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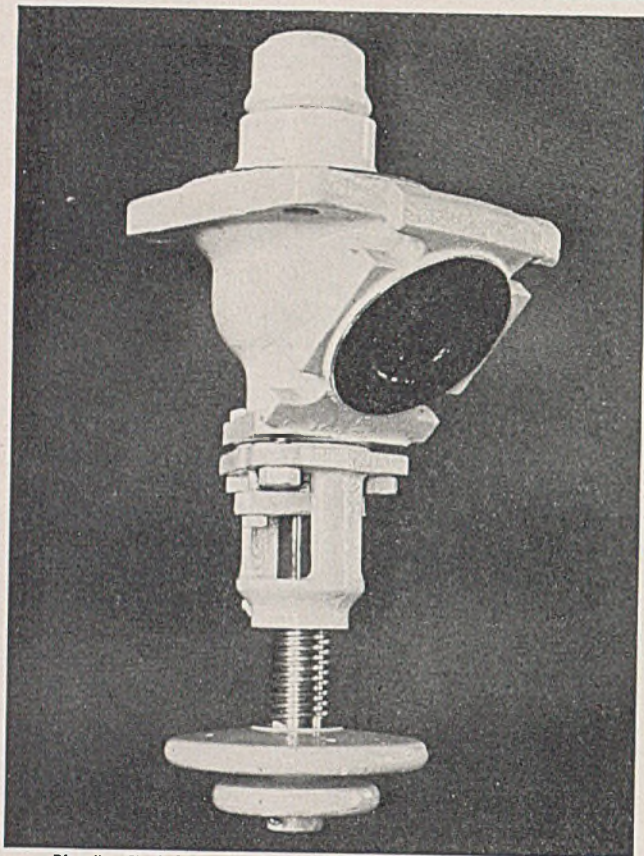
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Pfaudler Announces

HEAVY-DUTY ACID-RESISTING GLASS-LINED VALVES

Flush, Pop and Line Valves Available



Pfaudler Flush Valve is so designed that pressures within reactor tend to keep seat tight. It holds with the pressure. Valve and seat are ground in at the factory, locked into position, then assembled to reactor outlet or as a line valve fully assembled. When opened it should be opened fully and not used for regulating flow

To meet the need for corrosion resistant valves, all parts of which have the same acid resisting properties as Pfaudler Glass-Lined Steel Equipment, Pfaudler now offers a mechanically strong series of glass-lined flush, line and pop safety valves. These valves have been in commercial service for a sufficiently long period of time to prove their practicability.

Pfaudler Valves are made of a sturdy glass-lined cast iron body with porcelain valve seat and valve head. The valve head is carried on a glass covered stem that cannot break under tension. Porcelain parts are largely free of unequal temperature expansion and bear no pipe line strains.

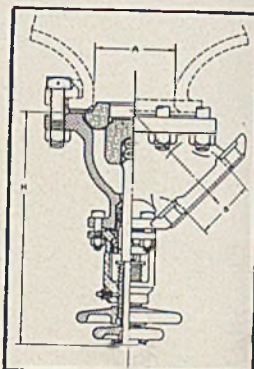
When it is necessary to regrind porcelain valve seats and heads, this can be done without special tools or dismantling the Pfaudler valve. It is only necessary to turn the lower

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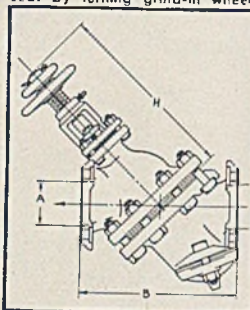
All Types Use Same Valve Body

The same valve body is used for all types of Pfaudler Valves so that by a change of operating mechanism and porcelain parts, a flush valve can be made into a globe, throttle, line or pop safety valve. They can be attached to 125-lb. cast iron or 150-lb. steel flanged fittings, as all of our valve flanges are drilled to these standards. They can also be substituted for standard flanged elbows or tees in existing pipe lines, as the overall length (face to face) of valves is the same as tees and elbows.

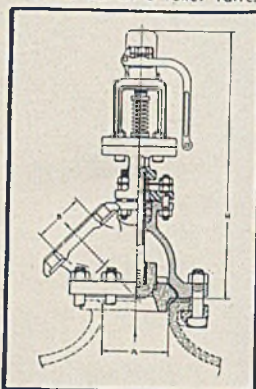
From the standpoint of corrosion resistance, Pfaudler Valves are highly satisfactory for any service glass-lined equipment withstands. If you are being balked in some of your process for lack of equipment which will withstand the corrosive action of the reagents, why not take up your problem with Pfaudler engineers? Glass-lined valves are only one of the many items Pfaudler has developed to cope with difficult process conditions.



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INDUSTRIAL AND ENGINEERING CHEMISTRY

REPORTS

ON THE CHEMICAL WORLD TODAY

Commerce and Industry

Future of Nitrogen Plants. Nitrogen is one of the basic elements of modern warfare. It is reported that the nine synthetic ammonia plants built by the Government in recent years to supplement prewar productive capacity represent an investment by the American public of approximately \$250,000,000, and have a combined maximum capacity of about 775,000 tons of fixed nitrogen per year. Obviously here is a tough nut to crack, for mixed up intimately in the problem are questions of national security and fertilizer production, the latter with political implications.

Secretary of Agriculture Wickard has just released the recommendations of a postwar planning group within his Department, suggesting that some of the synthetic ammonia plants now operated by the Federal Government be converted to the manufacture of solid nitrogen fertilizer:

A sound national policy with respect to these plants (the nine mentioned above) should (a) insure American farmers an abundant supply of fertilizer nitrogen in times of peace at prices that would be associated with free competition on the part of private concerns using the lowest cost methods available, and (b) provide a reserve nitrogen fixation capacity that would be an integral part of our military establishment. This reserve capacity would reduce the impact of any future war on fertilizer nitrogen supplies.

The USDA postwar planning group has refrained in this report from taking any stand on the question of whether private industry or government should operate the federally owned nitrogen-fixation plants. It does favor ultimate conversion of nearly 40% of the total rated nitrogen-producing capacity of existing government plants for the production of granular nitrogen fertilizer, ammonia, and ammonia derivatives to meet postwar requirements.

The USDA postwar planners base their estimates of nitrogen requirements on assumptions as to national and farm income, nitrogen fertilizer prices, and soil and crop needs. Briefly they estimate fertilizer nitrogen consumption under unfavorable conditions at 500,000 tons (in terms of nitrogen), at 750,000 tons under moderately favorable conditions, and at 900,000 tons under most favorable conditions. Just as a measure of these estimates, it is recalled that the average 1936-40 consumption of fertilizer nitrogen was about 390,000 tons. The report also estimates that industrial nitrogen consumption will range between 175,000 and 300,000 tons of nitrogen, and contemplates certain amounts of imports of Chilean nitrate and other nitrogen-bearing materials.

Grave doubts exist in the minds of many practical individuals that anything like 40% conversion of existing federally owned nitrogen-fixation plants is necessary in the postwar years. Those who take this stand are emphatic that no such consumption of fertilizer nitrogen is possible unless the farmer is to be subsidized directly or indirectly by public funds. This might take the form of direct gifts of fertilizer or fertilizer sold at a price well below the figure that private industry can afford to meet. Those who challenge the 40% conversion figure also point out that the Department of Agriculture appears to be in favor of two diametrically opposed schools of thought: (1) rigid production controls of agricultural products and (2) a policy of increasing output of agricultural products through the much wider use of fertilizer.

We face the same question of excess national and international nitrogen-fixation capacity that we did after World War I, in a more aggravated form; for new synthetic producing units have been erected, not only here but in many other parts of the world. In addition, one new plant in Chile has a rated capacity of some 200,000 tons of sodium nitrate annually, and we do have a "Good Neighbor Policy".

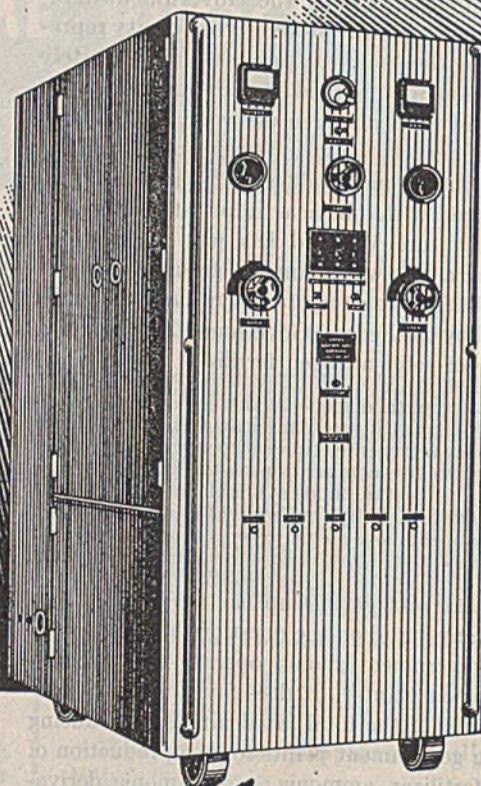
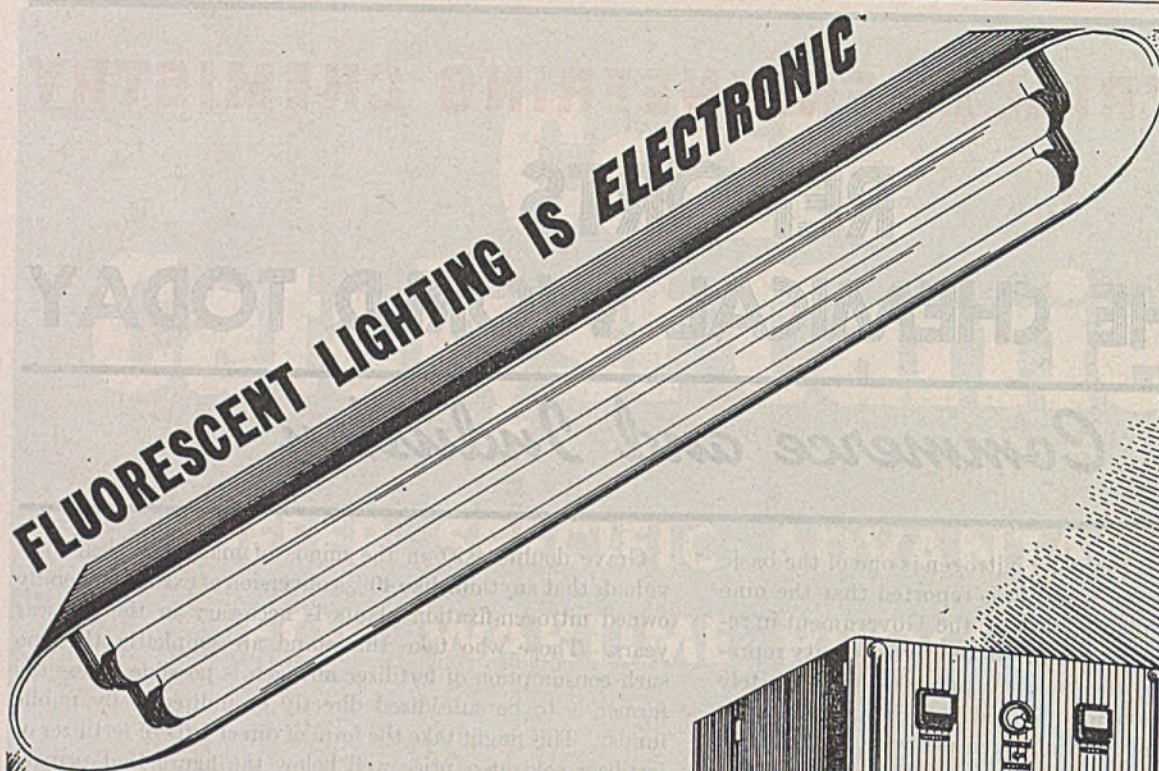
Finally, the appeal to hold part of our excess nitrogen-fixation capacity created in the war emergency in a stand-by condition has many advocates and appears, on the surface at least, to have much in its favor. Similar suggestions have been made in regard to our newly created synthetic rubber and government-owned magnesium and aluminum plants.

In any consideration of excess ammonia capacity it is more than a pious idea to do some straight thinking based on chemical facts. Much of the expected excess of ammonia capacity will fail to materialize for the reason that many of the plants will be converted to methanol production, once the war demand for explosives subsides. Our postwar requirements for methanol will be tremendous because of certain expansion in the plastics field.

A policy, however, of maintaining large numbers of stand-by plants presupposes that technology in these fields will remain static for many years to come. Few technologists will agree to any such contention. The same reason was given for holding the old cyanamide nitrogen-fixation plant at Muscle Shoals in stand-by condition following World War I, but the plant became hopelessly obsolete in a relatively short time.

(Continued on page 8)

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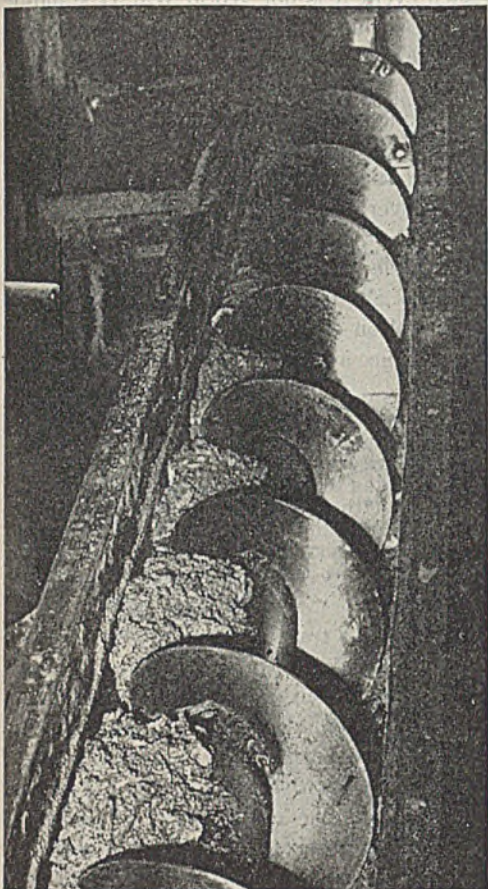
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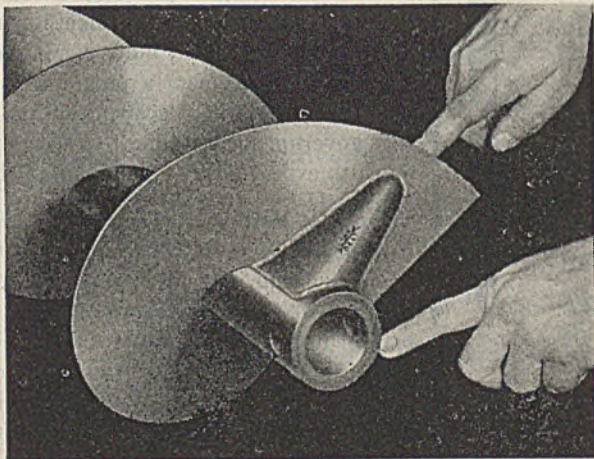
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*bring copra and sesame seed
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Above: Inclined Link-Belt screw conveyor delivering copra and sesame cake to crusher. Trough cover plate removed for photographing.

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OILS for soap, salads, and medicines are extracted from copra and sesame seed in many plants in which Link-Belt screw conveyors and elevators are used. One of these is the modern Fabrica de Aceita Hidrogenado y Manteca Vegetal, "La Polar," S.A., Mexican producer of high grade vegetable oils. Here Link-Belt screw conveyors carry copra and sesame cake to the crushers, and from a bucket elevator to expellers, which extract the oils.

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

Commerce and Industry

It is hardly likely that we will be called upon to fight another World War five years after the end of this one. We may be called upon to fight one twenty-five or fifty or a hundred years hence. In any such event it is not World War II stand-by plants that we will need but the very latest in technological advances; these will be available only if we maintain a healthy atmosphere that will permit continuous fundamental and applied research, not only in the field of fertilizers but of all other human endeavor.

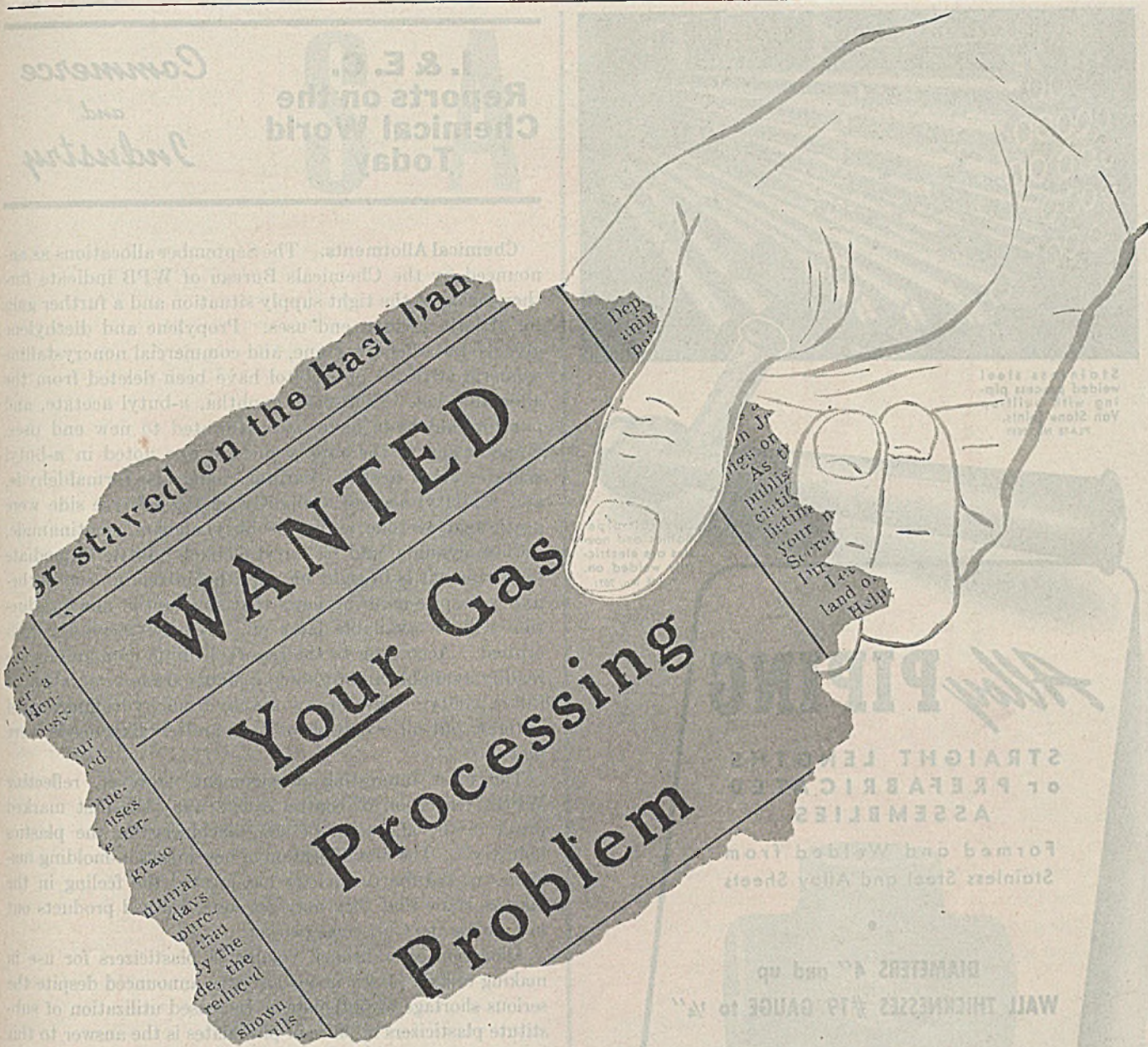
How best to attain this goal? Obviously by intelligent cooperation between government and industry, each recognizing the logical role of the other in an economy based on private enterprise. In the article "Liquid Fuel from Nonpetroleum Sources" (*Chemical and Engineering News*, August 10, pages 1244-50) Robert E. Wilson offers a pattern that might well be followed in this instance and others like it:

If the Bureau of Mines is in general accord with the principles and the program above outlined, the writer is of the opinion that the petroleum industry would be willing, if the Government so requested, to set up an advisory committee of technologists, well versed in these fields, to bring together and analyze existing data from various sources. On the basis of this correlation of information, they could advise and cooperate in recommending detailed research programs designing pilot plants, and keeping the investigations guided along the most useful and practical lines.

It will be nothing short of a tragedy if our nitrogen-fixation capacity in this country again becomes a political football. The same is true of excess capacity for production of sulfuric acid, synthetic rubber, magnesium, aluminum, and many other materials required in stupendous amounts in modern warfare. If such excess capacity is dealt with intelligently and private industry is treated fairly in the reconversion to peacetime economy, its leaders will certainly realize the full responsibility that such action automatically places upon it to keep America technologically strong to meet any future emergency. Such responsibility requires something more than the stimulus of an immediate profit motive. It requires a willingness to share with government a program on vital fundamental research and a spirit of cooperation on both sides. It means that government is willing to trust industry. Is all this too much to expect? We do not think it is.

On Not Painting the Town. The extensive damage to Europe's villages and cities may seem to be, as the work of reconstruction gets underway, an opportunity for a vast increase in the exportation of paint. Experts in the Bureau of Foreign and Domestic Commerce believe this to be a false hope, however, for a variety of reasons. Probably foremost in their negative analysis is the almost certain lack of exchange value that will exist in Europe after the war. Further, the preponderance of stone construction limits the use of paint, and lastly, many small though antiquated paint plants are still alive in most European towns. Unharmed by bombs, these will be able to swing into action very quickly. All in all, it appears that our foreign trade will not increase much above the export average of \$8,700,000, or 2% of the total sales of paint in the United States.

(Continued on page 10)



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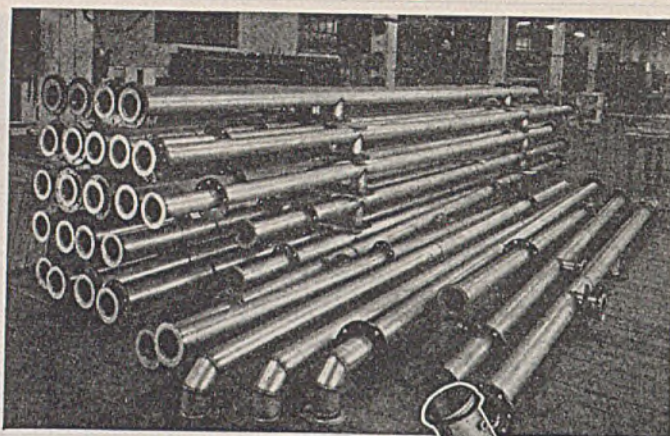
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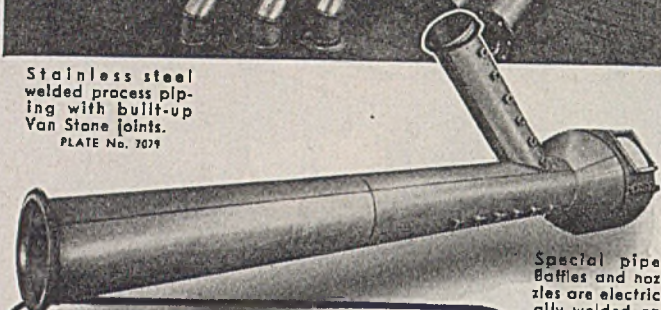
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I. & E. C. Reports on the Chemical World Today

*Commerce
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Chemical Allotments. The September allocations as announced by the Chemicals Bureau of WPB indicate further easing of the tight supply situation and a further gain for strictly civilian end uses. Propylene and diethylene glycols, butadiene, styrene, and commercial noncrystalline isomeric mixtures of sorbitol have been deleted from the allocation list. High-flash naphtha, *n*-butyl acetate, and paraformaldehyde have been allocated to new end uses. Some easing of the supply picture was noted in *n*-butyl acetate, ethyl acetate, barium chemicals, formaldehyde, and *sec*-butyl acetate. Slightly on the adverse side were acetic acid, acetone, aniline, isobutyl alcohol, nicotinamide, sodium cyanide, and *sec*-butyl alcohol. Little immediate improvement is in sight on naphthenic acid and naphthenates, despite assuring news that substantial new production will be available later on. *n*-Butyl alcohol is still critical. According to the report, lithium compounds are readily available and producing plants are not operating at full capacity. The supply of anhydrous hydrofluoric acid is tight, but all essential military and civilian needs were met.

The most interesting development, however, reflecting WPB's relaxation of control orders was "the first marked break in the allocation of new machinery for the plastics industry". The first allocation of new injection-molding machines in the fourth quarter has created the feeling in the plastics trade that they may get some finished products out in time for the Christmas market.

Allocation of additional volume of plasticizers for use in making certain plastic goods also was announced despite the serious shortage of phthalates. Increased utilization of substitute plasticizers in place of phthalates is the answer to this move.

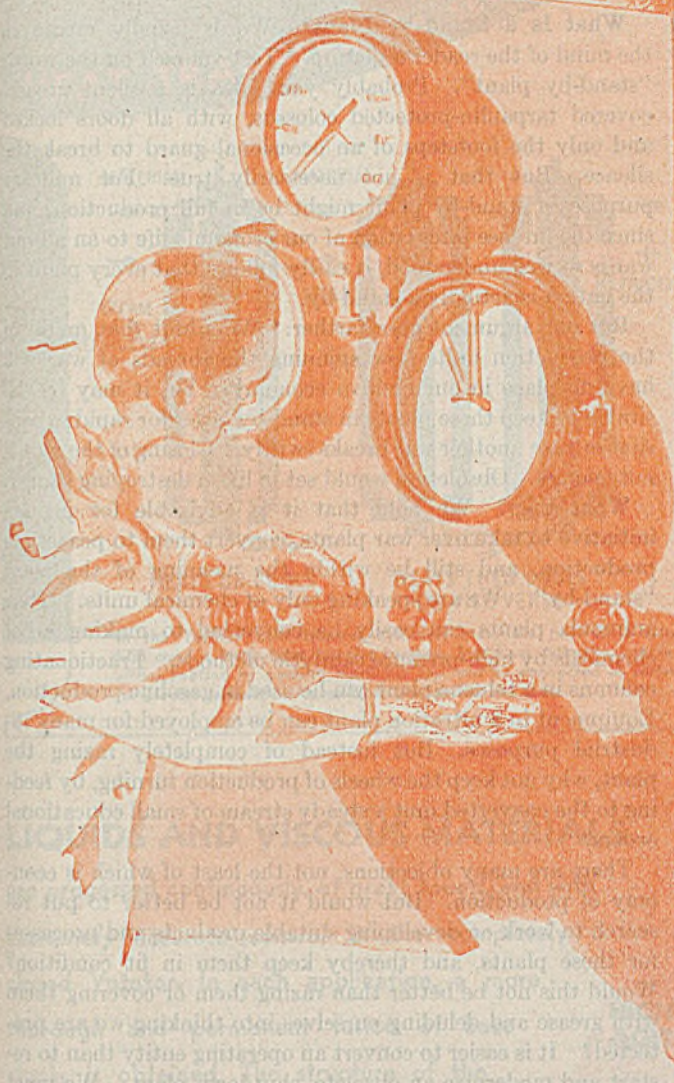
Progress in Containers. A new era in shipping of chemicals was inaugurated last month when the Pittsburgh Plate Glass Company's Columbia Chemical Division shipped 380 tons of chlorine, by barge, some 203 miles from Natrium near New Martinsville, W. Va., to the plant of the Carbide & Carbon Chemicals Corporation at Charleston, W. Va.

The chlorine is carried in four fusion-welded steel tanks, with a minimum wall thickness of 1 1/4 inches and built to withstand a pressure of 300 pounds per square inch. The cylindrical tanks are 55 feet 4 1/2 inches long and 7 feet 8 1/2 inches in diameter, and are mounted in the barge in pairs of steel cradles. The arrangement of the dome fittings is slightly different from that on a tank car, and each dome is equipped with added safety devices in addition to those which are standard to chlorine tank cars. Chemical producers are keenly interested in the expanding possibilities of large bulk shipments, especially through the inland waterways.

Lower distributing costs are going to receive greater attention in the postwar period. Two rather expensive factors have been container and shipping costs, and these are relatively high, percentage-wise, for products selling for a few cents per pound.

(Continued on page 12)

SAFE



High pressures, high velocities, high temperatures . . . stresses and strains, corrosion and erosion . . . *all* factors which tend to undermine safety in piping are resisted by *Tube-Turn seamless welding fittings*.

Laboratory and field tests conducted regularly demonstrate how Tube Turns' *exclusive*

forging processes increase serviceable life by improving grain structure in the metal itself, and thus reduce wear at the most vulnerable points of a piping system — where flow direction changes! Write for Catalog 111 — it contains data valuable to all who buy, specify and install piping and welding fittings

VALUABLE WALL CHARTS



Dimensional data on Tube-Turn fittings and flanges are shown on these two handy wall charts, sizes 24 x 36 inches—sent free on request.

Selected Tube Turns Distributors in every principal city are ready to serve you from complete stocks.

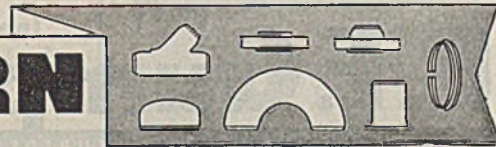
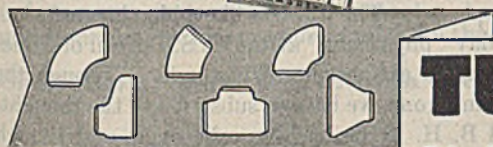
TUBE TURNS (Inc.) Louisville, Kentucky. Branch Offices: New York, Chicago, Philadelphia, Pittsburgh, Cleveland, Dayton, Washington, D. C., Houston, San Francisco, Seattle, Los Angeles.



TUBE-TURN

TRADE MARK

Welding Fittings and Flanges



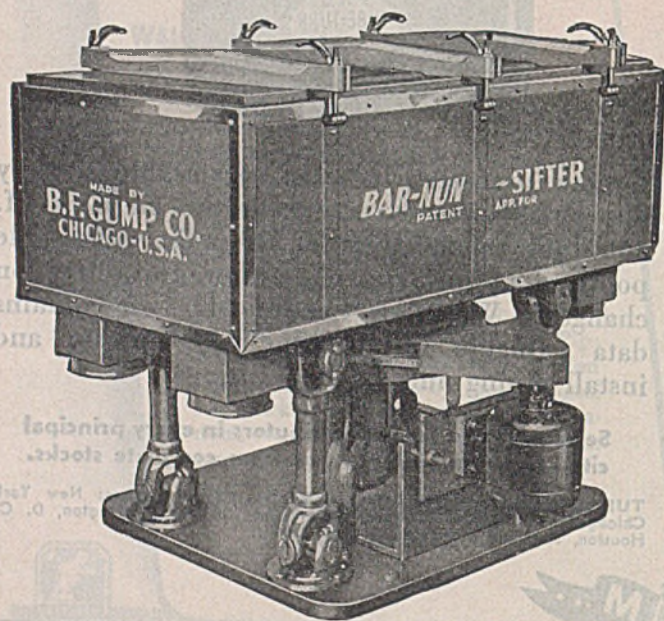
BAR-NUN

ROTARY

SIFTERS

Proved Satisfactory Under Severe Tests In Vital War Plants

THESE efficient units are measuring up to the severe continuous service required in vital war industries. When more capacity is needed extra BAR-NUNS are usually ordered to supplement the capacity of the first machines that have proved so satisfactory. Some of the reasons for the popularity of the BAR-NUN are: complete rotary motion, mechanically controlled; sturdy heavy-duty construction; and, large capacity for small space and power requirements. Available in 9 sizes — 4 to 60 square feet of cloth surface, for sifting or grading of dry, powdered, granular or flaked materials.



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ENGINEERS AND MANUFACTURERS SINCE 1872

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

Technology

What Is a Stand-by Plant? Words usually create in the mind of the reader a picture. Test yourself on the words "stand-by plant". Probably your idea is a silent grease-covered tarpaulin-protected colossus, with all doors locked and only the footsteps of an occasional guard to break the silence. But that is not necessarily true. For military purposes a stand-by plant might be in full production, and since the intense integration of our economic life to an all-out war is so well understood, it easily follows that every plant in the nation is actually a stand-by.

But our argument goes farther. We admit that many of the production units now spinning the threads of war will have no place in our civilian economy. Yet it may be desirable to keep these plants in stand-by order for rapid expansion in case another war breaks swiftly. Closing of the unit is not enough. Obsolescence would set in like a destroying cancer.

What then? We hold that it is advisable for private initiative to take over war plants, convert them to peacetime production, and still be within the meaning of the word "stand-by". We are speaking only of chemical units. Thus ammonia plants can easily be converted to making other chemicals by high-pressure catalytic methods. Fractionating columns in a toluene plant can be used in gasoline production. Equipment in a nitration plant can be employed for many industrial purposes. But instead of completely razing the plant, why not keep the wheels of production turning, by feeding to the converted unit a steady stream of small educational orders?

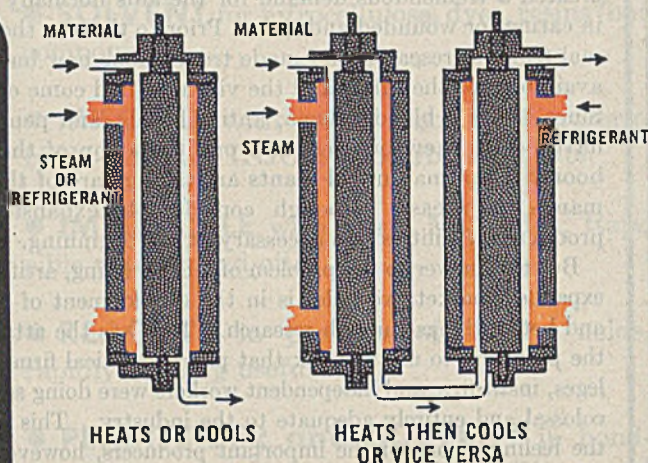
There are many objections, not the least of which is economy of production. But would it not be better to put research to work on developing suitable products and processes for these plants, and thereby keep them in fit condition? Would this not be better than razing them or covering them with grease and deluding ourselves into thinking we are protected? It is easier to convert an operating entity than to restart and modernize an obsolete, shutdown plant. We must emphasize that this is a problem for industry to consider and a matter on which industry will advise Government. However, the first job is to reach unanimity on the definition of a stand-by plant. An idle out-of-date plant is no protection; a stand-by plant is a running plant, not a rotting hulk.

Farewell B. H.? An old friend was given his certain death sentence the other day. And not for the first time, for predictions of his demise have been forthcoming since he contracted a seemingly fatal illness during the first World War. But he has managed to revive during this war and fight a good fight for his country even though everyone said it would be his last. B. H. has been dead, by all accounts, since his life processes became uneconomical. In the last depression he sheltered meanly, but as well as he was able, many hordes of unemployed. The war was like a blood transfusion, but the other day "physicians" at the U. S. Bureau of Mines predicted his certain extinction. We wonder. Though the flicker of life seems gone, we hate to subscribe to the thought. Our old friend B. H. is the beehive coke oven, and though others may, we cannot say "bye-bye beehive".

(Continued on page 14)

VOTATOR *2 in 1* PERFORMANCE

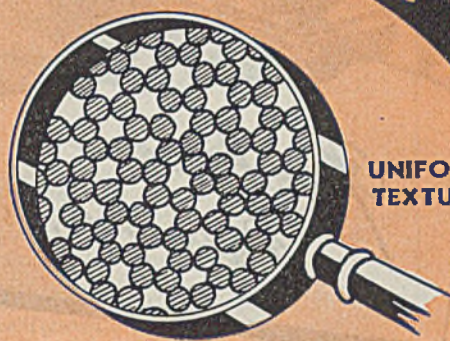
HEAT TRANSFER in seconds



In the Votator heat transfer cylinder, materials pass in a thin film over a large heat transfer surface. Standard cylinders handle either heating or cooling mediums and can be connected in series for greater capacity or for multiple temperature changes.

**LEADS TO IMPROVED
PRODUCT QUALITY
AND LARGE PRODUCTION
ECONOMIES**

PROCESSING at same time



LIQUIDS AND VISCOUS MATERIALS

are processed continuously, at *great speed*, and with *extremely accurate control* in the completely closed Votator. In each application, a more thorough and permanent fusion of base stocks is obtained. The structure of the finished product is more refined and uniform. Often many items of ordinary processing equipment are eliminated — with corresponding savings of floor space, power, heat, refrigerant and labor.

Votator units are available in standard models or can be especially engineered to fit individual requirements. We can give you more specific information if you will request and fill out our convenient data questionnaire. Address your inquiry to The Girdler Corp., Votator Div., Louisville 1, Ky.

**HIGH SPEED
AGITATION**



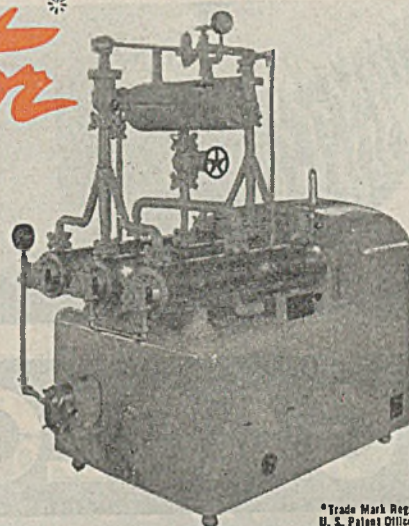
The rapidly revolving scraper blades on the shaft agitate thoroughly. Many processing operations can be accomplished more effectively—heat transfer and mixing, aerating, plasticizing, emulsifying, crystallizing or compounding.

THE

Votator

A GIRDLER
PRODUCT

A typical
Votator unit



HEAT TRANSFER AND PROCESSING EQUIPMENT

*Trade Mark Reg.
U. S. Patent Office



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"And don't forget how well those KLOZURE Oil Seals are working out."

Yes, GARLOCK products give superior performance for our Armed Forces and for industry everywhere. You can rely on their dependable service.

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PALMYRA, NEW YORK

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GARLOCK LATTICE-BRAID PACKING. The unique structural design imparts semi-automatic pressure action. Available in several styles for various types of service.



GARLOCK

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

Postwar

Drugs and Pharmaceuticals. A peculiar set of circumstances brought about, in recent years, the largest boom ever experienced in the history of the drug and pharmaceutical industry. One of the circumstances is the war, which created a tremendous demand for the aids normally used in caring for wounded and sick. Prior to the war the normal fruits of research had made tremendous new business available, for the sulfas and the vitamins had come of age. Since the war blood plasma, antimalarials, and penicillin have heaped new business and profits on top of the two booms. Pharmaceutical plants are taking care of the demands with ease, although considerable expansion of production facilities was necessary at the beginning.

But the answer to the problem of a contracting, artificially expanded market, we hold, is in the development of newer and better things through research. This was the attack in the past, and to us the work that pharmaceutical firms, colleges, institutes, and independent workers were doing seemed colossal and entirely adequate to the industry. This is not the feeling of one of the important producers, however, for Theodore G. Klumpp, president of Winthrop Chemical Company, stated before the Division of Medicinal Chemistry at the recent ACS meeting that "in comparison with research in other fields, plastics, metallurgy, petroleum, communications, and aviation, medical research is small time and amateurish". In view of the accomplishments of that "small time" research, if the industry is contemplating going into "big time" research, our advice to the germ is "duck, brother".

Industry Advisory Boards. Considerable duplication of effort and some working at cross purposes has been noted in the present system of one industry advisory board for the War Production Board in each important industry and almost identical setups in the Office of Price Administration. Once again an attempt will be made, it is reported, to simplify cooperative action between industries, WPB, and OPA by the creation within each field of one industry advisory board to function with both agencies.

A growing sentiment is also noted for the ultimate consolidation of WPB and OPA. Such action, according to the proponents of the idea, would be more efficient in handling reconversion and postwar problems. Those who favor the plan point out that prices and production are too closely allied to be handled by separate agencies. While considerable reluctance to any wedding of the two groups may be expected in many quarters, the idea has too much merit to be dismissed.

However, the main problem is the reluctance of industry executives to serve on industry advisory committees, through a fear that any participation in such programs will ultimately bring severe condemnation from the Department of Justice. The *can* and *cannot* pronouncements from Attorney General Biddle's office have frightened executives. They are likely to refuse invitations to participate unless the present Department of Justice attitude is clearly defined or unless new legislation is passed specifying the duties, rights, and privileges of such committees. Much good could come from cooperation between industry committees and government agencies in formulating postwar planning and reconversion policies.

DO YOU KNOW WHAT *Furfuryl* ALCOHOL CAN DO?

- **SOLVENT** for nitrocellulose, dyes, resins (both synthetic and natural), and many organic compounds.
- **MISCIBLE** with water, alcohol, chloroform, ether, coal tar solvents and most other NON-PARAFFINIC hydrocarbon solvents.
- **IMMISCIBLE** with Lard, Menhaden, Rape Seed and similar oils; only slightly miscible with linseed oil.
- **REACTIVE** in presence of mineral acids, rapidly forming useful resins.
- **PLASTICIZER and SOLVENT** in bonding abrasive grain for grinding wheels of improved temperature and moisture resistance.
- **WOOD-PENETRATING VEHICLE** for organic substances.
- **PAINT, VARNISH, and LACQUER REMOVER.**
- **WETTING AGENT** for uniform Plastic Mixes.

Furfuryl ALCOHOL (Refined) is available for uses requiring a narrower boiling, light colored product, completely miscible with water.

OUR TECHNICAL STAFF will be glad to help you secure more complete information about the application of *Furfuryl* Alcohol to your problems.

Quaker *Furfuryl* ALCOHOL

(TECHNICAL)

 $C_4H_3O-CH_2OH$

Molecular Weight	98.10
Freezing Point, °C	-31
Boiling Range, °C (95%)	167 to 177
Specific Gravity (25-25°C)	1.130
Flash Point (open cup) °C	75
Refractive Index (25/D)	1.4868
Vapor Pressure at 30°C, mm Hg.	2
Surface Tension (dynes/cm)	38.2

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Standard Containers: 9, 45, 90 and 500 lb. drums (net).
 Carload of Drums (80) 40,000 lbs.
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 All LCL quantities F.O.B. Cedar Rapids, Iowa.
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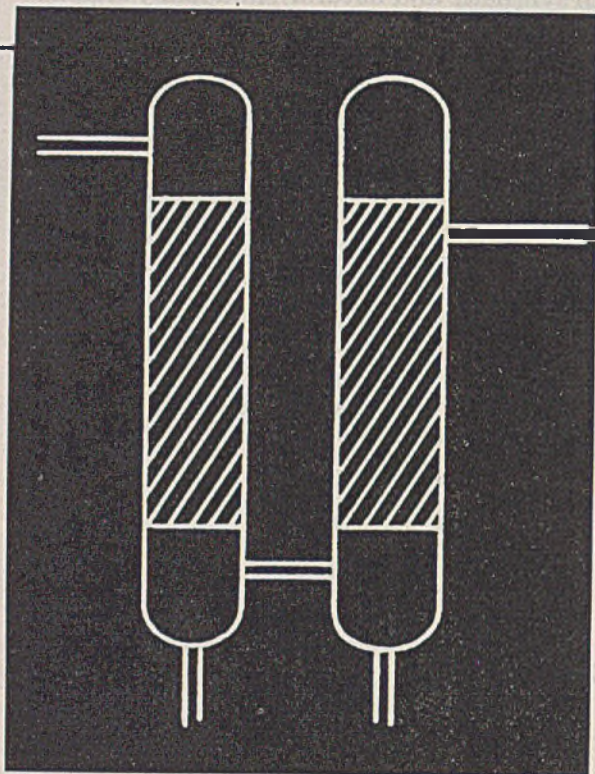
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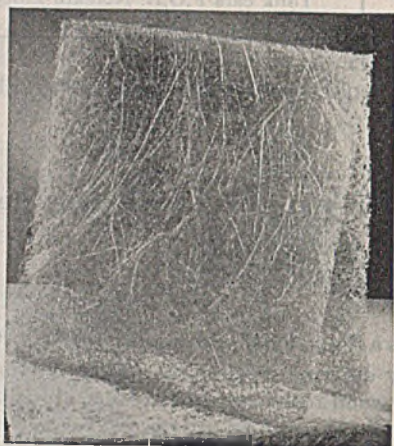


**FURFURAL - FURFURYL ALCOHOL - HYDROFURAMIDE
... TETRAHYDROFURFURYL ALCOHOL ...**

FIBERGLAS* TOWER PACKING OUTSTANDING MATERIAL FOR SOLVENT-RECOVERY



FOR SOLVENT-RECOVERY. Fiberglas Tower Packing comes in the convenient form illustrated at right. Packs are bonded with a water-soluble binder. Standard size packs—20" x 20" x 1".



Because of its great surface area and large free volume, Fiberglas Tower Packing is an exceptionally good medium for use in liquid-liquid extraction processes. Especially is this true, in the operation involving fractional distribution of the components of a mixture between two partially miscible solvents.

For the same reasons Fiberglas Tower Packing is highly desirable in precipitative extraction.

Fiberglas Tower Packing possesses, to an exceptionally high degree, all the properties that a tower packing medium should have:

Low Weight: 3½ pounds per cubic foot.

Large Surface Area: 135 feet per cubic foot of material.

Large Free Volume: 97.75% per cubic foot at 3½ pounds density.

Large Free Cross Section: Small force required to send the vapor through the tower.

Mechanical Strength: Water-soluble binder provides rigidity for easy handling during application.

Small Weight of Liquid Retained: Exceptionally small, varying with the viscosity of liquids involved.

High Productivity: Low vapor resistance results in greatly increased production per column.

Surprisingly Low Cost: Considerably less than commonly used packing materials.

Readily Available: Made of native materials, obtainable without delay.

If you require the benefits of Fiberglas Tower Packing in your process, write, giving details: Owens-Corning Fiberglas Corporation, 1951 Nicholas Bldg., Toledo 1, Ohio. In Canada, Fiberglas Canada, Ltd., Oshawa, Ontario.



FIBERGLAS

*T. M. Reg. U. S. Pat. Off.

...A BASIC MATERIAL

Free SAMPLES

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● Behind the door of America's chemical industry is being conducted one of science's most important pieces of unfinished business—the exploration of coal-tar.

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Niacin, in the Vitamin B Complex... many of the new life-saving sulfa drugs... scores of compounding materials, helping to make possible our vitally essential synthetic rubber industry... DDT... and finally, one of the most notable of modern chemical syntheses—the exact duplication of the complex quinine molecule.

For the even more memorable advances to be anticipated in the future, Barrett stands ever available as a key source of supply for coal-tar chemicals. If you are working on any problems involving coal-tar, or any of its derivatives, Barrett invites your inquiries.

THE BARRETT DIVISION

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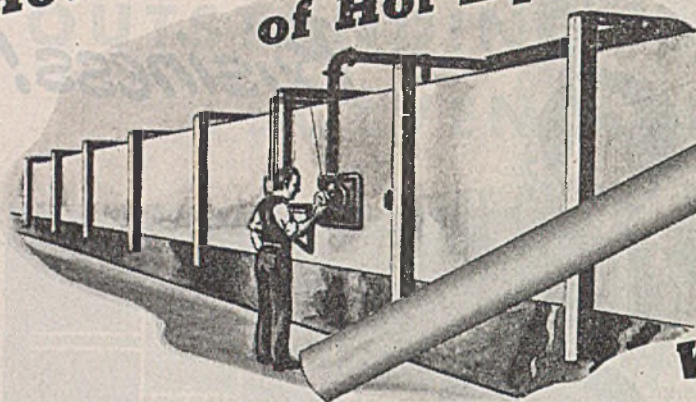
BARRETT COAL-TAR CHEMICALS: Tar acids: Phenols, Cresols, Cresylic Acids, Naphthalene • Phthalic Anhydride • Dibutyl Phthalate • Pyridine • Cumar* (Paracoumarone-indene Resin) • Rubber Compounding Materials • Bardol* • Barretan* • Pickling Inhibitors • Benzol • Toluol • Xylol • Solvent Naphtha, Hi-Flash Solvent • Hydrogenated Coal-Tar Chemicals • Flotation Agents • Tar Distillates • Anhydrous Ammonia • Ammonia Liquor • Ammonia Nitrate • Sulphate of Ammonia • Arcadian*, the American Nitrate of Soda.

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ONE OF AMERICA'S GREAT BASIC BUSINESSES



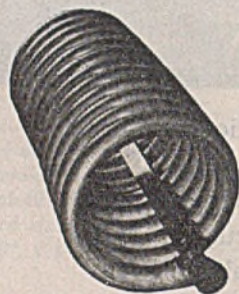
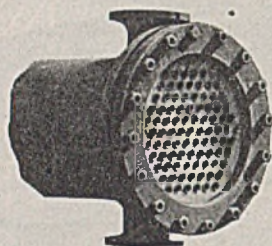
How to Prolong Life of Hot Equipment



with
**WELDED STAINLESS
TUBING**

Carpenter Welded Stainless Tubing, selected primarily for its heat resistance, is used as the "hot leg" to protect this thermocouple from corrosion, contamination and abrasion.

This tubing helps lengthen the service life of heat exchangers, condensers and other processing equipment.



Coils are fabricated easily without damage to the metal's structure.

Perforated Carpenter Welded Stainless Tubes are used as holders for catalysts.



When tubular parts must function in heat resistant or heat transfer applications, particularly where highly corrosive conditions exist, look to Carpenter Welded Stainless Tubing for the solution to your problem. You'll find that its physical and metallurgical structure contribute substantially to longer service life of process equipment.

The uniform walls of this tubing mean that there are no thin spots to "give out" under constant heat, corrosion, pressure or wear. And made in various analyses, you are assured of protection against many different corrosive elements and oxidation at high temperatures.

This is no time to experiment with heat or corrosion problems, so it will pay you to take advantage of Carpenter's "know how", gained first hand as a pioneer in the development of Welded Stainless Tubing. We'll be glad to share with you our experience in any problem affecting its selection, use or fabrication.

THE CARPENTER STEEL COMPANY
Welded Alloy Tube Division • Kenilworth, N. J.



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If you use Stainless Tubing—or are planning on its use—ask for a series of our Quick Facts Bulletins. A note on your company letterhead will start them on their way to you.



U.S.I. CHEMICAL NEWS

October



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



1944

U.S.I. Announces Two New Phenolics

Unusual Properties Exhibited by New "Arochem" Resins

Of timely interest to formulators of varnishes and vehicles for protective coatings, and to ink manufacturers and other resin users, is U.S.I.'s introduction of two phenolic-type resins, especially developed for present-day use with soft oils. Both of these resins are currently available for many civilian end-uses, although application must still be made, as usual, under W.P.B. Order M-246.

S&W Arochem 337

S&W Arochem 337 is especially useful in quick-drying varnishes, quick-drying enamels for either general or industrial use, floor paints, spar varnishes, over-print varnishes and printing inks. This high melting point, modified-phenolic resin imparts faster bodying rate, faster drying properties, superior resistance to alkali and water, and greater film hardness and mar resistance than most modified phenolics in varnishes of equivalent oil lengths.

Ease of handling is another feature. Although it has an exceptionally high melting point, it is readily soluble, without special cooking procedures in most high viscosity oils. In nearly all cases, the total resin and oil content may be charged into the kettle at the start and taken to top heat without any "kick-out" or formation of gel particles. Due to the short cooking schedules required, varnishes made with S&W Arochem 337 are light in color.

While this resin is too reactive to be used with tung oil alone, satisfactory varnishes may be produced by the addition of moderate amounts of less reactive resin or oil to the cook.

S&W Arochem 338

S&W Arochem 338 is particularly well suited for use in gloss ink vehicles and over-print varnishes as well as varnishes and enamels for general and industrial use.

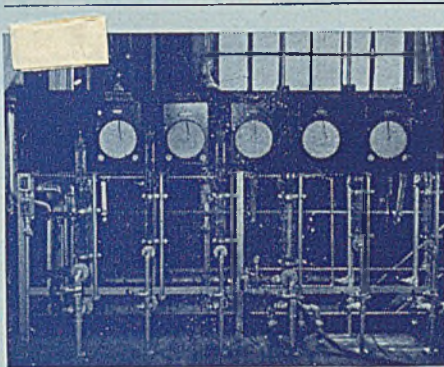
This resin, like S&W Arochem 337, is a modified phenolic, but it has a higher melting point, and being less soluble in solvents and oils, is more rapid in its bodying action. Developed primarily for use in printing inks and over-print varnishes, it produces ink vehicles of exceptionally high viscosity when cooked with linseed or other drying oils. This shortens the manufacturing holding times. Due to the unusually large molecular structure of the resin, the resulting vehicles dry to extremely

(Continued on next page)

Tonnage Production of Indalone Involves Novel Claisen Reaction

Manufacture of U.S.I.'s War Important Insectifuge Among First Large-scale Commercial Uses of this Type Condensation

Although every organic chemist has had laboratory experience with Claisen-type condensations, until recently only few have done much with these interesting reactions on a large commercial scale. The sudden demand for atebirin, sulfa-



Centralized control has played an important part in the successful tonnage-scale production of Indalone. Here you see one group of sensitive controllers, and recording instruments in U.S.I.'s Baltimore plant.

merazine, vitamin B₁, and U.S.I.'s Indalone, as a result of the war, has focused wide attention on the tonnage production of such chemicals and has brought many developments of both present and postwar significance. First of these from the standpoint of tonnage is U.S.I.'s manufacture of Indalone, vital ingredient in the government's new all-purpose insect repellent.

War Demands Met

Starting in the early 1920's with the first commercial production of acetoacetic ester, U.S.I. followed with the commercial-scale operation of a second Claisen reaction to produce sodium oxalacetate. This, in turn, was followed by the commercial introduction of Indalone in 1939. Tremendously stepped-up production of all of these products has been necessary to meet the huge war demands. This is particularly true of Indalone, production of which has been multiplied ten fold.

Basic Reaction

The reactions employed in the production of Indalone are shown on the next page. Mesityl oxide and dibutyl oxalate are first combined in a Claisen reaction using sodium butoxide as the condensing agent. This forms the sodium salt of Indalone which is then neutralized with dilute sulphuric acid. The process is carried out in the following stages.

Condensation Stage

Carefully measured quantities of mesityl oxide and dibutyl oxalate are added to the

(Continued on next page)

Finds New Short Cut to Zein Solutions

Current practice in preparing zein solutions calls for use of dry extracted zein to which is added a suitable solvent. Production of dry zein is a laborious and costly process involving the separate steps of precipitation, filtering, settling, washing and drying.

A newly patented process claims to greatly simplify the production of zein solutions and coating compounds by preparing them directly from the corn gluten. In the new method the granular or powdered gluten is first treated with a low boiling point zein protein solvent such as ethanol, or a mixture of such solvents.

Next the extract solution is separated from the residual gluten by filtration or centrifuging, and is then mixed with a base solvent of relatively high boiling point, such as ethylene glycol. Distillation removes the low boiling extracting solvent, leaving behind the zein dissolved in the base solvent and ready for use.

New Hydroscopic Ink For Recording Meters

One problem presented by recording meters of various kinds has been to find an ink which in the recorder pen will be able to withstand considerable exposure to the atmosphere without thickening or clogging, regardless of outside temperature or humidity, yet be fast drying after application.

A recent patent calls for a combination of a brilliant red dye with a tartrazine yellow for luminosity in a medium composed of water, ethanol, glycol and acetic acid. The hydroscopic effect of the glycol tends to absorb moisture from the air, thereby preventing the ink in the recorder pen from drying out. However, once the line is traced on the paper chart, the glycols are readily absorbed by the paper, thus producing a fast-drying ink. The acetic

RESIN SPECIFICATIONS

	S&W AROCHEM 337	S&W AROCHEM 338
Acid Number:	30-40	25-35
Melting Point: (Mercury)	150-160°C.	160-170°C.
Color:	N-K	N-K
Specific Gravity:	1.1	1.1
Soluble in:	Coal-tar and petroleum hydrocarbons and the usual solvents; in oils, both high and low viscosity.	Coal-tar hydrocarbons and lacquer solvents; medium and low viscosity oils.

NOTE: S&W Arochem 337 is insoluble in ethyl alcohol. S&W 338 is insoluble in petroleum hydrocarbons, although solutions will tolerate a high proportion of these solvents; it is completely insoluble in ethyl alcohol.

Novel Use of Solvents Improves Moulded Plastics

Color, transparency, and strength of certain transparent moulded plastics, formerly was impaired by small quantities of unreacted olefin and catalyst residue remaining after the reaction was completed. These impurities caused opacity after moulding and adversely affected the mechanical strength of the moulded article.

According to the claims appearing in a recent patent on olefin-sulphur-dioxide resins, a new process entirely eliminates these detrimental features. Crude olefin-sulphur-dioxide resin, in finely divided form, is treated with a blast of air or inert gas carrying vapors of a resin solvent such as acetone. The solvent penetrates the fine resin particles, and softens them.

Best moulding results are obtained when minute traces of the vaporized solvent are allowed to remain in the resin until it is moulded. According to the inventor, articles moulded from the new resin possess greater transparency and strength, and due to absence of unreacted ingredients, do not undergo a secondary reaction which changes their color after moulding.

Two New Phenolics

(Continued from preceding page)

hard, tough films with maximum "hold-out" and gloss.

In the production of varnishes and enamels, S&W Arochem 338 usually requires special cooking when used with most pre-bodied oils, and is too rapid in its bodying action for use with oils like tung, without modification. Thus Arochem 337 is generally preferred for these products.

U.S.I. will be glad to send samples and further data on both resins to anyone interested.

Tonnage Production of Indalone Involves Novel Claisen Reaction

(Continued from preceding page)

reaction vessel together with sufficient benzene to assure complete solution of the sodium salt of Indalone at the end of the reaction. After thorough mixing, a carefully measured quantity of sodium butoxide (in butyl alcohol solution) is added. The reaction vessel is equipped with heat exchangers for removal of heat generated by the reaction.

Neutralization

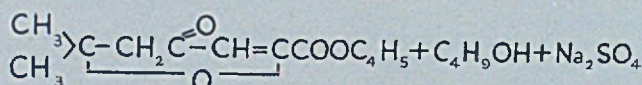
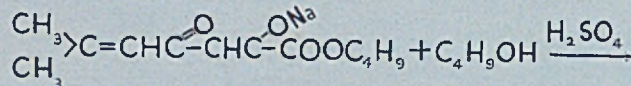
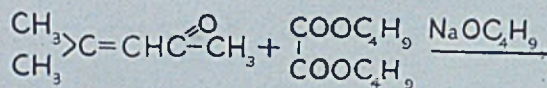
After the reaction has been completed (12-24 hours) the alkaline crude is neutralized with diluted sulphuric acid. This operation is critical and in the past has always been done on a batch basis. However, it is now being done with complete success using a continuous method developed at U.S.I.'s Baltimore plant.

Distillation and Recovery

The neutralized crude obtained from the above step is stripped of volatile solvents—benzene, butanol, and water—by a series of continuous vacuum distillation columns. The benzol and butanol are subsequently refined and returned to succeeding condensations. The stripped crude contains Indalone and a small amount of tars. The Indalone is recovered from the stripped crude by a continuous flash-distillation process, operating at 2 to 4mm. Hg, absolute pressure.

Approximately 90% of the Indalone is recovered in the flash-distillation process. The remaining 10% is present in the tar residue withdrawn continuously from the process. The Indalone present in these tars is subsequently recovered by a batch, low-pressure distillation process.

SYNTHESIS OF INDALONE



TECHNICAL DEVELOPMENTS

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

A water-resistant resin adhesive has been developed for use in mounting and over-coating paper and for other industrial applications where moisture resistance is needed. It is claimed that this new, clear adhesive will withstand a 48 hour immersion test, and that its long wet-life prevents paper wrinkling, makes registration easy. (No. 859)

U S I

Flame-proofed felt for vibration damping and insulation in high-temperature areas has been announced. It is claimed that this chemically treated felt can be exposed to the direct flame of a bunsen burner without either combustion or after glow. (No. 860)

U S I

A new rust-removing compound is claimed to facilitate pre-painting preparation of metal surfaces. The crystals of the preparation are said to become part of the metal and to be paint absorbent. (No. 861)

U S I

A tackifier for synthetic rubber, which is said to have added use as an extender, has been announced. The new product is claimed to be soluble in aromatic hydrocarbons, vegetable and mineral oils, and synthetic rubber. Some tack remains after vulcanizing. (No. 862)

U S I

Rubber heel marks and dirt may be removed from wood, cement and linoleum floors by a new cleaner, according to its manufacturer. (No. 863)

U S I

New flux for brazing preparation of cast iron, has been developed. It is said to produce a uniformly successful tinning prior to brazing. (No. 864)

U S I

A non-slip liquid wax, which, according to the manufacturer, requires no buffing and which may be applied with cloth, mop or spray equipment, has just been put on the market. (No. 865)

U S I

Two new protective creams have been designed to protect worker's hands. One is water soluble for dry work; the other is for protection where water and mild chemical solutions are present. (No. 866)

U S I

New dye for vinylite plastics, designed for dip application is available in yellow, orange, rose and green. A dip of 5 seconds is claimed to give a pastel shade, while a 60 second dip gives deep tones. (No. 867)

U S I

A new plastic resin adhesive, said to be colorless, of low viscosity and water-soluble, has been placed on the market. It is intended to be used with a co-agent in laminating and sizing textile fabrics and paper. (No. 868)

U.S.I. INDUSTRIAL CHEMICALS, INC.

60 EAST 42ND ST., NEW YORK 17, N. Y.



BRANCHES IN ALL PRINCIPAL CITIES

ALCOHOLS

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

Ethanol (Ethyl Alcohol)

Specially Denatured—all regular and anhydrous formulas
Completely Denatured—all regular and anhydrous formulas
Pure—190 proof, C.P. 96%, Absolute
*Super Pyro Anti-freeze
*Solox Proprietary Solvent

*ANSOLS

Ansol M

ACETIC ESTERS

Amyl Acetate
Butyl Acetate
Ethyl Acetate

OXALIC ESTERS

Dibutyl Oxalate
Diethyl Oxalate

PHTHALIC ESTERS

Diamyl Phthalate
Dibutyl Phthalate
Diethyl Phthalate

OTHER ESTERS

*Diatol
Diethyl Carbonate

INTERMEDIATES

Acetoacetanilide
Acetoacet-ortho-anis'dide
Acetoacet-ortho-chloranilide
Acetoacet-ortho-toluidide
Acetoacet-para-chloranilide
Ethyl Acetoacetate
Ethyl Benzoylacetate
Ethyl Sodium Oxalacetate

ETHERS

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

RESINS

ACETONE

Chemically Pure

FEED CONCENTRATES

*Curbay B-G
*Curbay Special Liquid
*Vacatone 40

OTHER PRODUCTS

Collodions
Ethylene
Ethylene Glycol
*Indalone
Nitrocellulose Solutions
Urethan



Citation for the veterans of a never-ending Battle

Paper-makers depend on Jenkins Valves where pipelines must do extra duty...

When America entered the war, the paper industry began a battle which is still in progress. It is the fight to supply the endless needs of the armed forces and war industry for paper products of every description.

The Oxford Paper Company, one of the industry's largest producers, has worked its plant far beyond its normal peacetime capacity in the past 2½ years, turning out a *thousand miles of paper a day*.

Even in normal times, there is no tougher spot for valves than in paper mill pipelines, because of corrosion, clogging, etc. With the pipelines doing *extra* duty, only valves of exceptional endurance could set such a gratifying record of trouble-free performance as that reported for the Jenkins Valves in the Oxford Mills in Rumford, Maine.

Such performance is no accident. It is the direct result of the better design, better materials, better workmanship of Jenkins Valves.



OXFORD PAPER COMPANY
GENERAL OFFICES
230 PARK AVENUE

NEW YORK 17, N.Y.
July 31, 1944

Jenkins Bros.
80 White Street
New York, N.Y.

Gentlemen:

Attn: F. C. Ernst, Chief Engineer

The information you sent on the new Malleable Iron Valves is just what we needed, and our engineers are considering their use for the special service we described to you.

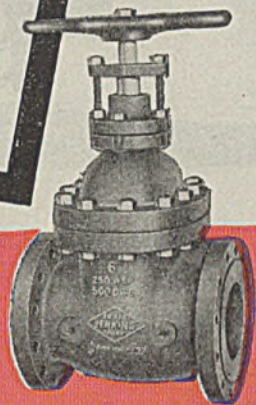
For several years, now, we have been installing Jenkins Valves in the toughest spots on our process lines, and if we ever needed any justification of our choice, we have certainly had it since the war greatly increased our operating schedules.

Meeting the demand for map paper, packaging paper, and other special stocks for the armed forces, and for the endless varieties needed by war plants, has kept us going full tilt. There hasn't been any time to nurse along "sick" valves. Fortunately, in spite of the punishment they've taken, our Jenkins Valves haven't needed any more attention than normal maintenance, and that was often pretty sketchy.

All told, we think you've got a product that has done a tough wartime job with extraordinary merit.

Very truly yours,

Everett Shea



Let this war record — only one of many "citations" that are coming in from leading producers in many industries — guide you in specifying valves for reconversion and renovation in your plant. You'll find it will "cost least in the long run" to specify Jenkins Valves — for every service.

Jenkins Bros., 80 White Street, New York 13; Bridgeport, Conn.; Atlanta; Boston; Philadelphia; Chicago. Jenkins Bros. Ltd., Montreal; London.



Jenkins Bros.

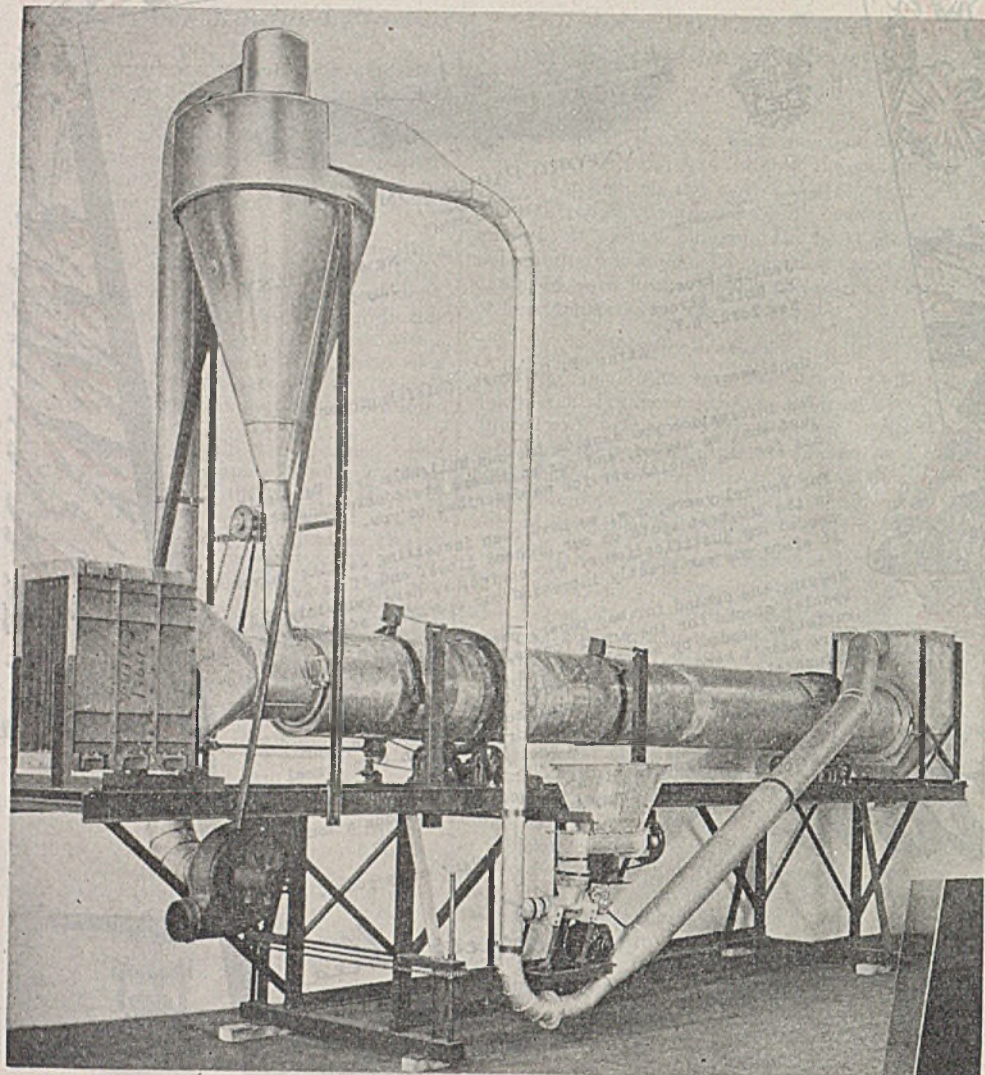
JENKINS VALVES

SINCE 1864

For every Industrial, Engineering, Marine and Commercial Service . . . In Bronze, Iron, Cast Steel and Corrosion-resisting Alloys . . . 25 to 600 lbs. pressure.

Sold Through Reliable Industrial Distributors Everywhere.

The Hersey INTERMEDIATE FEED SYSTEM



for
DRYING

- Root Starches
- Vegetable and Fruit Waste
- Sweet Potato Meal
- Bagasse
and
Similar materials

This system was designed for the efficient drying of materials having—

1. A relatively high initial moisture content
2. A wide variance in particle size
3. A moderate temperature limit

The system comprises a direct or indirect-fired concurrent dryer with a cyclone type separator, and provision is made for feeding the product to be dried into a conduit carrying the gases from the discharge end of the dryer to the cyclone.

Two primary advantages in this system of drying

are the substantially complete dust recovery due to the pick-up by the wet material of fine particles carried by the exhaust gases.

The second advantage is that the system combines the humidity and temperature balance efficiency of the common counter-current flow type of dryer with the particular advantage of the concurrent system.

Hersey Engineers have specialized in the design and construction of atmospheric drying systems for over 60 years. More than 1100 Hersey Dryers are now in use.

Write for catalog and information sheet.

HERSEY MANUFACTURING COMPANY — Drying Machinery Division
E. and 2nd Streets, SOUTH BOSTON, MASS.



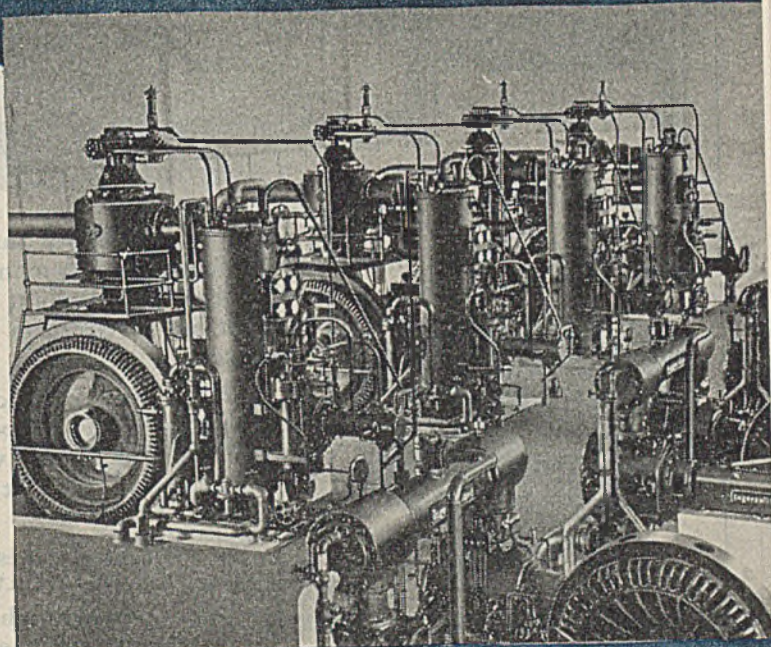
AIR POWER for SEA POWER

Inside a modern torpedo, compressed air supplies the oxygen needed to burn alcohol in a tiny boiler which generates the steam for running the torpedo's turbine and propellers. It also operates the gyroscope, and controls the torpedo.

In order to store a lot of air within a small space, this air is compressed to about 3000 pounds per sq inch pressure. For charging torpedoes on board Navy fighting ships and at Army and Navy airfields, Ingersoll-Rand has built hundreds of high-pressure heavy-duty compressors of small, compact design. Some of these are small enough to fit into the baggage compartment of your car.

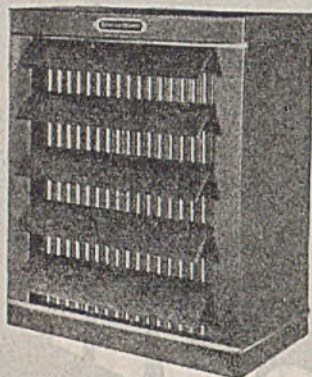
Compressed-air power is also essential to the manufacture and testing of torpedoes. Shown here is a battery of Ingersoll-Rand air compressors consisting of four 400-horsepower, 4-stage units supplying 4000-pound air for testing, and four 2-stage machines furnishing 100-pound air power needed in the manufacturing process. Identical installations of these compressors are in two other torpedo plants.

Ingersoll-Rand has built air and gas compressors for pressures from vacuum to 15,000-pound per sq inch for all kinds of services. Call upon this experience when you need compressors.

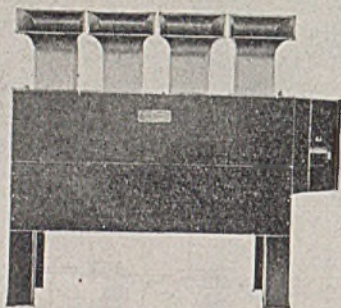


Ingersoll-Rand

11 BROADWAY, NEW YORK 4, N. Y.



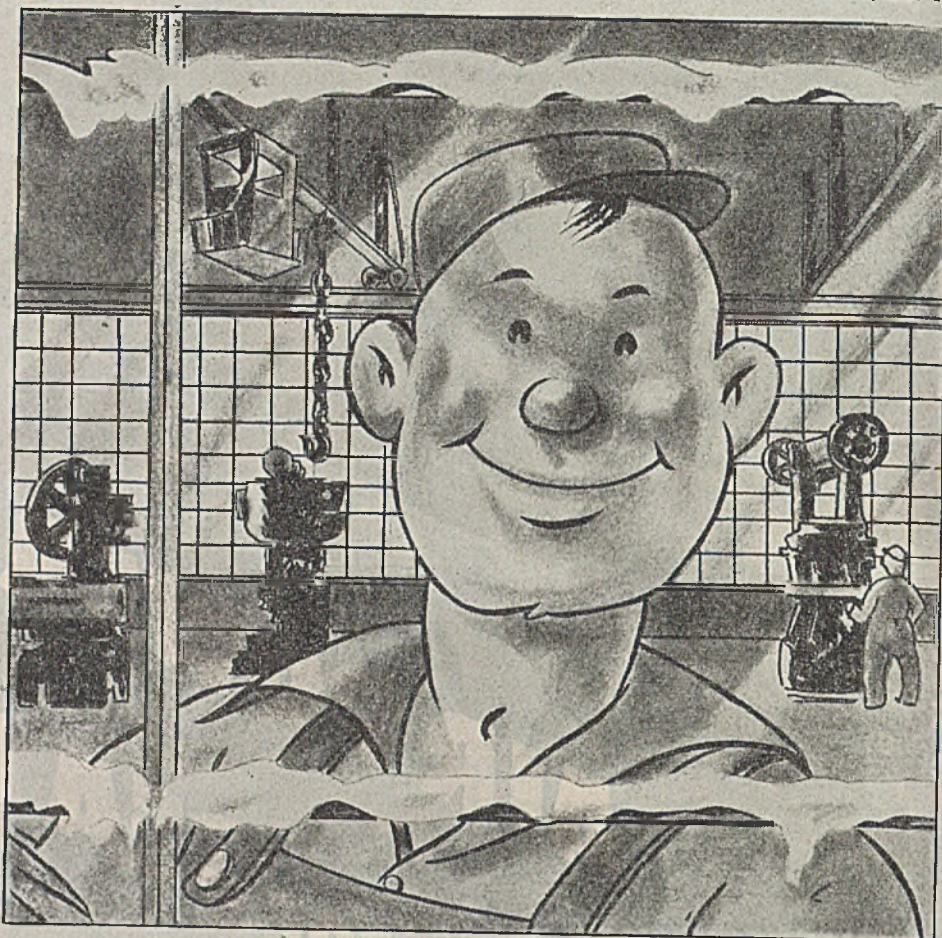
American Blower Venturafin Unit Heater (Horizontal Type).



American Blower Sirocco Unit Heater (Blower Type).



American Blower Vertical Type Unit Heater.



June in January

ALL WINTER LONG!

Yes, you can enjoy June in January and in every other month when heating is required, right in your own plant with American Blower Unit Heaters.

No hot spots or cold corners, but steady, healthful temperatures with heated air forced into working areas—where you want it—when you need it.

There are three types of American Blower Unit Heaters—Vertical Units for heating large, high-ceilinged industrial plants and other areas where heated air must be forced over wide spaces—Horizontal Type for wall or ceiling mountings in factories, plant

offices, garages, warehouses, etc., where it is advisable to force heated air over wide areas at desired levels—and the Blower Type of Sirocco Unit Heater for ceiling applications or floor installations in large, hard-to-heat industrial plants, airplane hangars and shops.

Best of all, you can buy these units now with an order carrying a Priority Rating of AA-5 or better, with a specified delivery date.

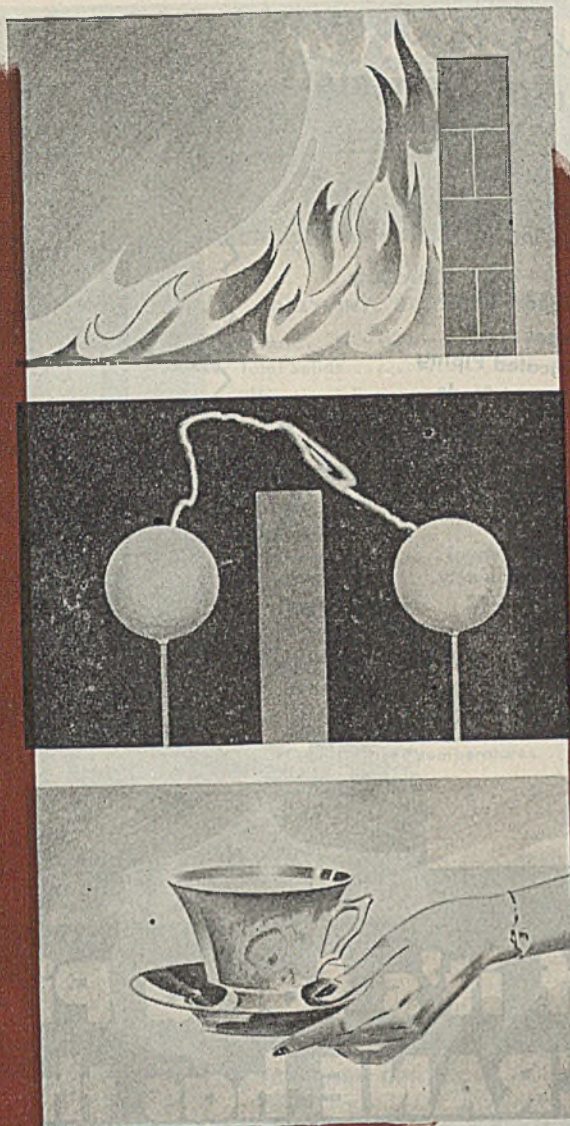
American Blower Unit Heaters save you up to 20% or more in fuel consumption, and provide ideal working conditions.

AMERICAN BLOWER

AMERICAN BLOWER CORPORATION, DETROIT, MICHIGAN
CANADIAN SIROCCO COMPANY, LTD., WINDSOR, ONTARIO

Division of AMERICAN RADIATOR & Standard Sanitary CORPORATION

For
**thermal,
 electrical
 or social
 exposure**



Many ceramic products for the "quality" market are quite likely to be formulated around Alorco Aluminas. For example—

Firebricks for high-duty service have these aluminas as their base. The bricks are strong and tough, and withstand terrific temperatures and exposure to flame. Also Alorco Aluminas supply the excellent electrical insulating properties and thermal shock resistance needed by airplane engine spark plug "porcelains".

Now into the picture steps high-grade table ware as a potential user of Alorco Aluminas. Thereby establishing these aluminas in a social spot, adding this distinction to the enviable industrial position they already hold.

Where Alorco Aluminas are employed in the manufacture of ceramic products, faithful reproduction with accuracy is possible. Close dimensional tolerances simplify and speed the assembly of products in which the parts are used.

Alorco's ability to vary the properties of these aluminas to suit your needs should enable you to employ them to advantage in many ways. Tell us what you want an alumina to accomplish, and we'll supply the alumina for your use or several aluminas for trial. Write ALUMINUM COMPANY OF AMERICA (Sales Agent for ALUMINUM ORE COMPANY), 1911 Gulf Building, Pittsburgh 19, Penna.

ALUMINUM ORE COMPANY

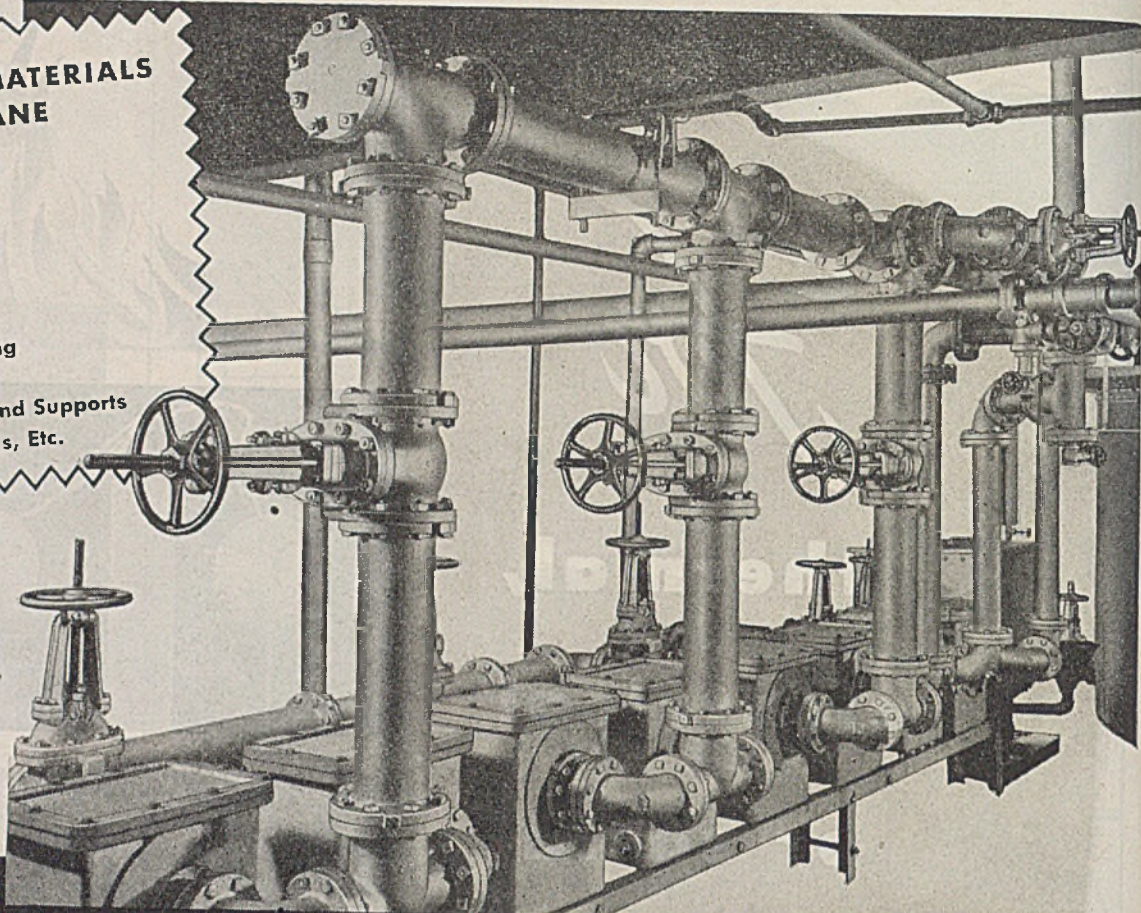


Aluminum and Fluorine Compounds

ALL PIPING MATERIALS BY CRANE

Gate Valves
Globe Valves
Check Valves
Pipe
Flanged Fittings
Flanges
Fabricated Piping
Bolts and Studs
Pipe Hangers and Supports
Screwed Fittings, Etc.

*Installation in
Chemical Processing
Plant.*

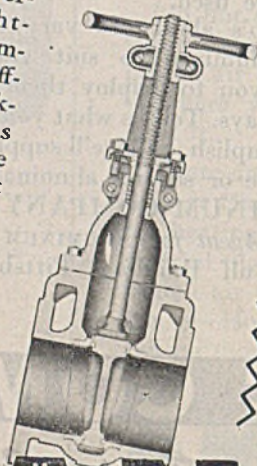


If it's for a Piping System... CRANE has the Part you need

ONE STANDARD OF QUALITY

Insure equally dependable quality in every part of piping systems by using Crane materials throughout. For example, in Crane Iron Body Wedge Gate Valves: Strong body sections resist severest strains. Straight-through ports give streamline flow. A deeper stuffing box lengthens packing life. Extra long guides keep disc travel true, while finest design throughout assures smooth and positive operation.

**STANDARD
IRON BODY
WEDGE GATE
VALVES**



ONE SOURCE OF SUPPLY

From a single fitting to a complete system—Crane is your *one source of supply* for all piping equipment needs. For power or processing lines—high or low pressure—Crane offers you the world's greatest selection of valves, fittings, pipe, fabricated assemblies, and all accessory parts for any installation. You need merely name the service.

ONE RESPONSIBILITY FOR ALL MATERIALS

Help yourself to better piping installations by starting with materials whose quality and craftsmanship are backed by *single responsibility*. Ordering, maintenance work, keeping of parts stocks—all such operations are simplified by Crane complete materials service. And you're sure of getting all the benefits of Crane Co.'s 89 years' experience and leadership in the piping equipment field.

Crane Co., General Offices: 836 South Michigan Avenue, Chicago 5, Illinois.

Branches and Wholesalers Serving All Industrial Areas

CRANE

**VALVES • FITTINGS • PIPE
PLUMBING • HEATING • PUMPS**

DU PONT PRODUCTS YOU SHOULD INVESTIGATE

POLYVINYL ACETATE
EMULSIONS

These emulsions are effective adhesives for such materials as wood, paper and other cellulose products, cloth, leather, cork, metals, glass and ceramics. Can be used as binders for paper pulp, sawdust, scrap leather, sand, clay, and other organic and inorganic molding or modeling masses. Suitable as wet-bond or heat-sealing adhesives. Today they serve as superior replacements for rubber latex and other essential materials, particularly in the adhesives field. Colorless, durable films, useful as heat-sealing tapes, can be made by evaporation of water.

PROPERTIES

Polyvinyl Acetate Emulsions are available in two grades. Both have the same resin content and viscosity but differ in the softening point (heat sealing temp.) of the contained resin.

The emulsion obviates use of organic solvents and special equipment. It can be diluted as desired by adding water; readily accepts plasticizers, pigments, and other materials commonly used in adhesive, binder and coating formulations.

COMPATIBILITY—Solutions of starch, dextrans, glue, casein and emulsions of asphalt, paraffin wax, rubber, natural and synthetic resins may be added to these Polyvinyl Acetate Emulsions.

Polyvinyl Acetate Emulsions have other properties of interest to paper makers and converters, and to manufacturers of textile sizes, water paints, leather finishes and dressings, and other aqueous preparations requiring an adhesive constituent or binder.

USES AND APPLICATIONS

ADHESIVES—Polyvinyl Acetate Emulsions are used commercially as adhesives for joining textiles, paper, cork, leather, metal, wood, ceramics, etc. Use of heat is not always necessary, but in many instances application of heat during or after drying will increase bond strength. Plasticizers may be used to modify both the tack or initial "grip" of wet or

partially dried emulsion coatings. Sealing temperatures and flexibility of the bonding films can also be modified by plasticizers.

Mixtures of Polyvinyl Acetate Emulsions and starch solutions are superior to starch alone in water resistance and strength of final bond.

Adhesives for use in fabricating shoes and other leather products and in food packaging are prepared by simply adding to the diluted emulsions the amount and type of plasticizer necessary to give desired tack and flexibility. In some cases emulsions of other resins or rubber latex are added to meet special requirements.

BINDERS—Paper pulp, wood flour, shredded asbestos, ground cork, textile fibers, sisal fiber, hemp and similar materials may be mixed with diluted emulsion and the resulting plastic mass subjected to heat and pressure to produce sheets, containers, casting molds and cores, repro-

CHARACTERISTICS
POLYVINYL ACETATE EMULSIONS

Form Free flowing, milky white liquids
Total Solids 55% minimum
pH 4-6
Color Milk white
Unpolymerized Vinyl Acetate Less than 2%
Weight per gallon Approx. 9 lbs.

FILMS AND COATINGS

Physical Properties

Form Tough, resinous solid
Color Water-white to cloudy
Density 1.19 at 20° C.
Specific volume 23.2 cu. in./lb.

Heat Sealing Temperatures

RH-460A 125° C. (approx.)
RH-460 100° C. (approx.)
Note: Plasticizers may be used to modify these temperatures.

Chemical Properties

Stability to light Excellent
Burning rate Slow
Effect of reagents Hydrolyzed by strong acid or alkali

ducing impressions, models, etc., of remarkable strength and durability.

FILMS AND COATINGS—Adherent films of Polyvinyl Acetate may be deposited on wood, cloth, paper, metals, ceramic ware, etc., by coating with emulsion, followed by water evaporation. They are stable to light, oxidation and aging; unaffected by aliphatic hydrocarbons, vegetable oils or animal fats.

★ ★ ★

These emulsions offer a means of extending the established usefulness of Polyvinyl Acetate. Limited quantities are available for research and experimentation. Further details may be obtained from: Electrochemicals Department, E. I. du Pont de Nemours & Co. (Inc.), Wilmington 98, Del.

EVERY BOND BRINGS VICTORY NEARER — BUY ANOTHER TODAY!

DU PONT
ELECTROCHEMICALS



REG. U. S. PAT. OFF.

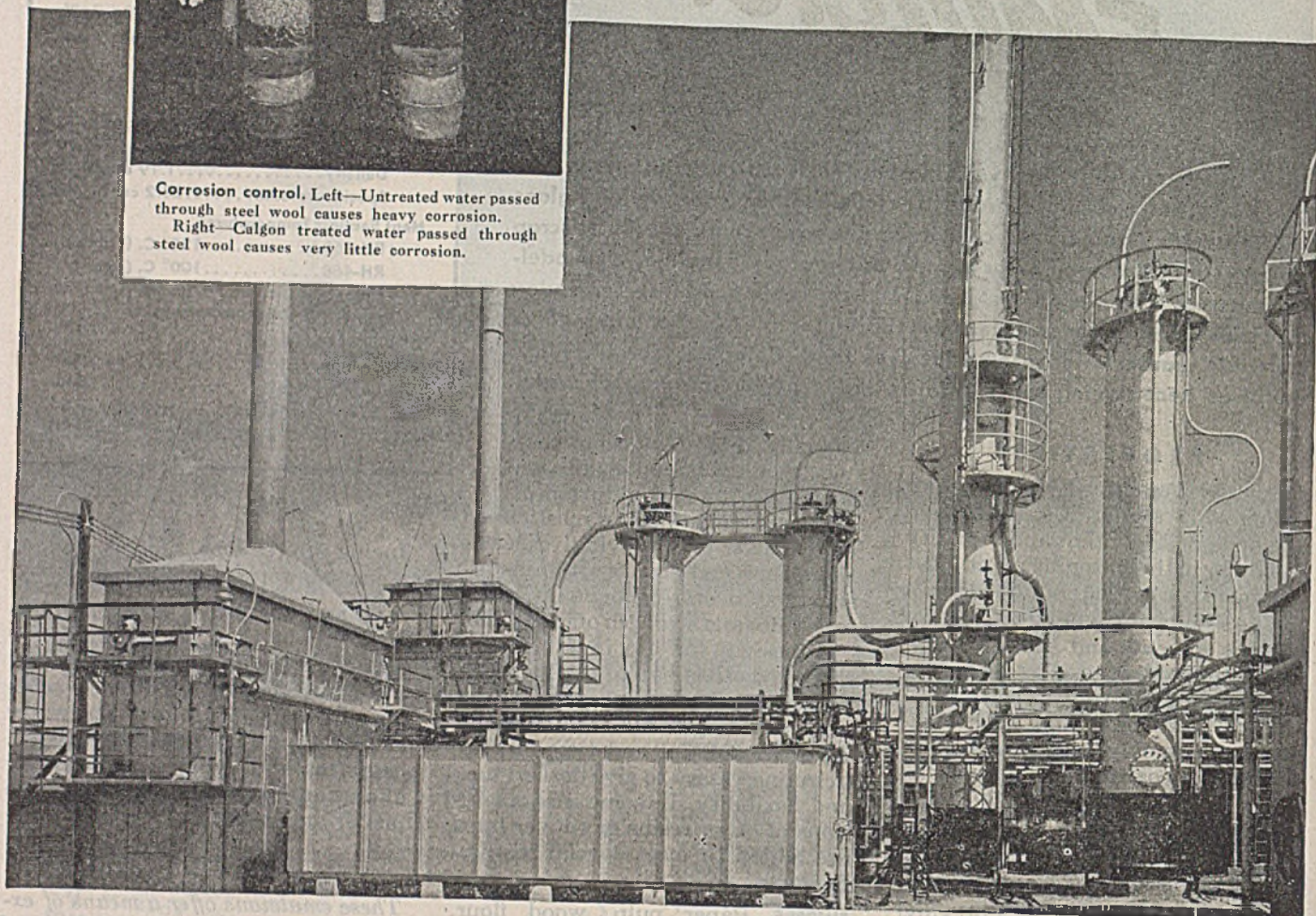
BETTER THINGS FOR BETTER LIVING...THROUGH CHEMISTRY

Quick relief for plants suffering from

"Hardening of the arteries"



Corrosion control. Left—Untreated water passed through steel wool causes heavy corrosion. Right—Calgon treated water passed through steel wool causes very little corrosion.



MOST plants are troubled with either scale or corrosion in pipe lines and cooling water systems. Scale cuts down the capacity of pipe lines and causes shut-downs for cleaning. Corrosion destroys the piping and equipment itself.

With Calgon* water treatment you can stop scale completely. Corrosion

can be controlled to such an extent that it is no longer a serious problem. The treatment can be started at once and begins to take effect in a few days' time. New scale does not form, old scale loosens and can be readily removed. Corrosion is controlled by the formation of a thin film over metal and metal oxides, at

pH values of 5.0 and higher, which reduces the attack of oxygen.

You can quickly prove that Calgon treatment works. We'll send you instructions for setting up an experiment in your own laboratory. Only 1 to 5 ppm. Calgon stops scale . . . 2 to 10 ppm. controls corrosion. Write for complete information.

*Calgon is the registered trade-mark of Calgon, Inc., for its glassy sodium phosphate products.

**HAGAN
HALL
BUROMIN
CALGON**

calgon, inc.

A SUBSIDIARY OF
HAGAN CORPORATION

HAGAN BUILDING
PITTSBURGH 30, PA.

ALOYCO VALVES

STAINLESS STEEL

**FOR A LONG LIFE
FREE FROM SHUTDOWNS!**

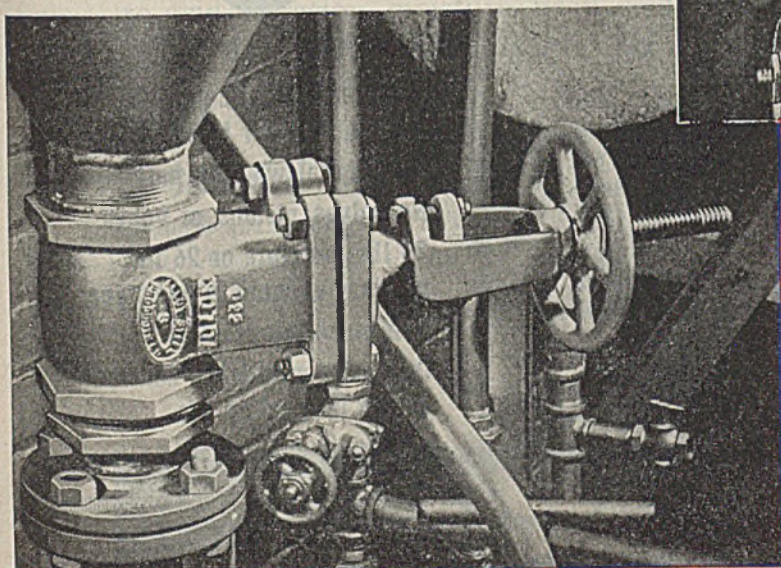
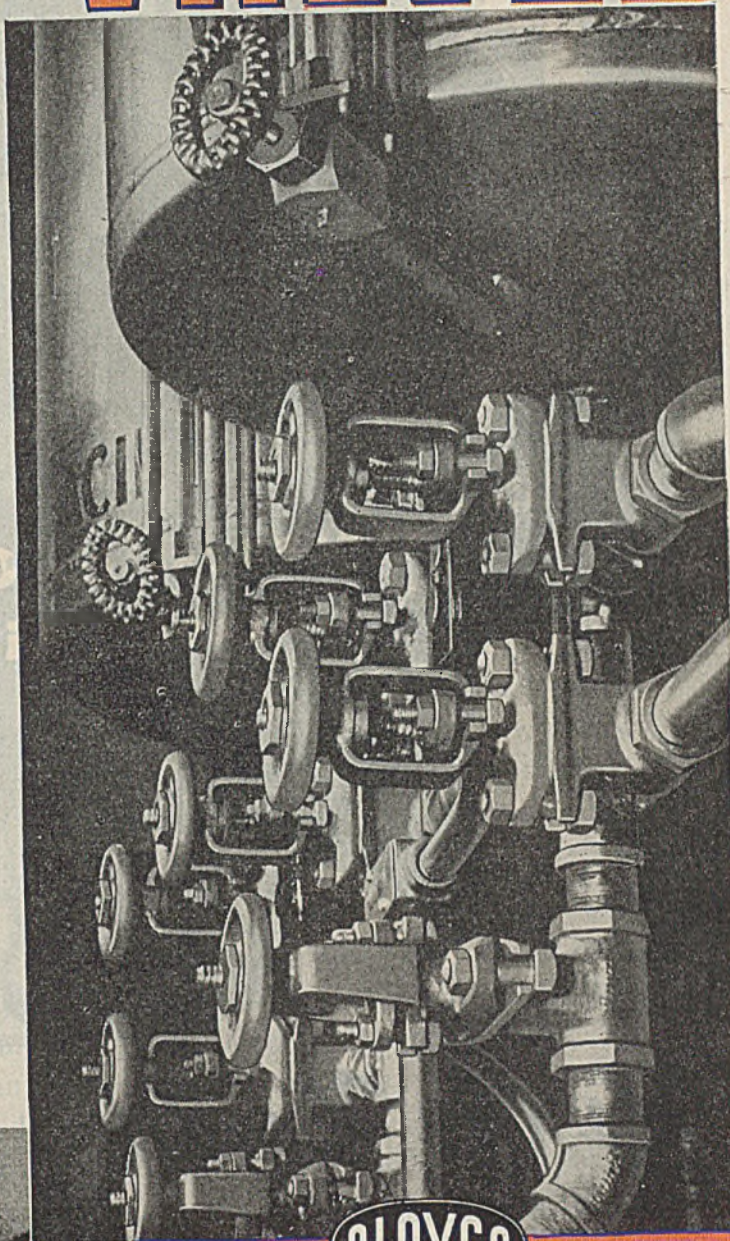
Pipe line shutdowns in process industries can be very costly. That is why important producers of high octane gasoline, synthetic rubber, explosives, pharmaceuticals and other precious materials use Alloyco Stainless Steel Valves.

The exceptional durability that has resulted in this customer preference springs from the sound design, correct analysis, experienced foundry practice, careful heat treatment, accurate machining and rigid inspection that are standard procedure at Alloy Steel Products Company. Only a company that specializes in the manufacture of stainless steel valves can afford these safeguards.

Alloyco Stainless Steel Valves and Fittings are available now for new installations on high priorities and for maintenance and repairs under M. R. O. regulations.

ALOYCO VALVES GUARD CRITICAL LINES AT CIBA

Precious fluids flow through the many Alloyco Valves used in the Summit, New Jersey, plant of Ciba Pharmaceutical Products, Inc. It is essential that these valves be of the highest quality and that they can be disassembled for cleaning in one minute. Not only must they remain chemically inert in the presence of all kinds of organic mixtures and acids, but they must function with absolute reliability when extremely costly substances are being handled.

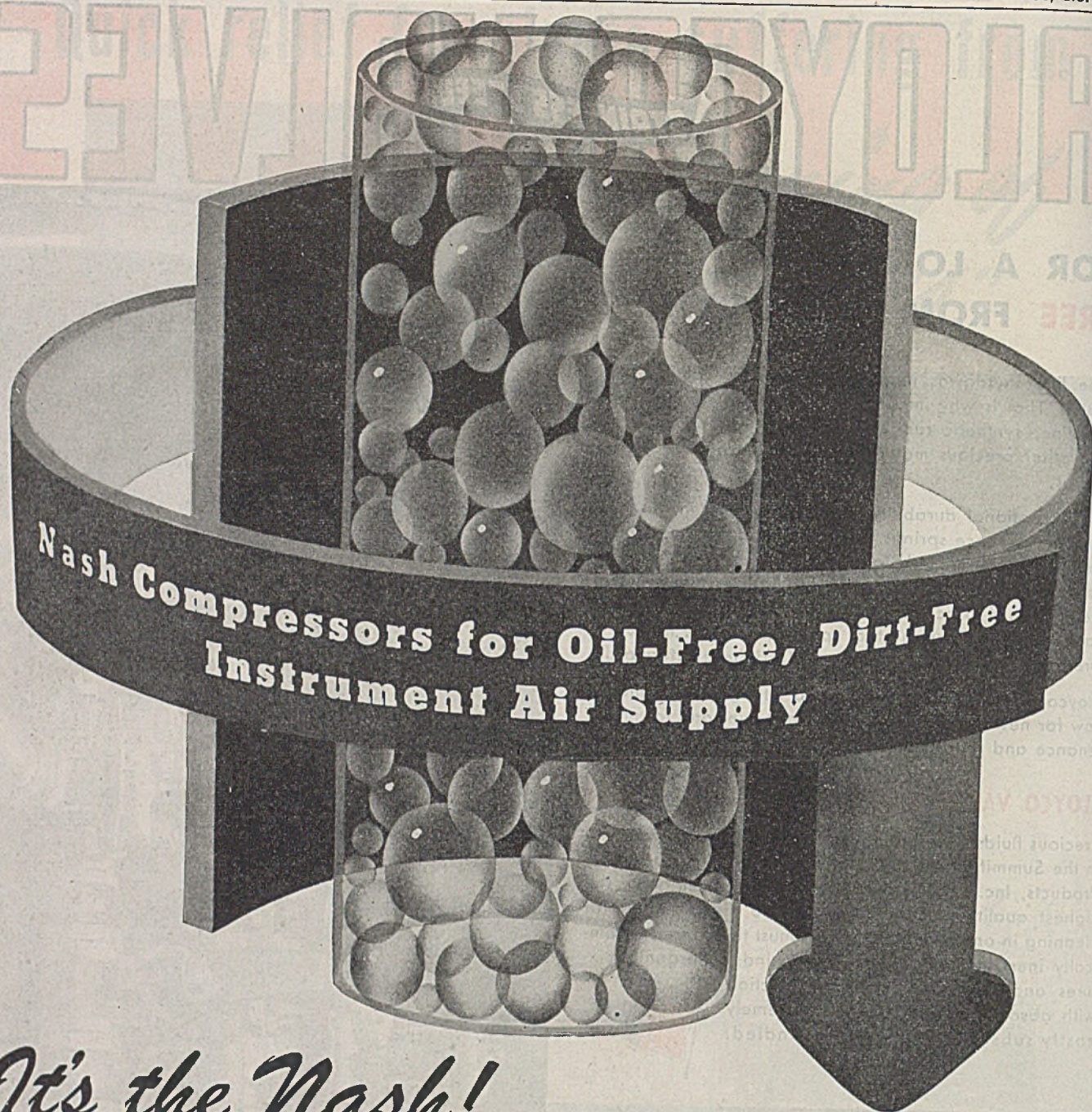


ALOYCO

Stainless Steel
VALVES and FITTINGS

GATE VALVES • GLOBE VALVES
Y VALVES • CHECK VALVES
LEVER THROTTLE GATE VALVES
TANK VALVES • SCREWED FITTINGS
FLANGED FITTINGS
GAUGE GLASS FITTINGS

Alloy Steel Products Company, Inc., 1310 West Elizabeth Avenue, Linden, N. J.



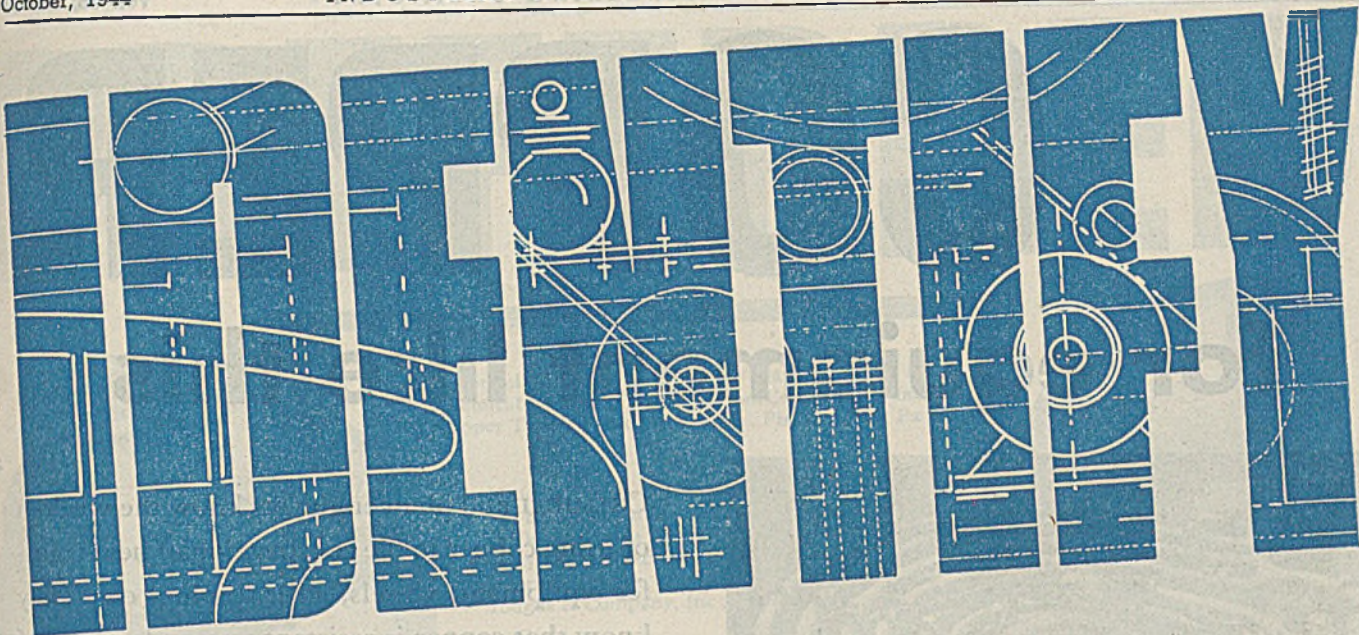
It's the Nash!

Because Nash Compressors have no internal lubrication and because delivered air is thoroughly washed within the pump, the Nash delivers only clean air, free from dust, heat, or oil. Therefore, instrument air supplied by a Nash assures immediate instrument response and eliminates all troubles resulting from fouled instrument lines, gummed orifices, and rotting instrument diaphragms. Also avoided are trouble and expense of the usual oil filters, dust filters, and after coolers, as none are used. Nash means dependable, low cost instrument operation.

Nash Compressors produce 75 lbs. pressure in a single stage, capacities to 6 million cubic feet a day in a single structure. No valves, gears, pistons, sliding vanes, or other enemies of long life complicate a Nash. Original capacity is maintained throughout a long life. Investigate the Nash Compressor now.

No internal lubrication to contaminate air handled.
No internal wearing parts.
No valves, pistons, or vanes.
75 lbs. pressure or 26 in. mercury vacuum in one stage.
Non-pulsating pressure.
Original performance constant over a long pump life.
Low maintenance cost.

NASH ENGINEERING COMPANY
297 WILSON, SO. NORWALK, CONN.



Your Post-War Products with **MEYERCORD DECALS!**

A wide variety of successful war uses under gruelling combat and climatic conditions have even more firmly established Meyercord Decalcomania as the perfect material for post-war product identification and instructions.

Meyercord Decal nameplates, lubricating guides, wiring diagrams, instructions, dial faces, serial and patent numbers, etc., can now be made resistant to acid, abrasion, moisture, heat, cold, petroleum vibrations, fungus growth.

Meyercord Decals are washable, durable and easily applied with water or cement to any commercial surface at production line speed. They save time, cost, materials and weight.

Designs may be reproduced in any size or number of colors, and can be applied to flat, convex or concave surfaces...even *rubber* and *crinkled* finish. Investigate the amazing variety of uses for Meyercord Decals in every branch of your business. Address Dept. 90-10.

FREE DESIGNING SERVICE

Manufacturers and designers are invited to avail themselves of Meyercord's free designing and technical consultation service on postwar identification.

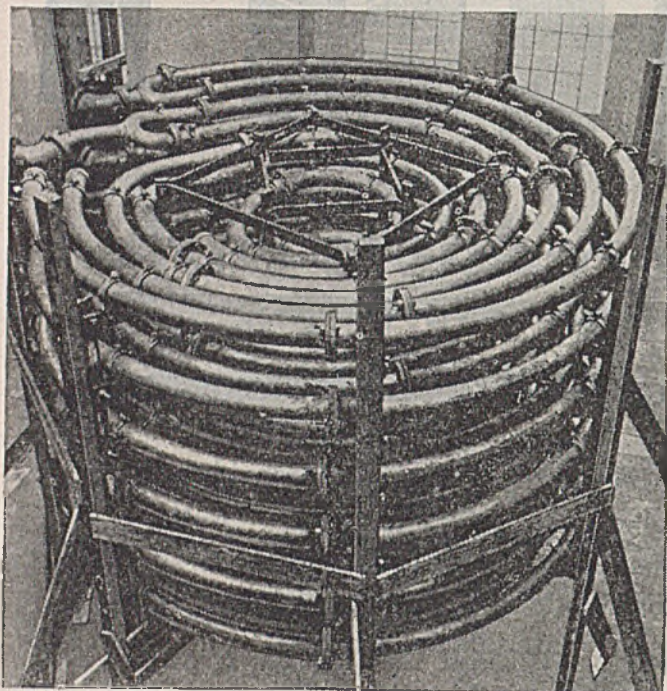
the **MEYERCORD Co.**
CHICAGO 44, ILLINOIS

BUY AN EXTRA BOND NOW!



COPPER

for equipment like this

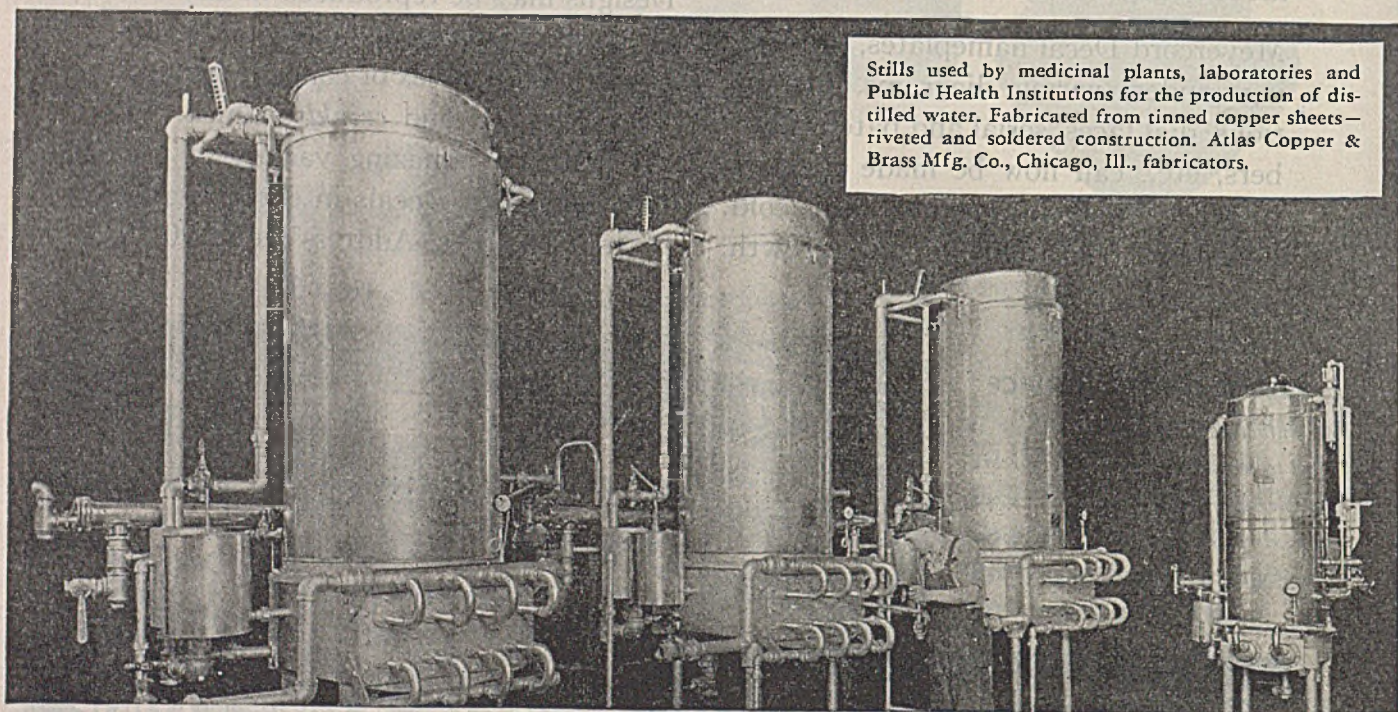


CHEMICAL and plant engineers know the wisdom of using copper in the construction of heat transfer equipment, vessels, stills, piping, etc. They know that copper is resistant to a wide range of normally corrosive solutions and compounds.

Copper is ductile and malleable far beyond the limits of ordinary metal. Many complex parts and fittings can be economically fabricated of copper, where other less workable metals would often require costly patterns and castings. Copper equipment requires little attention and will give maximum service life.

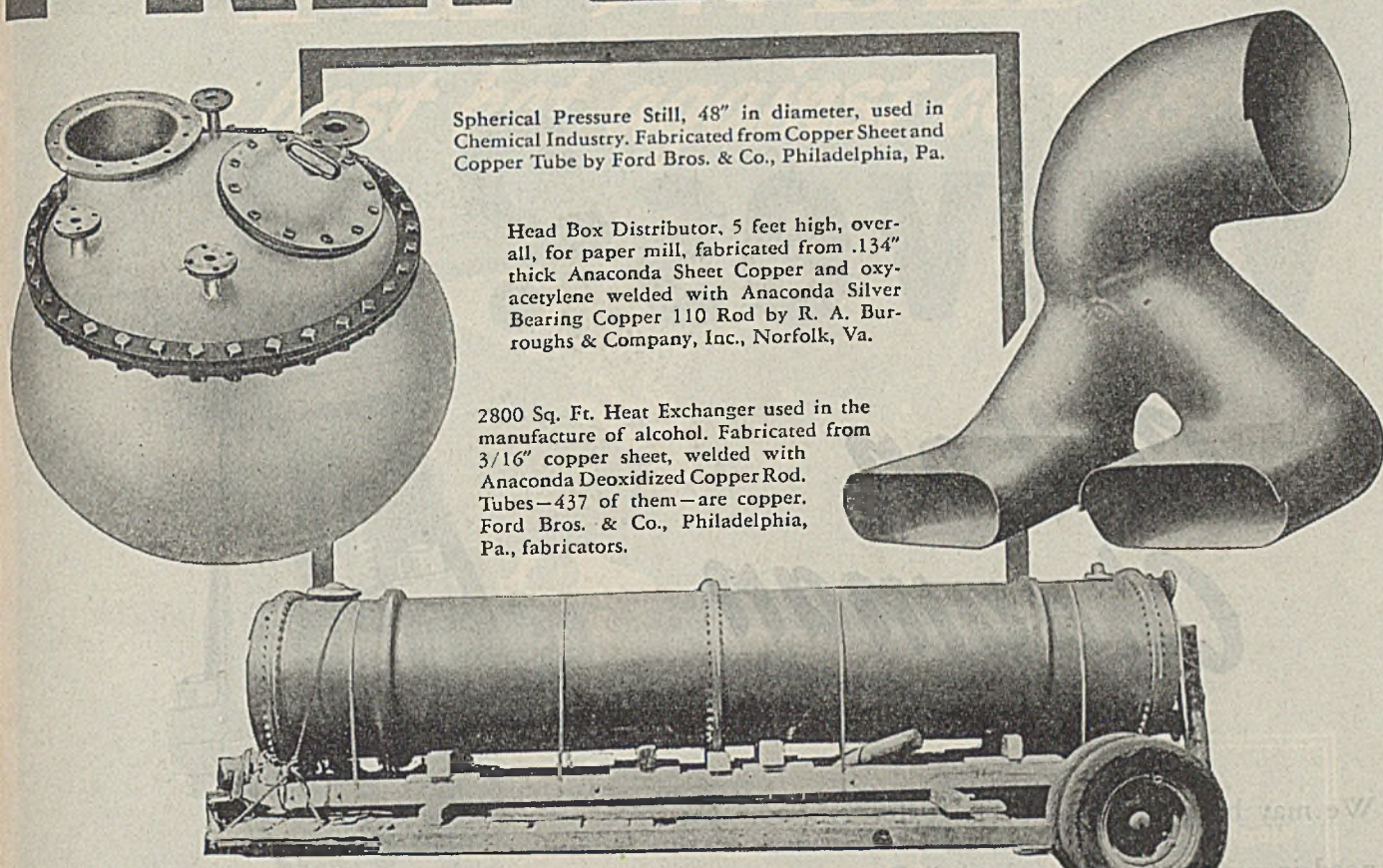
44123

Steam Pressure Coil used in Sugar Refining. Fabricated from 4" O.D. x No. 12 Stubs' Gage Copper Tube by Ford Bros. & Co., Philadelphia, Pa.



Stills used by medicinal plants, laboratories and Public Health Institutions for the production of distilled water. Fabricated from tinned copper sheets—riveted and soldered construction. Atlas Copper & Brass Mfg. Co., Chicago, Ill., fabricators.

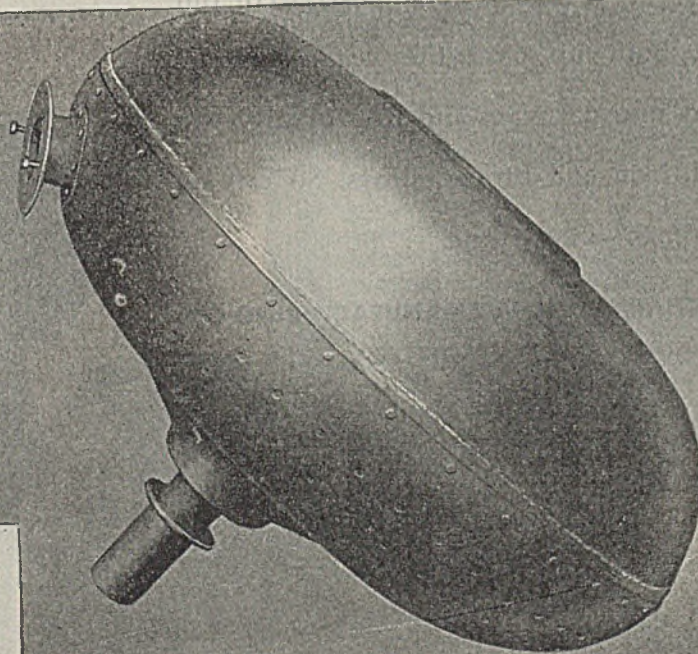
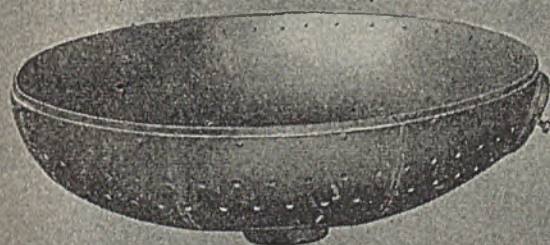
PREFERRED



Spherical Pressure Still, 48" in diameter, used in Chemical Industry. Fabricated from Copper Sheet and Copper Tube by Ford Bros. & Co., Philadelphia, Pa.

Head Box Distributor, 5 feet high, overall, for paper mill, fabricated from .134" thick Anaconda Sheet Copper and oxy-acetylene welded with Anaconda Silver Bearing Copper 110 Rod by R. A. Burroughs & Company, Inc., Norfolk, Va.

2800 Sq. Ft. Heat Exchanger used in the manufacture of alcohol. Fabricated from 3/16" copper sheet, welded with Anaconda Deoxidized Copper Rod. Tubes—437 of them—are copper. Ford Bros. & Co., Philadelphia, Pa., fabricators.



Powder Blenders formed and welded by Matt. Corcoran Company, Louisville, Ky. Vessel is 38" deep by 6 feet in diameter, fabricated from 3/16" thick copper, welded with Anaconda Phosphor Bronze 310 Welding Rod. Photo, courtesy of Air Reduction Sales Co.

THE AMERICAN BRASS COMPANY

Subsidiary of Anaconda Copper Mining Company

General Offices: Waterbury 88, Connecticut

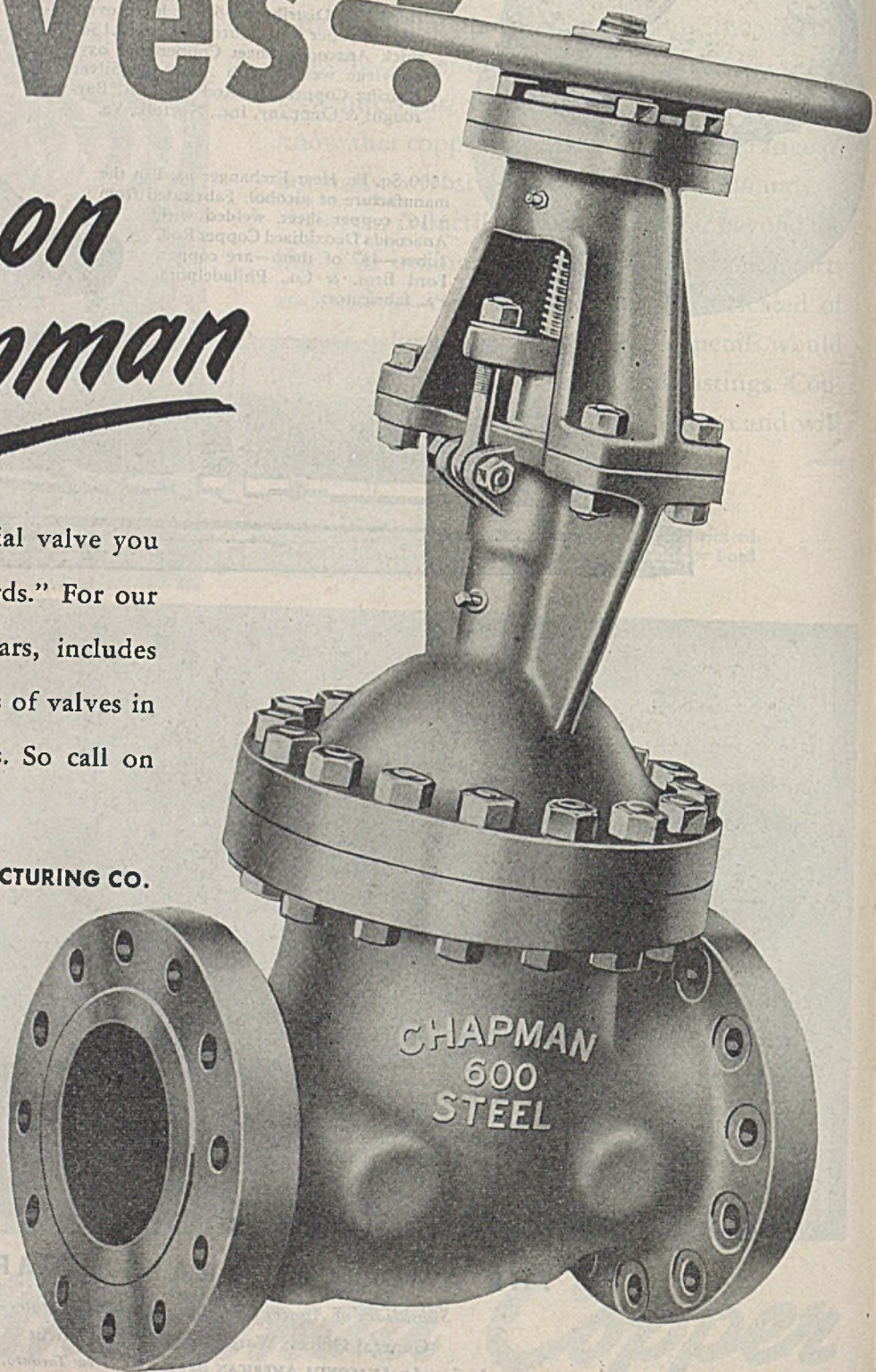
In Canada: ANACONDA AMERICAN BRASS LTD., New Toronto, Ont.

Need Special Valves?

*Call on
Chapman*

We may have just the special valve you need in our line of "Standards." For our line, built up over the years, includes many unusual types and sizes of valves in steel, iron and bronze alloys. So call on Chapman — next time.

THE CHAPMAN VALVE MANUFACTURING CO.
INDIAN ORCHARD, MASSACHUSETTS



PLIOWELD

your best bet against corrosion



Goodyear experts applying Plioweld lining to large pickling tank.

IN these days when all chemical equipment is working overtime — and spares are hard to get — you need permanent, foolproof protection against corrosion. That's the best reason for specifying Goodyear's new Plioweld synthetic rubber lining — it's longer lasting, requires minimum maintenance.

Plioweld lining is specially compounded by Goodyear from highest-quality, acid-resisting synthetic rubber and is comparable to natural rubber in its protective features.

It bonds permanently to all kinds of metal by an exclusive Goodyear process. It does not split or loosen from severe external impacts or vibration, and is not affected by temperature changes. It is not subject to chemical attack and will not contaminate materials in process.

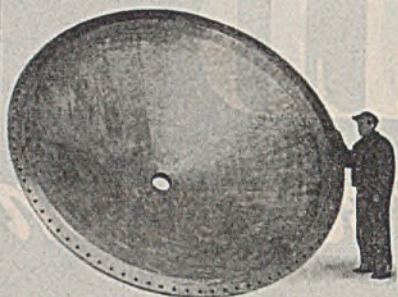
Beyond this, each Plioweld installation is individually compounded to provide maximum protection for the type of chemical handled — to insure best service. To get full particulars consult the G.T.M. — Goodyear Technical Man — or phone the nearest Goodyear Industrial Rubber Products Distributor.

7 REASONS why you should investigate PLIOWELD

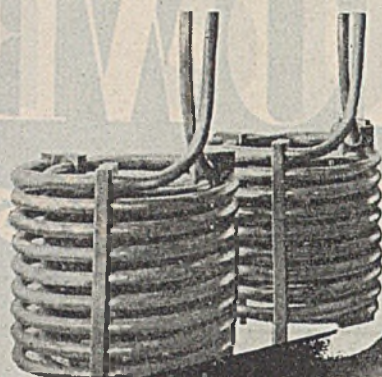
1. Effectively seals in corrosives that cannot be handled in metal.
2. Bonds permanently to metal surfaces by an exclusive Goodyear process.
3. Does not split or loosen with vibration or severe external impacts.
4. Does not crack or buckle under alternate wetting and drying, or temperature changes.
5. Surface will not disintegrate or slough off.
6. Protects chemicals from discoloration, iron "pick-up" and other contaminations.
7. Each installation specially formulated to provide maximum protection against chemical used.



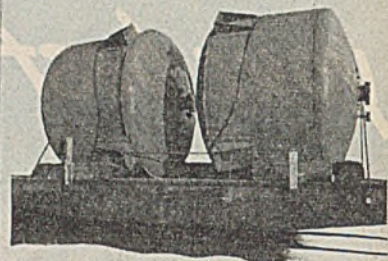
LEAD LINING OF TANKS, VATS,
CHAMBERS, AGITATORS, ETC.



CONVEYING LINES, HEATING
COILS, COOLING COILS, ETC.

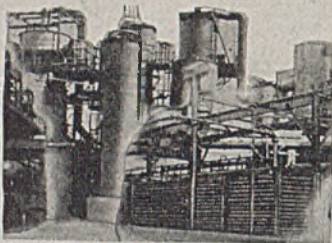


LEAD LINING OF TANKS ENCON-
TERING HIGH TEMPERATURE AND
PRESSURE, VIBRATION AND VACUUM

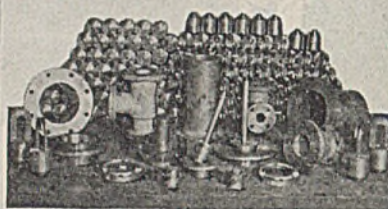


LEAD LINED APPARATUS...

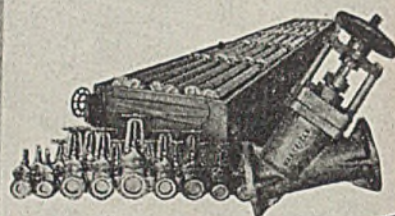
LEAD INSTALLATION, CONSTRUCTION AND
MAINTENANCE THROUGH LEAD BURNING



CHEMICAL LEAD SPECIALTIES, RETURN
BENDS, ELECTRODE WEIGHTS, ETC.



CONVEYING LINES, HEATING COILS, COOLING
COILS, ETC., ENCOUNTERING HIGH TEMPER-
ATURE AND PRESSURE, VIBRATION AND VACUUM



PRESENTS NO PROBLEM!

ASARCO OFFERS THE WORLD'S MOST COMPLETE SERVICE ON LEAD PRODUCTS AND THEIR INSTALLATION!

THOSE who rely on lead lined apparatus can eliminate almost all problems attendant upon its use by selecting the American Smelting and Refining Company as their source of supply.

We mine, smelt, refine, fabricate and install lead for Chemical Industry usage, and therefore

can supply not only your requirements for all lead products, but for finished apparatus as well.

To those interested in placing contracts for lead burning and construction in the field, we offer the services of our subsidiary, the Andrews Lead Construction Corporation.

AMERICAN SMELTING AND REFINING COMPANY

LEAD PRODUCTS DIVISION



120 BROADWAY, NEW YORK 5, N. Y.



Smashing molecules TO SPEED RESEARCH

Free electrons are now being used to speed both research and routine testing . . . and with more accurate results than ever before. At the Hercules Experiment Station the mass spectrometer analyzes gases and liquids in two to four hours. Former methods often-times required two to three weeks!

