high resistance to fatigue, coupled with its freedom from rust and excellent resistance to a wide range of corroding agents, have made it the Number One metal for the construction of chemical and process equipment such as that illustrated and listed below.

*Trade Mark Reg. U. S. Pat. Off.

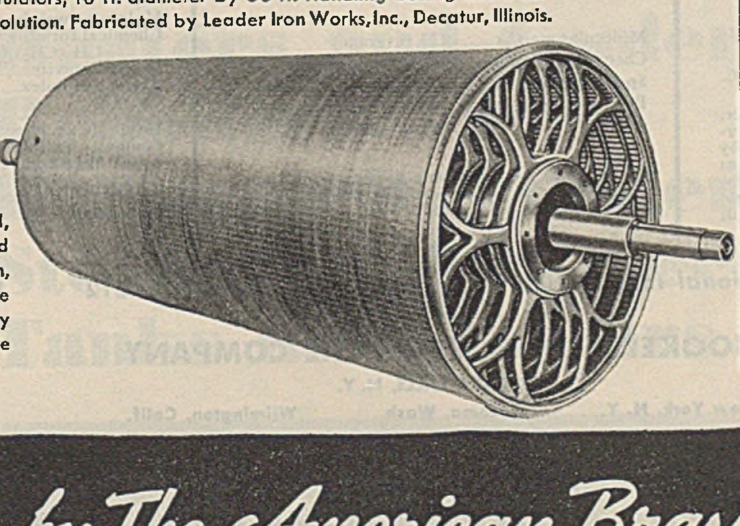
And from the fabricator's point of view also, Everdur is a favored metal—it machines readily, can be rolled, spun, stamped, cast, forged and welded. Furthermore, Everdur's availability in all commercial forms makes possible the economical fabrication of long-lasting, low-maintenance, "All Everdur" equipment.

43122

THE AMERICAN BRASS COMPANY
General Offices: Waterbury 88, Connecticut
Subsidiary of Anaconda Copper Mining Company
In Canada: Anaconda American Brass Ltd., New Toronto, Ont.



Everdur Acidulators, 10 ft. diameter by 30 ft. Handling boiling dilute sulphuric acid solution. Fabricated by Leader Iron Works, Inc., Decatur, Illinois.



Paper Making Cylinder Mold, fabricated by The Bagley and Sewall Company, Watertown, N.Y. Anaconda Signal Bronze Winding Wire is supported by Everdur Rods. Cast spiders are also Everdur.

Everdur Metal Uses in the Chemical and Process Industries . . .

- KETTLES
- CALANDRIAS
- VAPOR SCRUBBERS
- SCREENS
- FILTERS
- FILTER DRUMS
- FRACTIONATING COLUMNS
- CONE BLENDERS
- VALVES
- STORAGE VESSELS
- SCREWS, BOLTS, FASTENINGS
- STILLS
- VATS
- PRESSURE VESSELS
- VACUUM TANKS
- CONDENSATE TRAPS
- STORAGE HEATERS
- ACIDULATORS
- ELECTRICAL CONDUIT
- PIPE AND TUBES
- FABRICATED FITTINGS

Made by The American Brass Company

KNOCKING at the Chemist's Door

Thirteen new chemicals developed by Hooker Electrochemical Company are waiting for adventure. Consider their properties—send for research samples. It may be that one or more of these chemicals are what you have been seeking.

HIGHLY CHLORINATED PARAFFIN

Light colored, almost white, brittle resin, softening at about 100° C. and remaining very viscous at 140° C. Contains 76 to 78% Chlorine. This product is more stable than other chlorinated paraffins containing lesser amounts of Chlorine. Suggested uses: Resin for paints to withstand severe weather conditions.

CHLORPROPANE WAX

Molecular weight	320
Chemical formula	$CCl_3CCl_2CCl_3$
Softening point	110 to 120° C.
Boiling range	210 to 270° C.
Color	White crystalline wax
Odor	Mild camphor-like

Insoluble in water, soluble in alcohol, ether and chlorinated solvents. Suggested uses: plasticizer; dielectric wax; pyrotechnic compositions; lubricant to withstand chemical attack.

HEXACHLORBENZENE

Molecular weight	284.7
Chemical formula	C_6Cl_6
Melting point	230° C.
Color	White to cream

Insoluble in water, soluble in carbon tetrachloride, monochlorbenzene, toluene. Suggested uses: pyrotechnic compositions; ingredient of water proofing and flame proofing compounds.

HEXACHLORBUTADIENE

Molecular weight	261
Chemical formula	$CCl_2{=}CCl{-}CCl{=}CCl_2$
Melting point	−20 to −25° C.
Boiling range	210 to 220° C.
Specific gravity	1.65 to 1.70 at 25°/15.5° C.
Color	Water white

Insoluble in water; miscible with alcohol, ether, chlorinated organic solvents. Chemical properties: highly stable, is not easily hydrolyzed by water or mild alkalies. Suggested uses: solvent for rubber, synthetic rubber and other polymeric substances; high boiling non-flammable solvent; non-flammable heat transfer liquid; transformer fluid and hydraulic fluid.

HEXACHLORETHANE

Molecular weight	237
Chemical formula	C_2Cl_6
Melting point	186° C.
Boiling point	186° C.
Color	White crystals
Odor	Mild camphor-like

Insoluble in water, soluble in alcohol and carbon tetrachloride. Suggested uses: pyrotechnic compositions; insecticide; plasticizer and chlorinating agent.

HEXACHLORPROPYLENE

(Perchlorpropylene)

Molecular weight	249
Chemical formula	$CCl_3{-}CCl{=}CCl_2$
Boiling range	205 to 215° C.
Specific gravity	1.76 to 1.78 at 25°/15.5° C.
Color	Water white
Odor	Mild

Insoluble in water; miscible with alcohol, ether and chlorinated solvents. Suggested uses: solvent and plasticizer for rubber and other polymeric materials; non-flammable hydraulic fluid.

LAURYL CHLORIDE

(Dodecyl Chloride)

Molecular weight	213 (average)
Chemical formula	$C_{12}H_{25}Cl$ (approximate)
Specific gravity	0.8618 at 25°/15.5° C.
Color	Light yellow

Insoluble in water, soluble in organic solvents. Suggested uses: production of esters for plasticizers.

LAURYL MERCAPTAN

Molecular weight	211 (average)
Chemical formula	$C_{12}H_{25}SH$ (approximate)
Specific gravity	0.8420 at 25°/15.5° C.
Boiling range	125 to 225° at 15 mm.
Color	Water white

Insoluble in water, soluble in organic solvents. Suggested uses: catalyst in the production of copolymers such as Buna S.

METHYL PENTACHLOR STEARATE

Molecular weight	470 (approximate)
Chemical formula	$C_{17}H_{30}Cl_5COOCH_3$ (approximate)
Specific gravity	1.200 at 25°/15.5° C.
Color	Clear yellow to deep reddish brown

Insoluble in water, soluble in hydrocarbons. Suggested uses: plasticizer for polyvinyl chloride films to impart flexibility at low temperatures and to increase fire resistance; plasticizer for other film forming materials.

PELARGONYL CHLORIDE

Molecular weight	176.5
Chemical formula	$CH_3(CH_2)_7COCl$
Specific gravity	0.955 at 20°/15.5° C.
Boiling range	80–115° C. at 25 mm., 170–220° C. at 760 mm.
Color	Colorless to light yellow

Is hydrolyzed by water; reacts with alcohols to produce esters, soluble in ether. Suggested uses: intermediate to produce esters for plasticizers; to produce the peroxide for polymerization catalyst.

POLYCHLORPROPANE LIQUID

Molecular weight	268.3 (average)
Chemical formula	$C_3H_2Cl_6$ and C_3HCl_7
Boiling range	185° to 250° C.
Specific gravity	1.70 to 1.75 at 25°/15.5° C.
Color	Water white

Insoluble in water; miscible with alcohol, ether and chlorinated solvents. Viscous liquid at temperatures below −50° C. Suggested uses: plasticizer; dielectric wax; pyrotechnic compositions; lubricant to withstand chemical attack.

SODIUM TETRASULFIDE

Molecular weight	174
Chemical formula	Na_2S_4
Specific gravity (40% solution)	1.335 at 20°/15.5° C.
Color	Clear, deep red water solution

Suggested uses: soaking of hides and skins prior to unhairing; reduction organic nitro bodies; insecticide and fungicide for fruit tree spray; ore flotation reagent; reduction of cyanide plating baths; manufacture of sulfur dyes.

TETRA HYDRO FURFURYL OLEATE

Molecular weight	366.5
Chemical formula	$CH_3(CH_2)_7CH{:}CH(CH_2)_7COOCH_2OC_4H_7$
Specific gravity	0.926 at 15.5°/15.5° C.
Refractive index	1.4640
Color	Yellow to light brown

Insoluble in water; soluble in alcohols, esters, ketones, hydrocarbons, and chlorinated solvents. Suggested uses: plasticizer for polyvinyl chloride films to impart flexibility at low temperatures; plasticizer for other film-forming materials.

If additional information is desired, write our Dept. E12

KEEP ON BUYING WAR BONDS

HOOKER ELECTROCHEMICAL COMPANY

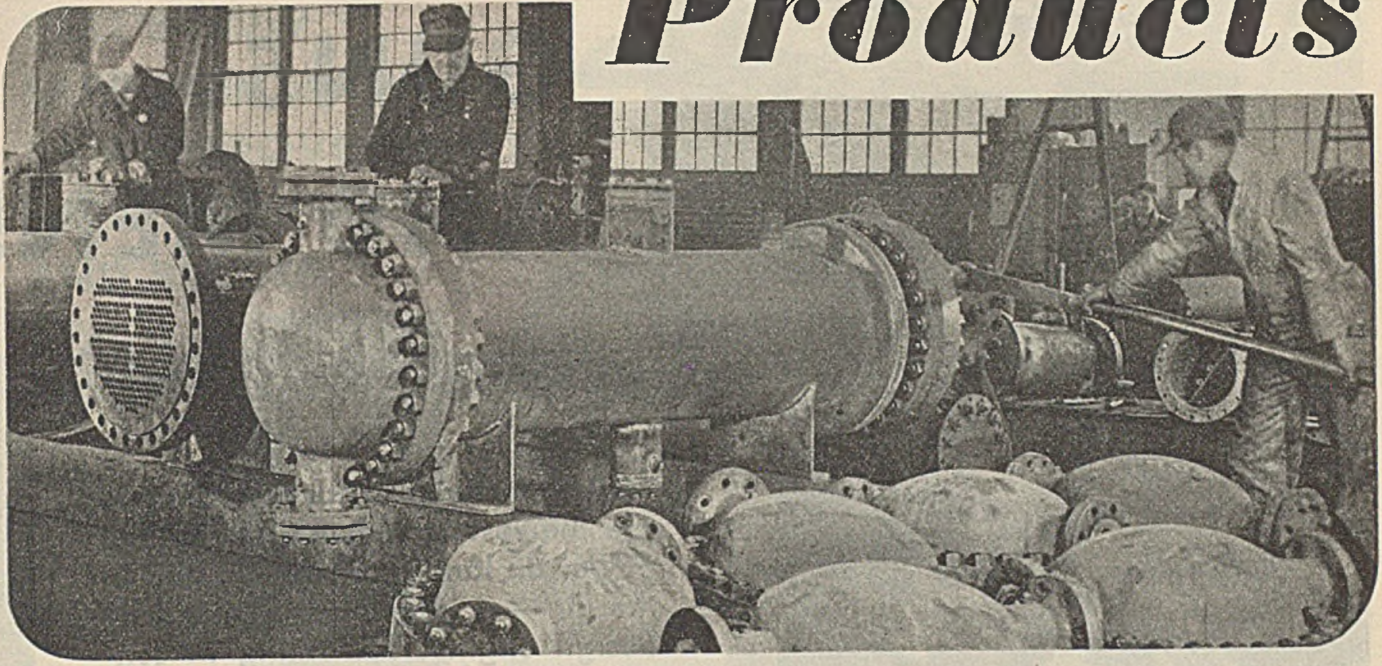
NIAGARA FALLS, N. Y.

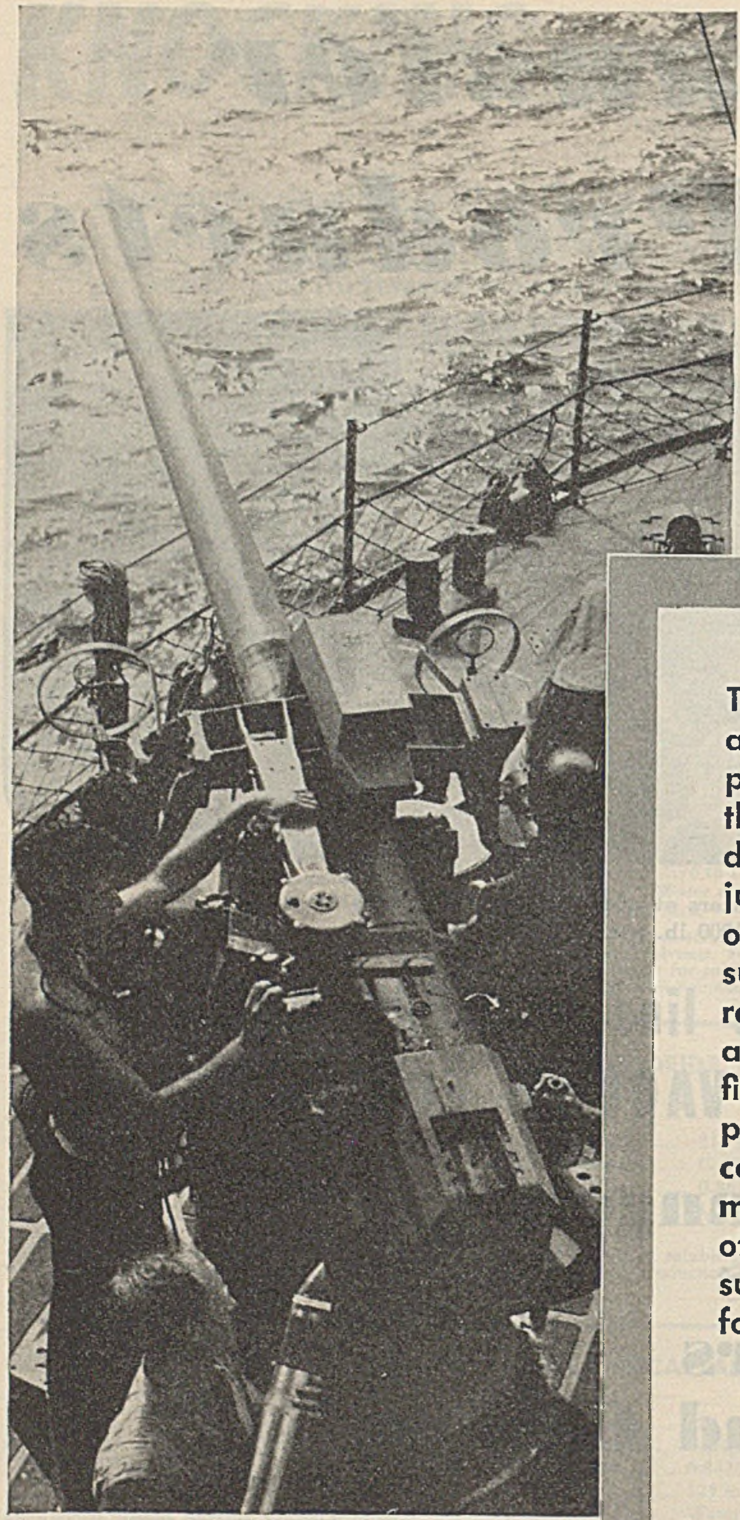
New York, N. Y. Tacoma, Wash. Wilmington, Calif.

ARMY E NAVY

HOOKER ELECTROCHEMICAL COMPANY

HOOKER CHEMICALS





Official Navy Photograph

GEARS... GUNS... AND MEN!

Today's victories of our armed forces are the result of their superior fire power on land and sea . . . and in the air — a superiority attained by design engineers working in conjunction with the army and navy ordnance departments. Victory and success depend on gun calibre and range . . . also its maneuverability and the clock-like precision of the firing mechanism . . . . D.O.James precision-made gears are important controlling factors in attaining the maximum fire power and efficiency of many of the guns now being so successfully used by our armed forces.

Accurately conforming to these design requirements has been an every-day "must" in our organization for over 55 years in the design, engineering and manufacture of all types of gears and gear speed reducers.

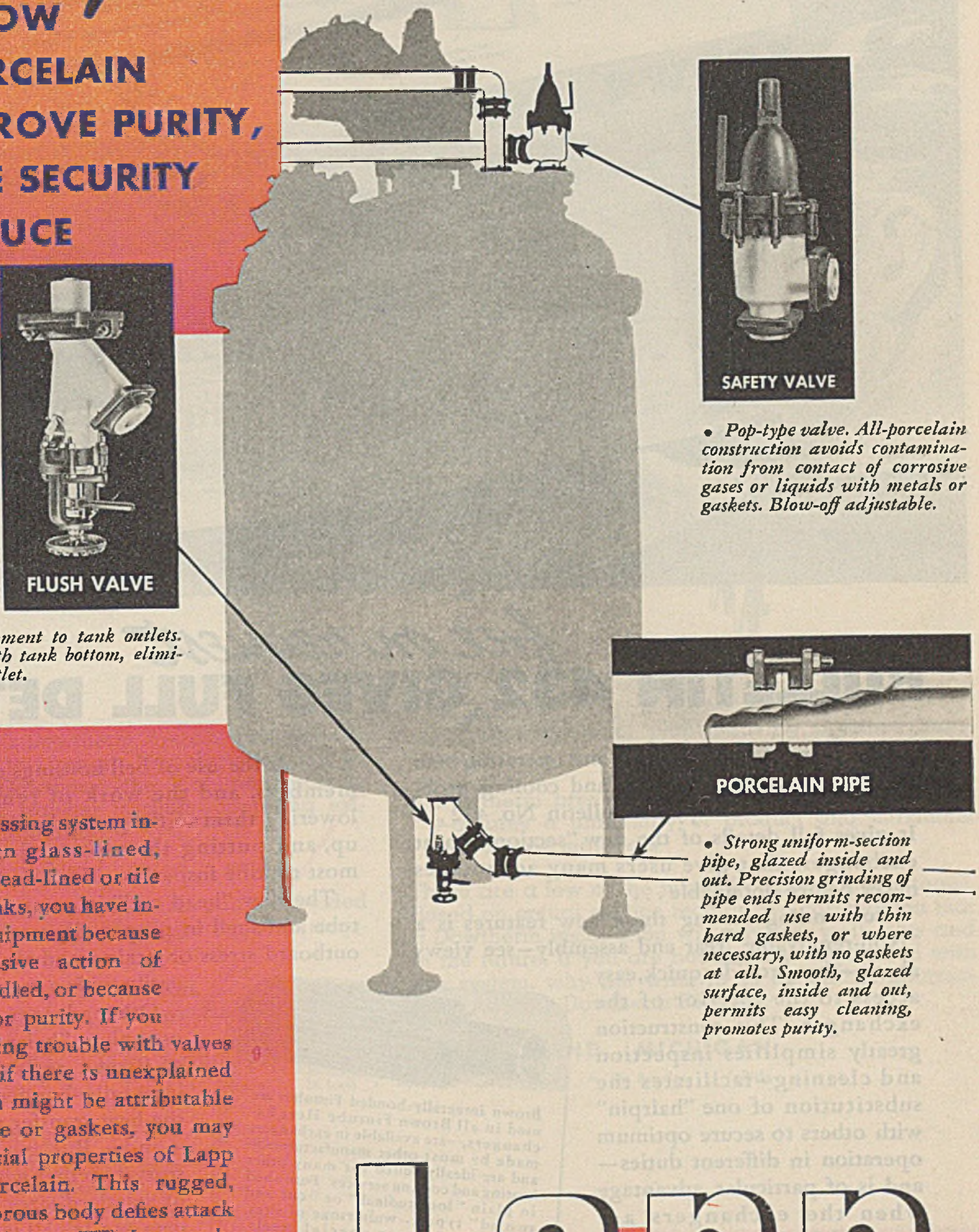
D.O.James

Established 1888

D.O. JAMES MANUFACTURING CO., 1140 W. MONROE STREET, CHICAGO, ILL.

Processing Corrosive Chemicals?

HERE'S HOW LAPP PORCELAIN CAN IMPROVE PURITY, INCREASE SECURITY AND REDUCE COSTS



- *Standard attachment to tank outlets. Poppet lines up with tank bottom, eliminating pocket at outlet.*

- *Pop-type valve. All-porcelain construction avoids contamination from contact of corrosive gases or liquids with metals or gaskets. Blow-off adjustable.*

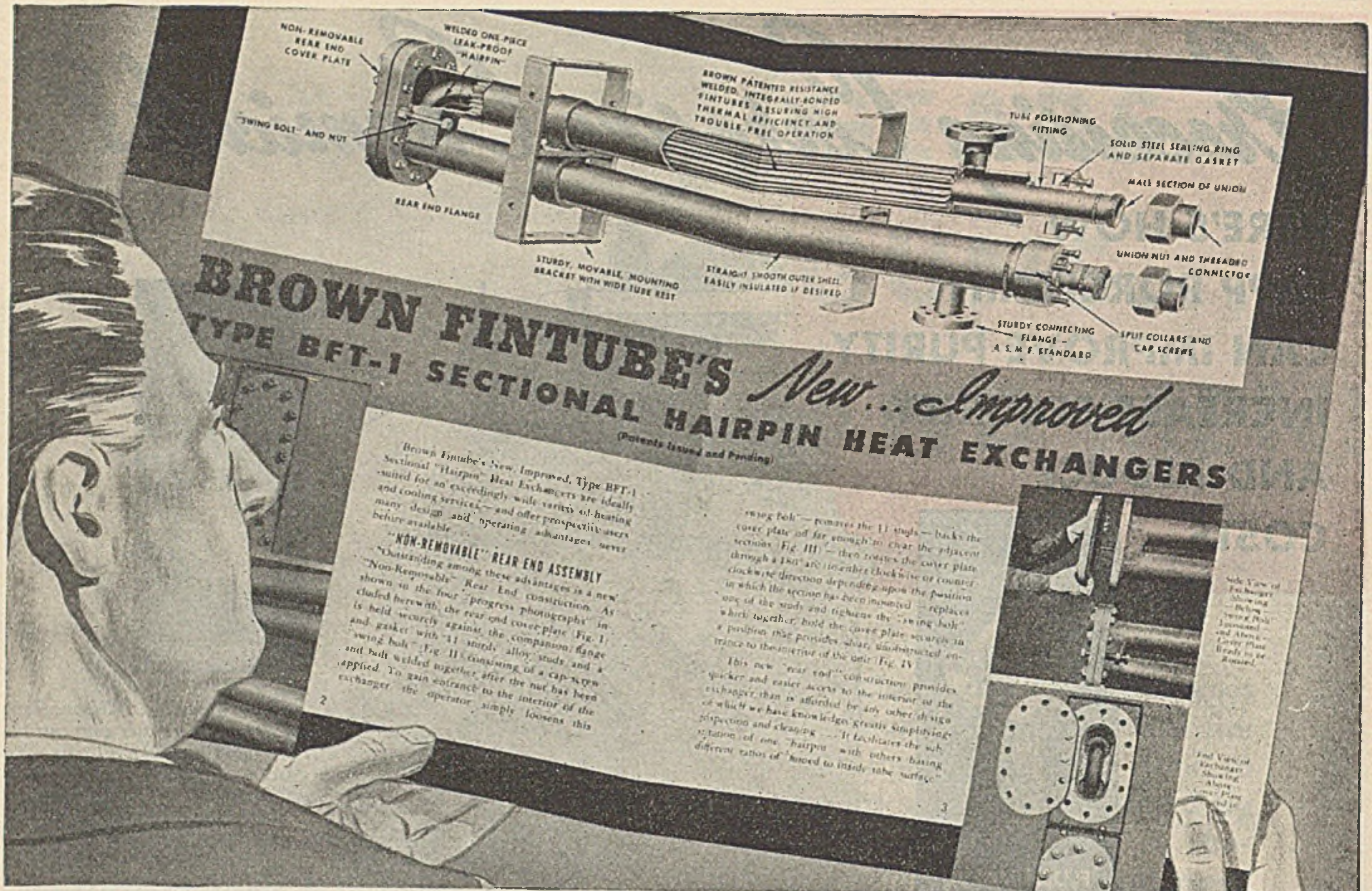
- *Strong uniform-section pipe, glazed inside and out. Precision grinding of pipe ends permits recommended use with thin hard gaskets, or where necessary, with no gaskets at all. Smooth, glazed surface, inside and out, permits easy cleaning, promotes purity.*

- If your processing system includes modern glass-lined, rubber-lined, lead-lined or tile processing tanks, you have installed this equipment because of the corrosive action of chemicals handled, or because of the need for purity. If you are experiencing trouble with valves or piping, or if there is unexplained trouble which might be attributable to valves, pipe or gaskets, you may need the special properties of Lapp Chemical Porcelain. This rugged, dense, non-porous body defies attack from any acid (except HF), is smooth, easily cleaned, and gives long, low-cost service. *Lapp Insulator Co., Inc., Chemical Porcelain Div., LeRoy, N.Y.*

ARMY E NAVY

Lapp

Chemical Porcelain



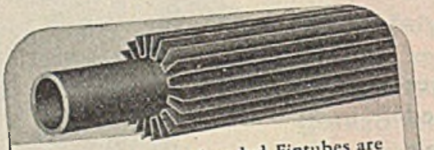
BULLETIN 432 ^free on request GIVES FULL DETAILS

● Engineers, works managers and operating men in all plants having heating and cooling problems, will want a copy of Bulletin No. 432... It gives full details of the new "sectional" heat exchangers that give users many advantages never before obtainable...

Outstanding among these new features is a "Non-removable" rear end assembly—see views above—that provides quick, easy access to the interior of the exchanger. This construction greatly simplifies inspection and cleaning—facilitates the substitution of one "hairpin" with others to secure optimum operation in different duties—and is of particular advantage when the exchangers are mounted high overhead, since it avoids the use of bell housings or other heavy members, and the work of removing these, lowering them to the ground, raising them back up, and putting them on again, for even the most routine inspection.

The new "head seal" is compact—holds the tube and shell in proper alignment—avoids any outboard stress or strain,—and can be assembled easily with a standard wrench.

Other advantages are welded one-piece "hairpins",—the use of Brown resistance-welded, integrally-bonded Fintubes as the heat transfer medium—and —and— But get the *complete* story, together with dimensions of standard sizes, performance data, etc. It's all in Bulletin 432. Send for a copy today!

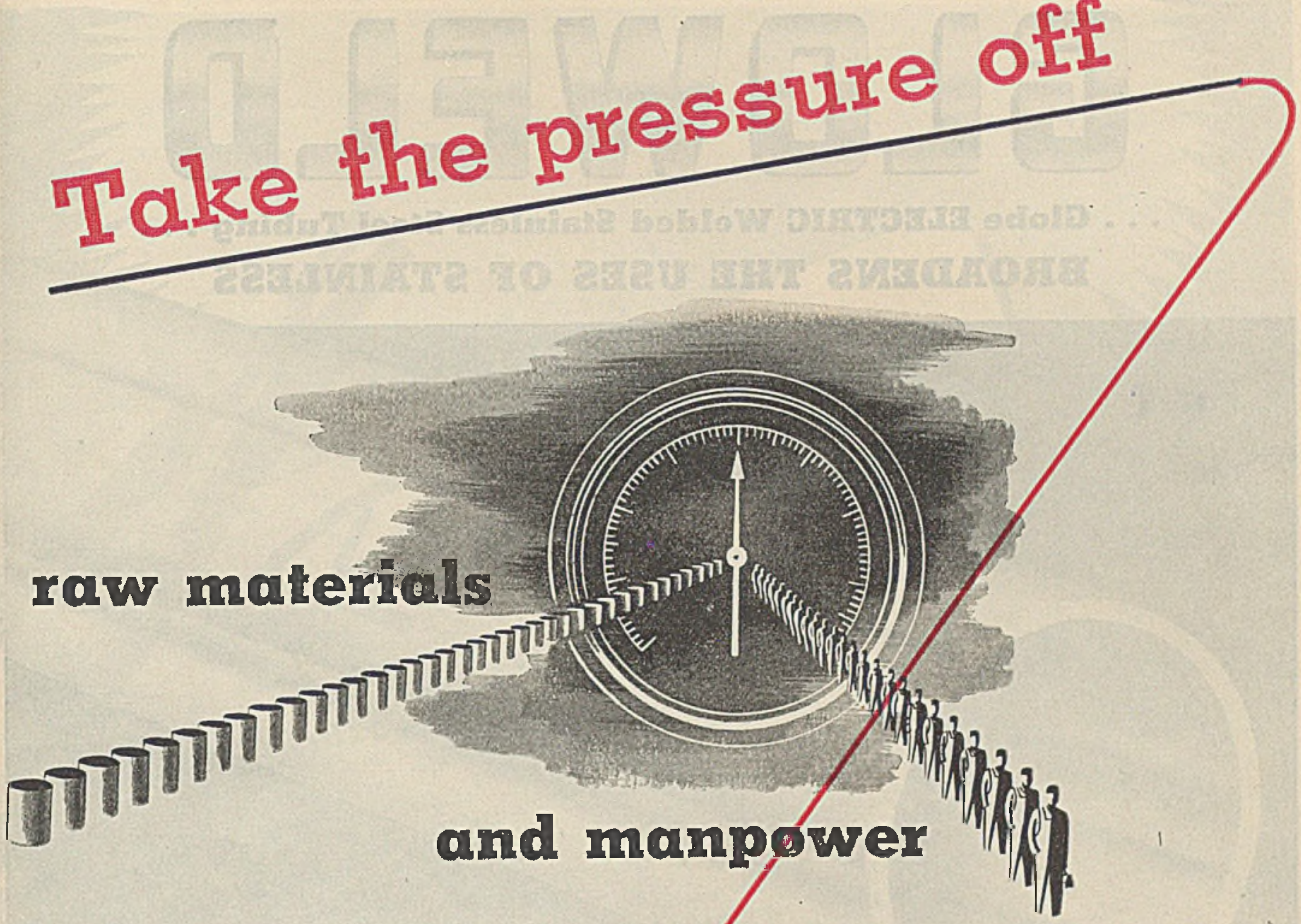


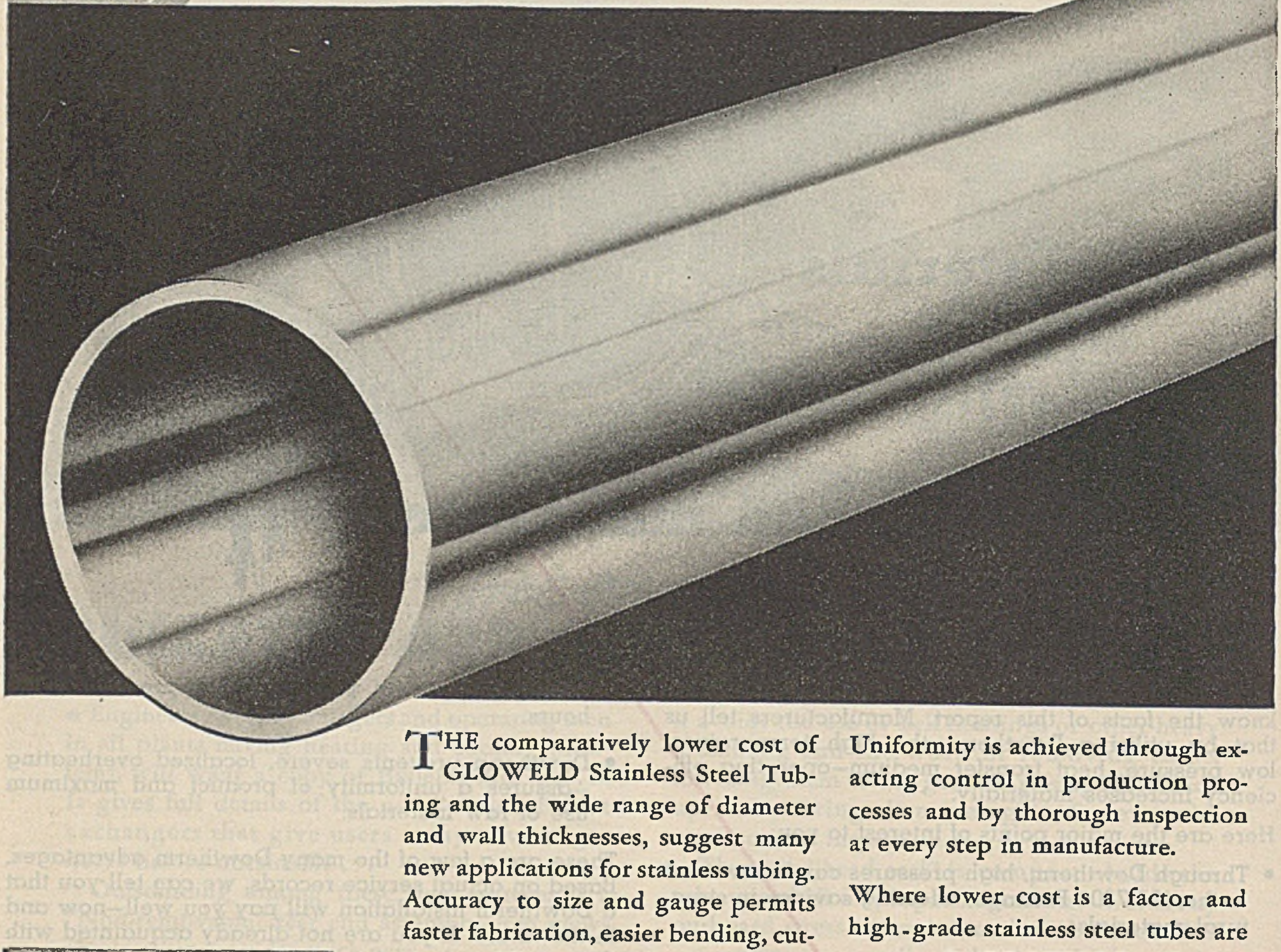
Brown integrally-bonded Fintubes are used in all Brown Fintube Heat Exchangers,—are available in exchangers made by most other manufacturers,—and are ideally suited for many other heating and cooling services. Furnished in plain "longitudinal" or "cut and twisted" types,—wide range of sizes, in low carbon or special steels. Design assistance furnished gladly.

THE BROWN FINTUBE CO.

120 FILBERT STREET • ELYRIA, OHIO

MANUFACTURERS OF INTEGRALLY BONDED FINTUBES AND FINTUBE HEAT EXCHANGERS


Take the pressure off
raw materials
and manpower



Photomicrograph of weld zone, showing grain structure of weld and parent metal.

Resoweld

A better lining than rubber for many jobs

ON many a tank-lining job where rubber would not be satisfactory, Goodyear's new resinous-base synthetic product — RESOWELD — will give ample and lasting protection.

Besides being resistant to all acid, alkali and salt solutions ordinarily handled by rubber, RESOWELD works where rubber would fail, with nitric and chromium acids, alcohol, petroleum oils, gasoline, linseed and vegetable oils, soaps and similar materials.

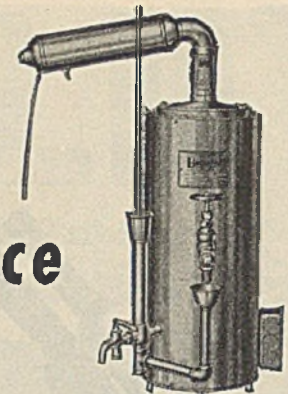
Other advantages: RESOWELD can be field applied to all types of metal, wood and concrete tanks by trained Goodyear workmen, whenever equipment cannot be shipped to or from our Akron factory. Pipe and fittings must be factory lined in all cases. RESOWELD withstands temperatures up to 150° F. It doesn't deteriorate with age, or crack under mechanical shock. And, since it is a less critical material than natural or reclaimed rubber, RESOWELD can be supplied, under war regulations, to plants having reasonable needs.

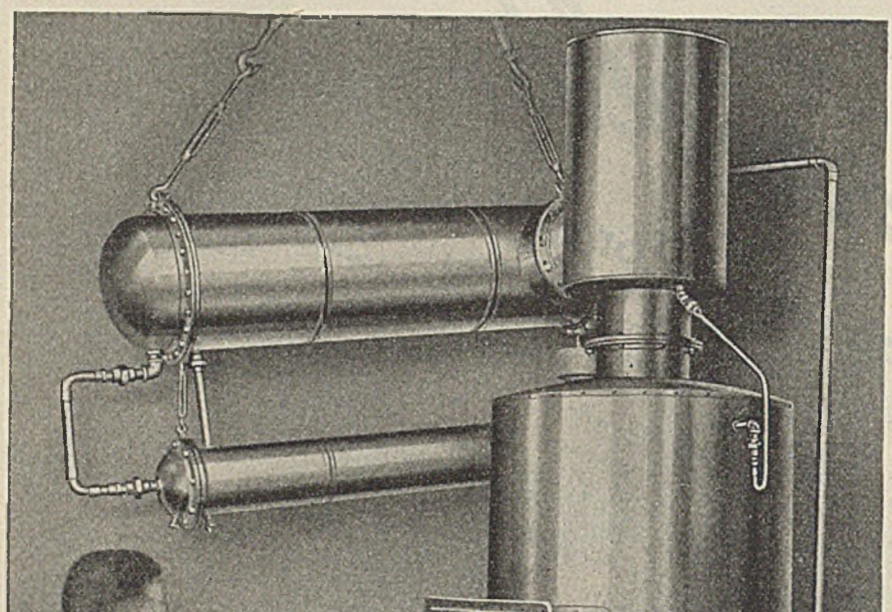
Resoweld—T.M. The Goodyear Tire & Rubber Company

BUY WAR BONDS to Speed Victory

For complete data on any corrosion-proofing job, consult the G.T.M.—Goodyear Technical Man. Or write Goodyear, Akron 16, Ohio or Los Angeles 54, California.

GOODYEAR
THE GREATEST NAME IN RUBBER



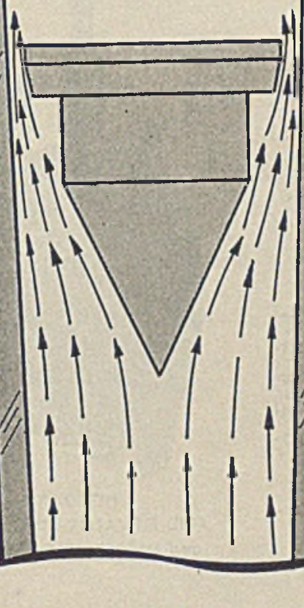


The ROTAMETER

—its basic advantages over head-type meters

8 BASIC ADVANTAGES

1. Metering elements and fluid being metered clearly visible
2. Wide flow range—20-to-1 easily obtained
3. Evenly spaced scale divisions—no compression of scale at low flows
4. Low, constant pressure drop—reduces pumping costs
5. New Stabl-Vis rotameter compensates for viscosity and density variations
6. 10″ to 24″ travel of metering float—accuracies correspondingly high
7. Instantaneous response to flow change—no friction or hysterisis
8. Measures corrosive gases, liquids and slurries that no other meter will handle accurately



EVENLY spaced scale divisions

The big advantage of the linear calibration of the rotameter is apparent when you are operating in the lower portion of its range. The scale divisions at low flows are just as far apart as at high flows. Low flow rates may therefore be set or read with the same high accuracy. This feature of the Rotameter, which makes it of such great help in controlling process flows closely, can be scientifically explained as follows:—

In Toricelli's fundamental flow equation, $Q=CA\sqrt{2gh}$, the area-type meter (rotameter) measures by varying the value of "A" (area of flow passage) whereas head-type meters (fixed orifices) vary the value of "h" (head). Thus, the rotameter "gets out from under the square root sign" which results in a linear calibration scale, instead of a square root scale with crowded divisions at the lower end. Consequently with the rotameter the same high accuracy of reading or of setting the flow rate may be obtained over the entire flow range.

The rotameter's straight line calibration curve is but one of its many advantages as a flow rate instrument. These advantages are rapidly causing instrument and operating engineers to replace fixed orifice meters by the rotameter in many important metering applications. The full details are told in a comprehensive and highly interesting booklet just printed, entitled "A New Era in Flow Rate Measurement." Large illustrations and a modern cartoon style make it easy and instructive reading. We will gladly send you this pamphlet without obligation—write us if you wish a free copy.

FISCHER & PORTER PRODUCT INFORMATION

For hazardous flow rate services . . .

The Magna-Bond Recorder-Controller!

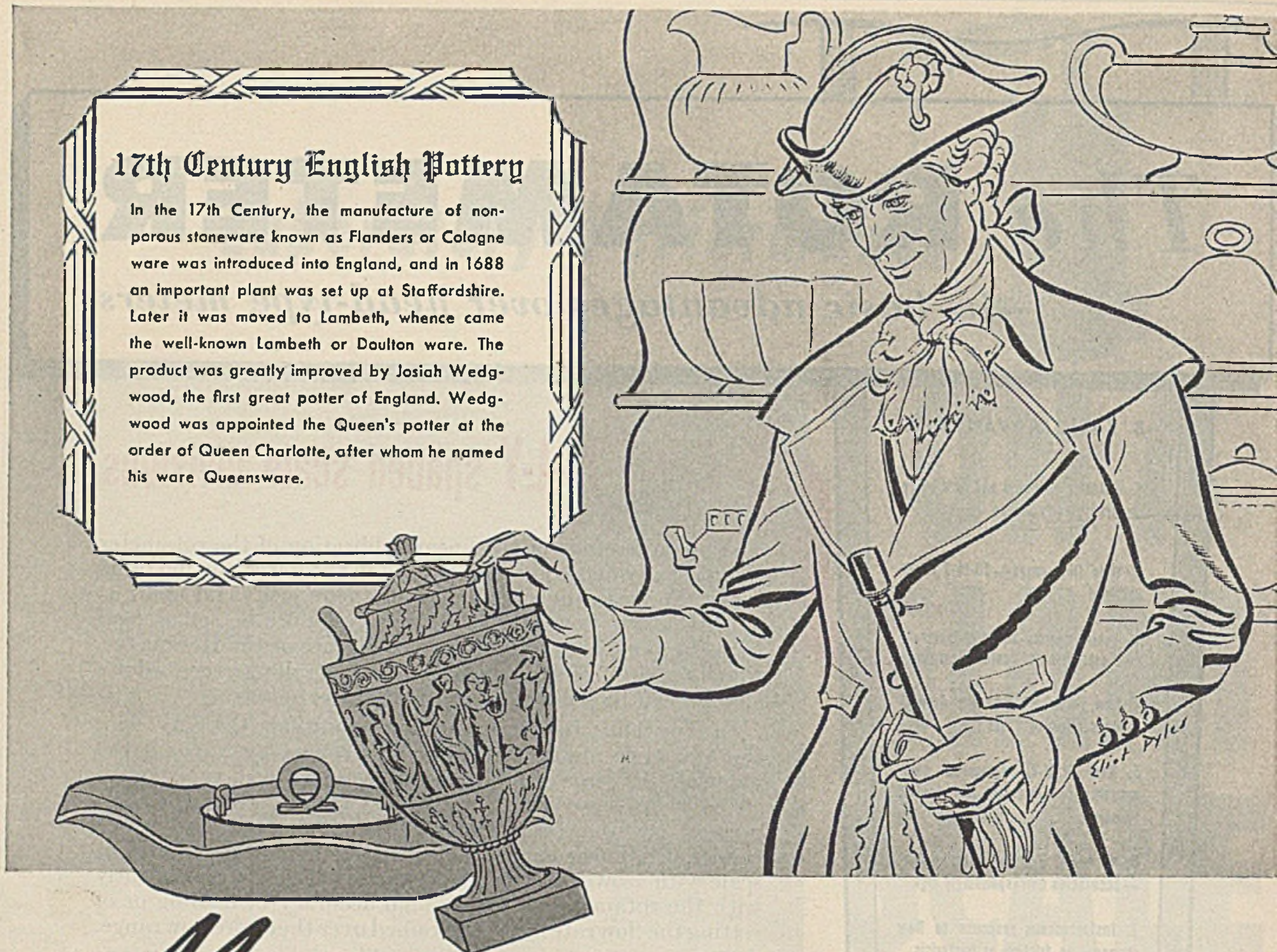
Where high pressure, or explosive or inflammable materials make it dangerous to use an electrical flow rate recorder or controller, the Fischer & Porter Magna-Bond Rotameter is the perfect answer. The meter is completely metal-enclosed and the position of the rotameter float is indicated externally by a magnetic clutch. With a spring-wound clock to drive the chart, there are no electrical connections required to obtain a recording or recording-controlling flow rate rotameter. The details of this remarkable new development are given in our bulletin 50-A. We will gladly send you a copy if you will write for it.

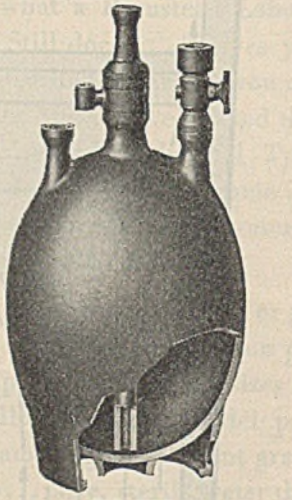
You will be able to see our latest developments at BOOTH 304-306—CHEM. SHOW, NEW YORK—DEC. 6 to 11.

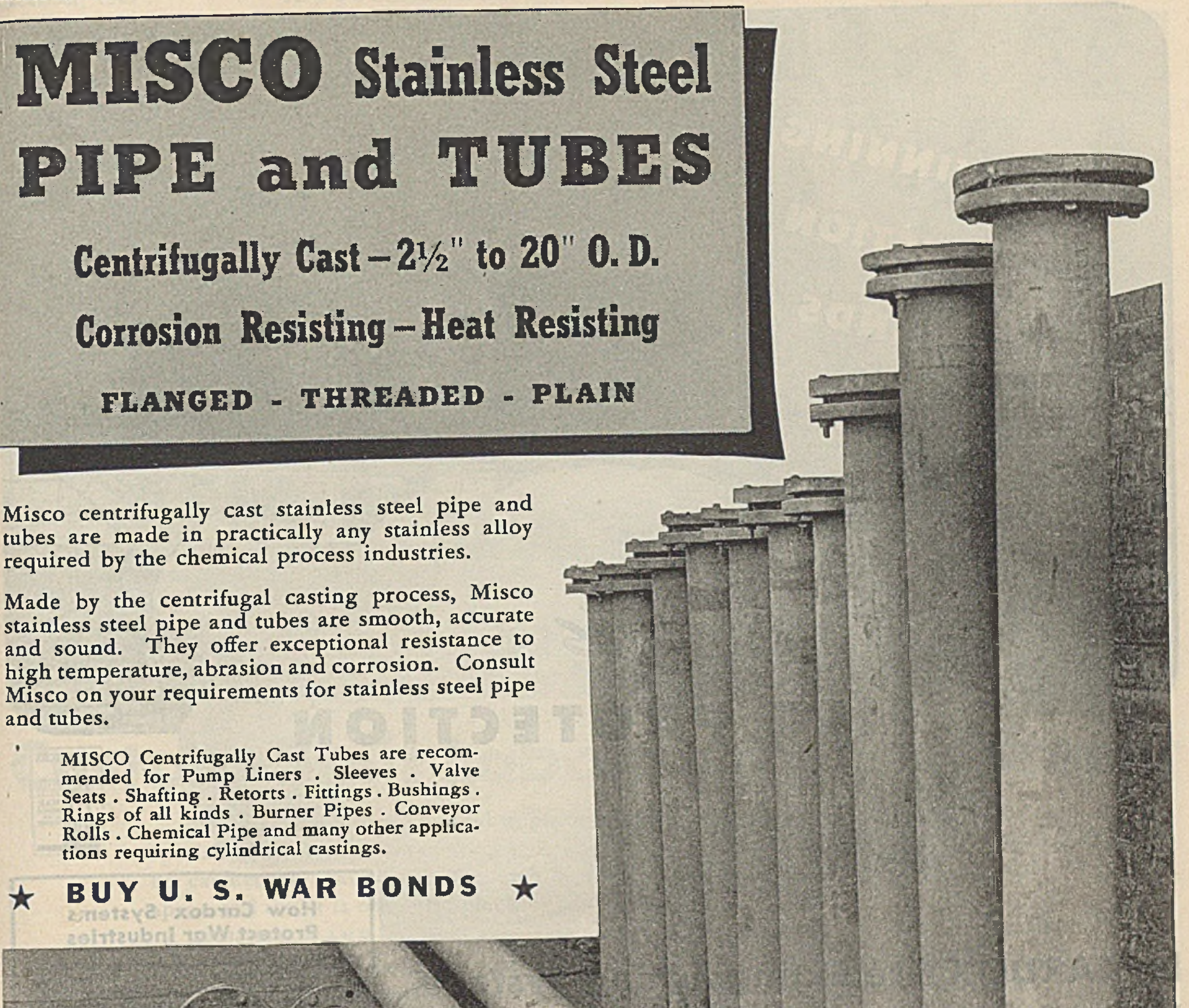
FISCHER & PORTER CO.

712 COUNTY LINE ROAD, HATBORO, PA.

RATE OF FLOW INDICATING, RECORDING OR CONTROLLING ROTAMETERS FOR ANY LIQUID OR GAS


Eliot Dyles





by CARDOX Fire Extinguishing Systems

More war goods from fewer man-hours is one of America's most urgent needs today! Every hour saved here is another step toward victory.

One major fire—or a small fire that results in crippling damage by the extinguishing medium—can cut the flow of vital war goods to a trickle over night. Such fires may halt or slow down production on a dozen different types of essential fighting tools . . . waste precious man-hours and critical materials.

Cardox Fire Extinguishing Systems provide distinctive advantages in protecting production against these war-prolonging fires. They smother the fire and "cool out" combustibles through timed mass discharges of *pounds* or *tons* of CO_2 . . . with no damage by the extinguishing medium. Consequently, when fire strikes, men and machines are usually back in production quickly. Losses of vital materials are reduced to a minimum.

Industries guarding War-Winning Production with engineered Cardox Fire Extinguishing Systems include leading manufacturers of *Airplanes, Airplane Parts, Armor Plate, Aviation Carburetors, Aviation Engines, Cold Strip Steel, Electric Power, Engine Parts, Forgings, Motor Fuel, Plastics, Processed Fabric, Rubber Products, Solvents, Tanks, Tank Engines.*

Today, the facilities of Cardox are concentrated on two activities: (1) Providing fire protection for War-Winning Production; (2) Applying the technological knowledge gained here to help industrial, municipal, state and national fire fighting organizations perfect plans to increase the efficiency of fire protection both today and after the war.

If more information would help—in solving your fire protection problems of today or tomorrow—write on your company letterhead for Bulletin 20123.

★ ★ ★

CARDOX CORPORATION
BELL BUILDING • CHICAGO 1, ILLINOIS

District Offices in New York • Washington
Detroit • Cleveland • Atlanta • Pittsburgh
San Francisco • Los Angeles • Seattle

How Cardox Systems Protect War Industries

- Timed discharges, as needed, through built-in piping systems . . . supplied instantly from a single storage unit holding tons (if required) of liquid Cardox CO_2.
- Mass discharge of Cardox CO_2 "knocks out" fire, by . . .
- Reducing oxygen content of the atmosphere below the concentration necessary for combustion, and . . .
- Cooling combustibles and fire zone below ignition temperature . . .
- Extinguishing fire quickly and completely *without* damage from extinguishing medium.

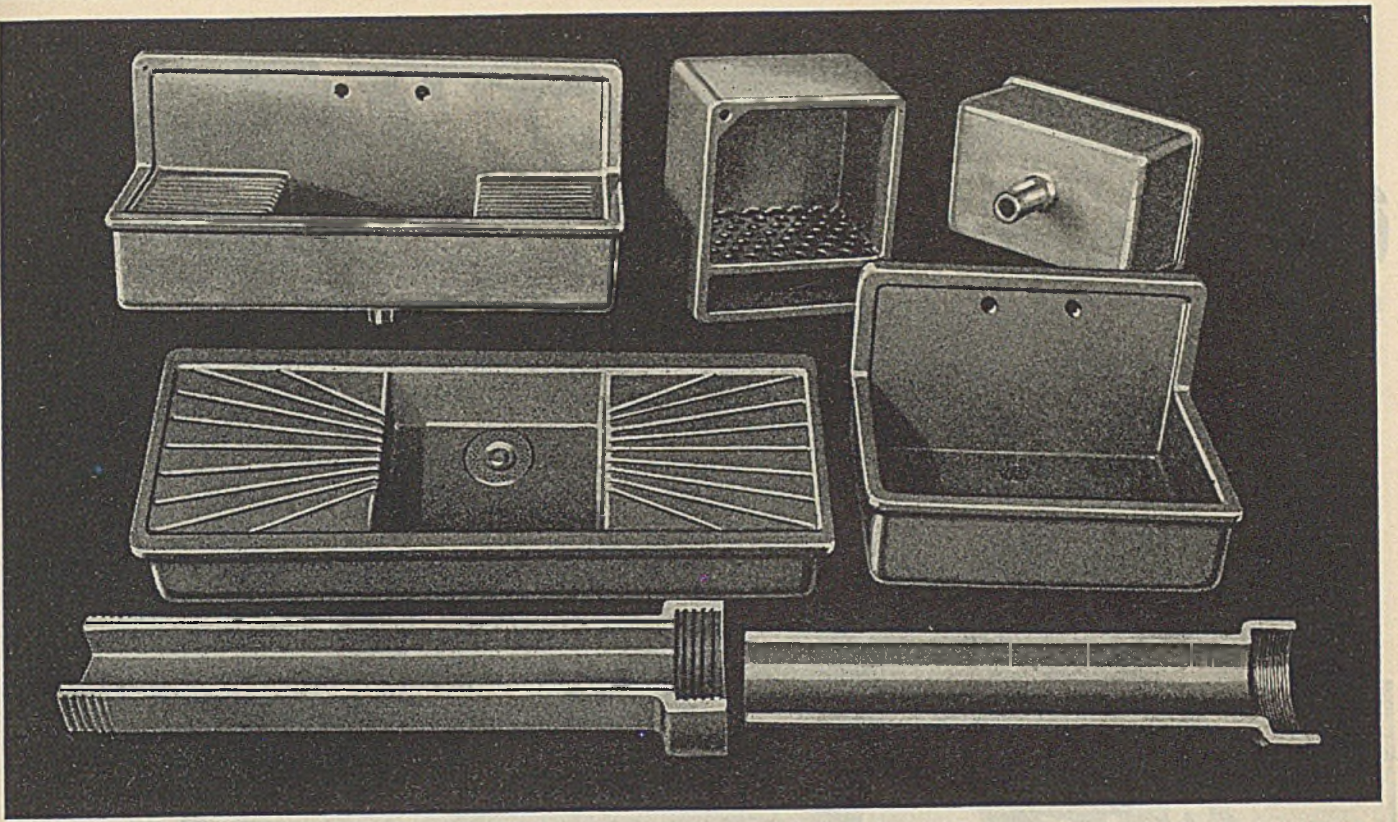
CARDOX—CO_2 Systems with Enhanced Fire Extinguishing Performance

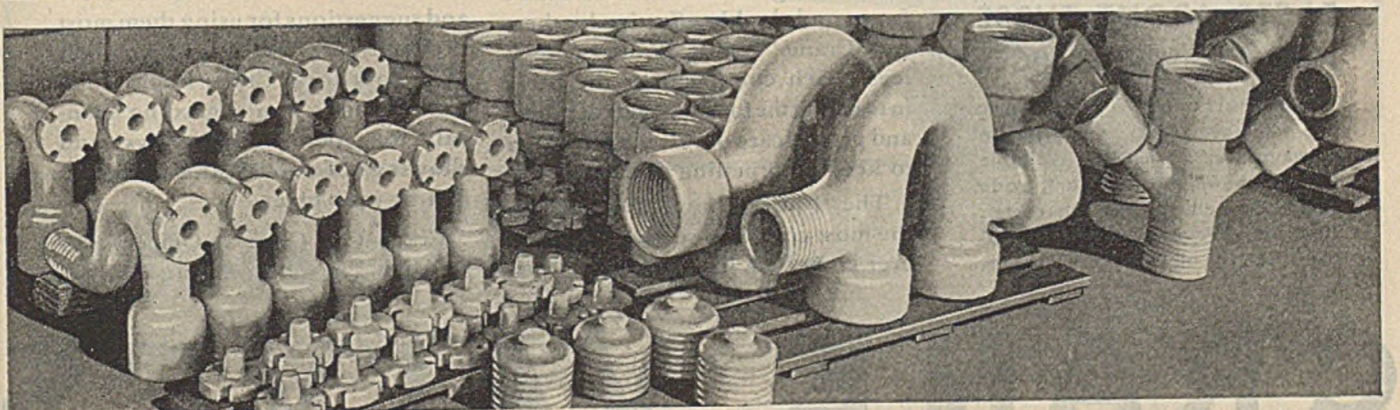
A. Uniformity of CO_2 characteristics.
B. Extinguishing medium with uniformly greater cooling effect.
C. Accurate projection of CO_2 through greater distances.
D. Timed discharges, as needed, through built-in piping systems . . . supplied quickly from a single tank holding tons of liquid Cardox CO_2.

MASS DISCHARGE OF CO_2 · ENHANCED COOLING EFFECT · CENTRAL STORAGE UNIT · AMPLE CO_2 RESERVE · ENGINEERED SYSTEMS · MANUAL OR AUTOMATIC CONTROL

CARDOX

NON-DAMAGING FIRE EXTINGUISHING SYSTEMS





Ready Now!

NEW TRAINING AIDS FOR PIPING MEN

❶ "PIPING POINTERS" SOUND FILM

❷ "PIPING POINTERS" MANUAL

FACTS ABOUT THESE NEW CRANE SERVICES

The "Piping Pointers" film is 16 mm. size with sound track. Approximate showing time, 30 minutes. Available free for showing in any plant, trade school, or industrial training center. The "Piping Pointers" manual is supplied free for all viewers of the film.

ARE your piping maintenance trainees learning fast enough to replace skilled men gone to war? Can they assure your plant of dependable piping service while replacement materials are far from plentiful?

Training of workers is made faster and doubly effective by these new Crane "Piping Pointers" services. Each complements the other in teaching the fundamentals of piping and proper care of valves and fittings to keep up pipe-line efficiency.

The "Piping Pointers" Manual is the most complete service of its type ever compiled, its chapters ranging from "The Language of Piping" to "Playing Safe on the Job." In the film, trainees see and hear how the manual's content is actually applied.

Available Free to Any Plant

Full information about these services and suggestions for using them most profitably are available on request from your local Crane Representative. Consult him regarding manuals for your piping crews, and showings of the "Piping Pointers" film in your plant.

Crane Co., General Offices: 836 S. Michigan Ave., Chicago 5, Ill.

CRANE VALVES

THE ROSS TWIN BANK CONDENSER DESIGN *has become a general trend*

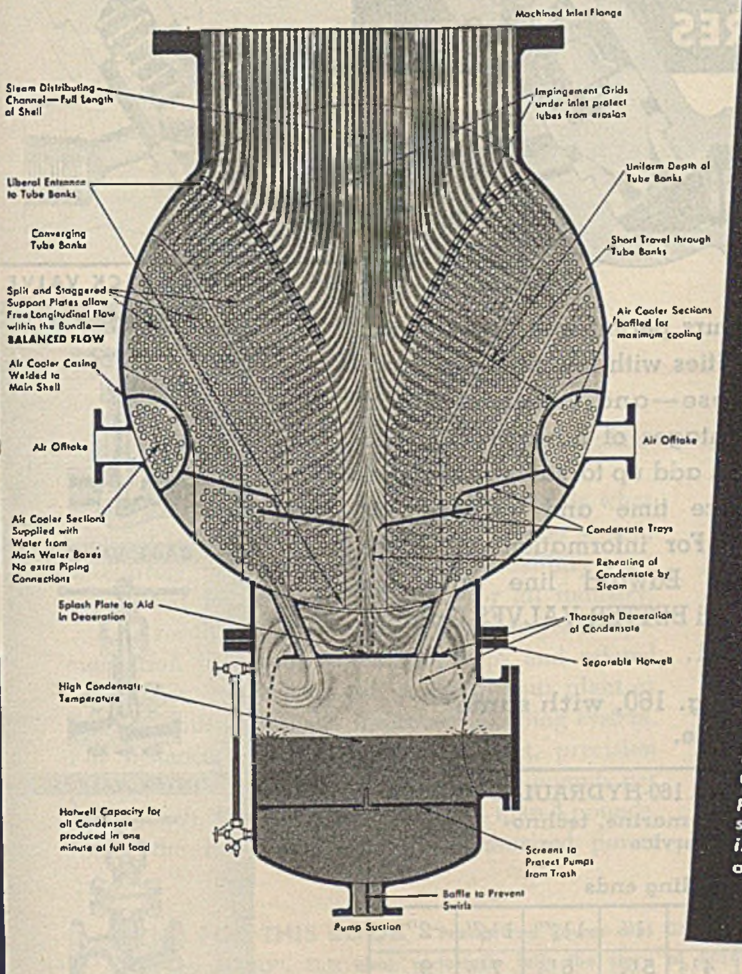
There is a definite trend towards divided tube bank layout in Surface Condensers. More and more condenser manufacturers are using it. Today most of the leaders are producing this design.

But, this divided bank idea is nothing new to Ross. Many years ago, Ross engineers started working on it — doing exhaustive research, building units, making performance tests and numerous trial installations. Soon the layout became standard with Ross.

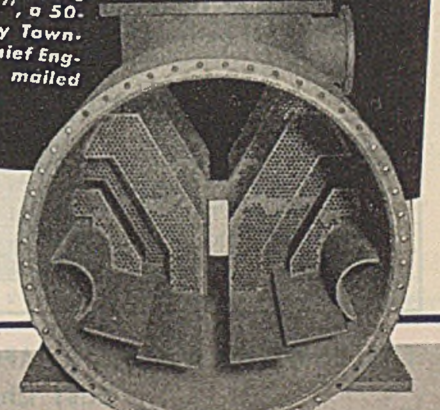
The first broad disclosure of this type of tube layout was made in a paper* presented by the chief engineer of Ross Heater & Mfg. Co. before the American Society of Mechanical Engineers in 1933.

So Ross points with pride to another "First" in Surface Condenser engineering and fabrication, which holds a position of great importance alongside all-welded steel construction—also a Ross innovation.

★ *"Surface Condenser Design and Operating Characteristics", a 50-page paper by Townsend Tinker, Chief Engineer of Ross, mailed on request.*



TYPICAL ROSS TUBE BUNDLE
In Cross Section, showing Steam Distributing Features.



INTERNAL ARRANGEMENT
Divided and Offset Tube Support Plates, Condensate Trays and Air Cooler Shells.

ROSS HEATER & MFG. CO., Inc.
Division of AMERICAN Radiator and "Standard" Sanitary Corporation

GENERAL OFFICES AND PLANT · 1423 WEST AVENUE · BUFFALO 13, N. Y.

EDWARD 6000 LB HYDRAULIC VALVES

FIG. 158 GLOBE

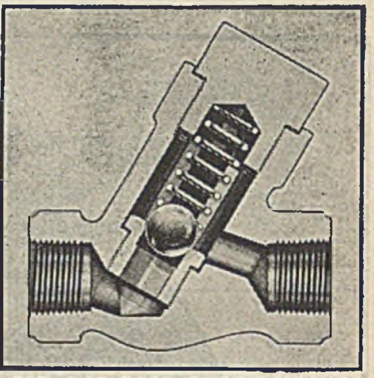


FIG. 160 BALL CHECK VALVE

THOUSANDS of excessive pressure systems operating under 300 F depend on Edward Fig. 158 globe hydraulic valves for fast, certain shut-off or accurate pressure control.

The seat and swivel needle disk are made of EValloy, Edward's own development in abrasion resisting stainless steel. The inside screw construction, the extra deep stuffing box and the special gland and packing nut design lengthen packing life and prevent leakage along the stem. Streamlined body contours permit free flow at high velocities with low pressure drop.

These—and other—specific advantages of Edward Fig. 158 valves add up to savings in maintenance time and replacement parts. For information on valves in the Edward line write for Edward BETTER VALVES Catalog No. 101.

Corresponding ball check valves, Fig. 160, with same ratings, also available.

DIMENSIONAL DETAILS OF EDWARD Fig. 158 and 160 HYDRAULIC VALVES
For power, petroleum, chemical process, marine, technological or general industrial service
Rating 6000 lb at 125 F
Globe type, screwed or socket welding ends

SIZE	¼″	⅜″	½″	¾″	1″	1¼″	1½″	2″
End to End, Fig. 158 and 160	3¾	3¾	3¾	4½	5⅛	6½	7½	9
Center to Top Open, Fig. 158	8¼	8¼	8¼	9¼	10⅞	13¾	14⅞	18
Handwheel Diameter, Fig. 158	5⅜	5⅜	5⅜	6⅜	8½	10⅛	10⅛	11½
Weight—lbs, Fig. 158	3¼	3¼	4¾	7	12	22	37	62
Weight—lbs, Fig. 160	1½	1½	2¾	4½	7¼	13½	19¾	40

THE EDWARD VALVE & MFG. CO., INC., 1210 W. 144th Street
East Chicago, Indiana

OTHER *Stop* VALVES

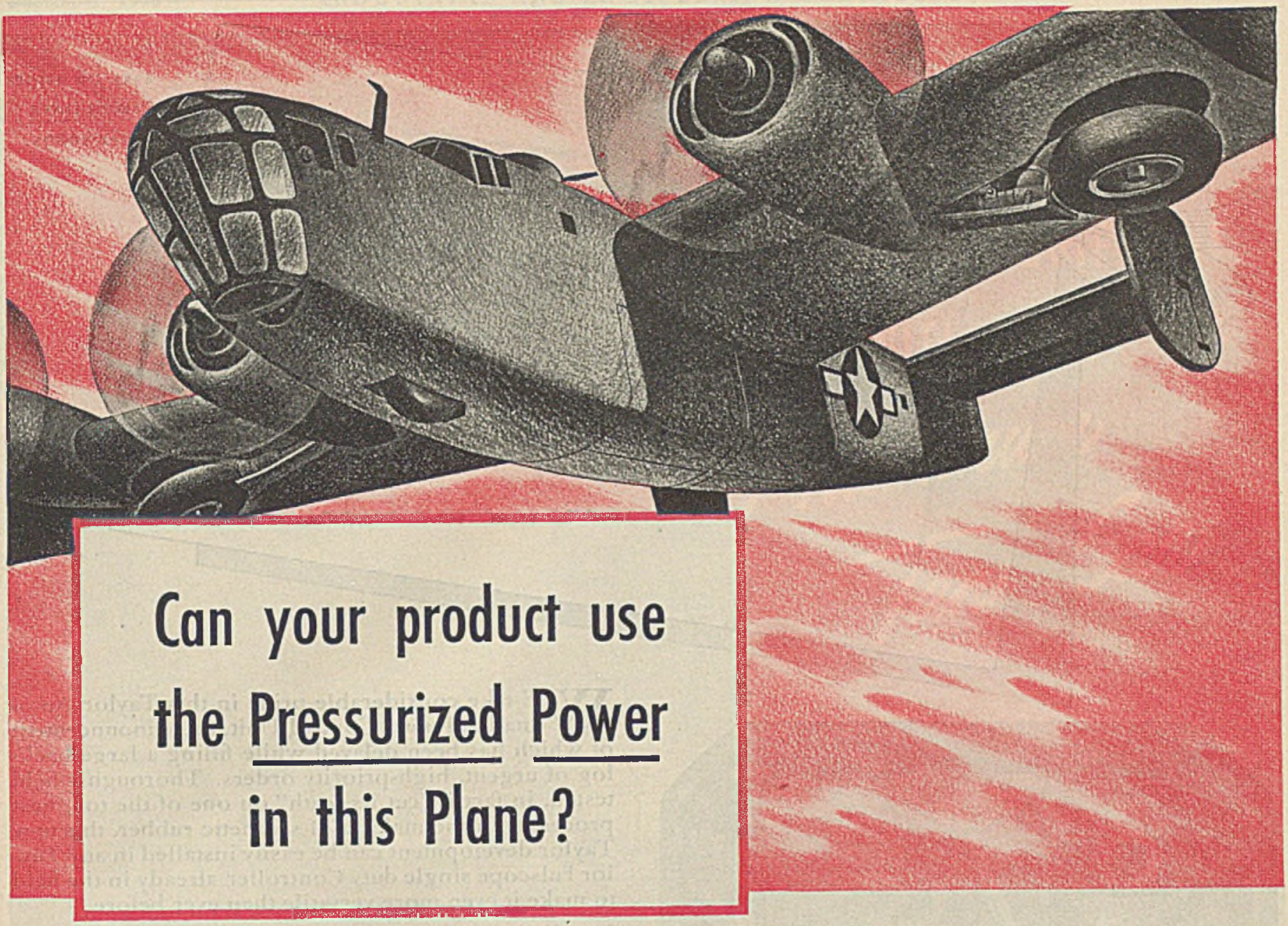
GAGE VALVES

INTEX VALVES

GLOBE VALVES

ANGLE VALVES

EDWARD *Steel* VALVES



Can your product use the Pressurized Power in this Plane?

★Have you ever watched a bomber fold its giant landing wheels into its wings?

The pressurized power that does this job is what we want to sell you. It is a hydraulic power system of entirely new efficiency and dependability . . . engineered for aircraft, available for all industry.

As a result of PESCO's more than ten years' specialization in making aviation pumps and related accessories, you will be able to equip your plant or product with a radically improved pumping system. For instance, you can have a compact, precision pump that delivers pressures up to 3000 pounds per square inch. This pump, weighing less than 4 pounds, forms the heart of a PESCO pressurized power system with endless uses in industry for transmitting or controlling power.

In addition to hydraulic pumps, PESCO builds pneumatic, vacuum and fuel pumps of equally high efficiencies, meeting practically all needs for pressurized power or controlled liquid flow.

The performance of PESCO equipment in your plant or product . . . its greater efficiency, dependability, and longer years of service . . . is assured by the fact that it has been engineered to operate under flying conditions which are far more extreme and demanding than any encountered down on earth. Won't you let us tell you more about PESCO Pumps and PESCO Engineering Service?

SEND FOR THIS BOOK "Pressurized Power and Controlled Flow by PESCO". This book pictorially tells the story of PESCO equipment, manufacturing facilities and engineering service. A copy will be mailed promptly upon request.

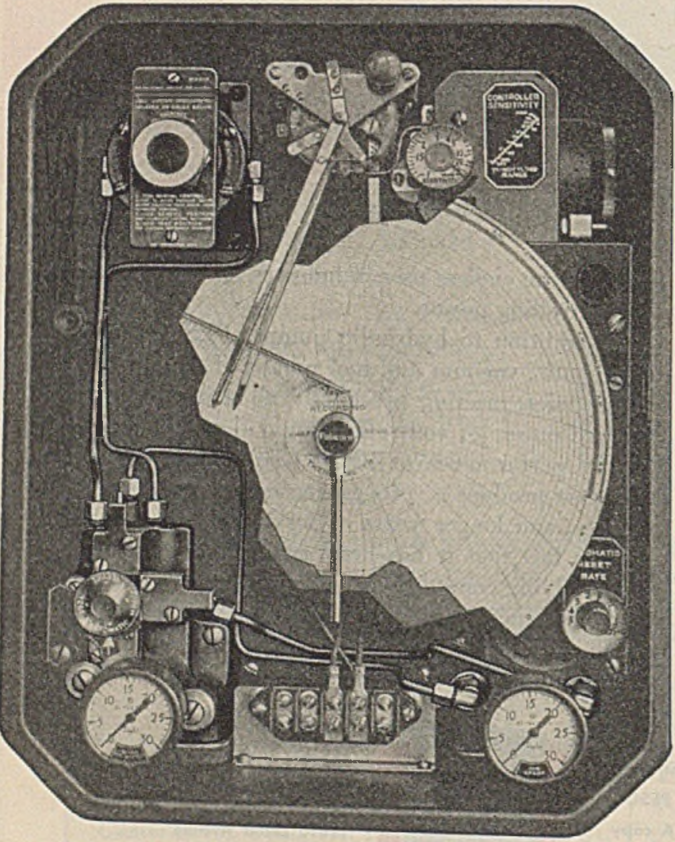
WRITE TO . . .
PESCO Products Co.
Industry Service E
11610 Euclid Avenue
Cleveland 6, Ohio

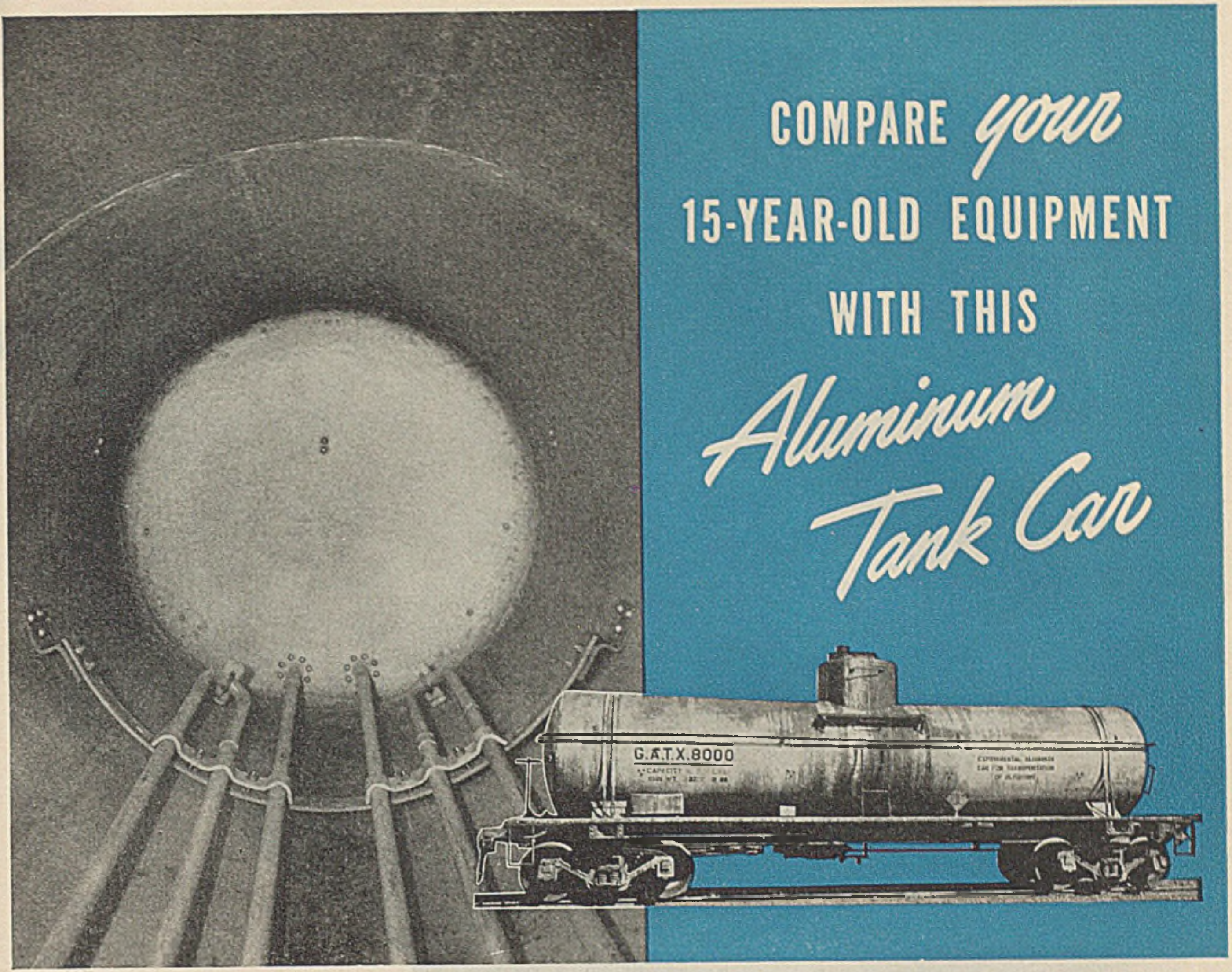
Division Borg-Warner

In Precision Hydraulics, Fuel Pumps, Air Pumps, Related Accessories . . .

PERFORMANCE POINTS TO Pesco FIRST


Taylor announces a new Baby!




COMPARE *your*
15-YEAR-OLD EQUIPMENT
WITH THIS
Aluminum
Tank Car
G.A.T.X. 8000

This is Synthetic Rubber

If America now has only a mere "handful" of natural rubber, it doesn't matter so much because synthetic rubber production is well on its way.

Pictured here is a handful of just one of the five basic commercial types of synthetic rubber—basic materials that are being turned into all of the things for which we used to rely on natural rubber.

Like natural rubber, the synthetic rubbers lend themselves to a great variety of processing treatments. Each type has distinct properties and characteristics that fit it for specific tasks.

For instance, one synthetic rubber, when treated a certain way, can be fabricated into the remarkable bullet-sealing hose which has so vastly increased the safety of our fighter plane and bomber crews . . . a different type, differently processed, may be the one that will produce rotary drilling hose for oil fields, or the compressed air hose for manufacturing plants.

Still other types of synthetic rubber may go into transmission or conveyor belts, mechanical packings, or any of the innumerable other mechanical rubber goods that serve on our battle fronts and in our war industries today.

You need not worry about *this* type of synthetic rubber or *that* one. Your great good fortune is that they will be available—at hand for skilled and experienced hands to transform as needed into what is needed.

Since 1921 the United States Rubber Company has been experimenting with and developing the possibilities of synthetic rubber . . . has been in practical production of synthetic rubber products since 1931.

Listen to the Philharmonic Symphony program over the CBS Network Sunday afternoon, 3:00 to 4:30 E.W.T. Carl Van Doren and a guest star present an interlude of historical significance.

1230 Sixth Ave., Rockefeller Center, New York 20

UNITED STATES RUBBER COMPANY

The portable extinguisher 80 feet long!

No, not the container...that's a handy unit only 7 inches in diameter by 27½ inches high. But the carbon dioxide it contains, stored under high pressure, expands 450 times in volume when it's released. That's enough of the fire-smothering gas to fill a cylinder 80 feet long by 2 feet in diameter! And that's why this Kidde product is one of the fastest fire-fighters known.

Walter Kidde & Company has prepared a booklet, "How to Teach Fire Fighting." It describes the various classes of fire, tells how to fight each of them. It explains why the most modern extinguisher can actually be a dangerous fire hazard, if it's used against the wrong fire! Write for your copy—it's free.

Kidde

WALTER KIDDE & COMPANY, INC., 1230 MAIN STREET, BELLEVILLE, N. J.

The Case of Product #3

ANOTHER DRYING PROBLEM SOLVED BY PROCTOR RESEARCH SPECIALISTS

Back in the early days of this war, one of America's largest chemical companies was confronted with the drying of an entirely new product. This product, a high explosive, they referred to simply as "Product #3".

Almost immediately, the complex problem of finding the correct way to dry this product was turned over to the Research Laboratory of Proctor & Schwartz, Inc. Delivered to the conveyor of the dryer from a continuous filter, Product #3 presented more than the usual number of difficulties. Our research men went to work, tests were made and the product observed. The mass of material as delivered from a rotary vacuum filter to the conveyor of a dryer would not permit uniform and quick drying. Preforming of this mass was accomplished by incorporating certain features of design in the dewatering equipment, as recommended by our research engineers. Further tests were made on preformed material and data secured. On the basis of this data three single conveyor dryers were designed and built. Upon completion, the machines were installed in the chemical company's plant under the direction of a Proctor & Schwartz engineer. He stayed on the job until the performance of the dryers was a proven fact.

This case history is just one of many taken from our files. It illustrates just how Proctor research works for you. Whether you have a new product to dry; a regular product that you want to dry more efficiently; or a wartime substitute that presents a different drying problem from your regular peace-time product, PROCTOR & SCHWARTZ Research Engineers are ready, willing and able to help you. Early consideration of your drying problem may well repay you in attaining the best possible type of process equipment and plant design.

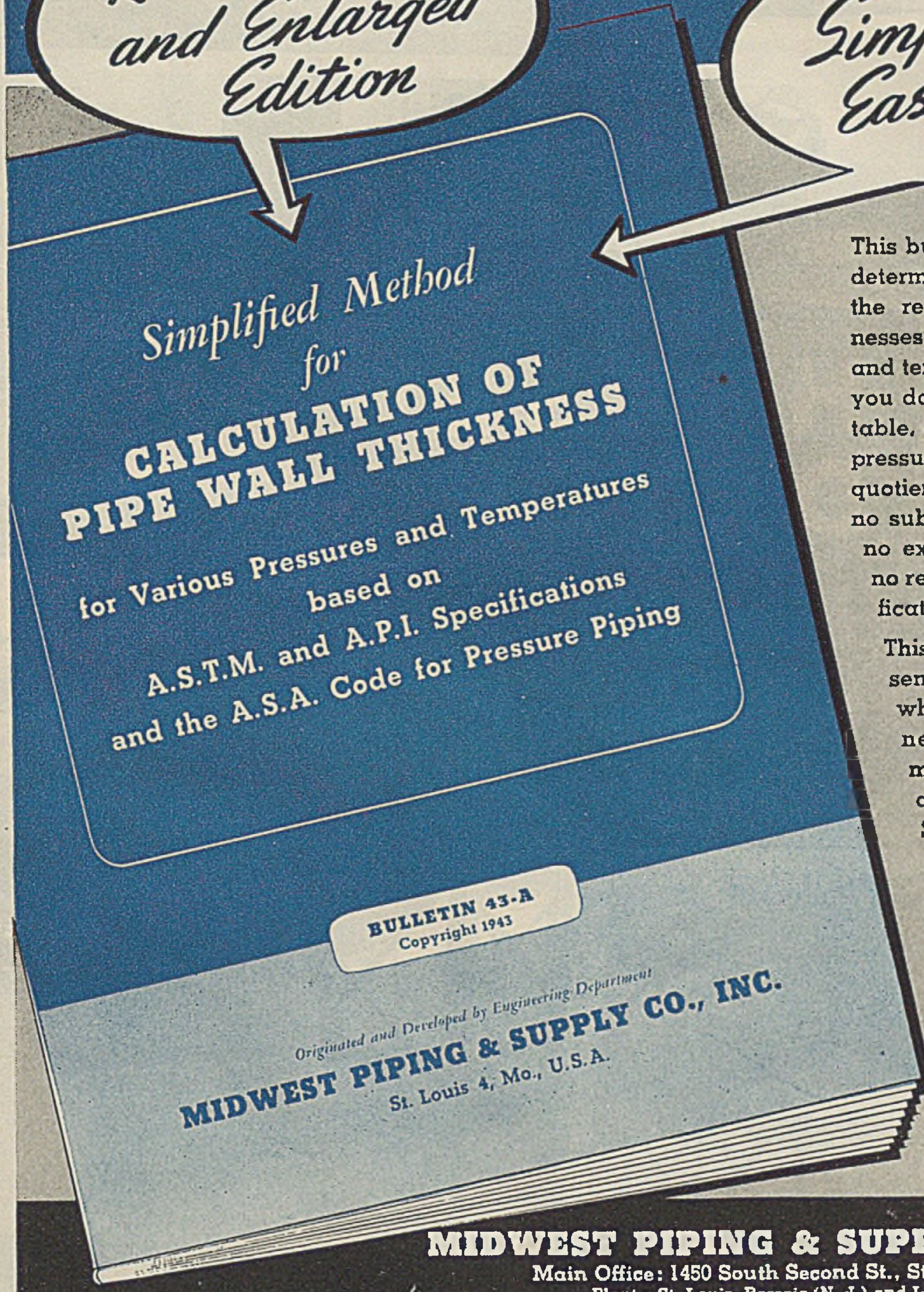
PROCTOR & SCHWARTZ • Inc • Philadelphia

The World's Largest Builders of Industrial Drying Equipment

SAVES TIME
FOR THE PIPING DESIGNER

Revised and Enlarged Edition

Simple and Easy to Use



Simplified Method for

CALCULATION OF PIPE WALL THICKNESS

for Various Pressures and Temperatures based on A.S.T.M. and A.P.I. Specifications and the A.S.A. Code for Pressure Piping

BULLETIN 43-A
Copyright 1943

Originated and Developed by Engineering Department
MIDWEST PIPING & SUPPLY CO., INC.
St. Louis 4, Mo., U.S.A.

This bulletin will enable you to determine quickly and easily the required pipe wall thicknesses for commercial pressure and temperature conditions. All you do is select a factor from a table, divide it into the working pressure and then refer the quotient to a chart. You have no substitution in formulae . . . no extensive calculations . . . no reference to codes or specifications.

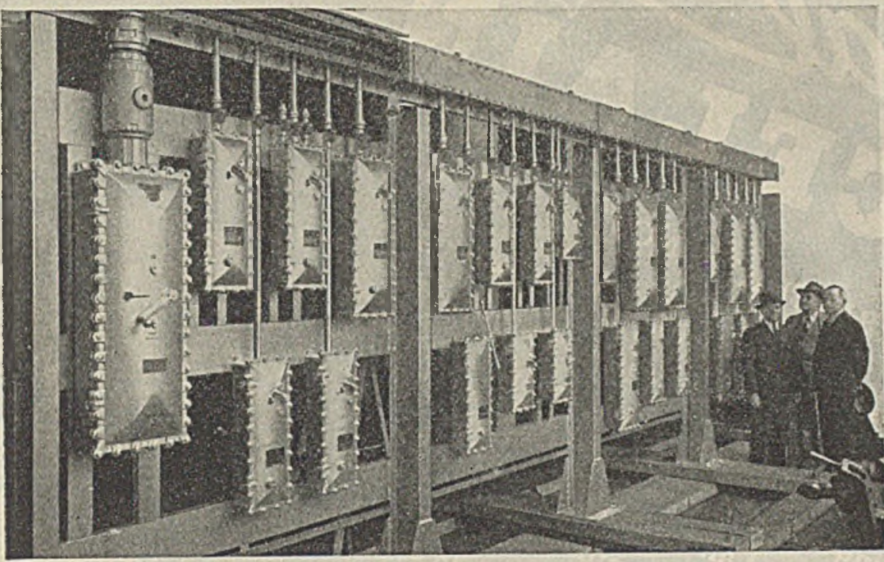
This bulletin will gladly be sent to anyone interested who requests it upon a business letterhead. Simply mention Bulletin 43-A and address the main office at St. Louis, Missouri.

MIDWEST PIPING & SUPPLY CO., INC.

Main Office: 1450 South Second St., St. Louis 4, Mo.
Plants: St. Louis, Passaic (N. J.) and Los Angeles
Sales Offices: Chicago—645 Marquette Bldg. • Houston—229 Shell Bldg. • Los Angeles—520 Anderson St. • New York—(Eastern Division) 30 Church St. • Tulsa—533 Mayo Bldg.

PIPING FABRICATORS AND MANUFACTURERS OF PIPE WELDING FITTINGS

Now You Can Order a Complete Low-voltage Control System as Easily as You Order Motor Starters



An assembly of 25 explosion-proof combination starters being installed outdoors at an oil refinery. For motors from 3 hp to 100 hp, 440 volts. Note the explosion-proof bus trough and seal-off fittings

G-E Factory-assembled Group Control

Simplifies **layout problems**

Cuts **installation time**

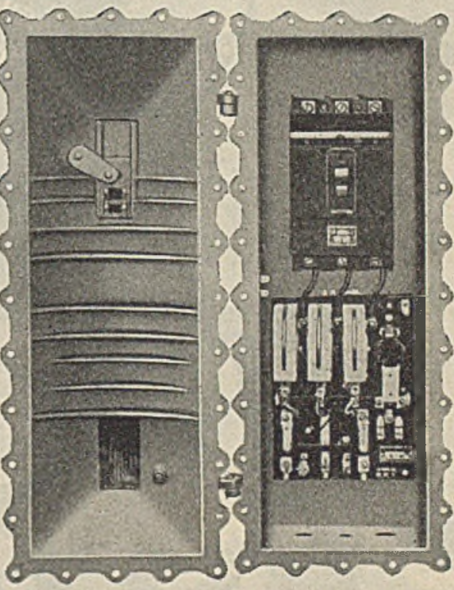
Saves **critical material**

WHEN you get everything you need in a *single* purchase, you avoid the disadvantages of piecemeal buying and piecemeal installation.

These controls are factory-assembled in a group, then wired and shipped as one complete unit. You save valuable time in selection, ordering, and layout. You have only to place the unit and connect the incoming line and the outgoing motor leads.

These starters are made of cast, high-strength alloy, and have the strength to withstand internal explosions. The flanges, which are securely bolted on all sides, are ground to tolerances that will not permit the escape of hot gases.

These pre-assembled units save critical materials required for conduit, junction boxes, and special fittings on separately mounted devices. For complete details on the advantages and applications of group controls, get in touch with our local office. *General Electric Company, Schenectady, N. Y.*



A G-E enclosed, combination magnetic switch (Size 2) and air circuit breaker, for hazardous gas locations, Class I, Group D

Every week 192,000 G-E employees purchase more than a million dollars' worth of War Bonds

MOTOR CONTROL FOR HAZARDOUS AREAS

GENERAL ELECTRIC

676-96-8900

No. 4 in a series of case studies on dust and fume conditions in the process industries.

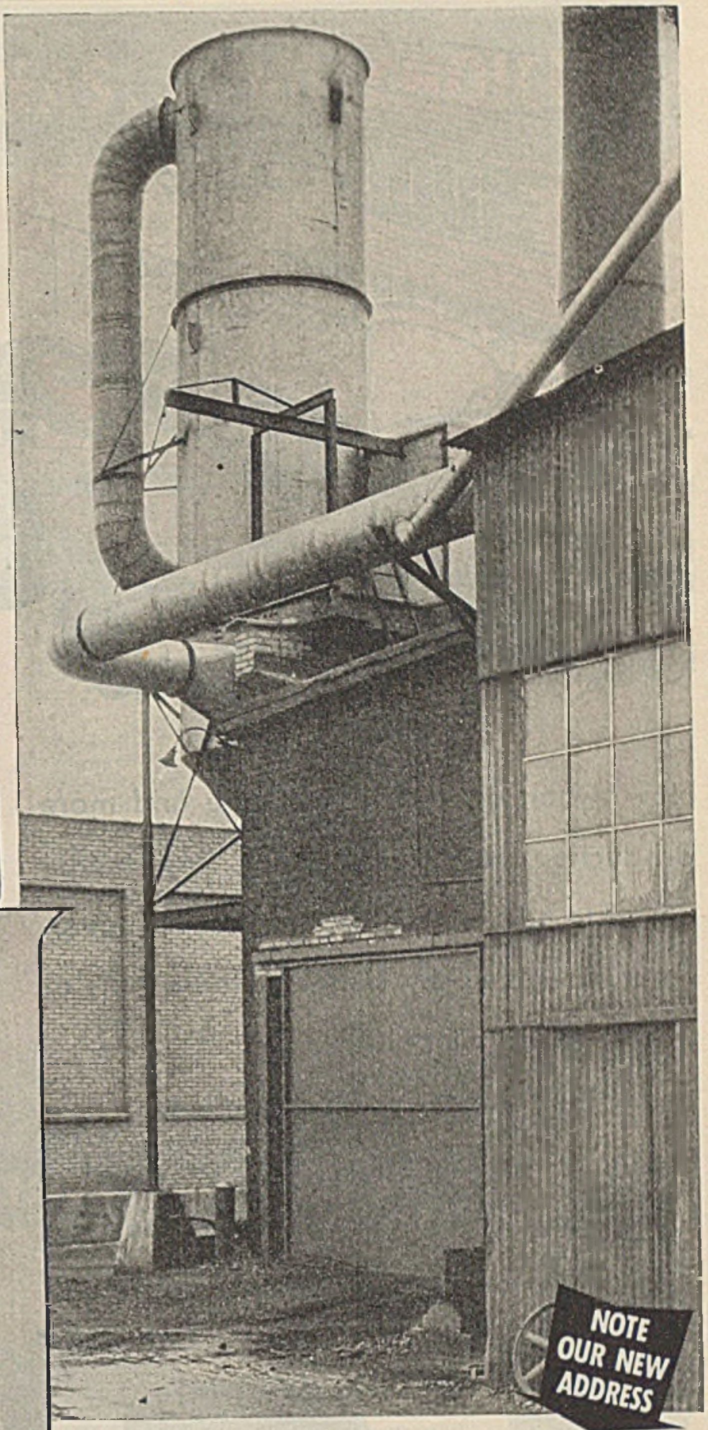
THE PROBLEM

Control of dust arising from the batching and handling of chemical mixtures for rubber manufacturing.

THE SOLUTION

The batch boxes on platform scales mounted on racks are suspended from an overhead rail and move to the various stations in front of the material bins. These racks are enclosed except for the front opening to form an exhaust hood. The connection from this hood indexes with a connection to the main duct system to carry the exhausted air and dust to a conveniently located Schneible Multi-Wash Dust Collector system.

This efficient dust control system has provided a number of advantages. The batching room is now a clean place for the operators to work without breathing contaminated air. Dust is not spread to other parts of the plant to settle on finished goods or on operating machinery.



What Dust and Fume Conditions Are Handicapping Your Plant?

Peak production and contaminated air do not go together. In many process plants with enviable production records, the air is kept clear of dust, fumes and odors with Schneible Multi-Wash Systems. Practically every dust and fume condition, whether it affects the entire plant or an individual operation, can be overcome with Schneible Multi-Wash Collectors of standard design, built of the material most resistant to the operating conditions. The water or other suitable liquid is usually recirculated. Valuable dusts may be profitably recovered.

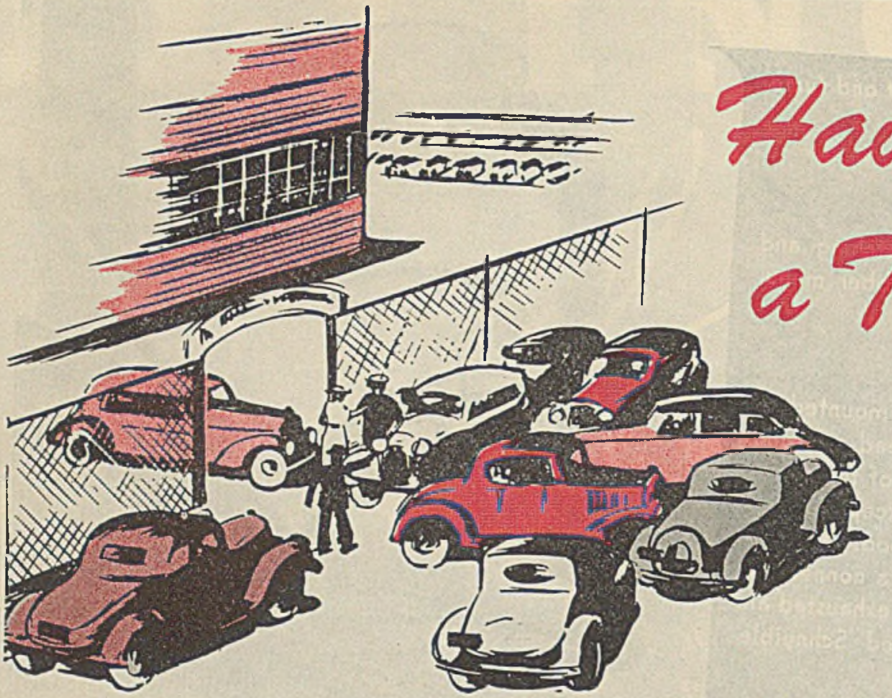
Consult us about your dust and fume problems.

CLAUDE B. SCHNEIBLE CO.
2827—25th Street Detroit, Michigan

(Our general offices have been moved to our plant)
Engineering Representatives in Principal Cities

SCHNEIBLE

DUST, ODOR AND FUME CONTROL EQUIPMEN



Have You a Traffic Jam

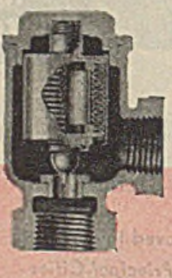
IN YOUR STEAM LINES?

Now, when the call is for more and more production, faster and faster, you cannot afford to have steam heated process equipment slowed up by sluggish steam coils or water-logged supply lines.

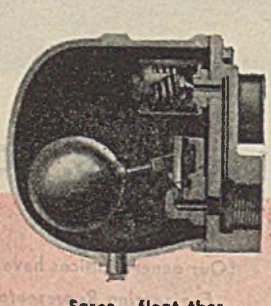
In other words, good steam traps now are more important than ever. Sarco makes four distinct types and can select the type to give you quickest air venting and maximum heating efficiency without lag or waste.

We can also suggest simple temperature controls which will prevent spoilage and stop wasteful overheating.

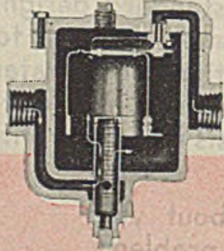
The Sarco Hook-Up Book contains helpful suggestions on proper selection of steam saving equipment and many tested hook-ups not published elsewhere. A copy is yours for the asking.



Sarco No. 9 thermostatic steam trap for individual trapping of steam coils.



Sarco float-thermostatic steam trap for tanks, lines, and temperature controlled hook-ups.



Sarco bucket trap for heavy duty and intermittent service.

Sarco No. 87 steam trap-control

Sarco temperature controls hold tank and process temperatures within a few degrees.

SARCO COMPANY, INC.
475 FIFTH AVENUE
NEW YORK 17, N. Y.

SARCO Saves Steam

Represented in Principal Cities

SARCO CANADA, LTD., 85 Richmond Street, West, TORONTO, ONTARIO

FOR HAZARDOUS AREAS....101 CHOICES

ALL THESE MOTOR TYPES

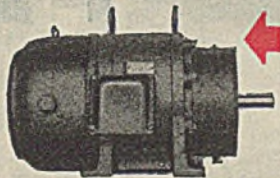
	Class I, Group D*	Class II, Groups E, F, G
Polyphase, squirrel-cage	✓	✓
Polyphase, wound-rotor	✓	✓
Single-phase	✓	✓
Direct-current	✓	✓
Gear-motors	✓	✓
Brake-motors	✓	✓
Vertical motors	✓	✓**
Multispeed motors	✓	✓
Navy motors ***	✓	✓
Marine motors	✓	

Tested and listed by Underwriters' Laboratories, Inc.
*Limited sizes also available for Class I, Group C.
**Not applicable to Class II, Group G.
***Also explosion-tested by other Laboratories.

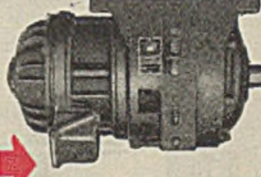
ALL THESE MODIFICATIONS

	Class I, Group D	Class II, Groups E, F, G
Face-type end shields	✓	✓
Flange-type end shields	✓	✓
Footless frames	✓	✓
Hollow-shaft designs	✓	✓
Thrust bearings	✓	✓
Oil-lubricated ball bearings	✓	
Sleeve bearings (250 hp up)	✓	
Class B (high-temperature) insulation	✓	✓**
Various voltages (32–6600 volts)	✓	✓
Various frequencies (25–60 cycles)	✓	✓
Intermittent ratings	✓	✓
Special-duty	✓	✓

In STANDARD MOTOR CONSTRUCTIONS such as these—



G-E squirrel-cage motor with face-type end shield for close-coupled mounting. Listed by Underwriters' Laboratories, Inc., as suitable for Class II locations.



G-E squirrel-cage gear-motor in explosion-proof construction, arranged for ceiling mounting. For low-speed conveyor drives, etc., in chemical plants.

G-E vertical motor (hollow shaft with flange base) for Class I, Group D, locations. Used for pumping gasoline from underground tanks.

NAME YOUR HAZARD—TELL US YOUR SPECIAL DRIVE PROBLEM—The chances are that G.E. can meet your *combination* of requirements with standard or "modified-standard" motors listed by Underwriters' Laboratories, Inc., as suitable for specific hazardous locations. If you need a motor for war work in any sort of hazardous spot, just call our local office. *General Electric Co., Schenectady, N. Y.*

EXPLOSION-PROOF
MOTORS

The best investment in the world is in this country's future—BUY WAR BONDS

GENERAL ELECTRIC

750-221-8030

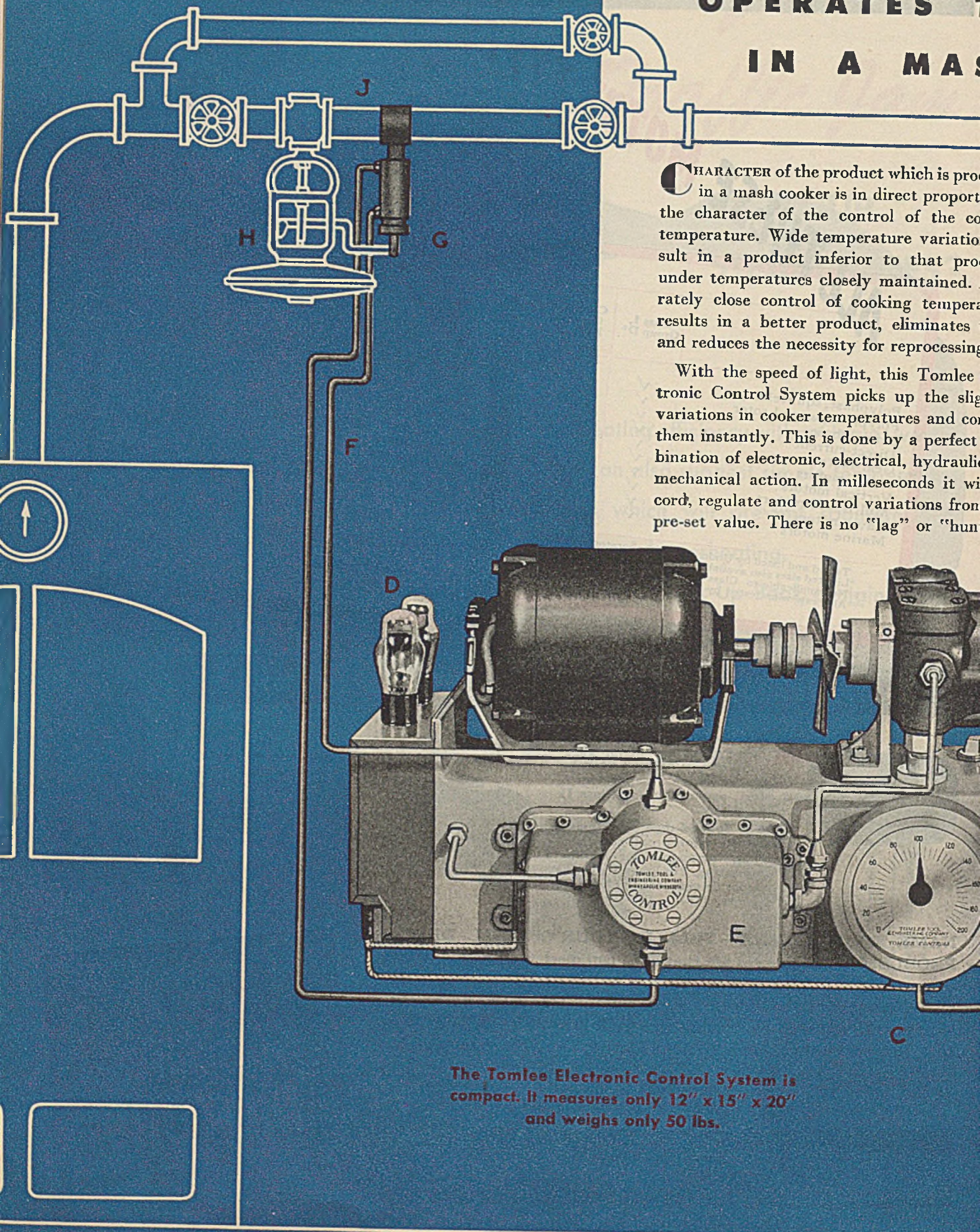
How the TOMLE

OPERATES

IN A MAS

CHARACTER of the product which is pro
in a mash cooker is in direct proport
the character of the control of the co
temperature. Wide temperature variatio
sult in a product inferior to that pro
under temperatures closely maintained.
rately close control of cooking tempera
results in a better product, eliminates
and reduces the necessity for reprocessing

With the speed of light, this Tomlee
tronic Control System picks up the slig
variations in cooker temperatures and co
them instantly. This is done by a perfect
bination of electronic, electrical, hydrauli
mechanical action. In milleseconds it wi
cord, regulate and control variations fron
pre-set value. There is no "lag" or "hun



The Tomlee Electronic Control System is compact. It measures only 12" x 15" x 20" and weighs only 50 lbs.

Electronic Control System

CONTROL THE TEMPERATURE

COOKER FOR ACCURATE PROCESSING

with their accumulation of repeated errors. Waste time and repeated processing of materials are completely eliminated by employment of the Tomlee Electronic Control Systems.

Wherever control and regulation of time, temperature, pressure, quantity or flow is required, Tomlee Electronic Control Systems furnish the ultimate in accurate control.

The Tomlee Electronic Control is the product of a young, aggressive organization, highly skilled in the production of precision apparatus. Our engineers are in a position to apply the Tomlee principle of electronic control to practically any control problem. Write for complete information. TOMLEE TOOL AND ENGINEERING COMPANY, 253 Third Avenue, South, Minneapolis 15, Minnesota.