The mass spectrometer employs free electrons to smash molecules of a compound into fragments. From the number, mass, and concentration of these fragments it is possible to determine the exact chemical structure of compounds with accuracies well over 99%. Progressive research such as this is constantly going on at Hercules to improve present products or discover new ones for industry. Perhaps some of our findings or the chemicals we have developed will be of interest in your current or post-war problems. Write Hercules Powder Company, Wilmington 99, Delaware.



Plastic safeguards fighting equipment

Packaging and shipping guns and other military equipment puts to an important new use the many excellent protective qualities of cellulose acetate.

The new packaging consists of paper sheets laminated with thin layers of the acetate. From one to five layers of kraft or creped paper are usually employed. The acetate coatings act not only as an oil barrier, but also help protect the contents of the package against water, dust, dirt,

and mechanical injury. The wrapping also keeps intact any previously applied corrosion-preventive film.

Flexible at room temperature, the laminated sheets are wrapped to the contours of the equipment being packaged. Sealing is accomplished by the use of pressure-sensitive adhesives, wax dippings, or other sealing methods. Hercules will gladly furnish names and addresses of suppliers. Write the Cellulose Products Department.

Flameproofers

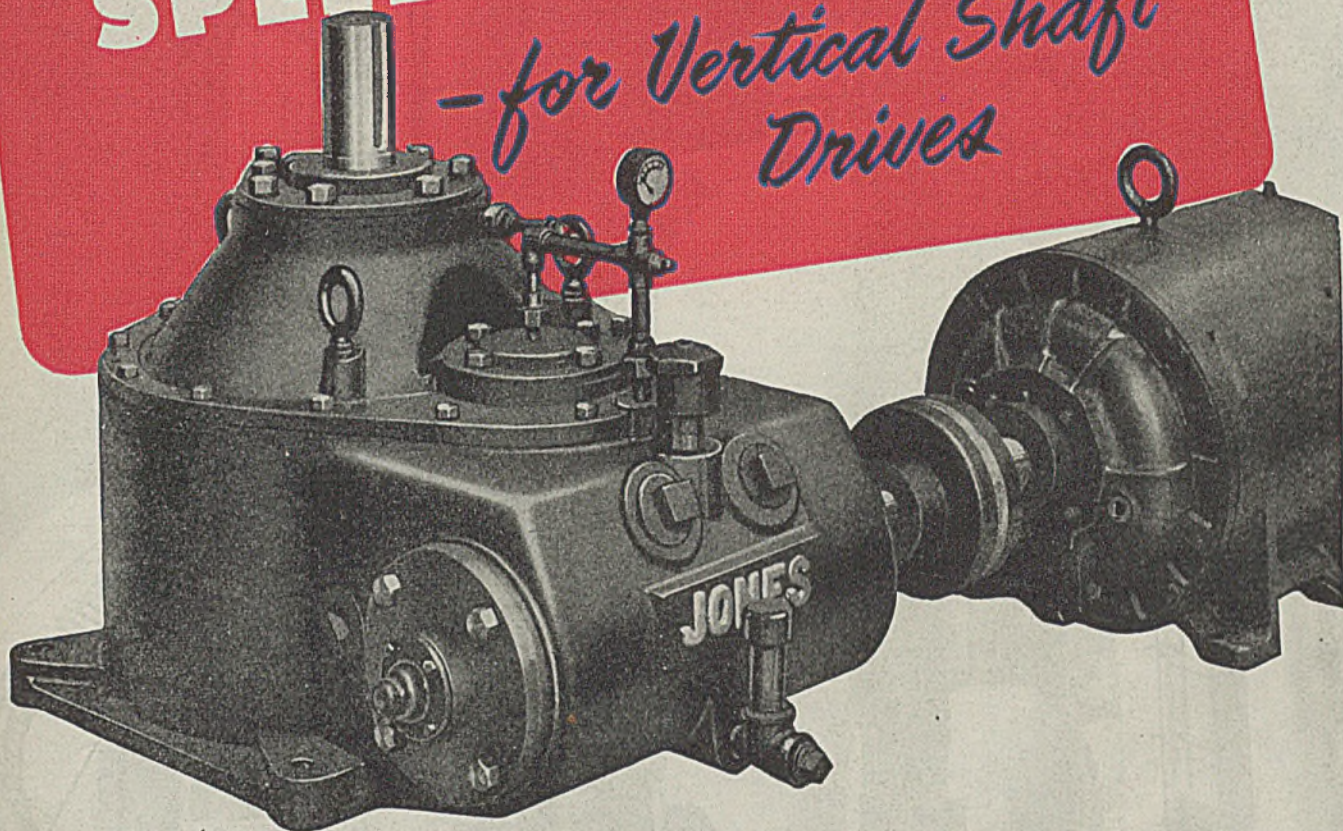
Now available for civilian uses are the Clorafins.* These are Hercules chlorinated paraffins for flameproof and waterproof coatings for textiles, and for flameproof paints and adhesives. Productive capacity is now ample for both military and civilian uses. Clorafin 42 is a viscous, nonflammable plasticizer, 42 to 43% chlorine; Clorafin 70 is a hard resin, 69 to 72% chlorine. Both are *stable*, easy to use, and compatible with most of the cellulose derivatives, resins, waxes, and plasticizers. Write Cellulose Products Department for new booklet.



Jones

WORM-HELICAL SPEED REDUCERS

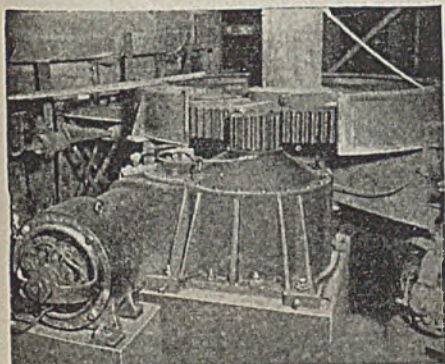
*- for Vertical Shaft
Drives*



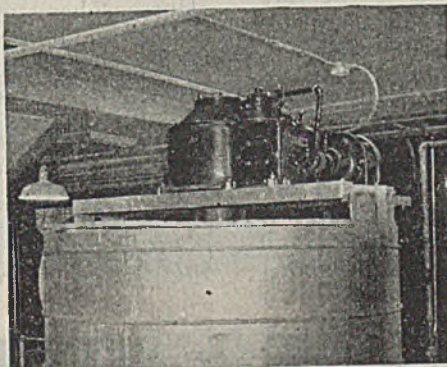
THESE machines fill a long felt need for double reduction units of the fully enclosed type to be used for agitators, mixers, ore roasters, bending rolls, etc., requiring a vertical shaft drive. Built in standard ratios in various types of assemblies ranging from 40 to 1 to 250 to 1 for all common motor

speeds and a wide range of horsepower ratings.

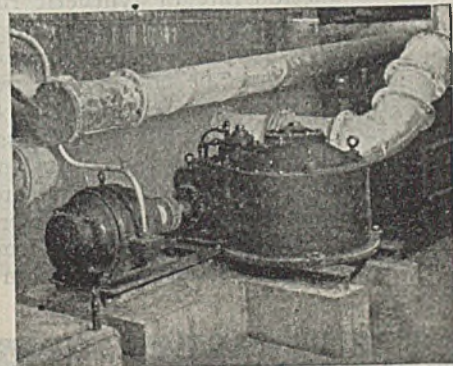
Jones Bulletin No. 75 covers complete details on these Worm-Helical Speed Reducers, with rating tables, dimension diagrams, torque charts and other application information. We shall be pleased to send you a copy.



• Jones Worm-Helical Speed Reducer on ore roaster with section of dust guard removed to show final gear reduction.



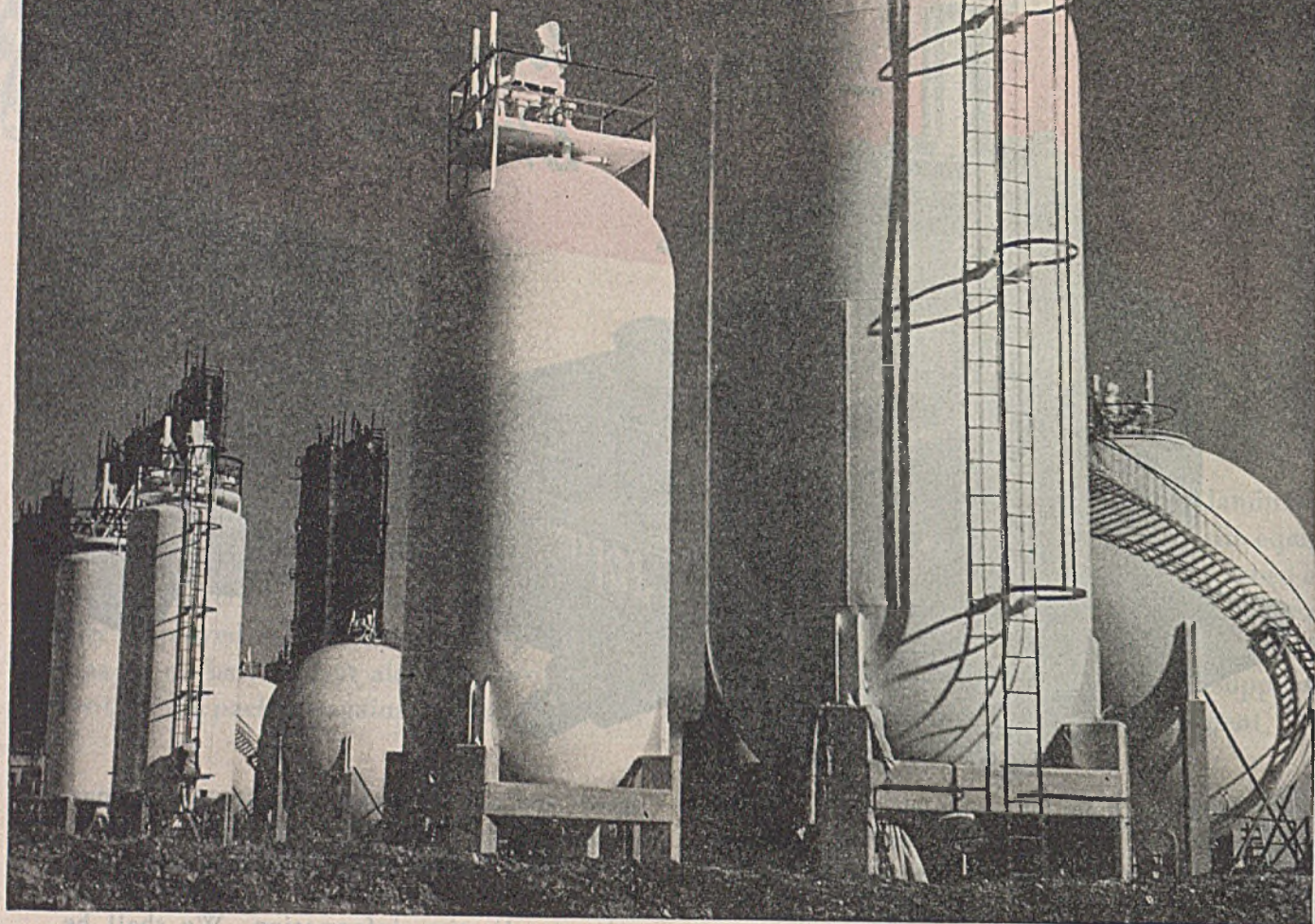
• Jones Worm-Helical Speed Reducer driving a lacquer agitator. A simple design prevents leakage of oil along the vertical low speed shaft.



• Jones Worm-Helical Speed Reducer on a paper mill agitator drive.

W. A. JONES FOUNDRY & MACHINE CO., 4445 Roosevelt Road, Chicago 24, Illinois

More *Butadiene*
for the Nation's
Compounding Plants!



CHIEF among the factors controlling the production rate of synthetic rubber is the rate of production of the components of this man-made product. *Butadiene*, key ingredient of GR-S type rubbers, must be produced in tremendous quantities. To maintain a steady flow of this product to the compounding plants it is essential to provide various types of storage tanks and pressure vessels in the production lines. Pressure storage, as provided by Hortonspheres, is the preferred method of handling and storing Butadiene. This type of storage guards the product from loss by evapora-

tion and also protects the quality of the product.

Hortonspheres and other types of pressure vessels, designed and fabricated in our plants, have become a common sight throughout the synthetic rubber industry, as well as at chemical and process plants.

The Hortonspheres and "bullets" shown above are a part of the storage facilities at the Houston plant of Sinclair Rubber, Inc. The Hortonspheres range in size from 30 ft. 3 in. in diam. to 51 ft. in diam. The "bullets" are 9 ft. in diam. by 20 ft. high and were designed for 75 lbs. per sq. in. pressure.

CHICAGO BRIDGE & IRON COMPANY

Chicago 4.....2482 McCormick Bldg.
New York 6.....3374—165 Broadway Bldg.
Philadelphia 3.....1636-1700 Walnut St. Bldg.
Cleveland 15.....2253 Guildhall Bldg.
Birmingham 1.....1574 North Fiftieth St.

Plants in BIRMINGHAM, CHICAGO and GREENVILLE, PA.



Washington 5.....330 Bowen Bldg.
Houston 1.....5639 Clinton Drive
Tulsa 3.....1636 Hunt Bldg.
Greenville.....York Street
San Francisco 5.....1067 Rialto Bldg.

In Canada: HORTON STEEL WORKS, LIMITED, FORT ERIE, ONT

Hardinge Equipment



HARDINGE BALL MILL
IN CLOSED CIRCUIT WITH HARDINGE COUNTER CURRENT CLASSIFIER



371 HARDINGE MILLS IN 9 INSTALLATIONS
(157)



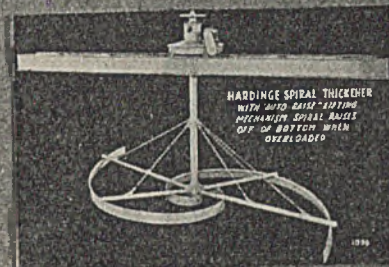
HARDINGE MILL
WITH AIR CLASSIFIER
(152)



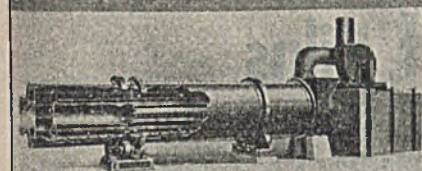
TWO HARDINGE BEAM TYPE CLARIFIERS
(1090)



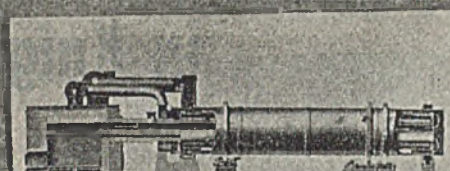
HARDINGE CONSTANT WEIGHT FEEDER
FOR FEEDING AND WEIGHING MATERIALS FROM SKY



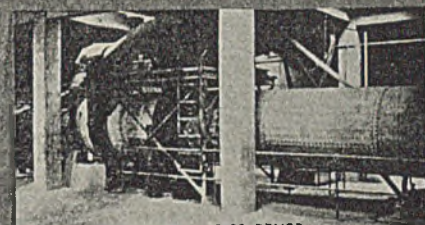
HARDINGE SPIRAL THICKENER
WITH AUTO RAISE-LOWERING
MECHANISM SPIRAL RAISES
OFF OF BOTTOM WHEN
OVERLOADED



PRINCIPLE OF CONSTRUCTION OF CLASS "XA"
RUGGLES-COLES DRYER
(5045)



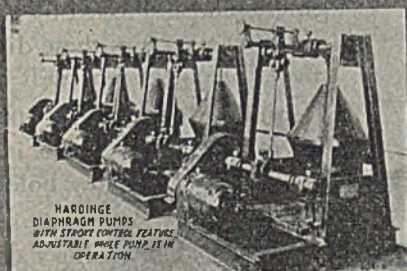
PRINCIPLE OF CONSTRUCTION OF
"XB" RUGGLES-COLES DRYER
(5086)



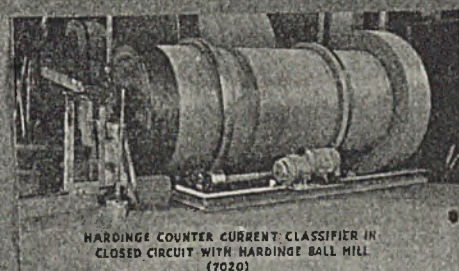
"XB" RUGGLES-COLES DRYER
DRYING WITHOUT CONTAMINATION AND LOSS OF DUST
(5087)



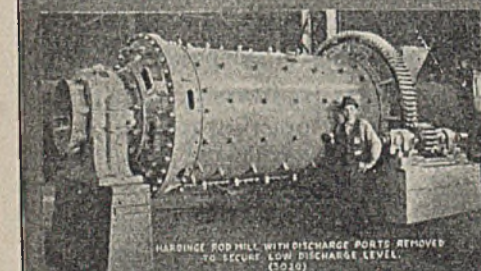
HARDINGE AGITATOR
WITH BALL BEARING SUPPORT AND
OIL FILLED GEAR HOUSING



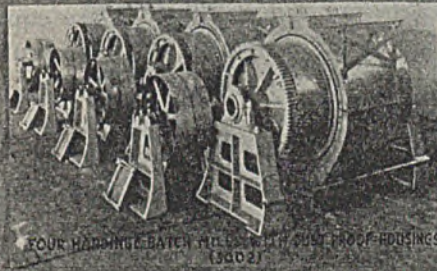
HARDINGE
DIAPHRAGM PUMPS
WITH STROKE CONTROL FEATURE
ADJUSTABLE WHILE PUMP IS IN
OPERATION



HARDINGE COUNTER CURRENT CLASSIFIER IN
CLOSED CIRCUIT WITH HARDINGE BALL MILL
(7020)



HARDINGE ROD MILL WITH DISCHARGE PORTS REMOVED
TO SECURE LOW DISCHARGE LEVEL
(5910)



FOUR HARDINGE BATCH MILLS WITH DUST PROOF HOUSINGS
(3002)

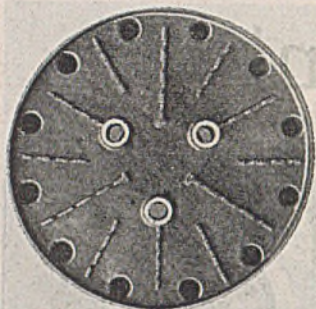


HARDINGE TUBE MILL ASSEMBLED
IN SHOP BEFORE SHIPMENT
(3005)

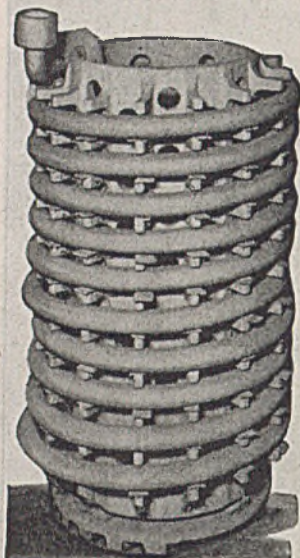
HARDINGE

COMPANY, INCORPORATED - YORK, PENNSYLVANIA

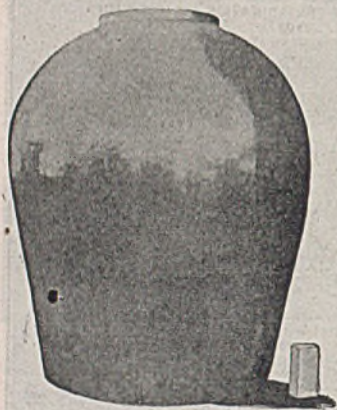
New York, 122 East 42nd Street Chicago, 205 West Wacker Drive San Francisco, 501 Howard Street Toronto, 200 Bay Street



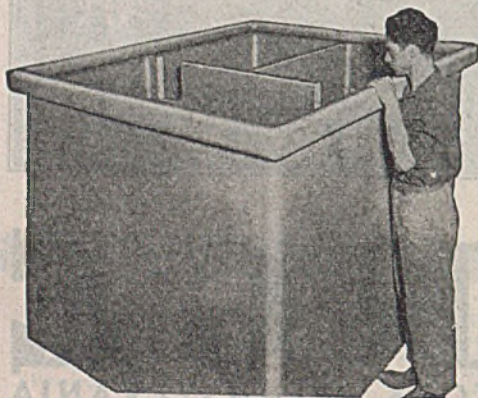
Section of Disc Cooler



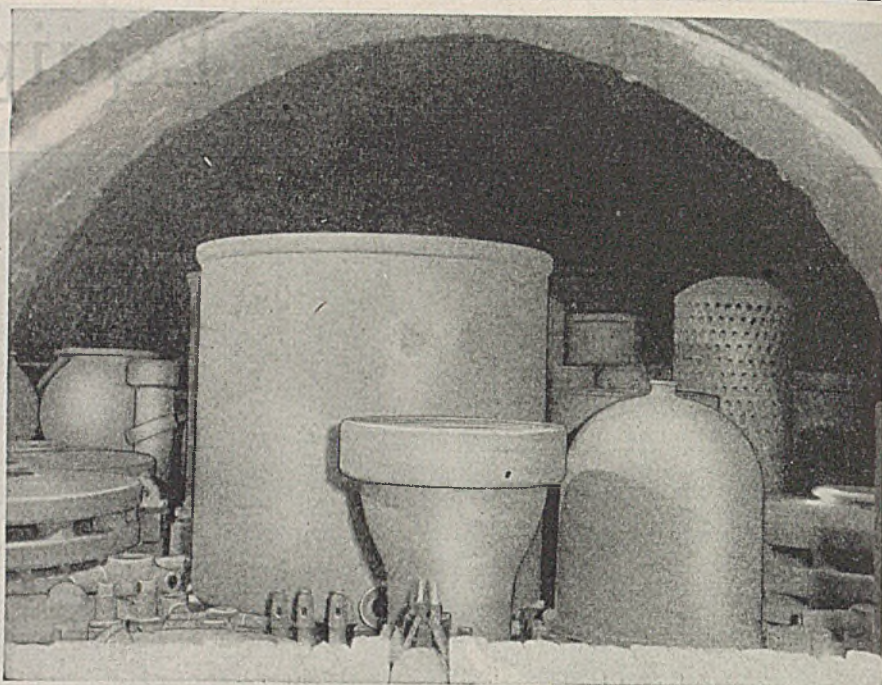
Acid-Cooling Coil



Acid-Proof Jar



One-Piece Tank



Strange Things Are "Hatched" in Knight Kilns

IT is quite an experience to peek into Knight kilns and see the great variety of chemical stoneware pieces they contain.

In these kilns temperatures of over 2200° F. thoroughly vitrify chemical ware designed by Knight engineers and fashioned by Knight craftsmen. One wonders for what purposes these diverse and intricately patterned pieces of equipment will be used.

In the kiln above is a 500-gallon storage jar for storing and mixing acids. Beside it, upside down, is a large kettle. The piece with many holes is a roof ventilating cap.

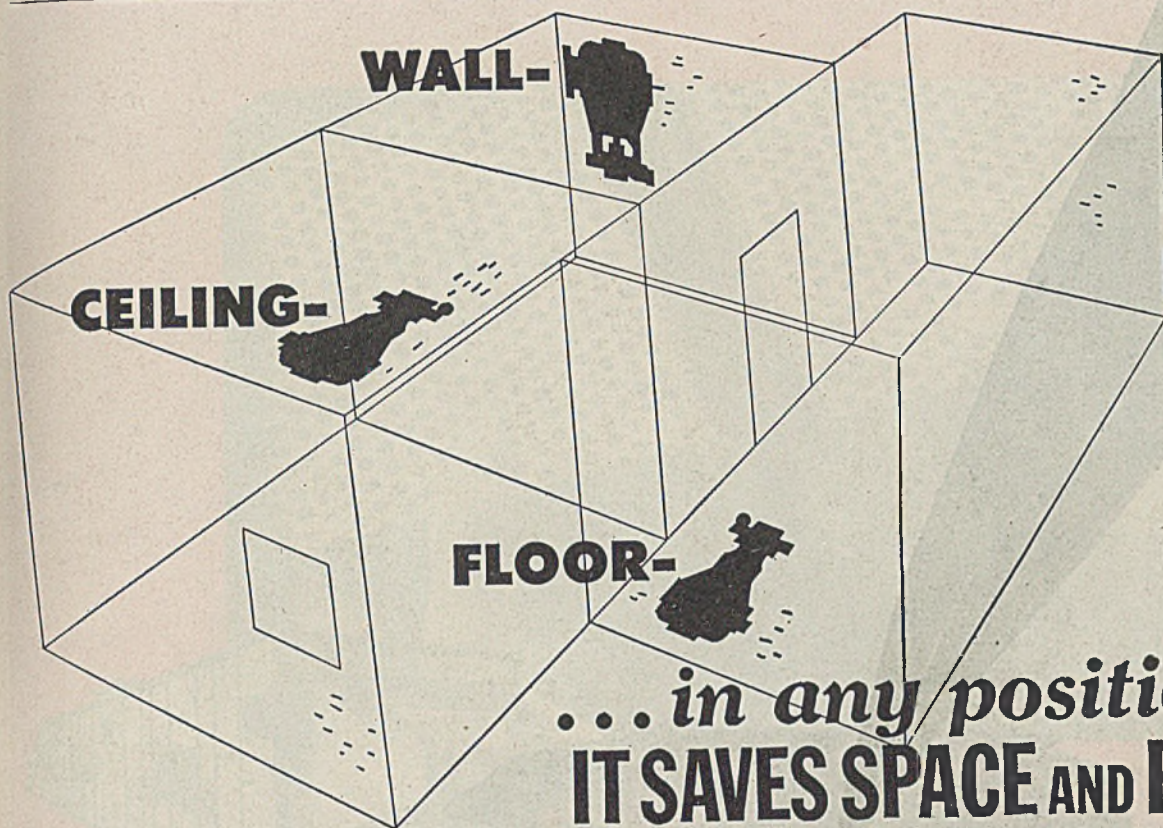
Just in front of the big storage jar is a reducer pipe fitting. On the left, lying flat, are disc coolers or condensers (42" in diameter) used in the manufacture of chlorine. Other kilns disclose equally interesting types of equipment designed for a multitude of chemical purposes.

The experience of Knight engineers is always at your disposal in helping you choose the most practical type of acid-proof equipment to meet your needs. When writing, please give complete data.

MAURICE A. KNIGHT

310 Kelly Ave., Akron 9, Ohio





... in any position
IT SAVES SPACE AND POWER!

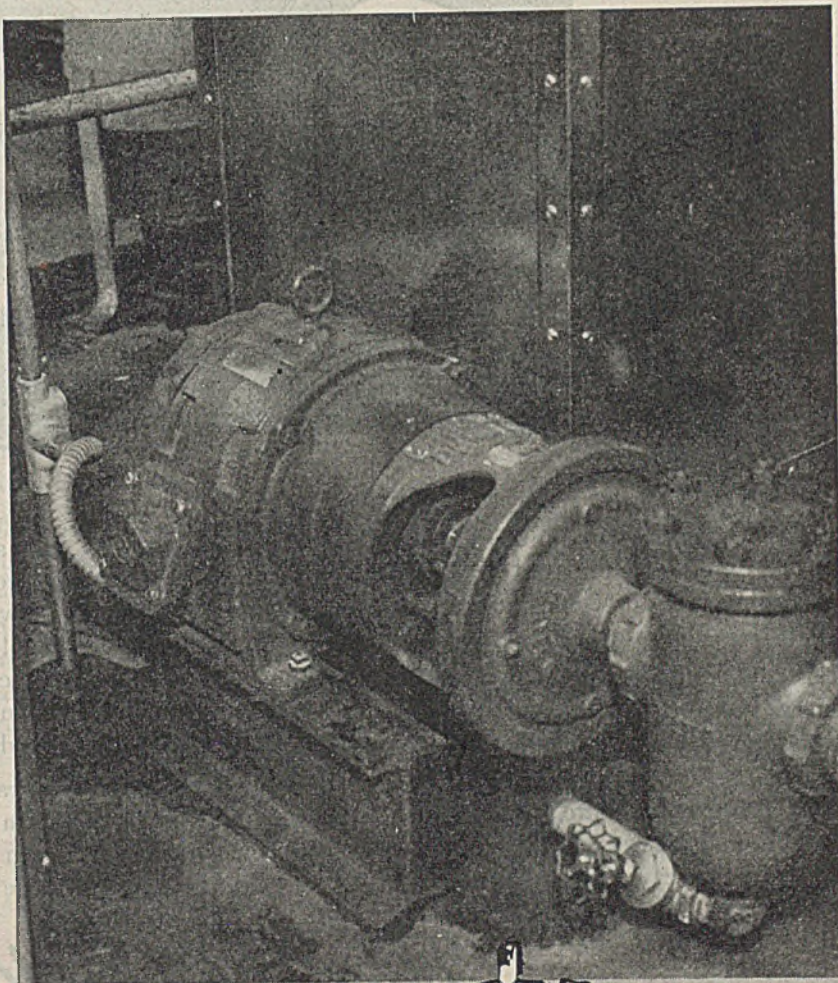
NO MATTER where you install a Gardner-Denver Close-Coupled Centrifugal Pump . . . floor, wall or ceiling . . . horizontally or vertically, you'll get a new high in low-cost, efficient pumping performance.

Pump and motor form a complete unit, ready for quick, easy installation. They save space, with no sacrifice in capacity. For convenience in fitting installation requirements, discharge nozzle can be turned in any one of eight different directions.

For complete information on sizes, capacities and performance data on Gardner-Denver Close-Coupled Centrifugal Pumps, write Gardner-Denver Company, Quincy, Illinois.

HERE ARE A FEW OUT- STANDING DESIGN ADVANTAGES:

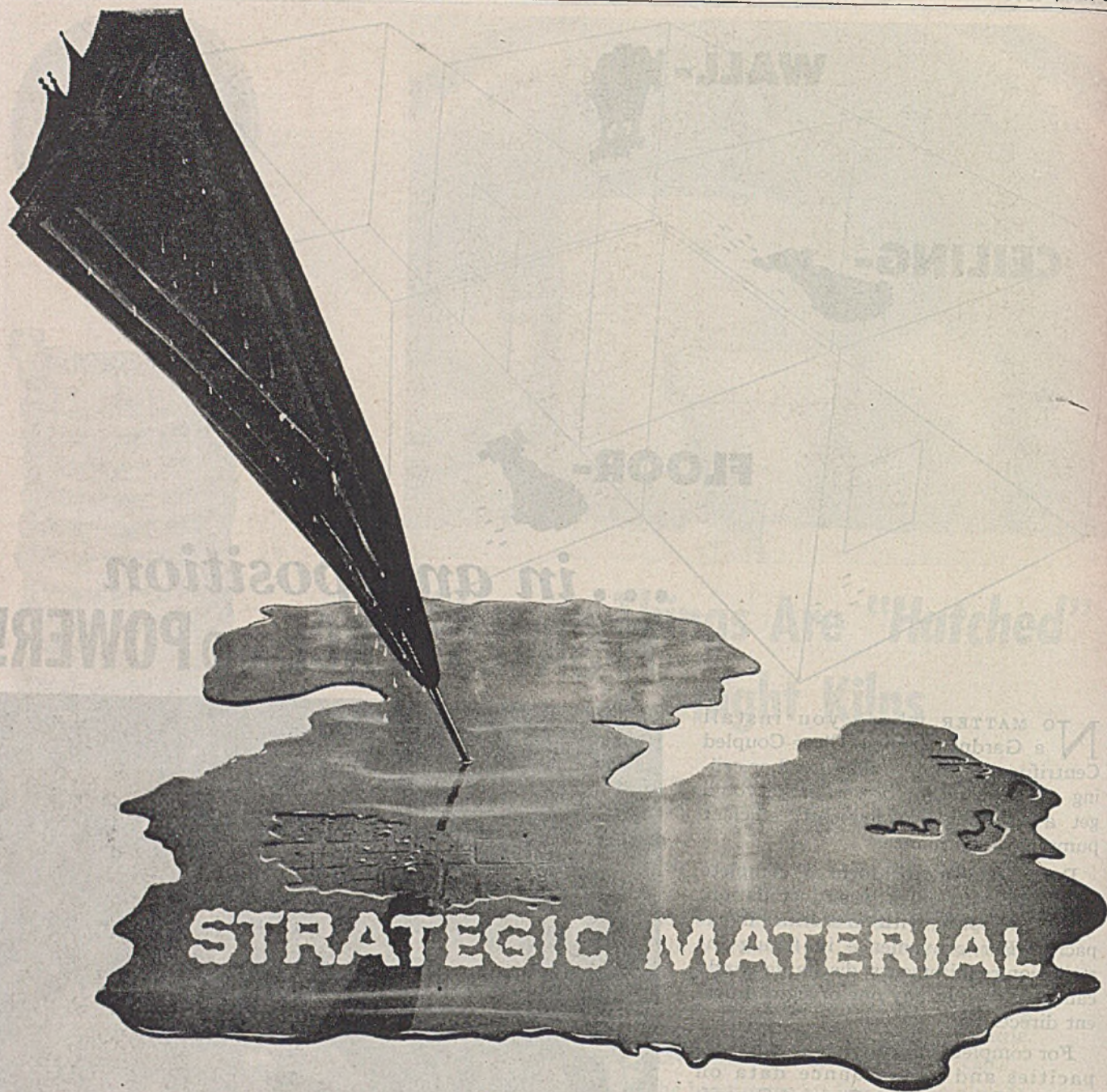
1. Rigidly controlled foundry practices assure smooth castings . . . minimum obstruction to flow.
2. Water passages and impeller blades carefully proportioned for efficient operation.
3. All vital parts cast in GarDurloy for greater strength and longer life.
4. Splash-proof, explosion-proof motor available if desired.



GARDNER-DENVER



Since 1859



Water... enormous quantities of it... are used in industrial cooling operations. Water comes into the plant *cool*—goes down the drain *hot*.

But war has caused acute water shortages in many industrial localities. Plant engineers then face a real problem... especially where continuous processes require continuous cooling, and lack of water can stop production or cause serious damage.

Solving this problem in many a war plant, G-E *evaporative* cooling equipment makes as little as five gallons do the work of 100 gallons! With evaporative cooling, water is cooled and used again and again. Comparatively little fresh water is needed.

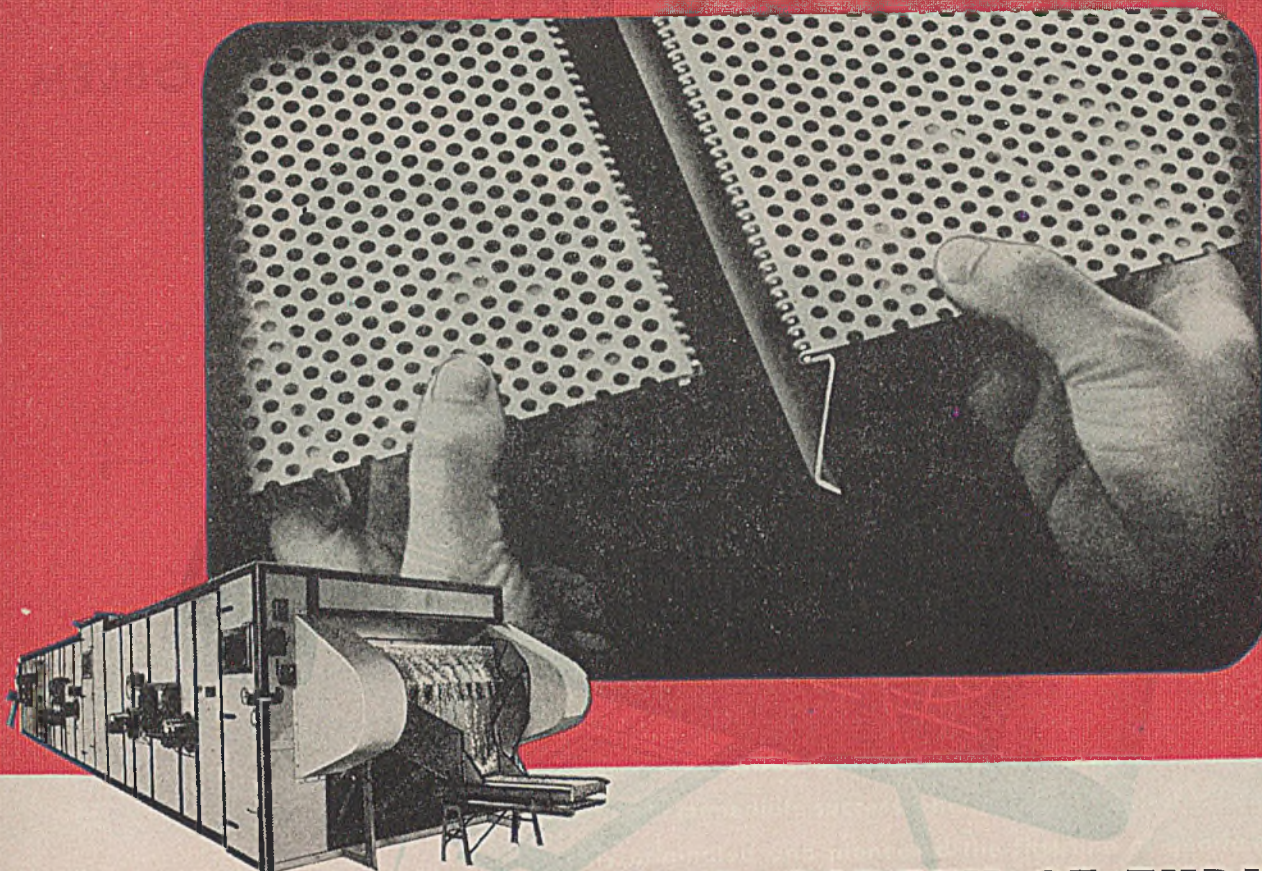
If water has become a strategic material in your plant, learn how G-E evaporative cooling can help conserve it. And remember, the same

equipment that saves *water* also saves money—by reducing water costs. In fact, in most installations, water savings *alone* are sufficient to pay for the cost of the equipment!

For information write: *General Electric Company, Air Conditioning and Commercial Refrigeration Divisions, Section 445, Bloomfield, N. J.*

☆ BUY WAR BONDS ☆

Industrial Cooling by
GENERAL  ELECTRIC



CONVEYOR SCREEN OF ENDURO PREVENTS CONTAMINATION—IS EASY TO CLEAN

In one end wet—out the other end dry! Through this and similar type dryers and dehydrators move textile fibres, pharmaceuticals, chemical products, foods and many other materials on continuous conveyors of Republic ENDURO Stainless Steel.

The design of the conveyor, illustrated above, consists of perforated plates hinged together and carried by side bar chains on steel rollers with frictionless bearings.

Whether it's for conveyors—or for tanks, kettles, vats, chutes, tables, tubing or any other equipment in the chemical processing industries—ENDURO is the ideal material.

ENDURO is highly resistant to most acids and alkalis, both hot and cold. It does not rust or corrode. It does not contaminate deli-

cate products—does not alter color, flavor, purity or composition. Its smooth, hard surface is remarkably easy to clean. And there are no surface pores to carry substances from one batch to another.

ENDURO is exceptionally strong and tough, too. It resists wear and abuse—cuts maintenance and replacement costs. It maintains its strength well in high temperature applications. It resists scaling when exposed to high heat ranges. And it can be fabricated economi-

cally to almost any desired shape.

Many equipment manufacturers standardize on ENDURO for important parts of their equipment. Others are glad to use it on your specifications. Ask your equipment manufacturer what priorities are necessary—or write us for further information and literature.

REPUBLIC STEEL CORPORATION

Alloy Steel Division • Massillon, Ohio

GENERAL OFFICES • CLEVELAND 1, OHIO

Berger Manufacturing Division • Culvert Division
Niles Steel Products Division • Steel and Tubes Division
Union Drawn Steel Division • Truscon Steel Company
Export Department: Chrysler Building, New York 17, N. Y.

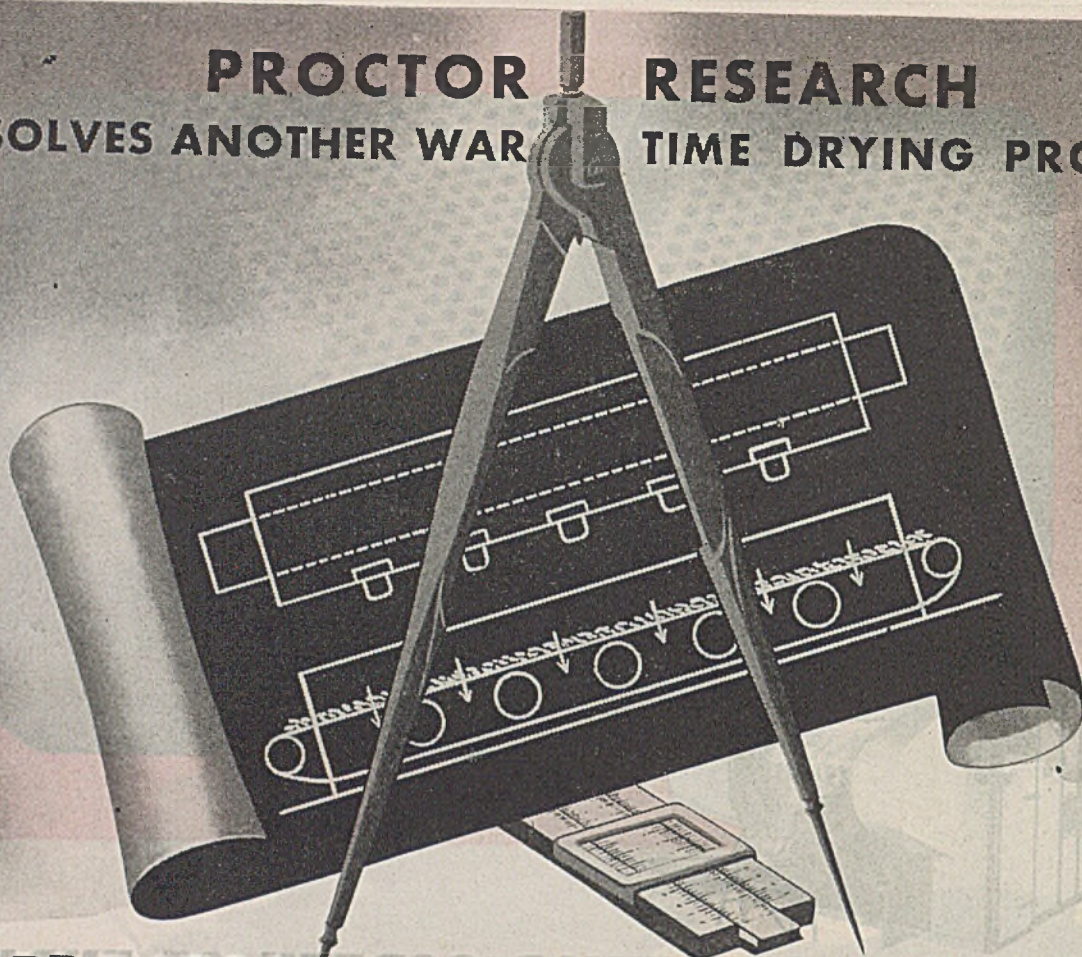


Republic
ENDURO STAINLESS STEEL

Reg. U. S. Pat. Off.

Other Republic Products include Carbon and Alloy Steels—Pipe, Sheets, Strip, Plates, Bars, Wire, Pig Iron, Bolts and Nuts, Tubing

PROCTOR RESEARCH SOLVES ANOTHER WAR TIME DRYING PROBLEM



with PROCTOR BUILT DRYERS FOR CATALYSTS

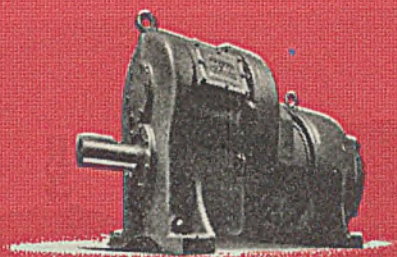
The same Proctor coordinated research which contributed so largely to the solution of literally hundreds of peacetime industrial drying problems, has, since the beginning of the war, been devoted almost exclusively to solving drying problems brought about by the war. One of the latest contributions Proctor research men and engineers have been able to make was the successful solution to the problem of drying catalysts for use in the manufacture of high octane aviation gasoline. Perfect drying uniformity is essential in the drying of catalysts. Due to the physical characteristics of the catalysts, temperatures and humidity conditions inside the dryer must be carefully and accurately controlled

to achieve the required uniformity. Making use of our research facilities and drawing on the wealth of available information, gathered in the solving of industrial drying problems for the past 60 years, our research engineers were able to cooperate with the catalyst producer's engineers and reach the successful solution to this vitally important war time drying problem. These same research facilities are available to you—and will continue to be available to you in the postwar period—without cost or obligation. It makes good business sense to call on Proctor engineers for help before investing in any new piece of drying machinery.

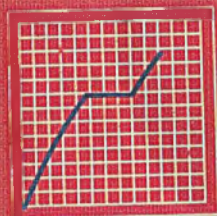
PROCTOR DRYERS
for the
CHEMICAL INDUSTRIES

manufactured by

PROCTOR & SCHWARTZ • INC •
PHILADELPHIA • PA •



1/10 TO 100 HORSEPOWER
Five types of gearhead motors have reduction ratios ranging up to 432:1.



HIGH EFFICIENCY
More efficient than other types of slow speed drives not only for power loss in each stage of reduction, in parallel shaft types.



GEARHEAD MOTORS

These are the **good reasons why** gearhead motors met with such immediate success when The Master Electric Company originated and pioneered the first line of gearhead motors, years ago.

These are the **good reasons why** more gearhead motors in use today carry the Master name than all other makes . . . **COMBINED**.

These are the **good reasons why** Master Gearhead Motors will help you save money and still add greatly to the convenience, compactness and safety of your motor driven machinery. For best results, use them for either your plant or your products.

THE MASTER ELECTRIC COMPANY • DAYTON 1, OHIO



available in combinations of all these types



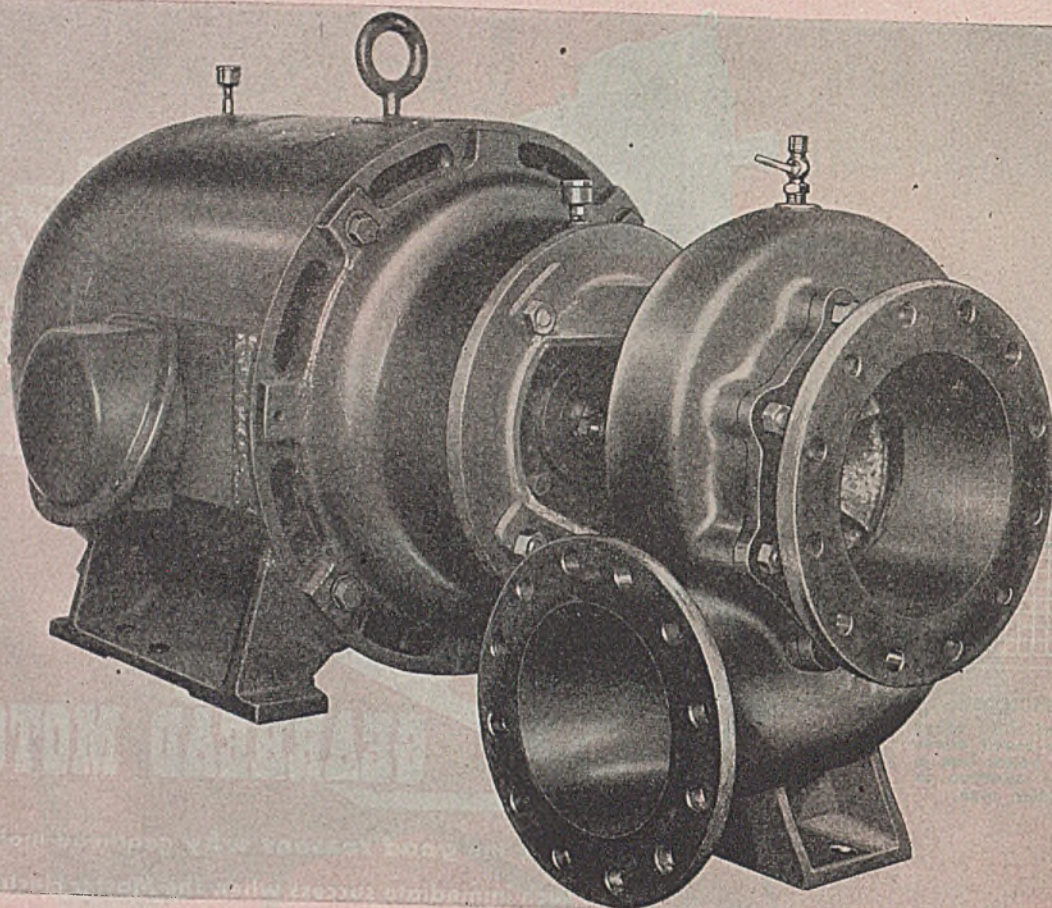
PROVEN RELIABILITY
Their durability and sturdiness have been proven with millions of hours of service all over the world.



UNDEVELOPED RESPONSIBILITY
The complete Gearhead Motor is designed and built by one man—known to one plant.

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





EASY to install **E**CONOMICAL to operate

Close-coupled pumps are usually installed in cramped quarters, or as part of a larger piece of equipment.

In either case, they are apt to get little attention, hence should be built to stay-on-the-job.

Buffalo Close-Coupled Pumps have the right hydraulic design to give high efficiency, plus the heavy-duty construction necessary for

steady operation without attention. You can see, from the No. 6 Pump illustrated above, that heavy-duty construction means what it says. Buffalo Close-Coupled Pumps installed in your plant, or as part of equipment you sell, will give years of trouble free operation. Write for bulletin 975-B which gives ratings and full construction details.



BUFFALO PUMPS INC.

153 MORTIMER ST.

BUFFALO, N. Y.

Canada Pumps, Inc., Kitchener, Ont.

"Buffalo"

**Close Coupled
PUMPS**

MAKE HEAT WORK

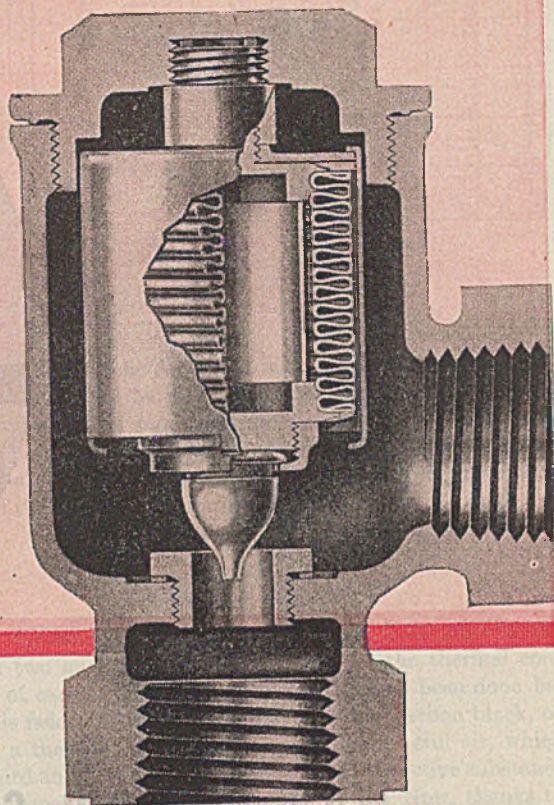


Delivery of heat units to the coils is not enough. If condensate dogs them or air is trapped in the coils, heat sits down and waits. If the wrong steam trap is used, heat will escape before its work is done.

Nor will just any trap do, because there are four kinds, each having a special function. Below we show examples of the No. 9 thermostatic trap used extensively in the heavy heat-consuming industries.

One of these should be used on each coil. They will keep every coil alive, let no unused heat escape. Wide open when cool, they remove air instantly. They cannot stick or freeze. The No. 9 works on all pressures within its range, without seat change.

If your equipment manufacturer did not supply one for each coil, better put them on. Also ideal for air vents. Small, inexpensive, easy to install. Catalog No. 250.

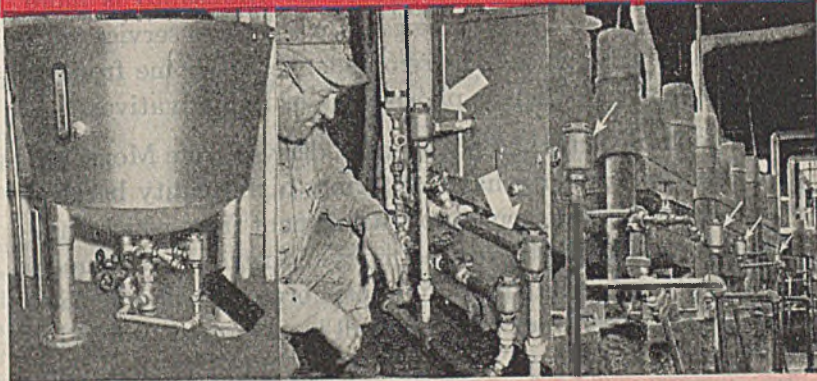


The Sarco No. 9 Steam Trap is a high pressure trap designed especially for process work. More heat is utilized before discharging condensate. The trap works over a wide range of pressures without adjustment. It is ideal for removing both air and condensate from practically all types of steam heated equipment. It is also suited to remove moisture from live steam lines.

CHEMICAL

FOOD

PLASTICS



Sarco No. 9's
on Kettle

Sarco No. 9's
on bottle washer

Sarco No. 9's
on plastic presses

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

Represented in Principal Cities

SARCO

Saves Steam

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

workmen



who seldom see their product

Skilled workmen, who operate the plant in which Monsanto extracts elemental phosphorus from phosphate ore seldom see the product of their labors. Elemental phosphorus made in modern electric furnaces is kept out of contact with air. Incidentally, it always is hidden from view.

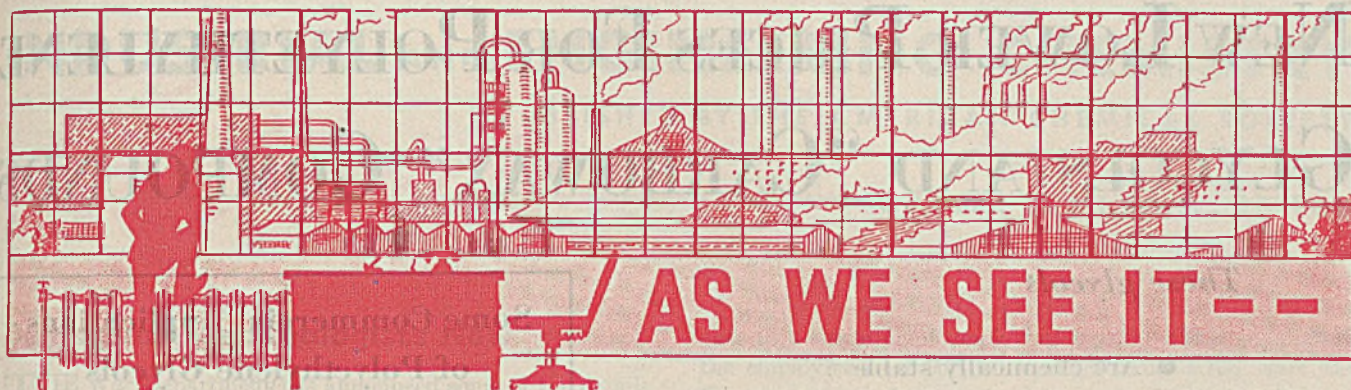
Elemental phosphorus produced by Monsanto is more than 99.9% pure. Much of it goes directly into service with Allied Armed Forces. The remainder serves home front or war industries, either as phosphorus or its derivatives.

Phosphoric acids and phosphates, derived from Monsanto elemental phosphorus have uniformly high quality because of the near-absolute purity of the element from which they are made. This quality has led many industries to look upon Monsanto as headquarters for phosphorus, phosphoric acids and phosphates. Your inquiries will be answered promptly. MONSANTO CHEMICAL COMPANY, Phosphate Division, 1700 South Second Street, St. Louis 4, Missouri. District Offices: New York, Chicago, Boston, Detroit, Charlotte, Birmingham, Los Angeles, San Francisco, Montreal, Toronto.

Phosphorus and Related Products By the World's Largest Producer of Elemental Phosphorus

PHOSPHORUS (YELLOW)
PHOSPHORIC ANHYDRIDE
PHOSPHORIC ACID—TETRA
PHOSPHORIC ACID—85%
PHOSPHORIC ACID—75%
MONO SODIUM PHOSPHATE
DI SODIUM PHOSPHATE (ANHYDROUS
AND DUOHYDRATE)
TRI SODIUM PHOSPHATE
SODIUM ACID PYRO PHOSPHATE
TETRA SODIUM PYRO PHOSPHATE
AMMONIUM PHOSPHATES
CALCIUM PHOSPHATES (MONO-DI-TRI)
CALCIUM PYRO PHOSPHATE
POTASSIUM PHOSPHATES
MAGNESIUM PHOSPHATES
SODIUM IRON PYROPHATE
FERRO PHOSPHORUS
SPECIAL PHOSPHATES FOR SPECIAL
APPLICATIONS





AS WE SEE IT--

This Month

WE SEARCH in vain for an article on Brown October ale to give our column a flavorsome approach in keeping with the spirit of the month. Found it is not, and the best we can do is to talk about a component of ale such as an azeotrope (in this case alcohol and water) leading to the article in the No. 1 spot by Ewell, Harrison, and Berg on Azeotropic Distillation. A new concept based on the hydrogen bonds present in a system is advanced in this contribution. The authors arrange liquids into five different classifications and from this, develop a theory to explain the formation of azeotropic mixtures. Likelihood of an azeotropic mixture in a binary system can be predicted from the data given, and the authors say that selection of an entrainer to help separate a constant-boiling mixture is greatly simplified.

Yeast is not too far from ale, since it concerns compressed yeast, a by-product of the brewing industry. De Beeze and Liebmann survey the part that aeration has in the efficient manufacture of yeast, and mention in passing that the technique of aeration removed the production of compressed yeast from the status of a brewery by-product and made it possible to become an independent operation. Which is as far as the ale analogy can go.

Heberlein and Clifton of Continental Can Company have studied vitamin retention in dehydrated foods. They find that, although an inert gas present during storage is beneficial to retention of vitamins, increases in storage temperature will effectively destroy all the vitamins present except riboflavin. If the dehydrated product is kept at room temperature, however, ascorbic acid and carotene are protected by the inert gas; thiamine reacts little to the gaseous protection.

Steinour, in the third article on Rate of Sedimentation, reports on the applicability of his rate equation, developed in our September issue, to flocculated suspensions of powders. This is an important continuation of a thorough investigation into the mathematical prediction of sedimentation rates, for although the equation was developed on uniform particles, the author finds that it can be made to work for powders of varying sizes.

Calcium chloride as a dehydration agent for solvents was reported on in the September issue; continuing the series, Meissner, Stokes, and co-workers follow up this report on batch dehydration with data on countercurrent systems. Spray and packed towers were used, and the results in a packed tower are better when the solvent is the dispersed phase than when strong calcium chloride is dispersed.

Considerable quantities of pork luncheon meat have been packed for the armed forces; American Can Company and American Meat Institute have joined in research and report on the vitamin retention of the meat after heat processing. The conclusions are that, if the processed meat were heated at high temperatures for a short time, there was better vitamin retention than the alternative method of lower temperatures and longer times. It was also found that the position of the meat in the can had a direct bearing on vitamin content.

Frear, Ogg, and Hull of the Tennessee Valley Authority have studied the preferential oxidation of phosphorus in the presence of carbon monoxide, with the intriguing objective in mind that

the phosphorus could be converted into pentoxide while the carbon compound would be retained as monoxide for use as fuel. Both phosphorus and monoxide are present in the gases that come from phosphorus blast furnaces, so the idea is of great practical interest. The reports indicate that results were successful, for most of the cases little monoxide was lost.

Next Month

LIGHT is thrown on a dark subject in our November issue, when two authors combine to report on the thermal conductivity of carbon black. Strangely, little had been done before in this field. It was always assumed that carbon black, or soot, had a thermal conductivity nearly that of still air, which is a standard and heretofore the lowest heat-conductive substance that ever came to a scientist to be measured. Now, thanks to the report that we will publish in November, it is proved that, in certain forms, soot is a better thermal insulator than still air. It is a tough world for standards because the chemist is always perfecting something better. Iso-octane (as we will see next month) had to move over because we made fuels that are more powerful, and now still air, below which nothing was better for not transferring heat, has a black outlook. "Soots" us!

Intriguing ideas are always springing to attention in the field of water softening. Not many years ago the sole argument for softening water was the saving of soap, or the prevention of metallic soaps from forming on delicate fabrics during textile processing. Since the advent and perfection of various new water softening methods and equipment, many more valid reasons have been advanced for the use of softening methods. One major saving that can be effected is to prevent scale and corrosion from ruining equipment such as heat exchangers, boilers, and stills. This leads to the discussion of a paper that will appear in the next issue. The authors propose that, instead of removing all the hardness, only the calcium portion be treated, leaving the magnesium behind. This, they claim, is especially adapted to the treatment of water scheduled for use in coolers, because often, depending on the water, a balanced product may be made that will not deposit calcium carbonate on the heat exchange surfaces. The cost of removing the calcium hardness is less than that of removing both calcium and magnesium hardness. Examples from actual installations treating from 1,500,000 to 24,000,000 gallons per day will serve to supply operating data.

If imitation is the sincerest form of flattery, rubber would feel flattered indeed, were it not for the fact that uneasy is the head that wears a crown. Some of the rubber substitutes that the chemists are thinking up today are extremely good, and we report on the latest of the new rubber-like substances in November with three articles. This time the material is vulcanized copolymerized ethyl acrylate and allyl maleate. Sulfur is the vulcanizing material only in some of the trials, and there are reports on a number of catalytic polymerization agents.

F. S. Van Antwerpen

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Film lubricant.

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Lubricant and film-former; spreading agent.

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INDUSTRIAL AND ENGINEERING CHEMISTRY

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY

Editorials

WALTER J. MURPHY, EDITOR

Demobilize Technologists Now

THE War Department has announced some of the details of the plan for the gradual demobilization of the men in the Army. A rather complicated point system has been devised, based upon the findings of the Army's Research Division after questioning some 30,000 G. I. Joes as to what they felt was the fairest method of handling this ticklish question. One thing is plain—G. I. Joe wants to get home just as quickly as possible and rightfully expects that a job will be there for him when he does. A little intelligent foresight exercised now in developing demobilization plans will go a long way toward seeing that the job is there when he again dons civies and that it is not one raking leaves or selling apples.

Certain industries are famous as job-creators. The chemical industry and the industries which employ chemical principles and methods stand high in this list. There are now between 12,000 and 15,000 chemists and chemical engineers in the Armed Services and the vast majority of these are not utilizing their technical skills. These men never should have been taken out of the Production Army and away from research. They should be returned promptly to civilian status where they can create worthwhile jobs for thousands of returning veterans.

England, Canada, and Russia did not permit their trained technologists to be inducted into the military forces and, because of this farsighted policy, these countries will have immediately available a well-trained, well-staffed body of technologists to meet postwar requirements. We, on the other hand, have drafted bona-fide students of chemistry and chemical engineering and many of the younger instructors and assistant professors of these subjects despite the fact that it takes between seven and nine years to turn out a chemist or chemical engineer and several additional years to train men to teach in these fields. Chemists and chemical engineers now in the Armed Forces are desperately needed in industry. Various employment bureaus and agencies and the records of the AMERICAN CHEMICAL SOCIETY'S Employment Clearing House clearly prove this statement to be true. With the output of young chemists and chemical engineers largely stopped because of the prevailing draft policies in regard to technical students, the scarcity of chemists and chemical engineers may continue for a decade. The prompt return of those now in the Armed Forces would assist to some extent at least in alleviating this condition.

We are delighted to note that at least one government agency in Washington has demonstrated an enlightened viewpoint on the vital importance of technical brainpower in reconversion and postwar planning. The War Manpower Commission has already outlined an immediate program for the release and assignment of civilian planning engineers and technologists for blueprinting production. Chairman Paul V. McNutt reports WMC estimates that less than 200 technolo-

gists in a single plant employing 16,000 workers may affect the employment of 500,000 workers immediately after the European phase of the war ends.

There are indications that the Army is considering early releases for many doctors and dentists. We endorse such a policy, but feel it is significant that medical officers in uniform are employed in the Armed Forces in a professional status, while the overwhelming majority of the 12,000 to 15,000 professional chemists and chemical engineers now in uniform are not engaged in chemical work of any kind. If released promptly they will help to create the jobs that G. I. Joe confidently expects to be here when he returns, perhaps in a ratio as high as 100 to 1.

What the Younger Chemists Complain About

A FEW weeks ago a young and promising chemist visited with us and, as might be expected, the conversation soon turned to "shop" talk. He told us about some of the problems of the young professional in the chemical field. It so happens that this particular chemist is employed by a company with progressive ideas on the proper monetary compensation for professional employees, so that salaries did not loom large in his list of "complaints". We did suggest that he list for us some of his ideas where improvements could be made, and we quote from two paragraphs:

First, I would like to propose a "rotation of jobs". This does not imply a chronic and continual change from one organization to another. Within an organization where a group of chemists are doing similar work a rotation of various phases of that work would be advantageous. As you well know many men are unhappy because they are kept on a job too long. The job becomes routine, dull, and uninteresting; the saturation point is reached and nothing more can be learned. When, or better even before, that point is reached, why not move the man to a new job where he has a chance to use more of his knowledge and ability and gain new and varied experience? In his place bring in another man to learn the previous chemist's work. There are many jobs in my opinion which should have much lower maximums than one year. The maximums and minimums could be set by the employer and employees and a definite schedule of rotation could easily be planned. This setup would eliminate a lot of the chronic griping about being in a rut and would abolish the necessity of a young chemist continually having to approach his employer for a chance at something new.

The second suggestion you've probably heard many times but it is good enough, I think, to bear repeating. Weekly, semi-monthly, even monthly discussions between the older men and the younger men would do a world of good. Discussion, exchange of ideas, a little more cooperation, trust—all will help toward bringing about a better state of mind for all concerned. A great many of the younger fellows feel that the work they do is not appreciated, not recognized. They develop inferiority complexes and often persecution complexes—believe it or not. This could all be so easily avoided if a spirit of mutual assistance and cooperation prevailed. All too many chemists don't use good psychology and common sense in their dealings with each other. If only the older men would recognize and acknowledge the presence of youth, so much more could be accomplished.

These points are well taken. Fortunately they can be corrected very easily if we but have the determination to do so. The older men in the profession do have a very definite obligation and responsibility.

A more active interest in the work of the younger members, frequent words of encouragement from the "elder statesmen", rather than formal advice and admonition, and practical demonstrations of the spirit of comradeship, will reap worthwhile rewards for the profession as a whole. Proper recognition of accomplishments in the minds of most young chemists is quite as important as compensation.

Gently Red

ALONG with about 2500 other members of the AMERICAN CHEMICAL SOCIETY, we were seated last month in the Grand Ballroom of the Waldorf-Astoria, listening to Bernard Baruch discuss the power of chemistry. It was not apparent to any one except the editors who caused the phenomena, but soon in two spots of the hall a gentle red glow slowly began to gather as the great financier developed his theme. The cherry aurora borealis started when Baruch advocated the use of science and scientists to help solve the "many economic and social problems that face us", for the editors remembered that in the September issue, just off the press, an editorial entitled "Scientists as Leaders" complained that seldom did the proposals for use of science in the formulation of political, social, and economic policies come from "statesmen, politicians, clergymen, or editors of the lay press".

The blaze gathered in intensity as Baruch continued and said "how helpful it would be if we could have more trained (scientific) minds to pass judgment and guide action before it is too late", for the editors remembered saying "we are forced to report a growing tendency on the part of . . . these groups to criticize the scientists for deserting science". The luminescent spots were connected by a ruby rainbow when Baruch finished by saying, "so I hope that in the future, even in the fields of economic, political, and social matters, national and international, more of these trained scientific minds, these experienced searchers after facts, truths, and realities, will be asked to help solve them." The glow continued for days, and now has subsided to a resemblance of a third degree sunburn. Our hats, suddenly too big for us, we have now remedied by pasting in copies of Baruch's speech.

Continuing Technologically Strong

SCIENTIFIC research and technical development plus our well-known ability quickly to devise efficient mass production methods are the fundamental reasons why our entrance into World War II spelled the doom of the Axis powers. The greatest safeguard of the future peace of the world is the continuance of the present predominant position of American technology. That strength, however, will depend upon the numbers and quality of the scientists we have available. Doctor Conant, the recent Priestley Medalist, in his thought-provoking speech of acceptance, offered one suggestion to ensure to a greater degree a proper flow from the reservoir of scientific talent latent in each generation of our youth. Specifically, he proposes that the Federal Government institute a national scholarship program for young men who give promise of becoming leaders in science and technology, such

scholarships to be awarded to members of the graduating class of the high schools through appropriate committees of a non-political nature in each state. The terms, according to Doctor Conant's proposal, should include support on a modest basis through four to seven years of further education. The recipient in return would agree to make himself available in time of national emergency for national service under whatever conditions the Government should then set.

Doctor Conant's suggestion is a practical one for obtaining an adequate number of well-qualified students of chemistry, chemical engineering, and the other branches of science and engineering. There is still, however, the necessity of securing more adequate numbers of capable instructors and assistant and associate professors in the postwar period. The solution of this problem has been made much more difficult because our technical schools and colleges have been stripped of most of the younger members of the teaching staffs as a result of the drafting of students and instructors and the demands of war research and production.

To make certain that we have well-rounded teaching staffs in our schools of chemistry and chemical engineering in the years to come, we must provide by one means or another higher rates of compensation, salaries more in line with what industry is willing to pay.

Unfortunately, our chemistry and chemical engineering teaching staffs are frequently tied into the schools of arts and sciences, and salary ranges on such staffs are based largely, if not wholly, on what the going rate is for teachers of languages, history, economics, etc., rather than bearing any relation to what the chemical and closely allied fields are paying for individuals of comparable ability. This is the principal reason why the teaching staffs in our schools of medicine and law receive much higher salaries than men devoting their lives to turning out chemists and chemical engineers.

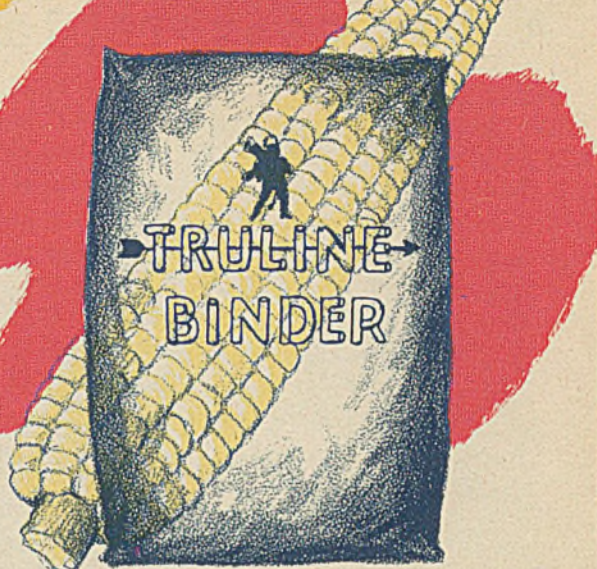
Industry has a direct stake in the end product of our technical schools and colleges and the chemical industry should consider very seriously ways and means of raising funds to increase the incomes of young instructors and assistant and associate professors. No plans have been formulated, but we are encouraged to learn that important leaders in the chemical industry are giving considerable thought to this problem.

Planning Postwar Germany

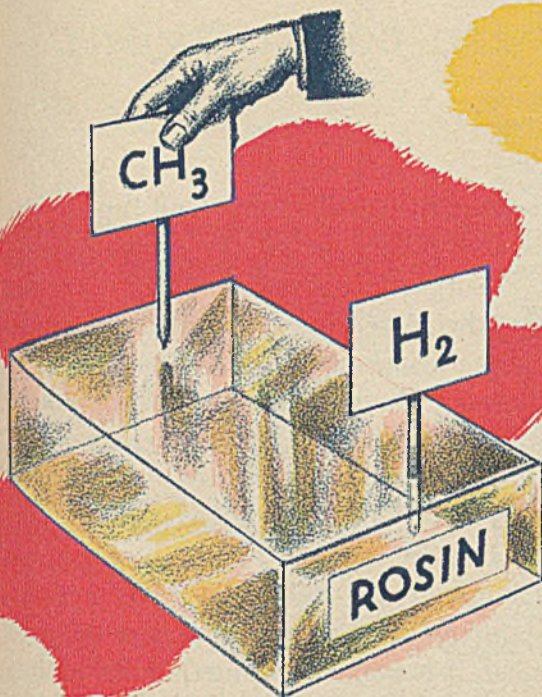
THE idea of turning a nation of some 80,000,000 people, in fact the most industrialized nation in Europe, into an agricultural country exclusively is utter nonsense. We are, indeed, admitting complete mental bankruptcy if this is the only plan we can devise to assure peace in Europe. Germany's criminal and militaristic classes must be punished according to their crimes against civilization. Her industries must be directly supervised for many years to come by scientifically trained individuals who will be able to detect and prevent the prostitution of science and industry for war purposes. She must provide the labor to help restore the devastated countries, the close tie between the military and industry must be eliminated, and the large trusts broken up. This, together with gradual re-education of the German masses, constitutes the best means of preventing another world holocaust. Now is the time when our scientific leadership must assume a great responsibility and statesmen must accord it an opportunity to assist in maintaining the peace of the world.

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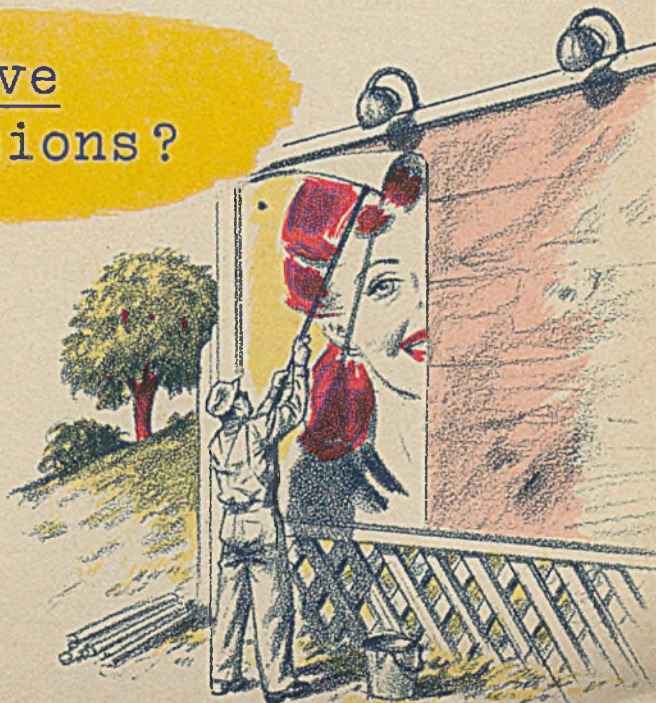


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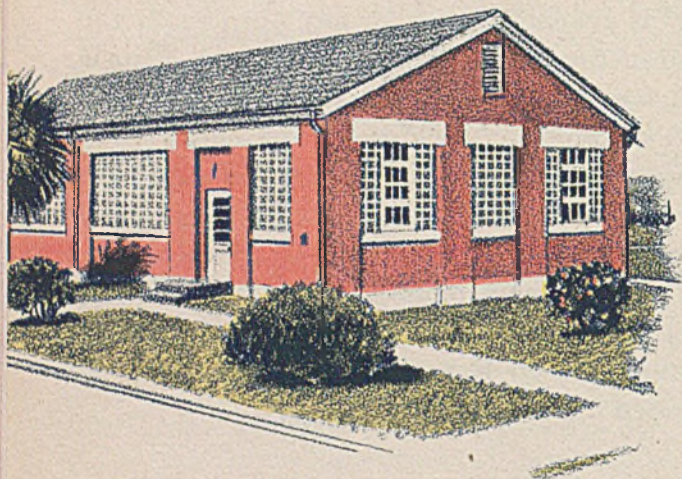


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AZEOTROPIC DISTILLATION

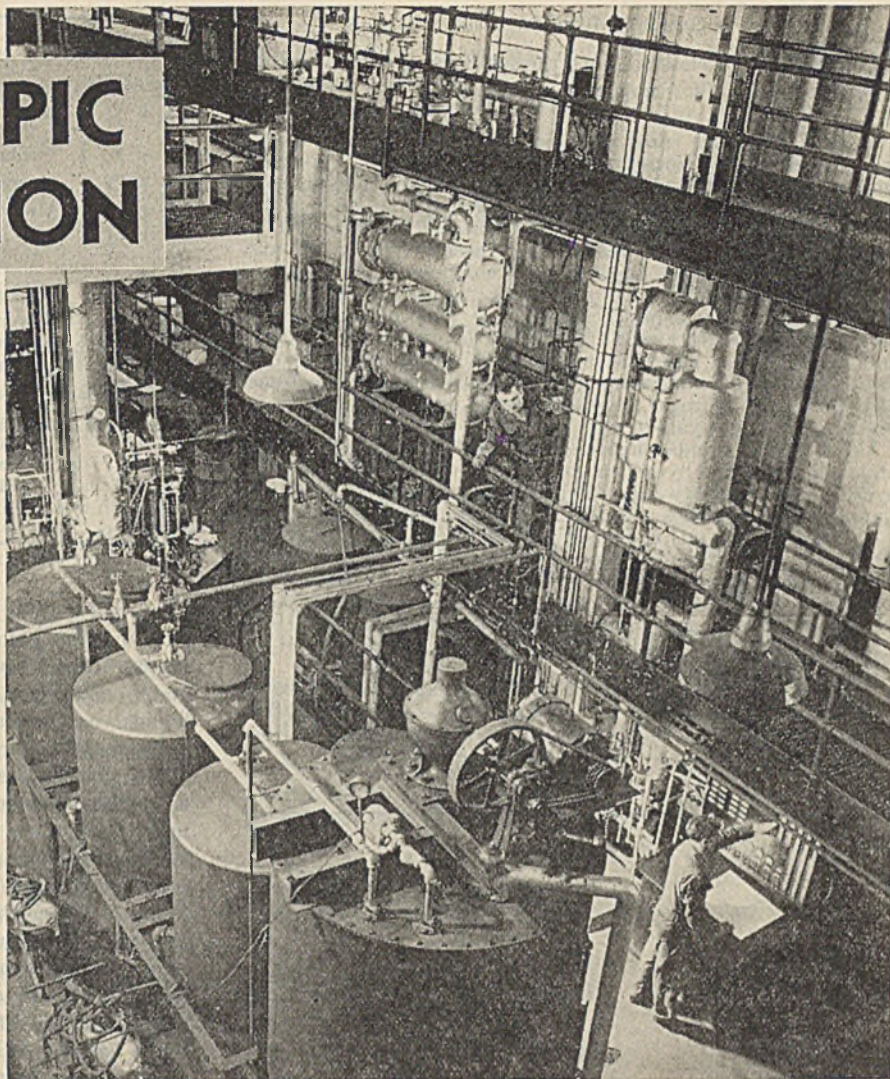
R. H. Ewell

PURDUE UNIVERSITY, LAFAYETTE, IND.
(Present Address, National Defense Research
Committee, Washington, D. C.)

*J. M. Harrison and
Lloyd Berg*

GULF RESEARCH & DEVELOPMENT
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Liquids may be divided into five classes based on their hydrogen-bond-forming tendencies. On the basis of this classification, a systematic summary of deviations from Raoult's law can be derived and the tendency for the formation of azeotropes can be predicted. This summary will minimize the experimental work required in the selection of an entrainer to effect a desired separation by azeotropic distillation. ~ Gulf's pilot plant for azeotropic distillation is shown at the right.



AZEOTROPIC is the term applied to distillations or rectifications which involve the formation of constant-boiling mixtures. The word "azeotrope" is synonymous with "constant-boiling mixture". An understanding of azeotropes is desirable for two reasons. First, they often occur in fractionation and make a given separation impossible by ordinary rectification. Secondly, they may be utilized to separate mixtures not ordinarily separable by straight rectification.

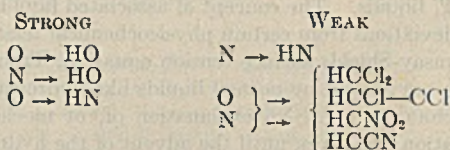
The formation of constant-boiling mixtures is a function of the difference in temperature between the two components and the nonideality of the resulting solution. In an ideal solution there is no change in the average intermolecular forces of attraction on mixing; there is no change in internal energy or in volume, no heat is absorbed or evolved, and the vapor pressure of the mixture is a linear function of the molar composition (Raoult's law). Raoult's law is sometimes taken as the definition of an ideal solution; although it is necessary, it is not a sufficient condition.

Since the formation of constant-boiling mixtures is a function of the nonideality of the mixture, a correlation of the deviations from ideality for various mixtures would greatly aid in the prediction and selection of azeotrope formers.

Many attempts have been made to predict and correlate the phenomenon of constant-boiling mixtures (1, 3, 4, 5, 7, 9, 10, 12). In the light of present knowledge on the subject, the deviation from ideality can be attributed to the effects of hydrogen bonds

or internal pressure, of which the former is the more important. The concept of hydrogen bonds (Figure 1) is that hydrogen can coordinate between two molecules of oxygen, nitrogen, or fluorine. It can also coordinate between one of these donor atoms (oxygen, nitrogen, or fluorine) and a carbon atom, provided a sufficient number of negative atoms or groups are attached to the carbon atom. Hydrogen cannot coordinate between two carbon atoms.

The strength of hydrogen bonds depends upon the nature of the atoms between which the hydrogen is coordinating. They may be classified generally into strong bonds and weak bonds as follows:



Based on hydrogen bonds, it is possible to arrange organic liquids into five classifications. It is then possible to generalize regarding binary systems composed of combinations of these classes. Thus, by assigning two liquids to their proper hydrogen bond classes, the nature of the deviations from ideality and the likelihood of azeotrope formation may be predicted.

CLASSIFICATION OF LIQUIDS

Liquids may be classified into the following groups based on their potentialities for forming hydrogen bonds:

CLASS I. Liquids capable of forming three-dimensional networks of strong hydrogen bonds—e.g., water, glycol, glycerol, amino alcohols, hydroxylamine, hydroxy acids, polyphenols, amides, etc. Compounds such as nitromethane and acetonitrile also form three-dimensional networks of hydrogen bonds, but the bonds are much weaker than those involving OH and NH groups. Therefore, these types of compounds are placed in class II.

CLASS II. Other liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen, and fluorine)—e.g., alcohols, acids, phenols, primary and secondary amines, oximes, nitro compounds with α -hydrogen atoms, nitriles with α -hydrogen atoms, ammonia, hydrazine, hydrogen fluoride, hydrogen cyanide, etc.

CLASS III. Liquids composed of molecules containing donor atoms but no active hydrogen atoms—e.g., ethers, ketones, aldehydes, esters, tertiary amines (including pyridine type), nitro compounds and nitriles without α -hydrogen atoms, etc.

CLASS IV. Liquids composed of molecules containing active hydrogen atoms but no donor atoms. These are molecules having two or three chlorine atoms on the same carbon as a hydrogen atom, or one chlorine on the same carbon atom and one or more chlorine atoms on adjacent carbon atoms—e.g., CHCl_3 , CH_2Cl_2 , CH_2CHCl_2 , $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, $\text{CH}_2\text{Cl}-\text{CHCl}-\text{CH}_2\text{Cl}$, $\text{CH}_2\text{Cl}-\text{CHCl}_2$, etc.

CLASS V. All other liquids—i.e., liquids having no hydrogen-bond-forming capabilities—e.g., hydrocarbons, carbon disulfide, sulfides, mercaptans, halohydrocarbons not in class IV, non-metallic elements such as iodine, phosphorus, sulfur, etc.

Table I. Summary of Deviations from Raoult's Law

CLASSES	DEVIATIONS	HYDROGEN BONDING
I + V	Always + deviations; I + V, frequently limited solubility	H bonds broken only
II + V		
III + IV	Always - deviations	H bonds formed only
I + IV	Always + deviations; I + IV, frequently limited solubility	H bonds both broken and formed, but dissociation of class I or II liquid is more important effect
II + IV		
I + I	Usually + deviations, very complicated groups, some - deviations give some max. azeotropes	H bonds both broken and formed
I + II		
I + III		
II + II		
II + III		
III + III	Quasi-ideal systems, always + deviations or ideal; azeotropes, if any, will be minima	No H bonds involved
III + V		
IV + IV		
IV + V		
V + V		

water will dissolve in water (or tend to dissolve in water). Class II liquid—e.g., alcohols—can form hydrogen bonds with water in two ways: from oxygen of water to hydrogen of alcohol, and from oxygen of alcohol to hydrogen of water. Class III liquids—e.g., ketones—can form hydrogen bonds with water in only one way: from oxygen of ketone to hydrogen of water. While all class II and class III liquids tend to dissolve in water, the extent to which they actually do dissolve depends on how many CH_2 groups have to be pulled into solution by the hydrogen-bond-forming groups. For instance, the lower alcohols are completely soluble in water—*n*-butyl about 10%, *n*-amyl about 3%, etc. When the hydrocarbon part of the molecule is so large that the solubility is very small—e.g., decyl alcohol—the tendency of the hydrogen-bond-forming group to dissolve in water causes the liquid to form a monomolecular oriented layer on the water surface. Ethyl ether is soluble in water only about 7%, but it has four CH_2 groups to pull into solution just as *n*-butyl alcohol does. However, methyl ether with only two CH_2 groups and dioxane with four CH_2 groups, but two ether oxygens, are completely soluble in water. Even high-molecular-weight substances, such as carbohydrates, proteins, gums, and other hydrophilic materials, are soluble in water since they can form many hydrogen bonds per molecule.

The old generalization that polar substances dissolve polar substances and nonpolar dissolve nonpolar is obviously incorrect. This generalization is based on a few fragmentary observations such as the following: Water (polar) dissolves glycerol (polar); benzene (nonpolar) dissolves naphthalene (nonpolar); water (polar) does not dissolve benzene (nonpolar). The following, however, are contrary: Water (polar, $\mu = 1.8$) does not dissolve ethyl iodide (polar, $\mu = 1.8$). Ethyl iodide (polar, $\mu = 1.8$) does dissolve naphthalene (nonpolar, $\mu = 0$). Water (polar, $\mu = 1.8$) does dissolve pyrazine (nonpolar, $\mu = 0$).

These examples further demonstrate the idea developed above that solubility is largely a hydrogen bond phenomenon and has little, if any, relation to polarity (dipole moment) of substances. Where hydrogen bonds are not involved, solubility is determined by internal pressures, and the internal pressure also has a minor effect on solubility when hydrogen bonding is the dominating factor. Any correlation of properties such as solubility, vapor pressure, etc., based on internal pressures of the components of the binary mixtures would hold only when no hydrogen bonds are either broken or formed on mixing. Internal pressure data measured from the properties of two pure compounds cannot be expected to apply to the binary mixture when additional and probably dominant forces of hydrogen bonds are created upon mixing.

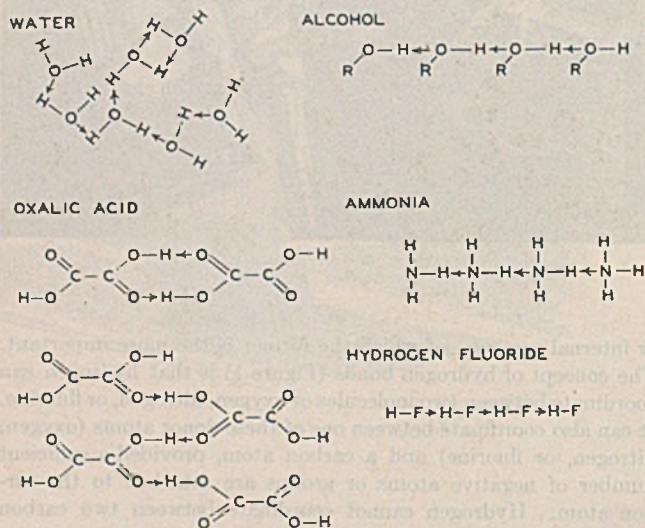


Figure 1. Concept of Hydrogen Bonds

Classes I and II include the liquids usually called "associated" or "abnormal" liquids. The concept of associated liquids has been based on deviations from certain physicochemical relations, such as the Ramsay-Shields surface tension equation, Trouton's rule, etc., which are obeyed by normal liquids like hydrocarbons, carbon tetrachloride, etc. No explanation of, or mechanism for, the association was given until the advent of the hydrogen bond concept, although the general relation to the presence of OH and NH groups had been recognized for some time. The term "hydrogen-bonded liquid" should now replace "associated liquid", although the term "association" should still prove useful to describe the general phenomenon. Class I and class II liquids have relatively high dielectric constants.

Classes I, II, and III include water-soluble substances. In general, any liquid (or solid) that can form hydrogen bonds with

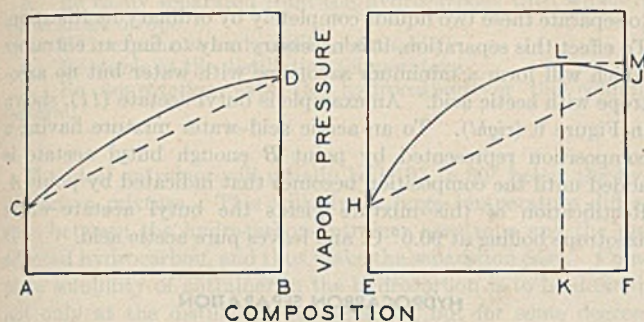


Figure 2. Vapor Pressure Curves

When deviations from ideal are insufficient to give an azeotrope, pure component *B* has the highest vapor pressure, *D*. When deviations are sufficient to give an azeotrope, some mixture of components *E* and *F*, such as *K*, will have the highest vapor pressure, *M*.

The solubility of ionic substances, such as salts, is determined by the dielectric constant of the solvent; and since hydrogen-bonded liquids have high dielectric constants, they are more or less solvents for salts.

Class IV liquids might be expected to be soluble in water, but the hydrogen bonds formed between water and these liquids (from oxygen of water to active hydrogen of class IV liquid) would be quite weak and do not compensate for its water hydrogen bonds which are broken.

Class V liquids are all very insoluble in water, since many of the water hydrogen bonds would have to be broken to make room for the class V molecules and no compensating hydrogen bonds are formed.

By this system of classification it is possible to predict the nature of the deviations from Raoult's law, and the hydrogen bonding in a mixture makes it possible to judge approximately the extent of these deviations. The actual formation of an azeotrope or constant-boiling mixture depends upon (a) the magnitude of the deviations from Raoult's law and (b) the difference in boiling point between the two pure components. The smaller the deviations from Raoult's law for a pair of substances, the smaller the difference in boiling point must be before an azeotrope will form (Figure 2).

When a system which shows positive (+) deviations from Raoult's law forms an azeotrope, it will be a minimum-boiling azeotrope. When the deviations are negative (-), the azeotrope, if formed, will be maximum-boiling. On the basis of the liquid classification presented above, a systematic summary of deviations from Raoult's law is derived in Table I. These rules may be exemplified by the following actual cases.

An example of II + V is ethanol (class II) and benzene (class V) which gives a minimum azeotrope boiling at 68.2° C. and containing 44.8 mole % ethanol.

An example of III + IV is acetone (class III) and chloroform (class IV) which gives a maximum azeotrope boiling at 64.5° C. and containing 34.5 mole % acetone.

Boiling point relations for water solutions are well known. The minimum constant-boiling mixture ethanol-water, boiling at 78.1° C. and yielding 89.2 mole % ethanol, is an example of I + II. The minimum constant-boiling mixture 1,4-dioxane-

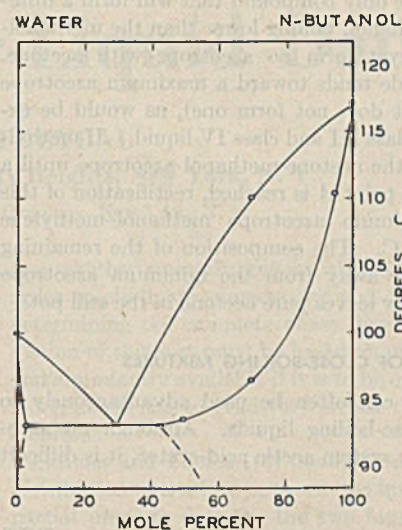
water, boiling at 87.8° C. and having a composition of 47 mole % dioxane (13), is an example of I + III. Water forms a few maximum azeotropes with certain compounds—for instance, with formic acid, ethylenediamine, and hydrazine. Water also forms maximum azeotropes with the strong acids—hydrochloric, hydrobromic, hydriodic, and nitric. Because of the insolubility of class IV and class V liquids in water, heterogeneous or two-phase minimum azeotropes are invariably formed by these classes of compounds with water.

An example of II + III is methanol (class II) and acetone (class III) which gives a minimum azeotrope boiling at 54.6° C. and containing 14 mole % methanol. The dissociation of the methanol is the principal effect.

An example of binary mixtures consisting of class II and class IV liquids is methanol (class II) and chloroform (class IV) which yields a minimum azeotrope boiling at 53.5° C. and containing 35 mole % methanol.

All combinations of class III, IV, and V liquids, except III + IV, are quasi-ideal solutions and only occasionally show a minimum azeotrope. They occur when the boiling points of the two constituents are very close. An example of III + V which gives a minimum azeotrope is acetone (class III) and *n*-hexane (class V), boiling at 49.8° C. and containing 68 mole % acetone. An example of two class V liquids forming a minimum azeotrope is benzene-methylcyclopentane boiling at 71.4° C. and containing 90 mole % methylcyclopentane (2). These azeotropes are caused by internal pressure differences (Table II).

Minimum azeotropes are much more numerous than maximum azeotropes. About three thousand minimum azeotropes have been recorded in the literature but only about two hundred fifty maximum azeotropes (6). All known maximum azeotropes may be classified as follows; as far as present knowledge goes, all other combinations of liquids yield minimum azeotropes, if any:

Figure 3. Diagram of a Heterogeneous Azeotrope, Water-*n*-Butanol

1. Water + strong acids—e.g., water + HCl, HBr, HI, HNO₃.

2. Water + certain associated liquids—e.g., water + formic acid, hydrazine, ethylenediamine.

3. Donor liquids (class III) + non-associated liquids containing active hydrogens (class IV)—e.g., acetone + chloroform, cyclohexanone + bromoform, butyl acetate + 1,2,2-trichloropropane.

4. Organic acids + amines—e.g., acetic acid + triethylamine, propionic acid + pyridine.

5. Phenols + amines—e.g.,

phenol + aniline, *o*-cresol + dimethylaniline.

6. Organic acids + donor liquids containing oxygen—e.g., formic acid + diethyl ketone, butyric acid + cyclohexanone.

7. Phenols + donor liquids containing oxygen—e.g., phenol + methylhexylketone, *o*-cresol + ethyl oxalate.

8. Phenols + alcohols—e.g., phenol + *n*-octanol, *o*-cresol + glycol.

The above discussion applies only to homogeneous azeotropes. Limited solubility always gives heterogeneous minimum azeotropes. An example of a heterogeneous azeotrope is shown in Figure 3 for water (class I) and *n*-butanol (class III) (14). All maximum azeotropes are homogeneous.

Table II. Internal Pressures

Compound	Atmospheres	Compound	Atmospheres
Neopentane	1,535	Carbon disulfide	4,140
Isopentane	1,842	Bromoform	4,220
<i>n</i> -Pentane	2,020	Methylene iodide	4,950
<i>n</i> -Octane	2,420	Bromine	5,700
Cyclohexane	2,780	Phosphorus	7,000
Carbon tetrachloride	3,070	Sulfur	7,420
Ethyl bromide	3,150	Iodine	7,600
Benzene	3,450	Mercury	38,750
Iodobenzene	3,640	Sodium chloride	72,900
Acetone	3,940		

ENTRAINERS

The purpose of an entrainer in azeotropic distillation is either to separate one component of a closely boiling pair or to separate one component of an azeotrope. In ordinary batch rectification it is necessary to produce minimum-boiling azeotropes to affect the distillation favorably. Since the lowest boiling component or the minimum azeotrope boils first, the formation of maximum boiling azeotropes will have no effect on the course of distillation.

The general methods of using entrainers to effect a separation may be summarized as follows:

1. To separate a closely boiling pair or a maximum azeotrope:
 - a. The entrainer forms a binary minimum azeotrope with only one component.
 - b. The entrainer forms binary minimum azeotropes with each component, but one minimum is sufficiently lower than the other.
 - c. The entrainer forms a ternary minimum azeotrope which is sufficiently lower than any binary azeotropes. The ratio of the original components in the ternary must be different from their ratio before the entrainer was added.
2. To separate a minimum azeotrope:
 - a. The entrainer forms a binary minimum azeotrope with one component which is sufficiently lower than the original minimum azeotrope.
 - b. The entrainer forms a ternary minimum azeotrope which is sufficiently lower than any binary minimum azeotrope and in which the ratio of the original components is different from their ratio in the binary minimum azeotrope.

SEPARATION OF AZEOTROPES

Figure 4 (left) indicates graphically how the minimum azeotrope acetone-methanol can be separated by azeotropic distillation. Methanol and acetone form a minimum azeotrope boiling at 54.6° C. and containing 86 mole % acetone. Methylene chloride appears to be the only compound that will form a minimum azeotrope with methanol, boiling lower than the methanol-acetone azeotrope, and yet form no azeotrope with acetone. Indeed, methylene chloride tends toward a maximum azeotrope with acetone (although it does not form one), as would be expected of a mixture of a class III and class IV liquid. If methylene chloride is added to the acetone-methanol azeotrope until a composition indicated by point A is reached, rectification of this mixture yields the minimum azeotrope methanol-methylene chloride boiling at 39.2° C. The composition of the remaining liquid moves rectilinearly away from the minimum azeotrope composition and ultimately leaves pure acetone in the still pot.

SEPARATION OF CLOSE-BOILING MIXTURES

Azeotropic distillation can often be used advantageously to separate mixtures of close-boiling liquids. Although no azeotrope forms in the binary system acetic acid-water, it is difficult

to separate these two liquids completely by ordinary rectification. To effect this separation, it is necessary only to find an entrainer which will form a minimum azeotrope with water but no azeotrope with acetic acid. An example is butyl acetate (11), shown in Figure 6 (right). To an acetic acid-water mixture having a composition represented by point B enough butyl acetate is added until the composition becomes that indicated by point A. Rectification of this mixture yields the butyl acetate-water azeotrope boiling at 90.6° C. and leaves pure acetic acid.

HYDROCARBON SEPARATION

Hydrocarbons usually occur as mixtures, and the isolation of a relatively pure compound from other similar-boiling hydrocarbons is a problem of considerable importance. The manufacture of butadiene, benzene, toluene, and xylene from petroleum fractions, to mention just a few, necessitates separations from similar-boiling hydrocarbons.

A given entrainer may form azeotropes with each type of hydrocarbon in a specific boiling range; however, the azeotropes will not all have the same boiling point. The amount of lowering between the boiling points of the hydrocarbons and their azeotropes increases in the order aromatic, olefin, naphthene, paraffin (8). Such an entrainer, which forms azeotropes with all the hydrocarbon types, is referred to as a nonselective entrainer.

Some liquids, however, form azeotropes with some types and fail to form azeotropes with other types of hydrocarbons in the same boiling range. Such a liquid is known as a selective entrainer. For example, all the types of hydrocarbons (paraffin, naphthene, olefin, aromatic) boiling in the range 100–110° C. form minimum azeotropes with methanol, a nonselective entrainer. Methyl ethyl ketone, on the other hand, is a selective entrainer for this range of hydrocarbons; it forms minimum azeotropes with the paraffin, naphthene, and olefin types but not with the toluene.

The proximity of the boiling points of the entrainer and the hydrocarbons is important in selecting an entrainer. When the boiling point of an entrainer is considerably below that of a close-boiling hydrocarbon mixture, first, the azeotrope boils a few degrees below the pure entrainer to give a large spread between the undesired hydrocarbon azeotrope (nonaromatic) and the desired hydrocarbon (aromatic); secondly, the composition of the azeotrope is low in removed hydrocarbon. On the other hand, when the boiling point of an entrainer is considerably above that of a close-boiling hydrocarbon mixture, first, the azeotrope boils but a few degrees below the hydrocarbon mixture to give a small spread between the nonaromatic azeotrope and the aromatic compound; secondly, the composition of the azeotrope is high in removed hydrocarbon. Thus both lower- and higher-boiling entrainers have advantages. Since a successful azeotropic distillation must effect a greater ease of separation than is possible by ordinary, fractional distillation, temperature spread must be obtained even at some sacrifice of hydrocarbon recovery efficiency. A commercially suitable entrainer, therefore, invariably has a boiling point below that of the hydrocarbon mixture to be separated.

Entrainers suitable for the separation of close-boiling hydrocarbon mixtures show the following desirable properties (8):

1. Boil within a limited range (0–30° C.) of the hydrocarbon which it is desired to separate.
2. Form, on mixing with the hydrocarbon a large positive deviation from Raoult's law, to give a minimum azeotrope with one or more of the hydrocarbon types in the mixture.
3. Be soluble in the hydrocarbon at the distillation temperature and for some degrees below it.

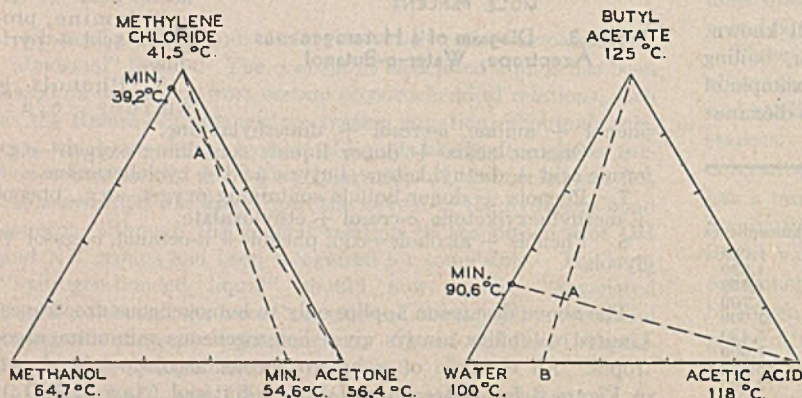


Figure 4. Separation of Azeotropes

4. Be easily separated from the hydrocarbons with which it forms an azeotrope.
5. Be inexpensive and readily obtainable.
6. Be stable at the distillation temperature.
7. Be nonreactive with the hydrocarbons or the column material.

The ideal entrainer will usually boil 10° to 30° below the hydrocarbon mixture. This will give a large temperature difference between the hydrocarbon-entrainer azeotrope and the unaffected hydrocarbon, and thus make the separation easy. Complete solubility of entrainer in the hydrocarbon is to be desired, not only at the distillation temperature, but for some degrees below it, so that two phases will not exist at reflux in the overhead assembly.

In a commercial process it is necessary to recover the entrainer from the azeotrope in order to recycle it to the azeotroping column. This is an economic aspect and demands an entrainer which can be separated easily and cheaply. The easiest separation occurs when the entrainer and hydrocarbon are insoluble at room temperature. When they are miscible, it is desirable that the entrainer be water soluble so that water washing can be accomplished. The water-entrainer mixture should be easily separated. In the case where the entrainer is water insoluble, a different washing component must be used. It should be inexpensive and easily removed from the entrainer.

A hydrocarbon mixture to be separated by azeotropic distillation should be a close-boiling fraction. This can be accomplished by fractional distillation into concentrates prior to azeotropic distillation. Contamination with material of a different boiling range tends to nullify the effects obtained by azeotroping.

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TERNARY LIQUID EQUILIBRIA

Predicted from Binary Vapor-Liquid Data

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THE increasing use of the unit operation liquid-liquid extraction as a means of separating the components of a binary solution has made it necessary to have at hand for design purposes a large amount of solubility data for ternary liquid systems. The lack of such data will prevent the application of the various design methods which have been described in detail (18); for the proper evaluation of a proposed solvent extraction process, the complete ternary liquid phase diagram must be known. In the absence of such data, it will frequently be desirable to predict from the properties of the components of a sys-

tem whether a certain solvent will be useful in such processes, in order to eliminate unnecessary and tedious laboratory work in determining the complete phase diagram. Any method of prediction of this sort must be based on properties which are readily and abundantly available if it is to be of general utility. Furthermore, unless it is to yield very precise results, it should not be too laborious.

Othmer and Tobias (16) described a method of predicting the distribution of a solute between two immiscible solvents based on partial pressure data for the two binary solutions formed with

The graphical method proposed by Hildebrand (10) for predicting ternary liquid equilibria from activity coefficients of binary solutions has been applied to a number of systems, using constant pressure and constant temperature vapor-liquid equilibrium data, and azeotropic measurements. No data on the ternary system are necessary for its application. The results at low concentration compare favorably with the observed data, and prove the method to be reliable in predicting which solvent will be useful in solvent extraction processes. The use of the van Laar equations for extending the applicability of the method is discussed. Two modifications to allow for mu-

tual solubility of the contacted solvents are tested; these frequently reproduce the distribution curve at high concentrations more accurately and thus make it possible to estimate roughly the position of the plait point. A simple analytical method of calculating an index of the usefulness of a proposed solvent in extraction processes for which no ternary data are available is described. The distribution coefficient of Hand (9) is shown to be predictable in certain cases. A modification of his empirical method of plotting distribution data is presented which makes it possible, in the case of some systems, to determine accurately the distribution curve with one measured tie line.

the solute and the two solvents. Perhaps a more generally applicable method, described by Hildebrand (10) and applied by him to one system, was referred to by Carlson and Colburn (7). It is based on the departure from ideality of the two binary solutions of the distributed solute and the immiscible solvents, and utilizes the fact that the activity of the distributed solute must be the same at equilibrium in the two immiscible solutions.

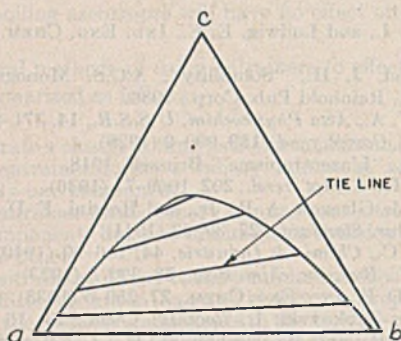


Figure 1. Typical Ternary Phase Diagram for Solvent Extraction Processes

Since there is a wealth of data with which to calculate activity coefficients, and hence activities, of binary solutions, the method becomes a powerful tool in predicting the usefulness of solvents in solvent extraction processes. The principal purpose of this paper is to investigate the general reliability of the method and certain of its modifications when the activity coefficients are calculated from vapor-liquid equilibrium data of the two binary solutions.

The ternary systems most frequently encountered have isothermal phase diagrams of the general triangular type shown in Figure 1. Component *c* is the solute distributed between the substantially immiscible solvents *a* and *b*. The area under the curve is a two-liquid area, and solutions at equilibrium are joined by tie lines. As the concentration of *c* increases, the mutual solubility of *a* and *b* increases, until finally the system becomes completely miscible at high concentrations of *c*. The slope of the tie lines is an important property of this diagram. If the tie lines slope downward toward the *a* apex, as in Figure 1, then *b* can be used for separating solutions of *a* and *c*. If their slope is toward the *b* apex, then *a* is useful in separating solutions of *b* and *c*. This can be shown more conveniently by plotting a simple equilibrium distribution curve, where the concentrations of *c* in the *a*-rich layer are plotted as ordinate against the concentrations of *c* in the *b*-rich layer as abscissa. If the resulting curve has a slope greater than unity, then component *a* can be used to extract *c* from *bc* solutions, and the greater the slope, the more useful will *a* become. The slope of the distribution curve becomes, therefore, an index (16) of the usefulness of solvent *a*.

PREDICTION FROM BINARY VAPOR-LIQUID EQUILIBRIA

Method 1, proposed by Hildebrand (10), for predicting the distribution curve just described, ignores the mutual solubility of *a* and *b*. From the vapor-liquid equilibrium data of binary solutions *ac*, the activity coefficients, or the departure from ideality, of *a* and *c* in these solutions are calculated by methods to be discussed later. For this purpose boiling-point curves, partial or total vapor pressure data of the binary solutions, or even azeotropic data can be used, and they are extensively available. A plot of these activity coefficients against concentrations will frequently have the general appearance indicated in Figure 2, although occasionally the values of $\log \gamma$ will be negative. Similar data are calculated for the binary system *bc*. Although only the values of γ_{31} and γ_{32} are necessary, any thermodynamic

inconsistencies in the data will be immediately evident (7) if γ_{11} and γ_{22} are also calculated, and consequently some estimate of the reliability of the data can be made. From the smoothed plots, values of the activity of *c* in the two binary solutions are calculated:

$$\alpha_{31} = \gamma_{31}x_{31} \quad (1)$$

$$\alpha_{32} = \gamma_{32}x_{32} \quad (2)$$

On a single sheet of graph paper, a plot is made of α_{31} against x_{31} and α_{32} against x_{32} , giving rise to curves of the type of Figure 3, although the relative positions of the curves may be reversed from that shown. From these, at equal values of α_{31} and α_{32} it is possible to read corresponding values of x_{31} and x_{32} , the predicted equilibrium concentrations of *c* in the *a*- and *b*-rich layers, respectively, and to plot a distribution curve with x_{31} as ordinate.

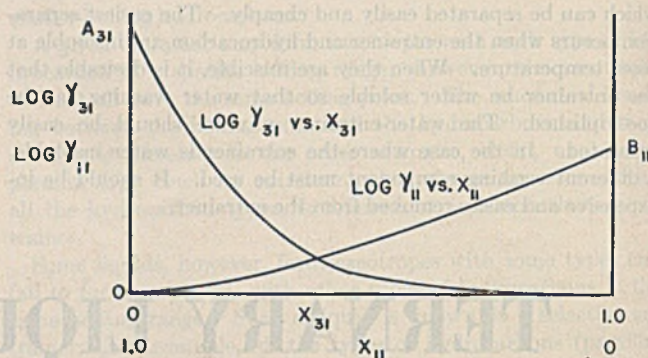


Figure 2. Activity Coefficients for Binary System *ac*

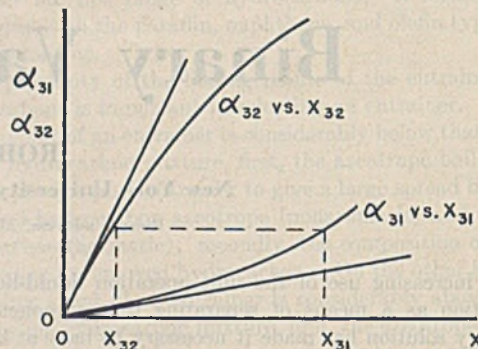


Figure 3. Activity-Concentration Curves for Binary Systems *ac* and *bc*

If curves of the type of Figure 3 result, it is evident that the slope of the distribution curve will exceed unity, and *a* will be a useful solvent for separating mixtures of *b* and *c*, from the point of view of extraction equilibrium at least. The principal feature of this method lies in the fact that no previous knowledge of the nature of the ternary diagram is necessary.

EFFECT OF HIGH SOLUTE CONCENTRATIONS

Method 1 must become an approximation, at best, when the mutual solubility of components *a* and *b* becomes appreciable. Although the distribution curve previously described ordinarily has a slope different from unity at the origin, it must, for a system of the type indicated in Figure 1, eventually meet the line $x_{31} = x_{32}$ at a concentration of *c* less than 100% (the plait point). In so doing, it will frequently go through a maximum in either x_{31} or x_{32} . Knowledge of this effect of mutual solubility, even approximately, prior to the actual experimental determination of *a*

complete phase diagram is desirable, since solvent extraction processes should not operate at concentrations of c near the plait point. Method 1 ordinarily will not yield this information. Accordingly, two empirical modifications, to take into consideration the increased mutual solubility of the initially immiscible solvents have been attempted.

Method 2 is a simple modification which may be used if the solubility curve of the ternary system (without tie lines) is available. It is based on the assumption that the activity of c in the a -rich layer, when determined from curves of the type of Figure 2 calculated from the properties of binary ac , are properly a function of the effective solute concentration $x_{31}/(x_{31} + x_{11})$ rather than simply x_{31} . Accordingly, Figures 2 and 3 are plotted as before, with data from binary solutions ac and bc . From the concentrations along the ternary solubility curve, ratios $x_{31}/(x_{31} + x_{11})$ for the a -rich solutions are calculated. With these as abscissas, from Figure 3 the predicted values of $x_{32}/(x_{32} + x_{22})$ at equilibrium in the b -rich layer are obtained at equal values of α_{31} and α_{32} . These can be converted to predicted equilibrium values of x_{32} in the b -rich layer by reference to a curve of x_{32} against $x_{32}/(x_{32} + x_{22})$ calculated from the solubility curve of the b -rich solutions. Again a predicted distribution curve can be plotted.

Method 3 attempts empirically to make still further correction for the increased mutual solubility of the initially immiscible solvents, and again requires that the ternary solubility curve be available. Carlson and Colburn (7) suggest that for ternary solutions, in some instances, an interpolation of the logarithms of γ_3 is satisfactory between values in binary mixtures ac and bc , depending on the relative amounts of a and b present. Accordingly, curves of $\log \gamma_3$ against x_3 are plotted as before, from data on the binary solutions. Assuming the ternary solubility curve to be available, values of x_{11} , x_{21} , and x_{31} for a single point in the a -rich layer will be known. With x_{31} as abscissa, reference to the activity coefficient curve of the type of Figure 2 ($\log \gamma_{31}$ against x_{31}) will give a value of $\log \gamma_{31}$. Using the same value of x_{31} as abscissa, the activity coefficient curve, $\log \gamma_{32}$ against x_{32} , will give a value of $\log \gamma_{32}$. A weighted average is made so that

av. $\log \gamma_{31} =$

$$\log \gamma_{31} + \left(\frac{x_{21}}{x_{11} + x_{21}} \right) \times (\log \gamma_{32} - \log \gamma_{31}) \quad (3)$$

and an average value of α_{31} can be obtained. The procedure is repeated for b -rich solutions:

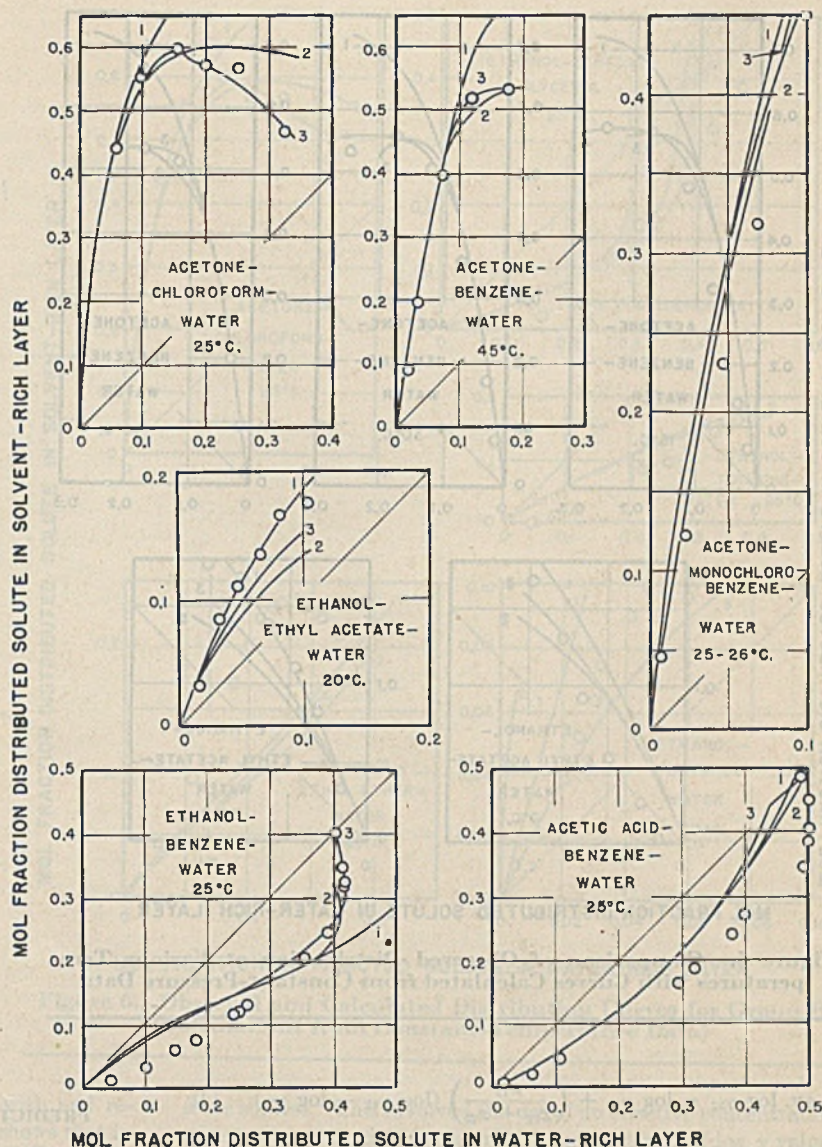


Figure 4. Observed and Calculated Distribution Curves for Group A (Calculations from Constant-Pressure Data)

TABLE I. GROUPING OF SYSTEMS ACCORDING TO VAPOR-LIQUID DATA

Distributed Solute c Solvent a -Solvent b	Ternary Liquid Temp., ° C.	Vapor-Liquid Data					
		Binary ac			Binary bc		
		Mm. Hg.	° C.	Cita- tion	Mm. Hg.	° C.	Cita- tion
GROUP A							
Acetone-chloroform-water	25(9)	760	56.2-64.4	(18)	760	56.5-100	(6)
Ethanol-benzene-water	25(20)	750	67.8-79.7	(18)	760	78.3-100	(12)
Ethanol-ethylacetate-water	0, 20(5)	760	71.8-78.3	(18)	760	78.3-100	(12)
Acetone-benzene-water	15, 30, 45(6)	760	56.1-80.1	(16)	760	56.5-100	(6)
Acetone-monochlorobenzene-water	25-26(17)	760	56.1-131.6	(16)	760	56.5-100	(6)
Acetic acid-benzene-water	25(9)	760	80.2-118.7	(18)	760	100-118.1	(18)
GROUP B							
Acetone-chloroform-water	25(9)	248.4-344.5	35.17	(26)	23.7-229.6	25	(2)
Ethanol-toluene-water	25(23)	93.0-249.2	32.3 ^a	(11)	17.5-44.2	20	(11)
Ethanol-benzene-glycerol	25(14)	103-198	34.8 ^a	(11)	<0.002-32.5	15 ^a	(11)
Ethanol-ethyl ether-water	25(11)	59.7-537	25.0 ^a	(11)	17.5-44.2	20	(11)
Ethanol- <i>n</i> -butanol-water	20(8)	760	79.1-114.3	(6)	17.5-44.2	20	(11)
GROUP C							
Ethanol-cyclohexane-water	25(21)	760	64.9 ^b	(18)	17.5-44.2	20	(11)
Isopropanol-ethylacetate-water	20(3)	760	74.8 ^b	(18)	760	80.04-100	(6)
Isopropanol-toluene-water	25(22)	760	80.6 ^b	(18)	760	80.04-100	(6)
<i>tert</i> -Butanol-ethylacetate-water	20(3)	760	75.2 ^b	(11)	760	79.91 ^b	(11)

^a Total pressure data reported.

^b An azeotrope.

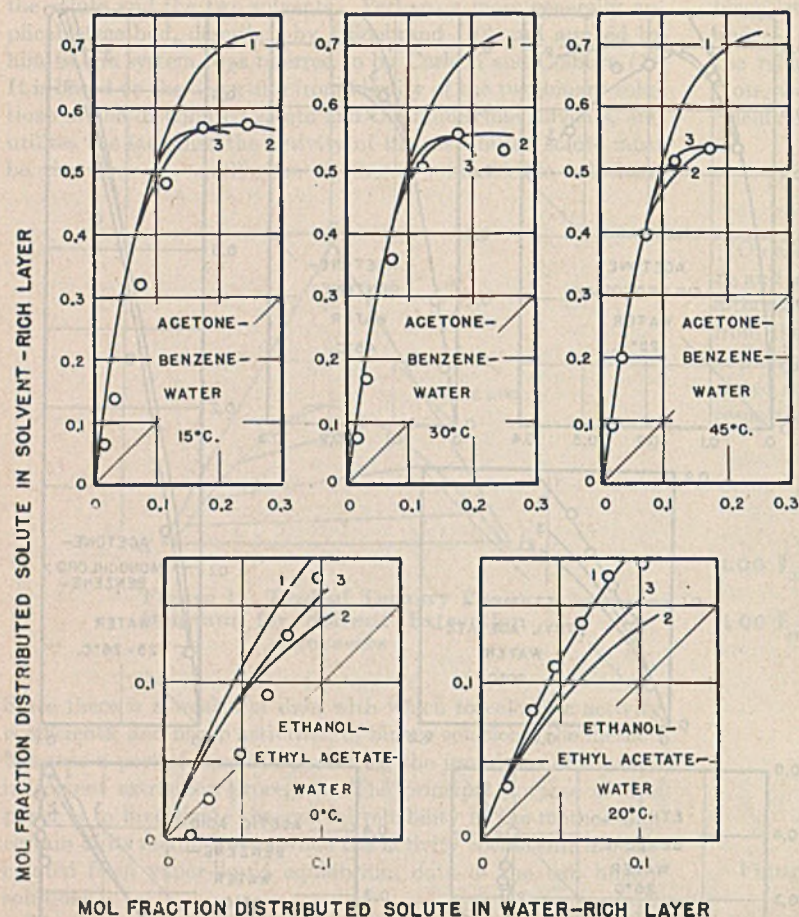


Figure 5. Comparison of Observed Distribution at Various Temperatures with Curves Calculated from Constant-Pressure Data

served data reported in the references cited in Table I, as plotted points.

It is evident that, with the exception of the system ethanol-benzene-water, the abnormalities of which have been discussed (21, 24), the initial portion of the distribution curve is predicted by all three methods exceedingly well. The curves calculated by method 1, as would be expected, frequently depart markedly from the observed data at high concentrations; methods 2 and 3, which account for some change in mutual solubility, if only empirically, in general give a truer prediction of the observed data, particularly with respect to the maximum in x_2 that may be reached. Although it is known that acetic acid solutions are in many respects abnormal and that Equation 5 does not apply, the system acetic acid-benzene-water was included deliberately. Although agreement between observed and calculated distribution is not so good as with other systems, the qualitative conclusion that water is a preferred extracting solvent for acetic acid-benzene solutions, rather than the reverse, nevertheless is predicted.

In order to show the effect of temperature on the activity coefficients in this work, two of the systems for which ternary equilibrium data were available at several temperatures were calculated, and the results are presented in Figure 5. Although method 1, which does not require a ternary solubility curve, must inevitably yield the same results for a given set of vapor-liquid equilibria, calculations by methods 2 and 3 are influenced. It is evident that better agreement is obtained, the more nearly the temperature of the predicted ternary liquid data agrees with that of the binary vapor-liquid data used, although discrepancies are not large in any case.

$$\text{av. } \log \gamma_{32} = \log \gamma_{32} + \left(\frac{x_{12}}{x_{12} + x_{22}} \right) (\log \gamma_{31} - \log \gamma_{32}) \quad (4)$$

Curves of the type of Figure 3 are plotted, and again predicted equilibrium concentrations are obtained.

The three methods were tried on a number of systems where fairly extensive distribution data are available, so that a comparison of the predicted and observed results can be made. The systems, together with the vapor-liquid equilibria from which the predictions were made, are listed in Table I. They are classified into three groups, depending upon the type of vapor-liquid data utilized.

USE OF CONSTANT-PRESSURE DATA

Group A includes systems whose distribution curves were calculated from binary vapor-liquid data at or near one atmosphere total pressure. Since the ternary liquid data with which the predicted values are compared were all reported at near room temperature, the additional assumption is made that the effect of temperature upon the activity coefficients is negligible. The activity coefficients were calculated from the relation,

$$\gamma = p/Px \quad (5)$$

where p = partial pressure of a component in equilibrium with liquid solution of mole fraction x and P = vapor pressure of the component at temperature of equilibrium measurement.

This, in turn, implies that the vapors follow the perfect gas laws; for most purposes this assumption is justified, particularly at the low pressures involved. Figure 4 shows the distribution curves so calculated by the three methods, together with all of the ob-

PREDICTIONS WITH CONSTANT-TEMPERATURE DATA

Group B includes those systems for which binary vapor-liquid data at constant temperature were available. Calculated and observed results are shown in Figure 6. In the case of the system acetone-chloroform-water, which was included in group A as well, a slight improvement is obtained, since the effect of temperature on activity coefficients is not so great. It is of special interest that in the case of the binary systems ethanol-toluene, ethanol-benzene, ethanol-ether, and ethanol-glycerol, only the total pressures of the solutions were reported in the references cited. Since partial pressures are required, it was assumed that the van Laar equations (13) accurately describe the variation of activity coefficient with concentration in a binary solution. By a trial-and-error procedure (7) it is then possible to fit these equations to the total pressure data and so obtain the necessary γ values. This was done in the case of the first three of the above binary pairs. Good fits were obtained in all cases with the exception of ethanol-ether, where the van Laar equations apparently do not apply very well. It is clear that this device greatly extends the usefulness of the methods discussed here. In the case of ethanol-glycerol solutions, the total pressure was taken as the partial pressure of ethanol, since the vapor pressure of glycerol is exceedingly low at 15° C. (19).

USE OF AZEOTROPIC DATA

Frequently the only binary vapor-liquid equilibrium datum available for a given system is a determination of a condition of azeotropism. If the van Laar equations are again assumed to be

applicable, the activity coefficients can be approximated from this single measurement by a simple procedure described by Carlson and Colburn (7). Group C (Table I, Figure 7) includes those systems in which the method was used for at least one of the binary pairs and, in the case of *tert*-butanol-ethyl acetate-water, for both binaries. Since considerable azeotropic data are available, the use of this method extends to a large degree the applicability of this approach to estimation of distribution curves. In this group, insufficient data were available to permit the use of methods 2 and 3 on the system ethanol-cyclohexane-water.

The distribution curves are plotted here in terms of mole fractions. It may be preferred, however, to base a prediction of the usefulness of a solvent on the basis of weight fractions, since most ternary diagrams are ordinarily plotted on this basis. If the ternary solubility curve is at hand, the predicted distribution data are readily converted to a weight basis. If no ternary data are available, the predicted mole fractions may be converted to weight fractions on the basis of binary solutions alone, and this will result in a distribution of the solute compatible with the observed data. Ordinarily, if the distribution curve on a mole fraction basis indicates that the distributed solute favors the *a*-rich layer, the data on a weight fraction basis will also favor it. Occasionally, with a peculiar combination of molecular weights the condition is reversed. For example, with the system ethanol-ethyl acetate-water the observed data indicate that the higher concentrations of ethanol are in the water-rich layer on a weight basis, and in the solvent-rich layer on a mole basis. The methods used here for predicting the distribution also lead to this conclusion.

Of the three, method 1 is the simplest to work with and requires least data. A careful study of Figures 4 to 7 shows that in every case, particularly if attention is focused on the initial slope of the calculated curve, method 1 does not fail to predict properly which of the two solvents is favored by the distributed solute. Frequently the agreement between observed and calculated results, up to moderate concentrations, is excellent. This is the case even though many of the systems considered exhibit considerable abnormality, discussions of which can in most cases be found in the literature citation for the observed ternary liquid data. The only system tried where the method has not given the correct results is isopropanol-tetrachloroethylene-water (4) (not shown); in that case an attempt was made to predict distribution from the binary azeotrope of isopropanol and tetrachloroethylene, which occurs at an isopropanol mole fraction of 0.92. However, as Carlson and Colburn (7) point out, the van Laar equations cannot be used with confidence to give γ_3 when the mole fraction of *c* in the azeotrope is much above 0.75; this point should be kept in mind when this variation of the method is applied.

Methods 2 and 3 are more limited in applicability, since they require the solubility curve. However, either will frequently give an excellent indication of the general position of the plait point; consequently when available data permit, they will be worth while. Although method 3 is more complicated to work out, it generally gives better results. For the systems isopropanol-toluene-water and ethanol-ethyl ether-water, where methods 2 and 3 both fail to show properly the effect of mutual solubility of the solvents, a fourth modification was tried with

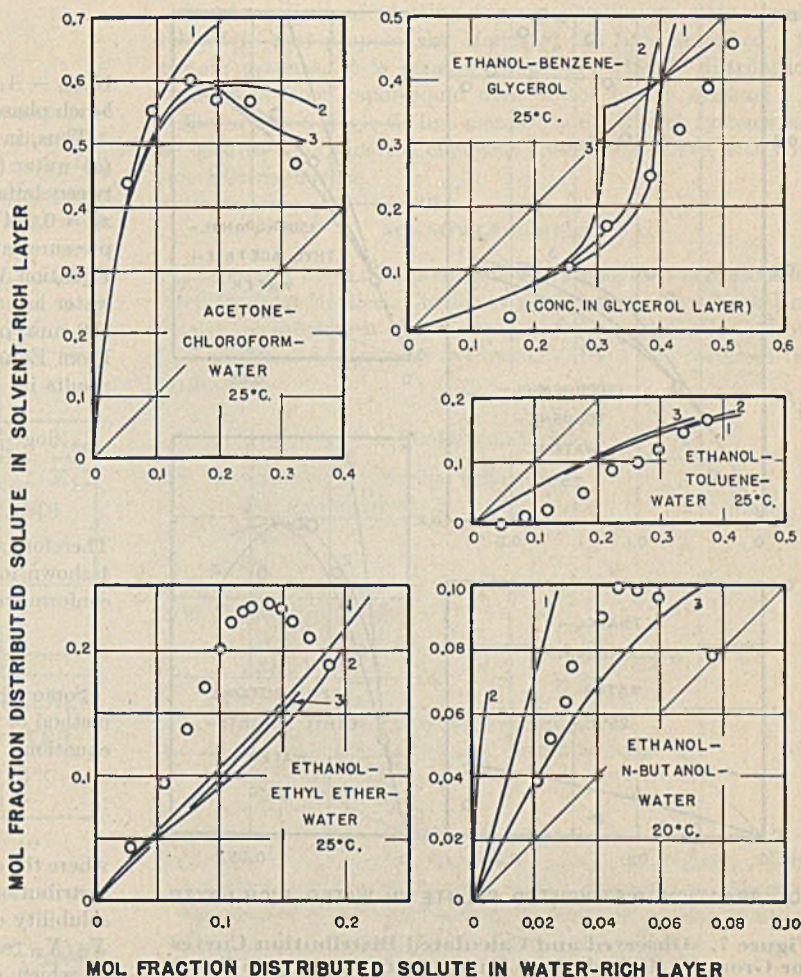


Figure 6. Observed and Calculated Distribution Curves for Group B (Calculations from Constant-Temperature Data)

some success. This involved the use of an effective concentration as noted in method 2, together with an averaging of $\log \gamma$ values as in method 3. The method is too complicated to be of great utility, however, and in general cannot be relied upon to give improvement in every case.

ANALYTICAL METHODS

The initial slope of the predicted distribution curve by method 1 is an index of the usefulness of a solvent for extraction purposes, and this initial slope may be calculated without plotting the entire curve. The equation of the tangents drawn to the activity curves at the origin (Figure 3) must be

$$\alpha_{31} = \gamma'_{31}x_{31} \quad (6)$$

$$\alpha_{32} = \gamma'_{32}x_{32} \quad (7)$$

where γ'_{31} and γ'_{32} are the activity coefficients of *c* in the binary solutions at zero concentration. At equal activities and at the origin of the curves,

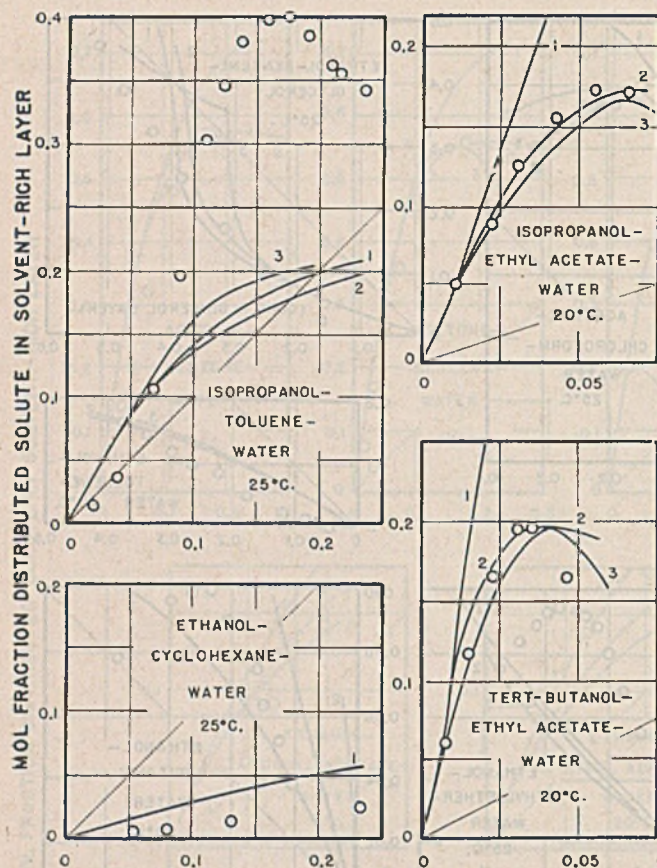
$$\gamma'_{31}x_{31} = \gamma'_{32}x_{32} \quad (8)$$

Consequently, the initial slope of the distribution curve becomes:

$$\frac{x_{31}}{x_{32}} = \frac{\gamma'_{32}}{\gamma'_{31}} = k \quad (9)$$

If *k* is greater than 1, the distribution favors the *a*-rich layer, and the activity curves of Figure 3 need not be plotted to determine this. The value of a simple index of this sort was discussed by Othmer and Tobias (16).

For the special case where the only vapor-liquid data available are the two binary azeotropes of *ac* and *bc* (or any reliable



MOL FRACTION DISTRIBUTED SOLUTE IN WATER-RICH LAYER

Figure 7. Observed and Calculated Distribution Curves for Group C (Calculations Partly from Azeotropic Data)

isolated measurement), and if the van Laar equations are assumed, the index k can readily be calculated analytically. Carlson and Colburn (7) wrote the van Laar equations in terms of the terminal values of the activity coefficients. Thus, for the binary ac ,

$$\log \gamma_{31} = \frac{A_{31}}{\left(1 + \frac{A_{31}x_{31}}{B_{11}x_{11}}\right)^2} \quad (10)$$

$$\log \gamma_{11} = \frac{B_{11}}{\left(1 + \frac{B_{11}x_{11}}{A_{31}x_{31}}\right)^2} \quad (11)$$

where $A_{31} = \log \gamma'_{31}$ and $B_{11} = \log \gamma'_{11}$. If these are solved simultaneously, the result (7) is:

$$A_{31} = (\log \gamma_{31}) \left[1 + \frac{x_{11} \log \gamma_{11}}{x_{31} \log \gamma_{31}}\right]^2 = \log \gamma'_{31} \quad (12)$$

Since at the azeotrope,

$$\gamma_{11} = P_i/P_1 \quad (13)$$

$$\gamma_{31} = P_i/P_3 \quad (14)$$

then A_{31} can readily be calculated. Similarly, for the binary azeotrope bc ,

$$A_{32} = (\log \gamma_{32}) \left[1 + \frac{x_{22} \log \gamma_{22}}{x_{32} \log \gamma_{32}}\right]^2 = \log \gamma'_{32} \quad (15)$$

and A_{32} can be calculated. The initial slope of the distribution curve becomes:

$$k = \frac{x'_{31}}{x_{32}} = 10^{A_{32} - A_{31}} \quad (16)$$

$$\text{or } \log \frac{x'_{31}}{x_{32}} = A_{32} - A_{31} \quad (17)$$

If $A_{32} - A_{31}$ is positive, c favors the a -rich phase; if negative, the b -rich phase.

Thus, in the case of the system *tert*-butanol (c)-ethyl acetate (a)-water (b), two binary azeotropes are formed (11). That between butanol and ethyl acetate has a mole fraction butanol $x_{31} = 0.284$ at 75.2°C . and 760 mm. of mercury. From the vapor pressures at this temperature, $\gamma_{31} = 1.147$ and $\gamma_{11} = 1.074$. By Equation 12, $A_{31} = 0.3185$. The azeotrope of *tert*-butanol and water has a mole fraction butanol $x_{32} = 0.6459$ at 79.9°C . and 760 mm. of mercury, for which $\gamma_{32} = 1.089$ and $\gamma_{22} = 2.149$. From Equation 15, $A_{32} = 1.2973$. Substitution in Equation 17 results in

$$\log \frac{x'_{31}}{x_{32}} = \log \text{limiting} \frac{\text{concn. butanol in ester layer}}{\text{concn. butanol in water layer}} \\ = A_{32} - A_{31} = +0.9788$$

Therefore $x'_{31}/x_{32} = 9.52$, which checks the initial slope of curve 1 shown for this system in Figure 7 (obtained graphically) and conforms to the observed data closely.

PLOTTING TERNARY LIQUID DATA

Some years ago Hand (9) introduced a successful empirical method of plotting ternary liquid equilibrium data, based on the equation,

$$\frac{X_{31}}{X_{11}} = K \left(\frac{X_{32}}{X_{22}}\right)^n \quad (18)$$

where the concentrations are in weight fractions. This is a type of distribution curve, where n is introduced to account for mutual solubility of the solvents (1). A log-log plot of X_{31}/X_{11} against X_{32}/X_{22} results in good straight lines for most systems, the slopes of which equal n . Two experimentally determined tie lines would serve to plot this line.

Since, in binary ac , $x_{31} = x_{31}/x_{11}$ as x_{31} becomes zero, Equation 9 can be written:

$$\frac{x'_{31}}{x_{11}} = \frac{\gamma_{32}}{\gamma_{31}} \left(\frac{x'_{32}}{x_{22}}\right) \quad (19)$$

If n is introduced as in Equation 18, a similar equation for plotting in terms of mole fractions results:

$$\frac{x_{31}}{x_{11}} = m \left(\frac{x_{32}}{x_{22}}\right)^n \quad (20)$$

where m is a constant. The n values for the two plots are the same, and the coefficients are related:

$$K = m \left(\frac{MW_3}{MW_1}\right) \left(\frac{MW_2}{MW_3}\right)^n \quad (21)$$

If $n = 1$, then $m = k = \gamma'_{32}/\gamma'_{31}$, and Hand's K can be predicted:

$$K = \frac{\gamma'_{32}}{\gamma'_{31}} \left(\frac{MW_2}{MW_1}\right), \text{ for } n = 1 \quad (22)$$

Typical plots are shown in Figure 8 for the system acetone (c)-benzene (a)-water (b) at 15°C . (5). For both lines $n = 1.33$. Since $m = 14.0$, then

$$K = 2.20 = 14.0 \left(\frac{MW_{\text{acetone}}}{MW_{\text{benzene}}}\right) \left(\frac{MW_{\text{water}}}{MW_{\text{acetone}}}\right)^{1.33}$$

For the system acetone (c)-chloroform (b)-water (a) at 25°C ., Baneroft and Hubbard (1) report $K = 0.494$ and $n = 1.02$, and Hand (9) reports $K = 0.4084$ and $n = 1.07$. Since n is so nearly unity, Equation 22 should apply. For this system $\gamma'_{31} = 6.1$ at 25°C . and $\gamma'_{32} = 0.4$ at 35.17°C . Consequently, the predicted

$$K = \frac{0.4}{6.1} \left(\frac{MW_{\text{CHCl}_3}}{MW_{\text{H}_2\text{O}}} \right) = 0.435$$

which falls between the reported values.

Further practical application of this development is also possible. Suppose in a ternary system that one tie line measurement is available. This single datum can be plotted on x_{31}/x_{11} vs. x_{32}/x_{22} coordinates, using log-log paper. On the initial assumption that $n = 1$ or nearly so, γ_{32}/γ_{31} can be calculated from

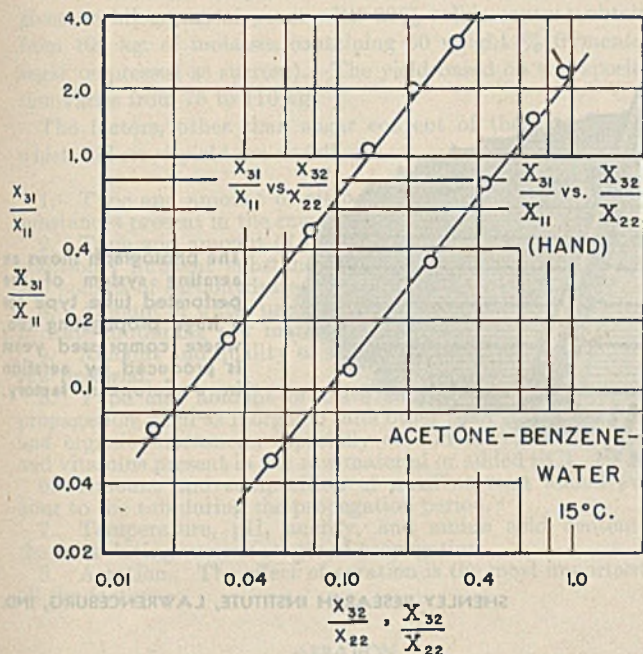


Figure 8. Rectilinear Plots of Distribution Curves (Data of Briggs and Comings, 5)

vapor-liquid data; if $n = 1$, the ratio will equal k , or the value of x_{31}/x_{11} at $x_{32}/x_{22} = 1$. This point is then plotted, and a line drawn through the two points. If the line has a slope other than unity, it should be discarded until further data are available. If the slope is 1, then the line may be taken as representing the entire equilibrium distribution with considerable confidence.

SUMMARY AND CONCLUSIONS

1. Method 1 of predicting ternary liquid equilibrium distribution data described by Hildebrand (10), and two modifications, methods 2 and 3, introduced to account for the mutual solubility of the contacted solvents, have been worked out for a number of systems and compared with the observed data. Binary vapor-liquid equilibrium data of three types were used—constant pressure, constant temperature, and azeotropes.

2. Method 1, which requires no information about the ternary system and which, if necessary, can be applied when merely two binary azeotropes are known, is reliable in predicting which solvent may be used for extraction, particularly if attention is focused on the predictions at low concentrations for the distributed solute.

3. Method 2 is a simple modification requiring the ternary solubility curve and is, therefore, more limited in applicability. It is generally successful in predicting the trend of the distribution curve at higher concentrations of the solute.

4. Method 3, likewise requiring the ternary solubility curve, leads to slightly better results than method 2, although it is more complicated to work out.

5. A simple analytical method of determining an index of the usefulness of a solvent in extraction processes, which requires a minimum of graphical work, has been described.

6. A method of plotting ternary equilibrium data closely related to that proposed by Hand (9) has been described. In certain systems, it is possible to predict Hand's distribution coefficients from vapor-liquid data of the binary systems. It is shown how a single tie line measurement for such systems can be used to determine the complete distribution curve with considerable confidence.

ACKNOWLEDGMENT

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NOMENCLATURE

- a, b = relatively immiscible solvents
- c = distributed solute
- $A_3 = \log \gamma'_3$
- $B_1 = \log \gamma'_1$
- k, K, m, n = constants
- MW = molecular weight
- p = partial pressure
- P = vapor pressure
- P_t = total pressure
- x = concentration in terms of mole fraction
- X = concentration in terms of weight fraction
- α = activity of component
- γ = activity coefficient

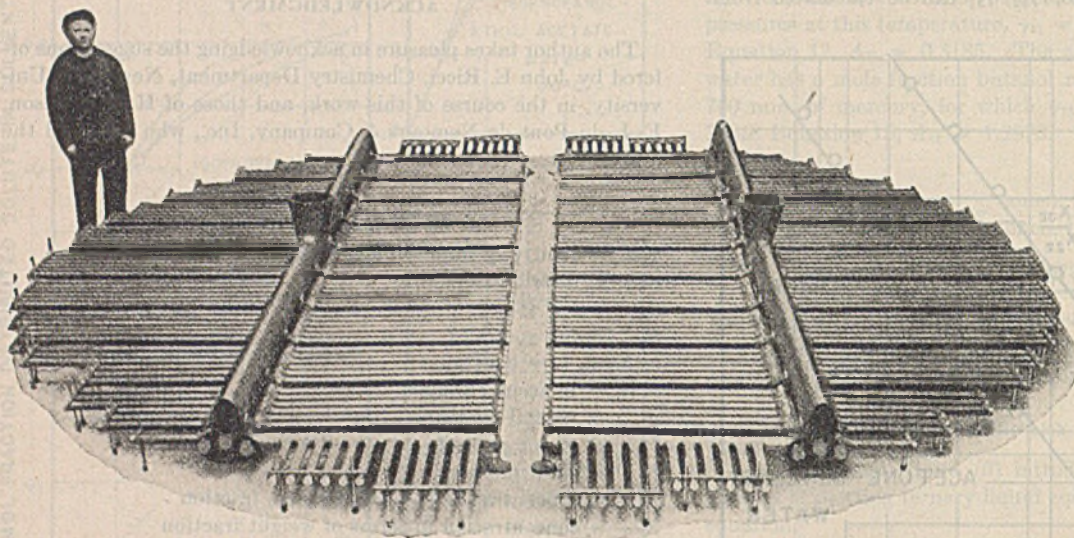
Superscript ' = zero concentration

Subscripts 1, 2, 3 = components a, b, c , respectively. First subscript refers to component whose property is indicated, the second to the predominant component of the solution. Thus, x_{31} = mole fraction of c in an a -rich solution.

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AERATION in the PRODUCTION of COMPRESSED YEAST



The photograph shows an aerating system of the perforated tube type for a huge propagating tub, where compressed yeast is produced by aeration in a European factory.

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COMPRESSED yeast, originally a by-product of alcohol and beer, has gained in importance during the past thirty years. Yeast is being consumed wet or dry, natural or irradiated, alone or mixed with other food substances and flavoring materials. In wartime yeast has become a partial substitute for meat. With the advent of the aeration of the wort in the early part of this century, the production of compressed yeast became independent from alcohol or beer manufacture. Aeration of the nutrient liquids in which the yeast propagates enabled manufacturers not only to multiply former yields four or five times, but also to control the quality of the product. Since the time of the old-fashioned foam yeast process early in this century, hundreds of new methods of producing compressed yeast have been developed; all have one principal step in common, aeration of the wort.

Air was generally believed to be a raw material which could be obtained free of cost. The cost of energy necessary to compress air, however, proved that a considerable amount (10–20%) of the total production expenses is due to aeration. Manufacturers, eager to reduce costs, began to study the attainment of optimum yield with a reduced amount of air. Especially between 1925 and 1940 dozens of patents were applied for, chiefly in Europe. Research was concentrated on proper technology rather than on the biological effect of aeration.

The primary purpose of this paper is to provide a basis for further research by discussing the facts connected with aeration in the production of compressed yeast, by enumerating some of the aerating systems used or recommended, and by tracing the course of their development. In recent years the interest of fermentologists has turned toward microbiological processes other than compressed yeast production, where aeration of the wort is essential. For those processes also, useful directions can be obtained from the methods used in aerating the yeast wort.

Little is known about the biochemical mechanism of aeration. The general belief is that oxygen is important chiefly for the

propagation of the yeast, and that the yeast can utilize only the oxygen dissolved in the liquid. The solubility of oxygen is low—0.0009% at 20° C. Aeration is necessary to replace used, dissolved oxygen. It is also believed that aeration takes away fermentation products from the surface of the cells and substitutes fresh nutrients for them. Staub (31) believes that the yield of yeast is in direct proportion to the cube root of the aerating intensity. This and similar conclusions may be true only to a limited extent.

On the other hand, there are facts which may at least modify the oxygen supply theory. Yeast may also multiply in the absence of air. In several experiments made on a pilot-plant scale in 1930–33, one of the authors obtained considerable yields of compressed yeast in mashes in which carbon dioxide or nitrogen was passed through instead of air. These yields were three to four times larger than those obtained in identical mashes in which no gas was distributed.

Weleminsky and Butschowitz (56) obtained the same yield in aerated wort as in unaerated but rapidly circulated wort. In the first case there was no alcohol, in the second case, normal alcohol yield in addition to yeast. Meyer (18) describes propagation of yeast without aeration. In closed tubs the wort is well agitated under vacuum to eliminate alcohol and carbon dioxide; in addition to alcohol, the same amount of yeast was obtained as in aerated wort. Jansen (11) recommends intensive circulation of the beer in a closed fermenter. All the beer is passed through a pump every 10 minutes. Besides excellent alcohol yield, a good yield of yeast is claimed.

Willkie and Prochaska (58) concluded: "In the absence of oxygen, growth is slow and fermentation is the predominant reaction. Whereas agitation with inert gases increases both growth and fermentation rate through better contact of yeast with mash ingredients, dispersion of air throughout the medium induces yeast growth specifically at the expense of fermentation. Pure oxygen is not as good a growth stimulant as air."

YIELD

The yield of compressed yeast is generally expressed as weight per cent of the carbohydrate-containing raw material, occasionally as weight per cent of the actual sugar used. The weight of yeast is normally given at 30% solids content. The carbohydrate-containing raw material is most often molasses and seldom grain; it is more frequently beet molasses than cane molasses. In the true yield statement, the fermentable sugar content of the molasses is also given.

In continental Europe, if not otherwise specified, the yield is given as kilograms of yeast with 30% solids content obtained from 100 kg. of molasses containing 50 weight % fermentable sugar (expressed as sucrose). The yield based on this specification varies from 75 to 110 kg.

The factors, other than sugar content of the raw material, which influence yield are as follows:

1. Type and amount of nitrogen and phosphorus-containing substances present in the raw material.
2. Type and amount of nitrogen and phosphorus-containing additional nutrient substances added to the wort with every 100 pounds of carbohydrate-containing raw material.
3. Amount of water used to dilute each 100 pounds of carbohydrate-containing raw material.
4. Amount and quality of seed yeast used per 100 pounds of raw material.
5. Type and amount of trace substances which stimulate propagation, such as inorganic salts other than those mentioned, and organic substances, especially certain nitrogen compounds and vitamins present in the raw material or added to it.
6. Amount and composition of nutrient wort added every hour to the tub during the propagation period.
7. Temperature, pH, acidity, and amino acid content of the wort during various stages of propagation.
8. Aeration. The effect of aeration is the most important of all the factors.

AERATION

QUANTITY OF AIR. The quantity is usually specified by the volume of air passing through the nutrient liquid. Unfortunately the volume of air is reported either in compressed form or at atmospheric pressure as free air. Naturally it makes a difference if the reported 100 cubic feet are understood to be at atmospheric pressure or at 5, 10, 20, or 30 pounds gage pressure. Table I records the volume, V , of 100 cubic feet of free air at 60° F. at various gage pressures and the volume, V_1 , of 100 cubic feet of compressed air when released from various gage pressures to free air at 60° F. The corresponding gage and water pressures are also given. Pressure of water at a certain height is slightly less than the pressure of yeast wort at the same height. Resistance of yeast wort to compressed air on a production scale is

generally between 6 and 10 pounds per square inch. Table II records corresponding volumes of free and compressed air and minimum power requirements for compression at various gage pressures, supposing single-stage compression. The air volumes differ from those given at constant temperature in Table I because of the increase in temperature during compression. The minimum power requirement given in Table II is less than that actually consumed by the best air compressor.

Air pressure is needed to counteract the following: height of wort, resistance of air distributor, resistance of air filter, resistance of air cooler, resistance of air meter and conducting pipe lines, and special local factors.

The height of the wort is determined by the propagating tub and the propagation method used. In a tall fermenter the resistance of the wort is greater than in a low fermenter. In the majority of the propagating methods (2) the height of the wort changes during the 12-14 hour propagating period. It gradually increases from an initial height of 30-50% to the final height of 100%; the pressure of the air must increase accordingly.

Resistance is one of the main characteristics of a given air distributor. While its value can be rather large (5-10 pounds or much more) as in the case of the porous ceramic or carbon tubes and plates, it can also be negative as in the case of certain mechanical air distributors.

The resistance of the air filter, cooler, meter, and connecting air lines is not characteristic of any propagating or air-distributing system. It may be large because of poorly designed and engineered equipment, but it is negligible if the devices are of proper dimensions.

The quantity of air must be computed on the basis of specified conditions of the propagation method. Propagation methods are also determined by a number of factors, the numerical values of which are subject to change during the propagation period. The change in any of these components will affect the yield.

It is not easy to relate the quantity of air to a given process; the customary specifications, where quantity is related to a single factor of the propagating method, give little or misleading information when methods must be compared on this basis.

It is customary to report the air requirement in volume units per minute: (I) per volume unit of wort (cubic feet of air per gallon of wort); (II) per square unit of liquid surface (cubic feet of air per square foot of liquid or tub bottom surface); (III) per weight per cent of yeast in propagating liquid (cubic feet of air per pound of yeast in 100 gallons of liquid); (IV) per weight unit of raw material (cubic feet of air per ton of total molasses or bushel of grain mashed); (V) per weight unit of newly produced yeast (cubic feet of air per pound of yeast produced).

The air requirement (method I) is most frequently reported as x cubic feet of air per minute per gallon of wort. The value of x when the same yield is obtained in a one-gallon jar in the laboratory may be fifty times as large as in a 20,000-gallon vat in the plant. The air is better utilized in a large vat. Without additional specification this type of report does not give any information to the expert.

The quantity of air is often reported as x cubic feet of air per minute per square foot of liquid surface (method II). This specification eliminates the height of liquid because the same amount of air will pass every inch in the upper liquid levels as well as in the lowest. This method of reporting quantity of air is more informative than the previous one, although it is still incomplete.

The weight per cent of yeast in the liquid (method III) can vary greatly according to the propagating process used. The finished beer may contain 5-25% yeast (with 30% solids). The air requirement per gallon or per square foot of liquid surface will be much larger in the second than in the first case. The initial concentration of yeast, with the exception of true continuous processes, is generally one fifth to one half the final concentration (2). With the exception of the short initial and final propaga-

This survey of aeration in compressed yeast production indicates that, despite the amount of work carried on so far, the problems involved are far from being solved. There is much left to explore in the biochemical interpretation of the effect of aeration. A uniform specification should be developed to characterize any aeration system; mathematical relation between propagation of yeast and air requirement should be studied more intensively. The main objective of future research remains to make aeration cheaper by further reduction of energy requirements and by further simplification of the equipment necessary to provide the mash with sufficient air. Aeration in the manufacture of yeast is generally provided by perforated tube systems; but fine aeration produced by porous substances or by mechanical air distributors is most promising for the future. The extensive consumption of yeast, the application of aeration technique, and its importance in other microbiological processes than compressed yeast production should stimulate further research.

Table I. Isothermal Compression of Air at 60° F.

Vol. V_1 , Cu. Ft.	Gage Pressure P_2 , Lb./Sq. In.	Water Pressure, Ft.	Vol. V_2 , Cu. Ft.
100	0	0	100
88.0	2	4.6	113
78.5	4	9.2	127
71.0	6	13.9	141
64.8	8	18.5	154
59.5	10	23.1	168
55.0	12	27.7	182
51.2	14	32.2	195
47.9	16	36.8	209
45.0	18	41.6	222
42.3	20	46.2	236
40.0	22	50.8	250
38.0	24	55.5	263
36.2	26	60.0	276
34.5	28	64.5	290
32.8	30	69.4	305

Table II. Air Compression and Minimum Power Requirements for Single-Stage Compression ($PV^{1.3} = \text{Constant}$)

Vol. V of 100 Cu. Ft. Free Air Compressed to P_2	Gage Pressure P_2 , Lb./Sq. In.	Vol. V_2 of 100 Cu. Ft. Com- pressed Air Released to Atm. Pressure	Power Required, Kilowatts	
			To compress 100 cu. ft. free air to P_2	To produce 100 cu. ft. compressed air at P_2
100	0	100	0	0
90.5	2	110.3	0.621	0.686
83.0	4	120.3	1.185	1.428
76.8	6	130.1	1.703	2.280
71.6	8	139.7	2.185	3.05
67.0	10	149.1	2.64	3.94
63.1	12	158.3	3.06	4.85
59.7	14	167.3	3.46	5.79
56.7	16	176.2	3.84	6.78
54.0	18	185.0	4.20	7.77
51.6	20	192.6	4.54	8.79
49.4	22	202.1	4.87	9.80
47.4	24	210.6	5.20	10.95
45.6	26	218.9	5.49	12.00
44.0	28	227.1	5.79	13.13
42.5	30	235.3	6.07	14.28

tion periods, the amount of air supplied to the tub is usually constant, regardless of the changes in volume of wort or in yeast concentration during the main propagation period (10–12 hours). Under the influence of a number of variants, only one particular phase can be characterized by this third type of report.

The production man likes to report and compare the air requirement in cubic feet per weight unit of raw material used or per weight unit of new yeast (methods IV and V). At first glance method V in particular seems a good way to compare production results. No proper comparison, however, based on this type of specification, can be obtained because of two major variants—height of liquid and yield. It has already been mentioned that the utilization of air depends considerably on the size and shape of the fermenter. Each method of propagation, in combination with a special method of aeration, may reach the optimum yield in a manner characteristic of the method. There are methods in which a 65–70% yield can be increased only slightly even if the quantity of air is doubled. There are other methods in which a 65–70% yield can easily be increased to 85–90% simply by increasing the quantity of air by 50%. These figures demonstrate that yield and liquid level cannot be eliminated from the definition of air requirement.

In spite of the fact, then, that it is common practice, the quantity of air cannot be satisfactorily related to a single characteristic of a method. For correct evaluation, quantity of air must be reported in units of volume (cubic feet) measured at atmospheric pressure, relating its value per unit of liquid per minute in any second during the propagation period. This must be completed with the following information: (A) height of the liquid at any

time, (B) the yeast concentration in the wort (possibly at any time, but at least at the start and finish of propagation), (C) yield per unit for a given raw material, (D) ratio of new yeast to seed yeast (factor of generation).

Items A, B, and C can be reported most conveniently by graphs. The values of air requirement related to other production factors can be calculated from the above specifications. If the air quantity requirements of two or more methods are to be compared, the specifications must be reported in connection with that yield which is normal for the less effective system. Then the increased yield and the factor of generation must be reported for each system, when the quantity of air is increased by 10, 20, and 50% of the basic requirement, all other conditions being kept identical. The method which requires less air to obtain the basic yield and will give the highest yields by increasing the quantity is superior to the others in the matter of air requirement (Table III).

Figures in Table III are partly taken from the authors' experience and partly calculated from limited information in the literature. They demonstrate that if air requirement is related to a single property, such as volume of wort or weight of raw material without other essential information, it does not characterize an aerating system.

The ratio of new yeast to seed yeast (factor of generation) is important, because the yield on seed yeast as well as the air requirement for its production is usually much lower than that on the final product.

QUALITY OF AIR. The quality of the air is more important to the yield than the quantity. It is even more difficult to define quality of air exactly than to define quantity. An attempt will be made to interpret the term by discussing its most important components. The conditions under which air is introduced, distributed, and kept in the wort determine quality. It is essential that the air (A) should pass through the entire height of the liquid, (B) should be distributed equally through the entire cross section of the tub, (C) should contact the wort at the largest possible surface, and (D) should be in contact with the wort for the longest possible time.

A. The air is generally introduced into the liquid at the deepest point, close to the bottom of the tub. By this means both tub and air capacity are best utilized.

B. A well-balanced network of aerating tubes covering the entire tub bottom, the proper position of the aerating candles or bodies, or the agitation of the mash are the means employed to maintain homogeneous distribution of air. If the air passes

Table III. Air Requirements of Yeast Production in Various Systems

Item No.	Source	Aerating System	Air Requirement, Cu. Ft.					
			Per gal. per min. during main fermentation	Total used per lb. molasses of 50% sugar content	Total used per lb. new yeast (30% solid content)	Height of Liquid, Ft.	Max. Air Pressure (Approx.), Lb./Sq. In.	Wort per Batch, Gal.
1.	a	Perforated tubes	0.20	375	530	12	6.0	13,000
2.	a	Perforated tubes	0.3	210	280	24	12.5	20,000
3.	a	Perforated tubes	0.21	315	400	20	10.5	20,000
4.	(55)	Perforated tubes	0.20	235	275	5,100
5.	(6)	Perforated tubes	0.06	260
6.	(5)	Perforated tubes	0.11	..	333	10,000
7.	(25)	Perforated tubes (assumed)	0.14	290	360	7,000
8.	a	Mechanical air distributor	0.40	180	200	7	3.0	550
9.	(30)	No. 60 carbon sparger	0.40	0.13
10.	(30)	Berkefeld candle	<0.07	0.13
11.	(47)	No. 60 carbon sparger	0.25	10	40.0	250
12.	(21)	Si carbide aerator	0.27	910	1820	1	..	13.2

^a Figures taken from actual production data in 1937 of three yeast factories in Central Europe.

Lb. Yeast (30% Solids) from 100 Lb. Raw Material
50% Sugar Content

through only one section of the tub, that part will be over-aerated while the other part will be underaerated. In the over-aerated mash the utilization of air is poor, and in the under-aerated mash the propagation is slow.

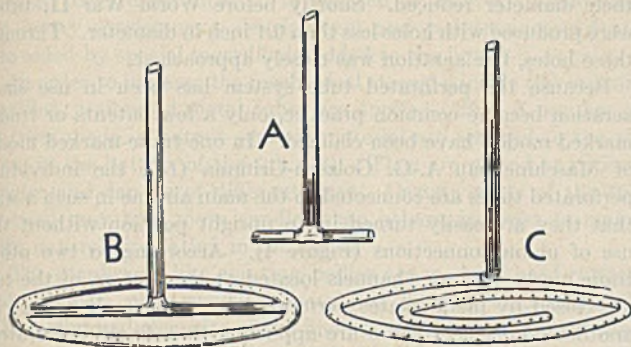


Figure 1. Early Forms of Perforated Tube Systems

- A. Inverted T
- B. Perforated ring
- C. Spiral sparger

C. In aeration the most important factor is to establish the largest possible contacting surface between air and liquid per unit of air. The largest possible surface of a given amount of air is offered by bubbles of the smallest size. The surface area of 1 cubic foot in a single bubble will be 697 square inches. If this is divided into bubbles 1 inch in diameter, its total surface area will be 10,368 square inches. Going farther, the total contacting surface of 1 cubic foot of air divided into bubbles with a diameter of 0.1 inch will be 103,680 square inches; with a diameter of 0.01 inch, it will be 1,036,800 square inches, etc. The total surface area of a definite amount of air will increase in inverse proportion to the diameter of the individual bubbles.

In the practical aeration of yeast mashes, the diameter of the air bubbles is estimated to be from 0.0001 to 1 inch. By the old aerating systems, practically every size between these limits was represented. The greater part passed in the form of large bubbles, and only a small fraction of air formed the smallest bubbles. The total contacting surface per unit of air was relatively small. Those methods which produce only the small bubbles are called "fine aerating systems", and they result in yields identical with or larger than the old systems, while using only 10-50% of their air requirement. Naturally, the yield does not increase in direct proportion to the contacting surface. Several of the aerating systems disperse the liquid in the air in the form of a fine spray. The contacting surface increases with the decreased size of the liquid drops.

D. The next important factor in aeration is the contacting time, the time the bubbles spend in the wort. Fine aeration creates not only a large contacting surface, but also a longer contacting time. The floating time is much longer for a small bubble than for a larger one because of its lower elevating power. A small bubble may spend minutes in the liquid before leaving it; a large one may pass through within a few seconds.

In order to lengthen the floating time, several systems keep the liquid in a slow rotating movement, the bubbles thus reaching the surface of the liquid through a long spiral course instead of by a straight vertical line. The floating time is also influenced by the height of the liquid. That is the explanation of the lower air requirement in cubic feet per gallon of wort in a tall vat.

The floating time is not in direct proportion to the height of the liquid, because the rising speed is constantly accelerated by the elevating power of the bubbles. Even the elevating power increases with the course of elevation, because the size of the bubbles will increase as the liquid pressure decreases in the upper liquid layers.

ENERGY REQUIREMENT

The investigator in the laboratory as well as the industrial operator will profit by an analysis of the air requirements. The production man will look only for the energy requirement of the aeration. He will report it in horsepower or kilowatts per 100 pounds of yeast produced. The energy requirement is dependent upon the quantity and the pressure of air used, and the energy requirement of the agitators, mechanical distributors, or circulating pumps. The quantity of air per unit of product depends mainly upon the height of the liquid level and the contacting surfaces of the air. For the higher liquid level, the producer pays with the higher pressure; for the smaller bubbles he pays with additional air pressure when porous air-distributing bodies are used, and with additional energy when mechanical air distributors are utilized.

When energy requirements are held to the minimum, local conditions must be carefully considered. Generally the actual energy consumption due to unbalanced local conditions is higher than the theoretical consumption calculated from minimum air requirement. On the other hand, local conditions may reduce the cost of the energy requirement below the theoretical. When, as is customary, steam-driven air compressors are used, utilization of exhaust steam for sterilization, distillation, etc., will considerably reduce the costs of air compression.

Next to the energy requirement, the production man is interested in the necessary maximum air pressure, because the price of the air compressor, air cooler, filter, conducting pipe lines, etc., is higher for high-pressure than for low-pressure operation.

CLASSIFICATION OF METHODS

Methods developed by processing engineers have generally aimed at high yields and low air requirements. Methods developed by machine factories have generally produced simple, dependable devices designed for large consumption without requiring many changes in other equipment. Many of the recommended methods are simple reproductions of previous ones, with only slight improvements. Most patents seek to secure advantages over existing patents or to protect promising ideas.

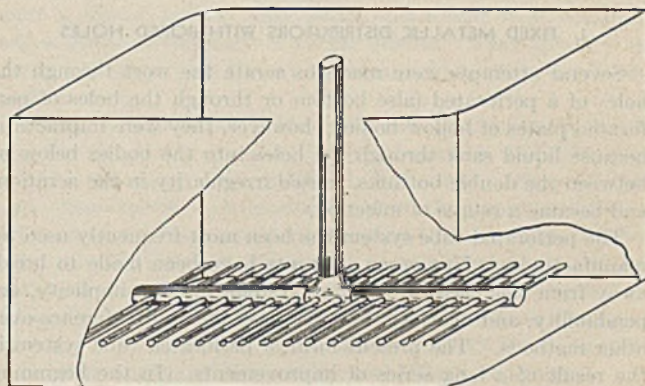


Figure 2. Network of Perforated Tubes

Groupings of the systems recommended or used may be approached from different angles—for instance: Grouping 1: (a) systems where air is distributed in the liquid; (b) systems where liquid is distributed in the air; (c) systems where air and liquid are placed in contact on bodies with large surfaces. Grouping 2: (a) systems where the liquid is aerated in the tub; (b) systems where part of the liquid is withdrawn from the tub and, after being subjected to intensive aeration, is returned. Grouping 3: (a) air distributors with moving parts; (b) air distributors without moving parts. Grouping 4: (a) rough

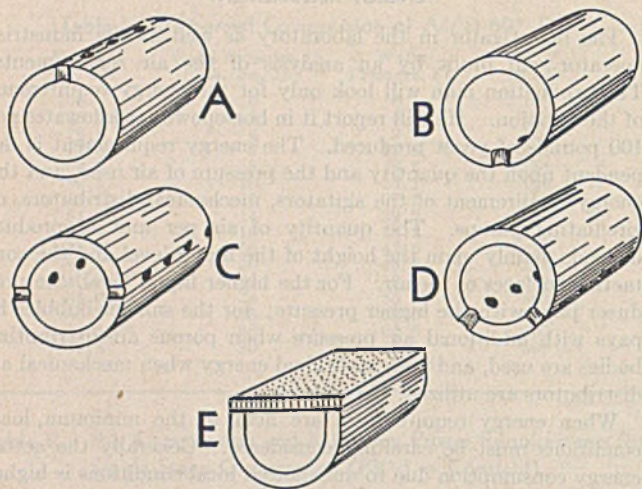


Figure 3. Position of Holes in Tubes

aeration; (b) fine aeration. Such and similar groupings may be set up to classify the various aerating systems according to one or another basic point.

Disregarding systematic classification, the following grouping will deal with the various systems in seven major groups, according to the similarity of the devices used to distribute air. No sharp line can be drawn even between these groups.

I. Compressed air enters the liquid through perforated metallic plates, tubes, or tube systems fixed on the bottom of the tub.

II. Air enters the liquid through hollow bodies, plates, tubes, candles, or false bottoms, made of porous material such as ceramic substances, porous carbon, porous copper, hard rubber, soft rubber, fibrous substances, etc.

III. Air enters the liquid through hollow bodies, plates, or tubes made of metal and provided with openings other than bored holes.

IV. Mechanical air distributors.

V. Liquid spray aerators.

VI. Packed columns.

VII. Miscellaneous.

I. FIXED METALLIC DISTRIBUTORS WITH BORED HOLES

Several attempts were made to aerate the wort through the holes of a perforated false bottom or through the holes of perforated plates of hollow bodies; however, they were impractical because liquid sank through the holes into the bodies below or between the double bottoms, caused irregularity in the aeration, and became a source of infection.

The perforated tube system has been most frequently used by manufacturers. Numerous attempts have been made to break away from this classical aerating system, but its simplicity, dependability, and relatively low cost have assured preference over other methods. The present form of perforated tube system is the result of a long series of improvements. In the beginning air was introduced into the liquid through the two open ends of an inverted-T pipe line (Figure 14). This was soon replaced by perforated rings and spiral spargers. The next arrangement was a network of perforated tubes covering the bottom of the tub; individual parallel tubes branched out on both sides of a horizontal main line, into which the air passed through one or more vertical lines inside the tub (Figure 2). The iron pipes originally used were replaced by tin-coated copper, occasionally by brass, and recently by stainless steel tubes. The tubes, few in number at first, increased rapidly until the bottom surface was nearly covered by them. Union connections, later well-grooved surface connections, were applied. The diameter of the tubes varied, according to the size of the tubs, from $\frac{1}{4}$ to 2 inches.

The holes were moved from the top to the bottom of the

tubes in order to prevent the flow of liquid into them. Later the holes were placed on two sides or at the lower part of the tubes 90° apart. Recently very small holes occupy the upper surface of the tubes (Figure 3). The size of the holes as a rule was $\frac{1}{25}$ – $\frac{2}{25}$ inch. The number of holes was increased and their diameter reduced. Shortly before World War II, tubes were produced with holes less than 0.1 inch in diameter. Through these holes, fine aeration was closely approached.

Because the perforated tube system has been in use since aeration became common practice, only a few patents or trade-marked models have been claimed. In one trade-marked model of Maschinenbau A.-G. Golzern-Grimma (15), the individual perforated tubes are connected to the main air line in such a way that they are easily turned in an upright position without the use of union connections (Figure 4). According to two other trade marks (16) air channels located at the bottom of the tub are closed by metal plates perforated by very small holes. In another model (17) tubes are applied with a finely perforated, horizontal top plate (Figure 3E).

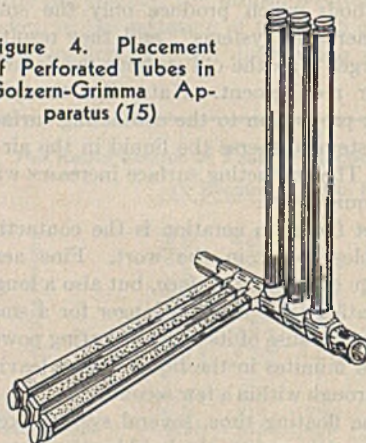
A patent (45) of Strauch & Schmidt specifies an aerating system in which the individual perforated tubes branch out from submain lines which, in turn, stem from the main air line. By this arrangement the individual tubes are parallel to the main air line. In another patented system (46) the aerating tubes are provided with water and steam connections for cleansing and sterilizing. Aerating systems are built by Strauch & Schmidt for vats up to 200,000-gallon capacity. They claim 30–40% less air requirement for their latest models and still less for double-tube aerating systems (Figure 5). Aerating systems built by Golzern-Grimma are also generally used in European yeast factories.

II. FINE AERATION THROUGH POROUS SUBSTANCES

By devices classified in this group, air enters the liquid in the form of fine bubbles through the tiny openings of porous substances. The air may be compressed into hollow bodies, into tubes placed on the bottom of the propagating tub, or between double bottoms, the upper of which is built of the porous substance. Practically all materials used in bacteriological and serological filtration have been tested for fine aeration.

The earlier recommendation of Peter (23) that porous substance be used did not receive much attention. Stich is credited with calling the attention of yeast manufacturers to the importance of fine aeration and with presenting practical ways of attaining it. His basic patent (35) recommends the introduction of air into the wort through diaphragm bodies with orifices 0.16 to 0.6μ

Figure 4. Placement of Perforated Tubes in Golzern-Grimma Apparatus (15)



in size, and the lengthening of the floating time by slow rotation of the liquid. This was a revolutionary recommendation at that time, when the diameter of the holes of the perforated tubes varied from 1000 to 2000 μ .

Stich's basic patent was followed by many others. For example, pore sizes in the diaphragm plates are increased to 1 – 25μ in order to reduce the pressure requirement of the air (42). The diaphragm plates or bodies are built with two layers (38). The thick inside layer with large holes assures mechanical

strength; the thin outside layer with small pores assures the fine distribution of air. This change was necessary to reduce the resistance of the ceramic plates and candles.

At the beginning of propagation, the wort is converted into a foam by fine aeration (41). During the course of propagation, enough finely distributed air is supplied to the wort to maintain its foamy consistency; development and maintenance of foam are aided by special ingredients added to the liquid.

In order to increase the mechanical strength inside the ceramic candles, perforated metal tubes are applied (39). A number of candles made of porous ceramic material are screwed to the air lines in the bottom of the tub (43). They are placed at various angles and can be of different sizes. Certain parts of the tub bottom may hold more candles than others, in order to maintain natural circulation in the liquid.

The diaphragm-like aerating bodies are made of hard rubber, soft rubber, glass powder, metal, or fibrous material (40). The individual elements of the fine-aerating system are provided with separate air control and liquid-releasing devices (36); if liquid gets into the candles or other aerating bodies, it is returned to the tub.

A fine perforated rubber tube covers the perforated metal pipes of any conventional aerating system (33). The holes of the rubber tube are tight and open only under an excess of air pressure. The porous, ceramic, aerating candles are mounted at the outside surface of the perforated metallic pipes (34). The pipes are covered by elastic rubber rings or perforated rubber tubes which allow air from the metal pipe to go through the candles, but they close when inside pressure decreases.

Almost every yeast factory in Europe in 1930 and the following years attempted to apply Stich's method or to avoid his patents. A number of laboratory and semipilot-plant tests were made, but only a few factories made actual use of the process. They placed hundreds of ceramic candles upright in the bottoms of the tall yeast tubs and used screw connections to the copper air-line systems.

Several disadvantages of the method handicapped its broader use. If the ceramic candles were strong enough, excess air pressure (8-14 or more pounds per square inch) was required; with the resistance of the liquid, this amounted to 14-20 pounds or more. Thus, despite the greatly reduced amount of air, the energy requirement was just below that of other methods developed at the same time. The air compressors of the older plants were designed for a maximum pressure of about 6-8 pounds per square inch. When a plant was converted to the Stich method, the compressors had to be replaced. The maintenance expense of the easily broken candles, the danger of spoiling a mash if any of the candles broke during aeration, cleaning and sterilization difficulties, and the frequent changing of the candles because of clogging kept manufacturers from using them generally.

Numerous methods embody the elements of the Stich method or improvements upon it; several will be mentioned as examples. Braasch and Braasch (4) improved the fine-aerating process by adding small amounts of organic acid (acetic or lactic) to the wort. The addition of 0.01% or more lactic acid changes the surface tension of the mash so that the dimensions of the air bubbles will decrease to a fraction of their original size. By this method ceramic candles can be used with much larger pores, and less excess air pressure is required. Gosda (10) provided the candles with safety valves, introduced the air at both ends of the candles, and improved the screw connections between candles and metallic air lines. Bermann (3) recommended glass filter plates with pores of 40 to 70 μ for fine aeration. Schattaneck (26) recommended porous plates made of copper.

In the United States a number of devices made of ceramic substances or porous carbon available for filtration purposes are easily adapted to fine aeration. They are used for filtering beverages, serological, bacteriological, and other preparations,

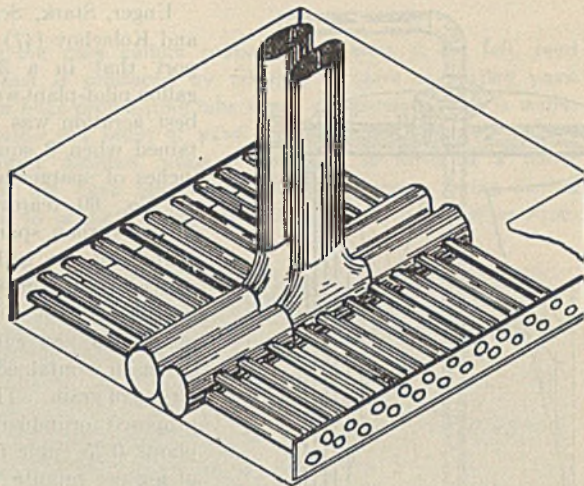


Figure 5. Double-Tube Aerating System of Strauch & Schmidt

and air. Recently some of them were specially designed⁷ and used for distributing gas in liquids. Carbon dioxide is⁷ dispersed through such porous substances in carbonated beverage production.

Porous substances are marketed in the form of plates, candles, or tubes. Plates are used as false bottoms. Tubes are connected on one or both ends to the air line for aeration. Tubes in horizontal position are also prepared with porous flat upper plates for fine aeration, when the semicylindrical part of the tube facing the side and bottom of the tub is impermeable. The characteristics of most of these devices are described in the commercial bulletins of the producers (19, 28). Carbon tubes are made up to 36 inches in length and $\frac{5}{8}$ -3 $\frac{3}{4}$ inches in inside diameter, with porosity from 5 to 190 μ . Air permeability of the various porosities per square foot per minute at various pressures is presented in charts.

In recent years American scientists have reported the use of porous substances to distribute air in yeast worts on a laboratory and pilot-plant scale. Pavcek, Peterson, and Elvehjem (21) used a silicon carbide tube as air distributor in a fermenter which dispersed 100 liters of air per minute. They obtained ten and a half to thirteen times as great a yield in aerated as in unaerated wort.

Stark, Kolachov, and Willkie (30) used aloxite stones, No. 30 and No. 60 carbon spargers, Berkefeld candles, and open glass tubes as air distributors in 500-ml. fermenters. Many of their data connected with air distribution prove the great importance of fine aeration. Their results also confirm that data on air requirement related to a single factor such as cubic feet per minute per gallon have limited value. The extremely low air consumption when Berkefeld filters are used correlated with facts previously stated. The orifices of a Berkefeld filter are very small and result in very fine air distribution at the cost of high air pressure.

Stark, Scaif, and Kolachov (57) report the effect of aeration on the growth of distiller's yeast. In selected experiments (which included their earlier work, 30) they used aloxite stone, Berkefeld candles, glass tube, and No. 30 and No. 60 carbon spargers as air distributors to provide the wort with 3, 0.8, 0.4, and 0.07 cubic foot of air per gallon per minute. They report optimum results when 0.4 cubic foot of air per minute per gallon of wort is distributed through 17 square inches of effective area of No. 60 carbon sparger.

The National Carbon Company (19) discloses that No. 60 carbon tubes contain pores of 33 μ diameter and require 34 pounds of air pressure per square inch for every 5 cubic feet per minute per square foot. Table II indicates the relation between pressure and power consumption.

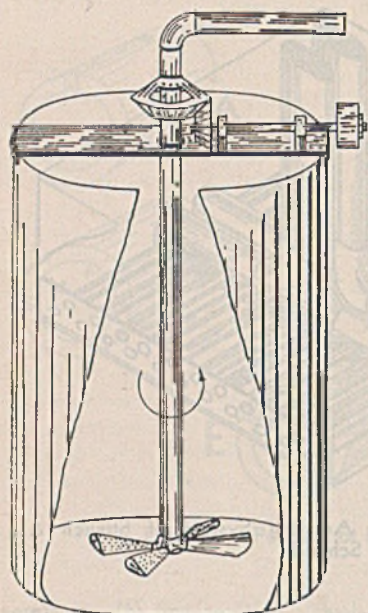


Figure 6. Fast-Rotating Mechanical Air Distributor of Vogelbusch (54)

Unger, Stark, Sealf, and Kolachov (47) report that in a 300-gallon pilot-plant wort, best aeration was obtained when 3 square inches of sparger area of No. 60 teardrop-shaped carbon sparger were used per gallon. Air consumption was 0.25 cubic foot of air per gallon; 80 gallon of mash contained 1 bushel of grain. They proposed for industrial plants 0.25 cubic foot of air per minute per gallon of wort, 10 cubic feet of air per minute per square foot of sparger surface, and air pressure of 40 pounds per square inch. Yeast concentrations are expressed in number of cells per

milliliter. The experiments of the four reports (21, 30, 47, 57) were made on a laboratory or pilot-plant scale. In one (30), growth factors and vitamin B₁ content of yeast were studied; in the other three, the production of distiller's yeast (simultaneously with alcohol). The same critical attention cannot be paid to the economy of aeration in propagating yeast for such purposes as in compressed yeast production. For instance, the power requirement where high air pressure was used is extremely high. These reports are still of great importance because fine aeration through porous substances was used and close specifications of conditions were reported.

III. FIXED DISTRIBUTORS WITH VARIOUS OPENINGS

The large reduction in the air requirement achieved by Stich's method left no doubt about the economical possibilities of fine aeration. To overcome the disadvantages of a nonmetallic substance, a number of devices were constructed in which the air was forced into the liquid as fine bubbles, through the small space between well-fitting metallic surfaces.

Vogelbusch (52) recommends winding the large openings of metallic tubes or other bodies with wire or fibrous substances. The air compressed into the tubes or other hollow bodies will enter the liquid between the narrow space of the joining wires or fibers. He also compresses the perforated surface of a metallic tube (50) so that the round holes will be deformed into narrow openings. A number of rings cut from sheet metal (53) are compressed next to one another to form a tube-like body. Drawing the compressed air into the hollow space causes it to escape into the liquid between the rings, in the form of fine bubbles.

According to Lockey (14), the air is forced into the liquid through the lengthy cuts of two metallic tubes. The smaller tube fits into the larger, and one of them is rotated.

Rank and Hahn (24) describe aerating bodies made of parallel wire of square cross section. Using low excess pressure, 0.5 pound per square inch, the air enters the liquid between the wires in the form of fine bubbles. The fineness of bubbles is increased by the sharpness of the edge of the wires. They claim that 18.7 horsepower are sufficient to supply 450 cubic feet of air per minute in mash 11.5 feet high, in the form of fine bubbles. They also state that 29 horsepower are required when diaphragm bodies are used under identical conditions.

IV. MECHANICAL AIR DISTRIBUTORS

Devices in this group use mechanical force to produce air bubbles of the smallest possible size in the wort. The air entering the liquid through relatively large openings forms tiny bubbles because of the difference in speed between liquid and air which is usually created by rotating bodies. Mechanical air distributors can be divided into the following types: The liquid is moved with considerable speed above the fixed openings of the air supply; the openings of the air supply are moved with considerable speed in the liquid; the air bubbles are introduced into the liquid in the form of large bubbles and are disintegrated there by fast-moving agitators.

Klipfel (18) describes equipment to aerate liquids for breweries or for compressed yeast production. It consists of a hollow vertical shaft connected with perforated tubes in horizontal position close to the bottom of the propagating tub. The air passing through the rotating shaft and the horizontal tubes is dispersed throughout the cross section of the liquid. This device has the elements of a modern mechanical air distributor.

Peter (22) recommends a slow-moving agitator which forces fine air bubbles introduced at the bottom of the tub in a slow rotating movement instead of a rapid upright pass through the mash. He improved this method (23) by introducing air between the double bottoms of the tub, the upper bottom of which is porous. This patent (23) contains the elements of both Groups II and IV. The correct technical application of both groups, however, was made about ten years later by Stich and followers and by Vogelbusch and followers.

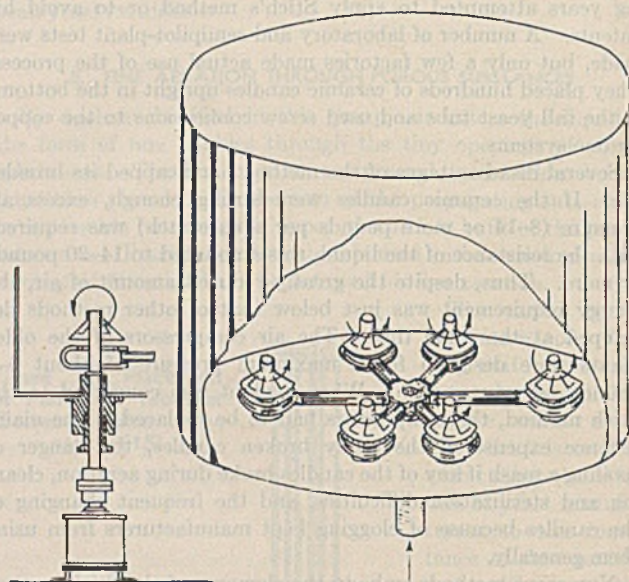
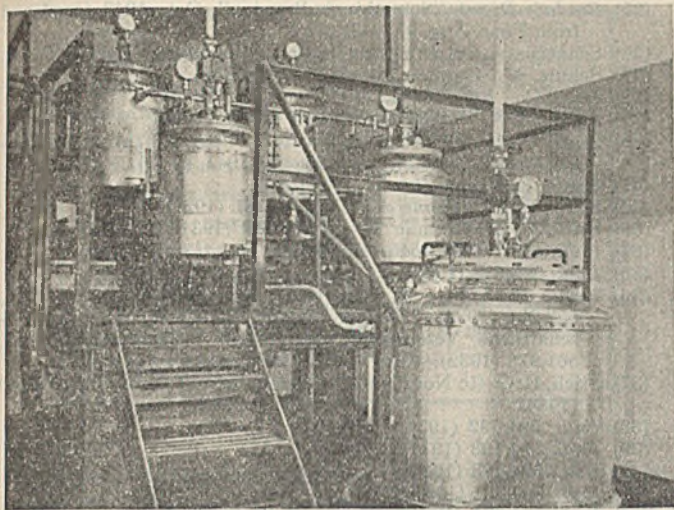


Figure 7. Simple Fine-Aerating Device of de Becq (1)

Vogelbusch (54) describes equipment in which air passes into the liquid through the holes of a fast-rotating, hollow metal device. Air is drawn into this container through a hollow vertical shaft which also provides the revolving motion. Baffle plates prevent the rotation of the liquid (Figure 6). Vogelbusch constructed several devices; the final form is a hollow propeller of perforated metal rotated at high speed (800-2000 r.p.m.). The speed of rotation permits the air passing through the relatively large holes (0.5 to 1 mm.) to enter the liquid in the form of very fine bubbles, which are further divided by the fast-moving propeller into microscopic particles. The fineness of the air bubbles increases with the difference in speed between liquid and propeller.



In the pure culture propagating system at the left, seed yeast is produced by aeration to serve as starting yeast for huge propagating tubs where compressed yeast is made. Below is a series of yeast tubs at one of Shenley's plants where distillers' yeast is produced to serve as a starter for the huge fermenters; attempts are now being carried on to propagate this distillers' yeast by means of aeration.

The air requirements of Vogelbusch's mechanical distributor are one fourth to one fifth the amount needed for perforated tubes. Zscheile (59) cites one commercial claim that the air requirement of the Vogelbusch distributor is 40-50 cubic feet per pound of new yeast. Compared with Table III, this figure is very low. As stated before, without data on other conditions and on the energy required by the mechanical air distributor, such figures are of little value.

De Beeze (1) describes a simple fine-aerating device. The air enters the liquid through relatively large openings ($1/25$ - $1/2$ inch in diameter), above which the liquid is kept in motion at high speed by a rotor or similar device. Baffle plates are placed near the rotor. The air may pass into the liquid through perforated tubes, plates, or even through the open end of a pipe line. The rotor can be a propeller, curved arms around a shaft, or some other device. The most practical arrangement is a reversed funnel with six to eight L-shaped cuts on the mantle, rotated at high velocity (500-1500 r.p.m.) above the upright open end of the air pipe. One or more units can be placed in a tub. The effects are similar to those obtained by the Vogelbusch system but are achieved by a simpler mechanical device (Figure 7).

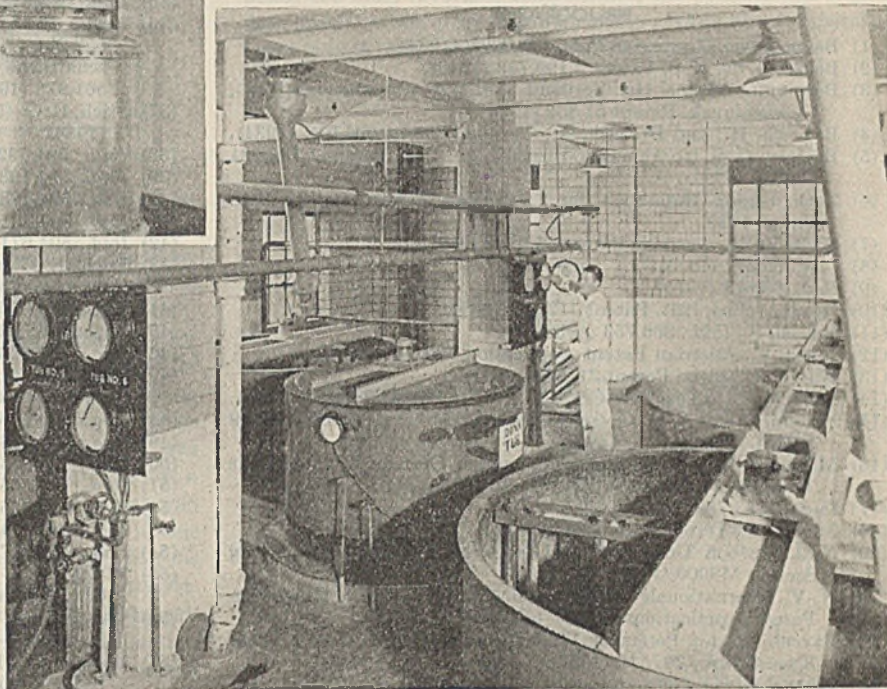
V. LIQUID SPRAY AERATORS

The devices in this group create maximum contact between liquid and air by distributing the liquid in the air in the form of a fine, dropping spray. These methods have no practical application at present. Two patents are mentioned as examples: According to the Schulz process (27), a portion of the wort from the tub is elevated by compressed air through a vertical pipe to a plate with zigzag edges. As it falls back into the tub in the form of a spray, the wort contacts the air over a large surface.

Sigmond (29) pumps a portion of the wort continuously into a flat, screen-bottomed tub located above the propagating vat. From there, in the form of fine spray, it is returned to the vat in constant contact with air.

VI. PACKED COLUMNS

The liquid in which the yeast propagates floats down in a column and there contacts the air which is blown in counter-current to the liquid. N.-V. Internationale Suiker en Alcohol



Compagnie (20) has used packed columns as fermenters to produce alcohol or yeast. The fermenting liquid, passing through a heat exchanger for temperature control, is pumped from the bottom of the column to the top. The liquid floats downward on the large surface of the contact material countercurrent to the air rising from the bottom. The air is compressed between the bottom plate and the perforated false bottom supporting the filling material.

The energy requirement for aeration is claimed to be small because of the small resistance of the column. When alcohol is produced, the fermentation time is reduced from the customary 40-70 hours to 7; when compressed yeast is produced, from the customary 12 hours to 2-3 hours. The method is chiefly used to ferment sugar obtained by wood cellulose conversion.

VII. MISCELLANEOUS

There are aerating systems which combine two or more of the fundamental principles. Many of them aerate only part of the wort at a time and then mix it with the bulk. These recommendations have hardly passed the pilot-plant stage.

Giesecke (7) suggests the continuous mixing of a portion of the wort with air by air jets placed in the bottom of the vat and returning the wort into the remainder of the liquid through perforated tubes. He improves the process (8, 9) by placing the air jets outside of the vat.

Vogelbusch (49) continuously withdraws part of the mash from the vat; after it is intensively aerated in a pipe line through an air distributor made of porous material, it is returned to the vat.

Jonas (12) continuously withdraws a portion of the yeast wort and returns it through a perforated tube network into the tub

after emulsifying it with air by passage through centrifuge-like equipment similar to yeast separators. No air compressors are required because the centrifuge sucks the necessary air. All the wort passes through the aerator every 25 minutes. Jonas claims that only 20 horsepower are needed to provide enough air for 13,200 gallons of wort.

ACKNOWLEDGMENT

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CATALYTIC VAPOR-PHASE OXIDATION OF Picolines over Vanadate Catalysts

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THE purpose of this investigation was to study the vapor-phase oxidation of the picolines over vanadate catalysts in an effort to determine the most favorable conditions for obtaining the pyridine carboxylic acids. The production of these acids by vapor-phase catalytic methods has not been reported previously. β -Picoline has received most attention in this study since its partial oxidation product, nicotinic acid, is of considerable importance.

The vanadates have been useful as catalysts in the oxidation of various organic compounds. In 1928 Maxted and Dunsby (3) oxidized several nitro and halogen derivatives of toluene to the corresponding benzoic acids over tin vanadate. Later Maxted (2) oxidized benzaldehyde, benzyl alcohol, and a number of

aromatic hydrocarbons over bismuth and tin vanadates. Bismuth vanadate was also used as a catalyst in the oxidation of furfural to maleic anhydride by Milas and Walsh (5). Kiprianov and Shostak (1) used bismuth, tin, and silver vanadates in the oxidation of benzene to maleic anhydride. Sulfur dioxide was also oxidized to sulfur trioxide over several vanadate catalysts by Neumann (6) and Maxted (4).

In this study the vanadates of five representative metals from different families of the periodic table were used as catalysts. From the results obtained a comparison of the catalytic activities of these various vanadates can be made.

Figure 1 is a diagram of the reaction chamber. Air was the oxidizing agent in all cases and was taken from a compressed air line. The rate of flow of air was measured by a differential level

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The vapor-phase oxidation of beta-picoline over five metallic vanadate catalysts was studied. Alpha- and gamma-picolines were oxidized over the most efficient catalyst. Favorable working conditions of each catalyst were determined by studying the effect of temperature, ratio of reactants, and velocity of reactants over the catalyst. The best results were obtained over a tin vanadate catalyst which gave 22.6% nicotinic acid at 275° C., with a 9 to 1 mole ratio of oxygen to beta-picoline.

flowmeter. After passing through a 12-inch column of anhydrous calcium chloride, the air passed through a preheater maintained at a temperature slightly lower than that of the reaction chamber, and then into the reaction chamber. The picoline was forced from a glass reservoir into the reaction chamber by means of compressed air. This air line contained an open-end manometer for measuring the pressure. By this procedure a constant flow of liquid from the reservoir could be maintained. The entering hot air vaporized the liquid and prevented formation of drops and fluctuations in liquid feed. The reaction chamber was heated electrically and the temperature was measured by a thermocouple. The catalyst bed, which was usually 1 inch and never more than 2 inches deep, rested directly on top of the thermocouple. The reaction temperatures of a number of runs were also measured by a thermometer embedded in the catalyst. Results closely comparable to these reported were obtained. The pyridine carboxylic acids were collected in two sublimation chambers connected in series. The exit gases then passed through two water-cooled spiral condensers to the carbon dioxide absorption train. In all experiments the $\frac{3}{4}$ -inch-diameter reaction chamber was fitted with a Pyrex liner (inside diameter, 16 mm.). In runs carried out without the glass liner, a loose scale of iron oxide formed inside the $\frac{3}{4}$ -inch iron pipe which served as the reaction chamber. The purpose of this glass liner was to prevent these oxides of iron from affecting the action of the catalysts. A 6-inch column of pumice which had previously been boiled in concentrated hydrochloric acid was placed in the reaction chamber above the catalyst to serve as a gas preheater and distributor.

Reilly Tar & Chemical Corporation furnished the α -, β -, and γ -picolines. Each of these picolines was dried over freshly roasted calcium oxide and fractionated. Fractions with 0.5° C. boiling ranges were used in all experiments.

PROCEDURE AND ANALYTIC METHOD

When a run was to be made, the temperature was adjusted and air was started through the furnace at the desired rate. A measured volume of picoline was delivered into the reservoir from a calibrated pipet, and sufficient pressure was placed on the reservoir to force the liquid through the capillary at the desired rate. Since the heat of reaction was considerable, it was necessary to effect some cooling. Experience showed that the temperature could be controlled fairly closely ($\pm 3^\circ$ C.) by directing a small electric fan toward the furnace during the course of the reaction. The exit gases from the reactor were passed through the carbon dioxide absorption train during the run and for 5 minutes thereafter. This time was sufficient to flush all carbon dioxide from the reactor. The furnace was flushed with air at least an hour before the sublimation chambers were removed. During this time all the solid products were removed from the furnace and the water from the reaction was evaporated from the condensers. The evaporation of this water was necessary since the small

amounts of dissolved carbon dioxide which it contained caused errors in the subsequent titration of the pyridine carboxylic acids.

After the flushing period was finished, the solid products were washed from the condensers and sublimation chambers with nearly boiling distilled water. The pyridine carboxylic acids formed were, in most cases, white. A melting point of 233° to 234° C. for the nicotinic acid and the fact that it did not lower the melting point of c.p. nicotinic acid indicated that the product was reasonably pure. In cases where the reaction was carried out below the most favorable temperature, the product was slightly discolored by the unchanged picoline. When the temperature was too high, the product was white but less abundant.

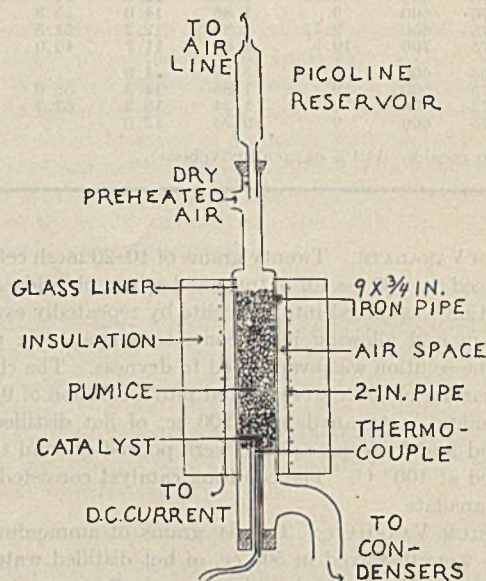


Figure 1. Reaction Chamber

The yields of pyridine carboxylic acids were estimated by titration with 0.05–0.10 *N* sodium hydroxide which had previously been standardized against c.p. nicotinic acid. To determine the extent of complete oxidation, the quantity of carbon dioxide in the exit gas was determined. In the carbon dioxide absorption train magnesium perchlorate was the dehydrating agent and ascarite was used to remove carbon dioxide. Precautions necessary in the combustion analysis of nitrogen containing organic compounds were taken. Since in most experiments pyridine carboxylic acid equivalent to 15–30 ml. of 0.05 *N* sodium hydroxide and 1.3–1.8 grams of carbon dioxide were formed, the yields could be determined fairly accurately. Oxidations carried out under identical conditions gave closely comparable results. The results reported are the average of at least two runs.

PREPARATION OF CATALYSTS

The vanadate catalysts were prepared in as nearly the same manner as possible. When the physical form of the catalyst permitted, no support was used. A celite support was used in cases where the vanadate was extremely fine and would not adhere on molding. The catalysts were not subjected to preliminary heat treatment. The reagents used in the preparations were c.p. grade.

TIN VANADATE. A solution of 12 grams of anhydrous stannic chloride in 200 cc. of distilled water was added to a solution of 20 grams of ammonium metavanadate in 500 cc. of hot distilled water until precipitation was complete. The red precipitate was washed by decantation with about 20 liters of distilled water, filtered, and dried at 100° C. Catalyst of 10–20 mesh size was used.

TABLE I. OXIDATION OF β -PICOLINE OVER TIN VANADATE
(0.93 g. β -picoline passed per run; volume of catalyst, 5.08 cc. or 6.0–6.2 g.)

Run No.	Temp., ° C.	Air, % of Theory for Nicotinic Acid ^a	Mole Ratio, O ₂ /β-Picoline	β-Picoline, Grams/Hr.	Nicotinic Acid, % of Theory	CO ₂ , % of Theory (by Complete Oxidation)	Nicotinic Acid, % Based on β-Picoline Oxidized
1	247	600	9	1.86	7.8	49.0	13.7
2	265	600	9	1.86	11.4	52.5	17.8
3	275	600	9	1.86	14.0	55.3	20.2
4	290	600	9	1.86	9.8	76.0	11.4
5	275	500	7.5	1.86	11.2	54	18.2
6	275	550	8.25	1.86	12.0	55.3	20.2
7	275	600	9	1.86	14.0	55.3	19.1
8	275	650	9.75	1.86	12.2	40.0	22.6
9	275	700	10.5	1.86	11.7
10	275	600	9	3.72	1.0	55.0	20.7
11	275	600	9	1.86	14.3	63.2	22.2
12	275	600	9	1.24	18.2
13	275	600	9	0.93	12.0

^a Dry air considered 21% oxygen (by volume).

BARIUM VANADATE. Twenty grams of 10–20 mesh celite chips were placed in 100 cc. of saturated barium chloride solution. The solution was forced into the celite by repeatedly evacuating the system and allowing it to come to atmospheric pressure. Finally the solution was evaporated to dryness. The chips containing barium chloride were poured into a solution of 9.5 grams of ammonium metavanadate in 200 cc. of hot distilled water. The liquid and loose precipitate were poured off and the chips were dried at 100° C. The resulting catalyst consisted of 11% barium vanadate.

POTASSIUM VANADATE. Twenty grams of ammonium metavanadate were dissolved in 500 cc. of hot distilled water. The quantity of potassium hydroxide theoretically necessary to liberate the ammonia was added and the solution was boiled until ammonia could not be detected with litmus. Twenty grams of 10–20 mesh celite chips were added and the solution was evaporated to dryness. The resulting catalyst consisted of 44% potassium vanadate.

FERRIC VANADATE. A solution of 20 grams of ferric chloride in 100 cc. of distilled water was added to a solution of 28 grams of ammonium metavanadate in 600 cc. of hot distilled water. The resulting precipitate was washed by decantation with approximately 15 liters of distilled water, filtered, and dried at 100° C. Catalyst of 10–20 mesh size was placed in the furnace.

SILVER VANADATE. A solution of 12 grams of ammonium metavanadate in 300 cc. of hot distilled water was added to a solution of 14 grams of silver nitrate in 200 cc. of distilled water. The resulting precipitate was washed with approximately 20 liters of distilled water, filtered, and dried at 100° C. Catalyst of 10–20 mesh size was placed in the furnace.

OXIDATION OF PICOLINES OVER TIN VANADATE

The variables which are most important in a vapor-phase catalytic oxidation are temperature, ratio of reactants, and flow rate of reactants over the catalyst or contact time. A summary of these variables in the oxidation of β -picoline over tin vanadate is shown in Table I.

The yield of nicotinic acid based on picoline oxidized was calculated on the assumption that all β -picoline not oxidized to nicotinic acid or carbon dioxide remained unchanged. This assumption was necessary since unreacted picoline was not recovered. The yield of nicotinic acid obtained in a single pass (nicotinic acid, per cent of theory) was measured directly.

The results in Table I indicate that a temperature of 275° C. is most favorable for the production of nicotinic acid over tin vanadate. It is interesting to note that this temperature checks

closely with the temperature used by Maxted in the oxidation of a large group of organic compounds over tin vanadate.

The results of runs 5–9 of Table I indicate that 600% of the air theoretically necessary for the production of nicotinic acid gives the most favorable ratio of reactants and contact time under the conditions described. When the air is in excess of 600% of theory or in excess of a 9:1 mole ratio of oxygen to β -picoline, the yields of both nicotinic acid and carbon dioxide decrease. This behavior is contrary to what might be expected at first glance. However, increasing the ratio of air to β -picoline increased the space velocity or decreased the contact time, which probably accounts to a great extent for the smaller yields of oxidation products. The results of runs 10–13 (Table I) show the effect of contact time at constant air ratio to be significant. A further explanation for this decrease in oxidation products is a possible lowering of the effective (reaction zone) temperature because of the additional heat capacity of the flowing mixture relative to the heat generated by the reaction.

The results of runs 10–13 also show that 1.25 grams of picoline per hour with a 9:1 mole ratio of oxygen to β -picoline is the most favorable flow rate of picoline over this catalyst. The most favorable conditions found here for the production of nicotinic acid are listed for run 12.

The results obtained in the oxidation of α - and γ -picolines over tin vanadate are summarized in Table II. Runs 1–6 show that

TABLE II. OXIDATION OF α - AND γ -PICOLINES OVER TIN VANADATE

(0.93 g. picoline passed per run; volume of catalyst, 5.08 cc.)

Run No.	Temp., ° C.	Air, % of Theory for Picoline Acid	Mole Ratio, O ₂ /β-Picoline	Picoline, Grams/Hr.	α-Pyridine Carboxylic Acid, % of Theory	γ-Pyridine Carboxylic Acid, % of Theory
1	210	600	9	1.86	..	4.9
2	220	600	9	1.86	..	8.5
3	230	600	9	1.86	16.9	8.5
4	255	600	9	1.86	18.8	10.5
5	265	600	9	1.86	14.7	8.9
6	290	600	9	1.86	13.0	7.5
7	255	400	6	1.86	3.6	..
8	255	500	7.5	1.86	15.0	1.2
9	255	600	9	1.86	18.8	10.0
10	255	700	10.5	1.86	17.0	10.6
11	255	800	12	1.86	10.0	11.1
12	255	900	13.5	1.86	..	11.0
13	255	{ 600 with α-, 9 with α- }		2.79	8.6	8.0
14	255	{ 900 with γ-, 13.5 with γ- }		1.86	18.8	11.0
15	255	{ 900 with γ-, 13.5 with γ- }		1.24	13.7	7.5
16	255	{ 900 with γ-, 13.5 with γ- }		0.93	11.8	6.5

TABLE III. OXIDATION OF β -PICOLINE OVER BARIUM VANADATE
(0.93 g. β -picoline passed per run; volume of catalyst, 20.3 cc. or 8.5 g.)

Run No.	Temp., ° C.	Air, % of Theory for Nicotinic Acid	Mole Ratio, O ₂ /β-Picoline	β-Picoline, Grams/Hr.	Nicotinic Acid, % of Theory	CO ₂ , % of Theory (by Complete Oxidation)	Nicotinic Acid, % Based on β-Picoline Oxidized
1	275	600	9	1.86	2.2	33.0	6.2
2	290	600	9	1.86	2.3	43.2	5.1
3	320	600	9	1.86	7.5	57.0	11.6
4	330	600	9	1.86	12.6	60.1	17.3
5	340	600	9	1.86	12.8	62.0	17.1
6	350	600	9	1.85	12.3	64.2	16.1
7	365	600	9	1.86	6.6	65.0	9.2
8	340	300	4.5	1.86	1.0	40.0	2.4
9	340	500	7.5	1.86	8.3	64.0	11.5
10	340	600	9	1.86	12.8	62.0	17.1
11	340	700	10.5	1.86	12.2	57.5	18.0
12	340	800	12	1.86	9.5	57.0	14.3
13	340	600	9	3.72	5.0	47.0	9.6
14	340	600	9	2.23	14.2	55.0	20.5
15	340	600	9	1.86	12.8	62.0	17.1
16	340	600	9	1.24	11.5	70.0	14.1

TABLE IV. OXIDATION OF β -PICOLINE OVER POTASSIUM VANADATE0.93 g. of β -picoline passed per run; volume of catalyst, 10.2 cc. or 6.6 g.)

Run No.	Temp., ° C.	Air, % of Theory for Nicotinic Acid	Mole Ratio, O ₂ /β-Picoline	β-Picoline, Grams/Hr.	Nicotinic Acid, % of Theory	CO ₂ , % of Theory (by Complete Oxidation)	Nicotinic Acid, % Based on β-Picoline Oxidized
1	290	600	9	1.86	Trace	6.6	...
2	317	600	9	1.86	1.1	15.2	6.7
3	335	600	9	1.86	2.4	22.3	9.7
4	340	600	9	1.86	2.5	24.1	9.4
5	353	600	9	1.86	4.5	36.0	11.1
6	365	600	9	1.86	9.3	57.0	14.6
7	380	600	9	1.86	9.5	74.0	10.2
8	365	700	10.5	1.86	6.7	48.0	12.3
9	365	600	9	1.86	9.7	57.4	14.5
10	365	500	7.5	1.86	12.3	58.0	17.5
11	365	400	6	1.86	13.4	70.0	16.1
12	365	300	4.5	1.86	Trace	68.0	...

TABLE V. OXIDATION OF β -PICOLINE OVER FERRIC VANADATE0.93 g. of β -picoline passed per run; volume of catalyst, 5.08 cc. or 1.4 g.

Run No.	Temp., ° C.	Air, % of Theory for Nicotinic Acid	Mole Ratio, O ₂ /β-Picoline	β-Picoline, Grams/Hr.	Nicotinic Acid, % of Theory	CO ₂ , % of Theory (by Complete Oxidation)	Nicotinic Acid, % Based on β-Picoline Oxidized
1	260	600	9	1.86	1.2	8.0	13.0
2	280	600	9	1.86	4.3	17.1	20.1
3	300	600	9	1.86	6.8	27.4	19.9
4	320	600	9	1.86	7.8	51.4	13.2
5	300	300	4.5	1.86	3.0	44.0	6.4
6	300	400	6	1.86	4.2	44.1	8.7
7	300	500	7.5	1.86	7.0	39.7	14.9
8	300	600	9	1.86	6.8	27.4	19.9
9	300	700	10.5	1.86	4.7	16.8	21.9

with α - and γ -picolines the catalyst is active in the same temperature range as in the oxidation of the beta isomer. However, the optimum yields of picolinic acids were obtained at a slightly lower temperature. The need for a fairly large excess of air in this reaction is demonstrated. When the amount of air dropped to 400% in the case of α -picoline and 500% in the case of γ -picoline (with contact times increased proportionately), the decreases in acid yields were extremely sharp.

The life of tin vanadate as a catalyst in this oxidation is not long; it is much longer-lived as a catalyst in the oxidation of toluene. In the oxidation of picoline a physical change takes place in the vanadate; it is much more finely divided and is covered with a black deposit when removed from the reaction chamber. Attempts to reactivate it by heating in a stream of air at 475° C. for 16-18 hours were unsuccessful. It is probable that the life of this catalyst might be lengthened by placing it on the proper support. The tin vanadate was much more active when first placed in the furnace. For example, 80-90% of the first 4-5 grams of β -picoline passed over the catalyst was oxidized to carbon dioxide and no nicotinic acid was detected. During the passage of the first 5-6 grams of picoline, the catalyst was gradually deactivated. The activity then remained rather constant while the next 25-30 grams of picoline were passed. The results in all the tables were taken while the activity of the catalyst was constant; i.e., a run made at the beginning of the study gave yields which correlated closely with the results of a run carried out under the same conditions at the close of the study.

OXIDATION OF β -PICOLINE OVER BARIUM VANADATE

The results obtained in the oxidation of β -picoline over barium vanadate are given in Table III. Optimum yields of acid can be obtained over a fairly wide temperature range (runs 1-7). Although this is an advantage over tin vanadate, the yields of acid

per pass were considerably lower over barium vanadate. Increasing the ratio of air to picoline (runs 8-12) caused the yields of nicotinic acid to pass through a maximum. A low mole ratio of air to β -picoline with the proportionately longer contact time was favorable to carbon dioxide production and unfavorable to nicotinic acid production. As the ratio of air to β -picoline increased beyond 9 to 1 (with contact time decreased), the yields of both carbon dioxide and nicotinic acid decreased slightly, the decrease in acid becoming more apparent at a 12 to 1 ratio. Barium vanadate had at least 50% longer life than tin vanadate. After more than 40 grams of β -picoline had passed over the barium vanadate, the yields of nicotinic acid had decreased only slightly.

OXIDATION OF β -PICOLINE OVER POTASSIUM VANADATE

The results obtained in the oxidation of β -picoline over potassium vanadate are summarized in Table IV. A fairly high temperature is reached before potassium vanadate becomes active. The outstanding feature of this catalyst is its extremely short life. After about 18 grams of β -picoline have passed over it, the yields of acid and carbon dioxide had decreased to about 70% of the yields obtained after 5-10 grams of picoline had passed. For this reason the study was discontinued before the effect of flow rate of picoline was determined.

OXIDATION OF β -PICOLINE OVER FERRIC VANADATE

The results of the oxidation of β -picoline over ferric vanadate are shown in Table V. Ferric vanadate was the least efficient catalyst studied. Above 300° C. the nicotinic acid was very dark colored. For this reason the later runs were made at 300° C. Because of the unsuitable product and the low acid yields the study was discontinued before the effect of flow rate of reactants was determined.

OXIDATION OF β -PICOLINE OVER SILVER VANADATE

The oxidation of β -picoline over silver vanadate was studied between 255° and 370° C. with an oxygen to β -picoline ratio of 1.5-10.5 to 1. Not more than 1-2% of nicotinic acid was produced in any experiment. At 350° C. and with a 9 to 1 oxygen to β -picoline ratio almost 70% of the picoline was completely oxidized. Less drastic conditions produced less carbon dioxide, but the acid yields did not increase appreciably. The silver vanadate was very light and porous but shrank considerably during use. A suitable support which would eliminate such shrinkage would probably make silver vanadate a more efficient catalyst.

SUMMARY

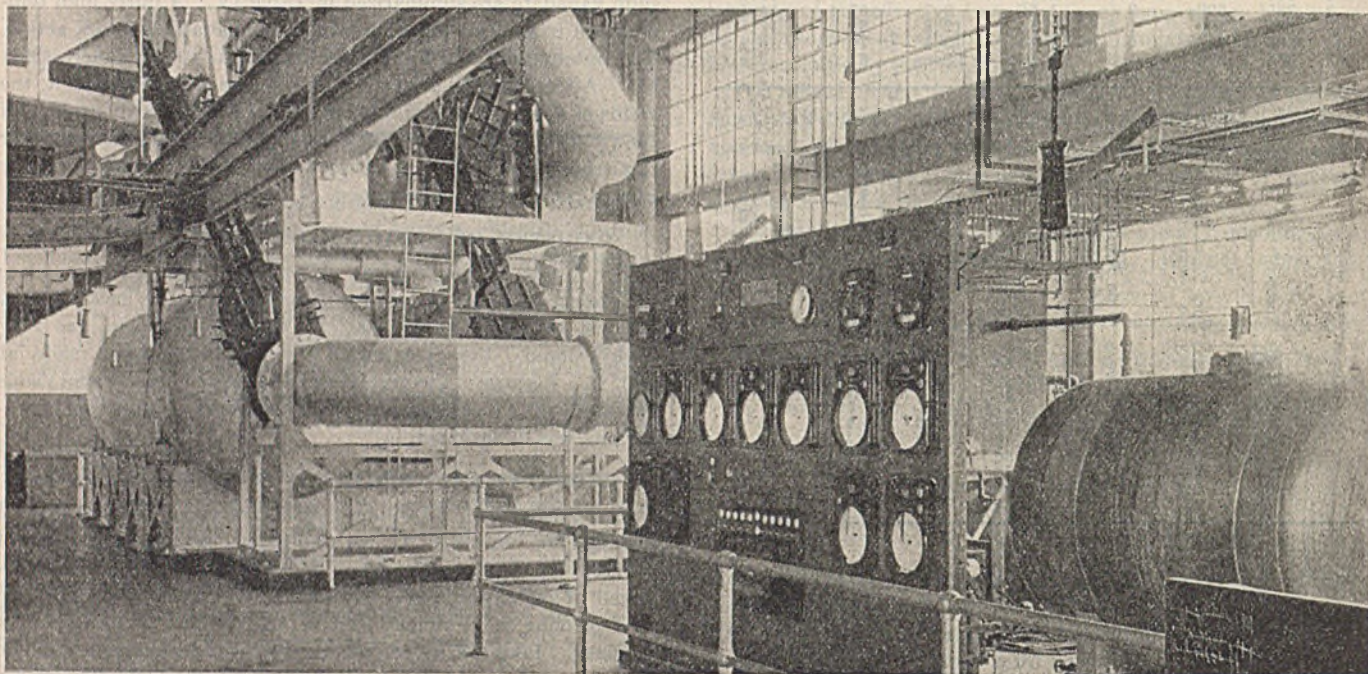
This investigation showed that the vanadate catalysts described were too active to produce good yields of pyridine carboxylic acids. With tin vanadate, the best catalyst studied, 81.4% of the β -picoline passed was used up while only 18.2% was converted to nicotinic acid. Barium vanadate was slightly less active under the most favorable conditions found here, and the yield of nicotinic acid based on picoline oxidized compared favorably with the results obtained over tin vanadate. Each catalyst required a large mole ratio of air to picoline and short contact time for most favorable results. Each catalyst underwent a preliminary deactivation period while the first few grams of picoline were passed. The activities of the catalysts then remained constant for some time.

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Adsorption of Solvent Vapors on COMMERCIAL ACTIVATED CARBON



THE major industrial applications of activated carbon are in solvent recovery, refining and production of foods, chemicals, water, and pharmaceuticals, and in certain catalytic reactions. At present large quantities of activated carbon are being used in gas masks. The value of this adsorbent lies in its ability to remove substantially all organic vapors from the surrounding medium, even though they are present in infinitesimal concentrations. Recovery of solvent vapors from some industrial processes is often uneconomic or even impossible by condensation or compression procedures, and solvent adsorption on activated carbon is used. The simplicity of the apparatus, its ease of operation and control, low recovery cost per pound of solvent, and high efficiency have combined to make this method important. Furthermore, the heat effects in adsorption seem to be particularly adapted to some types of cooling, such as might be used in refrigeration and air-conditioning thermodynamic cycles. The initial step in the design of an adsorption unit is the determination of equilibrium data to indicate the maximum possible adsorption under ideal conditions. Complete equilibrium data are available for the vapors of only a few solvents.

There are three general methods for measuring adsorption of vapors on solid adsorbents:

DYNAMIC (WEIGHT). Measured quantities of carrier gas containing definite concentrations of vapor are passed through an

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adsorbent bed. The quantity of vapor adsorbed is measured by weighing the bed.

STATIC (VOLUME). A measured quantity of vapor is placed in contact with the adsorbent. After the system has attained equilibrium, as recorded by unchanging pressure, the

volume of the unadsorbed vapor is calculated to give, by difference, the quantity adsorbed.

STATIC (WEIGHT). A helical spring (2, 8), supporting a bucket of adsorbent, is mounted in a closed system (9). The vapor is introduced and maintained at a constant pressure, and the adsorption is measured by observing accurately the deflection of the spring. The apparatus used has some disadvantages, while the method appears to be the best one available.

The purpose of this investigation was to determine and correlate fundamental adsorption data of equilibrium pressures and concentrations on a commercial activated carbon for certain industrially important solvents over wide ranges of temperature, vapor pressure, and adsorbate concentration.

APPARATUS

An apparatus was constructed of Pyrex (Figure 1) which included the best features of previous equipment (8, 9). It was designed so that the adsorbent could be maintained at a controlled temperature between room and 550° C. A fixed vapor pressure of the organic liquid being studied was produced by maintaining it at a fixed temperature. The glass parts were

mounted on a steel and wood support and cushioned with sponge rubber to minimize vibration.

ADSORPTION TUBE A. This vertical tube, about 90 cm. long, contained weighing spring *Q*, the carbon, and two thermometers, T_4 and T_1 , for measuring their respective temperatures. A quartz fiber, *V*, supported aluminum bucket *U* and the carbon. At the top of this tube was a hollow ground-glass stopper *J* into which had been sealed two 1-mm. glass cross bars. The tandem thermometers were suspended by a hook from one of the cross bars and the spring-bucket system from the other. When this stopper was raised, therefore, everything in the tube was removed.

The lower thermometer, T_1 , had a nominal range to 550° C. in order to withstand the high temperature of the degassing operation, later described. It was read during the runs (as well as thermometer T_2 in the bath outside of the adsorption tube) and recalibrated after each run. Corrections were made later to values read. This was necessary because of the tendency to give a different reading after exposure to the high temperature of degassing.

BERYLLIUM COPPER SPRING Q. The heart of the apparatus was weighing spring *Q*. The literature methods for fabricating quartz springs (2, 8) were tried and found laborious. A semi-automatic machine was constructed so that satisfactory springs could be fabricated with a minimum of difficulty. They are, however, very fragile, and it seemed desirable to find a better material.

Beryllium copper combines exceptional strength with corrosion resistance, high endurance strength, and heat hardening after forming, and therefore approaches most closely the ideal metal for springs (6). The final spring was made of this alloy by Instrument Specialties Company, Inc., and was calibrated by adding standard weights to a small mica pan suspended from the lower end. A perfect straight-line relation was found throughout the entire range of elongation vs. weight. Details of the spring follow:

Outside diam., mm.	8.28	Sensitivity, mm./g.	241.86
Diam. of wire, mm. (in.)	0.178 (0.007)	Compressed length, mm.	59
No. of turns	301	Suspended free length, mm.	257

BUCKET U. A piece of aluminum foil approximately 2.5 cm. square was formed around a piece of 7-mm. glass rod. Two hoops of extremely fine wire and a thin bail were added. The final bucket was 17 mm. long and 8.2 mm. in diameter and weighed 0.0427 gram. It was suspended from the spring by a long (55-cm.) link, *V*, of fine quartz fiber, to keep the spring above the heated base of the adsorption tube A.

CATHETOMETER P. This was mounted on a 2-inch steel pipe connected to a 1/2-inch steel plate which was bolted onto the stone desk top. It had a focal range of about 2 inches and was focused on the lowermost coil of the spring which was illuminated by a blue microscope light, *R*, from behind. The range of vertical motion was 50 mm.; the vernier scale was read directly to 0.005 mm. and could be interpolated to 0.001 mm. With a

The adsorption equilibria of pressures, temperatures, and concentrations on a commercial activated carbon were determined for the following organic solvents: acetone, methyl ethyl ketone, methyl isobutyl ketone, methanol, carbon disulfide, and ethyl ether. An improved apparatus is described which permits rapid measurement of the equilibrium adsorbate concentration over wide ranges of vapor pressure and adsorbent temperature. The apparatus is of the static weight type in which the weight of vapor adsorbed is measured by observing with a microscope the elongation of a sensitive beryllium copper spring carrying the adsorbent. The data are plotted initially as isotherms; from these isosteres are cross-plotted to give straight-line relations by the graphical method previously described (13). Heats of adsorption are calculated by the same method. Such data of adsorbent characteristics and vapor adsorbability over the wide ranges studied are important as the basis for industrial design and applications in solvent recovery operations. The photograph shows an instrument panel and adsorbers in a completely automatic Columbia activated carbon solvent-recovery plant (courtesy of Carbide & Carbon Chemicals Corporation).

spring sensitivity of 241.86 mm. per gram, weight changes of about 0.000004 gram could be measured.

VAPOR PRESSURE TUBE B. The organic liquid entered this tube via buret *G* and cock *H* and was maintained at the desired temperature by the constant-temperature bath in a Dewar flask, *N*. Temperatures below room were used, since above that point there was condensation within the system. A solid carbon dioxide-methanol solution was used as a bath and was thoroughly mixed by an electrically driven stirrer (not shown). The additions of the solid carbon dioxide were small and frequent; and the temperature was readily maintained within 0.5° C., as shown by thermometer T_3 .

MANOMETER C. Connected to the top of vapor pressure tube *B* was an open-end, U-bend, 7-mm. Pyrex manometer, filled with triple-distilled mercury. The end open at the atmosphere passed down into a small bottle stoppered with clean cotton; and a steel scale allowed measurements which could be estimated to 0.1 mm.

CONSTANT-TEMPERATURE BATHS L AND M AND COLD TRAP D.

Dewar flask *L* contained a mixture of methanol and solid carbon dioxide so that any diffusing mercury vapor would be condensed while the pumps were operating during the purging of the carbon. The entering line to the vacuum system was 22 mm. in diameter, and a 42-mm. jacket served as a condenser. Transparent Dewar flask *M* contained peanut oil, an electric agitator, and an immersion heater. A Variac transformer allowed temperature control within 0.5° C. Thermometer T_2 served to check internal thermometer T_1 .

PUMPS E AND F. The vacuum pump system consisted of a Cenco mercury diffusion pump and a Cenco Pressovac with the necessary accessories to reduce the pressure to 10^{-6} mm. mercury.

STOPCOCKS O, K, AND H. Vent cock *O* was a standard 2-mm. bore vacuum cock. A large 10-mm.-bore vacuum cock, *K*, with mercury seal closed off the pumps. Liquid supply cock *H* had a capillary bore, mercury seal, and pressure-equalizing connection to the base. The most satisfactory stopcock grease for acetone and methanol was Apiezon M (Shell Oil Company); and that most resistant to methyl ethyl ketone, methyl isobutyl ketone, ethyl ether, and carbon disulfide was Nonaq (Eimer and Amend).

MATERIALS. A commercial activated carbon from coconut shells was used; it was Columbia grade 4SXA, 6-8 mesh (Carbide & Carbon Chemicals Corporation). It was in the form of small cylinders and had the following standard commercial specifications and screen analysis:

Specifications		Screen Analysis, %	
Activity, %	85.5	4-6 mesh	2.6
Retentivity, %	43.8	6-8 mesh	87.3
Apparent density	0.462	8-10 mesh	7.2
Strength, %	98	10-14 mesh	2.4
Ash, total, %	1.15	Fines	0.6

The liquids were c.p. materials, further purified and distilled in an efficient laboratory rectifying column, with a discard of fractions above and below the accepted boiling points.

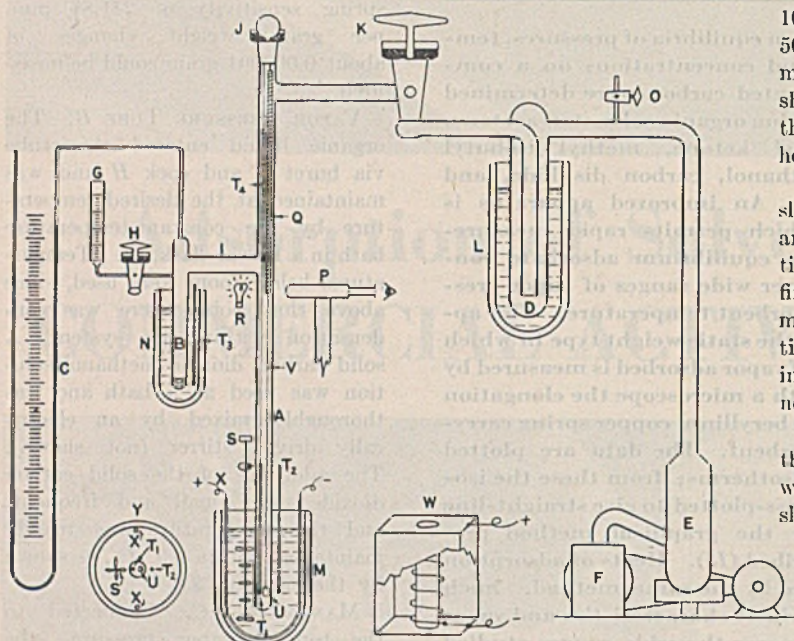


Figure 1. Diagram of Apparatus

- A. Adsorption tube containing weighing spring system
 B. Vapor pressure tube containing liquid being adsorbed
 C. Mercury manometer for measuring vapor pressure of liquid being adsorbed (equilibrium adsorption pressure)
 D. Cold trap for condensing mercury vapor
 E. Mercury diffusion pump to maintain 10^{-6} mm. Hg pressure
 F. Backing pump (Pressovac)
 G. Graduated buret for supplying liquid to system
 H. Capillary stopcock, mercury-sealed
 I. Connecting tube between adsorption tube and vapor pressure tube
 J. Adsorption tube stopper (mercury-sealed) for removing spring system
 K. Large mercury-sealed stopcock (10-mm. bore) for shutting off pump system after evacuation
 L. Dewar flask for cold trap, filled with low-temperature mixture
 M. Dewar flask for adsorption tube bath, maintained to give desired carbon temperature
 N. Dewar flask for vapor pressure tube bath, maintained to give desired liquid temperature and vapor pressure
 O. Vent stopcock (2-mm. bore)
 P. Cathetometer for measuring elongation of spring
 Q. Beryllium copper spring which elongates as carbon adsorbs and increases in weight
 R. Microscope light
 S. Agitator for constant-temperature bath
 T₁. Thermometer for measuring carbon temperature
 T₂. Thermometer for measuring temperature of bath around adsorption tube
 T₃. Thermometer for measuring temperature of liquid being vaporized and adsorbed
 T₄. Thermometer for measuring spring temperature
 U. Aluminum bucket for holding carbon as adsorbent
 V. Quartz fiber link to suspend adsorbent in heated zone, with spring itself sufficiently removed to be cold
 W. Removable electric furnace for heating carbon during degassing operation
 X. External heater for maintaining desired bath temperature
 Y. Cross section of adsorption tube system and surrounding constant-temperature bath

OPERATION

PREPARATION. The apparatus was thoroughly boiled out five times with the pure solvent to be studied. The plugs of the stopcocks were removed, cleaned, and greased. The weighing spring was recalibrated each time it was removed, although deviations from the initial calibration were always negligible. Approximately 0.2 gram (seventeen pellets) of activated carbon was placed in the bucket. The spring, link, and bucket with carbon were hooked to stopper J and lowered into tube A along with thermometers T₁ and T₄. An initial reading was then made of the spring length.

DEGASSING. Oil backing pump F was started, and large stopcock K was opened slowly. Removable electric furnace W was mounted around the lower portion of adsorption tube A with the bucket in the center, and was heated slowly until thermometer T₁ read 500° C. A shield of asbestos board, 6 inches above the furnace, prevented heating of the spring by radiation. After an hour of pumping, the pressure was approximately 0.01 mm. A solid carbon dioxide-methanol bath, L, was placed around mercury trap D to condense any mercury vapor. Then mercury diffusion pump E was started and allowed to pump for 5 hours to give a pressure of approximately

10^{-6} mm. During this time the charcoal was maintained at 500° C. and thus degassed. Large stopcock K was closed, mercury diffusion pump E and Pressovac pump F were shut off, and furnace W was shut down gradually so that the final attainment of room temperature took several hours.

PURGING. The next day 2 ml. of liquid were passed slowly through stopcock H. This vaporized immediately and was adsorbed by the carbon with consequent elongation of the spring. Gas molecules, not removed by the first degassing, were supplanted on the carbon surface by molecules of the substance to be studied. An exact repetition of the degassing operation served to put the carbon in final condition. The new length of the spring was then noted; this became the zero point.

DATA TAKING. With the carbon completely degassed, the system was ready for use. Fifteen milliliters of liquid were poured into buret G. Approximately 12 ml. were slowly passed into vapor pressure tube B around which had been placed a solid carbon dioxide-methanol bath N, with a temperature of -77° C. This condensed most of the flash vapor formed and decreased the surge of adsorption on the carbon. The temperature of this bath was allowed to rise to give the desired vapor pressure of the liquid, as shown by manometer C. This temperature was maintained. Electric furnace W was replaced by constant-temperature oil bath M, and the desired carbon temperature was obtained and maintained.

The weight of adsorbate per gram of adsorbent was calculated from the deflection of the spring observed with the cathetometer P. With fixed vapor pressure of the liquid and temperature of the carbon, sorption was considered at equilibrium when no change in length of the spring was observed during a half hour. This equilibrium condition was always attained within approximately 2 hours after changing either the charcoal temperature or the liquid temperature and vapor pressure.

During a series of runs the temperature of the liquid and hence the vapor pressure, as shown by manometer C, were maintained con-

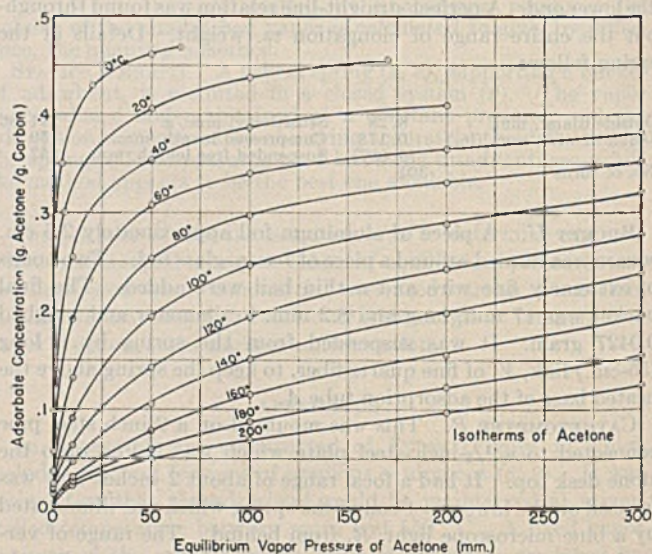


Figure 2. Isotherms of Acetone Adsorption

stant; and the carbon temperature was changed from 40° to 200° C. in uniform steps of 20°. While a series was usually made with increasing temperatures of carbon, these series were checked frequently by reversing the temperature steps and also at intervals the same day. Once or twice check runs were made after intermediate degassing. These duplications confirmed the equilibria measured as being absolute and indicated that there were no measurable hysteresis effects.

Different series of runs were made for each of several different liquid temperatures and vapor pressures. The upper limit of the liquid temperature was the room temperature, since, at higher liquid temperatures, vapors condensed in the apparatus. Liquid temperatures below about -30° C. were not used because of the correspondingly low vapor pressures.

TABLE I. ADSORPTION OF SOLVENT VAPORS ON ACTIVATED CARBON

Adsorbate		Adsorbate Concn., in Grams/Gram Carbon, at Carbon Temp. of:										
Temp., ° C.	Vapor pressure, mm.	0° C.	20° C.	40° C.	60° C.	80° C.	100° C.	120° C.	140° C.	160° C.	180° C.	200° C.
Acetone Vapor												
-70	0.4	0.0984	0.0578	0.0368	0.0243	0.0212	0.0202	0.0177	0.0156	0.0135
-32	10	0.3912	0.3264	0.2549	0.1920	0.1321	0.0905	0.0635	0.0476	0.0309	0.0278	0.0221
-5.8	50.2	0.4619	0.4060	0.3540	0.3079	0.2535	0.1942	0.1428	0.1050	0.0780	0.0596	0.0494
7.4	100	0.4390	0.3870	0.3401	0.2971	0.2489	0.1941	0.1519	0.1157	0.0882	0.0688
21.8	200	0.4100	0.3650	0.3308	0.2885	0.2430	0.1979	0.1551	0.1224	0.0968
31.1	300	0.4278	0.3818	0.3526	0.3212	0.2781	0.2389	0.1956	0.1552	0.1250
44.8	500	0.4017	0.3780	0.3512	0.3249	0.2941	0.2509	0.2161	0.1830
Methyl Ethyl Ketone												
-25	5.0	0.5118	0.4340	0.3500	0.2980	0.2040	0.1470	0.1065	0.0715	0.0520	0.0342	0.0240
-20	7.2	0.5257	0.4562	0.3990	0.3216	0.2467	0.1828	0.1266	0.0904	0.0653	0.0467	0.0350
-10	14.1	0.5511	0.4948	0.4300	0.3740	0.3120	0.2360	0.1760	0.1270	0.0960	0.0690	0.0500
0	26.5	0.5702	0.5259	0.4519	0.4073	0.3504	0.2870	0.2210	0.1676	0.1262	0.0960	0.0711
10	45.0	0.5551	0.4781	0.4360	0.3840	0.3280	0.2600	0.2060	0.1600	0.1270	0.0960
20	73.3	0.5070	0.4540	0.4134	0.3672	0.3053	0.2520	0.2000	0.1598	0.1300
25	88.1	0.5193	0.4365	0.3250	0.2210	0.1470
30	114.6	0.5381	0.4948	0.4603	0.4212	0.3678	0.3147	0.2580	0.2210	0.1818
Methyl Isobutyl Ketone Vapor												
-20	1.6	0.3420	0.3061	0.2608	0.2193	0.1734	0.1313	0.1036	0.0792	0.0500
-10	3.2	0.3600	0.3281	0.2851	0.2419	0.2040	0.1680	0.1317	0.1040	0.0764
0	7.6	0.3725	0.3440	0.3128	0.2760	0.2320	0.1980	0.1618	0.1300	0.1015
10	11.0	0.3827	0.3594	0.3319	0.2994	0.2631	0.2290	0.1940	0.1600	0.1300
20	17.3	0.3880	0.3677	0.3451	0.3160	0.2836	0.2488	0.2124	0.1771	0.1484
Methanol Vapor												
-20	7.6	0.0301	0.0103	0.0082	0.0069	0.0060	0.0060
0	29.8	0.2373	0.0905	0.0357	0.0247	0.0205	0.0181	0.0171	0.0165
10	54.7	0.3352	0.1693	0.0724	0.0380	0.0280	0.0229	0.0205	0.0190	0.0172
20	95.1	0.4000	0.2558	0.1280	0.0600	0.0380	0.0301	0.0260	0.0180
Carbon Disulfide Vapor												
-20	47.2	0.5580	0.4679	0.3720	0.2800	0.2085	0.1605	0.1187	0.0978	0.0738
-10	79.5	0.6002	0.5228	0.4280	0.3608	0.2705	0.2070	0.1680	0.1265	0.1028
0	134.4	0.6397	0.5678	0.4946	0.4450	0.3422	0.2693	0.2174	0.1736	0.1414
10	207.3	0.6595	0.5908	0.5312	0.4770	0.3958	0.3180	0.2682	0.2150	0.1780
20	297.3	0.6741	0.6128	0.5632	0.5031	0.4345	0.3711	0.3076	0.2460	0.1938
Diethyl Ether Vapor												
-20	64.0	0.3481	0.2945	0.2497	0.2072	0.1671	0.1243	0.0868	0.0641
-10	123.6	0.3702	0.3300	0.2945	0.2528	0.2123	0.1741	0.1379	0.1082
0	208.8	0.3879	0.3557	0.3224	0.2831	0.2442	0.2095	0.1810	0.1552
10	290.8	0.3996	0.3671	0.3331	0.2978	0.2620	0.2261	0.2005	0.1684
20	458.8	0.4000	0.3736	0.3472	0.3186	0.2792	0.2496	0.2162	0.1817

RESULTS

Data are shown in Table I for the lower ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone), and for methanol, carbon disulfide, and ethyl ether. Isotherms (Figure 2) were plotted as adsorbate concentration *vs.* equilibrium vapor pressures for all runs taken at the same carbon temperature. There are as many points on each isotherm as there were different liquid temperatures and vapor pressures. These isotherms were then cross-plotted to give isosteres (Figure 3) by picking off the intersections of the isotherms with uniformly spaced ordinates. The method of plotting logarithms of equilibrium pressures *vs.* logarithms of vapor pressures of a reference substance has been described (13). Acetone was chosen as the reference substance for the plot of the ketones; it is the initial member of the ketone series, and available thermodynamic data for it are most complete. With the other materials, each was used as its own reference substance for plotting.

The data points never deviated from straight lines by more than the experimental error. Since there are no published data for these materials on this carbon, no comparisons with other work can be made. The slopes of the lines were determined; by the method previously indicated (13), the instantaneous or partial heats of adsorption were obtained and plotted (Figure 4).

Vapor pressures of most of the liquids have not been reported in the literature for values below 0° C. (3, 5, 10, 14), and they are listed in Table II. Vapor pressures of the solvents studied are plotted in Figure 5 against the vapor pressure of acetone on log paper by the method previously described (11).

The lines are straight, and the calculated latent heats of vaporization agree with accepted values (5, 7).

The isotherms of acetone, methyl ethyl ketone, methyl isobutyl ketone, carbon disulfide, and ethyl ether have the same general shape. The rapid rise in the quantity of vapor adsorbed in the low-pressure region is marked at low carbon temperatures. This rate of increase flattens out with higher temperatures until the isotherms are almost straight lines. With increase of vapor pressure, the isotherms (especially those at low temperatures) tend to become horizontal. In this range a tremendous increase in vapor pressure gives only a small increase in adsorbate concentration on the carbon. This tapering off of the adsorption process infers that the initial forces which caused a great increase in the adsorbate concentration for a small pressure increase are now being diminished by interference of the adsorbed phase, owing to a "saturation" effect on the carbon.

In the case of methanol isotherms, instead of the initial steep

TABLE II. AVERAGED VALUES FOR TEMPERATURES AND VAPOR PRESSURES OF LIQUID TAKEN AT CONSTANT TEMPERATURES OF LIQUID AND DIFFERENT TEMPERATURES OF CARBON

Temp., ° C.	Pressure, Mm. Hg				Temp., ° C.	Pressure, mm. Hg	Carbon Disulfide	
	Acetone	Methyl ethyl ketone	Methyl isobutyl ketone	Methanol			Temp., ° C.	Pressure, mm. Hg
-30	10.8	3.3	-20.5	64.5	-19.6	47.1
-25	15.2	5.0	-8.3	124.1	-10.0	79.5
-20	21.4	7.2	1.6	7.6	+ 2.2	208.8	+ 1.1	134.2
-10	38.0	14.1	3.2	..	9.9	290.9	11.0	207.3
0	69.0	25.5	7.6	29.8	20.6	460.0	20.0	297.2
10	114.5	45.0	11.0	54.7				
20	184.5	73.3	17.3	95.1				
30	282.5	114.6				

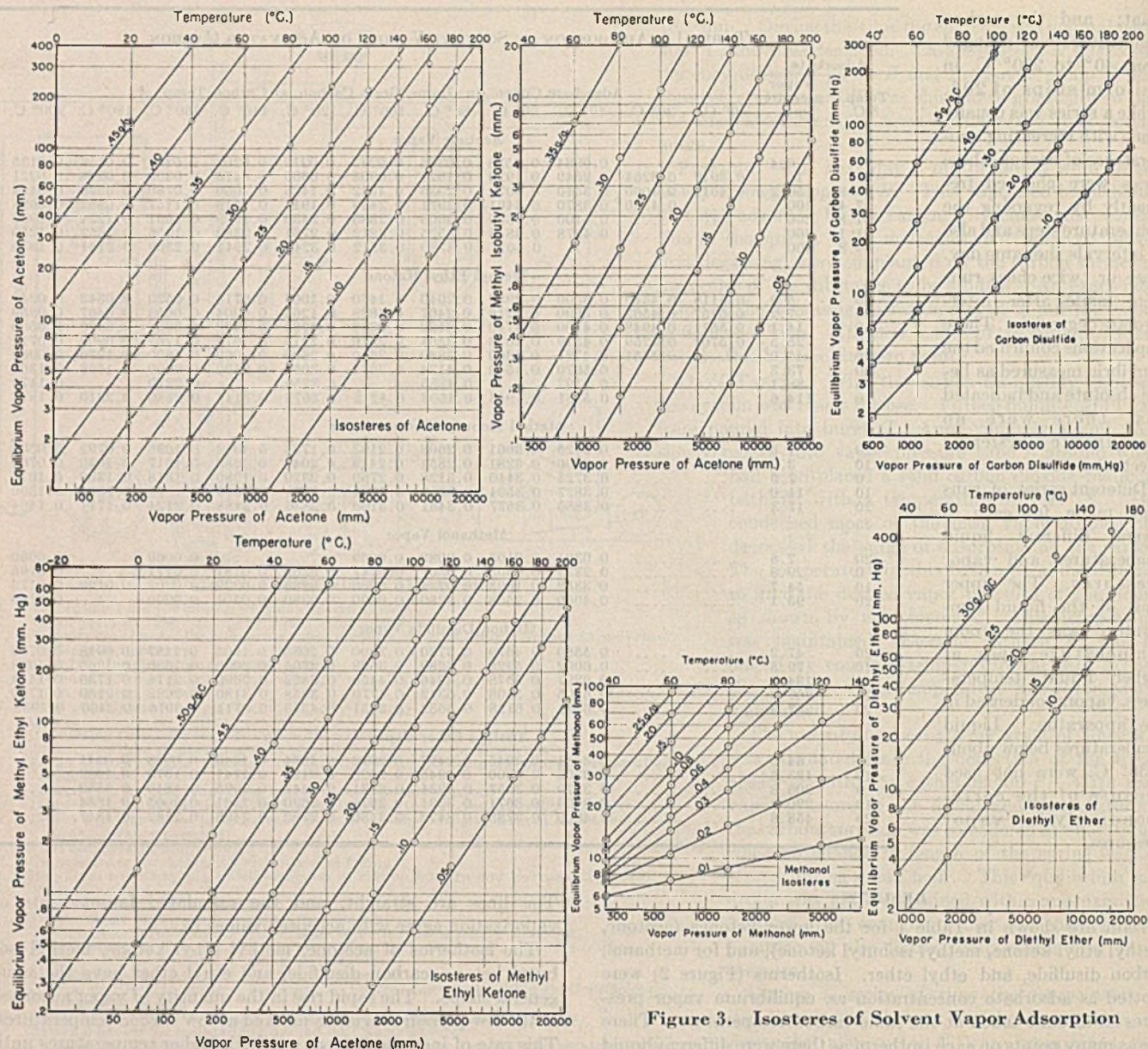


Figure 3. Isosteres of Solvent Vapor Adsorption

slope in the low-vapor-pressure region, there is a flat portion which bends upward at approximately 10 mm. pressure. This shape is observed mainly in the 40°, 60°, and 80° C. isotherms, whereas those at higher temperatures are practically straight lines at small angles to the horizontal. This peculiarity had been observed previously (1) when water was the adsorbate. Because methanol closely resembles water, it may be expected to have somewhat similar adsorption properties. This peculiar behavior may be explained when it is realized that water and methanol, both highly polar, can collect on the carbon surface, not as single molecules, but as associated molecules (4) which interfere with normal adsorption. When the temperature is increased, the associated molecules are broken up, and adsorption proceeds normally.

HEAT OF ADSORPTION

When vapors are adsorbed, heat is liberated in the range of one to two times the latent heat of condensation (13). When adsorption processes are used industrially for solvent recovery, the liberated heat may be removed by cooling. The amount of cooling required to cool an adsorbent bed can be calculated readily from adsorption isosteres. These values must be sup-

plemented by data concerning the effect of gas mixtures (carrier gas, etc.).

The slopes of the isosteres (Figure 3) were measured and plotted against adsorbate concentration with temperature as the other parameter (Figure 4). These slopes are equal to the ratio of the molar heats for the passage from the condensed to the gaseous phase of the adsorbed material and of the reference substance (13). The plots show that the differential heat of adsorption is usually affected by (a) the adsorbate concentration, since different isosteres have different slopes, and (b) the temperature of the adsorbent, since latent heats always vary with temperature.

The first requirement for heat calculations is the latent heat of the reference substance over the desired temperature range, 0–200° C. These data for acetone are available up to 100° C. Higher values were calculated (12) from reduced temperatures and pressures:

Temp., ° C.	Latent Heat of Acetone, Cal./Gram	
	Handbook value	Calcd. (12)
0	134.74	121.7
50	126.5	109.6
100	112.76	91.65
150	64.0
200

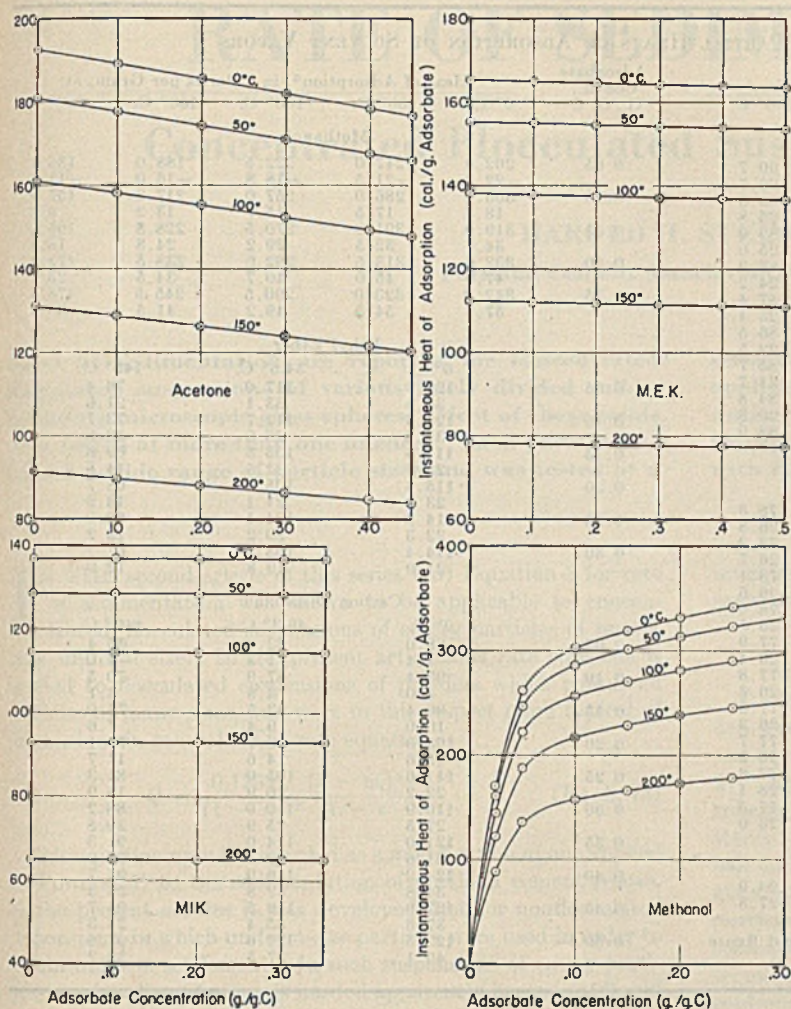


Figure 4. Instantaneous Heats of Adsorption of Solvent Vapors

Table III shows the adsorbate concentrations and instantaneous total and partial heats calculated at the various temperatures. Corresponding to each temperature and concentration are two numbers. The upper gives the total instantaneous heat of adsorption and condensation at these conditions; the lower is obtained by subtracting the value of the usual latent heat. The

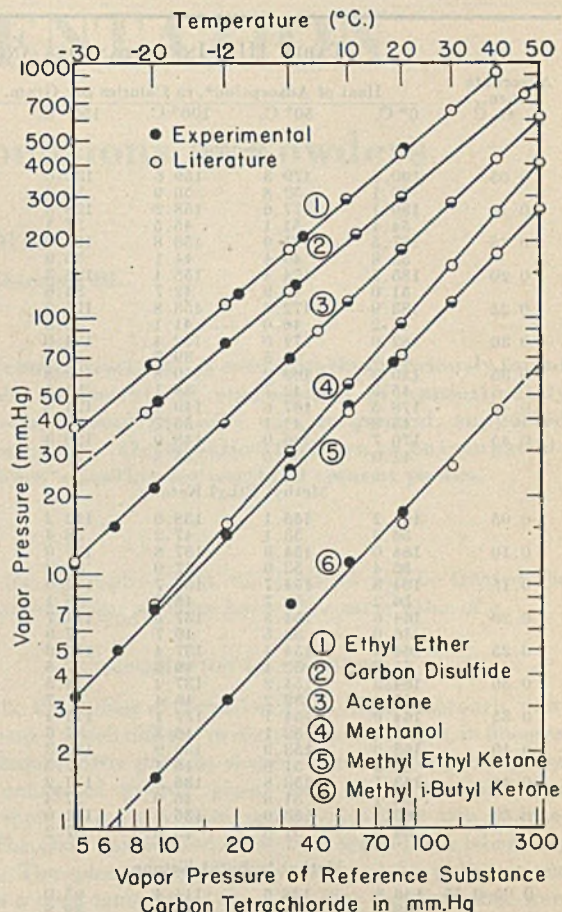


Figure 5. Vapor Pressure at Low Temperatures of Compounds Studied

lower number, therefore, is the value of the partial heat of adsorption alone under these conditions.

The change in isostere slope for the ketones runs in the following order: acetone, methyl ethyl ketone, methyl isobutyl ketone. The last substance evidently has no change in total instantaneous heat with change of concentration since it shows no appreciable change of isostere slope with adsorbate concentration. Other theoretical deductions from these data of the homologs of the ketone series and the substitute ethanes and methanes may also be made.

Using the methods of this investigation, it should be possible to predict the adsorption concentration and heat data for homologs by extrapolation and interpolation from data measured on only a few systems of the series.

The use of adsorption in refrigeration and air conditioning can be foreseen. The isotherms of a good refrigerant (liquid or adsorbate) in an adsorption process should be widely spaced, very steep, and abrupt in the low-vapor-pressure region. The greater the space between two particular isotherms, the more heat sensitive is the adsorbent, so that a lowering of a few

degrees will give a great increase in adsorption. Conversely, it should be possible to degas the adsorbent readily by increasing the temperature only a few degrees. The economics of the use of adsorption in refrigeration and air conditioning will depend on the selection of satisfactory vapors or gases as adsorbates and of satisfactory solids as adsorbents.

TABLE III. INSTANTANEOUS AND PARTIAL HEATS OF ADSORPTION OF SOLVENT VAPORS

Adsorbate Concn., G./G. C	Heat of Adsorption ^a , in Calories per Gram, at:					Adsorbate Concn., G./G. C	Heat of Adsorption ^a , in Calories per Gram, at:				
	0° C.	50° C.	100° C.	150° C.	200° C.		0° C.	50° C.	100° C.	150° C.	200° C.
Acetone											
0.05	190.8	179.3	159.6	130.0	90.7	0.05	262.0	247.0	222.5	188.0	136.5
	56.1	52.8	46.9	38.3	26.7		-22.3	-21.5	-18.8	-16.0	-11.6
0.10	189.1	177.6	153.2	128.8	89.8	0.10	303.0	286.0	257.0	217.2	157.9
	54.4	51.1	45.5	37.1	25.8		18.7	17.5	15.7	13.2	9.8
0.15	187.5	175.9	156.8	127.6	89.0	0.15	319.0	301.0	270.5	228.8	166.1
	52.8	49.4	44.1	35.9	25.0		34.7	32.5	29.2	24.8	18.0
0.20	185.7	174.4	155.4	126.3	88.2	0.20	332.0	313.5	282.0	238.5	173.2
	51.0	47.9	42.7	34.6	24.2		47.7	45.0	40.7	34.5	25.1
0.25	183.9	172.5	153.8	125.2	87.4	0.25	342.0	323.0	290.5	245.5	178.5
	49.2	46.0	41.1	33.5	23.4		57.7	54.5	49.2	41.5	30.4
0.30	182.0	171.0	152.4	124.0	86.5						
	47.3	44.5	39.7	32.3	22.5						
0.35	180.2	169.2	150.8	122.8	85.7						
	45.5	42.7	38.1	31.1	21.7						
0.40	178.5	167.6	149.4	121.5	84.8	0.05	0° C.	34.6° C.		140° C.	
	43.8	41.1	36.7	29.8	20.8		129.0	117.0		76.4	
0.45	176.7	166.0	148.0	120.3	84.0	0.10	36.5	33.1		21.6	
	42.0	39.5	35.3	28.6	20.0		124.3	112.7		73.7	
							31.8	28.8		18.9	
						0.15	117.5	106.5		69.6	
							25.0	22.6		14.8	
						0.20	115.8	105.0		68.7	
							23.3	21.1		13.9	
						0.25	114.8	104.1		68.0	
							22.3	20.2		13.2	
						0.30	114.4	103.7		67.7	
							21.9	19.8		12.9	
Methyl Ethyl Ketone											
0.05	165.2	155.1	133.0	112.2	78.3						
	56.6	53.1	47.2	38.4	26.8						
0.10	165.0	154.9	137.8	112.0	78.2						
	56.4	52.9	47.0	38.2	26.7						
0.15	164.8	154.7	137.7	111.9	78.1						
	56.2	52.7	46.9	38.1	26.6						
0.20	164.6	154.5	137.5	111.7	78.0						
	56.0	52.5	46.7	37.9	26.5						
0.25	164.4	154.4	137.4	111.6	77.9	0.05	0° C.	46.3° C.		140° C.	
	55.8	52.4	46.6	37.8	26.4		88.0	82.8		66.4	
0.30	164.2	154.2	137.2	111.5	77.8	0.10	-1.4	-1.3		-1.0	
	55.6	52.2	46.4	37.7	26.3		93.4	87.9		70.5	
0.35	164.0	154.1	137.1	111.4	77.8	0.15	4.0	3.8		3.1	
	55.4	52.1	46.3	37.6	26.3		99.4	93.5		75.0	
0.40	163.9	153.9	136.9	111.3	77.7	0.20	10.0	9.4		7.6	
	55.3	51.9	46.1	37.5	26.2		105.0	98.7		79.1	
0.45	163.7	153.8	136.8	111.2	77.6	0.25	15.6	14.6		11.7	
	55.1	51.8	46.0	37.4	26.1		111.6	105.0		84.3	
0.50	163.5	153.6	136.6	111.0	77.5	0.30	22.2	20.9		16.9	
	54.9	51.6	45.8	37.2	26.0		116.9	110.0		88.2	
						0.35	27.5	25.9		20.8	
							121.0	114.0		91.3	
						0.40	31.6	29.0		23.9	
							124.2	116.9		93.7	
						0.45	34.8	32.8		26.3	
							127.0	119.5		95.7	
							37.6	35.4		28.3	
						0.50	129.5	121.6		97.6	
							40.1	37.5		30.2	
Methyl Isobutyl Ketone											
0.05-0.35	136.8	128.5	114.4	93.0	64.9						
	68.6	55.1	49.1	39.8	27.8						

^a First figure at each concentration is instantaneous heat, second figure is partial heat.

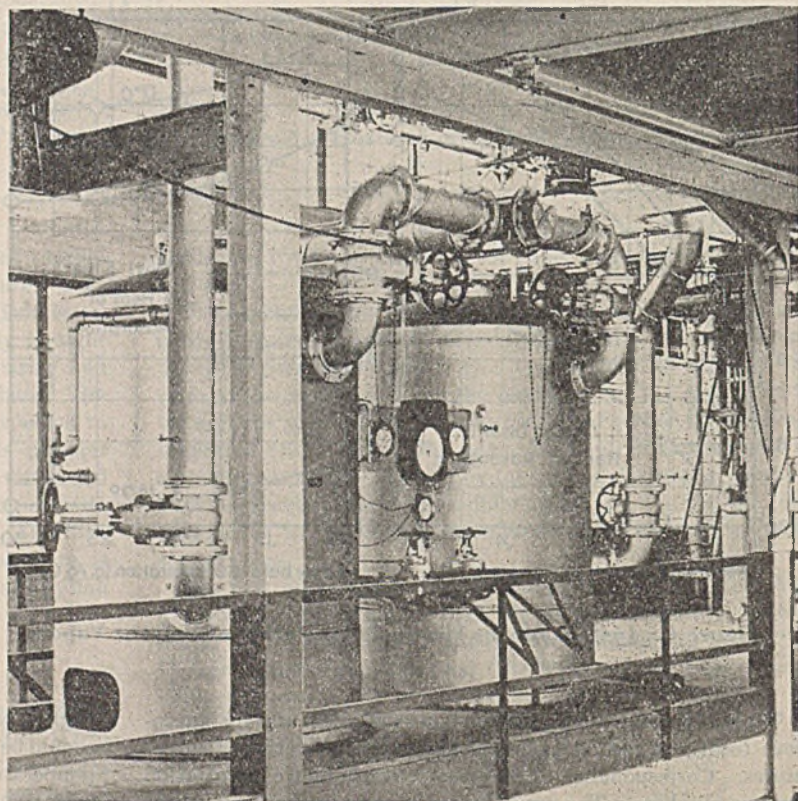
^a First figure at each concentration is instantaneous heat, second figure is partial heat.

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Typical Vertical Adsorbers in a Small Manually Operated, Solvent Recovery Plant (Columbia Activated Carbon System; Courtesy, Carbide & Carbon Chemicals Corp.)

RATE OF SEDIMENTATION

Concentrated Flocculated Suspensions of Powders

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Rates of sedimentation are reported for concentrated flocculated suspensions of various finely divided solids, including microscopic glass spheres. Most of these solids were tested at more than one fineness. Each powder embraced a wide range of particle sizes and was tested at a

series of concentrations. A rate equation previously found applicable to flocculated suspensions of approximately uniform-size emery particles was, in general, supported by the new data. The equation is shown to be compatible with Powers' equation for portland cement pastes.

IN THE second article of this series (13) Equation 3 for rate of sedimentation was shown to be applicable to concentrated, flocculated suspensions of emery particles of practically uniform size. In the present article this rate equation is applied to flocculated suspensions of powders which contained particles of many sizes, and were in this respect more typical of suspensions in general. The rate equation is

$$Q = \frac{0.123 V_s (\epsilon - w_i)^2}{(1 - w_i)^2 1 - \epsilon} \quad (\text{Eq. 3, 13})$$

This equation may be regarded as a modification of one applied by Powers (9) to the sedimentation of portland cement pastes. In the present studies it was developed first for nonflocculated suspensions, in which uniform-size particles were used in order to obtain uniform settlement. In such suspensions of emery particles, empirical constant w_i is needed apparently because of liquid which remains with the particles during their fall; during sedimentation the main mass of liquid moves relative to the particles, but a quantity of liquid equal to $w_i/(1 - w_i)$ per unit volume of solid appears not to take part in this flow but to remain stagnant at the surfaces of the angular particles. In the first article of this series (12) w_i was shown to be zero for nonflocculated suspensions of spheres; evidently the rounded surfaces did not keep any of the liquid out of the flow.

When concentrated suspensions of the emery particles were flocculated, Equation 3 (13) was still found to apply, but with a higher value of w_i . Apparently the conditions that control the rate of settlement remained much the same as before; indeed, experiments indicated that the initial resistance to settlement remained wholly of viscous origin, and the appearance of the suspensions was consistent with the assumption that the displaced liquid still flowed past the individual particles. That is, there appeared to be no opportunity, such as occurs at low concentrations, for the flow to by-pass groups of particles.

To apply Equation 3 (13) to powders containing particles of many sizes, V_s is formulated as follows:

$$V_s = \frac{2g(\rho_s - \rho_f)}{\eta \epsilon^2} \quad (1)$$

where σ = specific surface value, sq. cm./cc., calculated as if each particle were a sphere having same density as particle and same rate of fall when alone in a large volume of viscous liquid. For uniform-size particles it is equal to $3/r$, where r is radius of equal-settling sphere. Numerical value of σ is obtained from sedimentation analysis of a very dilute, nonflocculated suspension.

With V_s calculated as in Equation 1, the application of Equation 3 (13) to flocculated mixtures of particles of various sizes

involves the assumption that the particles can be treated the same as uniform-size particles having the same value of σ .