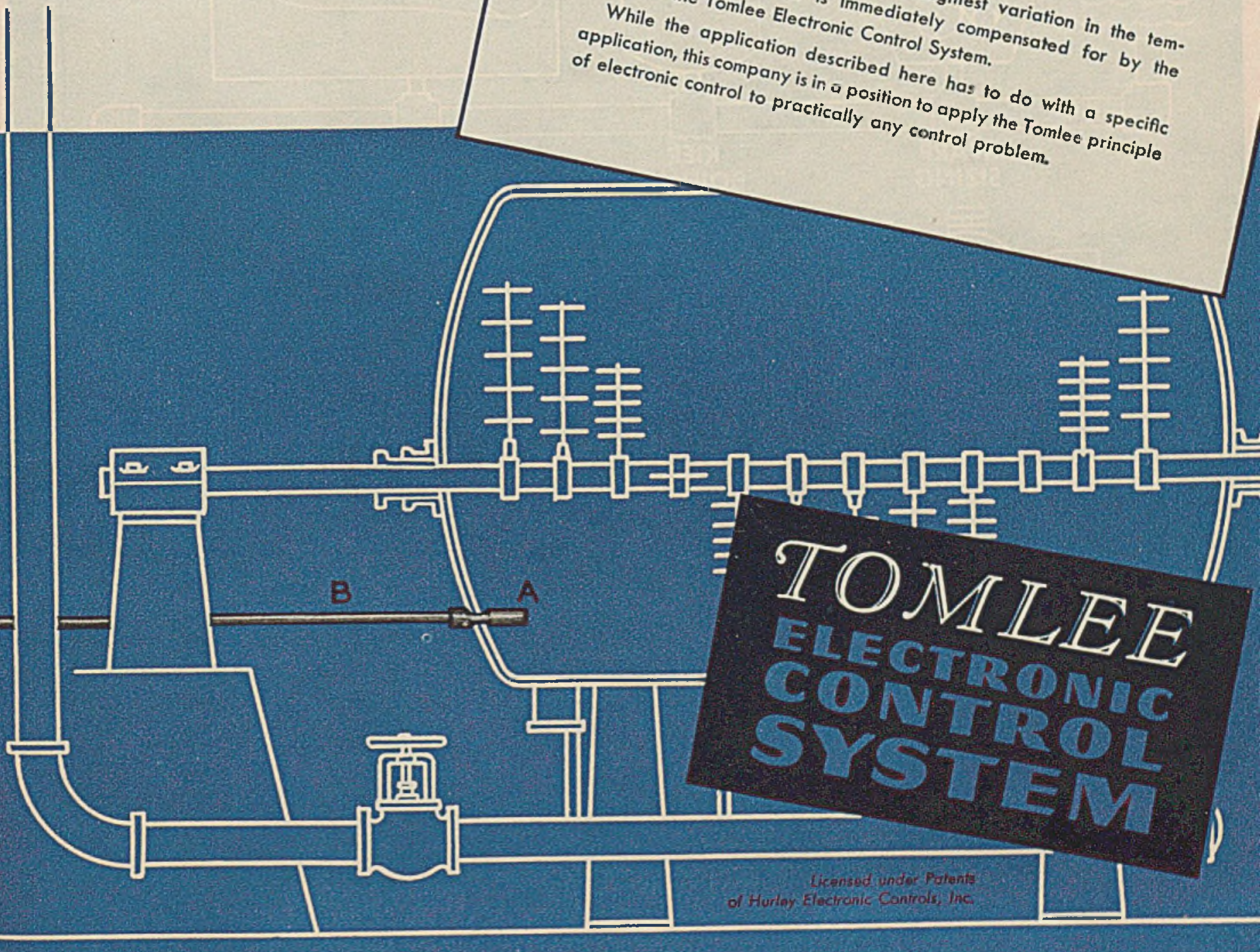
HOW THIS MASH COOKER OPERATE WITH TOMLEE ELECTRONIC CONTROL

As very slight changes in temperature occur at thermometer (A) they are transmitted through impulse tube (B) to diagnosing unit (C) which has been pre-set at the exact temperature which it is desired to have maintained in the mash cooker.

All variations even of the slightest degree from the pre-set value in diagnosing unit (C) are transmitted to tubes (D). A feeble current of only 2 milliamperes is amplified in the electronic unit to standard 110 volts and operates either of two electro-magnets, which in turn control the action of 4-way valve (E). This valve sends hydraulic pressure to either side of hydraulic piston (G) causing valve (H) to proportion the volume of steam in line (J) in the amount necessary to hold temperature in the mash cooker to the pre-determined value set in diagnosing unit (C).

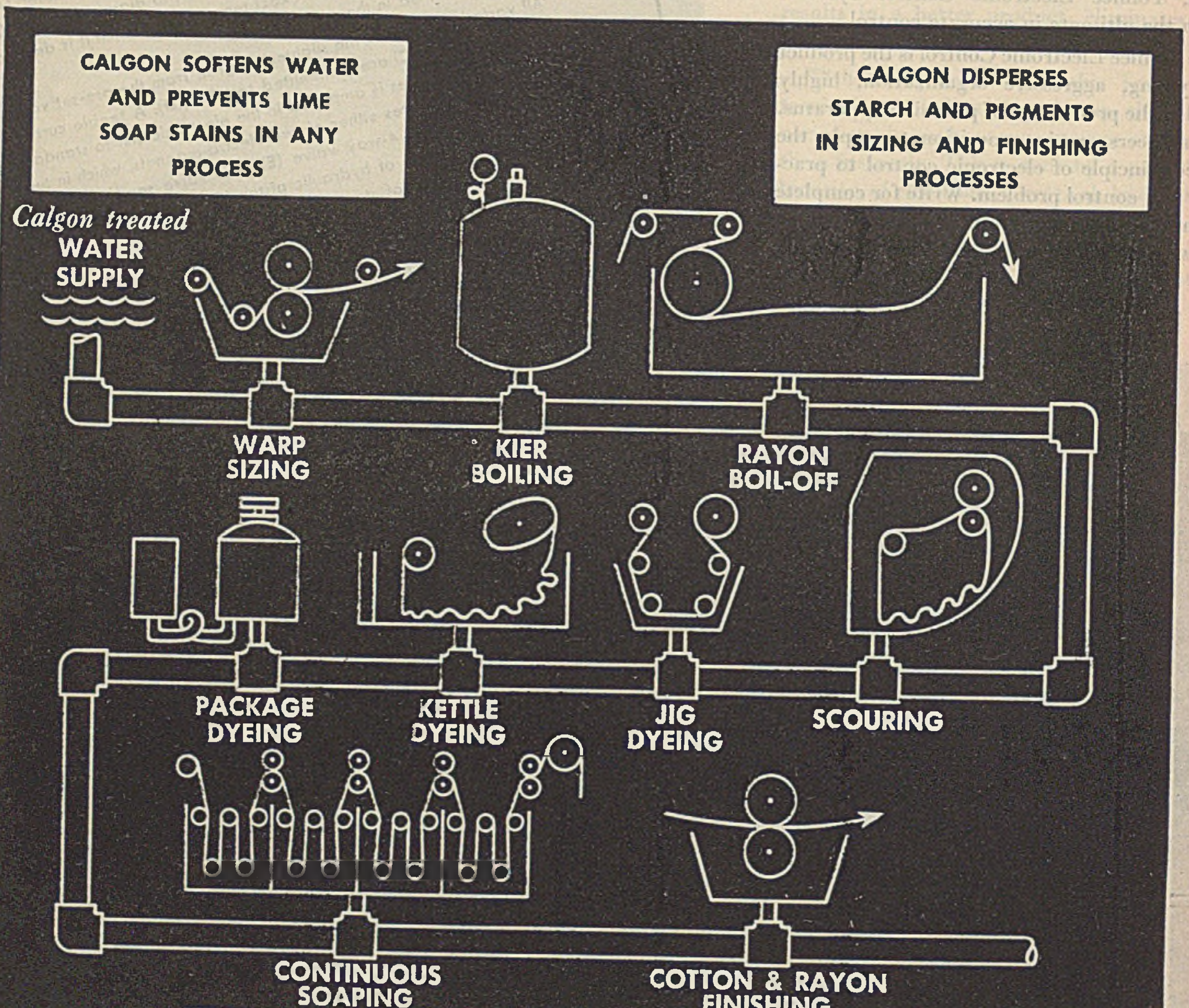
It can be readily seen that the slightest variation in the temperature in the cooker is immediately compensated for by the action of the Tomlee Electronic Control System.

While the application described here has to do with a specific application, this company is in a position to apply the Tomlee principle of electronic control to practically any control problem.

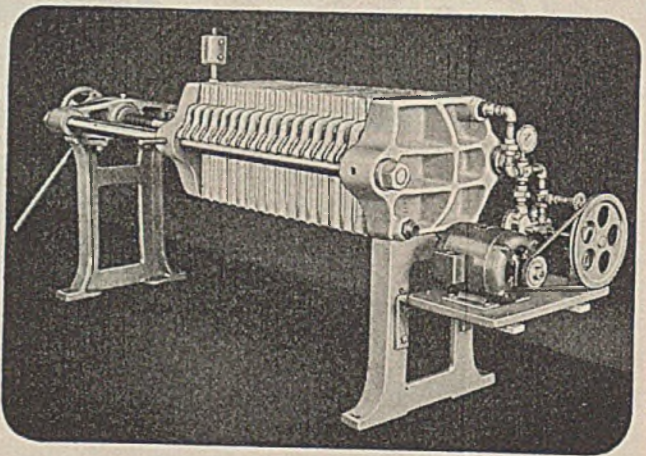


TOMLEE ELECTRONIC CONTROL SYSTEM

Licensed under Patents
of Hurley Electronic Controls, Inc.


CALGON SOFTENS WATER AND PREVENTS LIME SOAP STAINS IN ANY PROCESS
CALGON DISPERSES STARCH AND PIGMENTS IN SIZING AND FINISHING PROCESSES
Calgon treated WATER SUPPLY
WARP SIZING
KIER BOILING
RAYON BOIL-OFF
PACKAGE DYEING
KETTLE DYEING
JIG DYEING
SCOURING
CONTINUOUS SOAPING
COTTON & RAYON FINISHING

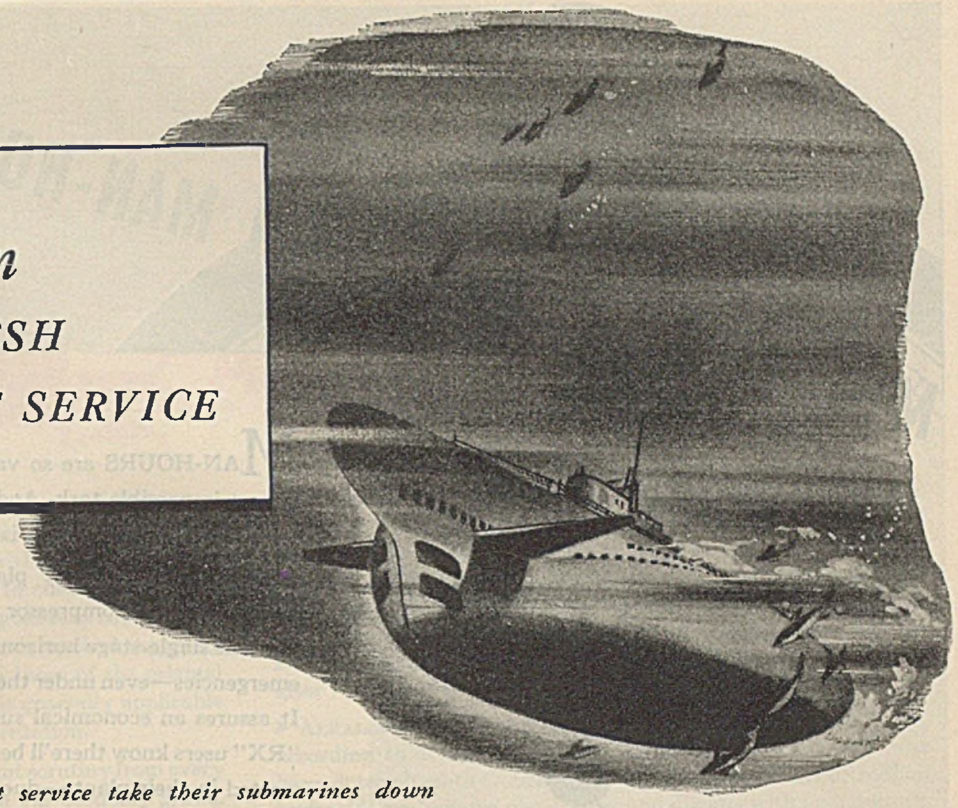

Peace Work!




SPERRY
FILTER PRESSES

Deep drawn

TO KEEP AIR FRESH FOR THE SILENT SERVICE



When men of the silent service take their submarines down beneath the surface—their "pig-boats" are air-conditioned. The air is kept fresh and healthful. The refrigerant gas is frequently stored and transported in Hackney Cylinders . . . deep drawn to specifications. They meet all requirements as to strength, weight and safety. This cylinder (at lower right) is only one of the many Pressed Steel Tank Company products being produced for the war effort.

In addition to submarine service, Hackney Cylinders are being used for the storage and transportation of many refrigerant gases which are being employed in vital applications, both war and civilian. In airplane factories, rivets are cooled in order to speed production. In locker plants, refrigeration is meeting important uses in the preservation of food. Pressed Steel Cylinders and refrigerant gases are used in the storage of blood plasma—and for refrigerated test compartments simulating weather conditions in the stratosphere.

For successful performance in these vital functions, the cylinder must meet a wide variety of strength, weight, safety and handling requirements. To assure the physical properties required for the various types of gases, the cylinders are made from flat, circular plates of steel—and they are formed into seamless cylinders by a series of cupping and forming operations. This Hackney Deep Drawing Process permits their being made to exacting specifications with uniform side-wall thickness. To further improve their physical properties, the cylinder is subjected to precision-controlled heat treatment. The result is a cylinder that is light in weight—and yet has adequate strength.

It may be that your war and postwar problems can be solved by Hackney designs and the production of deep drawn shapes and shells. Many manufacturers, through the use of Hackney Deep Drawn Shapes, have been able to conserve material, man-hours and equipment—assure adequate strength while reducing weight. Be sure to write for full details.

Pressed Steel Tank Company

Manufacturers of Hackney Products

GENERAL OFFICES AND FACTORY • 1451 SOUTH 66th STREET
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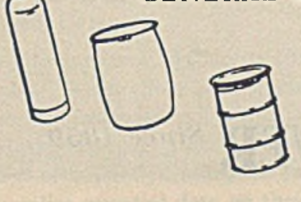
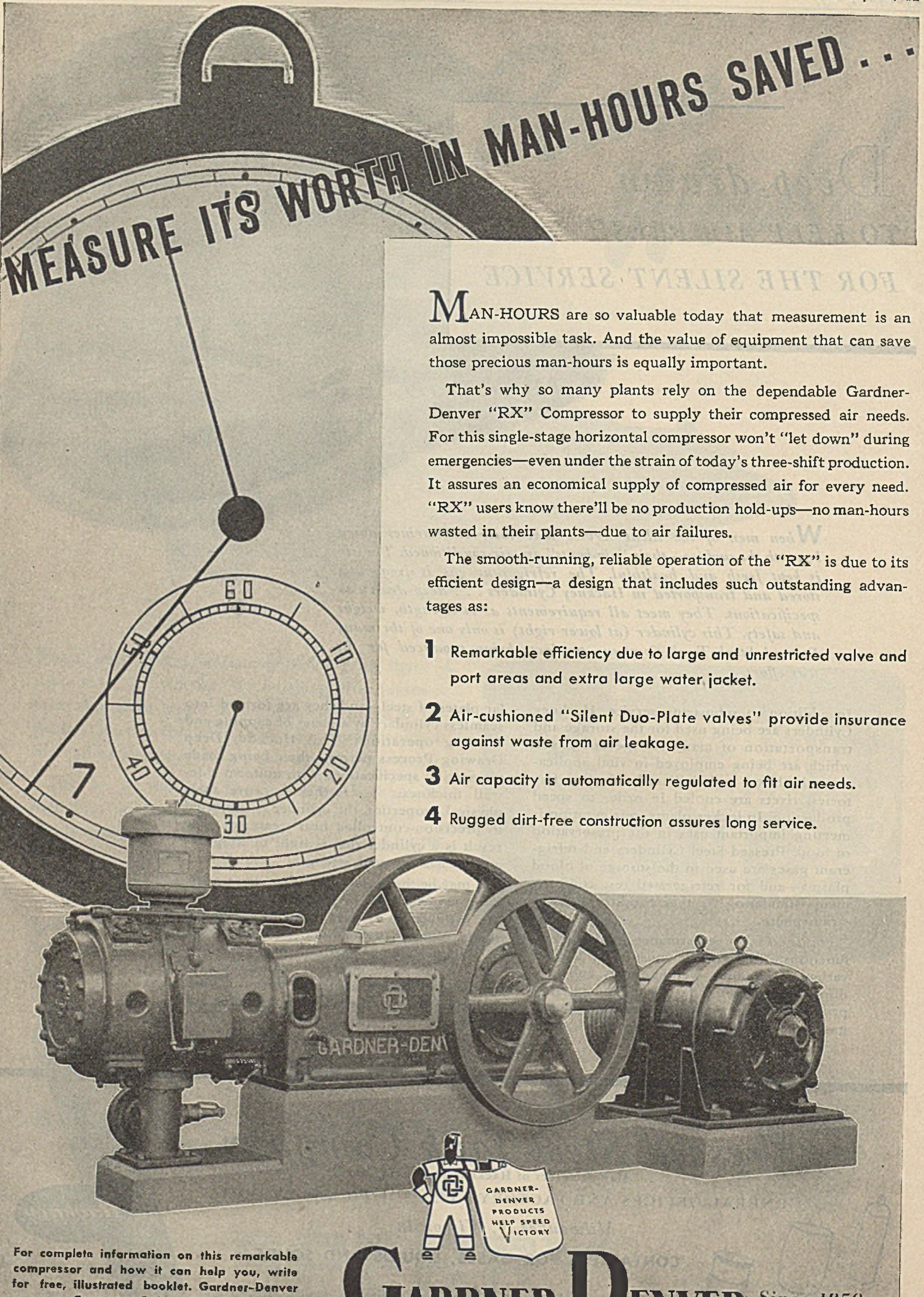


CONTAINERS FOR GASES, LIQUIDS AND SOLIDS


MEASURE IT'S WORTH IN MAN-HOURS SAVED . . .
60
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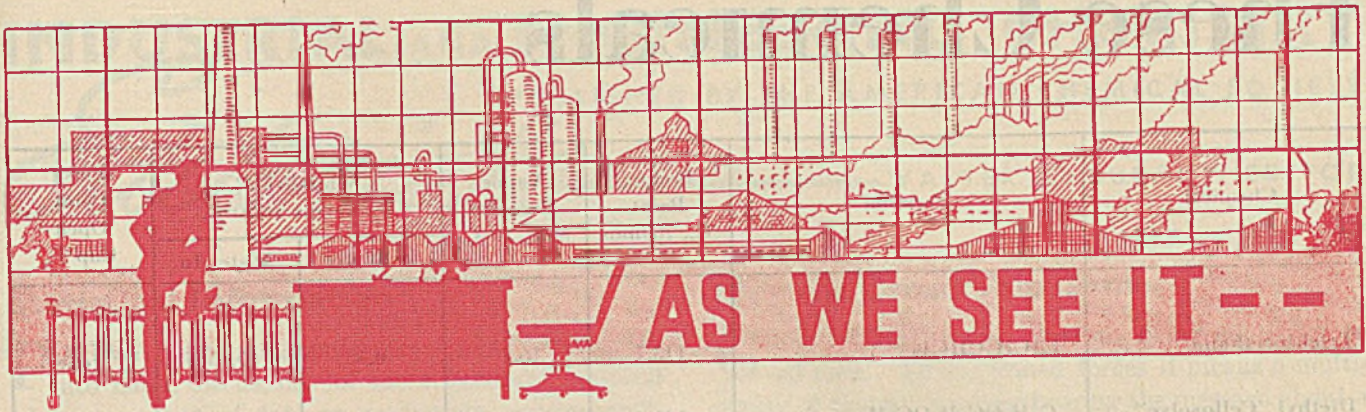
GARDNER-DENV
GARDNER-DENVER PRODUCTS HELP SPEED VICTORY



▶ **Automatic Control** of operations by instruments involves a number of important factors beyond simply placing the instruments themselves in working connection with equipment. One of these is the setting of each instrument to ensure its mastery of the job to be done. Allen (page 1223) goes into the problem of settings on the basis of the Ziegler-Nichols method, applying it to instruments of a different make from those of the original presentation. He shows that the method is generally applicable and thus provides valuable help in instrumentation.

▶ **Synthetic Elastomers** are under constant scrutiny from every point of view today as their importance in our economy grows. Fielding (page 1259) compares the life under flexing and the tendency to crystallization and fibering of several accepted synthetics with Hevea rubber.

▶ **Vapor-Liquid Equilibria** in systems made up of two phases present special problems of measurement. The industrial significance of such systems and the difficulties encountered in evaluating their equilibria under different conditions have prompted Colburn and his co-workers (page 1250) to approach the problem from a fresh point of view. Isobutanol-water and ethylene dichloride–toluene are the systems studied in confirming the value of the new equilibrium still.

▶ **Organic Fungicides** have long been sought to supplement or replace compounds of sulfur, copper, and mercury whose present scarcity and known limitations enlarge opportunities for our fungus enemies. Ter Horst and Felix (page 1255) describe in detail their investigations confirming the high value of 2,3-dichloro-1,4-naphthoquinone in frustrating fungi commonly destructive in agriculture and textiles. Present costs of fungi are of the order of a billion dollars annually which is a stake large enough to encourage much research.

▶ **Low-Boiling Hydrocarbons** occupy positions of growing importance as raw materials for an ever increasing variety of syntheses. Recovery of these compounds from gas mixtures by absorption in oils has consequently become substantial. Kirkbride and Bertetti (page 1242) provide valuable data on pressure absorption in oils of paraffinic, naphthenic, and aromatic character, and show how these differ in solvency under varying conditions.

▶ **Solvents** were subjects of an important group of papers presented before the Division of Industrial and Engineering Chemistry of the Society, featured in our October issue. Two of these papers (pages 1230 and 1240) were not ready for publication with the others in October. We are pleased to be able to include them this month.

▶ **Chlorinated Hydrocarbons** today are engaged in vital war jobs. When these are completed huge quantities of these important solvents will again perform useful tasks for civilians. McGovern (page 1230) reviews in considerable detail the properties of chlorohydrocarbons on which their values depend and supplies essential data on their many important applications.

▶ **Butanol and Acetone**, simultaneous products of a fermentation first developed for its probable value in the synthesis of rubber, have come to occupy important places as industrial solvents. Wynkoop (page 1240) describes them and their principal applications. Interesting historical footnote is the important role of the Weizmann fermentation process in persuading the British Government to grant rights in Palestine to the Zionists after World War I.

▶ **Alkaline Soap Builders** behave quite differently in solution, according to Kuentzel, Hensley, and Bacon (page 1286) who have determined the variation of the pH of solutions of sodium hydroxide, carbonates, phosphates, and silicates with temperature.

▶ **Hydroxy Compounds** react readily with boric acid to form esters of interesting properties. Irany (page 1290) describes this reversible reaction with polyvinyl resins and the use of the products, suggesting that the acid forms spatial interlinkages between the resin molecules.

▶ **Viscosity of *n*-Pentane** under a variety of conditions of temperature and pressure has been determined in a rolling-ball viscometer by Hubbard and Brown (page 1276).

▶ **Distribution of Ash Constituents** in coke has been studied by Shnidman (page 1262) for the light it may shed on the structure of coal.

▶ **Solubility of Water** in liquid carbon dioxide has been determined by Stone (page 1284). This problem is of immediate interest because of the widening use of liquid CO_2 in fire extinguishers.

▶ **Mixed Calcium Salts** of fatty acids and synthetic anionic detergents form in solution to suppress foaming and detersive powers of solutions containing mixtures of these materials, according to Miles and Ross (page 1298).

▶ **Gas Adsorption** is an important engineering operation in vapor recovery from air and in catalytic petroleum processes. Adsorption data (temperature, pressure, concentration, and heat involved) are correlated graphically by Othmer and Sawyer (page 1269). Their methods may be helpful in designing adsorption systems where only a few data are available.

▶ **Pectin's Emulsifying Properties** are compared by Lotzkar and Maclay (page 1294) with those of tragacanth, karaya, and acacia under various conditions and data are provided as a basis for using pectin to replace the imported gums, now scarce.

▶ **Chlorophosphate** is proposed by Fox and Clark (page 1264) as an intermediate product in converting phosphate rock to available fertilizer. The chlorophosphate process described is said to offer both economies in producing available phosphate and an outlet for by-product hydrochloric acid.

DHKilleffer

These Chemicals

Chemical	Formula	Boiling Point °C., 760mm.	Vapor Pressure mm., 20°C.	Solubility % by weight at 20°C.		Flash Point Open Cup°F.
				In Water	Water In	
Trichlorethane	$ClCH_2CHCl_2$	113.7	16.7	0.45	0.05	None
Diethyl "Cellosolve"	$C_2H_5OC_2H_4OC_2H_5$	121.4	9.4	21.0	3.4	95
n-Hexanol	$CH_3(CH_2)_4CH_2OH$	157.2	0.7	0.58	7.2	165
Methyl "Carbitol"	$CH_3OC_2H_4OC_2H_4OH$	194.2	0.2	Complete	Complete	200
Hexyl Ether	$C_6H_{13}OC_6H_{13}$	226.2	0.07	<0.01	0.12	170

are available in limited quantities

Here are five synthetic organic chemicals that were available in drum quantities at the time this magazine went to press. Have you investigated their possible uses in your processes? Some of them may help meet your present raw material needs.

Trichlorethane is colorless, nonflammable, and stable under ordinary conditions of use. It is a good solvent and extractant for most oils, fats, waxes, natural rubber, and some types of synthetic rubber.

Diethyl "Cellosolve," a stable ether, dissolves both oils and water and is an excellent mutual solvent. With alcohol, it is a solvent for nitrocellulose.

n-Hexanol is an excellent solvent for hydrocarbons, linseed oil, shellac, rosin, gums, and dyestuffs. It is also used in hydraulic brake fluids.

Methyl "Carbitol" is miscible with water and many organic solvents. It is used in perfumes, textile dye pastes, non-aqueous wood stains, and lacquers.

Hexyl Ether is a mild-odored, stable liquid, with a high boiling point. It is used as an inert reaction medium, and as an anti-foam agent particularly in certain types of adhesives.

For information concerning the use of these chemicals, address:

CARBIDE AND CARBON CHEMICALS CORPORATION
Unit of Union Carbide and Carbon Corporation
30 East 42nd Street UCC New York 17, N. Y.

PRODUCERS OF SYNTHETIC ORGANIC CHEMICALS

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

Statistical Information

POSTWAR planning conferences quickly degenerate into banal discussions of mere generalities unless adequate statistical data on production, consumption, etc., are readily available. The master of a luxury liner can regale his passengers with an interesting dissertation on the principles of navigation, but unless he has his instruments, tables, and charts available he can only make a hazy guess as to the actual position of his ship. Similarly, before executives can plan intelligently they must be provided with statistical material or they, too, are groping in a dark sea of ignorance and decisions are but wild guesses.

Most of the statistics gathered by government departments, war agencies, trade associations, and publications have been withheld in the past two years, for such information would be of great assistance to our enemies, particularly figures on construction and production in the earlier stages of the conversion-to-war period. Output of many items is now of such proportions that disclosure can only depress the morale of the Germans and Japanese still further and is, indeed, the very best kind of propaganda.

Statistical information on the chemical industry furnished in the prewar period by several governmental agencies was most helpful but in many phases it was not so complete or so up to date as to be truly valuable to executives required to make reasonably quick but accurate decisions. This statement should not be construed as adverse criticism. The plain truth of the matter is that the chemical industry in the past has been somewhat secretive and unwilling to cooperate to the same extent that, for example, the steel industry has done through the medium of the Iron and Steel Institute. Chemical manufacturers, of course, assisted the armed services and government defense agencies in every possible way prior to Pearl Harbor, and, indeed, the industry compiled a most remarkable record of cooperation then and in the past two years, but these data are confidential and rightfully so.

Now is a particularly good time to review the entire chemical statistical setup with a view to developing a more comprehensive and coordinated plan to be placed in effect as quickly as possible with due regard naturally to the present war status of the country. The Manufacturing Chemists' Association might find it possible to act as the spearhead in a program of revamping ways and means of collecting and collating chemical data for public release.

Play the Censorship Game

CENSORSHIP comes close to being all things to all men. To our armed forces it means a multiplicity of things: a poster bearing the message about a slip of the lip sinking a ship, being close-mouthed about cargoes, destinations, routes, departure times, training with new secret weapons, or even that the plane serviced this morning took off with some notable aboard.

At home censorship has the myriad meanings that are as diverse as the affected are diverse in their relationship with the function of censorship. Mechanics working on some new supermotor or rocket ship with the built-in traffic signs have a strict censorship imposed, whose beginnings and end are embodied in an acute realization of the importance of their project; and the conscience of each such individual supplies the policing necessary.

According to popular belief, editors have no conscience. Whether or not this is true or false, it must be admitted that a wartime ban is about the only power on earth that has the ability to muzzle all the press at the same time. All publications have agreeably, if not cheerfully, deleted sentences, paragraphs, yea, even articles, and once, in the case of this journal, a whole issue was revised—all to keep our enemies uninformed.

To break censorship into its component parts, for therein is a moral for personnel in the chemical field, it is seen that there are broadly two groups of publications affected—general magazines and newspapers catering to the general public, and technical journals for a select group of specialists. The first type of publication must be wary only of the broad aspects of censorship, such as the premature mention of a new tactical weapon, attack, operations in a new field, or other basic surprises. Thus, strict secrecy was maintained necessarily on all data concerning the bazooka prior to its use. When the Army became reasonably certain that the enemy knew of this rocket gun and had examined captured specimens, censorship had no function except to keep certain information, such as the names of manufacturers, from the general public. But now comes the real task for the technical press and the technical man. We are still under strict censorship, for even though the enemy may know about this new weapon, he can only obtain the know-how for its manufacture through his own extensive research or from publications.

Thus it becomes safe to assume, now that the enemy is using rockets, that the principles of rocket fuel are known to him and, therefore, bits of information may begin to appear. But, until that point is reached, our technologists must exercise a personal proscription. Using our bazooka analogy still further, though the revelation of the rocket fuel might be in order on the reasonable certification that the two nations are using the same materials, we cannot yet afford to publish vital information on its manufacture if the manufacturing operations deviate from normal practice to the slightest degree. Such information must not be disclosed. Do not talk about it except as an abstract problem, and then only if necessary. It is quite easy to piece together a whole story, as editors have done from time to time, with information that has leaked out in dribbles, and it is well within the ability of our enemies to do likewise. And while we are on the subject, there are still so many big secrets that even a slight hint about their nature would be of inestimable value to our enemies. Almost without exception every chemist and chemical engineer of this Nation possesses information and key data on some vital war operation yet unrevealed. If you are working on such a project, maintain your silence. The slip of the lip by a sailor may cause a ship to be sunk, but the slip of the lip by a scientist, the slip of the pen by an editor, the misplaced confidence of an executive, or the idle chatter of an equipment salesman may sink a whole nation—may result in the slaughter of thousands of young men needlessly.

Credit Where Credit Is Due

THE 19th Exposition of Chemical Industries, to be held in Madison Square Garden in New York, December 6 to 11, will be unique in many respects, but especially so because of a likely reduction in the physical display of heavy chemical manufacturing equipment. While many booths may resemble Mother Hubbard's cupboard, scientific brain power will be available as usual to those seeking technical information. Furthermore, it is comforting to remember that while the absence of full-scale models may be noticed and commented on, no really serious dearth of equipment now exists in our greatly expanded and widely diversified chemical and metallurgical manufacturing operations. To date little recognition has been given to the important contribution made by American plant designers and manufacturers of chemical equipment and scientific apparatus to the war effort.

How many heat exchangers, compressors, and a thousand and one other essential elements of construction and operation have been produced since Pearl Harbor is a deep dark secret known only to a few WPB officials, but a recent plant inspection in the South and Southwest is a partial indication at least to the editors of INDUSTRIAL AND ENGINEERING CHEMISTRY of the progress registered in the delivery of equipment to essential war plants in the short space of twenty-four months.

And, while rather belatedly bouquets are being presented to equipment designers and manufacturers, let us not forget to present another to the teaching profession primarily responsible for the notable achievements of American chemists and chemical engineers in the present national emergency.

Price Shouts (or Speaks)

FACTORS affecting the future of our lustily growing synthetic rubber industry have previously been discussed here. Utility naturally is the fundamental consideration, but barely less important is the question of price. Recent announcement by one of the leading companies in this field of sweeping reductions in the prices of its several grades of synthetics emphasizes this factor. It is by no means the first, nor will it be the last, cut in the prices of synthetic elastomers. Already production of specialty products in the field has attained the stature to justify passing substantial savings in manufacture on to consumers. This is, of course, characteristic of chemical industry. Repeated price reductions have consistently followed industrial progress and process development in the chemical field. Swift growth of output and continual development of processes is confidently anticipated. Both will inevitably benefit consumers.

Political thinking on the subject ignores this characteristic of chemical prices and thus is led astray. Announcements now that no protection will be afforded synthetic rubber manufacture in the postwar period are decidedly premature. No one can yet foresee the date of peace, and by the same token the state of the synthetic rubber picture at that time is unpredictable. If, meanwhile, further reductions in price accompany enhanced utility and value and if the condition of plantations continues to deteriorate, it is easily possible that the new industry may possess sufficient vitality to flourish without political protection.

Deferment of Chemical Operators

THE War Manpower Commission through Selective Service should take immediate steps to prevent any further inroads by the draft into the ranks of chemical operators by pointing out where necessary the definition of a chemical operator as given in Activity and Occupation Bulletin No. 17, which is still in full force and effect.

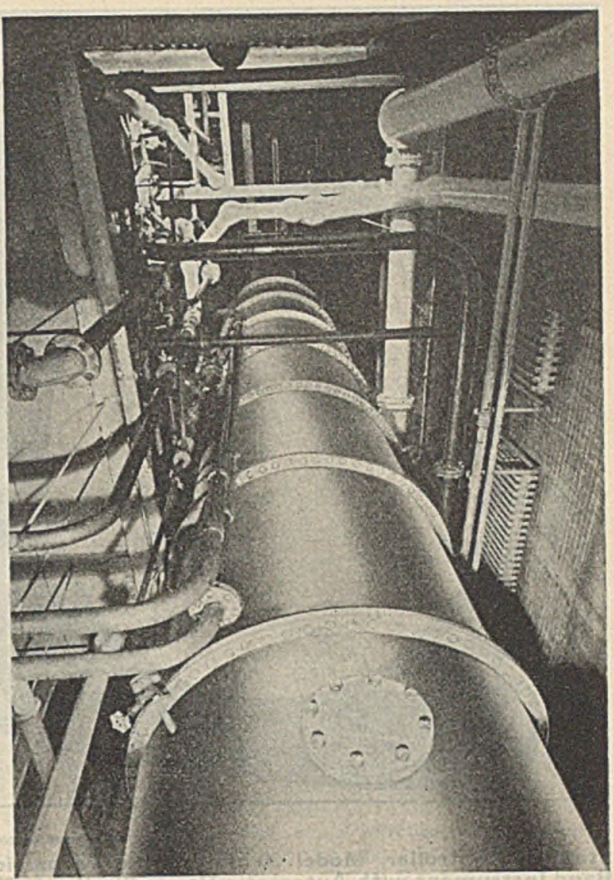
Our attention has been called to a recent occurrence in one state where the party in charge of Manning and Replacement Tables allows deferments of still operators but disclaims any knowledge of other chemical operators. The chemical industry will be hopelessly crippled unless such situations are speedily eliminated.

INDUSTRIAL CONTROL INSTRUMENT SETTINGS

Lyman H. Allen, Jr.

AMERICAN VISCOSE CORPORATION, MEADVILLE, PENNA.

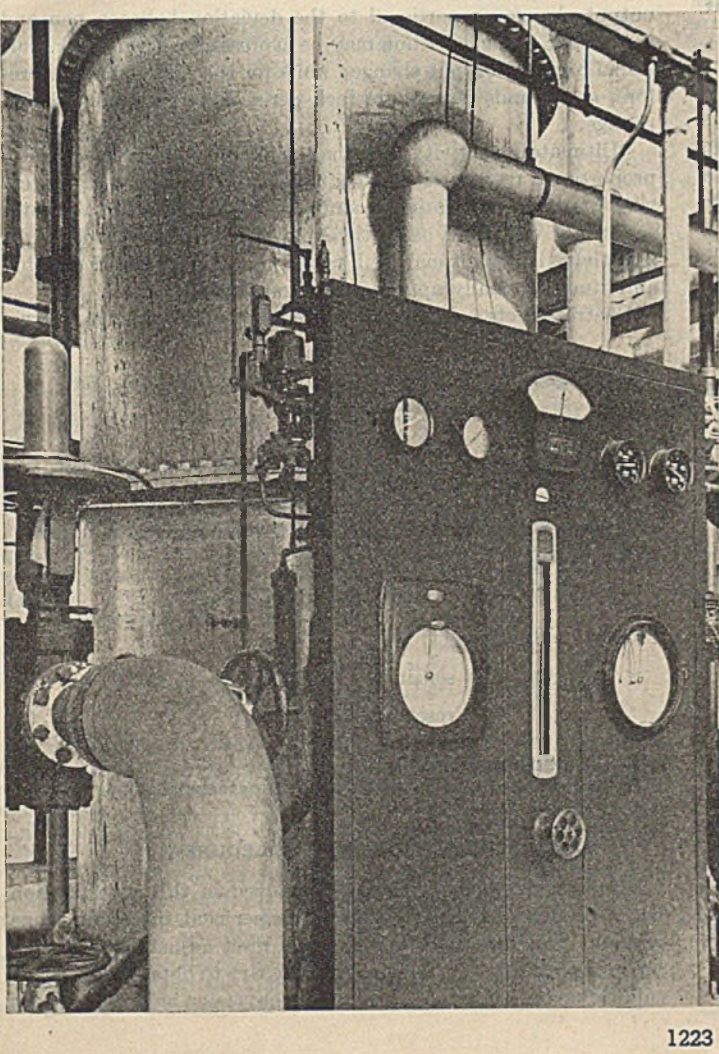
AT THE annual meeting of the American Society of Mechanical Engineers in 1941, a paper was presented by J. G. Ziegler[1] which offered a method of arriving at optimum instrument setting from a series of determinations made of process characteristics, including all lags involved. This method had a sound mathematical background and was simple enough to permit accurate establishment of settings in a few hours, instead of the weeks and sometimes months involved in the hit-or-miss, trial-and-error methods now practiced, with no assurance even then that the optimum settings had been obtained. Since the paper was based on controllers made by the Taylor Instrument Company, questions were raised concerning the universal applicability of the data to the adjustment of instruments manufactured by other companies. Therefore an investigation of the outlined procedure was initiated on a Foxboro controller, since that type was available to the author.



COURTESY, VULCAN COPPER & SUPPLY COMPANY

In June, 1941, a Foxboro Model 30 Stabilog temperature controller had been installed in the Acetone Recovery Department of the American Viscose Corporation to regulate the steam flow to an acetone recovery column. This column is a thirty-plate, 66-inch-diameter unit, with a tray spacing of 12 inches. It has a capacity sufficient to recover 140 pounds per minute of 99 per cent acetone from a 28 per cent aqueous acetone solution when operating at a reflux ratio of 1.5 to 1. Heat is supplied through the injection of live steam through a sparger pipe into the 42-inch-high base section of the column. Vapors are condensed in a horizontal multipass hot condenser, and the resulting hot condensate flows to a fixed ratio, weir type, split flow divider which divides the total overhead into product and reflux streams. Only the product stream is cooled. Hot reflux is returned to the top plate of the column, and the feed solution, preheated through a heat interchange with the column residue water discharging from the base, is introduced into the column on the tenth plate from the bottom.

The temperature bulb of the Foxboro control instrument is located in the vapor space above the seventh plate from the bottom of the column, and the temperature at this point is controlled through



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The Photographs Show Acetone Recovery Unit on Which the Method Outlined Was Tested. Above Is a Worm's-Eye View of the Thirty-Plate Column. At the Left Is the Control Board, Showing the Model 30 Foxboro Instrument and the Control Valve for Steam.

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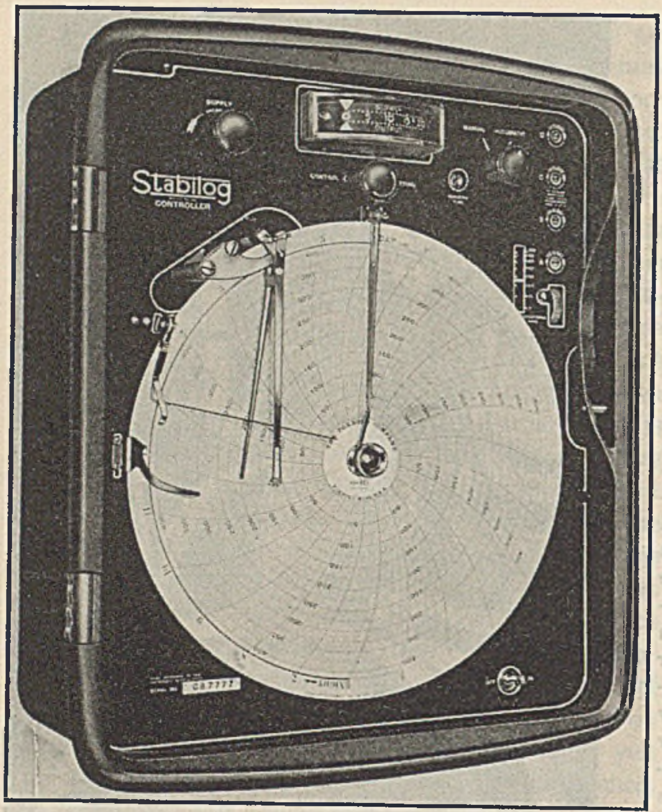
[1] Ziegler and Nichols, *Trans. Am. Soc. Mech. Engrs.*, **64**, No. 8, 759–68 (1942).



COURTESY, FOXBORO COMPANY

Stabilog Controller, Model 30, Adjustable Proportional Band Instrument with Automatic Reset, Similar to That Used in Investigation

the instrument action by positioning an air-operated diaphragm-type throttling valve in the steam line to the sparger pipe. Considerable time was spent in establishing the best settings for the instrument, those which would give a reasonable rate of recovery from upsets in the process resulting from changes in feed rate, feed composition, steam pressure, etc., and still give as close a control as possible of the temperature at the bulb location. It was found impossible to obtain straight-line control except at approximately 100 per cent throttling range (Taylor sensitivity of 2.75 pounds per square inch per inch), a setting which would not give a satisfactorily rapid recovery from process upsets. Furthermore, it was possible to detect very little change in the control characteristics obtained, as the reset resistance was progressively increased by cutting in additional spools of reset capillary through the closing of the reset valves provided in the instrument. The problem, therefore, was to calibrate the Foxboro control settings in terms of the Taylor units outlined in Ziegler and Nichols' paper, to determine the proper controller settings by the method presented, to try these settings in actual operation, and to compare them and the resulting control characteristics with those then being obtained.

DEFINITION OF TERMS

Control Effects. "Proportional response" is by far the most common of control effects, being found in most industrial air-operated controllers. As the name indicates, this effect gives an instrument air output or valve movement proportional to the amount of pen movement. In other words, a pen movement of 2° will give twice the valve movement or air output pressure change resulting from a pen movement of 1°. The ratio of valve movement to pen movement is called "instrument sensitivity" (percentage of full chart pen movement required for full valve movement is called "throttling range") and may be fixed or adjustable. An on-off controller is merely one with a fixed high sensitivity. The proportional response instrument has only one definite air output pressure or valve position for any given pen position and, as a result, is unable to compensate for changes in process load which require a change in the rate of flow of the controlled medium and still maintain the original control point. Changes in load with a proportional response instrument result in a pen deviation from the control point. This deviation of pen and pointer with load changes is called "offset"; the degree of offset varies inversely with the instrument sensitivity (directly with the throttling range) and directly with the size of the load change.

"Automatic reset" has as its only purpose the elimination of offset. In all other respects its effect is to create instability of control. Proper reset settings, however, enable this control effect to improve the degree of control, and a slightly decreased instrument sensitivity will eliminate its effect on stability. In operation, automatic reset detects pen deviation from the control point, and its action is to cause a slow continuous rate of valve movement in the direction necessary to eliminate this deviation. The rate of valve movement is proportional to the degree of deviation of the pen from the set point; in most industrial instruments this reset rate is adjustable, either in steps through the addition of lengths of capillary tubing to the instrument air circuit, or continuously through the adjustment of a precision needle valve.

Units of Measurement. Proportional response "sensitivity" is measured by the air output pressure change produced by an instrument and resulting from a pen movement of one inch on the chart. The units, therefore, are pounds per square inch per inch.

Automatic reset produces a continuous rate of instrument air output change proportional to the deviation between pen and set pointer. The deviation may be expressed in terms of proportional response output change; units for the "reset rate", therefore, are pounds per square inch per minute per pound initial change.

"Ultimate sensitivity" is that sensitivity adjustment in a proportional response instrument applied to a particular process which gives an oscillating record of fixed amplitude. A greater sensitivity will cause oscillations of increasing amplitude, while sensitivity below ultimate will result in oscillations of decreasing amplitude gradually approaching straight-line control.

Control effects according to Ziegler[1] are summarized as follows:

Response	Action	Measure	Unit
Proportional	$\frac{\text{Valve movement}}{\text{Pen movement}}$	Sensitivity	Lb./sq.in./in.
Automatic reset	$\frac{\text{Valve velocity}}{\text{Pen movement}}$	Reset rate	Per min.

Optimum controller adjustments[1] are summarized as follows:
Proportional:

$$\text{sensitivity} = 0.5S_u \tag{1}$$

Proportional plus reset:

$$\text{sensitivity} = 0.45S_u \tag{2}$$

$$\text{reset rate} = 1.2/P_u \tag{3}$$

where
S_u = ultimate sensitivity
P_u = period of oscillation at the ultimate sensitivity.

INVESTIGATION PROCEDURE

Since the Foxboro instrument involved in this investigation had a proportional band calibrated in per cent throttling range and was provided with four stepwise reset adjustments having no units of calibration, it was first necessary to obtain the missing calibrations and determine the actual conversion between per cent throttling range and sensitivity. The procedure followed is outlined below:

1. Place the instrument on remote hand control so that the controlled valve is operated by the pressure-reducing valve in the instrument case, and determine the amount of air pressure required on the controlled valve diaphragm to stabilize the process at the desired temperature.
2. Place the process on hand control and close the block valves on either side of the automatic controlled valve. Disconnect the pen from the measuring element, and fix it at the temperature at which the process is to be controlled.
3. Plug the air output line from the instrument at the case and open all reset valves to obtain the fastest reset rate possible.
4. Adjust the pointer to coincide with the pen, and set the throttling range to given an air output pressure equal to that determined in step 1. A sufficiently long waiting period should be allowed at this point to be sure that the instrument is in equilibrium and that there is no reset effect. If a reset change in the output pressure is observed, the pointer should be moved from the pen in that direction and to a sufficient distance necessary to stop the reset action. The pointer should then be readjusted to agree with the pen by means of the micrometer adjusting screw.
5. Close all reset valves to obtain the slowest possible reset rate. Disconnect the air piping between the reset capillary unit and the capacity tanks, and blank the connection from the tanks. This operation must be completed as rapidly as possible to avoid loss of pressure in the reset bellows. As a result of this step, the instrument is now of the proportional response type.

Table I. Conversion between Foxboro Throttling Range and Taylor Sensitivity

Throttling Range, %	Taylor Sensitivity, Lb./Sq. In./In.		Throttling Range, %	Taylor Sensitivity, Lb./Sq. In./In.	
	Exptl.	Calcd.		Exptl.	Calcd.
10	26.7	27.5	50	5.6	5.5
20	14.6	13.75	60	4.7	4.58
30	9.4	9.16	80	3.8	3.43
40	6.7	6.87	100	3.2	2.75

6. Adjust the throttling range at 100 per cent and then move the pointer away from the pen a distance sufficient to give an air output pressure change of 5 pounds. Measure the distance between the pen and pointer accurately and record this measurement. Repeat this measurement for pen and pointer deviation at increments of 10 per cent for the entire range of throttling range adjustment available.
7. The instrument sensitivity equivalent to the various throttling range adjustments can now be calculated thus:

$$\frac{\text{air output pressure change, lb./sq. in.}}{\text{pen and pointer deviation, inches}} = \text{sensitivity, lb./sq.in./in. of pen travel}$$

The results listed in Table I and plotted in Figure 1 show the conversion obtained between throttling range and instrument sensitivity in the Foxboro Model 30 Stabilog temperature controller. A plot of the reciprocal of throttling range against sensitivity gives essentially a straight line and thus confirms the relation between these two units of proportional response measurement. In the usual case, actual calibration is unnecessary since the conversion may be calculated thus:

$$\text{sensitivity} = \frac{\text{lb. air change for full valve travel} \times 100}{\text{\% throttling range} \times \text{chart width in inches}}$$

(In the procedure described here, the proportional response mechanism was first calibrated and then the ultimate sensitivity and period determined, followed by calibration of the reset mechanism. If desirable, however, calibration of the proportional response and reset mechanisms may be completed first and followed by the determination of ultimate sensitivity and period.)

8. Determine the throttling range adjustment necessary to produce exactly a one pound output air pressure change for a pen deviation from the pointer of one major chart division.

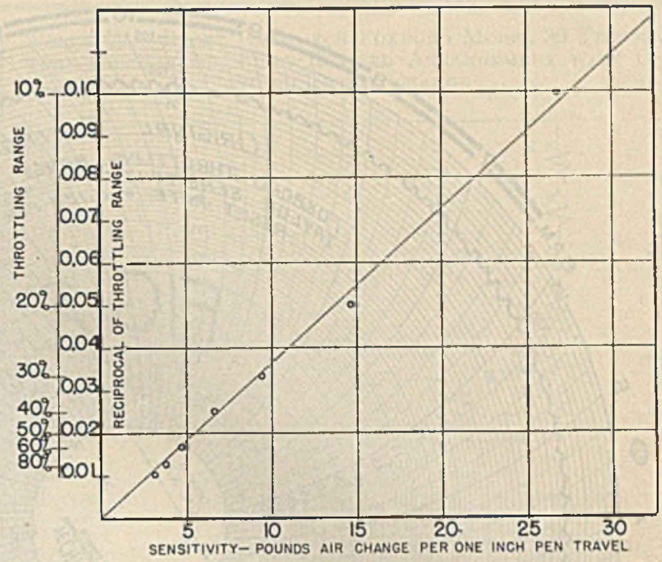
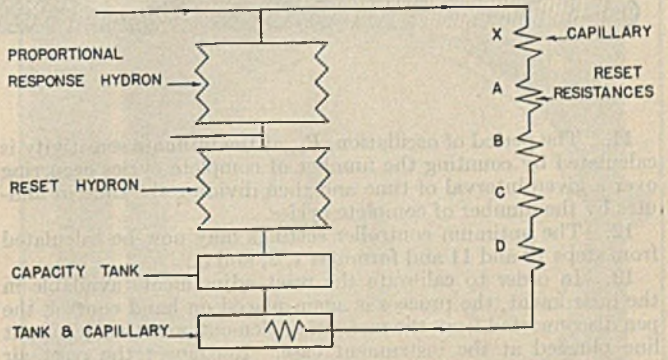


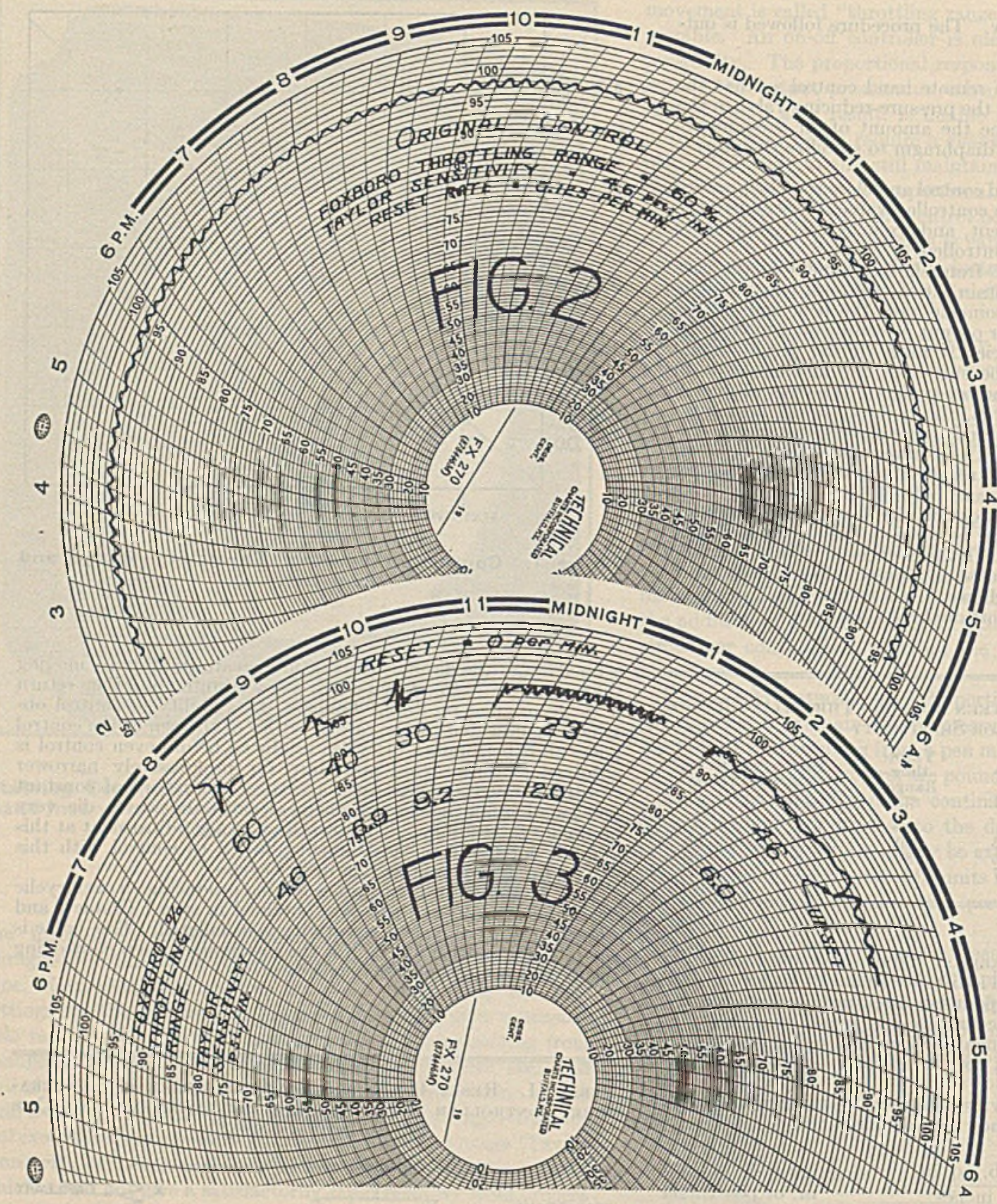
Figure 1. Conversion between Throttling Range and Sensitivity

9. Adjust the instrument for a wide throttling range, replace the connection between the pen and the measuring element, reconnect the output air line to the controlled valve diaphragm, and place the instrument in control of the process. After the pen is lined out at the desired temperature, create an upset by moving the pointer away from the pen for a few minutes, and then return it to its original position. Observe the stability of control obtained as indicated by the rate of return of the pen to the control point and the number of cycles produced before even control is obtained. Repeat this procedure for progressively narrower throttling range settings until a cyclic chart record of constant and small amplitude is obtained, or until the waves die very gradually to stability. The throttling range adjustment at this point is noted and the instrument allowed to control with this setting for approximately four or five cycles.
10. From the throttling range setting producing an even cyclic operation (step 9) and the data obtained in step 7 (Table I and Figure 1), the equivalent sensitivity is calculated. This value is the ultimate sensitivity, S_u, for the instrument when controlling the particular process under consideration.

Table II. Reset Rates for Foxboro Model 30 Temperature Controller with Original Arrangement and One Pound Initial Change



Resistance Open	Pressure Change, Lb./Sq.In.	Time		Reset Rate, Lb./Min./Lb.	
		Min.	Sec.		
A	9 to 11 11 to 9	14 17	55 11	0.134 0.116	0.125
B	9 to 11 11 to 9	15 18	21 21	0.13 0.109	0.119
C	9 to 11 11 to 9	15 18	45 14	0.127 0.11	0.118
D	9 to 11 11 to 9	15 18	42 24	0.128 0.109	0.118



11. The period of oscillation, P_u, at the ultimate sensitivity is calculated by counting the number of complete cycles occurring over a given interval of time and then dividing the time in minutes by the number of complete cycles.

12. The optimum controller settings may now be calculated from steps 10 and 11 and formulas 1, 2, and 3.

13. In order to calibrate the reset adjustments available in the instrument, the process is again placed on hand control, the pen disconnected from the measuring element, and the air output line plugged at the instrument case. Reconnect the reset air piping between the reset capillary unit and the capacity tanks, and set the throttling range at the value determined in step 8. Close all reset valves to give the slowest possible reset rate and check the throttling range setting to be sure that exactly a one-pound output air pressure change is obtained at a pen deviation of one major chart division from the pointer. This operation must be done rapidly to minimize the effects of air output change created by the reset action. Adjust the air output pressure to approximately 7 pounds. This may be done by moving the pointer away from the pen in the direction necessary to give the required air change. Wait for this air pressure change to occur, and then return the set pointer to the pen.

14. Make a def nite reset rate ad justment and the move the pointer on major chart divisio toward the outer edg of the chart. Th output pressure wi immediately chang 1 pound and the maintain a slow bu continuous rate o change resulting fron the effects of auto matic reset. Start stop watch when th output pressur passes the next ever pound graduation o the output air pres sure gage and obtai the time required fo an additional 3 or pounds. Let th pressure chang slightly more than additional pound from the end of th timing period, an then move th pointer to a positio one scale divisio from the pen towar the center of th chart. Allow the reset rate to become established and then obtain the time required for an air output pressure change in the reverse direction. Compute the average of these two times and record it as the time for that particular reset adjustment. Repeat for a check, make another reset rate adjustment, and obtain the time for this new setting. If the times become to long move the pointer a distance sufficient to give an initial change of 2 pounds or time over a range of only 2 instead of 3 or 4 pounds in air pressure change. Calculate the reset rates for the various adjustments as follows:

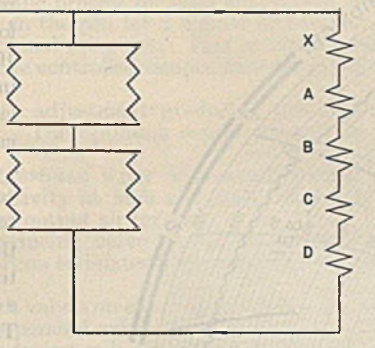
$$\frac{\text{lb. change in pressure during timed period}}{\text{av. time in minutes} \times \text{initial pressure change}} =$$

$$\text{reset rate} = \text{lb./sq.in./min./lb. initial pressure change}$$

RESET RATES

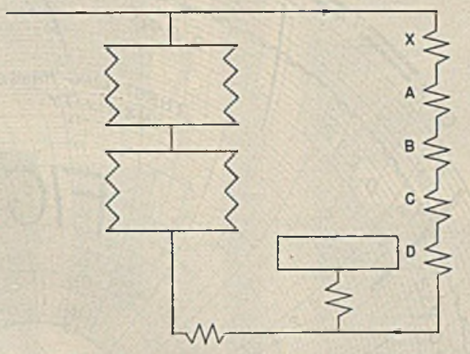
Before the work was initiated, the degree of control being obtained from the Foxboro temperature controller was similar to that shown on the actual recording chart record (Figure 2). The instrument settings of 60 per cent throttling range equivalent to a Taylor sensitivity of 4.6 pounds/sq. in./in. and a reset rate later determined by calibration to be equal to 0.125 pound/min./pound had been established after a considerable period of trial and error experiments. It is true that the variations in the controlled temperature record could have been decreased to some degree by widening the throttling range or reducing the sensitivity. This was, however, a step in the wrong direction since it would result in too slow a rate of recovery from the process upsets. Very little change in the appearance of the chart record was

Table III. Reset Rates for Foxboro 30 Temperature Controller with No Tanks and One Pound Initial Change



Resistance Open	Pressure Change, Lb./Sq.In.	Time		Reset Rate, Lb./Min./Lb.	
		Min.	Sec.		
A	9 to 13	..	45	5.34	4.77
	13 to 9	..	57	4.21	
B	9 to 13	1	12	3.33	3.07
	13 to 9	1	25	2.82	
C	9 to 13	1	23	2.89	2.47
	13 to 9	1	57	2.05	
D	9 to 13	1	46	2.26	1.87
	13 to 9	2	42	1.48	
All closed	9 to 13	2	36	1.54	1.38
	13 to 9	3	16	1.225	

Table IV. Reset Rates for Foxboro Model 30 Temperature Controller, First Revised Arrangement with One Pound Initial Change



Resistance Open	Pressure Change, Lb./Sq.In.	Time		Reset Rate, Lb./Min./Lb.	
		Min.	Sec.		
A	9 to 11	5	46	0.347	0.331
	11 to 9	6	23	0.314	
B	9 to 11	6	17	0.319	0.299
	11 to 9	7	9	0.28	
C	9 to 11	6	51	0.292	0.240
	11 to 9	10	38	0.188	
D	9 to 11	7	22	0.272	0.232
	11 to 9	10	22	0.193	

obtained through the use of the four different reset rate settings available in the instrument. Figure 3 shows the record of the determination of ultimate sensitivity, S_u, for the instrument and process under consideration. It will be noted that the ultimate sensitivity, S_u, was obtained at a throttling range setting of approximately 23 per cent, equivalent to a Taylor sensitivity of approximately 12.0 pounds/sq. in./in. The chart record on the right-hand side of Figure 3 illustrates the type of control that would have been received on a proportional response type of instrument operating with a sensitivity setting of half the ultimate. It is obvious from this record that process load changes are constantly occurring in the equipment, which points to the necessity for the automatic reset control effect if an even controlled temperature record is to be obtained. The record of the ultimate sensitivity shows that there are approximately $9^1/_2$ oscillating cycles per hour, equivalent to a time of $6^1/_3$ minutes per cycle.

Calculations follow for determining the optimum operating sensitivity S_o and reset rate RR required, based on the determinations for ultimate sensitivity and period of oscillation:

$$S_o = 0.45\,S_u = 0.45 \times 12.0 = 5.4 \text{ lb./in.} \tag{4}$$

$$5.4 \text{ lb./in. sensitivity} = 51\% \text{ throttling range} \tag{5}$$

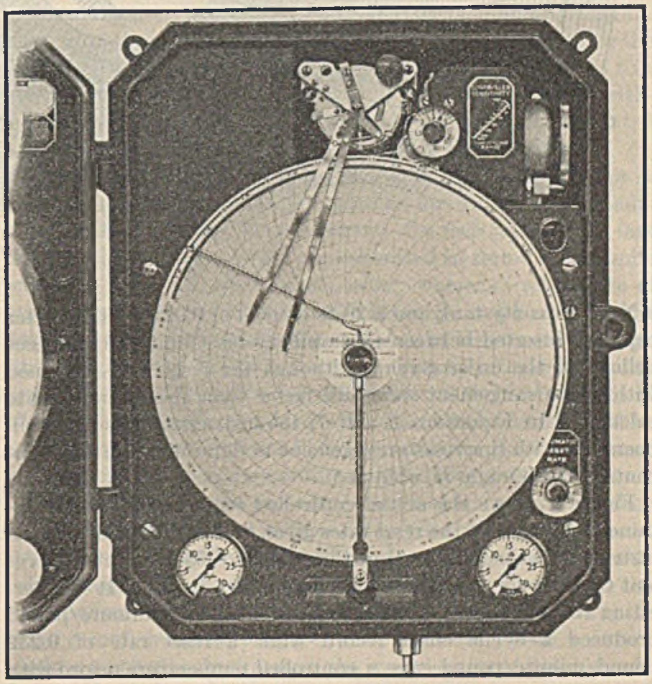
$$60/9.5 = 6.33 \text{ min. per cycle} \tag{6}$$

$$RR = 1.2/6.33 = 0.19 \text{ lb./min./lb.} \tag{7}$$

The reset rates for the original arrangement of the automatic reset adjustments furnished with the instrument were then determined and are listed in Table II. There is little change in the reset rate for the four possible adjustments, which explains the observation that there was very little change in the controlled temperature record obtained, regardless of the reset rate adjustment employed. Also, it was impossible to obtain the optimum reset rate calculated according to Equations 6 and 7.

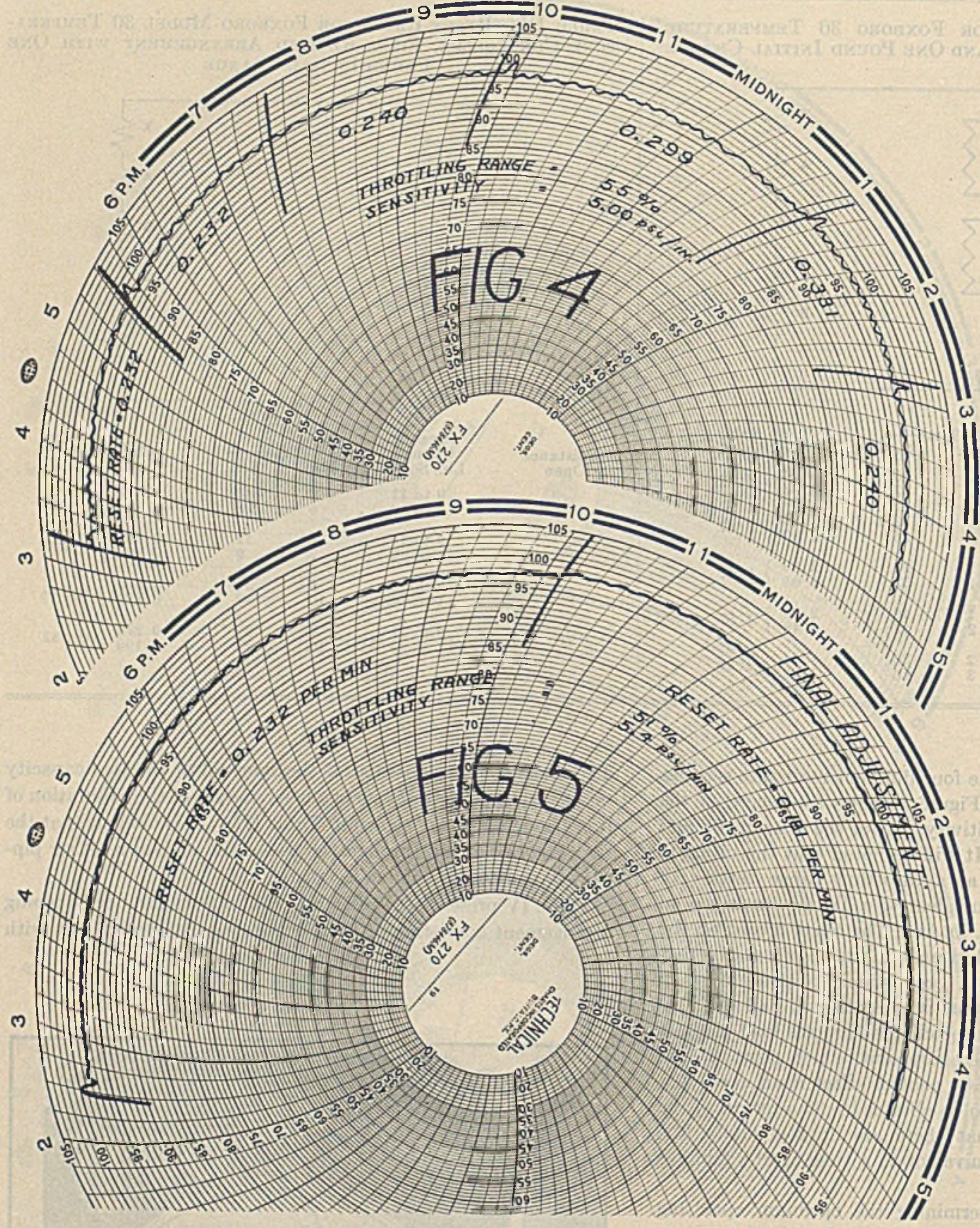
It was then decided to rearrange the capillary spools and capacity tanks in an attempt to obtain the calculated reset rates. The first attempt consisted of the removal of the two capacity tanks furnished with the instrument; results of the calibration of this arrangement are shown in Table III. It is obvious that the reset rates obtained through the use of the revised reset air piping arrangement are much too fast.

Table IV presents the reset rate calibrations for a reset piping arrangement consisting of the Foxboro capillary reset unit with



COURTESY, TAYLOR INSTRUMENT COMPANIES

Adjustable Sensitivity Type of Fulscope Controller with Automatic Reset



a No. 5 capacity tank and a 20-foot spool of 0.021-inch diameter capillary inserted between the capillary reset unit and the reset bellows in the order given. Although the reset rates obtained with this arrangement were still faster than the optimum rate calculated in Equations 6 and 7, the instrument was placed in operation with this reset arrangement to determine the degree of control which might be obtained.

Figure 4 shows the actual controlled temperature record obtained with each of the reset rates given in Table IV and with the instrument adjusted to a throttling range of 55 per cent, equivalent to a Taylor sensitivity of 5 pounds/sq. in./in. It is interesting to note that a reset rate of 0.331 pound/minute/pound produced a cyclic chart record while a reset rate of 0.232 pound/minute/pound gave a controlled temperature record with the minimum amplitude of fluctuation.

Table V gives the calibration of a reset arrangement with which it was possible to obtain approximately the calculated optimum reset rate. In this system the Foxboro capillary reset unit was followed in order by a 10-foot spool of 0.021-inch-diameter capillary and a number 5 capacity tank.

Figure 5 gives the controlled temperature record for a throttling range setting of 51 per cent equivalent to a Taylor sensitivity of 5.4 pounds/sq. in./in. (calculated optimum sensitivity). The record at the left is that obtained with a reset rate of 0.232 pound/min./pound in accordance with the last setting given in Table IV. The record on the right-hand side of Figure 5 was obtained with a reset rate of 0.181 pound/min./pound, which is approximately equal to the calculated value of the optimum reset rate as given in Equations 6 and 7. This record represents that obtained with the calculated optimum settings, and without doubt gives the best controlled temperature of all settings tried.

ADJUSTMENT OF TAYLOR INSTRUMENTS

Since the outlined procedure presented in the body of this paper applies only to the Foxboro Model 30 instrument, it was thought that a similar outlined procedure for Taylor instruments might be of value. An outline follows for both the Taylor proportional response controller and the Taylor proportional response and reset controller:

Proportional Response. 1. With the process on hand control and the instrument recording but not controlling, adjust the hand-operated valve to bring the pen to the desired control point.

2. Turn the pointer to the position of maximum output pressure, and guess the output pressure required to give the controlled valve a flow handling capacity equal to that of the hand-operated valve. Put this air pressure on the diaphragm of the controlled valve by regulating the reducing valve within the instrument case.

3. Adjust the proportional response dial for the lowest sensitivity adjustment, and set the pointer to coincide with the pen.

4. Close the hand-operated valve and open the block valves around the automatic controlled valve. If the temperature as recorded by the pen tends to rise or fall away from the pointer, make the necessary correction in the air pressure on the valve

diaphragm required to return the pen to the pointer by adjusting the large knurled wheel in the upper right-hand corner of the instrument case.

5. Adjust the instrument sensitivity upward in steps, creating a disturbance in the process for each adjustment by moving the pointer away from the pen for a minute or two and then returning it to the original set point. This procedure will finally produce an even cyclic controlled temperature record of constant amplitude.

6. The sensitivity adjustment producing this record is the ultimate sensitivity. The optimum sensitivity will be half the ultimate.

Proportional Response with Automatic Reset. 1. Set the instrument sensitivity at high and turn the pointer to the position of maximum output air pressure.

2. Adjust the reducing valve in the instrument to give a controlled valve position estimated to be sufficient to control the process.

3. Open the block valves on either side of the controlled valve and close the hand-operated valve.

4. Adjust the reducing valve in the instrument to stabilize the process.

5. Adjust the sensitivity dial for the lowest possible sensitivity and open the reset rate valve to graduation 5. Wait one minute and then set the reset rate valve to 0.

6. Set the supply air pressure to the instrument at 20 pounds and adjust the pointer to agree with the pen.

7. Adjust the instrument sensitivity as in the case of the proportional response instrument until the ultimate sensitivity is found. Allow the instrument to control at the ultimate sensitivity for approximately four or five complete cycles, and determine the time required for one complete oscillating cycle.

8. Set the sensitivity dial at 45 per cent of the ultimate sensitivity.

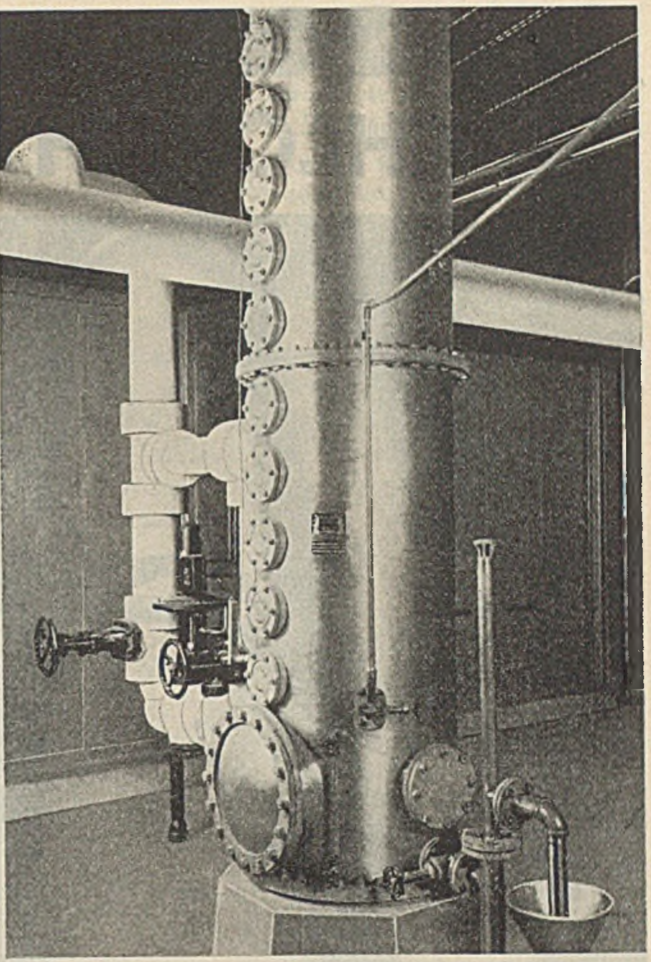
9. Set the reset dial at 1.2 over the time for one complete cycle at ultimate sensitivity.

CONCLUSIONS

The work described here confirms the data presented in the original paper by Ziegler and Nichols. The method for obtaining optimum settings proved to be straightforward and simple, and offered a more rapid method of obtaining optimum settings than the trial-and-error, hit-or-miss method of instrument adjustment commonly used. Furthermore, the settings obtained in this manner should be consistently closer to the actual optimum than those obtained by trial and error. In this particular case the Ziegler-Nichols procedure for obtaining optimum settings led to a revision of the reset arrangement in the instrument itself, without which it would have been impossible to obtain the calculated optimum settings and the degree of control finally achieved.

Naturally, the Ziegler-Nichols procedure has greater value in the establishment of optimum settings for Taylor instruments than for those of other manufacturers; the reason lies in the fact that the Taylor instruments are calibrated in terms of the units presented in the Ziegler-Nichols paper, whereas instruments of other manufacturers must be calibrated in these units in the field by the one whose duty it is to make the instrument settings. The acceptance by various instrument manufacturers of a universal system of units for the calibration of the various control effects which may be obtained with their instruments would be valuable in the establishment of optimum settings in accordance with the general procedure outlined in the Ziegler-Nichols paper.

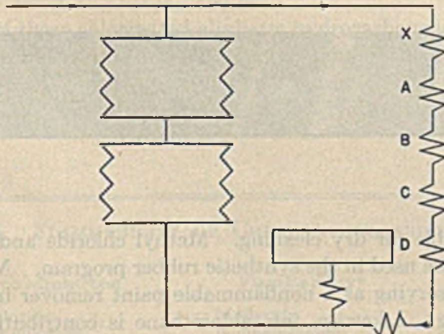
It is also felt that the preceding data disproves the contention of one instrument manufacturer that, once the optimum reset rate is established, slower rates of reset may be employed without damage to the control record. Evidence presented here not only confirms the fact that a too rapid reset rate produces a cyclic chart record, but also indicates that too slow a reset rate will produce an erratic chart record, the irregularities of which can be decreased only by reducing the instrument sensitivity. Often this is a step in the wrong direction, especially if the fastest possible rate of recovery from process upsets is required.



COURTESY, VULCAN COPPER & SUPPLY COMPANY

Alcohol Recovery Column, Showing Foxboro Stabilflo Steam-Control Valve with Integral-Mounted Vernier Valvactor

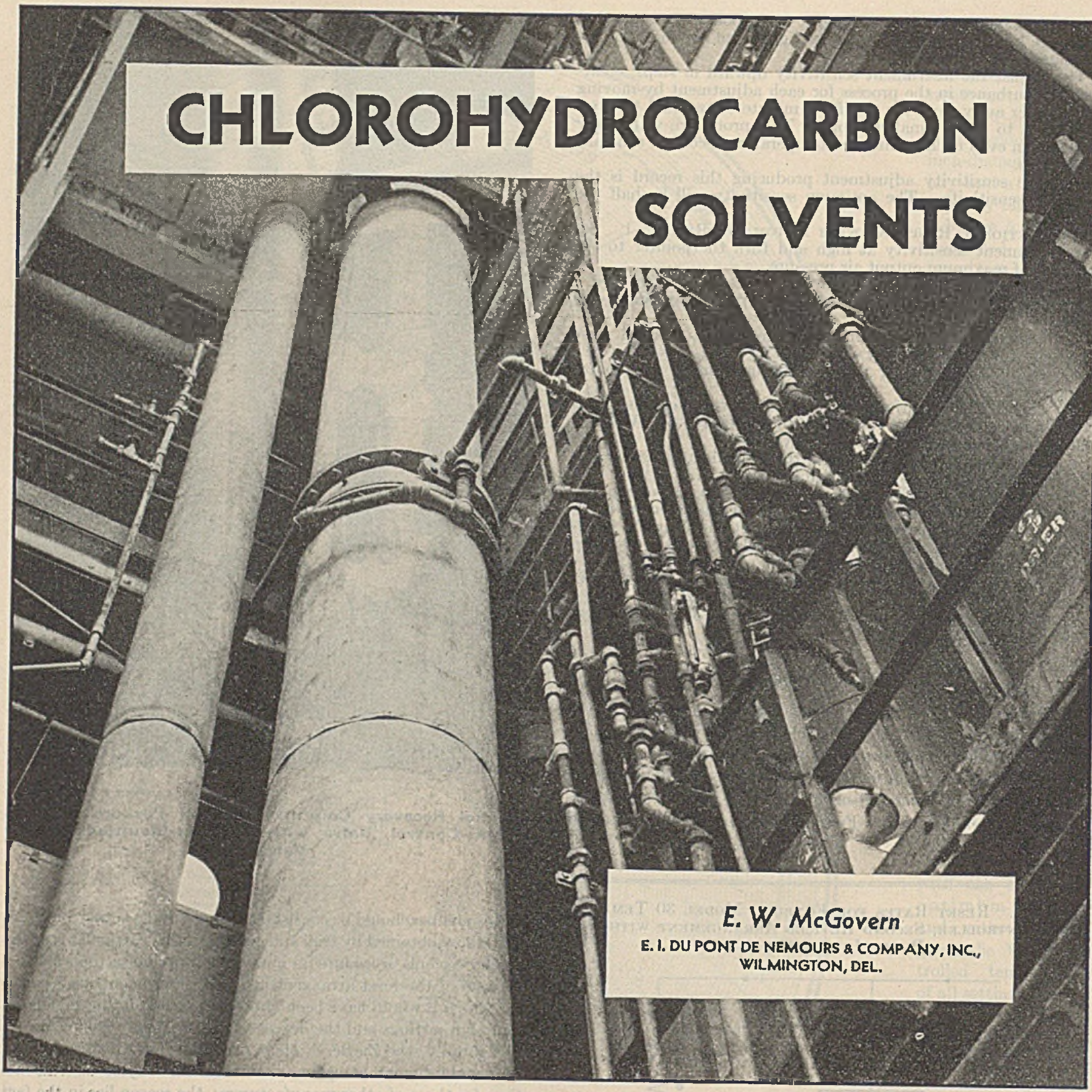
Table V. Reset Rates for Foxboro Model 30 Temperature Controller, Second Revised Arrangement with One Pound Initial Change



Resistance Open	Pressure Change, Lb./Sq. In.	Time Min.	Time Sec.	Reset Rate, Lb./Min./Lb.	
A	9 to 11	7	23	0.271	0.236
	11 to 9	9	58	0.201	
B	9 to 11	10	2	0.200	0.181
	11 to 9	12	25	0.161	
C	9 to 11	14	53	0.134	0.111
	11 to 9	22	45	0.088	
D	9 to 11	18	22	0.109	0.103
	11 to 9	20	50	0.096	
All closed	9 to 11	19	30	0.102	0.103
	11 to 9	19	12	0.104	

CHLOROHYDROCARBON SOLVENTS

E. W. McGovern
E. I. DU PONT DE NEMOURS & COMPANY, INC.,
WILMINGTON, DEL.



The photograph shows equipment for solvent distillation of crude trichlorethylene.

CHLOROHYDROCARBON solvents are finding even greater use in time of war than before. Production capacities for scarce raw materials as well as for the solvents themselves have had to be expanded repeatedly. Supplies of solvents for less essential civilian uses have been greatly curtailed or eliminated. Some peacetime uses, such as carbon tetrachloride for fire extinguisher fluid, have been directly transposed to war uses. Trichlorethylene is speeding production of tanks, airplanes, guns, and ammunition through its previously established use for solvent degreasing of metals. On the other hand, curtailment of civilian supply is often caused by diversion to purely war uses. Perchlorethylene is going into the manufacture of the smoke screen ingredient hexachlorethane, and for long periods little or none has been available for dry cleaning. Methyl chloride and ethylene dichloride are used in the synthetic rubber program. Methylene cholride is serving as a nonflammable paint remover in ship reconditioning. Likewise, tetrachlorethane is contributing in an important way to the war program. Many other peacetime and wartime applications of the chlorohydrocarbons depend to a great extent on their near or absolute nonflammability, coupled with their excellent solvent power for oils, fats, and other organic materials.

• • •

This discussion is confined to the commercially important groups of chlorinated aliphatic hydrocarbons—namely, the chlorine substitution products of methane, ethylene, ethane, and propane. Chlorinated derivatives, such as chloroalcohols and chloroethers, and the chlorinated aromatics are beyond the scope of the paper.

The most commonly used of the chlorinated aliphatics are methylene chloride (dichloromethane), chloroform, and carbon tetrachloride of the methane group; trichlorethylene and perchlorethylene (tetrachloroethylene) of the ethylene group; ethylene dichloride (1,2-dichloroethane) of the ethane group; and propylene dichloride (1,2-dichloropropane) of the propane group. Of lesser importance as solvents are methyl chloride, the *trans* and *cis* isomers of *sym*-dichlorethylene, ethyl chloride, β-trichlorethane (1,1,2-trichloroethane), *sym*-tetrachlorethane, and pentachlorethane.

Methods for commercial production of these chlorinated aliphatics show considerable variety. In general, the chloromethanes are derived from either methane or methanol. However, chloroform is also commonly made from acetone, and carbon tetrachloride from carbon disulfide. The chloroethylenes are most commonly obtained from acetylene. The chloroethanes are made variously from acetylene, ethylene, or ethanol. Propylene dichloride is manufactured by direct addition of chlorine to propylene.

FLAMMABILITY

The chief value of the chloro compounds over unsubstituted hydrocarbons is low flammability or nonflammability. Except for methyl chloride, ethyl chloride, dichlorethylene, ethylene dichloride, and propylene dichloride, all have flash points above 80° F. and therefore are considered nonflammable under Bureau of Explosives regulations. Methylene chloride is rated by the Underwriters' Laboratories as practically nonflammable at ordinary temperatures; chloroform and trichlorethylene are rated nonflammable and nonexplosive. Carbon tetrachloride, perchlorethylene, β-trichlorethane, tetrachlorethane, and pentachlorethane are also nonflammable. Of the nonflammables, methylene chloride, chloroform, and trichlorethylene, and some others with hydrogen in the molecule, form weakly combustible mixtures at higher temperatures with high concentrations of solvent in air.

Methyl chloride, ethyl chloride, and dichlorethylene are rated by the Underwriters' Laboratories as moderately flammable. Ethylene dichloride is likewise moderately flammable and is given a fire hazard rating of 60–70 by the Underwriters, which places it in a class with ethanol. Propylene dichloride is moderately flammable. Flash points of these flammable chlorohydrocarbons are shown in Table I.

The commercially important chlorinated aliphatic hydrocarbon solvents include methylene chloride, chloroform, and carbon tetrachloride of the methane group; trichlorethylene and perchlorethylene of the ethylene group; ethylene dichloride of the ethane group; and propylene dichloride of the propane group. Important properties affecting commercial applications of the solvents are discussed. They include flammability, stability, effect on common engineering metals, toxicity, and selective solvent action. A table and charts summarizing physical data are presented. Important fields of application and factors leading to the selection of the individual solvents are discussed. These applications include dry cleaning, extraction, and metal cleaning.

STABILITY

Each of these chlorinated aliphatic hydrocarbons is sufficiently stable for at least a narrow range of conditions of commercial application. Some conditions of use, however, may bring about a breakdown with formation of acidic decomposition products. It is, therefore, of considerable importance to outline for each chlorohydrocarbon the conditions under which it may be used without significant decomposition or corrosion of equipment. The terms "significant" or "appreciable" as used here do not refer to extensive decomposition but to a breakdown in one day of 0.001 to 0.01 per cent of the material.

Table I. Flammability of Chlorohydrocarbon Solvents

Chlorohydrocarbon	Flammability[a]	Flash Point, ° C.
Methyl chloride	Moderate	<0
Methylene chloride	Nonflammable	..
Chloroform	Nonflammable	..
Carbon tetrachloride	Nonflammable (0)	..
trans-Dichlorethylene (Di-48)	Moderate	4
cis-Dichlorethylene (Di-60)	Moderate	6
Trichlorethylene	Nonflammable (3–4)	..
Perchlorethylene	Nonflammable (0)	..
Ethyl chloride	Moderate	<0
Ethylene dichloride	Moderate (60–70)	13.3
β-Trichlorethane	Nonflammable	..
sym-Tetrachlorethane	Nonflammable	..
Pentachlorethane	Nonflammable	..
Hexachlorethane	Nonflammable	..
Propylene dichloride	Moderate	17

[a] Numbers in parentheses refer to Underwriters' Lab. flammability ratings based on ether = 100.

In general, chlorohydrocarbons may decompose through three fundamental causes—oxidation, hydrolysis, and pyrolysis. Some are also subject to a type of polymerization which might be termed "condensation". Oxidation is accelerated by high temperatures, light, and certain catalyzing impurities. Hydrolysis may be accelerated by metals such as iron or their salts as well as by higher temperatures. Reaction with water is comparatively slow when all water present is dissolved in the chlorohydrocarbon.

Decomposition of the oxidation or autoxidation type may be effectively controlled by very small amounts of inhibitors. However, no successful inhibitors for hydrolysis of chlorohydrocarbons are known, and therefore those which readily form acid in the presence of water must be used either in the absence of water or in specially designed acid-resisting equipment. Likewise, the chlorohydrocarbons must be used below the temperatures at which significant pyrolysis takes place. To avoid local overheating, they should not be allowed to come in contact with hot surfaces, such as heating coils, which are above the decomposition temperature of the particular solvent in question. All of the chlorohydrocarbons will break down in direct flame or when in contact with very hot surfaces (above 400–500° C.). The products of such thermal decomposition may include hydrochloric acid (if hydrogen is in the compound or in other substances present), phosgene (if air is present), and chlorine.

The conditions are outlined under which each of the chlorinated hydrocarbons may be used without appreciable development of acidity and without appreciable corrosion of properly

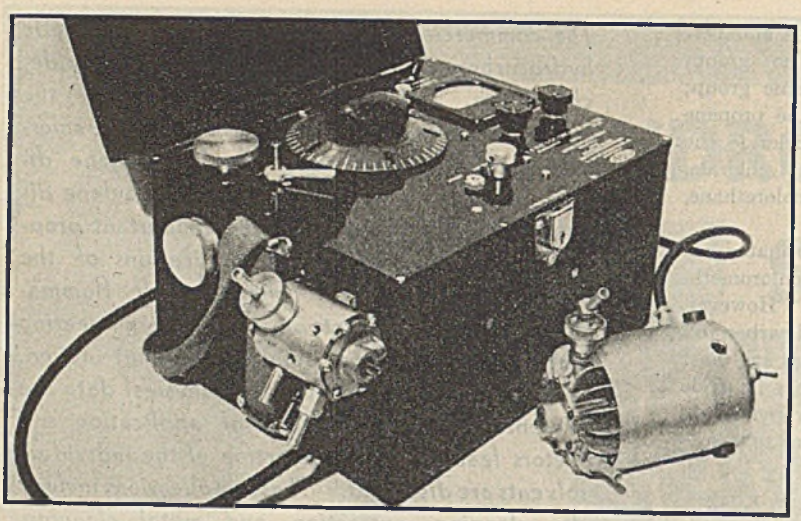


Figure 1. Ultraviolet Photoelectric Tri-Per Analyzer for Rapid Analysis of Vapors in Air

designed equipment. Trichlorethylene, perchlorethylene, and methylene chloride show the greatest stability over a wide range of conditions, although other chlorohydrocarbons may be satisfactorily stable for particular uses which provide suitable conditions:

Methyl Chloride has the highest thermal stability of the chlorohydrocarbons under consideration; in the absence of air and water it does not show appreciable decomposition below about 400° C. It hydrolyzes slowly below 100° and is highly resistant to oxidation at temperatures up to several hundred degrees centigrade.

Methylene Chloride may be used in the presence of air, water, light, and any of the common construction metals at temperatures up to 60° C., which is 20° above its boiling point. Small quantities of dissolved water do not appreciably affect its stability below 100°, but an excess of water (i. e., undissolved water) may cause noticeable hydrolysis at 60°. Steam distillation of the solvent from oils with low-pressure steam, however, is successfully employed, since in this case time of contact with water at higher temperatures is quite limited. A commercially available grade of methylene chloride containing a volatile oxidation inhibitor is stable in dry systems, even in the presence of air at temperatures up to 120° C.

Chloroform, either the stabilized technical grade or the U. S. P. grade, can be used in the presence or absence of light and water with common construction metals up to 120° C. The U. S. P. grade contains alcohol as an oxidation inhibitor, and a technical grade is available which contains an even more powerful inhibitor. However, in the presence of air, especially air and light, even stabilized chloroform tends to develop acidity on continued use.

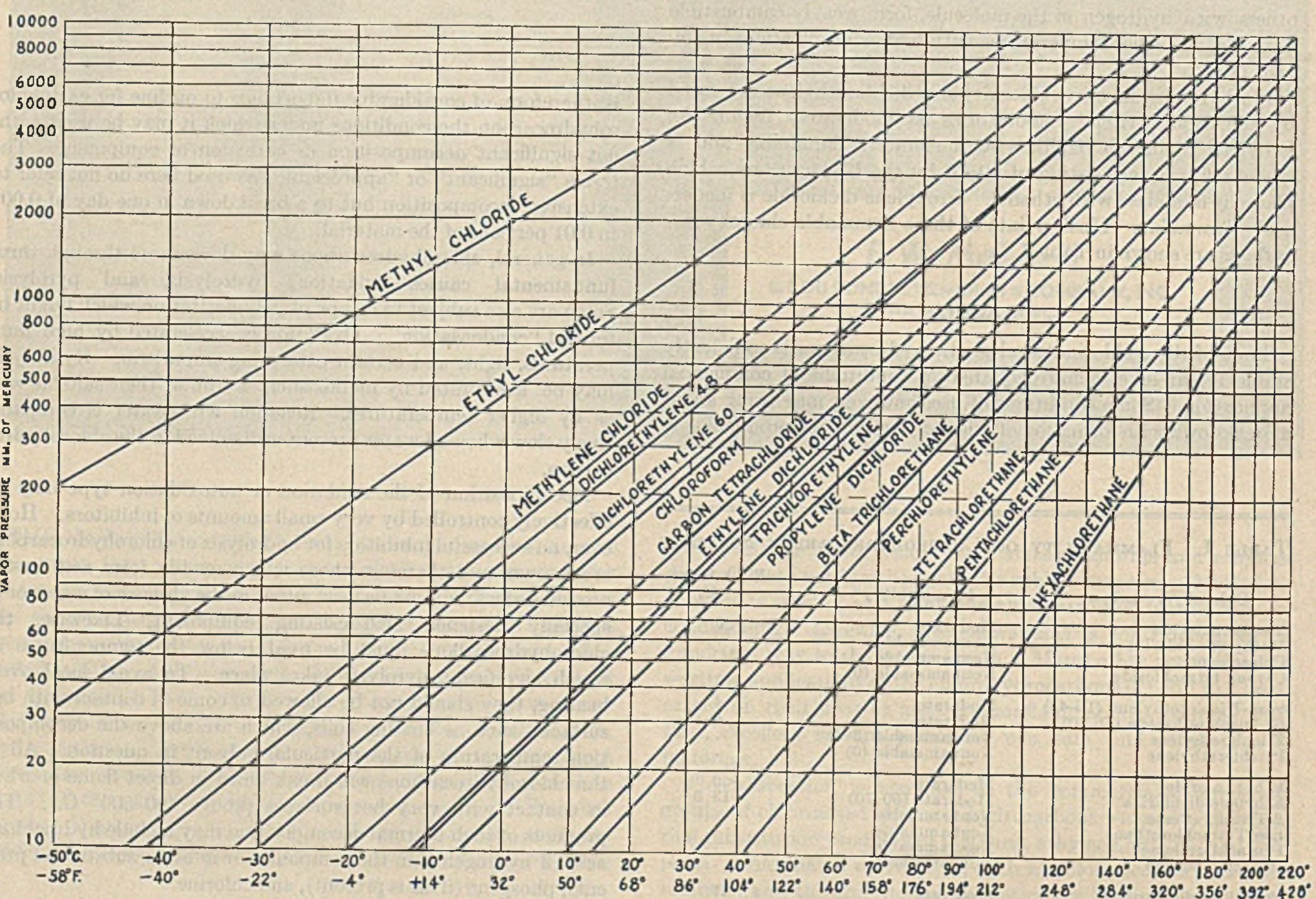


Figure 2. Vapor Pressures

Pressure-temperature relations are important in selecting for a particular application. Methylene chloride extraction of cocoa butter avoids deleterious effects of high temperatures. Metals are not too hot to handle after being degreased with trichlorethylene vapors.

The numbers on curves of Figures 3 to 14 refer in each case to the same compound, designated as follows:

1. Carbon tetrachloride
2. Chloroform
3. *trans*-Dichlorethylene (Di-48)
4. *cis*-Dichlorethylene (Di-60)
5. Ethyl chloride
6. Ethylene dichloride
7. Methyl chloride
8. Methylene chloride
9. Pentachlorethane
10. Perchlorethylene
11. Tetrachlorethane
12. Trichlorethylene
13. β-Trichlorethane

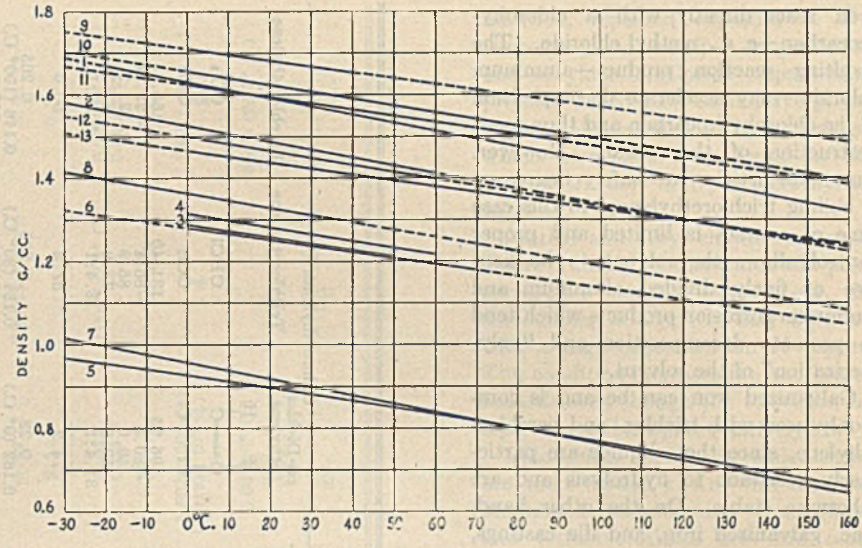


Figure 3. Density of Liquids

High-density liquids are more completely removed in centrifuging dry-cleaned garments. Pentachlorethane because of its high density is used for sink-and-float beneficiation of coal and other minerals.

Carbon Tetrachloride may be used in the presence or absence of air and light with the common construction metals up to 130° C. In the presence of undissolved water, carbon tetrachloride hydrolyzes readily, and at its boiling point wet carbon tetrachloride will corrode most of the common construction metals. Equipment to handle the wet solvent is, therefore, commonly constructed of nickel or Monel metal, both of which are resistant to this type of corrosion. In the absence of excess water, carbon tetrachloride containing dissolved water may be used with the common construction metals at various temperatures up to 90° C., depending upon the particular metal.

Dichlorethylene (*trans* and *cis*) may be used in the absence of air and water with the common construction metals at temperatures up to 120° C. Properly stabilized material can be successfully employed in the presence of air and water up to 60°.

Trichlorethylene, properly purified and stabilized, may be used in the presence or absence of air, water, and light, with any of the common construction metals at temperatures up to 120° C.

Perchlorethylene, properly purified and stabilized, may be employed in the presence or absence of air, water, and light, with any of the common construction metals, at temperatures up to 140° C.

Ethyl Chloride may be used in the absence of air and water at temperatures up to and, in some instances, considerably above 200° C. It is quite resistant to oxidation at ordinary temperatures, and hydrolysis is slow.

Ethylene Dichloride may be employed in the presence or absence of air and light with the common construction metals at temperatures up to 100° C. In the absence of air and water it is stable up to 160°. In contact with water, it hydrolyzes slowly at 80°, and at 100° hydrolysis is rapid.

β-Trichlorethane may be used in the absence of air and water at temperatures up to 110° C. In contact with water, it hydrolyzes appreciably at its boiling point (113.7°). It may be used in the presence of air at ordinary temperatures.

Tetrachlorethane may be employed in the absence of air and dissolved water up to 120° C. Excess water over that which will dissolve causes appreciable hydrolysis at room temperature. Hydrolysis and oxidation become comparatively rapid above 110°.

Pentachlorethane shows practically the same stability characteristics as tetrachlorethane. It may be used in the absence of air and excess water at temperatures up to 110° C. It cannot be distilled at atmospheric pressure without some decomposition.

MATERIALS OF CONSTRUCTION

All of the common engineering metals, including ordinary grades of iron and steel, tin (tin plate), brass, bronze, copper, lead, zinc, and galvanized iron, can be used with these chlorohydrocarbons under conditions which avoid the formation of acidic decomposition products, as outlined in the section on "Stability". Because of the highly corrosive nature of hydrochloric acid, the chlorohydrocarbons generally should not be used under conditions where they will show an appreciable degree of decomposition. Some measure of relief from corrosion may sometimes be afforded by special acid-resisting alloys when the presence of the acidic materials does not rule out the solvent for other reasons.

Aluminum, though satisfactory under favorable conditions with some of the more stable chlorohydrocarbons, should not be used generally as a material of construction. It is susceptible to corrosion by even small amounts of hydrochloric acid and may

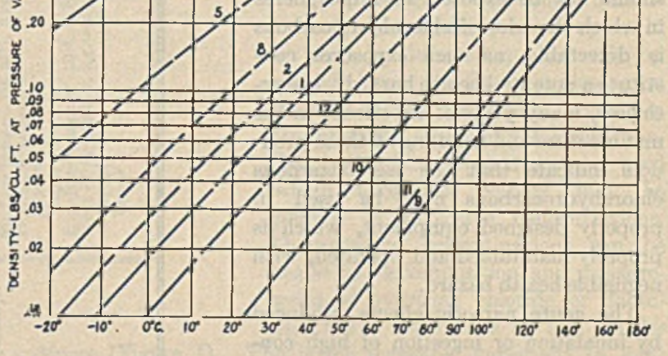


Figure 4. Density of Saturated Vapors

High-density vapors are characteristic of chlorohydrocarbons, and ventilation should generally be down-draft. High vapor density permits the use of trichlor- and perchlorethylene in open-tank vapor degreasers.

even react directly with a chlorohydrocarbon—e. g., methyl chloride. The resulting reaction product—aluminum chloride—may accelerate decomposition of the chlorohydrocarbon and thus speed destruction of the metal. However, aluminum articles are safely degreased in boiling trichlorethylene; in this case time of contact is limited and proper control allows the solvent to be kept free of finely divided aluminum and aluminum corrosion products which tend to promote decomposition and "polymerization" of the solvent.

Galvanized iron can be and is commonly used with trichlor- and perchlorethylene, since these liquids are particularly resistant to hydrolysis and are otherwise stable. On the other hand, zinc, galvanized iron, and die castings, especially those containing aluminum or magnesium, should not be employed as materials of construction with chlorohydrocarbons susceptible to hydrolysis at ordinary temperatures, or where time of contact is long and temperatures are high. These metals, however, can be degreased with chlorohydrocarbon solvents.

Carbon tetrachloride, ethylene dichloride, β-trichlorethane, tetrachlorethane, and pentachlorethane are best employed in the absence of free water because of their strong hydrolyzing tendencies and consequent corrosive effects. Nickel and Monel metal are sometimes used as materials of construction for carbon tetrachloride equipment in processes where free water may be introduced, conditions under which common construction metals such as iron and zinc-coated iron are attacked.

TOXICITY

The chlorohydrocarbons, like all solvents other than water, are toxic. There is considerable variation among them in degree of toxicity, and many can be used with a high degree of safety under proper conditions. However, human beings should not be exposed to atmospheres in which the odor of chlorohydrocarbons is detectable, as such exposures constitute a potential health hazard. Nevertheless, many years of experience in the manufacture and handling of these products indicate that the less hazardous chlorohydrocarbons may be used in properly designed equipment, which is properly maintained and operated, with negligible health hazard.

The acute narcotic effects produced by inhalation or ingestion of high concentrations of carbon tetrachloride, ethylene dichloride, dichlorethylene, trichlorethylene, and perchlorethylene

Table II. Physical Properties of Chlorohydrocarbons

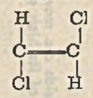
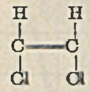
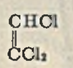
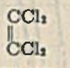
	Chloromethanes				Chloroethylenes			
	Methyl chloride	Methylene chloride (dichloromethane)	Chloroform	Carbon tetrachloride	*trans*-Dichlorethylene	*cis*-Dichlorethylene	Trichlorethylene	Perchlorethylene
Chemical formula	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4	 $\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}$	 $\underset{Cl}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}$	 $CHCl{=}CCl_2$	 $CCl_2{=}CCl_2$
Molecular weight	50.49	84.94	119.39	153.84	96.95	96.95	131.40	165.85
Freezing point, ° C.	−97.6	−96.7	−63.5	−22.85	−50.0	−80.5	−86.4	−22.35
Boiling point (at 1 atm.), ° C.	−23.76	39.8	61.2	76.5	47.5	59.0	86.9	121.2
Steam distn. point (at 1 atm.), ° C.	......	38.3	56.0	66.8	45.2	53.8	73.2	87.7
Solvent: water ratio, by wt.	......	66.3:1	34.1:1	23.5:1	51.0:1	31.4:1	13.4:1	5.32:1
Latent heat of vaporization (at b. p.), cal./g. or C.H.U./lb.	102.45	78.7	59.3	46.8	73.7	74.2	57.2	50.0
Sp. heat, cal./g./° C.								
Liquid (20° C.)	0.381	0.280	0.234	0.205	0.28	0.28	0.225	0.205
Vapor (1 atm.)	0.199 (25° C., 1.021 atm.)	0.155 (40° C.)	0.142 (61.2° C.)	0.140 (76.75° C.)	0.162 (0° C.)	0.162 (0° C.)	0.156 (80° C.)	0.146 (100° C.)
Critical temperature, ° C.	143	245.0	262.9	283.15	243.3	271.0	271.0	347.1
Critical pressure, atm.	65.9	60.9	53.8	44.98	54.4	......	49.5	....
Thermal conductivity, C.H.U./(hr.)(sq. ft.)(° C./ft.)								
Liquid (20° C.)	0.093	0.0920	0.0751	0.0683	0.0732	0.0848	0.0801	0.0732
Vapor (b. p.)	0.00486 at 0° C.	0.00438	0.00455	0.00422	....	......	0.00482	0.00505
Sp. gr. of liquid, d_4^{20}	0.920	1.326	1.489	1.594	1.257	1.282	1.464	1.623
Av. coefficient of cubical expansion of liquid (° C.)	0.00209 (−30 to +30)	0.00137 (0 to 40)	0.00129 (0 to 40)	0.00124 (0 to 40)	0.00136 (15 to 45)	0.00127 (15 to 45)	0.00117 (0 to 40)	0.00102 (0 to 25)
Vapor density (b. p. and 1 atm.), g./l.	3.58 (−15° C.)	3.30	4.36	5.37	3.68	3.56	4.45	5.22
Sp. gr. of vapor at 1 atm. and b. p. (air = 1 at same temp. and pressure)	2.52 (−15° C.)	2.93	4.13	5.32	3.34	3.34	4.54	5.83
Viscosity, centipoises								
Liquid (20° C.)	0.244	0.425	0.57	0.969	0.425	0.47	0.58	0.88
Vapor	0.01062 (20° C.)	0.0109 (40° C.)	0.0115 (61° C.)	0.0115 (70° C.)	....	......	0.0103 (60° C.)	0.0099 (60° C.)
Solubility (25° C.), g./100 g.								
Chlorohydrocarbon in water	0.74 at 30° C., 1 atm.	1.32	0.79	0.08	0.63	0.35	0.11	0.015
Water in chlorohydrocarbon	0.285	0.198	0.097	0.013	0.55	0.55	0.032	0.0105
Diffusivity in air (25° C., 1 atm.), sq. cm./sec.	0.105	0.091	0.079	0.071	....	......	0.073	0.067
Evaporation rate (ether = 100)	......	71	56	33	63	56	28	9
Refractive index, n_D								
Liquid	1.3712 (−23.7° C.)	1.4244 (20° C.)	1.4455 (20° C.)	1.4601 (20° C.)	1.4466 (18° C.)	1.4499 (17° C.)	1.4782 (20° C.)	1.5044 (20° C.)
Vapor	1.000703 (25° C.)	1.001055 (25° C.)	1.001436 (0° C.)	1.001796 (0° C.)	1.001473 (0° C.)	......	1.001784 (0° C.)	1.002009 (0° C.)
Surface tension (in air), dynes/sq. cm.	......	28.2 (20° C.)	26.2 (25° C., in N)	25.4 (25° C., in N)	....	......	Approx. 29 (30° C.)	32.32 (20° C.)
Dielectric constant								
Liquid	12.93 (−25° C.)	9.1 (20° C.)	4.785 (20° C.)	2.205 (20° C.)	2.35 (25° C.)	9.30 (25° C.)	3.42 (16° C.)	2.365 (25° C.)
Vapor	1.0109 (21° C.)	1.0082 (40° C.)	1.00462 (69.6° C.)	1.00302 (87.6° C.)	....	......	....	....
Dipole moment × 10^{18}, E.S.U.	1.86	1.59	1.00	0.0	0	1.85	0.9	0
Heat of formation, kg.-cal./mole								
Liquid	......	28.6	31.2	33.8	....	......	+1	+3
Vapor	20.1	21.7	23.6	25.9	....	......	−7	−6

TABLE II. PHYSICAL PROPERTIES OF CHLOROHYDROCARBONS (*Continued*)

	Chloroethanes						
	Ethyl chloride	Ethylene dichloride (1,2-dichloroethane)	1,1,2-β-Trichlorethane	1,1,2,2-Tetrachlorethane	Pentachlorethane	Hexachlorethane	Propylene Dichloride (1,2-dichloropropane)
Chemical formula	CH_3 CH_2Cl	CH_2Cl CH_2Cl	CH_2Cl $CHCl_2$	$CHCl_2$ $CHCl_2$	$CHCl_2$ CCl_3	CCl_3 CCl_3	CH_3CHCl CH_2Cl
Molecular weight	64.52	98.97	133.42	167.86	202.31	236.76	112.99
Freezing point, ° C.	−136.4	−35.5	−35.5	−42.5	−29.0	184.5 (sublimes)	below −70
Boiling point (at 1 atm.), ° C.	12.3	83.5	113.7	146.3	160.5	186.8 at 811 mm. (triple point)	96.4
Steam distn. point (at 1 atm.), ° C.	11.8	71.4	85.4	93.7	95.8	99.0	78.2
Solvent: water ratio, by wt.	256.3:1	11.3:1	5.38:1	2.41:1	1.845:1	0.48:1	8.17:1
Latent heat of vaporization (at b. p.), cal./g. or C.H.U./lb.	91.5	77.3	68.7	54.9	44.2 (147–158° C.)	46.4	72.3 (65–85° C.)
Sp. heat, cal./g./° C.							
Liquid (20° C.)	0.399	0.308	0.266	0.268	0.215	0.174 (25° C.)	0.22 (25° C.)
Vapor (1 atm.)	0.243 (40° C.)	0.255 (97.1° C.)	....	0.220 (146° C.)	....	.....	......
Critical temperature, ° C.	182.8	......	....	383.0	....	.....	......
Critical pressure, atm.	52.0	......	....	......	....	.....	......
Thermal conductivity, C.H.U./(hr.)(sq. ft.)(° C./ft.)							
Liquid (20° C.)	0.0848	0.0825	0.0778	0.0778	0.0751	.....	0.0726
Vapor (b. p.)	0.00550	......	....	......	....	.....	......
Sp. gr. of liquid, d_4^{20}	0.897	1.253	1.438	1.596	1.681	2.091	1.155
Av. coefficient of cubical expansion of liquid (° C.)	0.00156 (0 to 15)	0.00117 (0 to 30)	0.00100 (0 to 25)	0.00103 (0 to 30)	0.000912 (0 to 30)	.....	0.000813 (10 to 30)
Vapor density (b. p. and 1 atm.), g./l.	2.76	3.38	4.20	4.88	5.69	6.70 (811 mm.)	3.72
Sp. gr. of vapor at 1 atm. and b. p. (air = 1 at same temp. and pressure)	2.23	3.42	4.61	5.79	6.99	8.18 (811 mm.)	3.90
Viscosity, centipoises							
Liquid (20° C.)	0.26	0.84	1.2	1.77	2.5	.....	0.80
Vapor	0.0093 (12.3° C.)	......	....	......	....	.....	......
Solubility (25° C.), g./100 g.							
Chlorohydrocarbon in water	0.45 (0° C.)	0.84	0.44	0.29	0.05	0.005 (22.3° C.)	0.27 (20° C.)
Water in chlorohydrocarbon	....	0.16 (20° C.)	0.025 (−9° C.)	1.13	0.03	.....	0.04 (20° C.)
Diffusivity in air (25° C., 1 atm.), sq. cm./sec.	0.094	......	....	0.065	....	.....	......
Evaporation rate (ether = 100)	....	27	12	3	3	.....	......
Refractive index, n_D							
Liquid	1.3798 (0° C.)	1.4448 (20° C.)	1.4719 (22° C.)	1.4938 (20° C.)	1.5024 (20° C.)	.....	1.4371 (25° C.)
Vapor	1.001000 (25° C.)	1.001344 (0° C.)	....	1.001602 (0° C.)	1.001929 (0° C.)	.....	......
Surface tension (in air), dynes/sq. cm.	20.64 (10° C.)	30.1 (29.9° C., in N)	....	......	....	.....	......
Dielectric constant							
Liquid	6.29 (170° C.)	10.45 (20° C.)	....	8.00 (20° C.)	3.60 (25° C.)	.....	8.925 (26.1° C.)
Vapor	1.01285 (23.5° C.)	1.00481 (120° C.)	....	......	....	.....	......
Dipole moment × 10^{18}, E.S.U.	2.00	1.57	....	1.85	....	.....	1.85
Heat of formation, kg.-cal./mole							
Liquid	31.6	37.6	....	......	45	54 (macrocryst.)	......
Vapor	25.7	29.3	....	33	35	37	......

are apparently of approximately the same order of magnitude. From a practical standpoint, however, carbon tetrachloride and ethylene dichloride are somewhat more toxic than trichlor- and perchlorethylene because of their higher vapor pressures. In addition, repeated exposure to low concentrations of carbon tetrachloride and ethylene dichloride vapors may produce delayed or cumulative physiological effects, such as liver damage, which have not been found in the case of trichlor- and perchlorethylene vapors.

Methyl and ethyl chloride are gaseous at ordinary temperatures and pressures, and, should leakage occur, the surrounding atmosph re may be filled with a high concentration of vapors. This condition increases fire and health hazards even though the toxicities, on a percentage basis, are relatively low.

Chloroform and β-trichlorethane are more toxic than the above-mentioned compounds; pentachlor- and tetrachlorethane are still more toxic. Tetrachlorethane, in particular, must be used with greatest precaution because of its high toxicity, in spite of its relatively low vapor pressure.

Contact of the skin with any of the chlorinated hydrocarbons or their vapors should be avoided since absorption through the pores may produce the same physiological effects as inhalation. Contact with the liquid solvent may also cause excessive dryness with subsequent cracking of the skin due to extraction of the natural oils normally present, and this may be followed by infection.

At higher temperatures such as occur in gas flames and electric heaters, chlorinated hydrocarbon vapors, the nonflammable as well as the flammable, may decompose with the formation of toxic and corrosive substances. To prevent inhalation, the combustion products from open flames located near open equipment containing solvent must be conducted outside of the building.

Systems using chlorinated hydrocarbons should be well designed and maintained with a view toward preventing leakage of vapors into working spaces and thus minimizing hazards and solvent losses.

The presence of very small quantities of chlorohydrocarbon vapors in air may be detected qualitatively by a halide lamp; the flame, impinging on metallic copper, turns blue or green in the presence of a chlorohydrocarbon. The halide lamp should not be used where flammable vapors may be present in explosive concentrations. Quantitative determinations can be made by decomposition and measurement of hydrogen chloride or photoelectrically by means of the Tri-Per analyzer (Figure 1). The latter measures variations in light absorption by air containing solvent vapors and provides a quick method for the detection and estimation of trichlorethylene, perchlorethylene, and pentachlorethane in air (*10, 11*).

PHYSICAL PROPERTIES

Properties of importance in the practical application of chlorohydrocarbons to solvent uses are detailed in Table II and Figures 2 to 14. They are based on critical selections of data from available literature sources, supplemented by investigations carried out in du Pont laboratories where published values were not available or were of doubtful accuracy. Selected best values were correlated and checked with values for related properties. In a few cases the finally selected values are still of questionable accuracy, but they are considered good enough to be useful in engineering calculations. Data on hexachlorethane are included to complete the chloroethanes, although this material is a solid at ordinary temperatures and therefore is not used as a solvent.

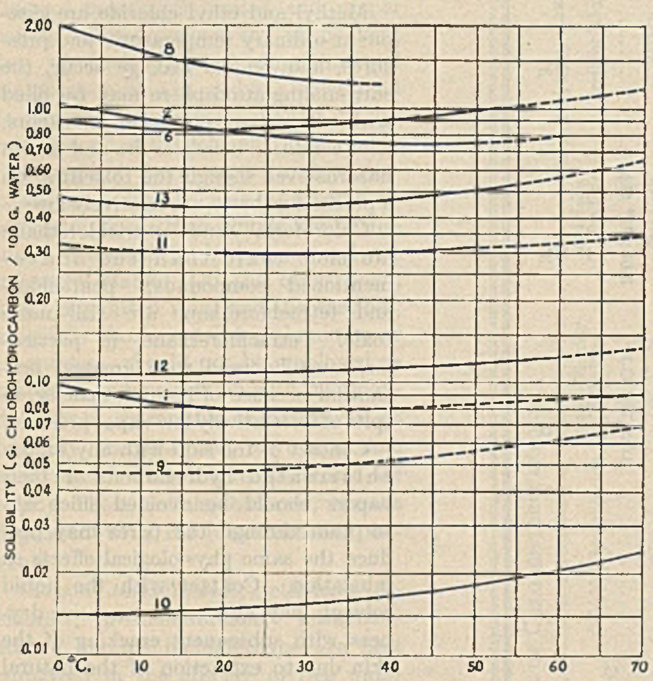


Figure 5. Solubility of Chlorohydrocarbons in Water

Low solubility makes recovery practicable by steam distillation in extraction processes The more polar solvents, such as methylene chloride, show highest solubility for water and other polar substances, such as cellulose acetate.

Data presented are differentiated according to experimentally determined values (solid lines), calculated values (long dashed lines), and extrapolations (short dashed lines). The exception is Figure 2 (vapor pressure) in which solid lines are drawn over the entire range; the accuracy of the modified Cox chart—log vapor pressure *vs.* $1/(230° + t° \text{ C.})$—used to correlate the data over the pressure range involved was great enough to justify this representation. The curious kink in the vapor pressure curve for hexachlorethane is attributed to the sublimation of this compound, and is corroborated by experimental data from several sources.

Calculations of the vapor viscosities of methylene chloride, trichlorethylene, and perchlorethylene were based on the Sutherland equation:

$$\mu = \frac{AM^{1/2}T^{1/2}}{S^2(T + C)}$$

where μ = viscosity, centipoises
A = universal constant equal to 2.7×10^{-3}
M = molecular weight of chlorohydrocarbon
S = diameter of molecule
C = Sutherland constant—i. e., 1.47 T_b, where T_b is boiling point on absolute scale

Latent heats of evaporation were calculated according to the Watson relation to supplement experimental data where required.

The specific heats of trichlor- and perchlorethylene vapors were calculated on the basis of the following two relations:

$$(C_v)_p = 0 = 3R + \frac{aR}{2} + \sum q_iC_{\nu i} + \frac{3n - 6 - a - \sum q_i}{\sum q_i}\sum q_iC_{\vartheta i}$$

$$C_p = (C_v)_p = 0 + R\left[1 + \frac{81}{32}\frac{p}{p_c}\left(\frac{T_c}{T}\right)^3\right]$$

where R = gas constant of 2.0 cal./mole
n = number of atoms in molecule
q_i = number of volume bonds
$C\vartheta_i, C\nu_i$ = Einstein functions for a given bond having characteristic frequencies ϑ_i and ν_i
a = number of bonds permitting free rotation

Thermal conductivities of trichlorethylene and perchlorethylene in the vapor state were computed from Jean's equation:

$$\frac{C_p\mu}{k} = \frac{4}{9 - 5/y}$$

where C_p = specific heat, C.H.U./(lb.)(° C.)
μ = viscosity, lb./(ft.)(hr.)
k = thermal conductivity, C.H.U./(hr.) (sq. ft.)(° C./ft.)
y = ratio of specific heats, C_p/C_v

The saturated vapor densities of the chlorohydrocarbons were calculated directly from the following equation based on the ideal gas laws:

$$V = \frac{M}{359} \times \frac{273}{T} \times \frac{P}{760}$$

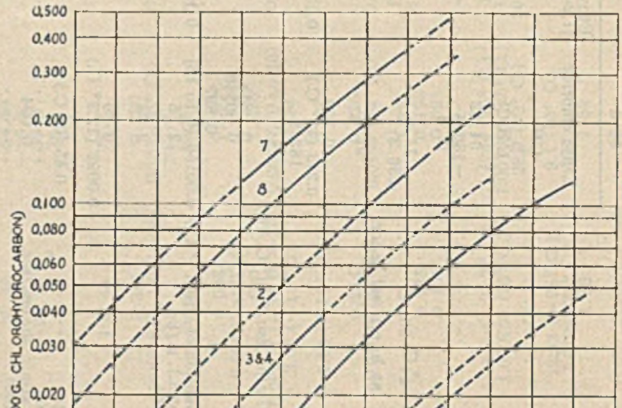


Figure 6. Solubility of Water in Chlorohydrocarbons

Low solubility of chlorohydrocarbons in water permits their application in processes such as dry cleaning and extraction where water dilution is undesirable.

where M = molecular weight of chlorohydrocarbon
P = vapor pressure of chlorohydrocarbon at absolute temperature T

Values thus calculated were in good agreement with available experimental data.

Diffusivities of the chlorinated hydrocarbons were determined by the formula:

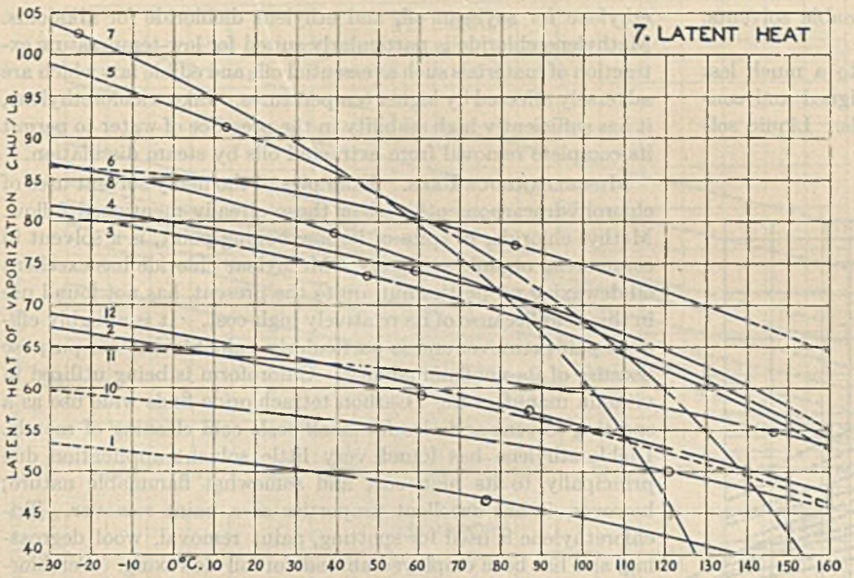
$$D = 0.0043 \frac{T^{3/2}}{P(V_A{}^{1/3} + V_B{}^{1/3})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$

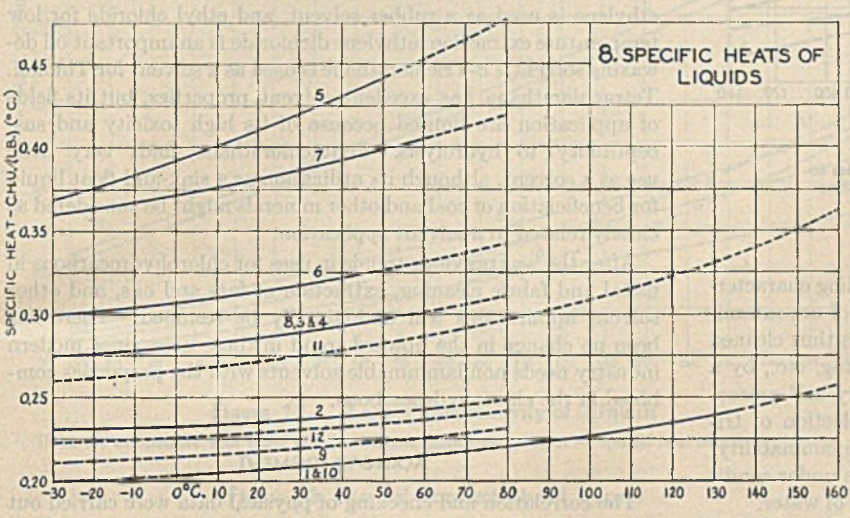
where D = diffusivity, sq. cm./sec.
T = absolute temperature
M = molecular weights of components
P = total pressure, atm.
V = molar volumes of components

SELECTIVE SOLVENT ACTION

As a class, the chlorinated hydrocarbons have a high and rapid solvent action on organic materials such as oils, fats, and waxes. Low surface tension and high wetting power contribute to this effect. Compared with other solvents, they have a high solvent power for free alkaloids although the solubility of such substances in chlorohydrocarbons is limited. In general, the chlorohydrocarbons dissolve only small quantities of water, water-soluble organic materials such as sugars and glycerol, and inorganic materials such as acids and salts. In other terms, it may be said that the chlorohydrocarbons in general are nonpolar or weakly polar solvents with some, such as methylene chloride, exhibiting a degree of polar solvent activity. Thus, many unsubstituted hydrocarbons are miscible in all proportions with the chlorohydrocarbons, while highly polar derivatives, such as glycerol and lactic acid, are only slightly soluble in the chlorohydrocarbons. Cellulose triacetate is soluble in methylene chloride, chloroform, or tetrachlorethane, preferably in the presence of a small amount of methanol, but the diacetate or hydroxy acetate is relatively insoluble in pure methylene chloride, chloroform, or tetrachlorethane. Other solvents, such as β-trichlorethane, methylene chloride, perchlorethylene, and trichlorethylene show distinctive solvent properties for natural and synthetic rubber. As a matter of fact, all of the chlorohydrocarbons have some swelling effect on rubber.

These solvent properties give some indication of the scope of the chlorinated hydrocarbons. Their commercial





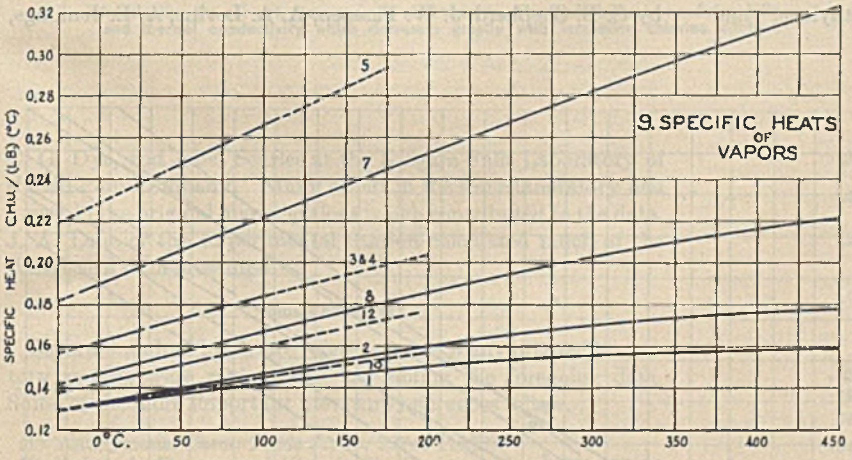


Figure 7. Latent Heat of Vaporization of Liquids

Low latent heats of chlorohydrocarbons contribute to rapid drying in metal degreasing and dry cleaning. Low latent heat is necessary to provide sufficient condensate on metals being cleaned by vapor degreasing. Circled points indicate latent heats at normal boiling points.

◆

Figure 8. Specific Heat of Liquids

High specific heat of liquid methylene chloride leads to its selection as a nonflammable low-temperature heat transfer medium. Trichlorethylene is used for heat transfer where a higher boiling liquid is needed.

◆

Figure 9. Specific Heat of Vapors at One Atmosphere

High specific heat of vapor is important in the application of chlorohydrocarbons as refrigerants.

applications, particularly those of the nonflammable solvents, are many. Some of the major uses follow.

Metal Degreasing. Trichlorethylene and, to a much less extent, perchlorethylene are used in specially designed and constructed equipment for vapor degreasing of metals. Liquid solvent as well as vapor may be used, but the outstanding characteristic of the process is a final rinse by condensation of uncontaminated vapor on the article being cleaned. Metal is thus cleaned prior to finishing, machining, heat treating, repairing, etc., by a rapid operation which leaves the metal surface dry and grease-free. Among the many factors leading to the selection of trichlorethylene for hot solvent degreasing are nonflammability, low latent heat, ideal boiling point, low solvent loss under conditions of use, and high stability even in the presence of water.

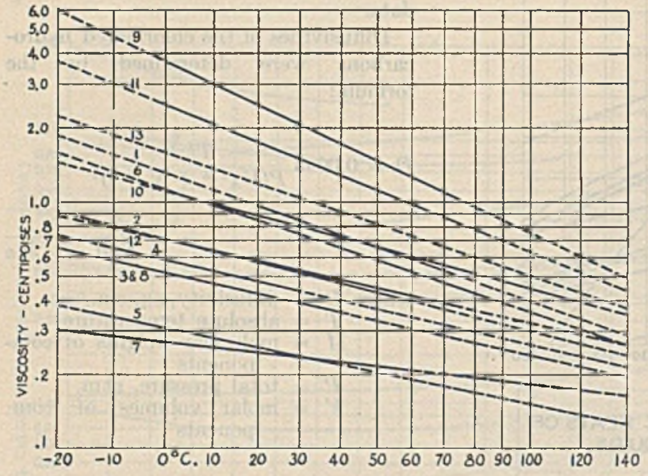


Figure 10. Viscosity of Liquids

Low viscosity of chlorohydrocarbon liquids contributes to their value in extraction, dry cleaning, and metal cleaning.

Dry Cleaning. Trichlorethylene, perchlorethylene, and carbon tetrachloride are in common use as dry cleaning solvents. Ethylene dichloride is used to some extent mixed with carbon tetrachloride. Here again, nonflammability and low over-all cleaning costs are of prime importance. Specially designed equipment is necessary to assure efficient, economical, and safe operation. All of these solvents will remove grease, dirt, and oil from garments in a short time, and garments are left free from odor. Since the solvents are low boiling, they can be recovered readily by the dry cleaners themselves by simple distillation.

Extraction. Most of the chlorinated hydrocarbons find use in the extraction field, the selection of the solvent depending upon many factors such as solubility of the material being extracted, cost, flammability, stability, and nature of extraction process. Some important examples are methylene chloride for cocoa butter, chloroform for medicinals, carbon tetrachloride for oils and fats from substantially dry materials, trichlorethylene for soybean oil, and ethylene dichloride for alkaloids. Methylene chloride is particularly suited for low-temperature extraction of materials such as essential oils and edible fats which are adversely affected by higher temperatures. Like trichlorethylene, it has sufficiently high stability in the presence of water to permit its complete removal from extracted oils by steam distillation.

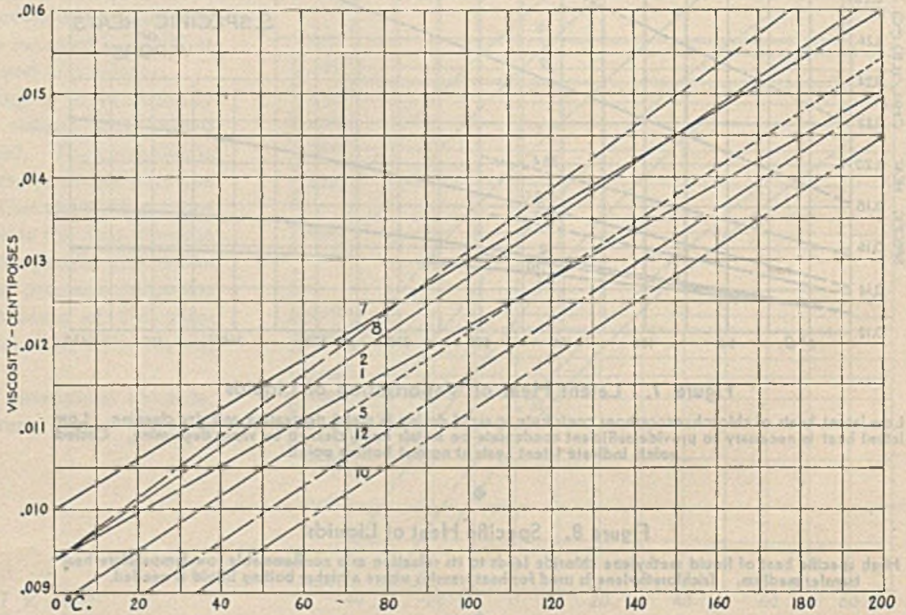


Figure 11. Viscosity of Vapors

In comparison to density, viscosity of chlorohydrocarbon vapors is a minor factor in fluid flow problems.

Miscellaneous Uses. Examples of the many solvent uses of chlorohydrocarbons other than those already mentioned follow. Methyl chloride, in spite of its low boiling point, is a solvent in commercial organic synthesis. Methylene chloride has excellent oil dewaxing properties but, up to the present, has not found use in this field because of its relatively high cost. It is a highly efficient paint remover and is particularly valuable for this purpose because of its nonflammability. Chloroform is being utilized in vitamin manufacture. Carbon tetrachloride finds wide use as a spotting solvent and also for small-scale cold cleaning of metals. Dichlorethylene has found very little solvent application due principally to its high cost and somewhat flammable nature; however, it has excellent properties as a paint remover. Trichlorethylene is used for spotting, paint removal, wool degreasing, and has been employed abroad for oil dewaxing. Perchlorethylene is used as a rubber solvent, and ethyl chloride for low temperature extraction; ethylene dichloride is an important oil dewaxing solvent. β-Trichlorethane is used as a solvent for Thiokol. Tetrachlorethane has excellent solvent properties, but its fields of application are limited because of its high toxicity and susceptibility to hydrolysis. Pentachlorethane finds very little use as a solvent, although its utilization as a sink-and-float liquid for beneficiation of coal and other minerals might be considered as closely related to a solvent application.

After the war previous trends in uses for chlorohydrocarbons in metal and fabric cleaning, extraction of fats and oils, and other solvent applications will undoubtedly be resumed. There has been no change in the upward trend in these uses, since modern industry needs nonflammmable solvents with the properties combined in the chlorohydrocarbons.

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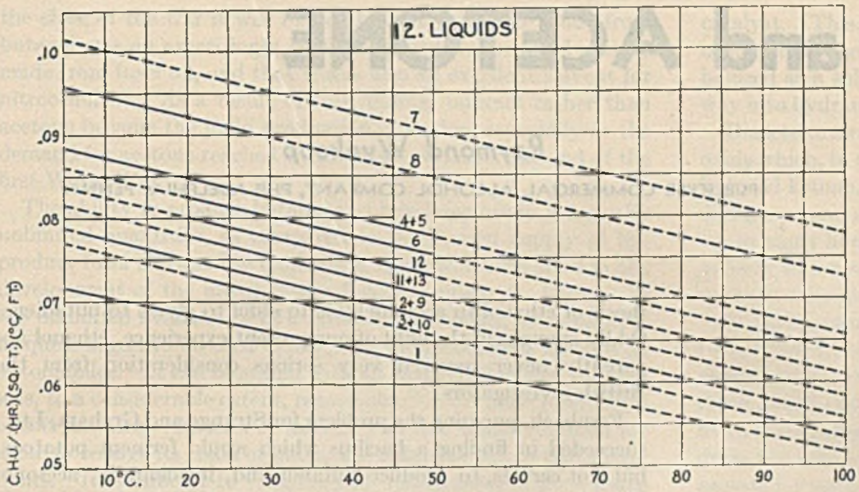

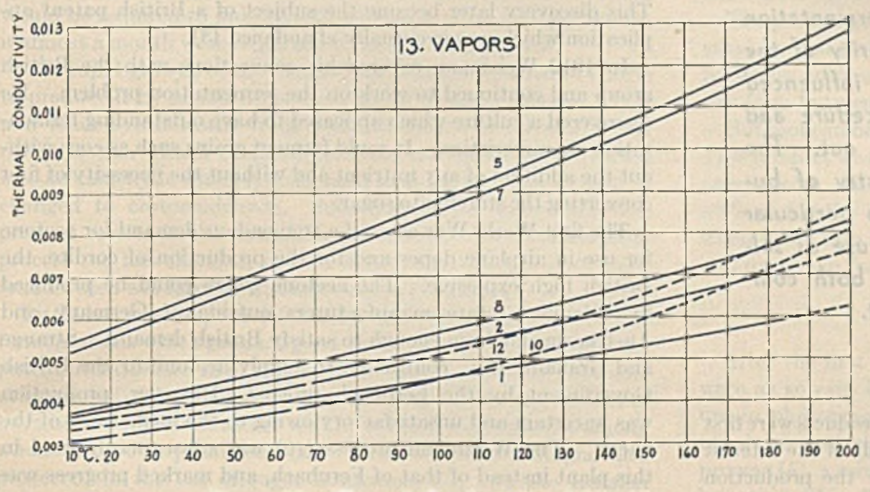

Figure 12. Thermal Conductivity of Liquids

These are comparable with those of other organic liquids and present no special heat transfer problems.

Figure 13. Thermal Conductivity of Vapors

In selecting the solvent, a compromise must sometimes be made between nonflammability and thermal conductivity which decreases greatly with increasing chlorine content.

C. G. Dye, and Janet Searles at the Niagara Falls Laboratory of the du Pont Company. Many others in the same laboratory had a part in the original investigations which contributed to the data. J. A. Lane of the Experimental Station calculated much of the theoretical data presented.

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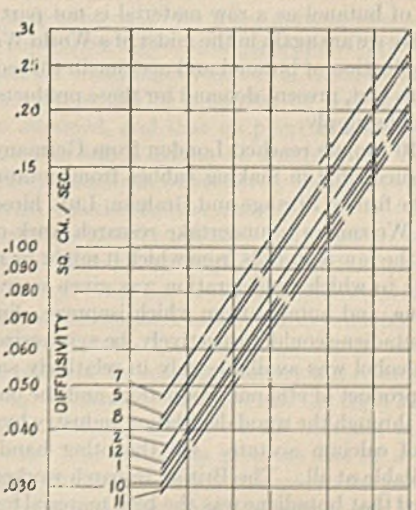

Figure 14. Diffusivity in Air at One Atmosphere

Diffusivity is lowest with the heavier molecules of higher chlorine content, in this case nonflammability is associated with decreasing tendency toward solvent loss in certain types of applications.

n-BUTANOL and ACETONE

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A brief history of the butyl-acetonic fermentation industry is given. The striking similarity of the past and present factors which have influenced the industry are noted. Process procedure and raw material economics are pointed out. The more important phases of the chemistry of butanol and acetone are discussed, with particular regard to the derivatives which find use as solvents. The uses and importance of both compounds and derivatives are pointed out.

THE investigations of processes to make these products were first carried out about thirty years ago as a result of the interest in the use of *n*-butanol as a starting point for the production of synthetic rubber. The commerical production of butanol, and the acetone simultaneously produced by the fermentation process, can be directly attributed to the demand for acetone brought about by the first World War. Thus, the search for synthetic rubber and the existence of a state of war furnished the impetus for the development of the butyl-acetonic fermentation industry.

Today this country is making a determined effort to bring about the rapid production of a huge tonnage of synthetic rubber, but the use of butanol as a raw material is not part of the program. Today we are again in the midst of a World War and there is a huge production of butanol and acetone in this country; but in spite of this fact, present demand for these products is in excess of the available supply.

About 1910 rumors reached London from Germany that Fritz Haber had succeeded in making rubber from potatoes. In the same year the firm of Strange and Graham, Ltd., hired Fernbach, Perkin, and Weizmann to undertake research work on synthetic rubber, and the raw materials from which it might be made. The raw products to which consideration was given were isoamyl alcohol, acetone, and butanol from which isoprene, dimethylbutadiene, and butadiene could, respectively, be synthesized.

Isoamyl alcohol was available only in relatively small quantities as a by-product of ethanol production, and the only source of acetone was through the wood distillation industry by destructive distillation of calcium acetate. On the other hand, *n*-butanol was not available at all. The British research workers prophetically surmised that butadiene was the best material for producing synthetic rubber, and decided that this could be made by the dehydration of butanol to butylene which, in turn, could be dehydrogenated to butadiene.

The use of ethanol also as a raw material was outlined by Perkin (*9*) who was the first to give the details of the now well known synthesis of ethanol to acetaldehyde to aldol to glycol to butadiene. Oddly enough, in the light of our present experience, ethanol apparently never received very serious consideration from the British investigators.

Fernbach, pursuing the problem for Strange and Graham, Ltd., succeeded in finding a bacillus which would ferment potatoes, but not cereals, to produce butanol and, incidentally, acetone. This discovery later became the subject of a British patent application which was eventually abandoned (*3*).

In 1912 Weizmann severed his connections with the British group and continued to work on the fermentation problem. He discovered a culture which appeared to have outstanding fermentation characteristics. It could ferment grains such as corn without the addition of any nutrient and without the necessity of first converting the starch into sugar.

The first World War created a tremendous demand for acetone for use in airplane dopes and for the production of cordite, the British high explosive. The acetone which could be produced by calcium acetate manufacturers outside of Germany and Austria was far from enough to satisfy British demand. Strange and Graham, Ltd., contracted to supply acetone to the British Government by the Fernbach process. However, production was uncertain and unsatisfactory owing to the inefficiency of the bacilli. The Weizmann process (*10*) was subsequently used in this plant instead of that of Fernbach, and marked progress was made in production.

However, at that time a bushel of corn weighing 56 pounds produced only 10 or 11 pounds of solvents made up of approximately 60 parts butanol, 30 parts acetone, and 10 parts ethanol. Thus, 56 pounds of material had to be shipped from America to England to obtain 3 pounds of much needed acetone. With shipping space at a premium, it became evident that the process had to be carried out closer to the source of raw material. A distiller was therefore converted to the Weizmann process at Toronto, Canada, and later when we entered the war, the process was utilized in two distilleries at Terre Haute, Ind. (*4*).

WEIZMANN PROCESS

The Weizmann process has already been described in detail (*6*) and will be merely outlined here. Corn is ground, digested under pressure with water, and cooled to 98° F., and the resulting mash run into fermenters. These are then inoculated with a culture of proved purity, and the fermentation is complete in about 40 hours. Although ethanol fermentation gives off carbon dioxide only, butanol fermentation produces a gas containing approximately 60 per cent carbon dioxide and 40 per cent hydrogen by volume. The butanol process must be carried out in closed fermenters which can be thoroughly sterilized to ensure satisfactory fermentations, whereas ethanol can be made in open-top fermenters. To obtain optimum yields, the butanol mash has a starch or sugar content of only about half that of the mash used for alcohol fermentation.

No use for butanol was found during the war except that at Toronto some of it was dehydrated to butylene, treated with sulfuric acid, and subsequently hydrolyzed to *sec*-butanol. This was catalytically dehydrogenated to methyl ethyl ketone which was used as a partial substitute for acetone. However, around the close of the war it was found that butyl acetate made from butanol was an exceedingly efficient substitute for amyl acetate made from fusel oil, and that it was also an excellent solvent for nitrocellulose. As a result of this finding, butanol rather than acetone became the main production objective, especially as the demand for acetone reached a rather low ebb after the end of the first World War.

The ability to produce butanol and butyl acetate in practically unlimited quantities, as compared to the limited supply of by-product fusel oil, was the foundation stone which resulted in the development of the nitrocellulose lacquer industry. Because of the unlimited availability of a satisfactory solvent, nitrocellulose lacquers began to be used in the place of oleoresinous finishes on automobiles. It can be stated without exaggeration that butanol was, to a considerable extent, responsible for the mass production of automobiles. Instead of the three to four weeks required for a car to receive its coats of finish, the time was cut to that many hours. It is difficult to visualize how many acres of floor space would be required to finish a half million or more cars per month if almost a month were required for the finishing process.

The rapid growth of the demand for butanol resulted in efforts to produce it by means other than the Weizmann process. It is now made synthetically from either acetylene or ethanol as the raw material. Each of these products can easily be converted into acetaldehyde which is condensed to aldol, and this, in turn, is changed to crotonaldehyde. Subsequent hydrogenation of this product results in the formation of butanol. The fermentation process too has changed, in that many new cultures have been found which will ferment molasses instead of grains.

Little has been reported formally concerning the many sugar fermentations which produce good yields of butanol, although the patent literature is full of claims. The descriptions and economic evaluations of sugar fermentations using blackstrap molasses have been worked out rather well by several investigators, among whom Arroyo is prominent (*2*). Mezzandroli and Magno also pioneered in the use of sugar fermenters (*7*), and the Russian literature reports use of the Weizmann bacillus to ferment mixtures of grain and molasses with the use of nutrients (*8*).

At the time the United States entered the present war, molasses had entirely supplanted corn and other grains as the raw material for butanol fermentation. However, the shortage of tankers and the submarine situation almost eliminated the importation of molasses so that the Weizmann process is again being used in butanol fermentation plants with grains as the raw material. With the exception of minor improvements, the process of producing butanol by fermentation is about back where it was twenty-five years ago. However, it should be borne in mind that the products of the butyl-acetonic fermentation must compete against synthetics which have a stable raw material cost, while agricultural products, cereals in particular, have fluctuated wildly in price in recent years. It is not unreasonable to assume, then, that substitution of molasses for grains, even in the grain belts, will continue to be common.

The availability of acetone as a by-product of the butyl-acetonic fermentation eliminated the production of the former by the wood distillation industry. However, the demand for acetone as a result of its low price and new uses has grown enormously so that today more is being produced synthetically than by fermentation. The production of synthetic acetone is based on propylene from oil refinery gases. This is converted into isopropanol by sulfation and subsequent hydrolysis, and the alcohol in turn is oxidized or dehydrogenated to acetone. Catalytic conversion of acetylene and steam and of acetaldehyde and steam to acetone over alkaline catalysts also seems promising.

CHEMICAL PROPERTIES

The chemical reactions of both butanol and acetone are well known, and only a few will be mentioned. Acetone is condensed to diacetone alcohol in the liquid phase by means of an alkaline catalyst. This ketoalcohol is an excellent solvent for both nitrocellulose and cellulose acetate. While it was originally made to be used as a solvent, the greater part of the production finds its way into hydraulic brake fluids.

Diacetone alcohol can be dehydrated with acid to form mesityl oxide which, in turn, can be catalytically hydrogenated to methyl isobutyl ketone. Mesityl oxide is an excellent solvent for esters, oils, gums, and rubberlike materials; methyl isobutyl ketone finds use in many liquid-liquid extraction processes, especially those involving water solutions of organic acids. It is one of the more easily obtainable water-insoluble ketones.

Of great commercial importance is the reaction by which acetone is pyrolyzed to ketene and methane. The availability of cheap acetone and the fact that ketene reacts directly with anhydrous acetic acid to form acetic anhydride has been of great benefit to the cellulose acetate industry. Less expensive acetic anhydride has resulted in substantially reducing the cost of cellulose acetate for use in fibers, plastics, and films.

The process of using *n*-butanol to make *sec*-butanol and methyl ethyl ketone at Toronto has already been referred to. This is no longer economical, as *sec*-butanol is now being made in quantity from butylenes from oil refinery gases.

Butanol can be catalytically dehydrogenated to butyraldehyde. This product was originally combined with amines to make rubber accelerators. However, far greater quantities are now being utilized for the manufacture of polyvinyl butyral resins which, when made into sheets and properly plasticized, are now in general use as the "sandwich filler" in safety glass.

USES OF ACETONE

After the first World War ended, the largest uses for acetone were as solvent in acetylene cylinders and for nitrocellulose for use in photographic films, cements, and dopes, but as the material became cheaper new uses were found. In the Govers process (*5*), a mixture of acetone and benzene is used to dewax lubricating oils. The rapidly growing cellulose acetate industry utilizes substantial quantities of acetone as a solvent, and it is used as the extraction medium in the production of insulin. However, probably as much acetone is converted into such products as acetic anhydride, diacetone alcohol, mesityl oxide, and substituted quinoline antioxidants as is used for direct solvent purposes.

USES OF BUTANOL

The Aronovsky process (*1*) for wood pulping uses a mixture of water and butanol in the digesters in place of the various chemicals usually utilized for wood digestion. It is claimed that cellulose of high alpha content can be produced by this process, that a pure lignin is obtained, and that no plant is needed for the recovery of chemicals which cannot be dumped into streams. In this process the butanol can be relatively easily recovered by injecting live steam into the digester mass.

The nitrocellulose lacquer industry continues to be the chief user of butanol. Here about 80 per cent of the butanol is employed in the form of butyl acetate so that until several years ago, 75–80 per cent of the butanol consumed in industry was in the form of the acetic ester. The expansion in the uses of urea-formaldehyde resins in the coating industry has recently changed this proportion. Butanol is used both in the resin kettle as the reaction medium and also as one of the solvents in the finish coating material. The result has been the sale of a larger proportion of butanol as such than was the case in the past.

Recently a great deal of interest has been shown in the large-scale production of 2,3-butyleneglycol by bacterial fermentation. Because of its low volatility, the recovery of the glycol presents a special problem. One proposal is to extract the glycol from the fermented mash with butanol; 2 gallons of butanol would be used for each gallon of mash.

Another relatively new material (cellulose acetate butyrate) for plastics and coatings involves the use of butanol. Butyric acid is made by the two-stage oxidation of butanol, first in the vapor phase to butyraldehyde, and then in the liquid phase to butyric acid. The use of butanol in the form of butyraldehyde for making polyvinyl butyral resins has already been mentioned.

Since a plasticizer may, in most cases, be considered a nonvolatile solvent, mention should be made of the more important plasticizers produced from butanol. Butanol itself is used to a small degree in the plasticizing of rubber. Dibutyl phthalate is one of the best plasticizers for nitrocellulose lacquers, for phenol-formaldehyde punch-stock resins, for other cellulose esters, and for flashless nonhygroscopic explosives.

Dibutyl sebacate is the preferred plasticizer for the polyvinyl butyral resin. Thus, in safety glass butanol finds use both in producing the resinous material itself and as a plasticizer for it.

Butanol owed its original growth to its use in nitrocellulose lacquers. Newer finishing materials have since appeared, although nitrocellulose lacquers continue to be sold in large volume. Even though the nitrocellulose lacquer usage may greatly diminish, it appears that the demand for butanol will continue; this product, either by itself or in the form of derivatives, plays an important part either as a solvent, a plasticizer, or an ingredient of many other products utilized in the finishing industry. Although born in the first World War at which time it was considered an almost unusable by-product, butanol is now playing an important part in our present war effort. There is every indication that it will continue to be needed for many peacetime uses.

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High-Pressure Absorption of LOW-BOILING HYDROCARBONS

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IN RECENT years there has been active interest in various methods of recovering distillate from high-pressure gas fields. This is particularly true of the Gulf Coast Region, inasmuch as state regulations have been established which do not permit wasteful processes for recovering the distillate. The regulations necessitate returning the residue gas to the reservoir from which it originated, unless the gas can be sold for a useful purpose. By returning lean gas to the reservoir, the pressure on the formation is maintained at the maximum, and there is very little loss of distillate due to retrograde condensation on the sand in the formation.

The return of lean gas to the reservoir entails considerable compressor capacity which is dependent upon the difference in pressure between the input wellhead and that of the lean gas before compression. It is desirable from the standpoint of maintaining compressor capacity at a minimum to carry out the recovery of distillate at as near wellhead pressure as possible. Of course, other factors must be considered to establish the optimum pressure. If retrograde condensation alone is used to recover the distillate, the separator pressure will ordinarily be about 500 to 1000 pounds per square inch at maximum distillate recovery. This leaves much to be desired since the wellhead pressures of many of the distillate fields are in excess of 3000 pounds; however, if higher separator pressure is used, the recovery of distillate declines rapidly. Furthermore, even at the optimum separator pressure, the efficiency of distillate recovery is not so high as desired.

High-pressure absorption, on the other hand, is a method which should permit more efficient recovery of distillate at higher pressure. The design of high-pressure absorbers, however, requires a knowledge of phase equilibrium at high pressure in systems with various types of lean oil. Few data are available which can be used as a basis for design. Few of the systems investigated and reported approach conditions which would be anticipated in a high-pressure absorber.

The first paper which even approached anticipated conditions in a high-pressure absorber was that of Katz and Hachmuth (*1*). They determined equilibrium constants of methane, ethane, propane, butanes, pentanes, and hexanes in a system of natural gas and a mid-continent crude oil at 40°, 120°, and 200° F. over a pressure range of atmospheric to 3500 pounds per square inch. Figure 1 represents an interpolation of their results for a temperature of 80° F. Their results showed that temperature affected the equilibrium constants much less above 800 pounds per square inch than at lower pressures; also, the effect of temperature increased with increasing molecular weight of the hydrocarbon.

Sage and Lacey (*4*) presented correlations of the equilibrium constant for methane in various binary systems, and showed that it is not only a function of temperature and pressure but also of the chemical characteristics of the system.

Sage, Hicks, and Lacey (*3*) recommended correlations, based on data available in the literature at the time, as the best available for solving problems on phase equilibria in production of crude oil and distillate. The most reliable of these correlations, however, were based entirely on the work of Katz and Hachmuth (*1*).

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Equilibrium constants are reported for methane, ethane, propane, *n*-butane, and *n*-pentane in three types of absorbing oil. The range of pressure was 125 to 3100 pounds per square inch, and the average temperature about 85° F. The three types of absorbing oil were paraffinic, naphthenic, and aromatic. The equilibrium constants at a given pressure and temperature are dependent upon the type of lean oil used. For the same pentane recovery at pressures above 1500 pounds per square inch the naphthenic type lean oil should absorb less methane than the paraffinic. Above 1750 pounds, however, the aromatic type should absorb less methane than the naphthenic. A higher lean oil rate would be required for aromatic type than either naphthenic or paraffinic, but the lean oil loss by vaporization into the lean gas with aromatic type would vary between 67 and 45 per cent of that for the paraffinic type at pressures of 1500 to 3000 pounds, respectively. At pressures around 125 pounds the paraffinic type lean oil is superior, both with respect to volume of lean oil required and to less methane absorption for the same pentane recovery.

The most pertinent publication thus far with respect to high-pressure absorption is that of Webber (*8*). He determined equilibrium constants for methane, ethane, propane, isobutane, *n*-butane, iso-pentane, *n*-pentane, and *n*-hexane in an absorbing oil with the following characteristics:

Aromatics, %	24.0	Distillation, ° F.	
Olefins, %	0.3	Initial b. p.	300
Naphthenes, %	36.7	10% over	421
Paraffins, %	39.0	50% over	511
Gr., ° A. P. I.	32.5	90% over	570
Mol. weight	183	97.7% over	650
Viscosity, centipoises			
At 100° F.	2.80		
At 200° F.	1.02		

His investigation was made at 33°, 100°, and 180° F. over a pressure range of 100 to 5000 pounds per square inch absolute. He showed that equilibrium constants are dependent upon the concentration not only of the less volatile component but also of the various components in the system, particularly above 3000 pounds per square inch. Unfortunately, insufficient data were presented to identify the exact composition of the system for each determination made.

Sage, Lavender, and Lacey (*5*) determined the equilibrium constant of methane in a system with decane, but they did not regard their results above 2000 pounds per square inch absolute as reliable.

Vink, Ames, David, and Katz (*7*) gave the equilibrium constants of methane, ethane, and propane in crude oil. Conditions were established such that a system of three phases, liquid-liquid-vapor, existed. The two liquid phases were obtained by precipitating asphalt with addition of sufficient propane. It is shown that the equilibrium constant of each component is quite different for each of the two phases used in its determination. This is conclusive evidence that the characteristics of the system are important in determining phase equilibria.

Roland, Smith, and Kaveler (*2*) determined equilibrium constants for methane, ethane, propane, butanes, pentanes, hexanes, and heptanes in a system of natural gas and distillate from one of the Gulf Coast fields. Their data extended to about 4000 pounds per square inch.

SCOPE OF INVESTIGATION

Inasmuch as high pressure absorption seemed to have possibilities for distillate recovery, an experimental program was initiated to provide the necessary phase equilibrium data to appraise the process. At the time the investigation was carried on, no information had been published dealing directly with phase equilibria of the low-boiling hydrocarbons in absorption oils at high pressure, although one paper (*8*) has been presented since then.

Although paraffinic lean oils are distinctly advantageous over naphthenic and aromatic types at low pressure, it was felt that the reverse might be the case at high pressure. Specifically, it was anticipated that the aromatic and naphthenic types should exhibit a selective absorption for butane and higher boiling components relative to methane over that exhibited by a paraffinic type. The objective of the experimental program was to determine the equilibrium constants for methane, ethane, propane, *n*-butane, and *n*-pentane in each of the three types of lean oil mentioned above. The equilibrium constants for each lean oil also were desired. This would permit evaluation of each type of

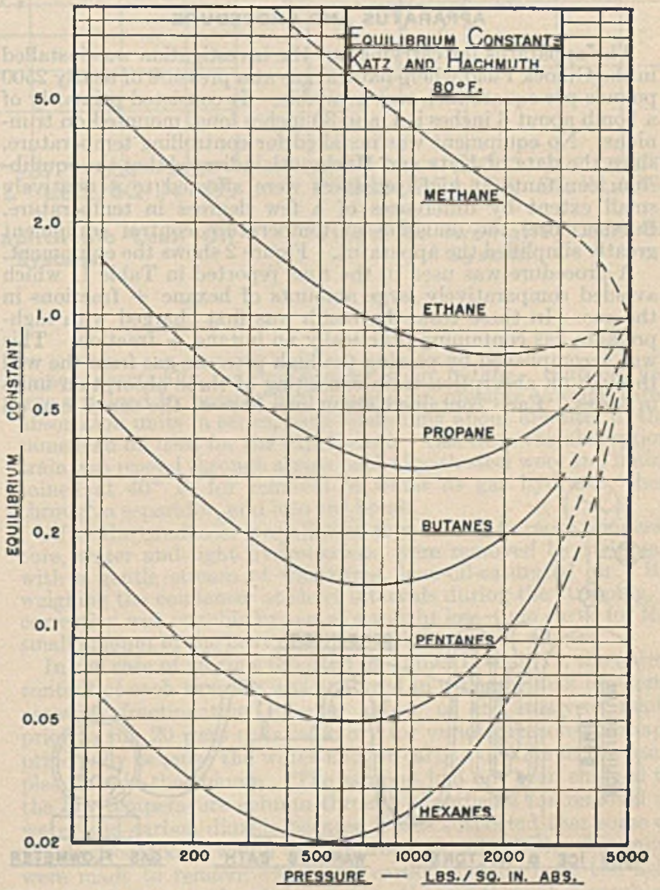

Figure 1. Natural Gas–Crude Oil System

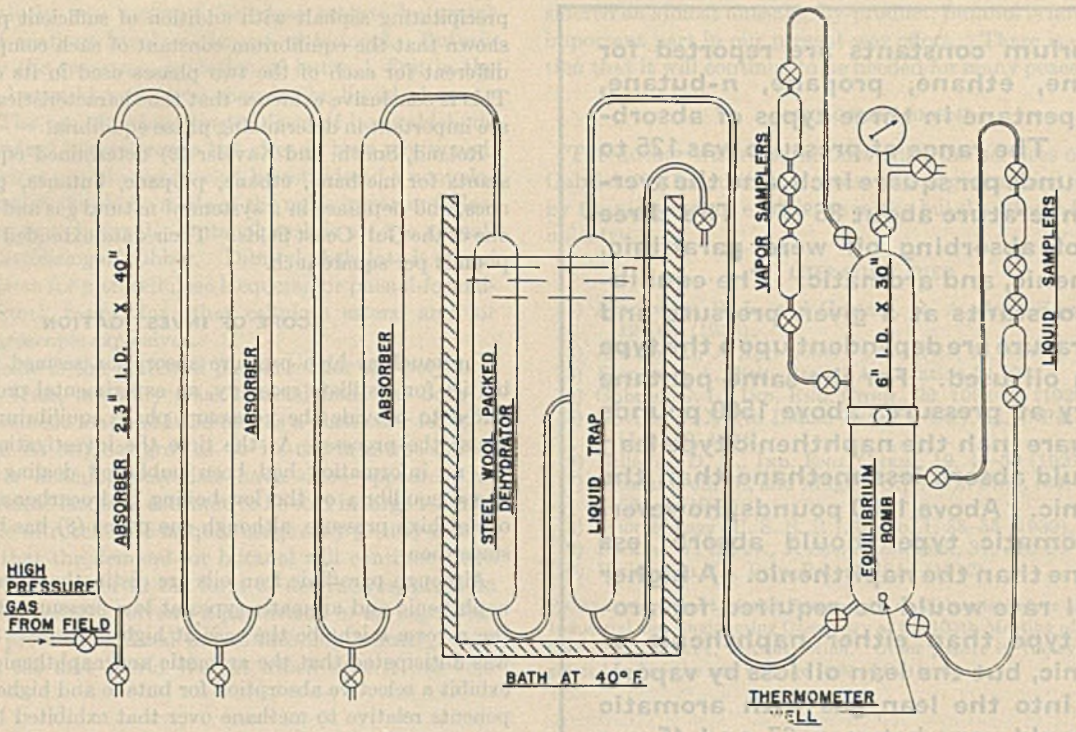

Figure 2. Experimental Equipment

lean oil with respect to: methane absorption at given butane and pentane recovery, lean oil rate at given butane and pentane recovery, and loss of lean oil by vaporization into the lean gas.

APPARATUS AND PROCEDURE

The apparatus for carrying out the investigation was installed in the Gillock Field where natural gas at a pressure of nearly 2500 pounds per square inch was available. It consisted primarily of a bomb about 6 inches i. d. and 30 inches long, mounted on trunnions. No equipment was installed for controlling temperature, since the data of Katz and Hachmuth indicated that the equilibrium constants at high pressures were affected to a relatively small extent by differences of a few degrees in temperature. Furthermore, the omission of temperature control equipment greatly simplified the apparatus. Figure 2 shows the equipment.

A procedure was used in the runs reported in Table II which avoided comparatively large amounts of hexane + fractions in the gas. In these tests the bomb was first charged with high-pressure gas containing practically no butane + fraction. This was accomplished by passing the high-pressure gas from the well through an absorption train consisting of three absorption units in series. Each contained about one liter of the same lean oil used for the experiment. A known quantity of lean oil was next pumped into the bomb followed by sufficient amounts of propane, n-butane, and n-pentane to permit accurate analyses for those components in samples of reasonable size (70 cc. for liquid and 100 cc. for vapor). Mercury was then pumped into the bomb to increase the pressure to the desired value for the series of experiments. The bomb was turned end over end on its trunnions for 30 minutes to ensure thorough mixing of the contents before samples were taken. The proportions of gas, oil, and mercury were roughly regulated to permit draining all of the mercury and little, if any, of the hydrocarbons when decreasing pressure for the second run of the series. Both gas and oil were drained to decrease the bomb pressure for runs beyond the second of the series. From the known volume of the bomb, the known amount of lean oil used, and the analyses of the samples, it was possible to check the accuracy of the data by component balance for pentane and establish the composition of the system for any test.

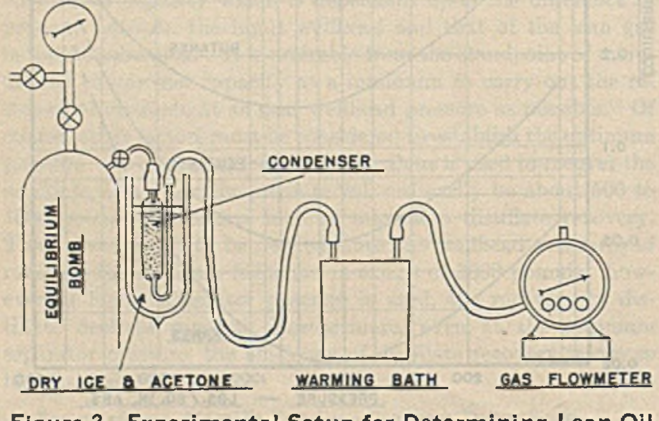

Figure 3. Experimental Setup for Determining Lean Oil Equilibrium Constants

Table I. Characteristics of Absorption Oils

	Paraffinic	Aromatic	Naphthenic
Gravity, ° A. P. I.	35.9	9.3	31.1
Density, lb./gal.	7.04	8.37	7.25
Mol. weight	230	160	220
Critical temp. (calcd.), ° F.	895	950	905
Viscosity at 100° F., Saybolt Universal sec.	38	39	...
Distillation, ° F.			
Initial b. p.	478	474	470
10% over	504	489	501
20% over	509	495	510
30% over	516	500	517
40% over	525	505	525
50% over	532	513	536
60% over	540	524	548
70% over	550	542	564
80% over	563	575	586
90% over	583	650	616
Final b. p.	647	760	682
Aromatics, wt. %	15.4	96.0	19.6
Naphthenics, wt. %	44.2	4.0	71.1
Paraffinics, wt. %	40.3		9.4

In the runs reported in Table III a procedure was also used to obtain equilibrium constants at a series of pressures with the same charge to the bomb. First, the bomb was charged with about 2 liters of lean oil. Then high-pressure field gas was

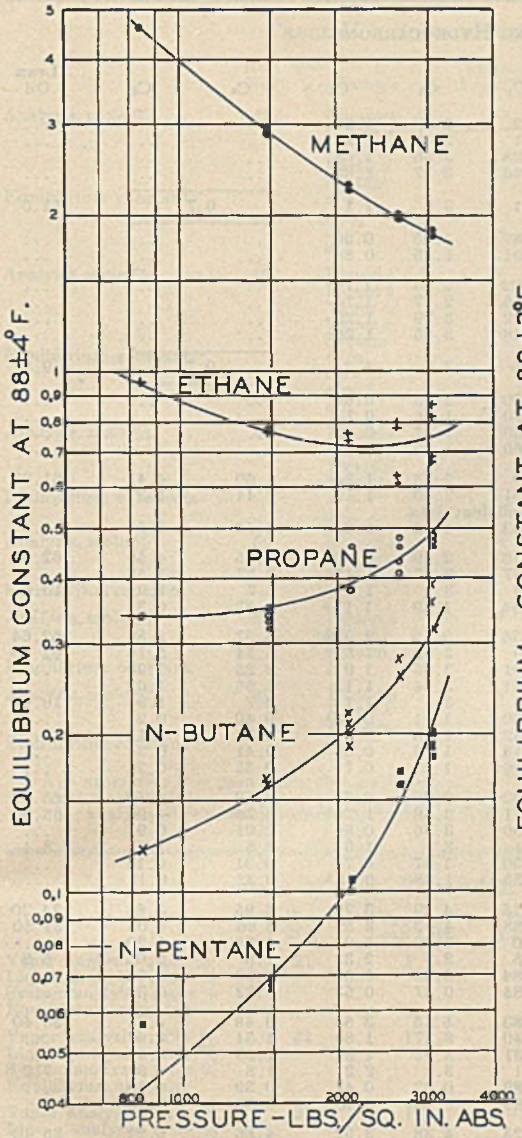

Figure 4. Paraffinic Lean Oil System

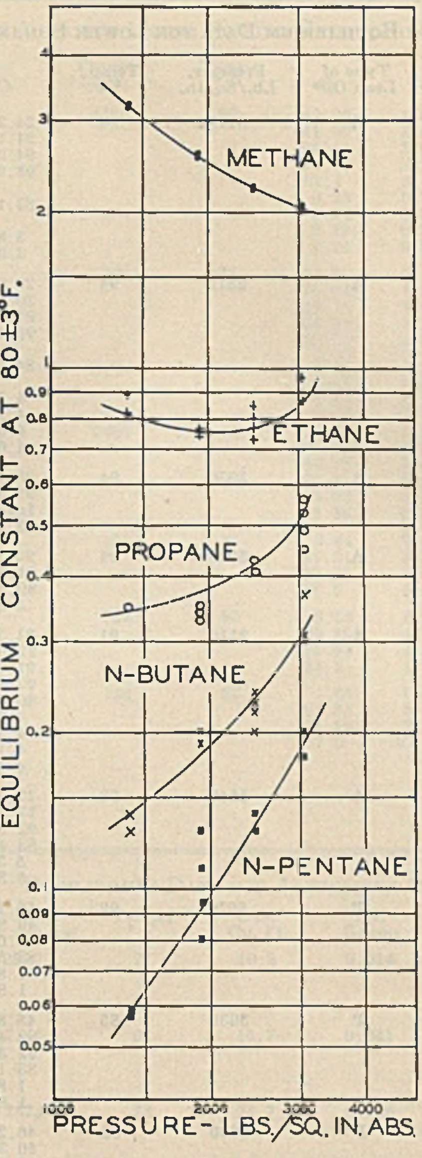

Figure 5. Naphthenic Lean Oil System

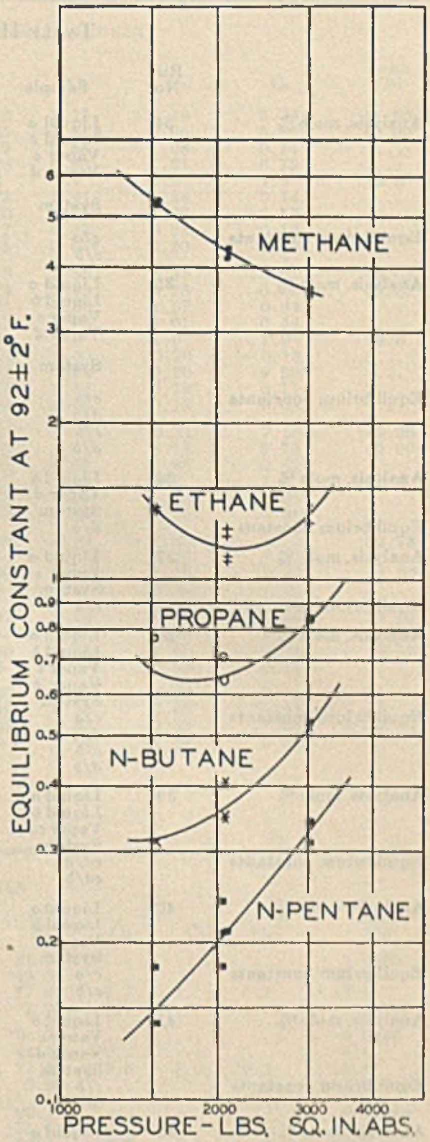

Figure 6. Aromatic Lean Oil System

passed into the bomb until maximum field pressure was reached. About 4 liters of the same lean oil was next pumped into the bomb, followed with mercury to increase the pressure to the desired value.

Determinations of the lean oil content of the vapor phase at various pressures was accomplished by obtaining the weight of lean oil in a measured volume of the vapor. Figure 3 shows the apparatus. Through a short connection, first flushed with a small amount of gas from the bomb, gas from the high-pressure bomb was throttled to substantially atmospheric pressure and passed into a weighed condenser maintained colder than −70° F. in a bath of solid carbon dioxide and acetone. Pressure in the bomb was maintained constant while removing gas by pumping in mercury. The condenser consisted of a glass chamber about 1.5 inches in diameter and 6 inches long. The chamber contained a depth of 4 inches of 14-mesh aluminum granules between plugs of glass wool. Noncondensables in the gas were warmed to about atmospheric temperature in a coil-in-water heater and then metered with a wet-gas meter. The rate of flow of gas was maintained at about 0.1 cubic foot per minute. The effectiveness of the condenser in stopping all lean oil was demonstrated in one run by placing a second condenser in series with the first. The lean oil condensed in the second was less than 1 mg. during the period of the run.

To avoid condensation of hydrocarbons not readily stripped from the condensed lean oil, the gas charged to the bomb contained practically nothing heavier than butane. Suitable gas was obtained by passing field gas at high pressure through three absorption units in series, each containing about one liter of the same lean oil used for the experiment. Gas from the absorption train was passed through a pipe packed with steel wool and maintained at 40° F. for removal of water as gas hydrates, then through a separator, and into the bomb.

After the condenser was allowed to warm up to room temperature, water and light hydrocarbons were removed by stripping with a gentle stream of water-free, lean-oil-saturated air. By weighing the condenser at short intervals during the stripping, a correction was possible by use of a weight loss-time curve for the small amount of the heavy oil removed during the process.

In the case of all runs reported in Tables II and III, the entire content of each sampler was analyzed in a Podbielniak low-temperature fractionation column. Most of the analyses made prior to run 20 were unsatisfactory for various reasons, perhaps principally because the water and/or carbon dioxide in the samples froze in the column. The samples had not been charged to the low-temperature column through absorbents for removal of water and carbon dioxide because it was suspected that some of the hydrocarbons would be absorbed or adsorbed. Attempts were made to remove water and carbon dioxide from the field gas charged to the bomb by passing the gas through a scrubber packed with sodium hydroxide pellets, and later by passing it

Table II. Equilibrium Data for Lower Boiling Hydrocarbons

	Run No.	Sample	Type of Lean Oil[a]	Pressure, Lb./Sq. In.	Temp., ° F.	C_1	C_2	C_3	C_4	C_5	Lean Oil
Analysis, mole %	34	Liquid *a*	A	3110	84	24.2	2.48	1.20	..	..	...
		Liquid *b*				24.1	2.66	1.23	..	..	...
		Vapor *c*				94.28	3.86	1.08	..	..	...
		Vapor *d*				93.96	3.77	1.35	..	..	...
		System				83.1	3.6	1.1	0.7		11.5
Equilibrium constants		*c/a*				3.89	1.55	0.90	..	..	...
		c/b				3.91	1.45	0.88	..	..	...
Analysis, mole %	35	Liquid *a*	A	2315	94	20.02	2.84	1.74	..	..	...
		Liquid *b*				20 06	2.77	1.74	..	..	...
		Vapor *c*				94.22	3.79	1.20	..	..	...
		Vapor *d*				94.18	3.85	1.26	..	..	...
		System				84.5	3.7	1.3	0.7		9.8
Equilibrium constants		*c/a*				4.70	1.33	0.69	..	..	...
		d/a				4.70	1.35	0.73	..	..	...
		c/b				4.69	1.37	0.69	..	..	...
		d/b				4.69	1.39	0.73	..	..	...
Analysis, mole %	36	Liquid *b*	A	3030	94	25.9	2.73	1.34	4.60	4.41	61.02
		Vapor *d*				91.51	3.50	1.12	2.44	1.37	...
		System				Insufficient data					
Equilibrium constant		*d/b*				3.53	1.28	0.84	0.53	0.31	...
Analysis, mole %	37	Liquid *a*	A	3030	94	25.16	2.49	0.96[b]	4.25	4.50	62.64
		Vapor *c*				91.57	3.47	1.12	2.27	1.53	...
		System				80.3	3.4	1.1	2.7	1.9	10.6
Equilibrium constant		*c/a*				3.64	1.39	1.17[b]	0.53	0.34	...
Analysis, mole %	38	Liquid *a*	A	2110	91	21.36	3.19	1.38[b]	5.57	5.86	62.64
		Liquid *b*				22.0	2.82	1.59	5.54	5.16	62.89
		Vapor *c*				91.91	3.55	1.01	2.25	1.23	...
		Vapor *d*				92.31	3.44	1.12	1.96	1.07	...
		System				80.5	3.4	1.1	2.7	1.9	10.4
Equilibrium constants		*c/a*				4.30	1.11	0.73[b]	0.40	0.21	...
		d/a				4.32	1.08	0.81[b]	0.35	0.18	...
		c/b				4.18	1.26	0.64	0.41	0.24	...
		d/b				4.19	1.22	0.71	0.35	0.21	...
Analysis, mole %	39	Liquid *a*	A	1540	93	17.52	2.60	0.77	6.50	6.50	66.11
		Liquid *b*				17.41	2.58	1.79[b]	6.36	4.96	66.90
		Vapor *cd*				92 90	3.56	0.59	2.01	0.91	...
		System				83.1	3.4	1.0	2.6	1.5	8.4
Equilibrium constants		*cd/a*				5.30	1.37	0.77	0.31	0.14	...
		cd/b				5.33	1.38	0.33[b]	0.32	0.18	...
Analysis, mole %	40	Liquid *a*	P	3070	92	50.15	4.29	3.79	3.95	3.62	34.20
		Liquid *b*				49.88	4.02	3.59	3.96	4.05	34.50
		Vapor *c*				92.0	3.52	1.91	1.28	1.20	...
		System				83.5	3.6	2.3	1.8	2.0	6.8
Equilibrium constants		*c/a*				1.84	0.82	0.50	0.32	0.33[c]	...
		c/b				1.84	0.87	0.53	0.32	0.30[c]	...
Analysis, mole %	41	Liquid *b*	P	3030	85	48.83	5.15	3.83	3.48	5.31	33.40
		Vapor *c*				92.40	3.47	1.80	1.34	0.97	...
		Vapor *d*				92.31	3.52	1.84	1.25	1.06	...
		System				83.1	3.8	2.2	1.8	1.9	7.2
Equilibrium constants		*c/b*				1.89	0.67	0.47	0.39	0.18	...
		d/b				1.89	0.68	0.48	0.36	0.20	...
Analysis, mole %	42	Liquid *a*	P	2630	88	46.23	4.38	3.92	4.86	5.21	35.40
		Liquid *b*				46.35	4.31	4.16	4.70	5.40	35.10
		Vapor *d*				92.92	3.41	1.81	1.28	..	...
		Vapor *ce*				93.76	2.66	1.87	0.78[b]	0.89	...
		System				83.0	3.6	2.3	2.0	1.8	7.3
Equilibrium constants		*d/a*				2.01	0.78	0.46	0.26	..	...
		ce/a				2.02	0.61	0.48	0.16[b]	0.17	...
		d/b				2.00	0.80	0.41	0.28	..	...
		ce/d				2.01	0.63	0.43	0.17[b]	0.16	...
Analysis, mole %	43	Liquid *a*	P	2110	84	41.32	4.54	3.90	5.76	6.66	37.82
		Liquid *b*				40.75	4.41	4.66	5.28	7.10	37.80
		Vapor *cf*				92 97	3.36	1.79	1.10	0.73	...
		Vapor *de*				92 96	3.34	1.79	1.15	0.71	...
		System				82.7	3.6	2.3	2.0	1.9	7.5
Equilibrium constants		*cf/a*				2.25	0.74	0.46	0.19	0.11	...
		de/a				2.25	0.74	0.46	0.20	0.11	...
		cf/b				2.28	0.76	0.38	0.21	0.10	...
		de/b				2.28	0.76	0.38	0.22	0.10	...
Analysis, mole %	44	Liquid *a*	P	1475	87	31.50	4.46	5.08	6.39	8.57	44.00
		Liquid *b*				31.70	4.44	4.89	6.31	8.77	43.90
		Vapor *cd*				93.27	3.40	1.72	1.03	0.58	...
		Vapor *efg*				93.24	3.48	1.63	1.06	0.59	...
		System				82.1	3.7	2.3	2.0	2.0	7.9
Equilibrium constants		*cd/a*				2.96	0.76	0.34	0.16	0.068	...
		efg/a				2.96	0.78	0.32	0.17	0.069	...
		cd/b				2.94	0.77	0.35	0.16	0.066	...
		efg/b				2.94	0.78	0.33	0.17	0.068	...
Analysis, mole %	45	Liquid *b*	P	820	84	20.05	3.78	5.27	7.72	10.90	52.73
		Vapor *d*				93.1	3.62	1.79	0.87	0.63	...
		System				Insufficient data					
Equilibrium constant		*d/b*				4.64	0.96	0.34	0.12	0.058	...
Analysis, mole %	46	Liquid *a*	N	3030	82	46.32	3.85	1.84	3.53	4.36	40.10
		Liquid *b*				45.37	3.42	1.72	4.33	4.86	40.30
		Vapor *c*				93.60	3.36	0.83	1.32	..	...
		Vapor *d*				93.48	3.33	0.97	1.29	0.88	...
		System				82.4	3.4	1.1	1.9	1.9	9.3
Equilibrium constants		*c/a*				2.02	0.87	0.45	0.37	..	...
		c/b				2.06	0.98	0.49	0.31	..	...
		d/a				2.02	0.87	0.53	0.37	0.20	...
		d/b				2.06	0.97	0.56	0.30	0.18	...

TABLE II. EQUILIBRIUM DATA FOR LOWER BOILING HYDROCARBONS (*Continued*)

	Run No.	Sample	Type of Lean Oil[a]	Pressure, Lb./Sq. In.	Temp., ° F.	C_1	C_2	C_3	C_4	C_5	Lean Oil
Analysis, mole %	47	Liquid *a*	N	2460	80	42.20	4.26	2.17	4.49	5.39	41.50
		Liquid *b*				41.90	3.85	1.44[b]	5.05	5.71	42.05
		Vapor *c*				94.14	3.09	0.88	1.08	0.74	...
		Vapor *d*				94.00	3.29	0.93	1.01	0.72	...
		System				82.4	3.4	1.1	1.9	1.9	9.3
Equilibrium constants		*c/a*				2.23	0.73	0.41	0.24	0.14	...
		c/b				2.24	0.80	0.61[b]	0.22	0.13	...
		d/a				2.22	0.77	0.43	0.23	0.13	...
		d/b				2.24	0.85	0.65[b]	0.20	0.13	...
Analysis, mole %	48	Liquid *a*	N	1915	77	36.80	4.18	2.58	5.35	5.01	46.08
		Liquid *b*				36.04	4.29	2.45	5.25	6.77	45.20
		Vapor *cd*				94.18	3.21	0.86	1.07	0.64	...
		Vapor *e*				94.42	3.15	0.85	1.01	0.54	...
		System				82.3	3.4	1.2	1.9	1.9	9.3
Equilibrium constants		*cd/a*			77	2.56	0.77	0.33	0.20	0.13	...
		cd/b				2.61	0.75	0.35	0.20	0.095	...
		e/a				2.56	0.75	0.34	0.19	0.11	...
		e/b				2.61	0.74	0.35	0.19	0.08	...
Analysis, mole %	49	Liquid *a*	N	1400	80	29.55	3.60	2.52	6.81	7.56	49.96
		Liquid *b*				29.70	3.94	2.55	6.18	7.73	49.90
		Vapor *d*				94.58	3.22	0.89	0.86	0.42	...
		System				83.1	3.3	1.2	1.8	1.7	8.9
Equilibrium constants		*d/a*				3.20	0.89	0.35	0.13	0.059	...
		d/b				3.19	0.82	0.35	0.14	0.058	...
Analysis, mole %	50	Liquid *a*	N	123	90	3.44	0.96	0.84	4.25	7.73	82.78
		Vapor *b*				89.31	5.30	1.57	2.30	1.41	...
		System				83.25	5.00	1.44	2.43	1.88	6.00
Equilibrium constant		*b/a*				26.0	5.5	1.9	0.54	0.18	...
Analysis, mole %	51	Liquid *a*	P	124	90	3.56	0.97	0.84	2.77	11.90	79.96
		Vapor *b*				90.80	4.65	1.29	1.44	1.82	...
		System				83.68	4.36	1.26	1.56	2.64	6.50
Equilibrium constant		*b/a*				25.5	4.8	1.5	0.52	0.15	...
Analysis, mole %	52	Liquid *a*	A	124	92	1.61	0.30	0.27	2.56	3.86	91.4
		Vapor *b*				91.85	3.18	0.96	2.66	1.35	...
		System				81.18	2.85	0.87	2.65	1.65	10.80
Equilibrium constant		*b/a*				57.0	10.6	3.55	1.04	0.35	...

[a] A = aromatic; P = paraffinic; N = naphthenic.
[b] Analysis doubtful.
[c] Poor analysis since pentane balance showed $K = 0.19$.

TABLE III. EQUILIBRIUM DATA FOR ABSORPTION OILS

	Run No.	Type of Lean Oil[a]	Pressure, Lb./Sq. In.	Temp., ° F.	Gas, Cu. Ft.	Oil, Grams	C_1	C_2	C_3	C_{4+}	Lean Oil
Vapor analysis, mole %	21	P	2890	77	10.2	0.914	95.7	...	...	...	0.0306
Liquid analysis, mole %							49.8	...	...	...	43.5
System analysis, mole %							77.6	3.7	1.0	0.7	17.0
Equilibrium constant							1.92	...	...	...	0.00070
Vapor analysis, mole %	22	P	2165	64	16.7	0.341	96.7	...	...	...	0.0069
Liquid analysis, mole %							42.1	...	...	...	51.0
System analysis, mole %							71.5	3.5	1.0	0.5	23.5
Equilibrium constant							2.30	...	...	...	0.000135
Vapor analysis, mole %	23	P	1675	73	21.7	0.156	96.1	...	...	...	0.00246
Liquid analysis, mole %							35.0	...	...	...	57.1
System analysis, mole %							66.6	3.6	1.3	0.6	27.9
Equilibrium constant							2.75	...	...	...	0.000043
Vapor analysis, mole %	27	A	3190	66	10.8	0.825	95.7	...	...	...	0.0377
Liquid analysis, mole %							23.3	...	...	...	73.4
System analysis, mole %							67.6	2.7	0.9	0.1	28.7
Equilibrium constant							4.1	...	...	...	0.00051
Vapor analysis, mole %	28	A	2240	62	17.4	0.274	96.0	...	...	...	0.00775
Liquid analysis, mole %							19.1	...	...	...	77.7
System analysis, mole %							65.8	2.7	0.9	0.1	30.5
Equilibrium constant							5.0	...	...	...	0.00010
Vapor analysis, mole %	29	A	1600	64	24.8	0.129	96.0	...	...	...	0.00256
Liquid analysis, mole %							14.6	...	...	...	82.5
System analysis, mole %							59.2	2.6	0.9	0.1	37.2
Equilibrium constant							6.6	...	...	...	0.000031

[a] P = paraffinic; A = aromatic.

through a sodium hydroxide solution followed by sodium hydroxide pellets or activated alumina. These methods appeared to fail as difficulty in analyses continued.

The method finally adopted for removal of water and carbon dioxide was to charge each vapor sample, and the vapor flashed from each liquid sample, to the Podbielniak column through a glass tube about 0.5 inch in diameter containing 1.5 inches of ascarite and 1.5 inches of Drierite. The liquid residue remaining after the liquid samples were flashed was charged through a by-pass around the Drierite and ascarite. At the same time a change in fractionation procedure was made to prevent excessive cooling of the upper part of the column with liquid nitrogen. Difficulty with freezing was eliminated except in a few cases.

EQUILIBRIUM DATA

Three oils were compared with respect to the equilibrium characteristics of the oil-natural gas system at various pressures. The first, a standard for comparison, was a gas oil obtained from East Texas crude, which is classified as paraffinic. The second was highly aromatic and consisted of topped Hydroformer bottoms. The third was a naphthenic gas oil obtained from Hastings crude. Various properties of the three oils are given in Table I.

Table II gives the equilibrium constants for methane through pentane in the paraffinic, naphthenic, and aromatic oil systems, together with the compositions of the systems on which the results were obtained. For each absorption oil the equilibrium constants are plotted against pressure (Figures 4, 5, and 6). The equilibrium constants as calculated from experimental results were smoothed by plotting, for any given experiment, the logarithm of the equilibrium constant against molecular weight.

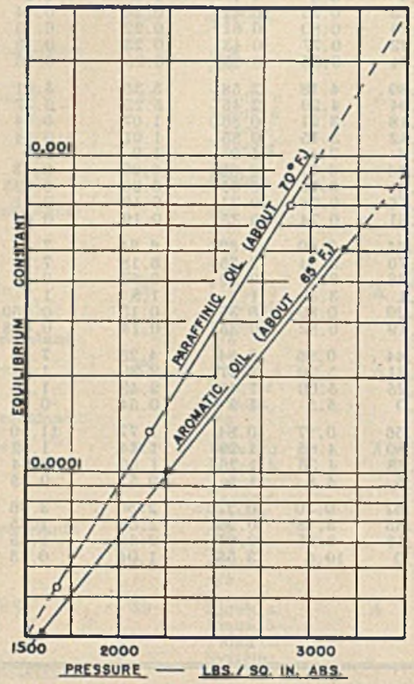

Figure 7. Equilibrium Constants for Paraffinic and Aromatic Lean Oils

The more reliable data obtained during this investigation and the data of others at high pressures, as reported in the literature, fall on a straight line when the constants for ethane through pentane are plotted in this manner. Using the straight line correlations as obtained, the curves in Figures 4, 5, and 6 were constructed. Too little propane was present in the aromatic oil system to permit accurate analyses for that component in several cases.

Data in Table II for the aromatic oil system represent the constants for methane in a system practically free of the heavier paraffinic hydrocarbons (first series). This represents very nearly the condition to be found in the upper part of an absorber. These equilibrium constants for methane are about 22 per cent higher than those given on Figure 6, despite the fact that the temperature was 28° F. lower. No such large divergence in methane constant with composition of the system was found in the paraffinic oil system.

The results obtained in the lean oil loss tests are given in Table III, and the equilibrium constants for the paraffinic and aromatic oils are plotted in Figure 7. If the concentration of lean oil in the system has a significant effect on lean oil equilibrium constants, curves such as those in Figure 7 are meaningless. The lean oil content of the system would be expected to have an appreciable effect on lean oil equilibrium constant if the temperature of the system was near (say, within 100° F. of) the critical temperature of the system. In this case, however, the critical temperature of the system is several hundred degrees above the temperature of the system.

METHOD OF CALCULATION

In the case of the aromatic oil system, it is of interest that the curve of equilibrium constant *vs.* pressure for ethane has a minimum at a value of equilibrium constant above unity. It is not known what happens above 3000 pounds per square inch, but it is apparent that a convergence pressure does not occur, since the critical temperature of the system is well above the temperature of the system.

In order to establish the relative advantages of each of the three types of absorbing oils, calculations were made to determine the lean oil rates, lean oil loss, and methane absorption based on 90 per cent pentane recovery in an absorber having three theoretical trays. Process calculations were made at pressures of 125, 1500, 2000, 2500, and 3000 pounds, based on a rich gas of the following mole percentage composition:

Methane	91.0
Ethane	4.5
Propane	2.0
n-Butane	1.5
n-Pentane	1.0
	100.0

The method of calculations is a modification of the absorption factor method presented by Souders and Brown (*6*):

1. The recovery of the key component is set (in this case 90 per cent *n*-pentane recovery). Based on the number of equivalent theoretical trays to be used, the required average absorption factor $(L/KV)_{av.}$ is calculated,

where K = equilibrium constant = y/x
L = liquid from tray, moles/time
V = vapor from tray, moles/time
y = mole fraction of component in vapor
x = mole fraction of component in liquid

2. Based on the results of step 1, the absorption factor for each of the other components in the rich gas is calculated. The recovery of each of the other components can then be determined from the relation between recovery and absorption factor as given by Souders and Brown (*6*).

3. Having the recovery of each component from step 2, the lean gas composition is calculated by material balance.

4. Based on the lean gas composition as calculated in step 3, the mole fraction of each component (except lean oil) in the liquid on the top tray is calculated as follows:

$$x_t = v/V_tK_t$$

where
v = moles of component in lean gas; subscript t = top tray

5. The mole fraction of lean oil in the liquid on the top tray is the difference between 1.0 and the sum of mole fractions obtained in step 4.

6. The lean oil rate is established so that the arithmetic average of the absorption factors at the top and bottom of the absorber is equal to the required average absorption factor as calculated in step 1. The L/V at the bottom may be taken as the ratio of moles of rich oil to moles of rich gas with no significant error (1 to 2 per cent, ordinarily):

$$(L/KV)_{av.} = (L_R/V_RK_B + L_t/V_tK_t)/2$$

which reduces to:

$$L_o = \frac{2(L/KV)_{av.} - L_a/K_BV_R}{1/K_tV_tx_{ot} + 1/K_BV_R}$$

where a = absorbed components
B = bottom tray of absorber
o = lean oil
R = rich oil or rich gas
t = top tray of absorber

Based on V_R = 100 and constant temperature, the above equation reduces to:

$$L_o = \frac{V_tx_{ot}}{100 + V_tx_{ot}}\left[200\left(\frac{L}{V}\right)_{av.} - L_a\right]$$

7. The lean oil v loss is calculated as follows:

$$v_{ot} = V_tx_{ot}K_t$$

TABLE IV. LEAN OIL RATE AND LOSS, AND METHANE ABSORPTION

(Basis, 100 moles of rich gas and 90 per cent pentane recovery)

Pressure, Lb./Sq. In.	125			1500			2000			2500			3000		
Type of Lean Oil[a]	P	A	N	P	A	N	P	A	N	P	A	N	P	A	N
Lean oil rate															
Gallons	732	1050	820	183	353	154	226	445	209	288	556	285	360	670	382
Moles	22.4	55	27	5.6	18.5	5.06	6.9	23.3	6.9	8.8	29.1	9.4	11	35	12.6
Pounds	5150	8800	5940	1290	2960	1115	1585	3750	1520	2020	4660	2070	2530	5600	2770
Relative lean oil rate[b]															
Gallons	1.00	1.435	1.12	1.00	1.93	0.84	1.00	1.97	0.925	1.00	1.93	0.99	1.00	1.86	1.06
Moles	1.00	2.46	1.21	1.00	3.30	0.90	1.00	3.38	1.00	1.00	3.31	1.06	1.00	3.18	1.14
Pounds	1.00	1.71	1.15	1.00	2.29	0.86	1.00	2.35	0.96	1.00	2.31	1.02	1.00	2.21	1.10
Lean oil loss, gal.	..	..	..	0.0645	0.0434	..	0.1300	0.083	..	0.47	0.232	..	0.945	0.426	..
Relative lean oil loss[b]	..	..	..	1.00	0.673	..	1.00	0.638	..	1.00	0.494	..	1.00	0.451	..
Methane absorbed, moles	0.90	0.94	1.06	3.74	3.32	3.18	6.30	5.51	5.71	10.15	8.29	9.28	16.28	11.65	14.55
Relative methane absorbed[b]	1.00	1.04	1.18	1.00	0.89	0.85	1.00	0.875	0.905	1.00	0.815	0.915	1.00	0.715	0.895

[a] P = paraffinic; A = aromatic; N = naphthenic. [b] Relative to that by paraffinic lean oil.

This procedure does not take cognizance of any temperature gradient in the absorber. It is felt that this is not necessary because latent heats of the hydrocarbons at such high pressures are small. A temperature rise of 20° F. with as much as 50 per cent increase in liquid volume is reasonable. However, in case temperature gradient were important, it could be evaluated by assuming the rich oil and top tray temperatures in step 1. Then, after step 7 the assumed top tray temperature could be checked by heat balance around the top tray and the assumed bottom temperature checked by over-all heat balance.

An example calculation to determine the relative merits of each type lean oil is presented for the following conditions: aromatic type lean oil, three theoretical trays, 90 per cent recovery of *n*-pentane, 3000 pounds per square inch pressure.

	Rich Gas, Moles	K	$(L/KV)_{av.}$	% Absorbed	Moles Absorbed	Lean Gas, Moles	Liquid from Top Tray, Mole %
C_1	91.0	4.30	0.128	12.8	11.65	79.35	22.2
C_2	4.5	1.35	0.406	39.0	1.76	2.74	2.26
C_3	2.0	0.83	0.661	57.5	1.15	0.85	1.23
C_{4n}	1.5	0.535	1.025	75.3	1.13	0.37	0.83
C_{5n}	1.0	0.327	1.68	90.0	0.90	0.10	0.37
	100.0				16.59	83.41	26.89
						Lean oil	73.11
							100.00

$$
\begin{aligned}
L_o &= \frac{(83.41)(0.7311)}{100 + (83.41)(0.7311)}\,[(200)(0.548) - 16.59| \\
&= 35 \text{ moles} = (35)(160)/8.37 = 670 \text{ gal.} \\
\text{lean oil loss} &= (83.41)(0.7311)(0.00037) \\
&= 0.0224 \text{ mole} = (0.0224)(160)/8.37 = 0.426 \text{ gal.}
\end{aligned}
$$

In the calculations on aromatic oil systems, the values of K for methane were taken from Table III because they were obtained under conditions more representative of the case under consideration. This is apparent by comparing the calculated methane content of the rich oil with the methane content given in Table III for the aromatic oil system.

The lean oil rates and quantities of methane absorbed by aromatic and naphthenic type lean oils relative to that by paraffinic type lean oils are listed in Table IV for five different pressures ranging from 125 to 3000 pounds per square inch. The lean oil loss for aromatic type lean oil relative to that for paraffinic type is also given.

In comparing the aromatic and paraffinic lean oil systems at the higher pressures (Table IV), at 2500 pounds per square inch and 90 per cent absorption of pentane, in the aromatic oil system about 93 per cent more volume of lean oil would be circulated, about 18.5 per cent less methane would be absorbed, and the volume of lean oil lost would be 50.6 per cent less. Similarly, comparing the naphthenic and paraffinic lean oil systems, the lean oil rates would be about the same in both systems, and about 8.5 per cent less methane would be absorbed in the naphthenic lean oil. It may be inferred from the results with the aromatic oil that lean oil loss in the naphthenic oil system would be no greater, and probably less, than in the paraffinic oil system.

Comparison of the three types of lean oil at low pressure (125 pounds) shows that there are no selective absorption characteristics of aromatic and naphthenic oils for pentane relative to methane. As a matter of fact, the paraffinic type oil has a slight advantage in this respect, although it is unimportant due to the small methane absorption for all of the three types. It is apparent also that, compared with paraffinic type, 12.0 per cent by volume more naphthenic and 43.5 per cent more aromatic type oil would be required for the same amount of pentane absorption at 125 pounds per square inch.

CONCLUSIONS

The results of the investigation show that at low pressure a paraffinic type lean oil is preferred to an aromatic or naphthenic type because substantially less volume is required for the same amount of pentane absorption. The amount of methane absorption for the same pentane recovery is essentially the same for each of the three types of lean oils.

At high pressure the aromatic and naphthenic type lean oils have a substantial selectivity of pentane absorption with respect to methane, compared with that obtained with paraffinic type lean oil of about the same boiling range. Furthermore, the lean oil loss with aromatic type is considerably less than that for paraffinic type. The volume of lean oil required in the case of aromatic type is somewhat more than and in the case of naphthenic type, about the same as that required with paraffinic type lean oil.

The proper lean oil to be used and the optimum absorption pressure for any specific case depends on an economic balance of the various factors affecting the investment and operating costs.

ACKNOWLEDGMENT

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EQUILIBRIUM STILL FOR Partially Miscible Liquids

Data on Isobutanol-Water

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The vapor over much of the soluble region of partially miscible mixtures will, on condensing, separate into two layers and prevent the use of the usual recirculation types of equilibrium stills. A new approach is employed where a vapor mixture is generated from separate boilers containing the pure components, and this vapor is bubbled through liquid in an adiabatic trap until the latter reaches equilibrium. Data were obtained on ethylene dichloride–toluene and on isobutanol-water. The former conformed with Raoult's law and with earlier data; the latter agreed well with those of Stockhardt and Hull (7) and showed general consistency when plotted as activity coefficients. These coefficients could not be accurately represented by van Laar equations. An application is suggested to ternary mixtures.

IN VIEW of the growing importance of industrial distillation systems involving the miscible region of partially miscible liquids, an adequate method of measuring the vapor-liquid equilibrium of such systems is greatly to be desired. In both the processes of azeotropic distillation and of liquid-liquid extraction, solvent is generally removed from one or more streams by stripping columns from which the condensed overhead separates into two layers. To make an accurate and economic design, vapor-liquid equilibrium of the miscible regions are required; although approximate methods of predicting these data are available (*1*), insufficient data are available to test these methods adequately. This is probably because of the experimental difficulties encountered.

There are two major difficulties encountered in studies of partially miscible systems in addition to those usually inherent in equilibrium stills (*4*). The first is that the vapor from any but the most dilute samples will, on condensing, form an immiscible mixture. Thus the recirculation types of apparatus cannot be used in the normal manner, since the condensate, on separating into two layers, cannot be returned to the still with the two liquid phases in proper proportion. While a stirrer might be utilized to maintain the condensate well mixed, there would be some question as to the proper assimilation of the two-phase return liquid by the contents of the still. Stockhardt and Hull (*7*) eliminated recirculation merely by distilling off small quantities from a mixture of known composition after first refluxing in a tilting condenser, but this method involves slight errors caused by differential condenser holdup and, in addition, encounters the second major difficulty discussed below.

The further difficulty offered by these systems lies in the great difference in composition between the vapor and liquid, and the small concentrations of the dilute component in the liquid. For example, in the miscible regions of isobutanol in water, which extends to about 2 mole per cent isobutanol, the vapor is from fifteen to thirty times as rich in isobutanol as the liquid. Therefore, if an equilibrium study is undertaken where a liquid sample is distilled, its composition will change extremely rapidly as vapor is formed, and the arrival at the desired steady-state conditions in the still becomes difficult or impossible.

These particular difficulties have led the authors to an entirely different philosophy of approach to this problem. Instead of attempting to determine the vapor in equilibrium with given liquid samples, the present thought is to make up certain vapor streams and to find the corresponding equilibrium liquids. Vapor streams of any composition can easily be formed by mixing the vapors from separate stills containing the pure components, and a liquid can readily be brought into equilibrium by bubbling the mixed vapor through the liquid. This paper describes such a still and supplies data taken to test the apparatus on the commercially important system, isobutanol-water.

SOURCE OF VAPOR

To supply a mixture of vapors of constant composition to the equilibrium liquid, the pure components are boiled separately at constant fixed rates in suitable distilling flasks. Any convenient source of heat can be used as long as the rate of heat input and, therefore, rate of vaporization can be controlled. The vapors thus generated are mixed and passed into the equilibrium chamber through tube *A* (Figure 1). Although the mixed vapor is apt to be slightly superheated, a slight loss of heat from the vapor line soon reduces it to saturation conditions; a small amount of condensate formed is withdrawn through a suitable capillary trap (not shown), connected to one arm of a tee in the vapor inlet tube, and is discarded. In the present apparatus it was found expedient to insulate the boilers and vapor lines with rock wool so that heat losses would be small and constant. Rheostat-controlled electric heaters and ordinary 1000-cc. distillation flasks provided a simple and flexible arrangement for vapor generation.

EQUILIBRIUM CHAMBER

To secure a liquid which is in true equilibrium with the vapor, the latter is bubbled through a quantity of the liquid in a suitable equilibrium chamber. The vapor enters the inner vessel (Figure 1) through tube *C*, the lower end of which, drawn into the shape of a small jet, dips slightly below the liquid surface. Passage of the vapor from the jet is directed upward and, with the aid of the small glass sleeve, *D*, surrounding it, causes smooth circulation of the liquid in the chamber and brings it rapidly to equilibrium. The location of the jet with respect to the liquid surface is important since any increase in pressure due to hydrostatic head, together with the frictional drop through the tube and jet, cause a small enthalpy gradient between the vapors in the two chambers. The dead-air cell, *K*, seems to prevent excessive heat transfer into the liquid, while the heat which is transferred into the vapor through the walls of the inlet and outlet vapor lines tends to superheat the vapor leaving the chamber and thus prevents partial condensation. Although the enthalpy gradient is small and of doubtful importance, it is present of necessity, and the above arrangement tends to reduce its effectiveness. Vapor leaving the equilibrium chamber through tube *G* is condensed and cooled in a suitable condenser.

Saturation conditions and thermal equilibrium are further effected by inclusion of the equilibrium chamber in the outer vapor jacket, *B*. Heat losses from the unit are compensated for by condensation of a portion of the entering vapor, the remainder being automatically left saturated. Excess condensate is siphoned through capillary tube *J* and discarded. This vapor chamber serves the further purpose of providing a store of vapor of large volume compared to the throughput which tends to absorb any slight fluctuations in the composition of the vapors entering the equilibrium vessel. The entire unit is enclosed by the outer dead-air jacket, *L*, and finally by a suitable insulating material such as rock wool. All parts described are constructed of glass to permit observation during operation, and they can be readily disassembled for ease in cleaning or minor adjustment.

In operation, liquid of the approximate equilibrium composition is first introduced into the equilibrium vessel through sampling tube *H*, and the liquid level is adjusted so as to facilitate a maximum of mixing by the vapor jet. When a run is begun, the initial liquid charge (about 15 cc.) is brought to the vapor temperature by condensation of a portion of the entering vapor. As the system approaches physical equilibrium, any heat requirements due to change in liquid composition are balanced either by condensation or vaporization in the equilibrium chamber. When equilibrium has been established, the liquid and vapor are at the same temperature, and any gain or loss of heat from the system is balanced by heat flow to or from the outer vapor space. At this point the liquid level remains constant.

A sensitive indication of the degree of equilibrium attained in the apparatus is also provided by thermocouple *I* whose junction is located in the well just above the vapor jet in the equilibrium chamber. When equilibrium is reached, the potentiometer shows no temperature variation greater than approximately 0.1° C.

• • • • •

The photograph on the facing page shows large distillation columns built by E. B. Badger & Sons Company for the separation of chemical products.

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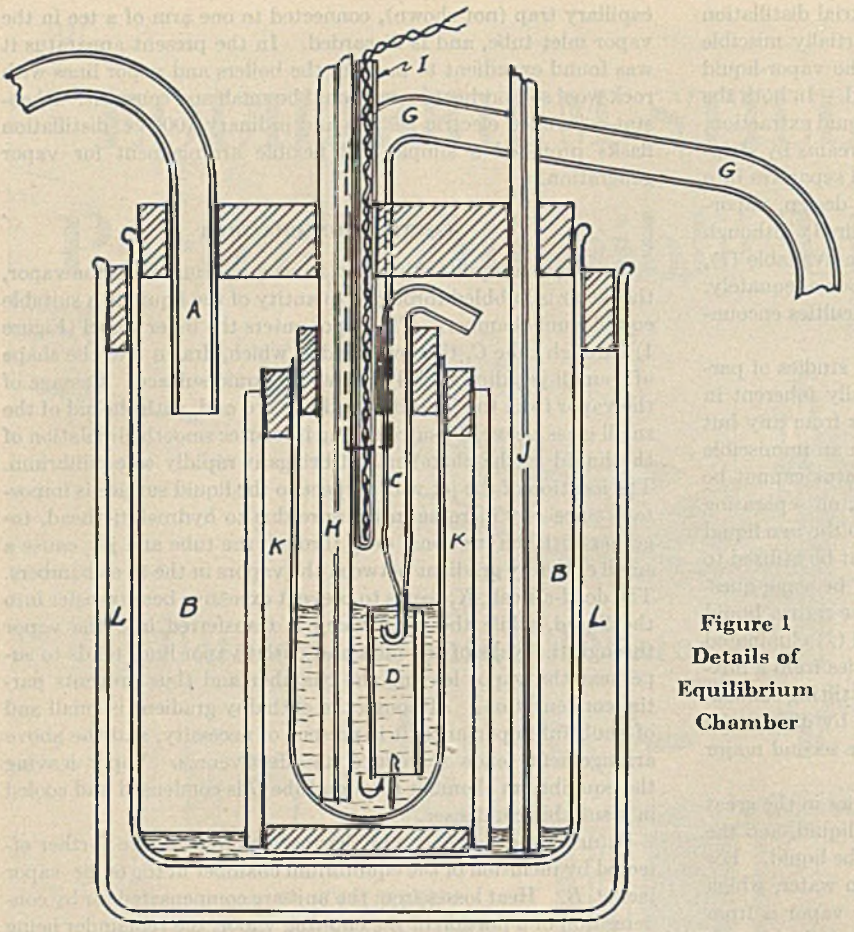

Figure 1 Details of Equilibrium Chamber

SAMPLING AND ANALYSIS

Since only a vapor of the exact heteroazeotropic composition can be in equilibrium with the two-phase liquid, the liquid in the equilibrium chamber was, in the present case, always a single-phase liquid; however, during operation with a vapor very near the azeotropic composition, the liquid, though single phase at the boiling point, separated into two phases when withdrawn and cooled for analysis.

Samples which were single phase at room temperature (including most of the liquid samples and some of the vapor samples) were analyzed by refractive index at 25° C. (±0.2°) with a Zeiss dipping refractometer. The isobutanol used was a narrow-boiling fraction (107.8–108.0° C.) obtained by distillation at high reflux ratio of a large quantity of the commercial material. The composition–refractive index data of Colburn and Welsh (*2*) for isobutanol-water solutions were used since the same liquids were employed in both studies.

Samples which formed two phases were analyzed by measuring the volumes of the two layers. The determinations were made directly in a graduated collecting cylinder, held (tightly stoppered) at 25° C. in a constant-temperature water bath for 15 to 30 minutes. The total volume of the samples taken ranged from 4 to 6 ml., and the collecting cylinder, previously calibrated with distilled water, could be read with a precision of about ±0.05 ml. The solubility data employed in the analytical calculations were obtained from International Critical Tables (*3*):

	Wt. %	*Mole %*
Isobutanol in water layer at 25° C.	8.25	2.14
Water in isobutanol layer at 25° C.	16.57	45.0

Density data used in the calculations were determined for each of the two phases by means of the graduated collecting cylinder as follows: Saturated solutions were prepared by prolonged shak-

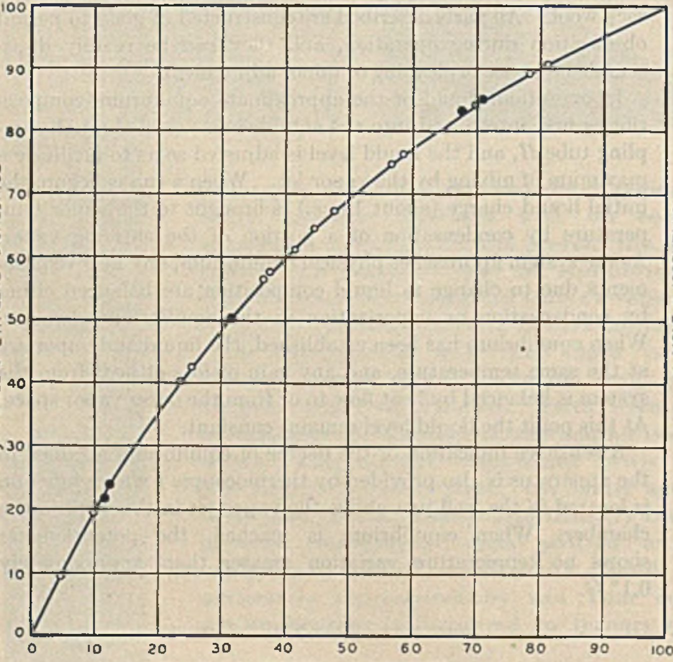

Figure 2. Data on Ethylene Dichloride–Toluene

● Experimental; ○ Jones *et al.*; — Raoult's law.

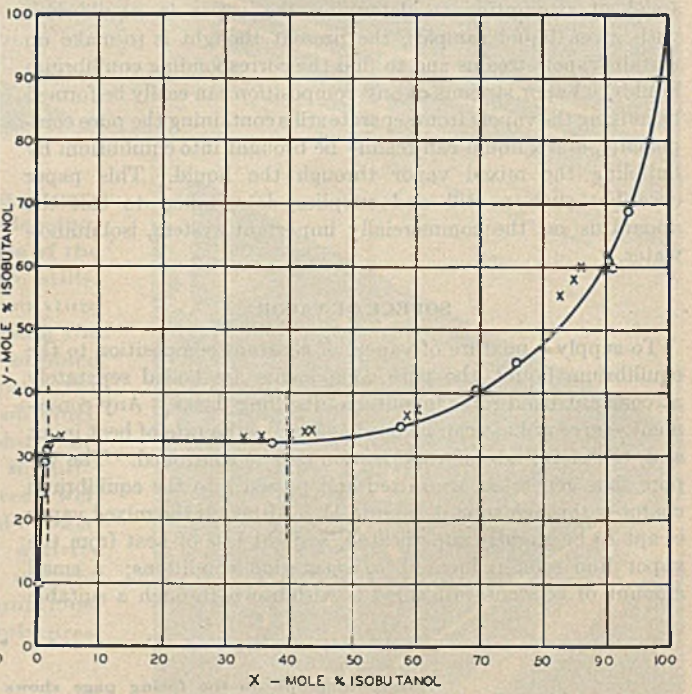

Figure 3. Data on Isobutanol-Water

○ Experimental; × Stockhardt and Hull.

ing of the two liquids in a separatory funnel at approximately 25° C. Each layer was carefully introduced into the previously weighed cylinder and held in the constant-temperature bath until temperature equilibrium was again established; the volume was then read and the cylinder again reweighed. In calculating compositions, the following average density values were used:

	Gram/ml.
Water saturated with isobutanol, 25° C.	0.983
Isobutanol saturated with water, 25° C.	0.836

Vapor pressure data for isobutanol and for water and barometric corrections were taken from the Chemical Engineers' Handbook (*5*). The temperature in the equilibrium chamber was measured with a copper-constantan thermocouple and semiprecision type potentiometer.