DESCRIPTION OF POWDERS

To make the testing of Equation 3 (13) fairly thorough, powders were used which differed in chemical composition, in fineness, and in characteristic particle shape. These powders comprised five finenesses of ground glass, two of microscopic glass spheres, three of burned shale, one of silica, and two of limestone. The glass and burned shale were ground in a laboratory ball mill. The spheres were made by feeding some of the ground glass into a blast lamp (10, 11). The silica and limestone were purchased already ground. To obtain different finenesses, air-separation and mixing were employed in some cases. Microscopic examination (12) showed that the preparations of spheres contained relatively few particles that were not well shaped. The particles of burned shale were shown to have a comparatively rough surface texture.

The values of σ , the specific surfaces of "equivalent" spheres, were determined from sedimentation analyses, essentially by the Wagner turbidimeter method (14), using the equipment specified for testing cement (A.S.T.M. standard test C115-42). All turbidimeter tests were made in water, using a little sodium hexametaphosphate as dispersant. The size analyses were commonly carried down only to a particle diameter of 5 microns, but the contribution of the finer sizes to the value of σ was estimated by a method devised by Dahl (5). By this method a cubic equation is assumed to fit the size-distribution curve below 10 microns.

Since σ enters Equation 3 (13) as a part of V_s , its determination by sedimentation analysis is wholly in accord with the theory of the equation. However, since the sedimentation of a concentrated suspension is in some respects similar to flow through a bed of particles, specific surface values determined by the air permeability method of Lea and Nurse (7) were obtained for comparison with the σ values. Indeed, since the glass spheres used in this investigation varied somewhat in density because of enclosed gas, the specific surfaces of both preparations were determined solely by this air permeability method; the method does not require that the particles have the same density, and it seems to give the actual specific surface of spheres (6, 12).

Table I shows the specific surface values obtained by each of the two methods, sedimentation and air permeability. Values calculated from air permeability tests (by the Lea and Nurse formula) are identified by symbol S_0 . All values, whether of S_0 or σ , are averages from two or more tests, except σ for burned shale 1 which is a selected result (4% above the average) believed to represent the best-dispersed sample. Table I gives some of the data from the turbidimeter size analyses and values of w_i .

TABLE I. PHYSICAL PROPERTIES OF MATERIALS AND VALUES OF w_i OBTAINED IN SEDIMENTATION TESTS

Powder	Density, Grams/ Cc.	Particle Size*, Cumulative % up to Particle Diam. of:				Sp. Surface, Sq. Cm./Cc.		S_0/σ	w_i in Sedi- mentation Tests
		5 microns	10 microns	25 microns	60 microns	σ	S_0^*		
Ground glass 1	2.50	2.3	6.9	24.0	80.5	2615	3,290	1.26	0.170
Ground glass 2	2.50	2.4	8.7	27.1	79.2	2720	3,570	1.31	0.195
Ground glass 3	2.50	5.2	11.8	31.6	83.0	3610	4,040	1.12	0.175
Ground glass 4	2.50	6.7	18.1	40.2	84.9	4220	5,240	1.24	0.190
Ground glass 5	2.50	12.8	29.2	59.8	87.6	6700	7,800	1.16	0.185
Glass spheres 1	2.35	2,980	(1.00)	0.100
Glass spheres 2	2.32	3,990	(1.00)	0.095
Burned shale 1	2.57	7.4	19.7	47.7	79.8	4710	9,130	1.94	0.315
Burned shale 2	2.57	(11.3)	(26.6)	(60.5)	(89.0)	(6320)	(11,160)	(1.76)	0.312
Burned shale 3	2.57	15.2	33.6	73.4	98.2	7940	13,200	1.66	0.315
Silica 1	2.65	12.7	22.1	44.9	82.9	5850	8,500	1.45	0.203 (lime) 0.165 (dye)
Limestone 1	2.78	11.7	19.0	36.2	63.2	5650	6,050	1.07
Limestone 2	2.78	18.0	29.4	54.6	82.9	8320	9,980	1.20

* Parentheses enclose values not obtained by direct experiment. Burned shale 2 was a mixture of 1 and 3. Glass spheres were not analyzed for size distribution, but microscopic inspections showed that particles varied widely in size.

* Porosity of test bed was sometimes varied in check tests, results of which were averaged. Mean porosities were: ground glass, 0.49, except 0.52 for No. 5; spheres 1 and 2, 0.47 and 0.45, respectively; burned shale, 0.47; silica, 0.49; limestones 1 and 2, 0.45 and 0.51, respectively.

which will receive attention later. All powders of a given material or type are numbered in the order of increasing fineness.

SEDIMENTATION TESTS

In the sedimentation tests on the flocculated suspensions the mixtures were stirred with an electrical mixer for at least 2 minutes and were tested in a cylindrical jar 100 mm. in diameter, using depths of sample between about 30 and 60 mm. Previous work had indicated that wall effects do not significantly influence the settlement at the center of the vessel under these conditions.

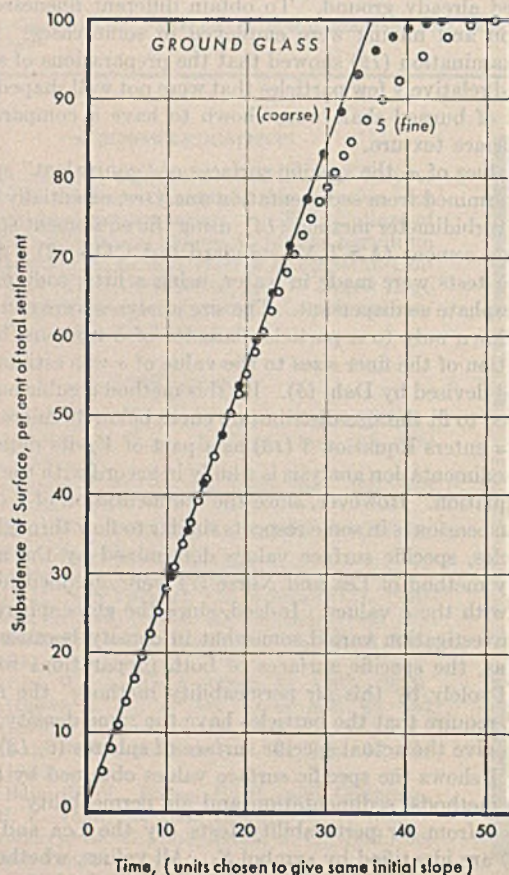


Figure 1. Sedimentation Curves for Ground Glass Powders 1 and 5 in 0.25% Zinc Sulfate Solution at $\epsilon = 0.60$

Readings were taken with a micrometer microscope sighted on a disk float which rode at the surface of the suspension (9, 13). Flocculants were chosen according to the requirements of the several powders and are given in Table II. Water was the suspension medium. The conditions of sedimentation ensured laminar flow of the displaced water in all cases as judged by comparison with the work of Carman (4) on flow through granular beds.

The curves of height of suspension against time were similar to those obtained in the previous studies of sized particles in that they exhibited an initial straight-line portion followed by some rounding off. The coarser the powder, the more dominant was the straight portion of the curve. This is illustrated by Figure 1 in which coarse and fine glass powders are compared by plotting so that the initial slopes of the curves are the same. In most cases the curves ended rather abruptly, but a somewhat prolonged slow final settlement was characteristic of the silica powder (Figure 2). Limestone 2 showed peculiar behavior; its fineness was about the same as that of burned shale 3, but the settlement was much slower at the same dilutions and continued for a long time at a rate that remained a large fraction of the initial rate (Figure 3). The greater the dilution of suspensions of limestone 2, the more the curves tended to round over and to fail to show a long initial straight-line portion, the opposite of the usual tendency.

Rates of sedimentation calculated for the initial constant-rate periods are given in Table II together with the porosities of the sediments and supplementary data.

RATES OF SEDIMENTATION

Figure 4 shows the degree of conformity between Equation 3 of the second article (13) and the rate data from Table II. If the equation is applicable, the data for a set of tests in which

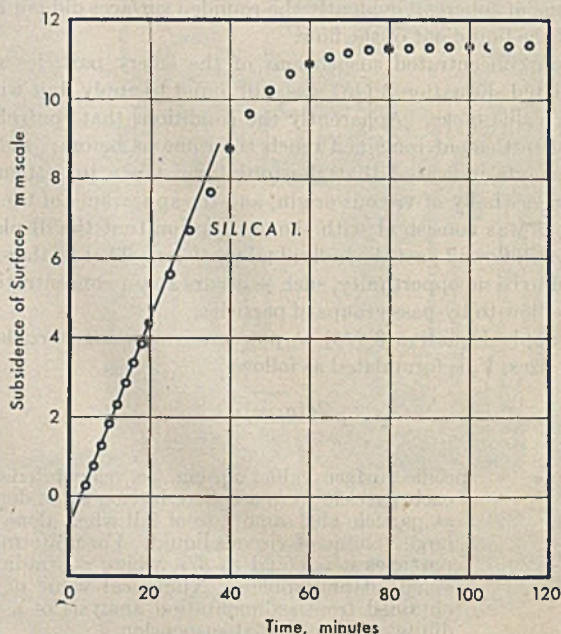


Figure 2. Sedimentation Curve for Silica Powder in One-Sixth Saturated Lime Water at $\epsilon = 0.62$ (Height of suspension, 57 Mm.)

TABLE II. SEDIMENTATION OF FLOCCULATED SUSPENSIONS AT VARIOUS DEGREES OF DILUTION

Flocculant, % of Water Wt.	Test No. (Chronological)	Initial Height, Mm.	Fluid Content, % in Total Vol. ($\epsilon \times 10^3$)	Settling Rate Q, Cm./Sec. $\times 10^4$	Settling, % of Initial Height	Porosity of Sediment, % of Settled Vol.
Ground Glass 1, 26.6° C.						
Zinc sulfate, 0.25	5	43.8	52.5	867	8.4	48.1
	1	43.8	52.5	863	9.1	47.8
	2	46.3	55.0	1121	11.9	48.9
	3	49.0	57.5	1389	14.2	50.5
	6	49.0	57.5	1380	13.7	50.8
	4	52.0	60.0	1770	17.1	51.8
	7	56.6	62.5	2220	20.6	52.8
	8	59.6	65.0	2890	22.7	54.7
Ground Glass 2, 26.1° C.						
Zinc sulfate, 0.25	8	43.8	52.5	680	8.3	48.2
	1	43.8	52.5	637	8.6	48.1
	2	46.3	55.0	843	11.1	49.4
	3	49.0	57.5	1088	12.6	51.4
	4	52.0	60.0	1360	14.8	53.1
	5	56.6	62.5	1810	17.1	54.8
	6	59.6	65.0	2320	20.3	56.1
	7	64.0	67.5	2930	22.7	57.9
Ground Glass 3, 25.2° C.						
Zinc sulfate, 0.25	1	37.4	52.3	426	8.4	47.9
	2	39.4	54.7	527	10.3	49.5
	3	41.4	56.9	689	12.3	50.8
	5	41.4	56.9	630	11.4	51.4
	4	44.0	59.4	906	15.6	51.9
Ground Glass 4, 25.7° C.						
Zinc sulfate, 0.25	1	36.7	50.0	174	4.7	47.5
	7	36.7	50.0	217	4.1	47.9
	9	36.7	50.0	237	4.0	47.9
	2	38.7	52.5	267	7.0	48.9
	3	39.5	55.0	360	8.5	50.8
	8	39.5	55.0	360	8.0	51.0
	4	43.2	57.5	475	11.2	52.1
	5	46.0	60.0	614	13.8	53.5
	6	49.0	62.5	845	16.6	55.0
	10	49.0	62.5	797	15.8	55.5
	11	52.5	65.0	1005	22.4	54.9
	12	56.6	67.5	1400	23.9	57.3
Ground Glass 5, 24.0° C.						
Zinc sulfate, 0.25	1	36.7	50.0	103	3.0	48.4
	10	43.2	50.0	90	3.8	48.1
	2	38.8	52.5	113	4.3	50.4
	3	40.7	55.0	138	6.2	52.0
	4	43.3	57.5	154	7.0	54.3
	11	39.7	57.5	202	5.6	55.0
	13	39.5	57.5	194	6.0	54.8
	5	46.0	60.0	242	11.2	55.0
	6	49.0	62.5	300	9.9	58.3
	14	46.3	62.5	310	9.3	58.7
	7	52.4	65.0	392	14.0	59.3
	8	56.6	67.5	533	18.4	60.1
	12	53.9	67.5	506	16.1	61.2
	9	61.2	70.0	679	23.2	61.0
Glass Spheres 1, 24.6° C.						
Zinc sulfate, 0.25	10	35.3	37.5	a	6.5	33.2
	11	36.7	40.0	231	5.9	36.2
	12	38.4	42.5	301	9.2	36.7
	13	40.0	45.0	391	11.5	37.9
	2	30.0	45.0	358	6.9	40.9
	3	31.5	47.5	486	11.0	41.0
	4	33.1	50.0	651	14.9	41.2
	5	34.8	52.5	797	18.1	42.0
	1	36.7	55.0	1025	19.1	44.4
	6	36.7	55.0	1074	22.0	42.3
	7	39.0	57.5	1421	24.7	43.6
	8	41.4	60.0	1865	25.1	46.0
	9	44.0	62.5	2550	30.8	45.9
Glass Spheres 2, 25.7° C.						
Zinc sulfate, 0.25	7	25.6	40.0	149	3.1	38.1
	8	25.6	40.0	144	3.3	38.0
	1	26.6	42.5	179	4.6	39.7
	2	26.6	45.0	218	7.0	40.8
	9	27.8	45.0	218	7.4	40.6
	3	29.2	47.5	304	10.6	41.3
	4	30.6	50.0	362	13.2	42.3
	5	32.2	52.5	444	18.1	42.0
	6	34.0	55.0	616	22.2	42.3
Burned Shale 1, 25.5° C.						
Lime water, satd.	7	38.9	58.3	205	6.3	55.5
	6	43.4	60.0	243	7.9	56.5
	4	46.0	62.5	354	9.9	58.6
	5	44.4	62.5	333	10.3	58.2
	8	44.9	65.3	442	13.3	60.0
	1	47.1	65.3	447	13.5	59.9
	9	45.2	67.5	593	17.0	60.8
	10	45.6	70.0	720	21.7	61.7
	2	47.1	70.0	782	21.6	61.7
	3	47.1	70.0	787	20.4	62.3
Burned Shale 2, 26.0° C.						
Lime water, satd.	1	39.1	57.5	125	4.2	55.6
	2	43.7	60.0	155	6.0	57.4
	3	45.1	62.5	193	7.8	59.3
	4	45.6	65.0	258	9.7	61.2
	5	46.2	67.5	351	11.8	63.1
	6	46.3	70.0	445	15.5	64.5
	7	46.4	72.5	570	20.2	65.5
	8	46.1	75.0	744 ^b	25.7	66.4
Burned Shale 3, 25.7° C.						
Lime water, satd.	3	39.2	57.5	76	2.4	56.4
	10	39.8	57.5	78	2.0	56.6
	2	42.0	60.0	92	3.6	58.5
	1	42.2	62.5	128	4.8	60.6
	4	43.7	65.0	150	6.9	62.4
	5	44.4	67.5	208	11.5	63.2
	6	44.1	70.0	281	11.1	66.3
	7	45.5	70.0	272	14.0	65.2
	8	46.2	72.5	370	19.7	65.8
	9	46.4	75.0	507	26.9	65.8
	11	45.7	75.0	485	22.9	67.6
Silica 1, 24.0° C.						
Lime water, satd.	1	49.0	56.0	199	6.4	53.0
	2	52.0	58.0	254	7.9	54.3
	3	54.0	60.0	318	12.0	54.5
	4	58.0	62.0	370	13.7	56.0
	5	60.5	64.0	470	16.3	57.0
	6	64.0	66.0	576	19.5	57.8
	7	68.0	68.0	761	23.0	58.4
Silica 1, 24.0° C.						
Lime water, 1/2 satd.	1	48.5	56.0	228	14.8	48.4
	2	49.0	58.0	258	16.1	50.0
	3	54.0	60.0	338	19.0	50.6
	4	57.0	62.0	422	21.2	51.8
	5	61.0	64.0	554	24.4	52.4
	6	64.5	66.0	683	27.4	53.2
	7	67.0	68.0	913 ^b	31.1	53.5
Silica 1, 24.0° C.						
Gentian violet 0.01	2	46.2	57.5	281	17.9	48.2
	3	45.0	57.5	296	13.2	51.0
	1	46.0	65.0	616	25.4	53.1
	4	47.0	65.0	600	23.6	54.2
Limestone 1, 25.2° C.						
Lime water, satd.	4	30.4	55.0	112	5.5	52.3
	3	30.2	57.5	153	6.6	54.5
	1	31.1	60.0	190	8.2	56.4
	2	31.9	62.5	208	9.2	58.6
	5	32.7	65.0	273	12.4	60.0
	6	33.3	67.5	304	14.5	62.0
	7	34.1	70.0	467	16.4	64.1
	8	34.2	72.5	910	23.0	64.2
Limestone 2, 25.8° C.						
Lime water, satd.	1	38.2	65.0	35
	3	31.7	65.0	33
	4	32.5	67.5	54
	5	33.0	70.0	56
	6	34.0	72.5	90
	2	46.1	75.0	169

^a Sedimentation curve for this highly concentrated suspension was exceptional in that the constant rate established initially changed abruptly to a higher one. Channeling was not observed and was improbable because of the high concentration. The curve was somewhat like those previously obtained with nonflocculated emery at high concentrations (13).

^b Channeling observed.

only ϵ has been varied should fall on a straight line for which

$$\text{slope} = \sqrt{\frac{0.123V_s}{(1-w_s)^2}} \quad (2)$$

where the value of w_s gives the intercept of the line on the ϵ -axis. The solid lines drawn through the data points in Figure 4 have these theoretical slopes.

The graphs for ground glass and glass spheres (Figure 4) show good agreement between the data points and the theoretical lines, except for glass spheres 1 at high values of ϵ . The lack of agreement in that case is similar to what was observed previously (13) at high dilutions of emery powder. The exceptionally high points can be attributed to flow of liquid through fine channels

developed in the floc structure because of the relatively low concentrations of solid.

Fair agreement with the rate equation is shown by the graph for burned shale. At the lowest values of ϵ the points are a little high, but otherwise agreement is good.

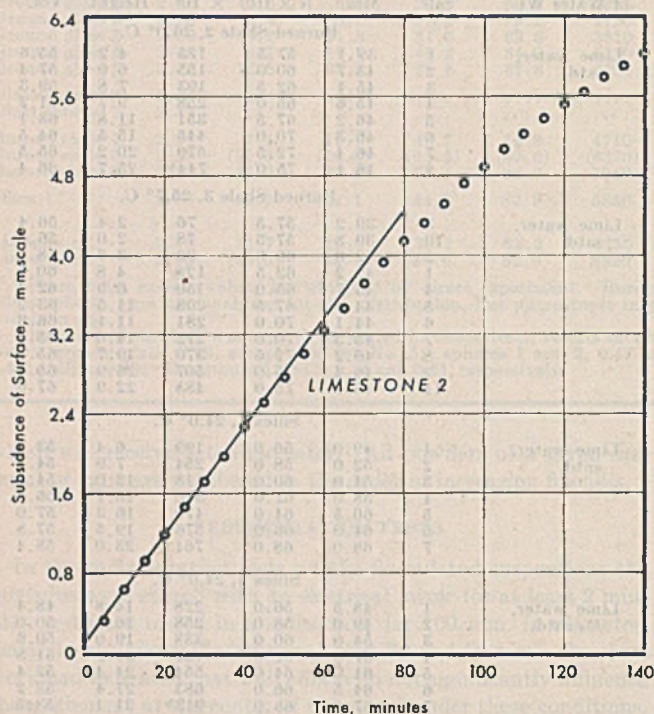


Figure 3. Sedimentation Curve (Incomplete) for Limestone 2 in Tap Water at $\epsilon = 0.725$
(Height of suspension, 34 mm.)

The tests on silica (Figure 4) agree in part with the theory. However, the high point at $\epsilon = 0.68$ for a test in saturated lime water and most of the points for tests in one-sixth saturated lime water are not represented by the theoretical line. These exceptions, like those for glass spheres 1, can be attributed to breaks in the floc structure. If this is the correct explanation, the breaks evidently occur at much lower values of ϵ in one-sixth saturated than in saturated lime water, an indication that the particles of silica have less cohesion in the weaker solution.

The breaks in floc structure assumed here were not, in general, actually seen. Only in the tests in one-sixth saturated lime water at $\epsilon = 0.68$ (and in a test on burned shale 2 at $\epsilon = 0.75$) were distinct channels detected. In contrast, Powers (9) nearly always found channels and "boils" in tests on cement pastes when the rates of sedimentation were too high to agree with his equation. This has also been the writer's experience in testing cement pastes. In suspensions in which channels are suspected but not seen, the cohesion between particles may be weaker and may result in many breaks but smaller, shifting ones.

At low fluid contents the rates of sedimentation of the silica were nearly equal in the two different lime solutions, even though the differences in total settlement were pronounced (Table II). Results of this kind had previously been obtained by Powers (9). The floc structure is evidently weaker in the lower concentrations of flocculant, but this weakness does not appear to affect the rate significantly unless actual breaks develop in the structure.

It is not clear from Figure 4 whether the suspensions of limestone 2 are exceptions to the theory, but obviously those for limestone 1 fail to conform. Apparently the nature of the floc structure is not the same in all suspensions, a fact that has been indicated also by tests with organic liquids which in some in-

stances have given unusual results (9). Some suspensions seem to be too strongly flocculated for Equation 3 (13) to apply; in such cases structural resistance may sometimes be involved. Certain other suspensions are apparently too weakly flocculated—for example, the less concentrated suspensions of silica in one-sixth saturated lime water. However, the fact that so many of the powders that have been investigated have settled in approximate conformity to Equation 3 (13) indicates that the equation has a considerable range of application (although only at concentrations great enough to avoid channeling and to permit of a continuous floc structure).

EFFECT OF SPECIFIC SURFACE

Since σ was varied widely, conformity of the experimental data to Equation 3 of the second article (13) (with V_s formulated as in Equation 1 of this paper) is support for the assumption that σ has the effect indicated by the equation. To show more directly the degree of this support, straight lines representing the data were first drawn on plots of $[Q(1 - \epsilon)]^{1/3}$ vs. ϵ without recourse to the theory. If these lines had conformed strictly to the theory, their slopes would have been given by Equation 2 which, with V_s expanded, is:

$$\text{slope} = \sqrt[3]{\frac{0.123}{(1 - w_i)^2} \frac{2g(\rho_s - \rho_f)}{\eta\sigma^2}} \quad (3)$$

Solved for σ this becomes

$$\sigma = \sqrt{0.123F} \quad \text{or} \quad \sigma = 0.35F^{1/2} \quad (4)$$

if $\frac{2g(\rho_s - \rho_f)}{\eta(1 - w_i)^2(\text{slope})^3}$ is designated by F . To show the degree to which the data conform to Equation 4, the experimental values of σ are plotted in Figure 5 against $F^{1/2}$ calculated from the slopes and w_i values found empirically from the plots of

$$[Q(1 - \epsilon)]^{1/3} \text{ vs. } \epsilon$$

A point for limestone 2 is not shown because its location was too uncertain. The single point for silica represents the tests in saturated lime water; the data for emery were obtained in previous work (13). The solid line has the slope 0.35 required by Equation 4.

As was to be expected, the point for limestone is distant from the rest. Otherwise, the points are represented rather well by the theoretical line. Thus, the use made of σ in determining the rate of sedimentation seems justified.

The specific surfaces determined by the Lea and Nurse air permeability method (designated S_0 as in Table I) are also plotted in Figure 5. Since the points are widely scattered and cannot well be represented by any straight line through the origin, it is evident that S_0 is, in general, unsuitable for use in place of σ in Equation 3 (13). Whether this situation may be altered by recently suggested modifications (3, 6) of the Lea and Nurse method is not apparent from this study.

FACTORS AFFECTING w_i

In the formula for rate of sedimentation, as given by Equation 3 (13), the w_i term differs from the others in not being determinable at present except by actual sedimentation tests on concentrated suspensions. The problem of prediction is complicated by the increase in w_i caused by flocculation. When a powder is reactive chemically, like portland cement, there are further complications. However, some qualitative inferences from present data are possible.

From Table I, w_i for inert powders seems to show no pronounced change as the fineness is changed. Although w_i increased with the fineness of flocculated emery powders of practically uniform particle size (13), inert powders that are not closely sized may ordinarily show no such effect. Aqueous pastes of portland cement show a consistent increase in the value of w_i with increase in fineness (9), but it seems probable that this is caused

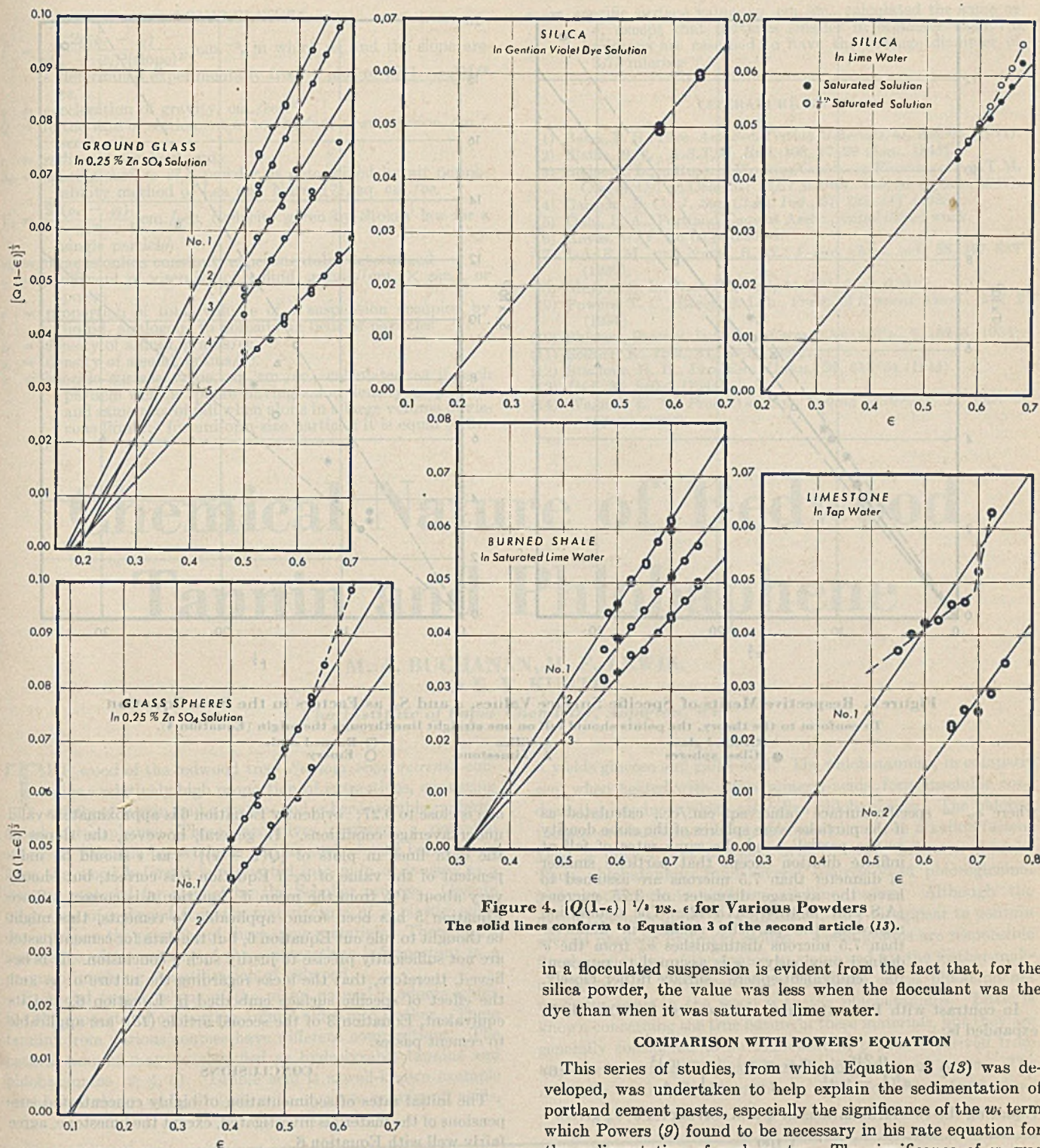


Figure 4. $[Q(1-\epsilon)]^{1/2}$ vs. ϵ for Various Powders
The solid lines conform to Equation 3 of the second article (13).

in a flocculated suspension is evident from the fact that, for the silica powder, the value was less when the flocculant was the dye than when it was saturated lime water.

COMPARISON WITH POWERS' EQUATION

This series of studies, from which Equation 3 (13) was developed, was undertaken to help explain the sedimentation of portland cement pastes, especially the significance of the w_i term which Powers (9) found to be necessary in his rate equation for the sedimentation of such pastes. The significance of w_i was given detailed consideration in the second article of the series (13), and views advanced there have now received further support. However, Equation 3 (13) which embodies those ideas differs somewhat from the Powers equation and, indeed, differs with respect to the use that is made of w_i . If w_i actually has the same significance for the cement pastes that it has been concluded to have for the other systems, then Equation 3 (13) may be expected to be practically equivalent to the Powers equation within the range of conditions that prevail in the pastes. That there is approximate equivalence can be shown as follows: Powers' equation is

$$Q = \frac{0.2}{\sigma_w^2} \frac{g(\rho_s - \rho_f)}{\eta} \frac{(\epsilon - w_i)^3}{1 - \epsilon} \quad (5)$$

by a layer of hydrate formed over the grains when they are first mixed with water. An added layer should have the same effect on w_i as stagnant liquid; the greater the quantity per unit volume of solid, the greater would be the value of w_i . Hence, since the quantity would probably be approximately proportional to the specific surface, w_i would increase with increase in fineness.

It is noteworthy that fair-sized values of w_i were found necessary in the rate equations for the flocculated glass spheres. Since the value of w_i for nonflocculated spheres has been shown to be zero (12), the data support the previous evidence from tests on emery (13) that flocculation increases w_i .

That the nature of the flocculant can affect the value of w_i

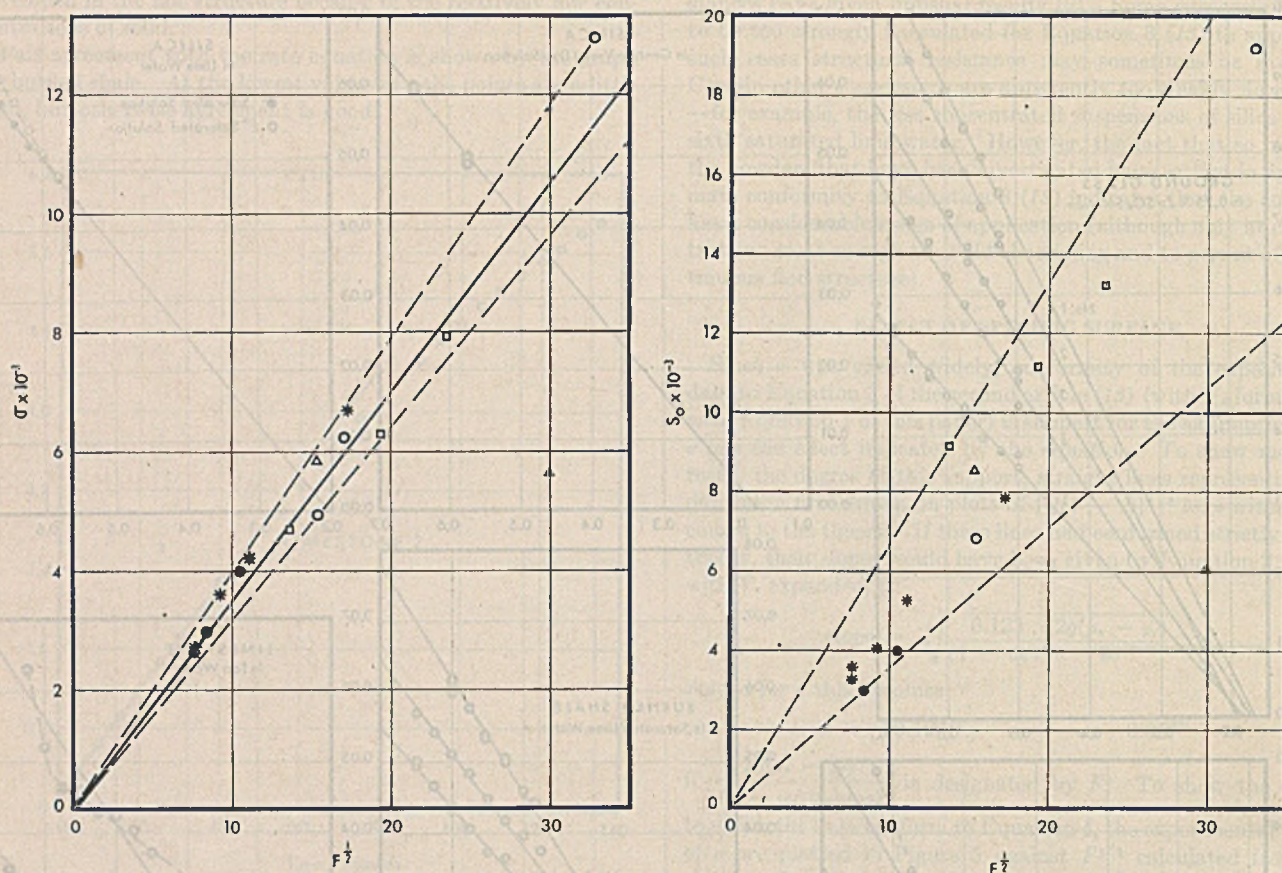


Figure 5. Respective Merits of Specific Surface Values, σ and S_0 , as Factors in the Rate Equation

To conform to the theory, the points should fall on one straight line through the origin (Equation 4).

* Ground glass
● Glass spheres
△ Silica
▲ Limestone
□ Burned shale
○ Emery

where σ_w = specific surface value, sq. cm./cc., calculated as if the particles were spheres of the same density as the particles and the same rates of fall at infinite dilution except that particles smaller in diameter than 7.5 microns are assumed to have the average diameter of 3.75 microns (A.S.T.M. method C115-42). The assumption regarding the particles smaller in diameter than 7.5 microns distinguishes σ_w from the σ defined previously; σ is assumed to represent the "equivalent-sphere" surface rather closely.

In contrast with Powers' equation, Equation 3 (13) with V , expanded is:

$$Q = \frac{0.246}{\sigma^2(1 - w_i)^2} \frac{g(\rho_s - \rho_f)}{\eta} \frac{(\epsilon - w_i)^2}{1 - \epsilon} \quad (6)$$

Equating the two formulations of Q and solving for σ/σ_w gives:

$$\frac{\sigma}{\sigma_w} = \frac{1.109}{1 - w_i} \quad (7)$$

The magnitude of the ratio σ/σ_w can be established as follows: Lea and Nurse (7) found that S_0/σ averaged 1.22 for cements. They also found that S_0/σ_w ranged between 1.6 and 1.8. However, in other investigations the ranges in S_0/σ_w have been 1.77-1.92, 1.70-1.99, and 1.70-2.00 (1, 2, 8). From these data and much additional unpublished work, a value of 1.85 appears to be reasonably representative of S_0/σ_w for American cements. Combining the ratio of S_0 to σ_w with the ratio of S_0 to σ , gives:

$$\sigma/\sigma_w = 1.52 \quad (8)$$

Equation 7 can then be solved for w_i , and the result is 0.27. For cements, w_i generally lies between 0.24 and 0.32, and the aver-

age is close to 0.27; evidently Equation 6 is approximately valid under average conditions. In general, however, the slopes of the data lines in plots of $[Q(1 - \epsilon)]^{1/2}$ vs. ϵ should be independent of the value of w_i if Equation 5 is correct, but should vary about 4% from the mean if Equation 6 is correct. Since Equation 5 has been found applicable to cements, this might be thought to rule out Equation 6, but the data for cement pastes are not sufficiently precise to justify such a conclusion. It is believed, therefore, that the ideas regarding the nature of w_i and the effect of specific surface embodied in Equation 6, and its equivalent, Equation 3 of the second article (13), are applicable to cement pastes.

CONCLUSIONS

The initial rates of sedimentation of highly concentrated suspensions of the materials investigated, except the limestone, agree fairly well with Equation 6.

Comparison of specific surface values determined by the air permeability method of Lea and Nurse (7) with σ values, which are the specific surfaces of "equivalent" spheres as determined by sedimentation analysis, indicates that the former are distinctly less suitable for use in the rate equation.

Comparison of Equation 6 with the equation developed by Powers (9) from studies on portland cement indicates that the two should give approximately the same results for cement pastes.

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NOMENCLATURE

- $F = \frac{2g(\rho_s - \rho_f)}{\eta(1 - w_i)^2(\text{slope})^2}$ cm.⁻², in which w_i and the slope are determined experimentally from a plot of $[Q(1 - \epsilon)]^{1/2}$ vs. ϵ
- g = acceleration of gravity, cm./sec.²
- Q = initial rate of settlement of top surface of suspension, cm./sec.
- r = radius of a sphere, cm.
- S_0 = specific surface of a powder as determined by air permeability method of Lea and Nurse (?), sq. cm./cc.
- $V_s = \frac{2g(\rho_s - \rho_f)}{\eta\sigma^2}$, cm./sec. (velocity given by Stokes' law for a single particle)
- w_i = dimensionless constant, experimentally determined
- η = coefficient of viscosity of a fluid, grams/(cm. X sec.), or poises
- ϵ = proportion of total volume of a suspension occupied by liquid, analogous to porosity in beds of particles
- ρ_f = density of a fluid, grams/cc.
- ρ_s = density of a solid, grams/cc.
- σ = specific surface value, sq. cm./cc., calculated as if each particle were a sphere having same density as particle and same rate of fall when alone in a large volume of viscous liquid; for uniform-size particles it is equal to $3/r$

σ_w = specific surface value, sq. cm./cc., calculated the same as σ , except that particles smaller in diameter than 7.5 microns are assumed to have the average diameter of 3.75 microns

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Chemical Nature of Redwood Tannin and Phlobaphene

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THE wood of the redwood tree (*Sequoia sempervirens*) contains a relatively high proportion of extractives, consisting chiefly of tannin and a water- and ether-insoluble material called phlobaphene. These extractives represent a potential source of valuable by-products and as such should be removed from the wood before it is converted into pulp or is used as a starting material for alcohol by the Scholler process. Certain other uses of redwood (i.e., the manufacture of a plastic pulp) depend upon the presence of these same materials. Therefore, a knowledge of the nature of these extractives is important in a program involving the utilization of redwood.

Redwood tannin is one of the many natural products which has the property of converting animal hides into leather. These tannins from various sources have different compositions. The natural tannins may be classified as hydrolyzable tannins and phlobatannins (2, 4, 6). Tannic acid is a well-known example of the first class; on hydrolysis with enzymes or mineral acids,

it yields glucose and gallic acid. The phlobatannins, in comparison, when heated with dilute mineral acids, form insoluble condensation products which are called phlobaphenes. The phlobatannins are built on the catechin model and, on alkaline fusion, yield a phenol and phenolic acid, or two different phenols. Thus, phlobatannins from several sources yield phloroglucinol and protocathechuic acid on alkaline fusion. Although the natural tannins differ in composition, they all appear to contain several phenolic hydroxyl groups. These groups are responsible for the solubility of the tannin in water and for the leather-making properties. Water-insoluble materials called phlobaphenes normally occur in the wood with the phlobatannins. Little is known concerning the true nature of these materials, but they are generally considered to be condensation products derived from the corresponding tannins by the elimination of water. The naturally occurring phlobaphenes differ somewhat from those

Tannin and phlobaphene have been isolated from redwood (*Sequoia sempervirens*), and their chemical nature has been investigated. Both tannin and phlobaphene can be acetylated and methylated. The purified tannin contains 2.8% methoxyl, 63.6% carbon, 5.6% hydrogen, 15.4% phenolic groups, and 20.3% total hydroxyl groups; it still contains 24% of material which is not adsorbed by hide powder but which contains approximately the same methoxyl and total hydroxyl groups as the total fraction. Classification reactions show that the product is a phlobatannin. The phlobaphene contains 6.9% methoxyl, 66.8% carbon, 5.9% hydrogen, 10.1% phenolic groups,

and 13.7% total hydroxyl groups. The high methoxyl content indicates that this fraction may contain some acetone-soluble lignin. Alkali fusion of both the tannin and phlobaphene yields only protocathechuic acid and catechol; the corresponding methylated products yield only veratric acid. Destructive distillation of phlobaphene yields catechol and small amounts of phenol. Ultraviolet absorption spectra for both tannin and phlobaphene are similar to those for mimosa tannin and alcohol-soluble spruce lignin. Methylation with diazomethane does not cause any significant change in the ultraviolet absorption spectra.

formed from the tannin on heating with acids (4). In this paper the term "phlobaphene" is used to designate the naturally occurring product. The water-insoluble fraction probably contains a certain amount of native lignin as defined by Brauns (1). At present no satisfactory method is known for separating this insoluble lignin from the true phlobaphene.

ISOLATION OF TANNIN AND PHLOBAPHENE

Many methods of isolating and purifying tannins are described in the literature (2, 4, 6). Because the tannins vary in solubility and because they are amorphous solids, none of the methods is ideal. Several of these methods have been applied to redwood in this laboratory.

The wood has been extracted with alcohol, acetone, or hot water (water does not remove the phlobaphene). The tannin has been isolated from its aqueous solution by precipitation with lead acetate or sodium chloride and by extraction with ethyl acetate. In one instance an attempt was made to purify the tannin by adsorbing it on hide powder and then extracting the hide powder with dilute alkali. Because only a small part of the tannin could be recovered from the hide powder, this procedure was discontinued.

The materials described in this paper were isolated and purified in the following manner: A total of 3400 grams (3050 grams on the oven-dry basis) of old stump wood in the form of sawdust was extracted with acetone by the countercurrent principle. Each portion was extracted ten times at room temperature. The combined acetone extracts were concentrated under reduced pressure to 900 grams, and the concentrate was poured into 5 liters of distilled water heated to 58° C. The phlobaphene separated as a thick tar and was washed with hot water. The aqueous layer was heated on the steam bath for 2 hours to remove acetone. A small amount of additional phlobaphene which separated was removed by filtration. The total crude phlobaphene, after drying, was extracted with ether in a Soxhlet apparatus. There were obtained 181 grams of ether-insoluble phlobaphene and 3 grams of ether-soluble material.

A 20-gram portion of the ether-extracted phlobaphene was purified by dissolving in 100 ml. of acetone and reprecipitating into 1500 ml. of water at 60° C. The product separated in a colloidal form and was flocculated by the addition of a small amount of anhydrous sodium sulfate. There were obtained 14.5 grams of reprecipitated phlobaphene and 5.5 grams of material which was mostly soluble in hot water but only partly soluble in cold water. The latter material appears to consist chiefly of difficultly soluble tannin.

The aqueous solution from the precipitation of the phlobaphene was treated with 1450 grams of 40% lead acetate to precipitate tannin. The tannin was liberated by suspending the lead salts in 6 liters of water at 60° C. and saturating with hydrogen sulfide. The resulting tannin solution was concentrated to 1800 ml., and the tannin precipitated by the addition of 432 grams of sodium chloride. The product, after drying, was separated from a small amount of salt by dissolving in acetone and evaporating the filtered acetone solution to dryness under reduced pressure. The resulting product was separated into two

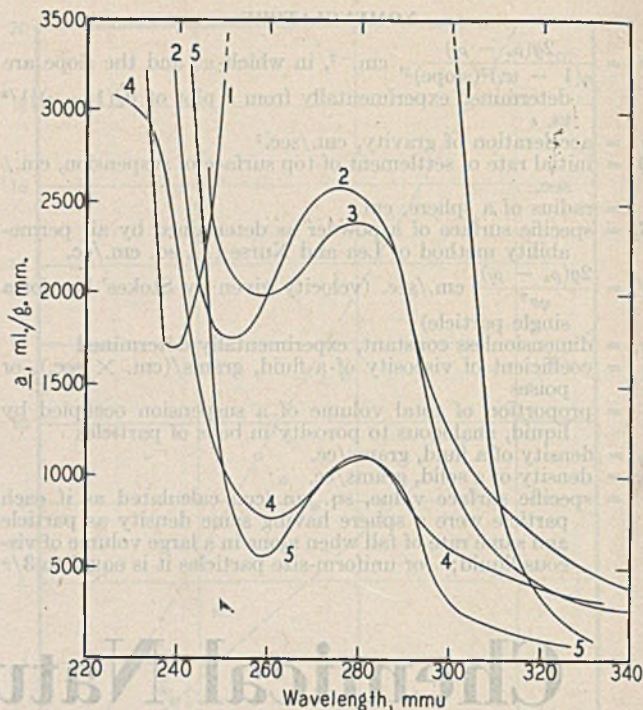


Figure 1. Ultraviolet Absorption Spectra

1. 0.04% tannic acid
2. 0.04% redwood tannin
3. 0.04% redwood phlobaphene
4. 0.02% native lignin
5. 0.04% mimosa tannin

fractions by extraction with ether in a Soxhlet apparatus. Sixty grams of ether-insoluble tannin and 18 grams of ether-soluble fraction were obtained. The latter fraction was insoluble in low-boiling petroleum ether and contained some material which was difficultly soluble in ether. The ether-insoluble fraction represents the purified tannin.

The yields are summarized in Table I. The purified tannin represents approximately one third of the total tannin present in the stumpwood used in this investigation. The other water-soluble fractions contain some tannin as well as the nontannins. Analysis of the purified tannin by the American Leather Chemists' Association method indicated that this fraction contains 24% of material which is not adsorbed by hide powder under the standard conditions of the test. Accordingly, a 6.1-gram portion of the tannin was treated with hide powder under conditions similar to the standard analysis. After the hide powder treatment, the aqueous solution did not precipitate gelatin. This solution was concentrated to dryness under reduced pressure. The residue (1.3 grams) was extracted with acetone, and the acetone-soluble fraction isolated and purified. An 0.8-gram yield of acetone-soluble nontannins was obtained which was found to contain 2.9% methoxyl. A sample of rootwood tannin which first had been adsorbed on hide powder and removed by sodium hydroxide contained 3.0% methoxyl.

CLASSIFICATION REACTIONS

Many qualitative tests have been described (2, 4, 6) which may be used to classify the tannins. The purified tannin was subjected to these tests and also was tested for glucose after hydrolysis. A 0.4% aqueous solution gave the following results: A green color with ferric alum, a dark precipitate with boiling hydrochloric acid, a reddish-brown precipitate with formaldehyde and hydrochloric acid, an immediate orange precipitate with bromine water, a pink color with sodium sulfite, a dark precipitate (soluble in acetic acid) with lead acetate, a brown precipitate with nitrous acid, a precipitate (soluble in ammonium hydrox-

TABLE I. DISTRIBUTION OF ACETONE-SOLUBLE EXTRACTIVES OF REDWOOD

	% of Oven-Dry Wood
Purified phlobaphene	4.3
Hot water-soluble fraction of phlobaphene	1.6
Ether-soluble fraction of phlobaphene	0.1
Total water-insolubles	6.0
Purified tannin	2.0
Hot water-soluble fraction of tannin	0.6
Other water-soluble fractions	4.9
Total water-solubles	7.5

ide) with iodine, a brown precipitate with gelatin, and no precipitate on boiling with acetic acid, ferric citrate, and ammonium chloride (Ware's test). A sample of the tannin, heated with 10% sulfuric acid for 110 hours, failed to form any sugar as determined by the osazone test. For comparative purposes all of these tests were also made on tannic acid (Baker's Analyzed) and a known phlobatannin (mimosa from *Acacia decurrens mollis*). The results show that redwood tannin is to be classified as a phlobatannin. On heating with acids or with hydrochloric acid and formaldehyde, redwood tannin is converted to insoluble condensation products more slowly than is mimosa tannin under the same conditions. This difference may be caused by the smaller proportion of phenolic hydroxyl groups in the redwood tannin.

ANALYSIS AND ACETYLATION

Samples of tannin and phlobaphene for analysis were purified by dissolving in dioxane and precipitating into petroleum ether (30–60° C.) and ether, respectively. The resulting products were thoroughly washed with petroleum ether and completely dried. The tannin contains a small but appreciable amount of methoxyl. Because a sample of rootwood tannin purified by adsorption on hide powder contained the same amount of methoxyl, this is believed to be an integral part of the tannin. The relatively high methoxyl content of the phlobaphene indicates the presence of 30–35% of native lignin in this fraction.

Both the tannin and the phlobaphene were acetylated with acetic anhydride in pyridine solution. The analytical results follow:

	Carbon, %	Hydrogen, %	Methoxyl, %	Acetyl, %
Tannin	63.6	5.6	2.8	...
Phlobaphene	66.8	5.9	6.9	...
Acetylated tannin	1.1	33.4
Acetylated phlobaphene	4.8	27.2

METHYLATION STUDIES

All of the known natural tannins contain phenolic hydroxyl groups; the phlobatannins, as pictured by Russell (6), also contain an aliphatic hydroxyl group. In addition, the conversion of tannin into phlobaphene is believed to be a condensation involving the loss of water from two hydroxyl groups. For these reasons it was desirable to estimate the number and kinds of hydroxyl groups present in the tannin and in the phlobaphene. Complete methylation with dimethyl sulfate and sodium hydroxide methylates both phenolic and aliphatic hydroxyl groups. On the other hand, methylation with diazomethane in an anhydrous solvent methylates phenolic but not aliphatic hydroxyl groups. This method has been used to determine the percentage of each kind of hydroxyl group present in both the tannin and the phlobaphene. Methylation with dimethyl sulfate was carried out in dioxane and acetone solutions, whereas methylation with diazomethane was carried out in anhydrous dioxane solution. In all cases the methylations were repeated until a constant methoxyl content was obtained.

The following equations were used to make the necessary calculations:

$$100 \frac{31(x)}{100 + 14(x)} + 100 \frac{\text{MeO content of original material}}{100 + 14(x)} = \text{\% MeO content of methylated material}$$

$$100 \frac{17(x)}{100} = \text{\% of methylatable hydroxyl groups}$$

where (x) = No. of methoxyl groups introduced per 100 grams of original material.

The total hydroxyl groups were calculated from the dimethyl sulfate methylation data, the phenolic hydroxyl groups from the diazomethane methylation data, and the aliphatic hydroxyl

TABLE II. ANALYSES OF TANNIN AND PHLOBAPHENE

	Methylating Agent	Methoxyl, %	Increase in Methoxyl, %
Tannin	Dimethyl sulfate	34.1	31.3
	Diazomethane	27.4	24.6
Phlobaphene	Dimethyl sulfate	28.6	21.7
	Diazomethane	23.4	16.5
Hydroxyl Groups	Total, %	Phenolic, %	Aliphatic, %
Tannin	20.3	15.4	4.9
Phlobaphene	13.7	10.1	3.6
"True phlobaphene"	15.3	13.1	2.2

groups by difference. (Diazomethane methylation of the dimethyl sulfate methylated products failed to produce an increase in methoxyl, an indication of the absence of carboxyl groups.)

The data in Table II show that the tannin contains more phenolic hydroxyl groups and more aliphatic hydroxyl groups than does the phlobaphene fraction. However, the redwood tannin contains less phenolic hydroxyl groups than the theoretical for other tannins such as tannic acid (pentadigalloylglucose), 25%, and mimosa tannin, 23.6%.

The high methoxyl content of the phlobaphene fraction is believed to result from the presence of native lignin. Brauns (1) showed that native lignin from black spruce contains 14.8% methoxyl, 4.0% hydroxyl groups which are methylated with diazomethane, and 10.5% hydroxyl groups which are methylated with dimethyl sulfate. Unpublished results by Brauns indicate that native lignins from certain other softwoods have approximately the same compositions. The data for the "true phlobaphene" in Table II are calculated on the basis that the phlobaphene contains 33% native lignin of the above composition. On the same basis, the methoxyl content is calculated to be 3.0%.

ULTRAVIOLET ABSORPTION SPECTRA

The absorption spectra of dioxane solutions of redwood tannin and phlobaphene, of the corresponding diazomethane-methylated products, and of mimosa tannin, tannic acid, and native lignin were determined by means of The Institute of Paper Chemistry multistep sector photometer (8) and the Bausch & Lomb medium quartz spectrograph. The curves showing extinction coefficients at the various wave lengths are given in Figure 1.

Extinction coefficient a was computed from the equation:

$$T = 10^{-acx}$$

where T = transmittance in fractional units

c = concentration, grams per ml.

x = solution thickness, mm.

The spectra for mimosa tannin and tannic acid do not show the secondary structure obtained by Russell (7). This difference may be due to the fact that Russell used absolute alcohol as solvent, whereas dioxane was the solvent in the present study. However, no secondary structure was obtained when water was the solvent. The curves of Figure 1 were drawn from a careful inspection of the spectrum plates, and no significant secondary structure was overlooked.

The peak for tannic acid on extrapolation is estimated to have a value of about 7000 $m\mu$. Tannic acid, mimosa tannin, redwood tannin, and phlobaphene show ultraviolet absorption in similar wave length bands but differ materially in the relative degree of absorption in those bands. The maximum at approximately 280 $m\mu$ is also exhibited by lignin preparations (3, 5).

The absorption curves for redwood tannin and phlobaphene lie between those for tannic acid and mimosa tannin. Methylation with diazomethane has only the effect of reducing the absorption because of the increased molecular weight.

FISSION PRODUCTS

On alkaline fusion of the tannin and the phlobaphene only protocatechuic acid and catechol were isolated. Other phenolic residues may be present, but it has not been possible to isolate other fission products. Alkaline fusion of methylated tannin and methylated phlobaphene yielded veratric acid. Oxidation of the methylated tannin also gave veratric acid. Vacuum distillation of the phlobaphene gave catechol and a small amount of phenol.

DISCUSSION OF RESULTS

Redwood tannin belongs to the phlobatannin class. It contains somewhat less phenolic groups than do other members of this class. It contains a small but appreciable amount of methoxyl.

The phlobaphene fraction appears to contain 30–35% of native lignin in addition to the true phlobaphene. This is not surprising, in view of the similar solubility behavior of the two materials. If the results are corrected for the presence of lignin, the true phlobaphene contains only a slightly higher methoxyl content and less phenolic and aliphatic hydroxyl groups than does the tannin. The true phlobaphene thus appears to be a condensation product of the tannin, in which both the aliphatic and the phenolic hydroxyl groups are involved.

Attempts have been made to establish a formula for redwood tannin on the basis of Russell's general type formula for the phlobatannins (6). However, it has not been possible to fit any single formula to all of the known data. This suggests that the tannin fraction is not homogeneous but consists of tannins of slightly different compositions which, however, possess similar solubility characteristics. Because protocatechuic acid is obtained on fusion, it appears that the 3', 4' positions are hy-

droxylated. The small amount of methoxyl which is present is believed to be attached to the 3' position. The small amount of phenolic hydroxyl groups suggests that the other aromatic ring is hydroxylated to a much lesser degree, if at all, than are the other phlobatannins. The carbon content is too low and the hydrogen too high for a structure similar to that picture by Russell but containing fewer hydroxyl groups.

The ultraviolet absorption spectra of both redwood tannin and phlobaphene are somewhat similar to that of lignin.

ACKNOWLEDGMENT

The authors are indebted to A. Russell for supplying the sample of mimosa tannin and for suggestions and comments relative to this work, and to J. A. Van den Akker for determination of the absorption spectra. Appreciation is expressed to The Pacific Lumber Company for permission to publish this work.

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Ferrous and Magnesium Chromites

Specific Heats at Low Temperatures

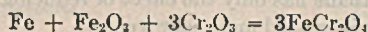
Specific heats of ferrous chromite and magnesium chromite have been measured throughout the temperature range 52° to 298° K. Ferrous chromite has two anomalies in its specific heat curve, one peak occurring at 75° and the other at 135° K. The following molal entropies at 298.16° K. were computed: ferrous chromite, 34.9 ± 0.4 E.U.; magnesium chromite, 25.3 ± 0.2 E.U.

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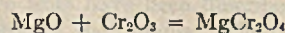
ONE of the recent programs of the Bureau of Mines has been a study of the beneficiation and utilization of low-grade domestic chromite ores. As part of this program the Pacific Experiment Station has made thermochemical studies of compounds of importance in the metallurgy of chromium. This paper presents low-temperature specific heat and entropy data for ferrous chromite and magnesium chromite.

The chromite samples were prepared in this laboratory by F. S. Boericke and W. M. Bangert. Ferrous chromite was made by heating in a vacuum to 1300° C. a finely ground stoichiometric mixture of high-grade sponge iron, reagent-grade ferric oxide, and chromic oxide of high purity. The reaction is represented by the equation:



Analysis of the final product showed 99.25% FeCr_2O_4 and 0.75% silica.

Magnesium chromite was prepared in a similar manner by reacting reagent-grade magnesium oxide with the chromic oxide at 1400° C. according to the reaction,



The sample analyzed 99.5% MgCr_2O_4 and 0.5% FeCr_2O_4 .

X-ray analyses of the crystal structures of the samples were made by E. V. Potter of the Salt Lake City Station of the Bureau of Mines. The ferrous chromite showed a cubic lattice with a parameter of 8.358 Å. The pattern for this sample checked well with those previously reported for synthetic and natural chromite. No impurity was present in sufficient quantity to exhibit addi-

TABLE I. SPECIFIC HEATS

FeCr ₂ O ₄ (Mol. Wt. = 223.87)		MgCr ₂ O ₄ (Mol. Wt. = 192.34)	
T° K.	C _p , cal./mole	T° K.	C _p , cal./mole
53.3	7.000	134.9	19.65
56.9	7.842	136.8	18.14
60.7	8.381	138.9	17.19
64.7	9.155	145.3	17.94
68.6	9.929	155.3	19.14
72.8	10.50	165.3	20.35
76.9	10.48	175.3	21.53
80.3	10.65	185.2	22.64
83.9	11.02	195.8	23.73
94.3	12.42	205.8	24.75
104.2	14.00	216.6	25.78
114.7	15.83	226.0	26.80
123.3	17.44	235.6	27.41
123.9	17.56	246.1	28.28
126.2	18.06	255.9	29.09
128.9	18.67	265.8	29.85
131.0	19.24	276.4	30.58
133.0	19.87	286.0	31.23
134.8	20.22	296.2	31.86
		205.7	22.36
		216.7	23.54
		226.0	24.44
		235.5	25.34
		246.1	26.28
		256.1	27.21
		265.8	27.97
		276.3	28.74
		286.0	29.46
		296.0	30.17

tional lines. The magnesium chromite also checked known spacings; its parameter was found to be 8.31 Å.

SPECIFIC HEATS

The method and apparatus used in the low-temperature specific heat measurements have been described previously (1, 3). The experimental results, expressed in defined calories (1 calorie = 4.1833 international joules), are listed in Table I and shown graphically in Figure 1. The molecular weights in Table I are in accordance with 1941 International Atomic Weights. Corrections have been made in the specific heat results for the previously mentioned impurities.

Magnesium chromite exhibited normal behavior throughout the temperature range studied. Two "humps", however, appear in the specific heat curve of ferrous chromite, the peaks being at 75° and 135° K. Anomalies such as these are not uncommon in ferrous iron compounds; similar humps have been reported in the specific heat curves of ferrous oxide, ferrous sulfide, ferrous chloride, and ferrous silicate.

ENTROPIES AT 298.16° K.

The evaluation of the entropies at 298.16° K. is obtained by graphical integration of a plot of C_p against $\log T$. This necessitates the extrapolation of the specific heat curves from the temperature of the lowest measurements down to the absolute zero of temperature. It was found that the function sum,

$$D\left(\frac{208}{T}\right) + 4E\left(\frac{531}{T}\right) + 2E\left(\frac{991}{T}\right)$$

adequately represents the magnesium chromite specific heat data in the measured range up to 200° K.; symbols D and E denote, respectively, Debye and Einstein functions. These functions were used for extrapolating the data down to 0° K. to obtain $S_{298.16}^{\circ} = 25.3 \pm 0.2$ entropy units (E.U.) per mole, of which 1.63 E.U. is extrapolation below 53.09° K.

Extrapolation of the specific heat curve of ferrous chromite down to 0° K. is difficult by any method because of the abnormal specific heats in the vicinity of the lower hump. A smooth "normal" curve was drawn, connecting the points above 138° K. with the points at 80.3° and 83.9° K., and with the lowest point at 53.3° K. Two functions sums were found to represent adequately this normal curve up to 150° K.:

$$D\left(\frac{140}{T}\right) + 2D\left(\frac{346}{T}\right) + 4E\left(\frac{794}{T}\right), \text{ giving } S_{53.09}^{\circ} = 4.13 \text{ E.U. per mole}$$

$$D\left(\frac{109}{T}\right) + 2E\left(\frac{264}{T}\right) + 4E\left(\frac{809}{T}\right), \text{ giving } S_{53.09}^{\circ} = 4.74 \text{ E.U. per mole}$$

The method of Kelley, Parks, and Huffman (2) also was used to extrapolate the normal curve to 0° K., using magnesium chromite as the standard substance in their extrapolation method. This extrapolation gives $S_{53.09}^{\circ} = 4.28$ E.U. per mole. A mean of these three values, $S_{53.09}^{\circ} = 4.38$ E.U. per mole, is adopted as the extrapolated portion of the entropy.

The entropy associated with the hump at 75° K. in the specific-heat curve of ferrous chromite was determined by actual summation,

$$\sum_{i=1}^n \frac{C_{pi} \Delta T}{T}, \text{ of the seven lowest specific heat determinations.}$$

This was a series of determinations with little or no intervening temperature gaps. Minor corrections were applied to bring the final temperature of each determination into exact coincidence with the initial temperature of the immediately following determination. The total entropy increase from 53.09° to 79.43° K. is 3.668 E.U. per mole, and the total heat absorption

in this interval, also obtained by summation, $\sum_{i=1}^n C_{pi} \Delta T$, is 243.4 calories per mole.

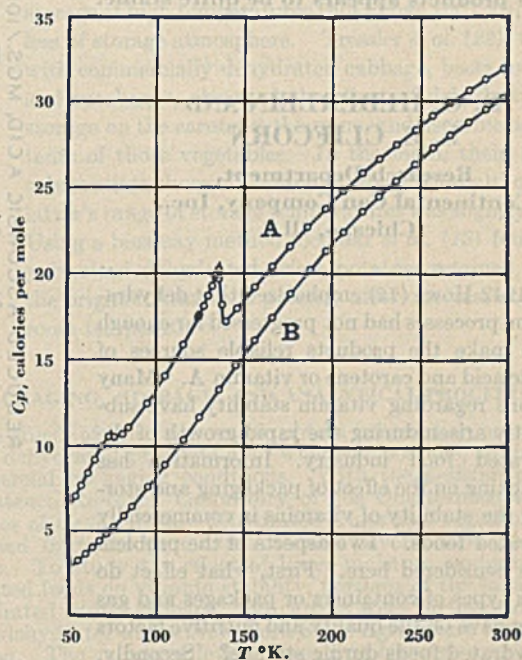


Figure 1. Specific Heats of Ferrous Chromite (A) and Magnesium Chromite (B)

A similar set of specific heat determinations was made over the region of the larger hump at 135° K. In addition, each of two determinations of the total heat absorption between 120° and 140° K. gave 366.2 calories per mole. The entropy increase from 120° to 140° K. is 2.820 E.U. per mole. The total measured entropy increase from 53.09° to 298.16° K. is 30.52 E.U. per mole. Adding to this the value adopted for the extrapolated portion of the entropy gives $S_{298.16}^{\circ} = 34.9 \pm 0.4$ E.U. per mole.

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Vitamin Content of Dehydrated Foods

EFFECT OF PACKAGING AND STORAGE

Dehydrated fruits and vegetables packaged in metal containers in an inert gas, in air, and in paper cartons, and stored at room temperature, 98° F., and 130° F., have been studied with regard to vitamin stability over a storage period of one year. The beneficial effect of inert gas packaging on carotene and ascorbic acid has been overshadowed by losses due to elevated temperatures of storage. Increased storage temperature had a detrimental effect on thiamine retention. Riboflavin in dehydrated products appears to be quite stable.

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IN 1942 Howe (12) emphasized that dehydration processes had not progressed far enough to make the products reliable sources of ascorbic acid and carotene or vitamin A. Many questions regarding vitamin stability have subsequently arisen during the rapid growth of the dehydrated food industry. Information has been lacking on the effect of packaging and storage on the stability of vitamins in commercially dehydrated foods. Two aspects of the problem will be considered here. First, what effect do various types of containers or packages and gas packing have on the quality and nutritive factors in dehydrated foods during storage? Secondly, how do increased temperatures of storage influence these variables? Packaged dehydrated food should be able to withstand temperatures varying from subarctic to equatorial, as well as moisture changes from arid desert to humid tropical. It has been estimated that the average Army storage period for dehydrated foods is nine months, from the dehydrator to the mess kit.

The scarcity of published information on this

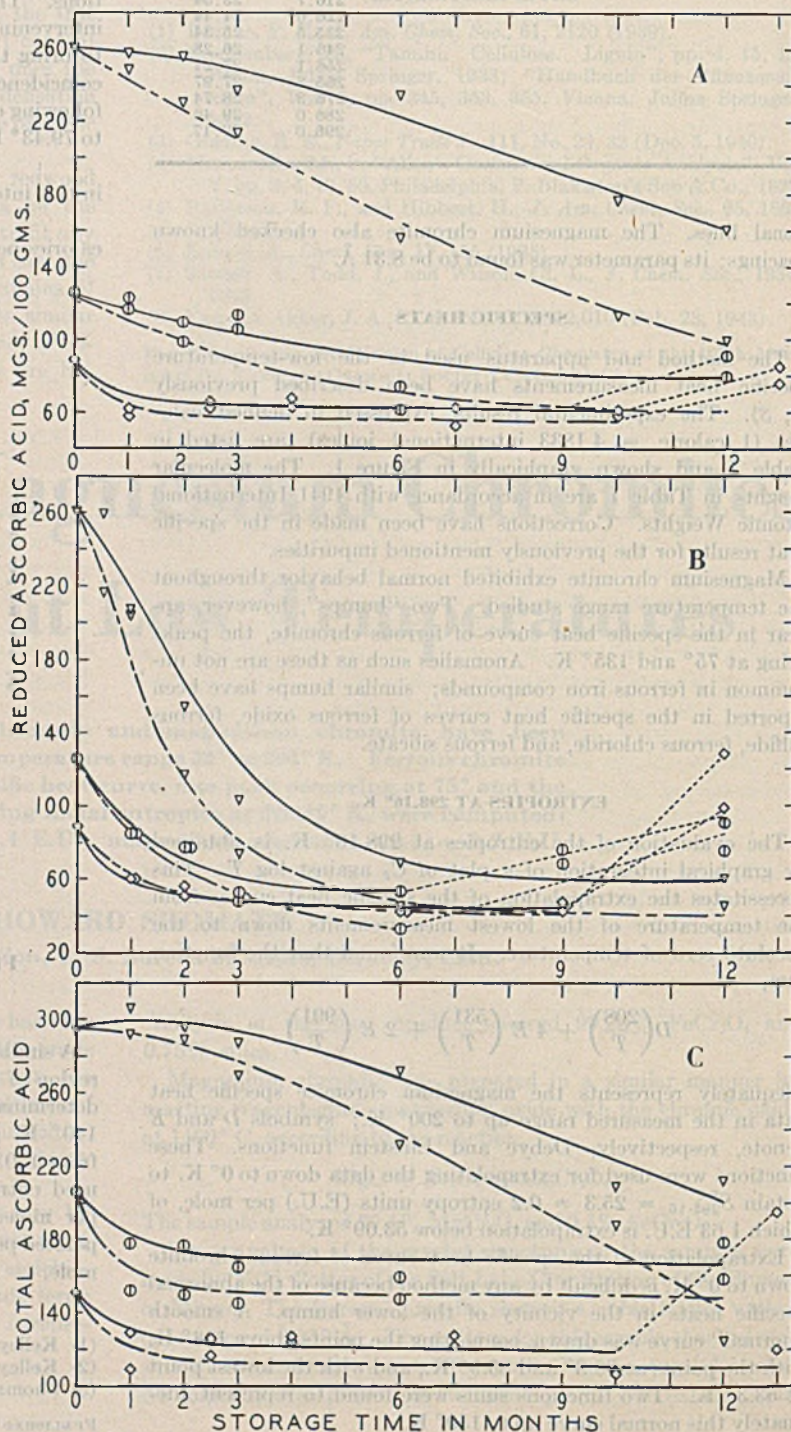


Figure 1. Effect of Gas Packing on Ascorbic Acid

▽ Cabbage (4.0% H₂O); ○ tomato juice cocktail;
◇ cranberries.
— Nitrogen pack; --- paper carton.
A. Reduced acid, room-temperature storage.
B. Reduced acid, 98° F. storage.
C. Total acid, room-temperature storage.

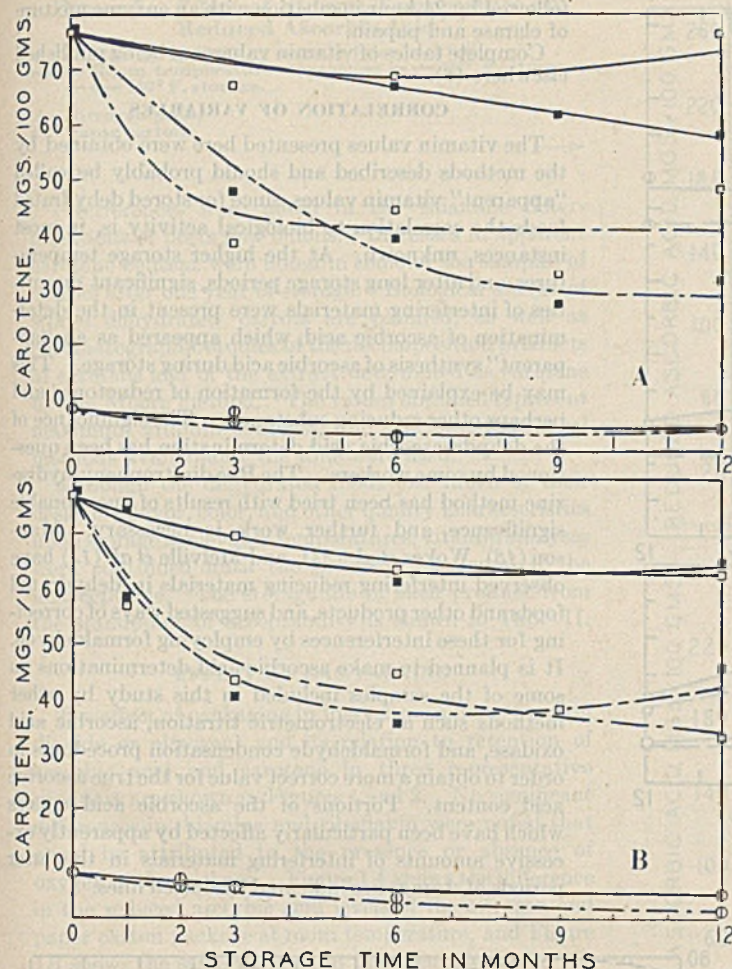


Figure 2. Effect of Gas Packing on Carotene

□ Carrots (5.6% H₂O); ■ carrots (4.6% H₂O); ○ tomato juice cocktail.
— Carbon dioxide pack; --- air pack.

A. Room-temperature storage.
B. 98° F. storage.

subject is due in part to the lack of interest in most dried foods during the period following World War I, and also to limitations of vitamin methods at that time. Tressler (21) and Cruess (7) in a review of the literature through 1941-42, observed contradictory data on the vitamin A or carotene and ascorbic acid values of dehydrated foods. Tressler found no reliable data on the effect of storage on the B vitamins in dried fruits and vegetables, but both reviewers concluded that the losses would probably be greatest during dehydration.

Chace (4) stored carrots, cabbage, and sweet potatoes at 90° F. in air, nitrogen, oxygen, and carbon dioxide, and found maximum retention of carotene in nitrogen and, to a lesser extent, in carbon dioxide. Ascorbic acid in cabbage seemed to be best retained in nitrogen while no significant changes in thiamine or riboflavin were observed. Farrell and Fellers (11) found that dehydrated green beans retained 98% of the original thiamine after dehydration with an over-all retention of 84% after one year of storage at 38° F. No changes in riboflavin were noted, but only 5% of the original ascorbic acid remained after dehydration and 4% after one year of storage at 38° F. Wall and Kelly (23) observed the disappearance of large amounts of carotene from several varieties of dehydrated plant materials on 3-6 month storage at room temperature. Aykroyd (1) found a 50% retention of ascorbic acid in cabbage, cauliflower, and knol-khol, stored 12 weeks at 98.6° F. in sealed containers. He also found only 25-30% retention of that vitamin in the same vegetables stored 6 weeks at 64-73° F. in unsealed containers. Dutton *et al.* (10) stored dehydrated spinach for 32 weeks under several ex-

perimental conditions, and correlated the chlorophyll, carotene, and ascorbic acid content. They found that carotene retention was decreased by oxygen in the storage atmosphere but was unaffected by moisture content.

Davis *et al.* (8), studying factors affecting the quality of a few laboratory-dehydrated vegetables, concluded that storage temperature was of prime importance, adequate blanching second, and the atmosphere of the package third. In an extensive study of fourteen laboratory-dehydrated vegetables, stored 6 months at 70° and 98° F., Beardsley *et al.* (2) observed that retentions of ascorbic acid and carotene were decreased considerably by the presence of oxygen in the storage atmosphere. Thiamine was unaffected, but its retention was appreciably decreased by increase in storage temperatures, as was retention of ascorbic acid. Storage temperature had no consistent effect on carotene.

In a study of the nutritive value of three commercially dehydrated vegetables—cabbage, potatoes, and turnips—Davis and MacArthur (9) reported that carotene and thiamine were quite stable during dehydration but ascorbic acid was not. They also reported that storage temperatures above 65-70° F. and oxygen in the storage atmospheres were detrimental to the retention of ascorbic acid. Carotene retentions were best in an inert storage atmosphere; thiamine was quite stable after 36-week storage at high temperatures (not above 100° F.), regardless of storage atmosphere. Tressler *et al.* (22), working with commercially dehydrated cabbage, beets, potatoes, and rutabagas, observed the effect of dehydration and storage on the carotene, thiamine, and ascorbic acid contents of those vegetables. In the main, their findings substantiate those of Davis and MacArthur although the latter's range of storage temperatures was slightly higher. Using a bioassay method, Seoular *et al.* (18) found that pulverized dehydrated sweet potatoes retained 83% of the original vitamin A potency after one-year storage at room temperature.

PACKAGING, STORAGE, AND ANALYTICAL PROCEDURES

The object of this work was to obtain information on commercially dehydrated products and, wherever possible, to duplicate commercial packaging conditions. With the assistance of the Subsistence Research Laboratory of the Quartermaster Corps, samples of eleven freshly dehydrated fruits and vegetables were obtained from the production lines of several food processing plants. To study the effect of lower moisture contents of dehydrated foods on vitamin stability, portions of the same lots of dehydrated beets, cabbage, and carrots were further dried in a small dehydrator at the New York State Agriculture Experiment Station. The moisture levels were thus lowered another 1 to 1.5%. Information on the dehydrated foods used is shown in Table I. As rapidly as possible all products were packaged in an inert atmosphere and shipped to the laboratory if sample containers were not available at the source of the product. When necessary, the product was repackaged so that four commercial conditions of packing were simulated for each product. Three packages were the conventional hermetically sealed metal containers; one had an atmosphere of air, one had carbon dioxide, and one had nitrogen. The latter two containers were packed with as low an oxygen content as was commercially feasible. A vacuum pack was not prepared since the usual commercial size container is too large (due to dangers of collapsing). The fourth package was an Army substitute 3-in-1 paper container supplied by Reynolds Metal Company; it consisted of a three-ply kraft paper-lead foil-cellulose envelope, heat-sealed and enclosed in a paper carton. Units of each of the packages were then stored at three different temperatures—namely, room temperature (75-80° F.), 98°, and 130°—with one exception. The substitute paper package only (98° F.) was stored in an atmosphere maintained at 93% relative humidity. Sufficient units were stored at each temperature to provide samples at intervals of 2 weeks,

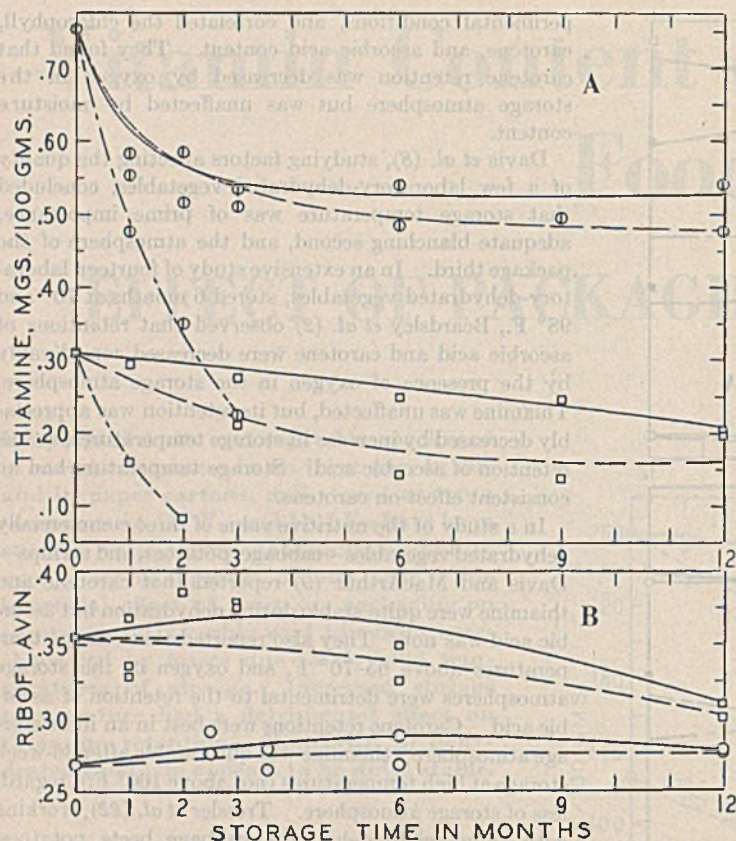


Figure 3. Effect of Storage Temperature on Thiamine and Riboflavin

○ Tomato juice cocktail; □ carrots (5.6% H₂O); ○ beets (4.9% H₂O).
— Room temperature storage; --- 98° F. storage; ··· 130° F. storage.

A. Nitrogen pack. B. Carbon dioxide pack.

1, 2, 3, 6, 9, and 12 months. Initial examinations were made at the time each product was placed in storage. Quality factors are reported elsewhere (6). Measurements of the nutritive factors of these samples are described here.

Attention is focused on ascorbic acid, carotene, thiamine, and riboflavin. Analyses were not made for factors occurring in insignificant quantities in the products included. Reduced ascorbic acid was measured by the Morell modification (17) of the Bessey (3) technique; a Coleman Model 11 spectrophotometer was used, and galvanometer readings were taken at 15- and 30-second intervals. Dehydroascorbic acid was estimated by reducing all oxidized ascorbic acid with hydrogen sulfide and measuring the total reducing power as recommended by Bessey (3). The color and turbidity of the extract of cranberries made it necessary to measure the ascorbic acid of this product by a modification of the Stotz procedure (20). The dye is permitted to react 15 seconds, excess dye is extracted with xylene, and the concentration of dye is measured on the spectrophotometer. Carotene was estimated by the modified chromatographic procedure of Moore (15), using Moore and Ely's method of extraction (16) and substituting denatured alcohol for ethyl alcohol in the foaming mixture. Thiamine was measured by the thiochrome method, as modified by Conner and Straub (5), in a Coleman Model 12 photofluorometer. Riboflavin was determined by the Snell and Strong microbiological method (19), modified by use of acid extracts neutralized to pH 4.5 with sodium acetate after autoclaving; in most cases it was

followed by 24-hour incubation with an enzyme mixture of clarsase and papain.

Complete tables of vitamin values are being published elsewhere (6).

CORRELATION OF VARIABLES

The vitamin values presented here were obtained by the methods described and should probably be called "apparent" vitamin values, since for stored dehydrated foods the correlation to biological activity is, in most instances, unknown. At the higher storage temperatures and after long storage periods, significant quantities of interfering materials were present in the determination of ascorbic acid, which appeared as an "apparent" synthesis of ascorbic acid during storage. This may be explained by the formation of reductones and perhaps other reducing substances. The significance of the dehydroascorbic acid determination has been questioned by some workers. The Roe dinitrophenylhydrazine method has been tried with results of questionable significance, and further work is necessary. Mapson (13), Wokes *et al.* (24), and Melville *et al.* (14) have observed interfering reducing materials in dehydrated foods and other products, and suggested ways of correcting for these interferences by employing formaldehyde. It is planned to make ascorbic acid determinations on some of the samples included in this study by other methods such as electrometric titration, ascorbic acid oxidase, and formaldehyde condensation procedures in order to obtain a more correct value for the true ascorbic acid content. Portions of the ascorbic acid curves which have been particularly affected by apparently excessive amounts of interfering materials in the later periods of storage are indicated by dotted lines.

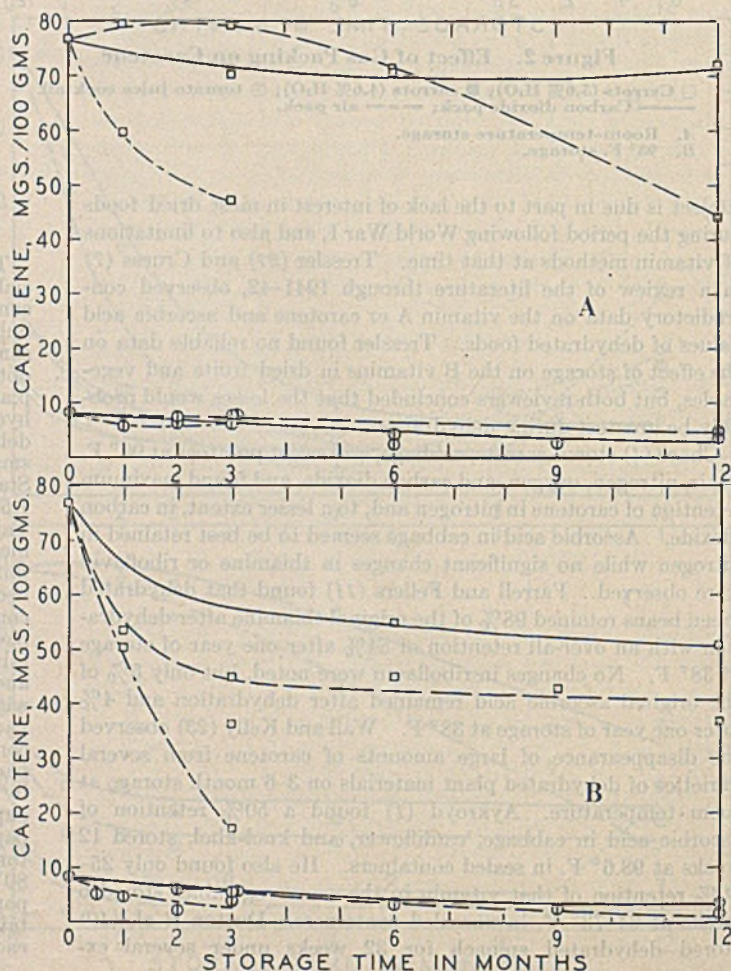


Figure 4. Effect of Storage Temperature on Carotene

□ Carrots (5.6% H₂O); ○ tomato juice cocktail.
— Room temperature storage; --- 98° F. storage; ··· 130° F. storage.

A. Nitrogen pack. B. Paper carton.

Figure 5. Effect of Storage Temperature on Reduced Ascorbic Acid

▼ Cabbage (2.9% H₂O); ○ tomato juice cocktail.
 — Room temperature storage; --- 98° F. storage;
 - - - 130° F. storage.

A. Nitrogen pack.
 B. Paper carton.

Interferences were noted in the thiamine determinations of beets and onions. Increases in apparent carotene content were noted in some of the samples of carrots after one year of storage. Biological assays of stored dehydrated carrots are planned, as well as chromatographic studies of the decomposition products of carotene and of the extract determined as carotene by the Moore method. The values obtained represent maximum vitamin contents, and the best analytical methods available at the time were used.

Although the dehydrated foods lost much of their desirable flavor, color, and other quality characteristics upon storage at elevated temperatures, vitamin analyses were continued until the product was found to be unacceptable. The storage life of each product from the standpoint of acceptability is shown in Table II.

EFFECT OF GAS PACKING

The effect of packaging in inert atmospheres (carbon dioxide or nitrogen) and its relation to retention of ascorbic acid and carotene in three representative products are shown in Figures 1 and 2. No significant differences in thiamine and riboflavin were noted that could be attributed to the presence or absence of oxygen in the package. Figure 1A shows the difference in the reduced ascorbic acid levels of the nitrogen and paper carton package at room temperature, and Figure 1B shows the same variable in these samples at 98° F. The effect of packaging on the apparent total ascorbic acid (reduced plus dehydroascorbic acid) level at room temperature is shown in Figure 1C. Results with the carbon dioxide package could be substituted on the graph for the nitrogen pack, and would give practically

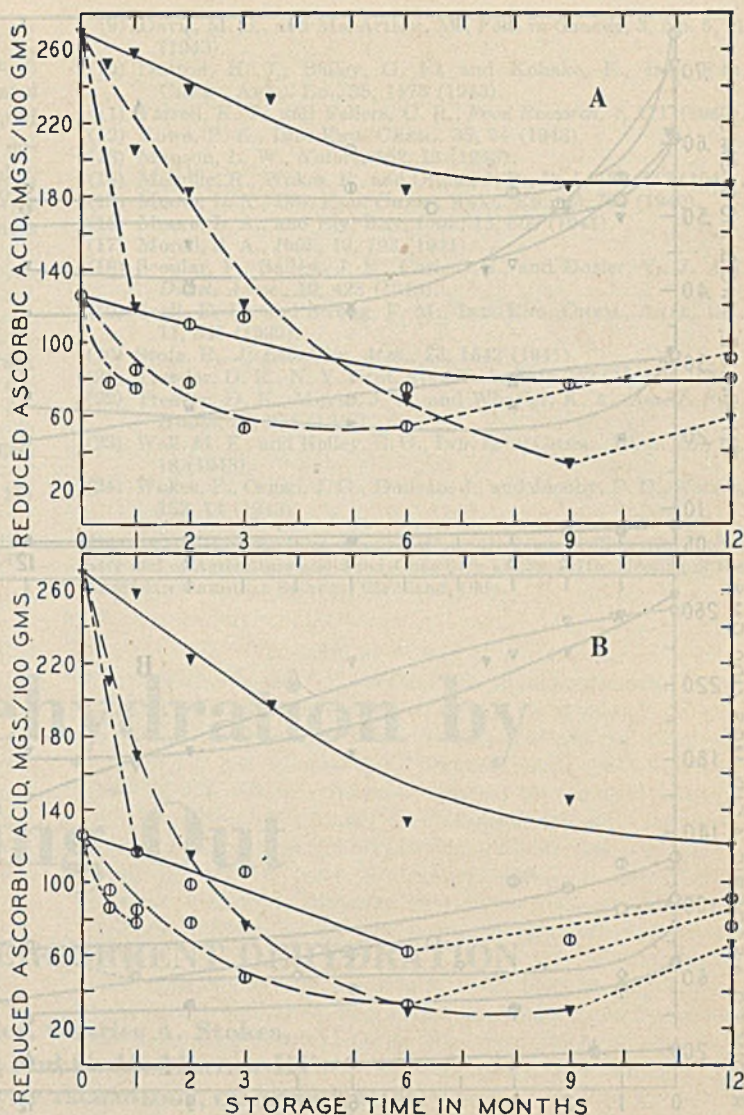


TABLE I. LIST OF FOOD PRODUCTS AND DEHYDRATION PROCESSES

Product	Variety	Form	Blanch		Type	Dehydration ^a Time, Hr.	Finishing Temp., ° F.	% Final Moisture
			Min.	° F.				
Apple nuggets	Unknown (northwestern U.S.)	Coarse ground slices	2, vacuum	..	0.8
Beets	Detroit Dark Red	Diced	7	240	Steam	4, tunnel; 18, finishing bins	140	4.9 & 3.7
Cabbage	Danish Ball Head	Shredded	4 1/4	205	Steam	7	135	4 & 2.9
Carrots	Red Core Chantenay	Diced	6 1/2	240	Steam	5, tunnel; 18, finishing bins	130	5.6 & 4.6
Cranberries	Unknown (Cape Cod, Mass.)	Pulp	Drum-dried	2	..
Irish potatoes	Unknown (Idaho)	Julienne	7 1/2	206	Steam	9	150	7.1
Rutabagas	Yellow Swede	Diced	?	210	Water	5	?	3.8
Tomato flakes	Unknown (N. Y.)	Pulp	Drum-dried	..	1.6
Tomato juice cocktail	Unknown (Calif.)	Pulp	Drum-dried	..	3.3

^a Unless otherwise specified, dehydration was carried out in a tunnel dryer.

TABLE II. STORAGE LIFE OF DEHYDRATED FOODS (IN MONTHS), BASED ON ACCEPTABILITY^a

Product	Room Temp.				98° F. Storage				130° F. Storage			
	Air	N ₂	CO ₂	Carton	Air	N ₂	CO ₂	Carton	Air	N ₂	CO ₂	Carton
Apple nuggets	12	12	12	12	9	9	9	3	1	1	1	1
Beets (4.9% H ₂ O)	12	12	12	12	3	9	9	3	<0.5	0.5	0.5	<0.5
Beets (3.7% H ₂ O)	12	12	12	12	3	12	9	3	<0.5	<0.5	<0.5	<0.5
Cabbage (4.0% H ₂ O)	3	12	12	6	0.5	1	2	0.5	<0.5	<0.5	<0.5	<0.5
Cabbage (2.9% H ₂ O)	9	12	12	6	1	2	2	1	<0.5	<0.5	<0.5	<0.5
Carrots (5.6% H ₂ O)	3	12	12	3	0.5	3	3	0.5	<0.5	<0.5	<0.5	<0.5
Carrots (4.6% H ₂ O)	3	12	12	3	1	3	3	1	<0.5	<0.5	<0.5	<0.5
Cranberries	3	12	12	3	3	6	6	1.5	0.5	0.5	0.5	0.5
Irish potatoes	6	9 ^b	9 ^b	9	1	1	1	1	<0.5	<0.5	<0.5	<0.5
Rutabagas	9 ^b	9 ^b	9 ^b	9 ^b	3	9 ^b	9 ^b	6	0.5	0.5	0.5	0.5
Tomato flakes	9	12	12	9	9	9	9	6	<0.5	<0.5	<0.5	<0.5
Tomato juice cocktail	9	12	12	1	2	2	2	1	<0.5	<0.5	<0.5	<0.5

^a Since the last examination was conducted at 12 months, the products so indicated may have a longer storage life.

^b Incomplete examinations; further storage may reveal the product is still acceptable.

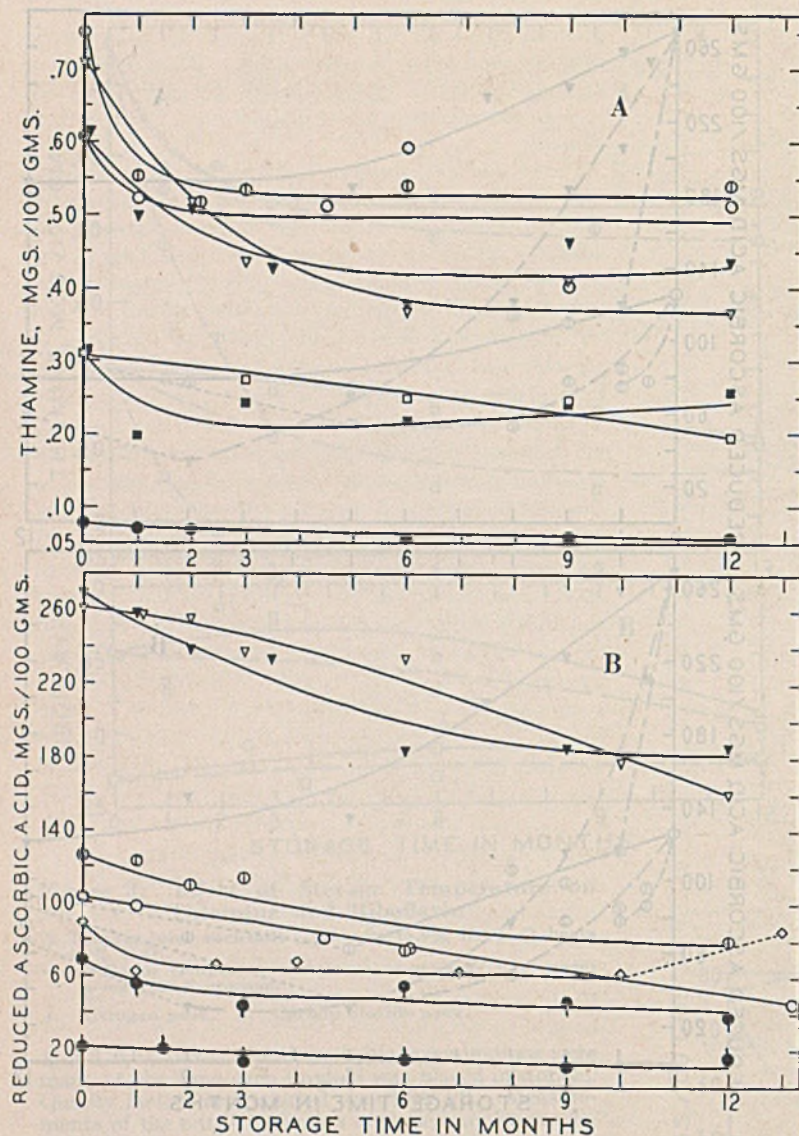


Figure 6. Effect of Specificity of Product on Thiamine and Ascorbic Acid Contents of Dehydrated Foods Stored in Nitrogen at Room Temperature

● Apple nuggets; ▽ cabbage (4.0% H₂O); ▼ cabbage (2.9% H₂O); □ carrots (5.6% H₂O); ■ carrots (4.6% H₂O); ○ tomato flakes; ⊙ tomato juice cocktail; ◇ cranberries; ● Irish potatoes; ● rutabagas.

identical curves. The dotted lines, usually from 9 months to 1 year for some of the products, indicate interferences.

In general, the curves show a greater retention of ascorbic acid and carotene in the gas pack samples. For ascorbic acid in cabbage, the benefits of gas packing were much more pronounced at room temperature than at 98° F. Gas packing was very beneficial in the retention of carotene in carrots and tomato juice cocktail at room-temperature and 98° F. storage (Figure 2).

EFFECT OF TEMPERATURE

The effect of storage temperature on the retention of ascorbic acid, carotene, thiamine, and riboflavin is shown in Figures 3, 4, and 5. The riboflavin content of carbon dioxide packs of carrots and beets (Figure 3B) showed little difference at room-temperature and 98° F. storage for one year. Data on storage of carrots at 130° F. indicated no loss. In consideration of the range or deviation of values usually obtained with the microbiological procedure, it is safe to assume that riboflavin was stable under the conditions of packaging and storage.

The rate of loss of ascorbic acid (Figure 5) was greatly increased with a corresponding increase in storage temperature. At 130° F. the rapid decrease in ascorbic acid content seemed to parallel the accelerated rate of chemical decomposition of the dehydrated products. Unpalatability resulted after short storage periods.

High storage temperatures had a deleterious effect on the stability of thiamine (Figure 3A) and also on carotene in carrots (Figure 4) even when gas packed. The carotene in the air package was retained no better at room temperature than at 98° F. (Figure 2).

EFFECT OF PRODUCT SPECIFICITY

The effect of specificity of the product on the thiamine and ascorbic acid contents of several dehydrated foods stored at room temperature is given in Figure 6. Carotene has already been shown in Figure 2A, but an insufficient number of products prevents any definite statement. Figure 6A gives the thiamine contents of five different products. The moisture content of the dehydrated product—for example, cabbage and carrots—has a variable effect. In consideration of the thiamine retention of cabbage of two moisture contents (2.9 and 4%), the greater loss of thiamine observed in the cabbage of higher moisture content may be significant. However, the differences in carrots are not significant, thiamine being quite stable at either moisture level. The apparent stability of thiamine in tomato flakes as compared to the sharper decreases of that vitamin in tomato juice cocktail may be due to the unavoidable storage period prior to the initial analysis of tomato flakes.

The effect of specificity of the product on riboflavin content is not shown, as riboflavin appears to be quite stable. The retentions of ascorbic acid (Figure 6B) appear to vary considerably. The difference in retentions of the nitrogen package and paper carton have already been discussed. In general, the products packaged in paper cartons showed about the same order of vitamin retention.

SUMMARY AND CONCLUSIONS

An inert atmosphere favored the retention of ascorbic acid and carotene at room-temperature storage. The protective effect of the inert gas was greatly reduced with increasing storage temperature, particularly with ascorbic acid. The storage atmosphere had no significant effect on thiamine or riboflavin.

The increase of storage temperature lowered the retention of ascorbic acid in most products. Carotene was somewhat adversely affected by elevated storage temperatures. Thiamine retention was decreased in most of the products by the higher storage temperatures. Tomato flakes and carrots indicated fairly good stability of thiamine at room-temperature. Riboflavin in dehydrated vegetables appeared to be quite stable.

From the data obtained in this study, it appears that specific product environments have no great effect on the stability of the vitamins studied.

With the possible exception of decreasing the thiamine content of cabbage, the additional drying of beets, cabbage, and carrots to obtain a lower moisture content demonstrated no significant effect on vitamin contents before or after storage.

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Solvent Dehydration by Salting Out

CONTINUOUS COUNTERCURRENT DEHYDRATION

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The continuous countercurrent extraction of water from methyl ethyl ketone by strong calcium chloride brines was investigated in a spray tower and in a packed tower, in which both $\frac{1}{2}$ -inch Beryl saddles and $\frac{1}{2}$ -inch Raschig rings were tested. When operating with ketone dispersed, the height of a transfer unit appeared to be about $2\frac{1}{4}$ feet in the spray tower and roughly half this value in the packed tower, independent of the type of packing used; the height proved independent of flow rates in either phase. When operating in a packed tower with brine dispersed, the H.T.U. values appeared somewhat greater than with ketone dispersed.

AN EARLIER paper (3) discussed the batch dehydration of an organic solvent by a dehydrating substance selected for its insolubility in the solvent being processed. It was pointed out that this method attained its maximum effectiveness when an excess of the dehydrating substance was used, so that the final product of the operation comprised a dehydrated solvent layer, a saturated brine layer, and the excess dehydrating substance. A general method for predicting the degree of dehydration obtainable in this case of maximum dehydration was presented.

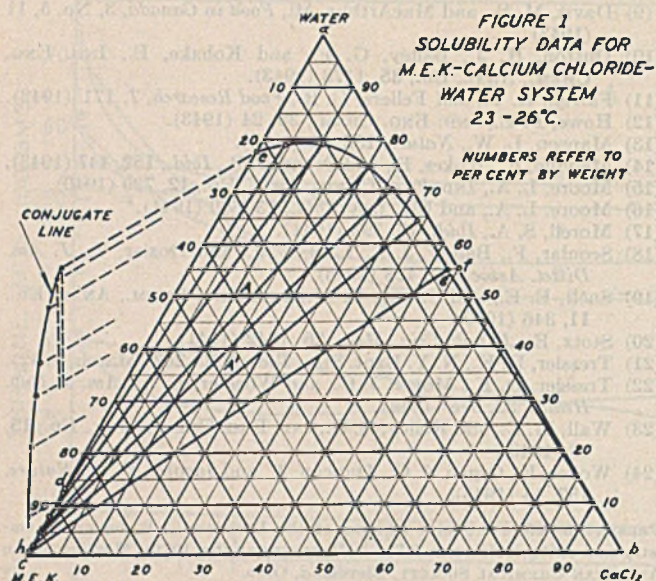
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For industrial operation, it is usually easier to deal with the system in which two liquid phases are brought into contact rather than one involving liquid and solid phases. It is interesting to note that saturated brines need not be used in such an operation, since even partly saturated brines possess marked dehydrating power, although never so great as that of a saturated brine. For example, Figure 1 shows that a 25 weight % solution of calcium chloride in water will exert a dehydrating effect upon any mixture of methyl ethyl ketone and water containing more than about 10% water.

It is apparent that this salting out technique, utilizing strong brines as a dehydrating agent, lends itself readily to countercurrent operation. This paper presents data on the continuous countercurrent extraction of water from a methyl ethyl ketone (M.E.K.) phase by a strong calcium chloride brine. This operation is of interest not only as an example of a technique generally applicable in solvent dehydration, but also because of its novelty. That is, in the studies of continuous countercurrent extraction previously reported in the literature, an organic molecule such as acetic acid was transferred between phases. The M.E.K.-water-calcium chloride system described here differs in that it involves the transfer of water, which behaves differently from organic molecules in many respects. The rate coefficients for this system are of interest in the general study of continuous countercurrent extraction.

The equilibrium data for the system M.E.K.-water-calcium chloride were discussed in some detail in the preceding paper (3)



and are presented graphically in Figure 1. Inspection shows that calcium chloride is not soluble in ketone containing 12.5 water or less, and therefore no salt enters the solvent phase in the extraction operation. Such solubility behavior of the dehydrating agent is necessary to preserve the purity of the solvent being processed. Further inspection of Figure 1 shows that M.E.K. is only sparingly soluble in strong brine; hence the transfer of M.E.K. from the solvent to the brine layer is relatively small. It is evident that a commercial extraction operation could recover all the M.E.K. so transferred by appropriate auxiliary operations.

Although a method exists for predicting the composition of the solvent phase in equilibrium with a brine saturated with a dehydrating agent (3), no reliable method exists for the prediction of the solvent layer compositions in equilibrium with brines not completely saturated. As a result, these solubility data must be obtained in the laboratory.

APPARATUS

The apparatus for continuous extraction is shown in Figure 2 and is essentially the same as that described by Sherwood, Evans, and Longcor (4). It consists of the extraction tower equipped with headers at each end for handling the solutions, and of the auxiliary equipment needed to supply strong brine and ketone saturated with water at a constant rate. The tower is Pyrex, 3.55 inches i.d. and 66 inches high. The incoming liquid enters the ends of the tower through six 0.120-inch i.d. brass nozzles projecting from each header into the tower. The liquids leave the ends of the tower through the center of each header. Operation of this tower and control of the disperse phase were described by Sherwood *et al.*

The brine system is comprised of a saturator, decanter, and constant-head box. In making a run, water and excess solid calcium chloride are placed in the brine saturator. The concentrated brine flows by gravity from here to the decanter, and is then pumped up to the constant-head tank, from which it flows into the top of the tower. The diluted brine from the tower is returned to the brine saturator and recycled. This diluted brine carries some M.E.K. in solution; however, it is salted out by the calcium chloride dissolving in the saturator and forms a ketone layer floating on top of the brine layer in the decanter. This ketone layer is drawn off when necessary and returned to the ketone system.

Operation of the ketone system, which likewise consists of the ketone saturator, decanter, and constant-head tank, is similar to that of the brine system. Appropriate amounts of M.E.K. and water are placed in the saturator at the start of each run. The liquid from the saturator flows by gravity to the decanter, where the liquid separates into two layers. The top layer containing 12.4% water by weight is decanted off and pumped to the constant-head tank, from which it flows into the bottom of

the tower. The dehydrated ketone from the top of the tower is returned to the saturator for re-use. Since calcium chloride is insoluble in the solvent phase being dehydrated, no salt enters the ketone system at any time.

In making a run, the tower was operated for 45 minutes under constant conditions before samples were taken, since tests showed that this allowed ample time for the apparatus to reach steady-state conditions. Record was then made of the flow rates and temperatures, and samples of the four liquid streams entering and leaving the tower were taken. In the runs marked M, the samples of entering and leaving solvent layer were analyzed for water content by adding water from a microburet to a known weight of sample at constant temperature until the appearance of a cloud indicated formation of a second layer, at which point the ketone phase contains 12.4% water. In the runs marked H, the water content of the ketone phase was determined with Karl Fischer reagent (5). The samples of entering and leaving brine were analyzed for calcium chloride by evaporating a known quantity to dryness and weighing the residue. The water and ketone in the brine phase were then determined from line *e-g* of Figure 1, since check analysis showed the composition of the brine leaving the tower to lie on this line, within limits of analytical error. The density of these brines may be assumed to be the same as that of aqueous calcium chloride brines containing an equal weight percentage of salt.

VARIABLES AND CALCULATIONS

Thirty-two runs were made in all. Fifteen were spray tower runs in which the tower contained no packing; the effective height of the tower was varied by extending the nozzles of the top header by attachment of glass tubes of appropriate length. In the remaining runs the tower was packed either with 1/2 inch ceramic saddles or 1/2-inch rings. The height of the packing was varied, the nozzles coming within 3 inches of the upper and lower faces of the packing in each case. Nozzle-mouth diameter was kept constant at 0.12 inch.

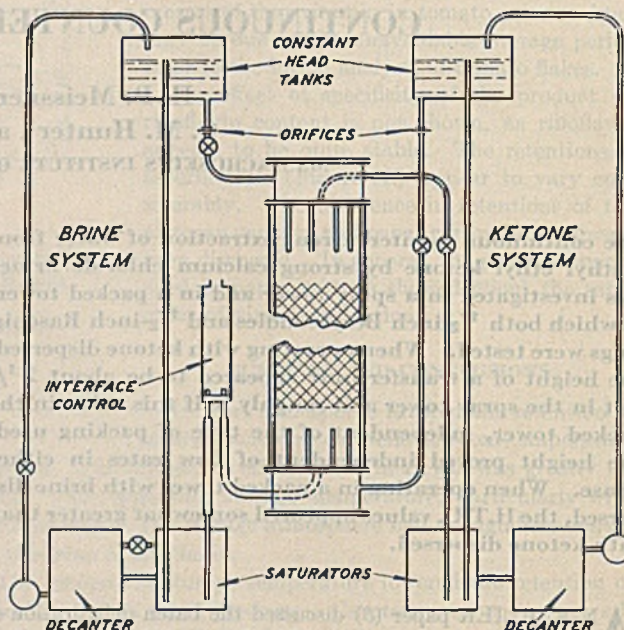


Figure 2. Schematic Diagram of Apparatus

In most of the runs ketone was the disperse phase. At all times transfer of water was from the ketone to the brine phase. The flow rates of the two phases were independently varied over rather wide ranges. The concentrations of the entering phases, however, were not changed significantly, as Table I shows. The inlet concentration of the brine varied from 54 to 67% water by weight while the inlet concentration of the ketone phase, with few exceptions, was constant at 12.4% water by weight. The temperature of all these runs was between 25° and 28° C.; over

this range there is no significant change in the lines on the equilibrium diagram shown in Figure 1.

The height of an over-all transfer unit (H.T.U.) and also the over-all transfer coefficient per unit of tower volume, K_{ka} , were calculated from the familiar equation,

$$N.T.U. = \int \frac{dC_k}{C_k - C_k^*} = \frac{K_{ka}V}{R_k} = \frac{l}{H.T.U.} \quad (1)$$

where C_k is the concentration of water in the ketone phase at any point in the tower, and C_k^* is the concentration of water in a ketone phase in equilibrium with the brine phase at the same point. These concentrations are based on the ketone phase since solubility relations indicate that the major diffusional resistance appears to be in the solvent rather than in the water phase. The integral term in the above equation was evaluated by the usual methods of graphical integration.

The rate of flow of the ketone phase, R_k , changes somewhat through the tower, since water together with a little M.E.K. passes from the ketone phase to the brine phase. In view of the small magnitude of this change (Table I), an arithmetic average of the inlet and outlet ketone phase rates was considered satisfactory for R_k in Equation 1.

Height l and volume V of the tower were always based on the space between the nozzles. In the packed tower runs, these nozzles extended within 3 inches of the packing, so that in a run on 24 inches of packing, for example, the distance between nozzles was actually 30 inches. This 3-inch spacing at either end seemed necessary for proper drop formation and smooth tower operation. The H.T.U.'s calculated for packed tower runs are therefore influenced by these end effects since they are based on a tower that is not completely packed.

SPRAY TOWER WITH KETONE DISPERSED

Transfer coefficients calculated for these runs are presented in Table I and graphically in Figure 3; the transfer coefficients

vary directly with the disperse phase rate. Previous investigators, who had similar findings, pointed out that this behavior is to be expected since at any given continuous phase rate the number of ketone bubbles formed per unit of tower volume increases as the disperse phase rate increases. Interfacial area a between the two phases, and hence K_{ka} , are increased. If the bubbles of ketone all have the same size distribution regardless of disperse phase rate, then K_{ka} should vary directly with ketone rate. Figure 3 shows this proportionality to be substantially true over the ranges covered; the relation between ketone rate and transfer coefficient is well represented by the equation:

$$K_{ka} = 0.4 L_d \quad (2)$$

Investigators of other systems report a marked dependence of transfer coefficients on continuous phase rate. They point out that this is to be expected, since increase in the continuous phase rate lengthens the time required for a disperse phase droplet to travel from one end of the tower to the other. As a result, the time for material transfer from one phase to the other is prolonged and thus increases the transfer coefficient. This point is illustrated by the findings of Sherwood *et al.* (4). Some of their results for the extraction of acetic acid from water solution with methyl isobutyl ketone are presented in Table II, where they are compared with selected runs for the M.E.K.-water-calcium chloride system taken from Table I.

Figure 3 shows that, within the accuracy of the data, the transfer coefficients for the M.E.K.-water-calcium chloride system are independent of the continuous phase rate. This disagreement with the findings of investigators of other systems may be explained as follows: The rate of travel of the disperse phase droplets was relatively so rapid in this case that the effect of continuous phase velocity was negligible. For example, the velocity of the continuous (brine) phase in the tower for run M17 was only 35.5 feet per hour. The rate of rise of the disperse phase through this tower, on the other hand, was perhaps $1/4$ to $1/2$ foot per second, or 900 to 1800 feet per hour, as judged by visual ob-

TABLE I. EXTRACTION OF WATER FROM METHYL ETHYL KETONE BY CALCIUM CHLORIDE BRINES

Run No.	Ht. of Packing, In.	Distance between Nozzles, In.	Water, % by Wt.				CaCl ₂ Brine in, % by Wt.	Ketone Rate, Cu. Ft./ (Hr.) (Sq. Ft.)		Brine Rate in, Cu. Ft./ (Hr.) (Sq. Ft.)	H.T.U., Ft.	K _{ka} , Lb. Moles/(Hr.) (Cu. Ft.) (Unit ΔC)
			Ketone in	Ketone out	Brine in	Brine out		In	Out			
Spray Tower Operation, Ketone-Dispersed												
M14	None	65.5	12.4	2.11	54.5	57.9	43.5	34.2	30.0	16.1	2.28	14.0
H4	None	65.5	12.3	3.0	67.1	72.1	30.5	66.6	59.9	18.8	1.67	37.9
H7	None	30.0	12.4	4.5	58.5	66.9	39.6	68.6	63.6	18.4	1.85	35.6
H2	None	61.5	9.1	3.0	64.7	67.6	33.1	47.0	44.2	24.7	2.50	18.3
M15	None	65.5	12.4	2.47	64.7	60.0	43.3	67.2	59.6	23.7	2.60	24.4
H3	None	61.5	12.1	3.0	63.1	68.5	34.6	58.2	53.2	29.2	2.28	24.5
M16	None	65.5	12.4	2.47	57.1	61.3	40.8	70.0	62.0	27.4	2.54	26.0
M17	None	65.5	12.4	2.21	54.2	57.6	43.8	28.0	25.3	35.5	2.49	10.7
M18	None	65.5	12.4	2.13	54.1	56.2	43.9	48.4	42.4	35.5	2.27	20.0
M19	None	65.5	12.4	2.13	54.9	56.8	43.1	65.0	56.3	35.6	2.27	26.7
Spray Tower Operation, Brine-Dispersed												
H5	None	66.5	12.4	6.5	62.2	64.3	35.8	68.6	63.5	19.0	6.6	10.0
H6	None	66.5	11.5	7.2	59.2	64.1	38.9	68.6	65.2	18.7	9.65	6.9
Half-Inch Berl Saddles, Brine-Dispersed												
M2	24	30	12.4	3.8	58.9	61.9	39.1	28.0	25.6	17.3	1.70	15.9
M4	24	30	12.4	3.38	58.4	61.0	39.6	28.0	25.4	30.0	1.49	18.0
M5	24	30	12.4	2.92	58.2	59.9	39.8	28.0	25.3	41.4	1.29	20.7
M6	24	30	12.4	2.76	57.1	58.5	40.9	28.0	25.2	49.6	1.33	20.0
M3	24	30	12.4	4.95	59.0	62.4	38.9	39.7	36.4	17.4	2.29	16.7
M7	24	30	12.4	5.75	55.3	60.2	42.7	65.7	60.8	17.0	2.89	22.0
M8	24	30	12.4	5.60	55.0	58.8	43.0	65.7	61.0	32.4	2.75	23.1
Half-Inch Berl Saddles, Ketone-Dispersed												
M1	24	30	12.4	5.0	62.75	65.1	35.0	28.0	25.7	17.4	2.08	12.9
M9	24	30	12.4	2.62	55.0	62.9	43.0	60.7	54.5	16.2	1.25	46.1
M10	24	30	12.4	2.77	55.4	63.2	42.6	73.4	65.6	16.2	1.32	52.8
M11	24	30	12.4	2.85	54.0	56.4	44.0	28.0	25.5	33.6	1.43	18.7
M24	36	42	12.4	1.60	54.5	55.9	43.5	28.0	24.2	33.6	1.24	21.0
M25	36	42	12.4	1.55	54.0	55.3	44.0	28.0	24.3	33.6	1.22	21.2
M12	24	30	12.4	2.44	54.0	58.5	44.0	61.3	55.0	33.6	1.30	44.9
M13	24	30	12.4	2.18	55.5	61.1	36.7	70.0	62.9	34.0	1.13	59.0
Half-Inch Ceramic Rings, Ketone-Dispersed												
M20	24	30	12.4	2.52	54.0	59.0	44.0	59.6	52.5	16.1	1.24	45.1
H8	22.5	30	12.4	3.7	62.2	68.2	35.8	68.6	62.1	17.3	1.37	47.8
M21	24	30	12.4	2.59	54.7	59.7	43.3	72.8	64.0	16.2	1.26	54.3
M22	24	30	12.4	2.16	54.5	55.7	43.5	28.0	24.4	33.8	1.12	23.5
M23	24	30	12.4	2.11	55.0	57.0	43.0	51.2	44.7	34.1	1.08	44.3

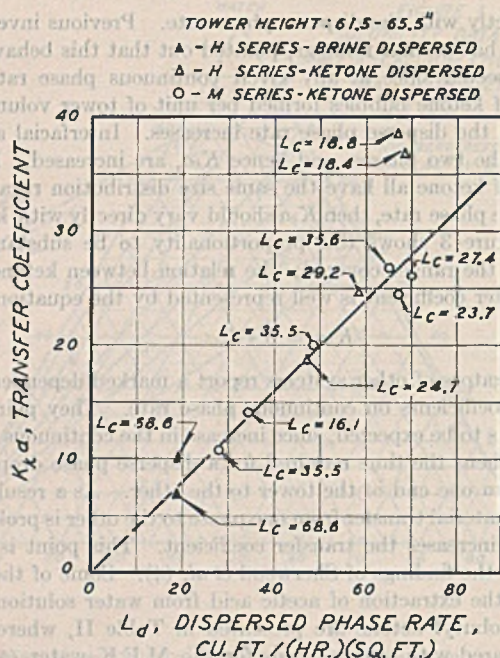


Figure 3. Transfer Coefficients for the Spray Tower

servation during several runs. Evidently, even doubling the continuous phase rate would cause little change in a droplet's travel time through the tower. Hence it is not surprising to find the transfer coefficient apparently independent of the continuous phase rate. This finding is further supported by the fact that calculation of the Reynolds number for the continuous phase shows a value well within the streamline range. Theoretically, at least, change of continuous phase rate within the streamline region should have no effect upon the transfer coefficient.

The high rates of disperse phase travel encountered in the M.E.K.-water-calcium chloride system were apparently not attained in systems reported by other investigators for two reasons: (a) The rate of disperse phase travel is roughly proportional to the difference in density of the two liquid phases; this difference for the system reported here, for example, is about four times that of Sherwood's methyl isobutyl ketone-acetic acid-water system. (b) The rate of bubble rise increases with increased bubble size, and somewhat larger bubbles may be expected to form in the system reported here than in Sherwood's system (other things being equal) because of the larger interfacial tension between the liquid phases. The dependence of bubble size on interfacial tension was pointed out by Holroyd (2).

The H.T.U. values for these spray tower runs are also presented in Table I, and inspection shows that they are substantially independent of the rates of either phase. This is to be expected from the foregoing discussion. That is, if $K_L a$ is independent of the continuous phase rate, then the H.T.U. value must likewise be independent. Since $K_L a$ varies directly with L_d , it follows from Equation 1 that H.T.U. must be independent of variations in L_d .

SPRAY TOWER WITH BRINE DISPERSED

Since conditions were almost identical for runs H5 and H6, it is evident that no conclusions regarding the effect of phase rates upon the coefficient can be drawn in this case. Moreover, too much confidence cannot be placed in the reported findings, since uncertainties are introduced by the tendency of the brine phase to wet ceramic surfaces preferentially as discussed below. Therefore an unknown percentage of the dispersed phase may be travel-

ing through this tower as a film along the inside walls rather than as dispersed droplets. It is interesting to note, however, that the value of the coefficient for these runs is about that predicted by Equation 2.

PACKED TOWER WITH KETONE DISPERSED

The results given in Figure 4 for the tower packed with $1/2$ -inch Raschig rings and $1/2$ -inch Berl saddles shows that the transfer coefficients again vary directly with the dispersed phase rate and appear largely independent of the continuous phase rate. These coefficients also appear independent of the packing used. Judging from the rather meager data available, it appears that these coefficients obey the following equation, which differs from Equation 2 only in having a larger coefficient:

$$K_L a = 0.74 L_d \quad (3)$$

The only available evidence which seriously conflicts with this finding is run M1, which can probably be neglected as subject to error since it is the first run of the M series.

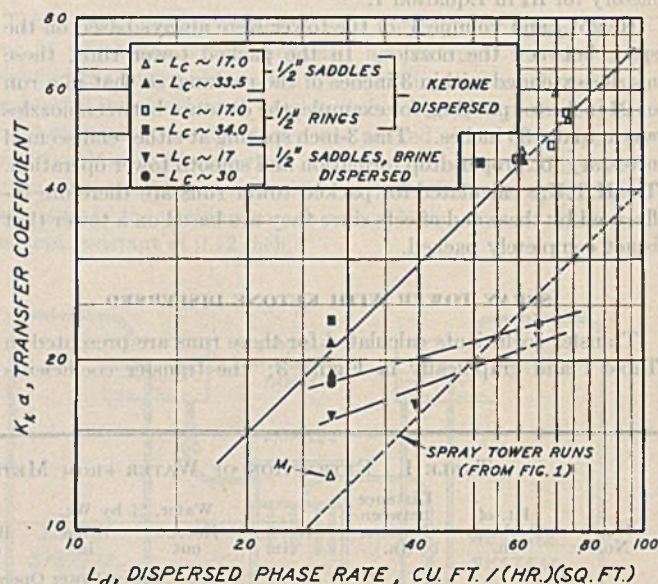


Figure 4. Transfer Coefficients for the Packed Tower

The data and Equations 2 and 3 indicate that the coefficients for this case are almost twice as great as in the spray tower runs for any given dispersed phase rate. Other investigators have likewise found larger coefficients for packed towers, as shown by Sherwood's results in Table II, although they have not found so simple a relation between the coefficients and the phase rate as Equation 3 indicates. The explanation usually presented for the higher coefficients in packed towers is that the packing breaks up the disperse phase into fine droplets. The packing also assists by increasing holdup time within the tower and developing turbulence within the droplets by deforming them. All these factors tend to increase the value of $K_L a$. On the other hand, it is not anticipated that this coefficient will be seriously affected by variations in the diameters of the nozzles used for the disperse phase, although no runs were made to explore this problem. Earlier investigators found that, for a given system, the packing rather than the nozzle dimensions determined droplet size in the tower, and this seemed borne out by observations made during these runs.

Study of the data indicates that the continuous phase rate again appears to have no significant effect upon the transfer co-

efficient. As in the spray tower, this can presumably be explained by the high rate of disperse phase travel as compared to the continuous phase rate. In a packed tower there is turbulence in the flow of the continuous phase through the packing, and since this turbulence increases with the continuous phase rate, there should be a corresponding increase in the film coefficient for the continuous phase. The finding here that the over-all coefficient is unaffected by increases in the continuous phase rate can best be explained by assuming that most of the transfer resistance is in the solvent phase.

TABLE II. COMPARATIVE DATA ON EXTRACTION OF WATER FROM M.E.K. WITH CALCIUM CHLORIDE BRINES AND EXTRACTION OF ACETIC ACID FROM WATER WITH METHYL ISOBUTYL KETONE (KETONE PHASE DISPERSED)

Run No.	Rates, Cu. Ft./ (Hr.) (Sq. Ft.)		Tower Ht., Ft.	H.T.U., Ft.	K_{La} , Lb. Moles/ (Hr.) (Cu. Ft.) (Unit ΔC)
	Ketone phase	Brine (or acid) phase			
M.I.K.-Water-Acetic Acid (4), Spray Tower					
23	40	40	5.15	2.5	16.1
24	40	70	5.04	1.27	31.5
25	40	90	5.24	0.86	46.3
M.E.K.-Calcium Chloride-Water, Spray Tower					
M17	28.0	35.5	5.5	2.49	10.7
M18	48.4	35.5	5.5	2.27	20.0
M19	65.0	35.5	5.5	2.27	26.7
H2	47.0	24.7	5.15	2.50	18.3
M.I.K.-Water-Acetic Acid (4), 1/2-Inch Berl Saddles					
17	40	10	4.5	2.0	19.8
18	40	25	4.5	0.76	52.5
19	40	40	4.5	0.45	88.3
M.E.K.-Calcium Chloride-Water, 1/2-Inch Berl Saddles					
M1	28.0	17.4	2.5	2.08	12.9
M9	60.7	16.2	2.5	1.32	46.1
M11	28.0	33.6	2.5	1.43	18.7
M13	70.0	34.0	2.5	1.13	59.0
M.I.K.-Water-Acetic Acid (4), 1/2-Inch Rings					
6	40	10	4.69	1.87	21.4
9	40	40	4.69	0.78	51.3
12	40	70	4.69	0.59	68.0
14	70	10	4.69	3.6	19.5
16	70	37.3	4.69	1.22	57.1
M.E.K.-Calcium Chloride-Water, 1/2-Inch Rings					
M21	72.8	16.2	2.5	1.26	94.3
M22	28.0	33.8	2.5	1.12	23.5
M23	51.2	34.1	2.5	1.08	44.3

The values of H.T.U. obtained appear to be little influenced by increases in the continuous and disperse phase rates. This contrasts with Sherwood's findings for 1/2-inch saddles and rings (Table II) which indicate a marked effect of rates of either phase on the H.T.U. values for this system.

BERL SADDLES WITH BRINE DISPERSED

Figure 4 shows that the coefficients for this case are smaller than for ketone dispersed over the range investigated. A small but definite tendency is evident for the transfer coefficients to increase with increases in the phase flow rates. Examination of the tower during these runs showed that the brine bubbles vanish immediately upon entering the packing, which they wet preferentially and cover with a film of brine phase. Previous investigators observed this same phenomenon in other systems, and explained the relatively small size of the transfer coefficient and its comparative independence of the phase flow rates as being due to the constancy of the interfacial area between the two phases. Coefficients are larger with ketone dispersed because no such restriction is imposed upon interfacial areas.

FLOODING

Flooding occurred in packed tower runs by the formation of a slug of disperse phase at the point where it entered the packing, the slug then being carried out with the continuous phase. It

was found impossible in this investigation to flood either the spray tower, or the packed tower with brine dispersed, at the maximum flow rates of about 80 cu. ft./ (hr.) (sq. ft.) attainable for each phase in this apparatus. On the other hand, flooding in a packed tower with ketone dispersed was approached in runs M10 and M13. More complete data on this effect are lacking because of the difficulty of determining the flooding points.

CONCLUSIONS

In the M.E.K.-water-calcium chloride system discussed here, in which water is transferred between phases, the values of H.T.U. and transfer coefficient are numerically about the same in magnitude as those of systems reported in the literature, in which an organic substance like acetic acid was transferred from a water to a solvent phase. It was found, however, that the dependence of the H.T.U. values and transfer coefficients upon phase rates differed somewhat from that of the methyl isobutyl ketone-acetic acid-water system investigated by Sherwood (4) and also showed no agreement with the results of Comings and Briggs (1), who found that the transfer coefficient in packed columns for benzoic acid, acetic acid, and aniline traveling between benzene and water phases could be expressed by the following equation:

$$K_a = BL_d^r L_c^s$$

where r and s were found to be 0.5 and 0.25, respectively. For the present system with ketone dispersed, r is unity and s is probably zero in both packed and spray towers. As was found by previous investigators of liquid-liquid extraction systems, transfer coefficients are largest in packed towers, but flooding rates are largest in spray towers. The coefficient is greater in packed columns if the disperse phase does not wet the packing.

Because of the somewhat limited range of variables covered in this study, it would seem of questionable value to make further comparisons with the literature data. It is clear, however, that transfer coefficients are amply large, so that countercurrent extractions of this sort could be carried out on a large scale in apparatus of reasonable size.

ACKNOWLEDGMENT

The solvent used in this investigation was donated by the B. F. Goodrich Company.

NOMENCLATURE

- A = internal cross-sectional area of tower B
 B = empirical constant
 C_k = concentration of water in ketone phase, lb. moles/cu. ft.
 C_k^* = concentration of water in ketone phase in equilibrium with brine phase, lb. moles/cu. ft.
H.T.U. = height of over-all transfer unit based on ketone phase, ft.
 K_{ka} = over-all transfer coefficient based on ketone phase, (lb. moles)/(hr.) (cu. ft.) (unit ΔC)
 l = tower height based on distance between nozzle tips, ft.
 L_d = disperse phase rate, (cu. ft.)/(hr.) (sq. ft.)
 L_c = continuous phase rate, (cu. ft.)/(hr.) (sq. ft.)
N.T.U. = number of transfer units
 R_k = rate of ketone phase, cu. ft./ (hr.)
 r, s = empirical constants in Equation 3
 V = tower volume $A \times l$

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Vitamin Retention in Processed Meat

EFFECT OF THERMAL PROCESSING

The effects of time and temperature of processing on the retention of thiamine, riboflavin, niacin, and pantothenic acid in pork luncheon meat are discussed. The rate of thiamine destruction is doubled with an 18° F. increase in temperature as contrasted with a tenfold increase in the rate of destruction of heat-resistant bacteria. Under conditions which permit uniformly rapid heating of the entire contents of the can, the higher processing temperatures are more favorable to thiamine retention. In commercial-size cans the processing temperature has little effect on B vitamin retention. Retention of B vitamins varies with the location in the can. Data are presented to show the effect of processing in commercial-size cans on the B vitamins.

THE literature relating to the effect of processing and other variants on the vitamin content of foods, including pork, has been reviewed in recent publications (4, 5, 6, 8, 12, 13, 20, 22). A number of studies have been made of the effects of various methods of cooking on a small scale on the retention of B vitamins in meat. Relatively few detailed studies have been made of the effect of different thermal processes on the retention of B vitamins in commercially canned meats. Rice and Robinson (17) and Reedman and Buckby (16) reported data relating to the vitamin content of commercially canned meat.

At present a considerable volume of pork luncheon meat is packed for the armed forces and civilians. The relatively severe heat treatment required to sterilize such a product commercially and the storage period between canning and consumption may materially influence the B vitamin content of the product as eaten. The variations from lot to lot in vitamin content of fresh raw pork, times and temperatures of heat processes employed, as well as differences in conditions under which the product may be stored, preclude the possibility of establishing one vitamin value applicable to all samples of pork luncheon meat at the time of consumption. Therefore, the retention of thiamine, riboflavin, niacin, and pantothenic acid during heating in thermal death time (T.D.T.) and commercial processing equipment has been studied. Information obtained from these studies should be of assistance in appraising the value of pork luncheon meat as sources of the B vitamins in terms of the vitamin content of the raw pork from which it is prepared. The data obtained may also suggest means of modifying present practices so as to permit retention of larger quantities of these vitamins in the canned product.

MATERIALS AND METHODS

CHEMICAL AND MICROBIOLOGICAL PROCEDURES. Moisture, protein, fat, sodium chloride, sodium nitrate, and sodium nitrite analyses were made essentially by the methods of the A.O.A.C. (2).

Thiamine was determined on quadruple aliquots from each sample by the U.S.P. XII thiochrome method (21). Two aliquots of each sample were analyzed independently in the research laboratories of the American Can Company and the American Meat Institute. Approximately 100-gram samples of the

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luncheon meat were mixed thoroughly with four times the weight of distilled water in Waring Blenders. Aliquots were taken for analysis while the Blender was mixing the slurry.

The microbiological procedures for riboflavin, niacin, and pantothenic acid were essentially the tentative U.S.P. XII techniques (21). Aliquots for microbiological assay were obtained from the slurry used for thiamine assay. The samples were prepared for the assay procedures by University of Texas methods (20). All samples were analyzed with two standard curves, and dilutions were made at five levels or concentrations.

The analytical error commonly accepted for the thiochrome method is ± 5 –10%. Most of the quadruple thiamine analyses checked within ± 5 % of one another. In a few samples the error amounted to 10%. The analytical error involved in the microbiological determinations was ± 10 %.

DESCRIPTION OF MEAT. The meat used in this study was secured from three different packing plants. In each case approximately 700 pounds of fresh pork picnics and butts and 300 pounds of shank meat were used. The meat was ground and mixed thoroughly with the quantities of sodium chloride, sodium nitrate, sodium nitrite, sugar, and spices customarily used in each packing plant. It was allowed to cure from 1 to 4 days. The temperature of the meat going into cure was approximately 49° F. (9.4° C.), and the temperature at time of canning was about 32° F. (0° C). Different packing plants use slightly different curing formulas and processing schedules. The meat was remixed before canning. Part of the 1000 pounds of luncheon meat was used for the experimental studies. The remainder was used in commercial production.

The proximate analyses of the uncooked pork luncheon meats used in the thermal processing studies are recorded in Table I. Under the conditions of these experiments, there was relatively little change in the proximate composition of the luncheon meat after thermal processing except in the concentration of sodium nitrite which decreased from 0.02–0.035% in the uncooked product to 0.002–0.004% in the cooked meat.

Previous studies (9) revealed that the inactivation of thiamine in lean pork muscle heated for 1 hour in boiling water was not greater in the presence of meat-curing ingredients than in fresh pork muscle.