TABLE I. EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR ETHYLENE DICHLORIDE–TOLUENE

Pressure, Mm. Hg	Temp., *t* ° C.	Mole % Ethylene Dichloride	
		Liquid x_1	Vapor y_1
772.7	88.2	71.0	85.3
772.7	98.3	31.4	50.3
763.3	88.2	67.8	83.8
763.3	105.7	11.7	21.8
763.3	104.4	12.3	24.0

RESULTS

To determine the dependability of the still, several preliminary runs were made on the system ethylene dichloride–toluene, since this mixture had been found to obey Raoult's law closely at atmospheric pressure (*4*). The results are given in Table I and are plotted in Figure 2. Since the data show fairly good agreement with Raoult's law, it was concluded that the apparatus involved no persistent or unaccountable errors and that the precision of the data obtained was primarily dependent upon the quality of control exercised.

The experimental data on the isobutanol-water system are given in Table II and plotted in Figures 3, 4, and 5. Figure 3 shows a few of the points at low concentrations of isobutanol and all the points at higher concentrations. The values all fall on a smooth curve, indicating consistency of the results. For comparison the data of Stockhardt and Hull (*7*) are shown, and agreement is good. Figure 4 is an enlarged diagram of the low isobutanol region. The data are remarkably close to a smooth curve. The points of Stockhardt and Hull are again in general agreement, although there is slightly more scattering of these values.

TABLE II. EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR ISOBUTANOL-WATER

Run No.	Pressure, Mm. Hg	Temp., ° C.	Mole % Isobutanol		Activity Coefficient	
			Liquid x_1	Vapor y_1	γ_1	γ_2
2*a*	756.2	93.53	0.65	18.52	49.5	1.031
c		90.00	1.52	29.0	38.2	1.040
d		96.05	0.27	9.00	52.5	1.060
e		98.12	0.11	3.27	43.0	1.029
3*b*	757.0	97.58	0.20	5.26	39.0	1.013
c		98.80	0.06	1.22	29.0	1.005
e		97.02	0.24	6.75	42.5	1.022
4*a*	761.4	88.0	2.08	31.6	33.1	1.090
b		90.9	1.00	22.6	43.8	1.088
c		89.0	1.92	31.0	33.8	1.055
d		89.4	1.93	30.4	32.4	1.051
5*a*	763.8	97.6	0.20	6.25	46.6	1.020
b		90.3	0.91	22.45	49.2	1.120
c		90.5	0.90	21.8	48.0	1.112
7*b*	762.0	98.95	93.8	68.9	1.037	5.17
d		96.80	90.6	61.0	1.032	4.65
e		96.73	91.1	59.8	1.010	5.06
8*c*	760.0	92.3	75.9	44.8	1.080	3.04
d		90.75	69.3	40.3	1.135	2.74
e		89.25	57.5	34.7	1.247	2.28
f		90.55	69.3	40.3	1.143	2.75
g		89.25	37.1	32.0	1.781	1.603
9	761.6	89.61	.....	32.0 32.8 32.5	......	.....

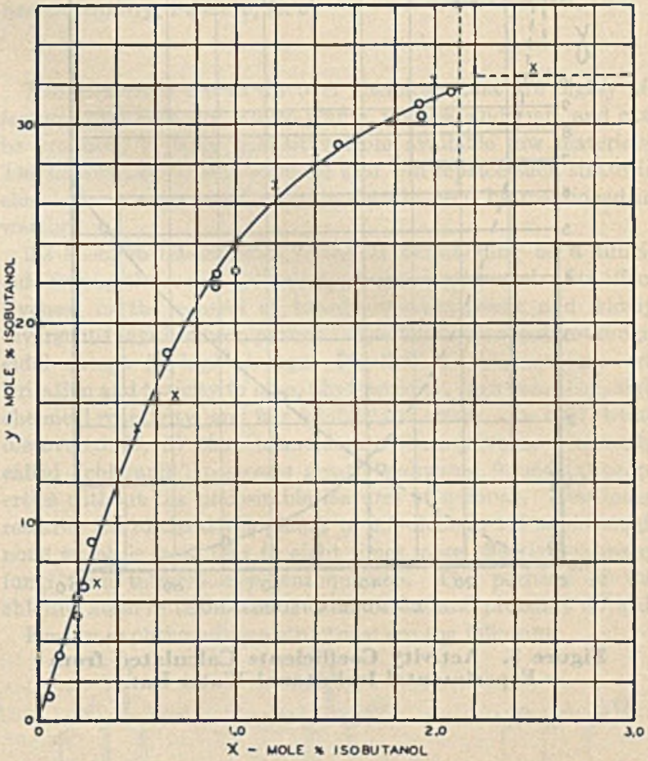

Figure 4. Data on Isobutanol-Water in Region of Dilute Isobutanol

○ Experimental; × Stockhardt and Hull.

A more definitive test of the equilibrium data, as previously pointed out (*1*), is to calculate from them the activity coefficients, γ_1 and γ_2, of the two components, and to plot them as shown on Figure 5 where

$$\gamma_1 = \frac{Py_1}{P_1x_1} \text{ and } \gamma_2 = \frac{Py_2}{P_2x_2} \qquad (1)$$

Here again the data are well correlated by smooth curves, particularly in the concentrated isobutanol region. At low concentrations of isobutanol, the activity coefficients of the concentrated component, water, would be expected to be practically unity, whereas they fall slightly high. This discrepancy is believed to be due to slight inaccuracies in the temperature readings which are apparently somewhat low. Correction of these temperatures were made by Shilling (*6*) to values which result in activity coefficients of unity for the water in this region; this lowered slightly the activity coefficients of isobutanol in this region, but did not change the liquid and vapor compositions. The observed temperatures in the concentrated isobutanol region are undoubtedly correct, since the activity coefficient curve of the concentrated component approaches unity in the expected asymptotic manner.

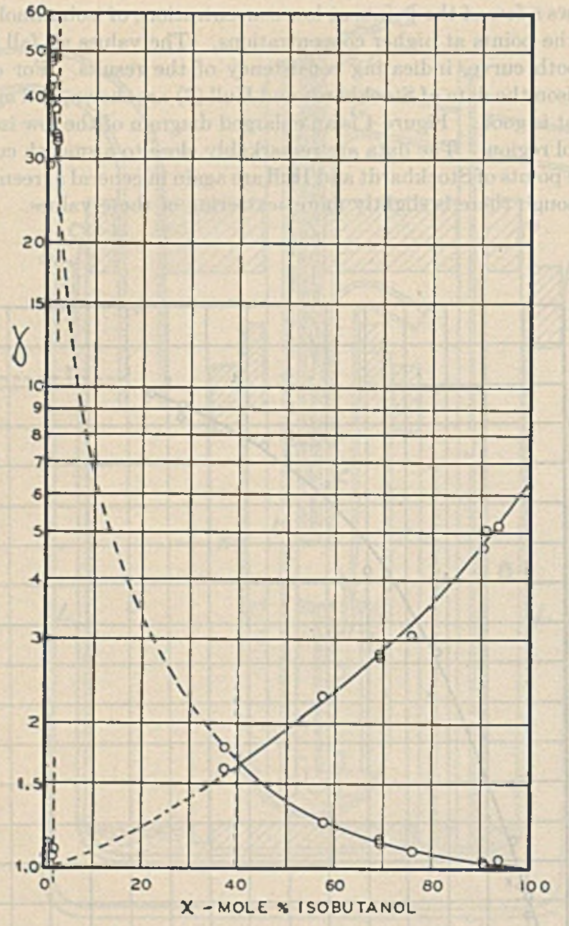

Figure 5. Activity Coefficients Calculated from Experimental Isobutanol-Water Data

An attempt was made to "fit" the activity coefficients with curves representing the van Laar equations:

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \quad (2)$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \quad (3)$$

The nearest fit was obtained by trial and error with equations having the following constants: $A = 1.7$ and $B = 0.7$. These curves were in close agreement for the water layer, but deviated from the data by 0 to 15 per cent for the isobutanol layer. The method discussed by Carlson and Colburn (*1*) for predicting van Laar constants from solubility data gives (for the boiling-point solubility values of 2.13 and 40.25 mole per cent isobutanol, respectively, at 90° C.) the following: $A = 1.66$ and $B = 0.4$. These values obviously do not represent the experimental data and cast doubt on this method of prediction as well as on the validity of the van Laar equations for systems where A and B differ so widely. Additional data are required to find whether this limitation on the use of the van Laar equations applies to other partially miscible systems where the mutual molal solubilities are so unsymmetrical in the two phases.

DISCUSSION OF RESULTS

The consistency of the experimental data as subjected to rigorous interpretation supports this new method of approach to the problem of securing reliable equilibrium data on partially miscible systems. It is obvious, however, that application of the apparatus need not be limited necessarily to such binary partially miscible systems.

TERNARY AND MULTICOMPONENT SYSTEMS. Because of its inherent simplicity, this type of apparatus seems particularly well adapted to the study of systems of more than two components, especially those known to possess a heteroazeotrope. Modification can be made simply by the use of an additional boiler for each component with but little increase in complexity of operation or control. The relative ease and rapidity with which a vapor which condenses to a two-phase liquid can frequently be analyzed by measurement of the volumes of the respective layers is an advantage not possessed by the usual recirculation type of still.

MISCIBLE MIXTURES. As indicated by the equilibrium data presented for ethylene dichloride-toluene, completely miscible systems of two or more components can be reliably evaluated with the still described, provided sufficient quantities of the pure components are available. While the present method utilizes somewhat greater amounts of material than do previous ones, this is not a serious disadvantage in most plant laboratories where the mixtures obtained may find use in subsequent distillation operations.

MODIFIED EQUILIBRIUM CHAMBER. The seeming complexity of the equilibrium chamber can be reduced by eliminating the outer jackets which serve to maintain thermal equilibrium, and replacing them by a coil of suitable resistance wire surrounding the inner vessel as employed in the still for miscible systems (*4*). The proper balancing of heat loss from the vessel would be achieved by controlling the height of the liquid, which should not change for some time as equilibrium is approached. The means of introducing vapor into the equilibrium liquid where a short glass tube permits smooth liquid circulation, results in a steady liquid level so that a slight increase or decrease in liquid height is readily apparent. Local superheating of the vapors evolved through tube *G* can similarly be affected by electric winding in order to ensure the elimination of reflux at this point where insulation may not prove adequate.

It is hoped that the apparatus and method described will stimulate the acquisition of much needed vapor-liquid equilibrium data for those systems without which the rigorous treatment of distillation column design and performance is impossible or of doubtful value.

NOMENCLATURE

A, B = van Laar constants in Equations 1 and 2
P = total pressure, mm. Hg
P_1, P_2 = vapor pressures of components 1 and 2, respectively, mm. Hg
t = temperature, ° C.
x_1, x_2 = mole % of components 1 and 2, respectively, in liquid
y_1, y_2 = mole % of components 1 and 2, respectively, in vapor
γ_1, γ_2 = activity coefficients of components 1 and 2, respectively

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2,3-DICHLORO-1,4-NAPHTHOQUINONE

A Potent Organic Fungicide

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2,3-Dichloro-1,4-naphthoquinone has proved to be a potent and safe fungicide for both agriculture and textiles. Its effectiveness in the control of numerous economic fungi has been demonstrated. In agriculture it may be used as a seed treatment or as a foliage spray to control plant diseases. On textiles 2,3-dichloro-1,4-naphthoquinone is an excellent mildew-proofing agent, has no harmful effect, and resists weathering. It should prove especially valuable in replacing metallic chemicals or in cases where a more suitable fungicide is desired.

THE annual fungous damage to agriculture in the United States has been estimated at a billion dollars. The annual loss due to mildew on raw cotton alone is placed at 25 to 75 million dollars (*1*). The importance of mildew-proofing in the war effort cannot be evaluated in terms of money alone. The fields of agriculture and textiles are related, particularly through the economically important cotton crop. Further, the fungus *Glomerella gossypii* (South.) Edg., causing anthracnose of the cotton plant, attacks and weakens the fibers in the boll (*3*, *7*) in the field. These fibers are lost largely at ginning.

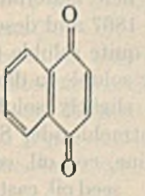
In agriculture, sulfur, copper, and organic mercury compounds are extensively used to control pathogenic fungi. While effective in many instances, they have disadvantages. Sulfur, for example, is ineffective in the control of a number of diseases, and during hot weather may burn the foliage. Repeated use increases soil acidity and in the greenhouse may render soil worthless. Elemental sulfur is of restricted value as a seed protector. Copper compounds do not control all diseases and may cause foliage or fruit injury, particularly during a cold spell. They may increase aphid population. As seed protectors, copper compounds are of limited usefulness. Organic mercury compounds, while often highly effective, are toxic to man and animals.

In the textile industry, fungicides such as copper carbonate, copper naphthenate, and chlorinated phenols are in extensive use. Copper compounds may cause weakening of the fibers as well as stiffness. Since copper is rubber's worst enemy, copper compounds cannot be used on rubberized fabrics. In view of the shortcomings of known fungicides, organic fungicides have been and are being developed that will augment and often replace sulfur or metallic fungicides of long standing.

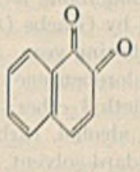
The objectives are to discover chemicals that are highly effective fungicides, are safe to plants, textiles, and man, and can be produced in large quantities from available raw materials. The importance of any chemical that can replace such strategic chemicals as copper and mercury hardly need be mentioned in wartime.

2,3-Dichloro-1,4-naphthoquinone is outstanding as a fungicide among the many quinone-type chemicals tested. Its effectiveness in the control of twenty-two important and widely divergent fungi has been proved. 1,4-Benzoquinone is not fungicidal except in high dosage. Its further disadvantages are irritation and toxicity to man, phytotoxicity, high volatility, high chemical reactivity, and fair solubility in water. In 1937 it was discovered (*6*, *9*) that tetrachloro-*p*-benzoquinone, commonly called "chloranil", possesses greatly enhanced fungicidal properties without the undesirable features of quinone. Continued research led to the development of 2,3-dichloro-1,4-naphthoquinone which is from four to eight times more effective on many fungi than tetrachloro-*p*-benzoquinone. The position of the chlorine atom in the molecule is important and probably critical.

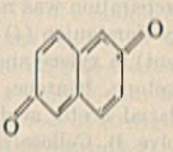
Known naphthoquinone structures are the following:



1,4-Naphthoquinone



1,2-Naphthoquinone



2,6-Naphthoquinone

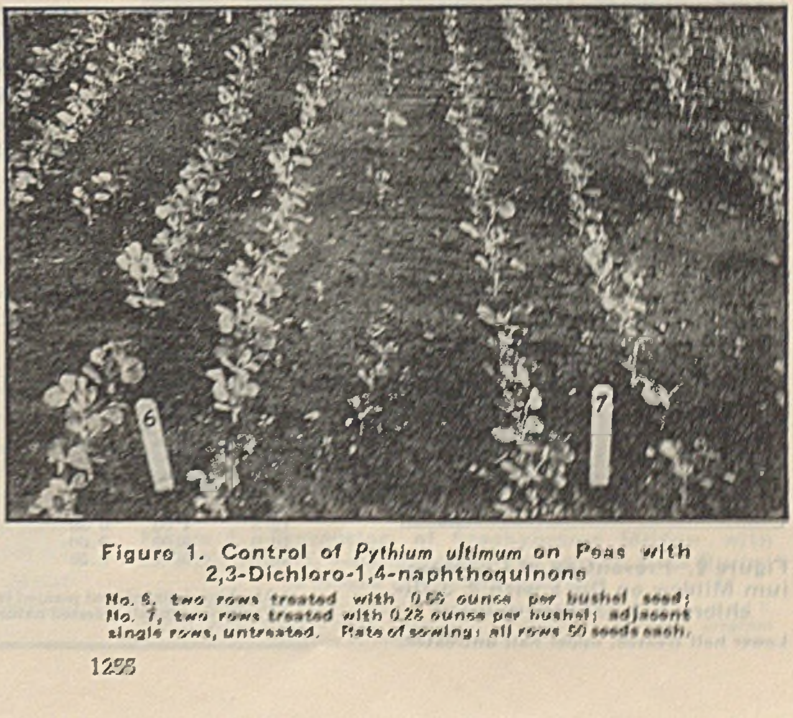
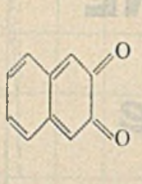


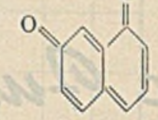
Figure 1. Control of *Pythium ultimum* on Peas with 2,3-Dichloro-1,4-naphthoquinone

No. 6, two rows treated with 0.56 ounce per bushel seed; No. 7, two rows treated with 0.28 ounce per bushel; adjacent single rows, untreated. Rate of sowing: all rows 50 seeds each.

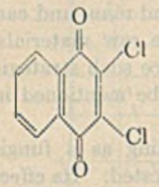
Others which do not exist, except possibly in derivatives are:


2,3-Naphthoquinone

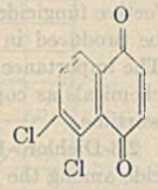

1,5-Naphthoquinone

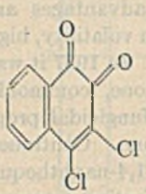

1,7-Naphthoquinone

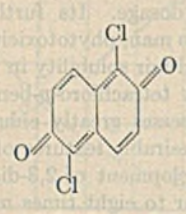
Of these six naphthoquinone structures, sixty-six possible dichloro isomers can be drawn. The literature (*4*, *5*, *10*, *13*, *14*, *19*, *20*) describes only six dichloronaphthoquinones:

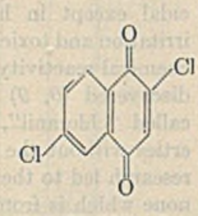

2,3-Dichloro-1,4-naphthoquinone


5,8-Dichloro-1,4-naphthoquinone


5,6-Dichloro-1,4-naphthoquinone


3,4-Dichloro-1,2-naphthoquinone


1,5-Dichloro-2,6-naphthoquinone


2,6-Dichloro-1,4-naphthoquinone

2,3-Dichloro-1,4-naphthoquinone is not a new material. Its preparation was recorded by Graebe (*10*) in 1867 and described by Carstanjen (*4*) the following year. It is quite soluble (4 per cent) in xylene and *o*-dichlorobenzene; fairly soluble in dioxane, acetone, benzene, and diethyl ether; and slightly soluble in glacial acetic acid, ethyl alcohol, carbon tetrachloride, Skellysolve B, Cellosolve, Stoddard solvent, gasoline, cod oil, cottonseed oil, castor oil, and Nujol. The solubility in water at pH 7.0 is in the order of 1 to 10,000,000, which is 2500 times less soluble than 1,4-naphthoquinone with a solubility of 1 to 4000. The vapor concentration of 2,3-dichloro-1,4-naphthoquinone at 100° C. is 0.2 mg. per liter.


Figure 2. Prevention of Chaetomium Mildew on Duck with 2, 3-Dichloro-1, 4-naphthoquinone

Lower half treated, upper half untreated.

USE AS AGRICULTURAL FUNGICIDE

The high fungicidal potency of 2,3-dichloro-1,4-naphthoquinone has been demonstrated repeatedly. It was determined first on the regularly employed test fungus, *Pythium ultimum* Trow, on peas in the greenhouse. Maximum control of Pythium (90 to 94 per cent plant stand) under the most favorable conditions for disease development was obtained at a dosage of 0.56 to 1.12 ounces per bushel of seed. Practical control was obtained at 0.28 ounce per bushel, equal to 1/32 per cent by seed weight (Figure 1).

The average pea stand at a dosage of 0.28 ounce per bushel of seed in twelve experiments was 80 per cent compared to 24 in the untreated, a significant mean difference of 56 per cent. Corresponding mean height of plants after about 10 days was 5.97 cm. for the treated and 4.67 for the untreated, a mean difference of 1.30 cm., which was highly significant with odds of 10,000 to 1. Analysis of variance on results from the twelve experiments in which the four dosages (2.24, 1.12, 0.56, and 0.28 ounce of 2,3-dichloro-1,4-naphthoquinone per bushel of seed) were employed showed no significant differences in plant height between dosages.

The chemical was applied also at dosages of 4.48 and 8.96 ounces per bushel of pea seed to determine any tendency to injure seed. The results were not significantly different from those obtained with a dosage of 1.12 ounces, showing the chemical to be safe on seed. The material appears to be noninjurious to foliage also and offers considerable promise as a plant spray against leaf diseases. The chemical is not compatible with nitrogen-fixing bacteria.

2,3-Dichloro-1,4-naphthoquinone has given good results also on Lima beans at 0.2 ounce per bushel and on corn (field and sweet) at 0.25 ounce per bushel. Its toxicity to Ustilago sp. in slide tests indicates possible value in the control of cereal smuts.

It has given fair control of the fungi causing cotton damping-off. The results obtained against Rhizoctonia and anthracnose damping-off in the greenhouse are shown in Table I.

2,3-Dichloro-1,4-naphthoquinone appreciably reduced both Rhizoctonia and Glomerella infection at a dosage of 0.5 ounce of active material per bushel of cottonseed applied just before planting. The percentage of anthracnose infection in the untreated seedlings always was high, although the percentage of actual damping-off from this disease was never exceptionally high, as in peas. Anthracnose control with the chemical may be observed in both criteria but is most striking in the percentage of healthy plants obtained.

2,3-Dichloro-1,4-naphthoquinone completely prevents germination of cotton anthracnose spores at 1 p. p. m. or less in slide tests. Test tube cultures of treated and untreated cottonseed highly infested with anthracnose revealed that 6 ounces per

TABLE I. CONTROL OF COTTON DISEASES WITH 2,3-DICHLORO-1,4-NAPHTHOQUINONE

			Individual Tests against:					
			Rhizoctonia[a]		Anthracnose[b]			
	Dosage, Ounces per Bu.		% Stand		% Stand		Healthy, % of Emerged	
% Concentration	Total	Active	Treated	Untreated	Treated	Untreated	Treated	Untreated
100.0	3.00	3.00	96	32	89	66	54	2
100.0	2.00	2.00	..	..	83	61	49	3
100.0	1.00	1.00	..	..	80	60	39	3
12.5	6.00	0.75	90	27	90	81	43	18
12.5	5.00	0.63	..	..	88	69	44	17
12.5	4.00	0.50	..	..	83	63	27	11
10.0	6.00	0.60	44	0	..	..	..	..
10.0	5.00	0.50	60	0	..	..	..	..

[a] Machine-delinted seed planted in Mississippi cotton soil.

[b] Fuzzy seed highly infested naturally and planted immediately after treatment.

bushel of the 12.5 per cent chemical (that is, 0.75 ounce of active material per bushel) completely kill *Glomerella gossypii* when applied 3 months in advance of planting. Possibly higher dosage would accomplish this in a shorter time.

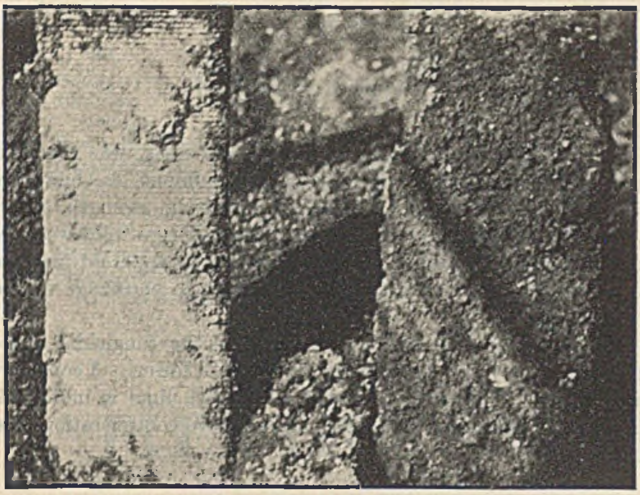


Figure 3. Soil Adherence in 2, 3-Dichloro-1, 4-naphthoquinone Treated (*left*) and Untreated (*right*) Fire Hose upon Removal from Soil 21 Days after Burial

USE AS A MILDEW PREVENTIVE

The armed forces need mildew prevention on numerous items. The ideal textile fungicide possesses the following properties: Effectiveness against both fungi and bacteria (for which property the term "bacterifungicide" is proposed); effectiveness at low temperatures; resistance to weathering, leaching, and heat; ease of application; no odor; no objectionable color alteration; no change in "feel" of fabric; no tendering; no undesirable effect on dyeing; nontoxicity and noncorrosiveness; no increase in flammability; inexpensiveness and availability.

2,3-Dichloro-1,4-naphthoquinone has proved in laboratory and soil burial tests to be a highly effective mildew-proofing agent for cotton fabrics against such molds as Chaetomium, Metarrhizium, Stachybotrys, Aspergillus, Penicillium, and others employed in U. S. Department of Agriculture test procedures for mildew preventives.

Stachybotrys spp. (probably *S. atra* Corda and *S. cylindrospora* Jensen) were important in the destruction of cotton fabrics in some of the soil burial tests. It has been demonstrated experimentally that *S. cylindrospora* is an active cellulose destroyer on cotton batting, absorbent cotton, and ashless filter paper (*16*). *S. papyrogena* Sacc. is destructive to cotton also (*12*). The occurrence and destructiveness of Stachybotrys spp. and related genera on paper has been known for a long time (*2*, *8*, *17*).

SLIDE TESTS

The toxicity of 2,3-dichloro-1,4-naphthoquinone to Metarrhizium and Stachybotrys was determined in slide tests, following the procedure of McCallan and co-workers (*15*), later adopted by the Committee on Standardization of Fungicidal Tests, American Phytopathological Society. Spores were from 4–7 day old cultures. Metarrhizium (N. R. R. L. No. 1875) was grown on strips of filter paper extending into a liquid medium suggested by Greathouse (*11*). This medium, of about pH 3.7, proved excellent for the production of spores in both Metarrhizium and *Glomerella gossypii*, and has the composition which follows.

NH_4NO_3	2.0	grams
K_2HPO_4	2.8	grams
$MgSO_4$	11.8	grams
Tartaric acid	2.0	grams
Fe, Zn, Mn as SO_4	0.001	gram each
Peptone	0.5	gram
Distilled water to make	1000.0	cc.

Stachybotrys was grown on potato dextrose agar. One tenth per cent ultrafiltered orange juice was added to the spore suspension to stimulate germination on the slide, although its necessity for either fungus was not determined. Metarrhizium, except for the smallness of its spores, is admirably suited to slide work, since spores capable of 100 per cent germination are produced in profusion.

The LD50 and LD95 values on Metarrhizium thus are found to be as follows:

Chemical	LD50 *P. p. m.*	LD95 *P. p. m.*
2,3-Dichloro-1,4-naphthoquinone	0.37	0.56
Tetrachloro-*p*-benzoquinone	2.5	4.00

The results show the potency of 2,3-dichloro-1,4-naphthoquinone, the LD50 as well as the LD95 values being only one eighth those of tetrachloro-*p*-benzoquinone.

The LD50 value for 2,3-dichloro-1,4-naphthoquinone on Stachybotrys is about 1.3 p. p. m., the LD95, 2.5 p. p. m. The ascospores of *Chaetomium globosum* Kze. failed to germinate satisfactorily for slide tests. The wholly submerged formation of mature perithecia by this fungus on plain agar is unusual and suggests possible internal fructification in fabric under certain conditions.

EFFECT ON STRENGTH OF COTTON FABRIC IN ABSENCE OF MILDEW

The effects of 2,3-dichloro-1,4-naphthoquinone on cotton fabric in the absence of mildew was determined by 60-hour exposure of the originally treated uninoculated and unincubated sample to the combined action of ultraviolet light, water spray, and heat (80° C.). The average bursting strengths of a sample of 8-ounce duck, originally testing 202 pounds, thus exposed in an accelerated weathering unit, was 62 pounds for the acetone-treated check and 79 pounds for the 2,3-dichloro-1,4-naphthoquinone treated (1 per cent in acetone). Thus no greater loss of strength over the check, due to the chemical, is indicated in controlled en-

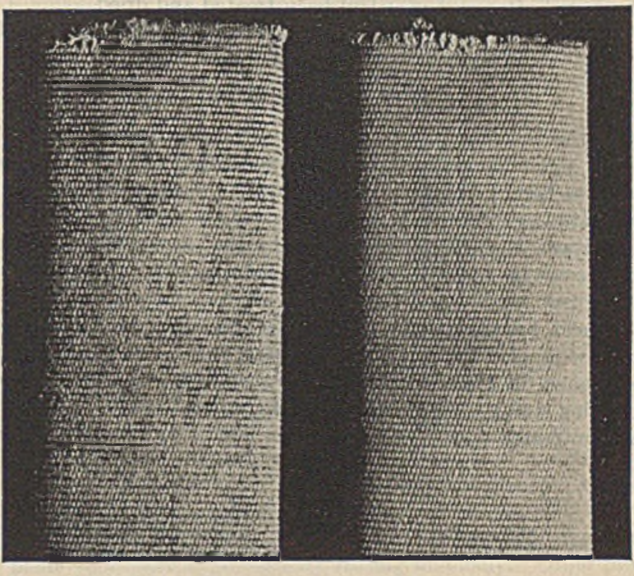


Figure 4. Prevention of Stachybotrys Mildew with 2, 3-Dichloro-1, 4-naphthoquinone on Fire Hose Buried 3 Weeks in Greenhouse Soil

Left: **Untreated hose; original tensile strength 29 lb./sq. in., final 0.**
Right: **Hose treated with 1 per cent chemical in acetone; original tensile strength 29 lb./sq. in., final 25.**

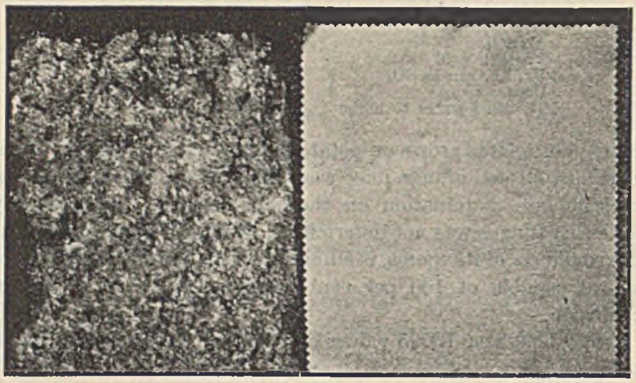


Figure 5. Prevention of Stachybotrys Mildew (Dark Areas) and Bacteriosis (Holes) with 2, 3-Dichloro-1, 4-naphthoquinone on Cotton Duck Buried 3 Weeks in Greenhouse Soil

Left: Untreated duck; original bursting strength 202 pounds, final 0.
Right: Duck treated with 1 per cent chemical in acetone; original bursting strength 205 pounds, final 215.

vironment, equivalent to several months of natural aging. The increase in strength over the check is probably due to shrinkage of the fabric.

FABRIC INOCULATION TESTS

Laboratory tests were conducted with Metarrhizium sp. or *Chaetomium globosum* as recommended by Thom *et al.* (*18*). The fabric under test was impregnated with a solution of 2,3-dichloro-1,4-naphthoquinone of known concentration and allowed to dry. Duplicate tests were made on dried treated samples, unwashed and washed for 16 to 24 hours in running tap water to determine resistance to leaching. Artificial inoculation with the desired mildew and 30-day incubation under optimum conditions for mildew development ensued. Fungicidal evaluation was based on visual observation and tensile and bursting strength determinations. The effectiveness of 2,3-dichloro-1,4-naphthoquinone in the control of Chaetomium is shown strikingly in Figure 2, in which the entire sample was inoculated and incubated after part of it had been treated and dried.

The tests on leached and unleached duck are shown in Table II.

SOIL BURIAL TESTS

In the soil burial tests, samples were buried horizontally $^{1}/_{4}$ to $^{1}/_{2}$ inch deep in good greenhouse soil of pH 7.2, using natural fungous flora as inocula. Soil moisture and other environment were kept at optimum conditions for mildew growth. Period of burial was 21 days. It is noteworthy that well mildew-proofed fabrics can be removed from the soil relatively clean, whereas untreated or poorly protected fabrics are covered with a layer of soil held by the mildew mycelia (Figure 3). Mildewed and mildew-proofed fire hose and duck after burial and soil removal are shown in Figures 4 and 5, together with some tensile and bursting strength figures. Further bursting strengths in treated and untreated duck, before and after 3-week soil burial, follow:

Acetone Check		1% 2,3-Dichloro-1,4-naphthoquinone in Acetone	
Before burial	After burial	Before burial	After burial
192	0	215	230
211	0	210	227
205	0	198	228
208	0	208	212
197	0	205	208
...	..	...	205
Av. 202	0	207	218

The 2,3-dichloro-1,4-naphthoquinone uptake by cotton duck from immersion in 1 per cent acetone solution is 1.5 to 1.7 per cent of the original duck weight.

Bursting strength determinations on cotton sheeting before and after 3-week soil burial follow:

Fabric Treatment	Lb./Sq. In.
Untreated, unburied	132
Untreated, buried	0
0.1% 2,3-dichloro-1,4-naphthoquinone, buried	150

Cotton sheeting, as well as fire hose and duck, was rendered mildew-proof by 2,3-dichloro-1,4-naphthoquinone, as shown by visual examination and tensile and bursting strength determinations. Both Chaetomium and Stachybotrys mildews were controlled effectively in soil burial tests. The apparent increase in strength due to treatment is attributed to shrinkage in the course of the tests.

2,3-Dichloro-1,4-naphthoquinone retains its fungicidal effectiveness at average temperatures of 50° F. or lower. A considerable degree of fungicidal compatibility with lime is indicated, provided somewhat above minimum effective concentrations are employed.

METHODS OF APPLICATION

2,3-Dichloro-1,4-naphthoquinone may be applied to fabric or leather in one of four ways: in organic solvent, in aqueous suspension, in a lacquer, or by vapor.

Solutions of the chemical are best prepared in such solvents as acetone, benzene, Cellosolve, Stoddard solvent, *o*-dichlorobenzene, or mineral, vegetable, and animal oils. Recommendations for light cotton sheeting are 0.1 per cent and for heavy fabrics, duck, etc., 0.5 to 1 per cent. Only simple immersion with subsequent drying is required.

Aqueous suspensions of pH 4 to 5, containing 20 per cent active chemical and the necessary protective agents, ball-milled, may be employed. Application is made from a dilution containing 1 per cent active ingredient, padding, and drying.

Table II. Tensile Strength (Pounds) of Treated and Untreated Duck after 30-Day Incubation Following Inoculation with *Chaetomium globosum*[a]

Untreated Check		Benzene Check		2,3-Dichloro-1,4-naphthoquinone			
				0.1% in Benzene		0.5% in Benzene	
Warp	Filling	Warp	Filling	Warp	Filling	Warp	Filling
Duck Unwashed before Incubation							
6	21	8	6	89	88	93	78
19	15	4	28	94	89	86	76
2	20	10	29	95	76	84	86
13	20	2	20	102	86	93	87
16	..	13	..	94	..	93	..
Av. 11.2	19	7.5	20.7	94.8	84.7	89.8	81.7
Duck Washed 24 Hours in Running Water before Incubation							
35	32	2	18	93	81	87	80
8	28	7	12	99	90	95	90
26	33	12	30	92	85	87	78
2	28	14	26	97	86	99	82
15	..	15	..	..	87	..	85
Av. 17.2	30.2	10	21.5	95.2	85.8	92.0	83.0

[a] Original tensile strength: warp 97, filling 71.

2,3-Dichloro-1,4-naphthoquinone can be applied to surfaces other than cotton, such as wood, rubber, etc., by painting with a lacquer containing the chemical.

The chemical can be applied easily and economically by exposure of the fabric to the vapor at 125° C. for at least one hour.

ACKNOWLEDGMENT

Grateful acknowledgment is made to E. C. Ladd, R. J. Norton, and J. L. Kurlychek of these laboratories for their part in the development of this fungicide, and to the management for permission to publish this paper. Anthracnose-infected cottonseed was kindly supplied by C. H. Arndt, Clemson Agricultural College.

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A PRELIMINARY paper on the same subject was presented before the Division of Agricultural and Food Chemistry at the 105th Meeting of the AMERICAN CHEMICAL SOCIETY, Detroit, Mich.

FLEX LIFE AND CRYSTALLIZATION OF Synthetic Rubber

J. H. FIELDING
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Natural rubber and Butyl B are similar in that stretching produces fibering; their flex life is good and high tensile gum stocks are possible. GR-S and Buna N lack all semblance of fibering. Gum stocks have low tensile and, in general, flex life is poor.

THE crystalline structure of stretched natural rubber has been the subject of much experimental work in the past. A great deal of this has been devoted to the more theoretical aspects such as x-ray patterns, thermal effects, and volume change. It is now known that neither Buna N nor GR-S has a fiber diagram when stretched and that Butyl B and neoprene do have such patterns.

Since the industry is now in the process of changing from natural rubber to GR-S, it is of interest to see just what this lack of crystallinity means from a compounding and performance standpoint. It is possible that many of our ideas based on rubber must change, that GR-S must be considered a new material, and that radical changes in formulation and construction must be made.

PHYSICAL EFFECTS OF CRYSTALLIZATION

When natural rubber is stretched, an alignment and fitting together of adjacent molecules or parts takes place which has many of the theoretical aspects of crystallization. The physical result is that the rubber becomes fibrous. It becomes stronger as it is stretched. Its resistance to rupture or tear is increased by the very force or deformation that tends to rupture it. At the same time it becomes weaker in a direction at right angles to this. The result is that tensile strength is high whether or not a reinforcing pigment is used, and rubber may be said to be reinforced by its own crystallization.

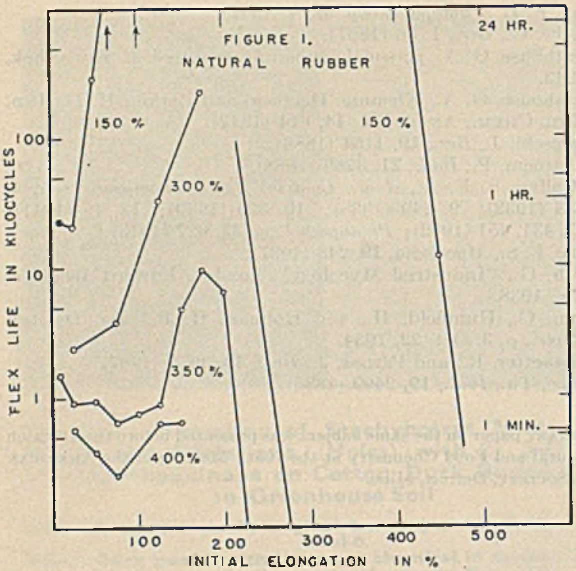
Tearing behavior of rubber was covered extensively some years ago by Busse (*1*). His work involved determining the relation between the depth of a transverse cut and the force required to rupture the strip. It was shown that, because of "semiracking", the force required to make a cut grow part way across a strip was under some conditions not sufficient to make it tear all the way across. Again, if the strip were stretched before cutting, there was a certain degree of elongation, somewhat less than the ultimate, at which the strip had to be cut three quarters of its width in order to produce complete rupture; at lower elongations a much smaller cut was sufficient. This same phenomenon of semiracking was used to explain the knotting of a carbon black stock, where the tear has a strong tendency to go at right angles to any chosen direction of tear.

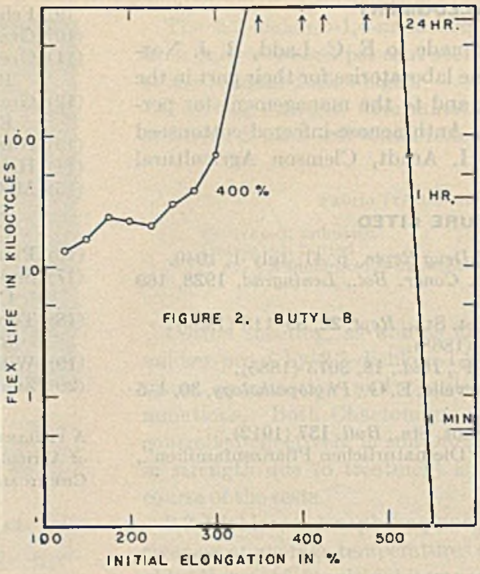
A totally different approach but equally effective was used by Cadwell (*2*). Rubber was flexed from various starting elongations greater than zero, with the result that flex life improved tremendously as elongation was increased and passed through a maximum at a point somewhat below the ultimate elongation.

This ability to resist rupture in the direction of strain is thought to be one of the greatest contributing factors to the toughness of vulcanized natural rubber. The object of this paper is to search for a similar behavior in synthetic rubber.

TEARING EXPERIMENTS

Four typical compounds were made up (Table I) and were subjected qualitatively to a tear test designed to reveal any tendency toward fibering. Wide dumbbell pieces were cut with a razor longitudinally and stretched in a Cooey machine, and an attempt made to continue the split by tearing manually. Other pieces were stretched, then razor cut longitudinally, and tearing was attempted. Still other pieces were stretched, then punctured with a pin, and an attempt made to force the pin along the strip longitudinally and thereby split it.





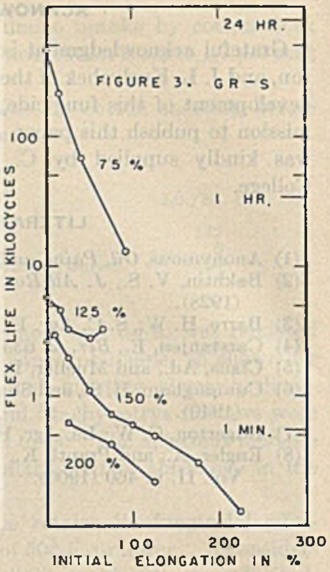


Table I. Formulation of Compounds

Natural rubber	100.00	....	....	....
Buna N	....	100.00	....	....
GR-S	....	....	100.00	....
Butyl B-1.45	....	....	....	106.50
Channel black	50.00	50.00	50.00	60.00
Stearic acid	3.00	2.00	2.00	3.00
Pine tar	3.00	....	....	....
SDO No. 10 (Barrett)	....	3.00	3.00	....
Medium process oil	....	....	....	3.00
ZnO	5.00	5.00	5.00	....
Sulfur	3.00	2.00	2.00	....
Mercaptobenzothiazole	1.25	1.50	1.50	....
Tetramethylthiuram disulfide	....	....	....	1.00
Total	165.25	163.50	163.50	173.50
Cure, min. (° F.)	70 (260)	50 (260)	50 (290)	70 (310)

Table II. Results of Tearing Experiments

	Natural	Buna N	GR-S	Butyl B-1.45
Min. elongation allowing split (approx.), %	350	...	...	700
Ultimate elongation, %	575	450	450	850
Splitting	Easy	No	No	Possible

These experiments were conducted at elongations from about 50 per cent of the ultimate to the ultimate. In the case of natural rubber splitting was comparatively easy. Butyl B behaved the same way, but splitting was a little more difficult. Buna N and GR-S could not be split; in fact they frequently tore completely across as soon as a longitudinal cut or a pinhole was made (Table II).

In this respect, then, rubber and Butyl B are in one class while Buna N and GR-S are in another.

FLEXING EXPERIMENTS

An experiment was designed to show the effect of flexing amplitude and starting elongation on flex life—in other words, to show whether or not flex life was greater when the test piece remained within the range of elongation where crystallization could occur.

Ring-shaped test pieces were flexed on a machine designed by G. J. Albertoni. The speed was 550 cycles per minute. It was possible to use amplitudes as low as 25 or as high as 400 per cent. Starting elongations were limited on the low side by the permanent set of the test piece. At low amplitudes the maximum elongation was limited by the machine as follows:

Amplitude, %	25	75	125
Max. elongation, %	115	90	65

At amplitudes of 150 per cent and above, the starting elongation was limited on the high side only by the nature of the stock under test. A further limitation was introduced that in most cases no run was made beyond 800 kilocycles, corresponding to 24 hours.

Table III and Figure 1 show several curves for natural rubber. The existence of a peak is marked. It is possible that the first few increments of initial elongation make flex life poorer, particularly at the higher amplitudes, but soon there is a sharp rise in flex life and finally a reduction again as the ultimate elongation is approached. The exact location of the peaks has not been determined, but it appears that all should occur at maximum elongations between 400 and 550 per cent.

Butyl B has a similar behavior (Table III and Figure 2). Its peak is just as sharp as natural rubber but falls at a higher elongation, possibly at a maximum elongation of 800 per cent.

GR-S shows no evidence of a peak (Table IV and Figure 3). All curves, within experimental error, start to fall immediately as initial elongation is increased above zero. The decline as the breaking elongation is approached is gradual rather than abrupt.

Table III. Flex Life of Natural Rubber and Butyl B-1.45[a]

Min. Elongation %	Flex Life of Natural at Amplitude of: 150%	200%	250%	300%	350%	400%	Flex Life of Butyl at Amplitude of 400%
	Kilocycles						
0	Too much set	..	...	..	..	..	
10	23	..	...	..	1.53	..	
25	21	..	...	2.4	0.91	0.57	Too much set
50	288	..	...	..	0.95	0.38	
75	(2120+)	..	...	3.9	0.65	0.25	
100	(450+)	..	...	..	0.77	..	
125	...	..	...	33.2	0.88	0.64	13.3
150	...	..	...	..	4.7	0.65	16.6
175	...	..	...	221[a]	9.7	..	24.2
200	...	..	...	..	6.5	..	22.6
225	...	..	...	..	0	..	20.8
250	...	..	...	..	..	..	30.6
275	...	..	...	0	..	..	38.0
300	...	..	...	..	..	..	72.7
325	...	..	0	..	..	..	..
350	...	..	...	..	..	..	(800+)
375	...	17	...	..	..	..	..
400	...	..	...	..	..	..	(800+)
425	...	..	...	..	..	..	(800+)
450	12	..	...	..	..	..	..
475	...	..	...	..	..	..	(800+)
500	...	..	...	..	..	..	..
525	...	..	...	..	..	..	71
550	...	..	...	..	..	..	0

[a] For example, the figure 221 means that strips flexed from 175 to 475% had a life of 221,000 cycles, or about 6$^1/_2$ hours.

Table IV. Flex Life of GR-S

Min. Elongation, %	Flex Life (Kilocycles) at Amplitude of: 25	75	125	150	200
0	.....	453	5.8	2.6	..
8.4	.....	...	...	2.9	..
15	(800+)	214	4.6	..	..
25	.....	...	3.2	2.0	0.63
40	(800+)	67	...	..	..
50	.....	...	2.8	1.1	..
65	(800+)	...	3.2	..	..
75	.....	...	...	0.72	0.43
90	.....	13	...	..	..
100	.....	...	...	0.61	..
115	.....	...	...	..	..
125	.....	...	...	0.50	0.22
150	.....	...	...	..	..
175	.....	...	...	0.31	..
200	.....	...	...	..	..
225	.....	...	...	0.13	..
250	.....	...	...	..	..
275	.....	...	...	..	..

Again rubber and Butyl B are in one class while GR-S is in another.

IMPLICATIONS

These experiments illustrate a type of behavior or a tendency which has a bearing on performance both in service and in laboratory tests. When a typical rubber tire is run under conditions that can produce tread cracking, it is found that many cracks are started before the first cracks have grown very large. On the other hand, since crack growth in a GR-S tire is not retarded by fibering, the first cracks may grow quite large before many are formed. The most successful flex tests for rubber in this laboratory have been those in which the crack has been permitted to start itself, such as the De Mattia and the perforated (cut round hole) strip test. These tests have not been successful with GR-S, but if either test piece is cut or nicked before test, it becomes a good measure of cut growth. A natural rubber test piece so nicked or cut will frequently "knot", and cut growth will be retarded until other points of failure have been started.

Lacking the benefit of fibering, the compounding of GR-S becomes a more delicate job than that of natural rubber. It is not expected that any compounding steps will produce fibering. Improved flex life must be obtained in spite of this lack.

The use of carbon black has been quite generally adopted in GR-S. This was done primarily to increase tensile strength. It was necessary because of the lack of crystal reinforcement in GR-S and its consequent low tensile strength. Its action is thought to be exactly the same as it is in natural rubber; but since natural rubber can crystallize, it is already well bound together and the possible increase in tensile is not so great as it is with GR-S. Obviously, the most highly reinforcing black permitted by heat build-up and processing should be used.

In polymer research, vigorous efforts should continue to get some degree of crystallization into the government tire rubber. It is already present in two synthetics. If this can be done and the other fine properties of GR-S still be maintained, it is predicted that flex life will be greatly improved and that gum stocks will be possible.

ACKNOWLEDGMENT

The writer wishes to express his thanks to W. W. Vogt, Development Manager of The Goodyear Tire & Rubber Company, for permission to publish this paper, and to G. J. Albertoni who performed much of the experimental work.

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

ALCHEMISTIC LABORATORY

◆ No. 156 in the Berolzheimer series of Alchemical and Historical Reproductions is a photographic view of the two rooms in the Deutsches Museum in Munich fitted up as an Alchemists' Laboratory of the Middle Ages.

Most of the apparatuses as shown appear unusual and differ from those presented by the various Dutch and other contemporary painters in the previous Reproductions in the series.

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With this reproduction it will be necessary to interrupt the series "for the duration" owing to the impossibility of obtaining material under present conditions. It is the hope that additional photographs can be obtained for a prompt resumption of the series.

A complete list of the 156 reproductions will be published in the January, 1944, issue. Copies of all of these can still be supplied.

D. D. Berolzheimer

50 East 41st Street
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ASH STRUCTURE in COKE

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Rochester Gas and Electric Corporation, Rochester, N. Y.

A series of thin sections of coke are studied, with and without the admixture of breeze, both before and after burning. It is found that the distribution and structure of ash in coke in relation to the combustible is dependent on the structure of the original coke. It is indicated that the combustible material surrounds and envelops the ash residue. The addition of 5 per cent breeze to the charged coal has little effect upon the structure of the resulting coke or its ash residue. The direction in which a coking coal expands in respect to its banded structure is indicated in a preliminary manner.

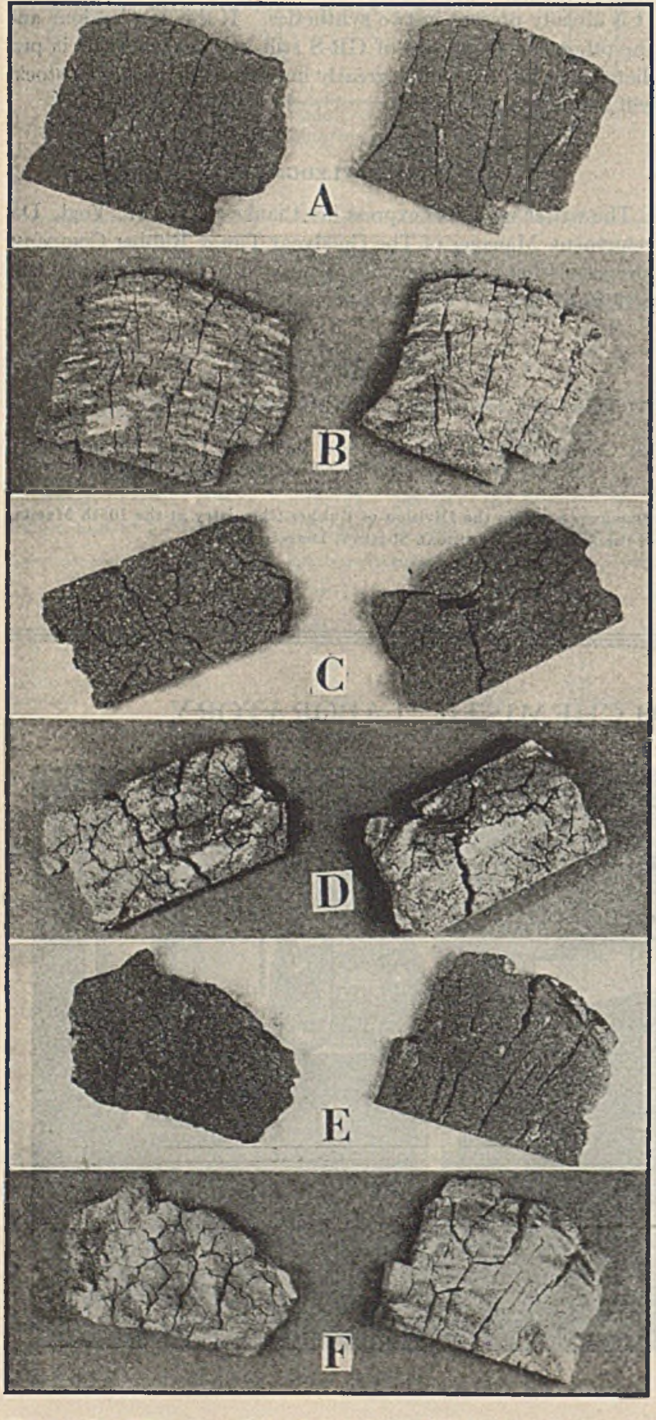

Figure 1. Photographs of Original Cokes and Residues after Combustion

COKE (*1*) has been defined as "the solid, cellular, coherent residue from destructive distillation of bituminous coal, said residue having such physical structure as results from the hardening of a fused or semiliquid mass". Pfluke (*4, 5*) reported that coke breeze could be added to 100 per cent high-volatile coal prior to carbonization without detrimental effects on coke strength, provided the following limits were observed:

1. Up to 5 per cent of breeze, no larger than minus $^1/_{32}$-inch square mesh.
2. Up to 3 per cent of breeze no larger than minus $^1/_{16}$-inch square mesh.
3. 1 per cent of any other size up to minus $^1/_4$-inch square mesh.

Pfluke further showed that, provided these limits are observed both with 100 per cent high-volatile coal and blended coal, the percentage of usable coke from the initial charge remains almost unchanged when breeze is added compared to the percentage of usable coke from the initial charge with no breeze added.

The term "ash structure in coke" is used here to indicate the probable distribution of the ash or mineral matter in relation to the combustible material—that is, the position of each particle of mineral matter with respect to the combustible. A survey of the literature indicated that little information was available relating to ash structure in coke. A number of investigations have been made on the distribution of ash in solid fuels (*2, 3*), but no study has been directed toward the manner in which the ash structure is built or distributed in the solid fuel sample in relation to the combustible. As a result an attempt was made to study this subject.

STRUCTURE AND DISTRIBUTION OF ASH

Since coke is an abrasive material, a Carborundum wheel was used to secure thin slices. Sections $^3/_{16}$ inch thick were cut from the lumps of coke in different directions. They were carefully placed on a lime asbestos board, photographed, inserted in a cold electric muffle furnace, and slowly raised to 1300° F. After remaining in the furnace for 16 hours, the lime asbestos board containing the ash from the coke was carefully removed, allowed to cool, and rephotographed in the same position as before burning. The coke samples were completely burned during this treatment, and only the ash or noncombustible matter remained.

The coke was made from Pittsburgh high-volatile gas coal crushed to $-1^1/_2$ inch size, charged into by-product coke ovens

(Koppers-Becker type), and carbonized at 2450° F. for 12 hours net. The approximate analysis of the coke follows:

Volatile matter, %	0.7
Ash, %	9.4
Fixed carbon, %	89.9
Sulfur, %	0.85
Fusion point, °F.	2600+
Heating value, B. t. u./lb.	12,810

PHOTOGRAPHIC RECORD

COKE ASH. Figure 1 shows how the coke behaved on burning and the structure and distribution of its ash. The photographs are typical of the results obtained from a large number and variety of samples examined in the course of this study. The samples of coke and ash shown are pieces of approximately half-oven width; when the sections are described as longitudinal, it means parallel to a line across the oven perpendicular to the walls; the opposite is meant for the cross section.

Figure 1*A* shows two samples of coke with the addition of 5 per cent breeze (fine coke) in the charged coal cut longitudinally from the coke sample. The characteristic fissures and porous structure of the coke is clearly seen. *B* presents the same samples after the combustible material has been burned away and only the ash remains; the shape and height of the ash samples are very similar to the unburned coke. Furthermore, the major fissures and minor cracks in the coke sample are clearly visible and maintained in the residue. The porous nature of the ash residue is also revealed. The light and dark areas in the residue give further indication as to how the component parts of the ash are distributed. Near the lower right-hand corner of the specimen at the left of Figure 1*A* is a piece of foreign matter (slate) which is somewhat darker than the remaining sample. The left-hand specimen in *B* indicates clearly the presence of this impurity in the ash in the same location as before burning.

Figure 1*C* shows two samples of coke with the addition of 5 per cent breeze in the charged coal, cut in cross section from the coke sample. The characteristic porous structure, major and minor fissures, as well as impurities are apparent. *D* represents the same samples after ignition. The ash structure is very similar to the coke structure.

The photographs show that the distribution of ash within a sample of coke is dependent upon the presence of foreign matter and impurities as well as upon the coke structure. Further, the distribution of the ash can be ascertained rather closely from a knowledge of the coke structure. It further indicates that the combustible matter surrounds and envelops the ash residue. The volume of the ash residue was almost the same as the original coke sample.

Figure 1*E* presents cross and longitudinal sections of the same sample of coke to which no breeze had been added in the coal charge. *F* shows the same samples after burning away the combustible material. As indicated previously, the ash structure follows closely the structure of the coke. The color, porosity, and general appearance of the ash structure of the cokes with and without breeze was the same. This study or ash structure corroborates the findings of Pfluke (*5*) who showed that the shatter, tumbler, and screen tests of coke, with and without the addition of breeze were the same.

In each case the photographs show that the combustible matter is built around the ash structure. The light and dark areas represent the distribution of the component parts of the ash.

COAL ASH. Figure 2*A* presents sections of bituminous gas coal from the Pittsburgh field. At the left is a section cut perpendicular to the bond structure; at the right, a section cut parallel to the bonds and comprising several bonds. The approximate analysis of the coal was:

Volatile matter, %	34.3
Ash, %	6.3
Fixed carbon, %	59.4
Sulfur, %	1.0
Fusion point, ° F.	2600+

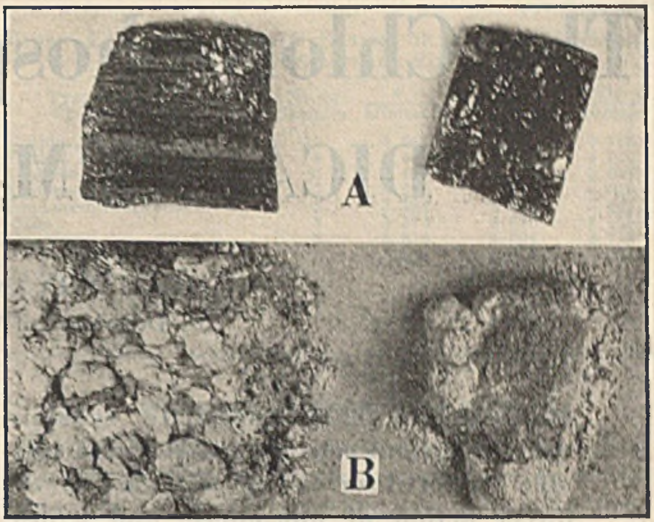

Figure 2. Photographs of Original Coal and Residues after Combustion

These samples were somewhat difficult to prepare, since the coal was soft and oily. The left-hand section shows the characteristic band structure of the coal. Figure 2*B* represents the same samples after slow burning by the method indicated for coke. Combustion of this sample was difficult because it was a coking coal and passed through a plastic stage before coking and final burning. This behavior obscured the true picture as to how ash is present in coal. However, *B* gives a preliminary indication as to the direction of expansion on heating. The left-hand section expanded considerably, but principally in the direction perpendicular to the plane of the bands in the unburned coal. This was further evidenced by the nature of the ash structure of the sample on the right. This ash residue was approximately the same size as the unburned coal but was considerably higher, an indication that expansion had occurred in the direction perpendicular to the plane of the bands. During softening and swelling of the coal there was no exuding of an ash-free pitch or tar, but an expansion of the coal as a whole. Figure 2*A* and *B* show individual lumps which do not correspond to the coal charge in a by-product oven. From this preliminary study it appears that this type of bituminous coal expands in a direction perpendicular to the plane of its banded structure.

It appears, then, that as the coal passes through the plastic state during the coking process, there is no segregation of ash; that is, the mineral matter does not separate from the combustible but remains thoroughly distributed.

The method employed may be applied to record the visible changes that take place in the ash and fuel at different periods during combustion. The behavior of the Pittsburgh gas coal indicates the difficulty of predicting how and where such coal ash would be distributed during the coking process or during combustion.

ACKNOWLEDGMENT

The author wishes to acknowledge the cooperation of Ralph M. Bishop of the laboratory staff in taking the photographs.

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PRESENTED before the Division of Gas and Fuel Chemistry at the 106th Meeting of the AMERICAN CHEMICAL SOCIETY, Detroit, Mich.

The Chlorophosphate Process for DICALCIUM PHOSPHATE

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Monocalcium chlorophosphate substantially free from calcium chloride and suitable for fertilizer can be obtained by the direct action of phosphoric and hydrochloric, of sulfuric and hydrochloric, or of phosphoric, sulfuric, and hydrochloric acids on phosphate rock. Monocalcium chlorophosphate can be converted to dicalcium phosphate by thermal treatment in the presence of water vapor with recovery of its hydrochloric acid content, or by ammoniation which yields a mixture of dicalcium phosphate and ammonium chloride. The manufacture of dicalcium phosphate by the chlorophosphate process would permit substantial economies in reagent materials over practices currently employed in the production of available phosphates. The production of monocalcium chlorophosphate, or of ammoniated chlorophosphate, would afford an outlet within the fertilizer industry for by-product hydrochloric acid.

THE use of dicalcium phosphate as a fertilizer was proposed by Way (*18*) in 1867. He described several methods for its production from hydrochloric acid solutions of natural phosphates, including the well known process of precipitation with milk of lime. Later Way (*19*) proposed to evaporate or otherwise concentrate such hydrochloric acid solutions of phosphate of lime to produce "chlorophosphate of lime" for fertilizer use. He considered the product to be "a compound of acid or monophosphate of lime with chloride of calcium in the proportion of one equivalent of each", and apparently was unaware that Erlenmeyer (*1*) previously had obtained such a compound in hydrated form by evaporation of a hydrochloric acid solution of tricalcium phosphate.

More recently Flatt (*2*) and Turrentine (*15, 16*) described the products formed by evaporation of hydrochloric acid solutions of phosphate rock as a mixture of calcium chloride and of a hydrated double salt of monocalcium phosphate and calcium chloride. Heating this mixture yielded hydrogen chloride, water, and basic chlorophosphates (Figure 8).

The chemistry of the phosphate rock–aqueous hydrochloric acid system was presented in a previous article (*5*) which showed that solid monocalcium chlorophosphate is produced on evaporating or otherwise concentrating solutions of calcium chloride and phosphoric acid. While the product thus obtained has physical and chemical properties suitable for fertilizer (*8, 19*), its production alone does not constitute the optimum use of reagent materials (*4*). The present article discusses the possible use of either sulfuric acid or phosphoric acid or both in conjunction with gaseous hydrogen chloride as reagents in the decomposition of phosphate rock for the production of calcium-chloride-free monocalcium chlorophosphate; methods are then described which have been developed for the conversion of the chlorophosphate to dicalcium phosphate.

REACTIONS YIELDING MONOCALCIUM CHLOROPHOSPHATE

Although monocalcium phosphate repeatedly has been reported to result from the action of hydrochloric acid on phosphate rock (*11, 14*) and other basic phosphates (*13, 17*), Fox and Clark (*5*) found no evidence of its occurrence in the system. The primary reaction involved in the decomposition of phosphate rock with hydrochloric acid was shown to be in accordance with the following equation where n is the $CaO:P_2O_5$ mole ratio of the original rock:

$$nCaO.P_2O_5 + 2nHCl = nCaCl_2 + 2H_3PO_4 + (n-3)H_2O \quad (1)$$

The ratio of calcium chloride to phosphoric acid in solution in contact with undecomposed rock remained constant as indicated, up to a concentration of about 2.3 gram moles of calcium chloride per kg. of solution at 25°, or 2.6 gram moles at 100° C.

Concentration of such solutions, whether or not in contact with undecomposed rock, resulted in a progressive increase of the $CaCl_2:H_3PO_4$ ratio of the solution accompanied by the appearance of monocalcium chlorophosphate, $CaClH_2PO_4.H_2O$, in the solid phase. In the absence of undecomposed rock a mole of hydrochloric acid was volatilized for each mole of calcium chloride converted to the chlorophosphate. Chlorophosphate formation, therefore, is equivalent to the replacement of half the chlorine of calcium chloride by the $H_2PO_4^-$ radical in accordance with the equation:

$$CaCl_2 + H_3PO_4 + H_2O = CaClH_2PO_4.H_2O + HCl \quad (2)$$

If, however, an excess of rock was present, the chlorophosphate was formed without appreciable loss of hydrochloric acid from the system. Consequently, crude chlorophosphate substantially free from calcium chloride can be prepared by treating phosphate rock with hydrochloric and phosphoric acids in the quantities required to form the chlorophosphate, and drying the mixture to complete the reactions (*3*):

$$nCaO.P_2O_5 + nHCl + (n-2)H_3PO_4 + 3H_2O = nCaClH_2PO_4.H_2O \quad (3)$$

Products obtained in this manner have been shown by vegetative tests to be a satisfactory source of phosphorus (*8*).

If, instead of phosphoric acid, sulfuric acid is added to combine with the excess of calcium present in phosphate rock, the reagent requirements are as shown in Equation 4.

$$nCaO.P_2O_5 + 2HCl + (n - 2)H_2SO_4 + (5 - n)H_2O = 2CaClH_2PO_4.H_2O + (n - 2)CaSO_4 \quad (4)$$

The product thus obtained is a mixture of chlorophosphate and calcium sulfate analogous in some respects to ordinary superphosphate, but containing one less mole of calcium sulfate per mole of P_2O_5. The production of monocalcium chlorophosphate according to Equations 3 and 4 is schematically shown in Figure 1.

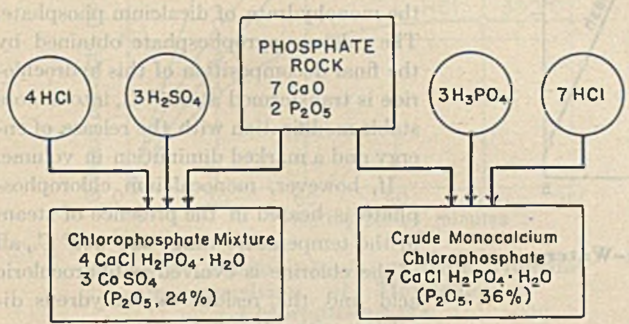

Figure 1. Acid Requirements for Monocalcium Chlorophosphate Production

If an excess of either phosphoric or sulfuric acid over the requirements shown in Equations 3 and 4 is used, a part of the phosphorus is obtained as monocalcium phosphate. It is possible, therefore, to treat phosphate rock with hydrochloric acid and either phosphoric or sulfuric acid, or both, and obtain mixed products free from calcium chloride as such. Products obtainable by the acidulation of rock phosphate with all possible combinations of sulfuric, phosphoric, and hydrochloric acids are indicated in Figure 2. The acidulation of rock with sulfuric acid, lower left-hand corner of the triangle, yields calcium sulfate, *A*, and monocalcium phosphate, *B*. Phosphoric acid, lower right-hand corner, yields only monocalcium phosphate. But with hydrochloric acid, represented by the apex of the triangle, a mixture of monocalcium chlorophosphate, *C*, and calcium chloride, *D*, is produced. Point *C* represents the proportion of hydrochloric acid to phosphoric acid indicated in Equation 3 for the production of the chlorophosphate only. Similarly, point *A,C* represents the proportion of hydrochloric to sulfuric acid indicated in Equation 4 for calcium sulfate and monocalcium chlorophosphate. For systems involving all three acids, represented by the surface area of the triangle, *A, C–C* is the boundary between those above yielding some free calcium chloride and those below that do not. The exact location of this line in the field of the diagram is a function of the lime-phosphate ratio, *n*, of the rock employed. Table I gives the minimum, maximum, and average values of *n* for representative samples of phosphate rock from various domestic and foreign sources, calculated from data published by Jacob, Hill, Marshall, and Reynolds (*9*, Tables 3 to 6). By substituting the appropriate values for *n* in Equations 1, 3, and 4, the number of moles of reagent acids required for these reactions per mole of P_2O_5 in each of the several rocks may be estimated. In general, the better grades of rock contain about 3.5 moles of CaO per mole of P_2O_5 and a rough approximation is obtained by writing the formula for the rock as $7CaO.2P_2O_5$, as indicated in Equations 10 and 11 (compare Figure 1). With rock containing 3.5 moles of calcium per mole of phosphoric oxide, 82 per cent of all possible combinations of sulfuric, phosphoric, and hydrochloric acids yield calcium-chloride-free mixtures of calcium sulfate, monocalcium phosphate, and monocalcium chlorophosphate. With rock for which *n* equals 4, about 78 per cent of all acid combinations yield calcium-chloride-free products; for tricalcium phosphate the estimate is about 87 per cent.

TABLE I. LIME-PHOSPHATE RATIOS OF VARIOUS DOMESTIC AND FOREIGN PHOSPHATE ROCKS (*9*)

Type of Source of Phosphate Rock	No. of Samples	*n* = $CaO:P_2O_5$ Mole Ratio		
		Minimum	Maximum	Average
Florida, land pebble	11	3.546	3.865	3.736
Florida, hard-rock	4	3.446	3.599	3.556
Tennessee, brown-rock	6	3.467	3.623	3.549
Tennessee, blue-rock	5	3.530	3.712	3.655
Tennessee, white-rock	2	3.584	3.598	3.591
Idaho	3	3.575	3.610	3.589
Montana	3	3.516	4.094	3.713
South Carolina	2	4.064	4.081	4.073
Foreign, including Morocco, Tunis, and Christmas, Curacao, and Ocean Islands	6	3.279	4.222	3.606

HYDROGEN CHLORIDE AS REAGENT

By using aqueous solutions of hydrochloric acid, water is introduced into the system which later must be removed by artificial means or by prolonged drying of the product in air at ordinary temperatures to obtain complete reaction of phosphoric acid. The disadvantages involved in such drying operations may be avoided by the direct absorption of hydrogen chloride in mixtures containing water limited to the amount necessary to promote the reactions involved. The absorption of hydrogen chloride in mixtures containing ground phosphate rock and water in the proportions required to yield monocalcium chlorophosphate and calcium chloride dihydrate is graphically shown in Figure 3. The charge was continuously agitated in a rotary type mixer while being exposed to the gas. For the production of chlorophosphate, it is not necessary to absorb more than *n* moles of hydrogen chloride per mole of phosphoric oxide, or one mole per mole of calcium in the rock. The addition of phosphoric or sulfuric acid, or both, may be made either before or after the absorption of hydrogen chloride. The preaddition of 75 per cent phosphoric acid would satisfy the theoretical requirements for water, according to Equation 3, but such a mixture would be too dry to give a satisfactory reaction with the hydrogen chloride. Practically, it has been found that about one part of water to five parts of rock, or a mixture containing 15–20 per cent of water is adequate. This

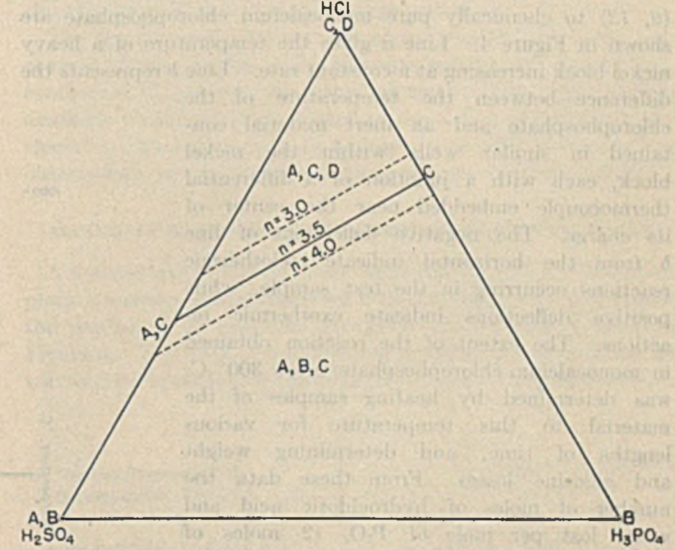

Figure 2. Composition of Reacted Phosphate Rock–Acid Mixtures

Reaction products: *A*, calcium sulfate; *B*, monocalcium phosphate; *C*, monocalcium chlorophosphate; *D*, calcium chloride.

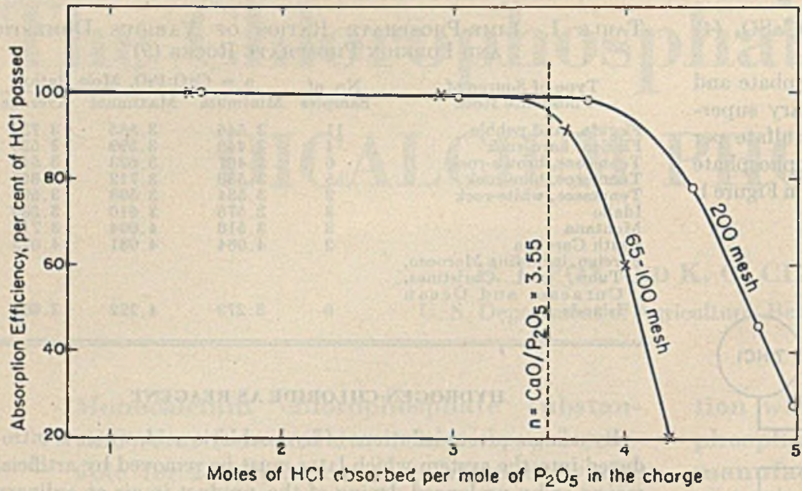

Figure 3. Absorption of Hydrogen Chloride in Phosphate Rock–Water (5–1) Mixtures

amount of water may be supplied with 65 per cent phosphoric acid. By such procedures products are obtained which may be further processed immediately for the production of dicalcium phosphate, treated with ammonia gas as indicated below, or readily dried in air for the production of monocalcium chlorophosphate (Figure 1).

THERMAL CONVERSION OF MONOCALCIUM CHLOROPHOSPHATE

The statement made by Way (*20*) and the implications of Newberry (*11*) to the effect that a simple heat treatment converts monocalcium chlorophosphate to dicalcium phosphate and hydrochloric acid were not experimentally confirmed.

The results obtained by applying differential thermal analysis (*6*, *12*) to chemically pure monocalcium chlorophosphate are shown in Figure 4. Line *a* gives the temperature of a heavy nickel block increasing at a constant rate. Line *b* represents the difference between the temperature of the chlorophosphate and an inert material contained in similar wells within the nickel block, each with a junction of a differential thermocouple embedded near the center of its charge. The negative deflections of line *b* from the horizontal indicate endothermic reactions occurring in the test sample, while positive deflections indicate exothermic reactions. The extent of the reaction obtained in monocalcium chlorophosphate below 300° C. was determined by heating samples of the material to this temperature for various lengths of time, and determining weight and chlorine losses. From these data the number of moles of hydrochloric acid and water lost per mole of P_2O_5 (2 moles of $CaClH_2PO_4.H_2O$) were determined. Similar data were obtained at 450° C. The results are shown graphically in Figure 5. The reaction occurring between 300° and 450° C. is obtained by difference. From these data it is evident that the thermal decomposition of monocalcium chlorophosphate proceeds in two separate and independent steps as follows:

$$2CaClH_2PO_4.H_2O \xrightarrow{225\text{–}330°\ C.} Ca_2ClH_3P_2O_8 + HCl + 2H_2O \quad (5)$$

$$Ca_2ClH_3P_2O_8 \xrightarrow{350\text{–}450°\ C.} Ca_2P_2O_7 + HCl + H_2O \quad (6)$$

The intermediate product obtained below 300° C. may be written as $(CaHPO_4)_2.HCl$ and for that reason may be regarded as the hemihydrochloride of dicalcium phosphate. This, undoubtedly, is what Newberry (*11*) identified by mistake as the monohydrate of dicalcium phosphate. The calcium pyrophosphate obtained by the final decomposition of this hydrochloride is transformed at 555° C. into a more stable modification with the release of energy and a marked diminution in volume.

If, however, monocalcium chlorophosphate is heated in the presence of steam in the temperature range 225–300° C., all of the chlorine is evolved as hydrochloric acid and the residue is anhydrous dicalcium orthophosphate (*4*):

$$CaClH_2PO_4.H_2O \xrightarrow[\text{steam}]{225\text{–}300°\ C.} CaHPO_4 + HCl + H_2O \quad (7)$$

Figure 6 shows the recovery of hydrochloric acid per mole of monocalcium chlorophosphate upon heating at different temperatures for various periods in an atmosphere of steam. Analyses of the residues are given in Table II.

Table II. Analyses of Solid Products Resulting from Thermal Decomposition of Monocalcium Chlorophosphate in the Presence of Steam

Temp., ° C.	Duration of Run, Min.	P_2O_5, Wt. %	CaO, Wt. %	Cl, Wt. %
...	$CaClH_2PO_4.H_2O$ (charged)	37.25	29.31	18.41
225	135	50.25	40.70	0.30
250	75	51.78	41.37	0.11
300	60	50.53	40.73	0.21
...	$CaHPO_4$ (theoretical)	52.17	41.21	..

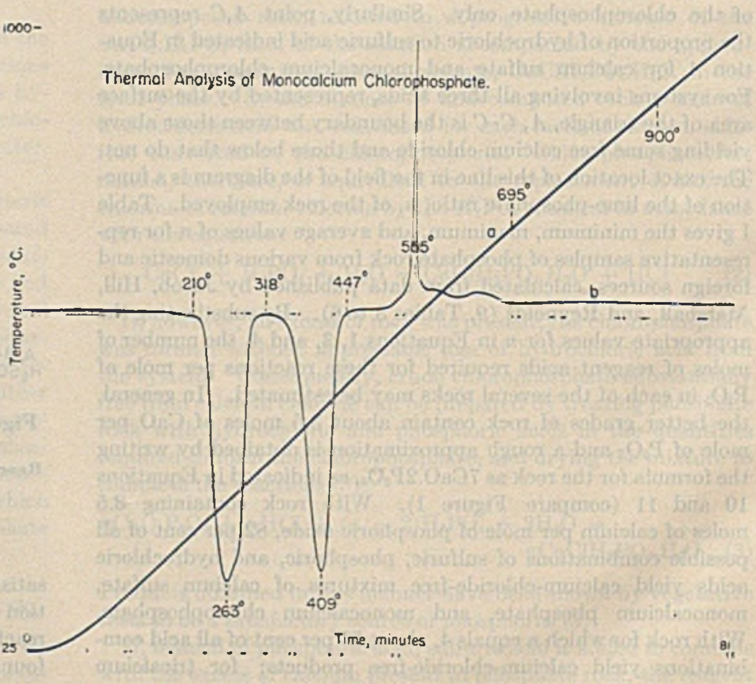

Figure 4. Thermal Analysis of Monocalcium Chlorophosphate

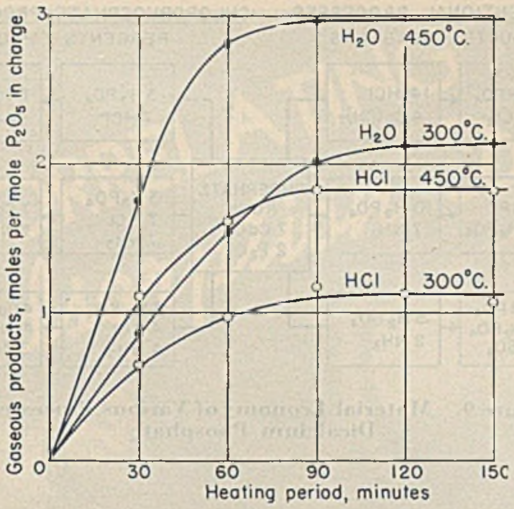

Figure 5. Gaseous Products from Thermal Decomposition of Monocalcium Chlorophosphate

Table III. Analyses of Air-Dried Monocalcium Chlorophosphate before and after Ammoniation

Constituent, %	$CaClH_2PO_4.H_2O$, Crude	Ammoniated Product
P_2O_5, total	35.95	35.71
P_2O_5, citrate-insol.	0.84	1.96
P_2O_5, available	35.11	33.75
P_2O_5, water-sol.	31.10	3.78
Cl, total	13.43	13.37
F, total	2.10	2.09
CaO, total	26.66	26.64
Ammonia N, total	...	6.17

The conversion of monocalcium chlorophosphates to dicalcium phosphate cannot be carried out in the presence of calcium chloride and the latter extracted by solvent methods because the chlorophosphate preferentially reacts with calcium chloride to yield more basic chlorophosphates (*15*, *16*). Thus, when equimolal quantities of the chlorophosphate and calcium chloride are heated, chlorospodiosite and hydrochloric acid result:

$$CaClH_2PO_4.H_2O + CaCl_2 = Ca_2ClPO_4 + 2HCl + H_2O \quad (8)$$

Characteristic reactions of monocalcium chlorophosphate are schematically shown in Figure 7.

AMMONIATION OF MONOCALCIUM CHLOROPHOSPHATE

Ammoniation of monocalcium chlorophosphate yields dicalcium phosphate and ammonium chloride in the proportions indicated by the reaction:

$$CaClH_2PO_4.H_2O + NH_3 \longrightarrow CaHPO_4 + NH_4Cl + H_2O \quad (9)$$

Since the chlorophosphate contains CaO and P_2O_5 in the combining proportions of dicalcium phosphate, the danger of overammoniation (*7*, *10*) is greatly reduced. Aqua ammonia or any of the ammonia liquors may be employed, but in so doing water from the ammonia solution as well as that released by the reaction must be evaporated to obtain a dry solid product. The ammoniation is most conveniently effected by placing ground monocalcium chlorophosphate in a closed rotating drum-type mixer (Figure 8) and admitting ammonia gas. The reaction rapidly proceeds to completion with the evolution of heat sufficient to vaporize the water formed by the reaction, so that the product discharging from the mixer needs only to be cooled in a current of air to produce a substantially dry granulated mixture of dicalcium phosphate and ammonium chloride. Table III presents analyses of crude monocalcium chlorophosphate before and after ammoniation in the manner indicated above.

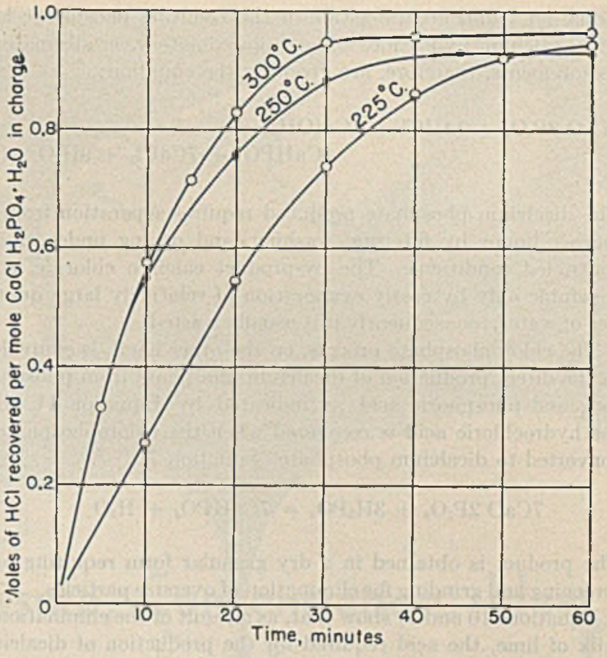

Figure 6. Recovery of Hydrogen Chloride from Monocalcium Chlorophosphate during Steam Treatment

The crude chlorophosphate which had been stored for 18 months in 100-pound fiberboard containers in the basement of the laboratory building showed insufficient caking to require regrinding before ammoniation; a light blow from a small scoop was sufficient to disintegrate the cake which had formed around the walls. The material in the interior was somewhat more dusty than when packaged, and a slight loss of moisture was indicated by the slightly higher values for calcium, phosphorus, and chlorine obtained at the end of the storage period.

The ammoniated product has approximately the same percentage of phosphorus as the chlorophosphate and, in addition, contains 6.17 per cent ammonia nitrogen. The slight loss in available phosphate is attributed to the action of impurities derived from phosphate rock, as no loss of available phosphate was observed on ammoniating pure monocalcium chlorophosphate.

MATERIAL ECONOMY OF CHLOROPHOSPHATE PROCESSES

A comparison of the material requirements of the chlorophosphate processes above described with a conventional process for the production of available phosphate for fertilizer is made in Figure 9. The milk of lime process for dicalcium phosphate involves decomposition of the phosphate rock in accordance with

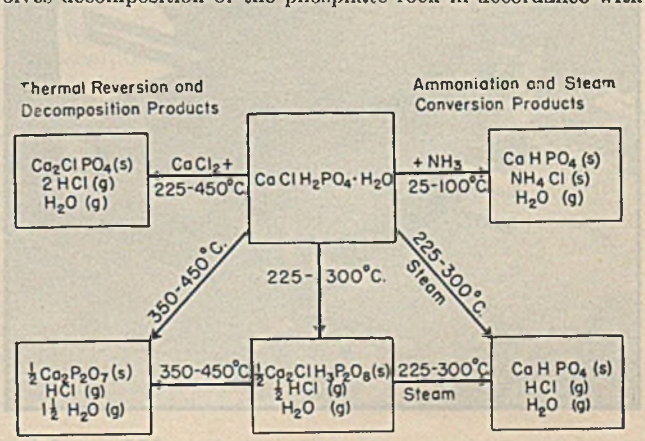

Figure 7. Monocalcium Chlorophosphate Reactions

Equation 1 and neutralization of the resulting phosphoric acid with calcium hydroxide. The approximate over-all material requirements, therefore, are given by the equation:

$$7CaO.2P_2O_5 + 14HCl + 4Ca(OH)_2 = 4CaHPO_4 + 7CaCl_2 + 9H_2O \quad (10)$$

The dicalcium phosphate produced requires separation from its mother liquor by filtering, washing, and drying under closely controlled conditions. The by-product calcium chloride is recoverable only by costly evaporation of relatively large quantities of water; consequently it is usually wasted.

The chlorophosphate process, on the other hand, is equivalent to the direct production of dicalcium phosphate from phosphate rock and phosphoric acid as indicated by Equation 11, since the hydrochloric acid is recovered when the chlorophosphate is converted to dicalcium phosphate (Equation 7):

$$7CaO.2P_2O_5 + 3H_3PO_4 = 7CaHPO_4 + H_2O \quad (11)$$

The product is obtained in a dry granular form requiring only screening and grinding for elimination of oversize particles.

Equations 10 and 11 show that, as a result of the elimination of milk of lime, the acid required for the production of dicalcium phosphate by the chlorophosphate process is 4 hydrogen equivalents less than the milk of lime process per mole of P_2O_5 in the rock.

In comparing ammoniated chlorophosphate with ammoniated superphosphate made with phosphoric acid, it will be noted (*a*) that approximately three and one third times as much rock can be treated by the chlorophosphate process per unit of phosphoric acid, which is the more costly reagent involved in these processes, and (*b*) that the ratio of nitrogen to phosphorus in ammoniated chlorophosphate is twice that in the ammoniated superphosphate.

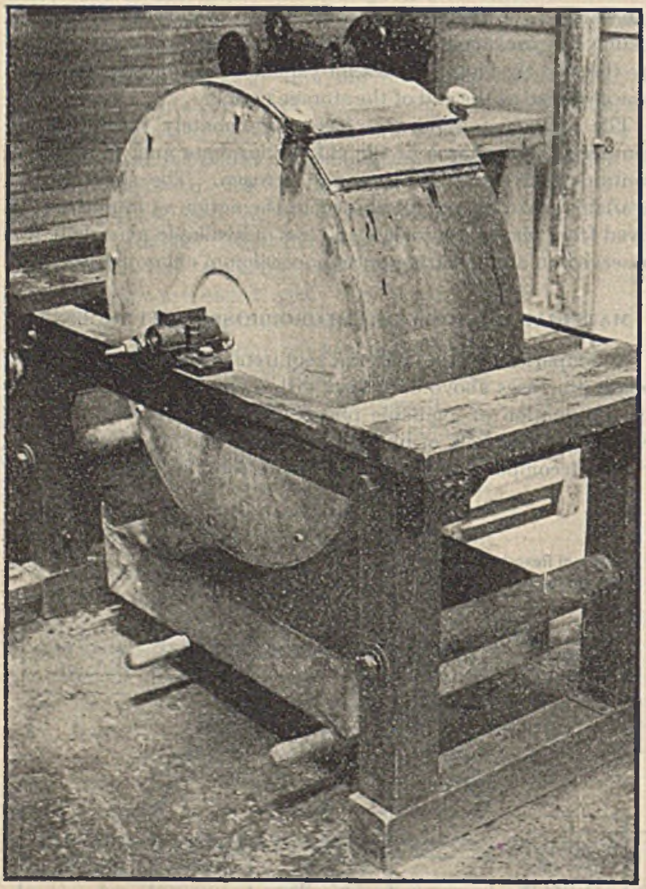

Figure 8. Equipment for Ammoniation of Monocalcium Chlorophosphate

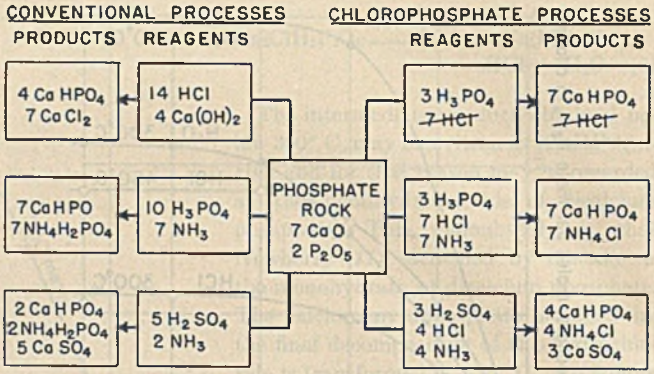

Figure 9. Material Economy of Various Processes for Dicalcium Phosphate

In comparison with ordinary ammoniated superphosphate, the same relative advantage is held by the chlorophosphate process, so far as the ratio of nitrogen to phosphorus is concerned. Under certain conditions it may also be advantageous to substitute hydrochloric acid for a part of the sulfuric acid ordinarily used for acidulating phosphate rock.

ACKNOWLEDGMENT

The authors are indebted to B. E. Brown and co-workers, Division of Fruit and Vegetable Crops and Diseases, for vegetative tests, and to R. Andrew Nelson and W. H. Ross of the laboratory staff, respectively, for the thermal analysis of monocalcium chlorophosphate and the use of equipment for its ammoniation. W. H. Ross kindly supplied the photograph reproduced as Figure 8.

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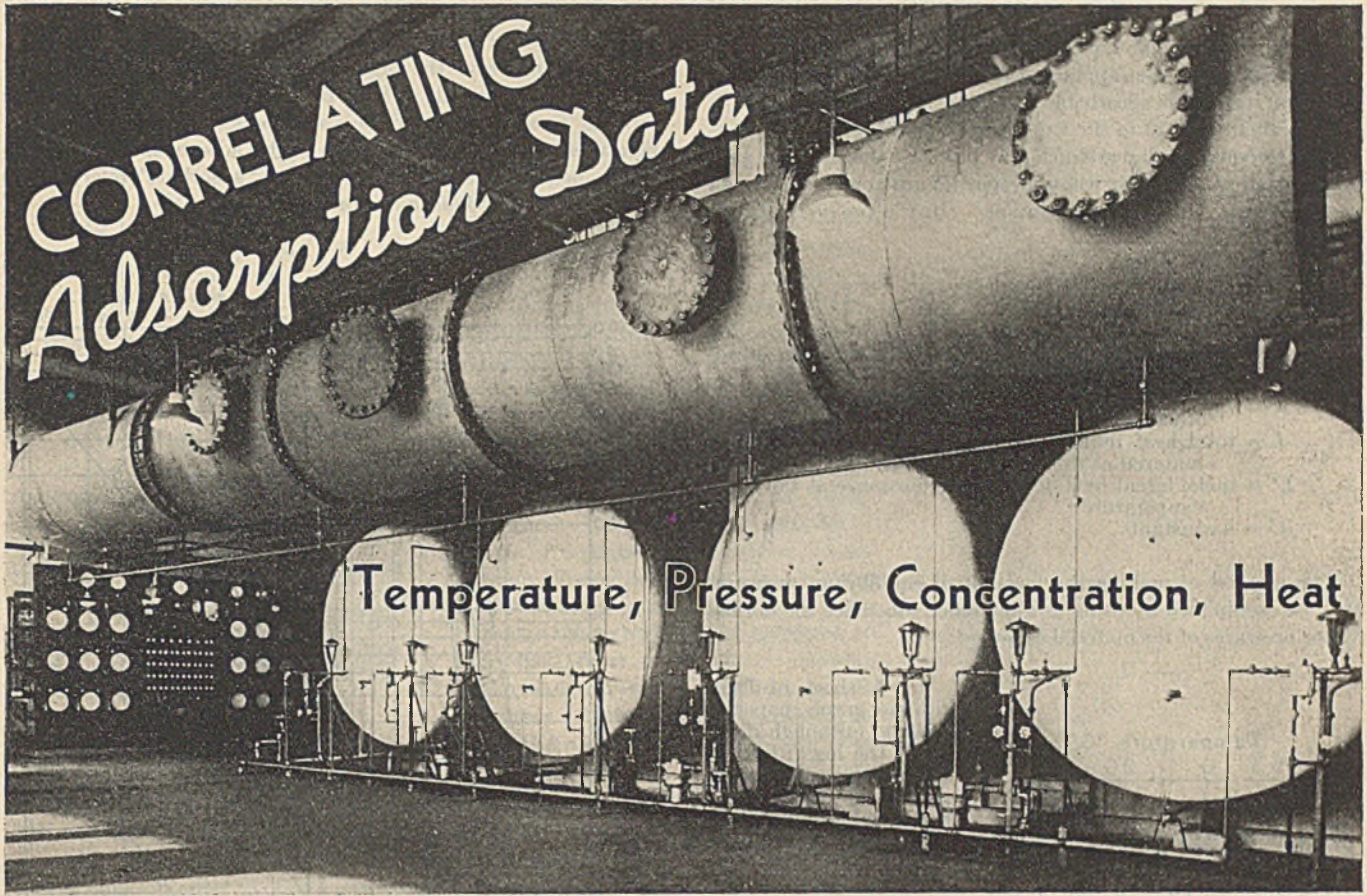
CORRELATING Adsorption Data

Temperature, Pressure, Concentration, Heat



Adsorbers, exhaust duct, and instrument panel in an automatically operated solvent recovery plant are shown above (courtesy, Carbide and Carbon Chemicals Corporation)

Donald F. Othmer and Frederick G. Sawyer
POLYTECHNIC INSTITUTE, BROOKLYN, N. Y.

Equilibrium vapor pressures of gas or vapor adsorbed on activated carbon or other substances are correlated with the temperatures of adsorption and the concentrations of gas or vapor by the graphical method previously described (*14*). The equilibrium vapor pressures of an adsorbate out of a solid adsorbent are plotted against the normal vapor pressures of the same or a different material at corresponding temperatures to give straight lines (isosteres) on a logarithmic plot. The usual advantages of a straight-line relation are obtained; and their slopes are equal to the ratios of the molal heats of adsorption to the molal latent heat of the reference substance. The heats of adsorption may be calculated from this relation; the calculations check calorimetric data closely. These methods of plotting and using data are of help in the design of adsorption systems when only a small amount of data are available.

VAPOR pressures of liquids, solids, hydrates, etc., were shown previously (*14*) to give straight lines when plotted on logarithmic paper against values of the vapor pressure of a reference substance at corresponding temperatures. Similarly, the partial pressure of a gas from a solution of given concentration was plotted against the vapor pressure of the solvent liquid at the same temperatures (*16*). The slopes of the lines are equal to the ratios of the total molal heat quantities involved in the evolution of the gaseous phase to the molal latent heat of the reference substance. An even better correlation was obtained (*15*) from the logarithmic plot of reduced pressure of the substance against reduced pressure of the reference material, always at the same reduced temperature. It was desired to apply this method of correlation to adsorption data of temperature, pressure, and concentration, where concentration is expressed as grams of material adsorbed on a gram of adsorbent, and to determine whether the heat evolved during the adsorption process can be predicted thereby without resorting to the difficult calorimetric measurement.

Gas adsorption is becoming an increasingly important unit operation of chemical engineering in the recovery of vapors from air and in catalytic petroleum processes (*1*, *6*, *13*, *18*). Adsorption data have usually been taken in such a way that the usual method of expression is concentration *vs.* pressure at constant temperature; i. e., the plot is made of isotherms. Various other ways have also been used, most of which are not readily adapted to engineering. As in gas absorption and solubility work, the important aspect from the standpoint of utilization and design is the pressure in equilibrium with a given concentration at a given temperature; and a simple and precise method of expression is desirable.

• • •

PLOTTING VAPOR PRESSURES

Following the method previously used, the basic equation is determined from the application of the Clausius-Clapeyron equation: (*a*) to the adsorbable substance in its equilibrium with the adsorbent and (*b*) to the vapor-liquid equilibrium of a standard or reference substance which may be either the adsorbed substance itself or any other whose properties are known and which has somewhat similar vapor relations. In the previous expression,

$$\log P = \frac{(L)}{(L')} \log P' + C \qquad (1)$$

where P = equilibrium pressure of given concentration of adsorbed material in adsorbent
P' = vapor pressure of reference substance (same or another) at the same temperature
L = total heat required to desorb one mole of adsorbed material at the given temperature
L' = molal latent heat of reference substance at the given temperature
C = a constant

The method of making the log plot of equilibrium pressures may be exemplified by using as a reference substance the normal vapor pressures of the material adsorbed:

1. A sheet of logarithmic graph paper is selected (although if desired, the logarithms of the pressure values to be plotted may be obtained from a table and plotted on a sheet of ordinary graph paper).
2. Temperatures are indicated on the X axis at the appropriate values corresponding to the vapor pressures of the material used as a reference.
3. A scale is laid off on the Y axis for the equilibrium pressures of the material when adsorbed. (The same pressure unit for this scale as for the X scale is not required, since there is a constant ratio between units; and the use of a different unit would merely have the effect of moving the line up or down by a distance equal to the conversion factor, without changing its slope or form.)
4. The equilibrium pressures are plotted on the respective temperature ordinates.
5. Points representing constant composition of adsorbed material in the adsorbent are connected by a line, usually straight.

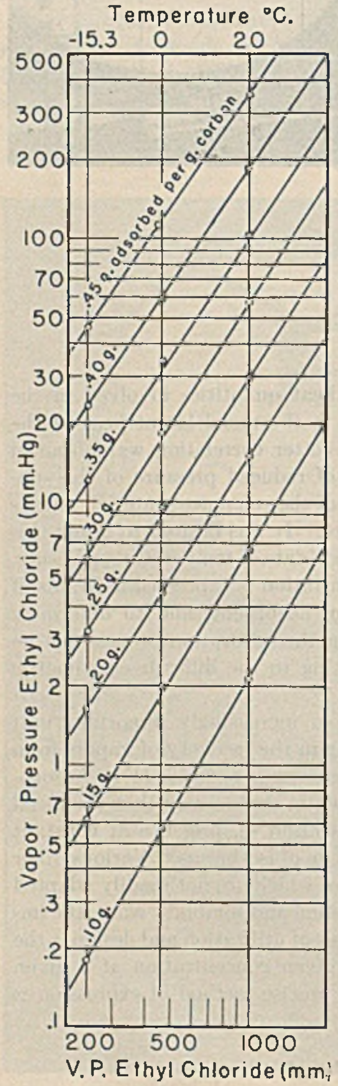


Figure 1. Isosteres of Ethyl Chloride Adsorbed on Charcoal

Most isothermal data are not tabulated to provide directly corresponding adsorbate concentrations for different temperatures. Therefore, the tabulations as provided are suitably graphed and the needed information is obtained by interpolation and cross-plotted as above. Figure 1 shows the straight lines obtained as a result of cross plotting from the original isotherms of ethyl chloride (*4*) adsorbed on charcoal. These lines are known as isosteres and provide a comparison of the vapor pressure at different temperatures when the concentration of the adsorbable substance is kept constant. In this paper the word "adsorbate" refers to the substance adsorbed on the adsorbent.

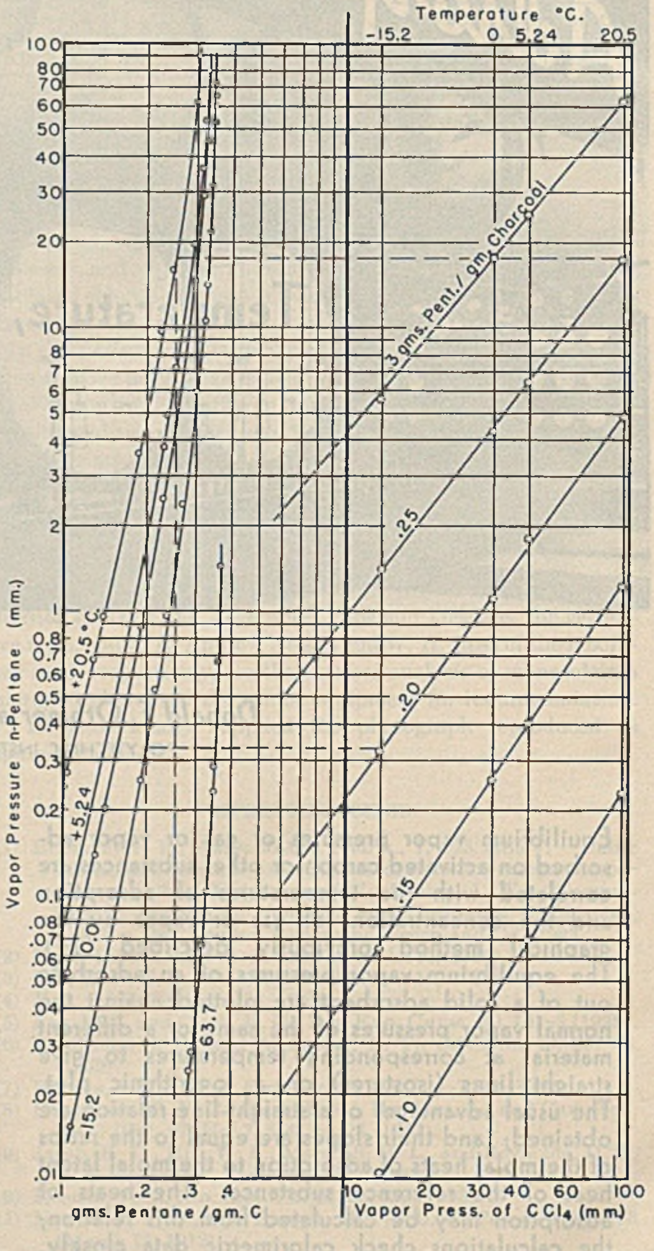


Figure 2. Freundlich Isotherms (*left*) of *n*-Pentane Adsorbed on Charcoal

The corresponding isosteres (*right*) are obtained by projection of intersections of the isotherms with the ordinates of concentration as shown.

The cross plotting may readily be done mechanically if the isotherms are first plotted on the left-hand side of logarithmic paper, as in Figure 2 for *n*-pentane adsorbed on carbon, with concentrations along the X axis and with equilibrium vapor pressures along the Y axis. To cross plot, the intersections of the isotherms with each ordinate of constant concentration are projected to the right until the projection lines intersect the corresponding tem-

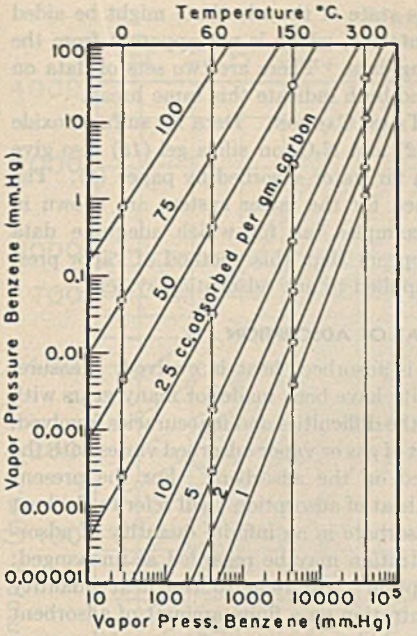


Figure 3. Isosteres of Benzene Adsorbed on Charcoal between 0° and 300° C.

perature ordinate on the main plot, which have been located on the right. The lines representing the equilibrium pressures are straight. The left-hand part of Figure 2 represents the logarithms of adsorbate concentration *vs.* logarithms of equilibrium pressure. This is the plot of the well known Freundlich isotherms. In the case of *n*-pentane the Freundlich isotherms are not straight; in fact, most of the data on the various systems considered here do not give straight Freundlich isotherms. The right-hand plot for the isosteres, however, does result in straight lines with the usual advantages of a straight-line plot.

Of particular interest in the *n*-pentane system is the wide pressure range of the data available which must be plotted on logarithmic paper in order to obtain any measure of accuracy within a graph of reasonable size.

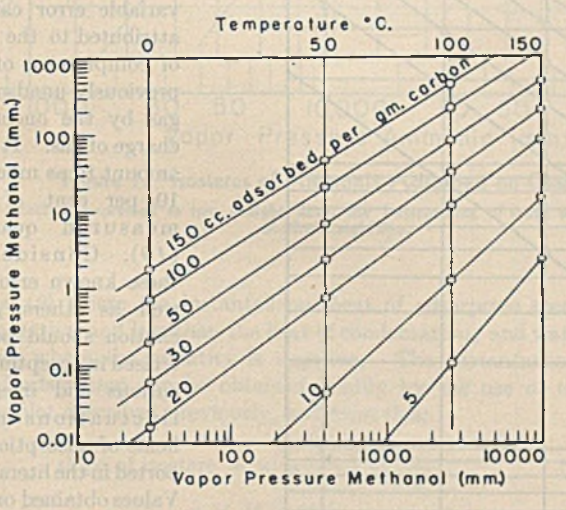


Figure 4. Isosteres of Methanol Adsorbed on Charcoal, Showing the Abrupt Change in Slope of Isosteres at Low Adsorbate Concentrations

Data are available and have been plotted for other materials normally liquid, such as chloroform, carbon disulfide, ethyl formate, methyl acetate, benzene (*2*) shown in Figure 3, methanol (*2*) shown in Figure 4, and ethyl ether (*4*) shown in Figure 5. The data for benzene cover a wide range of temperatures, from 0° to 300° C., slightly above the normal critical temperature. Data for ethyl ether and methanol are of interest because many experimental heat data are available, as will be mentioned later.

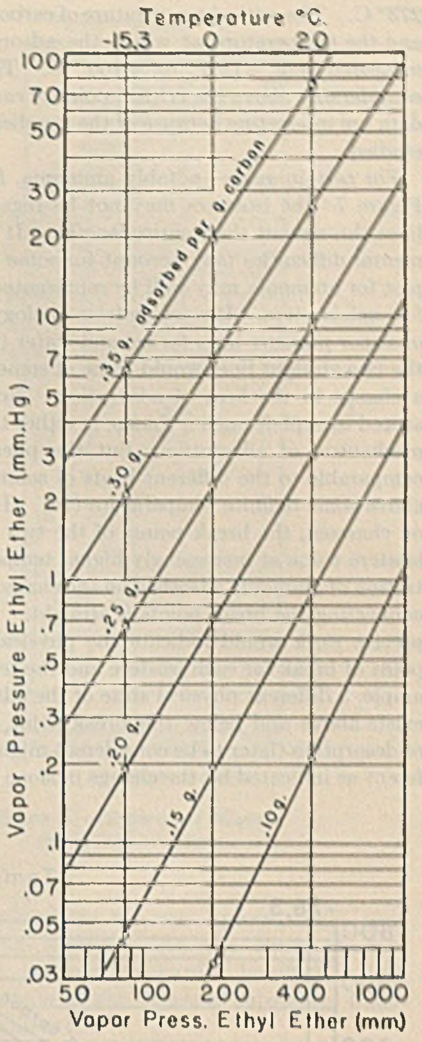


Figure 5. Isosteres of Ethyl Ether Adsorbed on Charcoal

In the range of materials which are normally gaseous, the data are plotted in Figure 6 for carbon monoxide and in Figure 7 for ammonia. Others studied were ethylene, carbon dioxide, nitrogen, methane, and ethyl chloride, Figure 1. In all these systems, with the exception of ethyl chloride and ammonia, it was necessary to select a reference compound other than the adsorbed material itself against which the plot could be made. It is impossible to plot equilibrium pressures of the material adsorbed from the charcoal against the normal vapor pressures of the material at temperatures above the critical, since the vapor pressure of a liquid terminates at the critical point, while adsorption and corresponding equilibrium pressures may be determined at much higher temperatures.

Graphical extrapolation may also be used at temperatures higher than the critical when the adsorption pressures are plotted against the vapor pressure of the adsorbate in the range below the critical. On the edge of a sheet of logarithmic graph paper are laid off the vapor pressure and temperature ordinates of another substance of higher critical temperature, usually water. When the edge of the paper is superimposed on the isostere graph some angle will be found where corresponding temperature lines coincide. For the temperatures above the critical point of the adsorbable substance, marks are placed on the isostere graph; and ordinates are drawn through these points designating the vapor pressures corresponding to the temperatures of adsorption above the critical point of the adsorbate. The isosteres can now be drawn through points on these temperature lines. This method was used in preparing the isostere graphs of ammonia in Figure 7 and benzene in Figure 3.

As an alternate method when the temperatures of adsorption data go above the critical, a reference substance may be used other than the material itself for which vapor pressure data are available. Data for carbon monoxide are plotted in Figure 6 against corresponding vapor pressures of carbon disulfide at the same temperatures. The range of experimental temperatures is far below the critical temperature of the carbon disulfide which is

273° C. The critical temperature of carbon monoxide is −139° C. and the temperature at which the adsorption on charcoal was measured was −78.3° to +100° C. Therefore all data were considerably above the critical point of carbon monoxide. These data are interesting because of the number of temperature points studied.

For certain gases—notably ammonia, for example, plotted in Figure 7—the isosteres may not be regarded as single straight lines throughout their entire lengths. It is possible that experimental difficulties may account for some discrepancies; but the plot for ammonia may well be represented by two straight lines for each isostere. Reasoning from analogy to the change in slope of vapor pressure lines for ice and water (*14*), the break between the two straight lines would come at some point where there was a change in the heat of adsorption. No theory has been presented to explain such a change in either the physical or chemical mechanism of adsorption; but the phenomenon may well be comparable to the different heats of solution of gases below and above some definite temperature (*16*). In the case of ammonia on charcoal, the break points of the two lines representing each isostere come at increasingly higher temperatures as the concentration of ammonia adsorbed on the charcoal decreases. The line connecting the break points is straight. It is possible that very precise work would indicate the physical relation between the point of break for each isostere and the temperature. If, for example, a different physical state of the adsorbate on the charcoal exists above and below this break point, the heat of adsorption or desorption (later to be considered) might be expected to be different as indicated by the change in slope of the lines. The general consideration of this state of the adsorbate might be aided by this graphic representation, which is not apparent from the other methods of plotting data. There are two sets of data on carbon dioxide (*7*, *20*) and both indicate this same break.

Adsorbents Other Than Carbon. Data for sulfur dioxide adsorbed on silica gel (*12*) and N_2O_4 on silica gel (*19*) also give straight lines, as do data for water adsorbed by paper (*8*). The straight isosteres obtained for the latter system are shown in Figure 8. From these examples (all for which adequate data could be found), it appears that this method of vapor pressure correlation can be applied to any adsorption system.

HEAT OF ADSORPTION

When a gas or vapor is adsorbed, heat is evolved. Measurements of this heat quantity have been made for many years with increasing cognizance of the difficulties and inaccuracies involved. The heat evolved per unit of gas or vapor adsorbed varies with the amount already adsorbed on the adsorbent. For the present purpose, "instantaneous heat of adsorption" will refer to the heat quantity per gram of adsorbate in an infinite quantity of adsorbent so that the concentration may be regarded as unchanged; "integral heat of adsorption" will refer to the heat quantity evolved when the concentration on a finite amount of adsorbent changes between two given values.

In experimental determinations, successive known quantities of gas are adsorbed and the heats evolved, temperature, and corresponding equilibrium pressure for each amount are measured. Although the largest part of the heat is evolved within a few minutes after admission of the gas, final equilibrium may be attained only after days of "drift", as this slow adsorption is called. Drift is essentially a nonreproducible effect, and the consequent thermal errors are variable. Another variable error can be attributed to the heat of compression of the previously unadsorbed gas by the oncoming charge of gas. It may amount to as much as 10 per cent of the measured quantity (*10*). Considering these known errors as well as others, great caution should be exercised in accepting the curious and irregular fluctuations in the heats of adsorption reported in the literature. Values obtained on different charcoals are sometimes widely divergent, probably as a result of great differences in the internal surfaces of adsorbents. In almost all cases the instantaneous heat of adsorption of a vapor is greater than its latent heat of condensation. Exceptions are: the adsorption of water on

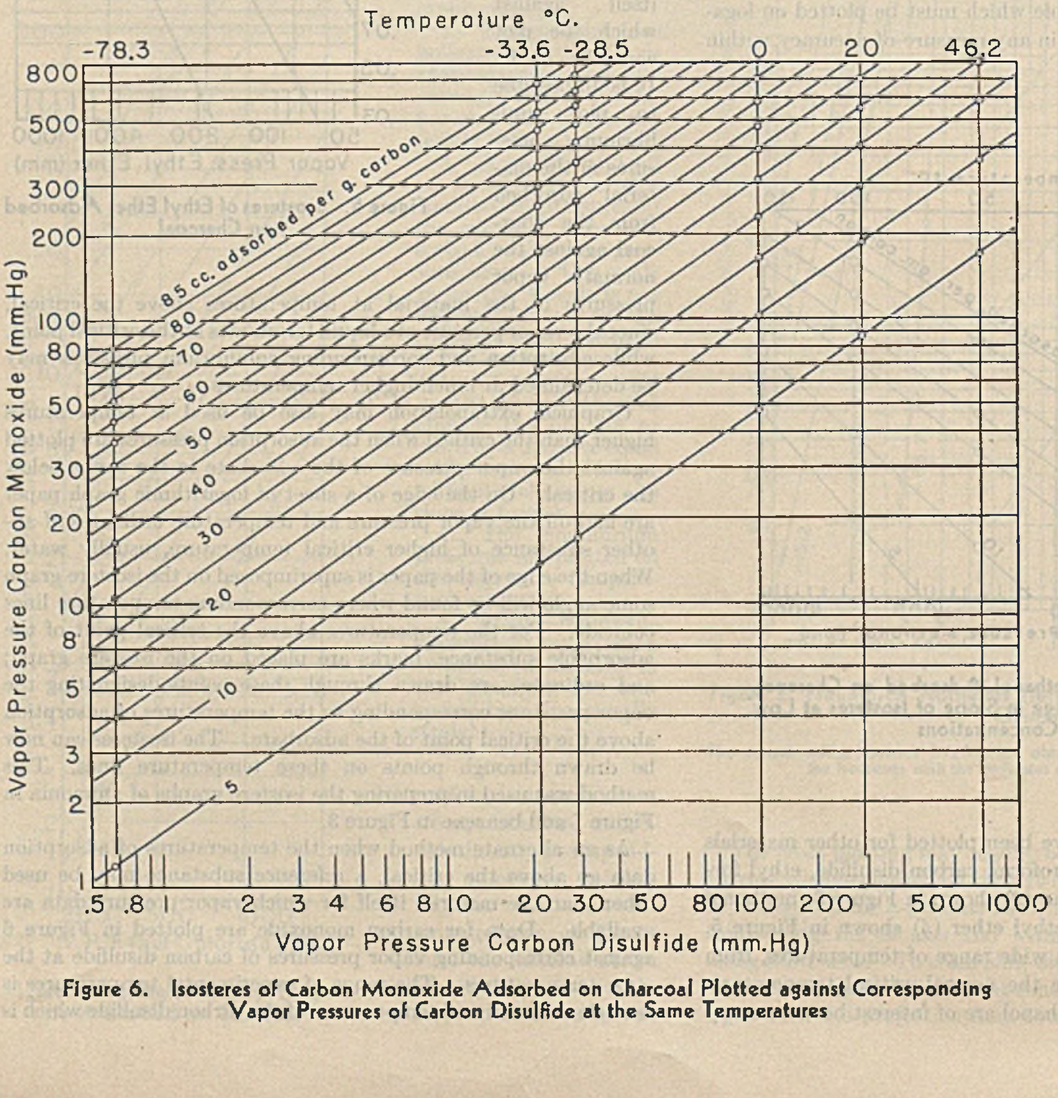


Figure 6. Isosteres of Carbon Monoxide Adsorbed on Charcoal Plotted against Corresponding Vapor Pressures of Carbon Disulfide at the Same Temperatures

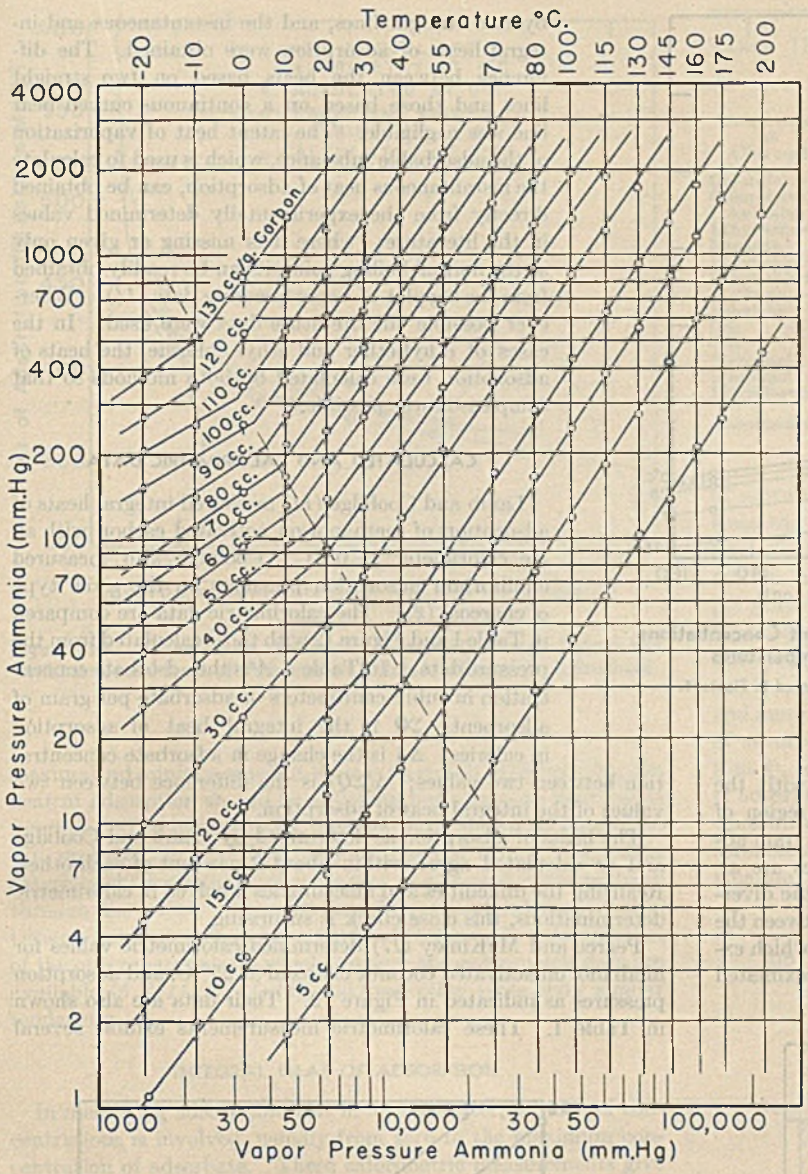


Figure 7. Isosteres of Ammonia Adsorbed on Charcoal

Each is expressed as two straight lines; the intersections of these lines fall on another straight line.

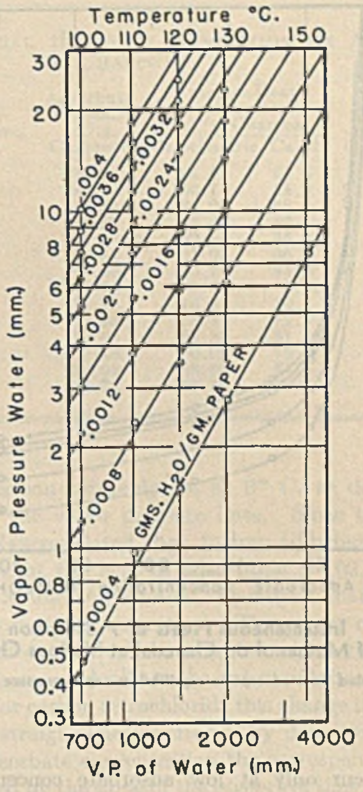


Figure 8. Isosteres of Water Adsorbed on Paper

charcoal (*9*) where the instantaneous heat of adsorption seems to be negative and less than the heat of condensation; and water on sand, where the quantity is negative. The instantaneous heat of adsorption can be obtained readily by the use of the isostere plot described previously, and from this:

$$\text{slope of isostere} = m = \frac{Q \times M_{\text{ads.}}}{l_{\text{ref.}} \times M_{\text{ref.}}} \qquad (2)$$

$$Q = \frac{m \times M_{\text{ref.}} \times l_{\text{ref.}}}{M_{\text{ads.}}} \qquad (3)$$

where at a common temperature

Q = instantaneous heat of adsorption, cal./gram of adsorbable substance
m = slope of isostere
$M_{\text{ref.}}$ = molecular weight of reference substance
$M_{\text{ads.}}$ = molecular weight of adsorbable substance
$l_{\text{ref.}}$ = latent heat of vaporization of reference substance, cal./gram

The instantaneous heat of adsorption may be separated into the heat of condensation and the heat of wetting; it has also been compared with the heat of sublimation (*3*) and the heat of compression (*11*). Because the exact physical condition of the material adsorbed is not known, any such hypothetic definition of the kind of heat quantity involved is hardly justified. With the adsorbate as the reference substance, Equation 3 reduces to:

$$Q = ml_{\text{ads.}} \qquad (4)$$

where $l_{\text{ads.}}$ = latent heat of vaporization of adsorbable substance, cal./gram at the given temperature

The slopes of the isosteres are determined, the latent heat values are known, and the instantaneous heat of adsorption may be determined immediately. In some cases it may be desired to plot all such thermal data for every concentration of adsorbate at all temperatures, and the following procedure is used:

1. From the plot the slope of each isostere is obtained, and these slopes are plotted against adsorbate concentration. A smooth curve is drawn which, in many cases, is a straight line.
2. A table is prepared with the instantaneous heats of adsorption calculated at various temperatures and adsorbate concentrations by multiplying known latent heats at given temperatures by the several isostere slopes as in Equation 3 or 4.
3. These instantaneous heats of adsorption are plotted against adsorbate concentration using several constant temperatures as parameters. In many cases these lines are straight and almost parallel so that accurate interpolation and extrapolation are possible. Examples of adsorption heat curves are methanol in Figure 9, ethyl ether in Figure 10, and carbon tetrachloride in Figure 11.

The shape of instantaneous heat of adsorption curves varies from a curved line with a sharp break (for example, benzene and of methanol, Figure 9) to those with a gradual curve such as ethyl ether (Figure 10), ethyl formate, methyl acetate, and ethyl chloride. A straight-line relation is found in the cases of ethylene, chloroform, *n*-pentane, carbon monoxide, carbon tetrachloride (Figure 11), methane, and carbon disulfide. Sharp-break

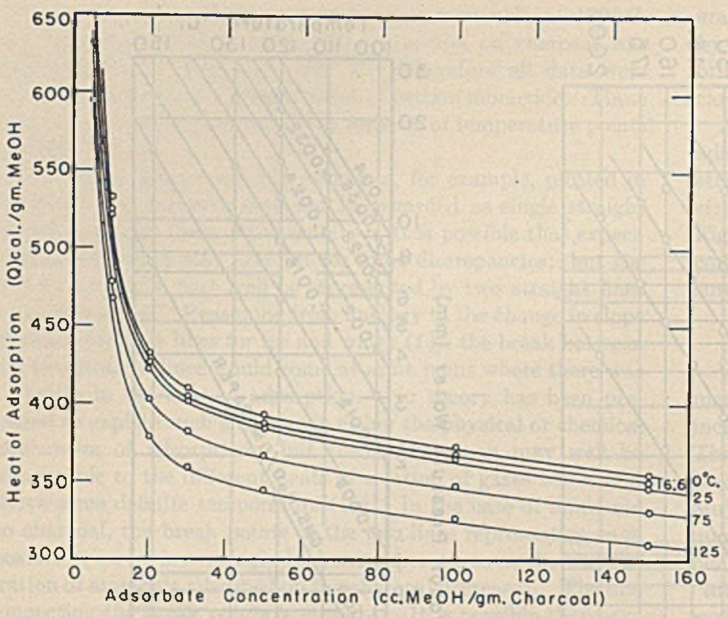


Figure 9. Instantaneous Heats of Adsorption of Different Concentrations of Methanol on Charcoal at Various Charcoal Temperatures

Calculated from adsorption equilibrium vapor-pressure data represented in Figure 4.

curves occur only at low adsorbate concentrations with the line becoming straight at high concentrations. The region of greatest slope change is from 10 to 30 cc. adsorbate per gram adsorbent. The instantaneous heat of adsorption curves are almost geometrically parallel to the isostere slope curve, the divergence from parallelism is due to the nonlinear relation between the latent heat and temperature. For the methanol curve which exhibits a sharp break in the heat data, the curve was approximated by two straight lines, and the instantaneous and integral heats of adsorption were obtained. The difference between the heats based on two straight lines and those based on a continuous curved heat line was negligible. The latent heat of vaporization of the adsorbable substance, which is used to calculate the instantaneous heat of adsorption, can be obtained directly from the experimentally determined values in the literature; where it is missing or given only at the normal boiling point, it can be readily obtained from the log plot of vapor pressure data (*14*). Wherever possible the literature data were used. In the cases of ethyl ether and ethyl chloride, the heats of adsorption were calculated by both methods so that comparison was possible.

CALCULATED AND CALORIMETRIC DATA

Lamb and Coolidge (*11*) measured integral heats of adsorption of methanol on activated carbon with an ice calorimeter at 0° C. Coolidge also measured equilibrium adsorption pressures on the same type of charcoal (*2*). The calorimetric data are compared in Table I and Figure 12 with those calculated from the pressure data. In Table I, A is the adsorbate concentration in cubic centimeters of adsorbate per gram of adsorbent; ΣQ is the integral heat of adsorption in calories; ΔA is the change in adsorbate concentration between two values; $\Delta(\Sigma Q)$ is the difference between two values of the integral heat of adsorption.

The heats of adsorption as determined by Lamb and Coolidge and as calculated agree within about 2 per cent of each other. Realizing the difficulties and inaccuracies involved in calorimetric determinations, this close check is surprising.

Pearce and McKinley (*17*) determined calorimetric values for methanol on activated coconut charcoal at 25° C. and adsorption pressures as indicated in Figure 12. Their data are also shown in Table I. These calorimetric measurements exhibit several

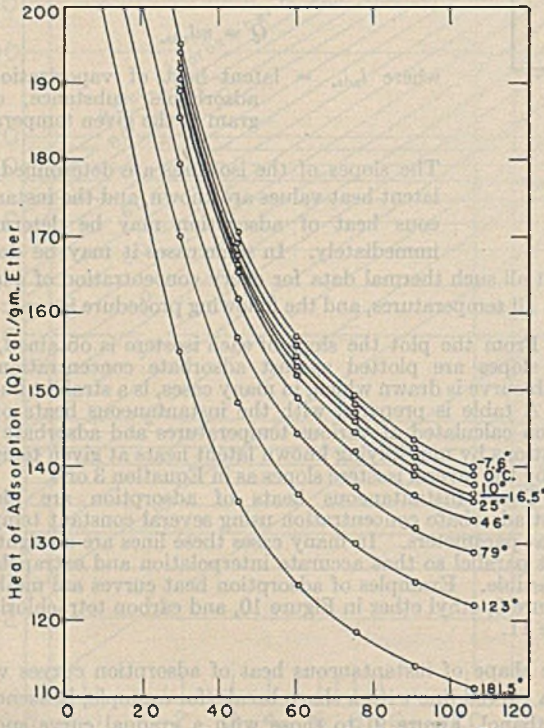


Figure 10. Instantaneous Heats of Adsorption of Ethyl Ether on Charcoal at Different Temperatures

Calculated from adsorption equilibrium vapor-pressure data represented in Figure 5.

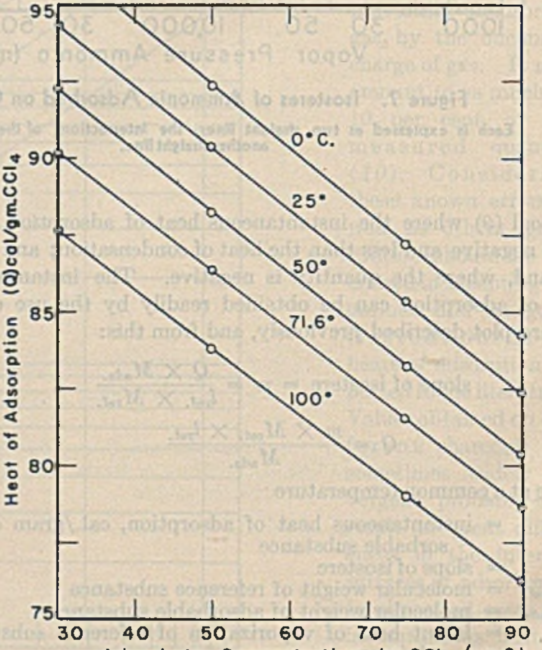


Figure 11. Instantaneous Heats of Adsorption of Carbon Tetrachloride on Charcoal at Different Temperatures

Calculated from an isostere plot of adsorption equilibrium vapor pressures similar to Figures 4 and 5.

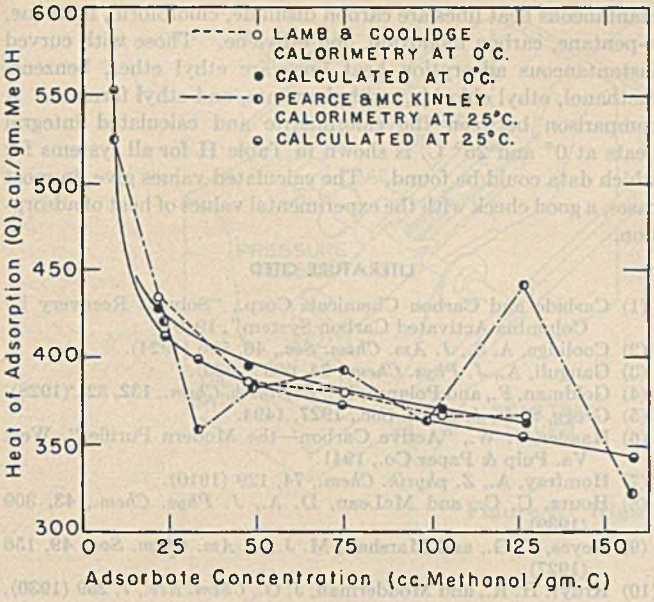


Figure 12. Comparison between Calorimetric and Calculated Instantaneous Heats of Adsorption Using Methanol as Adsorbate

maxima and minima, whereas there is no reason to believe that the heat of adsorption should be anything but a smooth continuous function. The irregularities, such as those shown in Figure 12, can probably be explained as experimental errors. The data determined from vapor pressures plot as a smooth curve midway through the widely divergent data determined calorimetrically. Other similar plots have been made of comparable data for most of the other materials for which pressure and calorimetric data are available (*5*, *8-11*, *17*, *21*, *22*), and these other plots show similar tendencies.

INTEGRAL HEAT OF ADSORPTION

In measuring adsorption heat in a calorimeter, a range of concentrations is involved, usually from zero to the maximum concentration of adsorbate. These calorimetric measurements give an integral heat rather than an instantaneous heat at a single concentration. This can be calculated graphically by measuring the area under a curve of instantaneous heat *vs.* concentration, in order to check further the heat quantities as determined from vapor pressures. Figure 13 shows the curve for the integral heat of adsorption of carbon tetrachloride at 0° C. as determined from the slopes of the vapor pressure lines. Since the line is straight, it may be extrapolated back to zero adsorbate concentration, at which point the heat of adsorption is 102.7 calories per gram of carbon tetrachloride; i. e., the largest heat quantity is at the lowest adsorbate concentration. The energy released in satisfying the initial demand of the adsorbent is at the highest level and then decreases gradually as these demands become more and more filled. For carbon tetrachloride this change in the heat of adsorption is a straight-line function. By definition (Equation 4), for any adsorbate concentration the corresponding heat of adsorption divided by the slope of the isostere of that particular concentration is equal to the latent heat of condensation of the adsorbable substance. Therefore, to test the validity of the extrapolation, the same procedure is used: 102.7 calories divided by

TABLE I. COMPARISON OF CALORIMETRIC HEAT OF ADSORPTION DATA WITH THOSE CALCULATED FROM PRESSURE DATA

Adsorbate Concn. A, cc./gram	$\frac{\Delta(\Sigma Q)}{\Delta A}$, cal./cc. Adsorbate	Instantaneous Heat of Adsorption, cal./g. Adsorbate: Calorimetric	Calcd.	Difference, %
		Data of Lamb and Coolidge		
21.62	0.620	434	428	−1.38
47.42	0.552	386	395	+2.33
75.27	0.543	380	381	+0.26
103.27	0.524	367	371	+1.09
127.40	0.523	366	363	−0.82
		Data of Pearce and McKinley		
8.96	0.750	525	553	+5.66
23.42	0.601	420	412	−1.94
33.13	0.513	359	398.5	+9.91
48.41	0.546	382	385	+0.77
74.65	0.561	393	373	−5.36
98.80	0.520	364	364.5	+0.13
126.41	0.632	442	355	−24.50
158.03	0.462	323	344	+6.10

TABLE II. INTEGRAL HEATS OF ADSORPTION ON ACTIVATED CHARCOAL

Adsorbate on Charcoal	Temperature, ° C.	Adsorbate Concn., cc./g. Charcoal	Integral Heat of Adsorption, cal./g. Charcoal: Calorimetric	Calcd.	Difference, %
Chloroform	0	107.1	65.67	62.8	4.38
Chloroform	25	94.45	56.7	54.5	3.88
Ethyl ether	0	99.34	60.61	58.1	4.13
Ethyl ether	25	65.83	45.41	40.1	11.80
Benzene	0	81.03	52.54	56.0	6.58
Ethyl chloride	0	124.80	61.03	56.4	7.54
Ethyl chloride	25	99.49	50.76	44.0	13.31
Methane	25	17.72	3.89	4.32	11.0
Ethylene	0	55.75	16.5	20.1	21.8
CS_2	0	15.32	76.87	72.6	5.55
CS_2	25	13.05	65.88	61.3	6.95
Methanol	0	127.40	70.08	75.9	8.31
Methanol	25	158.03	88.06	84.5	4.04
Ethyl formate	0	96.73	59.70	62.7	5.02

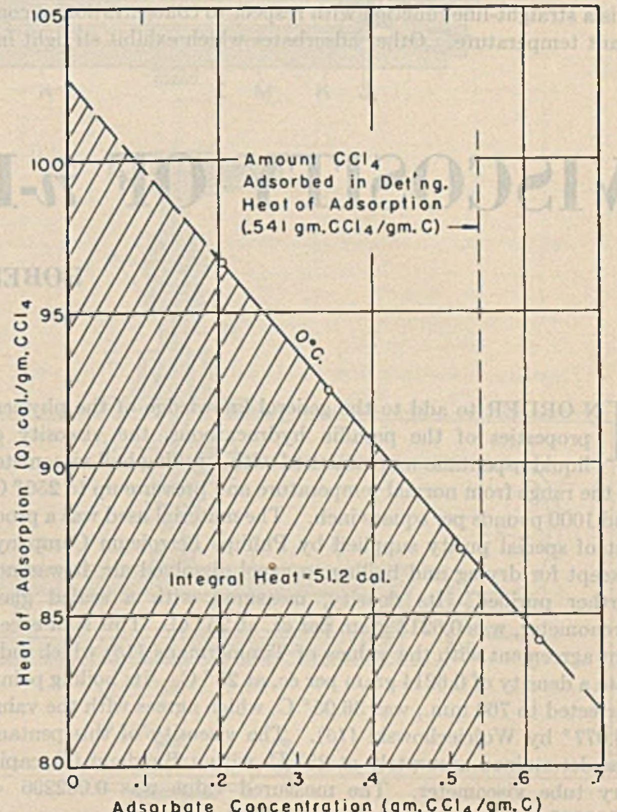


Figure 13. Integral Heat of Adsorption of Carbon Tetrachloride at 0° C.

Shaded area (plus that extending down to zero calories) presents the total heat liberated when 0.541 gram carbon tetrachloride is adsorbed on 1 gram charcoal.

1.993 equals 51.5 calories per gram of carbon tetrachloride, which checks exactly the latent heat of carbon tetrachloride at 0° C. (where 1.993 is the extrapolated value of isostere slope obtained by plotting the slope of the isostere against adsorbate concentration to zero concentration).

Adsorbate concentrations are usually expressed as cubic centimeters of adsorbate per gram charcoal; however, in order that the integral heat may be determined directly from the graph, the concentrations were plotted in Figure 13 as grams adsorbate per gram charcoal. To compare the calculated integral heat with that measured calorimetrically by Lamb and Coolidge (*11*), the shaded area in Figure 13 was measured from zero to the highest adsorbate concentration used by these investigators (0.541 gram carbon tetrachloride per gram charcoal); and the ordinate values were taken from zero up to the heat line. Expressed as an equation,

$$\Sigma Q = \int_{0 \text{ gram } CCl_4/\text{gram charcoal}}^{0.541 \text{ gram } CCl_4/\text{gram charcoal}} f(W)\, d(W)$$

where W = concentration of adsorbate

The integral heat was readily found as the area under the straight line, which gives calories per gram charcoal directly as the product of the length of the abscissa of maximum concentration multiplied by the average ordinate. A curved line could be handled equally well.

The comparison of integral heats at 0° C. follows:

Calorimetric heat (*11*)	51.4 calories liberated
Calculated heat	51.2 calories liberated
Difference	0.2 calorie or 0.39%

Because the check is so close, it is reasonable to assume that the plot of instantaneous heats is correct and that in this case, at least, it is a straight-line function with respect to concentration at constant temperature. Other adsorbates which exhibit straight instantaneous heat lines are carbon disulfide, chloroform, methane, *n*-pentane, carbon monoxide, and ethylene. Those with curved instantaneous adsorption heat lines are ethyl ether, benzene, methanol, ethyl chloride, methyl acetate, and ethyl formate. A comparison between the calorimetric and calculated integral heats at 0° and 25° C. is shown in Table II for all systems for which data could be found. The calculated values give, in most cases, a good check with the experimental values of heat of adsorption.

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VISCOSITY OF *n*-PENTANE

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IN ORDER to add to the general knowledge of the physical properties of the paraffin hydrocarbons, the viscosity of liquid *n*-pentane was measured with a rolling ball viscometer in the range from normal temperature and pressure up to 250° C. and 1000 pounds per square inch. The material used was a product of special purity supplied by Phillips Petroleum Company. Except for drying and boiling to expel dissolved air, it was not further purified. Its density, measured with a sealed glass pycnometer, was 0.6213 gram per cc. at 25° C. This is in excellent agreement with the values of Timmermans (*13*) which indicate a density of 0.6214 gram per cc. at 25° C. Its boiling point, corrected to 760 mm., was 36.05° C. which agrees with the value 36.077° by Wojciechowski (*15*). The viscosity of this pentane was determined accurately at 25° C. with a Bingham (*1*) capillary tube viscometer. The measured value was 0.002296 ± 0.000005 gram per cm. per second (poise).

VISCOMETER

Viscosity was measured with a rolling ball viscometer calibrated with fluids having known viscosity and density. Figure 1 is an isometric drawing of the viscometer assembly. The pressure vessel and tube are shown in Figure 2:

Pressure vessel *A*, 5.7 cm. ($2^1/_4$ inches) in diameter and 32 cm. ($12^1/_2$ inches) long, had an internal chamber 2.54 cm. (1 inch) in diameter and 25 cm. ($9^3/_4$ inches) deep. The end closure, *B*, contained an insulated electrode, *C*, and required a soft aluminum gasket, *D*, between grooved surfaces for tightness. This closure was the only pressure connection subject to high temperature that was opened during the use of the apparatus. Thermocouple *E* was inserted at the opposite end, and connection *F* conducted fluid from the trunnion to the pressure vessel. Inner tube *G* was drilled and reamed from a bar of steel to an internal diameter of 0.7991 ± 0.0005 cm. (0.3146 inch). Each end was closed by a cap, *H*, and sealed by a lead gasket, *J*. One cap only was drilled with a small hole to allow equalization of the applied fluid pressure. A sharp-pointed electrode, *K*, was permanently cemented into each cap in the axial position and insulated from the cap with a Bakelite bushing. The two electrodes were connected electrically outside the tube by means of a wire link, *L*, running through a glass tube. The steel ball, *M*, was 0.7938 ± 0.00005 cm. ($^5/_{16}$ inch) in diameter.

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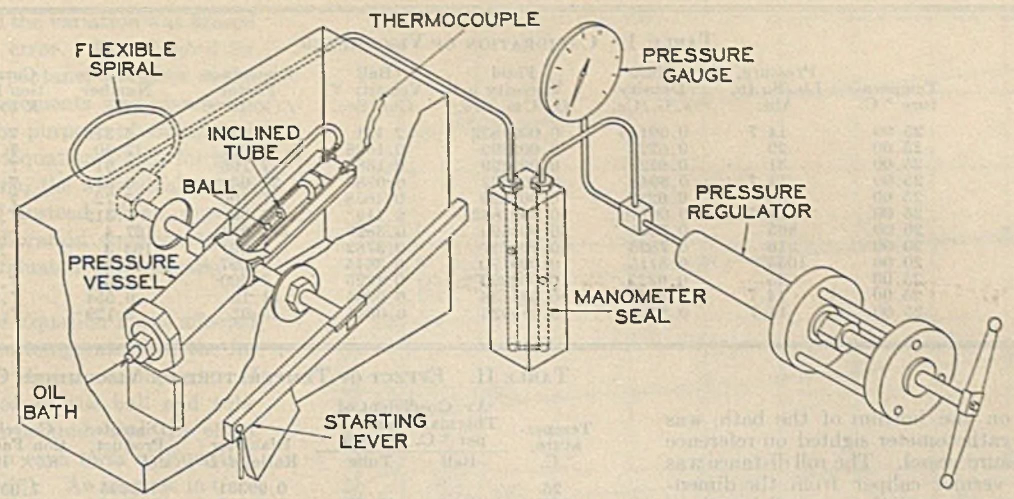

Figure 1. High Pressure Viscometer

The assembled pressure vessel was supported in an oil bath by trunnions *N* which were broken only at coupling *O* and union *P* outside the bath. On the end of one trunnion was a lever, pulled by a falling weight which furnished the power to move the pressure vessel and tube in the vertical plane about the horizontal axis. Pressure was applied to the system by a hydraulic press separated from the viscometer by a mercury-filled manometer seal. The connection to the seal was a very flexible copper tubing spiral. The pressure was read on a calibrated Bourdon tube gage.

In preparing the instrument for use, the manometer seal was first filled with the test fluid which was then forced through the connecting tubing. The inner tube and pressure vessel were filled, the vessel was placed in the oil bath, and the final connection was made at union *P*.

The oil bath was heated by immersion heaters controlled by a mercury-in-glass regulator. Temperature was measured by a thermocouple in the pressure vessel and by a thermocouple and calibrated thermometer in the bath. A sensitive potentiometer was used with the couples which were calibrated with a platinum resistance thermometer. The oil bath was maintained at a constant temperature until equilibrium between the inside and outside of the pressure vessel was reached before any measurements were made, and after each change in pressure time was allowed for the system to reach the test temperature again. The angle of inclination, fixed at 8° 20′ by the height of

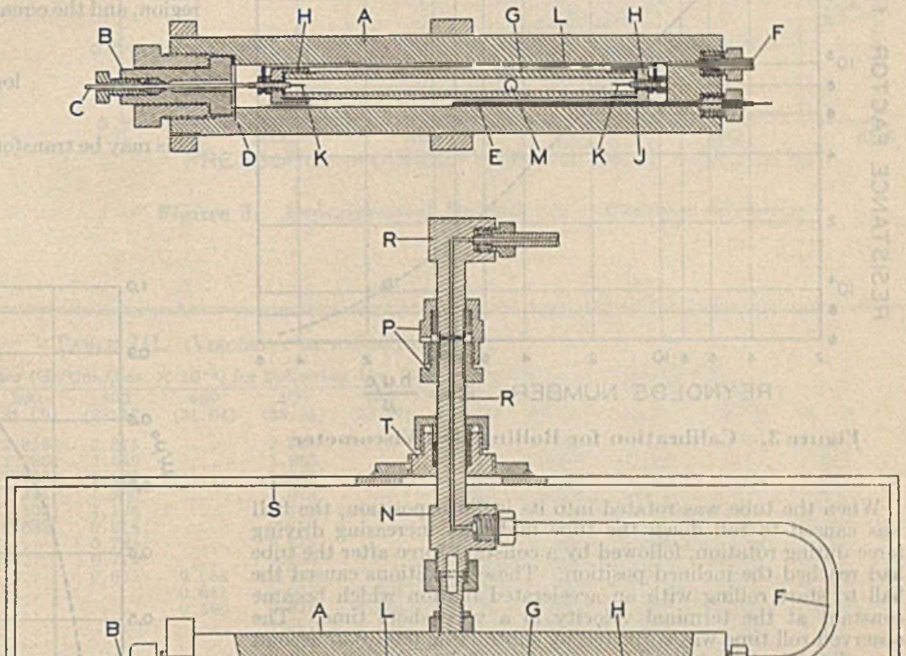

Figure 2. Pressure Vessel Assembly

The viscosity of *n*-pentane was determined with a rolling ball viscometer in the range from 25° to 250° C. and at pressures up to 1000 pounds per square inch. The resulting values are believed to be accurate within 5 per cent up to 150° C. and within 10 per cent at higher temperatures. A graphical comparison with data from the literature is shown.

Table I. Calibration of Viscometer

Fluid	Temperature ° C.	Pressure, Lb./Sq.In. Abs.	Fluid Density ρ, G./Cc.	Fluid Viscosity μ, G./Cm./Sec.	Ball Velocity V, Cm./Sec.	Resistance Factor f ($\times 10^{-4}$)	Reynolds Number Re	Correlation Factor K ($\times 10^7$)	$\frac{\rho_s - \rho}{V}$
Air	25.00	14.7	0.00116	0.0001832	2.121	25.23	5.316	7.46	3.66
n-Pentane, trial 1	25.00	29	0.6222	0.002299	0.1628	7.361	17.40	7.81	43.85
n-Pentane, trial 2	25.00	31	0.6222	0.002299	0.1582	7.796	16.91	7.58	45.10
Ethyl acetate	25.00	14.7	0.8948	0.004232	0.0787	21.03	6.571	7.24	87.19
n-Pentane, trial 3	25.00	32	0.6222	0.002299	0.1658	7.100	17.72	7.95	43.04
Air	25.00	14.7	0.00116	0.0001832	2.119	25.32	5.312	7.44	3.66
Liquid CO_2	20.00	865	0.7695	0.000696	0.3829	1.054	167.4	..	18.28
Liquid CO_2	20.00	916	0.7825	0.000717	0.3782	1.061	163.3	..	18.47
Liquid CO_2	20.00	1055	0.8115	0.000770	0.3644	1.097	151.9	..	19.09
n-Pentane, trial 5	25.00	25	0.6222	0.002299	0.1625	7.400	17.37	7.78	43.98
Ethyl acetate	25.00	14.7	0.8948	0.004238	0.0785	21.18	6.554	7.20	87.56
Benzene	25.00	14.7	0.8729	0.006025	0.0546	45.02	3.129	7.10	126.3

Table II. Effect of Temperature on Viscometer Calibration

Temperature, ° C.	Av. Coefficient of Thermal Expansion per ° C. ($\times 10^6$) Ball	Av. Coefficient of Thermal Expansion per ° C. ($\times 10^6$) Tube	Diameter Ratio, d/D	Diameter Product, $d(D + d)$	Correlation Factor K($\times 10^7$)	Calibration Coefficient C($\times 10^5$)
25	...	...	0.99331	1.2645	7.95	5.345
100	8.48	12.68	0.99299	1.2663	8.63	5.810
175	9.84	13.23	0.99280	1.2683	9.05	6.104
250	10.67	13.72	0.99263	1.2708	9.43	6.371

a block resting on the bottom of the bath, was measured with a cathetometer sighted on reference points on the pressure vessel. The roll distance was measured with a vernier caliper from the dimensions of the inner parts and the over-all length of the tube assembly. The viscometer could be rotated in the bath to incline in either direction; therefore the ball could be returned to its starting position. The roll time was measured with an electric chronoscope as the interval from the time the vessel passed the horizontal position to the time the ball reached the lower end of the tube. Breaking of the electrical connection and consequent arcing between the ball and upper contact was therefore avoided.

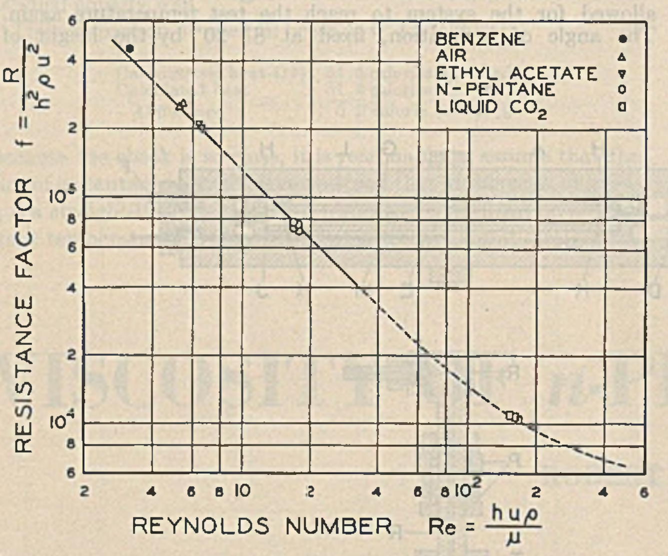

Figure 3. Calibration for Rolling Ball Viscometer

When the tube was rotated into its inclined position, the ball was caused to roll down the tube under an increasing driving force during rotation, followed by a constant force after the tube had reached the inclined position. These conditions caused the ball to start rolling with an accelerated motion which became constant at the terminal velocity in a very short time. The observed roll time was corrected by subtracting 0.05–0.07 second to make adjustment for this acceleration in starting the roll.

CALIBRATION

A general equation (*3*) for the rolling ball viscometer, valid only for the streamline region of fluid flow, is:

$$\mu = \frac{5\pi}{42} g \sin \theta\, K\, d(D + d) \frac{\rho_s - \rho}{V} \tag{1}$$

This equation can be simplified for any one instrument used under constant conditions to:

$$\mu = C \frac{\rho_s - \rho}{V} \tag{2}$$

Calibration data, consisting of the rolling velocity of a ball of known density in fluids having known viscosity and density, can be substituted directly in Equation 2 to obtain coefficient C.

To show the effect of turbulent flow on the calibration of the viscometer, two functions, Reynolds number Re and resistance factor f, were calculated and plotted on logarithmic paper. The calibration data are assembled in Table I, and the calculated values of these functions are plotted in Figure 3.

The relation between these functions is linear in the streamline region, and the equation of this relation is:

$$\log f = -\log Re - \log K \tag{3}$$

This may be transformed to

$$f = 1/KRe \tag{4}$$

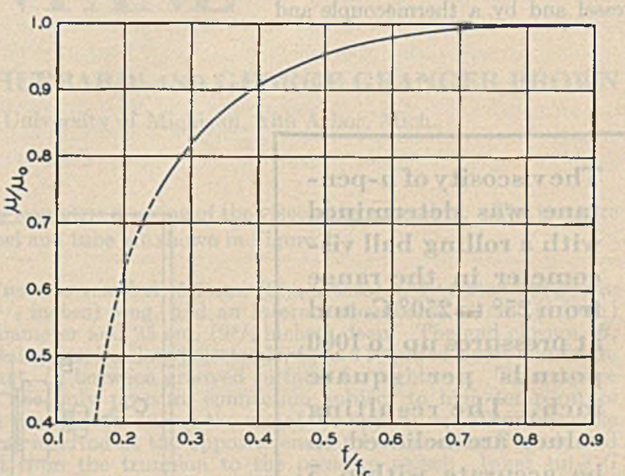

Figure 4. Correction for Rolling Ball Viscometer in Region of Turbulent Flow

The value of correlation factor K was calculated for each set of experimental data. The factor should be a constant if Equations 1 and 4 are obeyed rigorously in the streamline region. The value of K was found to decrease slightly as the fluid viscosity increased. Part of the variation was caused by experimental error. As indicated by the results for *n*-pentane, the error of the calibration measurements was about one per cent. For the purpose of calculating the coefficient of Equation 2 used for each trial on *n*-pentane, the individual values of *K* were used instead of an average value. Each calibration equation therefore correctly evaluated the viscosity of pentane at 25° C.

Coefficient *C* of Equation 2 was affected by changes in the temperature of the instrument. The linear coefficients of thermal expansion of the ball and tube were carefully measured, and the effect of temperature on each term of Equation 1 was calculated (*3*). An increase in temperature decreased the ball density and increased the roll distance and the product $d(D + d)$. Correlation factor *K*, a function of the diameter ratio, changed with temperature since the ball and tube had different coefficients of expansion. The value of *K* was numerically small, but the effect of the temperature increase to 250° C. was to increase *K* by 18.6 per cent. Table II shows the effect of temperature on the factors affecting the calibration coefficient, and Figure 6 shows graphically the effect of this correction on the calculated value of viscosity.

The turbulent region of fluid flow is shown in Figure 3 as a concave curve. The critical point designating the limit of the streamline region was assumed to have a constant critical Reynolds number, Re_c = 33.0, and a corresponding critical resistance factor, $f_c = 3.85 \times 10^4$ at 25° C. A correlation was obtained (*3*) between the ratio of the true viscosity μ to the viscosity μ_0 calculated from Equation 2, and the ratio of actual resistance factor *f* to critical resistance factor f_c. This correlation is shown in Figure 4.

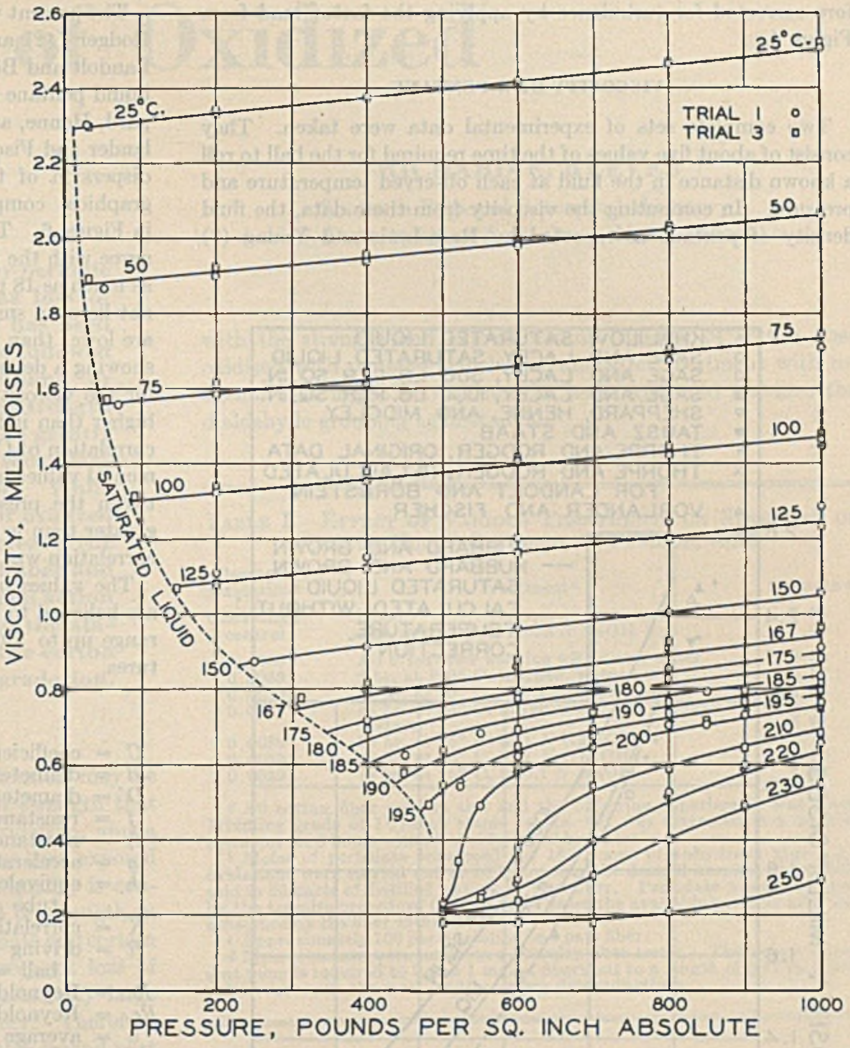

Figure 5. Experimental Results on *n*-Pentane Viscosity

Table III. Viscosity of *n*-Pentane

Temperature, ° C.	Saturation	100 (7.03)	200 (14.06)	300 (21.09)	400 (28.12)	450 (31.64)	500 (35.15)	550 (38.67)	600 (42.18)	700 (49.21)	800 (56.25)	900 (63.28)	1000 (70.31)
		Viscosity in Millipoises (G./Cm./Sec. × 10^{-3}) for Following Abs. Pressures in Lb./Sq. In. (Kg./Sq. Cm.)											
25	2.296	2.313	2.330	2.355	2.375	...	2.396	...	2.417	2.438	2.458	2.480	2.500
50	1.879	1.893	1.912	1.930	1.949	...	1.968	...	1.987	2.006	2.025	2.044	2.062
75	1.563	1.572	1.590	1.608	1.625	...	1.643	...	1.661	1.679	1.696	1.714	1.731
100	1.300	1.303	1.322	1.341	1.360	...	1.378	...	1.397	1.415	1.434	1.452	1.470
125	1.071	...	1.083	1.103	1.124	...	1.145	...	1.166	1.187	1.207	1.229	1.249
150	0.865	...	...	0.888	0.914	...	0.938	...	0.961	0.984	1.006	1.027	1.050
167	0.746	...	...	...	0.784	...	0.816	...	0.843	0.869	0.892	0.916	0.939
175	0.688	...	...	...	0.714	...	0.758	...	0.792	0.821	0.845	0.869	0.893
180	0.647	...	...	...	0.665	0.698	0.724	0.744	0.760	0.790	0.815	0.840	0.864
185	0.603	...	...	...	...	0.641	0.674	0.701	0.724	0.758	0.786	0.812	0.837
190	0.550	...	...	...	...	0.566	0.615	0.654	0.684	0.725	0.755	0.784	0.812
195	0.472	...	...	...	...	...	0.531	0.594	0.634	0.688	0.725	0.756	0.786
200	...	...	...	...	...	...	0.230	0.494	0.572	0.642	0.685	0.720	0.757
210	...	...	...	...	...	...	0.221	0.264	0.371	0.530	0.600	0.653	0.698
220	...	...	...	...	...	...	0.212	0.237	0.270	0.399	0.508	0.576	0.631
230	...	...	...	...	...	...	0.207	0.212	0.234	0.304	0.403	0.484	0.549
240	...	...	...	...	...	...	0.194	0.197	0.206	0.238	0.300	0.372	0.435
250	...	...	...	...	...	...	0.179	0.180	0.181	0.187	0.209	0.245	0.292

Liquid carbon dioxide, whose physical properties were obtained from Quinn and Jones (*6*), was used as a calibrating fluid in order to obtain data in the turbulent region at normal temperatures. Turbulent flow was encountered in the viscometer with *n*-pentane at temperatures above 75° C. This condition was recognized when the calculated resistance factor was numerically less than the critical resistance factor calculated for the temperature of the instrument. The viscosity calculated from Equation 2 was therefore corrected for turbulence by applying the factor read from Figure 4.

VISCOSITY OF n-PENTANE

Two complete sets of experimental data were taken. They consist of about five values of the time required for the ball to roll a known distance in the fluid at each observed temperature and pressure. In computing the viscosity from these data, the fluid density of pentane as reported by Rose-Innis and Young (*7*) and Sage, Lacey, and Schaafsma (*9*) were used. These computed values of pentane viscosity are shown as points in Figure 5. Isotherms were drawn through these data and cross-plotted. The coordinates of points read from the smoothed curves are given in Table III.

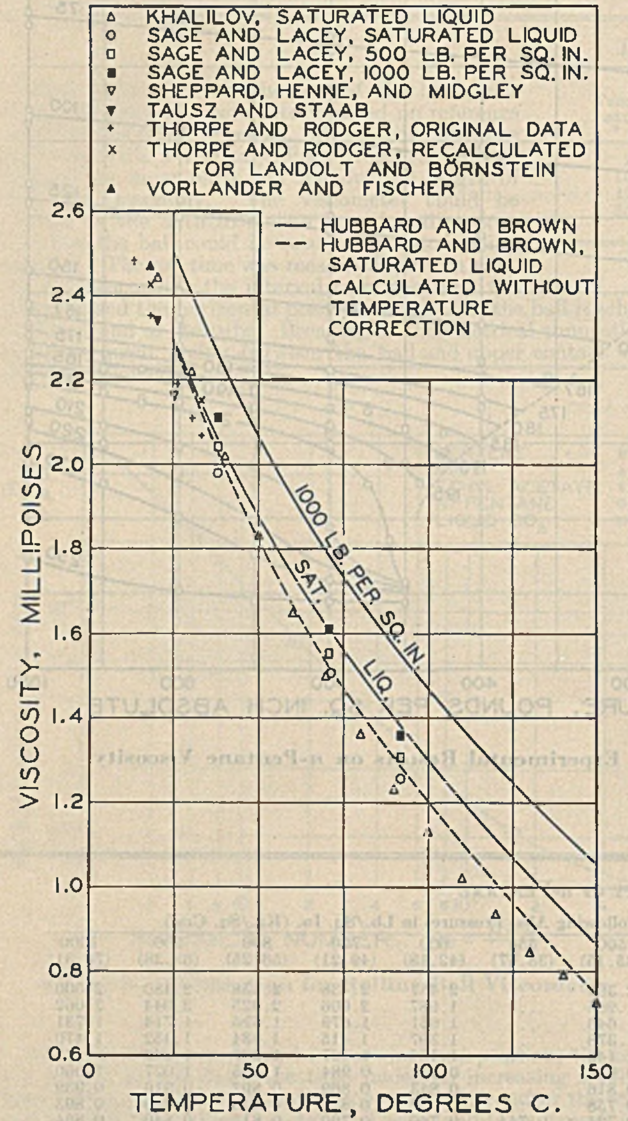

Figure 6. Comparison of n-Pentane Viscosity with Data in the Literature

The precision of the experimental measurements is high. In the streamline region the average deviation of the points from the isotherms is 0.5 per cent. For all points the average deviation from the isotherms is 1.4 per cent. Less than 3 per cent of all experimental values deviate more than 5 per cent from the isotherms.

The present viscosity values agree with the data of Thorpe and Rodger (*12*) and even better with these data recalculated for Landolt and Börnstein (*5*). Additional data on the viscosity of liquid pentane at atmospheric pressure are available from Sheppard, Henne, and Midgley (*10*), Tausz and Staab (*11*), and Vorlander and Fischer (*14*). At normal temperature the maximum dispersion of these literature values is about 5 per cent. A graphical comparison over a range of temperature is shown in Figure 6. The values of Khalilov (*4*) for the saturated liquid agree with the present work at normal temperatures but deviate as much as 18 per cent at the higher temperatures where they do not lie on a smooth curve. The values of Sage and Lacey (*8*) are lower than the present values by almost a constant quantity showing a deviation of 4 to 8 per cent. The pressure coefficient for the viscosity of pentane was found to be 50 to 70 per cent higher than indicated by the data of Sage and Lacey (*8*). The correlation of Comings and Egly (*2*) does not predict the experimental values in a satisfactory manner, but the disagreement between the present data on pentane and the correlation is no greater than is found between other reported data on which the correlation was based.

The values of the viscosity of n-pentane given in Table III are believed to be accurate within 5 per cent in the temperature range up to 150° C. and within 10 per cent at higher temperatures.

NOMENCLATURE

C = coefficient of Equation 2
d = diameter of ball, cm.
D = diameter of tube, cm.
f = resistance factor = $R/(h^2\rho\mu^2)$, dimensionless
f_c = resistance factor at critical velocity
g = acceleration of gravity = 980 cm./sec.^{2}
h = equivalent diameter of annular space between ball and tube = $D - d$, cm.
K = correlation factor. dimensionless
R = driving force on ball or resistance of fluid to motion of ball = $^5/_7(g \sin \theta)(\pi d^3/6)(\rho_s - \rho)$, gram cm./sec.^{2}
Re = Reynolds number = $(h\ u\ \rho)/\mu$, dimensionless
Re_c = Reynolds number at critical velocity
u = average fluid velocity through annular space between ball and tube = $Vd^2/(D^2 - d^2)$, cm./sec.
V = terminal rolling velocity of ball, cm./sec.
θ = angle of inclination of tube with horizontal
μ = viscosity of fluid, gram/cm./sec.
μ_0 = viscosity of fluid calculated when Equation 2 is used in turbulent region
π = 3.1416
ρ = density of fluid, gram/cc.
ρ_s = density of ball, gram/cc.

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Stabilization of Oxidized Cotton Fiber

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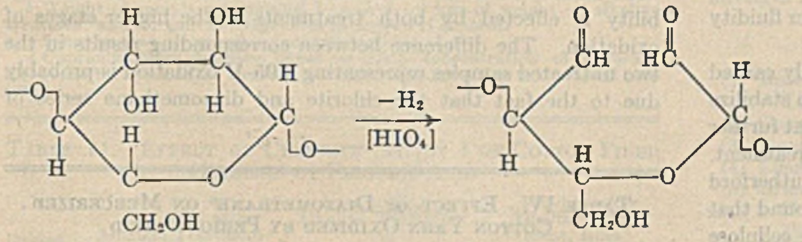
Damage to cotton fiber upon oxidation by periodic acid does not become fully apparent as loss of tensile strength until the oxidized fiber has been exposed to alkalies. If the oxidation is followed by treatment with ethereal diazomethane or sodium chloride at pH 4, the total loss of strength after subsequent exposure to alkali may be greatly decreased through the lessening of the secondary deterioration of the fiber after oxidation. While acting to diminish alkali deterioration of oxidized cotton fiber, these treatments also increase the cuprammonium viscosity of the oxidized fiber and decrease its alkali solubility. The beneficial action of these reagents is believed to be due to the stabilization of weakened positions within the cotton fiber and not to an actual reversal of degradation.

THE damage cotton fiber sustains upon oxidation may be divided into two phases: An initial loss of strength that may be observed immediately following oxidation, and a second loss that becomes evident after the fiber has been exposed to the action of dilute alkalies. As far as textile quality is concerned, the damage to the fiber is the total loss of strength in both phases. When oxidation is effected by periodate and certain other known types of oxidizing agents, the subsequent loss of strength upon alkaline treatment represents a relatively large proportion of the total damage to the cotton fiber. Therefore if suitable means could be found for preventing this second part of the deterioration, a part of the fiber damage could be averted.

Recent work by Jackson and Hudson (*6*), Mahoney and Purves (*8*), Grangaard, Gladding, and Purves (*5*), and Rutherford, Minor, Martin, and Harris (*10*) has shown that the principal reaction of periodic acid, or periodate, with cellulosic materials consists in cleavage of the 2,3-glycol position of certain glucose anhydride units, causing rupture of the carbon-carbon bond and formation of a dialdehyde configuration as shown in the following structural representation:



It is reasonable to explore the possibility that this dialdehyde configuration may be the grouping responsible for the alkali lability which Davidson (*3*) and Brownsett and Davidson (*1*) have observed in cotton fiber after periodic acid oxidation. Evidence presented by Rutherford and co-workers (*10*) makes it appear extremely likely that such is the case; they found that when the aldehyde groups of the oxidized fiber are converted to carboxyl groups under mildly acid conditions, the alkali solubility of the fiber is lessened. The present report deals chiefly with the strength and cuprammonium fluidity of cotton fiber oxidized with periodic acid before and after treatment with reagents that might be expected to react with and stabilize the dialdehyde grouping against alkali.

TABLE I. EFFECT OF VARIOUS TREATMENTS ON STRENGTH OF COTTON FIBER[a] OXIDIZED BY PERIODIC ACID

Degree of Oxidation[b]	Treatment[c]	Strength[d]
Unoxidized control	None	7.03
	1 hr. at 100° C. in 0.025 *N* NaOH	7.04
0.0089	Air dried after washing with distd. water	6.50
0.0089	1 hr. at 100° C. in distd. water	6.57
0.0089	18 hr. at 25° C. in 0.1 *N* HCl	6.28
0.0089	18 hr. at 25° C. in tap water, pH 9.9 (at start)	5.91
0.0089	18 hr. at 25° C. in 1 *N* $NaHCO_3$	4.75
0.0089	18 hr. at 25° C. in 1 *N* NH_4OH	4.73
0.0089	18 hr. at 25° C. in 0.1 *N* NaOH	4.57

[a] All cotton fiber used in this and the following experiments was Good Middling grade of 1$^{1}/_{8}$-inch staple length. It was extracted in a Soxhlet extractor for 8 hours with alcohol followed by water.

[b] Moles of periodate consumed per 162 grams of anhydrous fiber. All oxidations were carried out at 25° C., using the desired amount of periodic acid in 50 parts of distilled water to 1 part fiber. Periodate was determined by the arsenite procedure (*4*). In most cases the available periodic acid was consumed by the fiber within 24 hours.

[c] Approximately 100 parts solution to 1 part fiber.

[d] Measurements were made on a Pressley fiber tester. The values represent pounds required to break 1 mg. of fibers cut to a length of 0.47 in.; each value represents the mean of 10 or more determinations.

EFFECT OF REAGENTS ON OXIDIZED FIBER

The effect of certain common reagents on the strength of cotton fiber oxidized by periodic acid is shown in Table I. These data confirm earlier observations (*1*, *3*), in showing that the oxidation brings about a relatively small loss of tensile strength in comparison with the loss that occurs upon alkaline treatment after oxidation. The action of distilled water at high temperature or of dilute acids at room temperature does not have an adverse effect on the strength of oxidized fiber like that of alkalies. In order to prepare the oxidized fiber with the least possible loss of strength, it was necessary to wash out the oxidizing reagents with distilled water, since the tap water in this laboratory is alkaline (pH 9.6 to 9.9) and quickly brings about a large loss of strength in the oxidized fiber.

Some of the properties of a series of cotton-fiber preparations oxidized by increasing amounts of periodic acid are illustrated by the experiment reported in Table II. Increasing oxidation is accompanied by increasing alkali solubility and cuprammonium fluidity as well as loss of tenacity. After alkaline treatment a much greater loss of strength is apparent, but the cuprammonium fluidity is not increased, presumably because all unstable positions are broken by the alkaline cuprammonium hydroxide solution. This is in marked contrast to the behavior of hypochlorite-oxidized fiber, which is known to show increased cuprammonium fluidity as well as further loss of strength after alkaline treatment. Strict comparison of fluidity values before and after

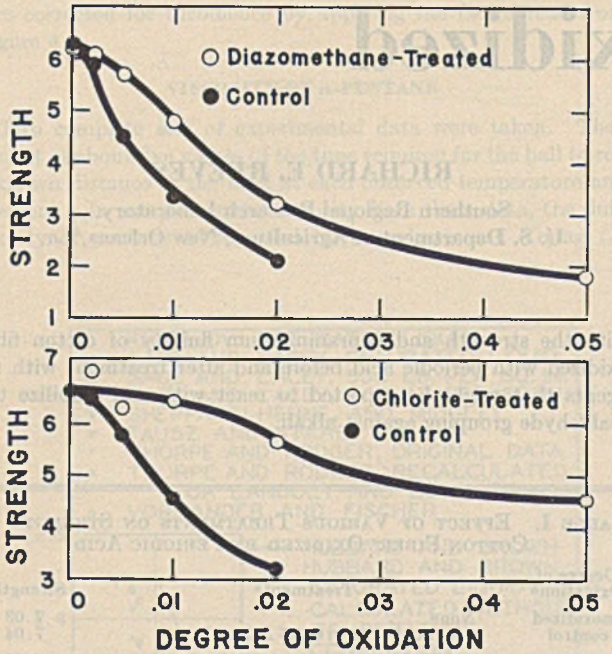


Figure 1. Stabilizing Effect of Treating Periodate-Oxidized Cotton Fiber with Diazomethane and with Chlorite before Exposure to Alkali

Table II. Alkali Stability of Cotton Fiber after Oxidation by Periodic Acid

Degree of Oxidation	Loss in Wt. on Alkaline Treatment[a], %	Strength[b] after Oxidation: Before alkaline treatment	Strength[b] after Oxidation: After alkaline treatment	Fluidity[c] of Oxidized Fiber, Rhes: Before alkaline treatment	Fluidity[c] of Oxidized Fiber, Rhes: After alkaline treatment
0.000	0.00	5.87	6.02	1.65	2.09
0.002	0.98	5.79	5.86	9.84	9.51
0.005	2.00	5.47	4.51	23.0	22.4
0.010	2.96	5.30	3.30	32.7	32.8
0.020	5.96	4.31	2.09	47.2	44.5
0.050	40.7	3.39	Disintegrated	55.3	..

[a] Treatment consisted of 100 parts 0.025 *N* NaOH in the water bath at 100° C. for 1 hr. Fiber was then washed with distilled water, allowed to stand in dilute acetic acid, washed free of acid with distilled water, and air-dried.

[b] See footnote [d], Table I.

[c] Cuprammonium fluidities were measured at 25° C., using Clibbens and Geake type viscometers and cuprammonium hydroxide solution containing 15 grams copper and 240 grams ammonia per liter (*2*). The cellulose concentration was 0.5% in each case. The units (rhes) represent reciprocal poise.

alkaline extraction is complicated by the fractionation which occurs when a portion of the fiber is dissolved by the alkali. The removal of soluble material would tend to result in a lower fluidity for the remaining material.

If the instability of the oxidized cotton fiber is actually caused by the dialdehyde configuration, it should be possible to stabilize the aldehyde groups by suitable chemical reactions so that further fiber degradation would not easily occur upon alkaline treatment. Such a stabilization has already been reported by Rutherford and co-workers (*10*), who employed chlorous acid and found that it converted the aldehyde groups of periodate-oxidized cellulose to carboxyl with an accompanying decrease in alkali solubility. A second reagent which stabilizes periodate-oxidized cotton fiber is ethereal diazomethane, which was used in the methylation of cotton fiber (*9*). Other treatments tested for their effect on the fluidity of oxidized fiber are listed in Table III.

It is apparent that sodium chlorite at pH 4 and ethereal diazomethane are the most effective of the reagents used. Other reagents which could be expected to react with aldehyde groups do so to only a slight extent or not at all under the conditions employed, or they form products not stable toward alkali.

Table III. Results of Treatments on Cuprammonium Fluidity of Cotton Fiber Oxidized with Periodic Acid

Treatment	Degree of Oxidation	Fluidity, Rhes: Before treatment	Fluidity, Rhes: After treatment
Aluminum isopropylate in isopropyl alcohol, refluxed 1 hr.	0.0089	31.1	29.9
Ammonium cyanide, 5% soln., 18 hr. at room temp.	0.0089	31.1	21.9
Phenyl hydrazine in alcohol, 18 hr. at room temp.	0.0089	31.1	22.4
Phenyl hydrazine hydrochloride + sodium acetate in water at 100° C., 1 hr.	0.020	56.0	54.7
Zinc dust and 25% acetic acid, refluxed 3 hr.	0.020	56.0	55.0
Hydrogen + active PtO catalyst in 50% alcohol, 50 lb., room temp., 3 hr.	0.020	56.0	55.0
Sodium bisulfite, 10% soln. at room temp., 2 hr.	0.014	38.3	37.5
Sodium chlorite at pH 4, 1% soln.			
1 hr. at room temp.	0.014	38.3	25.8
1 hr. at 50° C.	0.014	38.3	11.1
Diazomethane in ether at 0°, approx. 0.5 molar at start of expt.			
1¼ hr., 0.96% OCH_3	0.010	36.7	29.9
20 hr., 3.86% OCH_3	0.010	36.7	19.9
91 hr., 5.71% OCH_3	0.010	36.7	16.0
187 hr., 7.09% OCH_3 (2 treatments)	0.010	36.7	14.1
240 hr., 7.37% OCH_3	0.0089	31.1	8.0

STABILIZATION OF OXIDIZED FIBER

After it was established that certain reagents could reduce the fluidity of cotton fiber that had been oxidized with periodic acid, it was of interest to determine whether this effect would be accompanied by a decrease in the total loss of strength caused by the oxidation. Cotton fiber and yarn were oxidized with known amounts of periodic acid, and a portion of each sample was treated with ethereal diazomethane or, in some cases, sodium chlorite at pH 4. All samples were placed in contact with dilute alkali and then subjected to tensile strength measurements under comparable conditions. The samples treated with diazomethane or chlorite showed significantly less loss of strength than the untreated samples. The effectiveness of these two treatments on cotton fiber is shown in Figure 1. Table IV indicates the effect of diazomethane on the strength and alkali solubility of oxidized cotton yarn. In all cases it is evident that an appreciable portion of the total loss of strength induced by the oxidation can be prevented.

The effect of chlorite treatment in lowering the alkali solubility of periodate-oxidized cotton fiber has already been noted (*10*). This observation was confirmed by the present work and was found to apply as well to the diazomethane treatment. Tables V and VI compare the alkali solubility (loss in weight on alkaline treatment) of oxidized cotton fiber before and after treatment with diazomethane and chlorite. A marked reduction in solubility is effected by both treatments at the higher stages of oxidation. The difference between corresponding results in the two untreated samples representing 0.05 *M* oxidation is probably due to the fact that the chlorite and diazomethane series of

Table IV. Effect of Diazomethane[a] on Mercerized Cotton Yarn Oxidized by Periodic Acid

Degree of Oxidation	Loss in Wt. on Alkaline Treatment[b], %: Control	Loss in Wt. on Alkaline Treatment[b], %: Diazomethane-treated	Breaking Strength[c] after Alkaline Treatment, Lb.: Control	Breaking Strength[c] after Alkaline Treatment, Lb.: Diazomethane-treated
0.00	0.00	0.00	1.34	1.32
0.01	2.18	0.43	1.02	1.16
0.05	12.0	2.38	0.13	0.53
0.15	75.8	8.40	Disintegrated	0.31

[a] Treatment consisted of 0.42 *M* diazomethane in ether at 0° C. for 6 days. Approximately 7% methoxyl was introduced in this treatment.

[b] See footnote[a], Table II.

[c] Measured on a Scott yarn tester with 10 in. between jaws; each value represents the mean of 10 determinations.

oxidized samples were prepared under different conditions. Within each table, however, the treated samples were taken from the same batch of oxidized cotton fiber as the untreated samples. Also included are the values for strength and cuprammonium fluidity of the oxidized alkali-treated cotton fiber, with and without diazomethane or chlorite treatment. It is apparent that the treatments bring about a reduction of fluidity which persists after exposure to alkali at 100° C. Figure 1 shows how the diazomethane and chlorite treatments protected the strength of the oxidized fiber against the action of alkali.

DISCUSSION

The work of Jeanes and Isbell (*7*) and Rutherford and coworkers (*10*) indicates that the action of chlorite upon the oxidized fiber can be regarded as selective oxidation of aldehyde groups to carboxyl groups, the latter presumably not being susceptible to further deterioration in the presence of alkalies. That chlorite under these conditions does not harm the fiber by further oxidative side reactions is a remarkable fact which has received earlier mention by other workers (*11*). The properties of the carboxyl-containing cotton fibers are extremely interesting and offer various possibilities for further study. The behavior of the fiber and fabric toward certain dyes is markedly altered. Metallic salts of the carboxyl-containing fiber are easily prepared, and by means of double decomposition reactions it is possible to precipitate colored metallic salts throughout the fiber. Figure 2 shows a cross-sectional view of ordinary and carboxyl-containing yarns which were treated with a copper salt solution, washed, and then treated with potassium ferrocyanide. It is apparent that the copper salt was distributed quite uniformly throughout the oxidized fiber encircling the ordinary yarn.

The mechanism by which the oxidized cotton fiber is stabilized is much more obscure in the case of diazomethane than in that of the chlorite reagent. Diazomethane is known to react with aldehydic groups, but the simultaneous reaction with certain hydroxyl groups in the cotton fiber causes the picture to be confused. The diazomethane-treated fibers do not have the same dyeing properties as exhibited by the chlorite-treated samples. Further work is in progress to explore the nature of the diazomethane reaction products.

Table V. Effect of Diazomethane[a] on Cotton Fiber Oxidized by Periodic Acid

Degree of Oxidation	Strength[b] after Alkaline Treatment[c]		Loss in Wt. on Alkaline Treatment, %		Fluidity[d] after Alkaline Treatment, Rhes	
	Control	Diazomethane-treated	Control	Diazomethane-treated	Control	Diazomethane-treated
0.000	6.20	6.17	0.00	1.28	2.09	2.40
0.002	5.86	6.01	0.98	1.20	9.51	3.46
0.005	4.51	5.73	2.00	1.20	22.4	7.15
0.010	3.30	4.82	2.96	1.53	32.8	11.38
0.020	2.09	3.20	5.96	1.39	44.5	20.0
0.050	Disintegrated	1.80	40.7	2.74	..	28.3

[a] Treatment employed 0.45 *M* diazomethane in ether at 0° C. for 6 days; approximately 6% methoxyl was introduced.

[b] Weight of sample recalculated to adjust for loss of weight on alkaline treatment and for gain in weight due to methoxyl content.

[c] Same as that described in footnote[a], Table II.

[d] Cuprammonium fluidities based on 0.5% concentration of cellulose, allowance being made for increase in weight of samples due to methoxyl content.

Table VI. Effect of Chlorite[a] at pH 4 on Cotton Fiber Oxidized by Periodic Acid

Degree of Oxidation	Strength[b] after Alkaline Treatment[c]		Loss in Wt. on Alkaline Treatment, %		Fluidity after Alkaline Treatment, Rhes	
	Control	Chlorite-treated	Control	Chlorite-treated	Control	Chlorite-treated
0.000	6.58	6.57	0.90	1.82	2.02	3.23
0.002	6.49	7.01	2.30	1.22	9.73	3.81
0.005	5.73	6.30	2.60	0.87	18.8	5.86
0.010	4.53	6.46	3.66	0.79	21.7	7.24
0.020	3.16	5.57	5.16	0.73	42.0	12.95
0.050	Disintegrated	4.53	14.94	1.24	52.1	23.9

[a] Treatment consisted of 2% sodium chlorite buffered at pH 4.0 with 2% potassium acid phthalate and involved use of 50 parts of solution at 60° C. for 1 hour.

[b] Not recalculated to allow for loss of weight upon alkaline treatment.

[c] Same as that described in footnote[a], Table II.

Figure 2. Cotton Fibers (×250) after Being Treated With Solution of Copper Salt, Washed Free of Excess Copper, and Placed in Potassium Ferrocyanide Solution

Dark fibers had been oxidized by periodate and chlorite; light center fibers show behavior of unoxidized cotton.

It should be pointed out that the apparent reversal of the deterioration of cotton fiber by periodic acid represents a logical extension of results already published by other workers in this field. Although less is known of the mode of attack of many other common agents of fiber degradation, it has seemed worth while to apply to other types of damaged fibers the reagents which successfully lessen periodic-acid-induced fiber deterioration. To date, these reagents have been applied to fibers damaged by neutral and alkaline hypochlorite and by ultraviolet irradiation. In certain cases beneficial effects have been observed on these other types of damaged fibers, but protective effect has not approached in extent that shown on fibers oxidized by periodic acid.

ACKNOWLEDGMENT

The writer is indebted to William A. Posey and J. R. Jung, Jr., of the Southern Regional Research Laboratory, for a number of the determinations reported in this paper. J. M. Doebrick, of Tucson, Ariz., supplied the Pressley fiber tester used for strength measurements.

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Solubility of Water in
LIQUID CARBON DIOXIDE

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The solubility of water in liquid carbon dioxide is reported for several temperatures from −29° to +22.6° C. These temperatures involve a vapor pressure range for liquid carbon dioxide of 15 to 60 atmospheres. The values reported indicate a fairly regular increase in solubility from 0.02 per cent water at the lower temperature to 0.10 per cent at the higher.

THE composition of certain phases of the equilibrium mixtures of carbon dioxide and water, such as the solubility of carbon dioxide in liquid water, have been determined with satisfactory precision by a number of workers, especially Weibe (*3-6*); however, considerable uncertainty exists with regard to the solubility of water in liquid carbon dioxide. Lowry and Erickson (*2*) attempted to determine this from the density of the gaseous phase coexisting with the liquid carbon dioxide in the presence and absence of water and then computing the solubility by Raoult's law. Since the differences they observed were less than the experimental error, they concluded that water could not be soluble to more than 0.05 per cent in liquid carbon dioxide over a temperature range of −5.8° to 22.9° C.

The solubility is a matter of practical interest in the manufacture of commercial solid carbon dioxide (dry ice) where too much moisture often causes a freeze-up in the plant due to the accumulation of solid water. On the other hand, a certain amount of moisture has been regarded by some as essential to the production of dry ice with suitable physical properties. Without water the dry ice was thought to shatter easily, particularly after storage. Josephson (*1*) took out a patent covering the deliberate introduction of water for the purpose of improving the physical properties of dry ice. Although the desirability of any moisture in dry ice is doubtful, it is a point that is frequently raised in connection with the production of solid carbon dioxide. When carbon dioxide is used in certain types of fire extinguishers, the presence of too large an amount of water may cause serious trouble. Pressure drops in the carbon dioxide system may produce refrigeration resulting in the separation of solid water. This in turn may restrict the flow of the carbon dioxide. Hence the question of the solubility of water in the liquid carbon dioxide becomes of vital importance.

SOLUBILITY was determined directly by the apparatus shown in Figure 1. Although not indicated in the diagram, the carbon dioxide cylinder was immersed in a thermostat and the sodium-calcium hydrate tubes were placed in a water bath at room temperature. To charge the cylinder, a 25-ml. portion of distilled water was added to the clean cylinder; and after replacing the valve carrying the siphon tube, the cylinder was filled two thirds full with liquid carbon dioxide.

To ensure thorough mixing of the two liquids, the cylinder was placed on the rollers of a ball mill and revolved for 8 hours at about 80 r. p. m. The room temperature during this mixing was above that at which the solubility was to be determined. Next the cylinder was placed upright in a thermostat in which the temperature was controlled within ±0.05° C. The water of the thermostat covered the needle valve as well as the cylinder to take care of the cooling resulting from the change of state and the drop in pressure which took place at this point. After allowing 24–48 hours for the establishment of equilibrium at the temperature of the bath, the cylinder valve was opened fully. The needle valve was then opened gradually so that the gas, when bypassed through the flowmeter to adjust the rate, attained a rate of about 100 ml. per minute. After permitting sufficient flow to purge the siphon tube of any possible droplets of entrapped water, the stopcocks were adjusted to allow the gas to enter the absorption system. The magnesium perchlorate tubes were weighed filled with carbon dioxide while the sodium-calcium hydrate tubes contained dry air for both the initial and the final weighings. The completeness of the absorption of water by magnesium perchlorate and of carbon dioxide by soda lime was assured by the second tube of each of these reagents. The fact that the second tube showed little or no increase in weight during a run was evidence that neither the rate nor the amount of sample had been too great for the capacity of the absorbents. One charge of the perchlorate was adequate for many runs so that the final weighing of one run was used as the initial weighing for the next. The first sodium-calcium hydrate tube received a fresh charge for each determination, since each run was continued until the appearance of the reagent showed that the

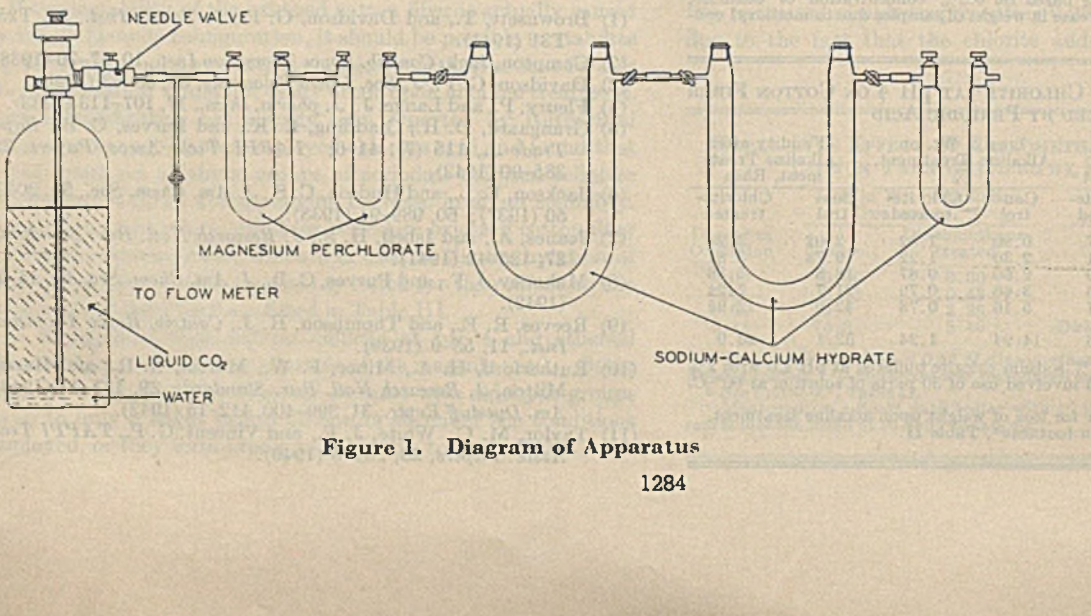

Figure 1. Diagram of Apparatus

Table I. Percentage of Water in Liquid Carbon Dioxide Saturated at Various Temperatures

Sample, Grams	Water, Grams	Water, Per Cent	Deviation from Mean
A. At 5.08° C.			
49.42	0.0301	0.0609	−0.0030
72.21	0.0476	0.0659	+0.0020
58.34	0.0365	0.0626	−0.0013
94.13	0.0587	0.0624	−0.0015
71.97	0.0465	0.0646	+0.0007
67.73	0.0442	0.0653	+0.0014
63.93	0.0413	0.0643	+0.0004
67.12	0.0402	0.0599	−0.0040
73.58	0.0499	0.0678	+0.0039
	Average	0.0639	0.0020
Average deviation from mean 3.2%			
B. At 15.0° C.			
118.63	0.0994	0.0838	−0.0062
99.41	0.0894	0.0899	−0.0001
91.37	0.0817	0.0894	−0.0006
88.66	0.0811	0.0914	−0.0014
89.22	0.0851	0.0954	+0.0054
	Average	0.0900	0.0027
Average deviation from mean 3.0%			
C. At 22.6 ±1° C.			
31.8	0.0316	0.0994	−0.0046
14.2	0.0155	0.109	+0.0050
13.3	0.0130	0.0980	−0.0060
25.4	0.0231	0.0910	−0.0130
11.7	0.142	0.121	+0.0710
67.7	0.0695	0.103	−0.0010
	Average	0.104	0.0078
Average deviation from mean 7.5%			
D. At −29° C.			
547.3	0.1121	0.0205	+0.0010
199.5	0.0363	0.0182	−0.0013
305.0	0.0631	0.0207	+0.0012
535.7	0.0991	0.0185	−0.0010
	Average	0.0195	0.0011
Average deviation from mean 5.1%			

reaction had progressed nearly to the exit end of the tube. The third sodium-calcium hydrate tube was included as a protection for the system against the water and carbon dioxide of the atmosphere. A sulfuric acid bubbler following the third soda lime tube showed a slight surge of pressure as the carbon dioxide was turned into the system at the start of a run. No further bubbles were observed during the run, an indication that practically all of the sample was absorbed by the two reagents. A single determination required a steady flow of gas from several hours to overnight. The sum of the weights of the water and carbon dioxide absorbed was taken as the weight of the sample.

The low percentage of water made difficult what otherwise would have been a simple determination. Each soda lime tube and contents weighed about 600 grams, and was capable of absorbing about 100 grams of carbon dioxide. The heavy-duty analytical balance used to weigh these tubes had a capacity of 2 kg. and a sensitivity of 0.1 mg. The 0.1 mg. sensitivity was not used with the carbon dioxide because the data for the water included only three significant figures. The magnesium perchlorate tubes and contents weighed approximately 100 grams each and were weighed on a balance with a capacity of 200 grams and a sensitivity of 0.1 mg. The method was developed after many less successful attempts had been made with various modifications.

TABLE I, *A* and *B*, records the results with the method just described.

The values listed under *C* and *D* were obtained in a different manner. In the case of *C* the entire experiment from the rolling of the cylinder to the absorption of the water was carried out in a room that showed a temperature variation of ±1° C. The weight of the sample was determined by the loss in the weight of the cylinder. Since the cylinder weighed some 12 kg., the sample was weighed only to within a few tenths gram. After the water had been absorbed by the magnesium perchlorate, the carbon dioxide was vented to the atmosphere instead of being absorbed by soda lime as above.

The results listed as *D* were obtained by the method of analysis used for *C*, but the sample was liquid carbon dioxide taken from the National Dry Ice Plant, Niland, Calif., where operating conditions indicated that the liquid carbon dioxide was saturated with water at −29° C. Since the author had no facilities for temperature control at such low temperatures, the values from this analysis are included as an indication of the trend of the solubility.

SEVERAL features of the experimental method should be considered. These include the fact that the carbon dioxide liquid and gaseous phases in equilibrium with water at the same temperature and pressure contain different percentages of water, the possibility that droplets or particles of water form stable suspensions in the liquid carbon dioxide, the effect of the iron dissolved from the cylinder walls by the water-rich phase, the refrigerating effect resulting from the change of state and the expansion at the needle valve, and the disturbance of the equilibrium resulting from the increase in volume of the gaseous phase as liquid carbon dioxide is drawn from the cylinder.

The fact that the liquid phase contains a different percentage of water from the gaseous phase made it necessary to take liquid carbon dioxide for analysis rather than samples from the gaseous phase. Analysis of the equilibrium mixtures of carbon dioxide in the two states with water showed that the gaseous phase contained about half the percentage of water that the liquid phase contained for the particular temperature and pressure.

The possibility that droplets of water or solid particles of water at low temperature might remain suspended in the liquid carbon dioxide appears to be very real. The fact that the method gives a somewhat regular decrease in solubility of water in liquid carbon dioxide with a decrease in temperature could hardly be explained if the suspension of water in the liquid carbon dioxide were at all stable. Hence, it has been assumed from a consideration of the densities of water, ice, and liquid carbon dioxide that, where water is in excess in the liquid state, the carbon dioxide liquid floats on top; at most temperatures at which the water is in the solid state, the water-ice floats on top of the liquid carbon dioxide.

The presence of iron in the water-rich phase was discovered when clear water which remained in the cylinder after the carbon dioxide had been exhausted was exposed to the atmosphere in an open beaker. On standing for some time open to the air, a brown gelatinous precipitate characteristic of hydrated basic iron appeared. If the carbon dioxide was swept from the clear solution by a rapid bubbling of air, the precipitate appeared at once. One of the cylinders was copper-plated on the inside to avoid this difficulty. Later the matter was disregarded when the applicability of the findings of Weibe and Gaddy (*4*) was recognized. They reported the probable formation of an iron bicarbonate and did quantitative work which indicated that the amount of iron dissolved under these circumstances was small. The error resulting from such small amounts of dissolved iron on the vapor pressure of water and hence its solubility in the liquid carbon dioxide is certainly of an order well outside the experimental limits of the work reported here.

WHEN liquid carbon dioxide changes to the gaseous state at the needle valve with a drop of pressure to that of the atmosphere, there is a refrigerating effect which might conceivably retain some of the water near the valve. Because the capacity for water of the gaseous carbon dioxide is much greater at one atmosphere than that of the liquid carbon dioxide at the relatively high pressure within the cylinder, because the valve was immersed in a thermostatically controlled water bath, and because the rate of flow was kept low (about 100 ml. per minute for the gas), it appears unlikely that this refrigeration effect resulted in incorrectly low values for the percentage of water found. Experimental variations in the rate of gas flow from 50 to 200 ml.

per minute were tried and gave no correlation with the deviation of the results. When the valve was not immersed in the water of the thermostat and the rate of gas flow was increased to 300 ml. per minute, moisture was seen to condense in the outlet tube from the valve. No such condensation was ever observed under the conditions at which the determinations were carried out.

The question of the disturbance of the equilibrium between the water-rich liquid phase and the carbon-dioxide-rich liquid phase was raised by the fact that, as liquid is drawn from the cylinder, the volume of the gaseous phase was increased. Since this phase is poorer in water at the 15–60 atmospheres range of pressure in the cylinder, the gradual loss of a greater percentage of carbon dioxide than of water to the gas phase might result in a supersaturation of the liquid carbon dioxide by water. Shaking the cylinder between determinations was tried with a view to minimizing this difficulty. However, this entailed the removal of the cylinder from the bath which upset the thermal equilibrium and introduced the possibility of entraining droplets of water in the siphon-valve part of the system. Since no noticeable change appeared in the values for the water content of the liquid carbon dioxide when this was done, much of the work was carried out without any other agitation than that provided by the vibration of the stirring motor of the bath. Also, the sample entered the siphon at a point close to the layer of water and at some distance from the interface between the liquid and the gaseous carbon dioxide; this fact likewise mitigated against the possibility that the sample of liquid carbon dioxide might become supersaturated with water as a result of the increasing volume of the gaseous phase.

It is realized that the values here reported leave much to be desired, but in view of the difficulties involved and the inadequacies of the existing published data, the results appear to be of fundamental importance.

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Properties of Detergent Solutions

THERMAL pH COEFFICIENTS OF ALKALINE SOLUTIONS

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THIS paper, the fourth of a series (*1*, *7*, *8*) concerned with the properties of detergent solutions, presents detailed pH data at 25°, 40°, and 60° C. on distilled water solutions of nine commercial alkalies sometimes used alone or in combination as laundry soap builders over concentration ranges of interest in laundry practice. Thermal pH coefficients, $\Delta pH/\Delta T$, for these builder solutions have been presented which permit the calculation of pH values at elevated temperatures from experimental data obtained at room temperature. The alkalies examined in the present work are: sodium hydroxide, sodium carbonate, sodium bicarbonate, trisodium phosphate, tetrasodium pyrophosphate, sodium tetraphosphate, sodium metasilicate, sodium sesquisilicate, and sodium orthosilicate.

In general, the technique and equipment were the same as that described in the first paper (*1*). Only electrometric methods were used, however. Some improvements in technique and apparatus design were made to secure greater accuracy and ease of manipulation. Both hydrogen electrode and glass electrode measurements were made on the same solution in most of the determinations. As a rule there was close agreement between the two measurements except for values obtained from solutions at elevated temperatures and very high pH where the sodium ion error was considerable.

METHODS AND APPARATUS

ELECTRICAL EQUIPMENT. Hydrogen electrode potentials were measured by a simplified Queen potentiometer with which readings could be made to the equivalent of less than 0.01 pH unit. Glass electrode potentials were measured by a Leeds & Northrup potentiometer-electrometer 7660-A which was calibrated to 0.002 volt (0.03 pH unit) and could be read accurately to the equivalent of the nearest 0.01 pH unit. National Technical Laboratories No. 1190E glass electrodes were used. These electrodes are especially adapted for use in alkaline solution and have very low sodium ion errors. All connecting electrical leads were well shielded.

PLATINUM ELECTRODES. 5 × 10 mm. electrodes were cut from platinum foil, mounted in the end of sealed glass tubes, and palladinized. A careful comparison of results obtained from both platinized and palladinized electrodes revealed negligible differences as long as the palladium coat was freshly formed. Upon continued use, a difference became noticeable and it must be assumed that the palladinized electrodes are in error; however, since they were much easier to clean and replate, they were used and freshly plated before each measurement. To secure uniform and reproducible coatings of palladium black, an apparatus was constructed whereby the cleaning and plating operations could be closely controlled. A current density of 160 milliamperes per sq. cm. applied to the electrodes for one minute while being electrolyzed cathodically in a 3 per cent palladium solution in hydrochloric acid produced a light, satisfactory coating. The palladium solution was prepared by electrolyzing a palladium wire in 1 to 1 hydrochloric acid until the proper weight of palladium had dissolved. The solution was maintained at approximately 3 per cent concentration by using a palladium wire anode for the plating operation.

ELECTRODE VESSELS. The vessels housing the electrodes and containing the test solution and saturated potassium chloride solution were made of Pyrex (Figure 1). Tubes *K* and *K'*, holding calomel electrodes *C* and *C'*, wet stopcocks *S* and *S'*, and all connecting capillary tubing to liquid junctions *J* and *J'*, are filled with saturated potassium chloride solution to which has been added a small amount of calomel. Tube *M* containing duplicate hydrogen electrodes *H* and *H'*, and tube *N* containing inter-

Improved apparatus for pH determination is described. pH data at 25°, 40°, and 60° C. are presented for distilled water solutions of nine commercial alkalies sometimes used alone and in combination as soap builders, including sodium hydroxide, sodium carbonate, sodium bicarbonate, trisodium phosphate, tetrasodium pyrophosphate, sodium tetraphosphate, sodium metasilicate, sodium sesquisilicate, and sodium orthosilicate. In general, multiple pH determinations check within 0.01 pH unit of the average. A linear equation and tables of constants provide for the calculation of pH values over the range 25–60° C. for the concentrations 0.01, 0.1, and 1 per cent to a close approximation. Thermal pH coefficients, in general, vary little with concentration and may be applied within the above limits to calculate pH at other temperatures from any base pH measurement.

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changeable glass electrode *G*, as well as drain tubes from these vessels to pinchcocks *P* and *P'*, are filled with the test solution to be examined. Hydrogen enters at *B* and is dispersed through a sintered glass disk, *F*, into a presaturator containing distilled water. Since the test solutions were dilute, there was not enough difference in vapor pressure to warrant the use of the test solution in the presaturator. Hydrogen thus presaturated carried into the test solution nearly the same amount of water as the escaping hydrogen carried out. Moreover, the hydrogen outlet at *E* was so designed that condensing vapor would not drain back into tube *M*. All electrical leads from the electrodes were run to switches which made it possible to connect any pair of electrodes to the potentiometers. Two complete assemblies were built. One of these was used at room temperature (25° C.) only, whereas the other was used at elevated temperatures.

Manipulating Technique. With all tubes filled and stoppered, all electrodes in place, hydrogen passing through the apparatus, and stopcocks and pinchcocks closed, the apparatus is allowed to stand in the constant-temperature bath until thermal equilibrium is attained. This requires from a few minutes to an hour or more, depending upon the temperature. The temperature of the bath is controlled to within 0.03° C. by thermoregulated heaters and ample stirring equipment. Stopcock *S* is then slightly opened to allow a small amount of saturated potassium chloride to flow up into the drain tube at *J* and is closed again. Electrical contact is readily obtained through the loosely closed stopcock which is covered with saturated potassium chloride solution. The pinchcock *P* is opened sufficiently to drain off excess potassium chloride in the drain tube and "wipe" a clean, sharp surface of contact between the potassium chloride solution and the test solution at opening *J* of the 1-mm. capillary tubing. The pinchcock is then closed. Hydrogen electrodes are adjustable vertically so that approximately half of the platinum foil is beneath the surface of the solution and the hydrogen gas bubbles strike them as they rise. Hydrogen electrode measurements may now be made.

The sequence of operations is repeated with corresponding parts of the equipment connecting with electrode vessel *N* which produces a liquid junction at *J'* and prepares the apparatus for glass electrode measurements. By interchanging two glass electrodes, *G* and *G'*, in vessel *N* and making proper connections between electrodes and potentiometers, it is possible to obtain eight e. m. f. measurements on two separate portions of the test solution. Four hydrogen electrode values result from electrode combinations *H* and *C*, *H* and *C'*, *H'* and *C*, *H'* and *C'*, and four glass electrode measurements from electrode pairs *G* and *C*, *G* and *C'*, *G'* and *C*, and *G'* and *C'*.

STANDARDIZATION

Potassium acid phthalate (sample 84a) as supplied by the National Bureau of Standards, was used as the primary standard (*2*). Beckman buffers, marked pH 4.00 ± 0.01, pH 7.00 ± 0.01, and pH 10.00 ± 0.01 at 25° C., were also used. The pH values for these buffers at elevated temperatures were supplied by the manufacturer; those obtained in the apparatus described checked within 0.01 pH unit of the specified values at all temperatures. A 0.05 molar sodium borate solution prepared from borax, which had been finely ground and stored in a large desiccator over saturated sodium bromide solution (*4*), proved to be a satisfactory buffer for routine checks. pH values for the borax buffer at elevated temperatures as calibrated against the phthalate buffer were 9.18 at 25° C., 9.06 at 40°, and 8.94 at 60°. Care was taken to avoid prolonged exposure of the buffers and solutions to atmospheric carbon dioxide.

Liquid-Junction Potential. Many factors in the construction and operation of the liquid-junction-forming apparatus described above ensure a minimum test solution || saturated potassium chloride liquid junction potential and maximum reproducibility. The contact area is about 1 sq. mm. and symmetrical, and never varies in shape or size (*3*). Saturated potassium

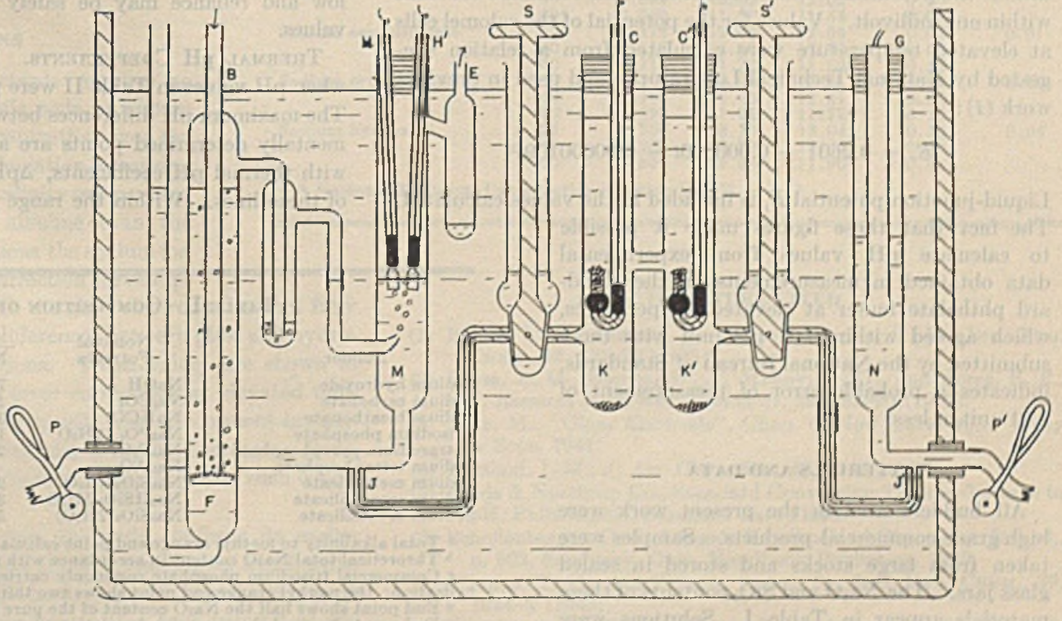
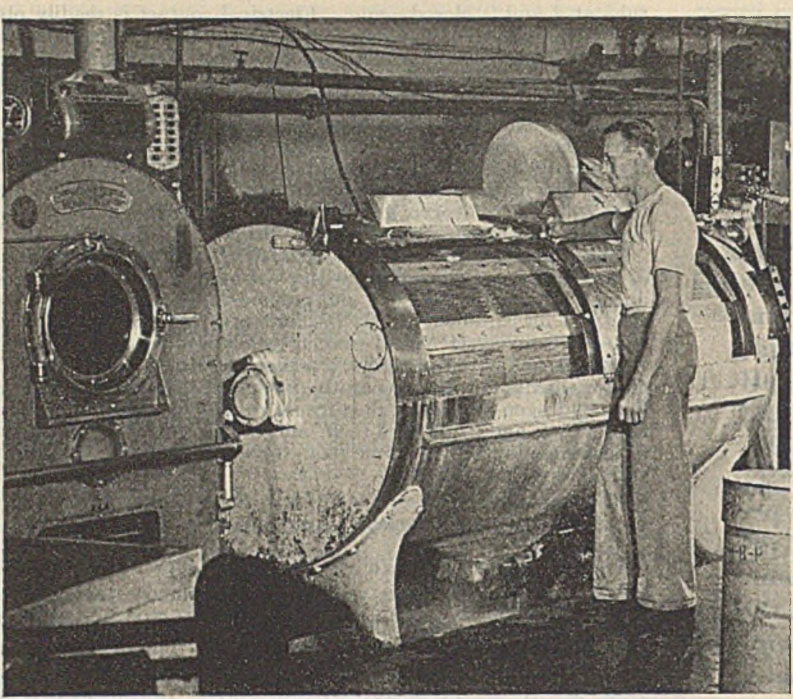


Figure 1. Glass and Hydrogen Electrode Assembly for pH Measurements



Modern Open-End and Shell Type Washers in a Commercial Laundry

chloride solution in contact with the dilute builder solutions provides a maximum difference in concentration and density. The potassium chloride solution contacts from below so that the action of gravity may be utilized in stabilizing the interface which is clearly visible during the pH measurements. Repeated measurements through newly formed liquid junctions have never indicated a detectable change in the liquid-junction potential.

Calomel Electrode Potentials. A number of saturated calomel electrodes were made and allowed to stand in saturated potassium chloride solution at the temperature under which they were to be used for several days. They were never allowed to change temperature during the entire series of measurements nor were they used at more than one temperature. Under these conditions the potentials of the calomel half cells remained constant within one millivolt. Values for the potential of the calomel cells at elevated temperature were calculated from a relation suggested by National Technical Laboratories and used in previous work (*1*):

$$E_c = 0.2601 - 0.000606t - 0.00000109t^2$$

Liquid-junction potential E_j is included in the values calculated. The fact that these figures made it possible to calculate pH values from experimental data obtained in measurements on the standard phthalate buffer at elevated temperatures, which agreed within 0.01 pH unit with those submitted by the National Bureau of Standards, indicates a probable error of measurement of 0.01 unit or less.

MATERIALS AND DATA

All builders used in the present work were high grade commercial products. Samples were taken from large stocks and stored in sealed glass jars. The Na_2O and SiO_2 contents of these materials appear in Table I. Solutions were made up in carbon dioxide-free distilled water. Measurements were always made on the solutions within a few hours after preparation.

Experimental data are presented in Table II. The pH values were calculated from hydrogen electrode data by the equation:

$$pH = (E + E_b - E_c) \div 0.00019832T$$

where E = observed potential
E_b = aqueous vapor pressure and barometric correction (*6*)
E_c = calomel electrode potential

pH values for glass electrode data were calculated from the following equation suggested by Leeds & Northrup Company (*5*):

$$pH = (E + 0.4529 + 0.00002t) \div 0.00019832T$$

where E = observed potential
t = ° C.
$T = 273.1 + t$

Each pH value recorded represents an average of the results of two to eight individual determinations. In general, these multiple pH readings were within 0.01 unit of the average. Since National Technical Laboratories No. 1190E electrodes were used for all glass electrode determinations, the sodium ion correction in solutions of 0.10 per cent or less are negligible at 25° C. Inasmuch as we had no correction table for sodium ion errors at elevated temperatures for use with the 1190E electrode, all glass electrode pH values are uncorrected. However, in every case where the error might be large, hydrogen electrode measurements were made. An examination of the differences in pH values as measured by the hydrogen electrode and glass electrode at high pH and temperature indicates that the sodium ion error increases not only with increasing pH but also with rising temperature.