PROCESSING EQUIPMENT. In order to study accurately the effects of heat treatment, it was desirable to obtain nearly instantaneous and uniform heating to the required temperature, a definite holding time at that temperature, and nearly instantaneous cooling to room temperature. A procedure previously

TABLE I. PROXIMATE ANALYSES OF UNCOOKED PORK LUNCHEON MEAT USED IN THERMAL PROCESSING STUDIES

Company No.	Moisture, %	Protein, %	Ether Ext., %	Sodium Chloride, %	Sodium Nitrate, %	Sodium Nitrite, %	B Vitamin Data
1	55.49	15.60	26.38	2.48	0.26	0.02	Table II A
2	56.83	15.84	25.08	3.00	0.13	0.035	Tables IIB & III
3	54.78	14.70	24.38	3.79	..	0.02	Fig. 4 (bottom)

TABLE II. B VITAMINS REMAINING IN PORK LUNCHEON MEAT AFTER THERMAL PROCESSING

Heat Treatment			Thiamine			Riboflavin		Niacin		Pantothenic Acid	
Min.	° F.	F ₀	Mg./100 grams		% re- tention ^a	Mg./100 grams	% re- tention	Mg./100 grams	% re- tention	Mg./100 grams	% re- tention
			No. 1	No. 2							
A. THERMAL DEATH EQUIPMENT											
Unheated cured meat			0.65	0.64	..	0.23	..	5.0	..	0.55	..
23	210	0.14	0.54	0.54	84	0.20	87	5.00	100	0.545	99
73	210	0.4	0.47	0.47	73	0.21	91	4.70	94	0.54	98
123	210	0.7	0.46	0.46	72	0.21	91	5.00	100	0.53	96
173	210	1.0	0.37	0.38	58	0.20	87	4.95	99	0.455	82
223	210	1.3	0.34	0.34	53	0.17	74	4.75	95	0.45	81
273	210	1.6	0.31	0.29	47	0.18	70	4.65	93	0.41	75
23	230	2.0	0.50	0.50	78	0.21	91	4.75	93	0.52	96
46 ¹ / ₂	230	3.6	0.39	0.43	67	0.21	91	4.95	99	0.51	93
73	230	6.0	0.36	0.36	56	0.21	91	4.95	99	0.51	93
123	230	10.0	0.30	0.31	47	0.21	91	4.95	99	0.50	91
173	230	13.0	0.22	0.20	33	0.21	91	4.90	98	0.50	91
223	230	17.0	0.16	0.17	26	0.20	87	4.70	94	0.47	86
273	230	21.0	0.14	0.14	22	0.20	87	4.45	89	0.445	81
5	245	2.6	0.59	0.59	91	0.21	91	4.95	99	0.52	95
7	245	3.6	0.56	0.56	87	0.21	91	4.95	99	0.51	93
28	245	15.0	0.43	0.43	67	0.22	96	4.75	95	0.40	73
68	245	36.0	0.29	0.28	45	0.22	96	4.70	94	0.44	80
108	245	57.0	0.19	0.19	30	0.21	91	4.70	94	0.44	80
148	245	78.0	0.10	0.10	16	0.21	91	4.90	98	0.425	77
193	245	100.0	0.07	0.07	11	0.21	91	4.90	98	0.38	69
1	260	3.60	0.62	0.61	96	0.22	96	4.95	99	0.54	98
3	260	11.0	0.60	0.60	94	0.20	87	4.90	98	0.48	87
13	260	47.0	0.45	0.45	70	0.21	91	4.30	86	0.44	80
48	260	170.0	0.23	0.23	36	0.22	96	3.30	66	0.40	73
88	260	320.0	0.09	0.09	14	0.22	96	3.45	69	0.37	67
118	260	420.0	0.03	0.03	5	0.20	87	3.15	63	0.34	62
158	260	570.0	0.04	0.04	6	0.20	87	2.90	58	0.35	64
B. COMMERCIAL-SIZE CANS ^b											
Uncooked sample			0.57	0.56	..	0.21	..	4.00	..	0.81	..
12-Ounce Cans (Round 300 × 308) ^c											
68	225	0.08	0.44	0.42	76	0.18	86	3.90	97	0.59	73
68	225	0.08	0.43	0.40	74	0.18	86	3.85	96	0.59	73
59	235	0.08	0.43	0.41	75	0.20	95	3.83	96	0.58	72
59	235	0.08	0.43	0.42	76
53	245	0.08	0.42	0.41	74	0.20	95	3.57	89	0.50	62
53	245	0.08	0.41	0.41	73
96	235	1.85	0.31	0.33	56	0.15	72	3.24	81	0.50	62
96	235	1.85	0.31	0.33	56	0.15	72	3.20	80	0.50	62
2 1/2-Pound Cans (Round 404 × 510) ^c											
166	225	0.24	0.32	0.32	57	0.15	72	2.67	87	0.50	82
166	225	0.24	0.33	0.35	60	0.16	76	2.94	89	0.53	86
146	235	0.26	0.31	0.29	53	0.15	71	3.14	79	0.50	82
146	235	0.26	0.29	0.29	51	0.17	81	3.21	80	0.50	82
136	245	0.29	0.27	0.27	48	0.16	76	3.22	81	0.56	88
136	245	0.29	0.26	0.26	46	0.16	76	3.22	81	0.50	82
200	235	2.2	0.19	0.22	36	0.15	72	2.78	70	0.46	57
200	235	2.2	0.20	0.20	35	0.14	67	3.02	75	0.48	59
6-Pound Cans (Rectangular 402 × 310 × 1208) ^c											
191	235	0.65	0.27	0.28	49	0.14	67	2.98	75	0.59	73
191	235	0.65	0.27	0.26	47	0.14	67	2.93	73	0.57	70

^a Average based on data from the two laboratories.

^b Two cans representing each heat treatment were analyzed separately.

^c The can size designation used in the industry is derived from the nominal dimensions. The first digit or digits represent inches, the last two, the extra fraction expressed as sixteenths of an inch. The diameter is cited first, followed by the height.

developed for bacteriological studies was admirably suited to this purpose. Small T.D.T. tin cans (approximately 2 1/2 inches in diameter and 3/8 inch high), containing approximately 14 grams of meat, were sealed under vacuum and heated in small-capacity T.D.T. steam-heated retorts. The heating was followed immediately by water cooling in the same retorts. These containers and retorts are described elsewhere (1, 19). The short lags in heating and cooling in these small containers have been measured, and corrections may be applied to the experimental heating times to determine the bactericidally effective heating time (18).

The bactericidal effect is expressed in *F* units; one unit is equivalent to one minute of heating at 250° F. (121.1° C.) with instantaneous heating and cooling. Thus, if a T.D.T. can of pork luncheon meat is heated experimentally for 5 minutes at 250° F., the corrected heating time is 3.1 minutes and the *F* value is 3.1 minutes. If another experimental heating tem-

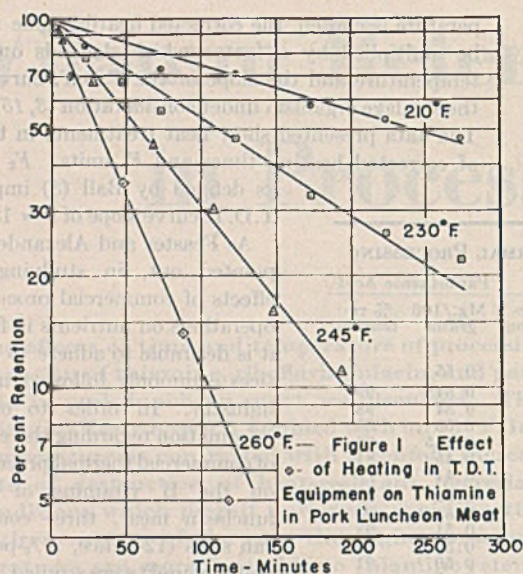
perature is chosen, the corrected heating time must be multiplied by a factor which depends on the temperature and the slope of the T.D.T. curve for the spoilage organism under consideration (3, 15, 19). The data presented show heat treatments in terms of corrected heating times and *F*₀ units. *F*₀ units as defined by Ball (3) imply a T.D.T. curve slope of *z* = 18° F.

As Feaster and Alexander (7) pointed out, in studying the effects of commercial processing operations on nutrients in foods, it is desirable to adhere to practices commonly followed in the industry. In order to obtain information regarding the effects of commercial thermal processing on the B vitamins of pork luncheon meat, three common can sizes (12-ounce, 2 1/2-pound, and 6-pound) were studied. The cans were filled on commercial stuffers and sealed under vacuum in commercial can-sealing machines. Thermal processing was carried out in the commercial manner using saturated steam as the heating medium in pressure retorts. Heat treatment was followed by immediate water cooling in the retort.

Lots of pork luncheon meat packed in the 12-ounce and 2 1/2-pound cans, respectively, were processed at three temperatures, 225°, 235°, and 245° F. (107.2°, 112.8°, and 118.3° C.). Table IIB gives the details as to processing times and *F*₀ values attained. The *F*₀ values were calculated by the methods of Ball (3) and Olson and Stevens (15), using heat penetration data obtained by thermocouple tests on pork luncheon meat in similar cans in similarly operated retorts. For each of these temperatures, a processing time for a 12-ounce lot was chosen that would give practically equal sterilizing values for the low-temperature points in each can, taking into consideration also the effect of the cooling operation. This minimum sterilizing value corresponded to that obtained in many processes currently used on this product. In addition, a fourth lot was subjected to a more severe heat treatment at 235° F.

An exactly parallel procedure was followed on four lots of the 2 1/2-pound cans; the method was typical of that currently used for this size of can. One lot of pork luncheon meat in 6-pound cans was given a processing at 235° F. comparable to common industrial practice.

SAMPLING. In sampling commercial-size cans to establish average B vitamin values for the entire contents, the loaf of meat was passed through a grinder. After thorough mixing of the ground meat, a sample was blended in water and sampled as described under "Chemical and Microbiological Procedures". Certain of the 2 1/2-pound cans were sampled so as to yield data regarding the degree of vitamin retention in meat from various



parts of the can. This was accomplished by cutting a slice $\frac{1}{2}$ inch thick from each end of the loaf representative of the meat from the ends of the can. An additional inch of meat (not analyzed) was cut from each end of the loaf; a cylinder of meat remained, 2 inches long and 4 inches in diameter, which had been mid-distant from the ends of the can during processing. This cylinder was then sampled with tools similar to cork borers to produce 2-inch-long cylindrical sections of the following diameters:

Inside, Inches	Outside, Inches
$\frac{3}{4}$	4
$\frac{21}{16}$	$\frac{31}{32}$
$\frac{13}{16}$	$\frac{21}{16}$
..	$\frac{13}{16}$ (solid cylinder)

These sections and the $\frac{1}{2}$ -inch slices from the ends of the loaf were analyzed separately.

In preparing samples from T.D.T. cans, the entire contents of six cans were made to a definite weight by adding distilled water. This mixture was blended and sampled as previously described.

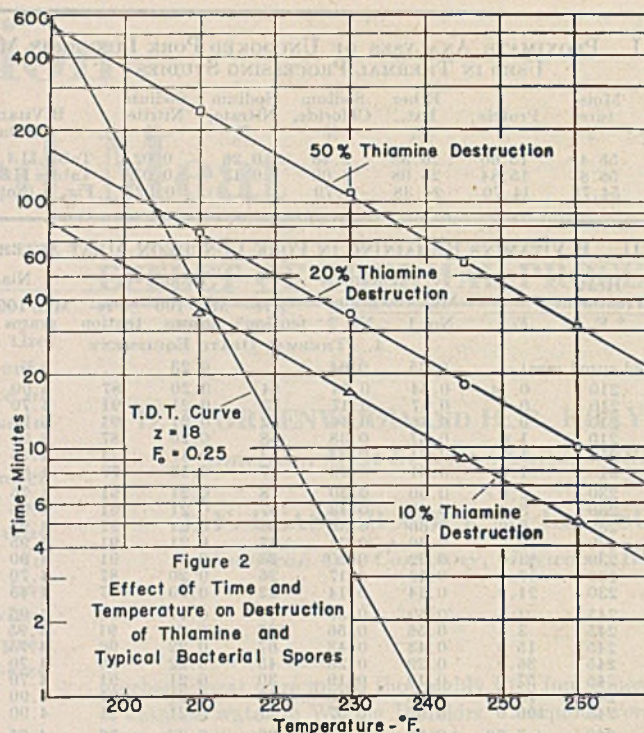
THERMAL DEATH TIME EQUIPMENT

The sterilizing, or F_0 , values for many of the heat treatments reported in Table IIA are far in excess of F_0 values of heat treatments used in commercial processing of pork luncheon meat. Because of the differences in heating characteristics of meat in T.D.T. cans and commercial cans, the data in Table IIA cannot be directly applied to samples in larger cans. The value of studies with T.D.T. equipment is largely confined to establishing rates of destruction of nutrients during heating under known conditions.

Since thiamine is generally considered to be heat labile, it was desirable to determine the rate of inactivation of thiamine in pork luncheon meat at different temperatures.

The order of a reaction may be determined graphically by plotting different functions of the concentration against time and determining which gives a straight line. A plot of log concentration against time gives a straight line for a unimolecular reaction. Figure 1 is a graph of log per cent retention of thiamine against time. It suggests that the inactivation of thiamine under these conditions may be a unimolecular reaction, since per cent retention is proportional to concentration, and the curves describe straight lines.

The times required for 10, 20, and 50% thiamine destruction at 210°, 230°, 245°, and 260° F. (98.9°, 110°, 118.3°, and 126.7° C.) read from Figure 1 were plotted in Figure 2. The latter demonstrates that with an 18° F. (10° C.) increase in temper-



ature the rate of thiamine destruction is approximately doubled. From the T.D.T. curve of spores of typical spoilage organisms in neutral phosphate medium (3, 19) it is observed that with an 18° F. increase in temperature the rate of destruction of such organisms is increased tenfold. Hence, with increase in processing temperature, the increase in rate of spore destruction is approximately five times the increase in rate of thiamine destruction.

Studies of this type do not take into account the lag of penetration of heat into meat in commercial-size cans. Because of the relatively large lag in heat penetration with products such as luncheon meat, which heat primarily by conduction, the outer portion of the can receives a much more severe heat treatment than the center (10, 11, 14), and the time-temperature- F_0 value relations are entirely different from those for the T.D.T. can (3, 15).

The data from these studies in T.D.T. equipment demonstrate that riboflavin and niacin in luncheon meat are quite stable thermally. Heat processing the entire mass of meat for periods up to 273 minutes at 230° F. or to 193 minutes at 245° F. permits retention of approximately 90% of the riboflavin and niacin.

The thermal stability of pantothenic acid in pork luncheon meat is intermediate between those of thiamine and riboflavin or niacin. Seventy to eighty per cent of the pantothenic acid in luncheon meat survived processing for 273 minutes at 230° F. or 193 minutes at 245° F. However, the data on pantothenic acid retention are not adequate for establishing rates of destruction of this factor at the different temperatures or increase in rate of destruction with increase in processing temperature.

COMMERCIAL-SIZE CANS

The effects of processing pork luncheon meat in 12-ounce, $2\frac{1}{2}$ -pound, and 6-pound cans on B vitamin retention, as judged by average values for the entire contents of the can, are summarized in Table IIB and Figure 3. Pork luncheon meat in the same can size (either 12-ounce or $2\frac{1}{2}$ -pound) subjected to heat treatments at 225°, 235°, or 245° F. of equivalent F_0 , or bactericidal, values retained approximately equivalent amounts of B vitamins. There is an indication that the 245° F. process is

slightly inferior to 225° or 235° F. processes for retention of thiamine. Thus it is evident that, for a slow-heating product such as pork luncheon meat, the lag in heating of material in the interior of the can may be sufficient to nullify the differences in rates of thiamine and bacteria destructions with increasing temperatures.

Retort times of 166 minutes at 225° F., 146 at 235°, and 136 at 245° F. for pork luncheon meat in 2½-pound cans have F_0 values of 0.24, 0.26, and 0.29, respectively; heat treatments of 6 minutes at 225° F., 1.8 at 235°, and 0.56 at 245° have F_0 values of 0.24, 0.26, and 0.29, respectively, for pork luncheon meat in T.D.T. equipment. By increasing the retort temperature from 225° to 245° F., the time required to give an approximately equivalent F_0 value is decreased by approximately 90% for luncheon meat in T.D.T. equipment. However, increasing the retort temperature from 225° to 245° F. decreases the time required to produce approximately equivalent F_0 values by only 18% for pork luncheon meat in 2½-pound cans. Hence, the use of higher processing temperatures for products, in commercial-size cans, which heat primarily by conduction does not increase the degree of thiamine retention. Any method of eliminating this heat penetration lag should make it possible to effect considerably better thiamine retention.

A comparison of vitamin values for pork luncheon meat in 12-ounce, 2½-pound, and 6-pound cans processed under conditions commonly employed in the canning of this product demonstrates that the degree of thiamine retention is materially greater for the meat in the smaller can. Thiamine retentions were quite similar for the product subjected to conventional heat treatments in 2½- or 6-pound cans. Retentions of pantothenic acid, niacin, and riboflavin were also somewhat better for pork luncheon meat processed in 12-ounce cans as compared to the meat in 2½- or 6-pound cans.

The retention of B vitamins in pork luncheon meat during heat processing and storage of the canned product was studied by Rice and Robinson (17). They found that the retention of thiamine in cured luncheon meat processed in 12-ounce and 6-pound cans was 67 and 43%, respectively. The retentions of niacin, riboflavin, and pantothenic acid were somewhat higher than those found in these studies. Retentions of 45 to 58% of the thiamine in spiced pork processed 200 minutes at 230° F., reported by Reedman and Buckby (16), are similar to the thiamine retention observed in this study of 48% for pork luncheon meat processed 191 minutes at 235° F. in the 6-pound can. Values of 0.3 to 0.4 mg. of thiamine per 100 grams of spiced pork in 12-ounce cans purchased on the retail market in Canada were also

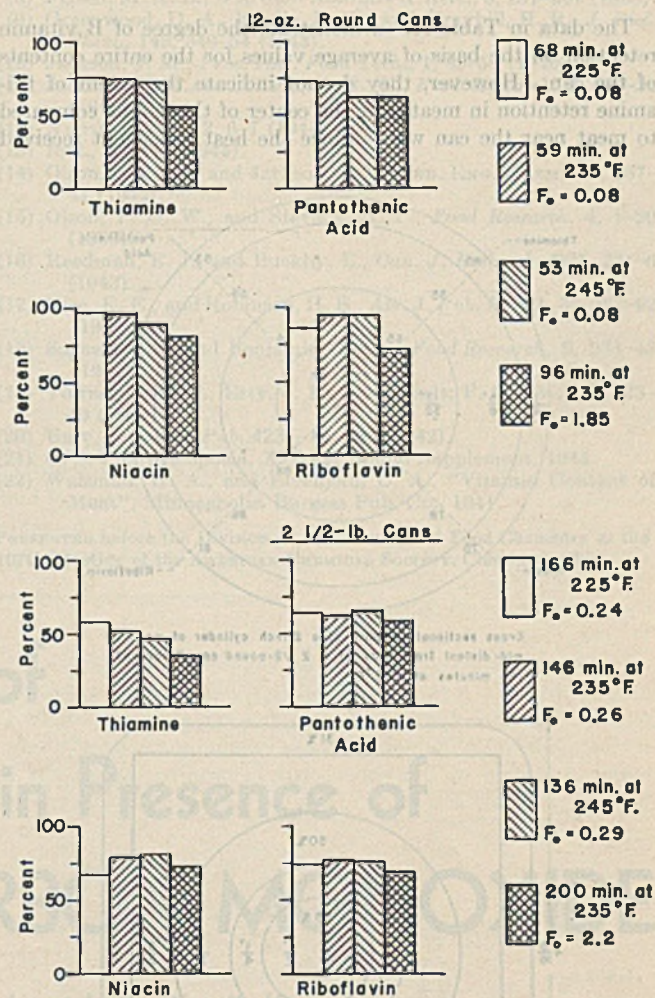


Figure 3. Retention of B Vitamins during Processing of Pork Luncheon Meat

reported by Reedman and Buckby. In the absence of thiamine values for the spiced pork before canning and of information regarding the heat process employed, it is not possible to compare the degree of retention of thiamine in their samples with that observed in the present studies.

TABLE III. RETENTION OF B VITAMINS IN PORK LUNCHEON MEAT IN VARIOUS PARTS OF 2½-POUND CAN AFTER THERMAL PROCESSING

Location in Can	Heat Treatment			Thiamine			Riboflavin			Niacin			Pantothenic Acid		
	Min.	°F.	F_0	Mg./100 grams No. 1	Mg./100 grams No. 2	% retention ^a	Mg./100 grams	% retention		Mg./100 grams	% retention		Mg./100 grams	% retention	
Av. of whole can ^b	146	235	0.26	0.30	0.29	52	0.17	76	3.18	80	0.50	62	0.50	62	
Disk ½ in. from each end	146	235	0.26	0.23	0.23	41	0.17	81	2.74	69	0.48	59	0.48	59	
	146	235	0.26	0.21	0.22	38	0.17	81	3.03	75	0.49	61	0.49	61	
Cylinder 3¼-4 in. diam.	146	235	0.26	0.25	0.25	44	0.17	81	2.78	70	0.50	62	0.50	62	
	146	235	0.26	0.28	0.25	47	0.17	81	3.22	81	0.56	69	0.56	69	
Cylinder 2¼-3½ in. diam.	146	235	0.26	0.31	0.32	55	0.18	81	3.03	75	0.48	59	0.48	59	
	146	235	0.26	0.30	0.32	55	0.18	86	3.20	80	0.61	75	0.61	75	
Cylinder 1½-2¼ in. diam.	146	235	0.26	0.36	0.37	65	0.18	86	0.58	72	0.58	72	
	146	235	0.26	0.38	0.35	66	0.18	86	3.30	82	0.62	77	0.62	77	
Cylinder 1¼ in. diam.	146	235	0.26	0.40	0.40	71	0.19	91	3.10	78	0.60	74	0.60	74	
	146	235	0.26	0.43	0.42	75	0.19	91	3.36	84	0.64	79	0.64	79	
Av. of whole can ^b	200	235	2.2	0.20	0.21	36	0.15	72	2.90	73	0.48	58	0.48	58	
Disk ½ in. from each end	200	235	2.2	0.16	0.16	28	0.14	67	2.92	73	0.50	62	0.50	62	
	200	235	2.2	0.16	0.16	28	0.14	67	2.93	73	0.50	62	0.50	62	
Cylinder 3¼-4 in. diam.	200	235	2.2	0.18	0.17	31	0.16	76	3.19	80	0.48	59	0.48	59	
	200	235	2.2	0.18	0.17	31	0.16	76	3.28	82	0.48	59	0.48	59	
Cylinder 2¼-3½ in. diam.	200	235	2.2	0.21	0.22	39	0.16	76	3.33	83	0.48	59	0.48	59	
	200	235	2.2	0.25	0.22	42	0.17	81	3.20	80	0.53	66	0.53	66	
Cylinder 1½-2¼ in. diam.	200	235	2.2	0.25	0.25	44	3.20	80	0.53	66	0.53	66	
	200	235	2.2	0.26	0.23	44	0.17	81	3.20	80	0.51	63	0.51	63	
Cylinder 1¼ in. diam.	200	235	2.2	0.28	0.27	48	0.17	81	3.29	82	0.50	62	0.50	62	
	200	235	2.2	0.27	0.26	46	0.17	81	3.26	82	0.50	62	0.50	62	

^a Average based on data from two laboratories.

^b Average based on analysis of two cans (Table IIB).

The data in Table IIB demonstrate the degree of B vitamin retention on the basis of average values for the entire contents of the can. However, they do not indicate the extent of thiamine retention in meat near the center of the can as compared to meat near the can wall. Since the heat treatment received

in Figure 4 were 0.92 and 0.36 mg. of thiamine per 100 grams, respectively.

The degree of pantothenic acid retention was found to be greater in the center of the can than at the outside of the loaf. The gradations in riboflavin and niacin retentions in various parts of the can are much smaller than are those for thiamine and pantothenic acid.

By placing thermocouples at definite points in 2½-pound cans of pork luncheon meat, the rates of heating at these points during a process of 146 minutes at 235° F. were determined. From this information schedules were designed for processing meat in T.D.T. cans comparable to the heat treatments received by meat at specific distances from the walls of a 2½-pound can. Lots of pork luncheon meat, from the same batch of meat used in stuffing the commercial-size cans, were filled into T.D.T. cans. These cans were processed according to time-temperature schedules calculated to reproduce the heating times and temperatures in meat 1/8 inch from the can wall and 1 1/8 inches from the can wall, and at the center of a 2½-pound can of pork luncheon meat processed 146 minutes at a retort temperature of 235° F. On analysis thiamine values for these samples from T.D.T. cans were found to be somewhat higher than those found for the corresponding cylindrical sections. However, the trends of increase in B vitamin retention with decrease in severity of heat treatment received by the meat near the center of the 2½-pound can were well substantiated by this type of study.

The data obtained demonstrate that one of the most important factors influencing B vitamin retention in pork luncheon meat during heat processing is the rate of penetration of heat into the product. The production of a bacteriologically acceptable product is, of necessity, based on the sterilizing value of the heat process at the slowest heating point of the product. Hence, the problem of increasing the degree of thiamine and other B vitamin retention during processing is dependent upon development of means of accelerating the rate of heating of the product at the center of the can and, this, of decreasing the difference in heat treatment received at the center and outside of the product.

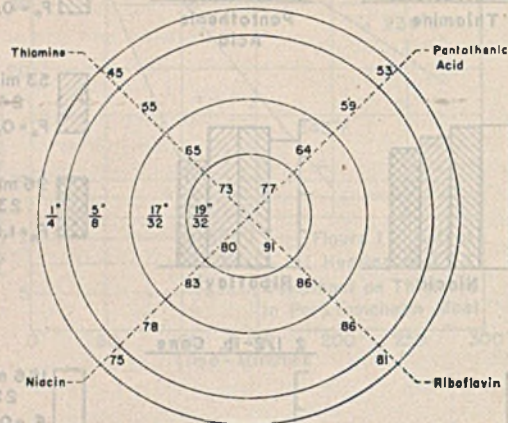
SUMMARY

1. The retentions of thiamine, riboflavin, niacin, and pantothenic acid were greater in cured pork luncheon meat processed at a high retort temperature in thermal death time (T.D.T.) cans for a short time than in the same product processed to the same sterilizing value at lower retort temperatures for longer periods. At a constant temperature the degree of thiamine destruction in a lot of pork luncheon meat is a function of time. The rate of thiamine destruction is approximately doubled with an 18° F. (10° C.) increase in temperature. Since the rate of destruction of heat-resistant bacteria is increased approximately tenfold with an 18° F. increase in temperature, the use of higher temperatures is more favorable to thiamine retention under conditions in which uniformly rapid heating of the product is possible. The influence of heat treatments on pantothenic acid appears to be similar to that on thiamine. Niacin and riboflavin in pork luncheon meat are relatively heat stable.

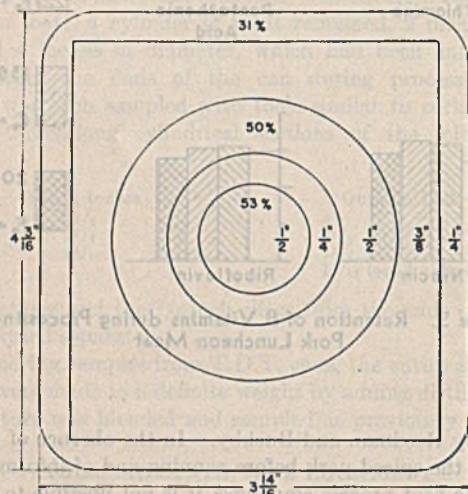
2. Because of the time required for heat to penetrate to the centers of commercial-size cans, the conclusions reached in studies of T.D.T. cans are not directly applicable to commercial procedures. In commercial sterilization of pork luncheon meat in 12-ounce or 2½-pound cans, the processing temperature did not appear to be a major factor influencing B vitamin retention. The retentions, on a percentage basis, of the B vitamins in pork luncheon meat in commercial cans subjected to heat treatments having F_0 values similar to processes commonly used in the industry were as follows:

Can Size	Thiamine	Riboflavin	Niacin	Pantothenic Acid
12-oz.	73-76	86-95	89-97	62-73
2½-lb.	46-60	71-81	71-81	62-68
6-lb.	38-49	67	73-75	70-73

3. The degree of B vitamin retention varies with the position of the meat within the can. The thiamine content of pork luncheon meat in the center of a 2½-pound can was found to be fully 50% higher than that of meat within 1/2 inch of the can wall.



Cross sectional sampling of a 2-inch cylinder of meat mid-distant from ends of a 2 1/2-pound can. Processed 146 minutes at 235° F.



Cross sectional sampling of a 2 1/2-inch block of meat mid-distant from the ends of a 6-pound can. Processed 200 minutes at 235° F.

Figure 4. Influence of Position in 2½- and 6-Pound Cans on Percentage B Vitamin Retention

by the product in the center of the can is markedly different in degree from that received by meat near the can wall, it was postulated that the extent of B vitamin retention, especially thiamine, would vary with the location within the can. The experiments represented in Table III and Figure 4 were designed to study this so-called core effect.

Thiamine retentions of 40 to 45% for meat from the ends or outside of the loaf as compared to 70 to 75% for meat from the center of 2½-pound cans processed 146 minutes at 235° F. demonstrate a decided variation in thiamine retention in meat from different parts of the can. Likewise, a definite core effect in the thiamine content of pork luncheon meat in a 2½-pound can can be processed 200 minutes at 235° F. was demonstrated. Data included in Figure 4, which were obtained in a previous study by one of the laboratories, show that thiamine retention in pork luncheon meat in 6-pound cans varies from the center to the outside of the can in a manner similar to that in 2½-pound cans. The average values for raw and canned luncheon meat shown

ACKNOWLEDGMENT

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Preferential Oxidation of PHOSPHORUS in Presence of CARBON MONOXIDE

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THE reduction of phosphate rock with coke in a blast furnace or an electric furnace yields phosphorus and carbon monoxide as gaseous products. When the phosphorus is oxidized to produce phosphoric acid or phosphates, it is desirable to conserve the carbon monoxide. In the operation of a phosphate blast furnace, fuel such as carbon monoxide is needed to pre-heat the blast. In electric-furnace operation, the by-product carbon monoxide can be utilized in nodulizing the phosphate for the furnace charge.

The phosphorus and carbon monoxide can be separated by condensing the elemental phosphorus from the furnace gases. An alternative is to oxidize the phosphorus preferentially in the presence of the carbon monoxide and to remove the resultant phosphorus pentoxide from the residual gases.

Either phosphorus or carbon monoxide, if burned alone with the stoichiometric proportion of air to yield phosphorus pentoxide or carbon dioxide, respectively, has a theoretical flame temperature (without allowance for dissociation of the products) above 2000° C. When a mixture of phosphorus and carbon monoxide is burned with a proportion of air slightly less than that required for complete oxidation of both substances and without provision for cooling, temperatures are reached at which practically all of the oxygen reacts and a state of equilibrium involving carbon monoxide, carbon dioxide, elemental phosphorus, phosphorus tetroxide, and phosphorus pentoxide is approached. Emmett and Shultz (8) found that at about 1000° C. an equilibrium mixture containing equimolar proportions of phosphorus

pentoxide and phosphorus tetroxide would contain 2 moles of carbon dioxide per mole of carbon monoxide. If this equilibrium is attained in burning phosphorus-carbon monoxide mixtures at high temperatures, both components are oxidized to a considerable extent. The equilibrium may be shifted, however, by removing one of the reaction products from the sphere of the reaction. By introducing phosphate rock, which reacts rapidly with phosphorus pentoxide at 1000° or 1100° C. to form calcium metaphosphate, Emmett and Shultz were able to shift the equilibrium so that practically complete oxidation of phosphorus by carbon dioxide was obtained. The same principle was applied in the work of Britzke and Pestov (2), Dunaev (7), and Brunauer and Shultz (4) who oxidized phosphorus with steam in the presence of solids capable of reaction with phosphorus pentoxide.

Phosphorus can be preferentially oxidized in the presence of carbon monoxide without introducing an absorbent for the phosphorus pentoxide by maintaining conditions under which the rate of oxidation of phosphorus to the pentoxide is much more rapid than the rate of oxidation of carbon monoxide, and under which the reduction of phosphorus pentoxide by carbon monoxide is negligible. Since the ignition temperatures of phosphorus and of carbon monoxide have been reported to be about 45° and 600° C., respectively, depending somewhat on experimental conditions, it seemed logical that there should be temperatures at which the relative rates of the oxidation reactions would be favorable to preferential oxidation of the phosphorus. Direct experimental evidence was desired, however, because chain

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mechanisms are involved in the oxidation of each substance, and it appeared that active intermediates formed in the oxidation of the phosphorus might induce oxidation of the carbon monoxide below the temperature normally required for ignition of pure carbon monoxide-air mixtures.

Britzke and Pestov (2) attempted to oxidize phosphine preferentially in the presence of carbon monoxide or hydrogen at 155° to 430° C. They also attempted preferential oxidation of phosphorus and phosphine in blast-furnace gas at 900° to 1100° C. Under these conditions they did not succeed in oxidizing the phosphorus completely. Dunaev (7) improved the apparatus and obtained practically complete oxidation of phosphorus with the formation of calcium phosphates by reacting mixtures of phosphorus and producer gas at 540° to 940° C. with air and steam in the presence of calcium carbonate. Preferential oxidation of the phosphorus in electric-furnace gas by burning with air sufficient to oxidize only the phosphorus was

The gases produced in reducing phosphates in a blast furnace or an electric furnace contain both phosphorus and carbon monoxide. It is advantageous to conserve the carbon monoxide for use as fuel, particularly for use in preheating air for the blast furnace. Since the ignition temperature of phosphorus is much lower than that of carbon monoxide, it appeared that the phosphorus could be oxidized preferentially, and the phosphorus pentoxide separated from the carbon monoxide. In gas containing 1% phosphorus and 39% carbon monoxide, the phosphorus was oxidized almost completely at 500° to 700° C. with about 160% of the theoretical air requirement for oxidation of the phosphorus to the pentoxide; about 1% of the carbon monoxide was oxidized. At 1100° C. preferential oxidation of the phosphorus in this gas was possible in the presence of phosphate rock, with which the P_2O_5 immediately reacted to form calcium metaphosphate. For gas containing 7% phosphorus and 90% carbon monoxide, substantially complete oxidation of the phosphorus occurred at 550° to 600° C. with 125% of the theoretical air requirement; about 2% of the carbon monoxide was oxidized. With gases of both compositions, the presence of water vapor increased the oxidation of carbon monoxide, and control of the rate of phosphorus input was found to be important.

proposed in patents by Klugh (10) and by Pistor and Suchy (11), but no detailed data were given. Britzke (1) proposed selective oxidation of phosphorus in the range 900° to 1300° C. Sigrist (12) patented a process for preferential oxidation with a mixture of carbon dioxide and air whereby a gas rich in carbon monoxide was obtained.

This paper presents the results of laboratory-scale investigations of the preferential oxidation of phosphorus with air in mixtures (0.94 to 1.02% P_4 , 35 to 40% CO ; and 59 to 64% N_2 , by volume) simulating phosphate blast-furnace gas, and in other mixtures (6.9 to 7.4% P_4 and 85 to 92% CO) simulating electric-furnace

gas. For brevity, these mixtures are termed "blast-furnace gas" and "electric-furnace gas", respectively, throughout this paper.

PREFERENTIAL OXIDATION IN ABSENCE OF SOLID REACTANTS

The experiments consisted in vaporizing phosphorus in carbon monoxide or nitrogen-carbon monoxide mixtures, burning the phosphorus vapor with air, and collecting and analyzing the products.

The carbon monoxide for the furnace mixture was generated by adding reagent-grade formic acid to concentrated sulfuric acid heated at 175° C. in a steel vessel. After removal of traces of oxygen by means of hot copper, the carbon monoxide was 95 to 98% pure; it contained 1% or less of carbon dioxide and traces of iron carbonyl, the chief impurity being nitrogen. The carbon monoxide was compressed hydraulically to a pressure of around 5 atmospheres and was stored in a steel tank without further purification. Cylinder-grade nitrogen was added if mixtures simulating phosphate blast-furnace gas were to be used.

As the gases were passed from storage to the phosphorus saturator, they were metered, freed from oxygen with hot copper, and dried with anhydrous calcium sulfate or sulfuric acid. The phosphorus saturator, shown at the bottom of Figure 4, was supported in an oil bath which was maintained at constant temperature within $\pm 0.5^\circ$ C. in experiments 1B to 17B and 8E to 17E, inclusive, and within $\pm 0.1^\circ$ C. in experiments 18B to 27B and 18E to 26E, inclusive. The saturator was calibrated over the ranges of temperature and flow employed in the experiments.

From the saturator the gas passed into the combustion furnace through a heated glass delivery tube (Figure 1). The gas entered at the top of the mullite combustion tube, which was supported in a vertical furnace. Metered dry air entered through a parallel inlet at the top of the combustion tube. When the presence of water vapor was desired, it was introduced in definite proportions with the air. The temperatures at different levels in the combustion zone were measured by a movable thermocouple.

The acid receiver used in collecting the liquid products from the experiments with moist air is also shown in Figure 1. A glass-wool filter removed acid mist from the effluent gas from the acid receiver. The acid receiver and filter were maintained at 250° to 270° C. to permit drainage of the metaphosphoric acid formed, which is extremely viscous at ordinary temperatures. In experiments with dry air, solid phosphorus pentoxide was

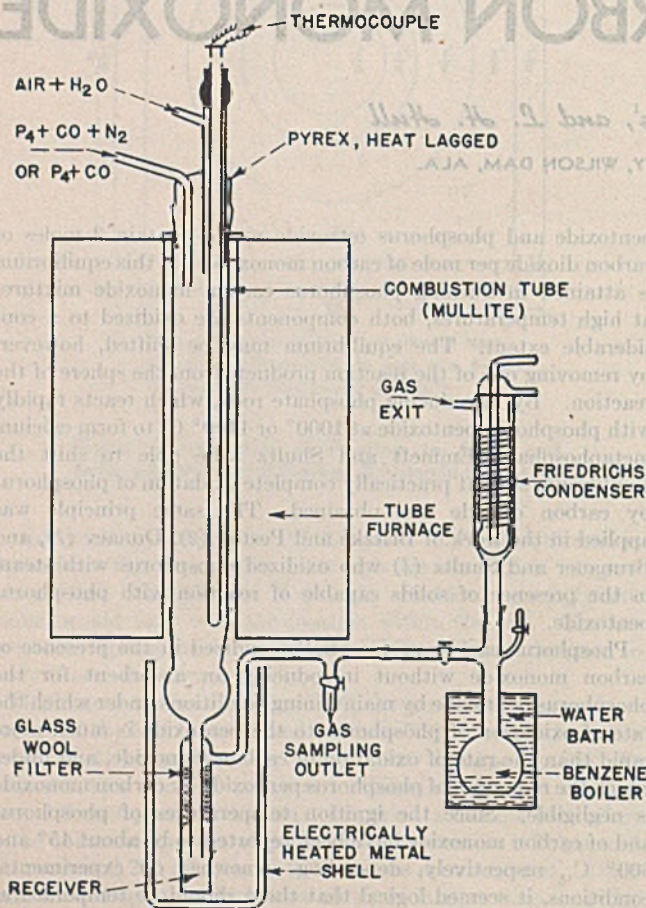


Figure 1. Apparatus for Preferential Oxidation of Phosphorus to Metaphosphoric Acid

collected at room temperature in a glass trap that replaced the acid collection system at the bottom of the combustion tube.

From the acid receiver (or trap) the gases passed through a heated tube to a tee connection from which samples were collected over mercury for determination of carbon dioxide, oxygen,

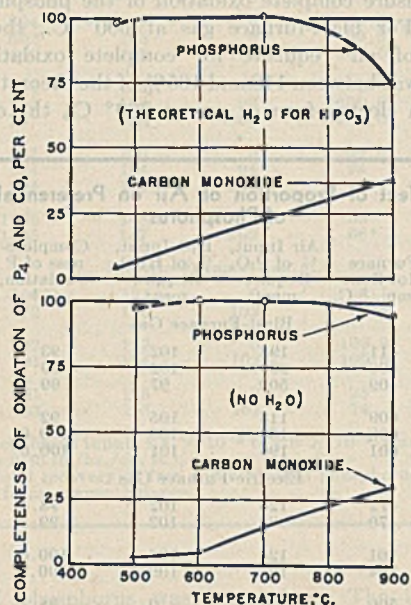


Figure 2. Observed Oxidation of Phosphorus and Carbon Monoxide Mixtures Simulating Blast-Furnace Gas
Air, 140-200% theoretical for P₄O₁₀; rate of phosphorus input, 1.2×10^{-4} to 1.6×10^{-4} gram/second/cc.

and carbon monoxide. Residual phosphorus and acidic products were effectively removed from the exit gases by passing them through a scrubber that consisted of a Friedrichs condenser in which a mixture of benzene and a small amount of water was refluxed. When measurement of the volume of exit gas was desired, the gas issuing from the scrubber was brought to a known benzene content by cooling in an ice bath and was passed through a wet test meter.

Efforts were made to maintain constant conditions throughout each experiment. By previous adjustment of the gas flows and temperatures, it was possible to establish the desired conditions within a few minutes after the start of an experiment. The measurements of the temperatures and flow rates, as well as the determinations of carbon dioxide, oxygen, and carbon monoxide in the exit gas, were made periodically throughout each experiment, and the respective results were averaged.

After each experiment the combustion tube, acid receiver or trap, and connecting tubes were washed out thoroughly, and the total free and combined phosphorus as well as the average extent of oxidation of the phosphorus was determined. In determining the average extent of oxidation in the material from these portions of the apparatus, samples were made up with 4 *N* sulfuric acid solution and known quantities of potassium iodate. A few drops of trichloroethylene were added, and the mixture was digested for at least 3 hours under a reflux condenser to convert the free phosphorus or lower oxides completely to the pentavalent state. The iodine was then boiled off, and the excess iodate was determined by adding potassium iodide and titrating the iodine liberated by the latter reagent with thiosulfate. This procedure was adapted from the method of Buehrer and Schupp (5). The total phosphorus in the resulting solutions was determined with ammonium molybdate. The quantity of iodate consumed in the digestion was a measure of the extent to which oxi-

dation of this phosphorus in the preferential oxidation experiment had fallen short of complete conversion to the pentavalent state. The average oxygen content of the products, expressed as percentage of the oxygen content that corresponded to complete conversion of the phosphorus to the pentavalent state, was termed the percentage oxidation of the phosphorus. An equimolar mixture of P₂O₃ and P₂O₅ thus corresponded to 80% oxidation of the phosphorus. The free and combined phosphorus in the exit-gas scrubber were determined separately by an adaptation of the method of Brown, Morgan, and Rushton (3), and the results were added to those found in the remainder of the apparatus. The phosphorus found in the benzene from the scrubber was regarded as free phosphorus. Experiment showed that the degree of oxidation of the combined (water-soluble) phosphorus from the scrubber could conveniently be assumed equal to the degree of oxidation of the phosphorus found in the acid receiver or trap.

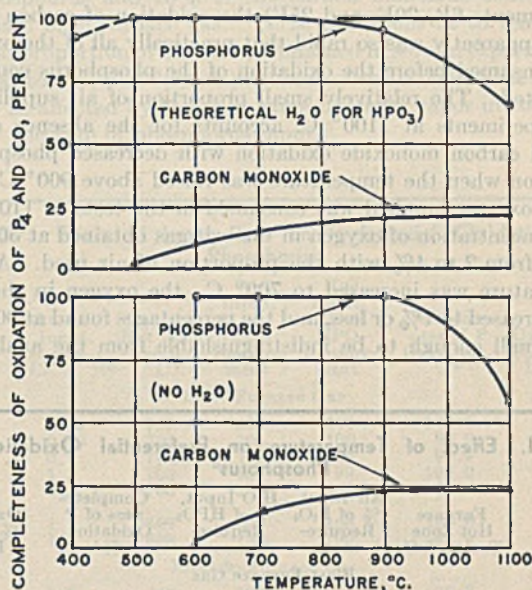


Figure 3. Observed Oxidation of Phosphorus and Carbon Monoxide Mixtures Simulating Electric-Furnace Gas

Air, 120-130% theoretical for P₄O₁₀; rate of phosphorus input, 1.3×10^{-4} gram/second/cc.

In the search for conditions conducive to complete oxidation of the phosphorus, little attention was given to the proportions of intermediate oxides and free phosphorus. When the average oxygen content associated with the free and combined phosphorus was less than 95% of that corresponding to complete conversion to the pentavalent state, the free phosphorus found in the exit-gas scrubber accounted for about half of the over-all oxygen deficiency. When the average degree of oxidation exceeded 97%, only traces of free phosphorus were found. The trivalent and pentavalent phosphorus produced were not determined individually. Trial experiments of the iodate digestion procedure with phosphites gave results in agreement with the iodometric procedure used by Emmett and Shultz (8) for determination of trivalent phosphorus.

The oxidation of the carbon monoxide was calculated from the carbon balance based on the average concentrations of carbon monoxide and carbon dioxide in the inlet and exit gases. In this calculation it was assumed that none of the carbon monoxide underwent decomposition to form carbon and carbon dioxide. Examination of the combustion tube gave no evidence that significant proportions of carbon monoxide had decomposed. Moreover, the average measured volume of exit gas, when

corrected for the gas withdrawn as samples and for the volume of benzene vapor present, agreed within 4% with the average volume of exit gas calculated from the carbon balance.

Effect of Temperature. The relation between the temperature in the hot zone of the combustion tube and the extent of oxidation of phosphorus and carbon monoxide is shown in Table I and Figures 2 and 3. The percentage oxidation of phosphorus was expressed in terms of total (free and combined) phosphorus recovered which was normally equivalent to about 96% of the phosphorus input. The results indicate that temperature control is of primary importance in preferential oxidation. The effects of the concentration of phosphorus and of carbon monoxide were apparently less significant, since similar results were obtained with blast-furnace gas and electric-furnace gas. Table I shows that the oxidation of phosphorus was almost complete at temperatures between 500° and 700° C. The oxidation of carbon monoxide increased rapidly in this range and at 700° C. appeared to exceed that permissible for practical purposes. At 900° C. (experiments 6B, 20E, and 25E) the oxidation of carbon monoxide apparently was so rapid that practically all of the oxygen was consumed before the oxidation of the phosphorus could be completed. The relatively small proportion of air supplied in the experiments at 1100° C. accounts for the absence of increased carbon monoxide oxidation with decreased phosphorus oxidation when the temperature was raised above 900° C.; all of the oxygen supplied was consumed in the tests at 1100° C. The concentration of oxygen in the exit gas obtained at 500° C. varied from 2 to 4% with the proportion of air used. As the temperature was increased to 700° C., the oxygen in the exit gas decreased to 1% or less, and the percentages found at 900° C. were small enough to be indistinguishable from the analytical error.

Table I. Effect of Temperature on Preferential Oxidation of Phosphorus^a

Expt. No.	Furnace Hot Zone Temp., ° C.	Air Input, % of P ₂ O ₅ Requirement	H ₂ O Input, % of HPO ₃ Requirement	Completeness of P Oxidation, % ^b	CO Oxidized, % of CO Input
Blast-Furnace Gas					
1B	411	198	102	93	2.2
3B	501	189	96	99.5	2.4
4B	601	196	101	100.0	11.6
5B	703	194	99	100.0	16.3
6B	904	184	94	94.5	20.3
25B	1105	147	202	66 ^c	21
27B	602	165	0	99.9	0.4
15B	704	185	0	100.0	15.4
17B	903	200	0	99.0	24
26B	1099	148	0	58 ^c	23
Electric-Furnace Gas					
21E	472	126	102	98.4	4.3
19E	701	124	102	100.0	22
20E	903	123	101	74	38
22E	500	121	0	98.1	2.2
26E	601	128	0	99.7	3.5
24E	702	122	0	100.0	14.6
25E	901	125	0	95	31

^a Rate of phosphorus input, 1.2×10^{-4} to 1.6×10^{-4} gram per second per cc. (0.26 to 0.36 lb./hr./cu. ft.).

^b Based on total recovery of free and combined phosphorus.

^c Calculated from oxygen balance.

The effects of temperature corresponded in general with predictions from the individual oxidation characteristics of phosphorus and of carbon monoxide. With respect to the minimum temperature for complete oxidation of phosphorus, it should be noted that Figures 2 and 3 give hot-zone temperatures, whereas there was evidence that the phosphorus oxidation took place near the gas-inlet tube where the temperature was 50° to 100° C. lower. Experiments beyond the scope of this paper demonstrated that complete oxidation of the phosphorus can be obtained at temperatures somewhat lower than those indicated by Figure 2.

Effect of Proportion of Air. Table II shows the effect of varying the proportion of air upon the oxidation. In the temperature range favorable to preferential oxidation, somewhat more air than the theoretical requirement (the quantity that contains the stoichiometric proportion of oxygen necessary for conversion of all of the elemental phosphorus to phosphorus pentoxide) was needed to ensure complete oxidation of the phosphorus to the pentoxide. For blast-furnace gas at 600° C., the minimum proportion of air requisite for complete oxidation of the phosphorus was between 118 and 165% of the theoretical requirement. With electric-furnace gas at 700° C., the oxidation of

Table II. Effect of Proportion of Air on Preferential Oxidation of Phosphorus^a

Expt. No.	Furnace Hot Zone Temp., ° C.	Air Input, % of P ₂ O ₅ Requirement	H ₂ O Input, % of HPO ₃ Requirement	Completeness of P Oxidation, % ^b	CO Oxidized, % of CO Input
Blast-Furnace Gas					
1B	411	198	102	93	2.2
11B	408	290	102	99.1	2.3
12B	409	500	97	99.2	1.5
9B	609	118	105	92	2.9
10B	609	165	108	100.0	5.9
4B	601	196	101	100.0	11.6
Electric-Furnace Gas					
21E	472	126	102	98.4	4.3
14-15E ^c	470	199	102	99.5	10.1
19E	701	124	102	100.0	22
18E	704	197	100	100.0	70
22E	500	121	0	98.1	2.2
13E	467	199	0	98.3	4.1

^a Rate of phosphorus input, 1.2×10^{-4} to 1.4×10^{-4} gram per second per cc. (0.26 to 0.31 lb./hr./cu. ft.).

^b Based on total recovery of free and combined phosphorus.

^c Average of two experiments.

phosphorus was complete with 120 to 125% of the theoretical air requirement. At about 400° C. the use of 500% of the theoretical air requirement did not markedly affect the oxidation of carbon monoxide; under these conditions, however, enough oxygen remained in the exit gas to make the mixture explosive. Explosive mixtures were obtained also in several experiments with electric-furnace gas that had been mixed with approximately 200% of the theoretical air requirement. Increase in the oxidation of carbon monoxide with increased proportions of air was apparent at 470° C. in electric-furnace gas and at 600° C. in blast-furnace gas. Therefore, at temperatures from 500° to 700° C. it seems desirable to use the minimum proportion of air consistent with complete oxidation of phosphorus. In this way the maximum proportion of carbon monoxide is conserved, the volume of gas to be handled by the P₂O₅ recovery system is minimized, and explosive compositions of exit gas are avoided.

Effect of Water Vapor. Table III shows that the oxidation of phosphorus in the presence of carbon monoxide was affected relatively little by admitting water vapor with the air. At temperatures up to 700° C. the oxidation of carbon monoxide was increased by admitting water vapor, but the effect decreased as the temperature was increased. In most of the experiments in which the air contained the stoichiometric proportion of water vapor to form metaphosphoric acid, the acid obtained in the receiver contained 87 to 91% P₂O₅, which is to be compared with 88.7% P₂O₅ in pure metaphosphoric acid.

Effect of Rate of Phosphorus Input. When phosphorus is burned, the gases should remain in the combustion chamber for a period sufficient to permit the completion of the oxidation reaction. In preliminary experiments on preferential oxidation, the phosphorus was passed too rapidly through the combustion zone; consequently, temperature control was imperfect, and

Table III. Effect of Water Vapor on Preferential Oxidation of Phosphorus^a

Expt. No.	Furnace Hot Zone Temp., ° C.	Air Input, % of P ₂ O ₅ Requirement	H ₂ O Input, % of HPO ₃ Requirement	Completeness of P Oxidation, % ^b	CO Oxidized, % of CO Input
Blast-Furnace Gas					
14B	604	140	0	99.5	2.7
27B	602	165	0	99.9	0.4
10B	609	165	108	100.0	5.9
15B	704	185	0	100.0	15.4
5B	703	194	99	100.0	16.3
8B	707	188	265	100.0	17.1
17B	903	200	0	99.0	24
6B	904	184	94	94	20
7B	904	184	261	96.6	17.8
26B	1099	148	0	58 ^c	23
25B	1105	147	202	66 ^c	21
Electric-Furnace Gas					
22E	500	121	0	98.1	2.2
21E	472	126	102	98.4	4.3
24E	702	122	0	100.0	14.6
19E	701	124	102	100.0	22
25E	901	125	0	95	31
20E	903	123	101	74	38

^a Rate of phosphorus input, 1.2×10^{-6} to 1.6×10^{-6} gram per second per cc. (0.26 to 0.36 lb./hr./cu. ft.).

^b Based on total recovery of free and combined phosphorus.

^c Computed from oxygen balance.

oxidation of phosphorus was incomplete. The influence of rate of phosphorus input, expressed as mass of phosphorus supplied per unit time per unit volume of combustion space, is indicated in Table IV for the principal series of experiments. When the rate of phosphorus input was increased from 1.3×10^{-6} to 9×10^{-6} gram per second per cc. (0.3 to 2 pounds per hour per cubic foot) of combustion space, the phosphorus oxidation decreased and the carbon monoxide oxidation increased. Determination of the maximum rate of phosphorus input consistent with effective preferential oxidation was not attempted inasmuch as the limiting rate is dependent upon the configuration of the combustion chamber and the conditions of heat dissipation; therefore, the limiting rate in the laboratory apparatus is not directly applicable in the design or operation of larger units. Although the oxidation of carbon monoxide to carbon dioxide, as well as the oxidation of phosphorus, contributes to the heat to be dissipated, the indications are that maximum permissible input rates for electric-furnace gas and for blast-furnace gas do not differ widely; in the apparatus used, the limiting rates for both gases were in the range 1.3×10^{-6} to 9×10^{-6} gram of phosphorus per second per cc. of combustion space.

The possibility that at low rates of input the phosphorus oxidation would be incomplete because of reaction of P₂O₅ with CO to form P₂O₄ and CO₂ was investigated at 700° C. in special experiments not shown in Table IV. One experiment was made at the slow input rate of 0.11×10^{-6} gram of phosphorus per second per cc. (0.025 pound per hour per cubic foot) of combustion space and with a moist air input of about 200% of the stoichiometric requirement for oxidation of the phosphorus to the pentoxide. In this experiment there was no evidence of reduction of the phosphorus pentoxide by the carbon monoxide, although the gas remained in the reaction chamber for about 110 seconds and the exit gas was found to contain no oxygen. In a parallel experiment at an input rate of 0.4×10^{-6} gram of phosphorus per second per cc. (0.088 pound per hour per cubic foot), practically identical results were obtained.

Effect of Area of Refractory Surface. To test the influence of refractory surface in the preferential oxidation of blast-furnace gas, one experiment was made under conditions similar to those of experiment 10B (Table III) except that the surface-to-volume

ratio of the combustion space was increased from 1.6 to 5.7 cm.⁻¹ by packing the combustion tube with mullite chips. As the results of the two experiments agreed within the probable reproducibility of the conditions, it appeared that the effect of packing upon oxidation was unimportant.

PREFERENTIAL OXIDATION OF PHOSPHORUS IN BLAST-FURNACE GAS IN PRESENCE OF PHOSPHATE ROCK

Since it was known that phosphorus can be oxidized with carbon dioxide in the presence of phosphate rock at high temperatures to form calcium metaphosphate, studies were made of the preferential oxidation of blast-furnace gas in the presence of phosphate rock. In making fertilizer-grade calcium metaphosphate by the reaction of phosphorus pentoxide with phosphate rock, a temperature near 1100° C. is necessary. It was estimated that this temperature could be maintained in a commercial-scale calcium metaphosphate unit of the type developed by TVA (6), provided the air admitted was sufficient to burn all the phosphorus and 13% of the carbon monoxide content of phosphate blast-furnace gas. These conditions as to temperature and proportion of air were maintained in several experiments designed to indicate the completeness of oxidation of the phosphorus as affected by the proportion of water vapor introduced and by the rate of phosphorus input.

Table IV. Effect of Input Rate on Preferential Oxidation of Phosphorus

Expt. No.	Rate of P Input, G./Sec. × 10 ⁶	Furnace Hot Zone Temp., ° C.	Air Input, % of P ₂ O ₅ Requirement	H ₂ O Input, % of HPO ₃ Requirement	Completeness of P Oxidation, % ^a	CO Oxidized, % of CO Input ^b
Blast-Furnace Gas						
18B	0.12	702	203	103	100.0	..
20B	0.40	702	201	100	99.9	..
21B	0.6	702	199	99	99.9	..
5B	1.2	703	194	99	100.0	..
23B	4.4	706	200	102	92	..
10B	1.2	609	165	108	100.0	..
13B	4.4	608	158	99	98.9	..
Electric-Furnace Gas						
13E	0.9	467	199	0	98.3	4.1 ^c
17E	8.9	479	194	0	95	58
21E	1.3	472	126	102	98.4	4.3
9E	8.9	440	120	102	95	25
26E	1.3	601	128	0	99.7	3.5
8E	9.3	611	118	0	<89	21

^a Based on total recovery of free and combined phosphorus.

^b Special experiments were made to determine effect of rate of phosphorus input on oxidation of CO in blast-furnace gas.

^c Exit gases from experiment 13E contained 6.6% free oxygen.

The apparatus used in studying the preferential oxidation in the presence of phosphate rock is shown in Figure 4. A column of -8 + 10 mesh Tennessee brown rock (35.5% P₂O₅, 49.6% CaO, 3.3% SiO₂, 2.6% Fe₂O₃, 1.2% Al₂O₃, and 3.8% F) was supported on a fused alumina disk in a vertical mullite tube heated by a resistance furnace. In contrast to the apparatus used in the previous series of experiments, the burner was at the foot of the tube, and the gases flowed upward around the disk and through the phosphate rock. The space between the burner and the rock column was provided as a combustion chamber. Temperatures were determined within the rock column by means of a thermocouple which was movable within a fused quartz sheath coaxial with the reaction tube and extending through the column to the supporting disk. To the top of the combustion tube were attached a tube for withdrawing gas samples for analysis and a heated tube for conducting unoxidized phosphorus and unabsorbed phosphorus pentoxide to a benzene-water reflux scrubber of the type previously described. After each

test the partially reacted phosphate rock was sampled and analyzed. The samples were examined for incompletely oxidized phosphorus by the iodometric procedure used by Emmett and Shultz (8).

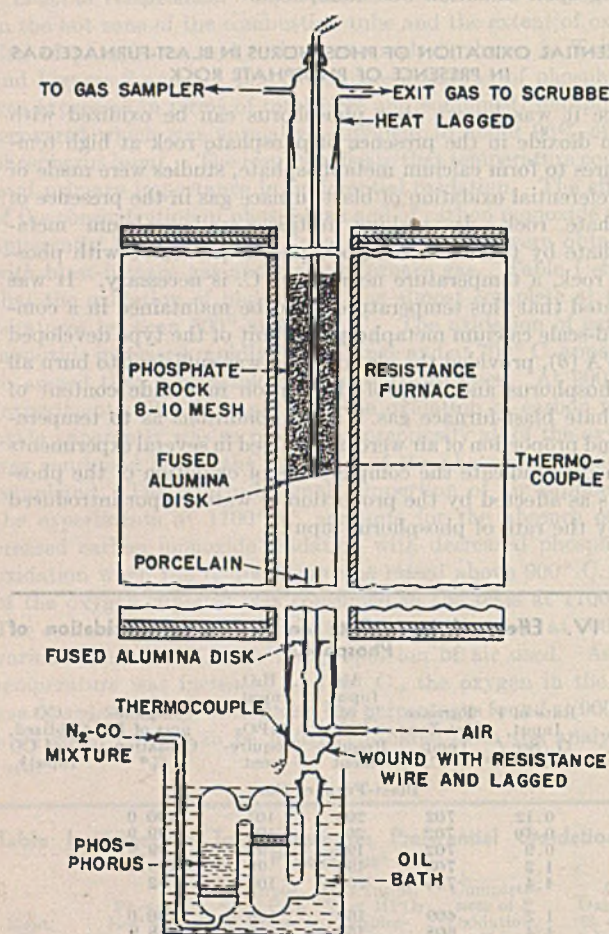


Figure 4. Apparatus for Preferential Oxidation of Phosphorus to Calcium Metaphosphate

The principal data from the experiments on preferential oxidation in the presence of phosphate rock are given in Table V. Experiments 25B and 26B are included to show the effect of omitting the rock. Comparison of experiments 1R and 3R with experiments 26B and 25B, respectively, shows that complete oxidation of the phosphorus occurred only when phosphate rock was used. The phosphate rock completely absorbed the phosphorus pentoxide that was produced by the oxidation of the phosphorus. Experiments 1R, 2R, and 3R showed that the oxidation of the phosphorus in the presence of phosphate rock was not affected significantly by the presence of water vapor. Other work (9) had shown that water vapor had no significant

effect upon the rate of reaction of phosphorus pentoxide with phosphate rock at elevated temperatures. The water vapor acted as an oxidizing agent, and its addition increased the oxidation of the carbon monoxide.

When the size of the combustion space was increased from 67 cc. in experiment 2R to 377 cc. in experiment 4R, thereby extending the average time in the combustion chamber from 2.3 to 12.9 seconds, the results were not affected noticeably.

REMOVAL OF TRACES OF PHOSPHORUS IN GASES

Preferential oxidation also may be applied to the purification of gases that are contaminated with small amounts of phosphorus. The carbon monoxide that remains after the condensation of phosphorus from electric-furnace gas contains, under some conditions of operation, about 0.01 to 0.05% by volume of phosphorus (P_4). The presence of this phosphorus in plant equipment is detrimental because of the corrosiveness of its oxidation products. The removal of phosphorus from gas mixtures simulating those obtained from phosphorus condensers was tried by preferentially oxidizing the phosphorus with air in contact with limestone. Carbon monoxide containing 0.01 to 0.05% phosphorus was mixed with 2% of its volume of air in the presence of a large excess of $-5 + 10$ mesh limestone and was heated to 265°, 470°, and 700° C. The time of contact with the bed of limestone was from 1.7 to 4 seconds (rate of phosphorus input, 0.06×10^{-6} to 0.3×10^{-6} gram per second per cc.). The quantity of phosphorus in the exit gas from the limestone was determined by absorption in copper at about 600° C. At 265° C., 60 to 90% of the phosphorus was removed from the gas, but at 470° and 700° C., the phosphorus was almost completely removed. The exit gas from these tests contained carbon monoxide, practically no free oxygen, less than 2% nitrogen, and about 0.2, 0.5, and 3.0% carbon dioxide at 265°, 470°, and 700° C., respectively.

CONCLUSIONS

The foregoing results demonstrate the possibility of complete oxidation of phosphorus with minimum oxidation of carbon monoxide in a mixture of the two gases with air. At 500° or 600° C. the phosphorus in gaseous mixtures simulating phosphate blast-furnace and electric-furnace gases was oxidized, respectively, with 1.6 and 1.25 times the stoichiometric proportions of air to convert the phosphorus to phosphorus pentoxide. Either dry air or air that contained sufficient water vapor to convert the pentoxide into metaphosphoric acid was used. The rate of phosphorus input was about 1.3×10^{-6} gram per second per cc. (0.3 pound per hour per cubic foot) of combustion space. Experiments beyond the scope of this paper demonstrated the applicability of the results to the preferential oxidation of actual blast-furnace gas.

The oxidation of the carbon monoxide is minimized by using the lowest temperature and proportion of air consistent with complete oxidation of the phosphorus, and by drying the air. The heating value of the by-product gas is thereby brought to its maximum. The highest concentrations of carbon monoxide

Table V. Oxidation of Blast-Furnace Gas in Presence of Phosphate Rock

Expt. No.	Air Input, % of P_2O_5 Requirement	H_2O Input, % of HPO_3 Requirement	Rock Input, % of $Ca(P_2O_5)_2$ Requirement	Av. Temp. at Different Levels from Foot of Rock Column, ° C.				Rate of P Input, G./Sec./Cc. $\times 10^6$	Time in Combustion Zone ^a , Sec.	Time in Contact with Rock, Sec.	CO Oxidized, % of CO Input	P Oxidized, % of P Input
				0	6 cm.	10 cm.	14 cm.					
1R	147	0	700	1095	1104	1064	940	1.7	2.5	2.5	10.1	100
2R	152	51	770	1099	1106	1070	959	1.8 ^b	2.3 ^b	2.3	13.2	100
3R	153	227	460	1093	1113	1082	999	2.5	1.5	1.7	17.9	100
4R	151	52	860	1108	1100	1109	974	0.5	12.9	3.0	14.3	100
25B	147	202	0	1105 ^c				1.6	21	66 ^d
26B	148	0	0	1099 ^c				1.6	23	58 ^d

^a Combustion zone included chamber below the rock column as well as voids in initial column. ^b Estimated.

^c Maximum temperature at center of furnace. ^d Calculated from oxygen balance.

obtained from mixtures simulating blast-furnace gas and electric-furnace gas were 30 and 34% by volume, respectively. The initial concentration of carbon monoxide in electric-furnace gas is much greater than that in blast-furnace gas, but the oxidation of the higher phosphorus content of the electric-furnace gas necessitates use of much more air. The final concentration of carbon monoxide obtained from electric-furnace gas by preferential oxidation of the phosphorus is therefore not greatly different from that obtained from blast-furnace gas.

In producing phosphoric acid from electric-furnace gas by a one-step process, preferential oxidation offers an advantage over complete oxidation, in that there is considerably less heat to be dissipated and the phosphorus pentoxide is diluted with less nitrogen.

In the preferential oxidation of blast-furnace gas in the presence of phosphate rock to form calcium metaphosphate, the percentage of CO in the exit gas was in the range 23 to 26%. In actual practice, somewhat higher concentrations of carbon monoxide probably could be obtained, because the normal blast-furnace gas contains a somewhat smaller proportion of phosphorus than was used in the experiments. To attain the carbon monoxide concentration of about 30% that would be required for preheating the blast, exact control of the operation of both the preferential oxidation furnace and the blast furnace would be required.

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HIGH-TEMPERATURE HEAT CONTENTS OF Ferrous and Magnesium Chromites

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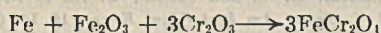
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The heat contents above 25° C. of high-grade synthetic samples of ferrous chromite and magnesium chromite were determined in the temperature range 25-1500° C. A table summarizes the heat contents and entropies above 25° C. of these substances at 100° intervals; the data are also adequately represented by equations.

INVESTIGATIONS at this Station on the metallurgy of chromium have revealed the need of accurate thermodynamic data for both ferrous and magnesium chromites. High-grade samples were prepared in the laboratory, and this paper presents high-temperature heat content data for both substances in the range 25° to 1500° C.

The measurements were made by a modification of the "method of mixtures"; in this case the samples, enclosed in platinum-rhodium capsules, were heated to a determined temperature and then dropped into a copper calorimeter, previously calibrated by electrical means (1 calorie = 4.1833 international joules). The method and apparatus have already been described (2). A platinum-rhodium capsule sealed with platinum was used for the ferrous chromite; an open-neck platinum-rhodium capsule having a tightly fitting cap was employed for the magnesium chromite.

The ferrous chromite was prepared by heating a stoichiometric mixture of high-grade sponge iron, reagent-grade ferric oxide, and chromic oxide of high purity according to the reaction,



at a temperature of 1300-1350° C. for several days in a slow stream of helium. Analysis of the product showed that it contained 24.77% Fe (theoretical 24.95%) and 46.09% Cr (theoretical 46.46%). A small amount of silica was also found. Treatment of the pulverized sample with hot concentrated hydrochloric acid for several hours revealed only traces of soluble iron.

The magnesium chromite was prepared in a similar manner by reacting reagent-grade magnesium oxide with reagent-grade chromic oxide at 1400° C. Analysis gave 12.58% Mg (theoretical 12.64%), 54.07% Cr (theoretical 54.08%), and 0.14% Fe. Treatment of this sample with hot concentrated hydrochloric acid showed that only traces of free MgO and Cr₂O₃ were present.

The crystal structures of the samples were examined at the Salt Lake City Station of the Bureau of Mines. The pattern of the ferrous chromite sample checked those previously reported for synthetic and natural chromite quite well, showing a cubic lattice with a parameter of 8.358 Å. No other material was present in sufficient quantity to show additional lines. Likewise, the magnesium chromite checked the known spacings. Its parameter was found to be 8.31 Å, and no lines corresponding to other substances were found.

The experimentally determined heat contents above 298.16° K. of ferrous and magnesium chromites are given in Table I. The columns labeled $T^\circ \text{K.}$ give the absolute temperature of the sample before being dropped into the calorimeter; the columns for $H_T - H_{298.16}$ list the heat liberated per gram molecular weight of material in dropping from T° to 298.16° K. Small correc-

TABLE I. HIGH-TEMPERATURE HEAT CONTENTS

FeCr ₂ O ₄		MgCr ₂ O ₄	
T° K.	$H_T - H_{298.16}$, cal./g. mol. wt.	T° K.	$H_T - H_{298.16}$, cal./g. mol. wt.
386.1	2,940	387.1	2,930
498.7	7,090	546.0	8,800
616.4	11,820	658.9	13,290
725.4	16,300	816.1	19,740
861.0	22,000	961.2	25,870
959.1	26,200	1077.6	30,810
1041.8	29,860	1232.4	37,570
1133.4	33,920	1370.7	43,600
1242.0	38,880	1400.7	44,980
1350.3	43,700	1473.3	48,270
1418.9	46,870	1581.6	53,050
1522.8	51,670	1644.4	55,900
1622.1	56,320	1782.8	62,140
1645.1	57,250		
1769.0	63,040		
1786.1	63,990		
1786.9	64,090		

TABLE II. HEAT CONTENTS AND ENTROPIES ABOVE 298.16° K AT 100° INTERVALS

FeCr ₂ O ₄			MgCr ₂ O ₄		
T° K.	$H_T - H_{298.16}$, cal./g. mol. wt.	$ST - S_{298.16}$, cal./g. mol. wt./° K.	T° K.	$H_T - H_{298.16}$, cal./g. mol. wt.	$ST - S_{298.16}$, cal./g. mol. wt./° K.
400	3,450	9.88	3,350	9.63	
500	7,100	18.03	7,040	17.86	
600	11,150	25.41	10,930	24.95	
700	15,280	31.77	14,920	31.10	
800	19,450	37.25	19,050	36.62	
900	23,660	42.31	23,280	41.60	
1000	27,960	46.84	27,500	46.04	
1100	32,390	51.06	31,800	50.14	
1200	36,920	55.00	36,120	53.90	
1300	41,460	58.64	40,460	57.38	
1400	46,000	62.00	44,920	60.68	
1500	50,550	65.14	49,390	63.76	
1600	55,200	68.14	53,880	66.66	
1700	59,860	70.97	58,360	69.38	
1800	64,600	73.67	62,860	71.95	

tions were made to the values in Table I for the silica (2) and iron impurities. The silica content of the ferrous chromite was taken as 0.75% and the iron in the magnesium chromite was considered to be present as 0.5% ferrous chromite.

All molecular weights accord with the 1941 International Atomic Weights. No discontinuity is discernible in the heat content curve of either substance. The heat contents, read from

the smooth curves, and calculated entropy increments at even 100° intervals from 298.16° K. to temperature T are summarized in Table II. No previous high-temperature heat content data of comparable accuracy appear in the literature. From the specific heats at 298.16° K., $C_p = 31.98$ and 30.30 calories per degree per mole for ferrous and magnesium chromites, respectively (1), and the heat content data, the following algebraic equations were derived. Below 600° K. the heat content equation for ferrous chromite may be in error by as much as 150 calories; at higher temperatures it has an average deviation of 0.2% with a maximum deviation of 0.4% around 1200° K. The heat content equation for magnesium chromite fits the data within 30 calories below 600° K.; above that temperature it has an average deviation of 0.15%, the maximum error being about 0.3%. The specific heat equations were obtained by differentiation:

$$\text{FeCr}_2\text{O}_4: H_T - H_{298.16} = 38.96T + 2.67 \times 10^{-3}T^2 +$$

$$\frac{7.62 \times 10^5}{T} - 14,410 \quad (298-1800^\circ \text{ K.})$$

$$C_p = 38.96 + 5.34 \times 10^{-3}T - \frac{7.62 \times 10^5}{T^2}$$

$$\text{MgCr}_2\text{O}_4: H_T - H_{298.16} = 40.02T + 1.78 \times 10^{-3}T^2 +$$

$$\frac{9.58 \times 10^5}{T} - 15,310 \quad (298-1800^\circ \text{ K.})$$

$$C_p = 40.02 + 3.56 \times 10^{-3}T - \frac{9.58 \times 10^5}{T^2}$$

ACKNOWLEDGMENT

Both samples were prepared and chemically analyzed at this station by F. S. Boericke, assisted by W. M. Bangert. The x-ray examination of the chromites was kindly carried out under the direction of E. V. Potter at the Salt Lake City Station.

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Nomogram to Convert Weight and Mole Percentages in Binary Systems

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ANALYTICAL results are almost always expressed as weight percentage, but the physical chemist, the engineer, or the operator in synthesis usually works with mole fraction or mole percentage. The physical chemist best understands ideal solutions and deviations from them when dealing in mole fractions. The chemist in synthetic work considers his reactions in terms of moles of reactants and moles of products. The chemical engineer designs much of his equipment in unit operations by working with mole fractions.

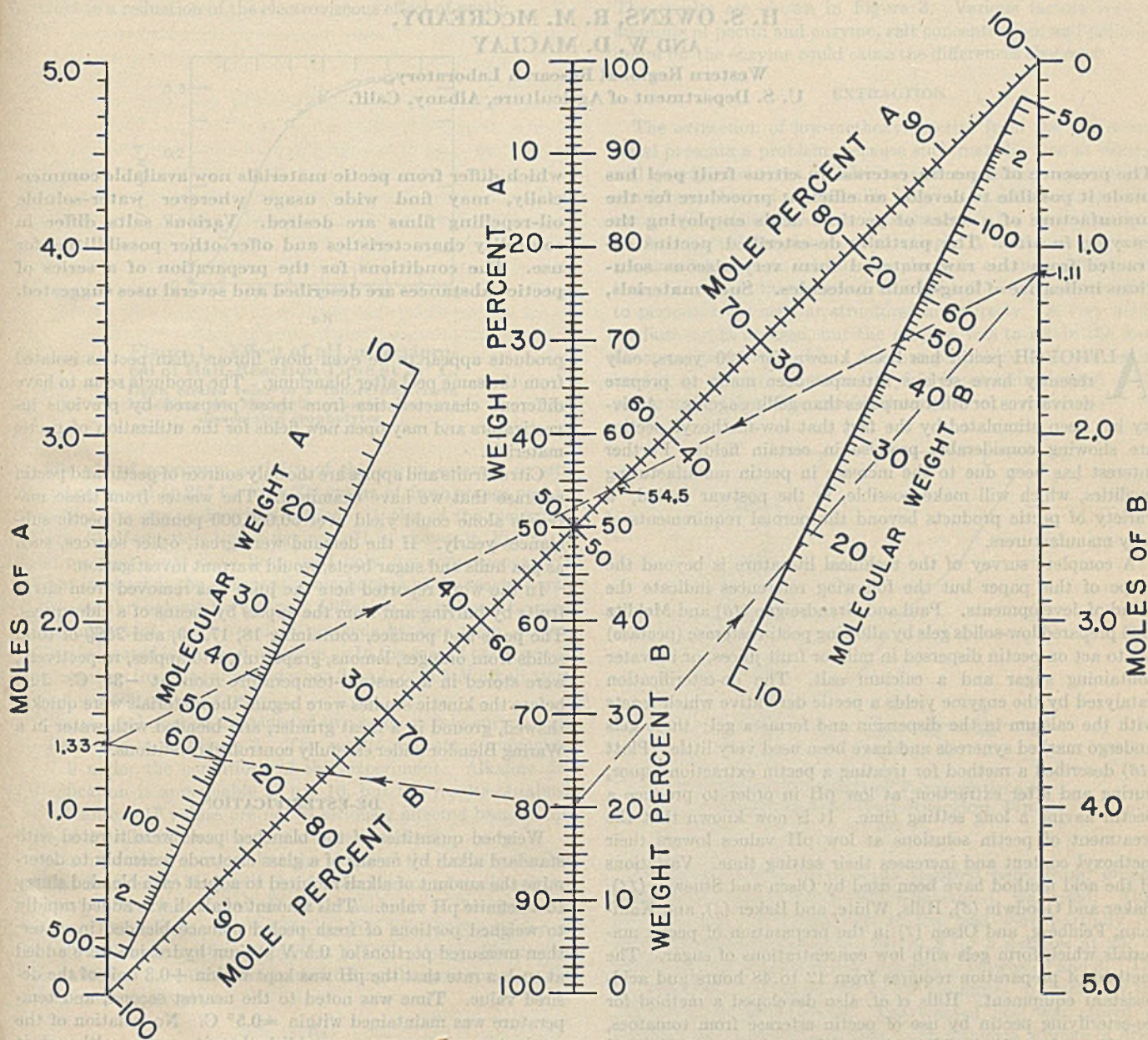
Since both additive and multiplicative operations are involved in this conversion, a mathematical solution is imposed to which no ready short cut is available even when a whole series of similar calculations is to be made. Several graphical calculators to effect

this conversion of weight per cent to mole per cent and vice versa have appeared in the literature¹. Each of these, however, requires an arithmetic calculation, and in some cases the chart is complicated. The nomogram presented here involves no calculation and furnishes a direct solution for mole per cent when composition by weight and molecular weight of the two components are known. A solution is also possible for weight per cent when mole per cent is known.

¹ Baker, J. S., *Chem. & Met. Eng.*, **45**, 155 (1938); Bridger, G. L., *Ibid.*, **44**, 451 (1937); Nevitt, H. G., *Ibid.*, **39**, 673 (1932); Patton, T. C., *Ibid.*, **41**, 148 (1934); Winnicki, H. S., and Chellis, L. N., *Ibid.*, **47**, 694 (1940); Underwood, A. J. V., *Trans. Am. Inst. Chem. Engrs.*, **10**, 145 (1932).

An expression of weight per cent is converted to mole per cent as follows: The point representing the weight composition of the system is located on the center vertical scale. Two lines are drawn from this point through the proper molecular weights and extended to extreme vertical scales representing number of moles of each constituent. The two points so obtained are connected with a straight line to give mole per cent on the long diagonal.

To solve for weight per cent from mole per cent, a short trial and error method is necessary. A point on the mole per cent line must lie on a straight line with points on the lines showing the number of moles. Therefore a point on weight per cent is guessed and tried until the above condition is fulfilled. Quick trials allow the point to be moved up and down until the correct answer is obtained.



An example is shown on the nomogram for converting an 80 weight per cent acetic acid-water solution to mole per cent. The point 80 per cent A-20 per cent B is located on the center vertical scale, and lines are drawn from it through 60 on molecular weight A and 18 on molecular weight B (representing the molecular weights of acetic acid and water, respectively). This shows 1.33 moles of acetic acid and 1.11 moles of water on the two extreme vertical scales. These two points are connected with a straight line to give an answer of 54.5 mole per cent acetic acid on the long diagonal. This compares favorably with the value of 54.5 obtained with a standard 10-inch slide rule.

This chart is interesting from consideration of nomograms in general. The unusual consolidation of a large Z-type chart with two smaller and related Z-charts results from the complex formula involved. It should be noted that the greatest space on the molecular weight scales is allotted to the lower molecular weight compounds, which places greatest accuracy where most desired.

For compactness the chart is presented in approximately square form. In a few cases the number of moles of A or B may be greater than 5. An extension of the outer lines is then required.

Enzymic Preparation and Extraction of PECTINIC ACIDS

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The presence of a pectin esterase in citrus fruit peel has made it possible to develop an efficient procedure for the manufacture of a series of pectinic acids employing the enzyme *in situ*. The partially de-esterified pectins extracted from the raw material form very viscous solutions indicative of long-chain molecules. Such materials,

ALTHOUGH pectin has been known for 120 years, only recently have serious attempts been made to prepare derivatives for other purposes than gelling agents. Activity has been stimulated by the fact that low-methoxyl pectins are showing considerable promise in certain fields. Further interest has been due to the increase in pectin manufacturing facilities, which will make possible, in the postwar period, a variety of pectic products beyond the normal requirements of jelly manufacturers.

A complete survey of the technical literature is beyond the scope of this paper but the following references indicate the trend of developments. Paul and Grandseigne (15) and Mehlitz (12) prepared low-solids gels by allowing pectin esterase (pectase) (8) to act on pectin dispersed in milk or fruit juices, or in water containing sugar and a calcium salt. The de-esterification catalyzed by the enzyme yields a pectic derivative which reacts with the calcium in the dispersion and forms a gel; these gels undergo marked syneresis and have been used very little. Platt (16) described a method for treating a pectin extraction liquor, during and after extraction, at low pH in order to produce a pectin having a long setting time. It is now known that the treatment of pectin solutions at low pH values lowers their methoxyl content and increases their setting time. Variations of the acid method have been used by Olsen and Stuewer (14), Baker and Goodwin (3), Hills, White, and Baker (4), and Kaufman, Fehlberg, and Olsen (7) in the preparation of pectic materials which form gels with low concentrations of sugar. The method of preparation requires from 12 to 48 hours and acid-resistant equipment. Hills *et al.* also developed a method for de-esterifying pectin by use of pectin esterase from tomatoes, but the product obtained has a low calcium tolerance and low gel strength. An alkaline method developed in this laboratory (11) overcomes the disadvantages of the acid method and has a high rate of reaction. The product is useful for many foods, such as puddings, pie fillings, desserts, and salads. Baier and Wilson (2) and Wilson (18) have prepared a fibrous sodium pectate by treating citrus peel with alkali, followed by extraction with alkaline phosphate solutions. This material has been suggested for latex creaming, for paper coatings (2), and as an agar substitute (1, 10).

The last-mentioned method depends upon a de-esterification of pectin *in situ* by the pectin esterase naturally occurring in the raw citrus materials and not upon an alkaline de-esterification as proposed by the original workers. The pH region of maximum activity is far removed from that for the pectinase (6), and the

which differ from pectic materials now available commercially, may find wide usage wherever water-soluble oil-repelling films are desired. Various salts differ in solubility characteristics and offer other possibilities for use. The conditions for the preparation of a series of pectic substances are described and several uses suggested.

products appear to be even more fibrous than pectins isolated from the same peel after blanching. The products seem to have different characteristics from those prepared by previous investigators and may open new fields for the utilization of pectic materials.

Citrus fruits and apples are the only sources of pectin and pectin esterase that we have examined. The wastes from these materials alone could yield over 50,000,000 pounds of pectic substances yearly. If the demand were great, other sources, such as pea hulls and sugar beets, would warrant investigation.

In the work reported here the juice was removed from citrus fruits by burring and from the apples by means of a cider press. The peels and pomace, containing 18, 17, 20, and 25% of total solids from oranges, lemons, grapefruit, and apples, respectively, were stored in a constant-temperature room at -35°C . Just before the kinetic studies were begun, the materials were quickly thawed, ground in a meat grinder, and blended with water in a Waring Blendor under carefully controlled conditions.

DE-ESTERIFICATION

Weighed quantities of the blanched peels were titrated with standard alkali by means of a glass electrode assembly to determine the amount of alkali required to adjust each blended slurry to a definite pH value. This amount of alkali was added rapidly to weighed portions of fresh peeled pomace blended in water; then measured portions of 0.5 *N* sodium hydroxide were added at such a rate that the pH was kept within ± 0.3 unit of the desired value. Time was noted to the nearest second, and temperature was maintained within $\pm 0.5^{\circ}\text{C}$. No isolation of the product was necessary to establish the rate curves, although it was done on most samples as a further check.

When the reaction had proceeded until enough alkali had been added to yield the desired information, the pH of the slurry was adjusted to 3 with 1:1 sulfuric acid, sodium hexametaphosphate (Calgon) was added, and the mixture was heated to boiling with steam. The time of the hot extraction was 15 minutes. The hot extract was filtered by suction with the aid of Hyflo Supercel. The filtrate was cooled and poured into an equal volume of 95% ethanol. The precipitate was strained on cheesecloth, hardened in ethanol, dried *in vacuo* at $60-70^{\circ}\text{C}$., and ground to pass a 60-mesh screen. The ash content of the pectins so prepared averaged about 18% and was primarily partially hydrolyzed products from the sodium hexametaphosphate. Methyl ester analyses were run by Hinton's method (5).

Viscosities were determined on 1% solutions of unpurified low-methoxyl pectins at pH 7 in a Stormer viscometer, calibrated with National Bureau of Standards oils No. H-1 and D, glycerol-water solutions, and water, at $25 \pm 0.5^\circ \text{C}$. The values reported have only relative significance because of the ash content. For each gram of pectin, 250 mg. of sodium hexametaphosphate were added to reduce the viscosity to a minimum and reproducible value. This reduction was apparently due in part to a reduction in the concentration of polyvalent ions, such as calcium, and in part to a reduction of the electroviscous effect of pectin.

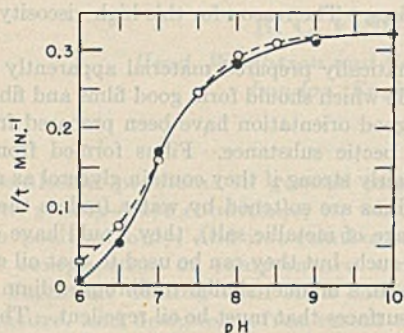


Figure 1. Effect of pH on Reciprocal of Half-Reaction Time at 25°C . Open circles refer to a theoretical curve based on the Michaelis equation for undissociated ampholytes.

The pH of maximum activity of the pectin esterase *in situ* was determined at 25°C . with 500 grams of fresh orange peel in 1.5 liters of water as described earlier. A plot of the reciprocal of the "half-reaction time" against pH is shown in Figure 1. Half-reaction times have been used only for convenience and do not imply that the order or the mechanism of the reaction was the same throughout its course. Diffusion phenomena become more important as the reaction proceeds because most of the pectin is located in the peel particles. In the case of orange peel, half reaction time was obtained when 35 ml. of 0.5 *N* alkali were added per 500 grams of peel.

Figure 1 is based on averages of two or more rate curves such as those shown in Figure 3. The results indicate a maximum near 9 under the conditions of this experiment. Alkaline de-esterification is appreciable at pH 10, but the results obtained at the lower pH values are not so seriously affected because the rate of the alkaline reaction is decreased markedly.

It is interesting to note that the shape of the curve is similar to that deduced by Michaelis (13) for the fraction of undissociated ampholyte as a function of pH on the acid side of the isoelectric region. If it is assumed that the enzyme has 100% activity at pH 10, half-activity is obtained at pH 7. Using this as the pK_2 value for the enzyme and substituting the corresponding K_2 value in the equation,

$$p = \frac{K_2}{K_2 + [H^+]}$$

where p = fraction of ampholyte undissociated

$$K_2 = K_w/K_{\text{base}}$$

the theoretical curve shown by the open circles in Figure 1 is obtained. The coincidence between the theoretical and experimental curves would indicate that, as the activity of the enzyme increases, it is changed from the anionic to the undissociated form. It would also imply that the isoelectric point is above pH 7. A similar theoretical treatment applied to the action of intestinal aminopeptidase by Wilson (19) indicates that this enzyme is also more active when in the undissociated form.

The influence of temperature was studied at pH 7 with 125 grams of fresh orange peel in 1.5 liters of water, using the constant

pH technique described earlier. A plot of the reciprocal of half-reaction time against temperature¹ in Figure 2 shows an almost linear increase in the rate of enzymic de-esterification with increase in temperature above 16°C . At 0°C . experimental errors were greater. Ninety-five per cent of the activity was destroyed when the esterase in orange peel was heated at pH 2 at 70°C . for 15 minutes.

The effect of kind of fruit was determined with a ratio of 125 grams of raw material to 1.5 liters of water at 25°C . and pH 7. The results are shown in Figure 3. Various factors such as amounts of pectin and enzyme, salt concentration, and pH maximum for the enzyme could cause the differences observed.

EXTRACTION

The extraction of low-methoxyl pectins from the source material presents a problem, because such metallic ions as calcium will precipitate them. Calcium and magnesium account for nearly one third of the metallic ions in the ash of citrus fruits; some of the calcium is known to be present in the form of pectates in the intercellular tissue. Accordingly it is necessary to add reagents which form calcium complexes to aid in the disintegration of the plant material and thus allow the extraction medium to permeate the cellular structures more freely. A very acidic medium could be used, but the purpose was to retain the most fibrous structure possible. Another possibility that was examined in an effort to improve the yield is solubilization (9) of the pectic materials with a suitable detergent.

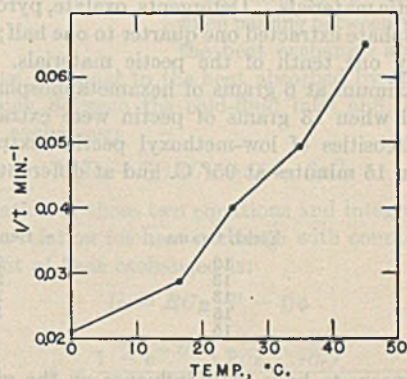


Figure 2. Effect of Temperature on Reciprocal of Half-Reaction Time at pH 7

In the extraction experiments reported here, fresh, ground citrus peel (orange unless otherwise stated) was used. After grinding, the pectic materials in the peel were partially de-esterified by maintaining the pH at 8 for 5 minutes at 25°C . The pH of the dispersion was adjusted to between 2 and 3. The dispersion was heated to 80°C . for 5 minutes to inactivate the enzymes and then filtered. The treated peel was stored at temperatures near freezing before use, although storage of dried peel would be more feasible commercially. An amount equivalent to 500 grams of fresh peel was dispersed in 1.5 liters of water, extracted with or without special extraction agents at various acid pH values at 90°C . and above for 15 minutes, and filtered. The cooled filtrate was poured into two volumes of ethanol. The precipitate was dehydrated in ethanol and further dried at $60-70^\circ \text{C}$. *in vacuo*. Quantities obtained in similar tests varied as much as 15% with the extraction technique used. The methoxyl contents of the products were between 3 and 4%. It is possible, however, by reducing the amount of alkali consumed

¹ The energy of activation was calculated from the variation in the rate constant with change in temperatures. Such calculations give 6×10^3 calories, which is near the value for the energy of activation found for other hydrolytic enzymes (17) and can be compared to 11×10^3 calories found for alkaline de-esterification of pectin (11).

in the de-esterification to prepare pectins having higher methoxyl contents. Products containing as much as 9.8% MeO have been made.

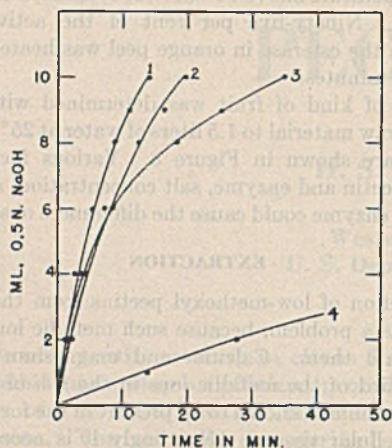


Figure 3. Rate of De-esterification with Different Fruits at pH 7 and 25° C.

Curve 1, grapefruit; 2, lemon; 3, orange; 4, apple.

Of the special extraction agents tried, only sodium hexametaphosphate and sodium tetrakisphosphate extracted the maximum amount of pectic materials. Detergents, oxalate, pyrophosphate, and metaphosphate extracted one quarter to one half; acid alone extracted only one tenth of the pectic materials. The yield reached a maximum at 6 grams of hexametaphosphate per 500 grams of peel when 13 grams of pectin were extracted. The yields and viscosities of low-methoxyl pectins extracted from treated peel in 15 minutes at 95° C. and at different pH values follow:

pH	Yield, Grams	η , Centipoises
2	10	28
3	13	28
4	13	25
5	15	15
6	15	7

The pH appears to have little influence on the yield, but at pH 5 and 6 there is marked degradation of the pectin. This influence of pH on viscosity makes it possible to prepare materials of diverse chain lengths. With an extraction period of 60 minutes at pH 3 the yield was 15 grams but the viscosity of a 1% solution decreased to 16 centipoises.

METHOD OF MANUFACTURE

The equipment ordinarily used for the isolation of pectin can be utilized for this series of pectic substances. The changes in the usual procedure permit determination of the amount of alkali required to neutralize the acids in the slurry of peel or pomace and the amount of alkali required to obtain the desired degree of de-esterification. The 1:3 ratio of peel to water is satisfactory. After the slurry of peel and water is prepared, the alkali required to neutralize the acids and give the desired pH may be added. Then the amount of alkali required to produce the de-esterification may be added while the pH is kept constant. A somewhat more practical method is to add all the alkali rapidly and allow the reaction to proceed until the pH has dropped to 7. The reaction is stopped by adding acid, such as sulfur dioxide or sulfuric acid, to pH 3-4. One pound of sodium hexametaphosphate per 100 pounds of peel is added, the pH is readjusted to 3-4, and the slurry is heated to boiling for 10-15 minutes, pressed, and filtered. After vacuum-pan concentration the filtered liquid may be used for many purposes. To obtain a solid product the concentrated filtrate is precipitated with alcohol, calcium, iron,

aluminum, or other effective metallic salts. These procedures and the subsequent washings and dryings are standard techniques in the pectin field and need no amplification.

POSSIBLE USES

Solutions of pectins prepared in this manner have unusually high viscosities compared to those of pectins extracted by the usual methods. A solution of the most fibrous low-methoxyl pectin from orange peel had a viscosity of 36 centipoises, whereas a similar solution of the most fibrous pectin extracted from the same orange peel with sodium hexametaphosphate had a viscosity of 22 centipoises. The reason for this high viscosity is being investigated.

The enzymatically prepared material apparently has a long-chain molecule which should form good films and fibers. Fibers which show good orientation have been prepared from metallic salts of the pectic substance. Films formed from them are flexible and fairly strong if they contain glycerol as a plasticizer. Since these films are softened by water (unless they contain a high percentage of metallic salt), they would have only limited usefulness as such, but they can be used to coat oil containers of various types, in a manner similar to fibrous sodium pectate (2), or for other surfaces that must be oil repellent. They have fair adhesive qualities and can be used to laminate cardboard and other paper products. They also appear to be useful in certain fireproofing compositions. Low-solid gels have been prepared from the calcium salt of pectins having lower methoxyl contents. Like the fibrous sodium calcium pectate gel (1, 10), this gel has been used in nutrient media for bacteria and molds in place of agar.

The metallic salts, except those of the alkali metals, are insoluble in water, but the organic amine salts tend to be soluble. The latter may be useful in certain types of emulsions and agricultural sprays (2).

Many other possibilities for the application of these fibrous materials are the same as those given by Baier and Wilson for fibrous sodium pectate (2). The method presented here, however, permits the production of pectins having high as well as low methoxyl contents. Consequently, products can be prepared which are less sensitive to precipitation by metallic ions, such as calcium, and are thus more adaptable than fibrous pectic acid.

ACKNOWLEDGMENT

We express our appreciation to Ruth Frenchman for the methoxyl determinations, to Harry Lotzkar for the viscosity measurements, and to Samuel Waisbrot for carrying out several of the extractions.

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Heating and Cooling Times in CIRCULATING SYSTEMS

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Heat transmission problems in general engineering are most frequently connected with steady-state conditions, in which temperature changes take place relative to position only, and not relative to time. There are, however, cases where the computation of temperature variations over a given time is important. Formulas dealing with such conditions appear infrequently in technical literature, and designers often resort to approximations based on average conditions prevailing during the processing time. Examination of the heat transfer mechanism based on first principles has shown that, once adequate formulas have been developed which include a relatively small number of simplifying assumptions, it is possible to carry out concise numerical computations which readily lead to practical results.

THE methods of calculation most readily available and commonly used in heat transfer problems are based on the assumption that a constant mean-temperature difference exists between the heat receiver and heat supplier. This is the case in most continuous operations. However, in a number of important industrial applications this assumption is not justified; indeed the mean temperature difference is constantly changing from the beginning to the end of the operation.

Examples of such applications are the heating or cooling of batches of liquids or solids by a heat supplier or remover. Particular cases selected at random from the petroleum and steel industries, respectively, are the heating of tanks containing fluids which are highly viscous at low temperatures such as lubricating oils, asphalts, etc., and the quenching of metal billets in liquid baths. For such conditions practical methods of computation are not readily available, and the formulas developed below are intended to meet this deficiency.

Although the numerical examples set out in this paper have been selected from cases arising in the petroleum and steel industries, the basic formulas are quite general and may be found useful, possibly with suitable variations, in similar types of heat transmission problems in other industries.

In the following study it is assumed that: (a) The thermal conductivity and the shape of the solid body under consideration are such that all its particles are at a uniform temperature at a given time. (b) The thermal conductivity of the fluid and arrangement of the bath are such that

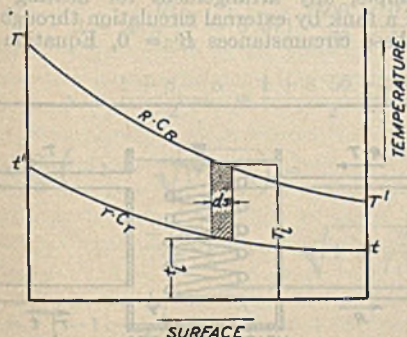


Figure 1. Temperature Conditions in a Surface Countercurrent Heat Exchanger

particles are at uniform temperature. (c) No heat is lost to the surroundings. (d) No heat is supplied from any sources other than those specifically mentioned. (e) Heat supplied to or removed from the bath fluid involves no change of state—i.e., vaporization, condensation, etc., are excluded. Provided the system under consideration is equipped with adequate circulation and insulation, these assumptions represent in many instances reasonably close approximations for practical purposes.

Analyzing the performance of a surface countercurrent heat exchanger of given dimensions and assumed constant over-all heat transfer coefficient when rates of circulation and inlet temperatures of the two fluids are varied, Figure 1 illustrates the temperature conditions. The heat transfer through a surface element of the exchanger must equal the heat loss of the hotter fluid when passing over this element:

$$-RC_R dT_i = (T_i - t_i) U dS \quad (1)$$

The heat lost by the hotter fluid, when passing between any point inside the heat exchanger and the hot-fluid

outlet, must be equal to the heat absorbed by the colder fluid, when passing between the cold-fluid inlet and the same point inside the exchanger:

$$(T_i - T') RC_R = (t_i - t) r C_r \quad (2)$$

Combination of these two equations and integration gives the well-known relation for heat exchange with countercurrent flow. The amount of heat exchanged is:

$$H = RC_R (T - t) \phi \quad (3)$$

$$\text{where} \quad \phi = \frac{1 - e^{-US \left(\frac{1}{RC_R} - \frac{1}{rC_r} \right)}}{1 - \left(\frac{RC_R}{rC_r} \right) e^{-US \left(\frac{1}{RC_R} - \frac{1}{rC_r} \right)}} \quad (4)$$

This amount of heat is defined by the dimensions of the exchanger, the over-all heat transfer coefficient, and the rates of circulation of the fluids of given characteristics. From Equation 4 it will be noted that ϕ assumes an indeterminate value for $RC_R = rC_r$. However, mathematical analysis of Equation 4 shows that the true value of ϕ for this case is:

$$\phi = \frac{1}{1 + \frac{RC_R}{US}} \quad (5)$$

The foregoing derivations are well known but have been included to facilitate the study of the subsequent extensions and developments.

The arrangement of the system under consideration is shown in Figure 2. Assuming no vaporization of the fluids, the sensible heat content of the entire system must be constant; in other words, the sum of all variations in heat contents must be equal to zero:

$$BC_B d\tau + AC_R dT + RC_R (T - t) \phi d\theta = 0 \quad (6)$$

The first and second terms in Equation 6 represent the change of heat content of the body and of the bath; the third term defines the heat removed from the system by the heat exchanger.

Furthermore, the heat lost or gained by the submerged body must be equal to the heat transferred through its surface:

$$-BC_B d\tau = S_B h_B (\tau - T) d\theta \quad (7)$$

Equation 7 can be rewritten:

$$d\theta = \frac{-BC_B}{S_B h_B} \frac{d\tau}{\tau - T} \quad (8)$$

Substituting this value of $d\theta$ in Equation 6 and rearranging,

$$\alpha \frac{dT}{d\tau} = \frac{T(1 + \beta) - \tau - \beta t}{\tau - T} \quad (9)$$

$$\text{where } \alpha = AC_R/BC_B \quad (10)$$

$$\beta = (RC_R/S_B h_B) \phi \quad (11)$$

Equation 9 represents the connection between the temperature of the body, τ , and the temperature of the bath, T . In order to solve this linear first-order differential Equation 9, the following groups are introduced:

$$\omega = \tau - t \quad (12)$$

$$v = (T - t)/(\tau - t) \quad (13)$$

$$\gamma = (1 + \beta - \alpha)/2 \quad (14)$$

$$p = \gamma/\alpha \left(-1 + \sqrt{1 + \frac{\alpha}{\gamma^2}} \right) \quad (15)$$

$$q = \gamma/\alpha \left(-1 - \sqrt{1 + \frac{\alpha}{\gamma^2}} \right) \quad (16)$$

$$\delta = \frac{1 + \gamma/\alpha}{p - q} \quad (17)$$

Equation 9 is integrated by the following substitutions:

$$\begin{aligned} T &= \mu + t & dT &= d\mu \\ \tau &= \omega + t & d\tau &= d\omega \\ \tau - T &= \omega - \mu \end{aligned}$$

This yields the homogeneous differential equation:

$$\alpha \frac{d\mu}{d\omega} = \frac{\mu(1 + \beta) - \omega}{\omega - \mu}$$

Solving in the conventional way by writing

$$\therefore \frac{d\mu}{\mu} = \frac{v\omega}{v\omega + \omega dv}$$

we obtain:

$$\frac{d\omega}{\omega} = \frac{(1 - v)dv}{v^2 + v \frac{1 + \beta - \alpha}{\alpha} - \frac{1}{\alpha}} \quad (18)$$

For brevity, the substitutions according to Equations 14, 15, 16, and 17 are introduced, and allocation of terms with the subscript zero to the beginning of the process results in the final equation:

$$\omega = \omega_0 \frac{v_0 - q/\delta + 0.5}{v_0 - p/\delta - 0.5} \frac{v - p/\delta - 0.5}{v - q/\delta + 0.5} \quad (19)$$

The vertical lines in Equation 19 represent the absolute or numerical value of the quantity enclosed—that is, the modulus of the quantity.

In the special case where $T_0 = t$, according to Equation 13, $v_0 = 0$ and Equation 19 takes the form:

$$\tau - t = (\tau_0 - t) \frac{q/\delta + 0.5}{p/\delta - 0.5} \frac{v - p/\delta - 0.5}{v - q/\delta + 0.5} \quad (20)$$

The groups $(\tau - t)$ and $(\tau_0 - t)$ have been substituted for ω and ω_0 , respectively, according to Equation 12.

To calculate the time element in the problem, Equation 8 must be integrated. Using the same substitutions as for integration of Equation 9,

$$\begin{aligned} T &= \mu + t \\ \tau &= \omega + t \\ v &= \frac{\mu}{\omega} = \frac{T - t}{\tau - t} \end{aligned}$$

we obtain:

$$\frac{d\tau}{\tau - T} = \left(\frac{d\omega}{\omega} \right) \frac{1}{1 - v}$$

substituting in the above for $d\omega/\omega$ from Equation 18 and introducing into Equation 8,

$$d\theta = - \frac{BC_B}{S_B h_B} \frac{dv}{v^2 + v \frac{1 + \beta - \alpha}{\alpha} - \frac{1}{\alpha}}$$

This standard form is integrated in the conventional way. For brevity, the substitutions according to Equations 14, 15, and 16 are introduced to give the final solution as:

$$\theta = \frac{BC_B}{S_B h_B} \frac{1}{p - q} \ln \left| \frac{v_0 - p}{v_0 - q} \frac{v - q}{v - p} \right| \quad (21)$$

Again, in the special case for which Equation 20 has been developed

$$\begin{aligned} v_0 &= 0 \\ T_0 &= t \end{aligned}$$

we obtain:

$$\theta = \frac{BC_B}{S_B h_B} \frac{1}{p - q} \ln \left| \frac{p}{q} \frac{v - q}{v - p} \right| \quad (22)$$

It is of interest to consider under what conditions the temperature of the body will become equal to the inlet temperature of the cooling water, t . Obviously this can occur only when the bath temperature is also equal to t .

Equation 13, $v = (T - t)/(\tau - t)$, assumes an indeterminate form for $T = \tau = t$, but the true value v for the equalization of body and bath temperatures can be obtained from Equation 20 which shows that $\tau - t$ will become zero; i.e., $\tau = t$ for $v = p$. Since, however, the body can reach cooling medium temperature only if the bath has also reached the same lowest temperature in the system (i.e., when $T = t$), it follows that $\tau = t$ when both are equal to t .

On the other hand, Equation 21 or 22 shows that equality between v and p , which is the condition for $\tau = T = t$, will occur at $\theta = \infty$. Consequently, complete equalization of all temperatures in the system takes place only after infinite time; that this does not coincide with practical experience is due to assumptions made to simplify the mathematical procedure. It is felt, however, that this discrepancy will not lead to any practical difficulties.

Two specialized cases of practical interest will be considered.

CASE 1 is a cooling or heating system with no solid submerged in the bath—for example, any arrangement for heating or cooling the contents of a tank by external circulation through a heat exchanger. In these circumstances $B = 0$, Equation 6 reduces to the form,

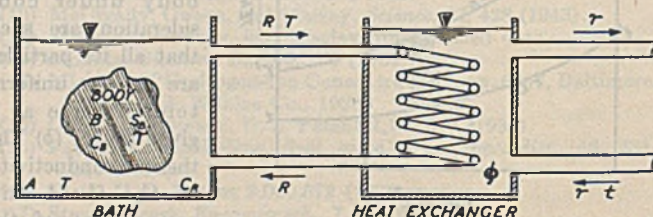


Figure 2. Diagram of Arrangement of Surface Counter-current Heat Exchanger

$$AC_R dT + RC_R (T - t) \phi d\theta = 0 \quad (23)$$

and Equation 7 disappears altogether. Integration of this simple expression yields, after some transformation:

$$\theta_{B=0} = \frac{A}{R\phi} \ln \left| \frac{T_0 - t}{T - t} \right| \quad (24)$$

CASE 2 is a cooling or heating system with no circulation through a heat exchanger—for example, in a quenching plant comprising merely a heat-insulated quenching tank. In these circumstances $R = 0$, and Equation 6 reduces to the form:

$$BC_B d\tau + AC_R dT = 0 \quad (25)$$

Equation 7 remains unaltered, and the general correlation in this case is:

$$\theta_{R=0} = \frac{AC_R}{S_B h_B} \frac{1}{\alpha + 1} \ln \left| \frac{\alpha(\tau_0 - T_0)}{\tau(\alpha + 1) - (\tau_0 + \alpha T_0)} \right| \quad (26)$$

This correlation is well known and appears as a special case of the general relation derived here.

The use of the foregoing correlations can best be demonstrated by numerical examples. The constants and coefficients are arbitrary, since the assessment of their precise values (for example, that of the average heat transfer coefficients) is not included in this study.

EXAMPLE I

A body with an initial temperature of 1560° F. is introduced into a quenching tank of given dimensions. The cooling liquid in the tank is circulated through an external cooler of known capacity. What time will it take for the body to reach a temperature of 260° F? What, then, will the bath temperature be? The following data are given:

TANK	BODY	COOLING SYSTEM
$A = 10,000$ lb. $T_0 = 1560^\circ$ F.	$B = 2000$ lb. $\tau_0 = 1560^\circ$ F. $C_B = 0.1$ $\frac{\text{B.t.u.}}{(\text{lb.}) (^\circ \text{F.})}$ $S_B = 50$ sq. ft. $h_B = 5$ $\frac{\text{B.t.u.}}{(\text{hr.}) (\text{sq. ft.}) (^\circ \text{F.})}$ $t = 260^\circ$ F.	$R = 7500$ lb./hr. $r = 3750$ lb./hr. $t = 80^\circ$ F. $C_R = 0.5$ $\frac{\text{B.t.u.}}{(\text{lb.}) (^\circ \text{F.})}$ $S_c = 100$ sq. ft. $U = 50$ $\frac{\text{B.t.u.}}{(\text{hr.}) (\text{sq. ft.}) (^\circ \text{F.})}$ $C_r = 1.0$ $\frac{\text{B.t.u.}}{(\text{lb.}) (^\circ \text{F.})}$

The solution follows. Since in this case $RC_R = rC_r$:

$$\phi = \frac{1}{1 + \frac{RC_R}{US_c}} = \frac{1}{1 + \frac{7500 \times 0.5}{50 \times 100}} = 0.571 \quad (5)$$

$$\alpha = \frac{AC_R}{BC_B} = \frac{10,000 \times 0.5}{2000 \times 0.1} = 25 \quad (10)$$

$$\beta = \phi \frac{RC_R}{S_B h_B} = 0.571 \frac{7500 \times 0.5}{50 \times 5} = 8.56 \quad (11)$$

$$\gamma = \frac{1 + \beta - \alpha}{2} = \frac{1 + 8.56 - 25}{2} = -7.72 \quad (14)$$

$$p = \frac{\gamma}{\alpha} \left(-1 + \sqrt{1 + \frac{\alpha}{\gamma^2}} \right) = \frac{-7.72}{25} \left(-1 + \sqrt{1 + \frac{25}{7.72^2}} \right) = -0.059 \quad (15)$$

$$q = \frac{\gamma}{\alpha} \left(-1 - \sqrt{1 + \frac{\alpha}{\gamma^2}} \right) = \frac{-7.72}{25} \left(-1 - \sqrt{1 + \frac{25}{7.72^2}} \right) = +0.677 \quad (16)$$

$$\delta = \frac{1 + \gamma/\alpha}{p - q} = \frac{\left(1 + \frac{-7.72}{25} \right)}{(-0.059) - (+0.677)} = -0.94 \quad (17)$$

$$\omega_0 = \tau_0 - t = 1560 - 60 = 1500$$

$$\omega = \tau - t = 260 - 60 = 200 \quad (12)$$

$$v_0 = \frac{T_0 - t}{\tau_0 - t} = \frac{1560 - 60}{1560 - 60} = 0.06 \quad (13)$$

$$\omega = \omega_0 \frac{v_0 - q/\delta^{0.5}}{v_0 - p/\delta^{0.5}} \frac{v - p/\delta^{0.5}}{v - q/\delta^{0.5}} \quad (19)$$

$$2.316 = \frac{v - 0.677/0.44}{v + 0.059/1.44}$$

This equation is probably best solved by trial and error, giving $v = 0.341$.

$$v = \frac{T - t}{\tau - t} = 0.341 = \frac{T - 60}{260 - 60}; T = 128^\circ \text{ F.} \quad (13)$$

$$\theta = \frac{BC_B}{S_B h_B} \frac{1}{p - q} \ln \left| \frac{v_0 - p}{v_0 - q} \frac{v - q}{v - p} \right| \quad (21)$$

$$= \frac{2000 \times 0.1}{50 \times 5} \frac{1}{(-0.059) - 0.677} \times \ln \left| \frac{0.06 - (-0.059)}{0.06 - 0.677} \frac{0.341 - 0.677}{0.341 - (-0.059)} \right|$$

$$\theta = 1.98 \text{ hr.} = 1 \text{ hr. } 59 \text{ min. (approx.)}$$

EXAMPLE II

Conditions are identical to those stated in example I, except that there is no circulation and consequently no heat removal through an external cooler. When will the body temperature become 260° F.? The solution is as follows:

$$\theta_{R=0} = \frac{AC_R}{S_B h_B} \frac{1}{\alpha + 1} \ln \left| \frac{\alpha(\tau_0 - T_0)}{\tau(\alpha + 1) - (\tau_0 + \alpha T_0)} \right| \quad (26)$$

Substituting values as defined in example I,

$$\theta = \frac{10,000 \times 0.5}{50 \times 5} \frac{1}{25 + 1} \times \ln \frac{25(1560 - 150)}{260(25 + 1) - [1560 + (25 \times 150)]}$$

$$\theta = 2.45 \text{ hr.} = 2 \text{ hr. } 27 \text{ min. (approx.)}$$

EXAMPLE III

The liquid in a storage tank is to be heated with low-pressure steam by circulation through an external heat exchanger. What time will it take to heat the tank from 100° to 150° F.? The following data are given:

TANK	HEATING SYSTEM
$A = 50,000$ lb. $T_0 = 100^\circ$ F. $T = 150^\circ$ F. $C_R = 0.5$ $\frac{\text{B.t.u.}}{(\text{lb.}) (^\circ \text{F.})}$	$R = 80,000$ lb./hr. $S = 200$ sq. ft. $U = 100$ $\frac{\text{B.t.u.}}{(\text{hr.}) (\text{sq. ft.}) (^\circ \text{F.})}$ $t = 250^\circ$ F. Latent heat = 945 B.t.u./lb.

SOLUTION. As steam condenses at constant temperature, the result in the heat exchanger is the same as if the heating medium had $C_r = \infty$.

$$\phi = 1 - e^{-\frac{US}{RC_R}} = 1 - e^{-\frac{100 \times 200}{80,000 \times 0.5}} = 0.393 \quad (4)$$

$$\theta_{B=0} = \frac{A}{R\phi} \ln \frac{T_0 - t}{T - t} = \frac{50,000}{80,000 \times 0.393} \ln \frac{100 - 250}{150 - 250} \quad (24)$$

$$= 0.644 \text{ hr.} = 39 \text{ min. (approx.)}$$

The foregoing leads to the conclusion that the problems covered by this study are rather complex because of the great number of variables and constants involved. External circumstances may impose considerable limitations on the assumptions which the designer is free to make. Some points which can be decided upon only in a particular problem are the relative sizes of the cooling system, the volume of the bath, and the circulating rate. In this connection, economic considerations will generally dictate the best design.

It does not seem possible to suggest a straightforward method of procedure which will lead to an optimum solution; unless data from similar cases are available, it will be necessary for the designer to assume arbitrarily the free variables and compute several arrangements from which to choose the best. Fortunately, however, the numerical computations, as set out in the examples, are neither involved nor time consuming.

ACKNOWLEDGMENT

In conclusion, the author wishes to thank F. Carr for useful suggestions on certain technical aspects of the problem, to H. Harper for his help in the presentation of the material, and to A. C. Mueller for checking the galley proofs.

NOMENCLATURE

A = weight of bath fluid, lb.
 B = weight of body, lb.
 C_B = specific heat of body, B.t.u./(lb.) (° F.)
 C_R = specific heat of bath fluid, B.t.u./(lb.) (° F.)
 C_c = specific heat of cooling fluid, B.t.u./(lb.) (° F.)

H = heat transferred in exchanger, B.t.u./hr.
 h_B = heat transfer coefficient from body to bath, B.t.u./(sq. ft.) (hr.) (° F.)
 p = characteristic group defined by Equation 15
 q = characteristic group defined by Equation 16
 R = circulating rate of bath fluid, lb./hr.
 r = circulating rate of cooling fluid, lb./hr.
 S = heat transfer surface in exchanger, sq. ft.
 S_B = external surface of body, sq. ft.
 S_c = heat transfer surface in cooler, sq. ft.
 T = inlet temperature of warmer fluid to exchanger, ° F.
 T' = outlet temperature of warmer fluid from exchanger, ° F.
 t = inlet temperature of colder fluid to exchanger, ° F.
 t' = outlet temperature of colder fluid from exchanger, ° F.
 T_i = intermediate temperature of warmer fluid in exchanger, ° F.
 t_i = intermediate temperature of colder fluid in exchanger, ° F.
 U = over-all heat transfer coefficient in exchanger, B.t.u./(sq. ft.) (hr.) (° F.)
 v = characteristic group defined by Equation 13
 α = characteristic group defined by Equation 10
 β = characteristic group defined by Equation 11
 γ = characteristic group defined by Equation 14
 δ = characteristic group defined by Equation 17
 θ = time, hr.
 τ = temperature of body, ° F.
 ϕ = characteristic group defined by Equation 4
 ω = characteristic group defined by Equation 12

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Viscosities of Molten COUMARONE-INDENE RESINS

COMPARED to most of the commercially important polymeric substances, coumarone-indene resins used in mastic flooring tile, in varnishes, and in extending rubbers have low average molecular weights. Various investigators (6) have reported molecular weights of almost 4000, but most of the commercial products are included within the brief range from 550 to 800. Furthermore, it is well known (10, 12, 13) that many of the physical properties of these resins change sharply within this molecular weight range.

The recent investigations of Flory on the viscosities of molten linear polyesters (7) and of Kauzmann and Eyring on the viscosities of linear hydrocarbons (9) have focused attention on the determination of molecular weights by viscosity measurements made directly on the material without the use of a solvent. Although there have been few other studies of the variation of the viscosity of molten synthetic polymers with molecular weight, Dunstan (5) proposed the formula:

$$\log \eta = AM + B$$

where η = coefficient of viscosity
 M = molecular weight
 A, B = constants

This equation was proved invalid by Albert for homologous esters (2) over a narrow molecular weight range and by Flory (7)

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for a wide molecular weight range. Flory demonstrated the applicability of the formula,

$$\log \eta = AM_w^{1/2} + B$$

where the relation was improved by the use of the weight-average molecular weight, M_w , rather than the number-average molecular weight.

It was decided to study the viscosities of the molten coumarone-indene resins in order to determine their variation with temperature and with molecular weight. The relations were also determined for mixtures of resins of different molecular weights. The latter results are of particular importance for many commercial formulations.

TREATMENT OF RESINS

The coumarone-indene resins were produced from a solvent naphtha having the following boiling range: 4% below 160° C., 28% between 160–175°, 66% between 175–185°, and 2% above

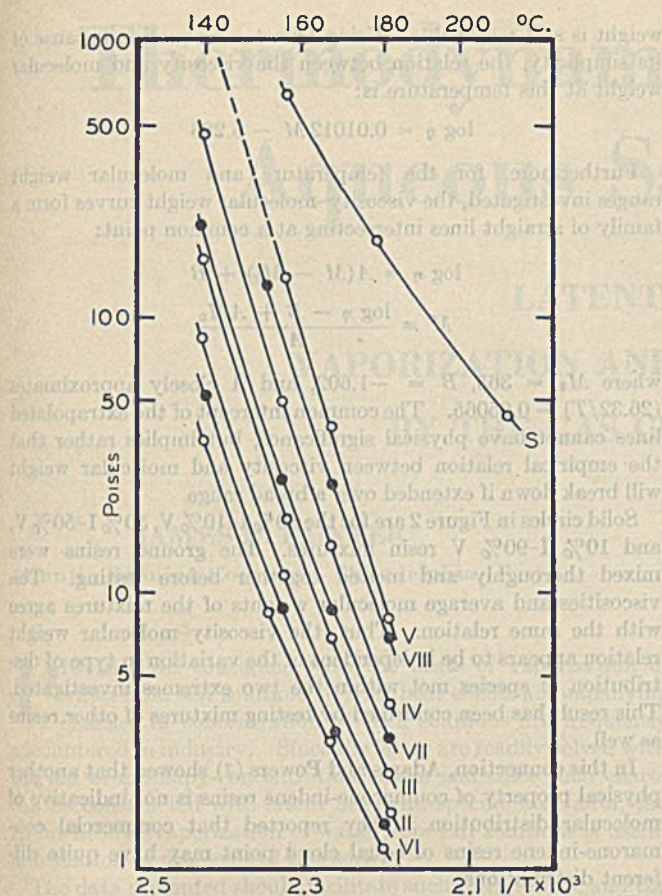


Figure 1. Log Viscosity vs. Inverse Absolute Temperature of Coumarone-Indene Resins

185° C. Undesirable polymerizable material was first removed by a dilute sulfuric acid wash. The degree of polymerization was controlled by the duration of the reaction and the amount of aluminum chloride used as catalyst (6). The temperature at the start was 0° C. and rose as the reaction proceeded. Salts were carefully removed by repeated agitation of the emulsion with water. This procedure was followed by vacuum distillation to remove naphtha and by steam distillation to remove oily polymers which are mostly dimers of indene and coumarone. Since the starting material was much richer in indene (boiling point 182° C.) than in coumarone (boiling point 172° C.), the resins consisted mostly of polyindenes. Because the polymerizable materials used commercially for coumarone-indene resins are always chiefly indene, the name is probably misleading.

The five coumarone-indene resins selected for viscosity studies were light brown, and had molecular weights and softening points as indicated in the following table. The molecular weights were determined by the cryoscopic method in benzene and the softening points, by the Ring and Ball method (3):

Resin No.	Mol. Wt.	Softening Point, ° C.	Resin No.	Mol. Wt.	Softening Point, ° C.
I	594	103.5	VI	604	106.5
II	620	109	VII	650	115.5
III	643	111.5	VIII	702	126
IV	678	119.5	S	826	115
V	716	129			

Resins VI, VII, and VIII were prepared by mixing I with V in 90-10, 50-50, and 10-90 parts by weight, respectively. S is a relatively tough resin obtained by polymerizing stock in which about 75% of the polymerizable material was styrene and the remainder was coumarone and indene fractions. This type is finding important uses in the flooring field. For comparison the

The average molecular weight of coumarone-indene resins may be determined by the measurement of their molten viscosities; a simple equation connects the viscosity and molecular weight at any temperature between 150° and 180° C. Viscosity measurements provide a simple and precise method. Since the viscosity-temperature coefficient is large, the temperature must be accurately known. On the other hand, since the viscosity appears in the equation as a logarithm, a 5% error in η produces an error of less than 1% in M . The relation determined here applies to mixtures of these polymers as well. Thus, any difference in the polymer distribution in two coumarone-indene resins is not important to the preparation of a mixture having intermediate viscosity properties. This result has an important bearing on the technological applications of these resins.

“ ” “ ” “ ”

viscosity of di-indene was also determined. Di-indene is a white crystalline solid recrystallized from benzene to a melting point of 56-57° C.

The method and apparatus were essentially the same as Flory's (7). The viscosities were calculated from the times t required to fill viscometers in the shape of volumetric pipets and from the pressure drops causing the molten resins to flow, corrected for the mean difference in height between resin in the viscometer and surrounding resin $P - P_A$. The equation is:

$$\eta = ct(P - P_A)$$

where $c = \text{a constant}$

The tube containing resin and viscometer was immersed in a vapor bath which remained within $\pm 0.1^\circ$ C. of constant temperature during any single experiment: 139° C., *m*-xylene; 157°, α -pinene; 168°, monoethanolamine; and 182°, aniline. The viscometers were calibrated with oils of known viscosities. Viscosities above 75 poises were measured in straight glass tubes used as viscometers. These techniques were described and discussed by Flory (7).

BEHAVIOR OF RESINS

The molten resins behaved as Newtonian liquids throughout the temperature range and stress range investigated. No change in the viscosity of the molten resins beyond the limits of the experimental method was noted for a sixfold variation in the stress applied. The significant temperature range was limited because at higher temperatures the viscosities decreased with time, probably as a result of depolymerization. For the range reported, no noticeable change in viscosity with time was noted.

Figure 1 shows that plots of $\log \eta$ against $1/T$ are nearly straight lines. As might be expected from the molecular configuration of the coumarone-indene resins, the viscosities are quite high for resins of such low molecular weight. They are also characterized by high viscosity-temperature coefficients. There appears to be a small dependency of the viscosity-temperature coefficient on molecular weight.

The values of C according to Andrade's (4) and Sheppard's (11) formula for the influence of temperature on viscosity,

$$\eta = A'e^{C/T}$$

at 140° and 180° C. are as follows:

Resin No.	$C \times 10^{-3}$ at 140° C.	$C \times 10^{-3}$ at 180° C.	Resin No.	$C \times 10^{-3}$ at 180° C.
I	21.5	14	V	23
II	20	14.5		11
III	23	16		
IV	23.5	20		

These are high values for C and are characteristic of amorphous materials (8).

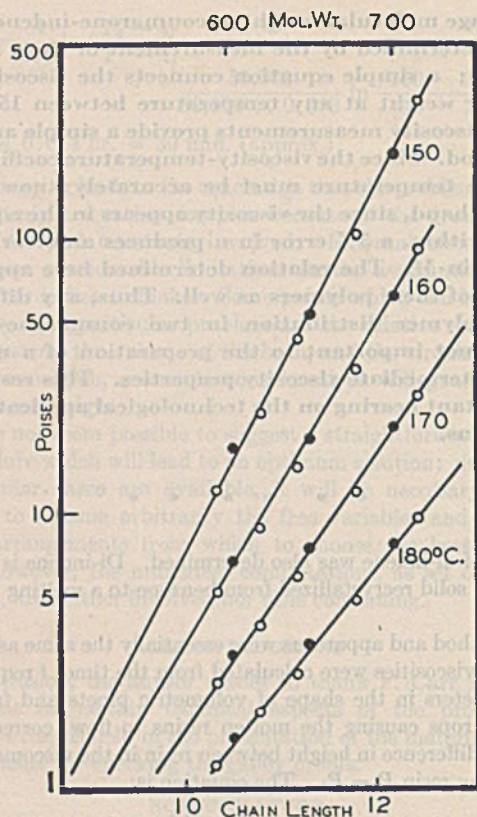


Figure 2. Log Viscosity vs. Molecular Weight or Chain Length

The styrene-coumarone-indene resins has a much smaller viscosity-temperature coefficient than the coumarone-indene resins. It is evident that viscosity measurements may be used to differentiate between the two types. There is a possibility that viscosity measurements may also be utilized to estimate the styrene content of such resins.

Plots of $\log \eta$ against molecular weight (number average) are shown at four different temperatures in Figure 2. Within the limits of error these plots are straight lines. The molecular weight range, however, is too brief to decide between Dunstan's and Flory's equations for the variation of viscosity with molecular weight or to find any deviation from linearity when number-average rather than weight-average molecular weight is used. No data are available for determining the weight-average molecular weight of these resins.

Probably the most practical temperature at which the viscosities of these coumarone-indene resins may be measured is 160° C. At this temperature the variation of viscosity with molecular weight is great, yet the viscosity of the resin of highest molecular

weight is still reasonable. Using Dunstan's equation because of its simplicity, the relation between the viscosity and molecular weight at this temperature is:

$$\log \eta = 0.01012 M - 5.296$$

Furthermore, for the temperature and molecular weight ranges investigated, the viscosity-molecular weight curves form a family of straight lines intersecting at a common point:

$$\log \eta = A(M - M_0) + B$$

$$M = \frac{\log \eta - B + AM_0}{A}$$

where $M_0 = 365$, $B = -1.602$, and A closely approximates $(26.32/T) - 0.05065$. The common intercept of the extrapolated lines cannot have physical significance, but implies rather that the empirical relation between viscosity and molecular weight will break down if extended over a broad range.

Solid circles in Figure 2 are for the 90% I-10% V, 50% I-50% V, and 10% I-90% V resin mixtures. The ground resins were mixed thoroughly and melted together before testing. The viscosities and average molecular weights of the mixtures agree with the same relation. Thus, the viscosity-molecular weight relation appears to be independent of the variation in type of distribution of species met within the two extremes investigated. This result has been confirmed by testing mixtures of other resins as well.

In this connection, Adams and Powers (1) showed that another physical property of coumarone-indene resins is not indicative of molecular distribution. They reported that commercial coumarone-indene resins of equal cloud point may have quite different distributions.

Figure 3 gives the viscosities of the di-indene; beyond 140° C., polymerization became noticeable. The molten di-indene was nearly water-white throughout the reproducible temperature range. At the xylene temperature, however, the readings had to be taken rapidly.

Temp., ° C.	Vapor Bath	Viscosity, Poise
67.2	Methyl alcohol	0.0953
79.2	Ethyl alcohol	0.0850
101.0	Water	0.0387
139.0	m-Xylene	0.0218

The viscosity-temperature coefficient is much lower than that of the resins. Viscosity values obtained by extrapolation of these results to the 150-180° C. range show no agreement with the viscosity-molecular weight relation given above.

ACKNOWLEDGMENT

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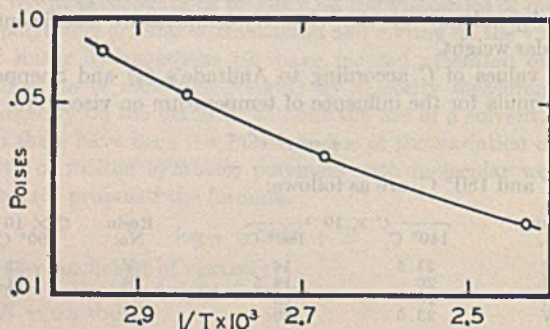


Figure 3. Log Viscosity vs. Inverse Absolute Temperature of Di-indene

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Thermodynamic Properties of Aqueous Salt Solutions

LATENT HEATS OF VAPORIZATION AND OTHER PROPERTIES BY THE GAS CURRENT METHOD

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PROBLEMS concerned with the heats of vaporization of water from salt solutions or with heat effects accompanying changes in concentration of such solutions are frequently encountered in industry. Since the latter are readily solved with the aid of enthalpy-concentration charts and since such charts can be constructed with latent heat and specific heat data, the latent heat of vaporization of water from salt solutions is useful information in problems of this sort.

The data presented should facilitate such calculations, and the equipment and method described should be generally applicable to similar measurements on other systems. The equipment is relatively easy to construct and operate, and the elimination of heat loss is probably easier than with latent heat measurements at the normal boiling point. The method and the thermodynamic analysis may be used for pure liquids and nonaqueous solutions as well as for aqueous solutions. This method also proved useful for the determination of other properties than latent heats.

The gas current method consists in the passage of an inert gas through a calorimeter, in the supply of heat to maintain a constant temperature, and in the analysis of the product gas. The theory of the method as it applies to the evaporation of pure water was developed by Goff and Hunter (6); they demonstrated that the method is suitable for measuring the latent heat of pure water.

The present work includes determinations of the latent heats and heats of dilution of water in three concentrations of potassium nitrate, four concentrations of calcium chloride, and three con-

centrations of potassium thiocyanate solutions at 30° C. In addition, the partial molal free energies, partial molal entropies, and vapor pressures were calculated for the thiocyanate solutions.

Smith (20) used the gas current method for measuring latent heat of pure water in 1907 and again in 1911. Goff and Hunter (6) explained his results, which were somewhat lower than the National Bureau of Standards values (15), in the light of interaction between air and water vapor molecules; information on the latter was not available at the time of Smith's work. Vrevskii and collaborators (21) studied the latent heats of pure water, aqueous solutions of sulfuric acid, and aqueous solutions of hydrochloric acid by this method.

THEORY

Latent Heat. The theory of the method as described by Goff and Hunter (6) will be reviewed here briefly and extended to include the treatment of salt solutions. The calorimeter is shown schematically in Figure 1. By means of the usual energy and material balances and an equation expressing the constancy of the calorimeter volume, Goff and Hunter (6) derived the following expression:

$$\bar{H}_w - \bar{H}'_w = q + (h_a^\alpha - \bar{H}_a) \frac{n_a}{n_w} - (1 - x) \frac{\bar{V}'_w}{v} q \quad (1)$$

Implied in the derivation of this expression are the following assumptions:

1. The entering air stream is carbon dioxide-free, containing neither water nor salt.
2. There is no salt in the vapor phase in the calorimeter or leaving the vessel.
3. The temperatures of entering and leaving air and of the calorimeter are the same and constant.
4. The pressure is uniform throughout and constant.
5. The quantity of water evaporated is so small that the changes in solution concentration and in solution properties are negligible.
6. There is no accumulation of air in the liquid phase.
7. The relative compositions of the vapor phase and of the leaving vapor stream are the same and constant.