Hydrogen electrode pH values are not recorded for solutions of sodium bicarbonate. There was a steady drift of potential during attempts to make such measurements. It would seem advisable to use a rocking-arm type hydrogen electrode for such measurements so that only a minimum amount of hydrogen passes through the solution. However, the pH values are relatively low and reliance may be safely placed in the glass electrode values.

Thermal pH Coefficients. Nearly straight lines resulted when pH values in Table II were plotted as pH *vs.* temperature. The maximum pH differences between these lines and the experimentally determined points are also shown in Table II, along with thermal pH coefficients, $\Delta pH/\Delta T$, representing the slopes of these lines. Within the range 25–60° C., pH values may be

Table I. Composition of Alkalies

Builder	Nominal Formula	Found, %		Theoretical, %	
		Na_2O[a]	SiO_2	Na_2O[b]	SiO_2
Sodium hydroxide	$NaOH$	76.5	...	77.5	..
Sodium carbonate	Na_2CO_3	58.1	...	58.5	..
Sodium bicarbonate	$NaHCO_3$	37.4	...	36.9	..
Trisodium phosphate	$Na_3PO_4.12H_2O$	18.5[c]	...	24.5	..
Tetrasodium pyrophosphate	$Na_4P_2O_7$	22.3[d]	...	46.6	..
Sodium tetraphosphate	$Na_6P_4O_{13}$	9.9[e]	...	39.6	..
Sodium metasilicate	$Na_2SiO_3.5H_2O$	29.5	28.15	29.2	28.3
Sodium sesquisilicate	$Na_3HSiO_4.5H_2O$	36.7	23.81	36.9	23.8
Sodium orthosilicate	$Na_4SiO_4(2H_2O)$	58.6	25.35	56.3	27.2

[a] Total alkalinity to methyl orange end point calculated as per cent.
[b] Theoretical total Na_2O content in accordance with formula.
[c] Commercial trisodium phosphate commonly carries less than 12 molecules of water of hydration; the methyl orange end point shows two thirds of the alkali present.
[d] End point shows half the Na_2O content of the pure compound.
[e] End point observed shows no simple relation to composition.

TABLE II. ELECTROMETRIC pH VALUES FOR SOLUTIONS AND THERMAL pH COEFFICIENTS[a]

Builder	Concn., %	25° C. H	25° C. G	40° C. H	40° C. G	60° C. H	60° C. G	A ΔpH/ΔT	B	Max. pH Deviation[b]
Sodium hydroxide	1.00	13.16	13.04	12.70	12.60	12.22	11.90	−0.026	13.78	0.02
	0.10	12.27	12.29	11.81	11.80	11.29	11.27	−0.028	12.96	0.02
	0.01	...	11.30	10.83	10.84	...	10.33	−0.027	11.96	0.03
Sodium orthosilicate	1.00	12.89	12.81	12.46	12.37	11.91	11.72	−0.028	13.59	0.00
	0.10	12.02	12.01	11.58	11.57	11.02	10.95	−0.028	12.72	0.00
	0.01	11.01	11.00	10.56	10.55	10.02	10.03	−0.028	11.70	0.01
Sodium sesquisilicate	1.00	12.68	12.64	12.23	12.14	11.72	11.59	−0.027	13.35	0.02
	0.10	11.80	11.79	11.34	11.34	10.83	10.83	−0.027	12.40	0.03
	0.01	10.71	10.69	10.28	10.28	9.86	9.87	−0.024	11.28	0.03
Sodium metasilicate	1.00	12.45	12.44	12.02	12.02	11.53	11.54	−0.026	13.08	0.01
	0.10	...	11.55	...	11.14	10.62	10.64	−0.026	12.20	0.01
	0.01	10.56	10.55	10.14	10.15	9.71	9.71	−0.024	11.15	0.02
Trisodium phosphate	1.00	12.00	11.99	11.60	11.59	11.22	11.22	−0.022	12.53	0.02
	0.10	11.31	11.31	...	10.91	10.65	10.63	−0.019	11.74	0.05
	0.01	10.29	10.29	9.84	9.85	9.65	9.65	−0.018	10.67	0.08
Tetrasodium pyrophosphate	1.00	10.16	10.17	10.04	10.03	9.64	9.65	−0.014	10.55	0.06
	0.10	...	10.03	...	9.89	9.65	9.64	−0.011	10.32	0.02
	0.01	9.50	9.50	9.36	9.36	...	9.23	−0.008	9.69	0.02
Sodium tetraphosphate	1.00	8.03	8.03	8.08	8.09	8.10	8.11	+0.002	7.99	0.02
	0.10	8.70	8.69	8.78	8.78	8.72	8.73	0.000	8.74	0.04
	0.01	8.83	8.82	8.67	8.68	8.50	8.51	−0.001	8.85	0.01
Sodium carbonate	1.00	11.25	11.26	10.99	10.97	10.61	10.62	−0.018	11.70	0.01
	0.10	...	10.94	...	10.65	10.29	10.30	−0.019	11.42	0.01
	0.01	10.40	10.40	10.09	10.09	...	9.74	−0.019	10.86	0.02
Sodium bicarbonate	1.00	...	8.18	...	8.10	...	8.14	−0.001	8.18	0.04
	0.10	...	8.43	...	8.37	...	8.48	+0.001	8.37	0.06
	0.01	...	8.28	...	8.07	...	8.08	−0.005	8.33	0.08

[a] H indicates hydrogen electrode values and G indicates glass electrode values.

[b] From linear relation.

calculated for the several builders at 0.01, 0.1, or 1.0 per cent concentrations from the relation,

$$\text{pH} = At + B$$

where t = temperature, ° C.,
A, B = constants from Table II ($A = \Delta\text{pH}/\Delta T$)

or for any concentration, if a base pH value is known, by the relation

$$\text{pH}_{t_2} = \text{pH}_{t_1} + A(t_2 - t_1)$$

where the approximate value of A is determined with reference to concentration range from Table II.

CONCLUSIONS

The No. 1190E glass electrode requires no sodium ion correction in caustic soda or silicate solutions at 0.1 per cent concentration over the range 25–60° C. but shows a deviation increasing with temperature and with alkalinity in 1 per cent solutions which are more alkaline than the metasilicate. For these solutions the sodium ion correction as obtained from a correction curve supplied by the manufacturer with the glass electrode does not fully account for the experimental differences between glass and hydrogen electrode pH determinations. These values are shown in Table III. Data for sodium error corrections at elevated temperatures are not available, but results from the present investigation included in Table III indicate a rapidly increasing divergence and the probable magnitude of the error under such conditions.

Nevertheless, the 1190E glass electrode confirms its earlier promise of greatly extending the alkaline ranges over which satisfactory pH measurements could be made, with or without sodium ion corrections. No difficulties have arisen from using it at elevated temperatures.

The data of Table II will aid in closing some of the gaps in the pH literature at higher temperatures. The effect of increased temperature is generally to lower pH in alkaline solutions. Thus for 1 per cent caustic soda solutions, an increase from 25° to 60° C. causes the pH to fall 0.94 pH unit; sodium metasilicate, 0.71 unit; tetrasodium pyrophosphate, 0.52; and sodium bicarbonate 0.04. These differences are reflected in the temperature coefficients, whose values are little affected by concentration for the stronger bases but become more variant for the milder alkalies.

Much theory attempting to relate pH and detergency in the past has suffered from nonavailability of reliable pH data at the elevated temperatures of detergent processes. The mutual effects on pH of soap and builder in combination at higher temperatures have been shown to be considerable for the modified soda-soap system (*1*). Much similar work for other soaps and other builders, correlated directly with detergency studies, appears to be prerequisite to further broad generalizations on pH-detergency relations.

TABLE III. GLASS ELECTRODE ERRORS

Substance	Temp., ° C.	Sodium Normality	pH Hydrogen	pH Glass	pH Difference	Na Ion Cor.[a]
Sodium metasilicate	25	0.099	12.45	12.44	0.01	0.01
	40	0.099	12.02	12.02	0.00	
	60	0.099	11.53	11.44	0.09	
Sodium sesquisilicate	25	0.118	12.68	12.64	0.04	0.01
	40	0.118	12.23	12.14	0.09	
	60	0.118	11.72	11.59	0.13	
Sodium orthosilicate	25	0.190	12.89	12.81	0.08	0.03
	40	0.190	12.46	12.37	0.09	
	60	0.190	11.91	11.72	0.19	
Sodium hydroxide	25	0.250	13.16	13.04	0.12	0.04
	40	0.250	12.70	12.60	0.10	
	60	0.250	12.22	11.90	0.32	

[a] National Technical Laboratories, drawing C-90E.

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BORATED RESINS

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Boric acid reacts readily with macromolecular substances such as cellulose esters and ethers and partially hydrolyzed polyvinyl esters and acetals, which contain a plurality of hydroxyl groups per molecule. The products formed are spatially linked, insoluble, infusible boric acid esters or esterlike association compounds. These compounds are hydrolyzed by mere contact with water or alcohols and regenerate the original thermoplastic resin without change. Various uses can be made of this effect—for example, in the production of thermoplastic and rubberlike materials in the form of fine powders or in temporary protective coatings; marginal additions of acid boric provide a means of sensitive control of molding materials and in film casting.

THE reactions of boric acid with monohydric alcohols follow the normal course of esterification. Combination takes place slowly in the absence of catalysts but is markedly accelerated by mineral acids. In the case of polyhydric alcohols, however, esters form readily, even without acid catalysts. This trend is still more pronounced in the action of boric acid upon macromolecular substances which carry multiple numbers of hydroxyl groups on every molecule. This description applies to many technically important plastics such as polyvinyl alcohol, partially hydrolyzed polyvinyl esters and acetals, and cellulose esters and ethers.

Solutions of these resins are viscous fluids. Upon addition of small amounts of boric acid these solutions change quickly into elastic gels which are insoluble, nonadherent soft solids, containing the original solvent as dispersed phase. The presence of water or alcohols prevents this phenomenon entirely, and their addition even in small amounts causes the gelled body to revert to the condition of a viscous fluid solution. When the solvents are evaporated, the resins are obtained in the form of insoluble and infusible masses from which, however, they can be recovered in their original condition by contact with water or alcohols. The same effect is observed if boric acid is added to the resins on hot mixing rolls: they lose their plasticity and are converted into loose infusible masses which, upon repeated passage, disintegrate into powder.

These observations are readily explained, considering that boric acid is tribasic and capable of forming spatially interlinked polyesters with the macromolecular polyalcohols. The resulting structures are a continuous phase whose formation forces solvents and plasticizers present to disperse within its network of fixed and bridged macromolecules. The whole system assumes the character of an insoluble and infusible gel.

That the bridging is brought about by the formation of boric acid esters or some type of more loosely bound complexes of analogous structure is supported by the following facts: Polyvinyl alcohol which is entirely insoluble in the lower aliphatic alcohols dissolves readily in warm methanol in the presence of one mole of boric acid, and this solution tolerates the addition of considerable quantities of benzene. This clearly indicates that polyvinyl alcohol is not present as such but in combination, evidently with boric acid. All insolubilized borated resins release boric acid and are recovered unchanged if treated with water. For example, a polyvinyl acetal resin (Alvar) rendered entirely insoluble by treatment with 2 to 5 per cent boric acid and drying, remains entirely unaffected by dioxane which is normally an excellent solvent for it; upon addition of a few per cent of water, it dissolves immediately. The same borated resin, suspended in water and heated, coalesces at exactly the same temperature as the untreated resin but fails to do so in a saturated aqueous solution of boric acid. The same observations can be made with plasticized cellulose acetate, using acetone. That the available alcohol groups of the borated resin are actually engaged is indicated by the fact that efficient esterification agents, such as acetic and phthalic anhydrides and benzoyl, phthalyl, and phosphorus chlorides, are almost without effect. Acetalization also fails.

Quantitative experiments were carried out by placing a resin solution of known concentration into a miniature mixing machine and adding successive small amounts of boric acid. Incipient gelation could be observed clearly by the motion, adhesion, and cohesion of the material. Beyond a certain minimum of boric acid sufficient to effect the phase inversion, further additions caused little change. Agents capable of restoring fluidity, such as water, methanol, cetyl alcohol, ethylene glycol, etc., seem to be effective in a stoichiometric ratio relative to the macromolecular alcohol but not to the boric acid present.

The minimum of boric acid required to cause gelation depends on the chain length of the macromolecules. Evidently, if at least two points of every chain molecule must be fixed in order to produce a continuous lattice, the effective amount of boric acid should be inversely proportional to the molecular weight of otherwise similarly constituted macromolecules. For example, two analytically comparable polyvinyl acetal resins made from different polyvinyl acetates (solution viscosities,15 and 95 centipoises, respectively) required 0.30 and 0.15 per cent boric acid to become completely insoluble. The smallness of these amounts shows that only a few bridges are required for effective lattice formation and that the yield per boric acid molecule must be high.

All polyvinyl resins are mixtures of polymer homologs varying greatly in molecular weight. If an insufficient amount of boric acid is added to a solution, the longest and most susceptible molecules are precipitated while the shorter ones remain in solution. By this means sharp fractionations can be effected without need of the exacting control of conditions on which the usual precipitation methods depend. For example, a polyvinyl acetal resin (Alvar 7-90, containing 8.2 per cent polyvinyl alcohol) in toluene solution was treated with 0.6 per cent boric acid which precipitated a firm gel and left an approximately equal quantity of resin in solution. The two fractions were boiled with water, dried, and compared (Table I, *A*). Fractionation of the same resin with the same amount of boric acid but in a different solvent (80 toluene–20 xylene) gave almost the same result. This is in accord with the fact that the insolubilized portion is generally insoluble because of its structure (Table I, *B*). The precipitated portion of *A* was redissolved, treated twice again under the same conditions, and yielded only negligible amounts of soluble materials whose viscosities fell within less than 5 per cent of that of the first crop. The data under *C* refer to another resin (Alvar 15-70, 5.6 per cent polyvinyl alcohol), similarly treated. The constancy of the analytical values shows that only the molecular weight is subject to fractionation.

The action of boric acid on macromolecular substances containing hydroxyl groups is essentially one of vulcanization or curing. However, unlike the permanent change brought about in rubber or thermosetting plastics, this effect is immediately and completely reversible, merely by contact with water. It is possible, therefore, to convert thermoplastic resins into inert, insoluble, and infusible masses for the convenience of some operation, and afterwards to recover them unchanged by washing or leaching with water.

TABLE I. ANALYSIS OF POLYVINYL RESIN FRACTIONS

Fraction	Viscosity in 5% Toluene Soln., Centipoises			Polyvinyl Acetate, %			Polyvinyl Alcohol, %		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Original	5.83	11.16		14.8	40.0		8.20		5.60
Soluble	3.56	3.36	5.62	....	....	....	7.35	....	....
Insoluble	7.46	6.95	13.47	15.0	15.1	....	8.22	8.25	....

FINELY POWDERED THERMOPLASTICS

The task of comminuting thermoplastic materials is limited by their nature. Devices based on attrition are useless because of the difficulty encountered in dissipating the generated heat. Crushers using the impact principle cannot reduce tough plastics below a particle whose mass is insufficient to provide the energy required for further shattering at any safe speed of the machine. This limit is usually between 30 and 50 mesh.

If, however, the thermoplastic material has been converted into a heat-insensitive form by treatment with boric acid, it can be ground or crushed in this condition by any effective means and to any required fineness (patents assigned to Shawinigan Chemicals Ltd.). This actually has been done with thermoplastic resins which are among the toughest types known: high-polymer polyvinyl formals (Formvars), acetals (Alvars), butyrals (Butvars, used in safety glass and rubber substitutes), as such or combined with large amounts of plasticizers; plasticized cellulose acetates and acetate-butyrates (Tenites); high-molecular cellulose ethers, etc. All these materials are converted into brittle infusible masses upon admixture of 2 to 5 per cent boric acid and can be reduced to fine powders with such ease that a single pass through a small impact crusher connected with an air-floating train yielded about 60 per cent fines passing 100 mesh, the remainder containing little material coarser than 80 mesh.

These fine powders can be leached free from boric acid by stirring with a few changes of water. They are then again thermoplastic and must be dried at a low enough temperature to avoid coalescence. The dry powders are dense, free flowing, and stable; they are in substance identical with the original materials.

Plasticizers do not interfere with the process even if present in high amounts. They are converted into dispersed phases and accompany the resin through all operations without imparting plasticity but assume again their original function in the recovered material. Their amount is limited only by considerations of stability of the powder under storage conditions.

These fine thermoplastic powders cannot be obtained by any other known methods and represent a new type of product. It is not improbable that their availability in quantity and variety may stimulate entirely novel applications in many fields. Promising trials have been conducted with unplasticized, high-polymer, polyvinyl formal (Formvar 15-95) powders in the Schori gun. The powder is sprayed through the flame of a gas torch upon metal surfaces where it forms a substantial, highly resistant coating. Borated or recovered resin powders of this type are of interest in the making of abrasive tools.

MOLDING

In making resin powders by the above method, enough boric acid must be used to assure the formation of rigid molecular lattices. By employing smaller or marginal amounts, various physical properties can be sensitively adjusted.

For example, the usefulness of thermoplastic resins for injection molding depends not only on their respective fluidities under given temperature conditions, but also on some constitutional factor which may be described as the ability to transmit a directed force as such, without dissipating it in form of hydrostatic pressure. It appears that this quasi solid quality is closely connected with the presence of a lattice structure which, in more or less effective disposition and continuity, is superimposed upon the essentially fluid substance of the resin. If it is lacking, proper performance in the injection machine cannot be assured by either higher temperatures or increased admixture of plasticizers. Thus, most plasticized cellulose acetates (Tenites) inject more easily into intricate molds than certain polyvinyl acetal (Alvar) compounds, in spite of the fact that their absolute fluidities (measured by outflow through a heated steel capillary under high pressures) are much lower. In Table II temperatures of equal fluidity are given together with temperatures at which molded articles begin to deform or "unmold". It appears that the more easily injectable Tenites are generally more rigid than the Alvar compounds. Addition of boric acid to the latter tends to narrow the differences among the recorded temperatures; at the same time it actually improves the injectability, form stability, tolerance for plasticizers, and resistance against solvent action of the Alvars.

TABLE II. FLUIDITY AND SOFTENING TEMPERATURES

Resin	Equal Fluidity Point, ° C.	Softening Point, ° C.
Tenite H[a]	125	125
Tenite MS[a]	125	120
Alvar 11-90[b], 5% plasticizer[c]	93	64
+0.5% boric acid	100	70
+1.0% boric acid	108	74
Alvar 11-90, 10% plasticizer	90	50
+0.5% boric acid	95	54
+1.0% boric acid	100	65

[a] Cellulose acetate (Eastman).
[b] Polyvinyl acetal (Shawinigan).
[c] Dibutyl phthalate.

Mottled moldings are made from mixed granulated plastics of different colors and flowing properties. The latter must be carefully adjusted in order to produce precisely repeatable effects; this is very conveniently done by addition of boric acid within a range of a few tenths of one per cent.

INSOLUBLE FILMS FROM SOLUTIONS

Where insoluble films are required, present practice employs solutions of heat-reactive resins which, after evaporation and baking, are rendered insoluble by an irreversible chemical process. Borated thermoplastic resins can be deposited from solutions which are maintained in fluid form by small additions of water or alcohol to the solvent. When evaporated to dryness, the coatings are insoluble except in solvents containing water or alcohol; they are also light colored and unaffected by heat. Films of this kind may find many practical applications as protective coatings for temporary use.

Table III. Effect of Boric Acid on Speed of Film Casting

Film	Min. after Casting	Load, Lb./Sq. In.	Sec. under Load	Elongation, %
Blank	6	15	Too soft	
Borated	6	15	Too soft	
Blank	9	20	10	Broke
Borated	9	20	30	150
Blank	11	30	5	Broke
Borated	11	30	60	100
Blank	15	30	30	Broke
Borated	15	30	Permanent	50
Blank	18	30	60	200
Borated	18	30	Permanent	Nil

For example, 25 parts of a polyvinyl acetal resin (Alvar 15-80) and 5 parts dibutyl phthalate are dissolved in 70 parts ethyl acetate containing 2 per cent water. To this solution are added 0.5 part boric acid, enough to cause complete insolubility of the evaporated film but not enough to make it brittle. In this condition it is neither dissolved nor softened by dry ethyl acetate or any other anhydrous nonalcoholic solvent but dissolves at once if small amounts of water or alcohol are added to the latter.

The capacity of borated resins to hold plasticizers or solvents dispersed as an internal phase is remarkable, amounting to proportions as high as 1:15 or more. These compounds are nontacky nonsweating gels which can be used in the preparation of hectograph masses, coatings for printing rolls, etc.

As an illustration, the above example of an insoluble coating can be modified to a mixture of 20 parts resin and 80 parts dibutyl phthalate, dissolved in 40 parts ethyl acetate containing 2 per cent water and 0.4 part boric acid. When cast, the viscous but entirely fluid solution leaves a firm nontacky gel, which absorbs and retains printing inks, stains, and dyes, and is little affected by temperature changes. It is generally insoluble but can be readily dissolved and recast using aqueous solvents.

FILM CASTING

An important factor in casting films from solutions by the usual methods is the rate at which the solvent is released in the final stage when the film is supposed to become self-supporting. In many cases small amounts of solvent are retained so tenaciously that subsequent operations are seriously delayed; in nearly all cases faster and more economical casting would result if the tensile strength of the "green" film could be improved without resorting to enforced drying methods. This is readily achieved by the phase inversion caused by small amounts of boric acid added to responsive film-forming media, such as all cellulose derivatives and polyvinyl acetal resins. Although the last remnants of solvent are not removed, these films gel upon reaching the stationary retentive condition and assume full physical strength which allows subsequent handling without delay.

The data in Table III show this effect in films cast from a solution of 100 parts polyvinyl acetal resin (Alvar 15-80) in 250 parts ethyl acetate containing 5 parts water and 2 parts boric acid. The films were cast on a glass plate, lifted after a given number of minutes, and immediately placed under load. Blank tests were carried out without boric acid.

Table IV. Effect of Boric Acid on Sintering Temperature

Boric Acid, %	% Elongation at 80 ° C. after: 5 min.	25 min.	60 min.	Sintering Point, ° C.
None	Infinite	...	..	135
0.2	300	Infinite	..	175
0.5	25	100	..	180
1.0	12	20	25	195
2.0	Nil	4	6	205

Entirely analogous results were obtained with the same resin plasticized with 15 per cent triethylene glycol hexoate, using the same solvent, and also with a solution of 60 parts cellulose acetate, 40 parts triacetin, and 2 parts boric acid in 400 parts methyl ethyl ketone containing 2 per cent water.

In amounts up to 2 per cent, boric acid remains dissolved or homogeneously dispersed in the films and does not interfere with their transparency. It contributes markedly to their heat resistance as shown in Table IV. Films of the polyvinyl acetal resin referred to in Table III (Alvar 15-80) were completely dried at 60° C. and suspended at 80° C. under a load of 50 pounds per square inch. The sintering temperatures were observed by slowly heating without load.

High-Temperature Heat Content of CALCIUM CARBIDE

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PART of the program of thermodynamic investigation of metallurgically important substances being conducted at this station involves measurement of heat contents above 25° C. by the so-called drop method; this paper presents some data obtained on a high-grade commercial sample of calcium carbide in the range 200° to 1000° C. This sample was part of that used by Kelley (*2*) in low-temperature specific-heat measurements, and it is probably of the highest purity available at present (91 per cent). Although there is considerable uncertainty in correcting for the impurities, it nevertheless seemed desirable to obtain and report these data on this important substance.

▶ THE method and apparatus were described previously (*5*). The sample was contained in a sealed platinum-rhodium alloy capsule; there was some action of the carbide on the container after the measurements at 1000° C., but it was insufficient to cause any appreciable error. The error in the measurements is certainly not more than one per cent throughout the entire range studied, and the results are in general reproducible to a few tenths per cent.

Correction was made for the major impurities reported by Kelley (*2*)—namely, 6.47 per cent CaO, 1.15 per cent SiO_2, and 0.77 per cent Al_2O_3—using data from his tables (*3*). The mate-

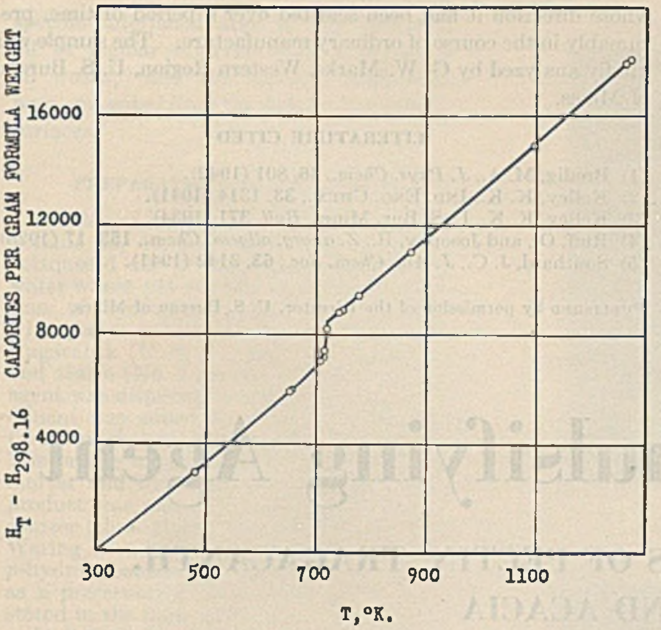

Figure 1. Heat Content of Calcium Carbide above 298.16° K.

rial was not reanalyzed, but it had been carefully preserved in a sealed glass container during the interim between Kelley's work (*2*) and the present measurements. The correction for these impurities averages about 2 per cent, and as the assumption of additivity of special heats may be considered only as an approximation, an over-all accuracy of better than 2 per cent cannot be claimed.

The results, expressed in defined calories (1 calorie = 4.1833 International joules) are assembled in Table I. Column 1 gives the absolute temperature, and column 2 the heat liberated per gram of material in dropping from temperature *T* to 298.16° K.; all results are corrected to this final temperature. Column 3 presents the result of correcting column 2 for the major impurities, and column 4 gives the heat content per gram molecular weight of calcium carbide (64.10 grams, in accordance with the 1941 International Atomic Weights). The latter are shown also in Figure 1.

Table I. High-Temperature Heat Content of Calcium Carbide

T, ° K.	$H_T - H_{298.16}$, cal./gram	$H_T - H_{298.16}$, cal./gram (cor.)	$H_T - H_{298.16}$, cal./gram mol. wt.
$652._3$	90.9_5	92.5_1	5,930
$653._3$	91.2_6	92.8_5	5,950
$657._2$	91.7_3	93.2_9	5,980
$873._3$	168.6	172.1	11,030
$873._2$	169.0	172.5	11,060
$1097._6$	230.3	234.0	15,000
$1096._9$	230.1	234.0	15,000
1271	277.7	281.4	18,040
1262	275.5	279.2	17,900
$481._2$	45.0_9	45.8_7	2,940
$480._8$	45.2_4	46.0_2	2,950
$778._6$	143.4	147.0	9,420
$715._5$	113.0	115.0	7,370
$741._5$	134.5	137.9	8,840
$719._9$	125.6	128.2	8,220
$708._1$	108.3	110.0	7,050
$749._4$	135.3	138.5	8,880

Table II. High-Temperature Heat Content and Entropy of Calcium Carbide above 298.16° K. at 100° Intervals

T, ° K.	$H_T - H_{298.16}$, cal./gram mol. wt.	$S_T - S_{298.16}$, cal./gram mol. wt./deg.	T, ° K.	$H_T - H_{298.16}$, cal./gram mol. wt.	$S_T - S_{298.16}$, cal./gram mol. wt./deg.
400	1600	4.62	800	9,790	18.32
500	3260	8.32	900	11,520	20.36
600	4995	11.47	1000	13,250	22.19
700	6760	14.19	1100	15,020	23.87
720[a]	7120	14.70	1200	16,780	25.41
720[b]	8450	16.55	1300	18,590	26.86

[a] Low-temperature form.
[b] High-temperature form.

Table II summarizes values read at even 100° C. intervals from the smooth curve through the data, together with the calculated entropy increments from 298.16° K. to temperature *T*.

▶ THE only previous measurements in this range are three results reported by Ruff and Josephy (*4*), which differ from the present values by an average of about 10 per cent. In view of the differences in experimental methods and the fact that uncertainties in both methods are greatest near room temperature, the data reported here agree satisfactorily with Kelley's results at room temperature.

* * *

Determinations of the heat content, above 25° C., of a sample of calcium carbide of 91.0 per cent purity were made in the range 200° to 1000° C. Correction for the major impurities was applied. The data show a transition at 447° ± 5° C., with a heat effect of 1330 calories per gram molecular weight. Below the transition temperature the data are represented by the equation:

$$H_T - H_{298.16} = 16.40T + 1.42 \times 10^{-3} T^2 + \frac{2.07 \times 10^5}{T} - 5710$$

and above the transition by the equation:

$$H_T - H_{298.16} = 15.40T + 1.00 \times 10^{-3} T^2 - 3156$$

* * *

The data show a transition at 720° ± 5° K. (447° C.) with an accompanying heat effect of 1330 calories per gram molecular weight. Bredig (*1*) reported the existence of a transformation in this region, to which he assigned the temperature 450° ± 20° C.; the work described in the present paper was done before Bredig's work was published and constitutes an independent observation. As the method employed in the present work involves mild quenching of the sample in each measurement, presumably the final form was the one designated "III" by Bredig, and the transformation observed here is III → IV (tetragonal → cubic). The other forms described by Bredig are not involved in these measurements. Assuming that the entropy obtained by Kelley at 298° K. is that of the usual tetragonal form (III) and hence that of the final state of these measurements, the application of these data above 450° C. is unambiguous.

The following equations express the heat content above 298.16° K. and the heat capacity per gram molecular weight for each of the two forms as a function of the absolute temperature within the indicated range. The equations for C_p were obtained by differentiating the heat content equations.

From 300° to 720° K.:

$$H_T - H_{298.16} = 16.40\,T + 1.42 \times 10^{-3}\,T^2 + \frac{2.07 \times 10^5}{T} - 5710 \quad (1)$$

$$C_p = 16.40 + 2.84 \times 10^{-3}\,T - \frac{2.07 \times 10^5}{T^2} \quad (2)$$

From 720° to 1275° K.:

$$H_T - H_{298.16} = 15.40T + 1.00 \times 10^{-3}\,T^2 - 3156 \qquad (3)$$

$$C_p = 15.40 + 2.00 \times 10^{-3}\,T \qquad (4)$$

Equation 1 was derived from $C_p = 14.93$ at 298.16° K. (*2*) and two heat content values from Table II; it fits the data to 0.4 per cent. Equation 3 represents the data to about 0.2 per cent.

ACKNOWLEDGMENT

The sample of calcium carbide was furnished by the National Carbide Corporation through the courtesy of F. Pruyn, Jr., under whose direction it had been selected over a period of time, presumably in the course of ordinary manufacture. The sample was kindly analyzed by G. W. Marks, Western Region, U. S. Bureau of Mines.

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Pectin as an Emulsifying Agent

COMPARATIVE EFFICIENCIES OF PECTIN, TRAGACANTH, KARAYA, AND ACACIA

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Pectin as an emulsifying agent is compared with gums tragacanth, karaya, and acacia in a study of aqueous emulsions of olive, cottonseed, and mineral oils under various conditions of acidity, ratio of oil to water, and concentration of agent by measurement of changes with time in the specific interfacial surface of the dispersed oil, hydrogen-ion concentration, and viscosity.

THE importation of gums tragacanth, karaya, acacia, and carob was approximately 24 million pounds in 1939 (*9*). Shipping difficulties have curtailed the importation of these gums, and it has therefore become advisable for the pharmaceutical, cosmetic, and food industries to look for satisfactory domestic substitute materials. Pectin, potentially available from the culls and cannery wastes of apples and citrus fruits in amounts in excess of 50 million pounds per year, has shown promise. Goldner and other investigators (*1*, *7*) have declared pectin unsatisfactory as a substitute emulsifying agent for tragacanth and acacia. However, in a subsequent paper Goldner (*2*) reversed himself and pronounced pectin satisfactory.

So far as can be ascertained, no quantitative study has been made on the relative merits of pectin and these gums as emulsifying agents. King and Mukherjee (*3*, *4*), in defining the stability coefficient of an emulsion as the reciprocal of the rate of change of the interfacial area per unit area of fresh emulsion interface, established a quantitative criterion of emulsion stability. The present study was undertaken to determine quantitatively the stability of emulsions of olive oil, cottonseed oil, and mineral oil with water, stabilized with pectin, tragacanth, karaya, and acacia under diverse conditions of acidity, ratio of oil to water, and concentration of emulsifying agent. Changes in the emulsions were followed by measuring the pH, viscosity, and

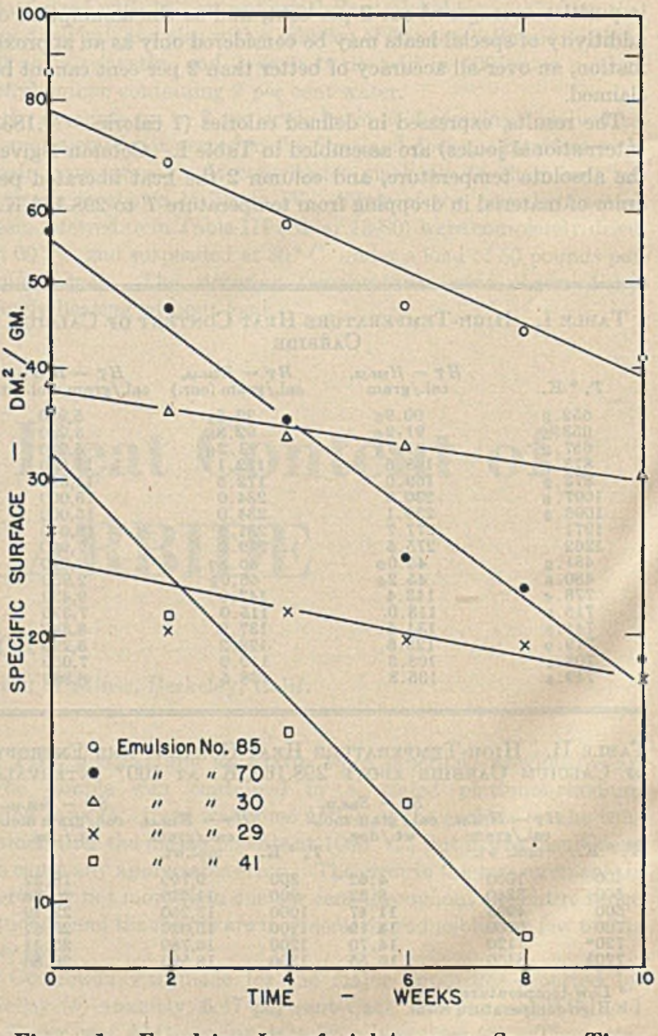


Figure 1. Emulsion Interfacial Areas *vs.* Storage Time

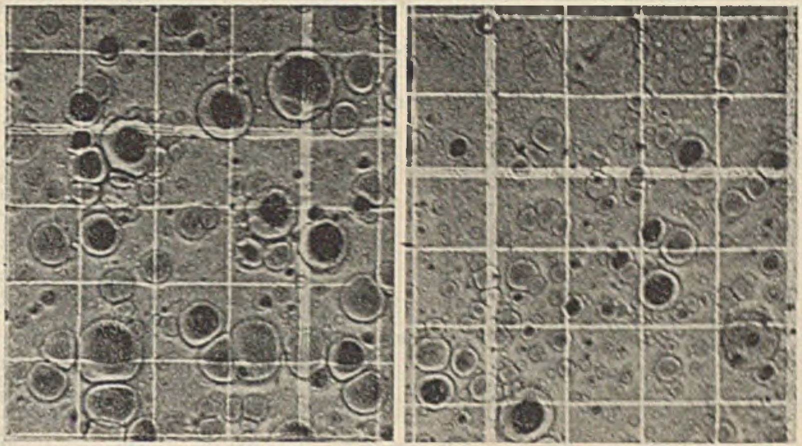
specific interfacial area of the dispersed oil at regular intervals over a period of 10 weeks; and the stability coefficients were computed from the data on the specific surfaces.

PREPARATION OF EMULSIONS

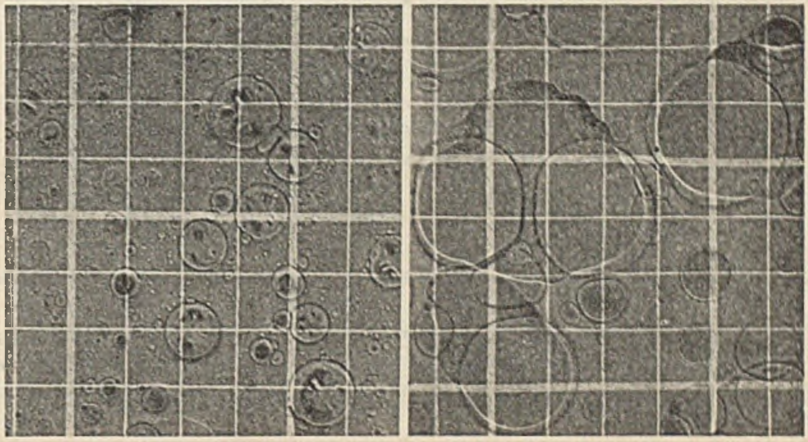
Emulsions were made up to contain by volume 25, 40, and 60 per cent olive oil, cottonseed oil, or mineral oil dispersed in water whose pH was adjusted by the addition of hydrochloric acid and stabilized with pectin (citrus, 200 grade, rapid set), tragacanth (U. S. P.), karaya (xxx grade), and acacia (No. 1 grade). The emulsifying agent was dispersed in the oil, and then the diluent was added at one time. The mixture was shaken in a jar until emulsified. The coarse emulsion was transferred to a mortar and triturated until smooth. The product was passed through a hand homogenizer (three times) and finally mixed in a Waring Blendor for 10 minutes. Methyl-*p*-hydroxybenzoate (0.1 per cent) was added as a preservative, and the emulsions were stored in the dark at 22° C.

At 2-week intervals photomicrographs of the emulsions were taken at a magnification of 144 to 200 times. A Spencer bright-line hemacytometer was used as a slide, and the exact magnification was determined from the lines on the hemacytometer. The method used in calculating the specific interfacial areas by means of size-frequency analysis of the photomicrographs was described by King and Mukherjee (*3*). A glass electrode potentiometer was used in measuring the hydrogen-ion activities; a Stormer viscometer, calibrated against a series of aqueous glycerol solutions of known viscosities (*8*), was used to measure the viscosities in centipoises of the emulsions at 22° C.

Pectin Emulsion 29 Tragacanth Emulsion 41



Freshly prepared (× 192) Freshly prepared (× 194)



After 10 weeks (× 144) After 10 weeks (× 144)

Figure 2. Degradation of Comparable Emulsions Stabilized with Pectin and Tragacanth

EMULSION STABILITY

To represent numerically the stability of these emulsions, it is convenient to assume that the specific surface changes with time in some simple mathematical manner. King and Mukherjee (*4*) assumed that the rate of change of the specific surface of an emulsion is proportional to the initial specific surface of the emulsion. However, in plotting their data they found it necessary to assume two rates, an initial rapid change followed by a much slower change. This behavior suggests that the change in the specific surface may be an exponential function of the time. Therefore, in treating the present data it was assumed that the rate of change of the specific surface at any time is proportional to the specific surface at that time. In other words,

Table I. Data for 40 Per Cent Olive Oil Emulsions

No.	Wt. % Stabilizer	pH of Diluent	pH of Emulsion		Viscosity, Centipoises		Initial Sp. Surface σ_0, Sq. Dm./G.	Stability Coefficient *k*, Weeks
			0 days	60 days	0 days	60 days		
			Pectin-Stabilized Emulsions					
1	0.5	6.5	4.5	4.6	98	B	17	5
2	0.5	2.6	2.9	3.0	79	60	26	17
3	0.5	1.6	1.7	2.0	74	43	51	4
4	1	6.5	3.8	3.9	500	380	24	50
5	1	2.6	3.0	3.8	400	12	46	3
6	1	1.6	1.9	2.0	325	275	46	50
7	1.5	6.5	3.9	4.2	1700	50	23	>200
8	1.5	2.6	3.0	3.0	1600	1500	37	43
9	1.5	1.6	2.0	2.0	1100	1000	56	>200
			Tragacanth-Stabilized Emulsions					
10	0.5	6.5	5.9	4.8	120	25	15	8
11	0.5	2.6	3.7	3.7	110	95	18	9
12	0.5	1.6	1.8	1.9	90	50	17	14
13	1	6.5	5.9	4.1	480	145	29	10
14	1	2.6	4.0	4.0	485	325	14	17
15	1	1.6	2.0	2.1	375	200	24	>200
16	1.5	6.5	5.8	4.4	2000	42	12	29
17	1.5	2.6	4.0	3.6	2000	43	17	17
18	1.5	1.6	2.1	2.3	1500	600	28	>200
			Acacia-Stabilized Emulsions					
19	1	6.5	5.6	5.6	10	9	89	17
20	1	2.6	3.7	3.8	8	7	55	33
21	1	1.6	1.9	2.1	7	6	17	50
22	3	6.5	5.2	4.6	26	20	117	25
23	3	2.6	4.0	3.9	18	18	101	25
24	3	1.6	2.7	2.7	14	11	80	17
25	6	6.5	5.1	4.3	50	47	145	29
26	6	2.6	4.0	4.2	50	41	128	>200
27	6	1.6	3.2	3.2	30	30	131	25

Table II. Data for 40 Per Cent Cottonseed Oil Emulsions

No.	Wt. % Stabilizer	pH of Diluent	pH of Emulsion		Viscosity, Centipoises		Initial Sp. Surface σ_0, Sq. Dm./G.	Stability Coefficient k, Weeks
			0 weeks	10 weeks	0 weeks	10 weeks		
			Pectin-Stabilized Emulsions					
28	0.75	6.6	4.2	3.5	210	15	16	11
29	0.75	4.0	3.6	3.6	200	85	24	33
30	0.75	2.9	3.2	3.2	195	140	38	40
31	0.75	2.1	2.5	2.5	170	160	48	>200
32	1.25	6.6	3.7	3.2	940	30	29	6
33	1.25	4.0	3.3	3.4	950	930	30	100
34	1.25	2.9	3.1	3.2	880	880	41	>200
35	1.25	2.1	2.6	2.6	735	680	54	>200
36	1.75	6.6	3.6	3.2	3400	*B*	34	5
37	1.75	4.0	3.3	3.3	2800	2800	36	67
38	1.75	2.9	3.1	3.4	2500	2800	38	67
39	1.75	2.1	2.7	2.8	2025	2075	52	200
			Tragacanth-Stabilized Emulsions					
40	0.75	6.6	6.1	4.4[a]	270	*B*	34	7
41	0.75	4.0	5.0	4.1[a]	240	*B*	32	6
42	0.75	2.9	4.2	4.3[a]	250	*B*	23	20
43	0.75	2.1	2.8	2.9	205	240	11	67
44	1.25	6.6	5.5	4.4[a]	880	*B*	44	2
45	1.25	4.0	5.0	4.1	800	440	21	12
46	1.25	2.9	4.3	4.1[a]	750	*B*	18	9
47	1.25	2.1	3.2	3.4	580	630	13	200
48	1.75	6.6	5.8	3.9[a]	*M*	*B*	16	12
49	1.75	4.0	5.1	3.9	1600	860	15	100
50	1.75	2.9	4.4	4.3	1750	600	16	15
51	1.75	2.1	3.4	3.6	1550	1060	14	100
			Karaya-Stabilized Emulsions					
52	1.25	4.0	4.3	4.5	*M*	1050	12	100
53	1.25	2.9	4.2	4.2	2050	1950	24	33
54	1.25	2.1	3.7	3.7	1300	1000	130	40
			Acacia-Stabilized Emulsions					
55	1.75	6.6	5.6	4.5	11	7	47	200
56	1.75	2.9	4.1	4.5	10	10	56	40
57	1.75	2.1	3.2	3.4	9	....	59	25
58	3.5	6.6	5.3	4.4	19	17	60	167
59	3.5	2.9	4.1	3.9	18	18	66	100

[a] At the end of 5 weeks.

$$\frac{-d\sigma}{dt} = k'\sigma = \frac{\sigma}{k}$$

where σ = specific surface, k' = instability coefficient, and k = stability coefficient.

In Figure 1 the specific surface as ordinate is plotted against the time as abscissa on semilog paper for several representative runs to illustrate the agreement between the data on the change of specific surface with time and the exponential hypothesis. The lines were determined by fitting the data to the above equation by the method of least squares. The instability coefficients, from which the stability coefficients were determined, were calculated to the nearest 5×10^{-3}, the estimated experimental error in k'. Values recorded as >200 imply that the apparent variation in the specific surface may be due to experimental error and that no significant change in the specific surface had taken place.

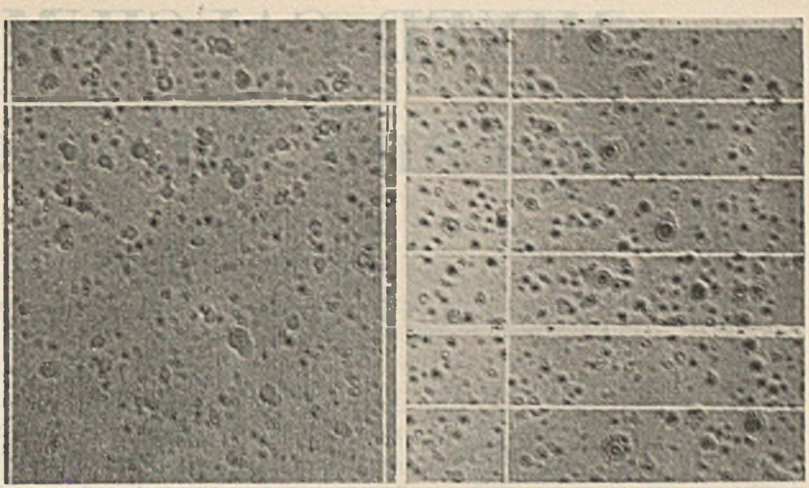
In several cases the emulsions either had broken within the period of observation or had deteriorated to such an extent that it was improbable the photomicrographs taken under these conditions were representative. Thus, deformities of the oil particles and evidence of free oil in the photomicrographs were interpreted as gross deterioration of the emulsions; these photomicrographs were discarded, and the calculations of the stability coefficients were made from the photomicrographs that were considered acceptable. Representative photomicrographs are shown in Figures 2 and 3.

The data on viscosity, pH, the graphically determined initial specific surface, and the calculated values of the stability coefficients are recorded in Tables I, II, and III. Because the generalizations deduced from the study of the 40 per cent oil emulsions are likewise applicable to the 25 and 60 per cent oil emulsions, the tables for the latter are omitted. The values for initial specific surface (σ_0) are expressed in units of square decimeters per gram of dispersed oil; those for stability coefficient are expressed in dimensions of weeks. *B* denotes that the emulsion broke within the period of observation and *M* denotes mayonnaise consistency—i. e., too viscous to be poured from the container.

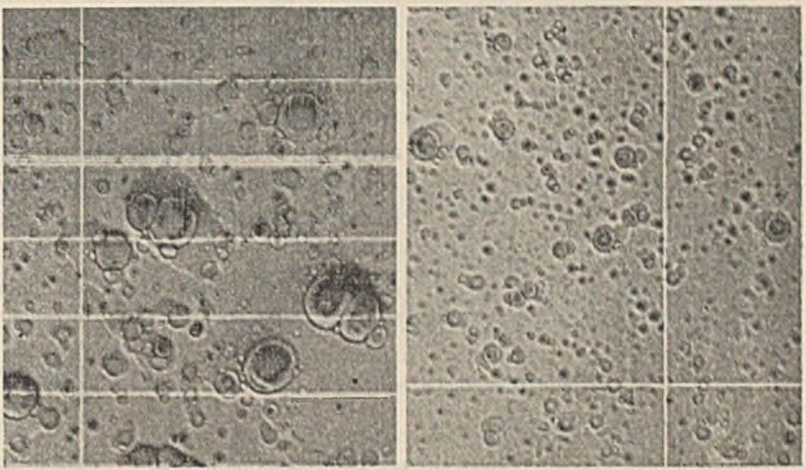
Table III. Data for 40 Per Cent Oil Mineral Emulsions

No.	Wt. % Stabilizer	pH of Diluent	pH of Emulsion		Viscosity, Centipoises		Initial Sp. Surface σ_0, Sq. Dm./G.	Stability Coefficient k, Weeks
			0 weeks	10 weeks	0 weeks	10 weeks		
			Pectin-Stabilized Emulsions					
60	1	5.9	3.2	3.3	410	380	99	>200
61	1	4.0	3.2	3.3	425	390	97	>200
62	1	3.0	3.3	3.2	415	385	97	200
63	1	2.0	2.5	2.5	350	330	76	200
64	1.5	5.9	3.2	3.2	1275	1080	129	>200
65	1.5	4.0	3.2	3.2	1300	1070	132	>200
66	1.5	3.0	3.2	3.2	1220	1080	121	200
67	1.5	2.0	2.7	2.6	1030	880	100	200
			Tragacanth-Stabilized Emulsions					
68	1	5.9	5.5	4.1	510	340	51	6
69	1	4.0	5.5	4.1	490	335	56	6
70	1	3.0	4.9	4.6	500	350	56	9
71	1	2.0	2.9	3.0	410	395	14	43
72	1.5	5.9	5.5	4.1	970	635	50	2
73	1.5	4.0	5.5	4.0	970	665	44	2
74	1.5	3.0	5.0	4.1	900	700	48	2
75	1.5	2.0	3.3	3.3	820	785	15	200
			Karaya-Stabilized Emulsions					
76	1	5.9	5.2	4.5	1070	695	113	100
77	1	4.0	4.4	4.4	940	770	103	>200
78	1	3.0	4.4	4.3	975	665	121	100
79	1	2.0	3.7	3.7	650	645	116	200
80	1.5	5.9	5.1	4.4	*M*	*M*	120	100
81	1.5	4.0	5.1	4.4	*M*	*M*	135	200
82	1.5	3.0	4.4	4.3	*M*	*M*	127	200
83	1.5	2.0	3.8	3.8	*M*	*M*	129	200
			Acacia-Stabilized Emulsions					
84	2	5.9	5.0	4.8	16	13	71	17
85	2	4.0	4.4	4.7	15	11	78	15
86	2	3.0	4.4	4.5	15	15	84	15
87	2	2.0	3.4	3.4	12	13	63	33
88	4.5	5.9	5.1	4.4	32	29	120	40
89	4.5	4.0	4.4	4.4	32	30	127	40
90	4.5	3.0	4.4	4.3	31	34	115	>200
91	4.5	2.0	3.7	3.7	26	27	119	200

The scope of this investigation limited the study to the effect of acidity, concentration of emulsifying agent, and ratio of oil to water on the pH, viscosity, and initial specific surface. The present data are adequate for comparison of the instability of the emulsions but are inadequate for reaching conclusions—for example, on the mechanism of the degradation of the emulsions or on the effect of acidity or concentration of emulsifying agent on particle size. The assumption of exponential change of specific surface with time is purely arbitrary, for the surface measurements reported here are not sufficiently precise to establish the correct mathematical dependence.



Pectin emulsion 64 Karaya emulsion 80



Tragacanth emulsion 72 Acacia emulsion 88

Figure 3. Particle Size of Stabilized Mineral Oil Emulsions (× 196)

PARTICLE SIZE AND VISCOSITY

Table II reveals a definite effect of acidity of the cottonseed oil emulsions on the average size of oil droplets as indicated by initial specific surface. The average particle size decreases with increasing acidity, except for the tragacanth-stabilized emulsions where it increases. Tables I and III also reveal trends in particle size with acidity, but some of these trends are not consistent with those in Table II. The data show that the viscosity of the emulsions decreases with increasing acidity. In general, the tragacanth-stabilized emulsions are coarse and viscous, the acacia emulsions are fine and fluid, the karaya emulsions are gelatinous, and the pectin emulsions are fine and viscous.

STABILITY

The consistent trend in the stability coefficients of the tragacanth-stabilized emulsions with the acidity of the emulsions is in accord with the observations by Kranz and Gordon (*5*) that tragacanth-stabilized emulsions of Nujol and cottonseed oil have maximum stability between diluent pH 1.9 and 2.3.

The trend of the stability coefficients with acidity of pectin-stabilized emulsions of cottonseed oil is parallel to that of tragacanth-stabilized emulsions. However, there appears to be no particular trend for the pectin-stabilized emulsions of olive oil and mineral oil. The stability data for the acacia-stabilized emulsions are in agreement with the conclusion of Kranz and Gordon (*5*) that acacia-stabilized emulsions are stable over the entire pH range. Over the pH range investigated, the emulsifying efficiency of karaya does not vary appreciably with the acidity of the emulsions.

The present data support the view taken by King and Mukherjee (*4*) that the degree of dispersion of the oil is unrelated to the stability. Also, no dependency between initial viscosity and stability has been observed. Greater viscosity may prevent creaming but does not necessarily enhance stability. Thus, acacia-stabilized emulsions are much less viscous than the emulsions prepared with pectin and the other gums, yet they are as stable as the latter.

The stability of an emulsion may depend on factors influencing the chemical stability of the emulsifying agent as well as on the physical characteristics of the freshly prepared emulsion. The correlation between stability coefficients and the change in viscosity of the emulsions on storage lends some weight to this view.

The variation of emulsifying efficiency with acidity and from oil to oil limits generalizations that can be made on the comparative emulsifying efficiencies of pectin and the gums. There is little difference between pectin and tragacanth as emulsifying agents for olive oil. Both are more effective at the lower pH values. Pectin appears to be slightly better than tragacanth as an emulsifying agent for cottonseed oil. It is possible to make these comparisons because the stability trends of pectin and tragacanth are practically parallel. As an emulsifying agent of mineral oil, pectin is clearly superior to tragacanth and acacia, and is at least equal to karaya. This is in agreement with the results of Merrill (*6*) who measured the mechanical stability of emulsions 62, 70, 78, and 86 by means of the recently developed centrifugal force method.

In presenting these data the authors hope that this information will furnish the pharmaceutical and food industries and other users of difficultly obtainable emulsifying agents with a guide to what may be expected of pectin as an emulsifying agent under various conditions.

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MIXED CALCIUM SALTS OF Soaps and Anionic Detergents

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Evidence is presented for the formation of mixed salts of calcium with fatty acids and synthetic anionic detergents. The pH limits necessary for the formation of these salts is discussed. Consideration of the formation of these mixed salts in mixtures containing sulfated detergents, soap, and calcium salts leads to a plausible explanation of the decrease in both the foaming and detersive properties of such mixtures. No corresponding behavior has been found for magnesium salts.

WHEN soap is dissolved in water containing calcium and magnesium salts, the familiar curds of calcium and magnesium soaps are formed. If, in addition to these materials, a typical sulfated or sulfonated detergent is present, it has been stated that these soap curds will be either rendered soluble or dispersed (*2*, *4*).

The formation and colloidal behavior of calcium soaps were discussed by Frisch and Valkó (*3*). According to them, in the presence of insufficient calcium salt, a colloidal solution or a very fine suspension of particles is produced, whose constitution they expressed by the formula:

$$[x\text{CaOl}_2.y\text{NaOl}.z\text{Ol}] + z\text{Na}^+$$

where Ol = oleate radical

This view was in agreement with the theory of colloidal electrolytes of Pauli (*7*). Valkó (*10*) extended this theory to include the behavior of calcium soaps in the presence of the calcium salts of anionic detergents (presumably of the type of long-chain alcohol sulfates). He postulated the formation of the complex, $[x\text{CaOl}_2.yM] + y/2\,\text{Ca}^{++}$, where M is the soap ion stable to hard water. The greater the ratio of y/x, the greater the stability of the solution of the complex.

The so-called dispersing effect of anionic detergents has often been described in the literature as due to protective colloids or peptization. In order to examine the efficiency of these effects, Lindner (*6*) and Kuckertz (*5*) made determinations of turbidity and precipitation in mixtures of common soap with anionic detergents. Valkó pointed out that such measurements were arbitrary since these systems are unstable and vary with time.

FOAM STABILITY

In the course of study of foaming characteristics of solutions of sulfated detergents in the presence of soap and hard water, the foams were found to be stable only within a limited pH range. Taking the loss in foam stability as a guide, the variation in behavior of solutions of these mixtures was followed by the pour foam test described by Ross and Miles (*8*). In the following discussion, for the sake of simplicity all the foam stability values represent the initial foam observed immediately after the formation of the foam and do not indicate the stability of such foam to longer drainage and other changes which occur with time.

The height of foam of sodium lauryl sulfate as a function of the concentration of the solution in distilled water at 46° C. is shown in curve *A*, Figure 1. When an equivalent amount of calcium chloride is added to the solution of sodium lauryl sulfate, the foam is improved slightly as shown in curve *B*. For comparison, the variation of foam with concentration for sodium laurate is shown in curve *C*.

In the following experiment the effect of one molecular equivalent of soluble calcium salt upon a mixture of one molecular equivalent each of sodium lauryl sulfate and sodium laurate was examined:

To 400 cc. of a 0.005 molar solution of sodium lauryl sulfate in distilled water (400 cc. of solution will contain 0.002 mole of material), a solution of calcium chloride was added in increments so that finally there was 0.005 gram mole per liter of calcium salt present. The calcium chloride solution used was a relatively concentrated solution (5000 p. p. m.) so that dilution factors incurred may be considered negligible, since only a total volume of 40 cc. was added. After each addition the foam of the solution was measured and the results are shown in curve *D*, Figure 2. With the addition of calcium chloride the foam rises to a steady level. This procedure was repeated by adding calcium chloride solution to a solution which was 0.005 molar in sodium lauryl sulfate and 0.005 molar in sodium laurate. As the calcium chloride was added, a precipitate formed and the foam test was run in the same manner; the result is shown in curve *E*. The final total amount of calcium chloride added was equivalent to the sum of the amount of sodium laurate and sodium lauryl sulfate present. If insoluble calcium dilaurate were precipitated, the remaining solution should have contained a mixture of sodium lauryl sulfate and calcium chloride; for such a mixture curve *D* should have been followed, at least approximately. The falling off in foam may be explained by assuming that the sodium lauryl sulfate as well as laurate are no longer present in the same form or concentration as they were before the addition of calcium chloride. The solutions in this experiment were maintained at pH 7.5 and 46° C.

A modification of the experiment was made in which a large excess of sodium lauryl sulfate over the sodium laurate was present in the solution. The actual proportions used were 0.001 mole of sodium lauryl sulfate and 0.0001 mole of sodium laurate. Stepwise addition of calcium to this mixture resulted in a minimum foam stability of 60 mm. when two equivalents of calcium on the soap basis had been added; further addition of calcium did not alter the foam stability.

Effect of Time. The following experiment was performed to examine the effect of freshly precipitated calcium dilaurate upon the foam of lauryl sulfate: To a solution containing 0.001 gram mole of sodium laurate, a solution containing 0.0005 gram mole of calcium chloride was added so that precipitation of calcium dilaurate was approximately complete. Then, while

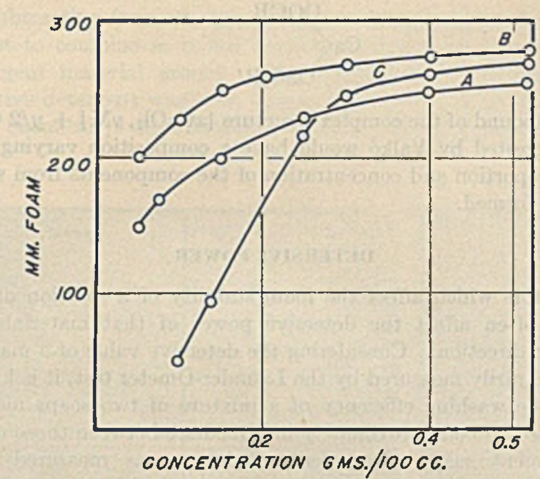


Figure 1. Variation of Foam with Concentration of Solution at 46° C. and pH of Approximately 7.0–8.0

A. Sodium lauryl sulfate in distilled water
B. Sodium lauryl sulfate + calcium chloride
C. Sodium laurate in distilled water

stirring and maintaining the same temperature of 46° C., a solution containing 0.001 gram mole of sodium lauryl sulfate was added and the pour foam test was made at definite time intervals after mixing. The result is shown in curve *F*, Figure 3. The initial height of foam for the sodium lauryl sulfate falls to a certain low level gradually with time. As the curve shows, it was some time before the loss in foam height was observed and 20 minutes before the final low value was reached. This result indicates that there is a slow interaction between the flocculent calcium dilaurate and the solution of sodium lauryl sulfate, resulting in a loss of foam stability.

EFFECT OF pH. The influence of pH was next examined with the results shown in Figure 4. The foam of a 0.1 per cent solution of sodium lauryl sulfate in distilled water at 46° C. as a function of pH is given by curve *H*. Curve *K* shows the effect of adding 100 p. p. m. hardness (in the form of calcium chloride) to a 0.1 per cent solution of sodium lauryl sulfate. Sodium laurate was then added to lauryl sulfate solution so that the solution contained 0.025 per cent sodium laurate (curve *J*). To this solution calcium chloride (to make 100 p. p. m. hardness) was then added, and curve *L* was obtained by varying the pH. Adjustments of pH were made by the addition of 0.1 *N* sulfuric acid or 0.1 *N* sodium hydroxide, and pH measurements were made with a Beckman glass electrode apparatus, using a type E electrode. Over the range examined, variation in pH had substantially no effect upon solutions of (*a*) sodium lauryl sulfate, (*b*) a mixture of sodium lauryl sulfate with sodium laurate, and (*c*) a mixture of sodium lauryl sulfate with calcium chloride. However, when all three components are present together—namely, sodium lauryl sulfate, sodium laurate, and calcium chloride—at a critical pH of about 5.2 a foam which is stable from pH 2.0 to 5.2 suddenly becomes unstable and falls to zero at about pH 7. This effect is reversible and, upon lowering the pH of the mixture below 5.2, the foam is restored to its original value. The critical pH 5.0–5.5 is also the pH below which the calcium laurate is converted into lauric acid and calcium salts.

FORMATION OF MIXED SALT

These results can be explained by assuming the formation of a mixed calcium salt of the fatty acid and detergent or of a variable complex composition as suggested by Valkó, if we postulate that such a complex or mixed salt, as a precipitate or some other form, has a deleterious effect upon foaming properties.

A mixed salt such as calcium laurate lauryl sulfate might be expected to show some chemical properties of both calcium dilaurate and calcium dilauryl sulfate. From titrations, the mixed salt and calcium dilaurate showed breaks at the same critical pH (5.0–5.5); the bearing of this critical value upon foaming properties was described above.

More direct evidence of the existence of such mixed salts was found in the preparation of these compounds by different methods which gave a product with constant stoichiometric proportions by analysis. The general procedure of preparation follows: To a solution of 1.1 grams of sodium laurate in 200 cc. of distilled water, a solution of 1.5 grams sodium lauryl sulfate in 100 cc. distilled water was added. To this mixture 0.55 gram calcium chloride in 60 cc. water was added gradually with stirring at 20° C. The pH of the solution at the end of the addition was 7.3. The fine precipitate was filtered off and washed free from chloride ion with water at 40–50° C. The product was dried in a vacuum desiccator over concentrated sulfuric acid. The yield was almost equal to the theoretical amount.

Analysis: Found Ca = 8.13%; S = 6.40%
Calculated for $Ca(O_2C_{12}H_{23})O_4SC_{12}H_{25}$: Ca = 7.93% S = 6.35%

A sample of this material (0.4000 gram) was mixed with excess dilute hydrochloric acid at 30° C. and the mixture extracted with petroleum ether. After washing and drying the extract, 0.1532 gram lauric acid was obtained. Theory required 0.1603 gram lauric acid. Calcium lauryl sulfate would have given no lauric acid and calcium laurate would give approximately twice this weight.

The following method using nonaqueous solvents, gave excellent results: Acid lauryl sulfate was prepared from pure lauryl alcohol and chlorosulfonic acid in liquid sulfur dioxide, as described by Ross *et al.* (*9*). To a solution of 1.40 grams of dry acid lauryl sulfate in 30 cc. of benzene, 2.2 grams of anhydrous calcium dilaurate were added, together with some glass beads

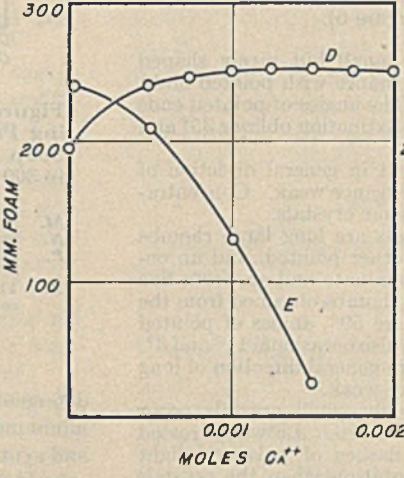


Figure 2. Effect of Adding Calcium Chloride to an Equimolar Solution of Sodium Lauryl Sulfate and Sodium Laurate at 46° C. and pH 7.5

D. 0.002 mole sodium lauryl sulfate + calcium chloride
E. 0.002 mole sodium lauryl sulfate + 0.002 mole sodium laurate + calcium chloride

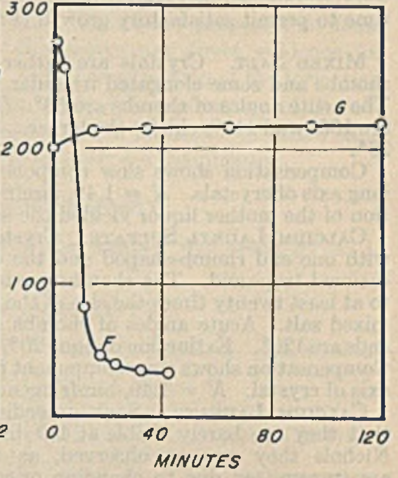


Figure 3. Effect of Time on the Addition of Sodium Lauryl Sulfate Solution to a Fresh Suspension of Hard Soap at 46° C. and pH 8.0

F. Sodium lauryl sulfate + calcium dilaurate
G. Sodium lauryl sulfate + magnesium dilaurate

in a stoppered flask. A clear gel formed from which a white solid precipitated when 50 cc. of dry ether were added. The solid was filtered off, washed with ether, and dried. From the solvents 1.07 grams of lauric acid were recovered (theory 1.00 grams). The solid salt was identical in properties with the mixed salt prepared by the wet method.

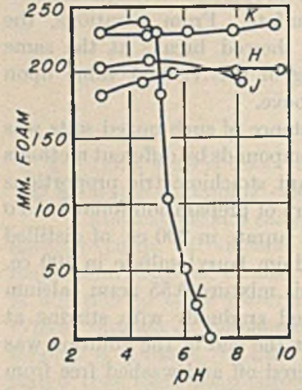


Figure 4. Variation of Foam with Hydrogen Ion Concentration at 46° C.

H. Solution of 0.1% sodium lauryl sulfate in distilled water
J. Solution of 0.1% sodium lauryl sulfate + 0.025% sodium laurate in distilled water
K. Solution of 0.1% sodium lauryl sulfate + 100 p. p. m. calcium hardness
L. Solution of 0.1% sodium lauryl sulfate + 0.025% sodium laurate + 100 p. p. m. calcium hardness

The method of preparation in aqueous solutions was varied by using excess of one reagent at a time, varying the temperature of preparation, and varying the pH of the aqueous solvent between 7 and 10. In all these experiments the product was essentially the same and analyses were remarkably close to the theoretical for the simple mixed salt. Furthermore, photomicrographs of crystals prepared from aqueous solutions illustrate the microscopic structure of the crystalline salts. The composition of these crystals was also checked by chemical analysis.

CRYSTAL EXAMINATION

In the following cases all of the products examined microscopically were prepared by adding a solution of calcium chloride to solutions of sodium laurate, sodium lauryl sulfate, or a mixture of both, all in equivalent amounts, to yield a liter of 0.001 *M* solution of the desired compound in water. The calcium chloride was added at 40° C. and the pH maintained between 7.2 and 8.0. Upon cooling to room temperature, the crystals which separated were examined microscopically after standing for a sufficient time to permit satisfactory growth (Figure 6).

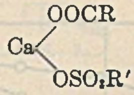
Mixed Salt. Crystals are rather small but nicely shaped rhombs and some elongated irregular shapes with pointed ends. The acute angles of rhombs are 56°. The angles of pointed ends are 105° and 110°, chiefly the larger. Extinction oblique 35° and 28°.

Compensation shows slow component in general direction of long axis of crystals. $N = 1.49$, birefringence weak. Concentration of the mother liquor yielded the same crystals.

Calcium Lauryl Sulfate. Crystals are long large rhombs with one end rhomb-shaped and the other pointed, and an occasional trapezoid. The rhombs predominate and are from five to at least twenty times the size of the rhombs obtained from the mixed salt. Acute angles of rhombs are 59°, angles of pointed ends are 120°. Extinction oblique 20°, also occasional 11° and 3°. Compensation shows slow component in general direction of long axis of crystal. $N = 1.49$, birefringence weak.

Calcium Laurate. Such exceedingly small crystals occur that they are barely visible at 450 diameters. Between crossed Nichols they can be observed, as flashes of polarized light are transmitted due to changing orientation when the crystals roll over and over under the cover glass; the effect is that of stars twinkling.

It is apparent that the mixed salt possesses characteristics which distinguish it from the calcium lauryl sulfate or calcium dilaurate. From these results it seems that a mixed calcium salt of a fatty acid and a sulfated detergent can be formed which has the following simple composition:



$$Ca\begin{cases}OOCR\\OSO_3R'\end{cases}$$

A compound of the complex structure $[xCaOl_2.yM] + y/2\ Ca^{++}$ as suggested by Valkó would have a composition varying with the proportion and concentration of the components from which it was formed.

DETERSIVE POWER

Factors which affect the foam stability of a solution of material often affect the detersive power of that material in a similar direction. Considering the detersive value of a material as arbitrarily measured by the Launder-Ometer test, it is known that the washing efficiency of a mixture of two soaps may be expected to be approximately intermediate between those of the component soaps. Detergent efficiency was measured in a modification of the Launder-Ometer described by Appel, Smith, and Christison (*1*). The soil on cotton cloth was prepared from Oil Dag (graphite and mineral oil) and cottonseed oil, and the relative light reflection of the sample after washing was determined with a B Lange Universal reflectometer. The reproducibility of this test may be ±10 per cent when the detersive efficiency is high.

Using 300 p. p. m. hard water and decreasing amounts of kettle soap, a detergency curve such as *M* in Figure 5 was obtained. Similarly, with a synthetic detergent in the same hard water, curve *N* was obtained. When mixtures of constant total concentration but variable ratios of soap to synthetic detergent were examined, curve *P* was obtained; it shows a minimum found to be characteristic of such mixtures of soaps and synthetic detergents in hard water. Assuming that calcium salts above pH 7 will combine with equivalent amounts of synthetic detergent and fatty acid whenever these are present together, to form a product which itself has substantially no detergent properties as measured in this test, theoretical curve *R* was calculated. Thus at any given concentration of the mixture, it was assumed that the material present in the higher molecular concentration was responsible for all detersive action and the effective concentration of this material was calculated

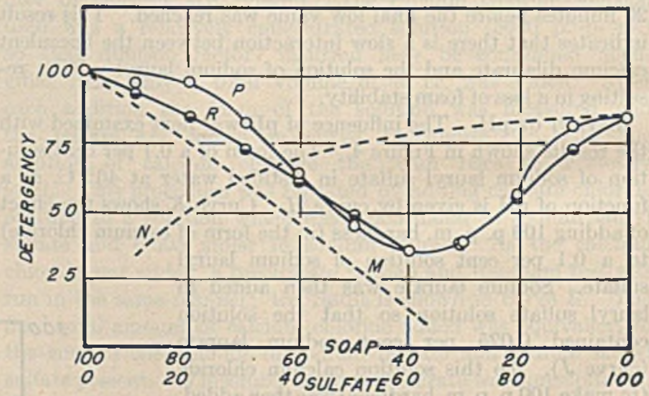
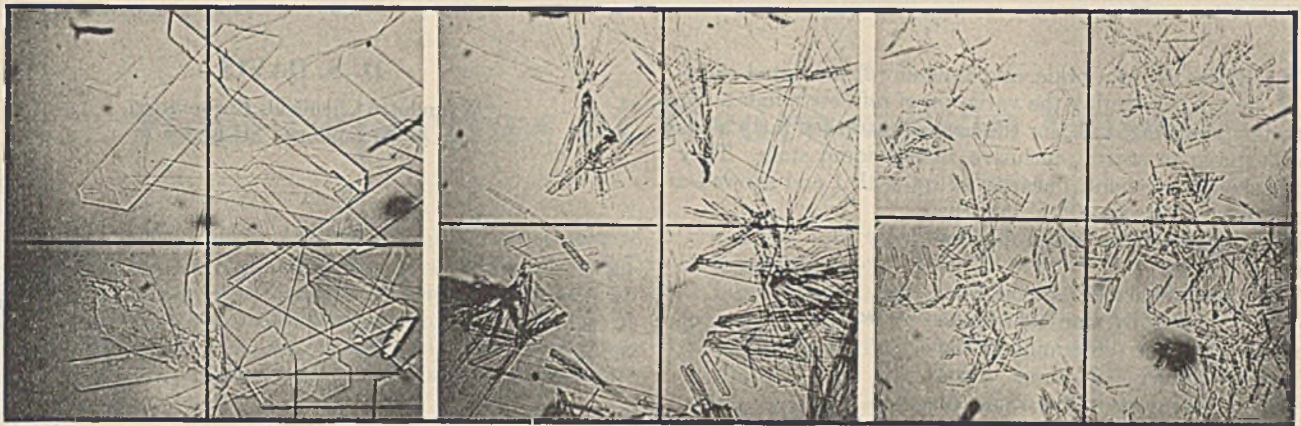


Figure 5. Variation in Detersive Efficiency for Varying Proportions of a Mixture of Commercial Tallow Soap with a Sulfated Synthetic Detergent at 43° C. in 300 P. P. M. Calcium Hard Water at a pH of Approximately 10

M. Soap alone
N. Sulfated detergent alone
P. Mixture soap + sulfated detergent at total concentration of 0.55%
R. Theoretical curve assuming removal of mixed calcium salt of soap and sulfated detergent

by subtracting from its apparent concentration an amount sufficient to combine as mixed calcium salt with all of the other detergent material present. This calculated concentration of effective detergent was then located upon curve *N* or *M* of the pure chemicals; the calculated effective detersive efficiency of the mixture was thus obtained which closely approximates experimental curve *P*. Thus the formation of mixed calcium salts of fatty acids and sulfated detergents also offers an explanation of the detersive behavior of the above mixtures.



Ca lauryl sulfate from water at 25° C. Ca laurate from 80% ethanol at 25° C. Mixed salt from water at 25° C.

Figure 6. Photomicrographs of Crystals (× 100)

The behavior of magnesium salts was also examined. To a solution of 0.001 gram mole of sodium laurate in distilled water, a solution of 0.0005 gram mole of magnesium sulfate was added with stirring at 46° C.; a solution of 0.001 gram mole of sodium lauryl sulfate was added immediately to the freshly precipitated magnesium dilaurate, and the foam test was measured at definite intervals. From curve *G*, Figure 3, it is apparent that magnesium dilaurate has no deleterious effect on the foam value of sodium lauryl sulfate. This is an interesting distinction between the properties of calcium and magnesium salts.

The magnesium laurate-lauryl sulfate was prepared in anhydrous media; but upon treatment with hot water, it showed the properties of a mixture of magnesium dilaurate and magnesium lauryl sulfate.

The mixed salts of calcium with fatty acids and anionic detergents in general appear to be definite solids of crystalline or pearly appearance. In the course of this investigation it has been shown that the reduction in foam stability cannot be accounted for by the presence of calcium, lauryl sulfate, laurate ions, or a solid precipitate. If, for example, it is assumed that the mixed salt does not behave as a strong electrolyte, the nonelectrolyte portion in solution could account for the reduction in foam stability.

In addition to the data reported, evidence was also found for the formation of mixed calcium salts in mixtures of a wide variety of soaps and synthetic commercial anionic detergents.

Comparison of the relative solubilities of the calcium soaps with the calcium salts of the anionic detergents studied does not suggest any relation from which the formation of the mixed salt as a precipitate might be predicted. The calcium soaps of the saturated fatty acids range in solubility at 50° C. from about 0.130 gram per liter for lauric to 0.03 gram for stearic; the calcium salts of the sulfates and sulfonates range from 0.75 gram per liter for calcium lauryl sulfate to over 100 grams for the calcium salts of sulfated glycerol monolaurate.

In order to demonstrate clearly the effects described, it was necessary to limit the concentrations of the components of the mixtures tested. For example, the effects of calcium salts in mixtures of soap and anionic detergents can occasionally be masked if the concentration of soap, synthetic detergent, or mixture of the two is too high. However, within a specific range of pH there is evidence that mixed salts can be formed with concomitant deleterious effects on both foaming and detersive properties of the mixtures to which calcium salts were added. The properties of the mixed salts vary widely with changes in the type and molecular weight of the fatty acid and anionic detergent employed.

In the above discussion the behavior of calcium and magnesium salts with sodium laurate and sodium lauryl sulfate was described because these materials demonstrate clearly the effects of mixed salt formation. Both sodium laurate and sodium lauryl sulfate are the lower members of the respective homologous series which exhibit certain of the characteristics of surface active materials. It seems permissible to suppose that certain behavior, such as compound formation, occurring in relatively concentrated solutions might have a parallel to some degree in dilute solution. The experimental observations do not support the conception of continuously variable composition as required by the theory of Valkó. We do not propose that foam stability or detergency in themselves are direct evidence for the existence of mixed salts, but the assumption of the formation of these simple salts leads to a plausible explanation of the observed effects. Strong support for the formation of mixed salts is given by the analytical and microscopic examination.

ACKNOWLEDGMENT

Microscopic examination of the crystals was made by A. I. Gebhart.

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Refractive Index Nomograph for Liquid Fatty Acids

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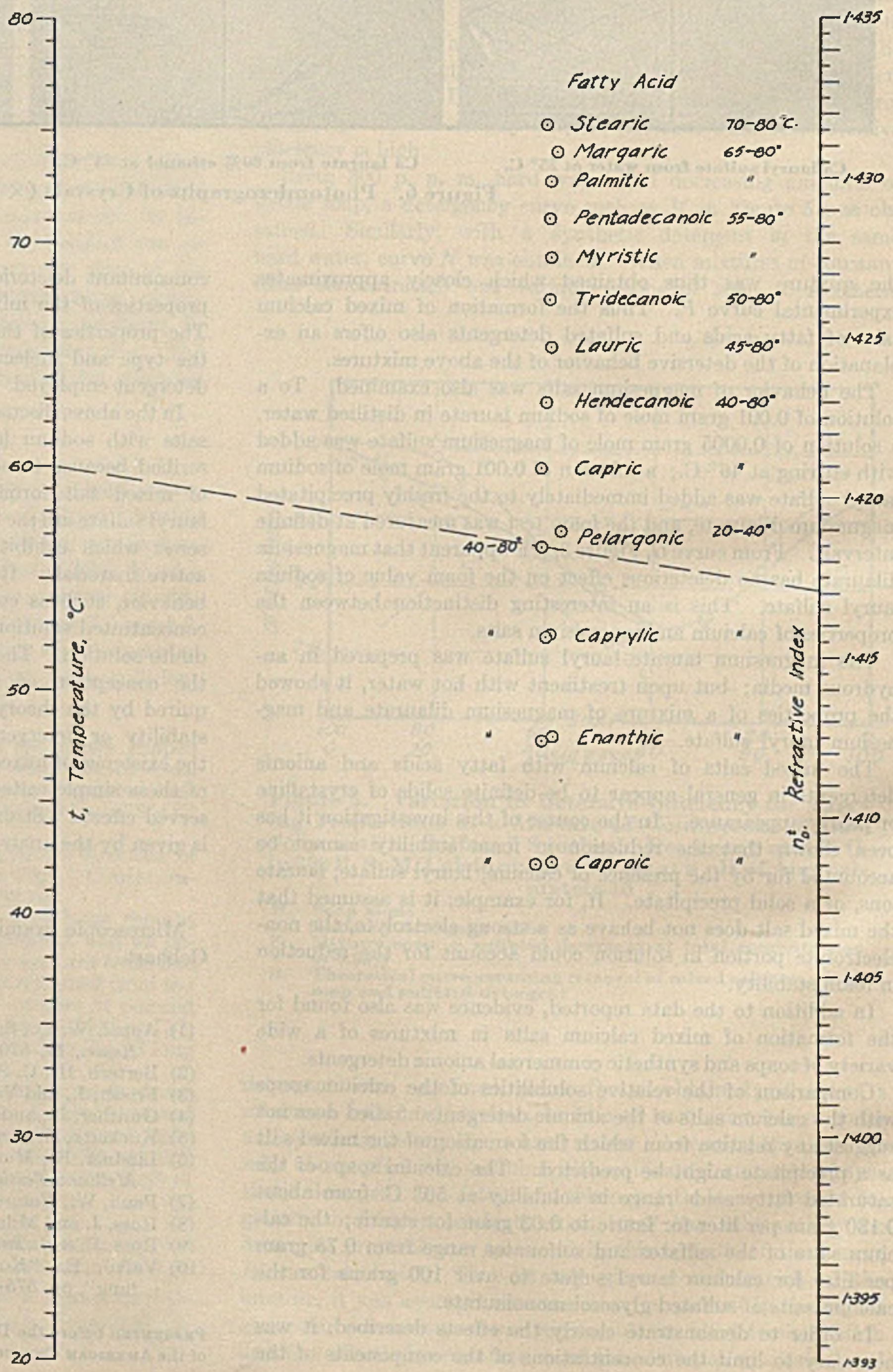
DORINSON, McCorkle, and Ralston (*2*) presented excellent data covering the variation of refractive index, n_D^t, with temperature, t ° C., for the normal saturated fatty acids from caproic to stearic, inclusive, in the liquid state. They established the general linearity of n_D^t with t and showed a break in the curve at 40° C. for the acids from caproic to pelargonic, inclusive.

These data enabled the construction of a chart, by line coordinate methods (*1*), for determining the refractive indices of these acids at any temperature in the range of applicability. The use of the chart is illustrated as follows: What is the refractive index of pelargonic acid at 60° C.? As shown by the broken line, connect 60 on the t-scale with the pelargonic acid point labeled 40 − 80° and produce the line to the n_D^t axis where the refractive index is read as 1.4171.

In a similar manner, using the other pelargonic acid point, the refractive index at 30° C. is found to be 1.4287 although the isopleth for these data is not shown. The full-scale chart (10 × 17 inches) yields values of n_D^t which agree with the original data within the probable experimental error.



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CORRESPONDENCE

Heat Capacities of Hydrocarbon Gases

SIR: In a previous paper (*21*) a method of calculating gaseous heat capacities of hydrocarbons at zero pressure was presented. Since that time it has been desirable to convert these heat capacity values to one atmosphere pressure; the Berthelot equation of state (*24*) was used, and may be written in the form of Equation 1 when converting heat capacities from zero to one atmosphere pressure:

$$\Delta C_p = 5.03\ T_c^3/P_c T^3 \qquad (1)$$

where ΔC_p = molar increase in heat capacity at T° K.
P_c = critical pressure, atm.
T_c = critical temperature, ° K.

Table I contains selected data for the critical temperature and pressure of the hydrocarbons concerned. By means of Equation 1 and Table I, the molar increase in the heat capacity was calculated and added to the heat capacities at zero pressure tabulated in the previous paper (*21*). The resulting heat capacities at one atmosphere pressure are presented in Table II.

In a private communication Herman D. Noether pointed out that the assignment of acetylenic frequencies (*21*) was not in agreement with those of Crawford (*7, 8*), or Glockler and Davis (*12*). The original frequency assignment was arrived at by taking the experimental heat capacity data of Kistiakowsky and Rice (*13, 14*), subtracting all the energy except that in the C≡C bond, and then distributing this energy between two frequencies to give the best fit with the experimental data. On practical grounds the original frequency assignment came well within the limits of accuracy possible (±4 per cent) by this method of calculating heat capacities, but from a theoretical standpoint it is not in line with the conception that the vibrational frequency of a bond increases as the binding force increases.

It seems best, then, in the light of this theoretical treatment to reassign the values of the acetylenic frequencies as follows: For the valence vibration of the C≡C bond ν = 2215 cm.$^{-1}$, and

TABLE I. HYDROCARBON CRITICAL CONSTANTS

	T_c, ° C.	T_c, ° K.	P_c, Atm.	Citation
Methane	−82.1	191.1	45.8	(*10*)
Acetylene	35.9	309.1	61.7	(*10*)
Ethylene	9.6	282.8	50.7	(*10*)
Ethane	32.3	305.5	48.2	(*5*)
Methylacetylene	121.6	394.8	54.7[a]	(*18*)
Allene	120.7	393.9	53.2[a]	(*16*)
Propylene	91.4	364.6	45.4	(*22*)
Cyclopropane	124.6	397.8	54.2	(*9*)
Propane	96.8	370.0	42.0	(*4*)
Dimethylacetylene	215.8	489.0	31.3	(*14*)
Butadiene	161.8	435.0	42.6	(*17*)
1-Butene	160.0	433.2	42.1	(*9*)
2-Butene	155.0	428.2	42.1	(*9*)
Butane	152.8	426.0	36.0	(*10*)
Isoprene	201.0	474.0	55.6	[a]
Pentylene	202.6	475.8	40.4	(*15*)
Pentane	197.2	470.4	33.0	(*25*)
Hexane	234.7	507.9	29.5	(*6*)
Heptane	267.0	540.2	27.0	(*3*)
Octane	296.4	569.6	25.2	(*1*)
Cyclohexene	251.8	525.0	36.6	[a]
Cyclohexane	281.0	554.2	40.6	(*2*)
Methylcyclohexane	301.5	574.7	34.4[a]	(*19*)
Benzene	288.5	561.7	47.8	(*25*)
Toluene	320.6	593.8	41.6	(*1*)
Phenylacetylene	312.8	586.0	40.0	[a]
Styrene	373.0	646.2	46.1	[a]
Ethylbenzene	346.4	619.6	38.1	(*1*)
Propylbenzene	365.6	638.8	32.3	(*1*)

[a] Calculated by one of two methods (*17, 23*).

TABLE II. MOLAR HEAT CAPACITIES OF HYDROCARBON GASES AT ONE ATMOSPHERE PRESSURE (C_p^1)

T° K.	250	300	350	400	450	500	600	700	800	900	1000	1100	1200	1300	1400	1500
Methane	8.39	8.89	9.55	10.30	11.08	11.84	13.28	14.59	15.78	16.84	17.79	18.63	19.38	20.03	20.60	21.10
Acetylene	8.90	10.72	11.48	12.14	12.70	13.14	13.92	14.58	15.16	15.69	16.17	16.60	17.00	17.35	17.67	17.95
Ethylene	9.67	10.49	11.57	12.69	13.81	14.89	16.87	18.51	19.96	21.45	22.62	23.63	24.51	25.26	25.92	26.50
Ethane	11.93	13.16	14.56	16.15	17.70	19.20	21.92	24.30	26.38	28.21	29.82	31.21	32.43	33.50	34.42	35.22
Methylacetylene	13.69	14.68	15.79	16.94	18.07	19.16	21.16	22.92	24.54	25.85	27.07	28.12	29.05	29.84	30.54	31.13
Allene	12.57	13.64	14.87	16.16	17.44	18.70	21.01	23.03	24.79	26.33	27.64	28.77	29.76	30.61	31.34	31.98
Propylene	14.11	15.63	17.37	19.19	20.99	22.72	25.86	28.57	30.93	32.98	34.76	36.29	37.63	38.79	39.79	40.66
Cyclopropane	14.82	16.54	18.42	20.33	22.18	23.91	27.00	29.64	31.92	33.90	35.61	37.10	38.42	39.56	40.56	41.43
Propane	15.71	17.64	19.89	22.24	24.55	26.75	30.70	34.11	37.06	39.64	41.88	43.80	45.50	46.96	48.24	49.35
Dimethylacetylene	18.24	19.67	21.43	23.29	25.12	26.88	30.06	32.83	35.32	37.35	39.19	40.78	42.17	43.36	44.41	45.32
Butadiene	16.49	18.28	20.28	22.35	24.38	26.33	29.86	32.90	35.53	37.79	39.74	41.42	42.88	44.11	45.19	46.14
1-Butene	18.03	20.24	22.67	25.35	27.90	30.31	34.67	38.43	41.65	44.28	46.84	48.92	50.74	52.28	53.63	54.81
2-Butene	17.32	19.64	22.24	24.94	27.55	30.04	34.48	38.29	41.54	44.21	46.78	48.88	50.70	52.25	53.00	54.79
Butane	19.65	22.26	25.27	28.41	31.46	34.36	39.54	43.98	47.81	51.11	53.99	56.48	58.65	60.50	62.15	63.54
Isoprene	20.18	22.78	25.59	28.48	31.28	34.04	38.69	42.78	46.27	49.27	51.85	54.07	55.99	57.63	59.06	60.30
Pentylene	21.96	24.85	28.13	31.52	34.82	37.94	43.52	48.28	52.38	55.74	58.93	61.56	63.84	65.79	67.48	68.97
Pentane	23.61	26.89	30.65	34.57	38.35	41.95	48.34	53.81	58.49	62.54	66.04	69.06	71.70	73.96	75.93	77.64
Hexane	27.71	31.61	36.10	40.78	45.31	49.59	57.20	63.69	69.64	74.02	78.15	81.72	84.82	87.48	89.80	91.83
Heptane	31.83	36.35	41.57	47.01	52.26	57.22	66.07	73.56	79.98	85.49	90.26	94.36	97.93	101.0	103.6	106.0
Octane	35.98	41.10	47.05	53.24	59.22	64.83	74.93	83.45	90.72	96.97	102.3	107.0	111.0	114.5	117.5	120.1
Cyclohexene	22.92	26.44	30.39	34.40	38.30	41.94	48.38	53.81	58.41	62.33	65.65	68.56	71.05	73.20	75.08	76.71
Cyclohexane	25.10	29.00	33.01	37.82	42.23	46.25	53.48	59.60	64.82	69.29	73.08	76.42	79.29	81.78	83.94	85.83
Methylcyclohexane	29.00	33.37	38.26	43.22	48.03	52.52	60.45	67.15	72.82	77.67	81.79	85.39	88.50	91.18	93.52	95.55
Benzene	17.97	20.61	23.62	26.66	29.62	32.36	37.19	41.21	44.58	47.40	49.77	51.81	53.54	55.04	56.33	57.44
Toluene	22.19	25.50	29.26	33.10	36.79	40.23	46.28	51.24	55.55	59.10	62.11	64.67	66.87	68.75	70.38	71.79
Phenylacetylene	24.24	27.61	31.33	35.06	39.65	41.98	47.79	52.62	56.69	59.96	62.75	65.13	67.15	68.86	70.34	71.60
Styrene	24.61	28.15	32.21	36.28	40.20	43.88	50.31	55.64	60.15	63.90	67.09	69.79	72.10	74.07	75.76	77.23
Ethylbenzene	26.27	30.23	34.73	39.33	43.76	47.89	55.16	62.20	66.30	70.58	74.21	77.32	80.01	82.27	84.25	85.96
Propylbenzene	30.54	35.05	40.27	44.60	50.76	55.57	64.04	71.11	77.05	82.07	86.32	89.97	93.11	95.78	98.01	100.1

for the deformation vibration of the C≡C bond $\delta = 333$ cm.$^{-1}$ Using these new frequencies, the acetylenic bonding contributions to the heat capacity are listed for a series of temperatures in Table III, and should be employed in place of their counterpart in the previous paper (*21*).

Table III. Acetylenic Bonding Contributions to Heat Capacity (calories/mole/bond)

T, ° K.	$\nu = 2215$, $\theta = 3178^a$	$\delta = 333$, $\theta = 478^a$	T, ° K.	$\nu = 2215$, $\theta = 3178^a$	$\delta = 333$, $\theta = 478^a$
250	0.0009	1.4782	800	0.6743	1.9290
300	0.0055	1.6152	900	0.7696	1.9409
350	0.0186	1.7052	1000	0.9104	1.9497
400	0.0445	1.7665	1100	1.0345	1.9560
450	0.0840	1.8103	1200	1.1423	1.9609
500	0.1398	1.8423	1300	1.2356	1.9648
600	0.2821	1.8853	1400	1.3156	1.9679
700	0.4466	1.9114	1500	1.3852	1.9703

[a] $\theta = 1.435 \times$ vibrational frequency.

Calculation of the heat capacity of acetylene with the new frequencies gives results as much as 12.5 per cent lower than the data of Frost (*11*). This is understandable, for the theoretical assignment of frequencies in acetylene (*20*) is considerably different from those for the substituted acetylenes (*7*, *8*, *12*), on which the new frequency assignment is based. Consequently, the data in Table II are those of Frost (*11*) converted to one atmosphere. Other acetylenic derivatives in Table II were from the new frequencies. The new data calculated for methylacetylene are 2.8 per cent or less below the experimental (*13*) and calculated (*8*) values; those calculated for dimethylacetylene are 1.4 per cent or less above the experimental values (*14*). Except for acetylene, the new frequencies reproduce the experimental heat capacities as well as the frequencies first employed (*21*).

ACKNOWLEDGMENT

It is my pleasant duty to thank Herman D. Noether for pointing out the shortcomings of the earlier acetylenic frequency assignment, and the Dow Chemical Company for permission to publish this work.

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Daniel R. Stull

The Dow Chemical Company
Midland, Mich.

Autoclaves for Pressure-Temperature Reactions

Sir: With reference to the section on "Safety Devices" on page 942 of this article (September, 1943), the following question has been asked: Was it intended that a frangible diaphragm with a rated bursting pressure of one and a half or two times the design pressure of the vessel should be used as the sole safety device? The answer is definitely negative, for the A. S. M. E. Code specifies that relief devices shall function at the design pressure; hence, it would be permissible to use a safety head with a bursting pressure fixed at one and a half or two times the design pressure (depending upon operating conditions) only when the vessel is equipped with another safety device set to let go at the design pressure. The discussion in question was strictly limited to such practice.

However, now that the question has been raised, it might be well to amplify this discussion. First, it might be pointed out that most engineers consider two pressures when designing autoclaves and other pressure vessels—the operating or working pressure and the design pressure; the latter should always be set at least 10 per cent above the operating or working pressure and would correspond to the setting of the usual safety valve.

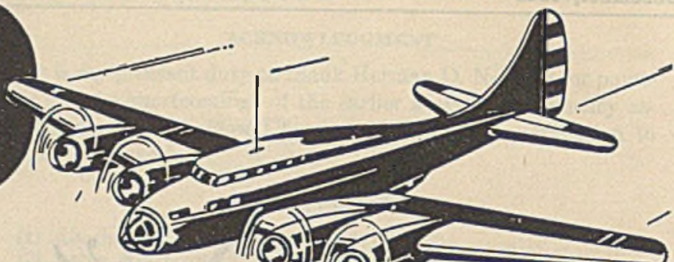
The writer knows of a number of cases in which safety heads are the sole safety device. In such cases the design pressure of the vessel should not be lower than the rated bursting pressure of the rupture disk; even then, in many instances the best practice might call for a safety valve in parallel with the safety head. Further, in such cases the design pressure should be at least 50 per cent above the working pressure, for if operated at a pressure too close to the rated bursting pressure, the rupture disk may be overstressed. This may result in premature failure which in some cases can entail the loss of valuable batches of chemicals being processed.

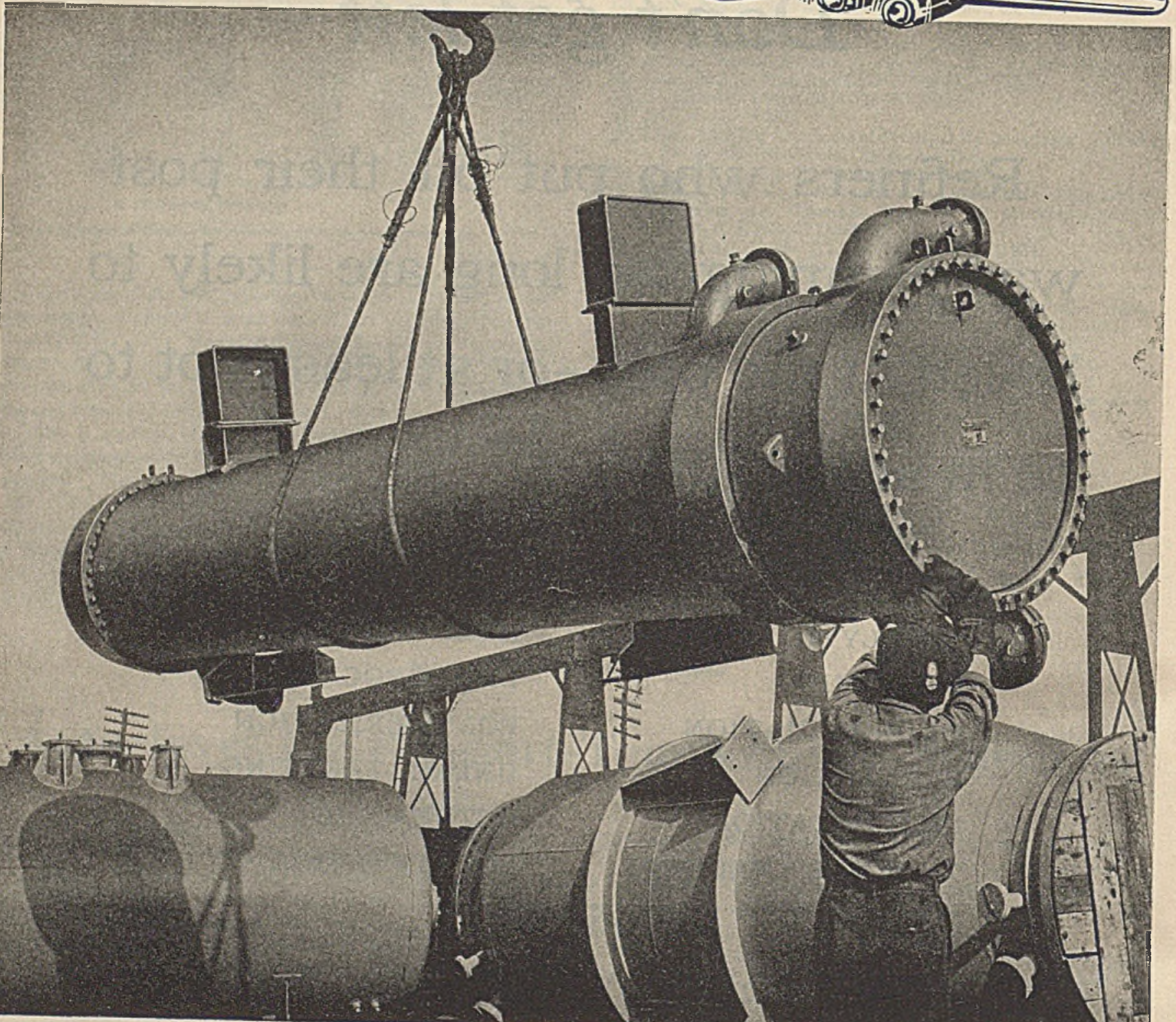
When vessels are used for comparatively low operating pressures, the design pressure can be 50 per cent higher than the working pressure without an excessive increase in the cost of the equipment; but for high-pressure autoclaves it is probably decidedly preferable (from the standpoint of initial cost) to use a safety valve set at the design pressure and then, solely as an emergency safety device, a safety head with a rupture disk having a bursting pressure of one and a half or two times the design pressure.

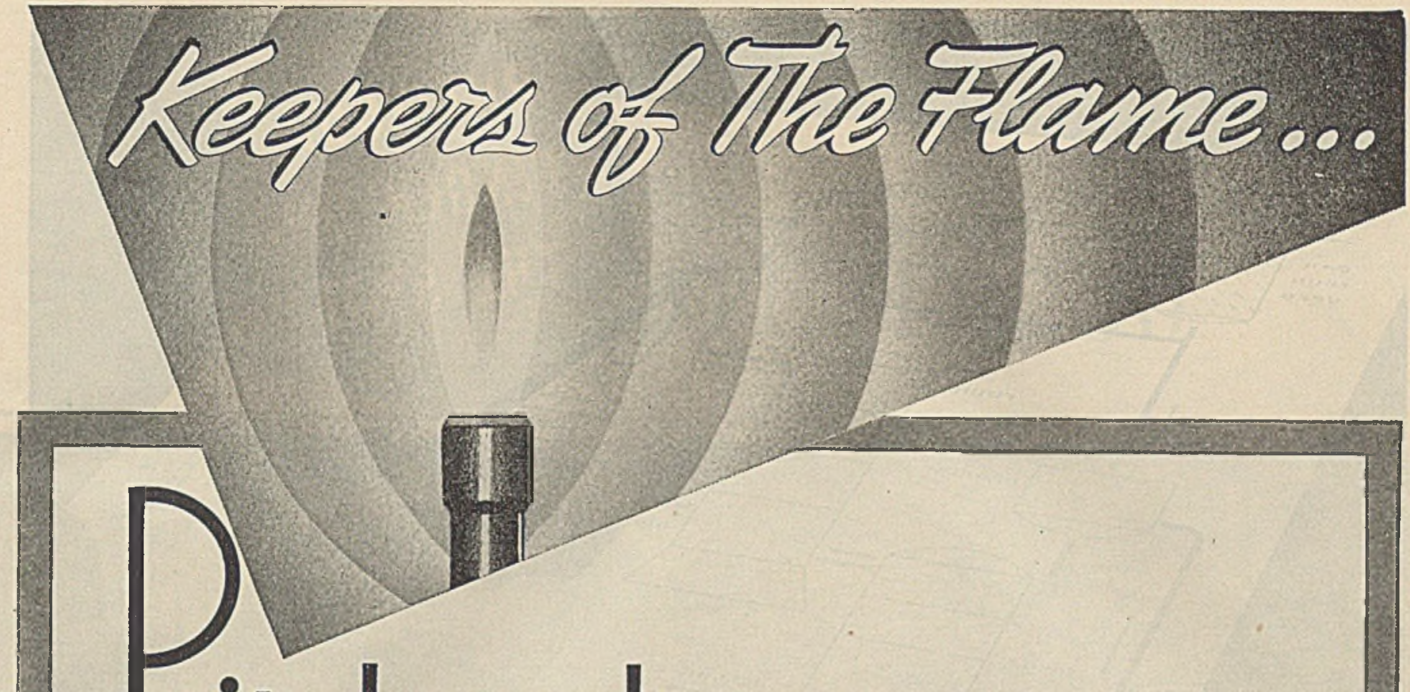
Finally it should be borne in mind that the above remarks apply only to cases where vessels are being operated at permissible maximum pressures. In many instances vessels are actually operated at much lower pressures than those on which design was based. This sometimes makes it possible to use a rupture disk with a rated bursting pressure equal to or lower than the design pressure of the vessel but still following the recommended practice of being 50 per cent above the actual operating pressure.

D. B. Gooch

Blaw-Knox Company
Pittsburgh, Penna.