Equation 1 is limited in utility as it stands, because it contains certain partial molal quantities of the vapor and liquid phases which are not known. Present methods of statistical mechanics (11) make possible the evaluation of such quantities for the vapor phase, however. Thus, at low pressure:

$$Pv = RT - [A_{aa}x^2 + 2A_{aw}x(1 - x) + A_{ww}(1 - x)^2]P \quad (2)$$

where x = mole fraction of dry air = $n_a/(n_a + n_w)$

The gas current method for measuring latent heats of vaporization of water from aqueous salt solutions is described, together with the equipment for experimental work. The thermodynamic analysis by which the results are interpreted is presented. This analysis shows that heats of dilution, partial molal free energy, partial molal entropy, and vapor pressure as well as latent heats can be computed from the data obtained. Aqueous solutions of potassium nitrate, calcium chloride, and potassium thiocyanate have been studied at 30° C., and the full list of properties determined for potassium thiocyanate. Only latent heats and heats of dilution are presented for potassium nitrate and calcium chloride. The sign and magnitude of the latent heats are shown to be consistent with those predictable from consideration of heats of solution. The method and equipment should be generally useful and not limited to aqueous solutions.

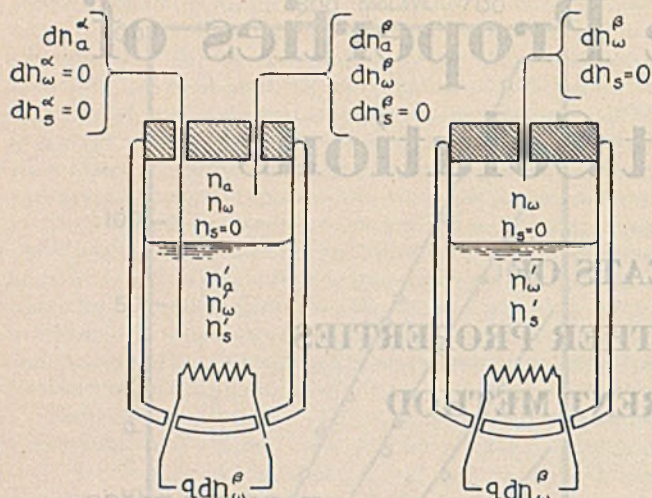


Figure 1. Calorimeter for Gas Current Method

Figure 2. Calorimeter for General Boiling Process

Equation 2 may be solved for v , multiplied by $(n_a + n_w)$ to yield V , and differentiated with respect to n_w at constant P , T , and n_a to yield:

$$\bar{V}_w = \frac{RT}{P} + x^2(A_{aa} - 2A_{aw} + A_{ww}) - A_{ww} \quad (3)$$

As Guggenheim (7) shows,

$$\bar{V}_w = \left(\frac{\partial \mu_w}{\partial P} \right)_{n_w, T} \quad (4)$$

Combining Equations 4 and 3 and integrating,

$$\mu_w = RT \ln P + P[x^2(A_{aa} - 2A_{aw} + A_{ww}) - A_{ww}] + C(T, x) \quad (5)$$

Guggenheim (9) evaluates $C(T, x)$ as follows:

$$C(T, x) = RT \ln(1 - x) + \mu_w^o(T) \quad (6)$$

where $\mu_w^o(T)$ = chemical potential of water in pure state at T

By combining Equations 6 and 5, a complete expression for μ_w results:

$$\mu_w = RT \ln P(1 - x) + P[x^2(A_{aa} - 2A_{aw} + A_{ww}) - A_{ww}] + \mu_w^o(T) \quad (7)$$

Equation 7 can be divided by T and differentiated with respect to T at constant P and x to yield:

$$\frac{-\mu_w + T \frac{\partial \mu_w}{\partial T}}{T^2} = Px^2 \left[\frac{d \frac{A_{aa}}{T}}{dT} - 2 \frac{d \frac{A_{aw}}{T}}{dT} + \frac{d \frac{A_{ww}}{T}}{dT} \right] - \frac{d \frac{\mu_w^o(T)}{T}}{dT} \quad (8)$$

This equation can be simplified by multiplying through by $(-T^2)$ and observing that, according to Guggenheim (8),

$$h_w^o = -T^2 \left[\frac{d \frac{\mu_w^o(T)}{T}}{dT} \right] \quad (9)$$

and by calling

$$-T^2 \frac{d \frac{A_{aa}}{T}}{dT} = B_{aa} \quad (10)$$

$$-T^2 \frac{d \frac{A_{aw}}{T}}{dT} = B_{aw} \quad (10A)$$

$$-T^2 \frac{d \frac{A_{ww}}{T}}{dT} = B_{ww} \quad (10B)$$

to yield:

$$\mu_w - T \frac{\partial \mu_w}{\partial T} = Px^2 [B_{aa} - 2B_{aw} + B_{ww}] - PB_{ww} + h_w^o(T) \quad (11)$$

$$\text{Since } \mu_w - T \frac{\partial \mu_w}{\partial T} = -T^2 \frac{\partial \left(\frac{\mu_w}{T} \right)}{\partial T} = \bar{H}_w \quad (12)$$

$$\text{and since } (B_{aa} - 2B_{aw} + B_{ww}) \text{ can be called } B \quad (13)$$

Equation 11 may be written:

$$\bar{H}_w = Px^2B - PB_{ww} + h_w^o(T) \quad (14)$$

Equation 14 assumes no enthalpy change due to mixing at zero pressure. In order to eliminate $h_w^o(T)$, Equation 14 can be solved for the condition of pure saturated water vapor, at which $\bar{H}_w = h_w^{sat}$ (molal enthalpy of saturated water vapor), $P = p_s$ (saturation pressure), and $x = 0$. Subtracting from Equation 14,

$$\bar{H}_w = h_w^{sat} + Px^2B - (P - p_s)B_{ww} \quad (15)$$

which is a complete and general expression for \bar{H}_w .

By the same methods Equation 2 may be multiplied by $(n_a + n_w)$, differentiated with respect to n_a at constant P , T , and n_w , and similarly treated to yield the corresponding relation for \bar{H}_a :

$$\bar{H}_a = h_a^o + (1 - x)^2BP \quad (16)$$

where h_a^o = enthalpy of dry air at entrance condition of calorimeter

Equation 16 also assumes no enthalpy change due to mixing at zero pressure.

Equations 15 and 16 may be substituted in 1 to yield:

$$(h_w^{sat} - \bar{H}_w') = q + B_{ww}(P - p_s) - xBP - (1 - x) \frac{V_w'}{v} q \quad (17)$$

This equation is much more useful than Equation 1 because all terms are measurable or easily estimable.

Goff and Hunter (6) applied Equation 17 only to pure water. Under such conditions, if the solubility of air in water is neglected, \bar{H}_w' becomes equal to h_w' , V_w' becomes v_w' , and Equation 17 simplifies to

$$r_w = h_w^{sat} - h_w' = q + B_{ww}(P - p_s) - xBP - (1 - x) \frac{v_w'}{v} q \quad (17A)$$

where r_w is the latent heat of water. In the present work, however, the limitation of pure water will be removed and the assumption of no air solubility will be retained.

To show the utility of Equation 17, it is necessary to consider the more general case of boiling an aqueous solution in which no air is present—i.e., the normal boiling operation. Considering the schematic representation of Figure 2:

A material balance yields:

$$dn_w^e + dn_w + dn_w^e = 0 \quad (18)$$

An energy balance (neglecting concentration change of salt) is:

$$-q dn_w^e + \bar{E}_w' dn_w^e + e_w dn_w + h_w dn_w^e = 0 \quad (19)$$

The expression for constancy of total volume is:

$$v_w dn_w + \bar{V}_w' dn_w^e = 0 \quad (20)$$

Solving these simultaneously and making the same assumptions as before except those relating to the presence of air,

$$r_w = q = \left(\frac{h_w - \bar{H}_w'}{1 - \frac{\bar{V}_w'}{v_w}} \right) \quad (21)$$

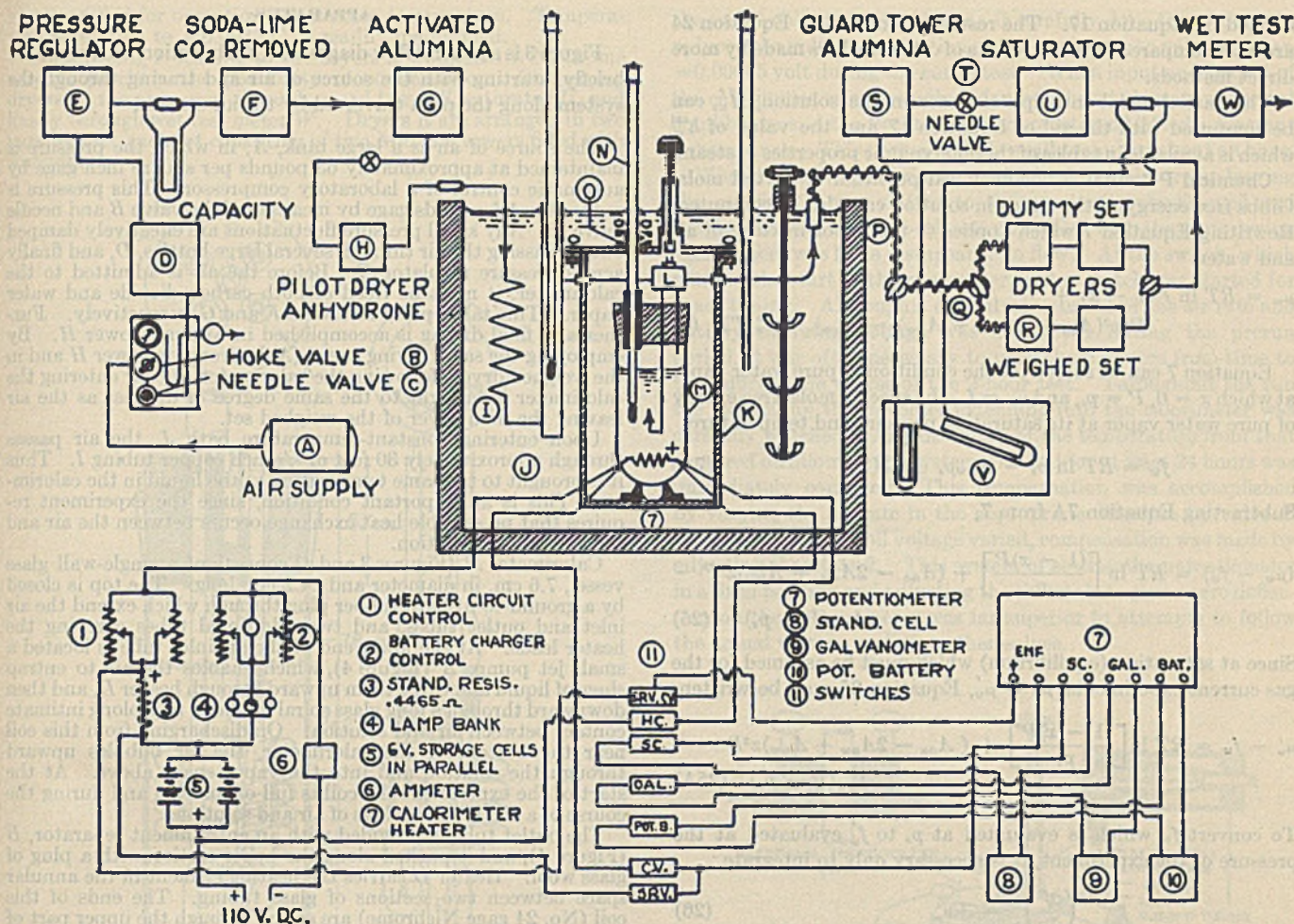


Figure 3. Assembly Diagram of Apparatus

where r_{ss} denotes the latent heat of water from the salt solution. Thus the latent heat of vaporization in the normal case is equal to $(h_w - \bar{H}'_w)$ multiplied by the correction factor above. Since \bar{V}'_w/v_w is a very small number, even if the liquid solution is far from ideal, the denominator is 1 for all practical purposes. It must be observed, however, that h_w in Equation 21 differs slightly from h_w^{sat} of Equation 17. The latter is evaluated at the vapor pressure of pure water at the temperature of the experiment, whereas the former is evaluated at the pressure of water vapor over the solution at the temperature of the experiment. Similarly \bar{H}'_w differs slightly from Equation 17 to Equation 21. In the former case it is evaluated at the temperature of the experiment and one atmosphere; in the latter, at the temperature of the experiment and the vapor pressure over the solution. Since the effect of pressure on the enthalpy of condensed phases is so small, and since the very small pressure difference acting on the gaseous enthalpy should also exert only a small effect, it is apparent that $(h_w^{sat} - \bar{H}'_w)$ defined by Equation 17 is, for practical purposes, the latent heat of vaporization. For this reason it is so called throughout this work; but we should bear in mind that the property computed and called "latent heat" is truly $(h_w^{sat} - \bar{H}'_w)$.

Equation 17 is therefore used throughout for the calculation of latent heat. In the last term of the equation \bar{V}'_w has been assumed equal to v_w for lack of better information and because this term is extremely small in magnitude.

The quantity q was measured in this work. Terms B and B_{ws} must be evaluated from other sources which can give insight into the interaction between air and water vapor molecules. Goff and Hunter (6) presented values of A_{as}/RT , B_{as}/RT , A_{ws}/RT , B_{ws}/RT , and B/RT . The first two were computed from the

equation of Beattie and Bridgeman (2) and the next two from that of Keyes (14). The last was computed from Equation 13 and the expression,

$$\lambda(T) = \frac{2A_{aw}}{A_{as} + A_{ws}} = 0.075 \pm 0.005 \quad (22)$$

inferred by Goff and Bates (5) from the data of Pollitzer and Strebel (18) and corroborated by Bates (1) and Goff and Bates (5). Thus all terms are known and r_{ss} can be determined from the measured value of q .

Apparently the first work in this country on such interaction in the vapor phase was carried out by Gillespie, Gerry, and Fraser (4A) with the system iodine vapor-air.

Heat of Dilution and Partial Molal Enthalpy. It is possible to compute the differential heat of dilution as follows: Consider a solution containing n_s moles of salt and n_w moles of water, the enthalpy of which is H' . If dn_w moles of water of enthalpy h'_w are added, the increase in enthalpy of the solution is $\left(\frac{\partial H'}{\partial n_w}\right)_{P,T,n_s}$ or \bar{H}'_w . If q_d represents the heat added to maintain constant temperature per mole of water added (the differential heat of dilution), an energy balance yields the expression:

$$q_d = \bar{H}'_w - h'_w \quad (23)$$

This can be related to Equations 17 and 17A as follows:

$$q_d = \bar{H}' - h'_w = (h_w^{sat} - h'_w) - (h_w^{sat} - \bar{H}'_w) \quad (24)$$

The first parenthetic expression is the latent heat of vaporization of pure water at the temperature in question, and the second is

defined by Equation 17. The results calculated by Equation 24 are later compared with the results of other workers made by more direct methods.

The partial molal enthalpy of water in the solution, \bar{H}_w , can be computed with the aid of Equation 17 and the value of h_w^* which is available in tables of thermodynamic properties of steam.

Chemical Potential. The chemical potential or partial molal Gibbs free energy of the water in solution can also be computed. Rewriting Equation 7 which applies to the vapor mixture of air and water:

$$\mu_w = RT \ln P(1-x) + P[x^2(A_{aa} - 2A_{aw} + A_{ww}) - A_{ww}] + \mu_w^*(T) \quad (7)$$

Equation 7 can be solved for the condition of pure water vapor at which $x = 0$, $P = p_s$, and $\mu_w = f_w$, the specific molal free energy of pure water vapor at its saturation pressure and temperature:

$$f_w = RT \ln p_s - A_{ww}p_s + \mu_w^*(T) \quad (7A)$$

Subtracting Equation 7A from 7,

$$(\mu_w - f_w) = RT \ln \left[\frac{(1-x)P}{p_s} \right] + (A_{aa} - 2A_{aw} + A_{ww})x^2P - A_{ww}(P - p_s) \quad (25)$$

Since at saturation (equilibrium) which must be assumed for the gas current experiments, $\mu_w = \mu_w'$, Equation 25 may be written:

$$\mu_w' - f_w = RT \ln \left[\frac{(1-x)P}{p_s} \right] + (A_{aa} - 2A_{aw} + A_{ww})x^2P - A_{ww}(P - p_s) \quad (25A)$$

To convert f_w which is evaluated at p_s to f_w' evaluated at the pressure of the experiment, it is necessary only to integrate,

$$\left(\frac{\partial f}{\partial p} \right)_T = +v_w' \quad (26)$$

where v_w' is the specific molal volume of pure liquid water, to obtain:

$$f_w = f_w' - v_w'(P - p_s) \quad (27)$$

$$\mu_w' - f_w' = RT \ln \left[\frac{(1-x)P}{p_s} \right] + (A_{aa} - 2A_{aw} + A_{ww})x^2P - (A_{ww} + v_w')(P - p_s) \quad (28)$$

This equation permits the calculation of the difference between chemical potential and specific molal Gibbs free energy at the temperature and pressure of the experiment.

Partial Molal Entropy. The partial molal entropy can also be computed by the basic thermodynamic relation,

$$\bar{S}_w' - s_w' = \frac{(\bar{H}_w' - h_w') - (\mu_w' - f_w')}{T} \quad (29)$$

Substituting the value of the second parenthetic expression as defined by Equation 28,

$$\bar{S}_w' - s_w' = \frac{(\bar{H}_w' - h_w') - RT \ln \left[\frac{(1-x)P}{p_s} \right] - (A_{aa} - 2A_{aw} + A_{ww})x^2P + (A_{ww} + v_w')(P - p_s)}{T} \quad (30)$$

by which the partial molal entropy can be calculated.

Vapor Pressure. This property can also be determined with the gas current method. The usual expression for the vapor pressure as measured in this way is

$$p_w = (1-x)P \quad (31)$$

even though this expression neglects the effect of intermolecular forces in the vapor (5). Since Equation 31 has been so widely used, however, it will be used here. Again, the attainment of equilibrium must be assumed.

APPARATUS

Figure 3 is a general flow diagram. Each section will be treated briefly, starting with the source of air and tracing through the system along the path traversed by the air stream.

The source of air is a large tank, *A*, in which the pressure is maintained at approximately 63 pounds per square inch gage by automatic control of a laboratory compressor. This pressure is reduced to 1.5 pounds gage by means of Hoke valve *B* and needle valve *C*. Any small pressure fluctuations are effectively damped out by passing the air through several large bottles, *D*, and finally across pressure regulator *E*. Before the air is admitted to the calorimeter, it must be freed of both carbon dioxide and water vapor. This takes place in towers *F* and *G*, respectively. Further and final drying is accomplished in Midvale tower *H*. By employing the same drying agent (Anhydron) in tower *H* and in the weighed dryers following the calorimeter, the air entering the calorimeter is brought to the same degree of dryness as the air leaving the final dryer of the weighed set.

Upon entering constant-temperature bath *J*, the air passes through approximately 30 feet of 1/4-inch copper tubing *I*. Thus it is brought to the same temperature as the liquid in the calorimeter. This is an important condition, since the experiment requires that no sensible heat exchange occurs between the air and the calorimeter solution.

Calorimeter *M* (Figures 3 and 4) consists of a single-wall glass vessel, 7.6 cm. in diameter and 24.2 cm. long. The top is closed by a ground-to-fit hard rubber plug through which extend the air inlet and outlet tubes, and two additional tubes carrying the heater leads. At the lower end of the air inlet tube is located a small jet pump, *A* (Figure 4), which enables the air to entrap slugs of liquid and carry them upward through heater *D*, and then downward through a long glass spiral intended to prolong intimate contact between air and solution. On discharging from this coil near the bottom of the calorimeter, the air bubbles upward through the solution and into the vapor space above. At the start of the experiment the coil is full of solution and during the course of a run is full of slugs of air and solution.

The outlet tube is provided with an entrainment separator, *B* (Figure 4), and is packed along the upper section with a plug of glass wool. Heater *D* carries the heating element in the annular space between two sections of glass tubing. The ends of this coil (No. 24 gage Nichrome) are sealed through the upper part of the glass tubes, and the annular space is filled with a heat transfer liquid (Aroclor). The free ends of the coil extend into vertical tubes *C*. These extend through the hard rubber plug but are filled with mercury to the level of the solution in the calorimeter. One other opening is provided in the top of the calorimeter, which carries a short section of soft rubber tubing serving to seal the stem of a Beckmann thermometer extending into the solution.

To provide more perfect adiabatic operation, the calorimeter is maintained in an air bath within a metal submarine (Figure 5). Four thin Bakelite supports center the calorimeter within the submarine, while several concentric cylinders of aluminum foil minimize thermal losses by convection and radiation between the calorimeter and the submarine wall. Near the top of the submarine is a four-way valve which can either direct the air stream into, or by-pass it around, the calorimeter. Copper tubing leads from this valve pass through the walls of the submarine and connect on one side to the tempering coil and on the other to the glass tubing leading to the dryers.

The top of the submarine is removable, but a watertight seal is provided by means of a rubber gasket and six equally placed thumbscrews. Projecting through this top are two small hollow copper tubes, *A*. These terminate at their upper ends in one section of a coaxial cable connection, *B*, and carry inside an insulated wire. The lower ends of these tubes dip into the mercury leads from the heater and are joined at this point to the insulated potential lead wires. The current is supplied through the copper

tube walls, and the voltage across the heater (at the mercury pools) is measured through these insulated potential lead wires inside the copper tubes. This ensures an exact determination of the energy input to the calorimeter. In addition, the submarine top carries a device for manipulating the four-way valve from the surface of the bath, and a watertight seal through which the stem of the Beckmann thermometer passes. The submarine is maintained at constant temperature by complete submergence in bath *J* (Figure 3). The temperature of this bath is regulated in the usual manner by a glass thermoregulator filled with alcohol over mercury. A Cenco supersensitive relay and a suitable resistance heater comprise the auxiliary equipment. A cooling coil is

also provided for operation below room temperature. Temperature regulation to $\pm 0.003^\circ \text{C.}$ is readily maintained.

Glass tubing *P* leading to the dryers is wound with Nichrome wire to preclude the possibility of condensation. On leaving dryers *R*, the air passes through guard tower *S*, saturator *U*, and finally through wet test meter *W*. Dryers *R* are arranged in two parallel sets, each set consisting of two Midvale towers filled with Anhydron.

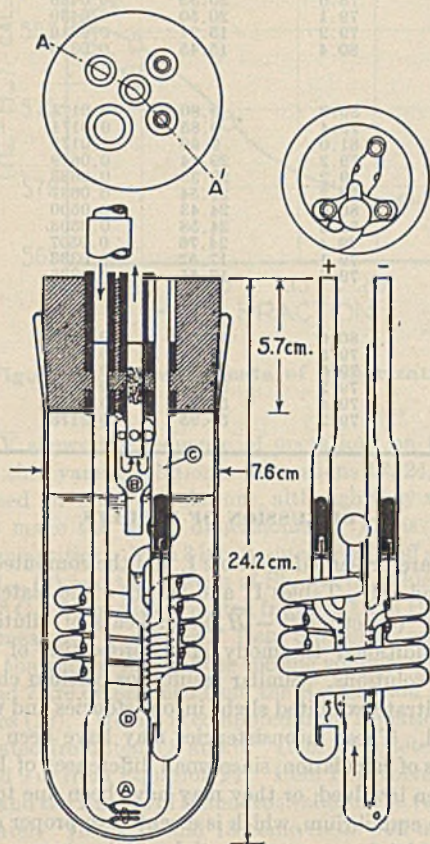


Figure 4. Glass Calorimeter

The electrical circuit (Figure 3) consists of the calorimeter heater, 7, two 15-ohm control rheostats, 1, connected in parallel, a standard resistance, 3, two battery-charging control rheostats, 2, and two 6-volt storage batteries, 5, in parallel. The standard resistance is a manganin coil having a resistance of 0.4465 ± 0.0001 international ohm as certified by the National Bureau of Standards. To maintain a constant voltage, the storage cells are continuously charged during the experiment, as nearly as possible at the same rate at which they discharge through the heater.

Voltage measurements across the heating coil and across the standard resistance are made with a type K Leeds & Northrup potentiometer, a Weston standard cell, and a suitable galvanometer.

Since only the time rate of supplying electrical energy to the calorimeter is measured, it is necessary to determine accurately the time during which water vapor is collected in the dryers. For this purpose a good laboratory stop watch is used; the necessary correction is obtained by comparing it with an electric clock over a number of 2-hour intervals.

GAS CURRENT METHOD

Before an experiment was begun, the practice was to precondition the adsorption towers by blowing them for an hour with dry air by-passing the calorimeter. Then a prerin period was started in which the dry air was sent through the calorimeter and into the dummy adsorption towers; the preconditioned towers were weighed in the interval. During this period it was necessary to balance the electrical input and the energy output for vaporization by varying both the air rate and the heater voltage. This balancing was accompanied by adjustment of the voltage across

the two 6-volt storage batteries; if carefully done this procedure reduced the voltage fluctuation across the heater to not more than ± 0.00005 volt during the entire test. When input and output of the calorimeter were properly balanced, the whole was in thermal equilibrium and the Beckmann thermometer exhibited a constant temperature. This prerin period usually required about an hour.

When thermal equilibrium was attained, the air stream leaving the calorimeter was shifted to the previously conditioned and weighed towers. Since both sets were filled with the same drying agent, there was little disturbance to flow. At the switch, which marked the start of the run proper, a stop watch was started for exact timing. Although a careful adjustment of the air rate and battery charging voltage was attempted during the prerin period, it was often necessary to vary these factors from time to time during the course of the 2-hour test. Throughout the run the Beckmann thermometer extending into the calorimeter was carefully watched. Any deviation of the temperature from that acquired on allowing the system to stand for at least 24 hours was immediately corrected. This compensation was accomplished by varying the air rate in the appropriate direction by valve *T* (Figure 3). If the coil voltage varied, compensation was made by adjusting rheostats 2. This system of setting the potentiometer in a fixed position and adjusting the rheostats to give a zero deflection on the galvanometer was far superior to attempts to follow the actual voltage variations themselves.

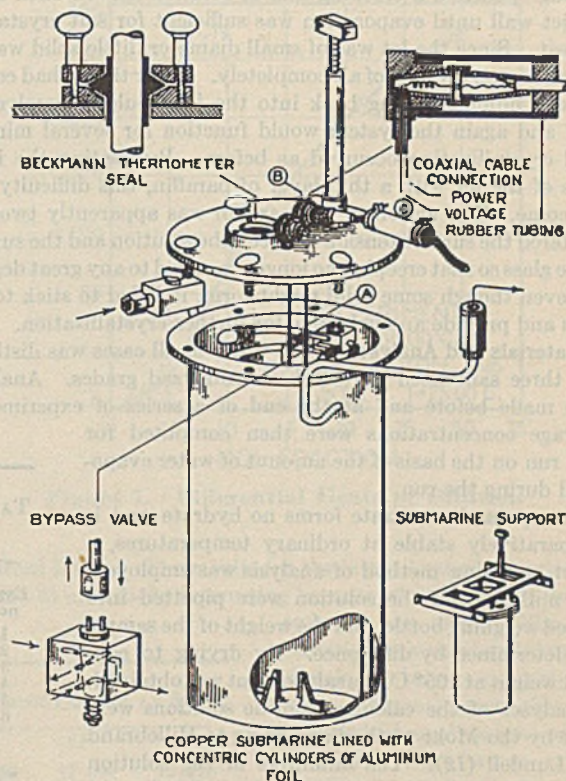


Figure 5. Metal Submarine

During the experiment voltage readings across the calorimeter heater and across the standard resistance were made at 15-minute intervals throughout the 2-hour period. These data, in conjunction with the time measurement as read from the stop watch and the resistance of the standard coil, constituted the information required for an energy accounting.

Although numerous difficulties were encountered throughout this work, particular mention should be made of one. This occurred only in the case of salt solutions and resulted from the deposition of salt in the small glass jet pump in the calorimeter.

TABLE I. TEST DATA ON SALT SOLUTIONS AT 30° C.

Expt. No.	Duration, Sec.	Heater Voltage	Standard Resistance Voltage	Water Collected, Grams	Wet Test Meter		Calorimeter Pressure, Cm. Hg	Av. Salt Concn.		
					Cu. ft.	° F.		%	Mole fraction	Molality
Potassium Nitrate										
1	7319.2	0.64857	0.62634	2.7541	3.4000	77	79.4	10.20	0.0198	1.123
2	7233.2	0.64768	0.62650	2.7101	3.3000	74	79.1	10.28	0.0200	1.133
3	7268.6	0.63403	0.61227	2.6165	3.3000	74	78.0	20.35	0.0436	2.527
4	7163.2	0.63812	0.61612	2.6172	3.3000	75	79.1	20.50	0.0439	2.550
5	7251.4	0.63740	0.61554	2.6361	3.3000	76	79.2	15.21	0.0310	1.774
6	7286.1	0.63955	0.61759	2.6685	3.3000	67	80.4	15.45	0.0315	1.807
Calcium Chloride										
7	7675.8	0.63071	0.60898	2.7214	3.3000	78	80.8	9.80	0.0173	0.9739
8	7361.1	0.63041	0.60846	2.5987	3.3000	77	79.4	9.85	0.0174	0.9844
9	7329.1	0.63126	0.60948	2.5938	3.3000	73	81.0	9.90	0.0175	0.9900
10	7492.1	0.53997	0.52163	1.9294	3.5000	77	79.2	29.24	0.0629	3.723
11	7241.0	0.53927	0.52094	1.8517	3.4000	80	79.2	29.39	0.0633	3.750
12	7407.5	0.53836	0.52000	1.8866	3.5000	80	79.3	29.54	0.0637	3.777
13	7196.8	0.55996	0.54087	1.9941	3.2000	81	80.6	24.43	0.0500	2.913
14	7342.6	0.56037	0.54121	2.0431	3.4000	88	81.3	24.58	0.0503	2.936
15	7193.4	0.56041	0.54125	1.9985	3.3000	89	79.4	24.76	0.0507	2.965
16	7252.6	0.59768	0.57722	2.3053	3.3000	89	79.1	17.52	0.0333	1.914
17	7286.9	0.59650	0.57610	2.3036	3.3000	87	79.6	17.65	0.0336	1.931
Potassium Thiocyanate										
18	7183.9	0.61498	0.59390	2.4271	3.3000	84	80.6	19.95	0.0442	2.565
19	7358.8	0.61318	0.59210	2.4711	3.4000	92	79.5	20.14	0.0447	2.595
20	7210.5	0.57041	0.55090	2.1150	3.3000	84	79.0	39.74	0.1090	6.787
21	7239.0	0.57069	0.55115	2.1244	3.3000	81	79.2	39.97	0.1095	6.852
22	7169.2	0.49660	0.47957	1.6079	3.4000	86	79.4	59.63	0.2150	15.201
23	7203.9	0.49455	0.47760	1.6029	3.4000	88	79.2	59.95	0.2173	15.405

During operation a creeping film of solution moved back along the jet wall until evaporation was sufficient for salt crystals to deposit. Since the jet was of small diameter, little solid was required to stop the flow of air completely. After the air had ceased to flow, liquid creeping back into the jet would redissolve the solid and again the system would function for several minutes until crystallization occurred as before. By coating the inner walls of the jet with a thin layer of paraffin, this difficulty was overcome. The action of the paraffin was apparently twofold: It altered the surface tension between the solution and the surface of the glass so that creeping no longer occurred to any great degree; and even though some solid might form, it failed to stick to the walls and provide an anchorage for further crystallization.

Materials and Analyses. The water in all cases was distilled. The three salts used were Baker's Analyzed grades. Analyses were made before and at the end of a series of experiments. Average concentrations were then computed for each run on the basis of the amount of water evaporated during the run.

Since potassium nitrate forms no hydrate and is comparatively stable at ordinary temperatures, a direct weighing method of analysis was employed. Ten milliliters of the solution were pipetted into a tared weighing bottle, and the weight of the sample was determined by difference. By drying to constant weight at 105° C. the salt content was obtained.

Analyses of the calcium chloride solutions were made by the Mohr method according to Hillebrand and Lundell (12). Ten milliliters of the solution were weighed into a tared weighing bottle and diluted to 500 ml. in a volumetric flask; 100 ml. of this solution were titrated with 0.1 *N* silver nitrate, using 2 ml. of 1% potassium dichromate as indicator.

The Volhard method for silver as given by Hillebrand and Lundell (12) was employed for potassium thiocyanate solutions. Ten milliliters were pipetted into a tared weighing bottle and diluted to 500 ml. in a volumetric flask. A solution of 0.1 *N* silver nitrate containing an indicator was titrated to a permanent pink color with this diluted solution. The indicator employed was a saturated solution of ferric ammonium sulfate, acidified with concentrated nitric acid.

DISCUSSION OF RESULTS

The data are presented in Table I, and the computed results in Tables II and III. Tables II and III show the "latent heats of vaporization" (strictly $h_{\text{vap}}^{\text{cal}} - \bar{H}_w$) and heats of dilution; Table III gives additional thermodynamic properties of potassium thiocyanate solutions. Similar results for calcium chloride and potassium nitrate exhibited slight inconsistencies and were therefore omitted. These inconsistencies may have been due to inherent errors of calculation, since small differences of large numbers are often involved, or they may have been due to failure to attain phase equilibrium, which is essential to proper calculation of partial molal free energy, partial molal entropy, and vapor pressure. It should be emphasized that the attainment of equilibrium is not required for the latent heat and heat of dilution determinations.

TABLE II. HEATS OF VAPORIZATION AND DILUTION OF SALT SOLUTIONS AT 30° C.

Potassium Nitrate				Calcium Chloride			
Expt. no.	Concn., mole fraction	Heat of vaporization ^a	Heat of dilution ^b	Expt. no.	Concn., mole fraction	Heat of vaporization ^a	Heat of dilution ^b
1	0.0198	578.4	+32.2	7	0.0173	580.5	-4.7
2	0.0200	579.3	+16.0	8	0.0174	581.9	-30.5
3	0.0436	577.8	+43.9	9	0.0175	582.5	-41.1
4	0.0439	577.0	+58.8	10	0.0629	586.0	-103.1
5	0.0310	578.3	+39.2	11	0.0633	588.5	-149.2
6	0.0315	577.9	+42.9	12	0.0637	588.8	-155.0
				13	0.0500	585.6	-95.9
				14	0.0503	584.0	-67.0
				15	0.0507	584.9	-84.3
				16	0.0333	581.5	-23.0
				17	0.0336	582.4	-39.4

^a $h_{\text{vap}}^{\text{cal}} - \bar{H}_w$, in cal. per gram H_2O .

^b $\bar{H}_w - h_w$, in cal. per mole H_2O .

TABLE III. THERMODYNAMIC PROPERTIES OF POTASSIUM THIOCYANATE SOLUTIONS AT 30° C.

Expt. No.	Concn., Mole Fraction	Heat of Vaporization ^a	Heat of Dilution ^b	Partial Molal Free Energy of Water ^c	Partial Molal Entropy of Water ^d	Vapor Pressure ^e
18	0.0442	579.2	+17.8	-61.5	+0.26	28.90
19	0.0447	579.3	+16.7	-61.8	+0.26	28.80
20	0.1090	574.0	+112.8	-153.4	+0.88	24.80
21	0.1095	574.2	+108.4	-155.1	+0.87	24.70
22	0.2150	568.8	+205.3	-324.8	+1.75	18.65
23	0.2173	568.7	+208.4	-324.1	+1.76	18.65

^a $h_{\text{vap}}^{\text{cal}} - \bar{H}_w$, in cal. per gram H_2O .

^b $\bar{H}_w - h_w$, in cal. per mole H_2O .

^c $\mu_w - \mu_w^0$, in cal. per mole H_2O .

^d $\bar{S}_w - s_w^0$, in cal. per mole H_2O per ° K.

^e $p_w = (1 - z)P$, in mm. Hg.

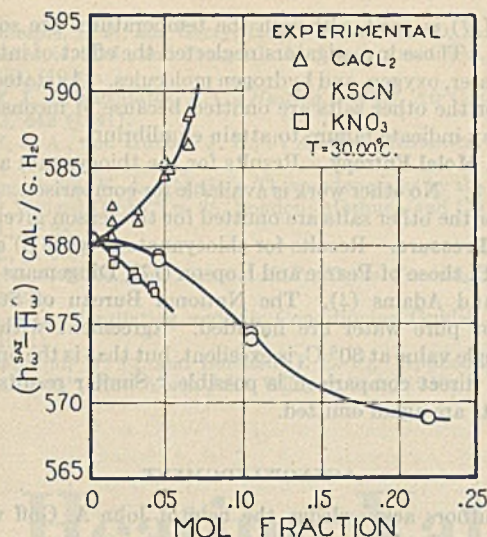


Figure 6. Latent Heats of Vaporization

Table IV shows the sequence of operations on the data for potassium thiocyanate solutions. Equations 17, 24, 28, 30, and 31 were used for these calculations, although they were divided by RT to make the terms dimensionless. Items 1 and 2 are measured quantities. Item 3 is computed from Goff and Hunter's value of B_{ww} (6) and the Bureau of Standards value of p_s , 31.80 mm. at 30° C. Item 4 is computed from Goff and Hunter's value of B and measured quantities. Item 5 involves only measured terms and the known value of the specific volume of liquid water. Items 6 and 7 are determined from the Keenan and Keyes steam table values (13). Item 8 is computed from Equation 17. Item 9 is calculated from items 8 and 6. Item 10 is determined from items 7 and 9 or from Equation 24. Item 11 involves only measured data and the Bureau of Standards value of the vapor pressure of pure water. Items 12 and 13 come from Goff and Hunter's values of the second virial coefficients and the interaction constant. Item 14 is calculated from the Keenan and Keyes steam table value (13) of v'_w and the Bureau of Standards value of p_s . Item 15 is computed with Equation 28, item 16 with Equation 30, and item 17 with Equation 31.

The latent heat results are presented graphically in Figure 6, those for the differential heat of dilution in Figure 7 and those for the chemical potential, partial molal entropy, and vapor pressure of potassium thiocyanate in Figure 8. Whenever possible, data of other workers are included, but the curves are drawn to weigh only the authors' points.

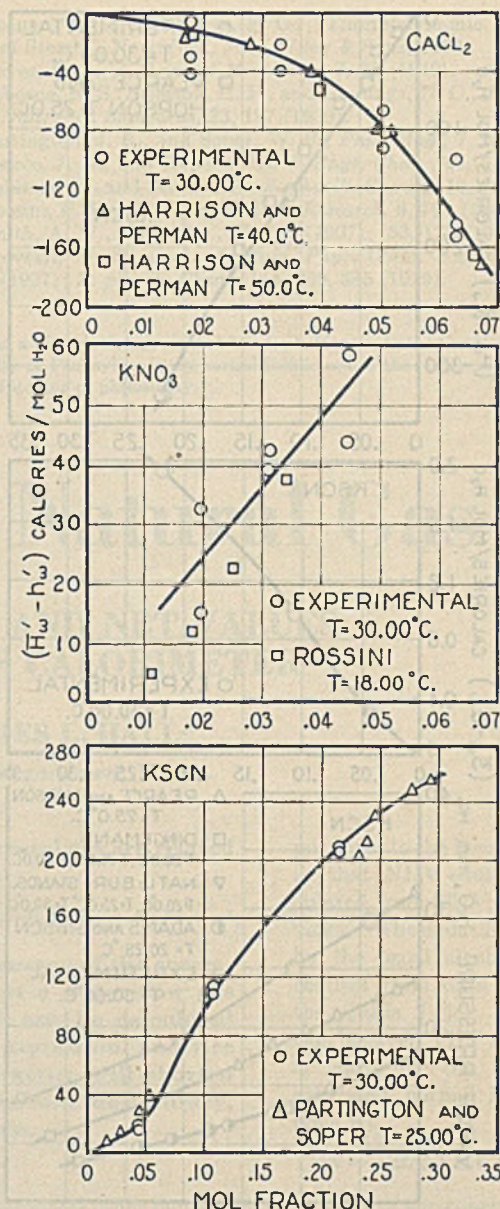


Figure 7. Differential Heats of Dilution

Latent Heats. The results for the latent heat of vaporization (Figure 6) are chiefly interesting because of the sign and magnitude of the effect. The two materials which absorb heat on dissolution behave similarly and quite differently from that material which evolves heat on dissolution. The former exhibit smaller latent heats than pure water, and the latter exhibits larger. The reduction of latent heat of water from a potassium thiocyanate solution of about 0.22 mole fraction thiocyanate below that of pure water is about 2%. The sign of these effects is in conformity with what one would predict from a consideration of the heat of solution. If solution is accompanied by the evolution of heat, the solution must possess less energy than it

TABLE IV. REDUCTION OF TEST DATA FOR SOLUTIONS OF POTASSIUM THIOCYANATE AT 30° C.

Item No.	Operation	Experiment Number					
		18	19	20	21	22	23
1	q/RT	17.307	17.310	17.152	17.159	17.000	16.995
2	$x = n_a/(n_a + n_w)$	0.9642	0.9637	0.9686	0.9688	0.9765	0.9764
3	$B_{ww}(P - p_s)/RT$	0.2959	0.2916	0.2897	0.2905	0.2913	0.2905
4	xBP/RT	0.2771	0.2732	0.2729	0.2736	0.2765	0.2758
5	$(1 - x)v'_w q/RT$	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
6	h'_w/RT^*	18.2529	18.2529	18.2529	18.2529	18.2529	18.2529
7	h_w/RT^{**}	0.8978	0.8978	0.8978	0.8978	0.8978	0.8978
8	$(h'_w - \bar{H}_w)$, cal./g. H ₂ O	579.2	579.3	574.0	574.2	568.8	568.7
9	\bar{H}_w/RT	0.9274	0.9255	1.0851	1.0778	1.2386	1.2437
10	$(\bar{H}_w - h'_w)$, cal./mole H ₂ O	+17.8	+16.7	+112.8	+108.4	+205.3	+208.4
11	$\ln(1 - x)P/p_s$	-0.0965	-0.0971	-0.2496	-0.2524	-0.5348	-0.5336
12	$(A_{as} - 2A_{aw} + A_{ww})x^2P/RT$	0.0434	0.0427	0.0429	0.0430	0.0438	0.0437
13	$A_{ww}(P - p_s)/RT$	0.0481	0.0474	0.0471	0.0473	0.0474	0.0475
14	$v'_w(P - p_s)/RT$	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
15	$(\mu_w - f_w)$, cal./mole H ₂ O	-61.5	-61.8	-153.4	-155.1	-324.8	-324.1
16	$(\bar{S}_w - s_w)$, cal./mole H ₂ O, °K.	+0.26	+0.26	+0.88	+0.87	+1.75	+1.76
17	$(1 - x)P$, mm. Hg	28.90	28.80	24.80	24.70	18.65	18.65

* The enthalpy of pure water vapor at 30° C. (13).

** The enthalpy of pure liquid water at 30° C. (13).

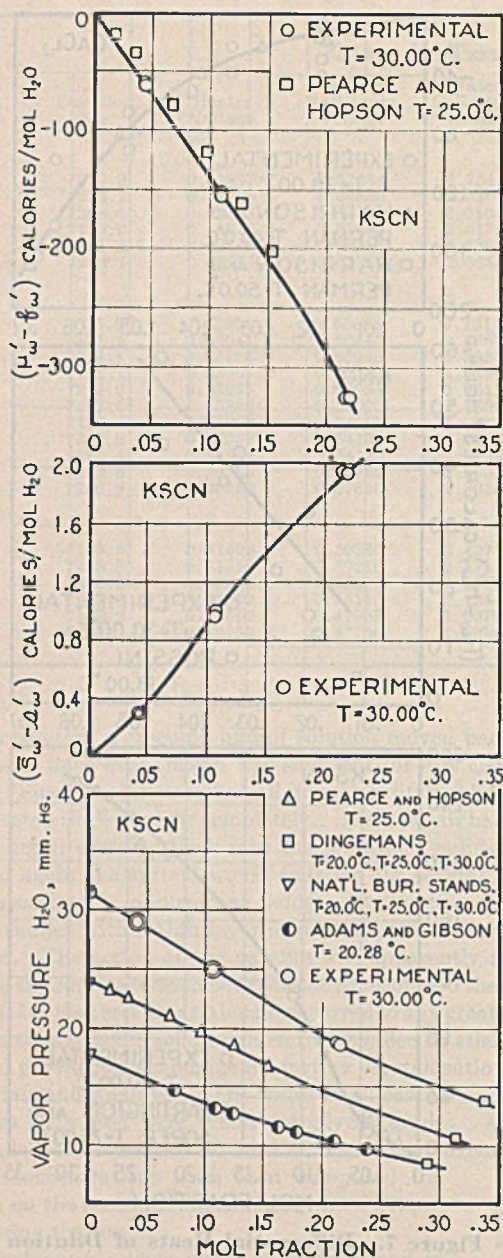


Figure 8. Chemical Potential, Partial Molal Entropy, and Vapor Pressure of Potassium Thiocyanate Solutions

original components; therefore more energy will be required to remove the water.

Heats of Dilution. The differential heats of dilution in Figure 7 reflect the difference between the latent heats of pure water and of water from salt solutions. Agreement between the present results for calcium chloride and those of Harrison and Perman (10) is good, although the temperatures are not strictly comparable. The agreement between the present results for potassium thiocyanate and those of Partington and Soper (16) is excellent, although again the temperatures are not exactly the same. Some disagreement between the present results for potassium nitrate and those of Rossini (19) can be observed, and the latter seem a little more self-consistent. This is undoubtedly due to the small magnitude of the effect and the inherent error of the present method of evaluation which involves the small difference of two large numbers.

Chemical Potential. Agreement of these data ($\mu'_w - f'_w$) for potassium thiocyanate (Figure 8) with the results of Pearce and

Hopson (17) is good, although the temperatures are somewhat different. Those investigators neglected the effect of interaction among water, oxygen, and hydrogen molecules. As stated before, results for the other salts are omitted because of inconsistencies which may indicate failure to attain equilibrium.

Partial Molal Entropy. Results for the thiocyanate are given in Figure 8. No other work is available for comparison. Similar results for the other salts are omitted for the reason given above.

Vapor Pressure. Results for thiocyanate (Figure 8) are compared with those of Pearce and Hopson (17), Dingemans (3), and Gibson and Adams (4). The National Bureau of Standards values for pure water are included. Agreement with Dingemans' single value at 30° C. is excellent, but that is the only point at which direct comparison is possible. Similar results for the other salts are again omitted.

ACKNOWLEDGMENT

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NOMENCLATURE

- A_{aa} = second virial coefficient of air (function of temperature only)
 A_{aw} = interaction constant for air-water (function of temperature only)
 A_{ww} = second virial coefficient for water vapor (function of temperature only)
 $B_{aa} = -T^2 \frac{d}{dT} \left(\frac{A_{aa}}{T} \right)$
 $B_{aw} = -T^2 \frac{d}{dT} \left(\frac{A_{aw}}{T} \right)$
 $B_{ww} = -T^2 \frac{d}{dT} \left(\frac{A_{ww}}{T} \right)$
 $B = B_{aa} - 2B_{aw} + B_{ww}$
 e = specific energy, cal./mole
 \bar{E} = partial molal energy, cal./mole
 f = specific free energy, cal./mole
 h = specific enthalpy, cal./mole
 H = total enthalpy, cal.
 \bar{H} = partial molal enthalpy, cal./mole
 $\lambda(T)$ = dimensionless interaction constant = $2A_{aw}/(A_{aa} + A_{ww})$
 μ = chemical potential, cal./mole
 n = amount of material, moles
 P = absolute total pressure within calorimeter, kg./sq. cm. or mm. Hg
 p_s = saturation pressure of pure water, kg./sq. cm. or mm. Hg
 q = electrical energy supplied to calorimeter, cal./mole water evaporated
 q_d = differential heat of dilution, cal./mole water
 r_w = latent heat of pure water, cal./mole
 r_{ss} = latent heat of water from salt solutions, cal./mole
 R = gas constant
 s = specific entropy, cal./mole/° K.
 \bar{S} = partial molal entropy, cal./mole/° K.
 T = absolute temperature, ° K.
 v = specific molal volume
 \bar{V} = partial molal volume
 x = mole fraction of dry air in vapor phase within calorimeter
 Superscripts and subscripts applying to n, μ, f, h, \bar{H}, s , and \bar{S}
 ' = liquid (if not primed, the vapor state is meant)
 a = air
 s = salt
 w = water
 α = entering condition
 β = leaving condition
 \circ = pure state
 sat = pure saturated state

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Heating Value of Natural Gas

DETERMINATION OF TOTAL AND NET VALUES WITH A WATER-FLOW GAS CALORIMETER

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THE heats of combustion of several thousands samples of natural gas have been determined in this laboratory during the past eight years. These data are of value in the operation of a water-flow gas calorimeter and also agree with an empirical relation between the total and net heating value of saturated hydrocarbons.

The heating value (2) is the number of B.t.u. produced by the constant-pressure combustion of 1 cubic foot of gas with air when the inlet and outlet gases are at the same temperature. The cubic foot of gas is measured at 60° F. saturated with water vapor, and under a total pressure of 30 inches of mercury at 32° F. under standard gravitational force. When the heating value is calculated as if the water formed by combustion is in the liquid state, it is known as the total heating value, THV; when in the vapor state it is known as the net heating value, NHV.

A water-flow gas calorimeter condenses out a portion of the water vapor of combustion so that the observed heating value, OHV, is between THV and NHV, and both are calculated from OHV. Corrections for the water of combustion that is carried out in the vapor state with the flue gases,

$$\text{THV} + \frac{\text{heat of condensation of combustion water leaving calorimeter as vapor}}{\text{of condensed water}} = \text{OHV} - \frac{\text{heat of condensation}}{\text{of condensed water}} = \text{NHV}$$

are necessary in calculating THV, and corrections for the water that condenses out are necessary for calculating NHV. The latter corrections are much greater in magnitude than those for THV. If the fuel gas consists of a homologous series such as the saturated paraffin hydrocarbons in natural gas, the quantity of water formed by complete combustion should be sufficiently pro-

The total and net heating values of natural gas are related by the empirical equation:

$$\text{THV} - 1.072 \text{ NHV} = 34 - 0.34 I$$

This equation is used to check the accuracy of the corrections for the water of combustion of a water-flow gas calorimeter. The net heating value can be calculated from the total heating value by this expression, and vice versa. The suggested calorimeter practice will shorten the number of man-hours per test, increase the accuracy, and decrease the size of the test sample.

portional to the heating value so that NHV could be calculated from THV, and vice versa. The equation derived by the usual algebraic procedures from data given in the Table I for the relation between THV and NHV of each of the first six saturated normal hydrocarbons is:

$$\text{THV} - 1.072 \text{ NHV} = 34 \quad (1)$$

Nitrogen and other inerts affect the value of the constant 34 in Equation 1. The equation, correcting for inerts, is:

$$\text{THV} - 1.072 \text{ NHV} = 34 - 0.34 I \quad (2)$$

where I = inerts, %

It is to be noted that 9% inerts affects the constant by only 3. Equations 1 and 2 hold for natural gas within the limits of deviation of the gas from the law of partial pressures.

HEATING VALUE TESTS

Recommendations of the National Bureau of Standards (1, 4) for the operation of water-flow calorimeters were followed, includ-

TABLE I. PROPERTIES OF GASES
Conditions specified in definition of THV and NHV; column 2 calculated from data of Rossini (3) at 25° C.

1	2	3	4	5	6	7	8
Hydrocarbon	THV	Water, Grams	Heat of Combustion, Col. 3 X 2.337	NHV, Col. 2 - Col. 4	Col. 5 X 1.072	Col. 2 - Col. 6	Sp. Gr. (Air = 1)
CH ₄	996	42.48	99	897	96	34	0.5544
C ₂ H ₆	1762	64.33	150	1612	1728	34	1.0492
C ₃ H ₈	2546	87.1	204	2342	2511	35	1.5623
n-C ₄ H ₁₀	3313	109.3	255	3058	3278	35	2.067
n-C ₅ H ₁₂	4080	131.4	307	3773	4045	35	2.57
n-C ₆ H ₁₄	4850	153.2	358	4492	4816	34	3.08

¹ On leave of absence with the Armed Forces.

ing all the suggested calibrations and corrections. Complete low-temperature fractional distillation analyses, using a Podbielniak apparatus with liquid nitrogen as a refrigerant, and specific gravity tests were made on most of the samples whose heating values were determined. The accuracy of the heating value determinations were checked with these data. Heating values of natural gases containing methane as the only hydrocarbon checked, within less than 2 B.t.u., the value obtained by Rossini for methane.

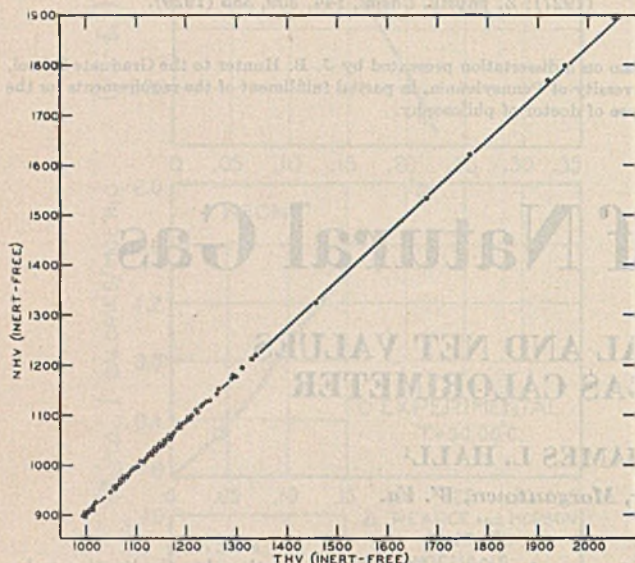


Figure 1. THV vs. NHV Curve through Methane and Ethane Points at a Burner Pressure of 0.11 Inch of Mercury plus Atmosphere

When a group of samples was used, they were arranged in order of increasing specific gravity, and the tests were made in this order; the next group of samples was run with the highest specific gravity first, the others following in order of decreasing specific gravity; the next group, in order of increasing specific gravity, etc. This reduced errors due to purging, variations in solubility of the gas in water, etc., and permitted uniform operation of the calorimeter. The Sargent automatic calorimeter was operated with the damper closed, under a constant pressure of 1.5 inches of water on the meter, and with the stopcock on the burner wide open at a gas rate of 3300 B.t.u. per hour. The damper was fairly tight fitting and had two $\frac{1}{2}$ -inch holes. The water condensed from the combustion of 0.4 cubic foot of gas was collected and measured after the preliminary burning of 0.4 cubic foot or more of the sample.

Experimental THV and NHV were plotted (Figure 1) in order to compare them with theoretical Equation 1. All first tests after the calorimeter had been idle a few hours were excluded from this curve. The experimental values were calculated to the inert-free basis. The curve was drawn through the points for pure methane and ethane. This figure indicates that the empirical equation holds for natural gas, so that any variation between THV or NHV as calculated from this equation and as experimentally determined is a measure of the correctness of part of the operating procedure.

Of twenty-nine samples having inert contents between 4 and 27%, fifteen showed higher calculated than experimental NHV and fourteen showed lower. When properly adjusted for an average natural gas, the calorimeter operates without further adjustments at the correct excess air rate, independent of the inert or hydrocarbon content.

Equation 1 was solved for 197 tests, and the difference between calculated and experimental NHV was plotted cumulatively (Figure 2, curve 1). The calculated values were assumed to be

correct; the negative scale represents higher experimental than calculated NHV's because insufficient water was collected, and the positive scale represents lower NHV's because more water was collected than was produced by the burning of the test sample.

The positive and negative portions of curve 1 are similar, so that the median value, -0.5 B.t.u., may be considered a measure of the amount of excess air beyond the 40% limit; the spread is due to fluctuations in runoff and errors of measurement.

CALORIMETER PERFORMANCE

WARMING-UP PERIOD. At the beginning of a group of tests the calorimeter was operated for 40 minutes so that operating conditions would be in equilibrium before an actual test was made. Curve 2 of Figure 2 shows that the water of combustion was not properly accounted for in about 45% of these first tests. Insufficient condensate water was collected during 40% of the first tests, while too much was recovered in 5%. The condensate water alternately holds back and floods out before it reaches a steady uniform runoff.

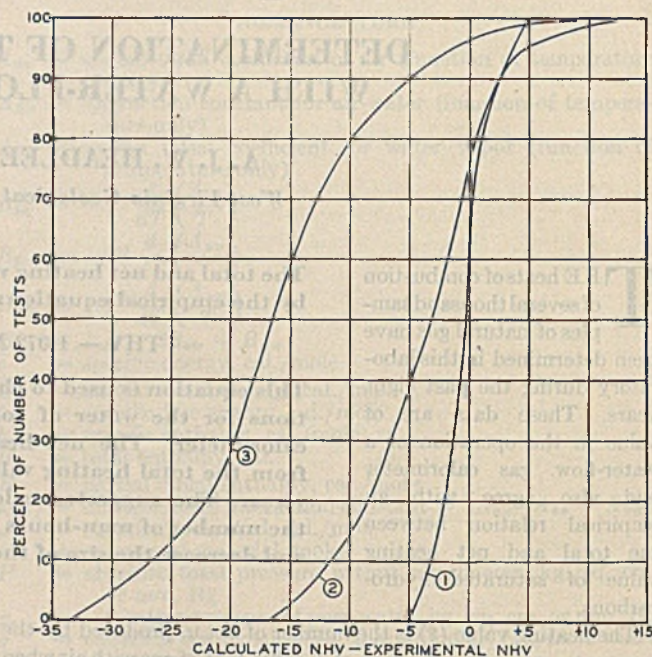


Figure 2. Cumulative Frequency Curves of the Difference between Calculated and Experimental NHV

Curve 1. Gas pressure, 0.11 inch mercury; 197 tests
Curve 2. First run of a group; gas pressure, 0.10-0.12 inch mercury; 98 tests
Curve 3. Gas pressure, 0.07 inch mercury; 73 tests

The warming-up period for two samples of natural gas was studied to determine the characteristics of the condensate water runoff. The condensate water from previous runs had evaporated from the condenser tubes, so that they were dry at the start of these tests. THV and NHV were calculated from the data for each 0.1 cubic foot of gas burned in order that the fluctuations would not be partially ironed out by too long a test period. These tests were plotted in the order made to show the progressive changes in the determined values (Figure 3). The test number scale is also a time scale; each test number represents the time necessary for one revolution of the meter (100 seconds). THV becomes steady in ten revolutions of the meter, equivalent to 17 minutes; NHV becomes steady after 40 minutes. The low points in the NHV curves are condensate floods. Two floods occurred during one of the tests before the condensate runoff became steady. NHV fluctuates much more than THV, even after the calorimeter is operating at its maximum steady state because of pulsating condensate-water drainage.

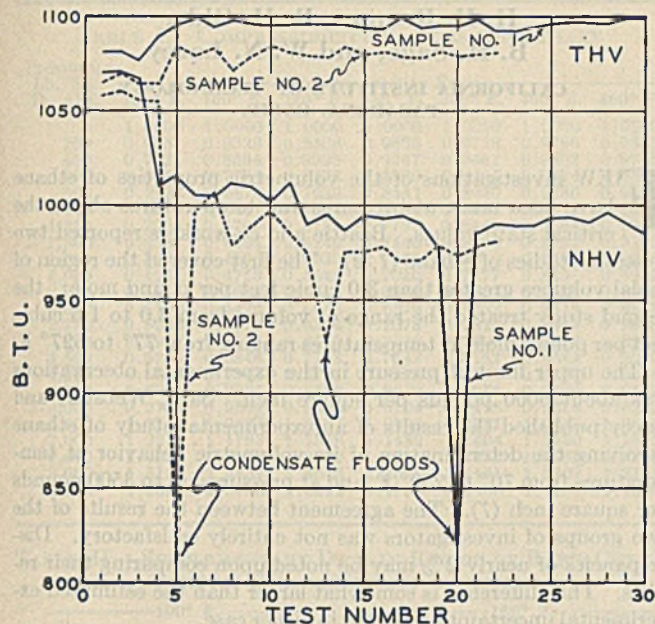


Figure 3. Calorimeter Performance While Attaining Equilibrium

OPERATION ABOVE 40% EXCESS AIR. Several tests were made with only 0.07 inch of mercury pressure on the meter at a gas rate of 2500 B.t.u. per hour. Wide variations were obtained between calculated and experimental NHV as indicated by curve 3 of Figure 2. The calorimeter was operating considerably above the 40% excess air limit, and the tables for calculating THV cannot be used with accuracy although the error involved was no more than 5 B.t.u. The condensate water runoff was pulsating even more than that shown in curve 2. These pulsations may have been partly due to the design of the collecting pan (shield) at the base of the calorimeter. If accurately uniform water runoff could be obtained, then accurate NHV tests could be made with any quantity of excess air, provided it remained uniform during a test. Atmospheric humidity and excess air would not be important factors so long as they remained uniform during a test, because Equation 1 could be used to calculate THV.

SUGGESTED CALORIMETER PRACTICE

A simple empirical relation (Equation 2) exists between the total and net heating value of natural gas. This relation can be used to check the operation of a water-flow calorimeter with respect to the water of combustion. It can be used to calculate NHV more accurately than it can be determined, provided THV is accurate to ± 1 B.t.u.

The fact that determined THV and NHV fit Equation 2 does not necessarily mean that they are the correct heating value for that gas; it indicates only that the water accounted for by the humidity and condensed water corrections was equal to the water formed by the combustion of the gas. THV and NHV may be high or low because of other errors.

If the NHV calculated from Equation 1 is consistently lower than the experimental value, then the calorimeter is being operated above the 40% excess air limit, and the experimental THV is too low by an amount equal to the heat of vaporization of the water vapor going out with the excess air, provided the proper amount of condensate was collected. If the drainage of condensate is less than that condensing out in the calorimeter, then the correction for condensate will be low and thus give too high an NHV. One or both causes may account for the high experimental NHV values as compared with those calculated from Equation 1. If too much condensate drains from the calorimeter or if less than

40% excess air (but always more than enough for complete combustion) passes through the calorimeter, then the experimental NHV will be less than that calculated by Equation 1.

Performance curves (Figures 2 and 3) should be made for each calorimeter and occasionally checked. They give the uniformity of operation of the calorimeter and the condensate water holdup and runoff. Test periods of even shorter duration than 0.1 cubic foot should also be charted. The chart of each reading of the outlet thermometer will frequently show fluctuations from the normal due to differential friction in the shaft of the wet test meter. This is especially true of new or reconditioned meters. The number of man-hours per test can be shortened by making such curves for a day's run of tests. The accuracy of the test will be increased and the sample size will be materially reduced.

The calorimeter should be operated for at least one hour before a test is made in order to ensure uniform runoff of condensate water after the calorimeter has been idle a few hours. Accurate THV can be obtained after a shorter warming-up period because the rate of runoff of the condensate water does not influence it. A calorimeter with accurately uniform condensate-water runoff would produce NHV's that could be used to advantage in calculating accurate THV's for natural gas and thus eliminate the necessity for humidity corrections.

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PRESENTED before the Division of Gas and Fuel Chemistry at the 105th Meeting of the AMERICAN CHEMICAL SOCIETY, Detroit, Mich. Published by permission of the State Geologist.

Process for Aminoguanidine (Correspondence)

SIR: My attention has been attracted to the following statement in the article by R. N. Shreve and R. P. Carter (line 12, column 1, page 423, May, 1944): "Wyler (29) in 1935 was granted a patent using zinc acetate instead of acetic acid with zinc dust, with yields claimed to be 90%. We were unable to obtain better than 50%." In the patent to which they refer, U. S. Patent 1,990,511 (1935), it is stated: "By my process I obtain a yield of aminoguanidine bicarbonate, for example, equivalent to 90% or more of the weight of the nitroguanidine used. . . ." This means that I claimed yields of at least 104×0.9 or 93.6 grams of aminoguanidine bicarbonate for 104 grams of nitroguanidine starting material, or about 71% of theory. Actually we obtain plant yields of more than 85% of theory under carefully controlled conditions and technique.

JOSEPH A. WYLER

TROJAN POWDER COMPANY
ALLENTOWN, PA.

SIR: Mr. Wyler is correct in that our article should have carried his claim of 71% yield rather than 90% as stated. It is true, however, that we got only 50%, but the reduction is not simple and we plan now to repeat the work in an effort to get up to 75 or 80% yield. Nothing would suit us better than to do this.

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Phase Equilibria in Hydrocarbon Systems

VOLUMETRIC BEHAVIOR OF ETHANE

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FEW investigations of the volumetric properties of ethane have been made at pressures and temperatures above the critical state values. Beattie and co-workers reported two separate studies of ethane (1, 2). The first covered the region of molal volumes greater than 3.0 cubic feet per pound mole; the second study treated the range of volume from 3.0 to 1.6 cubic feet per pound mole at temperatures ranging from 77° to 527° F.

The upper limit of pressure in the experimental observations was about 5000 pounds per square inch. Sage, Webster, and Lacey published the results of an experimental study of ethane involving the determination of its volumetric behavior at temperatures from 70° to 250° F. and at pressures up to 3500 pounds per square inch (7). The agreement between the results of the two groups of investigators was not entirely satisfactory. Discrepancies of nearly 2% may be noted upon comparing their results. This difference is somewhat larger than the estimated experimental uncertainty in either case.

In the course of studying the properties of ethane in binary mixtures of industrial importance (4, 5), it was deemed advisable to reinvestigate the volumetric behavior of this substance over somewhat larger ranges of pressure and temperature than were encompassed in the previous study of pure ethane (7). The results reported here extend to pressures of 10,000 pounds per square inch at seven uniformly spaced temperatures ranging from 100° to 460° F.

The equipment and methods have been described (6) and were found to yield reliable data in the case of methane (3), a substance whose volumetric behavior has been well established by many investigations. The instruments for measuring pressure, temperature, volume, and sample weight were carefully constructed and calibrated to ensure the determination of these quantities with an uncertainty of less than 0.1% of their absolute values.

Impure ethane was obtained from Carbide & Carbon Chemicals Corporation. It was fractionated three times at atmospheric pressure with a reflux ratio of approximately 50 to 1 in a 4-foot, vacuum-jacketed column packed with glass rings. The overhead was condensed in vacuo at liquid air temperatures with continuous removal of any noncondensable gases which might have accumulated during the condensation process. The purity of the material obtained in this way was verified by the nearly constant vapor pressure observed upon isothermally vaporizing a sample

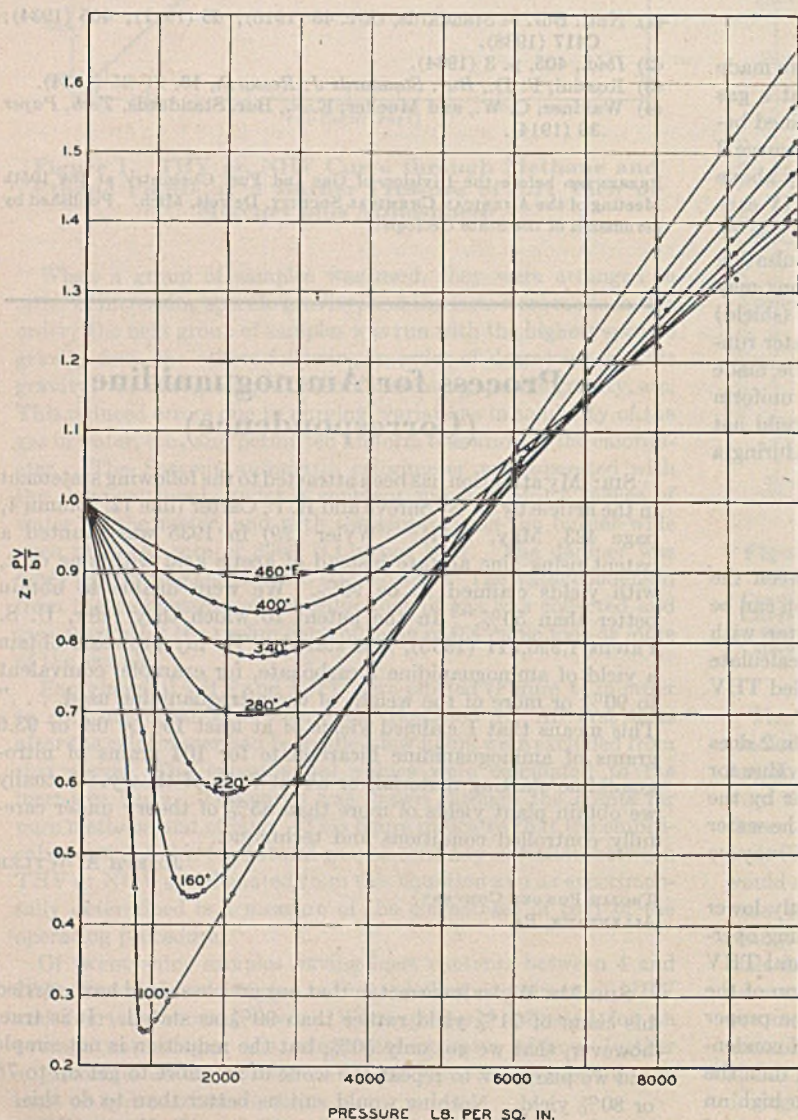


Figure 1. Effect of Pressure and Temperature on Compressibility Factor of Ethane

The volumetric behavior of ethane was investigated at pressures up to 10,000 pounds per square inch in the temperature interval between 100° and 460° F. The results of the experimental work are presented in tabular and graphical form. Comparisons are made with values obtained by others in recent investigations and with extrapolations based on Beattie-Bridgeman equation of state.

TABLE I. COMPRESSIBILITY FACTORS FOR ETHANE

Pressure, Lb./Sq. In. Abs.	Compressibility Factor						
	100° F.	160° F.	220° F.	280° F.	340° F.	400° F.	460° F.
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
200	0.9057	0.9328	0.9508	0.9635	0.9728	0.9798	0.9853
400	0.7921	0.8594	0.8999	0.9267	0.9461	0.9602	0.9713
600	0.6411	0.7784	0.8476	0.8900	0.9201	0.9414	0.9580
800	0.2935	0.6878	0.7939	0.8541	0.8950	0.9236	0.9455
1,000	0.2571	0.5881	0.7394	0.8194	0.8712	0.9071	0.9340
1,250	0.2955	0.4769	0.6753	0.7792	0.8440	0.8884	0.9210
1,500	0.3387	0.4391	0.6242	0.7440	0.8200	0.8722	0.9100
1,750	0.3820	0.4500	0.5939	0.7175	0.8010	0.8591	0.9006
2,000	0.4251	0.4753	0.5845	0.7010	0.7877	0.8494	0.8937
2,250	0.4676	0.5081	0.5915	0.6954	0.7807	0.8438	0.8898
2,500	0.5100	0.5426	0.6083	0.6979	0.7788	0.8419	0.8887
2,750	0.5520	0.5778	0.6314	0.7073	0.7827	0.8441	0.8903
3,000	0.5937	0.6134	0.6579	0.7218	0.7908	0.8494	0.8943
3,500	0.6756	0.6846	0.7158	0.7632	0.8162	0.8683	0.9099
4,000	0.7565	0.7563	0.7771	0.8114	0.8531	0.8957	0.9334
4,500	0.8362	0.8285	0.8398	0.8639	0.8955	0.9296	0.9619
5,000	0.9154	0.9004	0.9030	0.9184	0.9418	0.9674	0.9951
6,000	1.0714	1.0423	1.0287	1.0298	1.0387	1.0518	1.0658
7,000	1.2219	1.1793	1.1548	1.1439	1.1404	1.1430	1.1477
8,000	1.3688	1.3134	1.2799	1.2576	1.2431	1.2365	1.2332
9,000	1.5129	1.4454	1.4016	1.3698	1.3461	1.3309	1.3188
10,000	1.6530	1.5770	1.5211	1.4799	1.4488	1.4250	1.4050

TABLE II. SUPPLEMENTARY DATA IN REGION OF RAPID CURVATURE OF COMPRESSIBILITY ISOTHERMS

100° F.		160° F.	
Pressure, lb./sq. in. abs.	Compressibility factor Z	Pressure, lb./sq. in. abs.	Compressibility factor Z
700	0.5297	1100	0.5380
750	0.4443	1200	0.4949
775	0.3746	1300	0.4638
800	0.2935	1400	0.4462
820	0.2615	1500	0.4391
840	0.2532	1600	0.4408
860	0.2496	1700	0.4463
880	0.2485	1800	0.4540
900	0.2485	1900	0.4638
920	0.2493		
940	0.2509		
960	0.2527		
980	0.2548		

from bubble point to dew point at 80° F. At this temperature the observed bubble-point and dew-point pressures were, respectively, 630.6 and 630.4 pounds per square inch absolute.

For the determination of its volumetric behavior in the high-pressure region, 47.713 grams of ethane were distilled into the equilibrium cell; at each of the seven experimentally studied temperatures about eighteen volumetric observations were made at pressures ranging from 1000 to 10,000 pounds per square inch. The region of lower pressures was studied with a sample consisting of 13.804 grams of ethane at pressures varying from 300 to 3000 pounds per square inch. Where the two sets of observations yielded duplicate data, the discrepancy was less than 0.2%.

The experimental data were expressed in terms of molal volumes, compressibility factors, and residual molal volumes. Compressibility factor Z represents the ratio of observed volume to the corresponding perfect gas volume of the substance and is equal to PV/RT .

The residual molal volume \bar{V} is defined as the difference between the perfect gas molal volume and the observed molal volume of the substance at any given pressure and temperature and may be expressed as $(RT/P) - \bar{V}$. All calculations involving molal quantities are based upon a value of 30.069 for the molecular weight of pure ethane.

The compressibility factor and the residual molal volume have the useful property of remaining finite as the volume of system is indefinitely expanded. These quantities were plotted

as functions of pressure and temperature on 20 × 30 inch coordinate paper, and smooth curves were drawn through the points representing the experimental data. These curves served for interpolation of the experimental results to obtain the values at the pressures recorded in Tables I and II. The graphical operations described above are believed to have improved the consistency of the results without introducing significant uncertainties in the reported values with the possible exception of those for 460° F. at the higher pressures.

Figure 1 shows the isothermal relation between the compressibility factor and pressure at the temperatures involved in the study. The experimentally determined points are shown, and only at 460° F. and at pressures greater than 5000 pounds per square inch is there any appreciable discrepancy between the experimentally determined points and the smooth curves. The results reported in Table I were obtained from the smooth curves because it was believed that they represented the most probable behavior of ethane.

Table III presents a comparison of compressibility factors computed from the data of several investigations. The values obtained by the authors are everywhere larger than those obtained by Beattie and co-workers. The authors confirmed this discrepancy by recalibrating the volumetric apparatus and duplicating their initial results with another sample of ethane. The agreement between the present results of the authors and those obtained previously at this laboratory by Sage, Webster, and Lacey is not entirely satisfactory. The more recent data are believed to be the more reliable because many refinements in the design and operation of apparatus for measurement of pressure, volume, and temperature have been developed since the initial investigation. It is estimated that this work was performed with sufficient care and precision in regard to the calibration of instruments, measurement of primary variables, and graphical smoothing and interpolating of results so that the reported results are representative of actuality with an uncertainty of 0.2% at pressures less than 5000 pounds per square inch and with an uncertainty increasing to 0.4% at 10,000 pounds per square inch.

As an illustration of the hazards associated with the use of an equation of state to extrapolate curves outside the region of the experimental data, Figure 2 compares the extrapolated and ob-

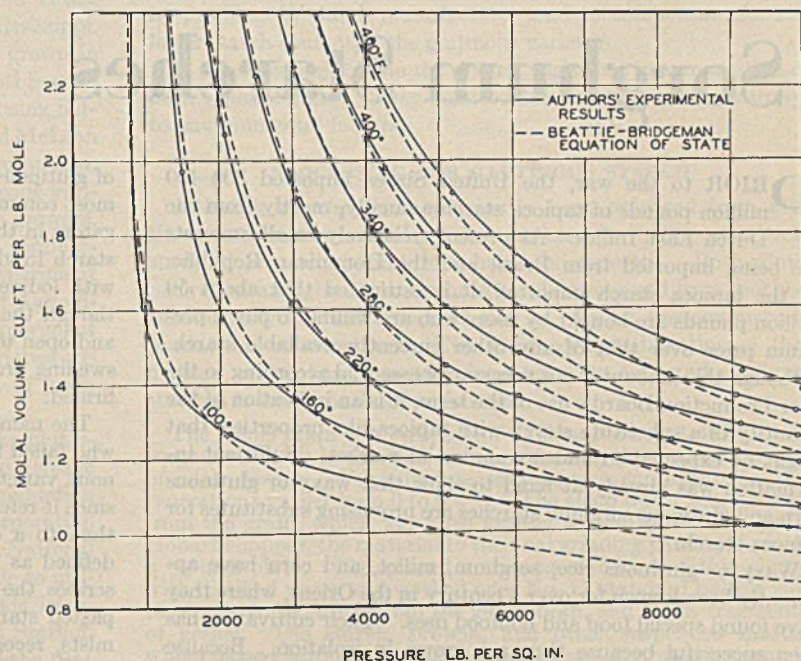


Figure 2. Comparison of Experimentally Observed Volumetric Behavior of Ethane with That Computed from Beattie-Bridgeman Equation of State

TABLE III. COMPARISON OF COMPRESSIBILITY FACTOR VALUES FOR ETHANE

Pres- sure, Lb./Sq. In. Abs.	100° F.		160° F.			220° F.		
	Sage, Webster, Lacey	Authors	Sage, Webster, Lacey	Beattie <i>et al.</i>	Authors	Sage, Webster, Lacey	Beattie <i>et al.</i>	Authors
500	0.7293 ^a	0.7235	0.8251	0.8165	0.8199	0.8782	0.8704	0.8739
1000	0.2529	0.2571	0.5572	0.5854	0.5881	0.7410	0.7351	0.7394
1500	0.3303	0.3387	0.4348	0.4371	0.4391	0.6248	0.6208	0.6242
2000	0.4132	0.4251	0.4658	0.4737	0.4753	0.5826	0.5822	0.5845
2500	0.4958	0.5100	0.5298	0.5426	0.6017	0.6055	0.6094
3000	0.6551	0.6579

	280° F.		340° F.		400° F.		460° F.	
	Beattie <i>et al.</i>	Authors	Beattie <i>et al.</i>	Authors	Beattie <i>et al.</i>	Authors	Beattie <i>et al.</i>	Authors
500	0.9047	0.9083	0.9284	0.9330	0.9436	0.9507	0.9551	0.9645
1000	0.8138	0.8194	0.8644	0.8712	0.8993	0.9071	0.9229	0.9340
1500	0.7403	0.7440	0.8134	0.8200	0.8641	0.8721	0.8990	0.9100
2000	0.6992	0.7010	0.7835	0.7877	0.8432	0.8495	0.8858	0.8937
2500	0.6955	0.6979	0.7766	0.7788	0.8386	0.8419	0.8842	0.8887
3000	0.7199	0.7218	0.7877	0.7908	0.8470	0.8494	0.8931	0.8942
4000	0.8078	0.8114	0.8507	0.8531	0.8931	0.8957	0.9318	0.9333
5000	0.9380	0.9418	0.9642	0.9675	0.9924	0.9951

^a Factor 0.7184 obtained by Beattie *et al.* at 100° F. and 500 pounds.

served volumetric behavior of ethane. The extrapolated values were computed by means of the Beattie-Bridgeman equation of state, the empirical constants of the equation having been determined by Beattie, Hadlock, and Poffenberger (1) from their experimental measurements of the volumetric properties of ethane at densities less than that of the critical state. Their calculations indicate that for densities less than the critical value, the equation represents the volumetric behavior of ethane with an average deviation of about 0.2% from the experimentally determined behavior. However, Figure 2 shows that for pressures of the order of 10,000 pounds per square inch the equation deviates from the actual volumetric behavior of ethane by nearly 20%.

A more reliable extrapolation of the volumetric data is accomplished graphically by plotting curves of constant volume on pressure vs. temperature coordinates. Such curves are usually

sufficiently linear to permit extrapolations of as much as 50% beyond the range of the experimental data. This technique was employed in testing the consistency and smoothness of the data obtained in the investigation.

ACKNOWLEDGMENT

Financial support from the American Petroleum Institute is acknowledged, this work having been a part of the activities of its Research Project 37. Assistance in the laboratory measurements and in the calculations was contributed by H. A. Taylor, E. Turner, and L. M. Reaney.

NOMENCLATURE

- P = pressure, lb./sq. in. abs.
 R = universal gas constant, 10.732 (lb./sq. in.) (cu. ft./lb. mole)/° R.
 T = temperature, ° R. (° F. + 459.69)
 V = molal volume, cu. ft./lb. mole
 \bar{V} = residual molal volume, cu. ft./lb. mole
 Z = compressibility factor

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PAPER 44 in the series "Phase Equilibria in Hydrocarbon Systems". Previous articles have appeared during 1934-40 (inclusive), 1942, 1943, and in January, March, and April, 1944.

Glutinous Corn and Sorghum Starches

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PRIOR to the war, the United States imported 300-400 million pounds of tapioca starch annually, mostly from the Dutch East Indies. At present, relatively small amounts are being imported from Brazil and the Dominican Republic. Of the tapioca starch imported, it is estimated that about 50 million pounds are bought by users who are willing to pay a premium price over that of any other currently available starch. Although this amount is not necessarily essential according to the War Production Board's use of the term, it is an indication of the quantity of a substitute starch with tapioca-like properties, that might be expected to find a commercial market. Sufficient information was already at hand to show that waxy or glutinous corn and glutinous sorghum starches are promising substitutes for tapioca starch.

Waxy or glutinous rice, sorghum, millet, and corn have apparently been known for over a century in the Orient, where they have found special food and nonfood uses. Their cultivation has been successful because they are grown in isolation. Because the waxy or glutinous characteristic is recessive, glutinous cereals under conditions favoring cross pollination with nonglutinous varieties tend to revert to the nonglutinous type. The fracture

of glutinous cereal grains appears dull and opaque, while that of most common varieties is horny or vitreous. European investigators in the latter part of the last century first recognized that starch in glutinous cereals is unique in that it stains red-brown with iodine rather than blue as does nonglutinous starch. Although the early chemical work on glutinous starch was crude and open to criticism, the microscopic observations and those on swelling properties were accurate and have been repeatedly confirmed.

The name "waxy" was applied to corn in 1909 by Collins (7) who failed to recognize the fact that he was dealing with a glutinous variety. The term "waxy" is unfortunate and confusing since it refers to the physical appearance of the endosperm rather than to a chemical characteristic of the starch. "Glutinous", defined as "sticky" or "gluey", is more suitable because it describes the most obvious characteristic of the cooked flour or pasted starch from this type of cereal. Botanists and agronomists, recognizing the applicability of the term, have used the adjective *glutinosus* as the varietal designation in the Latin name of glutinous cereals ever since the first European discovery of glutinous rice from the Orient.

The compositions of various glutinous and nonglutinous varieties of corn and sorghum have been determined. In general, the glutinous varieties have less starch and more oil and protein than the nonglutinous. The types of glutinous corn can be easily processed for high-quality starch by a method similar to that used for making corn-starch. The adaptation of this method to glutinous sorghums containing a nucellar layer yields off-color starches. This difficulty can be largely overcome by pearling the grain to remove the pigmented layer. Varieties lacking the nucellar layer yield white starch without the necessity for pearling. Compared to nonglutinous starch, the glutinous type is more sensitive to processing conditions. Excessive

grinding and increasing the concentration of the sulfur dioxide in the steeping operation tend to lower the viscosity of the glutinous starch. The gelatinization temperatures of the starch from the glutinous varieties are about the same as those of starch from the nonglutinous. Glutinous starch granules swell to a greater extent and exhibit a different structure than the nonglutinous. The viscosity of glutinous starch pastes is much higher than that of the ordinary type starch paste and is comparable to that of tapioca. Glutinous starch pastes are translucent, flavorless, and "long". Factors involved in the industrial utilization of glutinous starch as a replacement for tapioca starch are discussed.

Since about 1926 several investigators, in particular Brink (4, 5, 6), have shown interest in the composition, enzymic hydrolysis, and derivatives (8) of glutinous starch. Recently Meyer and Fuld (12), Schoch (13), Bates, French, and Rundle (2), and Whistler and Hilbert (16) have shown independently that glutinous starch, in contrast to nonglutinous, contains no amylose.

SOURCES OF GLUTINOUS STARCHES

Since there was little commercial interest in glutinous cereals before the war, it was fortunate that both corn and sorghum varieties had been developed to a point where they could be of immediate use for seed stocks. At the Nebraska Agricultural Experiment Station, T. A. Kiesselbach had produced an open-pollinated glutinous corn; N. P. Neal at the Wisconsin Agricultural Experiment Station was developing glutinous corn hybrids; and M. T. Jenkins and G. F. Sprague of the U. S. Department of Agriculture had produced a glutinous strain homologous to the nonglutinous double-cross Iowa 939 corn, one of the most popular hybrids grown in the corn belt.

The sorghum situation was in one respect better than that for corn. Two glutinous sorghum varieties have been in comparatively extensive production for some time. These are Schrock (including Sagrain) and Leoti. Schrock, a grain type, is grown in Kansas, Oklahoma, Arkansas, Mississippi, Louisiana, and Texas. Sagrain, a selected strain of Schrock, is grown in Mississippi. Leoti is adapted to a somewhat shorter season and is grown in Kansas, Nebraska, western Texas, and Colorado. Leoti is used almost exclusively as fodder, the whole stalk and head being harvested and fed as such. Gooseneck, Chinese Amber, and McLean are glutinous varieties of sorghums that are in minor production. The first two are seldom found unmixed with nonglutinous varieties, and the last has found little favor among sorghum growers. In addition to the glutinous varieties now being grown commercially, both R. E. Karper, at the Texas Agricultural Experiment Station, and A. F. Swanson, of the U. S. Department of Agriculture, working at the Fort Hays, Kans., Agricultural Experiment Station, have produced by hybridization glutinous varieties superior to either Sagrain or Leoti from the standpoint of grain production in the southern Great Plains.

Relatively small quantities of both Iowa and Nebraska glutinous corn and Texas glutinous sorghum from the limited acreage of the 1942 crop were available and were used for the production of starch on a commercial scale by General Foods Corporation (sorghum), American Maize-Products Company, and National Starch Products, Inc. (corn). An attempt was also made to utilize the commercial crop of Leoti sorghum. General Foods, in co-operation with the Nebraska Agricultural Experiment Station, after large-scale milling and processing experiments with the 1941 crop, made arrangements for the production and subsequent purchase of a large portion of the seed from the 1942 Leoti crop grown in Nebraska, but an unusually early frost prematurely killed a

large percentage of the crop, resulting in an immature grain unsuitable for starch production.

The 1944 crop of glutinous corn and sorghum should provide sufficient grain to furnish starch for the most essential industrial uses, and by 1945 all reasonable requirements should be met.

All glutinous corn and sorghum varieties previously described, except Gooseneck, McLean, and Chinese Amber sorghums, have been investigated and the results are included in this article.

COMPOSITION OF GLUTINOUS CORN AND SORGHUM

Analyses for moisture, protein, oil, and starch of representative glutinous and nonglutinous corns and sorghums, some from three or four crop years, were made. Moisture was determined by drying the grain in a Brabender moisture tester at 130° C.: corn for 2 hours; sorghum for 1.5 hours; nitrogen by the Kjeldahl-Gunning-Arnold method (1, page 26); starch in sorghum by diastase (1, page 359); starch in corn by a polarimetric method, essentially that of Hopkins (10); and oil by 20-hour Soxhlet extraction with Skellysolve F. The data are presented in Table I.

In general, the glutinous varieties of corn contain about 5% less starch than the nonglutinous. Only a few of the glutinous sorghum varieties contain as much starch as the nonglutinous. Leoti is exceptionally low in starch because of the large numbers of closely adherent glumes which constitute an appreciable portion of the entire sample. Higher contents of oil and protein, valuable by-products in starch manufacture, tend to compensate for the lower starch content of the glutinous varieties.

It is interesting to note the annual variations in composition of both types of grain. They must be due largely, perhaps entirely, to environmental factors.

PROCESSING FOR GLUTINOUS STARCH

Although starches have previously been prepared from glutinous sorghum or corn by other workers (6, 9, 11), no critical study of processing conditions has been reported. Both glutinous corn and glutinous sorghum can be processed by a method substantially the same as that now in use for the commercial production of cornstarch. The laboratory modification of this method, which has been used for separating corn and sorghum starches is briefly outlined as follows:

The whole grain was steeped for 24 hours (corn at 49° C. and sorghum at 44°) in distilled water containing the desired amount of sulfur dioxide. For experimental purposes, sulfur dioxide concentrations varied from 0 to 0.4%. The steep water was drained from the grain, which was then ground several times through a Hobart chopper, the material in the final grinding passing through a 1/8-inch plate. The ground grain was made into a thin slurry with distilled water and worked over No. 17 standard bolting silk to separate the starch from the germ, bran, and larger fragments of kernel. The starch, protein, and other suspended matter which passed through the bolting cloth were separated by centrifugation. The protein and fibrous material separated as an upper layer that was scraped from the surface of the starch. The starch was washed several times with distilled water and dried at a temperature below 50° C.

TABLE I. COMPARATIVE PROXIMATE ANALYSES OF REPRESENTATIVE GLUTINOUS AND NONGLUTINOUS CORNS AND SORGHUMS

Type	Variety	Crop Year	Mois- ture, %	% on Vacuum-Dried Basis		
				Protein ^a	Oil	Starch
CORN						
Glutinous	Iowa 939 hybrid	1939	9.2	12.16	5.11	67.4
	Same	1940	11.2	02.26	4.98	1.1
	Same	1941	8.1	12.44	4.80	67.0
	Same	1942	9.9	10.94	4.55	67.9
	Wis. hybrid	1939	11.4	10.09	5.60	67.7
	Same	1940	9.6	9.83	5.65	67.9
	Same	1941	8.4	9.61	5.59	68.7
	Same	1942A	8.8	10.81	4.89	68.9
	Same	1942B	7.8	12.58	5.98	62.2
		Iowa white	1938	11.8	11.90	4.32
	Nebr. open-pollinated	1941	8.9	11.55	4.72	65.6
Nonglutinous	Iowa 939 hybrid	1941	9.1	10.19	3.99	71.9
	Ill. 972 hybrid	1941	8.3	10.29	4.73	72.3
SORGHUM						
Glutinous	Sagrain	1939	12.6	13.16	4.24	63.5
	Leoti (Kans.)	1941	11.2	13.72	4.21	57.1
	Leoti (Nebr.)	1941	13.4	11.62	4.28	56.9
	Kafir (Texas)	1941	11.9	12.00	4.00	71.9
	Milo (Texas)	1941	12.6	11.30	3.60	67.8
	Atlas 40-17 (Kans.)	1942	12.4	13.00	4.25	68.3
	Atlas 41-13 (Kans.)	1942	10.5	13.57	4.02	69.5
	Club 397 (Kans.)	1941	11.0	14.76	3.80	71.1
	Same	1942	12.1	13.13	3.51	70.8
Nonglutinous	Blackhull kafir (Texas)	1941	12.6	12.46	3.70	72.0
	Milo (Texas)	1941	13.7	11.31	3.71	73.0
	Pink kafir (Kans.)	1940	12.4	13.43	4.16	70.0
	Same	1941	13.2	12.51	4.26	70.7

^a Protein calculated as N × 6.25.

From the standpoint of starch separation and color of starch extracted, glutinous corn was similar to nonglutinous in all respects.

Some sorghums presented processing difficulties not encountered with corn. In both Sagrain and Leoti the integument (or "nucellar" layer) is in the seed coat. In some varieties of sorghum this layer is resorbed as the seed matures. When present in the mature grain, however, it is apparently always pigmented (14). In both Sagrain and Leoti varieties, the pigment is water soluble and is strongly adsorbed by starch granules during processing. The color of the starch obtained is pale blue-gray and light tan, respectively. This difficulty can be overcome in part by pearling the grain to remove the major portion of the seed coat prior to processing. Starches prepared from the pearled grains have only a faint off-color. The nucellar layer in some white or tan sorghums is resorbed before maturity. Such sorghums, therefore, do not carry a pigment and yield colorless starches. On the other hand, white sorghums carrying a nucellar layer yield off-color starches. By hybridization, glutinous strains have been obtained with the nucellar layer largely resorbed, as in the Texas glutinous milo and kafir and the Kansas glutinous Club and Atlas sorghums. In the two former varieties the amount of pigment is small enough to allow nearly complete removal during processing. Pure white starches are obtained from the latter two varieties because of the absence of the red or purple pigment in the glume or pericarp. Pigment in the glume often produces spots on the seed coat.

DATA ON LABORATORY-PREPARED STARCHES

Analyses of the starches were made for moisture by drying to constant weight at 100° C. over P₂O₅ in an Abderhalden dryer; nitrogen, by the Kjeldahl-Gunning-Arnold method (1, page 26); phosphorus by Truog's method (15) after ashing with magnesium nitrate; ash (3-gram samples ashed at 700° C. for 3 hours); and methanol extract (20-30 gram, air-dried samples treated with absolute methanol and extracted 48 hours).

Viscosity determinations were made on 2% suspensions of starch in distilled water which had been pasted for 10 minutes in

a boiling water bath. Readings were taken on a Stormer viscometer, with a 100-gram weight, at 90° C. Eleven readings were taken on each sample, starting immediately after the paste was placed in the viscometer cup and continuing at one-minute intervals. First and eleventh readings are recorded for glutinous starches. Since the viscosity of nonglutinous starch did not change during this 10-minute interval, only one value is given.

Proximate analyses and viscosities of representative glutinous corn and sorghum starches are given in Table II, together with comparable data for typical nonglutinous cornstarches and tapioca. Disregarding Leoti sorghum starch, the glutinous starches contained only about half as much phosphorus as nonglutinous. Leoti starch contained high ash and high phosphorus, probably due to contamination from the glumes, which were very adherent on this sample. The glutinous starches showed considerable variation in viscosity, reflecting the influence of processing conditions and probably also of varietal source and conditions under which the grain was grown.

Both types of starch contained less nitrogen and phosphorus, the lower the sulfur dioxide concentrations of the steep used during processing. The glutinous also contained less ash after a steep with low sulfur dioxide concentration. While both types of cereal yielded starch of lower viscosity with increased sulfur dioxide content of the steep, the effect was more marked upon the glutinous. As will be pointed out later, glutinous granules are more easily broken during grinding.

GLUTINOUS STARCH CHARACTERISTICS

Microscopically, corn and sorghum starch granules, both glutinous and nonglutinous, are practically indistinguishable. Between crossed Nicols, they exhibit relatively strong birefringence; the four approximately equal bright quadrants of the granule are separated by the arms of a distinct dark cross.

The most striking characteristic of starch from the endosperm of glutinous cereal is the red or red-brown color which it gives with iodine. Only the starch from the endosperm exhibits this characteristic, that from the germ and the seed coat giving the usual starch-iodine blue. When a pure glutinous grain is processed for starch, usually a few blue-staining granules from tissues other than the endosperm are found in the product. As a rule, these are considerably smaller than the average endosperm starch granule, and are round rather than faceted; hence they are not readily confused with starch from nonglutinous endosperm, such as occurs in a sample made from glutinous grain contaminated with seed of nonglutinous.

Starches from glutinous varieties of corn, sorghum, rice, and barley have been examined and found to give a characteristic red to red-brown coloration with iodine. The shades, tints, and even the color of both glutinous and nonglutinous starch granules vary widely with the concentration of iodine reaching the starch.

TABLE II. COMPARATIVE ANALYTICAL AND VISCOMETRIC DATA ON REPRESENTATIVE GLUTINOUS AND NONGLUTINOUS CORN AND SORGHUM STARCHES

Source of Starch	Type of Steep, %	% on Vacuum-Dried Basis			Stormer Viscosity, Sec. ^a
		N	P	Ash	
Commercial cornstarch	SO ₂	0.05	0.015	0.08	7.4
Nonglutinous Iowa 939 corn	H ₂ O	0.03	0.013	0.06	7.7
Glutinous Iowa 939 corn, 1941	H ₂ O	0.03	0.006	0.03	21.6-13.0
Glutinous Iowa 939 corn, 1942	H ₂ O	0.03	0.009	0.05	14.8-11.0
Glutinous Iowa 939 corn, 1942	0.2 SO ₂	0.06	0.011	0.04	11.0-9.4
Nonglutinous Blackhull kafir	H ₂ O	0.05	0.072	0.28	7.8
Nonglutinous pink kafir	0.2 SO ₂	0.06	0.044	0.12	7.9
Glutinous Leoti sorghum	H ₂ O	0.05	0.014	0.33	18.8-12.8
Glutinous Club kafir, 1942	0.2 SO ₂	0.03	0.009	0.08	10.3-9.1
Glutinous Atlas 40-17 sorghum	H ₂ O	0.02	0.009	0.07	19.1-12.9
Glutinous Blackhull kafir	H ₂ O	0.05	0.009	0.07	12.6-10.6
Glutinous Blackhull kafir	0.4 SO ₂	0.06	0.012	0.08	6.8-6.4
Glutinous milo	H ₂ O	0.02	0.013	0.06	8.5-7.9
Commercial tapioca starch	...	0.01	0.011	0.09	10.7-9.9

^a Readings on a 2% suspension at 90° C.; distilled water reading at same temperature was 5.1 seconds. Readings for glutinous starches and tapioca indicate decrease over 10-minute period.



Figure 1. Glutinous Sorghum Starch Granules, Mounted in Distilled Water and Crushed by Pressure on the Cover Slip ($\times 500$)

Differences are especially noticeable if iodine solution is run into a water suspension of starch under a cover slip on a microscope slide, so that a concentration gradient results. Even in the absence of concentration gradients, both glutinous and nonglutinous barley starches exhibit a much wider variation in shades and tints in the presence of iodine than do other starches. The intensity and tone of color, in particular, of glutinous barley starch vary greatly with the concentration of iodine. At some concentrations individual granules exhibit different colors; some appear to be red-brown and others dark purple. Comparison of glutinous barley starch granules with nonglutinous, identically treated with varying concentrations of iodine, leaves no doubt but that the colors of the two varieties are dissimilar. In view of these results it is not believed that special significance should be attached to the statement of Hixon and Sprague (9) that glutinous barley starch differs from other glutinous starches in having both red- and blue-staining granules.

Glutinous corn and sorghum starches are very susceptible to injury and split into wedge-shaped fragments comparatively easily (Figure 1) if pressure is applied to the cover slip under which they are mounted for microscopic observation (compare Meyer, 11). Excessive granule breakage is effected during some types of grinding. This characteristic may assume importance if starch is broken or ground to the pearl or powder form under grinding conditions which do not affect nonglutinous starch. The viscosity of pastes made from such powdered starch is markedly lower than that of pastes from unpowdered, and approaches that of nonglutinous and even thin-boiling starches. This property has, therefore, considerable industrial significance.

No appreciable difference has been found between the gelatinization temperatures of glutinous cereal starches, as determined by loss of birefringence, and of those from the corresponding nonglutinous grains. Temperatures for initial loss of birefringence by a few granules and for complete loss of birefringence by all granules, respectively, follow: Cornstarch, initial 43–60° C., complete 70–77°; glutinous cornstarch, initial 40–59° C., complete 71–78°; sorghum starch, insufficient data available; glutinous sorghum starch, initial 49–58° C., complete 75–78°.

During the early stages of swelling immediately subsequent to gelatinization, glutinous starch granules appear lobed or segmented, in contrast to the more completely rounded forms commonly exhibited by the nonglutinous (Figure 2). Hixon and Sprague (9) mentioned this typical appearance.

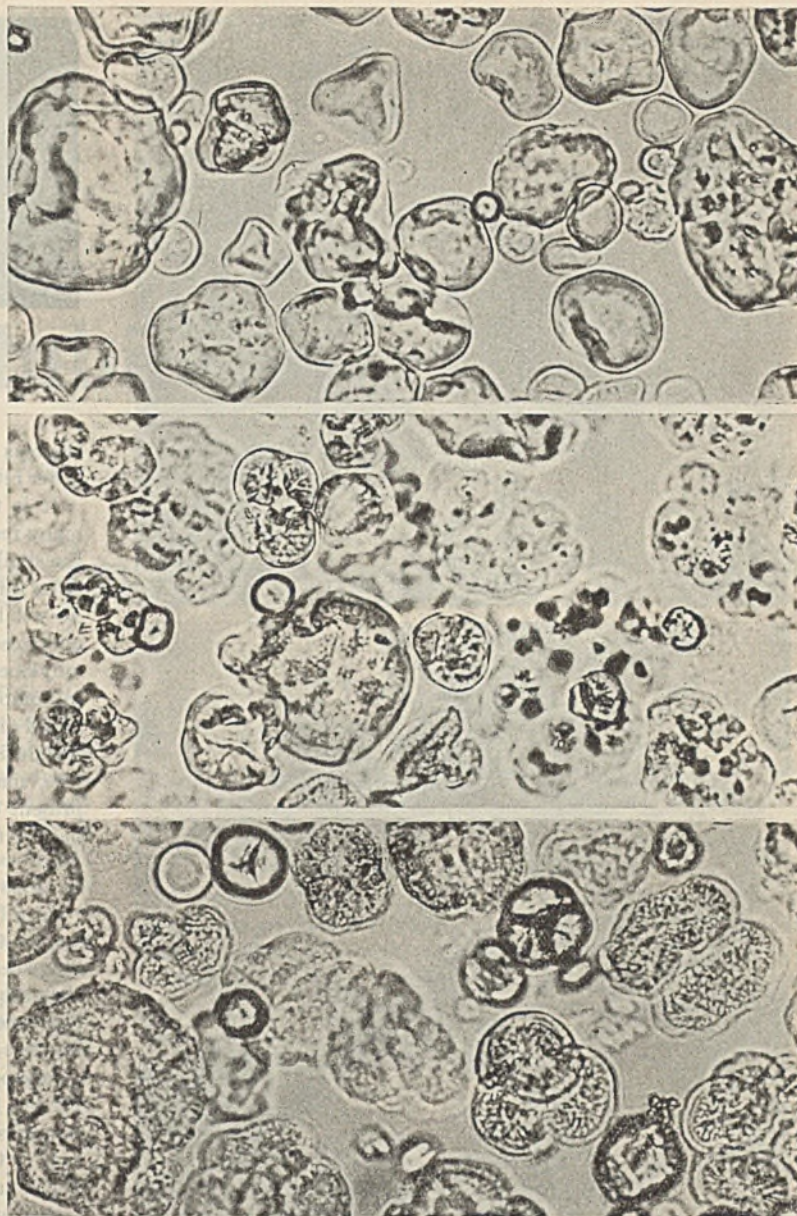


Figure 2. Starches Heated to 70° C. in Distilled Water—Corn (Top), Glutinous Corn (Center), and Glutinous Sorghum (Bottom), $\times 500$

On the basis of the present investigations, it is tentatively suggested that a structural difference exists between the two types of granules, which is responsible both for the difference in appearance of the two during swelling and for their dissimilar susceptibility to mechanical injury. As the granules swell with increasing temperature, the glutinous increase in size more rapidly than the nonglutinous; after reaching 95° C., they tend to form a stringy mass in which strongly convoluted granules appear to be embedded in and held together by heavy strands of thick, gelatinous starch material which seems to result by modification and fusion of some of the granules. Under similar conditions the nonglutinous granules remain intact, although considerably folded, and are surrounded by a colloidal suspension of finely dispersed material which has emanated from them (Figure 3). Because of these differences, the nonglutinous and glutinous pastes have dissimilar rheological properties. While the nonglutinous paste is "short", with high rigidity and low viscosity, the glutinous paste is "long" and tacky (Figure 4) with low rigidity and high viscosity (3). In concentrations above approximately 3.5% the nonglutinous cereal starch paste sets to a gel when cooled, but the glutinous remains mobile and viscous with little or no tend-

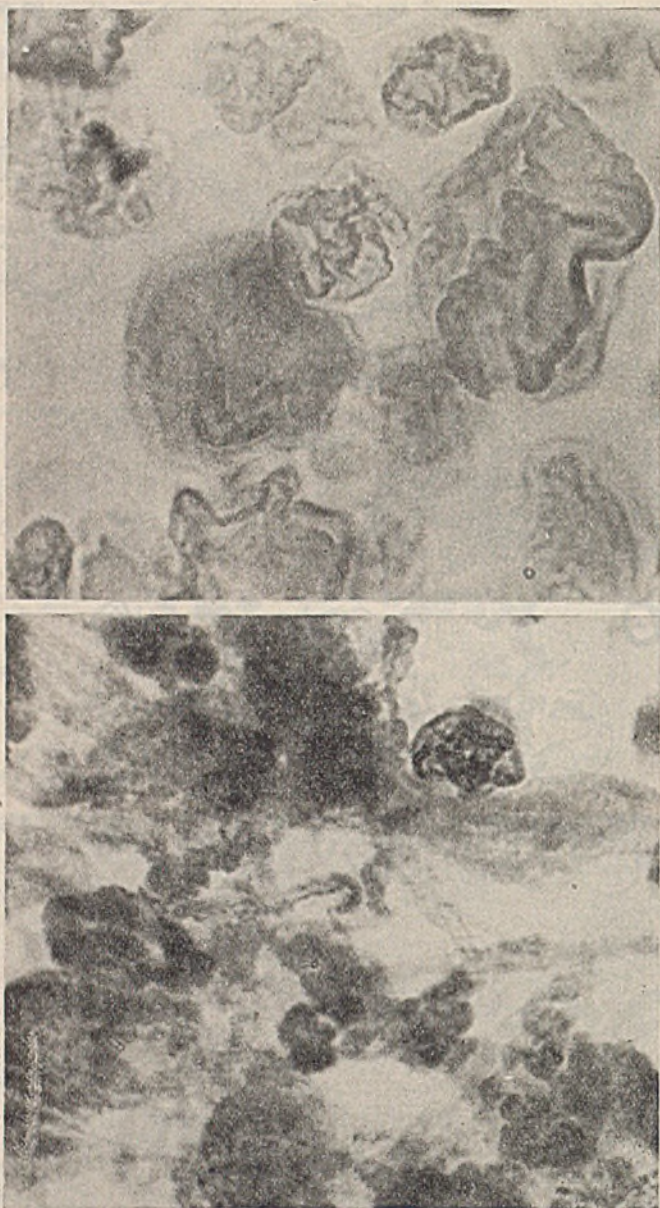


Figure 3. Starch Suspensions (0.5%) in Distilled Water, Heated One Hour in Boiling Water Bath—Corn (Top), Glutinous Corn (Bottom), $\times 500$

ency toward gel formation. In 2% suspension the hot viscosity (90°C.) of the glutinous paste is two or more times that of the nonglutinous, and decreases slowly with stirring or shear; that of the nonglutinous remains constant. Duplicate extractions give nonglutinous starches with practically the same viscosity. The properties of glutinous starches are far more sensitive to minor changes in the processing conditions, however, and are difficult to reproduce in duplicate samples. Comparison of data (Table II) shows the glutinous starches to be approximately equal to tapioca in viscosity. Observations in this laboratory, as well as those from various starch industries, indicate that some specimens of glutinous starches may change markedly in viscosity over 6 months to 2 years and may finally reach a condition which closely resembles that of a thin-boiling starch.

The nonglutinous cornstarch paste is nearly opaque and usually has a characteristic flavor, but that of glutinous corn or sorghum starch is translucent and flavorless. The translucency and lack of flavor of a glutinous starch paste are distinct advantages in the use of the starch in food products or adhesives for envelopes, etc. On standing, nonglutinous pastes or gels increase in opacity,

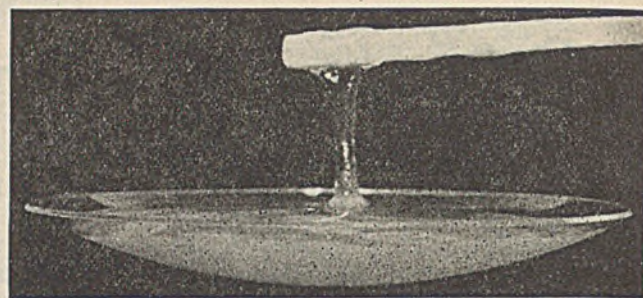


Figure 4. Tacky Character of 5% Glutinous Cornstarch Paste

whereas glutinous scarcely change over long periods; i.e., the latter retrograde slowly if at all.

It is to be emphasized that, although glutinous starches in many respects resemble tapioca and other so-called root starches, the similarity is to a large extent superficial. Glutinous starches differ fundamentally from nonglutinous by containing no amylose. As yet little or no formation is available on the nature of the amylaceous material of glutinous starch or on its relation to the amylopectin of nonglutinous starch. Because of the dissimilarity in composition, it seems not unreasonable to expect that profound differences between some of the properties of glutinous and nonglutinous starches will be found. Glutinous starches, therefore, may not only supplement or replace tapioca during the present emergency but also, because of their unique properties, may be found especially fitted for different purposes in the future.

INDUSTRIAL USES

Glutinous corn and sorghum starches give promise of commercial value for replacement of tapioca starch. When pasted they are equal or superior to the latter in translucency, viscosity, low speed of retrogradation, and lack of flavor. They should find use for textile sizing and finishing. For paper coatings, enzyme-converted starches are widely used. During enzyme conversion, cornstarch yields a turbid solution from which an amylaceous precipitate is deposited. This characteristic is a disadvantage in the use of cornstarch for paper coatings. Like tapioca, glutinous starch does not possess this unfavorable property but yields, on enzyme treatment, a clear solution. Glutinous starches are easily dextrinized, the products having more tack than those from tapioca produced under comparable conditions. They should, therefore, prove useful as British gums or envelope gums. Because of its desirable adhesive properties, considerable quantities of glutinous starch may find use in the plywood industry. Perhaps the largest potential user, however, is the food industry. Tests made by various commercial concerns have indicated that glutinous corn or sorghum starch can successfully replace tapioca in most of its present industrial and food uses.

ACKNOWLEDGMENT

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Gas-Liquid Solubilities and Pressures in Presence of Air

Gas-liquid equilibrium or solubility data are of fundamental importance in the study of gas absorption processes and for the proper design of equipment in which to conduct them. Data are needed on many new systems, and better data are needed on some systems previously studied. An apparatus has been assembled which is particularly suited for the determination of gas-liquid solubilities and corresponding pressures of systems in which air or other carrier gas is also present. The air is "saturated" with the constituent dissolved in the liquid phase. Partial pressure data for the system acetone-water are presented which have been determined in the presence of air, as previous data are incomplete and inconsistent. The solubilities and partial pressures of acetone in two mineral oils were also determined in the presence of air. These equilibrium data have been determined at the concentrations, temperatures, and pressure ordinarily encountered in gas absorption studies.

THE partial pressure of a component in a gas phase which is in equilibrium with a liquid phase may be determined by the static method and, when the component is a condensable vapor, by the ebullition method normally used for the determination of vapor composition data. Morton (4) and Beare, McVicar, and Ferguson (1) determined a few isolated points of the acetone-water system by the static method; but in each case the determinations were merely incidental to other work. No direct analyses of vapor compositions were made by the latter, and the results cannot be compared directly. Taylor (7) studied the same system without, however, determining equilibrium conditions.

In gas absorption operations, air or other carrier gas is present. It would be desirable to have equilibrium data obtained by a method more nearly comparable to the operation of gas absorption or desorption. In the air saturation method of determining gas-liquid solubility data, air is contacted with the liquid; the material to be distributed between the two is added to the liquid phase if it is normally liquid and to the air phase if it is normally

ACETONE-WATER AND ACETONE-HYDROCARBON OIL SYSTEMS

gas. Hartley (3) indirectly determined some few points of partial pressures of acetone and water at one temperature by the air saturation method. His data also cannot be correlated with those of the other experimenters.

Acetone vapor is a convenient material for experimental studies of gas absorption because (a) it is one of the few materials which, without being basic or acidic, may be simply and accurately determined by chemical analysis; (b) it is readily added quantitatively to a gas stream; (c) it is miscible with water and oils which might be used as wash liquids; (d) it does not attack or corrode the usual materials of construction.

Several methods may be used for saturating air with the components of a solution. It may be recycled over the liquid surface, it may be bubbled through the liquid, or the liquid may be sprayed in the air. The latter method was used in this investigation.

The desired data are at a total pressure of one atmosphere since gas absorptions or desorptions are usually carried out at this pressure. The work was planned with a series of runs at constant temperatures, each run being at a different liquid composition. Partial pressures were then calculated from the analysis of the vapor and liquid phases. The method and apparatus described may be used for determining solubilities of permanent gases by

adding them to the gas phase and absorbing them in the liquid. In any case, in relating the partial pressure exerted by a dissolved volatile liquid or gas to the composition (solubility) in the solution,

it is simpler for engineering work, as previously pointed out (6), to consider the pressure as a function of the liquid composition than liquid composition as a function of pressure.

DESCRIPTION OF APPARATUS

The apparatus used in determining the partial pressures of acetone from solutions in water and in oils is shown diagrammatically in Figure 1.

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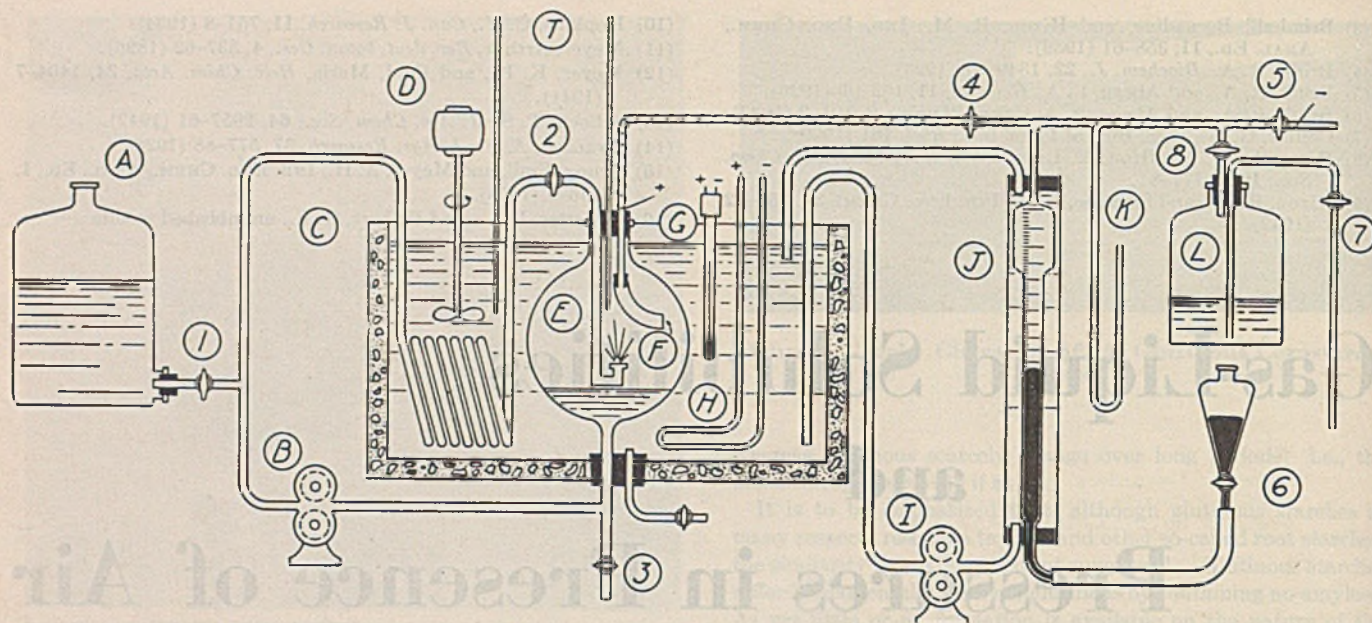


Figure 1. Apparatus for Determination of Solubilities of Gases in Liquid and Corresponding Partial Pressures

A. Reservoir for acetone solution
B. Circulation pump for acetone solution
C. Constant-temperature water bath
D. Agitator for water bath
E. Spray chamber

F. Spray trap
G. Thermo-regulator for water bath
H. Heater for water bath
I. Bath water circulation pump for gas buret

J. Gas buret
K. Manometer
L. Gas sample bottle
T. Thermometers for water bath and spray chamber

Constant-temperature bath *C* was an 11-gallon Alberene stone trough equipped with an efficient agitator, *D*. The temperature was maintained within $\pm 0.1^\circ \text{C}$. by thermoregulator *G* which operated a relay (not shown) and thus controlled electrical heating unit *H*. For temperatures below room temperature and above that of tap water, a small stream of tap water was constantly fed into the trough with the excess overflowing. For lower temperatures, ice water or iced brine from a separate small tank was used. The heating system maintained the temperature constant in every case.

Reservoir *A* was a 4.5-liter Wolff bottle with the outlet connected through a cock to a branched $\frac{3}{8}$ -inch copper tube. One arm led to the bottom outlet of a 3-liter flask used as a spray chamber *E* by way of circulating Beach-Russ gear pump *B*. This pump delivered 2-3 gallons per minute at a pressure of about 30 pounds per square inch. The other arm of the branched tubing formed a coil which was immersed in the water bath to ensure that the sprayed liquid attained the desired temperature. This tubing terminated in a standard spray nozzle (Whirl jet $\frac{1}{8}$ -inch-B 2 supplied by Spraying Systems Company) inside the spray chamber after passing through a tight-fitting rubber stopper in the mouth of the flask. A capillary gas sampling tube and a thermometer also passed through the rubber stopper.

By reversing the electric motor on the pump, the acetone solution was pumped from the reservoir into the spray chamber through its bottom drain by opening cock 1 and closing cock 2. By opening cock 2, closing cock 1, and operating the pump in the normal manner, it was possible to spray and recycle the liquid in the spray chamber; or by opening cock 1 and closing cock 2, the liquid was pumped back into the reservoir. Cock 3, which was used for draining the system, was closed during these operations.

Mercury-filled gas buret *J* had a water jacket maintained at the bath temperature by water circulated by a second Beach-Russ gear pump, *I*. The spray chamber and gas manometer, together with gas sample bottle *L*, manometer *K*, and vent cock 5, were connected with glass capillary tubing. This was electrically warmed to prevent condensation, which might occur during gas sampling, on runs above room temperature. A curved glass tube acted as a trap to prevent sprayed liquid from entering the

gas line. A siphon attached to the gas sample bottle served to withdraw displacement liquid as the gas sample was being collected.

OPERATION OF APPARATUS

Before a determination was made, the bath was brought to the desired temperature. The required amount of water was added to the sample bottles, and their siphon legs were filled.

The reservoir was charged with about 2500 ml. of the dilute acetone solution in water or oil which was to be studied in the particular run. Approximately 500 ml. were then pumped into the spray chamber, sprayed for 10-15 seconds, and pumped back into the reservoir. This process was repeated twice to rinse the apparatus thoroughly. The fourth time, spraying continued for 20 minutes. Cocks 4 and 5 were open thus far, so that atmospheric pressure was maintained.

A sample of the liquid was then withdrawn by a tube inserted through the hole that normally held the thermometer or from drain cock 3, and was discharged into a weighing buret. On replacing the thermometer, spraying was resumed for 10 minutes. Pump *B* was again stopped, cock 1 was opened, and approximately 100 ml. of acetone solution were allowed to flow slowly by gravity from the reservoir into the spray chamber. An equal volume of saturated air was thus displaced from the chamber and forced through the capillary tube to flush it. Cocks 1 and 5 were then closed. (Although the reservoir solution did not have the exact strength of the sprayed liquid, practically no diffusion would occur in the liquid phase; and even if there was complete mixing, no appreciable change in liquid concentration at the interface, or of the gas above, would take place during this and the next operation.)

The gas sample was collected by lowering the leveling bottle of the gas buret, cock 6 remaining closed. Cock 1 was opened, and more solution from the reservoir was allowed to flow slowly into the spray chamber. This caused a small pressure in the system which was equalized by cracking cock 6 of the leveling bottle and allowing the mercury to flow out. The two liquid movements (solution into spray chamber and mercury into leveling bottle) were balanced so that only slight deviations from atmospheric

pressure were indicated by the manometer. The manometer indicated no pressure difference when cocks 1 and 4 were closed, and the volume of gas in the buret was recorded.

The gas sample was transferred from the gas buret to the sample bottle by first closing cock 6 and raising the leveling bottle. Cock 8 was opened and siphon cock 7 cracked. The resulting negative pressure was equalized by opening cock 6 to let mercury flow back into the gas buret. As before, the relative rates of flow were regulated to keep the internal pressure close to atmospheric. The manometer always indicated atmospheric pressure at the end of the transfer of the measured volume, cock 8 was closed, and the gas sample bottle was removed. A second sample of the gas was then measured and taken in the same manner. It should be noted that the gas samples were taken in sample bottles already containing some air.

When the gas phase was so dilute that more than 100 cc. were required for analysis, gas samples were collected directly in calibrated quart bottles in which was placed the desired amount of water. The gas sample was allowed to reach room temperature and the pressure was adjusted to atmospheric before the volume was read.

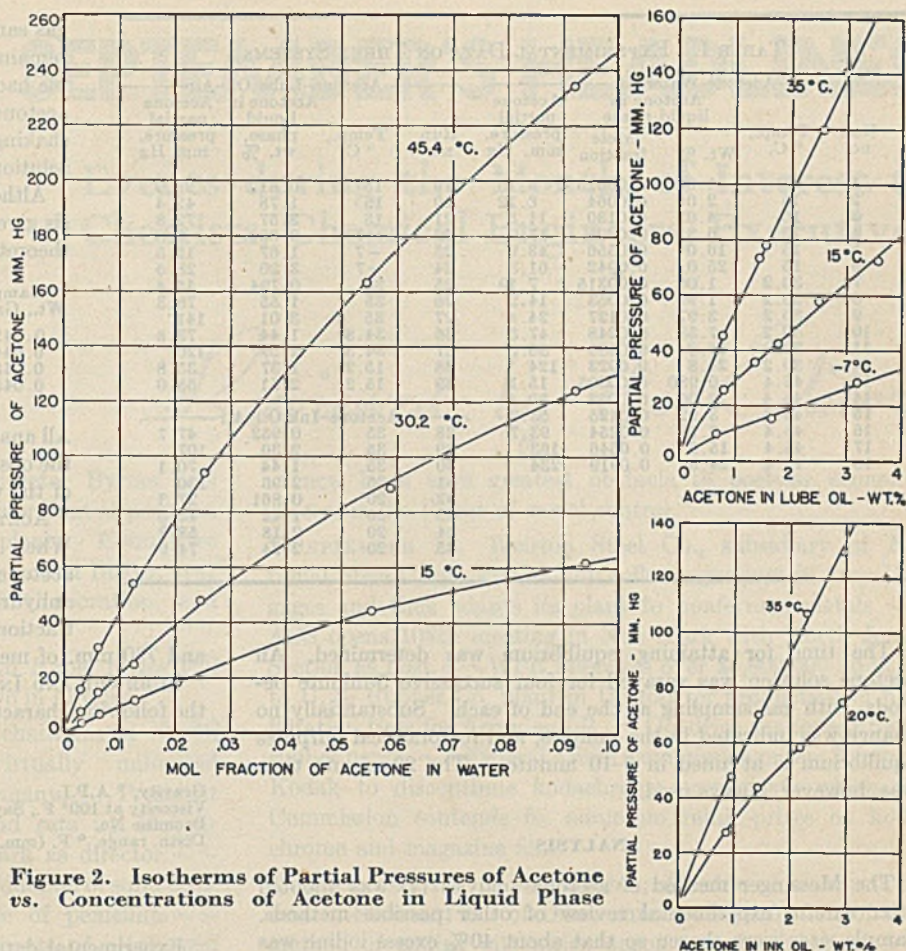


Figure 2. Isotherms of Partial Pressures of Acetone vs. Concentrations of Acetone in Liquid Phase

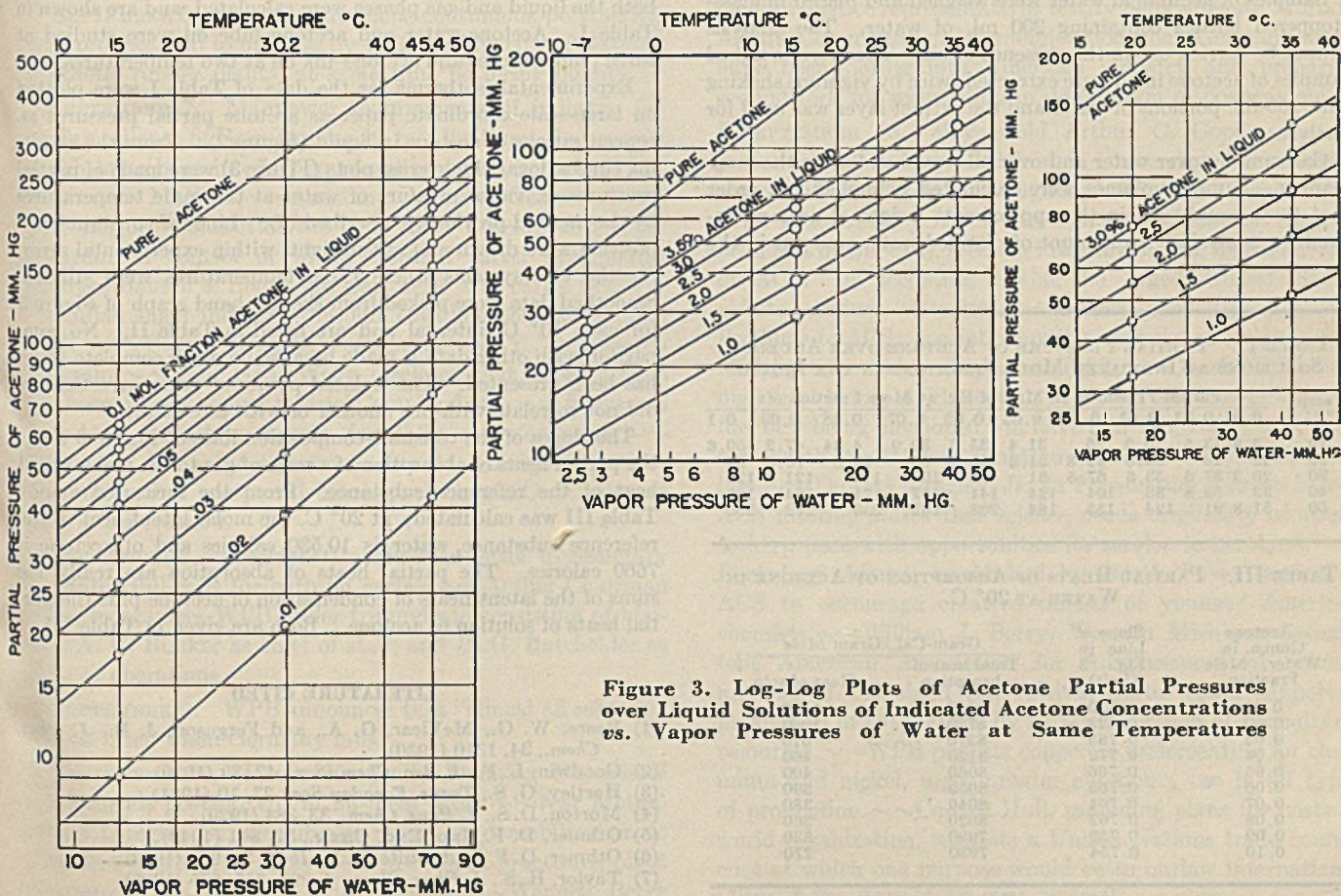


Figure 3. Log-Log Plots of Acetone Partial Pressures over Liquid Solutions of Indicated Acetone Concentrations vs. Vapor Pressures of Water at Same Temperatures

TABLE I. EXPERIMENTAL DATA ON THREE SYSTEMS

Acetone-Water-Air					Acetone-Lube Oil-Air				
Run no.	Temp., ° C.	Acetone in liquid phase		Acetone partial pressure, mm. Hg	Run no.	Temp., ° C.	Acetone in liquid phase		Acetone partial pressure, mm. Hg
		Wt. %	Mole fraction				Wt. %		
1	15	1.05	0.00325	3.15	19	15	0.812		25.9
2	15	2.05	0.0064	6.12	20	15	1.78		42.4
3	15	4.07	0.0130	11.5	21	15	3.57		72.8
4	15	6.31	0.0205	17.9	22	-7	0.682		9.8
5	15	16.0	0.0558	43.9	23	-7	1.67		15.5
6	15	25.0	0.0942	61.3	24	-7	3.20		28.5
7	30.2	1.00	0.00315	7.19	25	35	0.794		45.4
8	30.2	1.99	0.0063	14.2	26	35	1.55		78.3
9	30.2	3.97	0.0127	24.4	27	35	3.01		141
10	30.2	7.53	0.0248	47.5	28	35	1.44		73.8
11	30.2	16.8	0.0589	88.5	29	35	2.59		120
12	30.2	24.8	0.0923	124	30	15.2	1.37		35.8
13	45.4	0.980	0.00305	15.1	31	15.2	2.51		58.0
14	45.4	2.00	0.0063	30.4	Acetone-Ink Oil-Air				
15	45.4	3.92	0.0125	53.2	28	35	0.952		47.7
16	45.4	7.78	0.0254	93.7	29	35	2.30		107
17	45.4	15.6	0.0546	163	30	35	1.44		70.1
18	45.4	24.5	0.0919	234	31	35	2.96		130
					32	20	0.861		27.3
					33	20	1.42		43.6
					34	20	2.18		58.2
					35	20	2.94		74.9

The time for attaining equilibrium was determined. An acetone solution was sprayed for four successive 5-minute periods, with gas sampling at the end of each. Substantially no change was indicated in the samples, and for practical purposes equilibrium is attained in 5-10 minutes. The 20-minute time was, however, always used.

ANALYSIS

The Messinger method of acetone analysis (2) was adopted after careful experimental review of other possible methods. Sample sizes were chosen so that about 40% excess iodine was always present, and duplicate analyses were always made.

Samples of acetone in water were weighed and placed in glass-stoppered bottles containing 200 ml. of water. The analysis cannot be carried out in the presence of oil. Therefore, weighed samples of acetone in oil were extracted twice by vigorous shaking with 250-ml. portions of water and the extract layer was used for analysis.

Gas samples over water and over oil were handled in the same manner. Sample volumes were calculated beforehand in order that they would contain the approximate weight of acetone desired for analysis. An amount of distilled water was put in the

gas sample bottles such that approximately 200 ml. remained to dissolve the acetone after the gas sample had been taken. All but a negligible amount of acetone vapor was absorbed in the water by violently shaking for two 2-minute periods; then the aqueous solution was analyzed.

Although the Messinger method of acetone analysis gives consistent results, they were greater than theoretical:

Sample Wt., Gram	Water, Ml.	Approx. % Soln.	Acetone Found Gram.	%
0.0426	50	0.09	0.0431	101.3
0.0440	50	0.09	0.0450	101.9
0.0459	200	0.02	0.0464	101.2
0.0457	200	0.02	0.0464	101.6

All analyses were therefore corrected by multiplying the observed values by the reciprocal of the average of the values found above—i.e., 0.985.

ACETONE. Merck's C.P. product was used. When methods of analysis were compared, the acetone was allowed to dry for several days over anhydrous calcium chloride and then carefully fractionated, saving only that boiling at 56.5° C.

and 760 mm. of mercury.

LUBE OIL AND INK OIL. These two petroleum products had the following characteristics:

	Lube Oil	Ink Oil
Gravity, ° A.P.I.	22.8	37.6
Viscosity at 100° F., Saybolt Universal sec.	108.0	38.6
Bromine No.	1.3	0.6
Distn. range, ° F. (mm. Hg)	296-582 (10)	510-592 (760)

DATA

Experimental data were determined in the range of operation of absorption equipment; averages of the analytical results for both the liquid and gas phases were calculated, and are shown in Table I. Acetone-water and acetone-lube oil were studied at three temperatures and acetone-ink oil at two temperatures.

Experimental isotherms for the data of Table I were plotted on large-scale coordinate paper as acetone partial pressures *vs.* concentrations of acetone in liquid (Figure 2). From the resulting curves, logarithmic cross plots (Figure 3) were made of partial pressures *vs.* vapor pressure of water at the same temperatures by the method previously described (5). Lines of constant composition were drawn and are straight, within experimental error, for the two systems where three temperatures were studied. Smoothed data were picked from the left-hand graph of Figure 3 for each 10° C. interval and are listed in Table II. No comparison with other data is made because no other complete series has been presented. The isolated points of other investigators did not correlate with one another or with these data.

The slopes of the constant-composition lines of Figure 3 relate the partial heats of absorption of a mole of gas to the molar latent heat of the reference substance. From the measured slopes, Table III was calculated; at 20° C. the molar latent heat of the reference substance, water, is 10,530 calories and of acetone is 7660 calories. The partial heats of absorption are really the sums of the latent heats of condensation of acetone plus the partial heats of solution of acetone. Both are given in Table III.

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TABLE II. PARTIAL PRESSURE OF ACETONE OVER AQUEOUS SOLUTIONS AT INDICATED MOLE FRACTIONS IN THE LIQUID

Temp., ° C.	Partial Pressures, in Mm. of Hg, at Mole Fraction of:										
	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	
10	6.8	13.5	20.2	26	31.4	35.6	39.9	4.34	47.2	50.6	
20	12	23	33.6	42.8	51.3	58.2	65	70.8	76.5	82	
30	20.3	37.5	53.5	67.5	81	92	102	112	121	128	
40	33	59.8	83	104	124	141	157	171	184	197	
50	51.8	91	124	155	184	208	232	253	272	290	

TABLE III. PARTIAL HEATS OF ABSORPTION OF ACETONE IN WATER AT 20° C.

Acetone Concn. in Water, Mole Fraction	Slope of Line in Fig. 3 (Left)	Gram-Cal./Gram Mole	
		Total heat of absorption	Heat of soln.
0.01	0.879	9250	1590
0.02	0.828	8720	1060
0.03	0.785	8270	610
0.04	0.772	8120	460
0.05	0.766	8060	400
0.06	0.765	8050	390
0.07	0.764	8040	380
0.08	0.762	8020	360
0.09	0.759	7990	330
0.10	0.754	7930	270



SEPTEMBER'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ SEPTEMBER 2. War Mobilization Director Byrnes sets up interagency committee to formulate coordinated program for utilization of government-owned war plants. Committee will comprise representatives of War Production Board, War Manpower Commission, Defense Plant Corporation, and Surplus War Property Administration.

¶ SEPTEMBER 4. Sweden announces two Nobel prizes will be awarded this year in chemistry and two in physics.

¶ SEPTEMBER 5. J. A. Krug, acting chairman of WPB, announces drastic program for virtually unlimited civilian production after fall of Germany.~~President abolishes office of Rubber Director and sets up Rubber Bureau within WPB with James F. Clark as director.~~Census Bureau figures show decline in production of sulfa compounds owing to more widespread use of penicillin.~~Ordnance plants ordered to stop shipments of nitric acid to industry as Army requirements rise.

¶ SEPTEMBER 6. Goodyear develops continuous polymerization process, said to increase by 40% the capacity of Nation's synthetic rubber plants, at same time bettering quality.

¶ SEPTEMBER 7. Manpower requirements of industry following collapse of Germany can be met "without the controls which have been in effect in recent months", reports WMC Chairman McNutt.~~Assistant Attorney-General Berge tells Kilgore Committee the U. S. must develop and apply program to control or break German cartel agreements. Charges Bausch & Lomb and Carl Zeiss with cartel ties.~~Canadian sugar industry through 7 leading companies allies itself with Sugar Research Foundation, N. Y., in research program.~~Brig. Gen. Wolfe discloses that supergasoline has been developed by Matériel Command of armed forces and petroleum industry experts for B-29 superfortresses.~~Chairman Connally announces Senate Foreign Relations Committee has postponed hearings on Anglo-U. S. oil pact until after election.

¶ SEPTEMBER 8. President Roosevelt in letter to Secretary of State Hull calls for curb on cartels.~~Acting Chairman Krug reorganizes WPB under triumvirate consisting of himself, A. H. Bunker as chief of staff, and H. G. Batchelder as chief of operations.

¶ SEPTEMBER 9. WPB announces that "almost all controls" will be lifted when Germany falls.

¶ SEPTEMBER 10. House Economic Planning Committee recommends postwar cut in business taxes.~~War Mobilization Director Byrnes submits report on demobilization to President in which he urges speed in cutback procedure, plant clearances, and clear-cut price policies.~~Wendell Berge

in new book says greatest obstacle to postwar economic success is the threat of cartel control.

¶ SEPTEMBER 11. Weirton Steel Co., subsidiary of National Steel Corp., successfully rolls magnesium in very thin gages and thus adapts its plant to nonferrous metals.~~ACS opens 108th meeting in New York with North Jersey Section as host.~~WPB approves over \$5,000,000 addition to U. S. Rubber Co. plant in Detroit for production of high flotation tires for Army.~~B. F. Goodrich makes synthetic rubber bands.~~Federal Trade Commission orders Eastman Kodak to discontinue kodachrome agreements which the Commission contends fix minimum retail prices on kodachrome and magazine film.

¶ SEPTEMBER 12. E. C. Hughes, director of chemical research, Standard Oil of Ohio, announces perfection of new method of testing oils which opens way for lubrication of high-speed, high-compression postwar motors.~~Department of Justice representatives testify before Senate Military Affairs Committee on Demobilization that German cartels have been boring into American industry and preparing groundwork for resumption of domination in postwar era.

¶ SEPTEMBER 13. 35-year-old Arthur C. Cope, assistant professor of chemistry at Columbia University, receives ACS award of \$1000 for outstanding research in organic chemistry. Prize is donated by Alpha Chi Sigma.~~James B. Conant, president of Harvard, receives Priestley Medal, highest award of ACS. In accepting medal, he urged United States aid to student scientists.~~Owners offer Universal Oil Products to ACS; special committee appointed by President Midgley to consider acceptance of gift.~~Charles F. Kettering states before ACS meeting in New York that new motor fuel now being developed will have four times the power with one fourth less fuel consumption of present 100-octane gasoline.~~Thomas Midgley, Jr., in Presidential Address before ACS meeting states that science needs originality of youth to keep pace with opportunities for service to mankind.~~Baekeland Award¹ established by North Jersey Section of ACS to encourage creative talents of younger American chemists.~~William J. Berry, Western Michigan College, tells American Association for Advancement of Science meeting in Cleveland that United States could support a population of 551,000,000 by better utilization of agricultural resources.~~WPB permits copper as undercoating for chromium and nickel, urges greater aluminum use in all types of production.~~Cordell Hull, unfolding plans for postwar world organization, suggests a United Nations trade conference at which one purpose would be to outlaw international

¹ Chem. & Eng. News, 22, 538 (Sept. 25, 1944).

cartels.~~WMC Chairman McNutt outlines plans to assist industry in reconversion by releasing and assigning engineers and technicians for blueprinting civilian production.~~Post-war planning committee of U. S. Department of Agriculture recommends conversion of nearly 40% of nitrogen-producing capacity of 9 government-owned synthetic ammonia plants to manufacture of nitrogen fertilizer and ammonia for peacetime requirements (I. & E. C. Reports, advt. sect., p. 5).

¶ SEPTEMBER 14. Theodore G. Klumpp, president of Winthrop Chemical, tells ACS meeting that it is "biologically possible for many of our children or children's children to live in good health for 130 years". Says more time and money should be devoted to research in medical sciences.~~Seven British- and German-owned companies indicted on charge of monopolizing world supply of borax.~~George A. Hill, Jr., president, Houston Oil Co., in statement made public by Petroleum Industry War Council, assails Anglo-U. S. oil pact, now before Senate, as a cartel spur.

¶ SEPTEMBER 16. Secretary of Interior Ickes announces Bureau of Mines will soon send engineering survey parties to examine potential locations for synthetic liquid fuel and demonstration plants.

¶ SEPTEMBER 17. Food, chemical, and soft drink industries to get increased quotas of glass containers under WPB's revision of L-103-B.

¶ SEPTEMBER 18. Blaw-Knox, designers and engineer-contractors, announce 5 synthetic rubber pilot plants will be ready early in 1945.~~C. O. Rison, vice president of North Pacific Pipeline Co., announces plans for pipe line next year from Montana and Wyoming fields to supply projected \$5,000,000 refinery in Seattle.~~Basic Magnesium, Inc., on October 1 will start reduction of output in 4 units of 10-unit plant still in operation.~~House approves surplus property measure, establishing a 3-man board to direct disposal of estimated \$100,000,000,000 in surplus war matériel.~~Defense Supplies Corp. issues second monthly list of surplus war chemicals available for immediate sale to industry.

¶ SEPTEMBER 19. Senate accepts conference report to set up office of War Mobilization and Reconversion and dispose of surplus property to estimated value of \$100,000,000,000 under single administrator, nominated by President and confirmed by Senate.~~Standard Oil (N. J.) at Bayway plant demonstrates first full-scale aircraft engine test stand designed for research on aviation fuels.~~President Roosevelt orders Government to formulate plans for liquidation of wartime agencies.~~Texas oil men adopt resolution asking Senate not to ratify Anglo-U. S. world petroleum agreement.~~British Ministry of Supply retains Commercial Solvents as consultant in building and bringing into operation plants capable of producing 100,000,000,000 units of penicillin monthly.~~Borax Consolidated Ltd. denies that it and other companies monopolize world supply of borax.

¶ SEPTEMBER 20. House approves conference report on reconversion legislation adopted September 19 by Senate.

¶ SEPTEMBER 21. Pittsburgh Plate Glass opens new field for transportation with shipment of 380 tons of liquid chlorine by barge; announces that, in line with nationwide expansion policy, it will erect new paint plant at Springdale, suburb of Pittsburgh.~~Du Pont Co. announces chemical for transmuting lumber into new material, known as Arboreald.~~Coastal Chemical Co., Harlingen, Texas, acquired by Niagara

Sprayer & Chemical Co., Middleport, N. Y.~~American Tel. & Tel. establishes trust fund to finance five annual postdoctorate fellowships in physical sciences.~~Roosevelt urges a Missouri TVA in message to Congress before recess.

¶ SEPTEMBER 22. Mathieson Alkali starts production of ammonia at government-built plant at Lake Charles, La., with natural gas as raw material.~~According to State Department announcement, United States, Netherlands, and Great Britain will set up informal group to study common problems arising from production, manufacture, and use of rubber.

¶ SEPTEMBER 23. Monthly Chemicals Allocation report issued by WPB shows trend toward expansion in permitting civilian end uses for chemicals.

¶ SEPTEMBER 25. Shellac and balsa wood are removed from import control by WPB, effective October 1.~~FTC outlines policies under Webb-Pomerene Act for export associations engaged in foreign operations.~~Corning Glass purchases substantial interest in Brazil's leading glass company.

¶ SEPTEMBER 26. WPB reports Carbon Dioxide Producers Industry Advisory Committee seeks facilities for producing 90,000 tons CO₂ per quarter.~~Firestone Tire & Rubber announces development of first heat-tempered all-plastic tire.~~R. E. Gage, director of research and development, Mathieson Alkali Works, announces dichlorostyrene, from which heat-resistant plastic or synthetic rubber can be made.~~WMC Chairman McNutt lifts all manpower controls for veterans of present war.

¶ SEPTEMBER 27. McNutt says, with defeat of Germany, 4,000,000 workers will be released from present jobs, munitions program will be cut back 40%, manpower controls will end.~~Acting WPB Chairman Krug says Conservation Division will be discontinued October 31.~~J. N. Forker, vice president of Koppers Co., announces phthalic anhydride plant, annual capacity 7,000,000 pounds, will be built in Kobuta, Pa.~~WPB places silica gel under control because of heavily increased military demands.

¶ SEPTEMBER 28. Rubber shortage beaten by synthetic rubber production, Vice President Crossland, Rubber Reserve Co., tells representatives of 51 government-financed plants.~~B. F. Goodrich announces manufacture of 100 rubber tires from Russian dandelion.~~PAW issues order limiting output of premium motor fuel for nonmilitary use to 50% of current output.~~Interior Department officials seek information on Russia's plans for use of Romanian Ploesti oil refineries, owned in large part by Standard Oil Co. of N. J.

¶ SEPTEMBER 29. The President urges Foreign Economic Administration to relax export controls on V-E day in so far as possible.

¶ SEPTEMBER 30. F. B. Jewett retires as vice president of American Tel. & Tel., will devote full time to presidency of National Academy of Sciences and membership on National Defense Research Committee of OSRD.~~President Roosevelt accepts resignation of D. M. Nelson as chairman of WPB and appoints J. A. Krug as successor.~~WPB announces government-owned manganese plant at Las Vegas, Nev., is being closed.~~Senator Gillette accuses petroleum industry of trying to "squeeze out" the farmer to get a "post-war synthetic rubber monopoly".~~WPB Chairman Krug reports that, immediately following V-E day, most controls will be dispensed with, but certain controls must continue in chemicals, textiles, and forest products.

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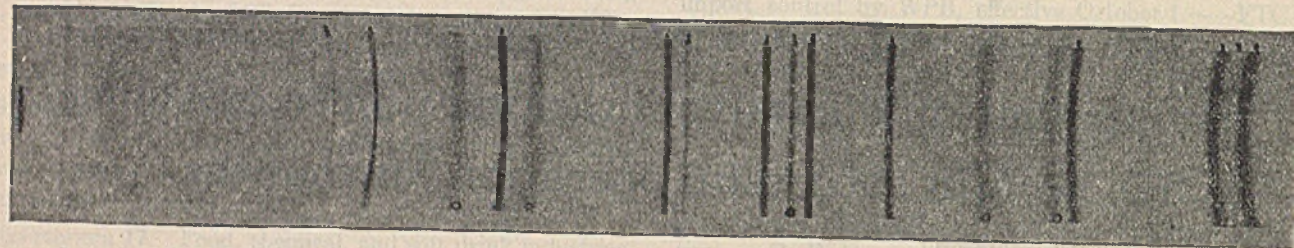
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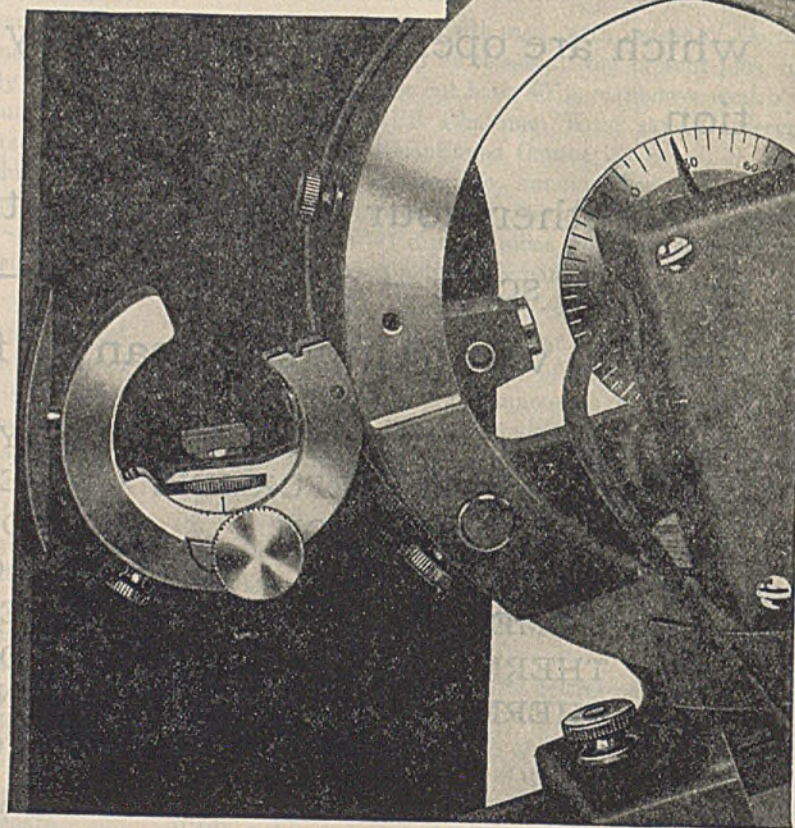
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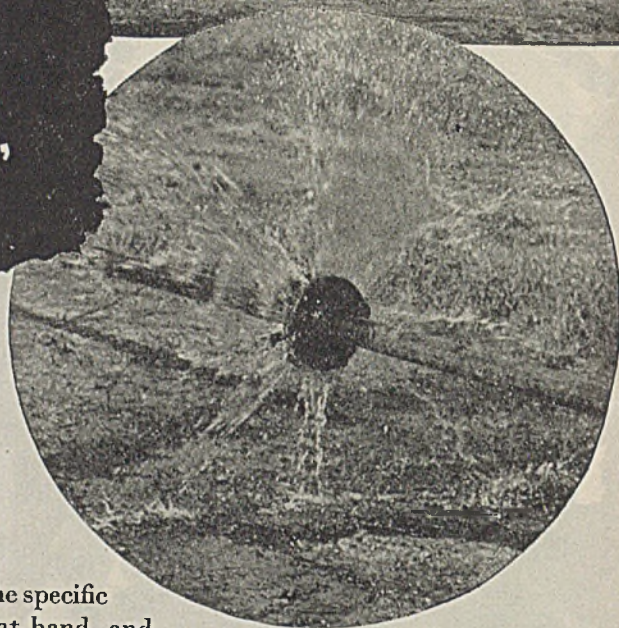
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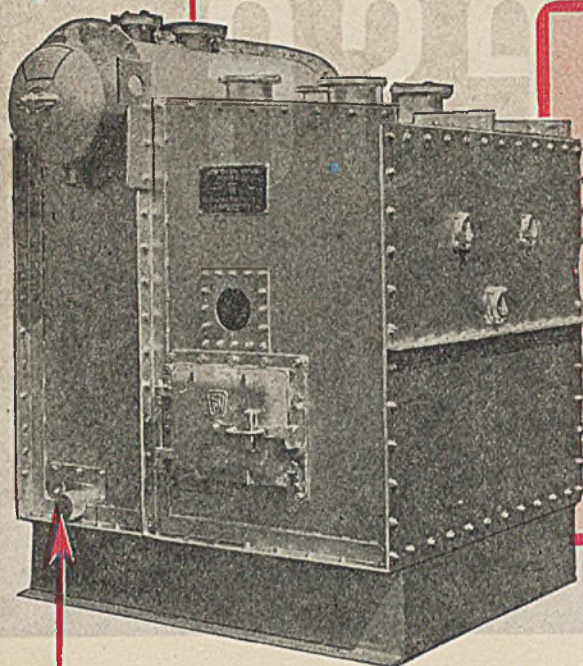
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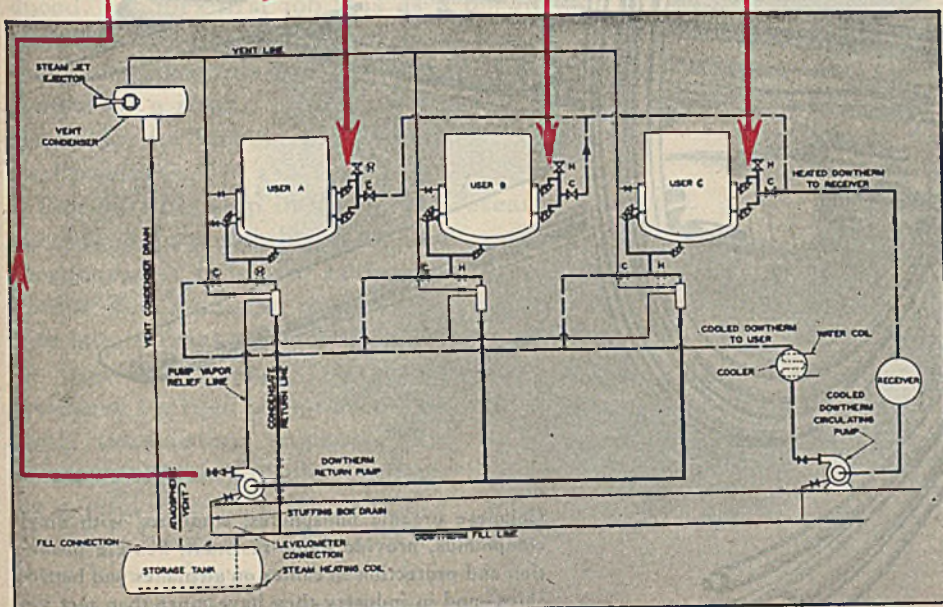
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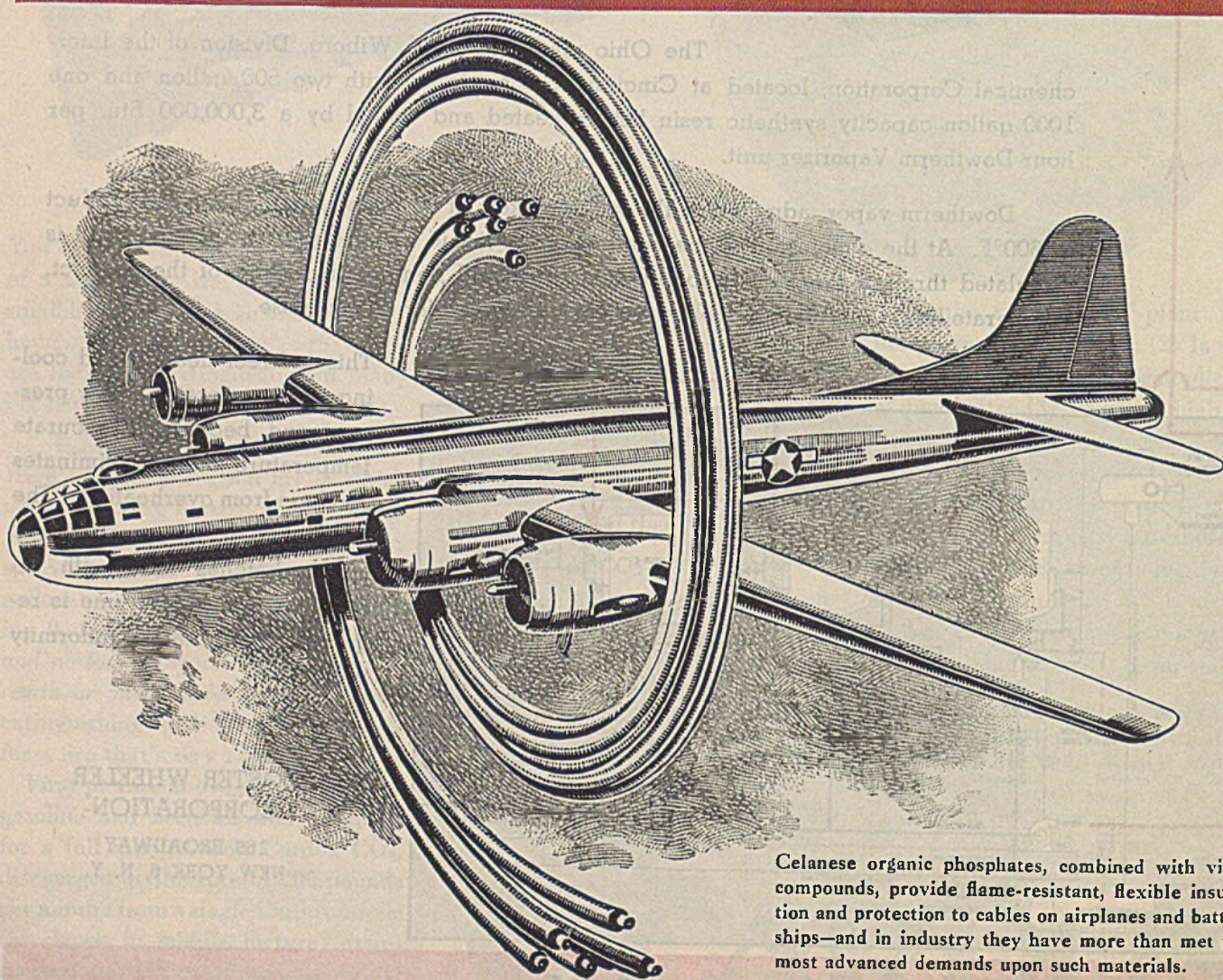


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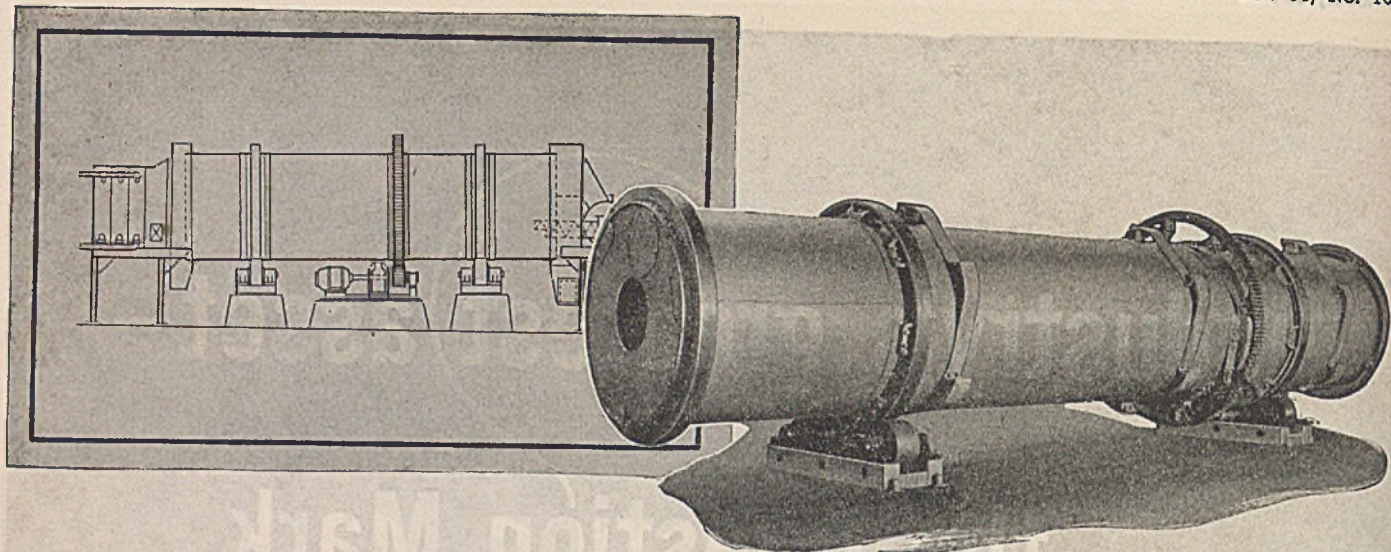
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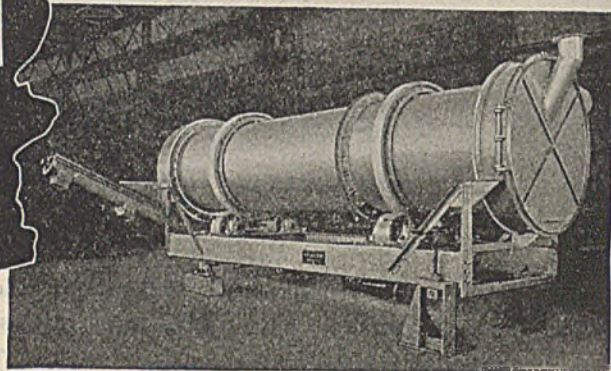
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Frequently these dryers are of stainless—stainless-clad—nickel-clad—monel lined or aluminum lined construction. They sometimes have totally enclosed screw feed and discharge conveyors, especially if the material is fine or powdery,—and are sometimes supported on a self-contained and adjustable steel frame so that the slope of the

dryer can be varied over a wide range, permitting a single equipment to meet the requirements of drying a wide variety of different products.

Style J dryers can be operated either parallel or counter-flow. They can be fitted with knockers to prevent damp material from adhering to the interior cylinder walls, if necessary. They are ideally suited for "2 stage" drying, and can maintain close pressure balance with the ambient atmosphere. But send for a copy of our Bulletin No. 89. It gives complete details about Bartlett-Snow dryers, coolers, calciners, autoclaves, kilns and other heat processing equipment—and contains much technical data of interest to engineers and operating men.

THE C. O. BARTLETT & SNOW CO.

6207 HARVARD AVENUE • CLEVELAND 5, OHIO

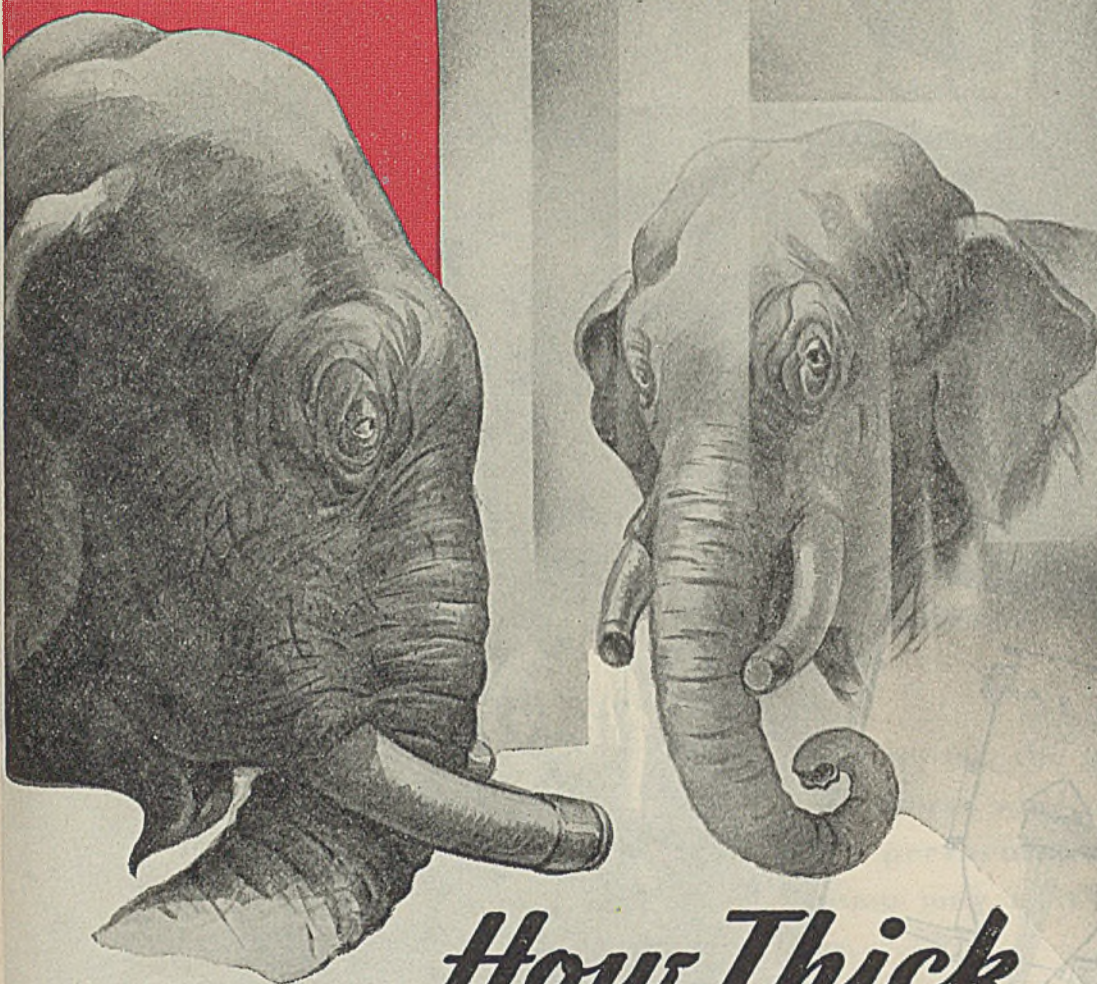
Engineering and Sales Representatives in Principal Cities

DRYERS • CALCINERS • KILNS • PRESSURE VESSELS

• COMPLETE MATERIAL HANDLING FACILITIES TO MEET ANY REQUIREMENT •
ONE CONTRACT • ONE GUARANTEE OF SATISFACTORY PERFORMANCE • UNIT RESPONSIBILITY

INGACLAD

STAINLESS-CLAD STEEL



How Thick should an Elephant's Hide be?

***Thick enough to withstand the attacks
of its enemies . . .***

That's also true of your stainless equipment . . . Why pay for more stainless metal than you need? . . . By using IngAclad you greatly reduce the material cost, yet have perfect stainless protection on the exposed surface . . . IngAclad consists of a 20% cladding of finest stainless steel bonded by the Ingersoll Process to a backing of mild steel.

If you are considering modernizing your plant with stainless equipment, be sure to investigate IngAclad . . . the only Stainless-Clad material with a 12-year record of satisfactory service in continuous use.

Write for Special IngAclad Folder

Users of IngAclad include:

American Cyanamid Co.
Armour & Co.
Coco-Cola Bottling Co.
Dow Chemical Co.
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General American Tank Car Corp.
Jeffrey Mfg. Co.
Eli Lilly & Co.
Liquid Carbonic Co.
Monsanto Chemical Co.
Procter & Gamble Co.
Sherwin-Williams Co.
Frederick Stearns & Co.
United States Potash Co.
and many others.

INGERSOLL STEEL & DISC DIVISION

BORG-WARNER CORPORATION

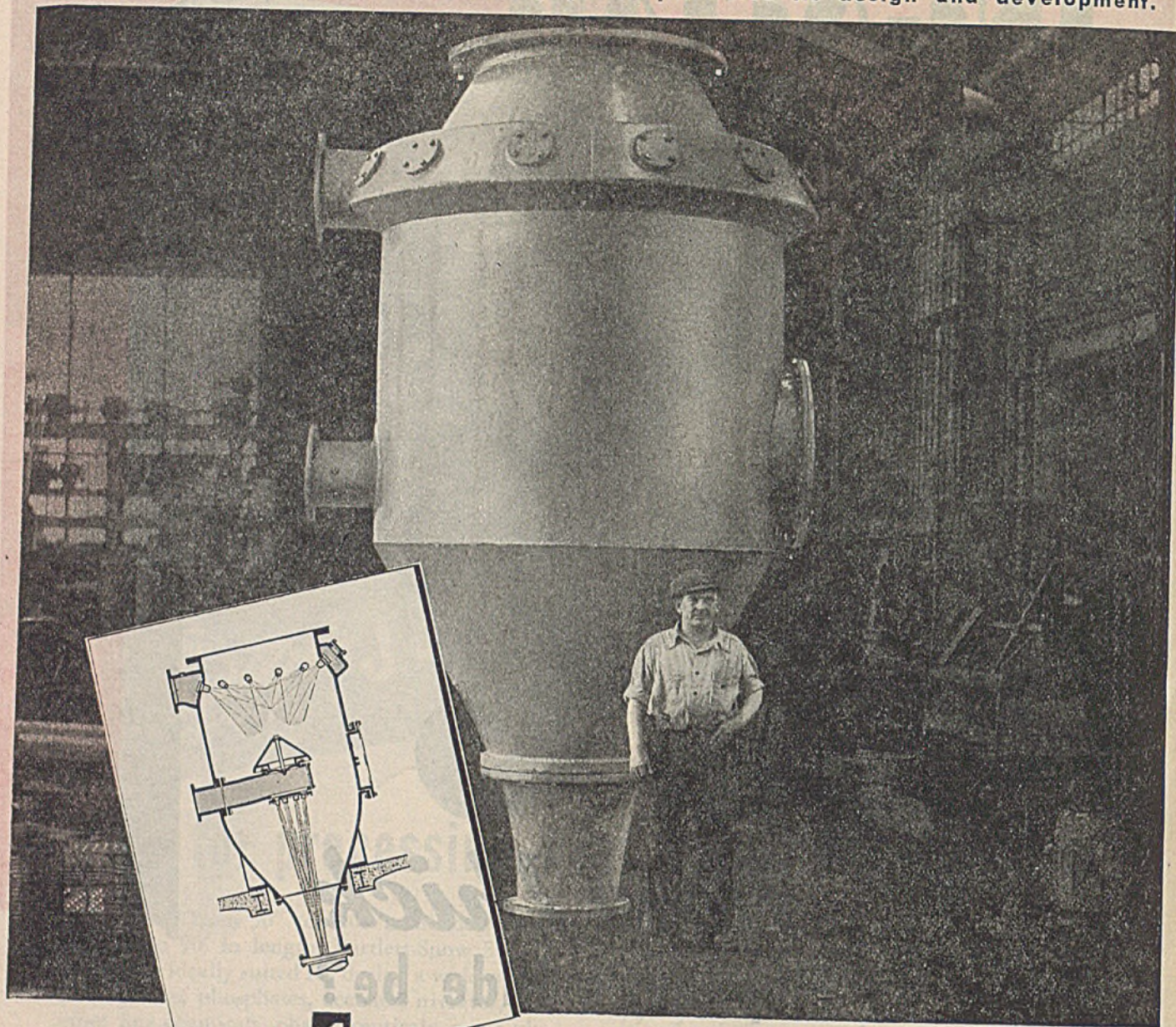
310 South Michigan Avenue

Chicago 4, Illinois

Plants: Chicago, Ill.; New Castle, Ind.; Kalamazoo, Mich.

Also Producers of Ingersoll Solid Stainless and Heat-Resisting Steels

NOTE: SCHUTTE & KOERTING are the **ORIGINATORS** of the Multi-Jet Spray Condenser principle and have, for many years, pioneered its design and development.



WELDED BAROMETRIC *Multi-Jet Spray* CONDENSERS of CORROSION-RESISTANT METALS

SK Barometric MJS Condensers are built in 13 standard sizes in capacities from 2000 up to 70,000 pounds of steam per hour. Write for Bulletin 5-AA.

This SK Barometric Multi-Jet Spray Condenser has a body of welded steel for a special application. Although many MJS Condensers are made of cast iron, they can also be supplied in 18-8 stainless steel, hard lead and other corrosion resistant materials, depending upon the process involved.

Absence of internal baffles is a feature of SK Barometric MJS Condensers. There are no moving parts in the

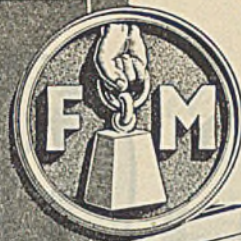
vacuum chamber and no air pump is required for operation, since condensed steam, air and non-condensable gases are removed by the combined action of the sprays, jets and barometric tail pipe. Separate control of water to the jets and sprays contributes to the flexibility and high efficiency under changing steam, vacuum and temperature conditions.



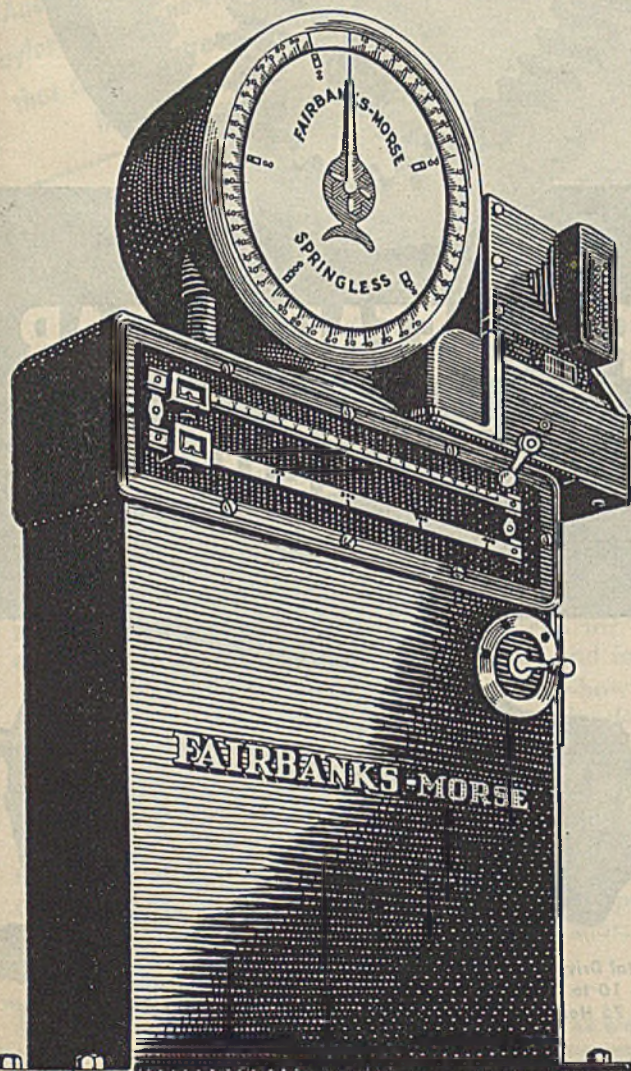
SCHUTTE & KOERTING CO. MANUFACTURING ENGINEERS
Main Office and Works: 1160 Thompson St., Philadelphia 22, Penna.

Also Producers of Ingersoll Solid Stainless and Heat-Resisting Steels

A name worth remembering!



FAIRBANKS-MORSE



After the war, the name Fairbanks-Morse will continue to mark performance-proved products only, as it has for 114 years.

No race to get civilian products onto the market early will tempt us to break this pledge.

Fairbanks-Morse Scales are precision-built instruments which provide mechanically perfect weight recording. Of sturdy scientific construction without springs or delicate parts, the countless types, styles, and modifications serve American business and industry by keeping books, records, and inventories, saving time, preventing errors, and speeding production.

BUY MORE WAR BONDS

DIESEL LOCOMOTIVES • DIESEL ENGINES • GENERATORS • MOTORS • SCALES • PUMPS • STOKERS • RAILROAD AND FARM EQUIPMENT

FAIRBANKS, MORSE & CO., CHICAGO 5, ILLINOIS

D.O. James

ESTABLISHED 1888

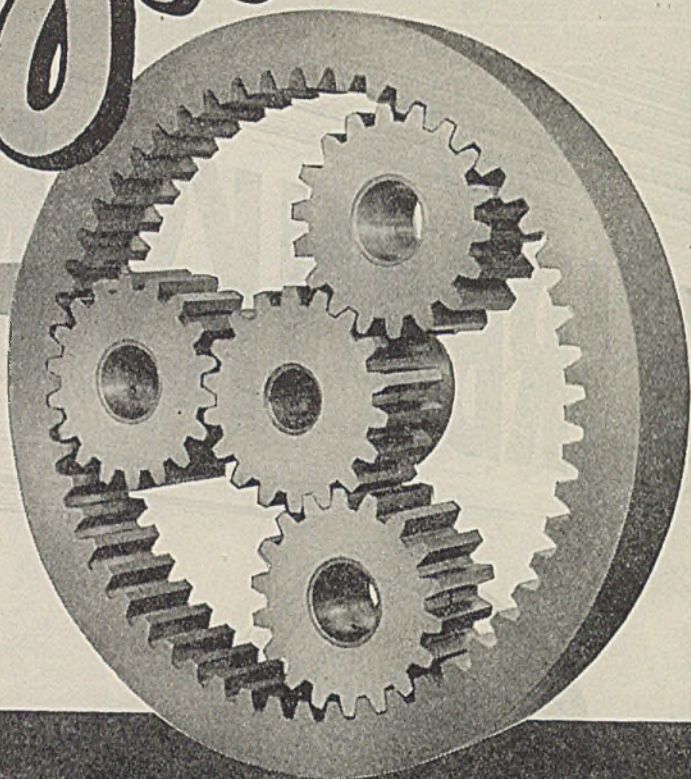
FOR LARGE SPEED REDUCTIONS AND GREATEST EFFICIENCY

SINCE 1903... D. O. James planetary Gear Reducers have been used on many industrial applications where large reductions were needed. The superior gear arrangement of this type of reducer obtains highest ratios and greatest efficiency. They are most compact and occupy very little floor space. The equal balance and similar revolving direction of the rolling contact of the gear teeth produces the maximum reduction with the minimum number of gears.

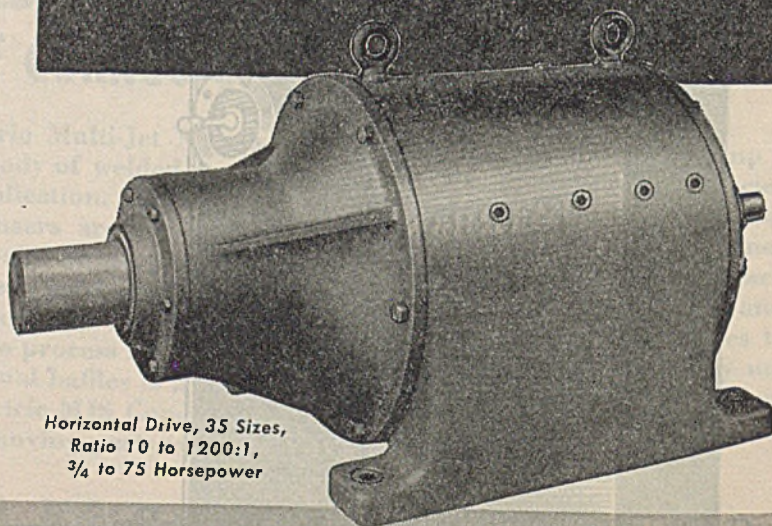
TODAY... Modern manufacturing methods and facilities, under the supervision of an experienced operating personnel, assure the utmost efficiency and durability to D. O. James Gears and Gear Speed Reducers.

D. O. JAMES MANUFACTURING
COMPANY

1140 W. Monroe St., Chicago 7, Ill.



PLANETARY GEAR SPEED REDUCER



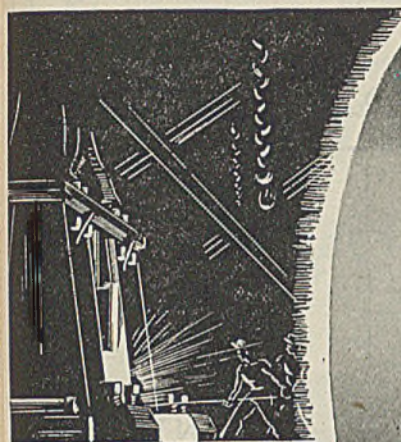
Horizontal Drive, 35 Sizes,
Ratio 10 to 1200:1,
3/4 to 75 Horsepower

56 YEARS MAKERS OF EVERY TYPE OF GEAR AND GEAR REDUCER

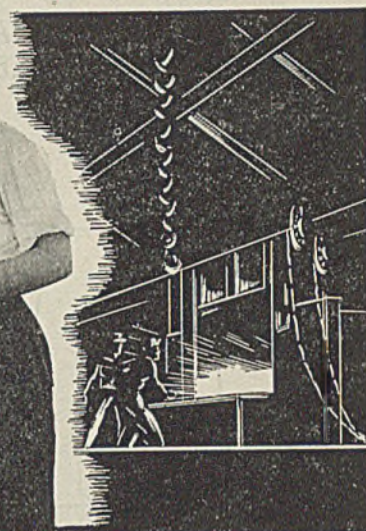
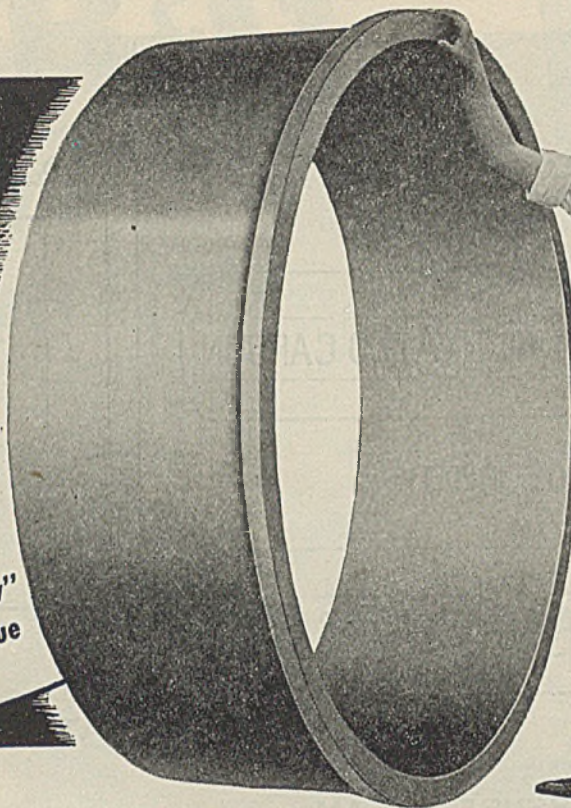
68



When bigger stub ends are built...



Another example of Taylor Forge "know-how" that means extra value in WeldELLS



• As you know, Lapped-joint Stub Ends are standardized only in pipe sizes through 24 inches. In this range thousands are used, but it's only on rare occasions that a real whopper like this one is needed. It's a seamless carbon-moly forging nearly seven feet in outside diameter and about two feet long with 1½ inch wall thickness.

Obviously, we aren't soliciting orders for 84 inch O.D. Lapped-joint Stub Ends. However, when "specials" of this kind are needed, it's a good bet that the job will be turned over to Taylor Forge.

Yes, for many years industry has considered Taylor Forge headquarters for those forging requirements that call for *unusual* knowledge of the behavior of hot metal under pressure and impact.

And isn't it true that this *unusual* "know-how" and facilities also make Taylor Forge headquarters for *unusual* value in your standard requirements for welding fittings?

You can be sure that it does, and if you want further confirmation you can find it in the features of WeldELLS listed opposite.

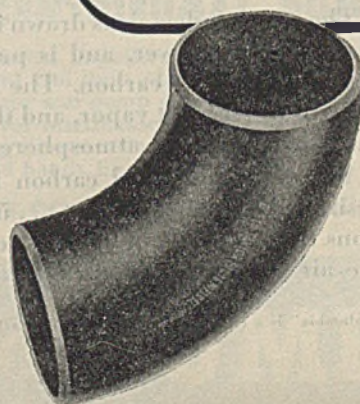
You will find features that are not combined in any other welding fittings . . . extra reinforcement where stresses are greatest . . . ample tangents . . . extremely accurate dimensions . . . permanent identifications . . . precision quarter marked ends. In short, you will find that

WeldELLS alone combine 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.

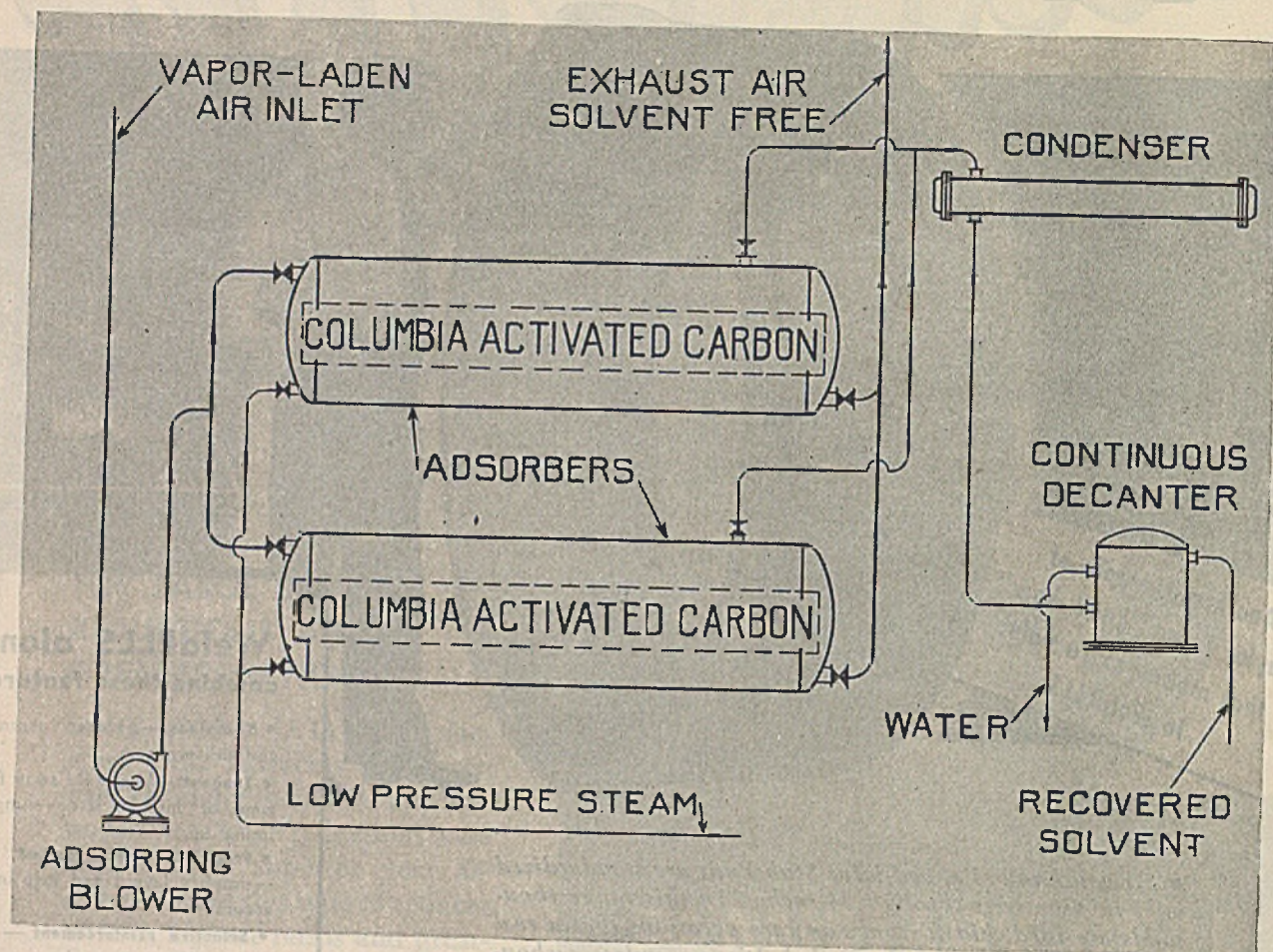
WeldELLS have everything

TAYLOR FORGE & PIPE WORKS, General Offices & Works: Chicago, P. O. Box 485
New York Office: 50 Church Street • Philadelphia Office: Broad Street Station Bldg.



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  New York 17, N. Y.
PRODUCERS OF SYNTHETIC ORGANIC CHEMICALS

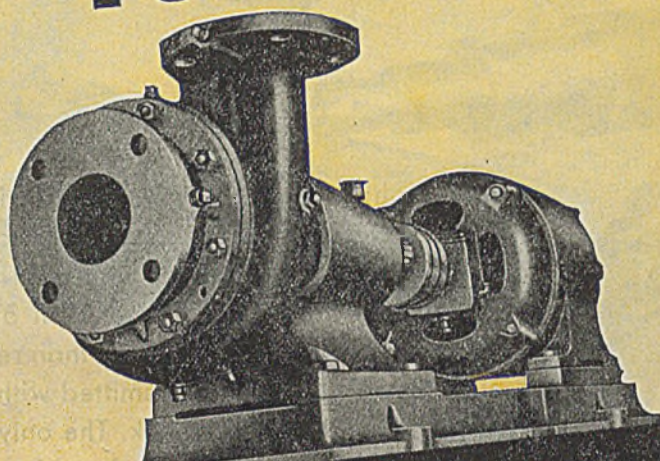
"Columbia" is a trade-mark of Carbide and Carbon Chemicals Corporation

== BUY UNITED STATES WAR BONDS AND STAMPS ==

B & G

centrifugal

PUMPS TYPE "W"



BELL & GOSSETT CO.
Morton Grove, Illinois

Bulletin
CP 843

**WRITE FOR
YOUR COPY!**

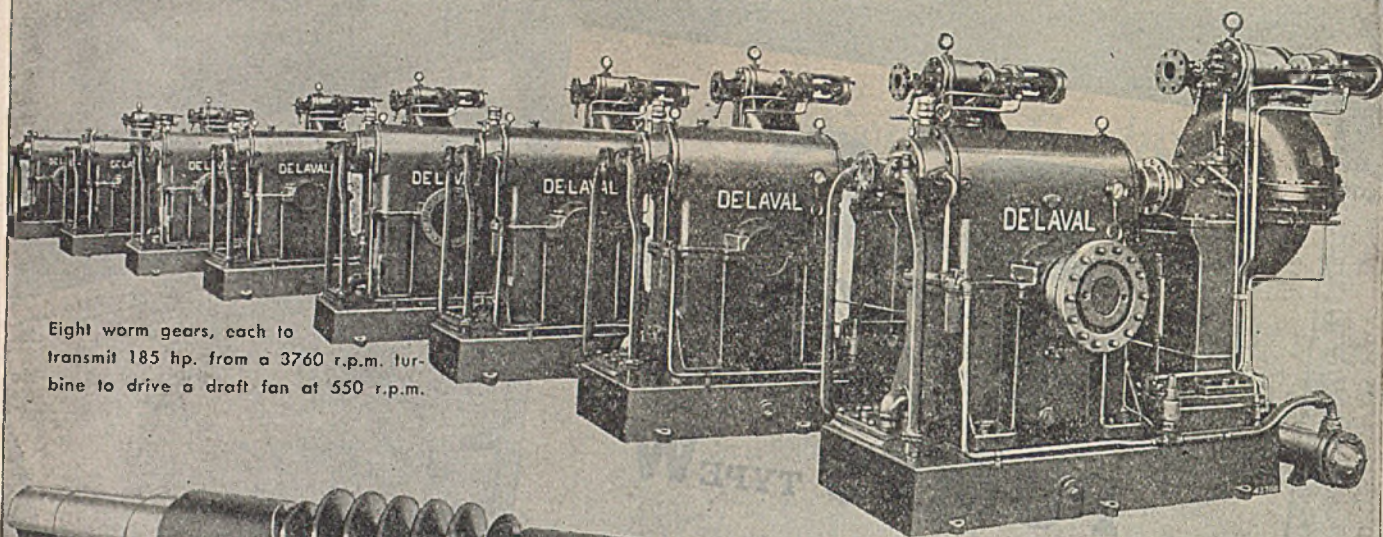
FEATURING EASY SELECTION TABLES FOR THIS COMPLETE LINE OF OPEN AND ENCLOSED IMPELLER CENTRIFUGAL PUMPS

What do you look for in a centrifugal pump? Design—workmanship—quality of materials—record of performance? You'll find them all in B & G Centrifugal Pumps... features that will appeal to your appreciation of good engineering... because they are based on twenty years' experience in the industrial field. The last word in centrifugal design—backed by precision manufacture and rigid factory inspection—built to stand up under continuous operation.

Semi-open and enclosed impellers are available in both Flexible Coupled and Uni-Built Models. B & G Uni-Built Pumps have the motor and pump combined into a single, compact unit, ideal for installation where space is limited. Send for the Catalog illustrated above—you'll like its easy Selection Tables and handy Engineering Data.

BELL & GOSSETT CO. Morton Grove, Illinois

B & G centrifugal PUMPS



Eight worm gears, each to transmit 185 hp. from a 3760 r.p.m. turbine to drive a draft fan at 550 r.p.m.



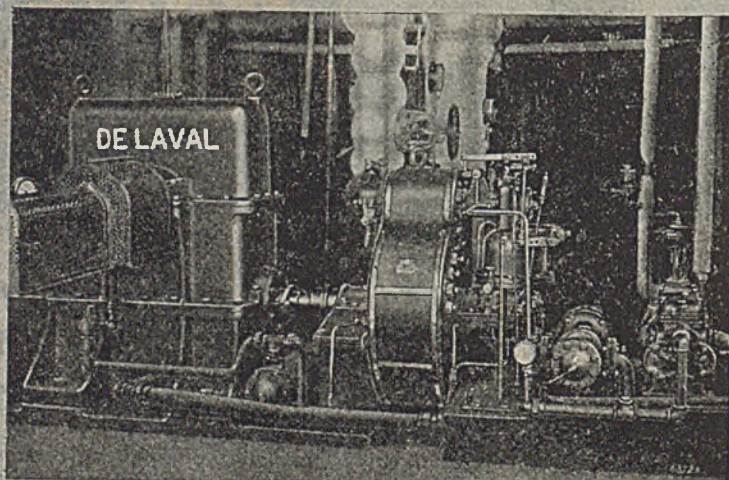
**FOR
SMALL
TURBINE DRIVES**
specify
DE LAVAL
**WORM
GEARS**

Ask for Booklet W-1130 on
"Industrial Applications of Worm Gears"

Worm gear transmitting 225 hp. from 3900 r.p.m. turbine to drive a paper machine. A De Laval worm gear in similar service has been in continuous operation for more than 15 years.

The high efficiency and reliability of De Laval worm gears is especially valuable in continuous, 24-hour service. The efficiency approaches 97 per cent at some ratios and increases, rather than recedes, with use. Power is transmitted without vibration, chatter or shock. The only maintenance required is occasional inspection of the oil level in the casing.

The driven shaft can be extended to either right or left, or both, or either up or down, or both.



DE LAVAL

WORM GEAR DIVISION

of the De Laval Steam Turbine Co., Trenton, N. J.

MANUFACTURERS OF TURBINES . . . STEAM, HYDRAULIC; PUMPS . . . CENTRIFUGAL, PROPELLER, ROTARY DISPLACEMENT, MOTOR-MOUNTED, MIXED-FLOW, CLOGLESS, SELF-PRIMING; CENTRIFUGAL BLOWERS and COMPRESSORS; GEARS . . . WORM, HELICAL; and FLEXIBLE COUPLINGS

PERMEABILITY OF POROUS CARBON AND GRAPHITE AVERAGE VALUES						
Grade Porous Carbon or Porous Graphite	Effective Porosity %	Pore Diameter Average		Filter Action Minimum Diameter Particle Retained Inches	Aver. Water* Permeability at 5 lb./sq. in. Pressure Gal./sq.ft./min.	Average Air** Permeability at 2 inch Water Pressure Cu.ft./sq.ft./min.
		Inches	Microns			
60	48	0.0013	33	0.00047	14.0	4.0
50	48	0.0019	48	0.00079	30.0	8.5
40	48	0.0027	69	0.00098	45.0	17.0
30	48	0.0039	99	0.00173	80.0	33.0
20	48	0.0055	140	0.00300	120.0	
10	48	0.0075	190	0.00590	175.0	

* Water at 70°F.—Plate 1 inch thick.

** Air at 70°F., 760 mm. Hg. pressure, 15% relative humidity—Plate 1 inch thick.

POROUS CARBON and GRAPHITE

For Filtration and Gas Dispersion in the Chemical and Metallurgical Industries

AS PLATES, open and blind-end tubes, and rods, "National" porous carbon and graphite are ideal materials for the diffusion of gases in liquids and for the aeration and filtration of liquids, particularly those of highly corrosive character.

They are inert to practically all acids, alkalis, and other solutions and are especially useful for the filtration of *molten salts, alkalis, and fluorides*. A special porous carbon is available for use in *caustic* filtration.

High and uniform permeability, and small pore size, make these materials unusually effective for gas dispersion . . . and ideal for steam

spargers for the heating of corrosive liquids with steam. They dissipate steam in minute bubbles, with resultant high heat absorption by the liquid and freedom from bumping. And they are not subject to fracture and spalling from thermal shock.

Available in six grades and a wide variety of standard and special sizes, porous carbon and graphite plates, tubes and rods may be easily machined and fabricated into virtually any type of apparatus. For complete details, write to our nearest Division Office.

Keep Your Eye on the Infantry . . .

the Doughboy Does It!

The registered trade-mark "National" distinguishes products of National Carbon Company, Inc.

NATIONAL CARBON COMPANY, INC.

Unit of Union Carbide and Carbon Corporation



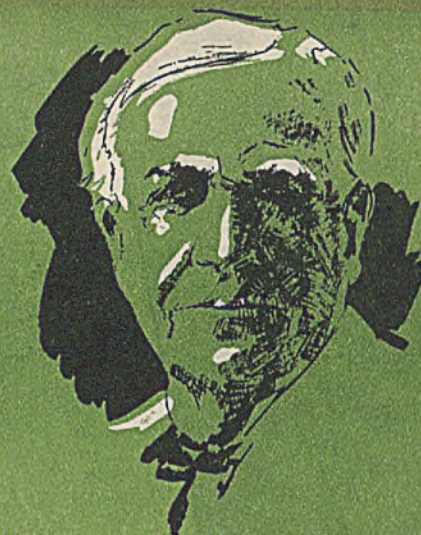
General Offices: 30 East 42nd Street, New York 17, N. Y.

Division Sales Offices: Atlanta, Chicago, Dallas, Kansas City, New York, Pittsburgh, San Francisco

IN INVENTION IT WAS

EDISON

Most renowned inventor of modern times, Thomas A. Edison knew that genius was primarily a matter of long, painstaking work. Asked to define the genius that produced such miracles as the electric light, he replied, "10% inspiration and 90% perspiration".

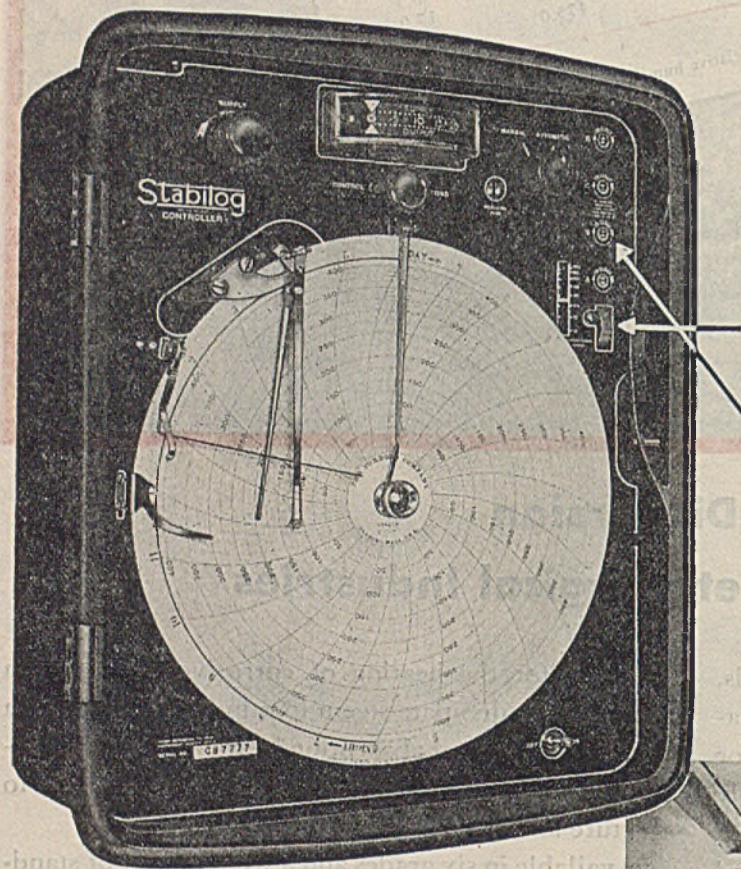


The only modern
process stabilizer that
requires just **2** adjustments

Only the Foxboro Stabilog Controller gives you optimum unit process control with only two simple adjustments:

1. **Proportional Band** is adjusted between zero and 100 per cent simply by turning the knurled knob at right of instrument. White marker indicates the setting. A lock screw at left of knob protects against any change in adjustment.
2. **Hyper-Reset values** are adjusted, when necessary, at the valve manifold above the Proportional Band control. Adjustment is not critical, and the factory setting of these valves will usually be satisfactory.

Only Foxboro offers a single adjustment on this type of instrument, because only Foxboro combines the reset or floating action with the rate sensitive action. Thus the Model 30 Stabilog Controller is extremely simple to put into operation. Yet, there's no sacrifice whatever in accuracy, flexibility, or performance.



This panel containing many Model 30 Stabilog Controllers in a leading chemical plant is typical of the chemical processing industry's reliance on Foxboro Instrumentation that creates and applies automatic instruments to improve production and reduce costs.



FOXBORO

Reg. U.S. Pat. Off.

MODEL 30

IN INSTRUMENTATION

...IT'S **FOXBORO!**

Reg. U. S. Pat. Off.

**Only genius in instrument making could have created
such an invaluable aid to unit process stabilizing as
the STABILOG CONTROLLER with HYPER-RESET**

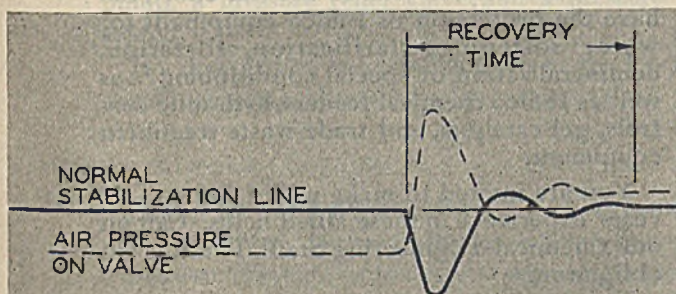
Foxboro Instrumentation means a great deal more than the mere ability to make automatic control instruments. It means a genius for creating as well as perfecting better instruments... a special talent gained only from years of the hardest kind of technical and practical experience.

As a case in point, the Foxboro Hyper-Reset Stabilog Controller has brought to air-operated control a degree of high performance that has never been approached. Operating on a principle entirely different from previous standard controllers, this remarkable instrument "feels" the rate of change of disturbance at the very start. Corrective action, measured and of the proper magnitude for any adjustment or distur-

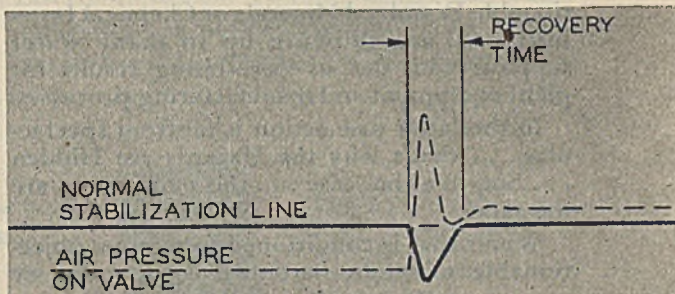
ance, is instantly in effect. The result is smoother and faster recovery from any process disturbance. Under average process conditions, recovery is often effected in as little as one-fourth the usual time - with as much as 50 per cent reduction in the amount of upset.

In appearance as well as action, too, the Model 30 Stabilog Controller reflects the advanced thinking of Foxboro Instrumentation. Its trim, rectangular housing "squares the circle" for compactness, high visibility, and broad utility. Its modern design permits true flush mounting for maximum efficiency and safety.

For complete details, write for illustrated Bulletin A-330. The Foxboro Company, 40 Neponset Ave., Foxboro, Mass. Branches in principal cities.



This curve is typical of results which may be obtained from efficient proportional control with reset - before the development of HYPER-RESET. Note the period required for recovery from this typical upset.



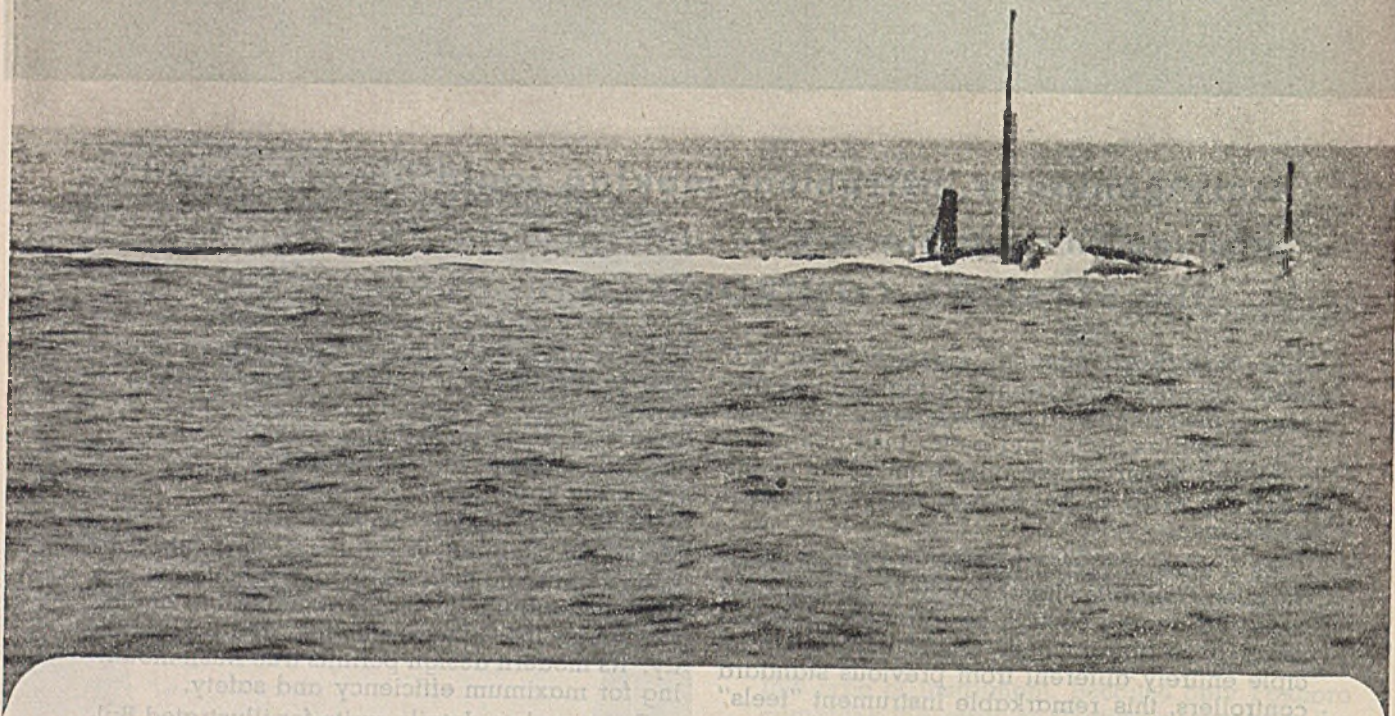
Here's what happens to the same curve with Model 30 Stabilog Control! With HYPER-RESET added to Proportional Control, stabilization is often achieved in $\frac{1}{4}$ the time, upset reduced as much as 50 per cent.

Stabilog Controller...

REG. U.S. PAT. OFF.

HIDDEN

Water Hazards



● Hidden Hazards . . . sponsored by Uncle Sam . . . are showing up in many waters with devastating results for the enemy.

Hidden Hazards . . . sponsored by Objectionable Dissolved Minerals or Chemical Instability . . . are showing up in many water supplies with just as devastating results for plant equipment and manufacturing processes.

In the latter case action is far from spectacular . . . that's why the Hazards are Hidden . . . but, in either case . . . the end results are the same.

Water that is conditioned to remove objectionable minerals, hardness, color, odor or

suspended matter will step up your production schedules, safeguard irreplaceable machinery, and protect materials in process.

Your industry, so vital to the war effort, can have the protection of Infilco equipment for water softening, clarification, filtration, demineralization or special conditioning . . . as well as Infilco chemical feeders, hydraulic controls, gel catalysts, and trade waste treatment equipment.

You are invited to make use of Infilco's 49 years' experience in these allied fields. Call on our Chemical Engineering Staff. There is no obligation.

INFILCO

INCORPORATED

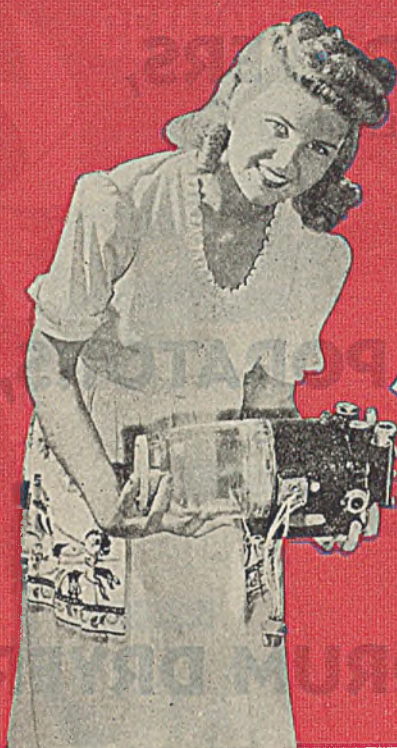
325 W. 25TH PLACE, CHICAGO 16, ILL.



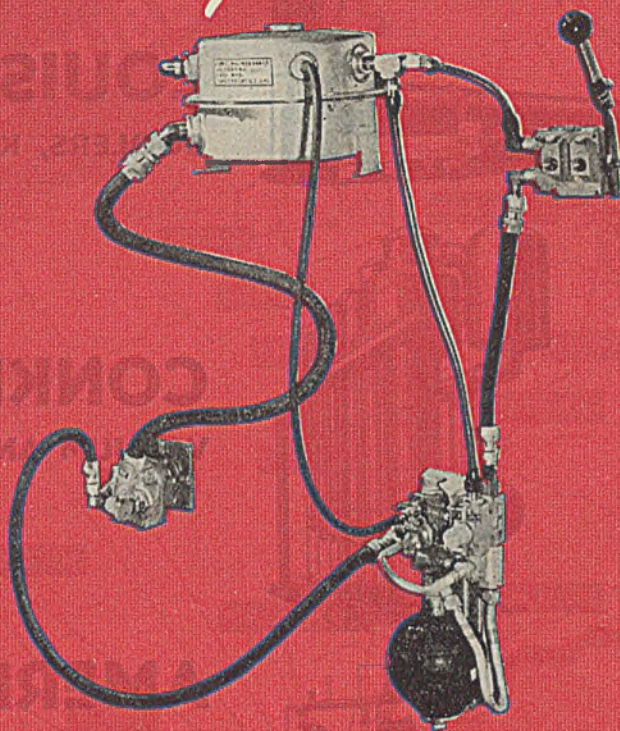
ACCELERATORS	•	ANEXERS	•	CHEMICAL FEEDERS
CATEXERS	•	CATALYSTS	•	FILTER PLANT EQUIPMENT
WATER SOFTENERS	•	FLOW CONTROLS	•	ION EXCHANGERS
CLARIFIERS	•	SETTLERS	•	ZEOLITES



NEW PESCO ELECTRO-HYDRAULIC *Power Package*



THIS
instead of
THIS



Here's another important PESCO engineering development that's destined to broaden the use and efficiency of hydraulic systems.

This new Electro-Hydraulic Power Package is a complete hydraulic system in itself . . . compact . . . light in weight . . . combining in one unit a reservoir, an electrically-driven pump, a pressure relief valve and a pressure switch.

It's designed to be installed close to the hydraulic cylinder, eliminating long runs of lines,

increasing the efficiency of the hydraulic system and reducing the number of operating parts to a new minimum. It will deliver pressures up to 3000 p.s.i., and features the superior performance made possible by PESCO pressure-loaded bushings.

Designed for the newest aircraft, the PESCO Electro-Hydraulic Power Package has many applications in modern industry. For now, you can transmit controlled hydraulic power wherever you can run a wire!

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.



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

Division Borg-Warner

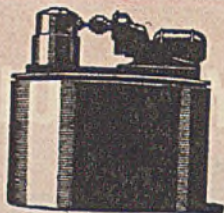


In Precision Hydraulics, Fuel Pumps,
Air Pumps, Related Accessories . . .

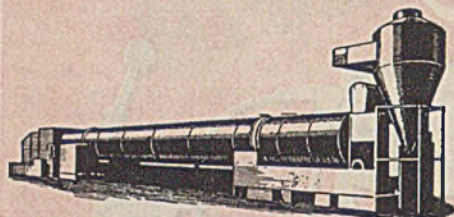
PERFORMANCE POINTS TO

Pesco

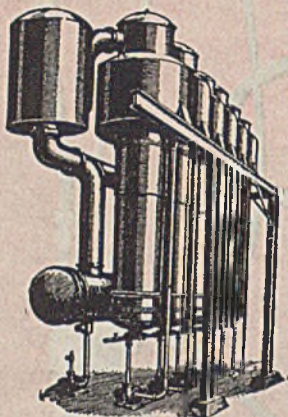
FIRST



TURBO-MIXERS, AGITATORS AND AERATORS



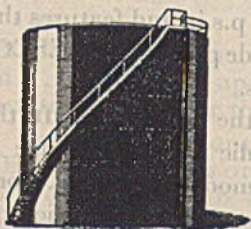
LOUISVILLE DRYERS, COOLERS, KILNS, DEWATERERS



CONKEY EVAPORATORS, VACUUM AND PRESSURE FILTERS



AMERICAN DRUM DRYERS AND FLAKERS



GENERAL AMERICAN TANKS AND PRESSURE VESSELS

Everybody in the process industries of course knows the famous products named above. Today they are being designed, built and sold by the self-same organizations as always—but with the *additional* engineering, manufacturing and research facilities now made possible by the econo-

mies and efficiencies of combined operation. The net result is that you can now purchase individual machines or completely integrated plants from one entirely dependable source—and with full assurance that you are getting the finest process equipment available in America.

GENERAL AMERICAN PROCESS EQUIPMENT

A Division of General American Transportation Corporation

Executive Offices: 433 BAXTER AVENUE, LOUISVILLE 4, KENTUCKY

New York Office: 420 LEXINGTON AVENUE, NEW YORK 17



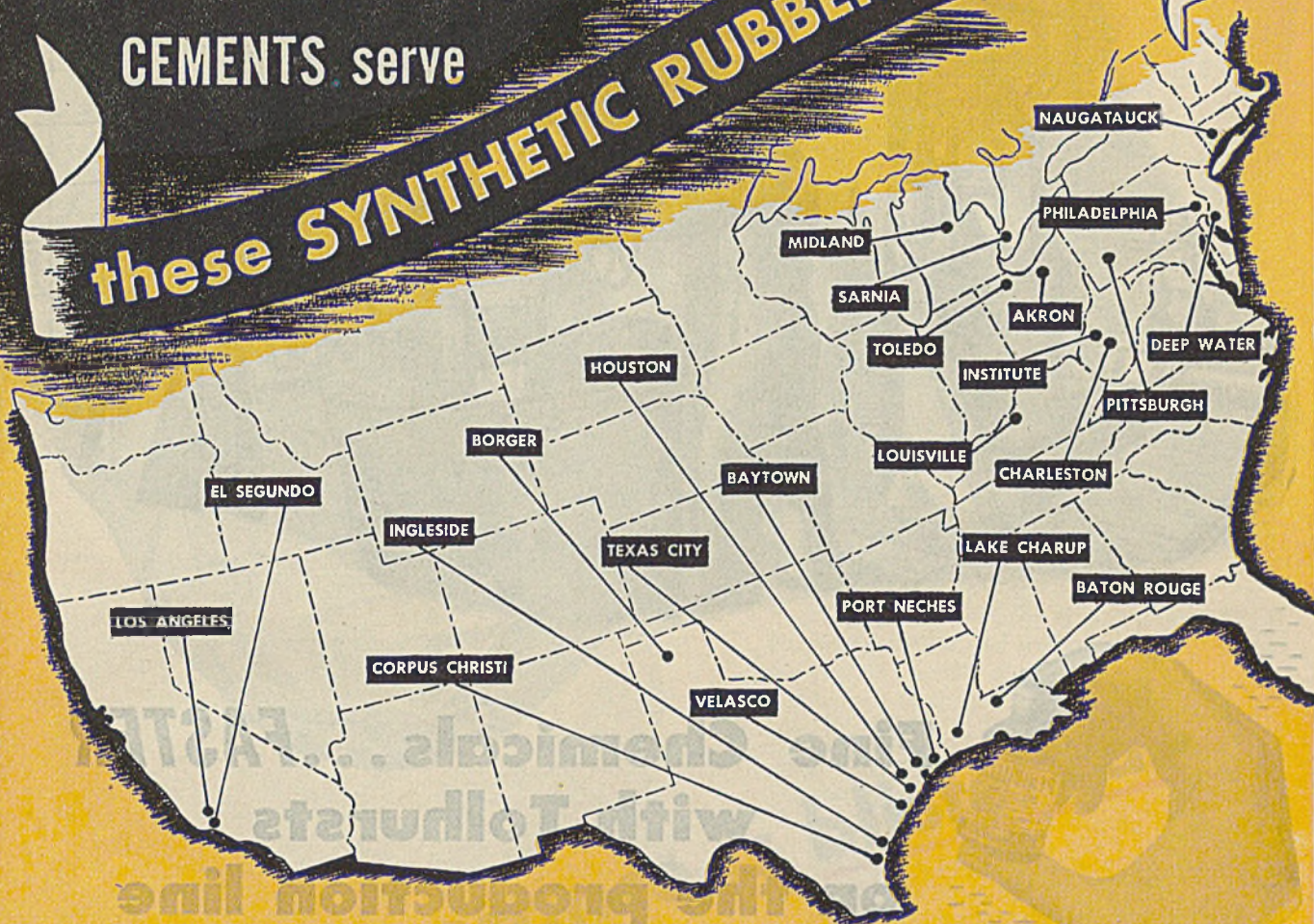
PENNSALT

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CORROSION RESISTANT

CEMENTS serve

these SYNTHETIC RUBBER plants...



Virtually overnight, America was faced with a grave need for rubber . . . and the sources of supply were shut off! Remember? Well, out of that crisis came the urgent call for synthetic rubber.

Industry's response has been one of the truly amazing stories of service. A few short years ago there were no Synthetic Rubber plants in America. Today there are 24. And Pennsylvania Salt is profoundly proud of the fact that Pennsalt Corrosion-Resistant cements have had a place in the building and maintenance of 22 of these all-important plants. *Penchlor**, *Asplit**, and *Causplit** are contributing to the success of synthetic rubber production.

PENCHLOR is a time-saving, quick-setting, self-hardening sodium silicate cement. Given punishing duty, it serves long and well under severe acid conditions.

CAUSPLIT is an exceedingly strong resin-cement, abrasion-resistant and easy to handle. Use it where conditions are alternately acid and alkali.

ASPLIT is an extremely strong resin-cement for use where conditions are always acid. Like Causplit, it is abrasion-resistant and easy to handle.

Consult Penn Salt technicians concerning your acid or alkali handling problems. Their wealth of experience is at your service without obligation on your part. Write fully or mail the attached coupon. **PENCHLOR** is available without restriction. **CAUSPLIT** and **ASPLIT** are available only for essential service.



*Trade-marks Reg. U. S. Pat. Off.

*Trade-marks Reg. U. S. Pat. Off.

Special Chemicals Division
PENNSYLVANIA SALT
 MANUFACTURING COMPANY
Chemicals

1000 WIDENER BUILDING, PHILADELPHIA 7, PA.

New York • Chicago • St. Louis • Pittsburgh • Cincinnati • Minneapolis
Wyandotte • Tacoma

SPECIAL CHEMICALS DIVISION
 PENNSYLVANIA SALT MANUFACTURING COMPANY
 Dept. IEC, 1000 Widener Bldg., Philadelphia 7, Pa.

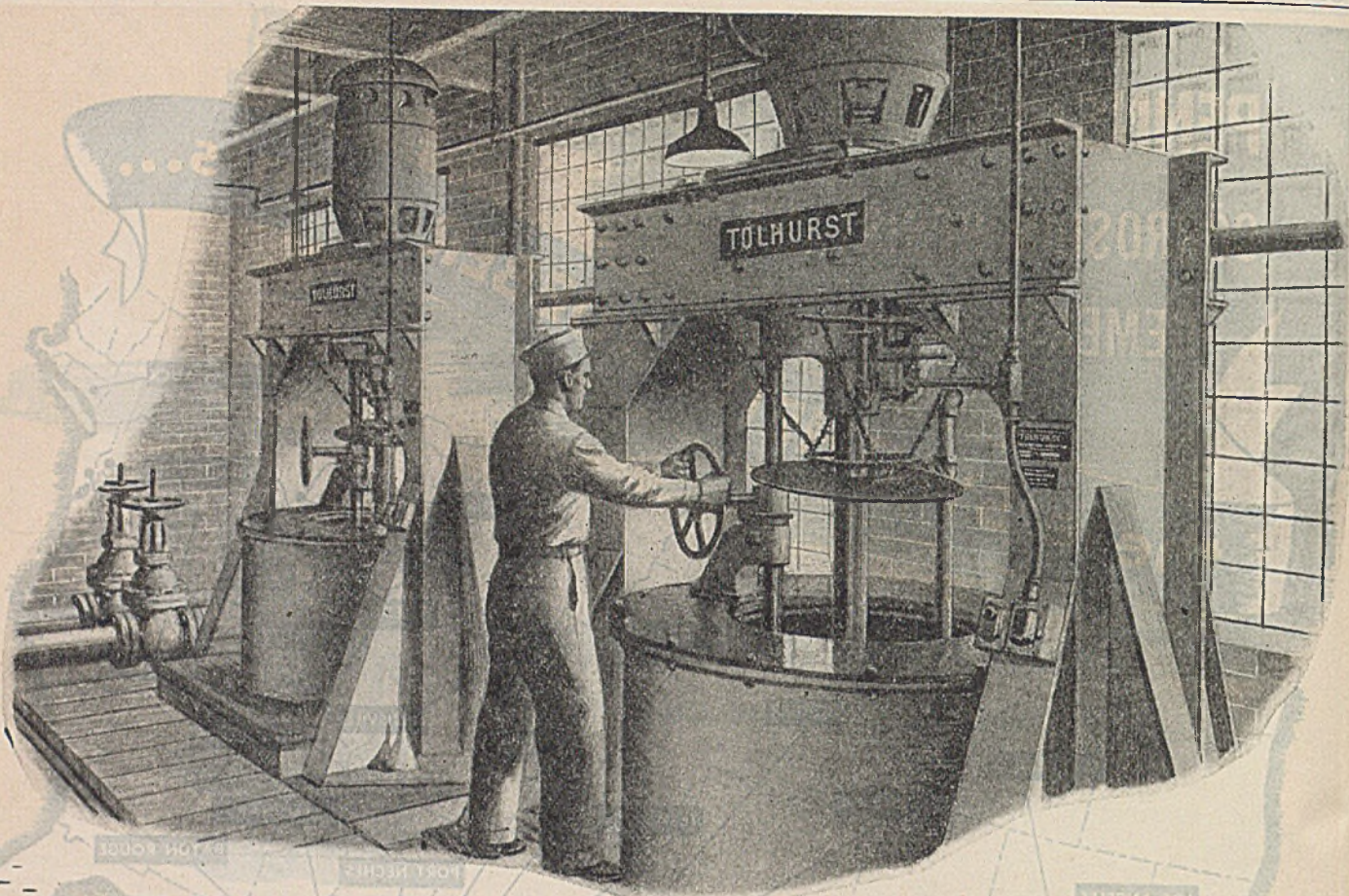
I would like to have a free copy of your new handbook No. 6 on Penchlor Acid-Proof Cement.

NAME _____

TITLE _____

COMPANY _____

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Fine Chemicals...**FASTER** with Tolhursts on the production line

EVER SINCE SYNTHESIS replaced herb or root extracts and scientific control took the place of human judgment, mass production methods have been adapted to the processing of fine chemicals.

For large-scale production of fine chemicals, Tolhurst centrifugals speed up many *draining, filtering, dehydrating, clarifying, thickening and separating* operations. Now

used extensively in the production of penicillin, sulfa drugs, vitamins and many other pharmaceuticals and medicinals, new processes which utilize Tolhurst centrifugals are being constantly developed. Tolhurst engineers offer their experience and cooperation for consultation on centrifugal equipment in connection with your present or planned processes.

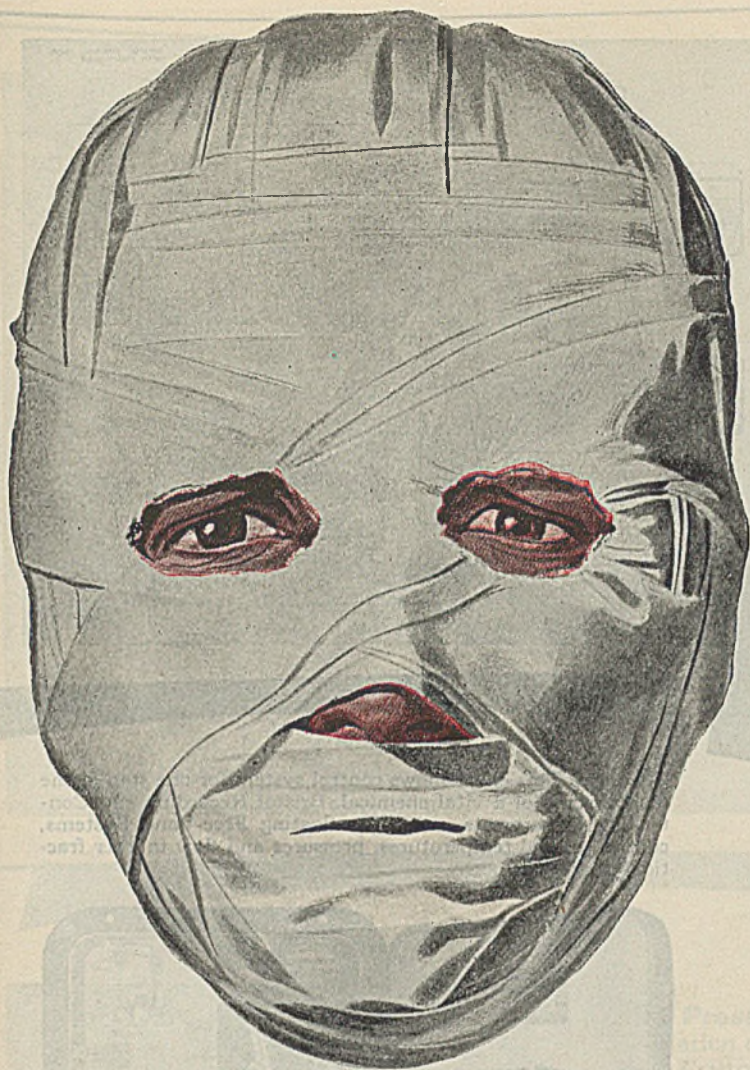


TOLHURST

Suspended Centrifugals

TOLHURST CENTRIFUGAL DIVISION OF AMERICAN MACHINE AND METALS, INC.

East Moline, Illinois



When ignorance is blistered!

● It's the ignorant men who make costly mistakes. Trained men don't get hurt by small fires. Trained fire-fighters don't let little blazes grow into big ones.

The way to train workers in fire extinguishing is by demonstrating use of extinguishing equipment. Show how to handle real fires. Show how various types of extinguishers are handled on different kinds of fires.

Walter Kidde & Company has prepared a booklet — "How To Teach Fire-Fighting." It tells how to stage a fast-moving, interesting, instructive fire class. Write for your plant's copy.

Walter Kidde & Company, Inc.

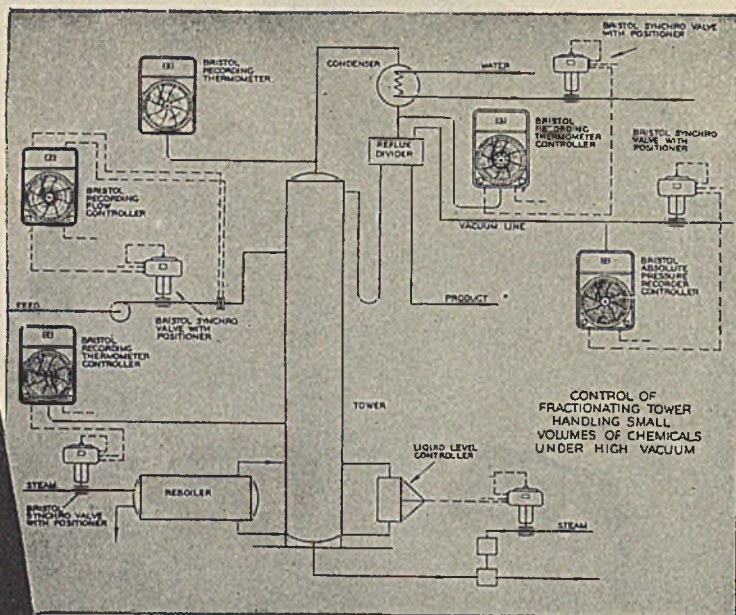
140 Cedar Street

New York 6, N. Y.



BRISTOL'S Free-Vane

The Unique
Convertible Controller for
PRESSURE, TEMPERATURE,
FLOW, LIQUID LEVEL, pH

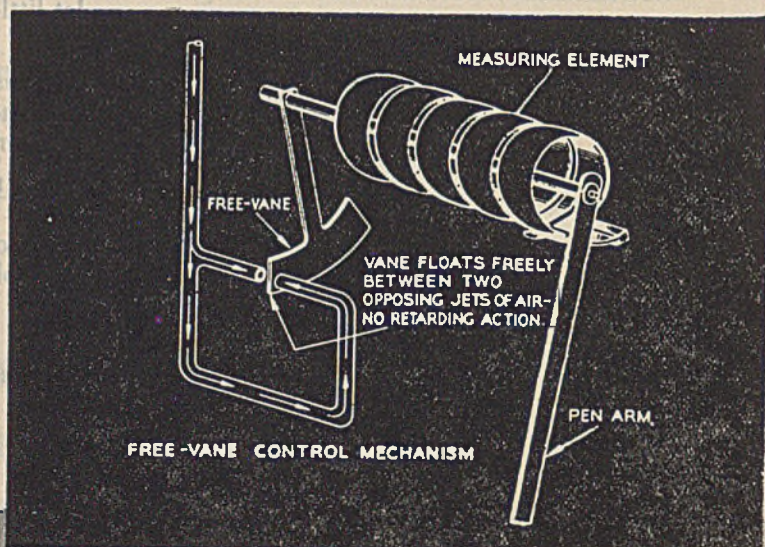
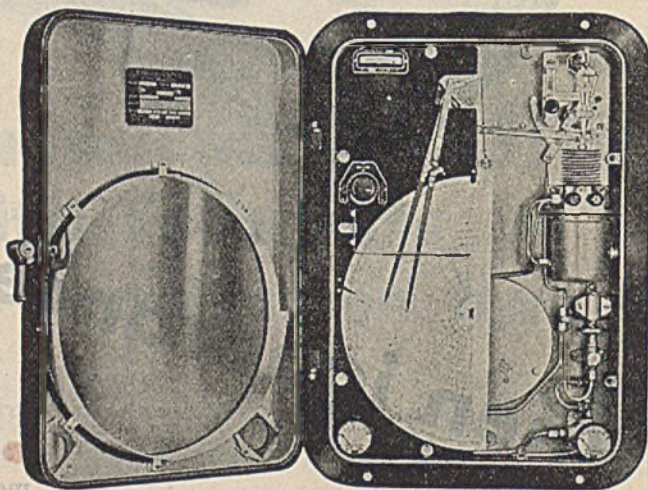


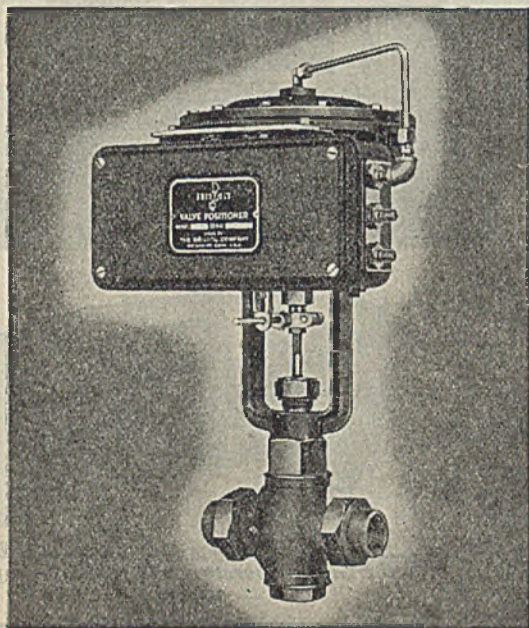
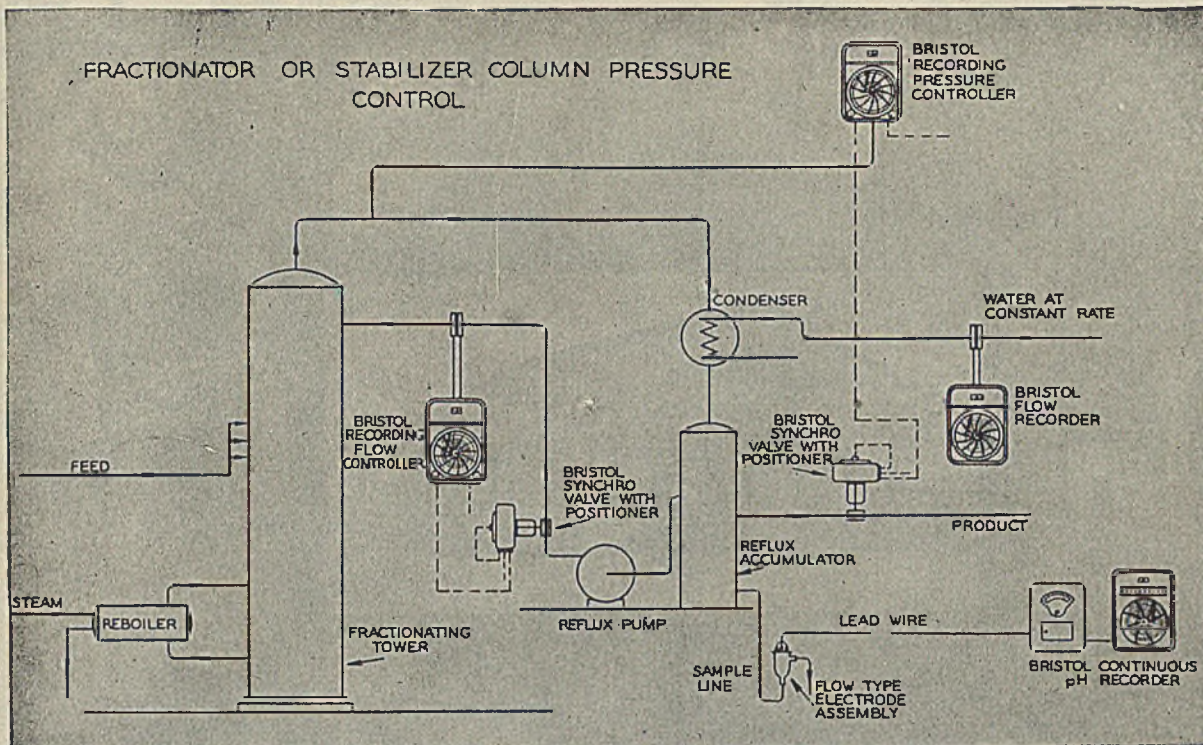
Chemical. This chart shows control system for one step in the manufacture of a vital chemical. Bristol Recording and Controlling instruments, using free-floating Free-Vane Systems, control critical temperatures, pressures and flow in this fractionating tower.

The basic Free-Vane principle, embodied in all types of Modern Bristol Air-Operated Controllers, offers you these important advantages in automatic process operation.

1. The convertible design enables you to change the type of control in your own plant, so as to fit any type of process that may develop.
2. The friction-less Free-Vane, actuated by sensitive, accurate measuring elements, floats freely between two air jets, eliminating any retarding action on the pen arm or pointer.
3. Five basic types of control, meeting any need, are available —
 - A. Monoset (off and on)
 - B. Ampliset (wide throttling)
 - C. Reset (wide throttling plus automatic reset)
 - D. Preset (wide throttling plus rate component)
 - E. Magniset (wide throttling plus rate component plus automatic reset)

Write for bulletin A-112, describing the Convertible Controller in detail. At the same time, tell us your problem and describe your process, if you wish. We may be able to make recommendations that will help you on your control problems. No obligation on your part, of course.





Back Pressure Control Systems. Efficiency with low installation cost characterizes this process control system using Bristol's Free-Vane Pressure and Flow Recording Controllers, and Bristol's Synchro Valves with Positioners. Locating the control valve in the product line from the reflux accumulator permits use of a small valve. No liquid level controller is necessary on the accumulator, since level is automatically maintained by variations in the condensing rate. This is only one example of how Bristol has helped achieve the precise column pressure controls necessary in producing ultimate yields of today's closely fractionated products.

Checks on Corrosion, too. Continuous automatic pH recording of the water separated from the tower-product, provides a close check on corrosion conditions existing in the tower, and shows if adequate preventive measures are being taken.



THE BRISTOL COMPANY

110 Bristol Road, Waterbury 91, Connecticut

The Bristol Company of Canada, Ltd.
Toronto, Ontario

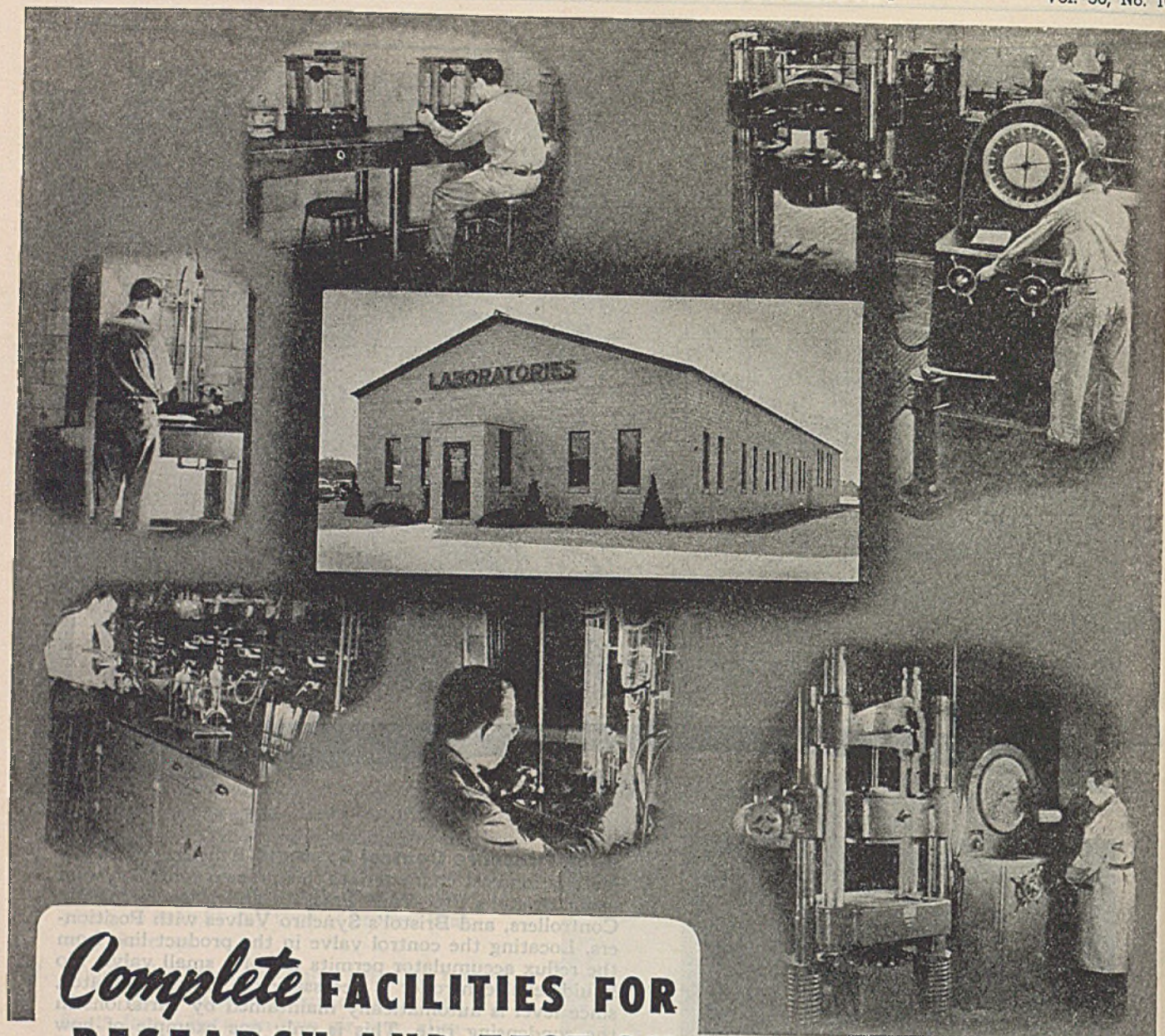
Bristol's Instrument Co., Ltd.
London N. W. 10, England



BRISTOL

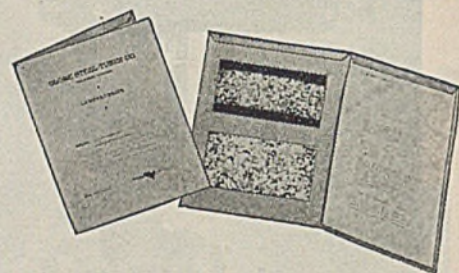
*Engineers Process Control
for Better Products and Profits*

AUTOMATIC CONTROLLING AND RECORDING INSTRUMENTS



Complete FACILITIES FOR RESEARCH AND TEST ON TUBING PROBLEMS . . .

Day in and day out, in a spacious building with complete and modern facilities, Globe chemists and metallurgists conduct research on tubing problems. Testing and inspection of Globe Steel Tubes are regular routine. Special problems of customers are studied, too, and physical and chemical tests, spectrographic and microscopic examinations are made, to select the correct analyses for each customer's particular needs. The Globe technical staff is available at the mill or in the field, for technical service on tubing problems.



A typical special report, prepared by the Globe laboratory and technical staff.



GLOBE
TUBES

- ★ Boiler and Pressure Tubes
- ★ Condenser and Heat Exchanger Tubes
- ★ Stainless Tubes (Seamless)

- ★ Mechanical Tubing
- ★ Gloweld Tubes (Welded Stainless)
- ★ Globeiron Tubes (Seamless Pure Iron)

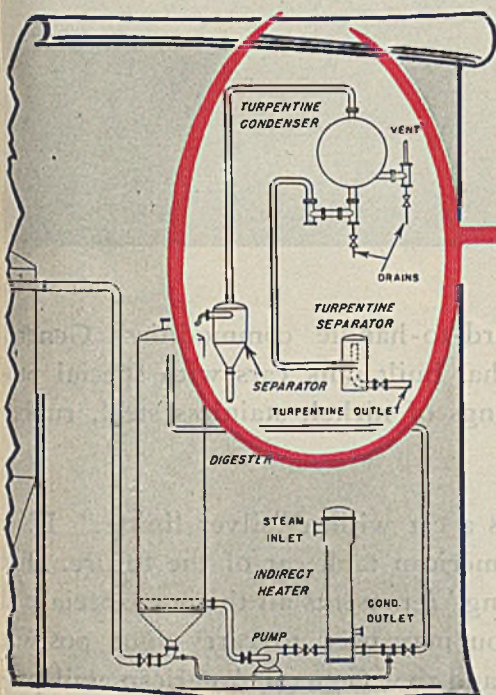
GLOBE STEEL
Tubes

GLOBE STEEL TUBES CO. *Milwaukee 4,
Wisconsin, U. S. A.*

TURPENTINE RECOVERY SYSTEM FOR PULP DIGESTERS



This unit, in operation at a large Southern pulp mill, is designed to recover 600 gals. of crude turpentine per day.



RECOVERY of turpentine vapors for pulp digesters can be economically effected in a unit comprised of a cyclose separator, turpentine condenser and turpentine separator. Not only is a valuable by-product salvaged, but heat is recovered from the steam and objectionable odors eliminated from pulp processing.

This system, designed and constructed by Foster Wheeler, is easy to install, low in maintenance and highly efficient in operation.

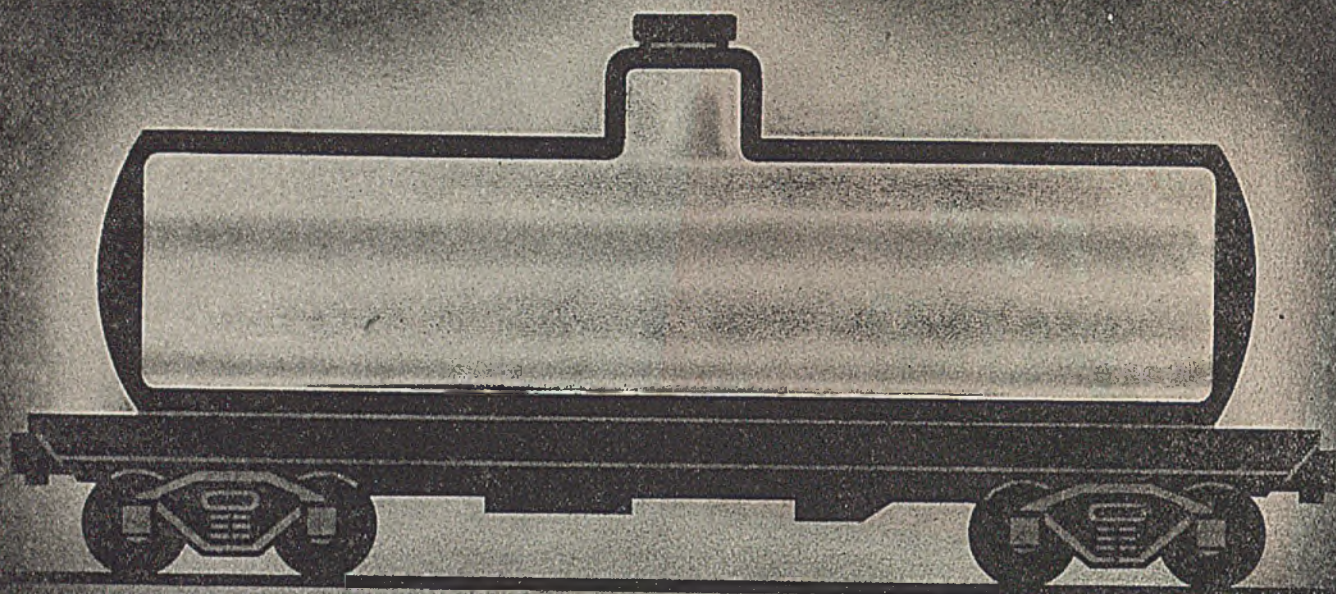
The crude turpentine can be further distilled and purified to meet specification requirements.



FOSTER WHEELER CORPORATION
165 BROADWAY
NEW YORK 6, N. Y.

FOSTER WHEELER

The Car With The "Silver Lining"



For Your Postwar Products

General American engineers are ready now to consult with you—to plan new tank cars with every feature needed to transport your products safely. Call or write our general offices—135 South LaSalle St., Chicago 90, Ill.




FOR hard-to-handle commodities, General American has built tank cars with special protective linings of nickel, stainless steel, rubber and lead.

Now here's a car with a "silver lining." It's a General American tank car of the future. The "silver lining" represents all the new specialized coatings you may need to carry your postwar products—and that General American will provide. You will have, then as now, definite advantages through use of General American cars for *safe, sure, low-cost* transportation.

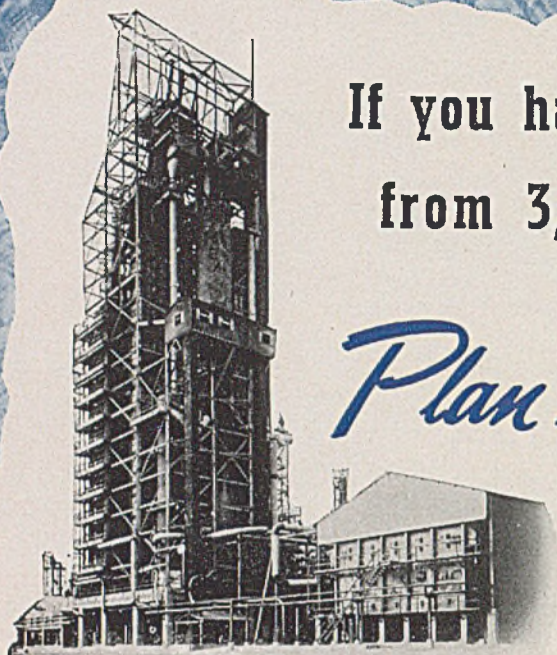
GENERAL AMERICAN TRANSPORTATION CORPORATION

Builders and Operators of Specialized Railroad Freight Cars ★ Bulk Liquid Storage Terminals ★ Pressure Vessels and other Welded Equipment ★ Aerocoach Motor Coaches ★ Process Equipment of all kinds ★ Fruit and Vegetable Precooling Service



MOTOR GASOLINE 80+ OCTANE ?
PREMIUM MOTOR GASOLINE . . . 85+ OCTANE !

Will small refining plants be ready?



If you have a plant that processes
from 3,000 to 10,000 B/D crude

*Plan NOW to meet Post-War
80-85+
Octane Ratings*

Every indication points to a post-war octane rating of 80 for regular gasoline and at least 85 for premium motor gasoline. Competition may send both ratings even higher.

The economical production of 85 and higher motor method octane motor gasoline with optimum T.E.L. addition points towards the wider use of catalytic cracking, a process now within the economic range of small refining operations.

Thermoform Catalytic Cracking* — with the yield-increasing TCC Synthetic Bead Catalyst — is well within the investment range of refiners processing from 3,000 to 10,000 B/D crude. Investment cost per barrel of charge for a small TCC plant now compares favorably with that of

larger plants; and in addition, the small plants using TCC Synthetic Bead Catalyst will also show high liquid recoveries of quality products.

TCC likewise gives higher yields of domestic furnace oil from heavy gas oil stocks — also from gas oils produced from coke still or visbreaker operations. TCC domestic furnace oil is stable and saleable without further treatment.

TCC and Synthetic Bead Catalyst open the way to post-war profits for the small refiner — at an investment cost well within the range of any company operating a 3,000 to 10,000 B/D crude refinery. Write for further data.

* Licensed by Houdry Process Corporation

THE LUMMUS COMPANY, 420 Lexington Avenue, New York 17, N. Y.

600 S. Michigan Ave., Chicago 5, Illinois
Mellie Esperson Bldg., Houston 2, Texas
634 S. Spring Street, Los Angeles 14, California
70 Barn Hill, Wembley Park, Middlesex, England



LUMMUS

PETROLEUM REFINING PLANTS

75S

88,000 pounds per sq. in. tensile strength in extruded shapes, 75,000 pounds in alclad sheet—stronger than any aluminum alloy in use today—nearly two times the yield strength of ordinary structural steel and one and one-third times the tensile strength. That's Alcoa's new high strength alloy, 75S.

No untried youngster, this alloy. Alcoa's research and development divisions have spent years in testing the performance of experimental quantities. In the fall of 1943, the first commercial run was put through Alcoa mills, and production has continued at an ever-increasing pace. Already, at

least eight major aircraft companies are building new experimental planes in which 75S is the principal structural material.

75S is now a standard alloy for alclad sheet and extruded shapes. Plain sheet, plate, rolled rod and bar made from 75S continue on an experimental basis, but may be obtained for certain projects.

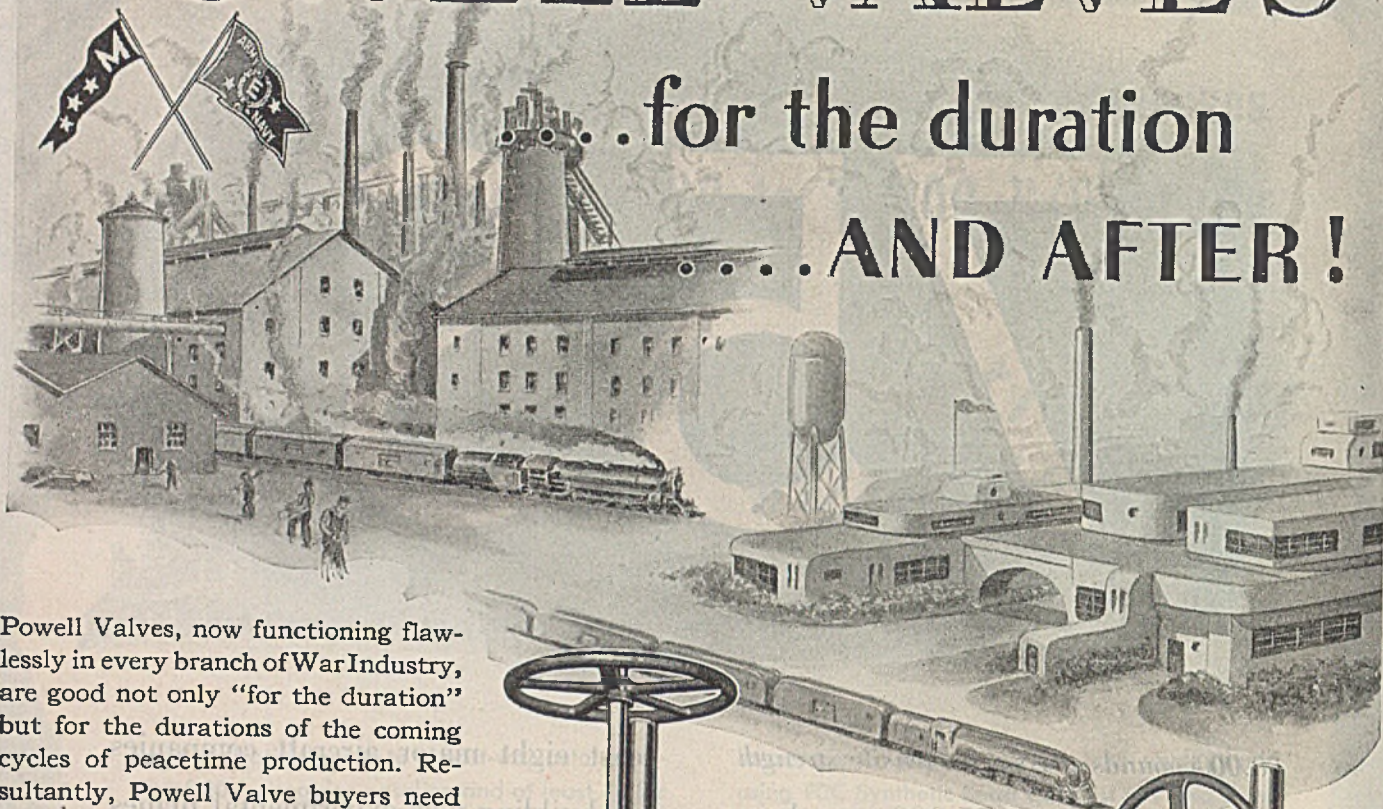
With WPB approval, you can employ 75S in your products. Our representatives will gladly help you work it into your designs. ALUMINUM COMPANY OF AMERICA, 2154 Gulf Building, Pittsburgh 19, Pa.

ALCOA



ALUMINUM

POWELL VALVES



...for the duration
.....AND AFTER!

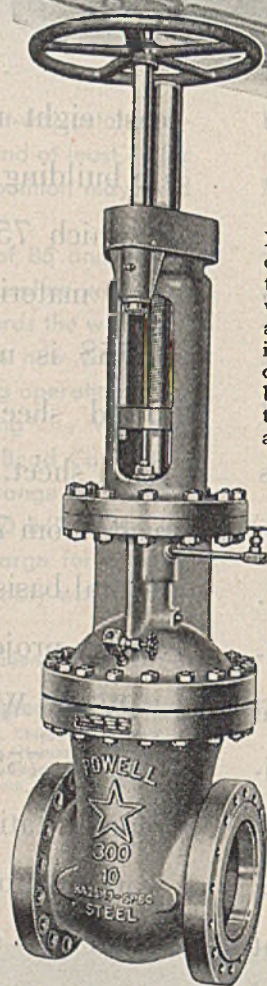
Powell Valves, now functioning flawlessly in every branch of War Industry, are good not only "for the duration" but for the durations of the coming cycles of peacetime production. Resultantly, Powell Valve buyers need face no scrapped installations when reconversion comes, whether it come by degrees or all at once.

The basic principle of efficient flow control is, at all times, the *right valve*, in the *right spot*, for the *right job*. It is on this principle that the complete POWELL Line of industrial valves of all types and materials has been developed through nearly a century of successful valve manufacture.

The gear operated gate valves shown here were specially designed by Powell Engineering to meet the specific and exacting requirements of high temperature hydrocarbon gas reforming and thermal catalytic cracking in a large western refinery.

The Wm. Powell Co.

Dependable Valves Since 1846
Cincinnati 22, Ohio



Both gate valves were specially designed and built for ultra-high temperature service. Double wedge discs, seats, disc guides and stem guides are Stellite faced. Cooling fins for dissipating heat and thereby lowering the temperature in the stuffing box are another feature.

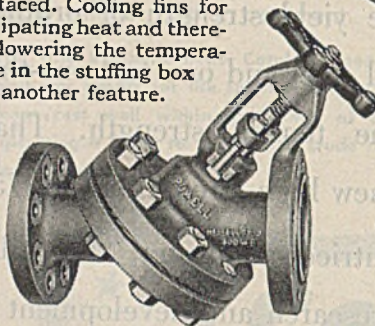
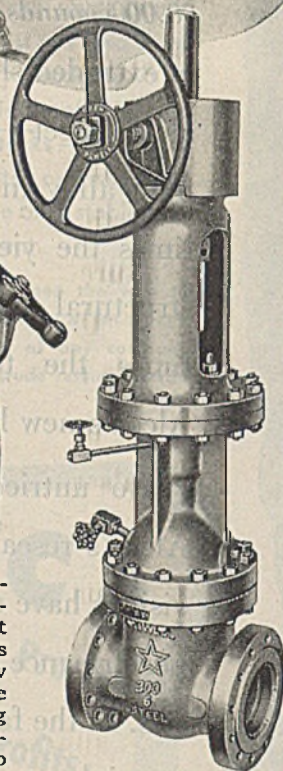


Fig. 1095—Specially designed, extra heavy, Separable Body, Reversible Seat "Y" Valve for 300-pounds W.P. Has straightway flow area through body. Available in special alloys for handling chlorine compounds in isomerization units. Sizes, $\frac{1}{2}$ to 4", incl.; flanged ends only.

10", Class 300-pound, Cast Alloy Steel O. S. & Y. Gate Valve. Spur-gear operated.



6", Class 300-pound, Cast Alloy Steel, O. S. & Y. Gate Valve. Bevel-gear operated.

POWELL VALVES

TWO SUPER REFRACTORIES THAT OPERATE SAFELY AT 3200° AND 4000° F

TAM Zircon (Zirconium Silicate) refractories operate safely at temperatures over 3200° F. while TAM Zirconium Oxide refractories are used in applications over 4000° F.

These two TAM super refractories resist acids and oxidizing atmospheres. They are being successfully used in the manufacture of phos-

phates, fused silica, aluminum melting and platinum smelting. They are also widely used as crucible backing and for various high temperature applications.

An experienced staff of field engineers located in various parts of the country are available for consultations without obligation. Write:

TAM PRODUCTS INCLUDE

Zircon bricks, special shapes and crucibles... Zircon insulating refractories... Zircon ramming mixes, cements and grog... Zircon milled and granular... Electrically Fused Zirconium Oxide Refractories... Electrically Fused Zirconium Oxide cements and ramming mixes... Electrically Fused Zirconium Oxide in various mesh sizes.



TITANIUM

ALLOY MANUFACTURING COMPANY

GENERAL OFFICES AND WORKS: NIAGARA FALLS, N. Y., U. S. A.
EXECUTIVE OFFICES: 111 BROADWAY, NEW YORK CITY

Representatives for the Pacific Coast States . . . L. H. BUTCHER COMPANY, Los Angeles, San Francisco, Portland, Seattle
Representatives for Europe . . . UNION OXIDE & CHEMICAL CO., Ltd., Plantation House, Fenchurch St., London, E. C., Eng.

TOO MANY IRONS..



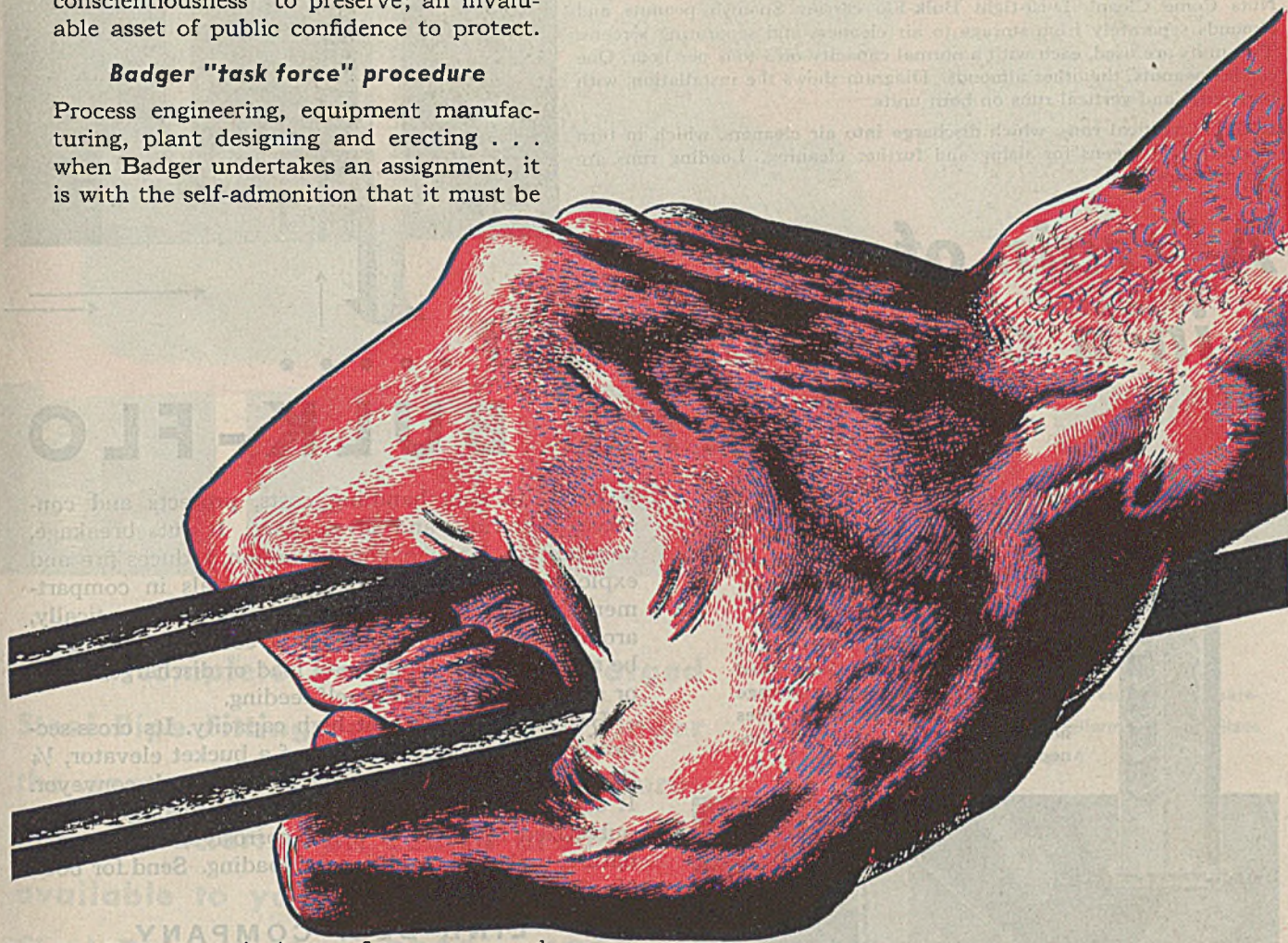
THOUGH wide in its scope of operations, it can never be said that this large and well-staffed organization has "too many irons in the fire" to do a thorough job on each.

Over the years and throughout the world, Badger has handled many projects—large-scale to small, and in extensive variety. Nevertheless, Badger has scrupulously refused assignments when overloading its facilities might prove detrimental to the exacting requirements of the job.

Such unwillingness to compromise its high standards of work is a Badger rule that has prevailed even in the days of heavy war-plant construction. For Badger has a priceless tradition of "New England conscientiousness" to preserve; an invaluable asset of public confidence to protect.