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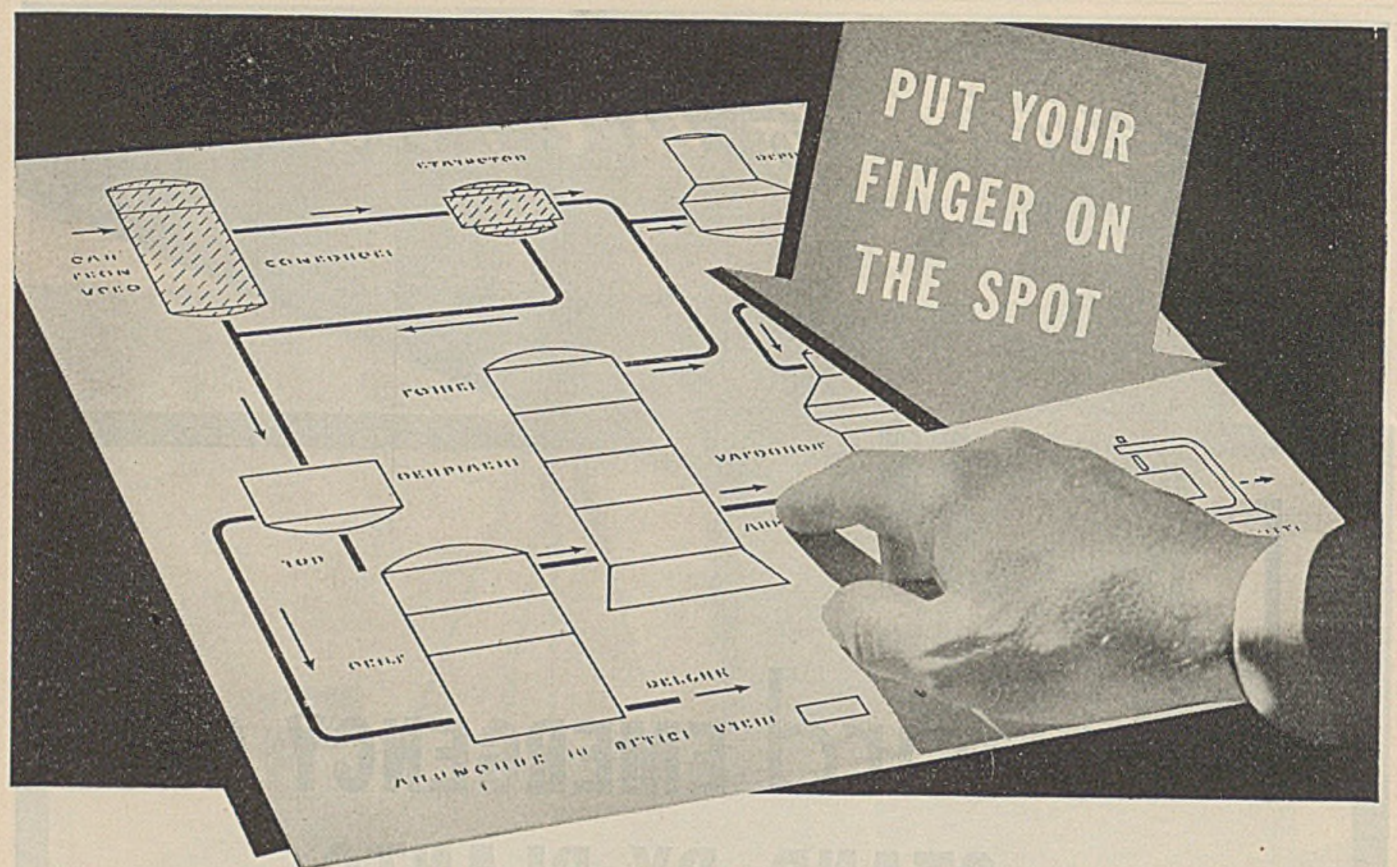
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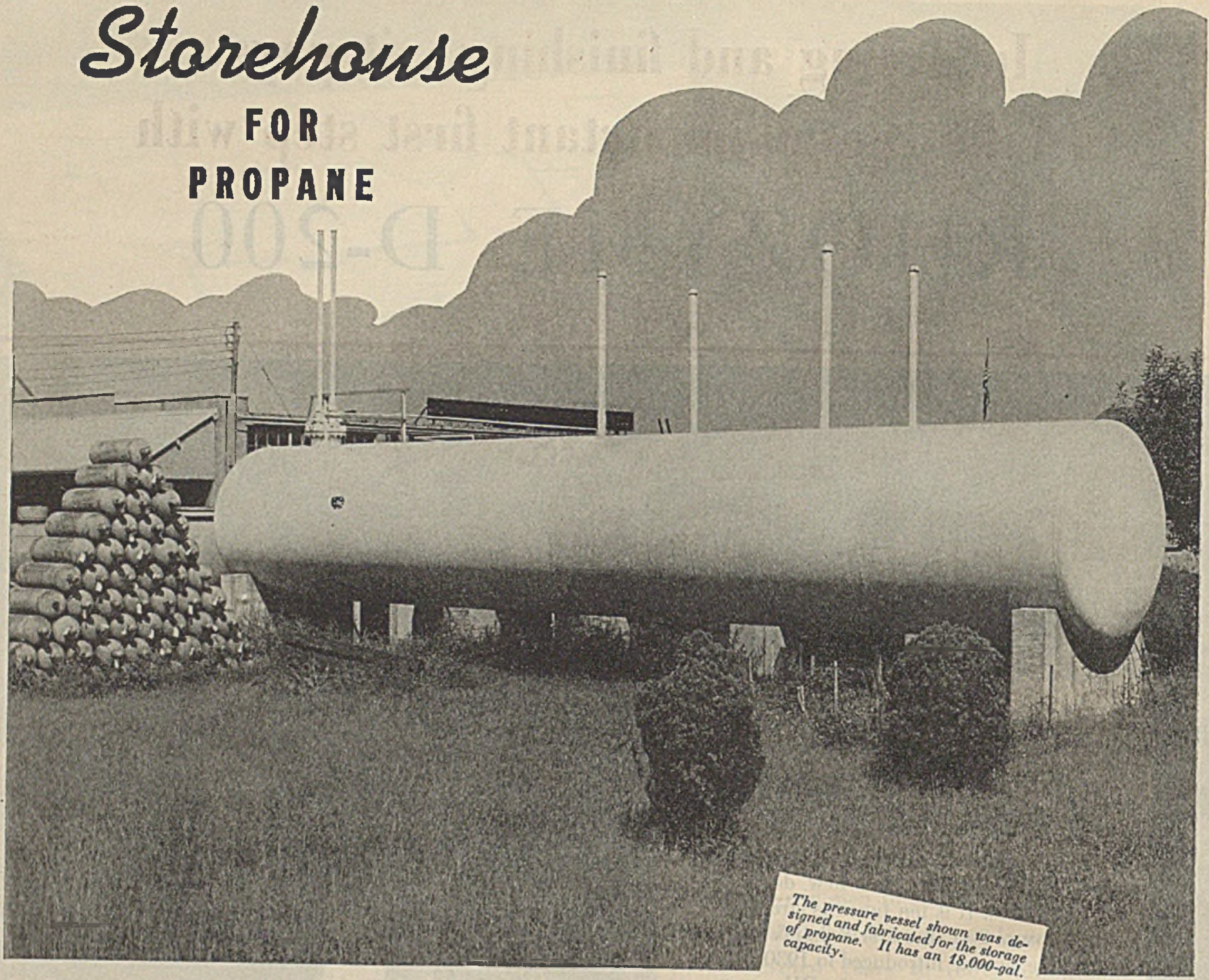

The pressure vessel shown was designed and fabricated for the storage of propane. It has an 18,000-gal. capacity.

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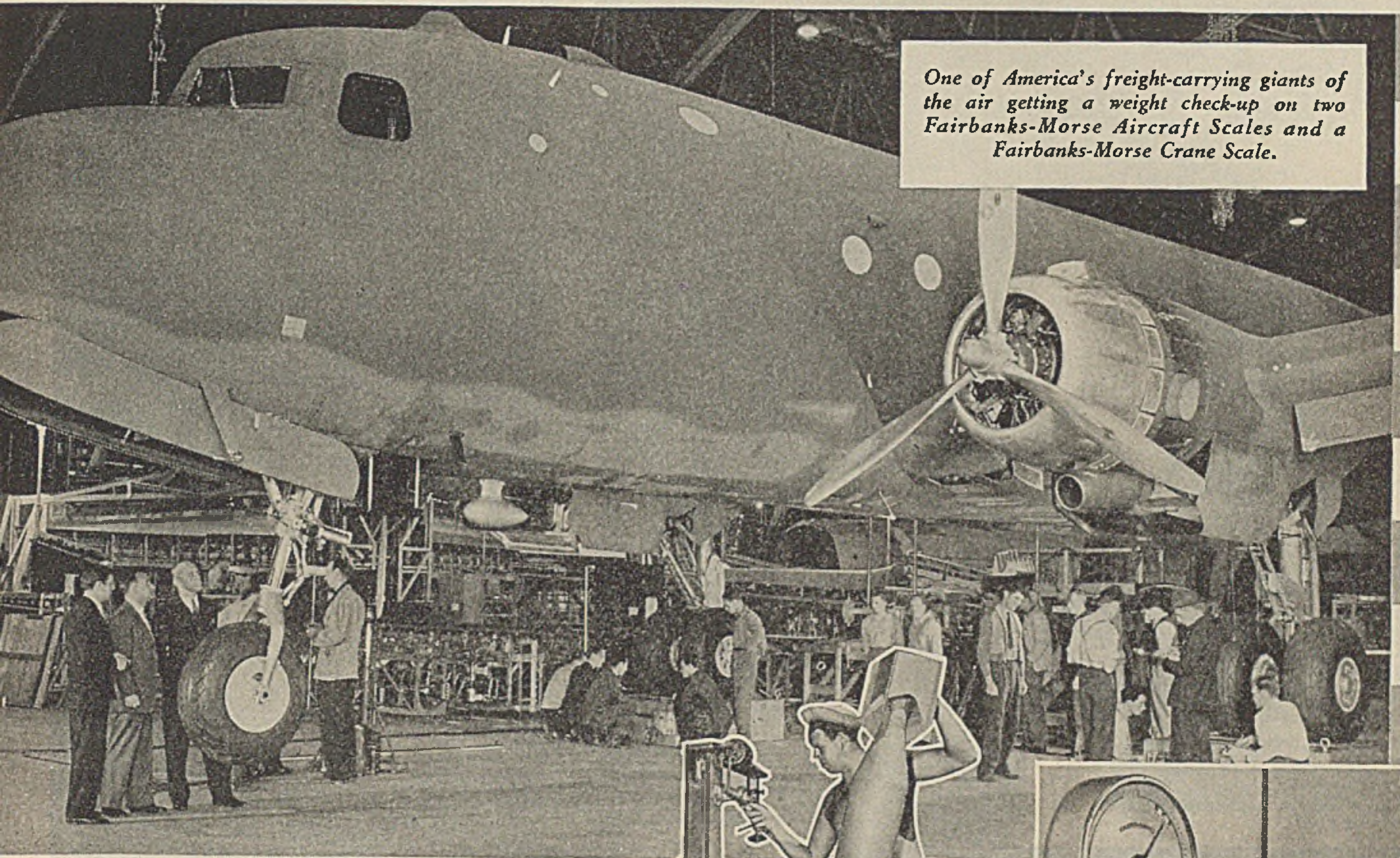
Fairbanks-Morse Scales in Warwork



One of America's freight-carrying giants of the air getting a weight check-up on two Fairbanks-Morse Aircraft Scales and a Fairbanks-Morse Crane Scale.

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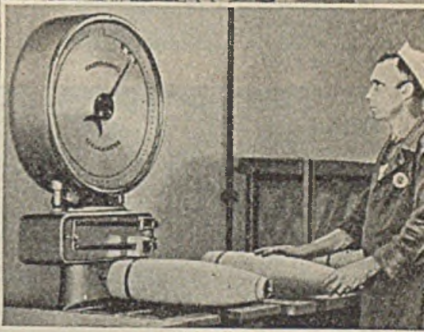
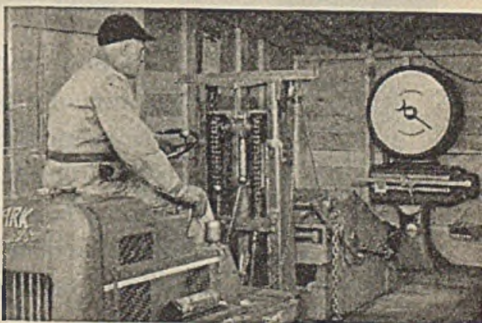
Weighing an "egg" for the Axis.



Correct weight for accurate gunnery.

Frozen eggs—NOT for the Axis!



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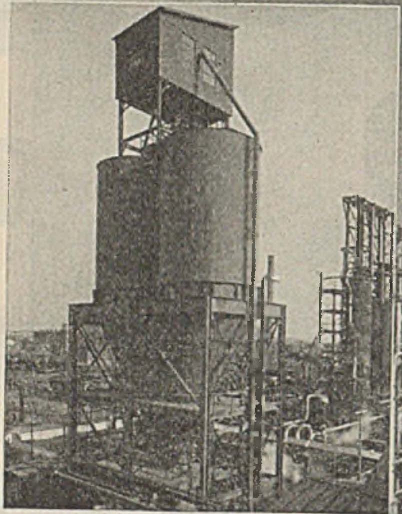
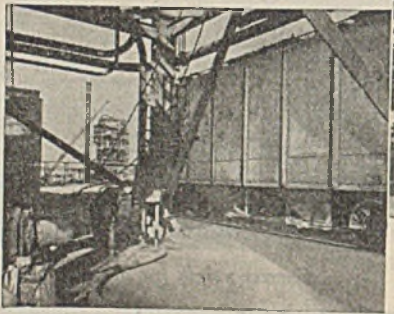
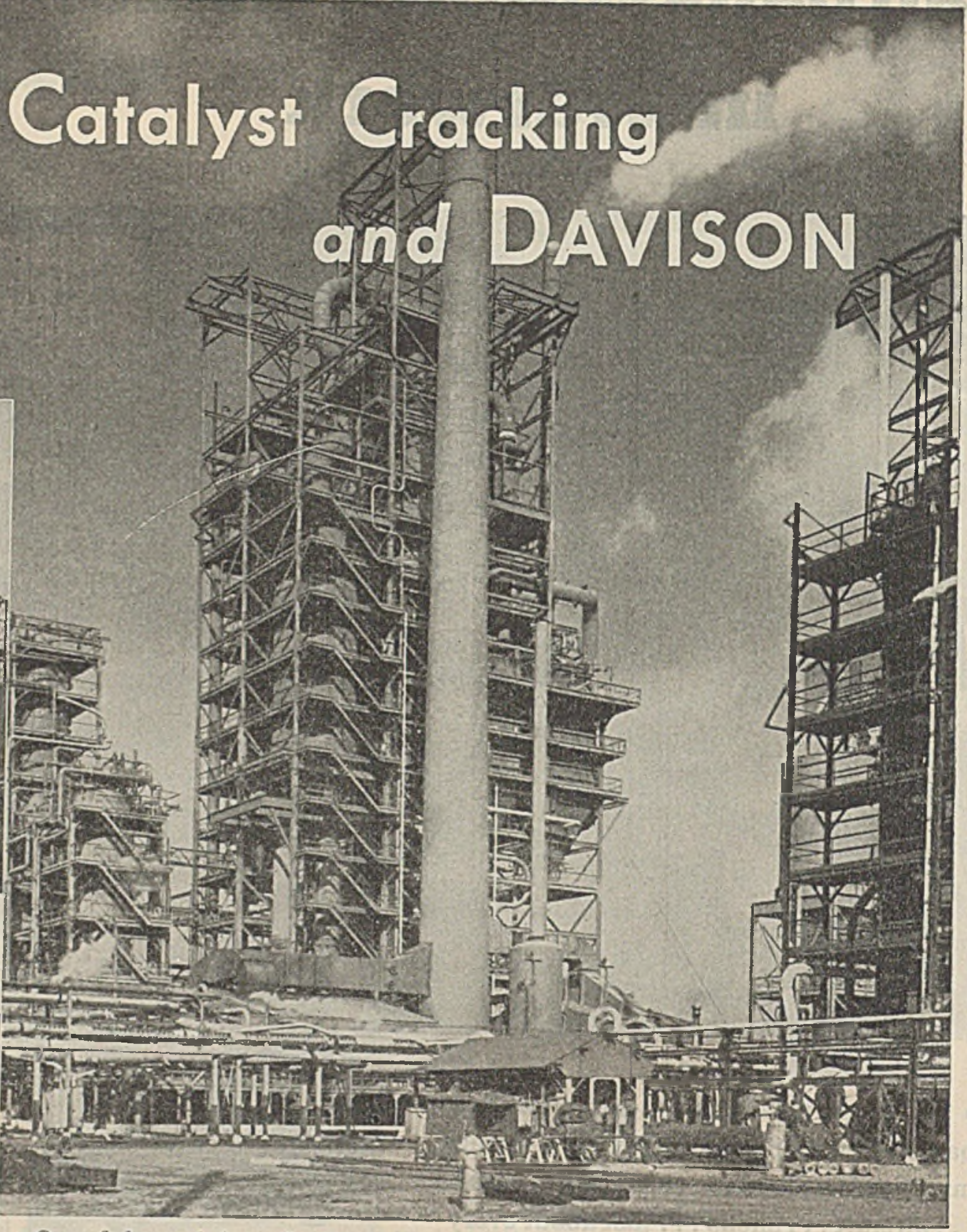


Separators for the separation of catalyst and vapor.

Davison gel type catalyst arriving at the "cat" cracking plant.





One of the catalytic or "cat" cracking plants of the Standard Oil Company (New Jersey)

Here, for the first time in a commercial plant large quantities of a solid catalyst are circulated with the vapors being cracked. After the reaction is complete, the catalyst is separated from the vapors in suitable separators.

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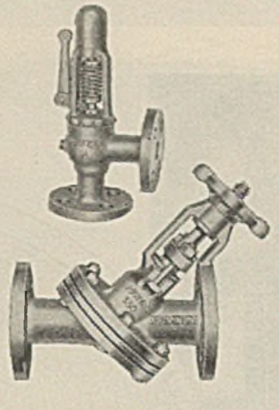

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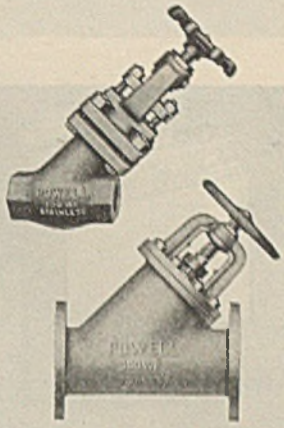

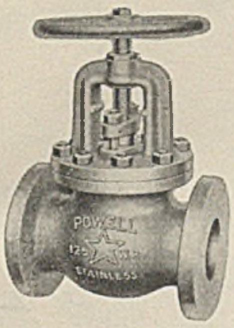

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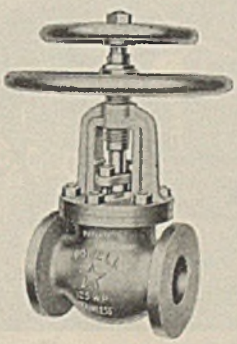

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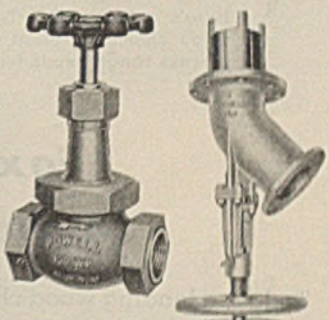

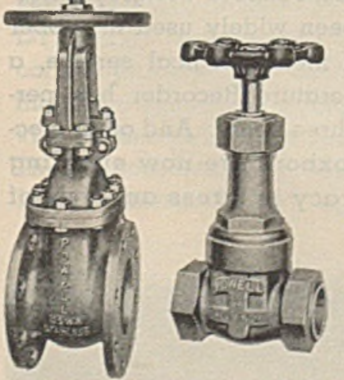

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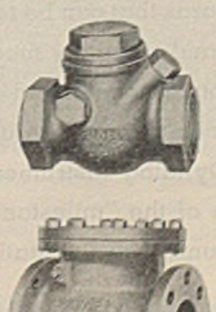

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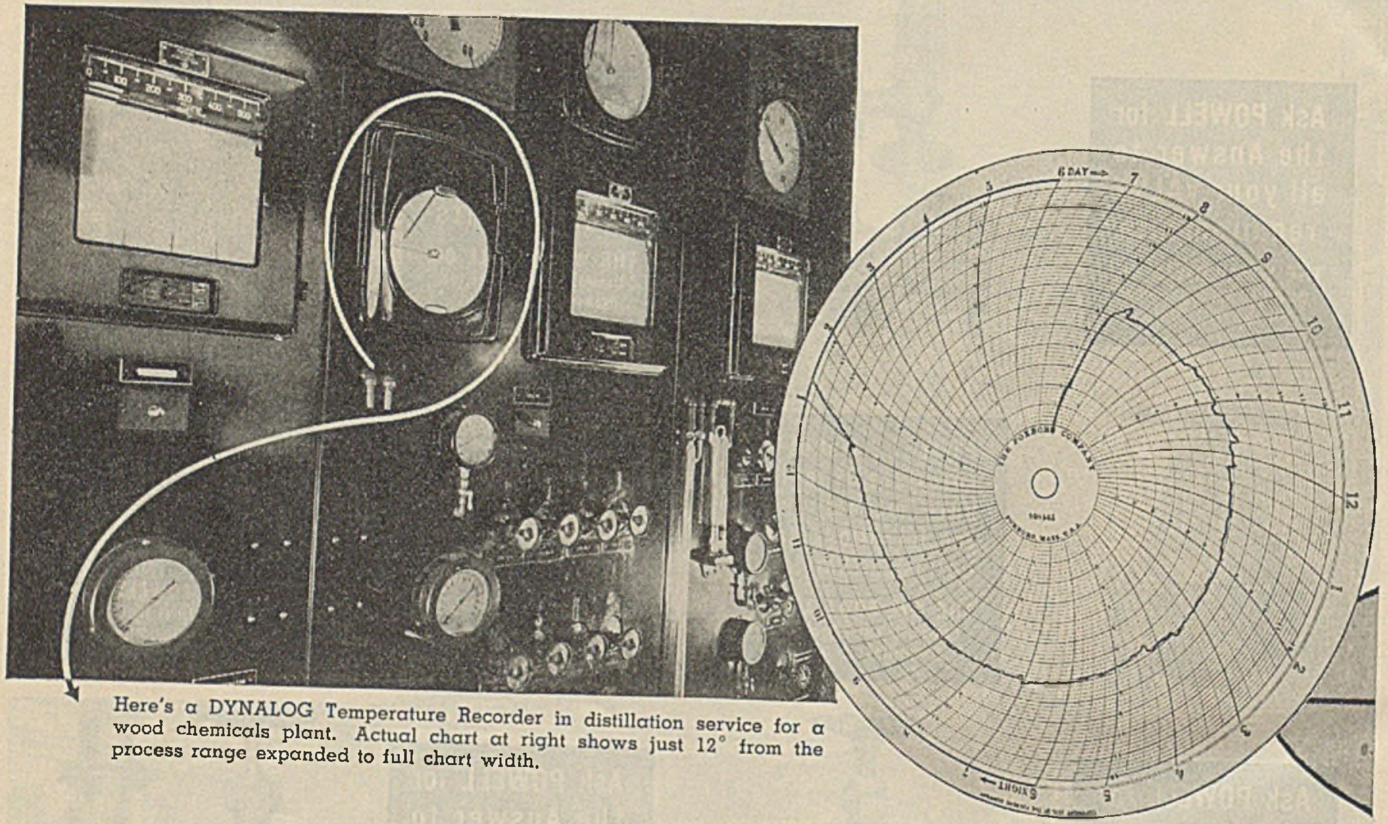

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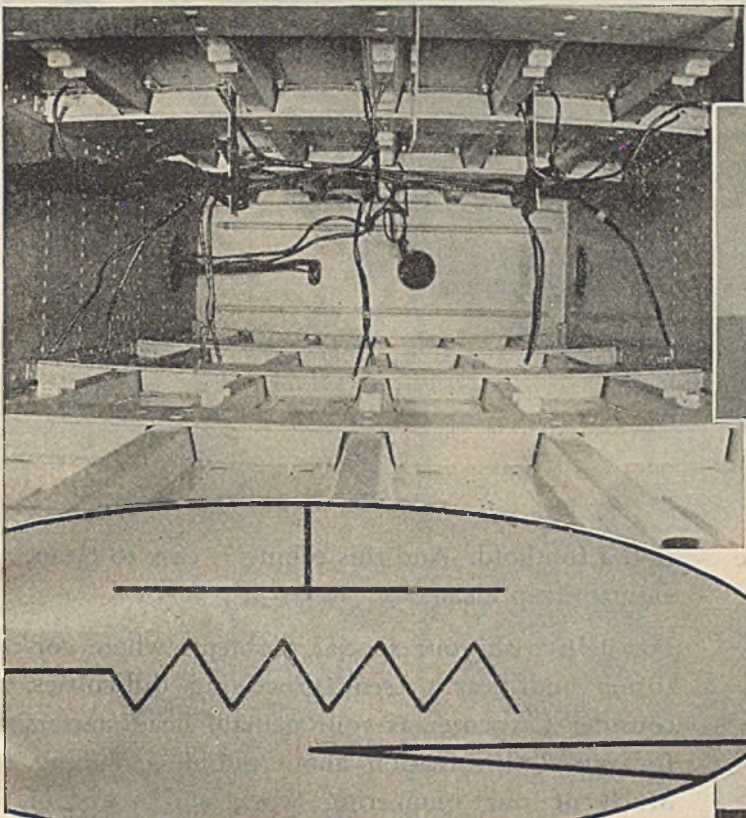
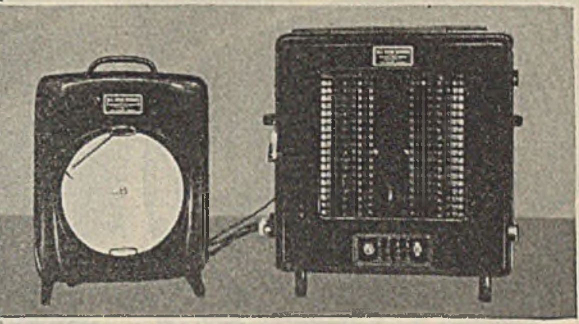
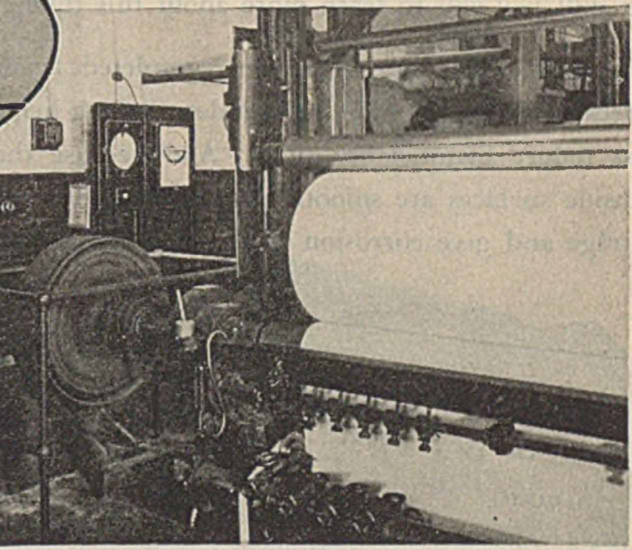




Interior view of warplane wing (left) shows installation of SR-4 strain gages. The automatic-switching Electronic Recorder (above) enables exact, speedy reading of 48-test-points under any loading!



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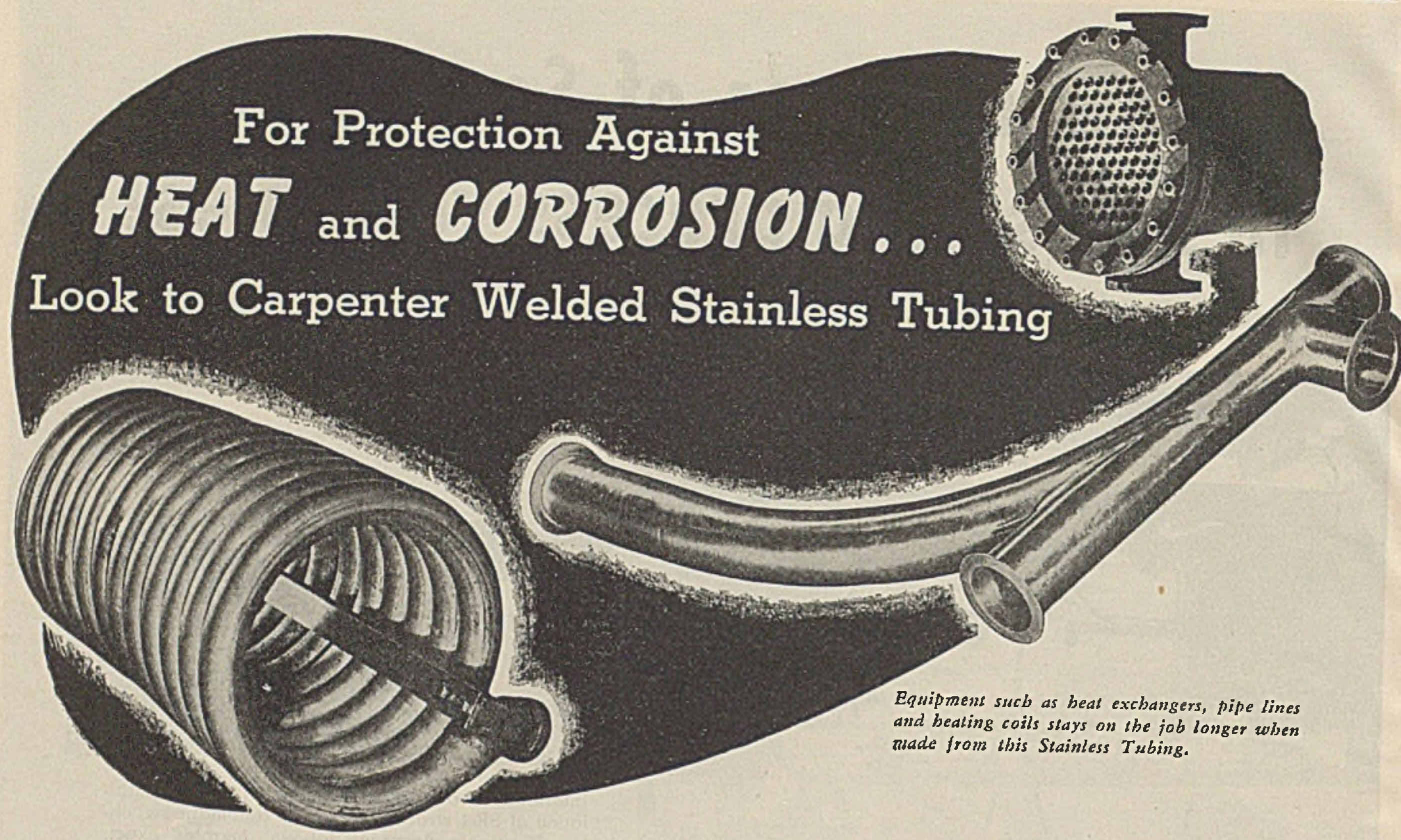

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For positive protection against specific corrosive elements, and oxidation from high temperatures, it will pay you to learn more about this tubing.

In many plants, processes are completed faster because Carpenter Welded Stainless Tubing helps to reduce maintenance time. And because the inside surfaces are smooth, no tiny particles can lodge and give corrosion or product contamination a foothold. And this tubing is easy to clean, easy to keep clean.

For help with your special problems where corosion and heat present processing difficulties, consider Carpenter as your general headquarters for useful information about Stainless Tubing. Much of our pioneering work and years of experience can probably be put to good use in solving your problems. Drop us a line today.

HERE'S WHY THIS STAINLESS TUBING IS EASY TO FABRICATE . . .

Uniform walls throughout mean that lighter gauges can be used without sacrificing strength. And *lighter gauges* permit savings in weight, as well as lower costs.

USE THIS PRINTED HELP TO GET THE MOST FROM THE STAINLESS TUBING YOU USE!

This convenient file folder provides some of the basic information you need when considering the use of Stainless Tubing. It gives data on corrosion resistance, physical properties of Carpenter Welded Stainless Tubing, sizes and shapes available, etc. A note on your company letterhead will start your copy on its way, so let us hear from you today.

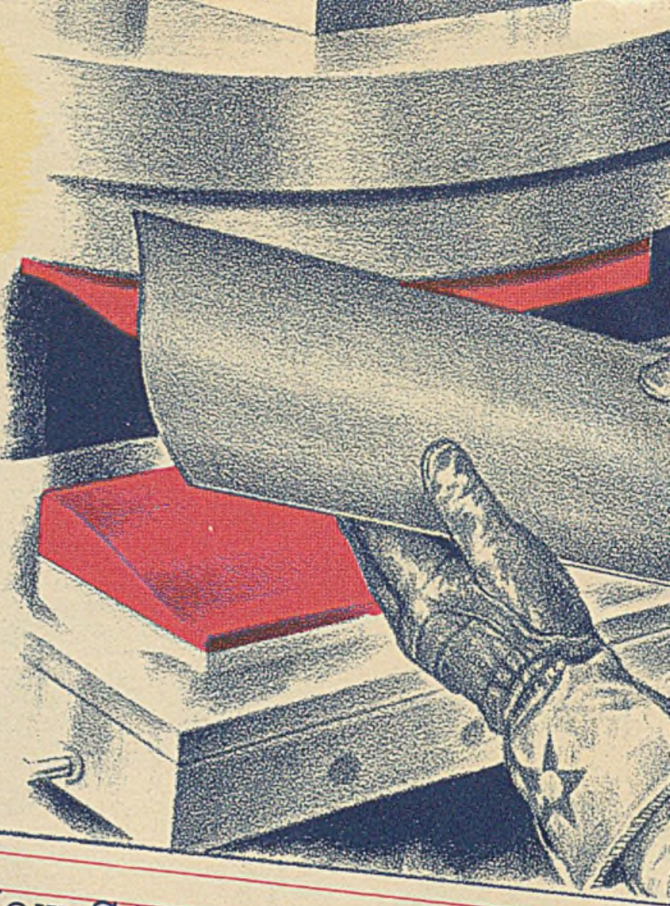
THE CARPENTER STEEL COMPANY
Welded Alloy Tube Division • Kenilworth, N. J.

Carpenter
WELDED
STAINLESS TUBING

YOUR PRODUCT, TOO, MAY BE IMPROVED through a "Partnership"

These products and many hundreds more were each improved through a "partnership" of knowledge. Your company, for example, possesses a wealth of product experience and manufacturing know-how. Hercules, on the other hand, has acquired in the past 30 years a vast storehouse of chemical knowledge. By sharing this knowledge with each other, your products and ours may be made better, more swiftly, more thriftily. Similar "partnerships" have produced tougher tires; longer-lasting cements; more powerful insecticides; better textiles, plastics, paints, papers; and an endless list of articles. Perhaps we can furnish you with technical data, literature, or assistance on some specific problem. Write Hercules Powder Company, Inc., Wilmington, Delaware.

New type plastic tools save manpower and metal



A new ethyl-cellulose based thermoplastic—cast like molten metal into forming blocks, drill jigs, stamping dies, and other tools—is speeding up the manufacture of aircraft parts and saving large quantities of metal.

These new plastic tools—capable of withstanding repeated hydraulic press and drop hammer pressures as high as 2 or 3 tons—are only one-sixth the weight of ordinary metal tools. They also permit lower casting temperatures and more exact mold dimensions . . . resulting in less machining and a 33% saving in forming time. The plastic tools may be recast and re-used several times. At the present time ethyl cellulose is so critical that its use for these tools is allocated to only the aircraft industry. Hercules will be glad to furnish you with names and addresses of producers of this plastic. Write Cellulose Products Department, Hercules.

New Stabilized Rosin. .

Hercules has now DEhydrogenated natural rosin to form a more stable material with *increased* resistance to light and oxygen.

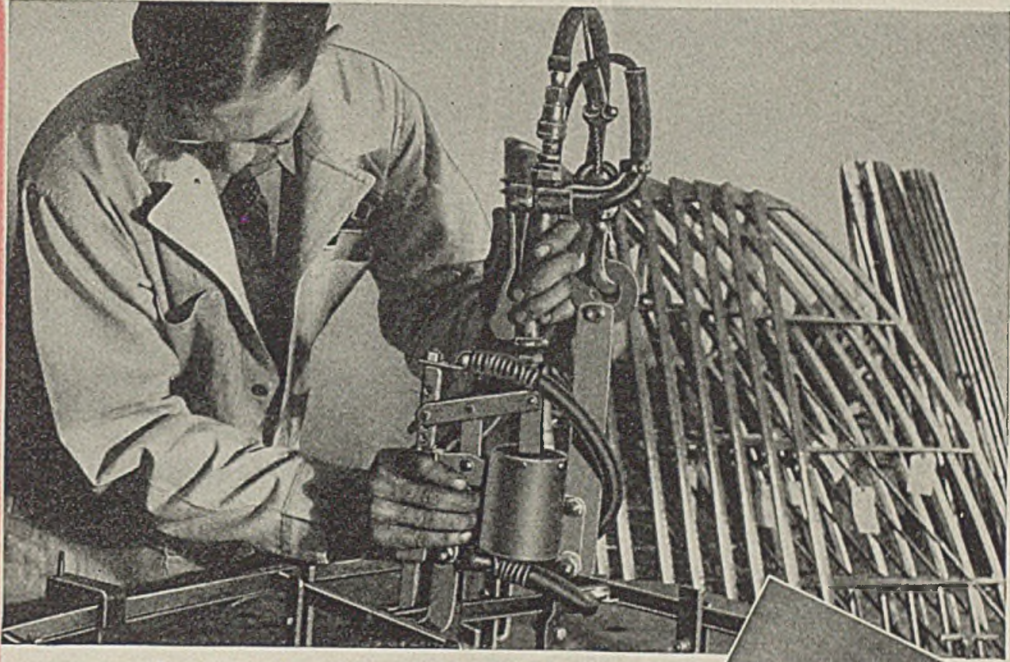
Called "PERMEX," this new dehydrogenated material is similar in its characteristics to Staybelite*, Hercules hydrogenated rosin. At the present time, "Permex" is available in small amounts only. Naval Stores Department.

Bad News for Flies

Recently concluded at Kansas State College was a 3-yea test on cattle and commercial insect sprays. In these tests Thanite*, the new toxic agent for insecticides developed b Hercules, showed greater knockdown and killing power tha any other toxic agent tested. The investigations have als shown that Thanite sprays offer longer-lasting repellency are non-toxic and non-staining even in high concentrations and leave no residual odor or taste to foods.

These and other findings are to be included in a new book now being prepared. If you would like us to send you a copy of this book as soon as it is published, or if you wish technica data regarding Thanite immediately, write Naval Store Department, Hercules Powder Company.

*Reg. U. S. Pat. Off. by Hercules Powder Company




THE FABRICATION OF
REPUBLIC
Enduro
STAINLESS STEELS


Compres

-sor Plant Operate

A MILE AT SEA!

How would you like to operate a seagoing compressor plant? These CLARK Balanced Opposed Compressors are operating over 20 feet of water, atop of piling — a mile from shore in Lake Maracaibo, Venezuela. If there were the least horizontal vibration, the plant would long ago have gone for a ride in the lake. But these compressors are electric driven and employ the balanced opposed principle of completely counterbalanced operation. Compressor cylinders are opposed, and pistons move in opposite directions simultaneously.

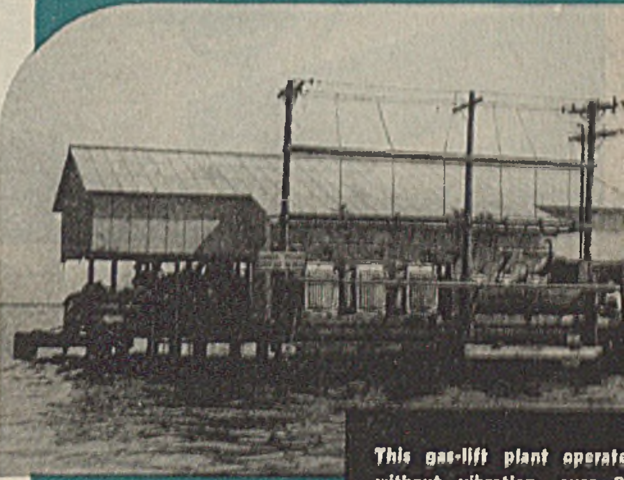
This unit is especially adapted for locations where it is impossible to construct firm, solid foundations. It is widely used for natural gasoline and vapor recovery plants, gas and air lift, refrigeration, and in special process work, for which automatic control of pressures or volume can be readily built in.

CLARK

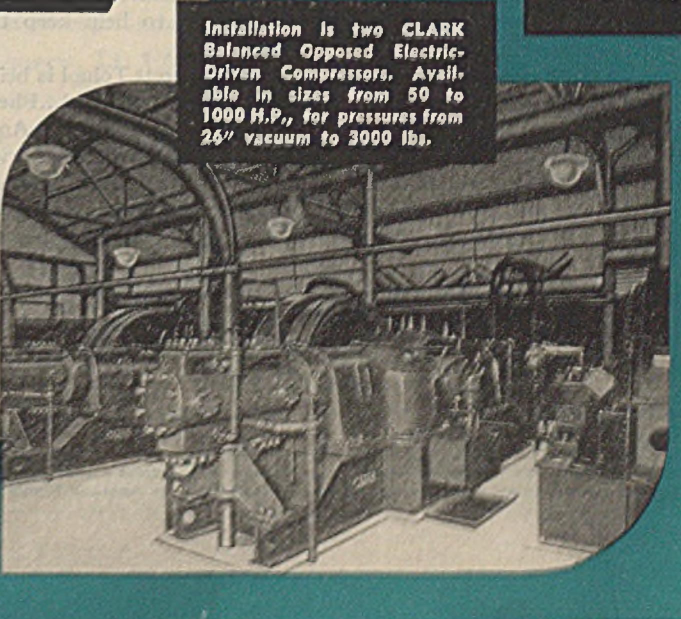
CLARK BROS. CO., INC.
Olean, New York, U.S.A.

Domestic Sales Offices and Warehouses: Tulsa, Okla.; Houston, Tex.; Chicago, Ill. (122 N. Michigan Ave.); Boston, Mass. (131 Clarendon St.); Huntington Park, Calif. (5715 Bicket St.) Foreign Offices: London, England; Avda Roque Saenz Pena, 832, Buenos Aires.

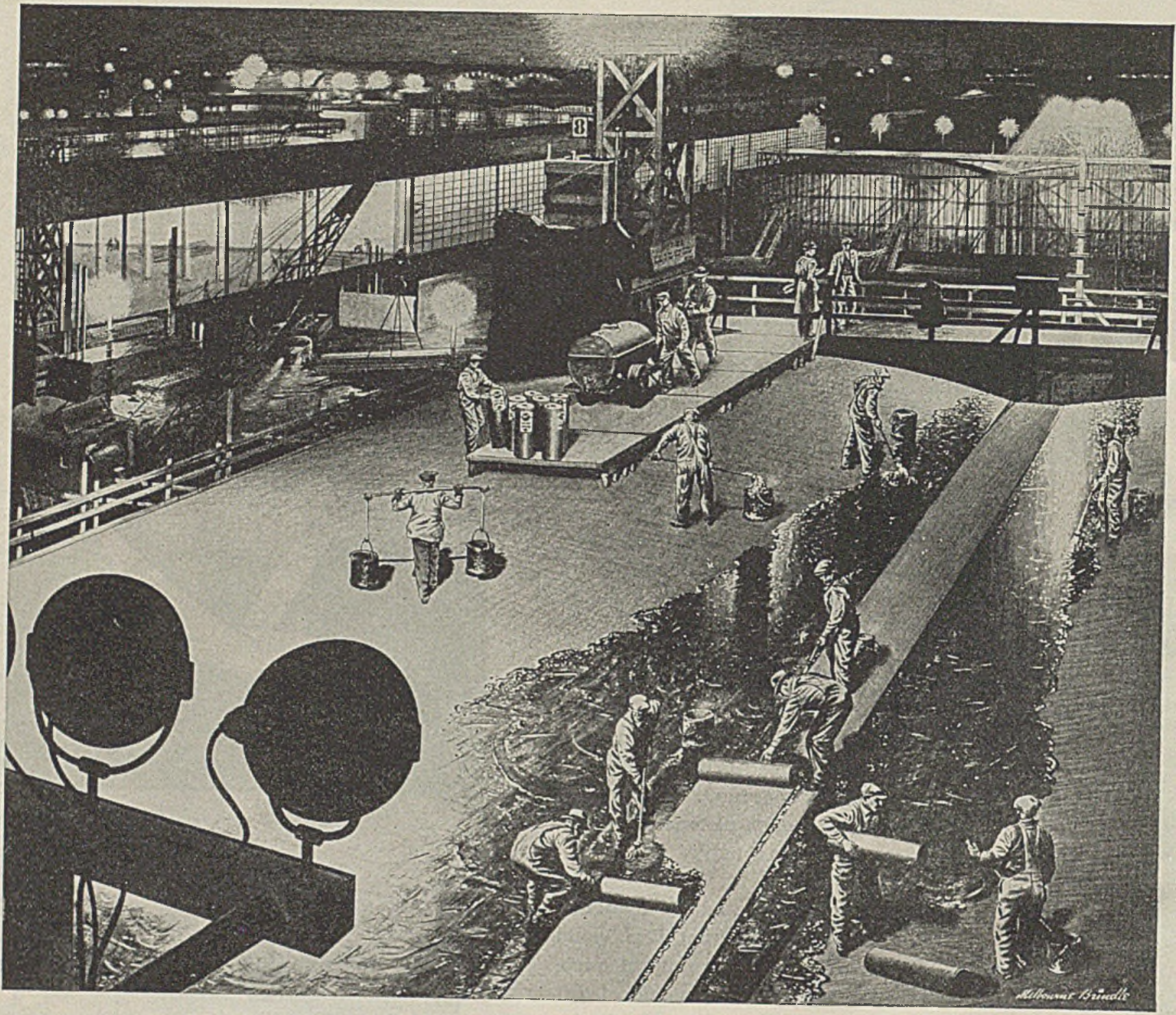
AFFILIATED COMPANIES: Dresser Mfg. Co., Bradford, Pa.; Pacific Pump Works, Huntington Park, Calif.; Bryant Heater Co., Cleveland, Ohio; Bovaird & Seyfang Mfg. Co., Bradford, Pa.



This gas-lift plant operate without vibration, over 2 feet of water, atop of piling



Installation is two CLARK Balanced Opposed Electric-Driven Compressors. Available in sizes from 50 to 1000 H.P., for pressures from 26″ vacuum to 3000 lbs.


8
Melbourne Brindle

"The pilots were quiet and solemn that night"...

Many tales have been told of men and tanks and planes. There is a story, too, of the drums of oil and gasoline that have gone with them to distant lands, and have played a part in strange adventures.

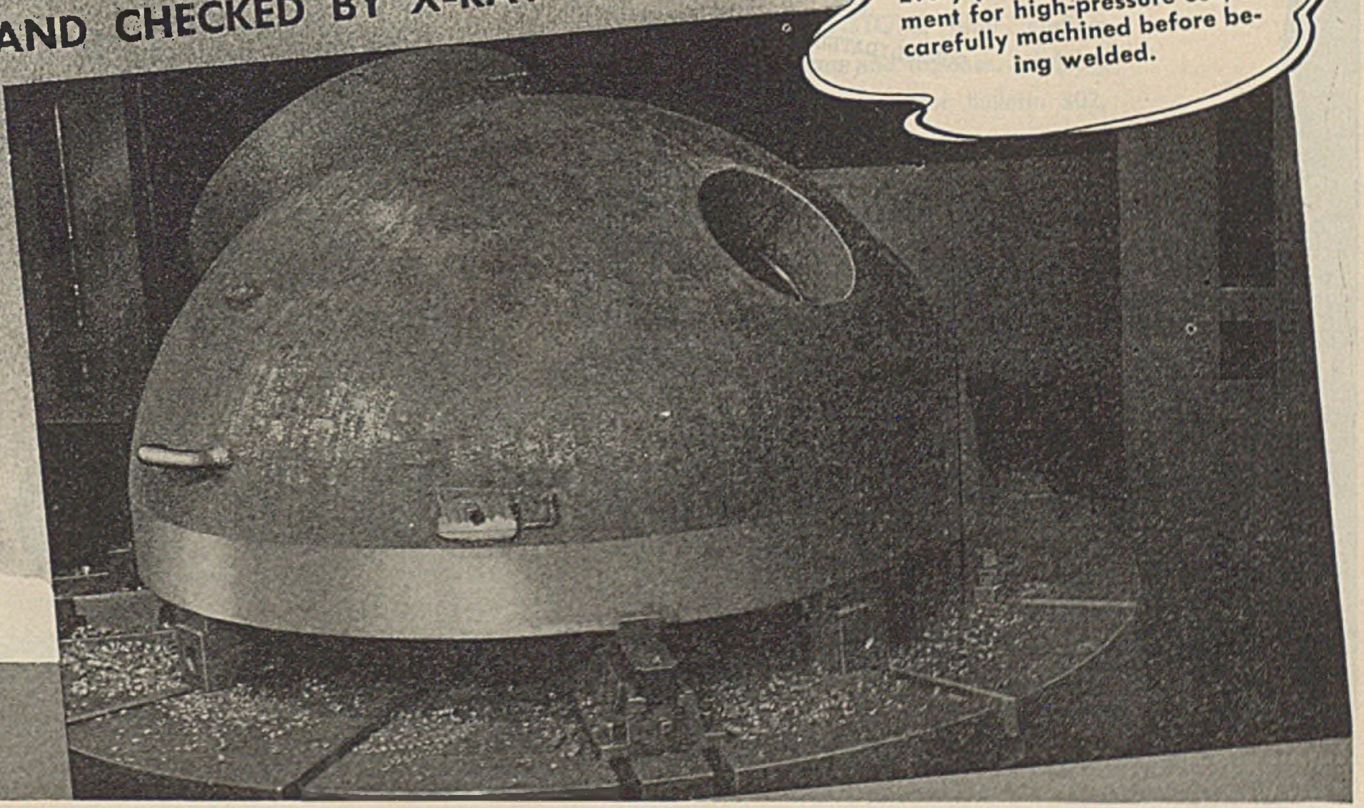
That story is told in "We Were There" — a modern odyssey that carries the reader through history-making exploits in Africa, the Pacific, Tunis, the Aleutians, Java and Alaska. It is profusely illustrated with original portraits of Winston Churchill, General Chiang Kai-shek, General Carl Spaatz, General Sir B. L. Montgomery, Lt. Col. Jimmy Devereux, and pencil studies of natives of Tunisia, the Aleutians and Java. A copy of the De Luxe Edition, beautifully bound, will be sent free upon request. Just mail the coupon.

De Luxe Bound Copy
Free Upon Request

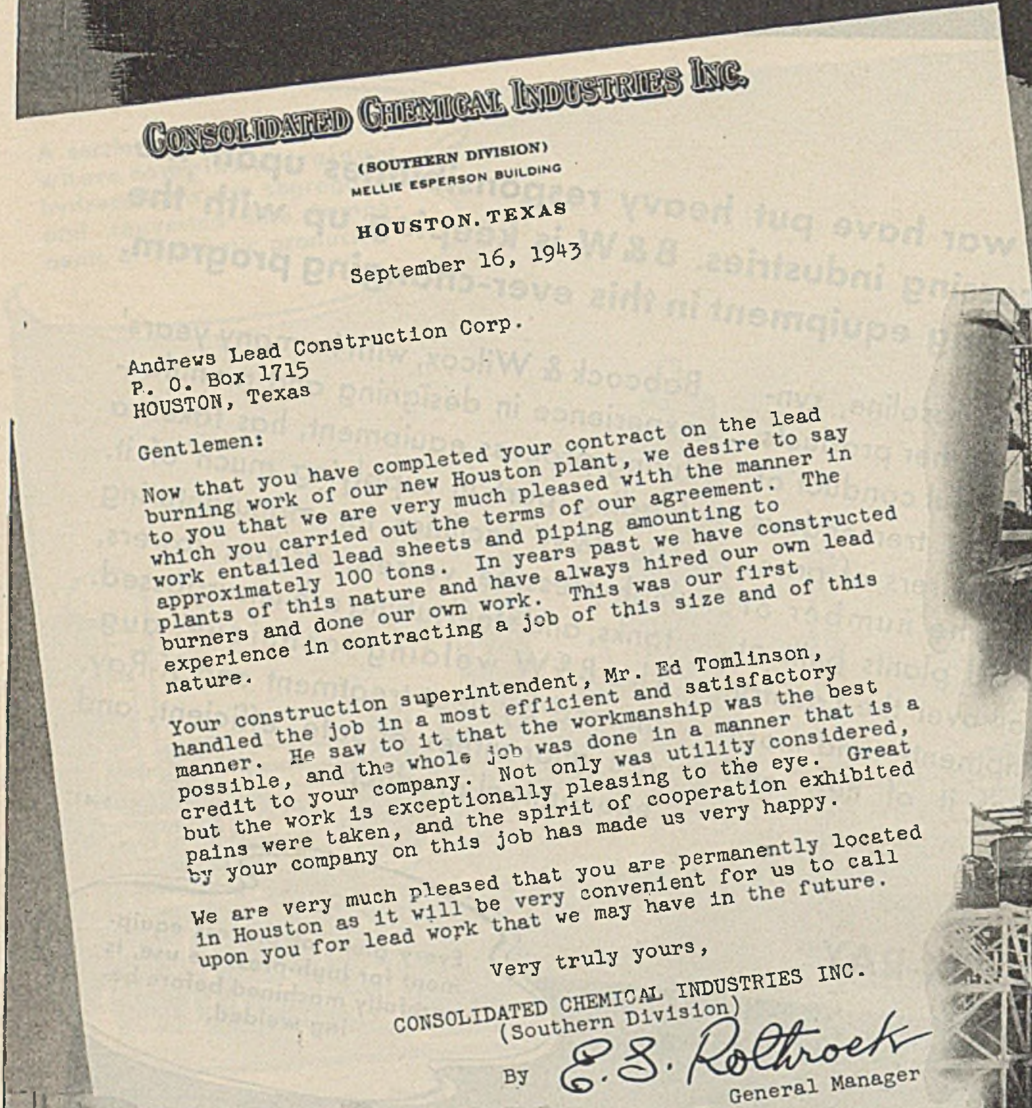
AMERICAN FLANGE & MANUFACTURING CO. INC.
30 Rockefeller Plaza, New York 20, N. Y.

Please send me, free of charge, a copy of the De Luxe Edition of "We Were There."

Name.................................... *Position*............
Firm...
Address..



Another Tough Lead Burning Job Simplified!



CONSOLIDATED CHEMICAL INDUSTRIES INC.
(SOUTHERN DIVISION)
MELLIE ESPERSON BUILDING
HOUSTON, TEXAS

September 16, 1943

Andrews Lead Construction Corp.
P. O. Box 1715
HOUSTON, Texas

Gentlemen:

Now that you have completed your contract on the lead burning work of our new Houston plant, we desire to say to you that we are very much pleased with the manner in which you carried out the terms of our agreement. The work entailed lead sheets and piping amounting to approximately 100 tons. In years past we have constructed plants of this nature and have always hired our own lead burners and done our own work. This was our first experience in contracting a job of this size and of this nature.

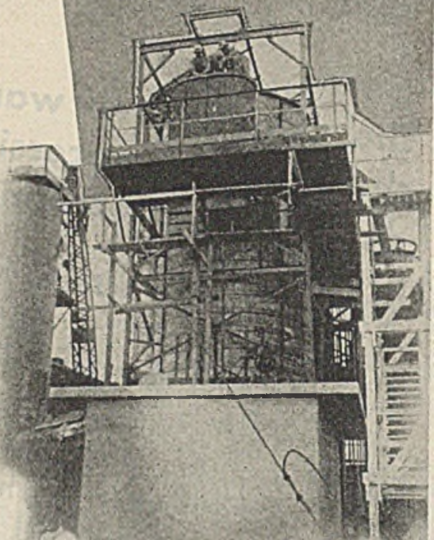
Your construction superintendent, Mr. Ed Tomlinson, handled the job in a most efficient and satisfactory manner. He saw to it that the workmanship was the best possible, and the whole job was done in a manner that is a credit to your company. Not only was utility considered, but the work is exceptionally pleasing to the eye. Great pains were taken, and the spirit of cooperation exhibited by your company on this job has made us very happy.

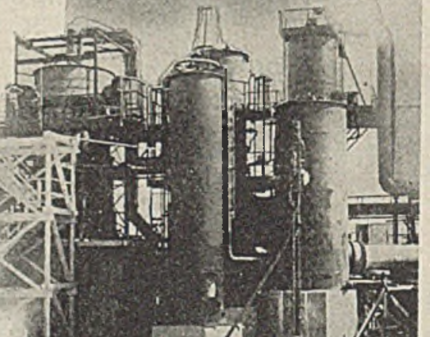
We are very much pleased that you are permanently located in Houston as it will be very convenient for us to call upon you for lead work that we may have in the future.

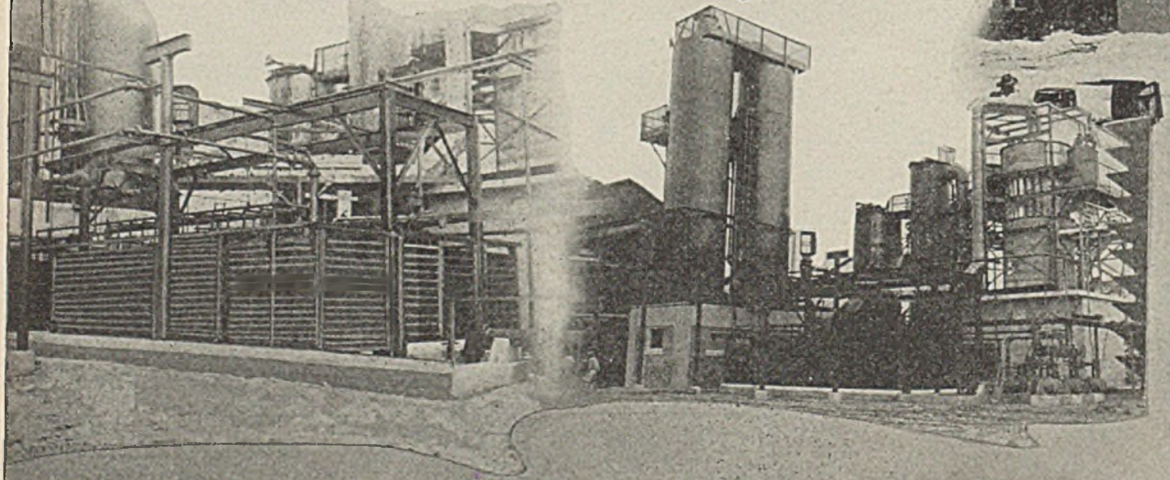
Very truly yours,

CONSOLIDATED CHEMICAL INDUSTRIES INC.
(Southern Division)

By E. S. Rothrock
General Manager





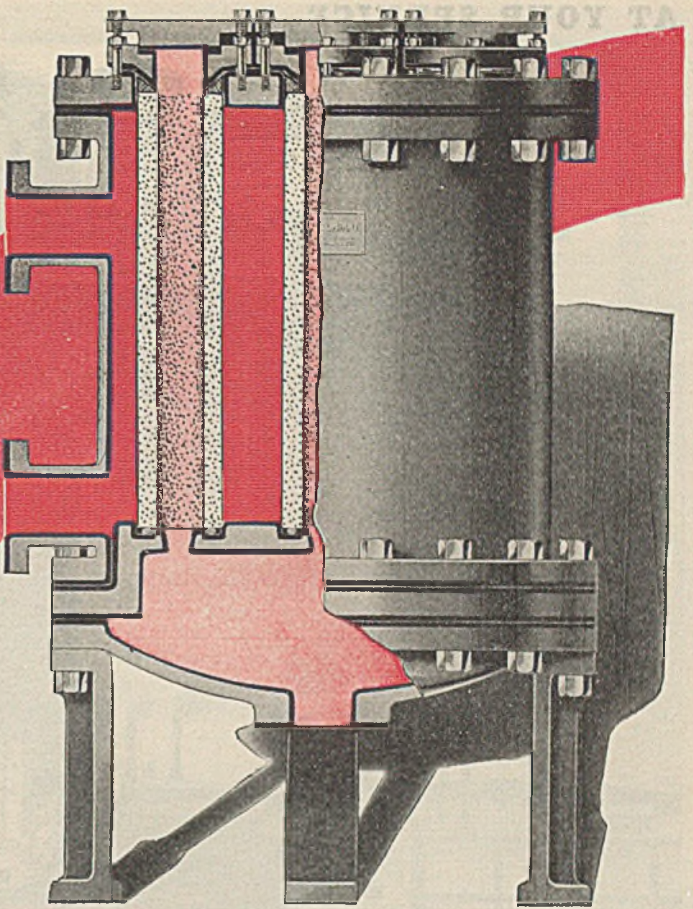


THE ANDREWS LEAD CONSTRUCTION CORP.

LEAD BURNING CONTRACTORS • 120 BROADWAY, NEW YORK 5, N. Y.

PORO-STONE *Filtration* *for* ACIDS

...AND CORROSIVE LIQUIDS



ADAMS PORO-STONE FILTERS embody the most advanced ideas in the design and construction of pressure filter equipment for acids and corrosive liquids. Supplied in two types—the rubber-lined "CFR" and the lead-lined "CFL"—each with its specific application depending on operating conditions. These totally enclosed filter units are compact, easily installed, readily cleaned by back washing. Special construction of PORO-STONE filter medium assures long life and a minimum of maintenance time and expense. Adaptable to a wide variety of industrial applications. Write for Bulletin 302, containing full details.

CORROSION RESISTANT

Heavy duty shell and all internal parts are lead or rubber lined. Corrosion resistant porous filtering medium and bonding material.

ACCESSIBILITY

Adams' design permits inspection or removal of tubes without disturbing shell or piping conditions.

CLEANING

The cleaning process is easily, quickly and neatly accomplished by backwashing a single tube at a time or the complete shell.

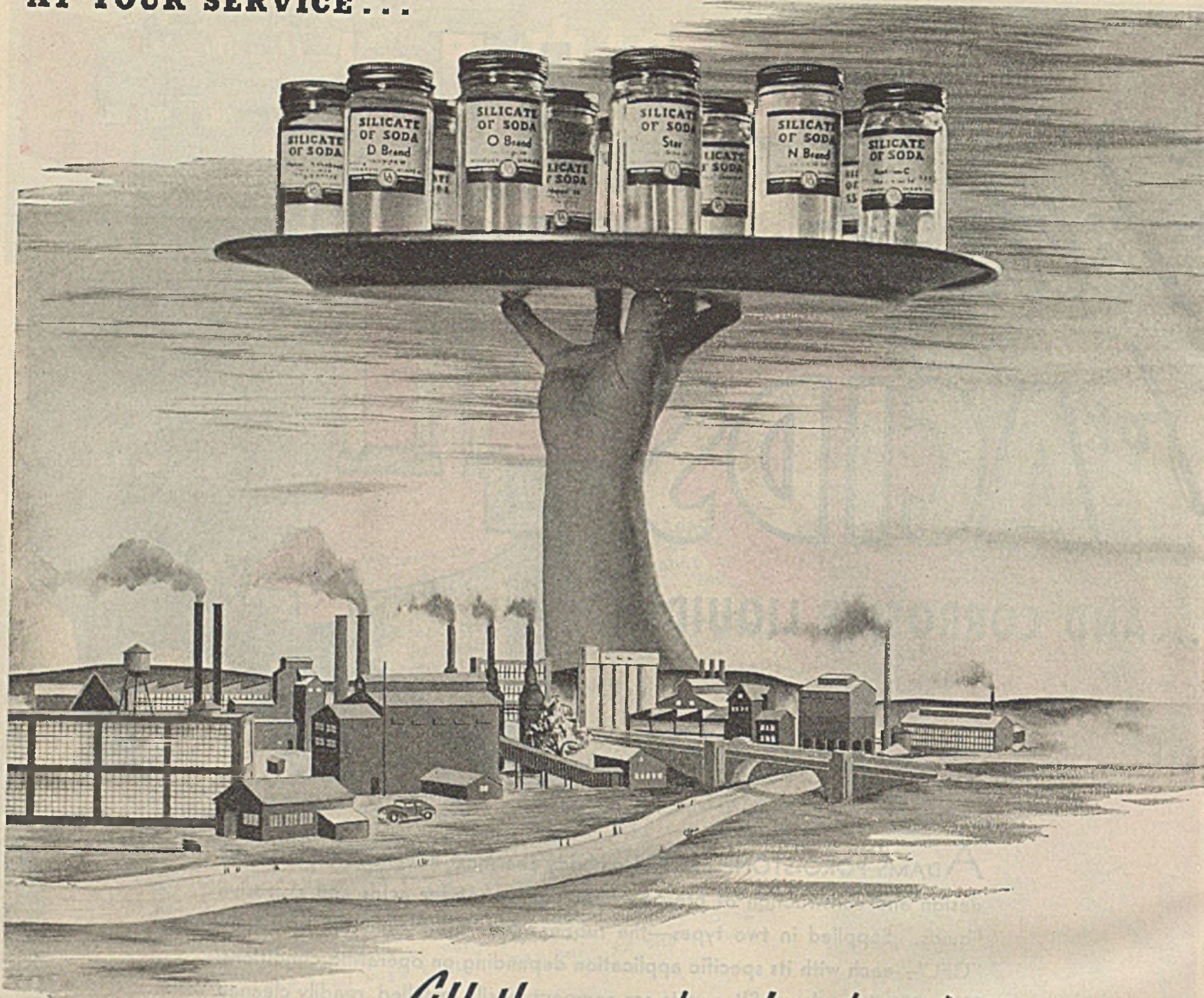
INSTALLATION

The compact, self-contained design permits installation at floor level or elevated. Only three connections required.

R. P. Adams Co. **Buffalo, N. Y.**

ADAMS *Poro-Stone* ACID FILTERS

AT YOUR SERVICE . . .



All these and potassium too

Fifty grades of sodium silicates are here for present day needs in numerous industries and for the needs to come. The useful combinations in the range from $3Na_2O: 2SiO_2$ to $Na_2O: 3.9\ SiO_2$ serve as detergents, adhesives, cements, colloids, inhibitors, coagulating and deflocculating agents and in many other ways.

In certain applications, such as film formation, the bloom that appears on sodium silicate may be objectionable. For non-blooming films, turn to potassium silicates. Several grades are offered under the general name of Kasil.

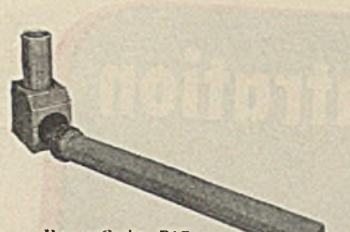
Kasil No. 1	Molecular ratio 1:3.9	29° Baumé
Kasil No. 2	Molecular ratio 1:3.9	32° Baumé
Kasil No. 6	Molecular ratio 1:3.29	40.5° Baumé

Yet another difference in the behavior of potassium as compared with sodium is in its use as a binder in carbon arc pencils. Kasil gives a quieter burning arc of greater length. Hence, formulas for welding electrodes used for metals such as stainless steel specify potassium silicate.

Would you like to have more information on Kasil Potassium Silicates? Perhaps they may open the way to new products or improved processes. We welcome the opportunity to explore these possibilities.

PHILADELPHIA QUARTZ COMPANY

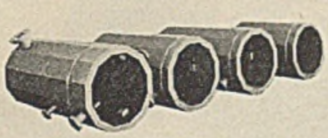
Gen'l Offices: 125 South Third St., Phila; 6, Pa.
Chicago Sales Office: 205 West Wacker Drive



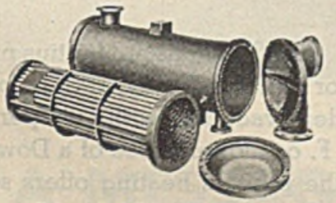
Porous Carbon Diffuser

Pipe, Fittings, Bubble Caps and Trays

Headers for heat exchanger



Sections of segmental type reaction tower



Tube and shell heat exchange unit

For Continuous and Reliable Service

NATIONAL AND KARBATE CARBON AND GRAPHITE PRODUCTS
TRADE-MARK TRADE-MARK

are extremely versatile and readily adapted to the construction of equipment of conventional design as well as special equipment of new design.

Outstanding performance and economies, along with simplification of design, are made possible by the following unique and advantageous combination of physical and chemical properties offered by these materials.

Resistance to severe thermal shock ✓ No deformation at high temperatures ✓ Not wet by molten metals—no sticking ✓ Mechanical strength maintained at high temperatures ✓ No reaction with most acids, alkalies and solvents—no contamination ✓ High rate of heat transfer (Graphite and graphite base "Karbate" products) ✓ Low rate of heat transfer (Carbon and carbon base "Karbate" products) ✓ Low thermal expansion ✓ Good electrical conductivity ✓ Self-lubricating ✓ Available in impervious grades ✓ Available in highly permeable (porous carbon and graphite) grades ✓ Easily machined and fabricated.

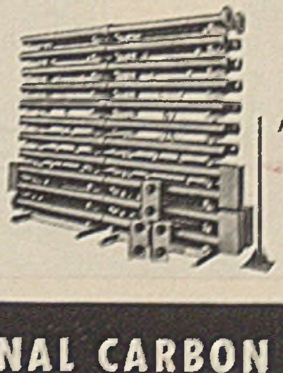
Practically any design can be machined or fabricated from available stock in the form of beams, blocks, slabs, brick, plates, round and rectangular rods, tubes and cylinders, pipe, fittings, valves, tower sections and tower accessories.

Special shapes or forms can be molded or extruded when quantity justifies.

The illustrations show only a few of the many diversified applications of these products.

Write for descriptive literature

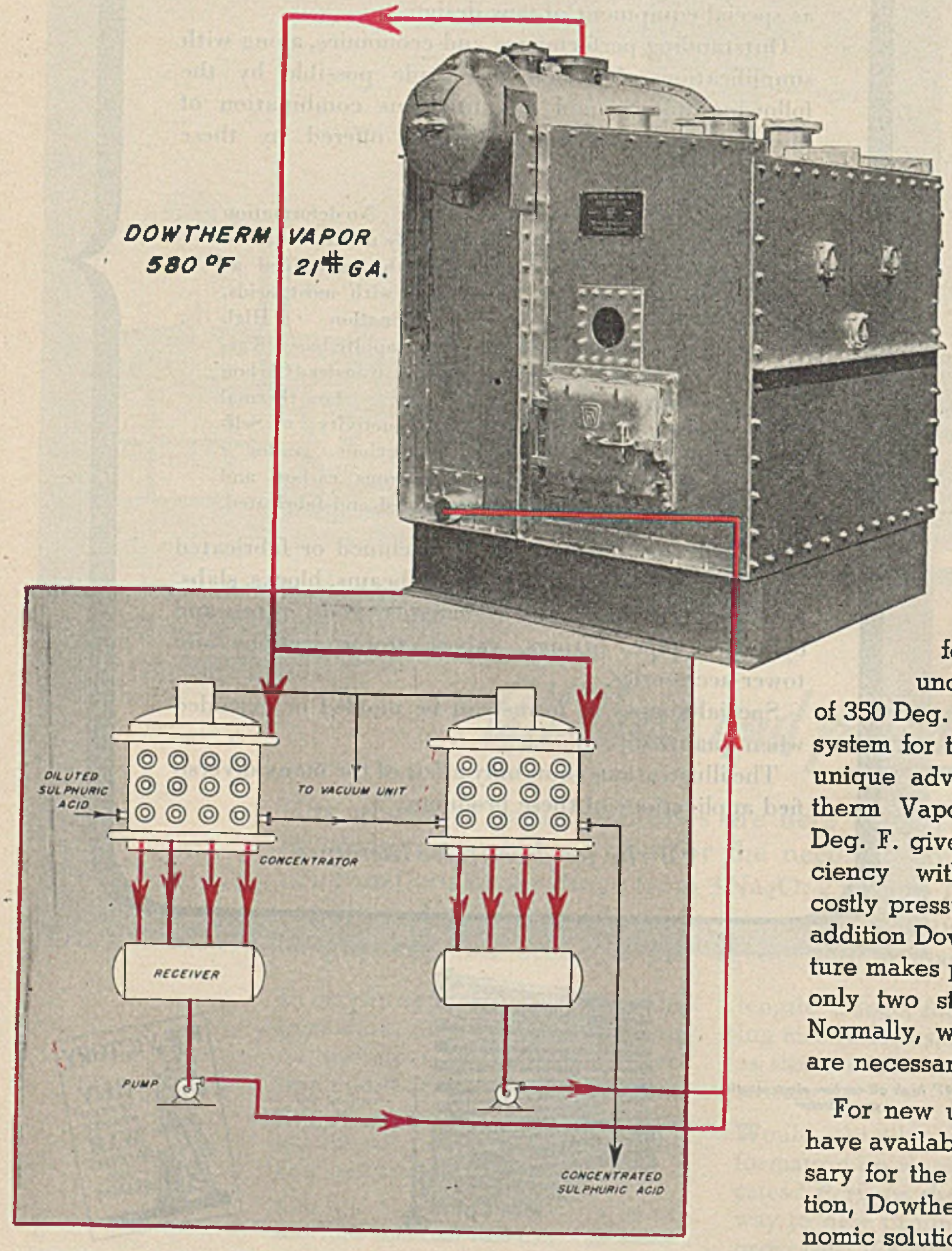
47' high all-carbon electrostatic precipitator



Return bend cooling coil

NATIONAL CARBON COMPANY, INC.
Unit of Union Carbide and Carbon Corporation
UCC
CARBON PRODUCTS DIVISION, CLEVELAND, OHIO
General Offices: 30 East 42nd St., New York, N. Y.
Branch Sales Offices: New York - Pittsburgh - Chicago - St. Louis - San Francisco

Sulphuric Acid Concentration with DOWTHERM PROCESS HEATING



The Simmonson-Mantius process for reconcentrating H_2SO_4 operates under vacuum with temperatures of 350 Deg. F. or higher. Use of a Dowtherm system for the process heating offers several unique advantages. The condensing Dowtherm Vapor at 21 psi pressure and 580 Deg. F. gives the maximum evaporative efficiency with minimum heating surfaces; costly pressure equipment is eliminated. In addition Dowtherm's high operating temperature makes possible successful operation with only two stages of the acid concentrator. Normally, when steam is used, three stages are necessary.

For new users of this process who do not have available the high pressure steam necessary for the higher stage of acid concentration, Dowtherm offers the practical and economic solution.

FOSTER WHEELER CORPORATION, 165 BROADWAY, NEW YORK 6, N. Y.

FOSTER FW WHEELER

(Painted from an actual war photograph,

A MESSAGE TO THOSE WHO FORGET

We have a photograph very much like the illustration on this page, but we cannot publish it.

Its grim reality is simply too shocking; and yet that very reality might serve a useful purpose. For, all too many of us read the casualty list in terms of numbers, forgetting that each unit in the number is an American boy lost or wounded or dead.

In very much the same way we read figures about production at home, forgetting that figures on production—and figures on lowered production due to slow downs—can be a real measure of the men who won't come back.

It is only when we think of these numbers of lost hours of production in life-and-death terms of men, that we realize how vital it is to win the *earliest* victory; and that the way we at home can best contribute toward this, is to eliminate industrial slow downs.

Fortunately many types of slow downs *can* be prevented.

Not among the least of these is the slow down due to valve failures. The way to prevent this type is *to avoid valve trouble before it starts.*

Have the valves in your plant inspected *regularly.* Have the operation and maintenance of valves entrusted to experienced hands. If workers *are* new, be sure that they are trained at the earliest moment to operate valves properly. When new valves are installed, make sure that they are selected and installed by experts.

Jenkins Engineers are ready to assist any management in developing a practical program of valve conservation.

Reprints of this advertisement are available for display in your plant.

Jenkins Bros., 80 White Street, New York 13, N. Y.; Bridgeport, Conn.; Atlanta, Ga.; Boston, Mass.; Philadelphia, Pa.; Chicago, Ill. Jenkins Bros., Ltd., Montreal; London, Eng.

TRADE JENKINS MARK

Jenkins Bros

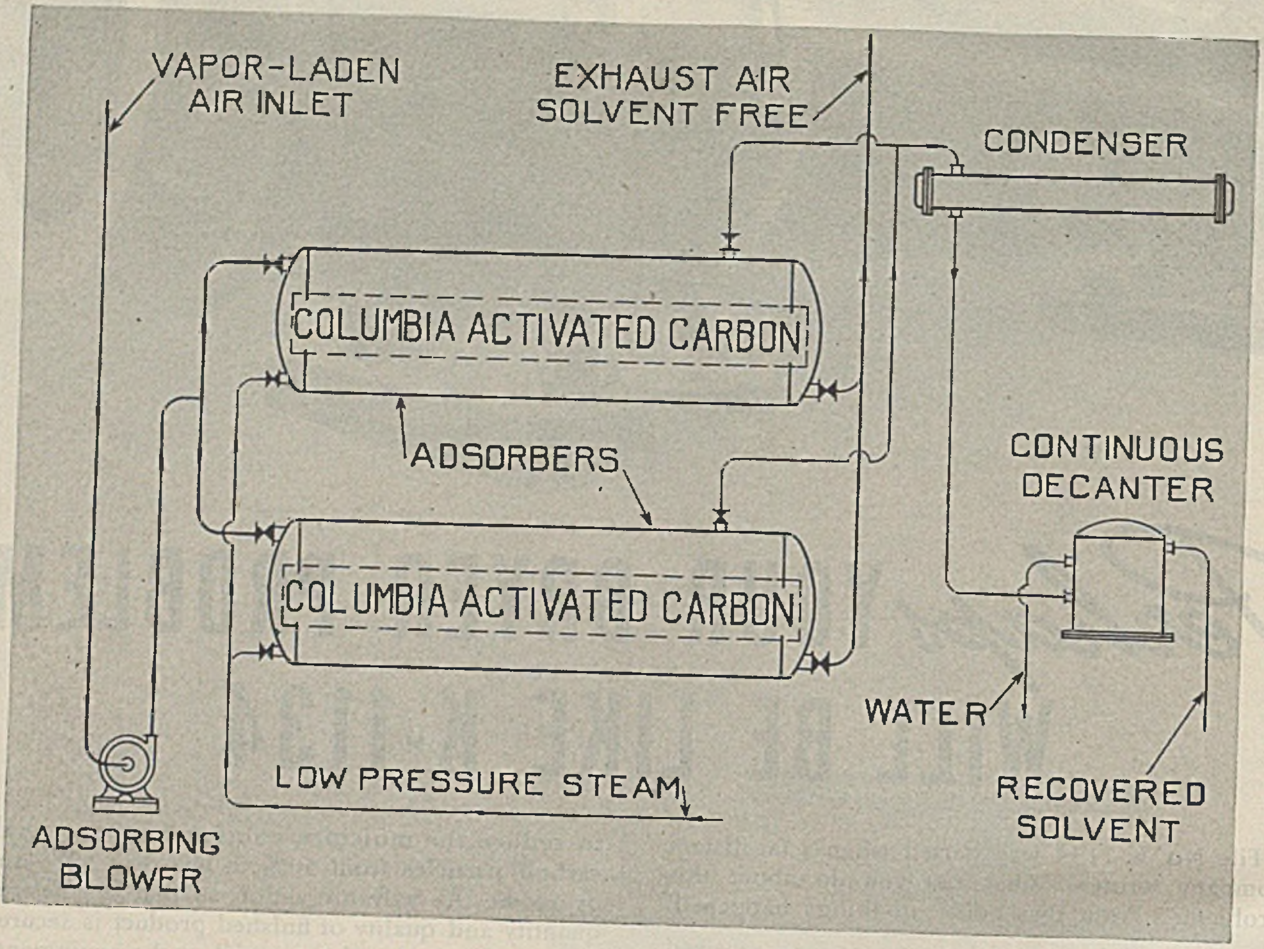
JENKINS VALVES

SINCE 1864

For every industrial, engineering, marine and power plant service . . . in Bronze, Iron, Cast Steel and Corrosion-Resisting Alloys . . . 125 to 600 lbs. pressure.

How Solvent Vapors Are Recovered From Air

With COLUMBIA Activated Carbon



SOLVENT recovery plants using COLUMBIA Activated Carbon are being used in many types of manufacturing operations where solvents are vaporized. All kinds of organic solvents—alcohols, chlorinated compounds, esters, ethers, hydrocarbons, ketones, and carbon bisulfide—can be recovered with high-operating efficiency and low recovery cost. Many of the large plants are automatically operated.

Here is how one simple type of solvent-recovery system works:

The vapor-laden air is drawn into the collecting plant by the blower, and is passed through the bed of activated carbon. The activated carbon adsorbs the solvent vapor, and the solvent-free air is discharged to the atmosphere.

When the activated carbon has adsorbed the desired amounts of solvent . . . in ordinary operations this takes about 30 minutes to one hour . . . the air stream is switched to another adsorber. The adsorbed solvent is driven out of the carbon bed with low-pressure steam and the steam-solvent vapor mixture is condensed.

If the solvent is not soluble in water, it is separated by an automatic decanter. When the solvent is water-soluble, it is separated by distillation.

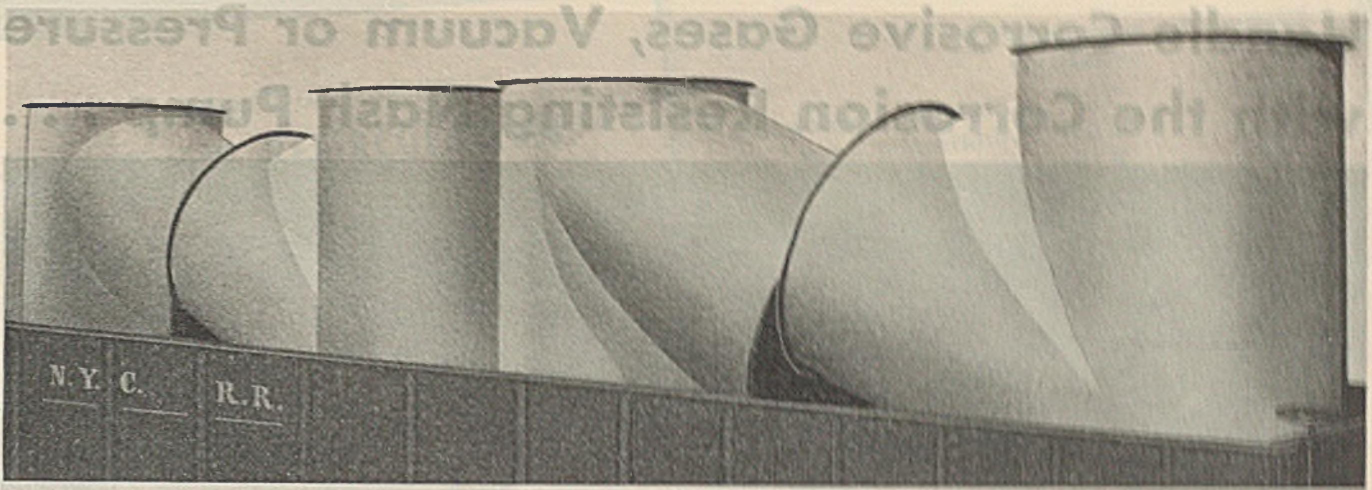
We design and supply complete solvent recovery plants to meet individual manufacturing problems. Write for our booklet, "Solvent Recovery by the COLUMBIA Activated Carbon System."

For information concerning the uses of COLUMBIA Activated Carbon, address:

CARBIDE AND CARBON CHEMICALS CORPORATION
Unit of Union Carbide and Carbon Corporation
30 East 42nd Street UCC New York, N. Y.
PRODUCERS OF SYNTHETIC ORGANIC CHEMICALS

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

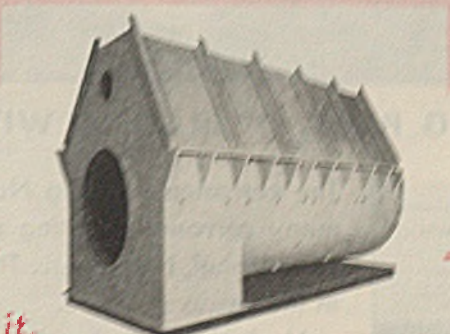
BUY UNITED STATES WAR BONDS AND STAMPS



. . . Part of a Single Job of

200 Car Loads of FABRICATED PLATE and SHEET WORK

The photo above shows four (4) special Y's for dust-collection system—7-foot diameter. The Y's are fabricated from $\frac{1}{2}$-inch plate with forged bar flanges and of all-welded construction. This equipment is part of **200 carloads of equipment** for ore collection systems preparatory to the manufacture of aluminum. Built in the Jay-Cee plant in Johnson City, Tenn.



At right: One of 31 fabricated steel chambers, each weighing more than 15 tons; fabricated by Jay-Cee in Johnson City, Tenn.

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

JAY-CEE

JOHNSON CITY

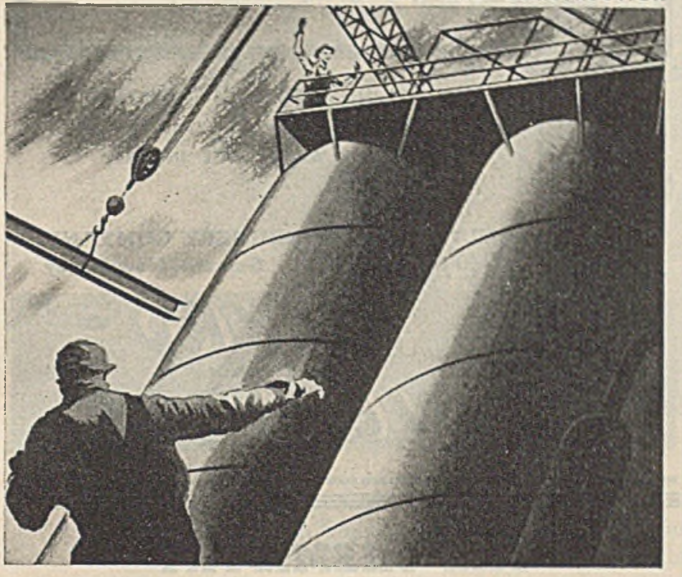
JOHNSON CITY, TENNESSEE . . SINCE 1882

GRAY IRON & ALLOY CASTINGS - STRUCTURAL STEEL - MISCELLANEOUS & ORNAMENTAL IRON WORK - SPECIAL MACHINE WORK


ALL HANDS AT
PROCESS ENGINEERING AND DESIGN

BATTLE STATIONS!

PROCUREMENT AND CONSTRUCTION



INITIAL PLANT OPERATION

War is still America's most serious business of the moment. Industrial efficiency is high—but not high enough. Production is huge—but still short of goals. Both objectives demand the redoubled effort of every loyal individual and concern.

Badger is knee-and-elbow-deep in the kind of large-scale work for which Badger's long experience is particularly suited. Since Pearl Harbor—and before—Badger services have been heavily engaged in process engineering, design and construction for both Government and private war-production plants in the chemical, petroleum and petro-chemical fields.

The total number of Badger employees engaged on war projects to date would populate a small city. The many construction operations in which Badger has had an important part during the past three years extend through many states and foreign countries. They represent a value approximating the cost of several "Alcan" highways.

Conspicuous are plants for the manufacture of butadiene, alcohol, toluol, tri-nitro-toluene, plus many complete refineries for the production of aviation gasoline.

Badger is thoroughly equipped and manned to assume full responsibility for the complete handling of any size project, from inception to final test-run operation. Around the key personnel of Badger's central organization are technical and laboratory engineers; design engineers and draftsmen; procurement, expediting and accounting experts; seasoned and efficiently supervised construction crews; experienced plant operators.

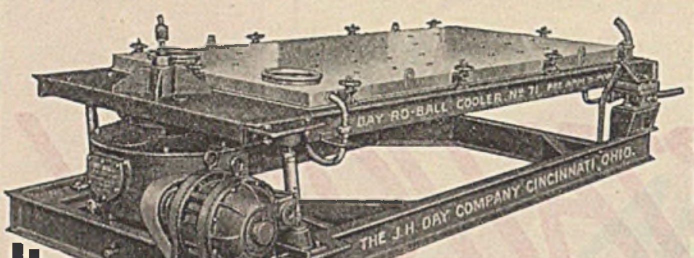
All these combine to afford the many advantages to be gained from placing everything in the hands of one qualified concern working in close co-operation with your own organization.

E. B. Badger & SONS CO.

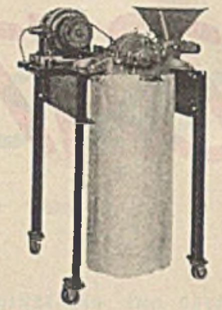
BOSTON **EST. 1841**

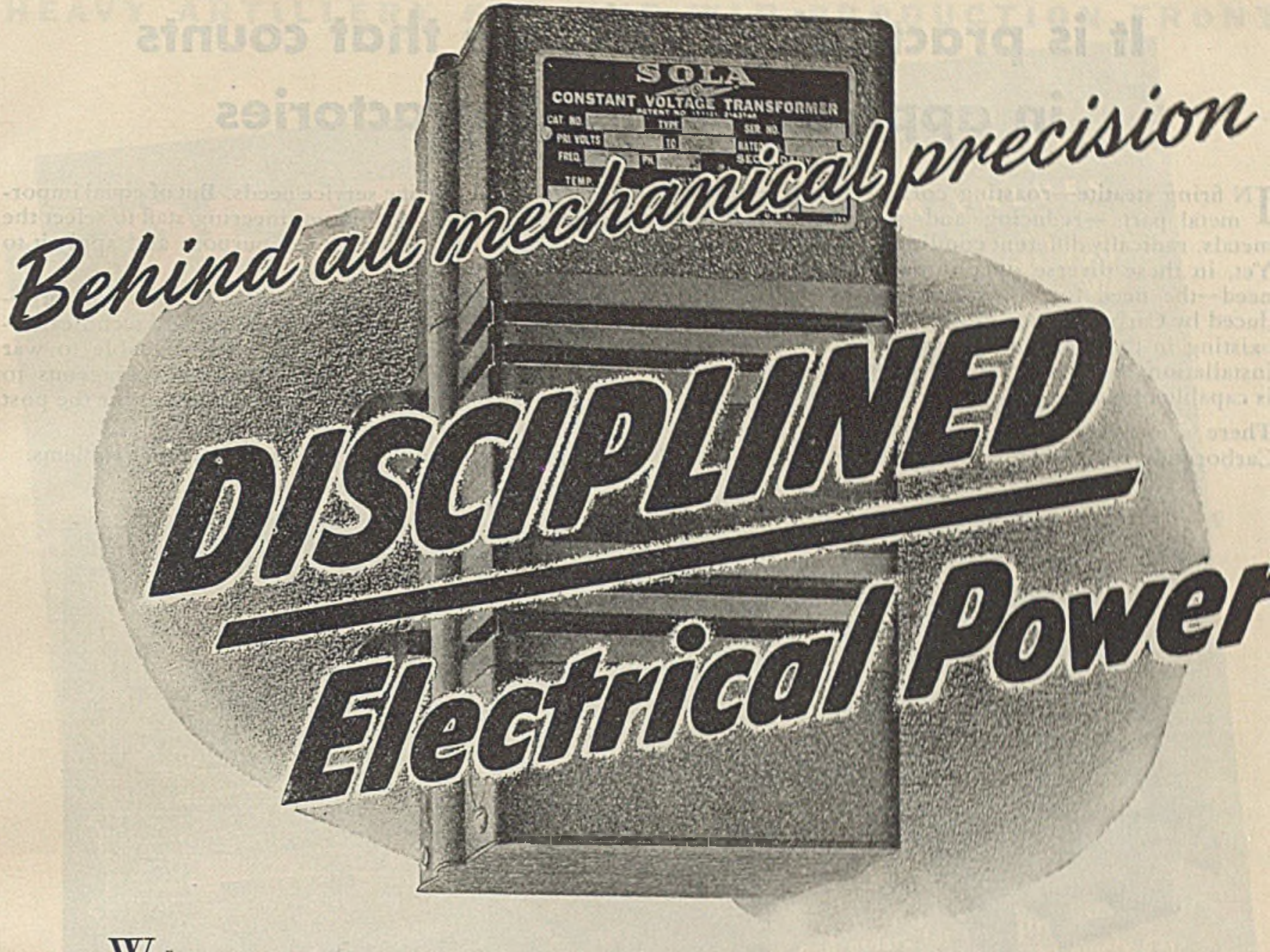
New York • Philadelphia • San Francisco • London

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


DAY RO-BALL COOLER No 71
THE J.H. DAY COMPANY CINCINNATI, OHIO.


RO-BALL DEWATERER No 71
THE J.H.DAY CO. CINCINNATI, OHIO.




SOLA
CONSTANT VOLTAGE TRANSFORMER
CAT. NO.
TYPE
SER. NO.
PRI. VOLTS
FREQ.
PH.
TEMP.

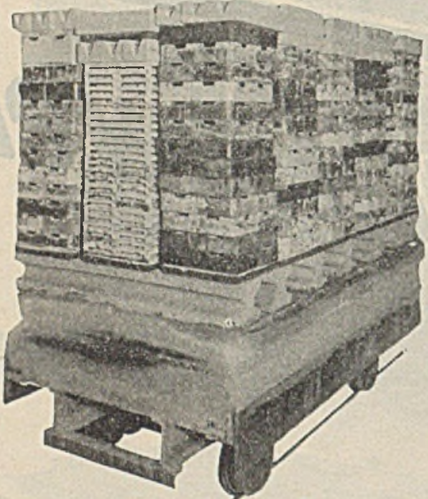
It is practical experience that counts in applying Super Refractories

IN firing steatite—roasting corrosive ores—treating metal parts—reducing and refining non-ferrous metals, radically different conditions are encountered. Yet, in these diverse operations there is a common need—the need for super refractories such as produced by Carborundum. With the variable conditions existing in these as well as numerous other types of installations, no one grade or kind of super refractory is capable of meeting their individual requirements.

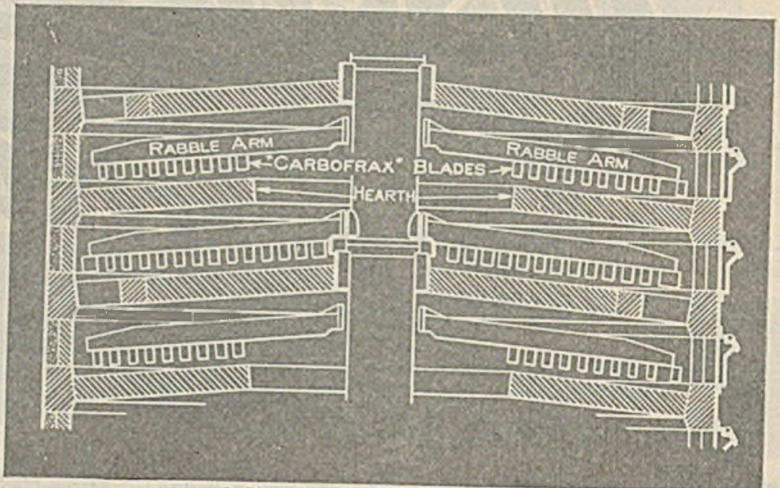
There are now more than sixty-five varieties of Carborundum Brand Super Refractories, each designed to withstand specific service needs. But of equal importance is the ability of our engineering staff to select the right super refractory for the purpose and apply it to a given installation.

Our comprehensive understanding of refractory problems—gained from years of practical and technical experience—has proved exceptionally valuable to war industry plants. It will be equally advantageous to operators of new and improved processes for the post war era.

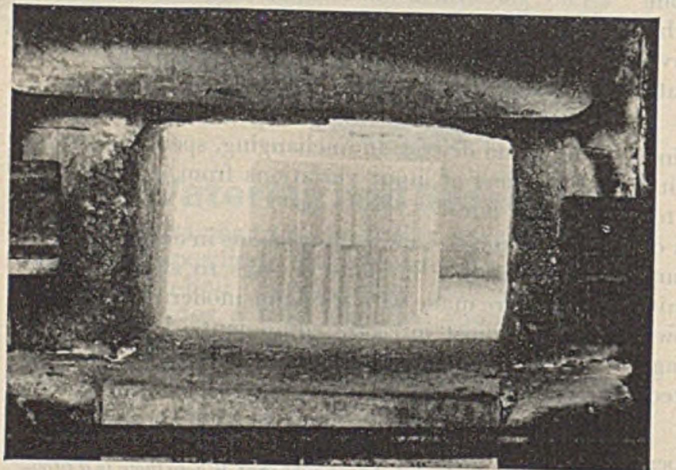
Let us consult with you on your refractory problems.



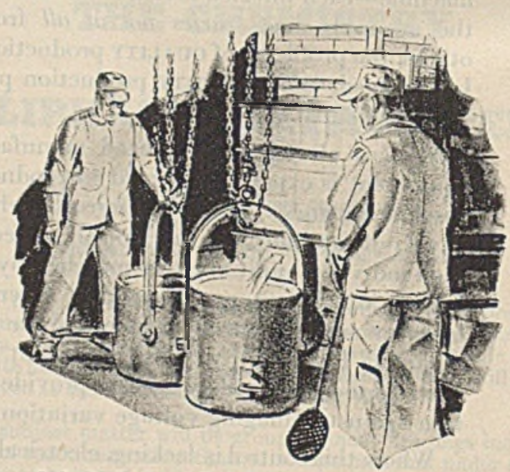
1 Firing Steatite



2 Roasting Corrosive Ores



3 Annealing



4 Reducing and Refining Non-ferrous Metals

Every hour this war is shortened will save $12,000,000. The lives it will save are priceless. Let's get it over with—quickly!

REFRACTORY CARBORUNDUM PRODUCTS

Refractory Division, **THE CARBORUNDUM COMPANY,** *Perth Amboy, N. J.*

REG. U. S. PAT. OFF.

MANUFACTURERS OF GRINDING WHEELS, COATED ABRASIVES, SUPER REFRACTORIES, HEATING ELEMENTS

District Sales Branches: Chicago, Philadelphia, Detroit, Cleveland, Boston, Pittsburgh. Distributors: McConnell Sales and Engineering Corporation, Birmingham, Ala.; Christy Firebrick Company, St. Louis, Mo.; Harrison & Company, Salt Lake City, Utah; Pacific Abrasive Supply Company, Los Angeles, San Francisco, Calif.; Denver Fire Clay Company, El Paso, Texas; Smith-Sharpe Company, Minneapolis, Minn.

(Carborundum, Carbofrax, Alfrax and Mullfrax are registered trade-marks of and indicate manufacture by The Carborundum Company)

HEAVY ARTILLERY FOR THE WAR PRODUCTION FRONT

READY ...TO SERVE YOUR NEEDS FOR NORDSTROM VALVES

We have made tremendous progress on our backlog of orders and within a few weeks, if not by the time this message appears, we will be largely in the clear on critical steel valves. We will then have open capacity to handle new steel valve business in the sequence received, subject, of course, to the priority rating assigned.

NEED VALVES AT ONCE? Right now we have available manufacturing facilities that are not suited to the production of steel valves and we can effect immediate stock delivery of Nordstrom Semi-Steel Valves in certain sizes and figure numbers.

AIM ...YOUR SIGHTS NOW ON LATE 1943 AND FIRST QUARTER 1944 CONSTRUCTION

Those booking orders now, in anticipation of late 1943 and early 1944 valve requirements will have first call on our facilities. Immediate action on your part is desirable so that we may establish firm delivery dates based upon amply foreseen needs for materials and carefully predicated manufacturing schedules.

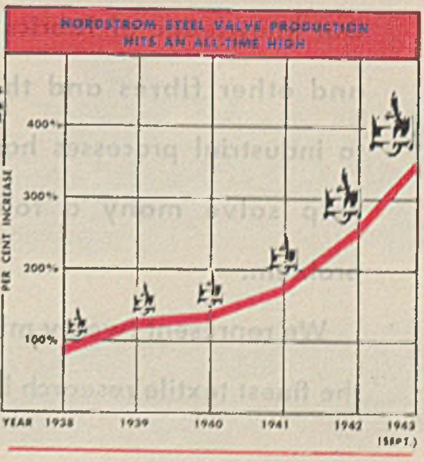
FIRE ...YOUR INQUIRIES AND ORDERS AT US

We can handle your immediate business in many lines and orders for Nordstrom Valves of any type can be accepted with excellent prospect of delivery within a maximum of ninety days after receipt of firm specifications. (The WPB lead factor for cast steel valves is 90 days.)

Merco Nordstrom Valve Company, in common with the entire valve industry, is emerging from a very trying period. Earlier this year the need for valves in vital wartime industries greatly exceeded all available facilities. Nordstrom was ordered to produce 600% over normal capacity during a short period and then was confronted with shortages ranging from man-power and machine tools through storage facilities and materials. These handicaps, we are pleased to report, have now been largely eliminated—thanks to a realization on the part of the War Production Board of the indispensable and unique position occupied by Nordstrom Valves.

Our tonnage of cast steel Nordstrom Valves has shown a progressive increase month by month. Our plant capacity is now geared to a production rate never before attained in our history. We know of no other valve company that has had a greater load thrust upon it or has used more vigorous efforts to satisfy the demands of their customers.

Out of all this has come a stronger more integral Nordstrom organization—one capable of handling the immediate needs of today and with adequate post-war facilities to service an increasing circle of Nordstrom Valve users.



MERCO NORDSTROM VALVE COMPANY

A Subsidiary of
Pittsburgh Equitable Meter Co.

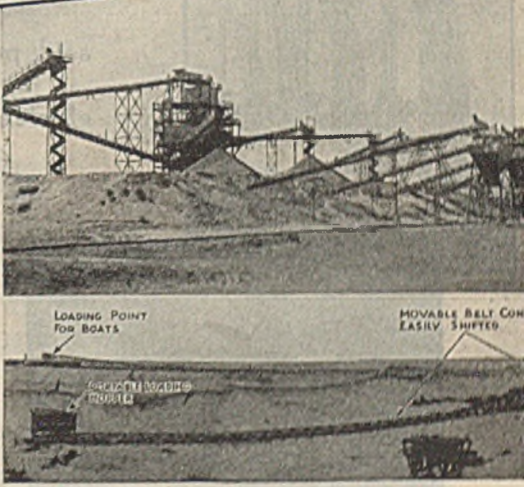
Main Office: Pittsburgh, Pennsylvania
Branches: Boston • Buffalo • Brooklyn • Chicago
Columbia, S. C. • Houston • Kansas City • Los
Angeles • Memphis • New York • Oakland
Seattle • Tulsa • San Francisco

NORDSTROM VALVES

KEEP UPKEEP DOWN

AS TIME GOES BY...

Designs Change . . . but S-A Quality Remains the Same



● Changing times bring changing needs. The need for new and better labor-saving, conveying methods is always present. We at Stephens-Adamson have always held it primarily important not only to stay abreast of new developments . . . but to anticipate and constantly plan for them.

Right now, this aspect of S-A activity has *double* significance . . . (1) the solution of your present problems . . . (2) the solution of new handling problems connected with new processes and products contemplated for the post-victory world.

STEPHENS-ADAMSON MFG. CO., 44 Ridgeway Ave., Aurora, Ill.

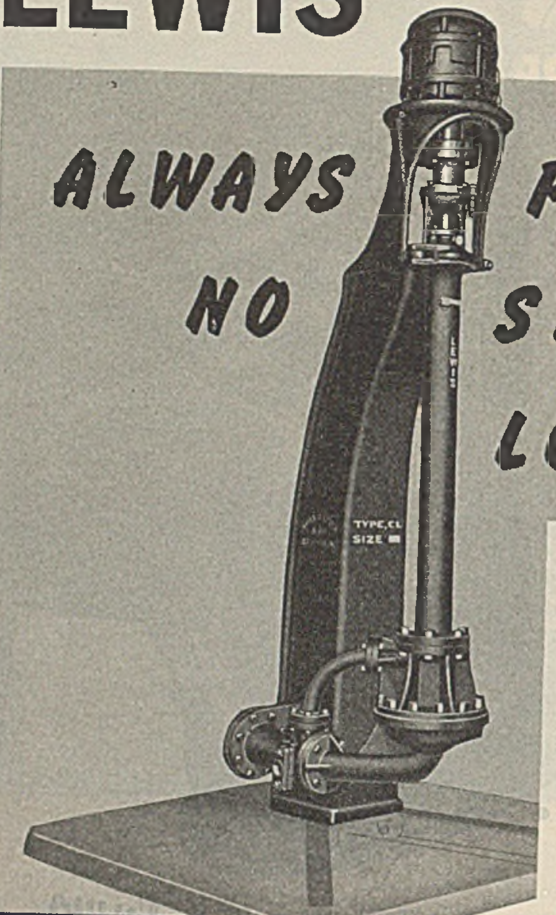
STEPHENS-ADAMSON

MFG. CO.

Designers and Manufacturers of All Types of

BULK MATERIAL HANDLING EQUIPMENT

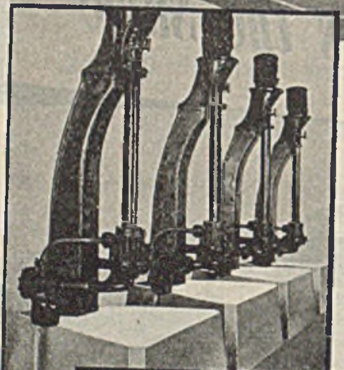
LEWIS VERTICAL ACID PUMPS

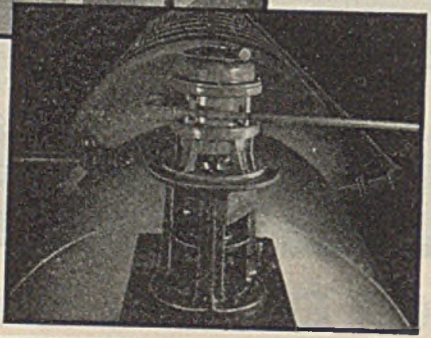


ALWAYS PRIMED
NO STUFFING BOX DRIP
LOW POWER COST

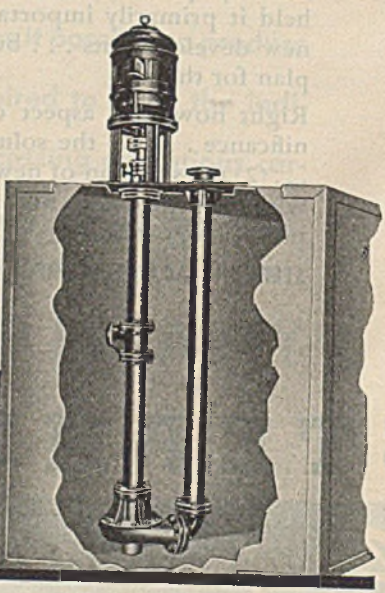
Since 1914, owners and operators of H_2SO_4 plants have learned that Lewis Vertical Acid Pumps are *continuously* reliable . . . whether the pumps are submerged or externally mounted—as single or multiple units.

When you specify "Lewis" on the next acid pump requisition, you will be certain that you are buying safe, efficient and reliable service—even under severe operating conditions.