Badger "task force" procedure

Process engineering, equipment manufacturing, plant designing and erecting . . . when Badger undertakes an assignment, it is with the self-admonition that it must be



handled with a singleness of purpose toward getting that job done well and quickly.

In line with this fundamental principle of customer serving, Badger sets up for each individual project a *complete "task force"* comprised of key men for planning and co-ordination, together with engineering, purchasing, expediting and construction personnel. Devoted to each assignment must be the *undivided time and attention*, the zeal and the talents of the planning board, engineers and other key men assigned to that particular "task."

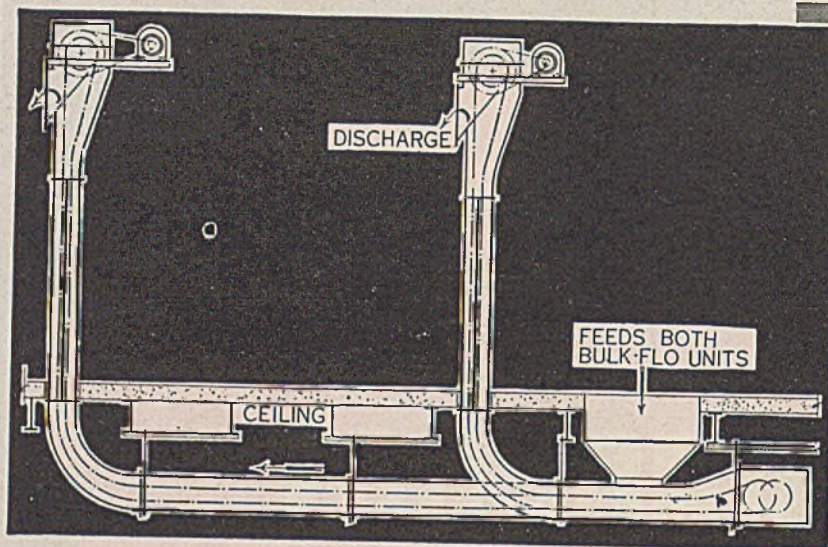
E. B. Badger & SONS CO.

BOSTON 14

EST. 1841

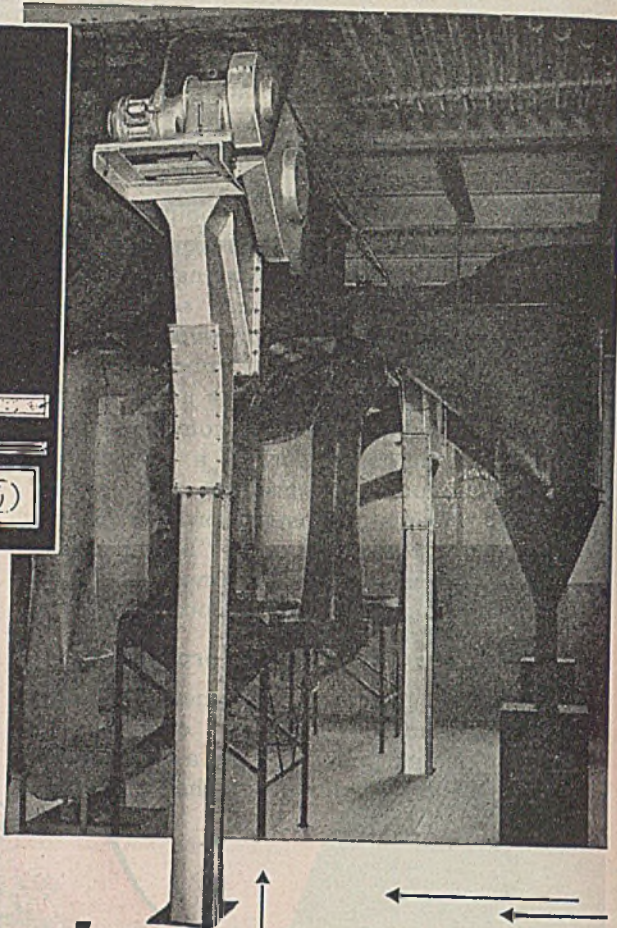
NEW YORK • PHILADELPHIA • SAN FRANCISCO • LONDON

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



Nuts Come Clean! Dust-tight Bulk-Flo carries Spanish peanuts and almonds separately from storage to air cleaners and separating screens. Two units are used, each with a normal capacity of 3 tons per hour. One carries peanuts, the other almonds. Diagram shows the installation, with horizontal and vertical runs on both units.

RIGHT: vertical runs, which discharge into air cleaners, which in turn discharge to screens for sizing and further cleaning. Loading runs are shown below.

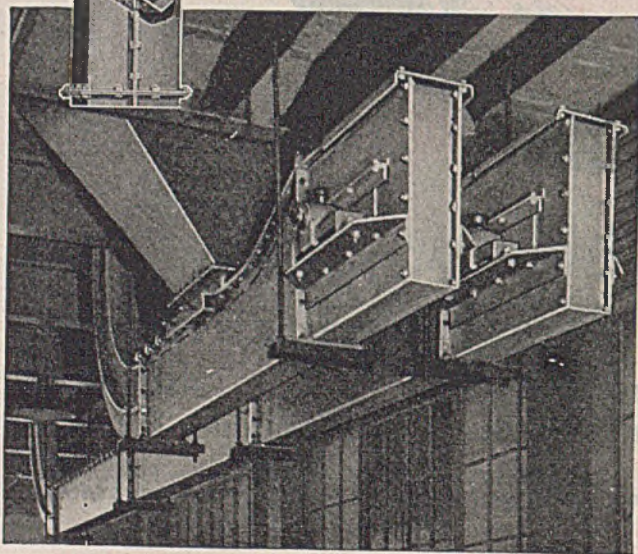


A "train of cars" in a dust-tight duct That's BULK-FLO

Material is carried in a succession of compartments in a dust-tight casing. It moves in a continuous mass. Bulk-Flo flights are peak-shaped, self-clearing, trouble-free.

. . .

Loading run of Bulk-Flo units shown below. Units are suspended from ceiling, loading from storage on floor above. Light weight makes heavy supporting structure unnecessary.



- Bulk-Flo cuts handling costs, protects and conserves materials, and saves space. It cuts breakage, degradation, leakage, contamination, reduces fire and explosion hazards. It moves materials in compartments, like an endless train—horizontally, vertically, around curves, up inclines, or in a combination. It may be arranged with loops; may load or discharge at one or several points, and is self-feeding.

Bulk-Flo has inherent high capacity. Its cross-sectional area is about $1/5$ that of a bucket elevator, $1/4$ that of a flight conveyor, $1/3$ that of a belt conveyor. It conveys any flowable granular, crushed, ground or pulverized material of a non-corrosive, non-abrasive nature, under all conditions of loading. Send for book No. 2075.

LINK-BELT COMPANY

Chicago 9, Indianapolis 6, Philadelphia 40, Atlanta, Dallas 1, Minneapolis 5, San Francisco 24, Toronto 8.
Offices in principal cities.

9836

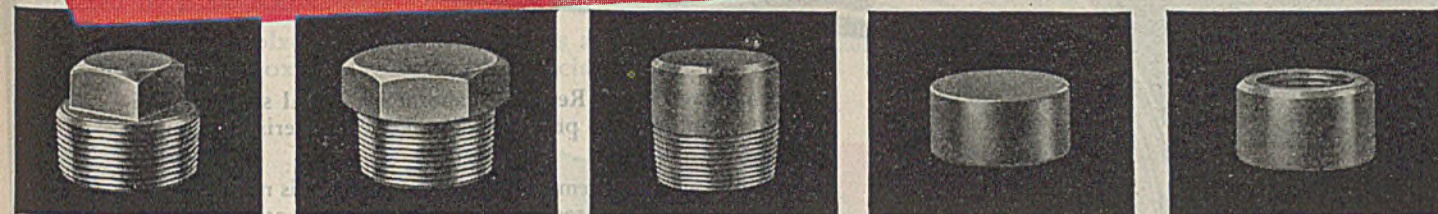
LINK-BELT
Bulk-Flo
ELEVATOR-CONVEYOR-FEEDER

LADISH

QUALITY FORGINGS

Controlled Quality

Forged Steel Pipe Fittings



• The complete line of Ladish Forged Steel Pipe Fittings manufactured under the same **Controlled Quality** procedures that characterize all Ladish products is available to you in Carbon and Alloy Steel. Pressures from 2000 to 6000 lbs.

Forged Steel Screwed Fittings

Full depth thread, accurately cut, results in pressure-tight joints. Pipe enters easily. Uniform thickness. Sizes clearly marked . . . $\frac{1}{4}$ " through 4".

Socket Welding Fittings

Speed up installation because deep sockets save time formerly required to cut pipe to exact length. Socket supports pipe and allows self-alignment. No machining of pipe necessary for fit. **ASSURED WELDABILITY.** Sizes clearly marked . . . $\frac{1}{4}$ " through 4".



TO MARK PROGRESS



FITTINGS DIVISION

LADISH DROP FORGE CO.

CUDAHY • WISCONSIN

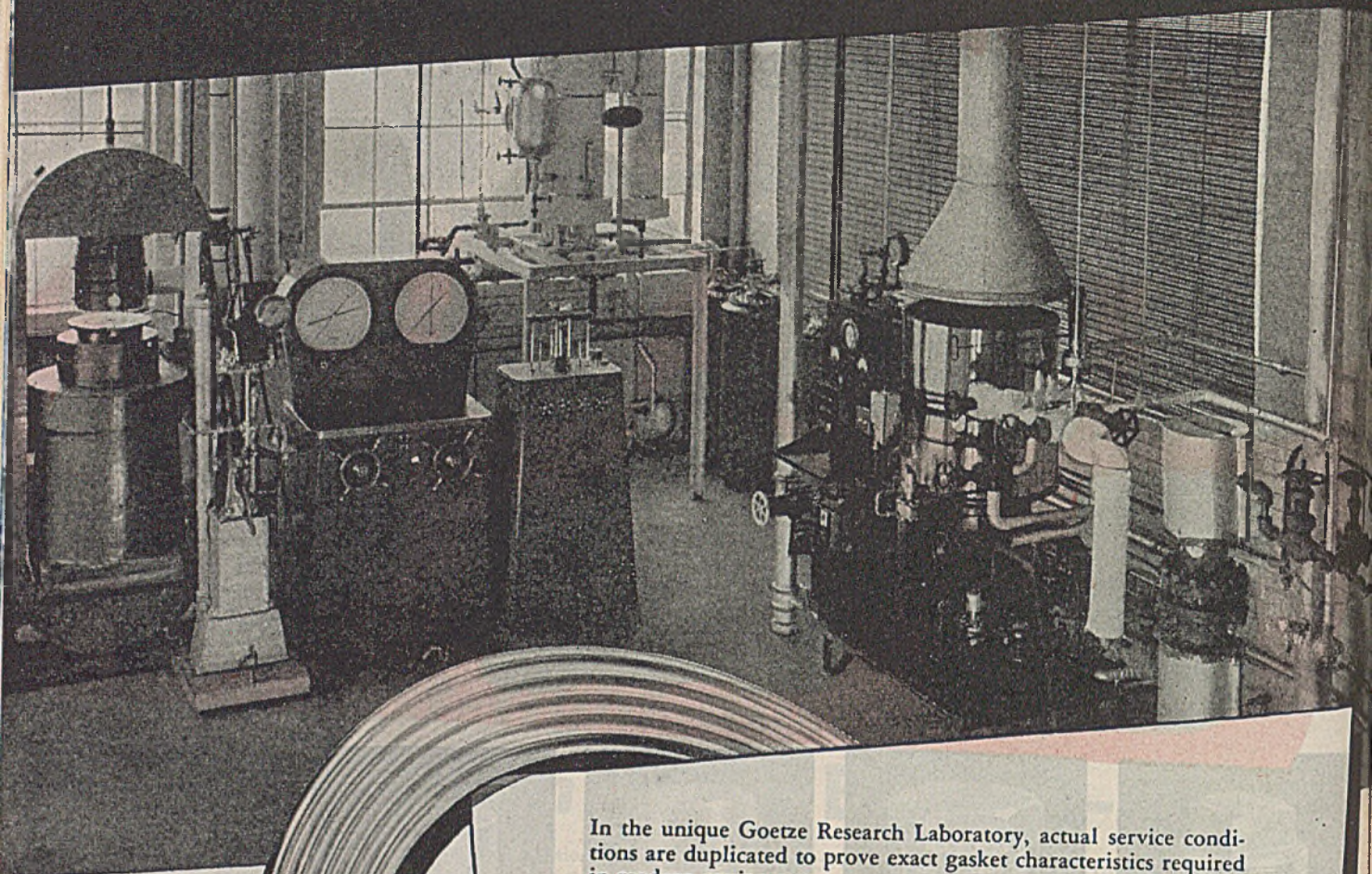
MILWAUKEE SUBURB

New York Office: 60 E. 42nd Street, New York City

From This Laboratory Come

FACTS ABOUT GASKETS

Vital to Industry



In the unique Goetze Research Laboratory, actual service conditions are duplicated to prove exact gasket characteristics required in modern equipment.

Higher pressures and temperatures necessitated this more accurate data on gasket yield stress and gasket factor. (In other words — what it takes to seal a particular closure and to keep it tight under specific operating conditions.)

A 600,000 lb Compression Testing Machine and a 2000 psi, 1000° F. Boiler are among the modern equipment employed, with accurate auxiliary equipment to determine not only initial gasket characteristics, but also changes that occur under normal and adverse service conditions.

Likewise the Goetze laboratory is equipped to study gasket raw materials for physical and metallurgical properties with particular reference to the effect of metal structure upon gasket performance.

Original data resulting from this research is available to interested engineers and designers of pressure equipment in a series of technical bulletins. If you wish to receive your copies of these bulletins regularly, write on your company letterhead, stating your position.

GOETZE GASKET & PACKING CO., Inc.
12 ALLEN AVENUE, NEW BRUNSWICK, NEW JERSEY

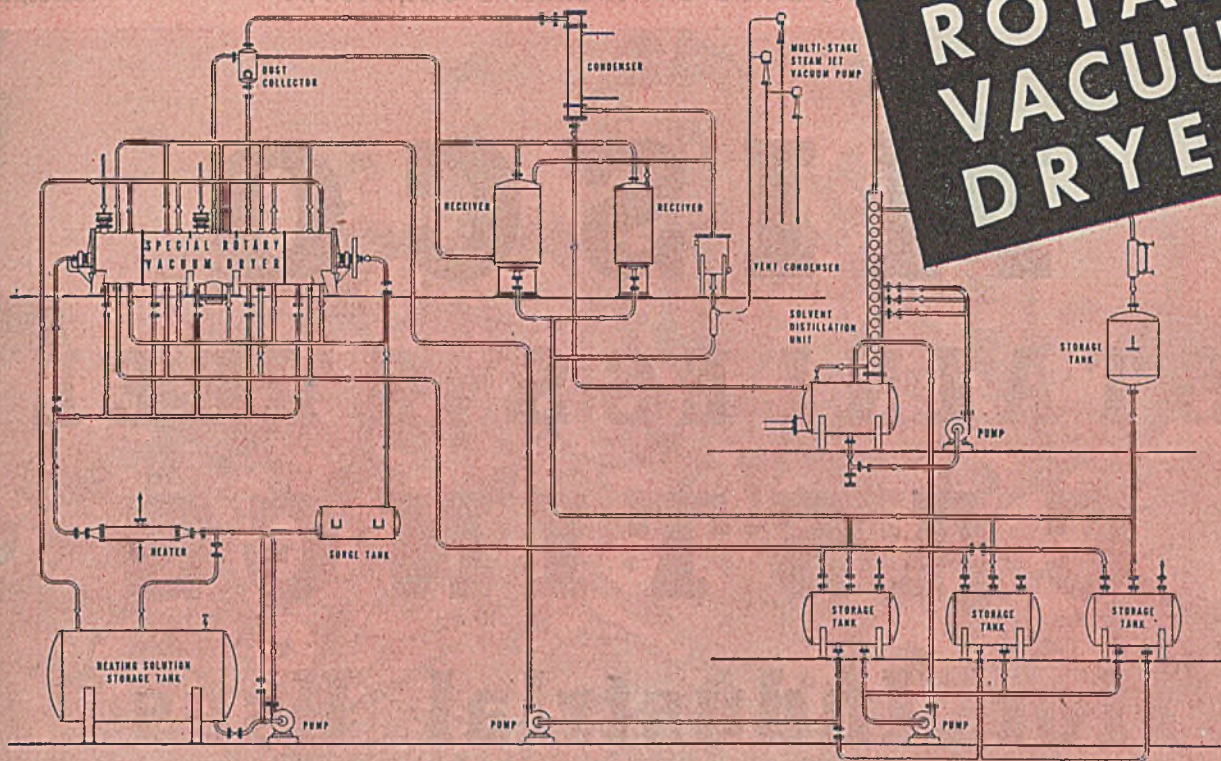
• NEW GASKET FILM AVAILABLE

See this Research Laboratory and other facilities of this highly specialized service to Industry — and hear Lowell Thomas, famous news commentator, describe them — in the new Kodachrome Motion Picture, "ONLY A GASKET." Available to employee groups, technical societies, engineering schools and other organizations. Write for full information.

Goetze for **GASKETS**



ROTARY VACUUM DRYERS



The plant indicated on the flow sheet involves the extraction and subsequent drying of an organic material at low temperature, and also includes recovery equipment to make the extracting solvent suitable for reuse. This complete unit was designed and constructed by Blaw-Knox.

The problems involved in these operations are well-known to Blaw-Knox engineers and technicians, who

have at their disposal the data and facilities necessary to see the job through from idea to operation . . . Your inquiry will receive prompt, intelligent attention.

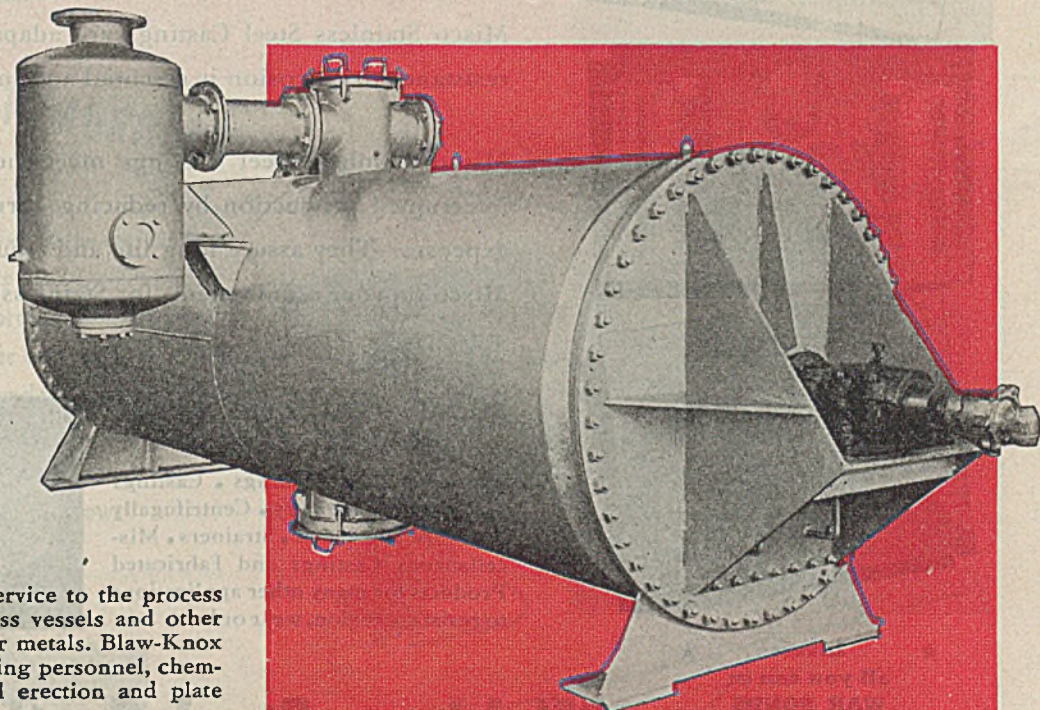
BLAW-KNOX DIVISION

OF BLAW-KNOX COMPANY

2081 Farmers Bank Building, Pittsburgh, Pa.

NEW YORK CHICAGO PHILADELPHIA BIRMINGHAM WASHINGTON

Representatives in Principal Cities



Blaw-Knox furnishes a complete service to the process industries, including welded process vessels and other equipment of steel, alloys and other metals. Blaw-Knox facilities include complete engineering personnel, chemical engineering laboratories—field erection and plate fabrication of every description.

BLAW-KNOX PROCESS EQUIPMENT



MISCO

STAINLESS STEEL

CASTINGS

for Industrial Uses

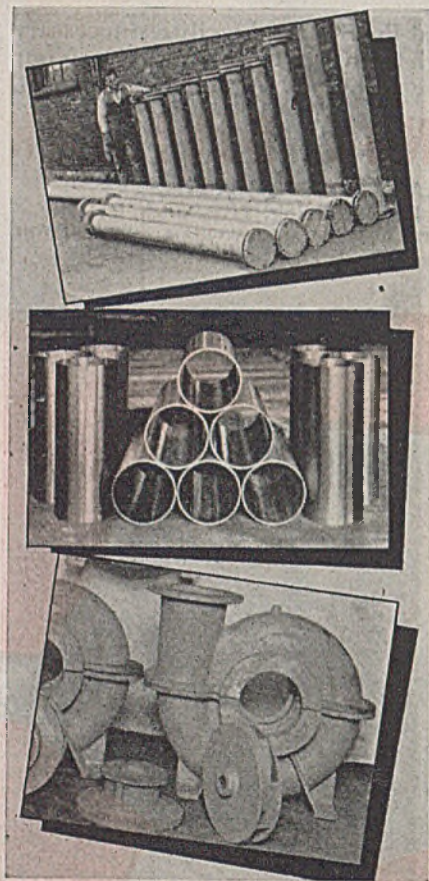
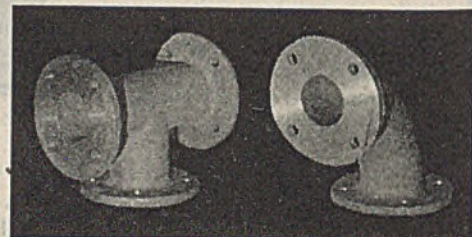
Misco specializes in the manufacture of Stainless Steel Castings for Industrial uses . . . The high quality of Misco Stainless Steel Castings is the result of specialized manufacturing experience accumulated during more than twenty-five years of metallurgical research and application.

Misco Stainless Steel Castings are adaptable to numerous uses where resistance to corrosion is essential and low cost operation is desirable.

Misco Stainless Steel Castings meet the demands of continuous, uninterrupted production by reducing corrosion losses and maintenance expenses. They assure long life and trouble-free performance. Consult Misco on your requirements for Stainless Steel Castings.

MISCO STAINLESS STEEL ALLOYS are used for

Fittings • Pump Castings • Castings for Mixing Machinery • Centrifugally Cast Pipe and Tubes • Strainers • Miscellaneous Castings and Fabricated Products for many other applications to resist corrosion, wear or heat.



★ Invest ★
all you can in
WAR BONDS



Michigan Steel Casting Company

One of the World's Pioneer Producers of Chromium-Nickel Alloy Castings

1999 GUOIN STREET, DETROIT 7, MICHIGAN

DO YOUR EXPERIMENTING AND PLANNING FOR THE USE OF DUCTILE ZIRCONIUM NOW

The production of ductile Zirconium is now out of the laboratory stage and we can offer prompt delivery of .005" or .002" sheet, and wire in various sizes from .002" to 1/8" rod.

CORROSION RESISTANT

Zirconium is a bright metal which takes an excellent polish. It is extremely corrosion-proof, and resists sodium hydroxide and acids of various normalcies up to temperatures of 100°C. with the exception of Hydrofluoric or hot concentrated Sulphuric Acids. Some idea of its value in this connection can be gathered from the following examples:

Concentrated HCl, 100°C.	No effect
Concentrated HNO ₃ , 100°C.	No effect
Concentrated H ₂ SO ₄ , 100°C.	Attacked
50% H ₂ SO ₄ , 100°C.	No effect
Aqua Regia, Room Temperature	Not attacked
10% NaOH, 100°C.	No effect
50% NaOH, 100°C.	No effect
HF	Attacked
H ₂ S	No effect

Ductile Zirconium Metal, as you can see, resists most acids. Most remarkable is its resistance to both sodium hydroxide and acids.

ADSORBS GASES

Ductile Zirconium Metal is perhaps best known because of its affinity for oxygen, nitrogen, carbon dioxide, carbon monoxide, water vapor, hydrogen, and other gases. It will adsorb up to 20 atomic volumes % of some of these gases. For this reason it is already vital in the manufacture of electronics tubes.

OTHER PROPERTIES

Any investigation of Ductile Zirconium Metal should not neglect other properties such as these:

Melting Point	1860°C.
Specific Gravity	6.4
Specific Resistance in Ohms Cms ² at 20°C.	45x10 ⁻⁶
Temperature Coefficient of Resistance, 0° to 100°C.	0.0045
Approximate Tensile Strength lbs./sq. in.	100,000

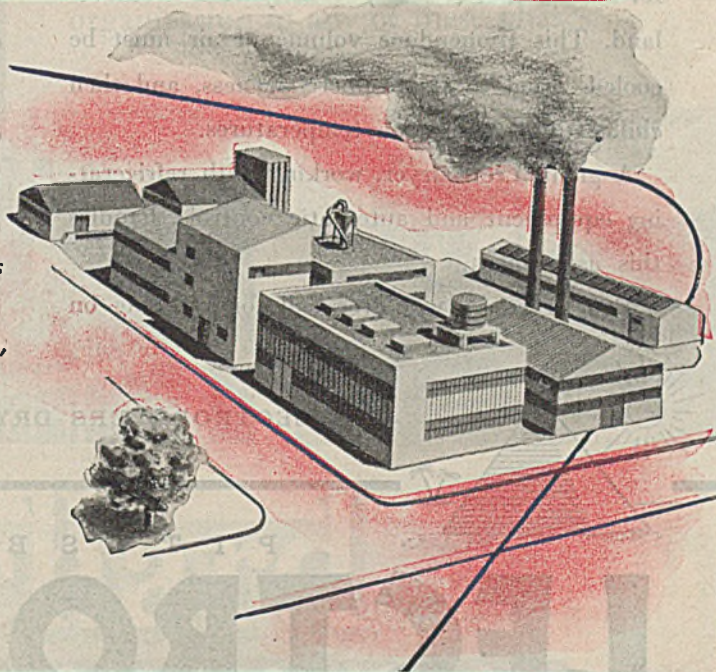
At present we are limited in offering it for use in chemical equipment as the sheet is still available only in relatively small sizes.

Further development work will probably permit us to supply sheets of greater area and we suggest you begin your preliminary work now.

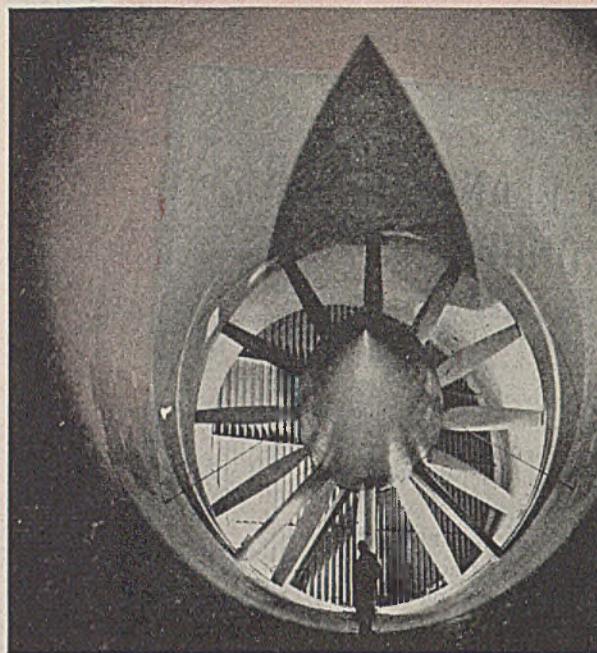
Inquiries are actively invited. Experimental and production quantities of Ductile Zirconium Metal sheets, and wire are now available.

"HOUSE OF TOMORROW"

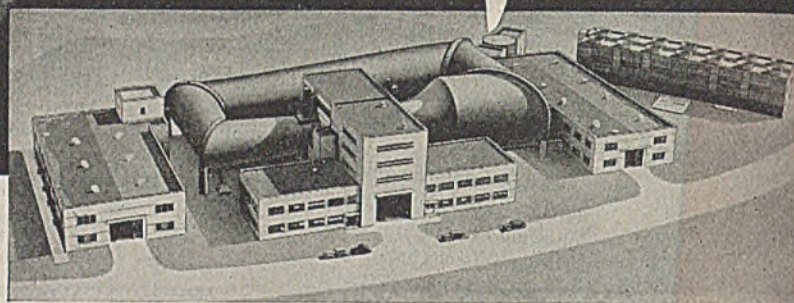
From our "house of tomorrow"—that is, the various Foote plants and laboratories, pour products used by hundreds of industries, and by our Armed Forces and those of our Allies on far flung battle fronts. Ores and minerals, chemicals and alloys, wrested from the earth, and new processes developed in our laboratories and plants, await your consideration, cooperation or application. Let Foote research and products help you today—for tomorrow.



PHILADELPHIA • ASBESTOS • EXTON, PENNSYLVANIA
Home Office: 1609 SUMMER STREET, PHILADELPHIA, PA.
West Coast Repr.: Griffin Chemical Co., San Francisco, Calif. • English Repr.: Ernst B. Westman, Ltd., London, Eng



Lectrodryer..



...IS DRYING

3 tons of air a minute TO STRATOSPHERE DRYNESS

Three tons per minute—approximately 85,000 cubic feet per minute—that's the rate at which make-up air can be moved into the new altitude wind tunnel the National Advisory Committee for Aeronautics (NACA) recently built at Cleveland. This tremendous volume of air must be cooled, dried to stratosphere dryness, and then chilled to extremely low temperatures.

A giant Lectrodryer, working with refrigerating equipment and automatic controls, handles this assignment.

Few processes will ever call for DRYing on

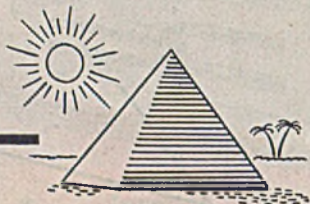
such a mammoth scale. But you'll recognize that the machine capable of doing this job, and the engineers responsible for designing it and helping to incorporate it into the process, can certainly handle any DRYing assignment that comes along.

Big job or little, working with air, gases or organic liquids, here is the place to turn to for DRYing assistance. PITTSBURGH LECTRODRYER CORPORATION, 305 32nd Street, Pittsburgh 30, Pa.

In England: Birmingham Electric Furnaces, Ltd., Tyburn Road, Erdington, Birmingham.

In Australia: Birmingham Electric Furnaces, Ltd., 51 Parramatta Road, Glebe, Sydney.

LECTRODRYERS DRY WITH ACTIVATED ALUMINAS



P I T T S B U R G H

LECTRODRYER

C O R P O R A T I O N

Reg. U.S. Pat. Off.



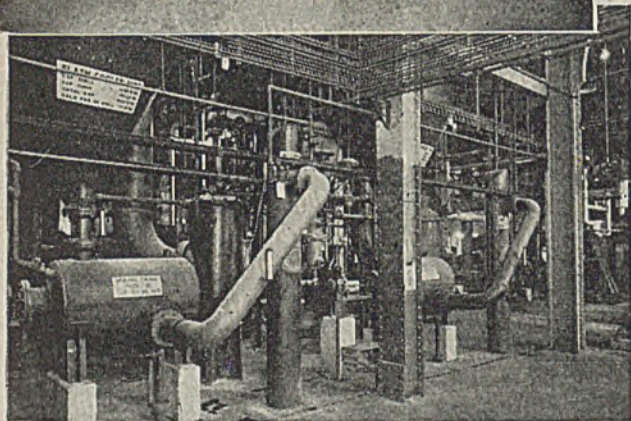
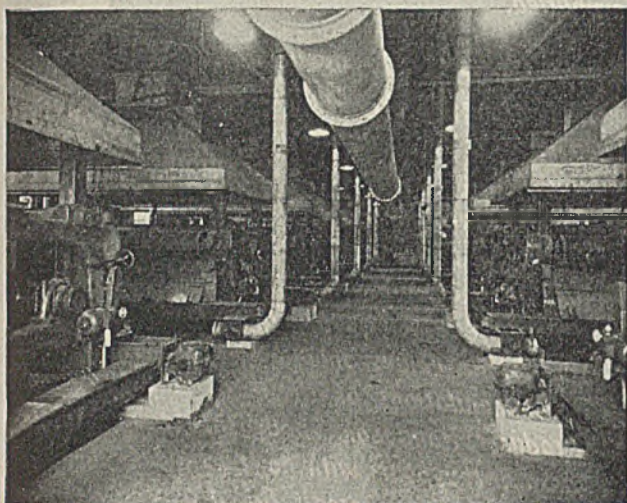
On Stream

DESIGNED • ENGINEERED • CONSTRUCTED

by Pritchard

Recent developments of industrial chemical processes give a view of what lies ahead. The field is without limit—but sound practical planning by experienced, capable chemical engineers is necessary.

The J. F. Pritchard & Company *Chemical Division* has recently completed a large mid-western distillery which was designed, engineered and constructed under its general supervision. This staff of engineers is ready to assist you in the development of your chemical process, assume full responsibility for design, purchasing and construction of plant or cooperate with your engineering organization in any of these phases.

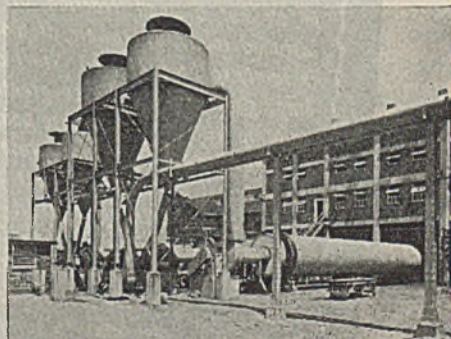
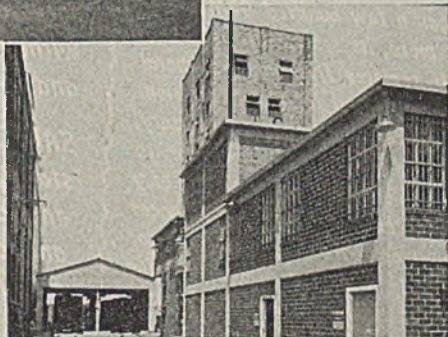


Top—A view through the soluble feed drying installation.

Center—Details picturing the mash cooling and instrument piping.

Lower Left—Grain scales and unloading station; alcohol still and receiving houses.

Lower Right—Showing the feed drying installation.



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HOUSTON
NEW YORK
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ENGINEERS AND CONSTRUCTORS
FOR THE CHEMICAL • PETROLEUM • GAS AND POWER INDUSTRIES
Manufacturers of Mechanical and Atmospheric Cooling Towers

Cooling Tower DOs and DON'Ts

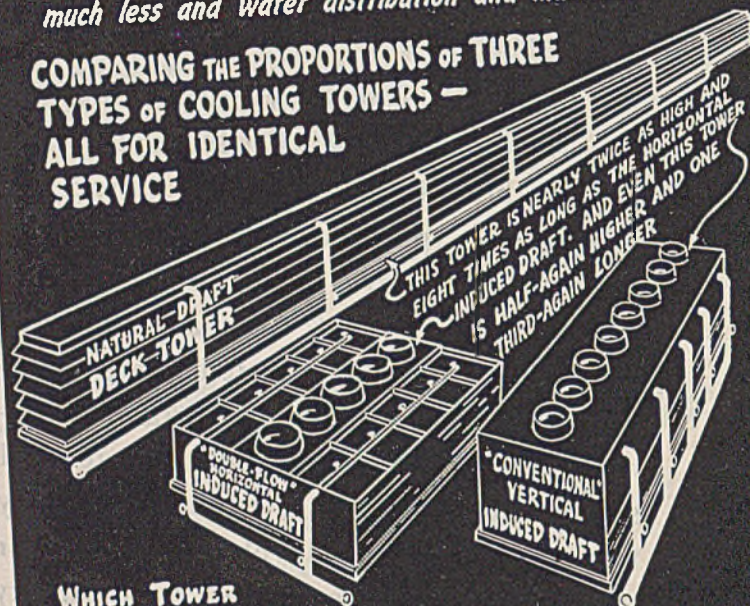
-by **MARLEY** (No. 5 of a series)

POINTERS ON CONSTRUCTION

In purchasing or evaluating any cooling tower these particulars of construction deserve attention:

GENERAL DESIGN—Towers of broad-and-low proportions are preferable over high-long-narrow designs. They can be better braced, their requirements for pumping, foundation and basin are much less and water distribution and maintenance are simplified.

COMPARING THE PROPORTIONS OF THREE TYPES OF COOLING TOWERS — ALL FOR IDENTICAL SERVICE



WHICH TOWER IS THE SOUNDEST STRUCTURE, LEAST VULNERABLE TO WIND OR QUAKE?
WHICH REQUIRES THE LEAST PIPING AND PUMPING?
WHICH CAN BE MOST CONVENIENTLY LOCATED AT MOST PLANTS?

REDWOOD vs. STEEL—Redwood is the principal structural material in all but small fraction of the total cooling tower capacity installed today. In towers of more than a few hundred GPM, steel is rarely preferred. Steel costs more, its service life is not as long, general maintenance greater. It requires frequent and liberal painting with aluminum-base paint inside and out to retard corrosion, whereas Redwood's natural preservatives render painting unnecessary. However if a Redwood tower is painted (for color harmony or to carry an advertising sign) it requires only standard paint, only infrequently, and only on the outside. Fire and safety ordinances which once banned any wood structures on roofs in business areas of some cities now have been modified widely in the case of Redwood due to its proven resistance to burning, its retention of strength in defiance of age and weather, its freedom from all forms of organic attack.

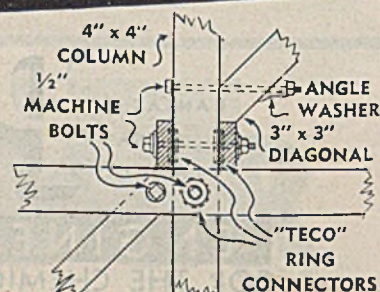
FRAMING—Equally as important as proper size, quality and quantity of members is that connections be sound, snug-fitting, full-bearing, with proven timber connectors (such as "Teco" rings) at critical joints; and footings, angle-washers and other structural hardware as required. Unit working stresses and other values should conform to recommendations of the U. S. Forest Products Handbook. Bolts should be used throughout, with no dependence on nails and no credit for structural strength given to the casing or other non-frame parts.

CASING—Walls should be double, with air space between, or otherwise provide for internal drainage of water on the inner surfaces to avoid seepage and unsightly exterior staining. Casing should be applied in a manner to permit necessary expansion and contraction without stress to frame or casing, and to present a smooth, neat exterior.

SAFETY & CONVENIENCE—Adequate stairs, ladders, walks, doors, guards and railings should be provided for safe and convenient access to all parts of tower requiring inspection and service.

DO YOU KNOW—

snug fit, full bearings, uniform workmanship and sound materials are assured in all frame members and other Redwood parts of Marley towers by 100% pre-fabrication in Marley's two large wood-working plants (Stockton, Calif. and Kansas City, Kans.) thoroughly equipped for this exacting service. Marley's structural superiority is a recognized fact, zealously maintained.



TYPICAL MARLEY FRAME JOINT

THE MARLEY COMPANY, INC. · KANSAS CITY · KANSAS

MARLEY COOLING TOWERS

HOMO-FLEX HOSE

10

10 ADVANTAGES

- 1—Extreme flexibility—easy to handle
- 2—Resists kinking
- 3—Light in weight
- 4—Practically inseparable cover and plies—balanced homogeneous construction
- 5—Withstands high pressures and surges with wide margin of safety
- 6—Uniform inside diameter
- 7—Less elongation and expansion
- 8—Less fatigue to operator
- 9—More production
- 10—Lower ultimate cost



—a MANHATTAN Development brings you 10 advantages important in war or peace

IN WAR—The homogeneous and extremely flexible construction achieved by MANHATTAN Strength Members of super-strength cords and the balanced, engineered method by which they are applied and inseparably combined with the FLEXLASTICS* tube and cover, together give a service impossible a few short years ago.

Every one of these advantages contributes to greater production through less fatigue to operator and to much longer hose life—therefore fewer interruptions.

Still another MANHATTAN advantage—Turnate Vulcanization—imparts added strength to Homo-Flex Hose. This process applies pressure progressively before and during vulcanization to give not only uniform inside and outside diameters, but

also uniform texture and resilient strength. The distinctive spiral marking identifies Turnate Vulcanization.

IN PEACE—All these advantages will have cumulative value for you in the forthcoming competitive period. Then the multiple economies of long service life; resistance to high working pressures and surges; easy handling with less operator fatigue because of its light weight; toughness to withstand wear, abrasion and kinking; will help keep costs down and profits up.

Manhattan's Condor Brand Homo-Flex Hose is now available in types for the following services: Air, Water, Steam Pressing Iron, Orchard Spray, High Pressure Mine Spray, High Pressure Oil Spray.

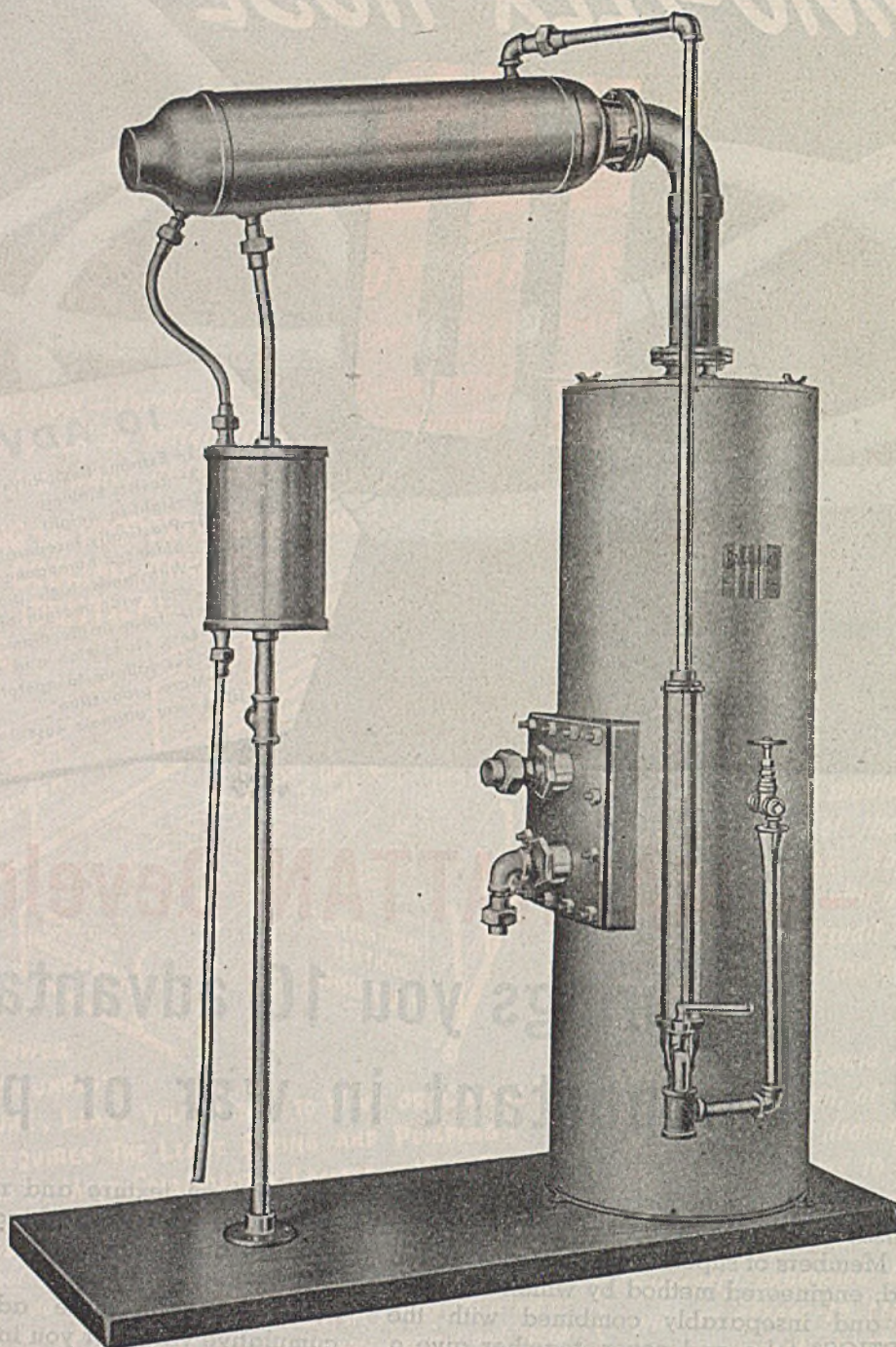
*The term FLEXLASTICS is an exclusive MANHATTAN trade mark. Only MANHATTAN can make FLEXLASTICS.

Buy more BONDS to bring the boys down the home stretch



Keep Ahead With

THE MANHATTAN RUBBER MFG. DIVISION
of Raybestos-Manhattan, Inc.



PURE AND STERILE ***EVERY DROP*** BARNSTEAD DISTILLED WATER

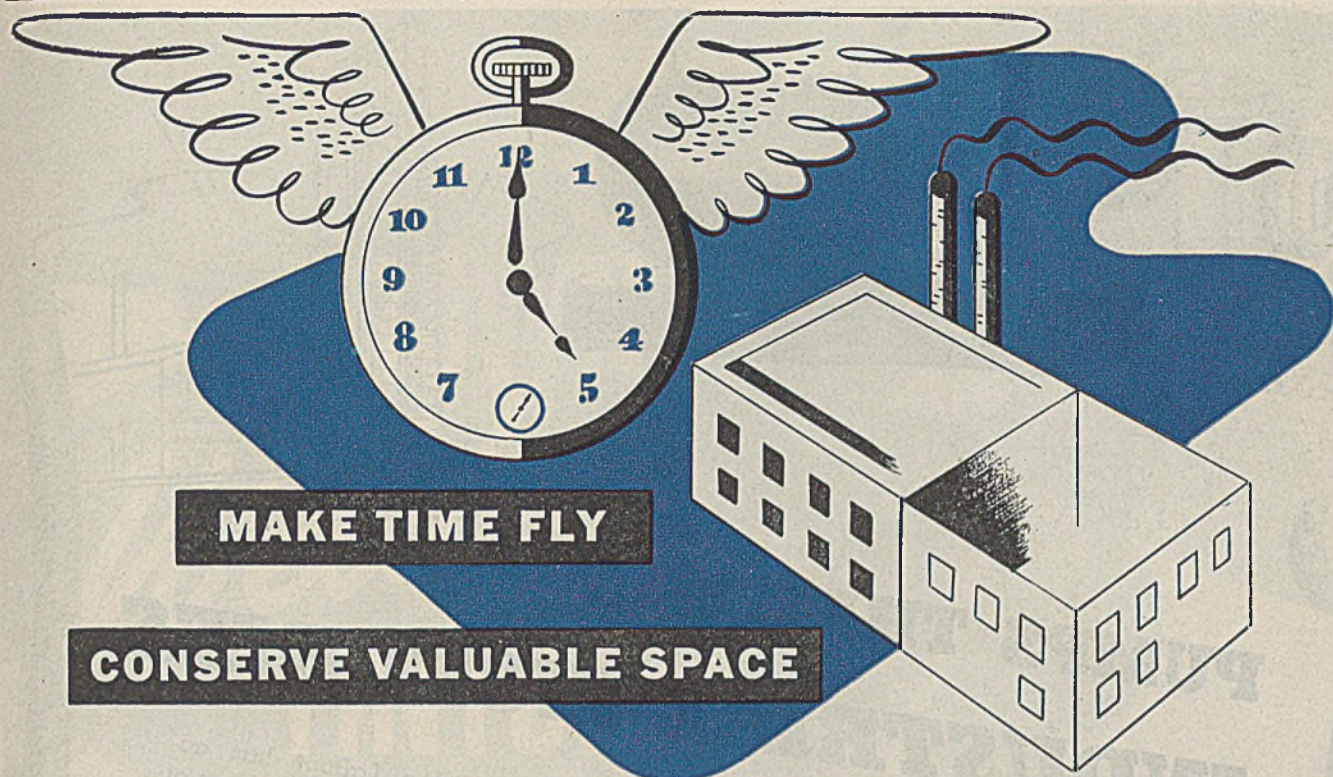
If you need pure water for your processes, you might as well go all the way and use Barnstead Distilled Water. The cost is low and you are sure of getting the results you want. For less than a $\frac{1}{4}$ of a cent per gallon a Barnstead water still will produce distilled water that is chemically and bacteriologically pure . . . free

from organic or inorganic solids . . . free from gaseous impurities . . . pure and sterile, *every drop of it.*

Sizes of Barnstead Water Stills range from $\frac{1}{2}$ to 500 gallons per hour. Operation is by gas, steam, or electricity. Write today for a copy of our new condensed catalog D.

Barnstead
STILL & STERILIZER CO. INC.

5 LANESVILLE TERRACE, FOREST HILLS, BOSTON 31, MASSACHUSETTS



MAKE TIME FLY

CONSERVE VALUABLE SPACE

with AT&M CENTRIFUGALS



EXTRACTION

AT&M Centrifugals 10 times as fast

By sheer force . . . many times greater than gravity, AT&M centrifugals have put wings on processing time to the great advantage of hundreds of manufacturers. They have been proven much faster for drying than filters, squeeze rolls, vacuum or suction boxes, or drying ovens.

AT&M centrifugals accomplish separation of materials so finely divided that they would never separate by gravity. They will even separate emulsions and some colloidal suspensions. Frequently AT&M centrifugals do two operations in one.

A very hush order for a special AT&M centrifugal, which requested that blueprints be kept under lock and key whenever not in use, resulted in

1. 95% recovery of a substance never before centrifuged.
2. Cut time for each batch from seven minutes to 35 seconds.

Consult AT&M for experienced engineering service (as war needs permit)
— no charge for study and recommendation. Strict confidence preserved.



FILTRATION

AT&M Centrifugals double production — no extra space

In place of unwieldy drying equipment—space-consuming tanks or slow, costly squeeze rolls, vacuum boxes or ovens—AT&M centrifugals are efficiently separating crystals from sticky fluids or, in one operation, 2 liquids from a solid—faster, cheaper, and in much less space. The space required for an AT&M Centrifugal, belt-driven, with a 36" basket, is only 6½ feet high, 4 feet wide and 8 feet deep.

One manufacturer converting for war found that limited head-room prevented centrifugals larger than 36" There was no additional floor space available yet expansion was imperative. AT&M engineers were consulted. Upon their recommendation he installed five 36" centrifugals. By quicker acceleration of the motor drives, **production was doubled.**

Investigate centrifuging for extraction . . . filtration . . . dehydration . . . precipitation . . . impregnation . . . coating

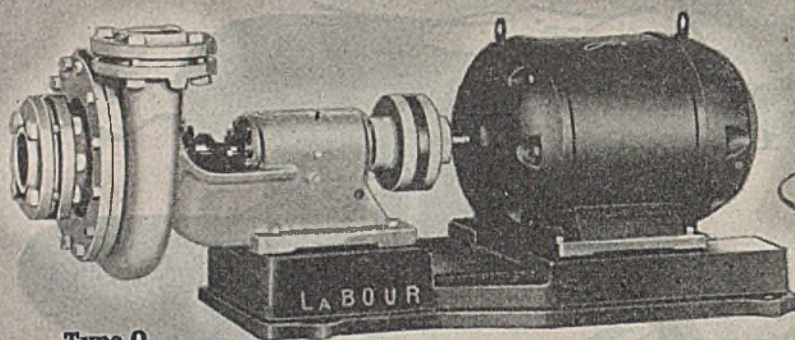
SAVE TIME
and **SPACE** with

A.T. and M.

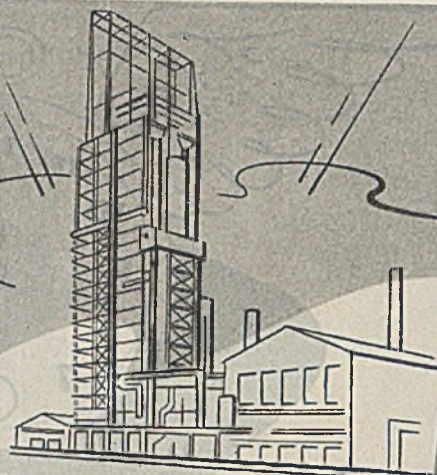
CENTRIFUGING

AMERICAN TOOL & MACHINE COMPANY

1421 Hyde Park Ave., Boston 36, Mass.
30C Church Street, New York 7, N. Y.



Type Q



PUMPS THAT WIN INDUSTRIAL VICTORIES

It's worth money to buyers of chemical pumps to know why LaBour pumps handle so many of today's toughest chemical moving jobs.

These pumps started winning industrial victories more than 21 years ago when LaBour produced the first commercially successful self-priming centrifugal pump. LaBour pumps have since simplified chemical pumping problems in chemical and fertilizer plants, in refineries, in steel, sugar, textile and paper mills.

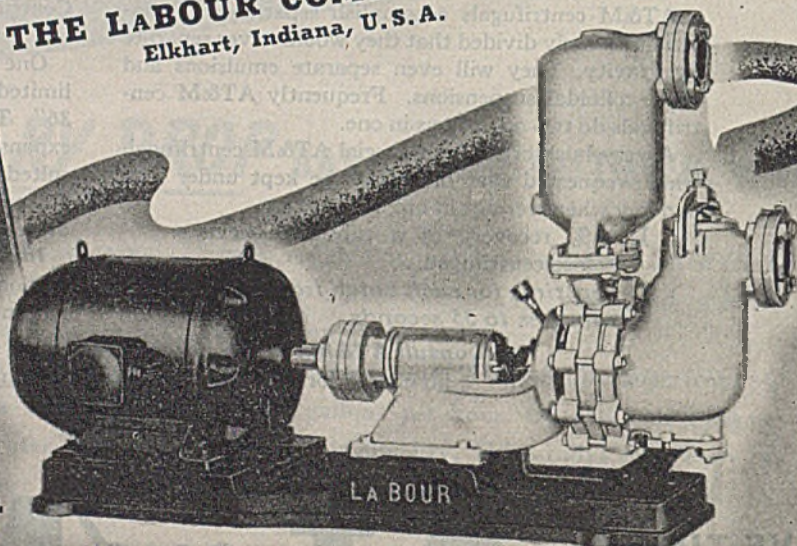
Obstacles encountered in chemical handling have been overcome by the

intimate knowledge LaBour has acquired through a continuous program of fact-finding and record-keeping. Out of that knowledge have come the many refinements and improvements that make LaBour pumps pre-eminent in their field.

If you would like to simplify your own chemical pumping problems, learn more about LaBour chemical handling pumps. Their efficiency, dependability, ease of maintenance and low operating cost can make your job easier.

Start by writing today for your free copy of Bulletin No. 50.

THE LABOUR COMPANY, Inc.
Elkhart, Indiana, U.S.A.



Type DPL



CENTRIFUGAL PUMPS

BROWN *Welded* FINTUBES

Sizes 1" to 8" in Diameter

● Conceived, perfected and available only from Brown Fintube, this welding of longitudinal U-shaped strip steel channels on the **outside** of the tube gives users the utmost in efficiency and performance. This construction avoids cutting grooves **into**,— and any weakening of the center tube. It permits the use of any number of fins that can be spaced advantageously around the tube diameter . . . And since the wall thickness of the center tube is determined by pressure only—not depth of groove—thinner walled center tubes can be used, increasing the effectiveness of the heat transfer.

The integral—and permanent—metallic bonding between the fins and center tube avoids the presence of an air gap,— with its restriction to heat flow, and any cracks to collect dirt, and other insulating materials. Consequently Brown welded Fintubes have high transferring efficiency—**permanently maintained**—and trouble free operation during the life of the tube. Available with center tubes 1" to 8" diameter, fins ¼" to 1½" in depth, to produce primary to secondary surface areas in any ratio from 4:1 to 15:1. Tube and fins may be carbon or alloy steel. Tubes can be lined with copper, zinc, lead, aluminum or admiralty for handling corrosives. Specify Brown **welded** Fintubes for your requirements. Samples for experimental and small pilot plant purposes furnished free on request. Inquiries handled promptly.



A Few of the 236 Brown Fintubes used in 2 Toluene Plants, Tubes, 6" OD, ¾" Wall, 36' Long 9% Chrome Steel. Fins, 4-6% Chrome Steel.



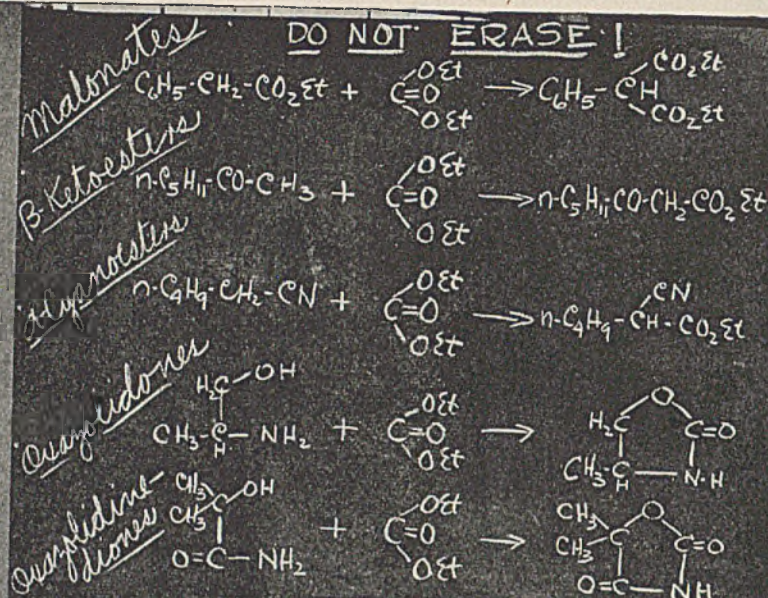
Part of 14,274 Salt to Air Heater Fintubes Awaiting Shipment. Tubes, 1" OD, 12 Gauge, 20' Long. Both Tubes and Fins Low Carbon Steel.

THE BROWN FINTUBE CO.

120 FILBERT STREET • ELYRIA, OHIO

MANUFACTURERS OF INTEGRALLY BONDED FINTUBES AND FINTUBE HEAT EXCHANGERS

*Today's
Blackboard Chemistry
Tomorrow's
New Products*



SEE FOR YOURSELF the many new products* which these reactions now put within your reach. You are cordially invited to visit the Mallinckrodt booth at the National Chemical Exposition, Chicago, Illinois, November 15-19, 1944. Our research chemists will be happy to discuss these new organics with you.

Among the Products on Display Will Be:

ESTERS

Diethyl Phenylmalonate
 Diethyl Phenylethylmalonate
 Diethyl Phenylbenzylmalonate
 Ethyl Phenylacetate
 Ethyl *Alpha*-phenylbutyrate
 Di-*n*-amyl Carbonate
 Dibenzyl Carbonate
 Dicyclohexyl Carbonate

ALPHA-CYANO ESTERS

Ethyl *Alpha*-phenylcyanoacetate

Ethyl Phenylethylcyanoacetate
 Ethyl Phenylbenzylcyanoacetate

BETA-KETOESTERS

Ethyl Isovalerylacetate
 Ethyl *Beta*-ketocaprylate
 Ethyl *p*-chlorobenzoylacetate

OXAZOLIDONES

2-Oxazolidone
 2-Hydroxyethyl-2-oxazolidone
 3-Phenyl-2-oxazolidone
 4, 4-Di-(hydroxymethyl)-2-oxazolidone

*Fundamental research on ester condensations by Mallinckrodt chemists have made potentially available a host of new organic compounds of diversified properties. See U. S. patents 2,338,220; 2,342,385; 2,346,059; 2,351,085. J. Am. Chem. Soc. 63, 2056, 2252 (1941); 64, 576, 578, 580 (1942).

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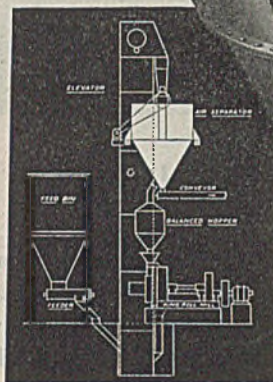
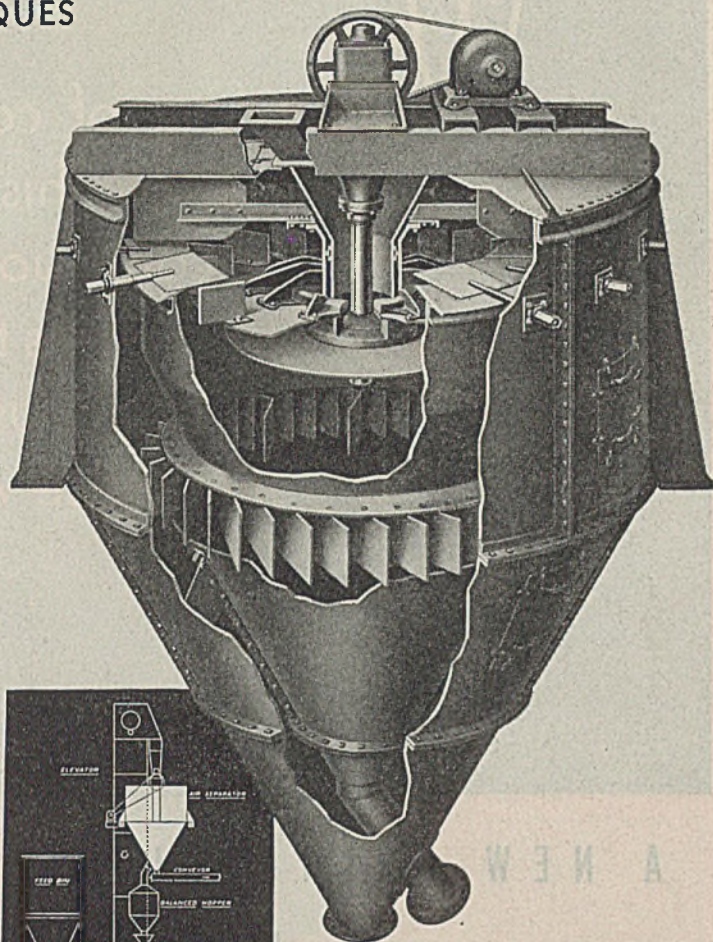
THE MODERN MACHINE THAT REVOLUTIONIZED PULVERIZING TECHNIQUES

The Sturtevant Air Separator . . . operating in closed circuit with a mill . . . selects and continuously removes the finished product in any desired fineness, thus permitting the mill to grind without cushioning fines.

In principle Sturtevant Air Separation employs the exact regulation and control of centrifugal force and air currents—one counteracting and overbalancing the other—so that by simple adjustments a product of any desired fineness is selected and collected while coarser sizes are rejected.

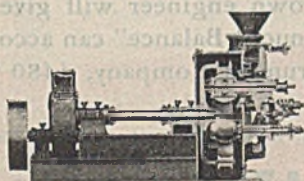
With this separator selective output is increased to as much as 300%, with a corresponding power reduction of from 10 to 50%. Costs, including upkeep, are cut to new lows, while finer and more uniform products are made possible.

Sturtevant Air Separators are built in sizes from 3 to 18 feet in diameter for capacities from $\frac{1}{4}$ to 50 tons, handling materials with a 40–350 mesh range. They are of rigid, compact construction capable of lifetime wear. Write for complete details.



The flow sheet (left) shows a "closed circuit" grinding unit incorporating a Sturtevant Air Separator and a Sturtevant Ring Roll Mill. Other variations in closed circuit grinding are available.

STURTEVANT AIR SEPARATOR



The STURTEVANT Ring Roll Mill indicated left is for medium and fine reduction (10 to 200 mesh) hard or soft materials. It features open door accessibility, employs no scrapers, plows, pushers or shields, is highly durable, requires little power and is built in many sizes for various capacities.

Ask for Sturtevant literature describing this modern line of processing equipment.

STURTEVANT MILL COMPANY 2 HARRISON SQUARE
BOSTON 22, MASS.

“Without fear of contradiction we state that this instrument, with its continuous balance principle, marks the greatest advance in industrial instrumentation since World War I”

A NEW PRINCIPLE IN INSTRUMENTATION

Introduced in 1941 as a flight recorder for testing army and navy aircraft, and since limited largely to direct war projects, the Brown Electronik Potentiometer is now available in increasing quantity to general industry. Without fear of contradiction we state that this instrument is the greatest advance in the art of industrial instrumentation since the days of World War I.

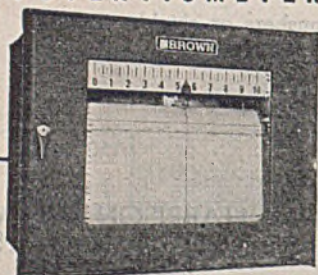
Used with conventional wiring and thermocouple installation, the Brown Electronik Potentiometer is rapidly outmoding all other forms of temperature controllers in the petroleum and other process industries.

Thousands of operation hours have proved its superior performance . . . accuracy . . . sensitivity . . . ruggedness. Its Electronik “Continuous Balance” Operating Principle means precise control every second, with uniformity hitherto impossible.

If the manufacture of your product involves temperature measurement or control — we invite your inquiry. A Brown engineer will give you a prompt opinion as to what Brown “Continuous Balance” can accomplish in your plant. Address The Brown Instrument Company, 4480 Wayne Avenue, Philadelphia 44, Pennsylvania.

LISTEN . . . The Blue Jacket Choir with Danny O’Neil every Sunday 11:05 to 11:30 A. M., Eastern War Time, C. B. S.

BROWN
Electronik
POTENTIOMETER



OPERATES ON
“CONTINUOUS BALANCE” PRINCIPLE

INSTRUMENTS BY **BROWN** CONTROLS BY
Honeywell
MINNEAPOLIS

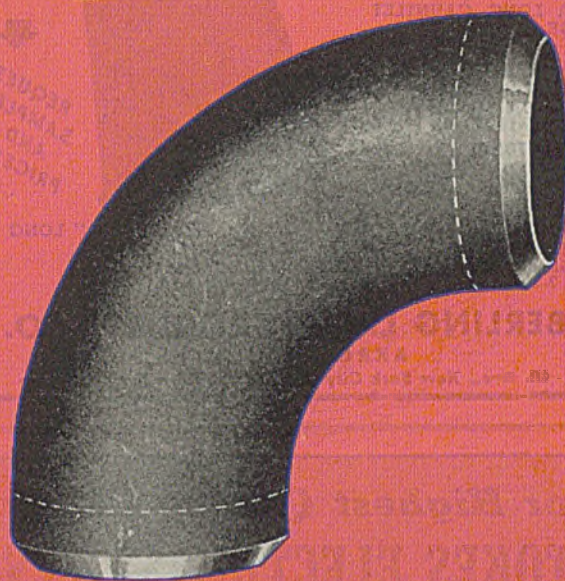
Only MIDWEST

OFFERS YOU THIS CHOICE

MIDWEST "STANDARD"
Butt-Welding Elbow



MIDWEST "LONG TANGENT"
Butt-Welding Elbow



The difference between the two types of welding elbows shown above is in their dimensions. The "American Standard" elbow has a center-to-end dimension equal to one and one-half times the nominal pipe size. The Midwest "Long Tangent" elbow has tangents (straight ends) equal to one-fourth of the nominal pipe size; the center-to-end dimension is one and three-quarters times the nominal pipe size. Important among the advantages of the long tangents are: (1) pipe and fitting more quickly and accurately lined up, (2) weld removed from point of maximum bending stress, (3) less pipe required, (4)

short nipple and extra circumferential weld frequently eliminated, (5) slip-on welding flanges easily used, etc. There is no increase in price for Midwest "Long Tangent" Welding Elbows.

Both types of elbows have all other advantages that result from the unique Midwest manufacturing process: final working of metal in compression (which means exceptional dimensional accuracy and uniformity), stress relieving, exact included angle, true circular cross-section and uniform wall thickness. For all the facts about Midwest Welding Fittings, ask for Bulletin WF-41.

MIDWEST WELDING FITTINGS IMPROVE
DESIGN AND REDUCE PIPING COSTS



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.

Now Also Available in NEW LIGHT DUTY STYLE

All-Neoprene Latex INDUSTRIAL GLOVES

Impermeable to practically
All Acids and Caustics

Highly Resistant to Oils
and Greases

5 POPULAR STYLES

★ No. 5760-5, 18" LONG
EXTRA LONG GAUNTLET
GAUGE .030 TO .040
SIZES 10, 11

★ No. 5737-2, 14" LONG
LONG GAUNTLET
GAUGE .030 TO .040
SIZES 9-10-11-11½-12

★ No. 5705-5, 11" LONG
SHORT GAUNTLET
GAUGE .020 TO .025
SIZES 9-10-11

★ No. 5703-5, 10½" LONG
STANDARD DUTY
GAUGE .015
SIZES 7-8-9-10-11

★ No. 5702-5, 10½" LONG
LIGHT DUTY
GAUGE .010 TO .012
SIZES 7-8-9-10-11



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SAMPLES
AND
PRICES

SEIBERLING LATEX PRODUCTS CO.

AKRON, OHIO

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For Highest Quality Water STOKES ELECTRIC STILLS

with
Automatic
Overheat-Protection



SIX SIZES

from ½ to 1½ g.p.h..
Also Gas and Steam
Heated Stills from ½ to
100 g.p.h.

CONTINUOUS DISCHARGE OF
IMPURITIES.

TRIPLE VAPOR BAFFLES prevent
entrainment.

LONG-LIFE, NON-CORROSIVE
METAL AND PYREX GLASS
CONSTRUCTION.

ECONOMICAL OF CURRENT
AND WATER. Large Boiling Area
and Counterflow Condenser.

MORE THAN 20,000 IN USE IN
EXACTING SERVICE.

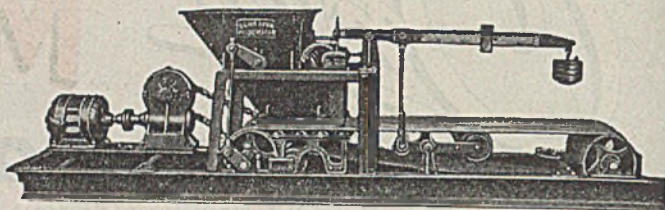
F. J. STOKES MACHINE CO.
5922 Tabor Road Philadelphia 20, Pa.

F.J. Stokes

WATER STILLs



FEED BY WEIGHT



THE AUTOMATIC FEEDER-WEIGHER-CONVEYOR

Schaffer Poidometers will proportion or feed your bulk material automatically with a high degree of accuracy. They are now being used for proportioning of feeding materials in the following industries — Cement, Process, Ceramic, Oil Refining, Feed, Soap, Ore, Gypsum, Lime and many others.

If you are handling a variety of materials, arrange your Poidometers in batteries — set one for each material and for the proportion wanted — then forget it! The Poidometers will do your bidding better than your most loyal employee. If any machine is not getting its full quota of material, the entire battery will automatically stop. Space does not permit of a thorough explanation of the many cost-saving qualities of Schaffer Poidometers.



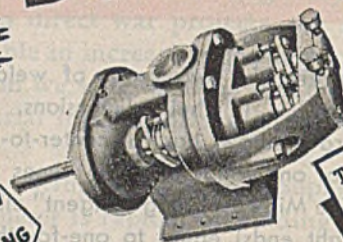
Install Schaffer Poidometers and Watch Results.
Write for catalog No. 3

SCHAFER POIDOMETER CO.

2828 Smallman Street

Pittsburgh 22, Pa.

BUMP PUMPS



The Original Designer
and Manufacturer
who Introduced BUMP
Pumps to the Industry.

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PRIMING

POSITIVE
ACTION

NO
CHURNING
ACTION

Positive displacement type that is capable of operating at slow speeds without agitation, or churning action within the pump, Bump Pumps have few parts so that maintenance is at a minimum. In use by chemical plants all over the country. Bump Pumps deliver a constant volume per revolution that is not affected by speeds or pressures.

Easy to install for any service.

Consult our engineers on your

pumping problems and your post-

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SLOW
SPEEDS

ONLY TWO
MOVING
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Principle
of Operation



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Number 5 of a Series: "Looking at the 5 essential things you never see in anodes!"



Webster defines it 55 ways!

BUT we'll stand on Definition 18.a:

"... conduct contributing to the advantage of another or others."

IT DEFINES what we mean by *customer service*... one of the five essential things you never see in "Acheson" graphite anodes.

Customer service includes such things as our continuing independent studies of anode behavior. It covers quick filling of your orders, and cooperative work with you to improve anode performance

in the electrolytic production of indispensable industrial chemicals and metals. It has helped to lower anode usage costs, to slow down voltage rise, and to lengthen cell-diaphragm life.

It is one of the most important of the five essential things you never see in the "Acheson" anodes used in the bulk of the nation's electrolytic cells. The others: Raw materials selection, manufacturing experience, manufacturing control, and continuing research. Your inquiries are invited.



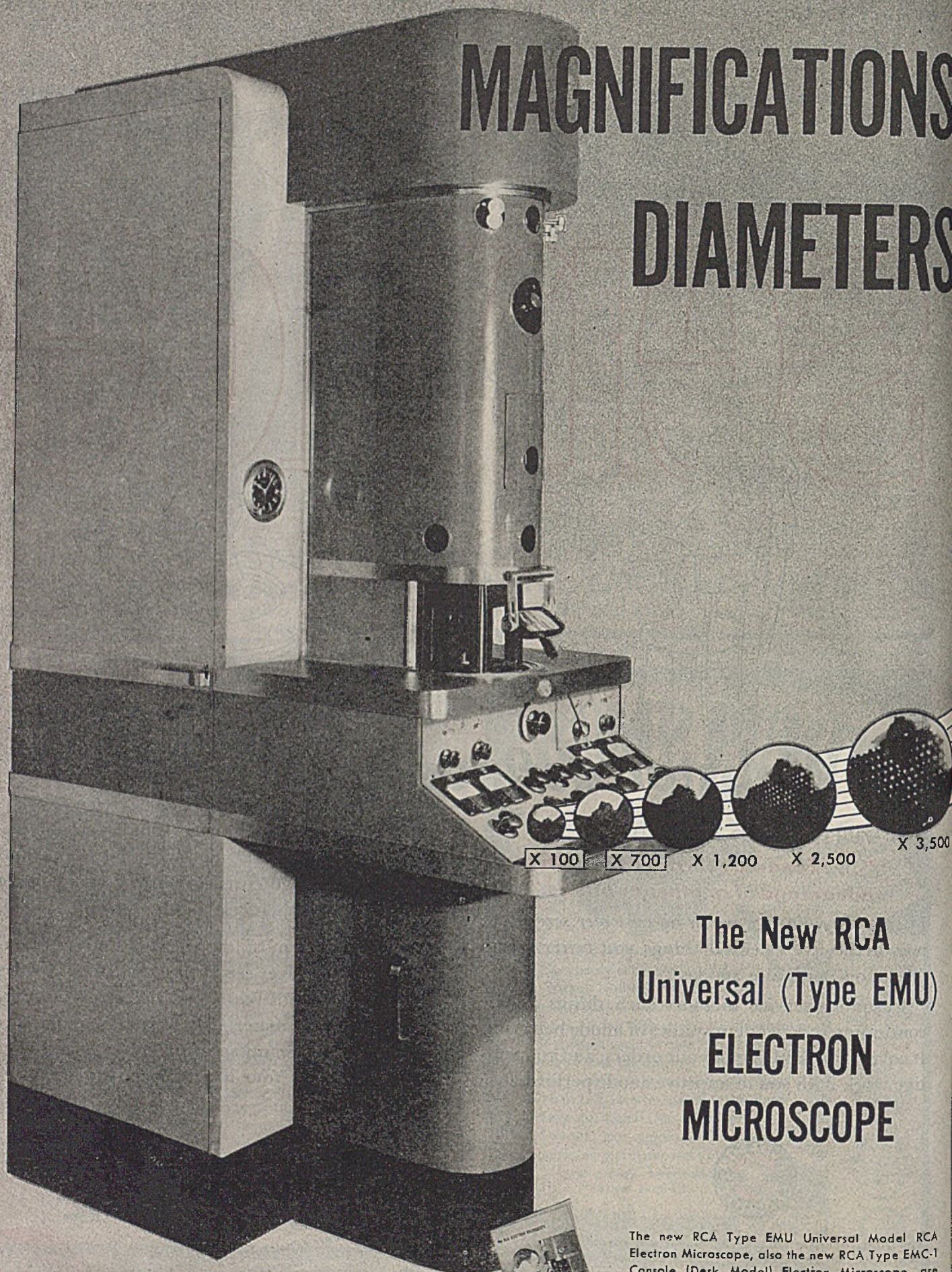
The word "Acheson" and the "Acheson" seal are registered trade-marks of National Carbon Company, Inc.

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Keep your eye on the infantry—the doughboy does it!

MAGNIFICATIONS DIAMETERS



The New RCA Universal (Type EMU) ELECTRON MICROSCOPE

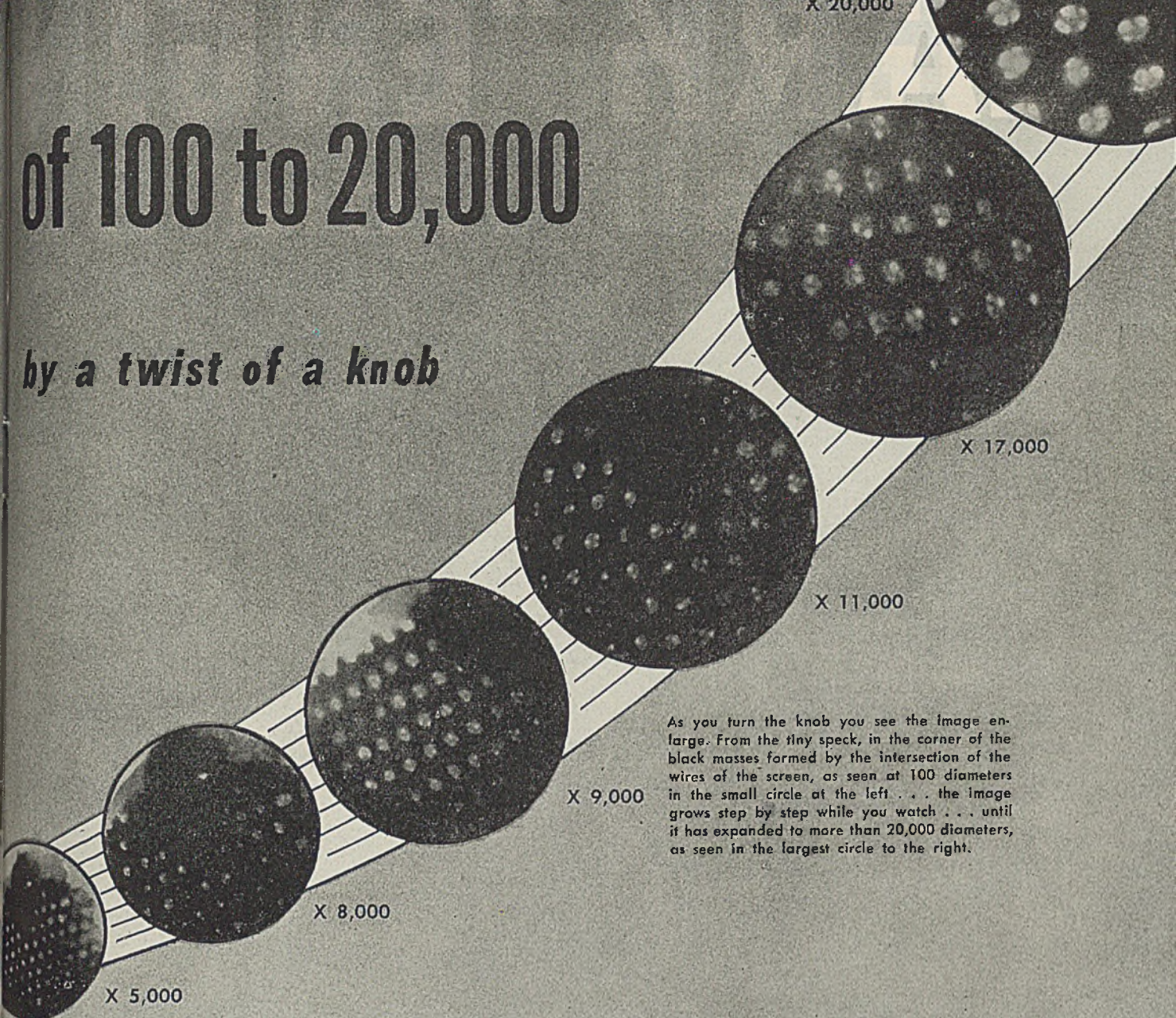
BUY WAR BONDS... AND KEEP 'EM



The new RCA Type EMU Universal Model RCA Electron Microscope, also the new RCA Type EMC-1 Console (Desk Model) Electron Microscope, are described and illustrated in this new RCA Bulletin. Copy sent promptly on request. In writing us for this bulletin, please use your business letterhead.

of 100 to 20,000

by a twist of a knob



As you turn the knob you see the image enlarge. From the tiny speck, in the corner of the black masses formed by the intersection of the wires of the screen, as seen at 100 diameters in the small circle at the left . . . the image grows step by step while you watch . . . until it has expanded to more than 20,000 diameters, as seen in the largest circle to the right.

THE new RCA Universal (Type EMU) Electron Microscope is designed to provide (1) maximum operator comfort and convenience, (2) maximum simplicity and flexibility, (3) consistent top performance, and (4) maximum ease of servicing.

The operator of this microscope, by merely turning a single knob, can enlarge the clear, sharp image he is observing through 40 steps of magnification ranging from 100 diameters up to 20,000 diameters.

This is but one example of the ease with which this instrument can be used in practice. Making micrographs at any magnification is equally simple.

Detailed descriptions of the new RCA Universal (Type EMU), and the new RCA Console (Desk Model, Type EMC) Electron Microscopes are contained in the booklet shown at the left.

Copy of this important and interesting new booklet will be sent promptly on request.



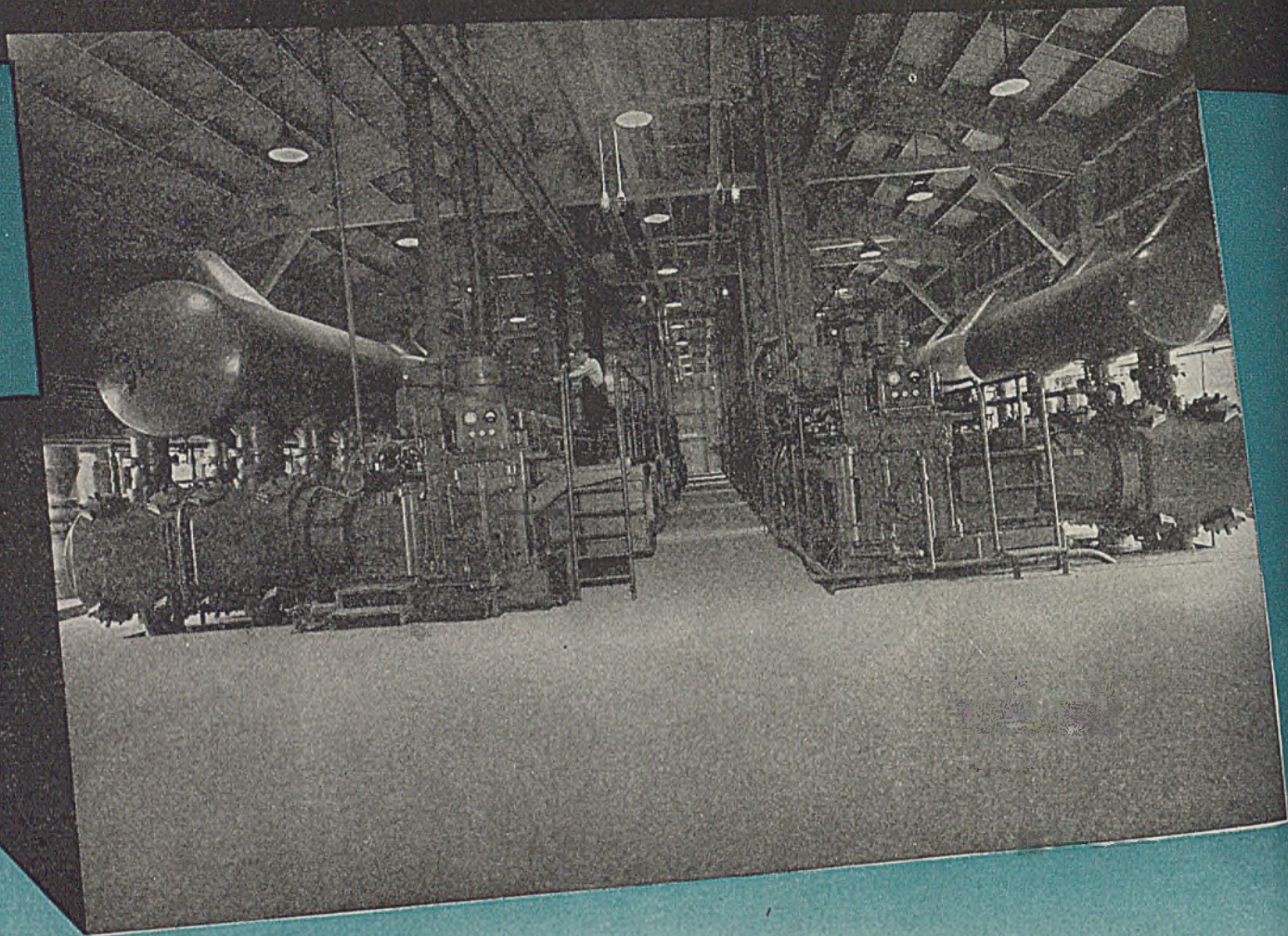
RADIO CORPORATION OF AMERICA

RCA VICTOR DIVISION • CAMDEN, N. J.

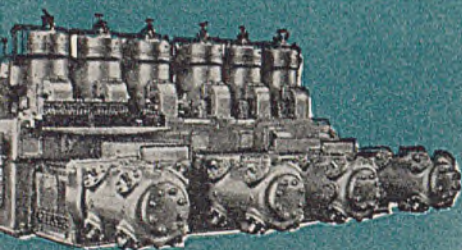
LEADS THE WAY . . . *In Radio . . . Television . . . Tubes . . .*

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CLARK ENGINE in California Bu



12 CLARK "Angle" Compressors totalling 7,500 BHP, in one of the Butadiene plants

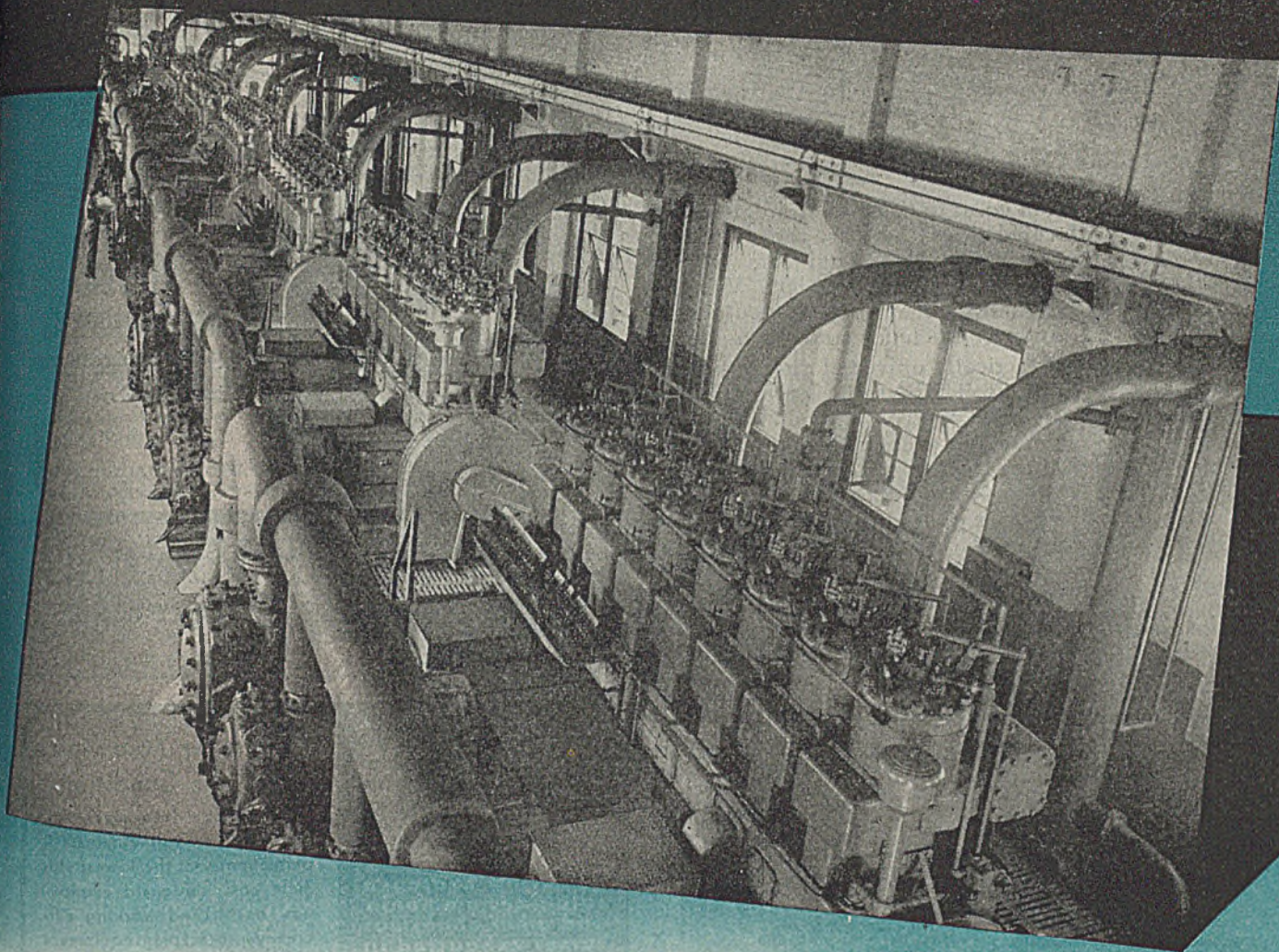


CLARK 6-cylinder, 750 BHP supercharged gas-driven "Angle"

The Clark Angles in the huge California Rubber project are typical of what the Clark organization can and is willing to do for special engineering problems in the handling of hydrocarbon gases.

The Clark Angles shown above, in one of the Butadiene plants, were specially engineered and built for the unusual operating conditions in this plant. In spite of the pressure of large and urgent war contracts, Clark engineered and built special tandem double-acting compressors needed for this application, in record time.

EERED" ANGLES tadiene Project

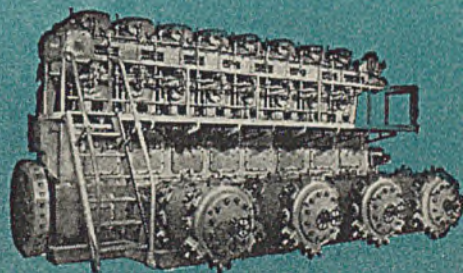


The Clark Angles for the above shown ammonia refrigeration installation were also built in an unusually short time.

For special compressors and unusual operating conditions get in touch with CLARK.

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7 CLARK 1000 BHP "Angles" in
refrigeration service in one of
the Butadiene plants



CLARK 4,000 BHP steam
driven "Angle"

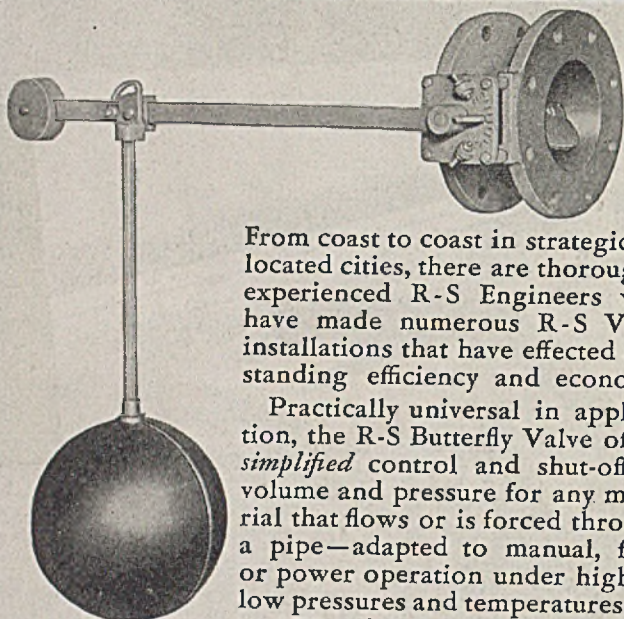
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ONE OF THE DRESSER INDUSTRIES



. . . SETS THE PACE IN COMPRESSOR PROGRESS

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No. 579

No. 579. Direct action float valve with counterweight assembly.

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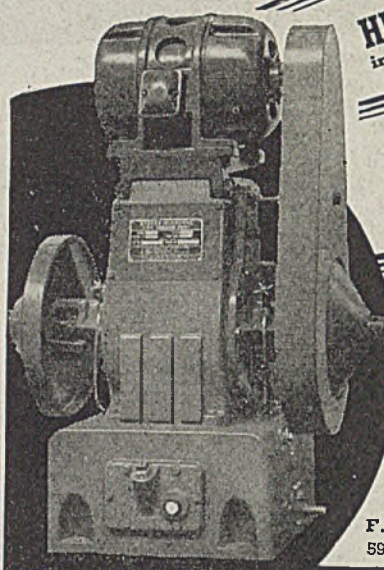
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PUMPS • GAUGES • EQUIPMENT**

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THE PROBLEM

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THE SOLUTION

A 12,000 c.f.m. Multi-Wash Collector was installed. The neighborhood nuisance was abated and working conditions in the plant were noticeably improved.

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FACE,
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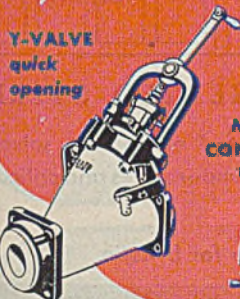


ANGLE
VALVE



Y-VALVE
hand
wheel

SAFETY
VALVE



Y-VALVE
quick
opening

MOTOR
CONTROLLED
VALVE



FLUSH
VALVE

OPERATING LEVER
(FULL-OPEN TO FULL-CLOSED
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LAPPED SEAT

● Study of the cut-away drawing of the Lapp Valve has determined many an engineer to try this equipment in his process. We've yet to hear of a case in which that judgment wasn't substantiated by the valves on the job. All the valves sketched at the left incorporate the same principles of construction. If you want to eliminate contamination, break-downs, shut-downs, slow-downs and maintenance, get some experience with Lapp Valves. *Lapp Insulator Co., Inc., Chemical Porcelain Division, LeRoy, N. Y.*



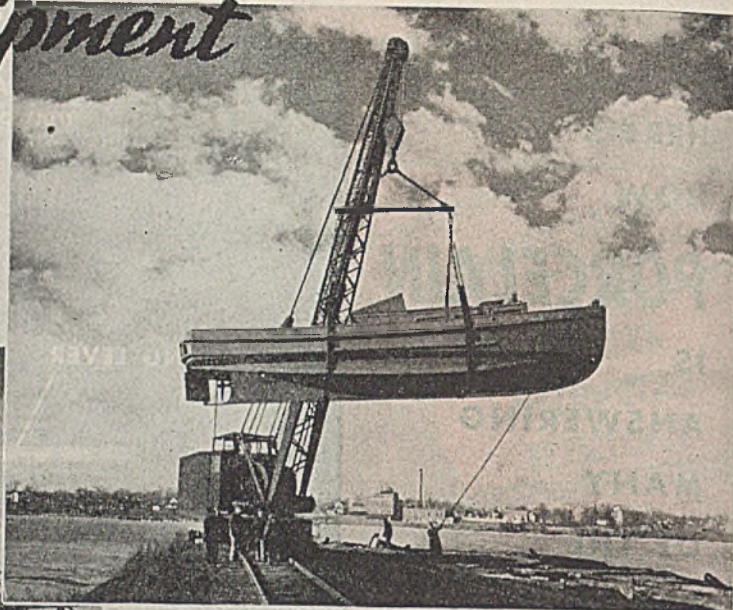
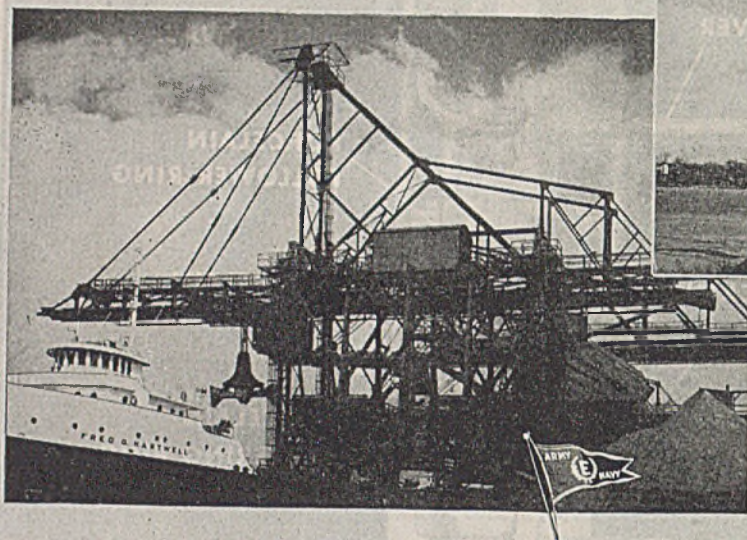
Lapp

Chemical Porcelain

Heavy Duty Equipment

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BY INDUSTRIAL BROWNHOIST

From Maine to California, in shipyards, dry docks, ports, steel mills, chemical plants, railroads and in nearly every other kind of industry where efficient material handling is required, Industrial Brownhoist equipment is speeding production and reducing man hours.



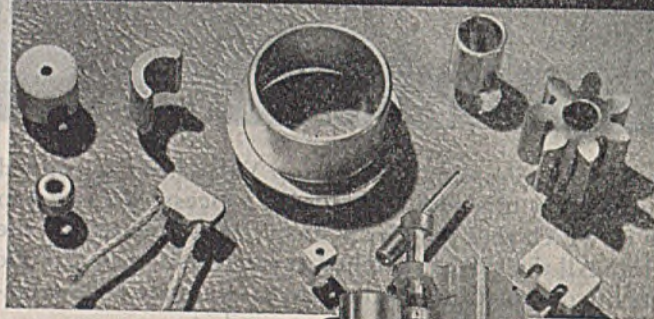
Above: An Industrial Brownhoist 40-ton Diesel locomotive crane at a Great Lakes yard easily swings an army boat to flat car after trial run. The patented Monitor-type cab provides 360° visibility, increases operator efficiency. Left: A 10-15 ton capacity I.B. fast plant for unloading iron ore from lake boats. Moveable lorry rides on runway, weighs ore and delivers it to railroad cars under span. Write for further facts about Industrial Brownhoist equipment to solve your material handling problems.

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Rugged Stokes Presses for forming powdered metal parts, dry pressing ceramics, debulking chemicals and many other services, stand up under the most severe operating conditions—retain their accuracy even under very heavy overloads.

No wonder nine out of ten powdered metal parts are produced on Stokes Presses and manufacturers of countless other products use Stokes Presses exclusively.

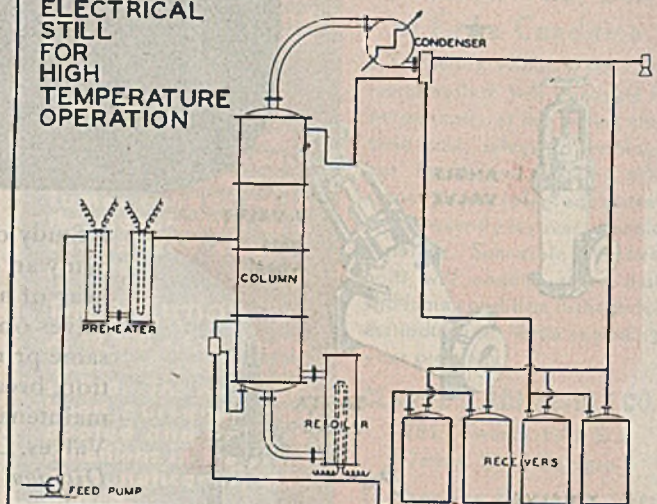
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ELECTRICAL STILL FOR HIGH TEMPERATURE OPERATION



ELECTRICALLY HEATED STILL

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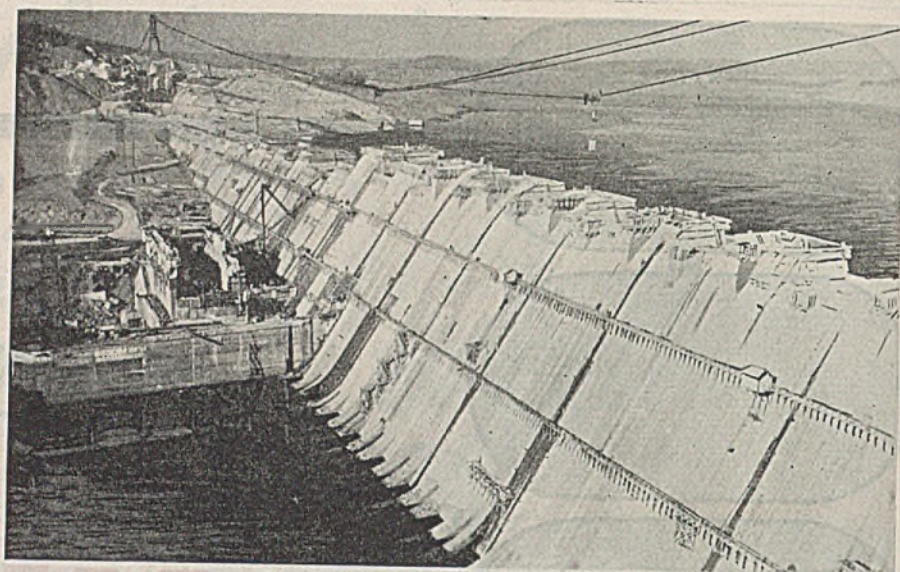
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WELLINGTON SEARS COMPANY, NEW YORK, N. Y.

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Refrigeration



Stretching across the North Fork of the White River, in Arkansas, Norfork Dam is 2624 ft. long and 220 ft. high — the fifth largest concrete structure of its kind in the U. S.

Frick Refrigeration played a triple rôle in hastening the building of this great Dam. To prevent dangerous heating as the concrete hardened, the water going into the mixers was chilled almost to the freezing point: in very hot weather, tons of crushed ice were also supplied; after being poured, the monolith was cooled for months by circulating chilled water through 900,000 ft. of pipe imbedded in the mass.

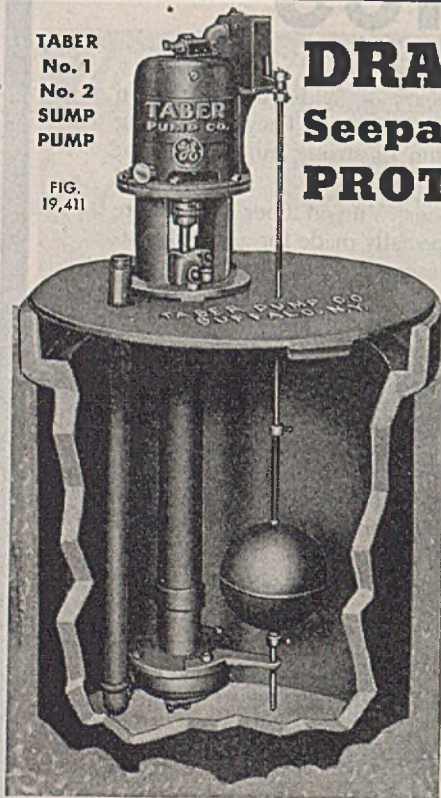
Frick Engineering and Frick Equipment served with distinction on this big project. Which leads us to repeat: "For the really important jobs, specify Frick Refrigeration."

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Write Frick Company for complete description of this unusual job.

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No. 1
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SUMP
PUMP

FIG.
19,411



Ad No. 541B

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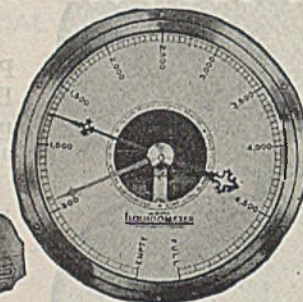
This sturdily constructed Taber Sump or drainage pump, unlike cheap "novelty" pumps, gives real protection.

Like all Taber Chemical Pumps, this Taber Sump Pump is built up to a standard of excellence that assures the protection intended.

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Stored Liquids Accurately With—*
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"THEY'RE ALWAYS DEPENDABLE"

100% automatic.

No pumps, valves, or auxiliary units needed to read them.

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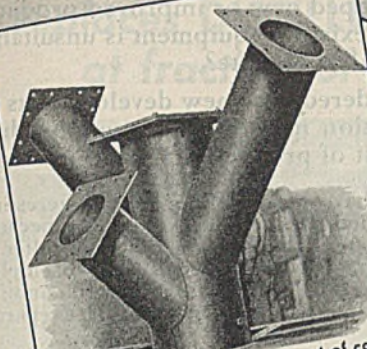
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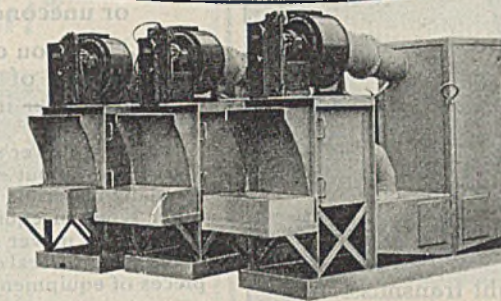
Write for complete details.

THE LIQUIDOMETER CORP.
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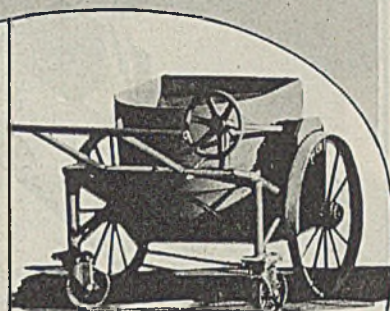
Produced in **JAY-CEE** CITY TENNESSEE



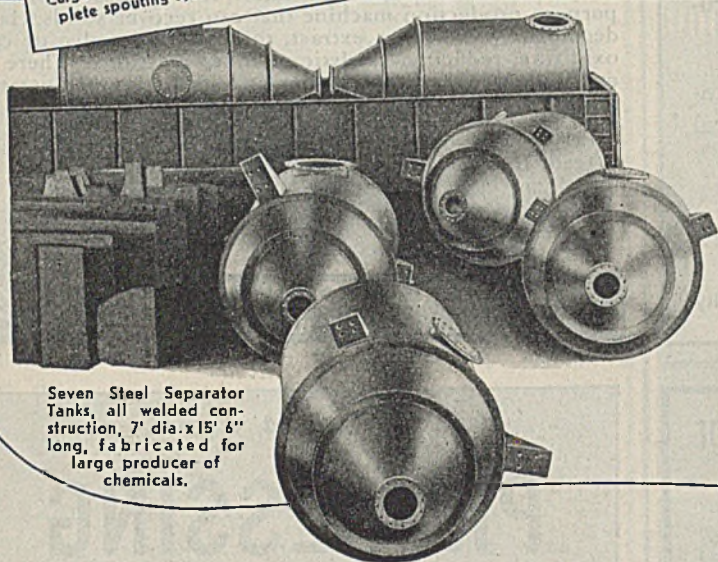
Large complicated "Y" Unit, part of complete spouting system built by Jay-Cee.



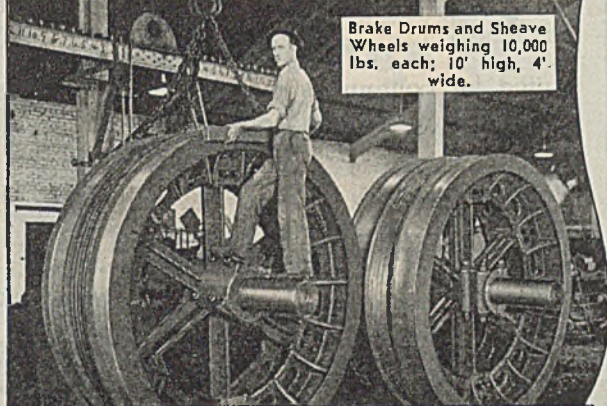
Three (3) of 12 Fume Eliminators fabricated and assembled by Jay-Cee, for aluminum tube mills.



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draw a picture of it . . . we'll build it.**

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Continuous-Flow Colorimeter



Mod. 400-S

A colorimeter for immediate and direct indication of the light transmission of a liquid flowing continuously through the instrument.

Suited for continuous registration of concentration, color or turbidity of solutions in chemical processes.

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(For High Chlorine Concentrations—
1.0 to 200 ppm. and above)

A special Chlorine Unit designed for uses where a high residual of 1.0 ppm. or more of chlorine is maintained. Price, complete with instructions, \$12.50.

The H-C Chlorine Comparator is one of a complete new line of LaMotte Chlorine Units. Embodies latest approved developments, such as control of color development, pH, etc., with a new series of interchangeable 15 mm. chlorine color standards embracing the entire useful range. The new LaMotte o-Tolidine reagent is used with all LaMotte units, and may be purchased separately, in various package sizes. Write for descriptive booklet.



LaMotte Roulette Comparator

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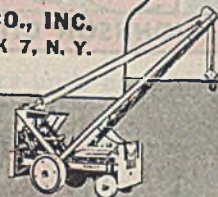


Sifters, Crushers, Cutters, Dry and Liquid Mixers,
Mills, Grinders, Pulverizers, Conveyor Systems,
Complete Installations.

The handling equipment construction "know-how" of the Mercer Engineering Works, Inc., Clifton, N. J. . . . The more than 40 years processing equipment experience of Robinson Mfg. Co., Muncy, Pa. . . . All are embodied in and represented by

MERCER-ROBINSON, CO., INC.
30 CHURCH ST., NEW YORK 7, N. Y.

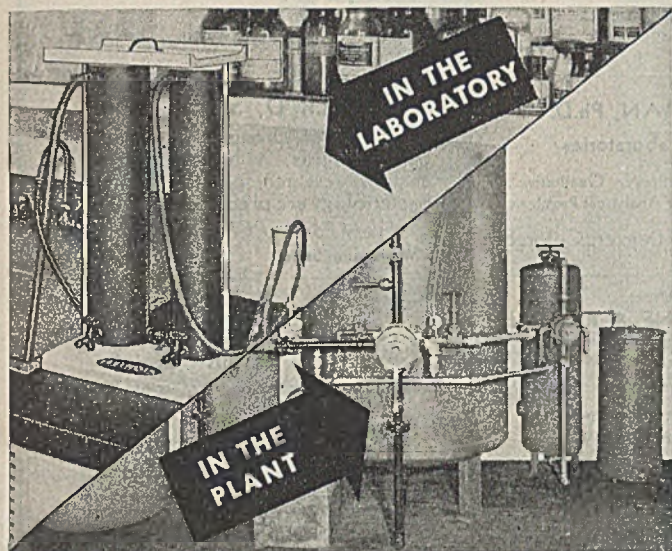
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Trailer Trucks (All Types) Wheel Tractor Cranes
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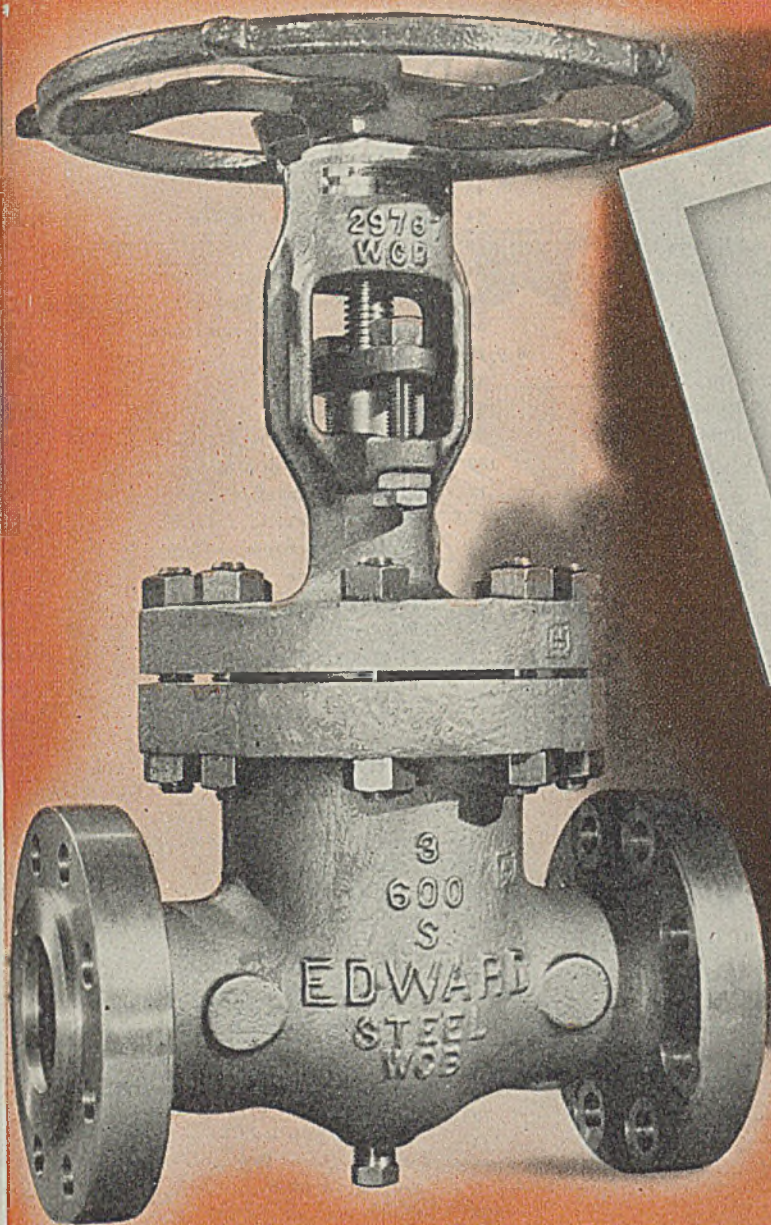
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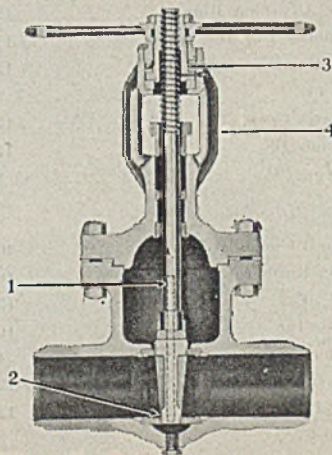
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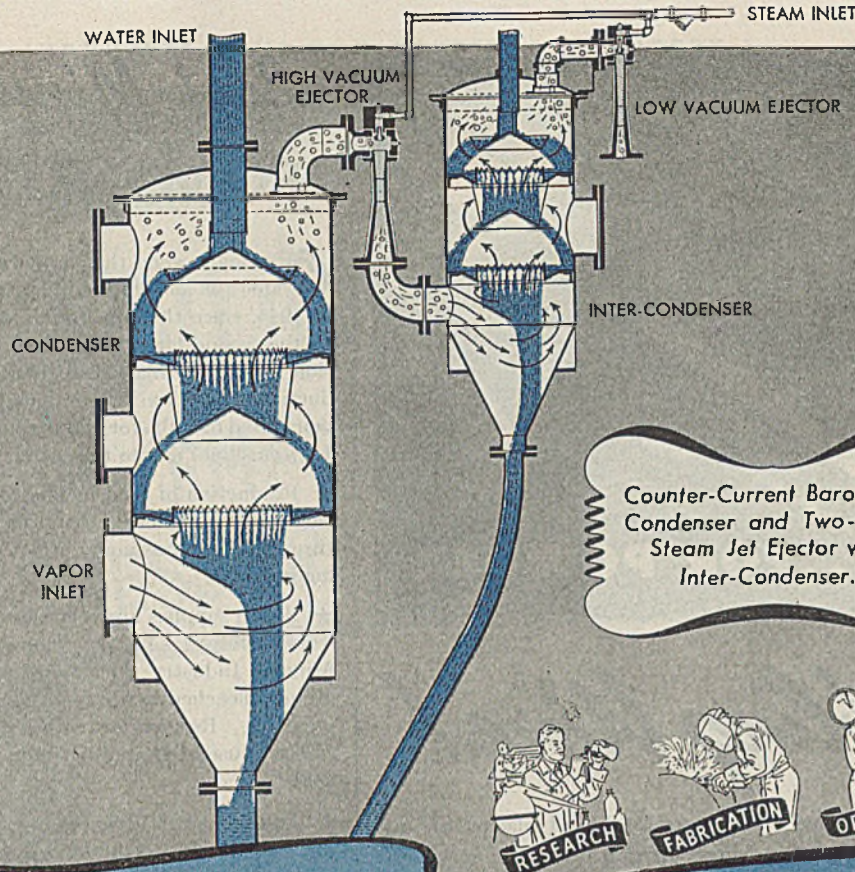
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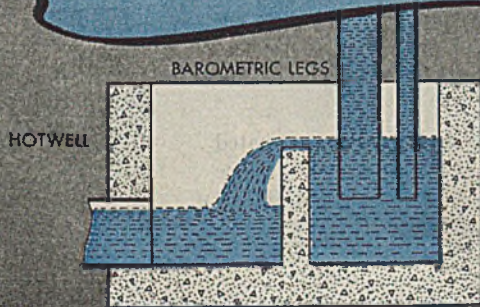
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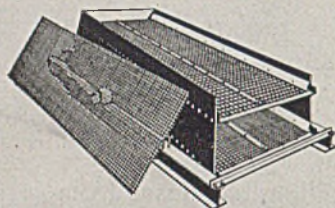


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Last-Minute Flashes

FROM THE EDITOR'S DESK

OUTLOOK is good that larger quantities of corn will be available for alcohol distilling plants and other industrial uses in 1945, since the crop estimated at 3,100,000,000 bushels may be the second largest on record. On the other hand, the situation on Cuban blackstrap molasses for industrial alcohol production is none too encouraging. Large quantities of alcohol are being used in Cuba for making fuel blends (reported 75% alcohol-15% gasoline) due to the scarcity of gasoline stocks.

★ Production of food in this country in 1944 is expected to be close to 40% higher than prewar years. Reconversion of agriculture will present as many, if not more, headaches than reconverting industry.

★ Barite supplies are very short, and the situation is likely to be worse before it is better. One exception is noted in a release by Mineral Industry Surveys of the Bureau of Mines—namely, ground bleached barite used in paint, rubber, and for other filler purposes. Reason for acute shortage is the tremendous increase in use of ground barite in oil well drilling in high-pressure fields.

★ Technological advances are not entirely in the field of synthetics and new products. According to the Dominion Bureau of Mines, Canadian consumption of common salt is increasing with its use in soil stabilization for the foundation of highways and for a surface veneer for gravel roads. It has been extensively used also in the development of soil-stabilized bases for runways at Canadian air fields.

★ We are trying to be helpful this month. Many readers are getting insomnia because of the shortage of metal drums. The Treasury Department, however, has dug up 270,000 or more 55-gallon drums. They are now available as surplus material, according to Ernest L. Olrich, Assistant to the Secretary of the Treasury.

★ Producers of chromium chemicals are discussing use of Turkish, Russian, Canadian, and domestic Montana ores, if adequate supplies of South African ores are not forthcoming because of lack of shipping facilities. Production of chromium chemicals requires high-grade ore, and ores of varying grades would cause considerable difficulties. Military applications take about 87% of the output of primary chromium chemicals.

★ War contractors facing termination of government contracts are advised to obtain Procurement Regulation 15 and the Termination Manual. Both are official documents and have been specially prepared to help the business man over the difficult hurdle this readjustment presents.

★ Government announcements say that V-day in Europe will see the end of job control in the strategic industries. According to McNutt, 4,000,000 workers will be released; but as Byrnes pointed out in a recent talk, this does not mean that these workers will be unemployed. Many will be wives who will leave industry permanently; civilian enterprises will undoubtedly find jobs for the rest.

★ It has been estimated that Canada will produce more than 12,000,000 bushels of flaxseed this year.



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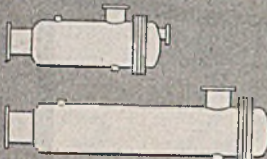

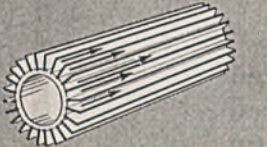
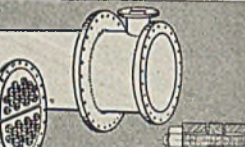
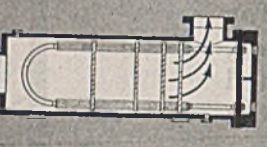


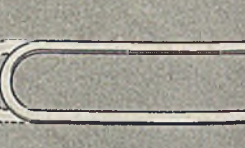
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	<p>MOST COMPACT UNIT . . .</p> <p>The increased heat transfer surface provided by the G-Fins in a given diameter of heater permits fewer tubes and a shorter shell requiring least space for a required duty.</p>	<p>ACCESSIBLE FOR COMPLETE CLEANING</p> <p>Since the G-Fin Storage Tank Oil Heater has fewest tubes for a required duty, and all tubes are accessible for cleaning throughout their entire length and diameter, the cleaning time is considerably shortened.</p>	
	<p>LEAST PRESSURE DROP . . .</p> <p>The straight-through flow of the oil passing through the heater results in a minimum pressure drop. The support plates for holding the heating elements in position are arranged so as to provide maximum free area for flow of oil.</p>	<p>EASILY EXAMINED AND CLEANED . . .</p> <p>Threaded bolt holes in the tube sheet permit removing the cover for examination of the tube joints while the tank is full of oil. After removal of the tube bundle from the shell, each U-bend element may be individually withdrawn for cleaning by backing off the lock-nuts at the tube sheet.</p>	
	<p>NO STRATIFICATION OR VAPOR BINDING</p> <p>The oil outlet is located at the top of the shell so as to prevent a dead pocket which would result in stratified, stagnant accumulation of hot oil or vapor.</p>	<p>LEAKPROOF JOINTS . . .</p> <p>The conical ends of the G-Fin heating elements are seated in the tube sheet with accurately machined metal-to-metal joints held tight by lock-nuts.</p>	
	<p>USES LESS STEAM . . .</p> <p>By heating the oil locally at the point of withdrawal from the tank, the G-Fin Storage Tank Oil Heater uses less steam than would be required by pipe coils located along the bottom of the tank.</p>	<p>NO TEMPERATURE STRAINS . . .</p> <p>The U-bend elements are free to expand and contract, so that there are no strains in the unit on change of temperature.</p>	



The G-Fin Tank Heater is built in two general types: for installation partly within the tank, as illustrated above, and also for installation outside the tank. The only difference between the two types is in the design of the shell at the floating end. Both types are built in a wide range of sizes.



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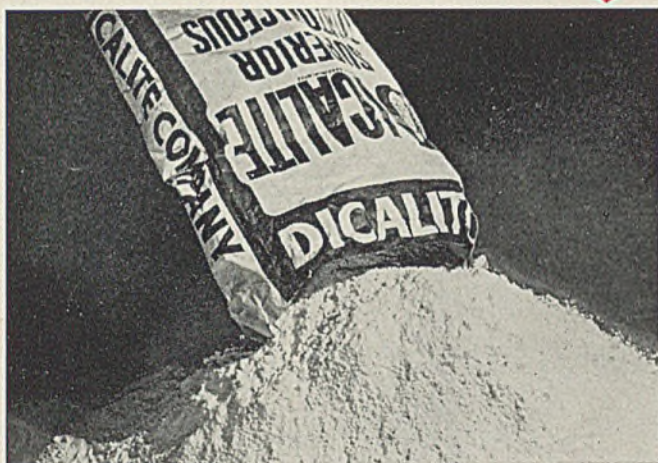
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Printing — Filler in printing ink rollers and roller core paint, and in printing ink.

Rubber — Filler in natural and synthetic rubber compounds, particularly mechanical rubber goods.



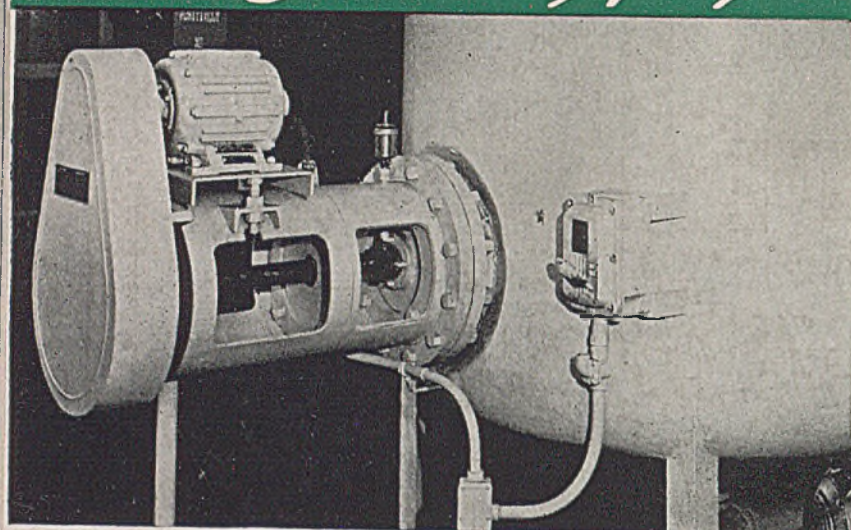
THE DICALITE COMPANY

CHICAGO 11, ILLINOIS • NEW YORK 5, NEW YORK • LOS ANGELES 14, CALIFORNIA

OFFICES AND WAREHOUSES IN PRINCIPAL CITIES OF U.S.A. AND IN CANADA

NEW DESIGN "LIGHTNIN" SIDE ENTERING MIXERS SET NEW STANDARDS IN...

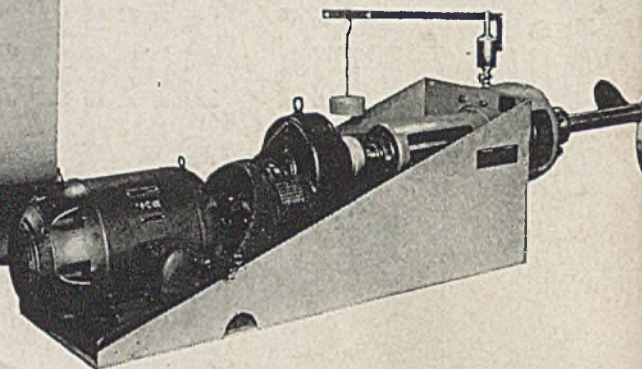
Process Adapted Agitation



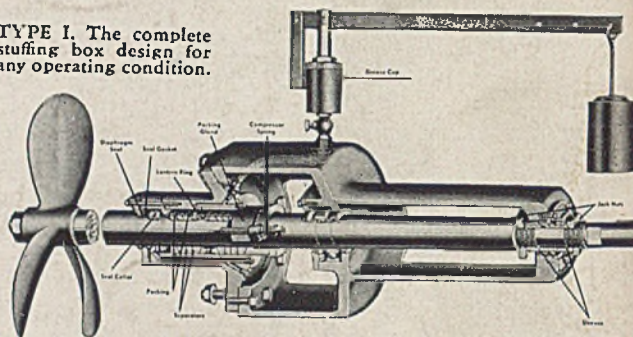
NEW MODEL SEV. Activated carbon slurry, chosen for low head room and economical tank head design.

THREE TYPES TO MEET YOUR REQUIREMENTS

THE MODEL SEG Gear Motor Unit is recommended for door installation, hazardous locations, where static is entered or where the atmosphere is gritty. (THE MODEL agitator unit without drive, motor or driving parts is mended for experimental jobs.)



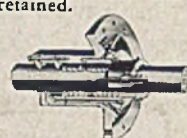
TYPE I. The complete stuffing box design for any operating condition.



TYPE II. If repacking with full tank is sole consideration, the diaphragm seal for controlling flushing liquid is omitted.

TYPE III. If abrasive conditions occur in tank which is empty at frequent intervals, the "shut-off" device is omitted but diaphragm seal is retained.

TYPE IV. For very duty conditions, a stuffing box is all that is required, with adequate lubrication but with features omitted.



WHERE TO USE SIDE ENTERING MIXERS

These "LIGHTNIN" Side Entering Mixers in capacities from 1 to 25 HP are designed primarily for use in large tanks. They can be used singly or in batteries depending upon the size of the tank, the materials to be mixed and the time desired to accomplish the agitation. They are also suited for use in smaller tanks where other types

of mountings are not practical as in those cases where head room is not available or where the top of the tank must be kept clear. The adaptability of "LIGHTNIN" Side Entering Agitators and the ability to do a thorough job of agitation have made mixing in tanks as large as 5,000,000 gal. capacity practical, economical, efficient.

ADVANTAGES OF NEW DESIGN

Now with the new design which has been just released for production after six years of exhaustive experiments and tests, these new "LIGHTNIN" Side Entering Mixers set a new standard for long life, ease of maintenance, economy and outstanding performance. In this new design are incorporated those features which operating and maintenance engineers want—those features which reduce wear, permit needed maintenance without

removal from tank, and which decrease the need for servicing. Among these are:

1. The mounting of the shaft on protected ball bearings outside the tank.
2. Constant pressure lubrication.
3. Special purpose stuffing box design.
4. Ability to repack with full tank.
5. Hard surfaced shafts and weight activated grease cup—optional.

HERE'S WHAT THE NEW OUTSIDE STUFFING BOX MEANS TO YOU

This new design of stuffing box now incorporated in "LIGHTNIN" Side Entering Mixers makes it possible to repack this member without removing mixer from the tank. Packing gland is spring actuated to provide uniform take up and is supplemented by adjusting nuts that provide means for regulating degree of take up or gland pressure. Gland is standard short length style, split body with solid head and is undercut to prevent drip spray and seizing. The standard stuffing box Type I is equipped with sealing collar for cutting off tank contents and flushing control diaphragm seal

for regulating flow of sealing liquid. This construction permits repair from outside the tank and without emptying. Three modifications of standard type are available: Type II for use where repacking with full is sole consideration; Type III for use where abrasive conditions occur tank is empty at frequent intervals; Type IV for very light duty conditions.

A new Bulletin (B76) just off the press gives more complete information on the new design Side Entering "LIGHTNIN" Mixers and specifications of Models and types available and methods of installation. Send for a



There is a Process Adapted Agitator for every size and shape of tank; for batch or continuous operation. Your savings will quickly repay the necessary modest investment. 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 Company engineers will gladly assist.

MIXING EQUIPMENT CO., INC.
1062 Garson Avenue, Rochester 9, N. Y.

Please send me the literature checked:

- ☐ B-76—Side Entering Mixers
- ☐ B-78—Top Entering Mixers
- ☐ B-75—Portable Mixers (Electric and Air Driven)
- ☐ B-77—Laboratory Mixers
- ☐ Mi-11—Operating Data Sheet

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