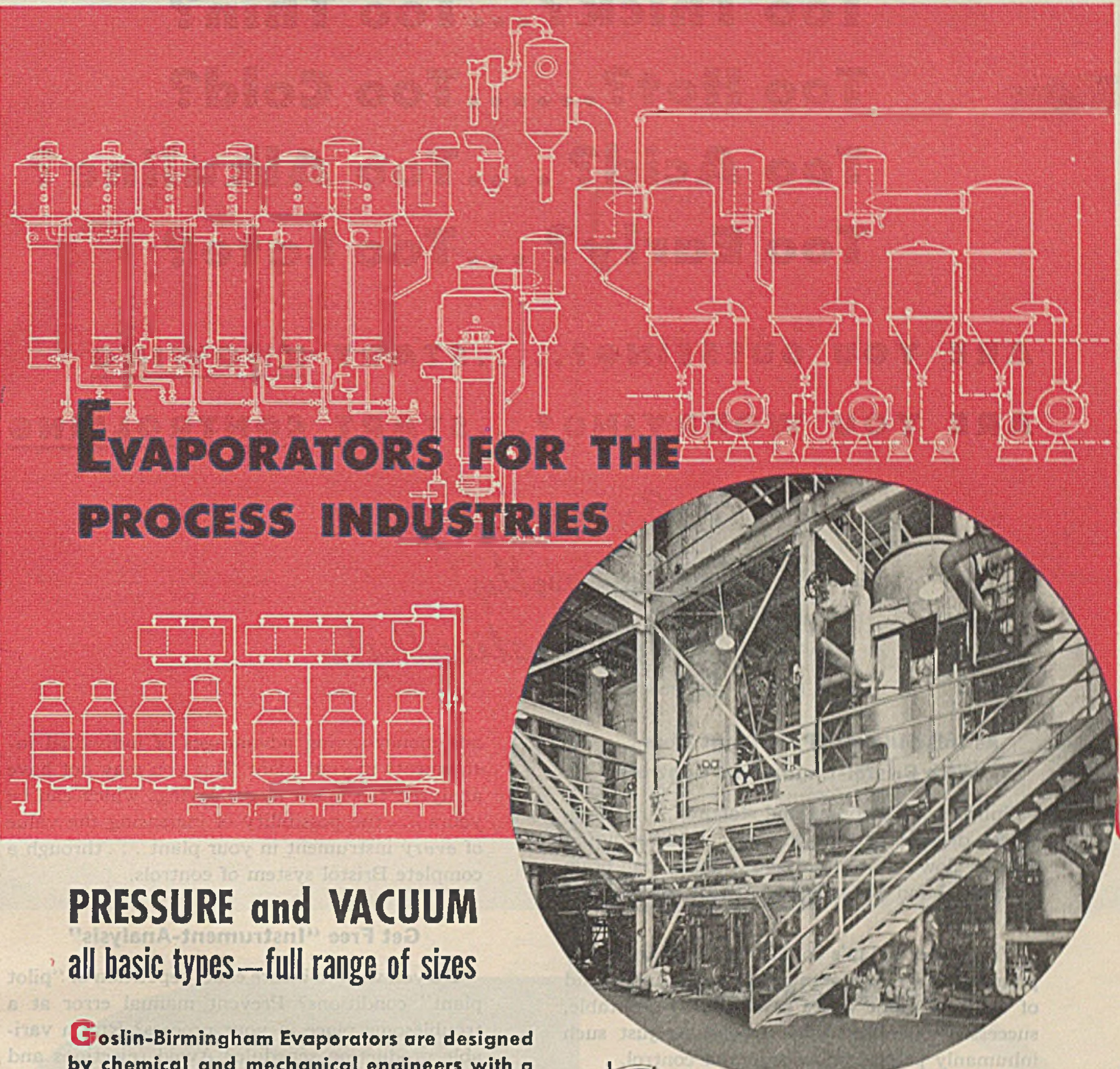




Many mounting arrangements are possible with Lewis Vertical Acid Pumps. Whatever your requirement, there is a way to meet it specifically with a standard Lewis pump.



CHAS. S. LEWIS & CO., INC.
ST. LOUIS, MO.



EVAPORATORS FOR THE PROCESS INDUSTRIES

PRESSURE and VACUUM

all basic types—full range of sizes

Goslin-Birmingham Evaporators are designed by chemical and mechanical engineers with a thorough background of technical and practical experience.

The evaporator units are of extreme simplicity in design, providing trouble-free operation with efficient heat transfer, low entrainment losses and definitely superior performance.

Installations cover such abnormal conditions as high viscosities, high boiling point elevations, heat sensitivity, extremely corrosive liquids, crystalization of products, severe foaming and the robbing of the effects for low pressure vapors for other process requirements.

Goslin-Birmingham Evaporators are built in all standard types, and modifications of evaporators, so our engineers can without prejudice recommend the evaporator type, material and construction best suited to your specific problem.

Write for Bulletin No. 301 for further information

BIRMINGHAM Long Tube Vertical Evaporators
BIRMINGHAM Forced Circulation Evaporators
BIRMINGHAM Standard Vertical Tube Evaporators
BIRMINGHAM Horizontal Tube Evaporators

GOSLIN-BIRMINGHAM MFG. COMPANY

CHICAGO
NEW ORLEANS
TULSA

BIRMINGHAM 1, ALABAMA
350 Madison Ave., New York 17, N. Y.

SALT LAKE CITY
SEATTLE
SAN FRANCISCO

Too Thick?...Too Thin?
Too Hot?......Too Cold?
Too Acid? ....Too Alkaline?
Too Early? ...Too Late?

ARE YOU GUESSING?.....START KNOWING

ARE YOU WORRYING?...START CONTROLLING

Accurately!
Instantly!
Automatically!

As this Sulphate Pulp Plant Does . . . With Bristol-Engineered Controls

Split-second stopping and starting . . . at fractional degrees of temperature, pressure, liquid level or flow . . . is often more than human brain or eye or hand can manage without costly errors and delays.

Yet, under today's conditions . . . when every pound of raw material must produce a full pound of value, without waste or error . . . profitable, successful operation may depend on just such inhumanly precise knowledge and control.

Automatic "Nervous Systems" Need Automatic "Brains"

Undoubtedly you already have tested the time-and-money-saving advantages of individual instruments in your plant. But you may not have analyzed the much larger savings which can be yours . . . the possibility of increasing the value of *every* instrument in your plant . . . through a complete Bristol system of controls.

Get Free "Instrument-Analysis"

Do you wish to insure exact repetition of "pilot plant" conditions? Prevent manual error at a troublesome place in your process? Run a variable production schedule? Avoid rejections and waste of vital raw materials? Bristol engineers are available to "case" your process in the light of modern developments in automatic recording and controlling. Write today, addressing 110, Bristol Rd., Waterbury, Connecticut.

THE BRISTOL COMPANY

WATERBURY, CONNECTICUT

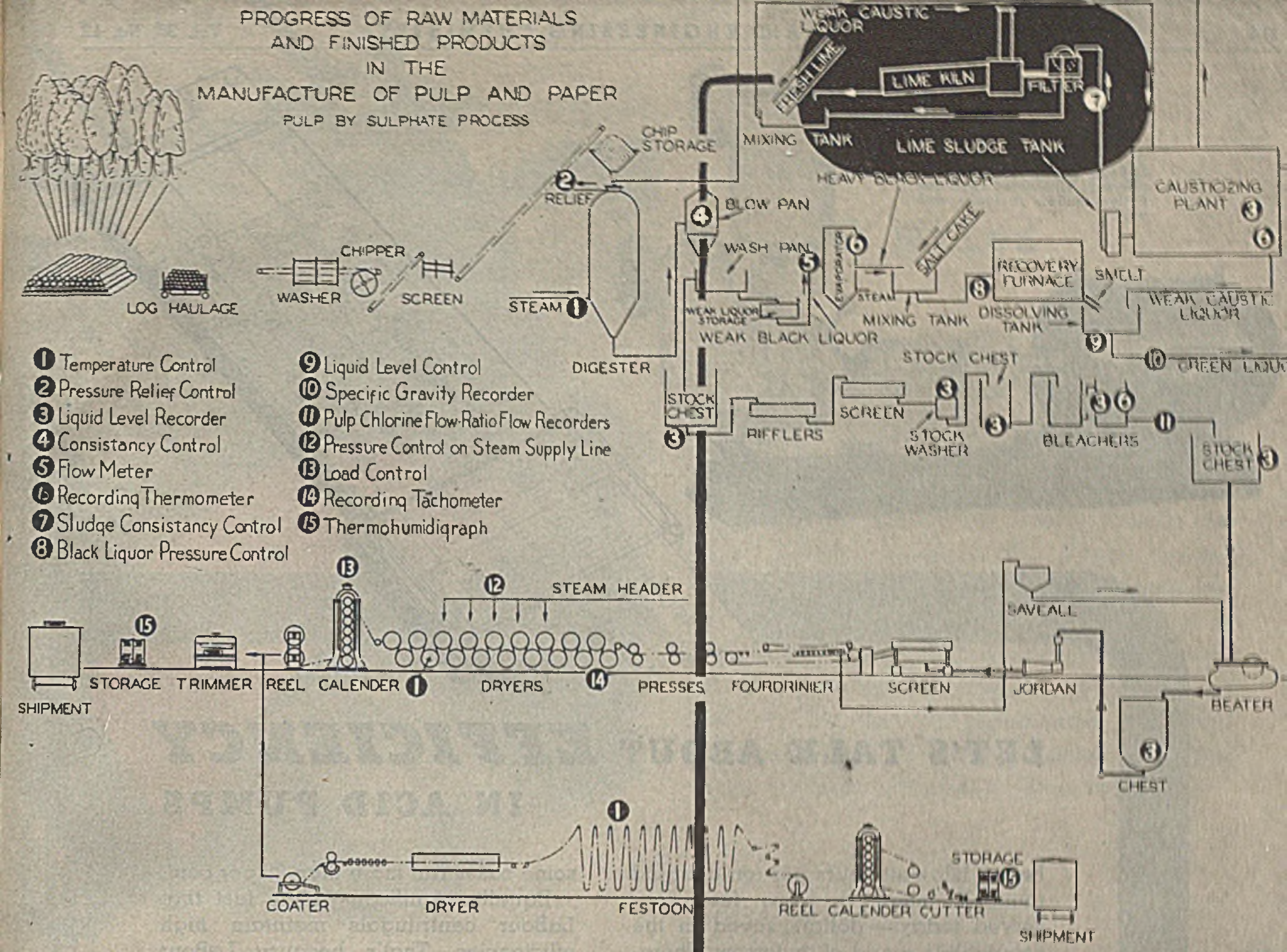
The Bristol Co. of Canada, Ltd.
Toronto, Ontario

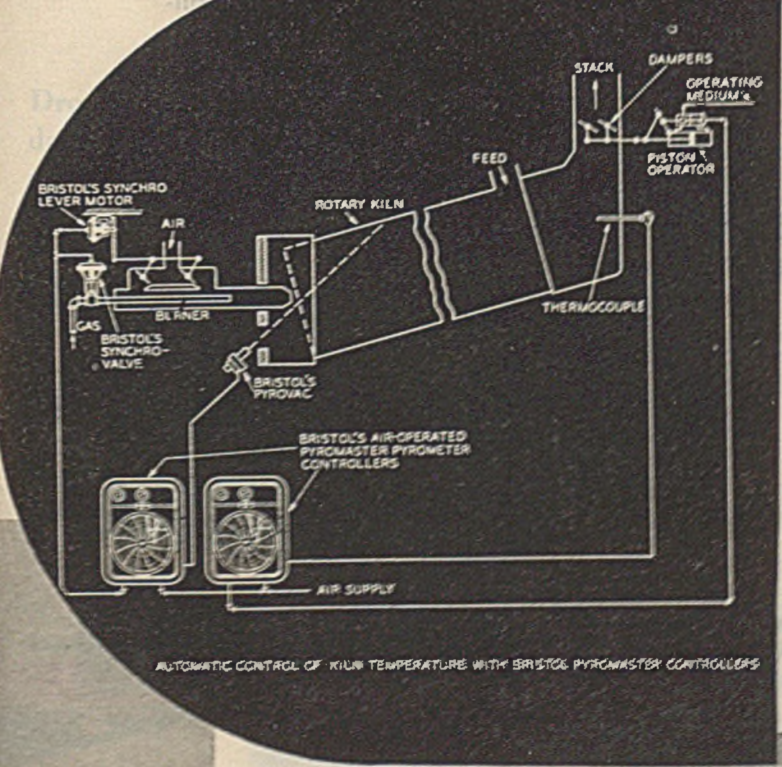
Bristol's Instrument Co., Ltd.
London, N. W. 10, England

BRISTOL

Engineers Process Control for Better Products and Profits

AUTOMATIC CONTROLLING AND RECORDING INSTRUMENT

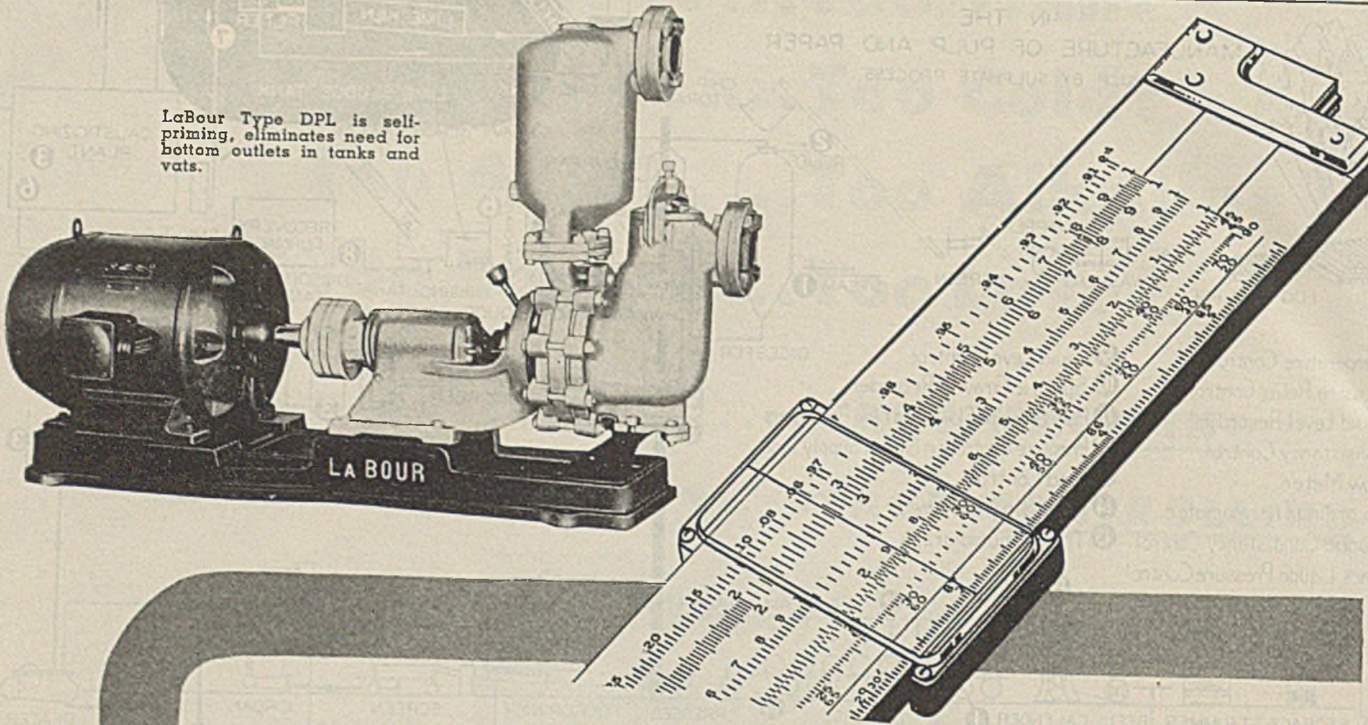




AUTOMATIC CONTROL OF KILN TEMPERATURE WITH BRISTOL PYROMASTER CONTROLLERS

Bristol's Pyromaster Control System Saves Fuel, Improves Quality, In Rotary Kiln Operation

Difficulties in manual regulation of heat in a large rotary lime kiln, with resulting waste of fuel and process time, were solved by a Bristol-engineered automatic temperature control system. Accurate temperatures, 2600° F. at front, 350° F. at back, were held to a virtually straight line on the chart, and a uniform temperature gradient was maintained throughout the length of the kiln. A considerable part of a large daily fuel bill was saved. Other advantages: better "pebble formation" of material leaving kiln and longer kiln lining life.



LaBour Type DPL is self-priming, eliminates need for bottom outlets in tanks and vats.

LET'S TALK ABOUT *EFFICIENCY* IN ACID PUMPS

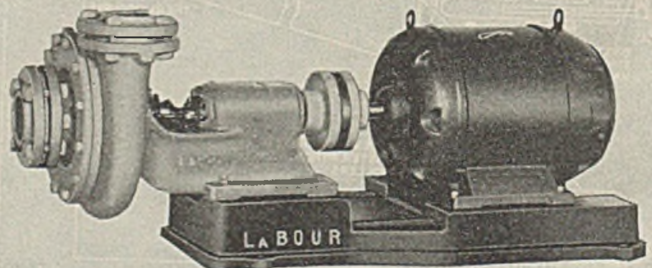
Fewer kilowatt-hours per ton of liquid pumped mean precious fuel conserved today — dollars saved in the competitive world of tomorrow. Therefore, the *efficiency* of the chemical pumps you buy is a matter of prime importance.

LaBour centrifugal pumps, of open impeller type construction without sealing rings or the like, attain efficiencies not commonly associated with centrifugal pumps. Your own comparisons, based on input and output specifications, will verify that quickly. With LaBour Type "Q" pumps, for example, efficiencies in some cases run more than 80 per cent.

Equally significant is the fact that LaBour centrifugals *maintain* high efficiencies. That's because LaBour design does not depend on close clearances or other wear-vulnerable features. It's the result rather of skill and experience gained in handling the chemical industries' most difficult assignments for more than 20 years.

So whenever you want to talk all-important efficiency, talk to LaBour. As a starter, let us send you a copy of Bulletin No. 50 containing interesting facts and useful information. Write for your free copy today.

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



LaBour Type Q is non-priming, but has sufficient air capacity to prevent binding.

LaBour

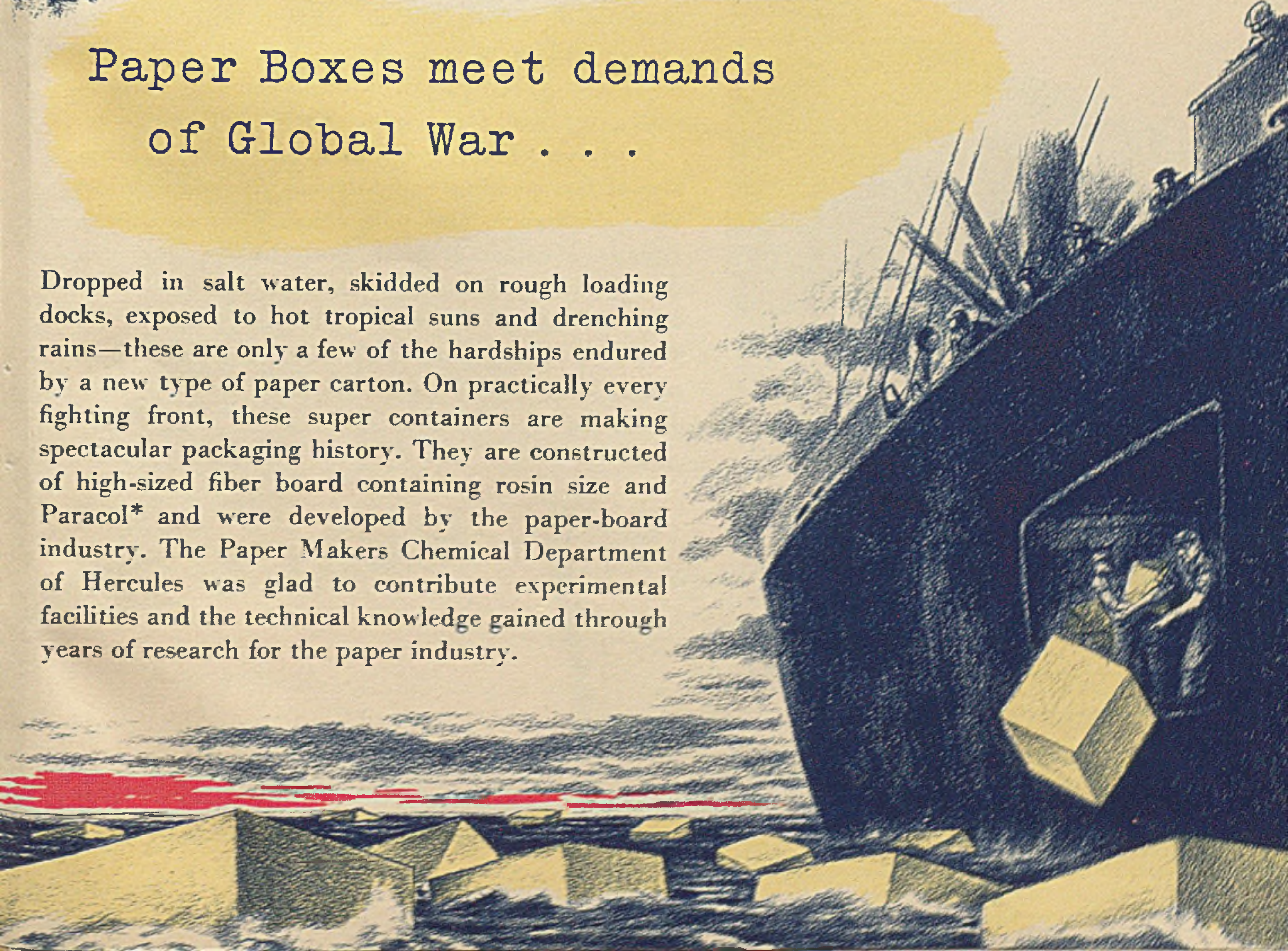
CENTRIFUGAL PUMPS

Plastic-coated fabric visible 2 miles

These brightly colored panel fabrics of the Signal Corps help identify the U. S. motorized equipment to our own airmen. Reflecting 90% of light, the glaring red, white, or yellow plastic-coated fabrics are clearly visible two miles. Ethyl cellulose is the plastic coating which meets the Army's stringent tests: No cracking or peeling at 20° F. below zero, or 140° F. above with 95% humidity . . . No sign of stickiness, no bleeding of color—even at 200° F. For further information regarding ethyl cellulose, the plastic of many war uses, write Cellulose Products Department.

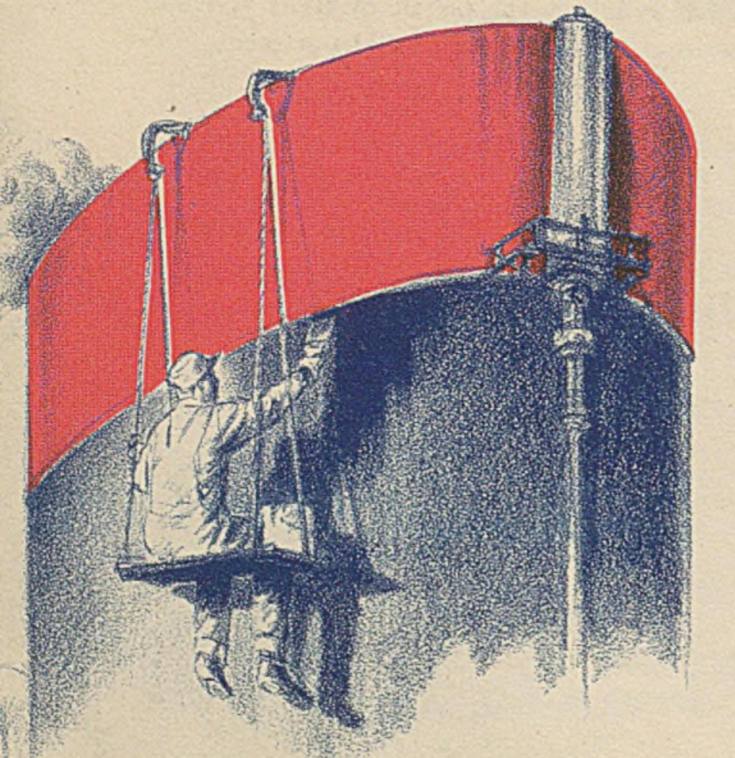
Paper Boxes meet demands of Global War . . .

Dropped in salt water, skidded on rough loading docks, exposed to hot tropical suns and drenching rains—these are only a few of the hardships endured by a new type of paper carton. On practically every fighting front, these super containers are making spectacular packaging history. They are constructed of high-sized fiber board containing rosin size and Paracol* and were developed by the paper-board industry. The Paper Makers Chemical Department of Hercules was glad to contribute experimental facilities and the technical knowledge gained through years of research for the paper industry.



A possible answer to solvent shortage for lacquer

Many lacquer manufacturers, seriously handicapped by the current shortage of ester solvents, are welcoming the recent re-introduction of Hercules SS Nitrocellulose. Almost soluble in ethyl alcohol, SS Nitrocellulose becomes a clear solution by simply adding a very small amount of some active solvent. Since offering trial samples to the industry several months ago, repeat orders of sufficient volume have been received to indicate its usefulness at this time. The supply of SS Nitrocellulose is ample and free of Government allocation. We shall gladly send you further information upon request. Use coupon below. Cellulose Products Department, Hercules Powder Company.



Hard varnishes from soft oils

Pentalyn* Resins — the Hercules pentaerythritol esters of selected rosins—are forming excellent varnishes with soft-drying oils such as linseed, or with dehydrated castor oils. At present, these varnishes are satisfying rigid strategic requirements—such as in salt-spray-resistant, marine spar varnishes.

Pentalyn varnishes combine the desirable properties of fast-cooking, rapid-drying, unusual hardness, alkali-resistance, and pale color. Because they are equally satisfactory with both linseed and dehydrated castor oil, manufacturers can now take advantage of changes in the supply situation . . . For technical information, address the Synthetics Department, Hercules Powder Company, Wilmington, Delaware.

*Reg. U. S. Pat. Off. by Hercules Powder Company

HERCULES POWDER COMPANY
INCORPORATED
922 Delaware Trust Building, Wilmington 99, Delaware

Please send me further information on:____________________

*Name*____________________

*Title*____________________

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IN-189

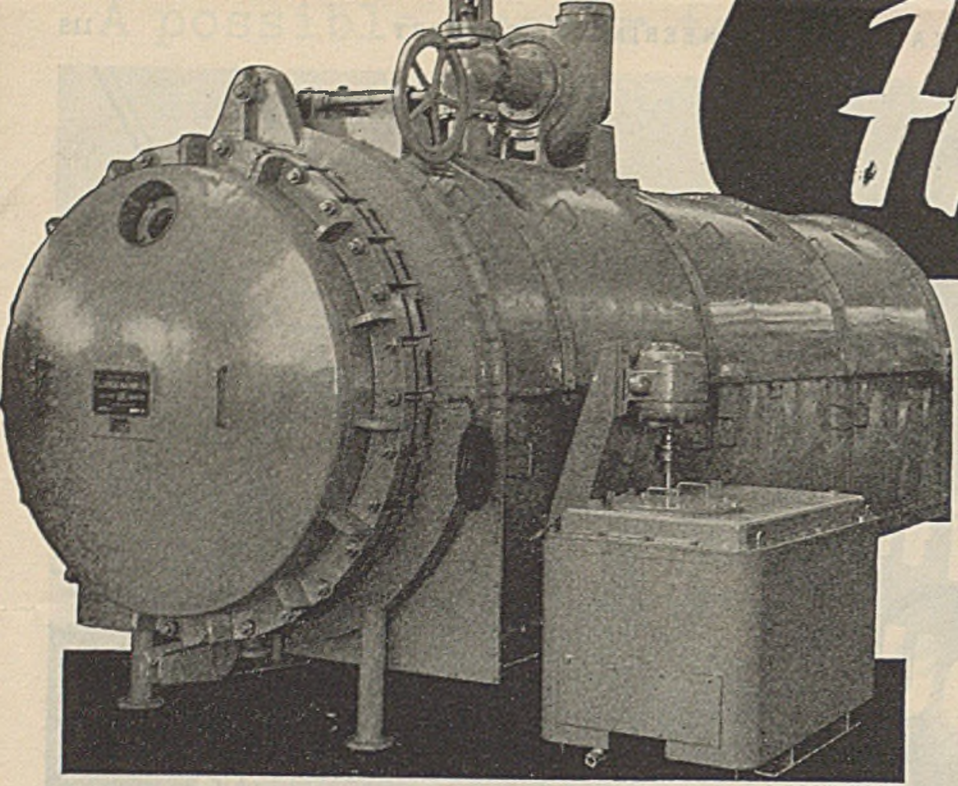
HERCULES

CELLULOSE PRODUCTS • TERPENE & ROSIN CHEMICALS • SYNTHETICS
CHEMICAL COTTON • EXPLOSIVES • PAPER MAKERS CHEMICALS

PRINTED IN U. S. A.

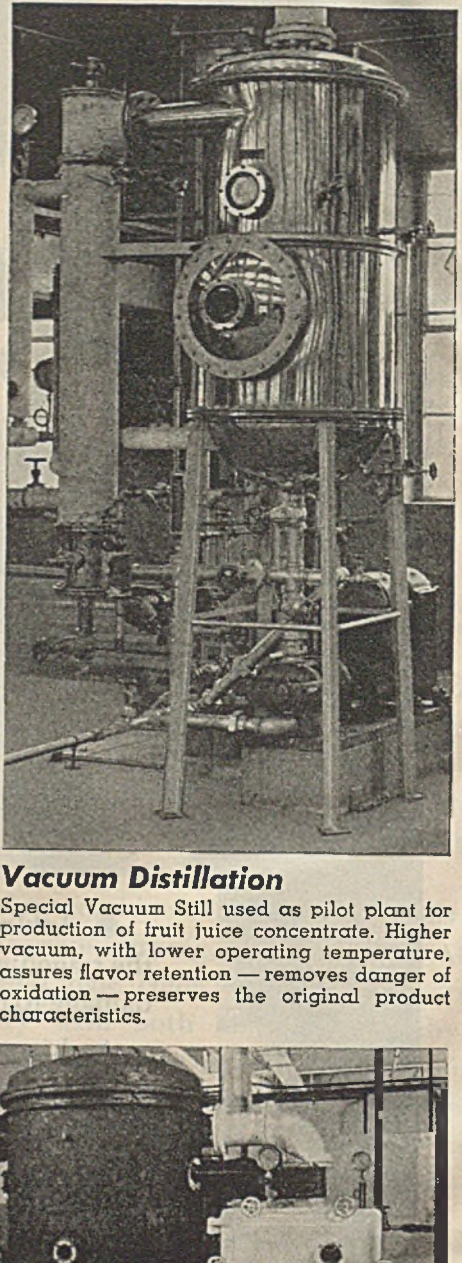

KEEP THE BIG GUNS
OF INDUSTRY FIRING!

Higher



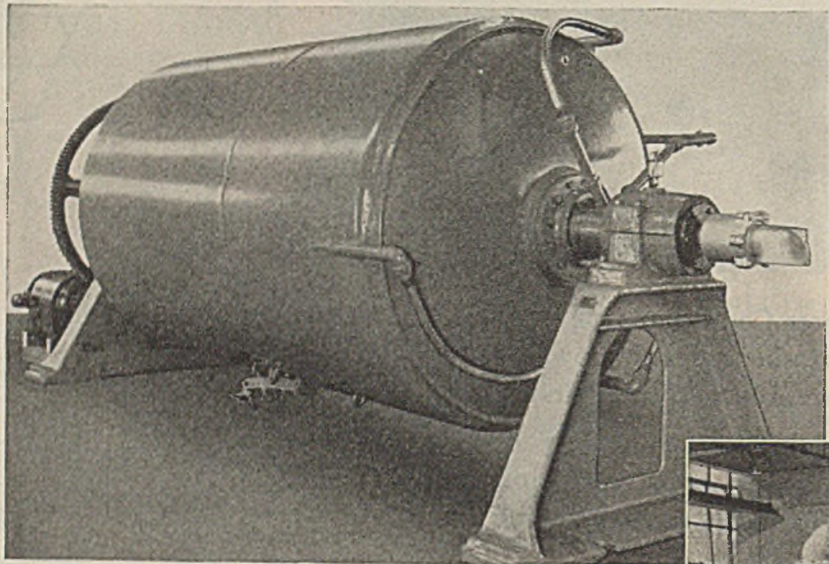
Vacuum Drying and Impregnating

Stokes Vacuum Impregnators are used for drying and impregnating power cable, radio coils, and condensers, armature and transformer coils, rope, lumber, and wood products, paper, fibre, felt, and other materials. Higher vacuum broadens their application.



Vacuum Distillation

Special Vacuum Still used as pilot plant for production of fruit juice concentrate. Higher vacuum, with lower operating temperature, assures flavor retention — removes danger of oxidation — preserves the original product characteristics.



Low Temperature Vacuum Drying

Rotary Vacuum Dryer. Higher vacuum with corresponding, lower temperatures, makes it possible to manufacture products heretofore impractical in the chemical, metallurgical and food fields.

Vacuum Drying from the Frozen State

At right: The Stokes pilot plant used in research on food and biological drying from the frozen state under vacuum in the low micron range by the Lyophile-Cryochem sublimation processes. Apparatus of this type is in use throughout the world for such services as the desiccation of Blood Plasma, Penicillin and other labile biologicals. Stokes assisted in the pioneering of this new method.

F.J.Stokes

Vacuum . . .

A New Tool..Making Possible New Processes and Profits

- **Desiccation of Blood Plasma, Penicillin, Serums**
- **Plating of Metals, Lenses, etc., by Molecular Bombardment**
- **Sublimation and Distillation of Pure Metals**
- **Drying of Heat-Sensitive Chemicals and Metal Powders**
- **Distillation of Essential Oils, Organic Chemicals, Food Concentrates**
- **Production of Magnesium by Ferro-Silicon or Carbo-Thermo Process**

These are but a few of many problems which are being solved, through higher vacuum and Stokes-engineered Equipment.

We have pioneered in the field of higher vacuum . . . for years have developed equipment, pumps, gauges and other auxiliaries, supplied completely engineered vacuum processing systems, making it easy and economically practical to obtain and utilize higher vacuum . . . to use lower temperatures in processing heat-sensitive materials, speed up processes, prevent oxidation, reduce operating costs by utilizing exhaust steam or other less expensive heat, minimize fire and explosion hazards, make it easier to control obnoxious fumes . . . and today, to open up entirely new fields of manufacture for tomorrow's products.

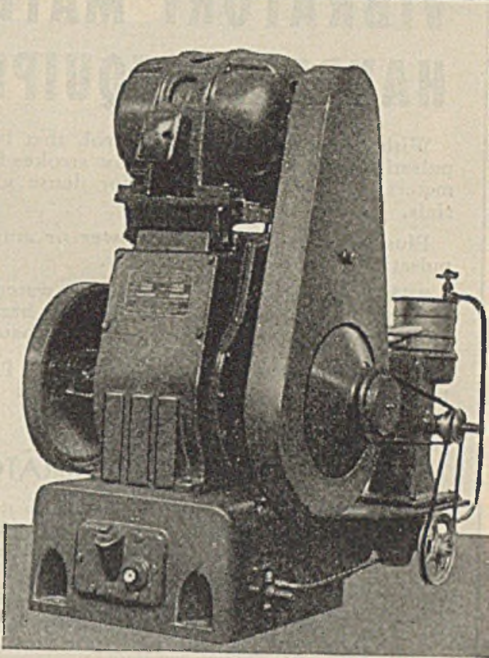
When you attend the Exposition of Chemical Industries, see the first display of the new Stokes Microvac Pump which is the heart of higher vacuum processing. (Described at right).

Also will be pictured the latest designs of high vacuum equipment for the processes listed above and other services in the rapidly expanding application of high vacuum practice in the biological, chemical, metallurgical, food and electrical industries.

Besides the field of Higher Vacuum, Stokes have also pioneered in Completely Automatic Plastics Molding and in Powder Metallurgy. See and hear about the latest Stokes developments in these fields — about the Completely Automatic "Press of the Future," one of several interesting and novel Stokes developments for post-war plastics production — about the new, high-capacity Powder Metallurgy Press which automatically controls uniform density of compressed parts.

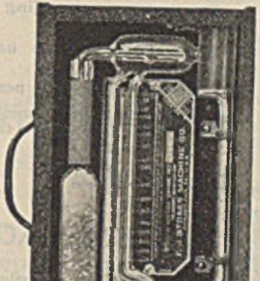
We invite you to use this opportunity to consult with us on new methods, new equipment, new economies as applied to your specific problems — both present and post-war.

F. J. STOKES MACHINE COMPANY
5922 Tabor Road Olney P. O. Philadelphia 20, Pa.
Representatives in New York, Chicago, Cincinnati, St. Louis, Cleveland, Detroit
Pacific Coast Representative: L. H. Butcher Company, Inc.



New Stokes Microvac Pump for Vacuum in the Low Micron Range

An entirely new oil-sealed Rotary Pump — the product of many years of high vacuum research and experience. Greater volumetric efficiency. Higher vacuum — in many cases these Pumps are operating in a narrow range of less than 10 microns. Smaller, more compact design for the same capacities. Rugged construction. New improved built-in motor-driven continuous oil clarifier. Many other features. See it at the Chemical Show.



New Stokes Vacuum Gauge

•

Requires no calibration. Accurate Readings in the Presence of Gases and Condensible Vapors.

This new, improved Stokes Portable (McLoed type) Vacuum Gauge provides rapid (2 to 5 seconds) readings within the micron range with permanent accuracy under all conditions. It will not require calibration against other gauges and retains its accuracy in the presence of all gases including hydrogen, and condensible vapors including water. See it at the Chemical Show.

See Our Exhibit — Booth 224 • Chemical Exhibition • Dec. 6 to 11, 1943

PROCESSING EQUIPMENT

FJS
Est. 1895

SYNTRON

WATER or AIR OPERATED

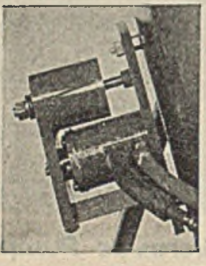
VIBRATORY MATERIAL HANDLING EQUIPMENT

With variable frequency control, that is, varying the pulsations per minute—long, slow strokes for light, fluffy materials—short, fast strokes for dense granular materials.

Plus valve control of the power or amplitude of the pulsations, and of the rate of flow.

"EXPLOSION PROOF"—air or water operated to suit the application—for operation in hazardous atmospheric locations, or handling explosive materials.

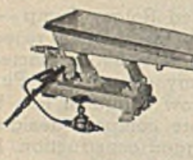
Operate efficiently on water, air or oil pressures of 40 psi. and up.



VIBRATORS

For application to those troublesome bins, hoppers and chutes, to keep their contents agitated and free-flowing.

Available in two sizes—the HV-15 for up to 750 lb. capacity hoppers, and the HV-55 for up to 5 tons capacity.



VIBRATING FEEDERS

For controlling the feed of and conveying bulk materials to grinders, pulverizers, screens, classifiers, etc.

Available in two sizes—HF-1 with a capacity of up to 4 tons per hour, and the HF-2 with a capacity of up to 10 tons per hour.

JOLTERS

For packing and settling bulk materials in containers.

Particularly effective on light, fluffy materials.

100 short, sharp jolts per minute.

Two models available—HJ-250 with a capacity of 250 lbs.—and the HJ-550 with a capacity of 550 lbs.

FEEDER MACHINES

For controlling the volume flow of dry chemicals and other bulk materials in all types of industrial processes.

Complete machines ready for operation with vibrated hoppers, and vibrating feeders with valve control of rate of flow.

Available in two sizes, with capacities of from ounces to tons per hour.

Illustrated and described in Catalog 435 which also includes information on Electric Vibrators, "Vibra-Flow" Feeders, Packers, Volumetric Feeder Machines and "Weigh-Flow" Gravimetric Feeders.

Write us about your problem.

SYNTRON COMPANY

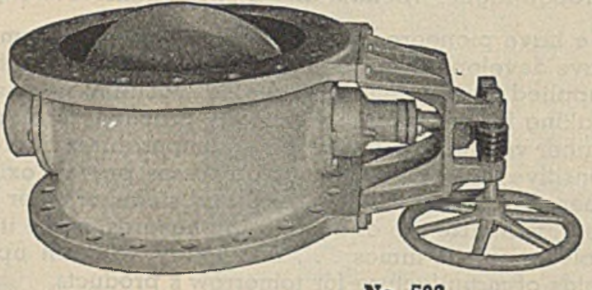
415 Lexington Ave. Homer City, Pa.

R-S Valve Engineering Service is NATION-WIDE

In strategically located cities from Boston to Dallas, and from New York to San Francisco, there are thoroughly experienced R-S Valve engineers who are eager to assist in the simplification of valve installations, willing to recommend the type of equipment best adapted to a particular control or shut-off condition and cooperative in pointing out possible changes in present equipment that will effect greater efficiency and economy.

Carefully selected for their engineering ability and experience in the installation and operation of valves, these men have been especially trained in the selection of alternate metals for resistance against heat, abrasion and corrosion as well as the application of R-S Valves under high or low pressures and temperatures whether the medium to be controlled is air, gas, steam, liquids or semi-solids.

The R-S representative is at your beck and call. Telephone the one nearest you for prompt service.



No. 502

20-inch, 125 pound American Standard Valve, hand wheel control, ball bearing mounted with stuffing box.

15 to 900 psi

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Rockefeller Bldg., Main 6192

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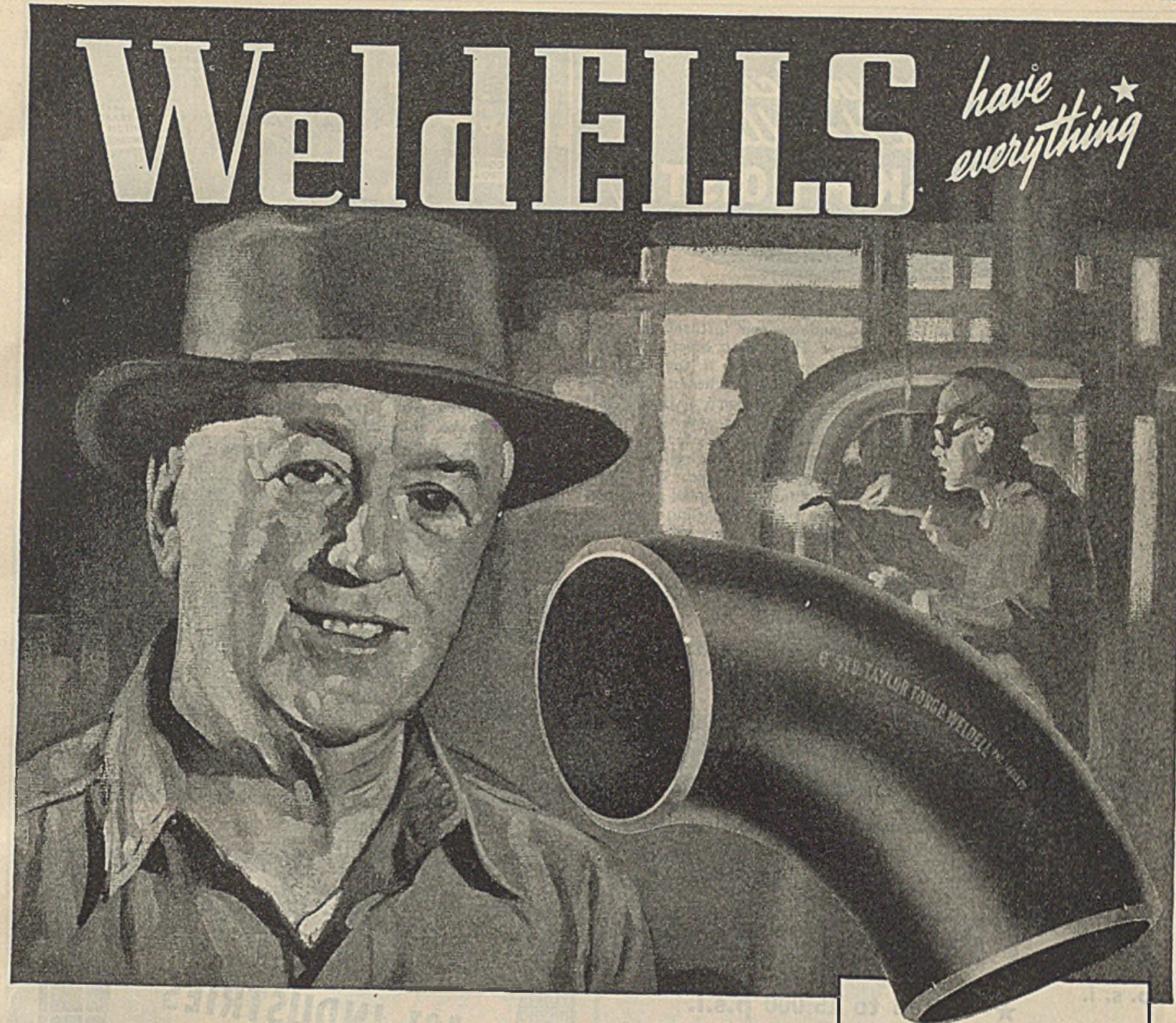

"They're built to give the man on the job a hand"

FROM the way they pile the work on me these days you'd think my job as foreman of the pipe crew is to put in the piping today that the front office won't finish planning till tomorrow!

The front office crowd might consider that laying it on a little thick. But whatever they think, they will have to admit that we have kept up with their wildest demands and done the job right, too.

Of course the main credit for that goes to fellows who do the work. But down to the last man they would be the first to agree that they couldn't have covered as much ground, or covered it as well, if it hadn't been for their old friend, WeldELLS.

WeldELLS and other Taylor Forge Welding Fittings are built to step in and give a hand. You don't have to grope for the proper size because size and weight are marked right there on the fitting. Tangents make them easy to line up. Accurate lathe bevels and lands make welding fast and sound. Precision quarter-marks guide the work.

If you want a fast job — a sound job — an economical job — take a tip from me and use the welding fittings that have *everything!*

★ WeldELLS alone have all these features:

- **Seamless** — greater strength and uniformity.
- **Tangents**—keep weld away from zone of highest stress—simplify lining up.
- **Precision quarter-marked ends** —simplify layout and help insure accuracy.
- **Selective reinforcement** — provides uniform strength.
- **Permanent and complete identification marking**—saves time and eliminates errors in shop and field.
- **Wall thickness never less than specification minimum**—assures full strength and long life.
- **Machine tool beveled ends**—provides best welding surface and accurate bevel and land.
- **The most complete line of Welding Fittings and Forged Steel Flanges in the World** — insures complete service and undivided responsibility.

* WeldELLS and many other Taylor Forge products are produced in Byers Genuine Wrought Iron.

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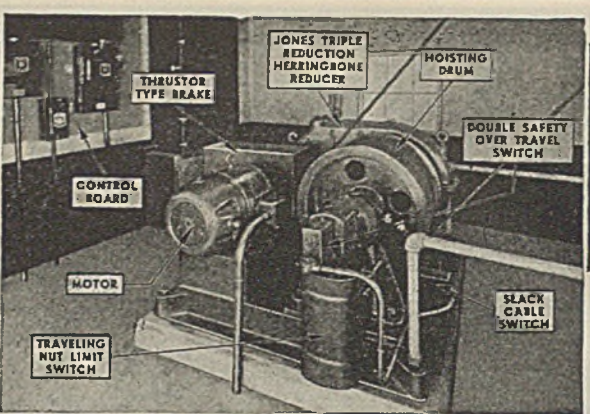
The list of Taylor Forge's contributions to the war effort only begins with WeldELLS. One of many examples is Taylor Corrugated Marine Furnaces, essential to many merchant ships and transports.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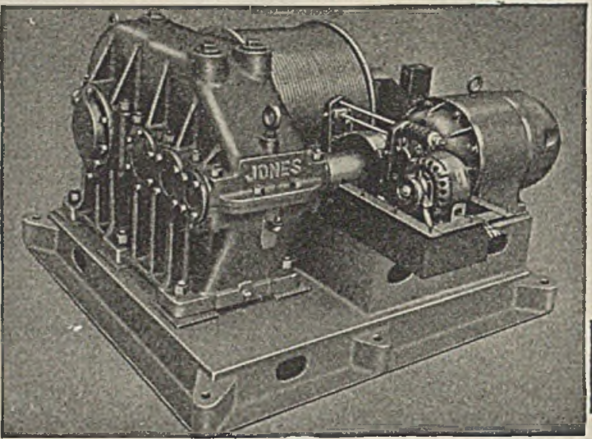
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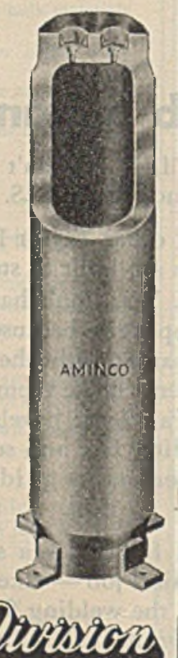
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Particle Size Table

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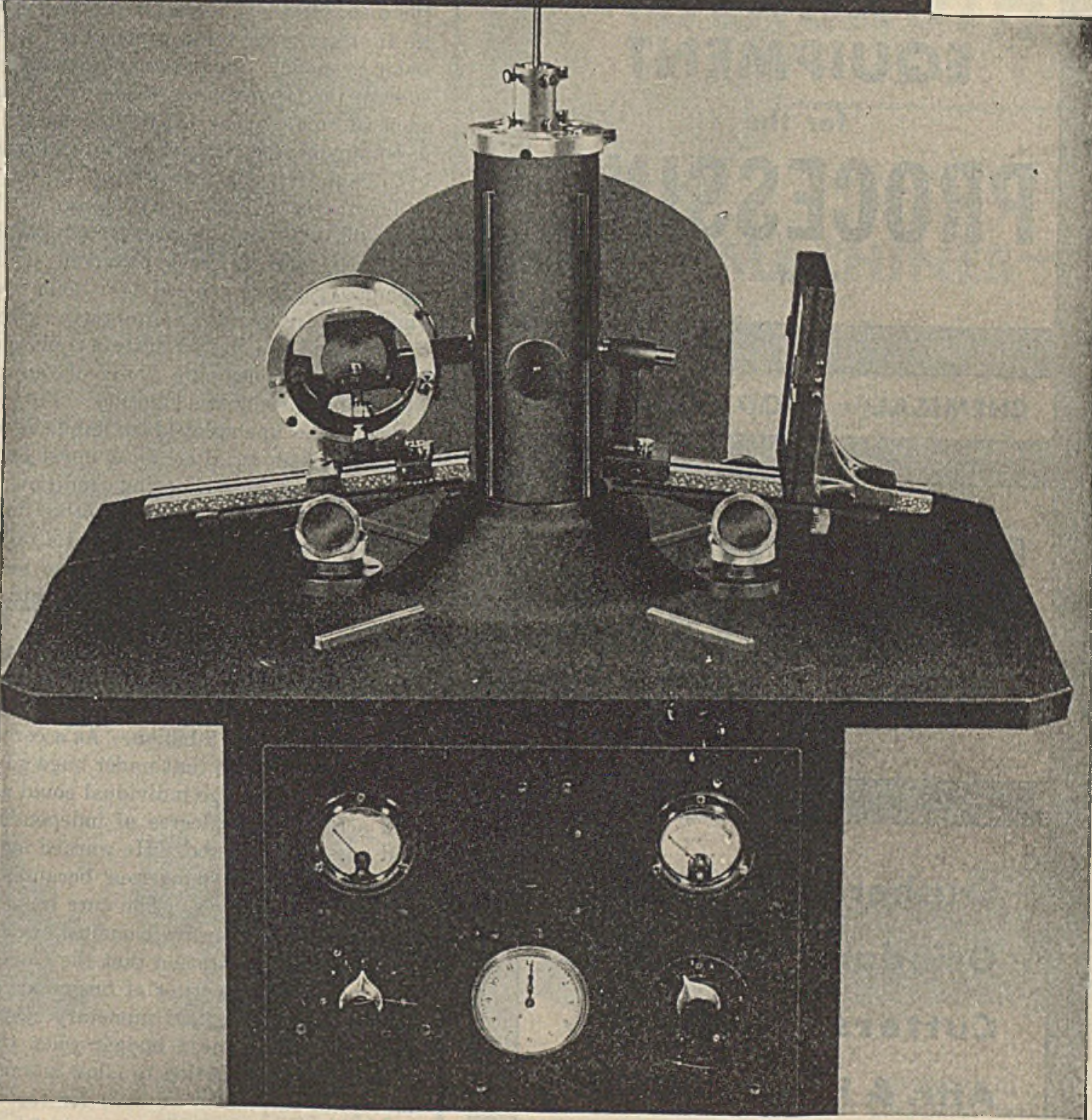

HIGH-SPEED x-ray diffraction analysis—an important contribution to war industry—is now available. The development of the G-E Model CA-6 beryllium window x-ray tube for use in the G-E Models XRD-1 and XRD-2 Units permits registration of patterns with exposure times which are from three to twenty times faster than was possible previously.

Today, with G-E X-Ray Diffraction Units, 15 to 30 minute exposures have replaced the four to eight hour tests which were formerly routine in diffraction studies of steel. Corresponding reductions in exposure times have materially speeded up the control of aluminum and magnesium refinement. Modern, progressive analytical laboratories have found in the G-E X-Ray Diffraction Units an exceedingly satisfactory method of quantitative and qualitative analysis. The diffraction method is ideal for the analysis of solid compounds, for example, because it provides information not obtainable by conventional analysis which generally identifies elements present rather than compounds.

An interesting new booklet which describes and illustrates G-E Equipment for X-Ray Diffraction will soon be available. To make sure that you receive your copy, address your request to Department N412.

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

Postwar Planning

plants ought to be maintained and not scrapped, but that the disposition of the plants will be made without regard to anything except the atmosphere at the time the decision is made. This means, he explained, that the attitude of the labor unions, deals with England, and conditions of employment will be among the decisive factors. If employment is needed, perhaps synthetic rubber could even be protected by a tariff.

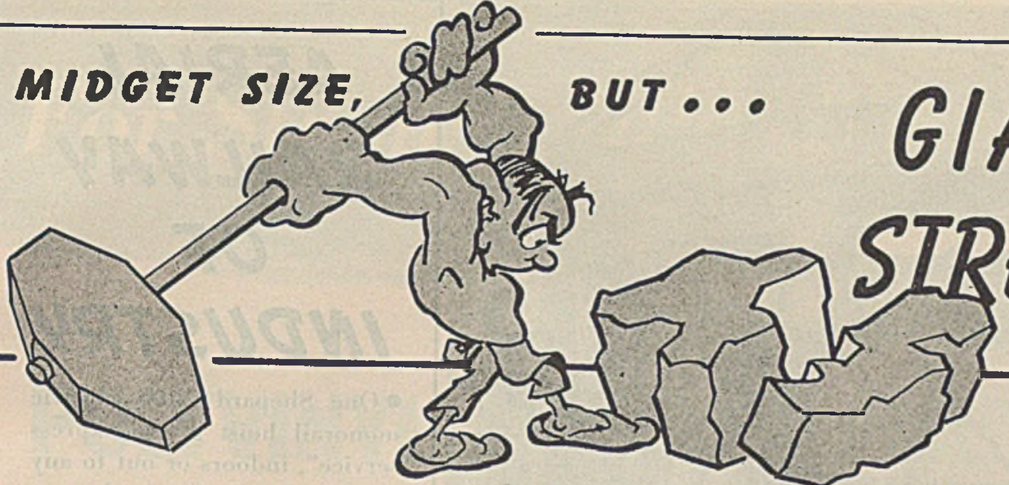
The recent meeting in Pittsburgh of the chemical engineers brought out more postwar thinking. First was P. W. Meyeringh, vice president of Hercules Powder Company, who expressed two main ideas: (1) The unemployed represent an already educated consumer market, and the United States should change its thinking to make the consuming power of the unemployed available to our productive capacity. Further, we should not consider the unemployed as liabilities or social pariahs. (2) Capitalism is, after all, a novel experiment and can be changed to meet changing conditions.

At the meeting's banquet, another postwar prophet was H. W. Prentis, Jr. He estimated a public debt of 250 to 300 billion dollars at war's end, and said that a drop of about ten points in the value of government bonds would bankrupt practically every banking institution in the country". This statement was based on the fact that the banks hold 40% of all the outstanding government bonds, some 70 billion dollars worth, against capital assets amounting to only 8 billion. As a corollary to this assertion, he maintained that under huge government debt the day when an average individual could save for his old age and achieve some degree of independence at retirement had passed into limbo. He warned against the idea that public debt is not dangerous because it is owed by the people to themselves. The cure seemed to Prentis, and to most of the attentive chemical engineers, to be a joint congressional declaration that the Government would not be a postwar competitor of business; and that Congress should provide a sound monetary system based on gold, declare for a balanced budget when the war is over, set up a system of taxation to allow a wartime accumulation of capital surplus to be used for reconversion of plants, provide for sharply reduced rates of taxation in the peace era, for the prompt adjustment of canceled war contracts, and for the disposition of war plants and inventories once the war ends.

To the editors at this time it seems that our major problem at the end of the war is going to be money and its attendant headaches. First of all we must reach a clear understanding of the meaning of government debt. We need a clarification of the currently popular idea: "Don't worry about the debt; we owe it to ourselves."

The industries of the nation can create wealth until they are figuratively blue in the face, but unless these efforts are backed by intelligent planning and real monetary policies in the Government, the created wealth is useless. In a later issue we will present the arguments of both sides in the public debt debate.

(*Continued on page 136*)



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Sturtevant Laboratory Machines are large machines in miniature — capable of running 24 hours a day with the full strength — and all of the features of full sized equipment.

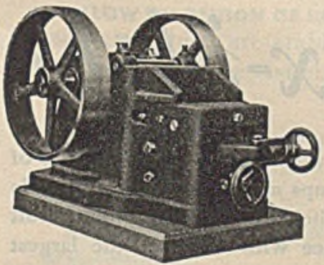
These great little machines are outstanding in design, construction and accessibility. They have an excellent reputation for the size and quality of their output as well as for their wide range of adjustment.

Although first designed especially for laboratory sampling work — they are used regularly in many plants where there are limited outputs.

Besides those described here, the line also includes: Screens, Air Separators, Vibrating Test Sieves and Automatic Coal Crushers and Samplers.

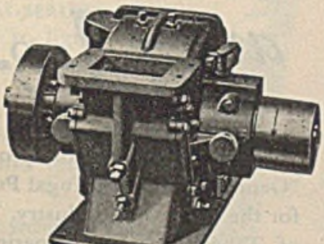
We're sorry that we've been too busy here at the plant to exhibit at the *Chemical Show* this year.

But we'll welcome your inquiries — give them our full attention. Write and tell us your needs and ask for a copy of our new catalog describing the complete line of Sturtevant Equipment.



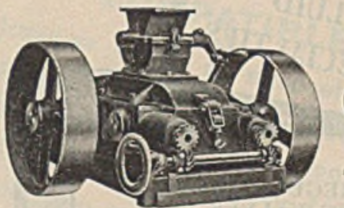
STURTEVANT LABORATORY JAW CRUSHERS

Special roll jaw action simplifies close regulation of the product. Capacities vary from 300 or 400 lbs. per hour at finest settings to 1000 or 2000 lbs. when opened for coarser work. Every part is accessible for quick and easy cleaning. These Crushers weigh from 900 to 1000 lbs. and are fitted with manganese steel jaw plates, reversible shields, and steel pitman.



STURTEVANT LABORATORY SWING-SLEDGE MILLS

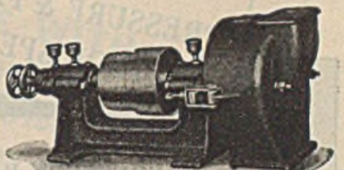
Capable of reducing soft, moderately hard and tough or fibrous materials to any degree of fineness between 1 in. and 20 mesh. The full feed opening of 5 × 6 in. may be utilized for soft substances. On harder materials the machine should be fed with pieces not larger than 2 to 3 in. The patented "Open Door" feature permits ready accessibility for cleaning.



STURTEVANT LABORATORY CRUSHING ROLLS

These machines have complete accessibility for quick and thorough cleaning. Adjustments are positive, accurate and automatic. The feeder also is automatic and adjustable. Tires are generally durable high carbon forgings. Two sizes are built in practically identical design. Range of output* for the 8″ × 5″ size is from ½ in. to 20 mesh—and for the 12″ × 12″ size from ¾ in. to 20 mesh.

* *Two stages are necessary for reductions greater than 4 to 1.*



STURTEVANT LABORATORY SAMPLE GRINDER

Laboratory Sample Grinders are of the "Open-Door" disc type and are capable of very fine work, producing products as fine as 100 mesh if desired, when working on dry, friable, soft or moderately hard materials. On many hard rocks and ores, they will operate with somewhat reduced capacities. Feed may be ¼″ and finer. Every part is accessible for quick and easy cleaning.

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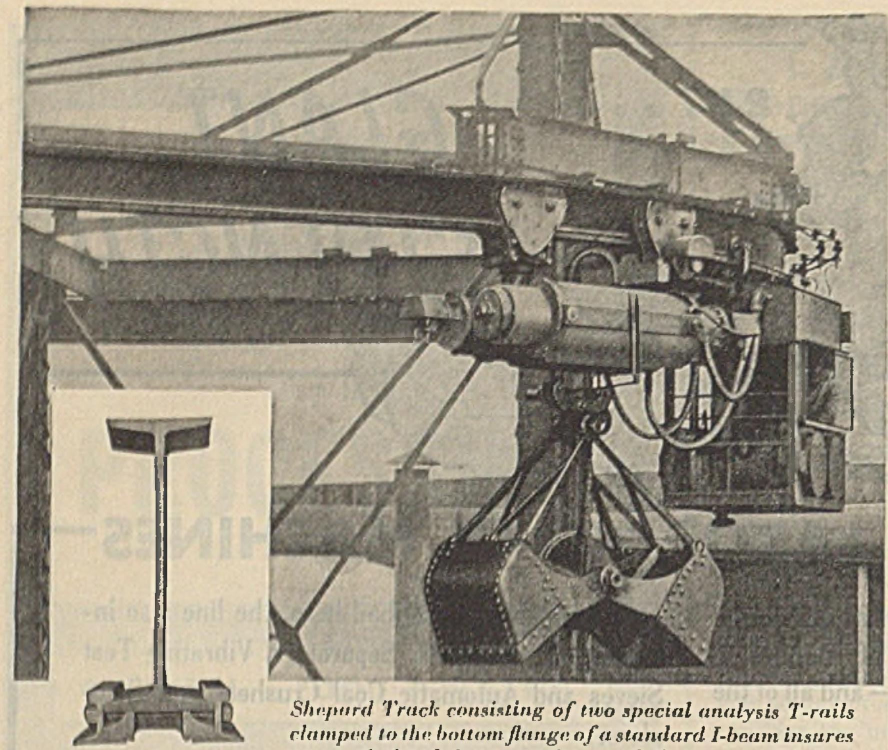

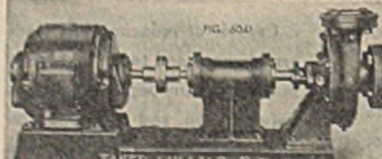
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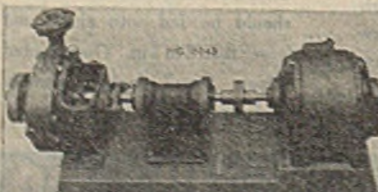

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Total solids	55% minimum
pH	4.0—6.0
Color	Milk white
Weight per gallon	9 pounds

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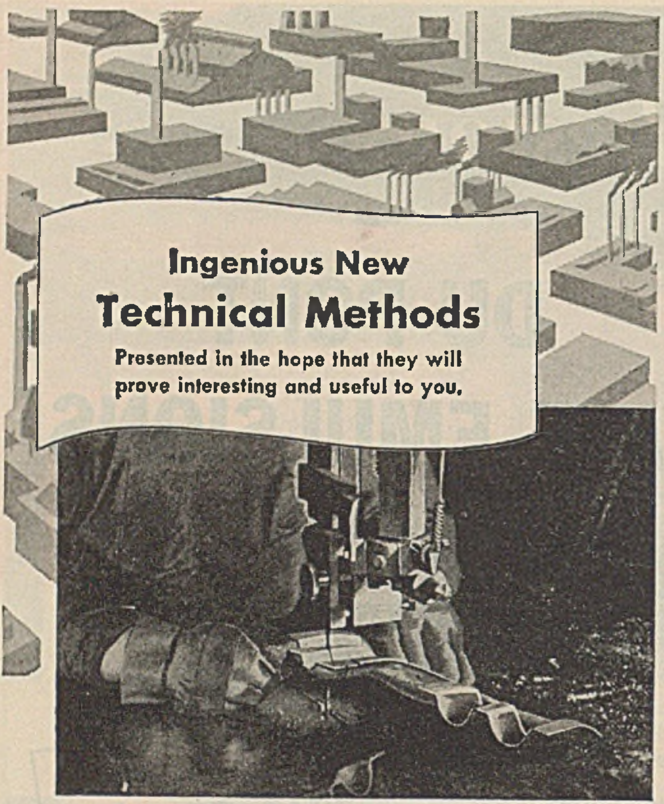

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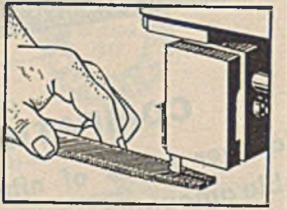
Hard Steels Cut by Heat Generated by Super High Saw Speeds

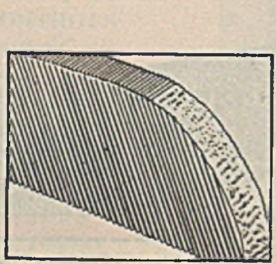
Ordinary band-saws, when operated at unbelievable high speeds up to 12,000 feet per minute, cut through hard steels and alloys by heat generated from the friction of the saw against the metal to be cut. The cutting effect is more that of burning through the metal than actual cutting. The heat generated is sufficient to melt or burn out the metal in the saw cut but not enough to draw the temper on the sides.

The hardness of either saw or metal to be cut is of little importance. Thin metal sheets are cut like paper, and plates up to one inch in thickness can be cut at speeds of ten inches per minute.

We hope this has proved interesting and useful to you, just as Wrigley's Spearmint Gum is proving useful to millions of people working everywhere for Victory.



Proof of ability of new method to cut hard materials is demonstrated by operator cutting a file.



The temper of curve cut section shown above is unaffected.

You can get complete information about this method from Bell Aircraft Corporation, Buffalo, New York.

X-61

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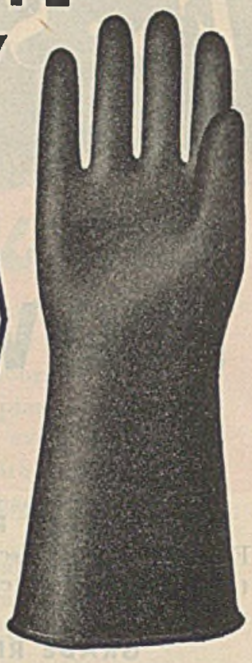

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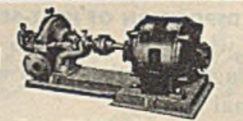

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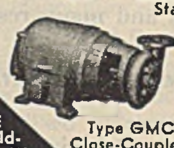

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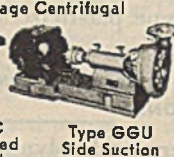

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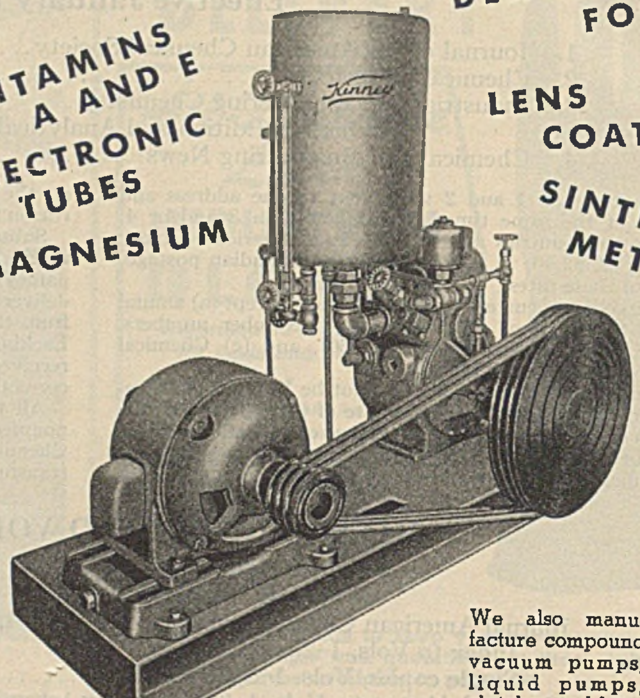
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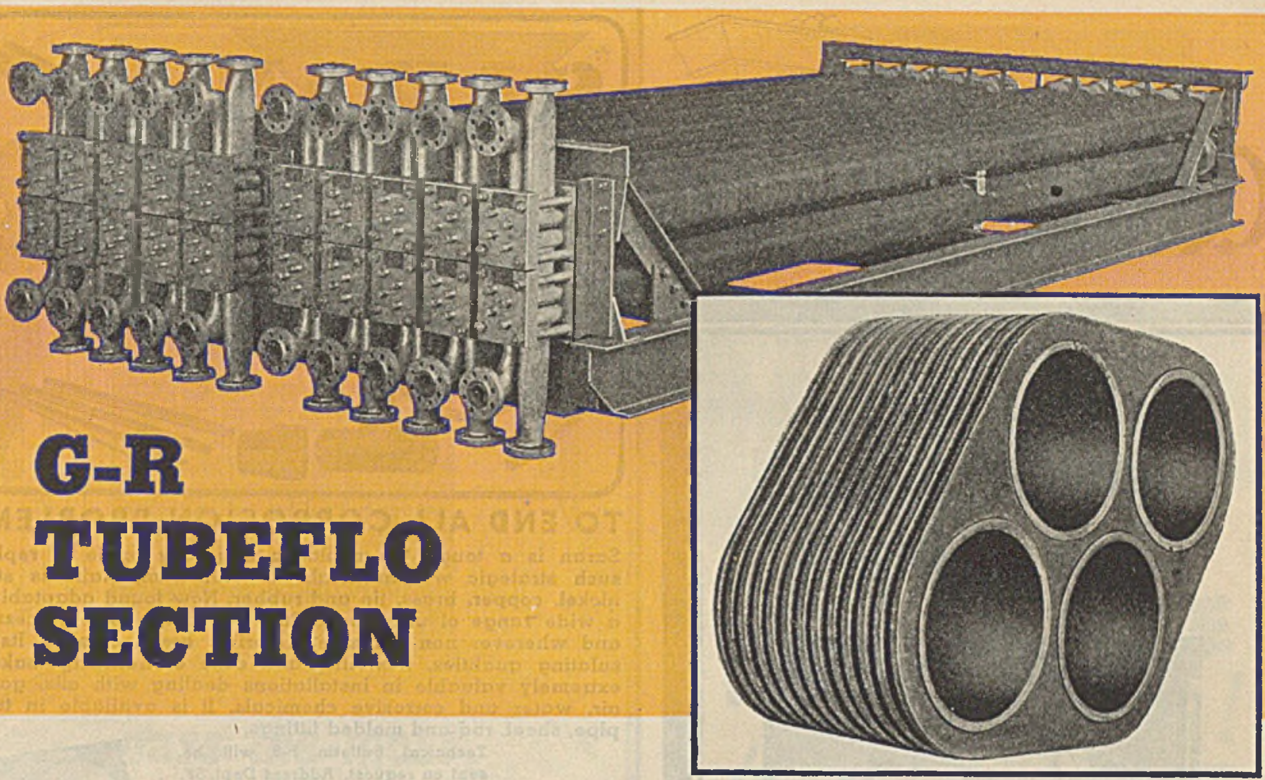

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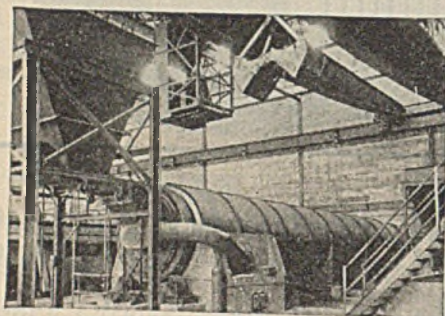

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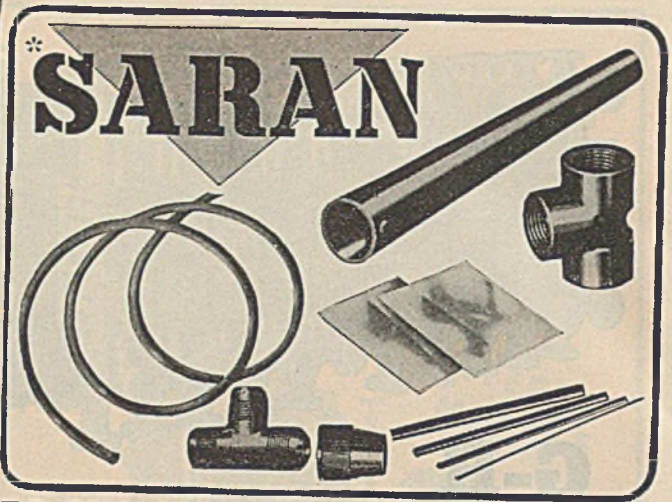

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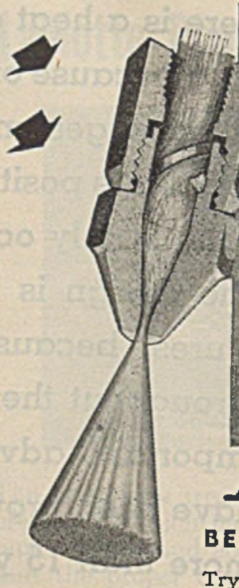

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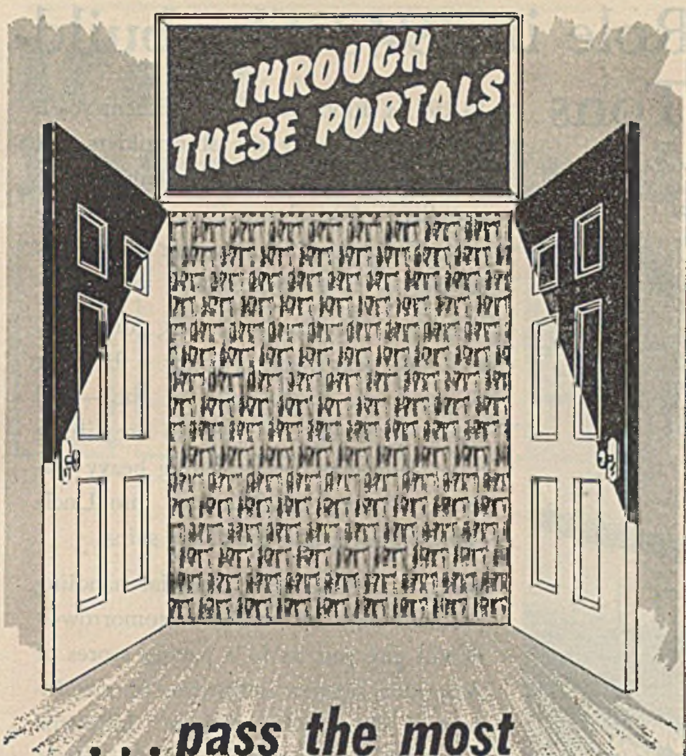

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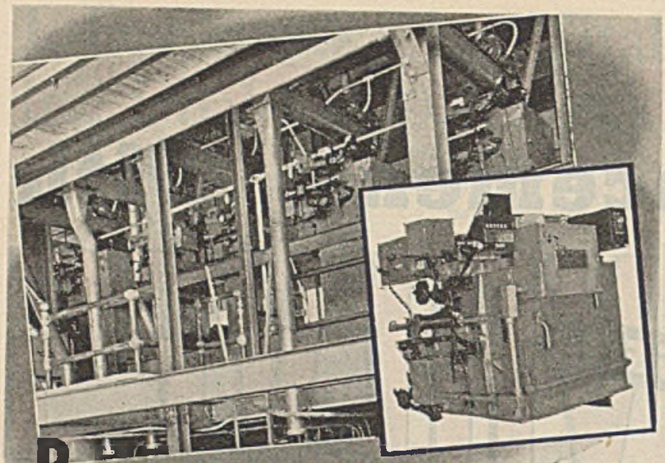


I. & E. C. Reports on the Chemical World Today

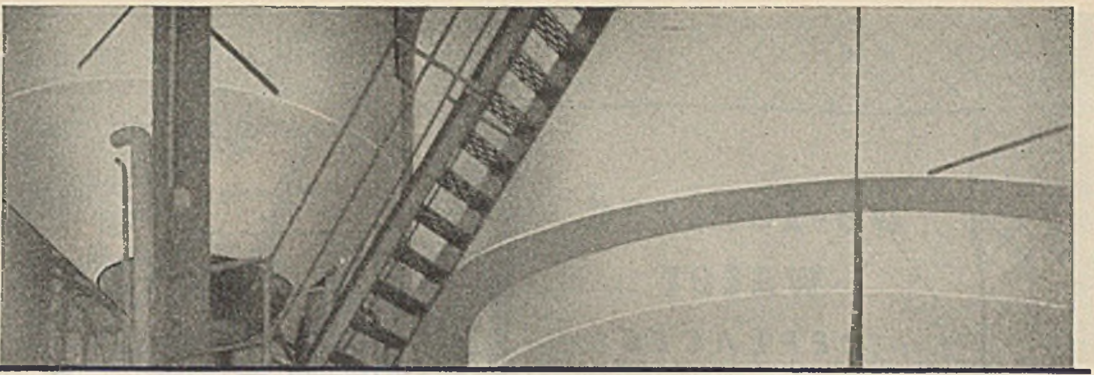
Industry

Package Problems. When returned tooth paste tubes, and others like them, have yielded a million pounds of tin with still another million and a half pounds awaiting its turn to be processed, the magnitude of America's container problem becomes readily apparent. New regulations are effective covering civilian use of containers of every type and establishing reduced quotas for all applications not in the most vital categories. Substitutions are prescribed all along the line to limit stringently the man-hours required to package each commodity. Glass replaces metal, ceramic replaces glass, paper and corrugated board substitute for both, and the chain continues in every direction. Meanwhile, permitted production of nonessential items shrinks and releases further package-producing capacity to supply containers for necessary products.

I. & E. C. Editors see in this necessary wartime trend an opportunity for complete revaluation of all our packaging techniques. The enormous growth of demand in past decades for individual packages for every item and every commodity is now forced into reverse. Larger packages will rule in the near future. Even the cracker barrel of blessed memory may return. When restrictions are ultimately lifted, industry and merchandisers may prefer not to return completely to multitudes of small, even tiny, packages that have for so long been the rage. We see a possible future economic compromise between the expensive, but convenient, small retail package and the now outmoded bulk package abandoned as unsanitary and uneconomical in a community of small families.

Return Cylinders. The critical shortage of cylinders for the transportation of chlorine is the chief problem associated with its wartime availability. Steel cannot be spared for cylinders. With greatly stepped-up manufacture, we now have sufficient chlorine, BUT it is at producing plants and will reach consumers only IF cylinders are kept in circulation. It is easy to set aside an empty cylinder and forget it, but doing so may and probably will mean delay in meeting a vital war need.

See the Job Through. David Lawrence, columnist and editor of *United States News*, performs a noteworthy service in calling attention to a growing exodus of business men from government posts. He courageously condemns this action in no uncertain terms. Postwar planning is vital and necessary at this time, but the war is not yet over. In our Washington meanderings we, too, have heard privately voiced opinions from many higher-ups bitterly complaining against the practice of a number of companies of recalling men from the capital. Not only are Germany and Japan yet to be defeated, but many important problems, such as renegotiation of contracts, procedures for cancellation of contracts, and disposition of government-owned plants, remain unsolved. Industry is myopic when it withdraws able administrators from government positions, and if it now turns it back on the Washington scene, it will have little ground on which to complain about future unsympathetic or even hostile attitudes.



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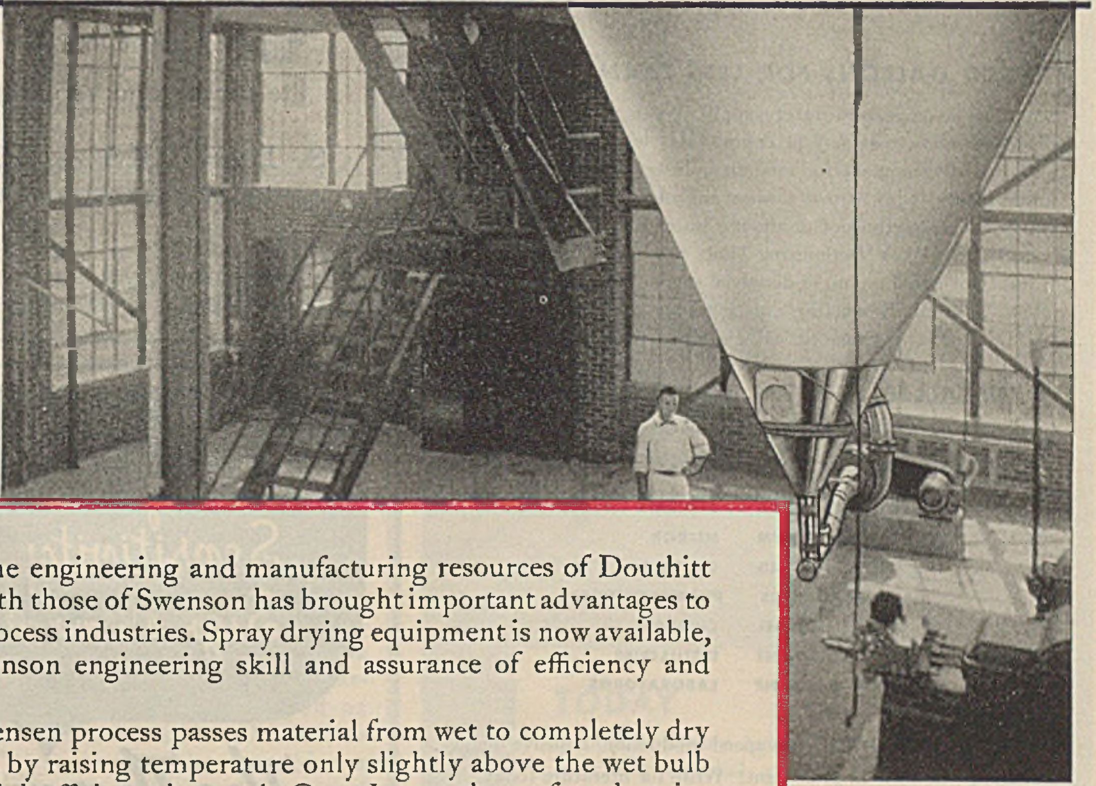

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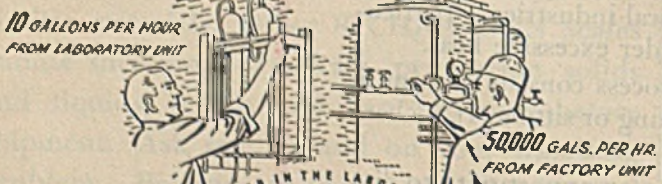
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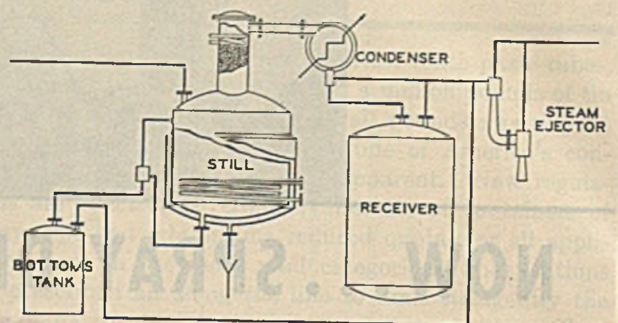
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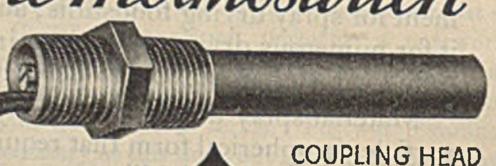
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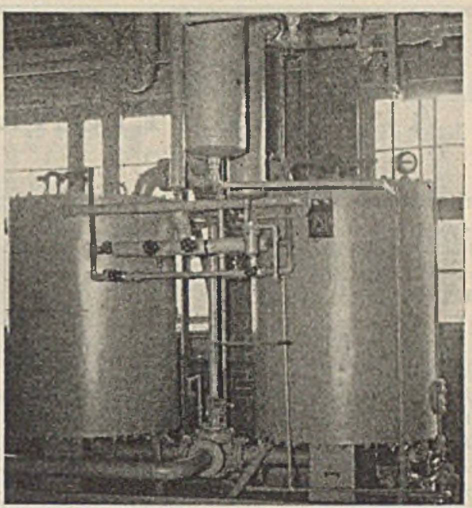

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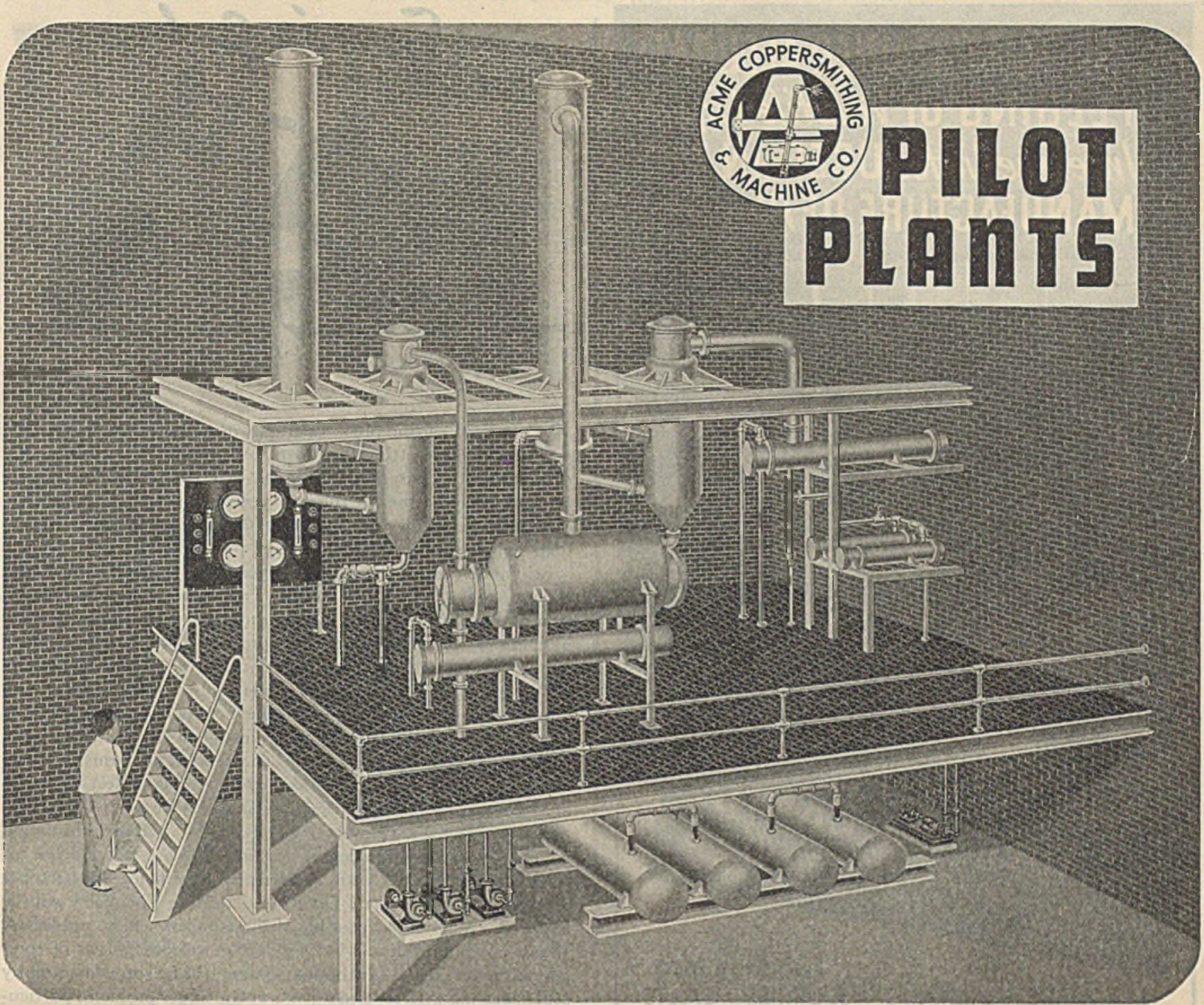
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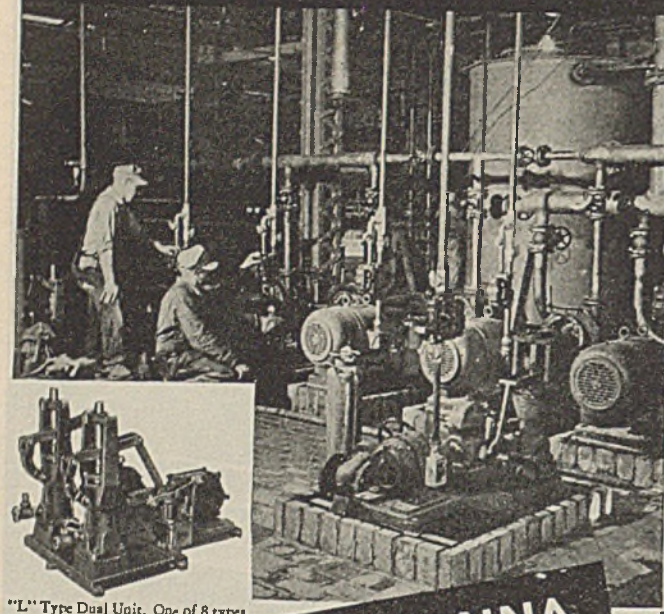

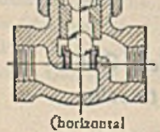

Despite a certain preoccupation with today's No. 1 publishing problem of getting the most from a limited allotment of paper, the editors are planning much of great value and general interest for our issues of the new year now swiftly approaching. While condensation will be the rule, the hope is to keep standards high and interest broad as always.

Still at the top of the chemical agenda is synthetic rubber, and thus it opens the new year for us. Prospects brighten as production of adequate amounts of the synthetics seems assured. Remaining is the equally important problem of adapting available materials to major uses, particularly in tires. The whole future course of plantation and of synthetic rubbers now pivots on our ability to modify and to adapt the new chemical products to serve better than rubber in its accustomed applications. The time available to accomplish this shortens as our arms continue victorious in the field, and thus haste is necessary lest the labor and effort spent building a new vital industry be wasted.

Against this background every scrap of usable information assumes magnified significance for both the present and the future. In our January issue, papers presented before the October meeting of the SOCIETY's Division of Rubber Chemistry will be featured. As many as possible of these papers will be published. Important information will be given on various phases of compounding and use of synthetics. These will be supplemented by others dealing with several aspects of the larger problem, particularly hydrocarbons and their polymers.

In a quite different field we shall learn of the nutrient values of by-products of corn coming from the distilling industry and the importance of these materials as sources of vitamins and nutrients as well as of roughage, always heretofore given special emphasis. Obviously this is an important source of feed for animals.

Next month we expect to use from Lacey and his co-workers the forty-first study on phase equilibria from the California Institute of Technology. These important papers have become, in the ten years the series has continued in our pages, a source of important data for the expanding petroleum industry. The researches behind these reports have been conducted as Project 37 of the American Petroleum Institute to provide trustworthy physical values essential to progress in the industry of hydrocarbons.

Also possessing primary significance is the method of determining the most economical size in selecting a heat exchange unit. Too often the selection of the size of any equipment units is based on guesses and hunches. Yet when installed, the unit chosen may eat up its cost many times a year by lack of full efficiency because it is either too large or too small for its job. In spite of the apparent complexity of its derivation, the formula given can be immediately applied to its intended calculation and with suitable modification to other related problems.

There will, of course, be other significant papers on equally useful subjects including a new synthesis for menthol and possibly the application of modern high-speed photography to the study of high explosives. But, meanwhile, we must save enough of this column to wish our readers the best the season affords in a year before Victory

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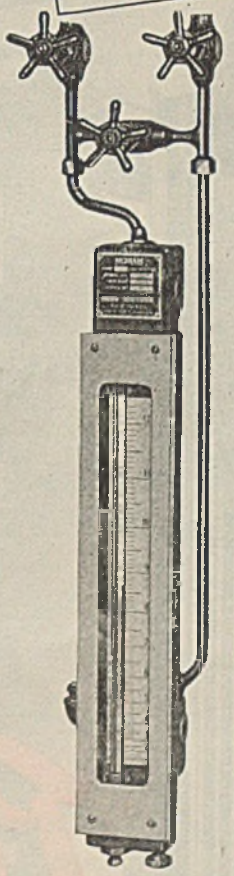

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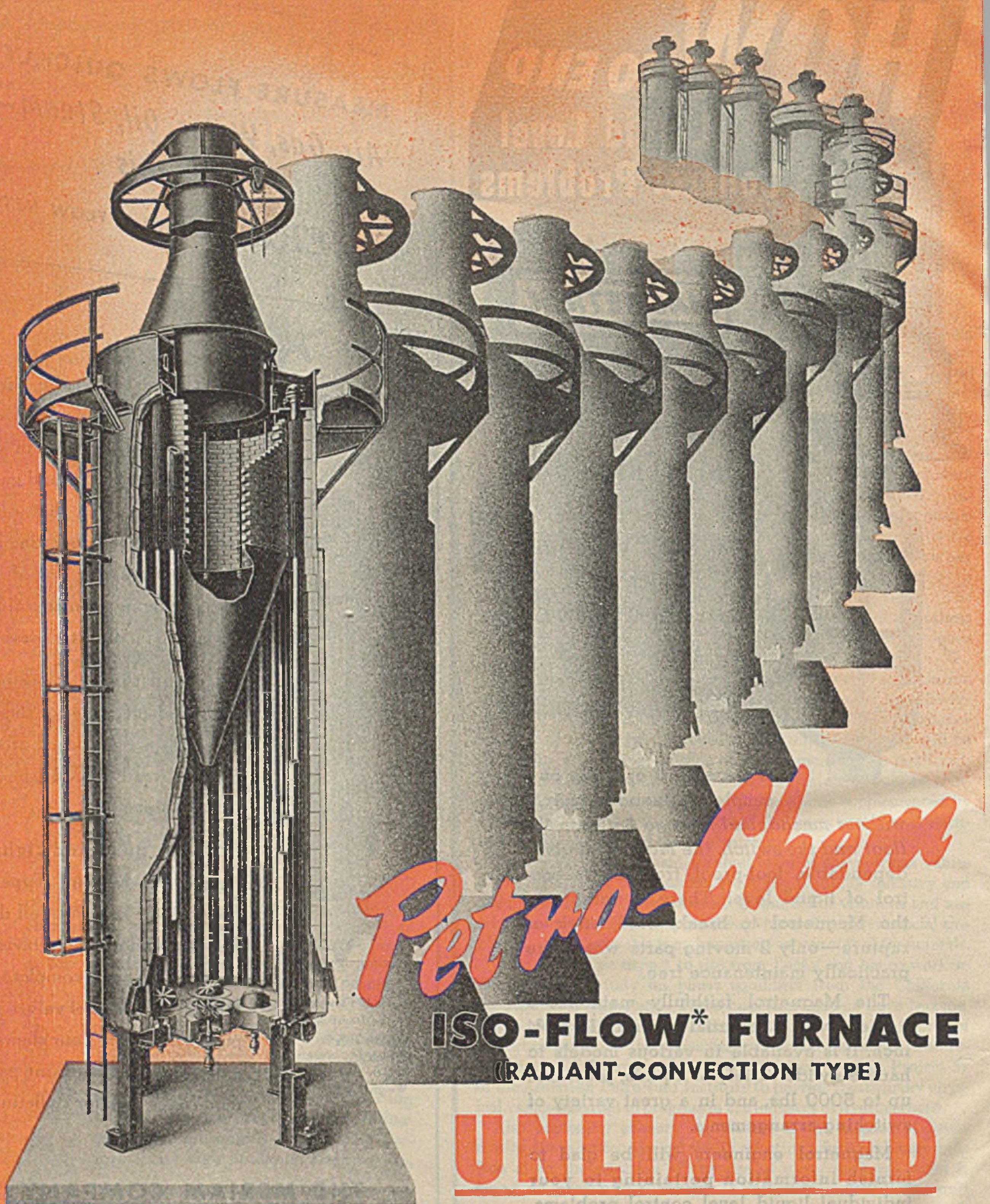
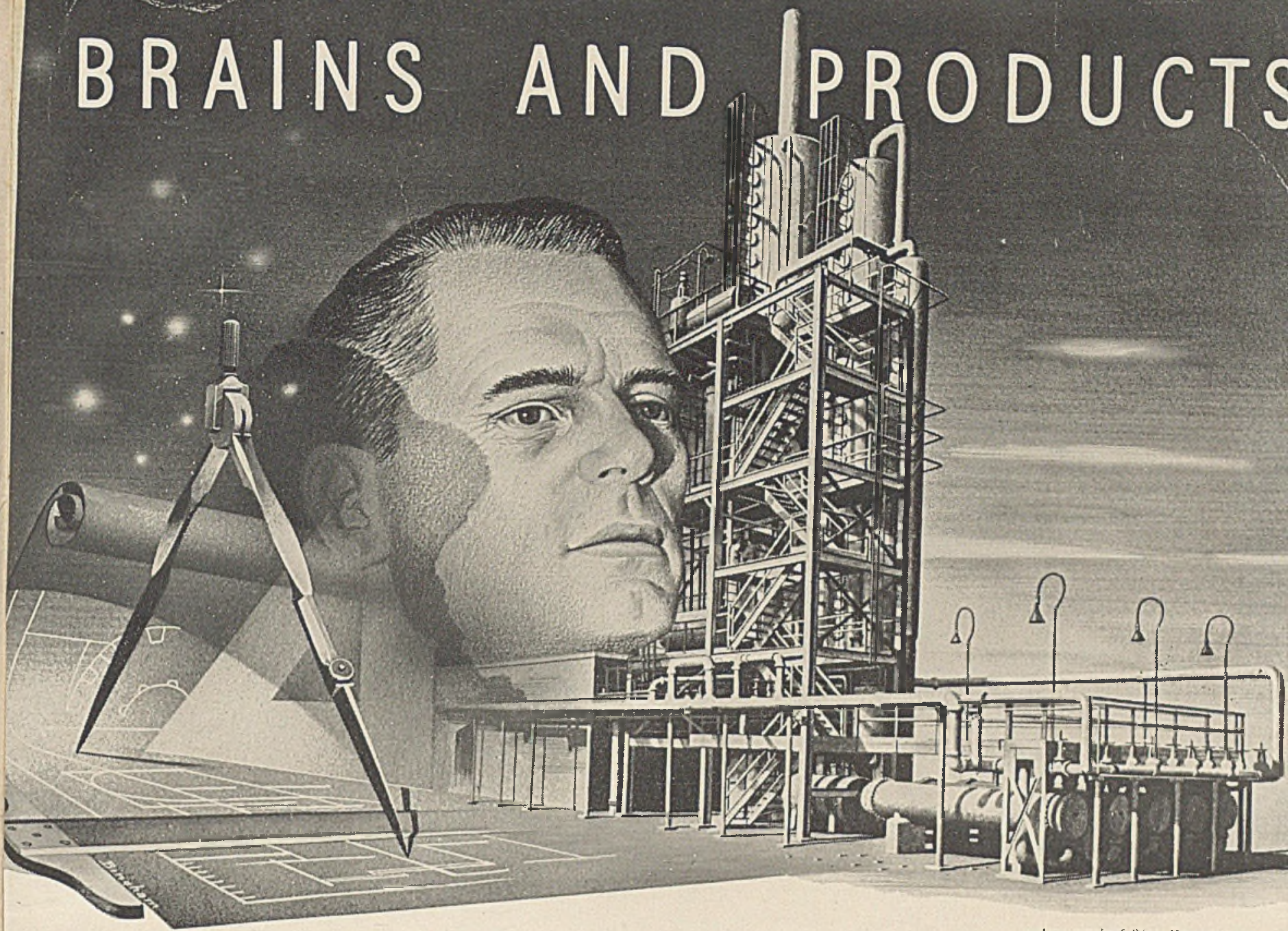

Petro-Chem



An example of Blaw-Knox design and construction for the rubber industry.

. . . to help you establish yourself profitably in tomorrow's market

Right now Blaw-Knox may have little to offer that is not connected with the war effort. It has, however, a wide line of engineered products, which, combined with long experience, knowledge and special skills, may be of value to you now or in connection with postwar planning.

To list everything that Blaw-Knox offers to industry would cover many pages. Those responsible for the postwar success of their business are invited to request a discussion with us to determine how Blaw-Knox thinking and products may best serve them.

Engineers . . . a complete organization including nearly all branches of engineering. Their knowledge can be applied to virtually every basic industry. They can think with you *now*.

Laboratories . . . research, metallurgical, chemical, well-equipped and competently staffed. From their systematized research come better materials, better methods.

Modern plants . . . steel fabricating, piping, machine shops, foundries, equipped with latest type tools and equipment and manned by workers trained in Blaw-Knox standards of precision.

Specialized knowledge and experience in building complete process plants—including research, engineering, design, construction of equipment and structure and test operation.

Unequalled facilities for designing and producing equipment for steel and non-ferrous industries. These play an important part in speeding production and reducing costs.

Pioneer and leader in designing and manufacturing construction equipment. This leadership is evident in great projects everywhere—dams, highways, waterways, harbor improvements.

PARTIAL LIST OF BLAW-KNOX PRODUCTS

INDUSTRIAL PRODUCTS & SERVICES

STEEL PLANT EQUIPMENT
ROLLS FOR STEEL & NON-FERROUS MILLS
ROLLING MILL MACHINERY
CONSTRUCTION EQUIPMENT
RADIO & TRANSMISSION TOWERS
POWER PIPING
STEEL GRATING
STEEL & ALLOY CASTINGS
CLAMSHELL BUCKETS
SPRINKLER SYSTEMS
DESIGN, FABRICATION AND ERECTION OF CHEMICAL, RUBBER AND OTHER PROCESS PLANTS AND EQUIPMENT

A FEW VICTORY PRODUCTS

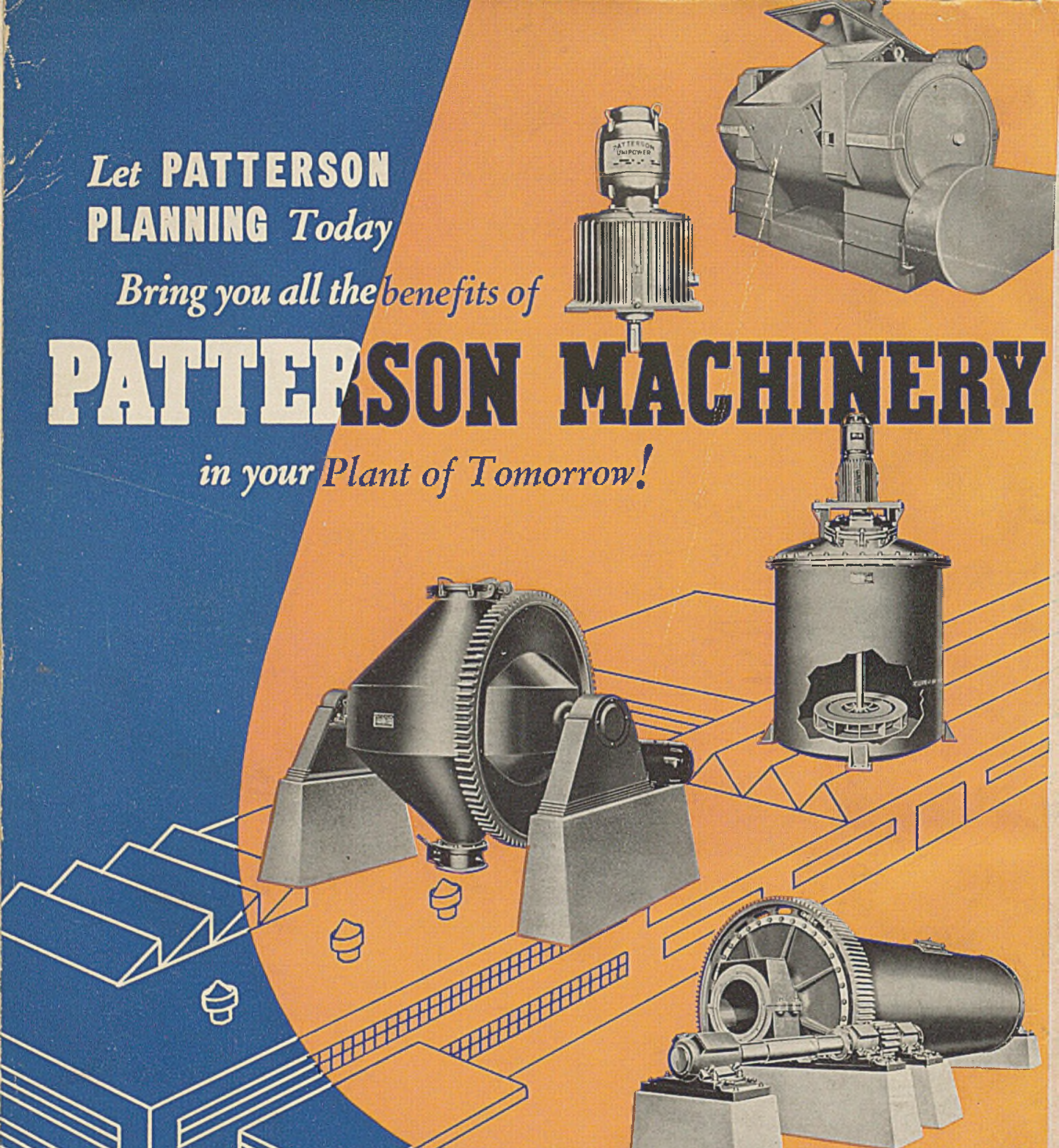
ANTI-AIRCRAFT GUNS
CHEMICAL PLANTS
PIPING FOR SUBMARINES
GUN SLIDES
AERIAL BOMBS
GUN MOUNTS
POWDER PLANTS
SYNTHETIC RUBBER PLANTS
CAST ARMOR FOR TANKS AND NAVAL CONSTRUCTION

BLAW-KNOX COMPANY

2081 FARMERS BANK BUILDING, PITTSBURGH, PA.

LEWIS FOUNDRY & MACHINE DIVISION • UNION STEEL CASTINGS DIVISION • POWER PIPING DIVISION • NATIONAL ALLOY STEEL DIVISION PITTSBURGH ROLLS DIVISION • BLAW-KNOX DIVISION • MARTINS FERRY DIVISION • BLAW-KNOX SPRINKLER DIVISION • BLAW-KNOX BOMB DIVISION

Four Blaw-Knox plants have been awarded the Army-Navy "E" for production excellence.


PATTERSON UNIPOWER